OXIDIZED SULFUR FUNCTIONALIZED POLYMERS VIA ADMET POLYMERIZATION

By

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To Mom and Steve
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There are so many who have been contributors to my success and I would like to thank all of them. This doctorate involved not only the four years in graduate school, but everything in life up until the degree’s competition. I have always tried to remember life’s little lessons. I cannot mention everyone who deserves thanks; otherwise, this section would comprise the entire document. But I believe those mentioned below have had the most profound effect on my life and especially my education.

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Most notably, my parents, Pam and Steve Hartley, two people who always put family first. My mother, like my grandparents, always put her kids first no matter what she had going on in her life. As rough as it must have been with my brother Chris and myself, she managed to do a great job, with both of us earning doctorate degrees. There is no doubt she is the common denominator and a major factor in our successes. My mother is always there for me and even for my friends. She was always looking out for us, demanding we “watch out for the crazy people” before leaving the house. Steve knew better. Steve always told me “don’t do anything stupid” before leaving the house. Steve was always tougher on me but definitely helped shape me into what I am today. These two never missed a school or sporting event. They were and remain dedicated parents, and they taught me this same devotion and discipline.

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OXIDIZED SULFUR FUNCTIONALIZED POLYMERS VIA ADMET POLYMERIZATION

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Precision placement of oxidized sulfur functionalities on and in polyolefin backbones via ADMET is described. Sulfonate esters, sodium sulfonates, sulfonic acids, sulfones, and sulfites have been incorporated with precise spacing using well-established ADMET methodology. This dissertation encompasses chemistry which cannot be produced through any other technique and will lead to a better fundamental understanding of oxidized sulfur functionalized polymers, and quite possibly lead to applications. As a result of this work, new polymers are now accessible, never before seen trends have been observed, and new synthetic techniques have been developed.

With the sulfonic acids and their conjugate bases, the sodium sulfonates, we have added yet another acid to the precision acid materials created via ADMET. These materials were created for the first time using novel synthetic chemistry and deprotection strategies presented here. The thermal behavior of precision sulfonic acids and sodium salts is similar to that of the precision carboxylic acids, but at higher temperatures.
With the capability to install oxidized sulfur groups, we have expanded the scope of ADMET. Along with pendent precision sulfur groups, this work details synthetic methods for precise installation of sulfites and sulfones into an aliphatic backbones. The precision polysulfites represent not only a first, but to the best of our knowledge a polymer containing a sulfite moiety within an aliphatic backbone has never been synthesized, prior to this work. The polysulfones (aliphatic polysulfones) display a trend unobserved in other ADMET chemistry: increasing functionalization results in increasing melting temperatures. Melting temperatures are as high as 175 degrees Celsius for these aliphatic precision polysulfones.

In the pursuit of these new materials, and in an effort to overcome synthetic boundaries, a new technique has been developed: microwave-assisted ADMET polymerization. Microwave step-metathesis polymerization overcomes the shortfalls of conventional heating methods, and in one case molecular-weights were found to be tripled those of traditional techniques in the same reaction time.

This work has provided new polymers, unique synthetic strategies, unique trends, and new techniques. This document details the foundation for each project mentioned. Furthermore, each of these chemistries and techniques continues to be studied following this introduction of original and innovative work.
CHAPTER 1
ADMET: FUNCTIONALIZED POLYOLEFINS

The use of acyclic diene metathesis (ADMET) in the synthesis of functionalized polyolefins is discussed. The nature of polymerizations, catalysts, and techniques are briefly covered. An overview of recent functionalized ADMET polymers and major contributions to its methodology is given. This chapter will place special emphasis on the use of ADMET to synthesize increasingly complex and new morphologies, resulting in well-defined polyolefin structures and functionalized materials unlocked as a result of this powerful polymerization method. Presented are polyolefins, materials, and architectures not possible through conventional polymerization techniques which have ultimately been applied to produce precision oxidized sulfur polymer.

Introduction

Functionalized polyolefins: incorporation of desired properties into the world’s most common plastics. Currently, the production of all forms of polyethylene (PE) total above 80 million tons each year.¹ This tonnage is attributed to the availability of cheap starting materials derived from fossil fuels and now even agricultural products. Commercially produced functionalized polyolefins are synthesized by the copolymerization of ethylene and other vinyl monomers, such as vinyl acetate and acrylates. However, due to the many side-reaction products, commercially produced functionalized PE structures are not well defined and are limited by defects such as uncontrollable and random branching. ADMET is recognized as the premiere polymerization technique for synthesizing complex polyolefin structures requiring accurate placement of functionalities.²
Since the emergence of Acyclic Diene Metathesis (ADMET) polymerization in the early 1990s, many sophisticated structures and functionalized polyolefins have been produced. Moieties including alcohols, acids, ketones, halogens, aromatics and others have been incorporated into PE.\(^3\) Because of the mild reaction conditions and limited number of side reactions, ADMET provides a level of control not possible in conventional techniques. Thus, ADMET is the leading polymerization technique for synthesizing complex architectures requiring accurate and precise placement of functionalities, while limiting reaction defects. Imperfections such as crosslinking and uncontrollable branching make conventionally polymerized materials difficult to study fundamentally.\(^4\) These side reactions are less desirable for advanced applications where precision is required.

Elimination of defects is made possible due to increasing availability of highly-selective olefin metathesis catalysts in recent years. Although metathesis polycondensation was first hypothesized as early as the 1950s, success was not achieved until 1991 with the successful polymerization of 1,9-decadiene and 1,5-hexadiene.\(^5\) The advent of ADMET coincides directly with the development of novel catalysts such as Schrock’s and Grubbs’ catalysts, which earned their developers (along with Yves Chauvin) a shared Nobel Prize in 2005.\(^6\) The continuing development of new, more tolerant catalysts allows for more sophisticated and functionalized polyolefin structures to be produced.

To better understand the effects of defects in PE, precision models of PE functionalized with branches have been synthesized via ADMET. More recently, high-polarity, acidic, ionic, renewable chemicals and drug moieties have been employed as
branches. These precision polymers have brought new properties to polyolefins and the potential for advanced applications, such as ion transport, renewable and biodegradable plastics, as well as drug therapeutics. This chapter describes ADMET, the reaction and techniques, followed by a discussion of precision functionalized polyethylenes, with an emphasis on major contributions as well as recent literature examples.

**ADMET**

Before discussing the details of various functionalized polyolefins synthesized by ADMET, it is first necessary to give the reader a brief description of the ADMET reaction and mechanism, including considerations and limitations. This section also provides a general procedure for performing a typical polymerization.

**Polycondensation of α,ω-dienes**

Although polyolefins are typically produced by chain-addition reactions, yielding molecular weights into the hundreds of thousands and even millions, the ADMET mechanism is based on stepwise-condensation. For every metathesis event between α,ω-diene monomers, a molecule of ethylene is evolved (Figure 1-1A). Removal of ethylene drives the reaction forward, slowly forming dimers, trimers, tetramers, and so on. All of these olefinic molecules may react at any time, continually increasing the molecular weight. Since, the reaction is step-growth in nature, the Carothers equation applies; i.e., only at near quantitative conversion of monomer is high molecular weight polymer formed (Figure 1-1B). Hence, monomer purity is absolutely crucial to prevent unintended chain capping and other side reactions.
Figure 1-1. ADMET polymerization. A) ADMET – polycondensation of α,ω-diene monomers with one molecule of ethylene released per number of repeat units \( x \), B) Carothers equation plot emphasizing that monomer conversion must approach 100% for high-molecular weight polymer via step polymerization.

Even with these precautions, molecular weights of ADMET polymers are slightly lower than those prepared by radical, Zeigler/Natta and metallocene reactions. Also, dienes are quite sophisticated and expensive to produce, compared to ethylene and substituted vinyl monomers. Thus, commercial polymerization of dienes to produce materials capable of competing with commodity plastics in the world market is not feasible from a cost perspective. However, high-end engineering plastics requiring fine-tuned properties are easily synthesized via ADMET. As mentioned above, molecular weight is also a factor, and currently commercial polyolefins may be produced with
much higher molecular weight (10^5 to 10^6 g/mol) than ADMET provides (ADMET upper limit ~100,000 M_w). On the other hand, functionalized polymers typically produced by step-growth conditions, while lower in molecular weight, have very strong intermolecular interactions (e.g., hydrogen bonding, pi stacking, ionic bonding), whereas polyethylene depends on mechanical strength provided by molecular weight and van der Waals forces. For example, nylon at a number average molecular weight of 11,300 (g/mol) has sufficient mechanical integrity for certain applications.\(^7\) Strong physical interactions along with structural control can be exploited to provide advanced polyolefin materials capable of new applications, like ion transport, while maintaining the crystallinity of linear polyethylene.

The advantage of ADMET is its utility in production of these precisely functionalized polyolefins, but the control arises from selective catalysts and symmetrical monomers, the key factors in ADMET sophistication. Design symmetry is built into the monomer and therefore transferred to the resulting polymer. This characteristic is particularly useful in precision systems and branch-functionalized models of PE varieties. While maintaining a linear, defect-free polyethylene backbone, a functionality or purposely placed defect is installed at a known concentration with known frequency. Thus, an equal number of carbons can be placed between each functionality if desired. Such precision allows scrutinizing defects at the molecular level to answer questions such as: What is the effect of a specified defect placed on every 21\(^{st}\) carbon versus every 75\(^{th}\) carbon?\(^8\) The ability to provide such fundamental morphological insight is unique to ADMET.
ADMET Catalysts

ADMET’s rise in the literature began shortly after efficient and robust olefin metathesis catalysts were introduced. However, olefin metathesis and metathesis polymerization were extensively theorized in the 1950s and 60s, building upon the polyolefin successes of Zeigler/Natta chemistry. In 1967 Nissim Calderon reported a successful polymerization of cyclic alkene monomers via metathesis using MoCl$_5$/EtAlCl$_2$/EtOH.$^9$ At that time, catalysis advancements were not sufficient for ADMET, but the efforts of Richard Schrock in the 1970s and Robert Grubbs in the 1980s led to catalysts later used to polymerize diene monomers via metathesis polycondensation.

![Figure 1-2. A variety of olefin metathesis catalysts.](image)

Schrock-type catalysts feature an early 4d or 5d transition metal, such as tantalum, and positively charged ligands. Such a complex is termed a “Schrock carbene.” More active Schrock catalysts feature tungsten and molybdenum metal centers (Figure 1-2). However, due to the highly electrophilic and oxophilic nature of early transition metals, these catalysts are not ideal for most functionalities.$^{10}$ Handling
and storage also complicate their usage. Ruthenium catalysts are the most popular and practical for producing functionalized ADMET polymers because of their tolerance to many functionalities and polymerization conditions.\textsuperscript{11} This versatility and robustness are attributed to the ruthenium metal center, which, unlike tungsten or molybdenum, is not as easily poisoned by oxygen-containing or other nucleophilic moieties.

To date, libraries of catalysts have been developed and are in use across the chemical industry. The chemistry of these catalysts will not be presented here, but it is worth noting that the catalyst should be selected with consideration of the desired functionalization and activity required.

**Mechanism**

The now widely accepted olefin metathesis mechanism was first proposed by Yves Chauvin in 1971.\textsuperscript{12} At the time, the mechanism was debated in the scientific community, but it was later substantiated by others in the field, including Grubbs. For his contribution to understanding the mechanistic details of olefin metathesis, Chauvin also shared the 2005 Nobel Prize with Grubbs and Schrock. Figure 1-3 displays the ADMET adaptation of Chauvin’s proposed productive pathway mechanism. The catalysts shown in Figure 1-2 are actually considered precatalysts 1, which react to afford the true catalyst, a methyldiene carbine 6. A double bond from a functionalized $\alpha,\omega$-diene monomer 2 coordinates to the catalyst 3 allowing for a $2 + 2$ cycloaddition and resulting in a metallocyclobutane intermediate 4. The metallocyclobutane then undergoes a $2 + 2$ cycloreversion, decomposing into styrene 5 (in the case of Grubbs’ first generation) and an $\alpha$-substituted metal alkylidene 6. At this point, coordination of another alkene occurs followed by another cycloaddition 7. The newly coordinating alkene can be monomer, polymer, or any olefin species present, even ethylene if equilibrium is reversed.
Assuming the reaction is driven forward towards polymer product, the final cycloreversion yields a larger olefin species 8 and the regenerated catalyst. Continuation will release ethylene gas 10 for terminal dienes. The catalyst remains active until poisoned or quenched (discussed in next section).

Figure 1-3. ADMET mechanism.

**Performing an ADMET Polymerization**

There exist a variety of polymerization setups possible for ADMET; this summary is in no way comprehensive of the techniques available, but is merely to serve as a starting point. Selection of an apparatus and conditions depends on the desired polymer product and monomer(s) to be polymerized. Typically, \(\alpha,\omega\)-diene monomers are viscous oils which can be polymerized in bulk. However, many monomers are solids...
even at high temperatures and require solution polymerization. The most crucial requirement to be met by any setup is the ability to remove the ethylene by-product, or adequate molecular weight is unachievable. Two effective methods for carrying out an ADMET polymerization of most monomers are: 1) bulk polymerization of liquid monomer under high vacuum (Figure 1-4A); and 2) solution polymerization in a high-boiling solvent (Figure 1-4B). Halogenated solvents prove to be the best for olefin metathesis reactions in general.\textsuperscript{13} A method published by Plenio in 1,2-dichlorobenzene has been exploited extensively.\textsuperscript{14} Opposed to the high-vacuum used in bulk conditions, a partial vacuum is used and is still adequate for removal of ethylene from solution, while maintaining the solvent. Another very crucial decision is the choice of catalyst. There are libraries of catalysts from which to choose, and each choice depends on a multitude of factors, including reaction temperature, substrate tolerance, and activity, to name a few.

![Typical ADMET Techniques](image)

Figure 1-4. Typical ADMET techniques. A) Bulk polymerization of a functionalized α,ω-diene monomer under high-vacuum. B) Example of solution polymerization utilizing both high-vacuum and argon flow to maintain a partial pressure, preventing high-boiling solvent from evaporating.
After the successful synthesis and purification of a functionalized \( \alpha, \omega \)-diene, the dry monomer or monomer solution is degassed in a Schlenk tube either by freeze-vacuum-thaw cycles or by bubbling argon through the monomer while stirring. To induce an ADMET reaction the catalyst of choice is simply added to the Schlenk tube, after which the flask is purged and subjected to the necessary conditions to drive the reaction forward. If Schrock-type catalysts are being used, a glove box is most likely necessary – another disadvantage ruthenium catalysts overcome. Polymerization temperatures for ADMET reactions are usually kept at 50 °C or below, due to the propensity for olefin isomerization at higher temperatures. Isomerization of alkenes presents a few notable issues, the most serious being the polymer structure, which will no longer be exactly as intended with known run-lengths purposely installed in the monomer. Another result of isomerization is reduced reactivity due to higher molecular weight condensates which must be removed. Propylene, butylene, and pentene are more difficult to completely remove than ethylene from a viscous reaction solution, and their presence will inevitably inhibit the equilibrium shift to product. If precision spacing is not a requirement, nor is a sophisticated model of PE the desired product, temperature control is less important.

Polymerization times can vary from hours to days, again depending on a multitude of factors. Longer reaction times are known to result in more isomerization. Reaction time and temperature, mentioned above, result in ruthenium-hydride formation caused by catalyst decomposition. The Ru-hydride species is known to cause isomerization and will alter the location of alkenes.\(^{15}\) However, all polymers will possess internal alkenes from cross-metathesis events. Because these alkenes are still active, to
avoid further reaction of the polymer with the catalyst, ethyl vinyl ether is added to "quench" the reaction by rendering the metathesis catalysts virtually inactive. This prevents reversal of the equilibrium (depolymerization if ethylene is present), cross-metathesis of the polymer chain, etc.

For conventional polyolefins to be mimicked through ADMET, the resulting unsaturated polymers must be completely hydrogenated. Saturation can be achieved through a variety of methods, including catalyzed high-pressure hydrogenations or the use of quantitative amounts of hydrazide reducing agents.\(^3,^{16}\) The limitations of saturation methods also depend on structural tolerance to the conditions and catalyst tolerance to the functional groups. A common technique is the use of Wilkinson’s catalyst, RhCl(PPh\(_3\))\(_3\), with a hydrogen pressure between 500 and 900 psi for periods of around 5 days. At these conditions, extreme caution should be exercised and choice of apparatus, as well as solvent, should be investigated prior to performing reactions in order to avoid mishaps. For example, ether solvents such as THF and dioxane (great solvents for some polymers) may form explosive peroxides under certain conditions required for alkene saturation.

**Functionalized Polyolefins by ADMET**

Now that the reader has some knowledge of how to make an ADMET polymer and the details of the reaction, the following section will provide a brief discussion of the wide array of possible functionalized polyethylenes successfully synthesized with ADMET since the technique’s emergence. This is not meant to be a comprehensive list of every polyolefin derivative; rather, it is meant to give the reader a review of important structural advances and insight into the vast realm of possibilities achievable with this powerful, yet controllable, polymerization technique. The development of ADMET began
in the early 1990s by Kenneth Wagener and his group when they discovered the polycondensation of terminal diolefins to high molecular weight polyethylenes. Wagener and his group have extended this initial development by publishing hundreds of studies. However, researchers now use the method in many countries and institutions, attesting to the technique’s power and versatility being realized worldwide.

Polyolefins display a range of properties, from those useful in commodity materials to those required of engineering plastics. These characteristics are suitable for many applications including cost-effective food storage, disposable bags, even artificial joints and bulletproof vests. Low cost, desirable properties, and practicality are the reasons why polyolefins are the most abundant plastics on Earth. However, alternative functionalization can improve and expand the use of polyolefins to new frontiers.

**Branch Functionalization**

Although hydrocarbon branches possess no heteroatoms nor are they particularly different from the backbone carbons, they do affect the properties of polyolefins. Branch sites act as impurities disrupting crystallinity, for example. Thus, branches are “functional” and serve purposes in regards to physical properties, and are therefore included as functionalities in this text. Commercial PE, especially low-density polyethylene (LDPE), contains random branching as a result of radical polymerization. Radical side reactions including chain transfer and back-biting result in LDPE with a mixture of long- and short-chain branches. Metallocene linear low-density polyethylene (LLDPE) has branches purposely installed by the copolymerization of ethylene with α-olefins, including 1-butene, 1-hexene, and 1-octene. Using various lengths and differing concentrations of branches, properties such as tensile strength can be tailored to a range of applications. However, placement of intentional branches is still random
and the fundamental understanding of their morphological effect remained a mystery for some time. An accurate and precise method of controlling branch frequency and concentration exactly was needed. This method is ADMET.

Perhaps one of the most significant contributions of ADMET to date is the ability to model these polyolefin systems by isolating the effect of branch defects. Utilizing the monomer symmetry mentioned previously, theoretically any desired length branch can be placed on a polyethylene backbone at any desired frequency. This structural precision allows for isolation and study of concentration and branch identity effects on PE morphology. Such information provides basic fundamental knowledge which may be used to improve upon an industry supplying billions of dollars in plastics.

The branch identity has a significant effect on PE behavior. The degree of crystallinity in PE types is a consequence of branching types, frequency, and distribution. Multiple studies by Wagener and coworkers have provided PE functionalized with over a dozen different branches spanning methyl to pentadecyl on backbones where some groups were placed every 15th, 21st, and 39th carbon. One particular study, provided insight into the effect a butyl group would have if placed every 75th carbon, a synthetic challenge. Even a butyl every 75 carbons affects the properties of polyethylene, lowering the melting point from 134 °C (linear PE) to 104 °C. Because of these investigations, a better understanding of PE crystallization, lamellar thickness, and crystal type due to branching is available.

PE modeling studies began with the simplest branch: methyl groups. Symmetrical monomers were synthesized as described previously with an equal number of -CH₂- units between the methyl and terminal alkenes, translating to PE
functionalized at precise intervals ranging from 8 to 20 carbons between methyls.\textsuperscript{19} To serve as a comparison, random copolymerizations of 1,9-decadiene and methyl-substituted monomers were performed.\textsuperscript{20} Very different behavior was observed for the precise and random methyl-containing polymers (Figure 1-5). Differential scanning calorimetry (DSC) data for PE with random methyl placement display a broad melting transition, in contrast to the sharp melting points of the precision methyl polymers. In other words, precision afforded by ADMET has a profound effect on polymer properties (an effect very important in other functionalized systems discussed below).
An ongoing synthetic challenge is the preparation of tactic branched polymers via ADMET. A regioregular, frequency-controlled polymer is one thing, but stereoregular polymers with long methylene run-lengths represent a supreme achievement, presently being addressed in the Wagener group.\textsuperscript{21, 22} To negate the atactic character of previous methyl studies, geminal dimethyl models were synthesized for comparison.\textsuperscript{23} The atactic polymer containing a single methyl every 9\textsuperscript{th} carbon is semicrystalline, whereas a gem-dimethyl group placed every 9\textsuperscript{th} carbon leads to an amorphous polymer. This work exemplifies that size of functionality affects crystalline behavior, morphology, and in turn the properties of the resulting polymer.

Next, a systemic study of larger branches was undertaken. Ethyl branched polymers were included in this endeavor to gain information regarding crystallization of short-chain branched PE.\textsuperscript{24} Utilizing small- and wide-angle X-ray scattering, PE functionalized with an ethyl group precisely located on every 21\textsuperscript{st} carbon (\textit{ethyl}\textsuperscript{21}) was studied, with particular attention to the temperature dependence of crystallization for ethyl-functionalized PE. Samples were isothermally crystallized at different temperatures from 5 to 28 \degree C. Above 21 \degree C, the crystal structure is triclinic with two ethyl branches included per lamella stem. Crystallization at 17 \degree C results in only one ethyl per stem and a stable hexagonal mesophase. Lowering the crystallization temperature below 8 \degree C excludes all branches from the precise \textit{ethyl}\textsuperscript{21} polymer lamellae.

Therefore, lamellae undergo thickening and include more ethyl branches as the crystallization temperature increases. This is not observed in random versions of ethyl-functionalized PE, as the polymer rapidly crystallizes in a disordered manner to very small, orthorhombic phases.
In contrast to the ethyl precision polymers, hexyl versions exhibit branch exclusion from the lamellae under all crystallization conditions. When incorporated into the unit cell, small groups such as ethyls and methyls alter the crystal, resulting in a melting temperature change. Even in radical chain polymerization, short-branch inclusion and long-branch exclusions are known, but the effect on melting temperature was determined from the study of larger precisely placed branches. As shown in Figure 1-6, a branch size of propyl or larger on every 21st carbon is excluded from the unit cell, and these excluded longer chain branches have no further effect on the melting temperature.  

![Graph](image.png)

**Figure 1-6.** PE branch inclusion and exclusion from the unit cell and effect on melting temperature. Reproduced with permission.  

These observations result directly from precision placement via ADMET functionalization. Although this discussion does not cover all PE modeling, it demonstrates some major findings. PE, although containing only carbon and hydrogen, is a treasure trove of fundamental polymer science knowledge still to be investigated.
Polar Moieties

Polar functionalization brings to polyolefins the properties attainable in all other walks of polymer science. Strong forces such as hydrogen bonding and interactions of carbonyl-containing functional groups introduce new structures, properties, and applications far beyond typical polyolefins.

Figure 1-7. IR spectra for PE with hydroxyl groups precisely placed every 21 carbons. Reproduced with permission. Copyright, 2015 Wiley.

Although, precision alcohol polymers were synthesized as early as 1998, only recently has morphological characterization shed additional light on the effects of hydroxy groups placed every 21\textsuperscript{st} carbon.\textsuperscript{25} X-ray scattering data confirmed hydroxyl groups are expelled from the unit cell, much like the branches mentioned in the previous section. Orthorhombic reflection planes are observed in the X-ray data at angles of 21° and 23.5° identical to those of PE. Evidence of hydrogen bonding was confirmed by DSC, in which the hydroxy functionalized polymer exhibits a melting transition of 100
°C, in comparison to other excluded-branch precision PEs (propyl through adamantyl) that melt below 20 °C. Temperature dependent IR analysis (Figure 1-7) showed that between 100 and 150 °C the hydrogen bonds weaken, as indicated by OH group stretching shifts from 3429 to 3475 cm\(^{-1}\). These results for precisely spaced alcohol functionalized PE are significant for multiple reasons: 1) OH exclusion from the unit cell may allow for easy PE surface modification; and 2) the stimulus-induced change in hydrogen bonding may make stimuli-responsive PE derivatives feasible.

Additional well-defined vinyl-alcohol copolymers were produced by Grubbs et al. via ADMET and ring opening polymerization (ROMP).\(^{27}\) The work was motivated by the concept that more controlled and defined polyvinyl alcohol (PVA) copolymers could lead to better gas barriers and biomaterials for more advanced applications, other than coatings and simple commodity packaging. Other polar functionalities such as acetals,\(^{28}\) carbonates,\(^{29}\) esters,\(^{30}\) phosphoesters,\(^{31, 32}\) sulfonate esters,\(^{33}\) and amides\(^{34}\) have been incorporated within the last 2 years. Additional examples of polar functionalities are discussed in a later section concerning renewable polyolefins via ADMET.

**Acidic Moieties**

Along with diverse polar functionalities (e.g., esters and alcohols), the ability to synthesize acid-functionalized PE is possible due to the development of robust, tolerant metathesis catalysts. With control and precision, shortfalls arising from commercially available materials may be overcome. For example, isolation of the acidic/ionic interactions from defects such as branching or random frequency/concentration of acid groups along a backbone leads to a better understanding of behavior. Acidic and ionic functionalized materials are presented in this section separate from other polar moieties because of their very different morphological trends. Neutral and ionic (acidic and basic)
forms of PE functionalized with carboxylic acids exhibit pH responsive behaviors resulting in altered microstructures dependent on ionization. Phosphonic acids (-PO(OH)₂) are also presented, because they display drastically different properties, due to the presence of two acidic hydrogens per group. Thus, phosphonics have twice as many hydrogen bond donors compared to carboxylic acids.

Figure 1-8. X-ray scattering for precise carboxylic acid functionalized PE displaying typical orthorhombic PE reflection and reflections pointing to the presence of acid layers. Reproduced with permission. Copyright, 2007 American Chemistry Society.

According to X-ray diffraction data (Figure 1-8 for COOH every 21st carbon), precise carboxylic acid polymers containing -COOH at known frequency dimerize between lamellae, forming layers of acids between crystalline regions of PE backbones. Random model polymers containing identical amounts of acids were synthesized for comparison via ROMP, a random polymerization method. Interestingly, random ROMP polymers, containing the same concentration of acid groups as precise
versions, dimerize similar to ADMET precision polymers. However, ordered acid layers were not present in polymers prepared by ROMP. A recent study of similar precision carboxylic acids, found that the run-length of the polyethylene backbone between precisely placed acid groups determines the crystal structure thickness, with 3 nm and 5-6 nm thicknesses observed for -COOH groups placed every 21\textsuperscript{st} and 45\textsuperscript{th} carbon, respectively.\cite{Winey2010}

![Diagram](image)

**Figure 1-9.** X-ray scattering of random and precise zinc carboxylates. High-concentration (22 mol\% and 66 mol \%) precision zinc carboxylate aggregates assume a cubic lattice. This is not observed in random ionomers with carbon backbones. Reprinted with permission.\cite{Winey2010} Copyright 2010, American Chemical Society.

Winey and coworkers presented an investigation of precision carboxylic acids in the anion-form (Figure 1-9).\cite{Winey2010} Upon neutralization of –COOH groups to the zinc carboxylates, aggregates form, in stark contrast to the layers which are present in the protonated forms. These precise aggregates show sharp X-ray scattering peaks, as opposed to the broad peaks displayed by random ionomers. With higher functionalization content (22 to 66 mol \%), the zinc carboxylate aggregates are present in a cubic lattice. Such order has not been witnessed previously. These observations
are no doubt by-products of the precision and control afforded by ADMET. Because other polymerization methods lack control over structure, most commercially produced ionomers are ill-defined, thus making them difficult to understand fully. However, with precision ionomers and aggregates continuing to be studied in such detail, the ionic behavior of precision systems could provide insight concerning random ionomer morphologies and interactions.

Figure 1-10. X-ray scattering analysis of precision geminal phosphonic acids every 21st carbon A) Room temperature X-ray scattering. Peak values at arrows are evidence for FCC lattice. B) FCC lattice shown with Bragg distances acquired by X-ray scattering as a function of Miller indices. Reproduced with permission.38 Copyright 2012, American Chemical Society.

Phosphoric acid-based materials are currently used in many applications, including high-temperature fuel cells.39 Studying phosphonic effects in defect-limited polyethylene may allow better understanding of ion transport and conductivity in these systems. Opper et al. synthesized precision phosphonic-containing polymers via
ADMET, including geminal phosphonic acid polymers having double the acid content on the same backbone.\textsuperscript{40, 41} These high-acid content polymers show very different properties from the carboxylics previously mentioned. Characterization of the geminal PA polymers by Winey and coworkers indicated the presence of a face-centered cubic lattice (Figure 1-10). Higher temperature X-ray scattering proved that the order of aggregates is virtually the same at 150 °C (high above the 47 °C $T_m$) as at room temperature.\textsuperscript{38} This is not the case with carboxylic acids, for which the acid dimers between layers dissociate when the temperature is above 120 °C.\textsuperscript{31} These investigations provide strong evidence that precision functionalization also leads to improved properties and that ADMET provides control of polymer architecture, much like other examples described in previous sections. Precisely engineered acid materials provided by ADMET may lead to improvements in ion transport and layered nanomaterials applications. ADMET itself may be used to make future conducting materials, as this behavior is not observed in random systems.

**Renewable Polyolefins**

Another group of functionalized polyolefins containing polar functionalities are presented as a separate category due to their synthesis from renewable materials, instead of fossil fuels.

Commercial polyurethanes are typically produced utilizing diols and diisocyanates. However, urethane functionalities have been installed into ADMET-capable $\alpha,\omega$-diene monomers using 10-undecenoic acid, a derivative of castor oil, as the starting material (Figure 1-11).\textsuperscript{42} These bio-based polyurethanes exhibit excellent thermal stability, decomposing well above 300 °C. Polyesters, polycarbonates, polyethers, and polyamides have also been prepared in a similar manner, with
polyethers having the best thermal stability, degrading only 5% at 409 °C.

Figure 1-11. Recently published functionalized polyolefins synthesized from castor oil derivatives. Adapted from references.37, 38, and 41

Another study was performed with polymers based upon the castor oil derivative 10-undecenoyl chloride. Two α,ω-diene monomers were synthesized by combining 10-undecenoyl chloride with either isosorbide or glucarodilactone, both derivatives of glucose, one of the most abundant and easily accessible renewable molecules.43 Copolymers containing both isosorbide and glucarodilactone-based monomers were also prepared and characterized. They exhibit degradation temperatures ranging from 206 °C to 369 °C. An important aspect of this work was the study of hydrolytic degradations. Isosorbide-containing backbones provide stability under all aqueous conditions (neutral, acidic and basic), while lactone functionalization was found crucial to degradability. Hence, any polymer synthesized using glucarodilactone was readily broken down in solution. One copolymer composition even showed an elongation of
640% at the break – displaying the wide array of properties possible for functionalized polyolefins.

Additional examples are documented in the literature. In fact, a large percent of recently published ADMET literature is devoted to bio-based or green materials. Products from natural oils and acids comprise the majority of these studies. Polyolefins functionalized with ferulic acid, abietic acid, and even benzoxazine have recently been prepared through ADMET polymerization.

**Biologically Active and Drug Functionalized Polyolefins**

The controllable nature of ADMET is ideal for preparation of biologically active materials and drug delivery vehicles, where the minutest defect could have a negative health effect. Leonard et al. reported early uses of ADMET with amino acid and peptide branches; specifically, lysine functionalities were precisely placed along a PE backbone on every 21st carbon. Four distinctly different polymers were synthesized all differing by lysine’s connectivity to the backbone. This project was synthetically challenging because free amines and carboxylic acids required protection due to their nucleophilicity and ability to poison metathesis catalysts. This highlights an issue faced with protecting groups in precision systems: quantitative removal is essential to retain precision.

A similar study involved the precision placement of drugs on a PE backbone. As proof of concept, diene monomers were synthesized with common drugs including ibuprofen and naproxen. Polymers with drugs attached directly to the backbone were prepared, as well as polymers containing hydrophobic (decanediol unit) or hydrophilic (tetraethylene glycol unit) spacers between the drug and backbone. Hydrolysis studies found that between 15 and 40% of drugs were hydrolyzed from the backbone over a 33 hour period, indicating a potential for timed release drug applications.
Knowing that large side chains and moieties are excluded from the crystal lattice of PE, one can imagine macromolecules similar to those described above to construct materials having bio-active surfaces with mechanical and thermal properties of polyethylene. Considering the importance and interdisciplinary nature of biology and medicine, there is no doubt that a controllable synthetic method like ADMET will become a go-to technique for future bio-olefins.

**Post-Polymerization Modification of Functionalized Polyolefins**

Post-polymerization chemistry has never been more popular, especially after the introduction of “click” chemistries that provide mild, efficient, and highly selective reactions. These are very useful in the preparation of some ADMET polymers, because the available catalysts do not allow installation of certain functionalities prior to polymerization. Also, the ADMET reaction alone is not as versatile in terms of accessing complex architectures directly, compared to the very popular ATRP and RAFT polymerizations. However, internal alkenes provided by the polymerization itself are now being exploited, as well as the reactivity of preinstalled compatible groups, to functionalize ADMET products further. Recently reported “click” reactions and other post-polymerization reactions are presented here.

Unverferth et al. have produced star polymers via ADMET polymerization of 10-undecenyl acrylate with hexaacrylate and tetraacrylate monomers, resulting in 4 and 6-arm polyester stars, respectively.\(^{30}\) Afterwards, the polymerization products were exposed to thiol-Michael conditions to functionalize the star-shaped systems with various mercaptoalcohols and methyl thioglycolates, as confirmed by \(^1\)H NMR. The thiol-Michael reaction was also used by Zhenshu and coworkers to synthesize star and linear-dendron (Figure 1-12) polyphosphoester functionalized ADMET derivatives.\(^{31, 32}\)
The star polyphosphoesters were subsequently used to make gold nanoparticle-containing composite materials, which are potentially suitable for biomedical applications.

Figure 1-12. Linear-dendron block polyphosphoesters synthesized by ADMET polymerization by Zhenshu and coworkers. Reproduced with permission. Copyright, 2014 Royal Society of Chemistry.

Thiol-Michael and thiol-ene reactions were utilized by Lowe and coworkers to synthesize a diversely functionalized group of materials containing alcohols, sugar derivatives, hydrocarbon tails, aromatics, fluorinated tails, silyls, and siloxanes. With an acrylate monomer, thiol-Michael reactions resulted in a series of drastically different linear functionalized polyolefins. However, the divalent sulfur present after thiol-Michael addition was found to inhibit ADMET polymerization. Thus, sulfide bonds were oxidized selectively (no alkene oxidation) with hydrogen peroxide and a catalytic amount of triazotriphosphorine chloride, a process termed “protective oxidation” by the authors. Post-polymerization, olefins were subjected to thiol-ene conditions to yield further functionalization of the backbones.
Other post-ADMET reactions have been performed, including other types of polymerizations. ATRP was utilized in coordination with ADMET by Opper et al. to create precision graft polymers containing phosphonic acids. This is just one example of how combination of polymerization methods can produce new, complex precision architectures. Li et al. used post-polymerization lactonization to form γ-butyrolactones on ADMET polymer backbones (Figure 1-13). The monomer design contained ethyl esters beta to the alkenes. After the initial ADMET polymerization, the alkenes were hydroxylated, and γ-lactonization was subsequently performed. The installed rings raised the $T_g$ of one sample by 160 °C (from -33°C to 127°C), dramatically changing the physical properties. These examples provide clear evidence that the emergence of click chemistry and efficient post-polymerization reactions has allowed even more functionalization of ADMET synthesized polymers.
ADMET allows researchers to produce new structures, which alone may have applications, or whose resulting properties may be elucidated to better understand existing commercial materials. And, with the development of even more efficient, tolerant and active catalysts, increasingly sophisticated structures, properties and morphologies will be possible through ADMET. Whether it be a drug, ionic group, renewable feedstock, or post-polymerization functionalization, ADMET is becoming an increasingly published and important technique for polyolefin functionalization.

**Purpose of this Dissertation**

The following chapters detail the expansion of this precision chemistry to oxidized sulfur functionalities using the ADMET methodology developed over the past three decades. The research presented in this dissertation is important not only polymer chemistry, but organic chemistry as well, with techniques and syntheses that may be applied elsewhere. ADMET is the tool by which new structures exhibiting completely new trends have been accessed and delivered here for the first time.

Chapter 2 describes the synthesis of precision sulfonic acid and sodium sulfonate polymers, which complete the precision acid polymer library. Chapter 3 details the synthesis of a new type of polymer, precision poly(sulfites). To the best of our knowledge, no other polymers have been prepared with the organic sulfite functionality, and ADMET was the method to provide it. Chapter 4 reports precision aliphatic polysulfones. In contrast to typical aromatic polysulfones, these aliphatic polysulfones possess methylene units adjacent to the sulfone. Precision aliphatic polysulfones display a trend never witnessed in ADMET precision polymers. Microwave-assisted ADMET is introduced in Chapter 5. Microwave ADMET polymerization was initially investigated to overcome hardships with solid oxidized sulfur monomers and insoluble
polymers. However, the technique has grown past this dissertation and is now being investigated independently as a new method of performing these precision inducing reactions. As a result of this research account, more sophisticated functionalized polymers may be produced and applications may arise as a direct result of precisely placed oxidized sulfur moieties and the techniques developed to produce them.
Introduction

This chapter details the first successful synthesis of precisely functionalized sulfonic acid and sodium sulfonate polymers. Prior to this work, carboxylic, phosphonic, and recently, boronic acids have been synthesized, but, until now, precision sulfonic acids and sodium sulfonates remained elusive. Each precision acid system requires a unique synthetic pathway, a challenge arising from the differences in properties of each acid group. Most acidic groups require protection for a successful ADMET polymerization. The major challenge is achieving complete deprotection of every acid group in order to maintain precision.

Figure 2-1. Protected precision acids and their deprotections. A) Precise carboxylic acid polymer deprotection B) Precise phosphonic acid deprotection C) Prior sulfonic acid deprotection attempts.

Previously synthesized precisely placed acids were achieved using fairly labile protecting groups. Carboxylic acids were protected with a hemiacetal group (Figure 2-
1A) and phosphonics were protected by an ethyl ester (Figure 2-1B). Boronic acids, a unique case, were synthesized directly utilizing an ionic liquid and found to be compatible with ADMET polymerization conditions. Figure 2-1C displays protected precision sulfonic acids with a variety of attempted protecting groups. Opper and Fisher both explored alternative protecting groups, including neopentyl, isobutyl, and perfluorophenyl. Alternatives to the directly attached protected ester route were also explored, of which two are notable: precise thiol polymerization followed by post-polymerization oxidation and an aromatic spaced sulfonate ester route. Neither route provided the desired precision sulfonic acids.

The pursuit of precision poly(sulfonic acid)s is motivated, in part, by the results from the precision carboxylic acid work. Acidic functionalities are well-known to enhance polymer properties by increasing strength and toughness, and by allowing for proton conduction. Applications include hydrogels, gas barriers, coatings, and adhesives, to name a few. Fuel cell applications have been of primary interest in recent years due to the expansion of alternative energy research. Commercial sulfonic acid-functionalized materials, such as Nafion®, make excellent proton exchange membranes for fuel cells, because the high acidity of sulfonic groups promotes proton conduction.

However, commercially produced sulfonic acid polymers lack definition and uniformity, inevitable features induced by defects arising from the random nature of most polymerization mechanisms. Also, sulfonation is often performed post-polymerization, and only the surface of the polymer is functionalized or not completely sulfonated. Methods of installing sulfonic acids after the polymer has been made,
lack sophistication and control. In the present study, the precision allowed by ADMET enables precise placement of sulfonate groups, which in turn, provides us more control over morphology, especially the proton conducting domains which exist within the architectures. There is precedence for this claim. Precision carboxylic acid polymers exist in layers, with the carboxylic groups hydrogen bonded between lamellae. Precision sulfonic acids may behave in the same manner, but with properties which give rise to proton conduction.

Figure 2-2. Precise and random sulfonic acid polymer structures discussed in Chapter 2. $\text{SO}_3\text{Et}$, $\text{SO}_3\text{Na}$, and $\text{SO}_3\text{H}$ denote ethyl sulfonate, sodium sulfonate, and sulfonic acid, respectfully. If U is present, the polymer is an ADMET product containing unsaturated double bonds. 9 and 21 indicate sulfonic placement on every 9th or 21st carbon, while Co denotes a copolymer made to mimic the 21st polymer’s sulfonate concentration, but in with random sulfonate placement. For 21 polymers, a dash and number at the end indicate molecular weights (e.g., –33K = 33,000).

This chapter details the recent developments and successful synthesis of precise sulfonic-acid and sodium sulfonate functionalized polyolefins. Improvements in the
monomer synthesis have made it possible to produce larger quantities of ester-protected sulfonic acids positioned on every 9th and 21st carbon of the polyolefin backbone to study the effect of acid concentration on morphology. To mimic the product of a conventional polymerization, a random copolymerization was performed using a sulfonate ester and 1,9-decadiene. Following descriptions of an improved protected monomer, novel sulfonate deprotection chemistry is presented, and structural and thermal characteristics of polymers are compared. Figure 2-2 shows the structures of polymers described in this chapter.

**Experimental**

**Methods**

All chemicals and materials were purchased from Sigma Aldrich and used as received, unless otherwise stated. Dry solvents were obtained from a solvent purification system. Grubbs’ 1st generation catalyst was graciously donated by Materia, Inc. and used as received. Flash chromatography was performed using SiliCycle SiliaFlash® P60, 40-63 μm, 60 Å silica. $^1$H NMR and $^{13}$C NMR spectra were acquired on a Varian Mercury-300 NMR Spectrometer using VNMRJ software. IR spectra were obtained on a PerkinElmer FT-IR Spectrum One with ATR attachment using Spectrum Software for data analysis. Mass spectroscopy was performed in the Department of Chemistry’s Mass Spectroscopy Laboratories at the University of Florida. Elemental Analysis was performed by Atlantic Microlabs. Molecular weights were obtained in THF at 40 °C relative to polystyrene standards using an Agilent 1100 GPC with a refractive index detector. Thermogravimetric Analysis (TGA) was performed on a TA Instruments Q5000 using a temperature ramp of 10 °C/min under nitrogen atmosphere. Differential Scanning Calorimetry (DSC) was performed on a TA Instruments Q1000 DSC.
Hermetically sealed aluminum pans were equilibrated at -80 °C and subsequently heated at 10 °C/min until the desired final temperature was reached. Pans were then cooled at 10 °C/min to -80 °C. Three of these heat/cool cycles were performed for each sample. Data are reported for the third cycles, which were reproducible.

**Pent-4-en-1-yl trifluoromethanesulfonate (1).** To a dry 1L round bottom flask containing 500 mL of dry DCM, 16 mL of dry pyridine was added. Then 47.68 grams (169 mmols) of trifluoromethanesulfonic anhydride was added dropwise over 15 mins at room temperature. The resulting reagent was stirred and cooled to 0 °C before 12.66 grams (147 mmols) of 4-penten-1-ol was added dropwise. The reaction was allowed to warm to room temperature and was stirred for 1 hour, at which point pyridinium triflate had precipitated. The precipitate was filtered, washed with dry DCM and discarded. The filtrate was concentrated and passed through a plug of silica (9:1, hexanes:DCM). The product flask was quickly purged with argon and placed into a freezer, while NMR spectra were acquired for confirmation. The triflate was subsequently used immediately to prevent degradation. Yield: 23.3 grams, 82%. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.84-5.70 (m, 1H), 5.13-5.05 (m, 2H), 4.55 (t, 2H), 2.20 (q, 2H), 1.94 (p, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 135.7, 120.7, 116.6, 76.7, 63.8, 29.0, 28.3.

**Undec-10-en-1-yl trifluoromethanesulfonate (2).** The procedure used for pent-4-en-1-yl trifluoromethanesulfonate above was employed: 16 mL of pyridine, 47.68 grams (169 mmols) of trifluoromethanesulfonic anhydride, and 25.03 (147 mmols) grams of 10-undecen-1-ol. Yield: 33.8 grams, 76%. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.86-5.76 (m, 1H), 5.03-4.91 (m, 2H), 4.53 (t, 2H), 2.03 (q, 2H), 1.83 (m, 2H), 1.45-1.27 (br,
13C NMR (75 MHz, CDCl$_3$)  δ 139.1, 120.8, 116.5, 114.1, 76.5, 33.7, 31.6, 29.3, 29.2, 29.0, 28.9, 28.8, 25.0.

**Monomer Synthesis**

To a three-neck round bottom flask, 5.00 grams (40.27 mmols) of ethyl methanesulfonate was added and dissolved in 40 mL of dry THF. The solution was cooled to -78 °C, approximately 39 mmols of freshly prepared LDA was added dropwise, and the solution was stirred for 15 minutes. The temperature was then raised to 0°C for 30 minutes to allow for thorough deprotonation. The flask was then lowered again into a -78 °C bath and stirred for 15 minutes before 39 mmols of the appropriate triflate was added dropwise in 50 mL of dry heptane. The reaction was raised to 0 °C for 30 minutes and then lowered back to -78 °C before repeating the addition of LDA and triflate once more to yield dialkylated product. Afterwards, the reaction was concentrated to half the original volume, flooded with deionized water, and extracted with diethyl ether (4x25 mL). The organic layer was collected and dried over MgSO$_4$. The MgSO$_4$ was filtered, washed with ether, and discarded, while the filtrate was collected and concentrated to yield crude oil-like products. Products were purified via column chromatography with an eluent mixture consisting of hexanes and ethyl acetate (19:1).

**Ethyl undeca-1,10-diene-6-sulfonate (3).** 8.51 grams of pent-4-en-1-yl trifluoromethanesulfonate (1) was added after each deprotonation. Yield: 4.57 grams, 45%. 1H NMR (300 MHz, CDCl$_3$) δ 5.83-5.74 (m, 2H), 5.07-4.96 (m, 4H), 4.32-4.25 (q, 2H), 2.99-2.97 (p, 1H), 2.13-2.05 (q, 4H), 1.98 -1.88 (m, 4H), 1.75-1.53 (m, 4H), 1.42-1.37 (t, 3H). 13C NMR (75 MHz, CDCl$_3$) δ 137.7, 115.3, 65.4, 60.9, 33.4, 28.3, 25.7, 15.2. HRMS (ESI) (m/z): (M+Na)$^+$ calcd for C$_{25}$H$_{48}$O$_3$S 451.3216; found 451.3213.
Elemental Analysis: calcd for C\textsubscript{25}H\textsubscript{48}O\textsubscript{3}S, C: 70.04, H: 11.29, N: 0.00; found C: 69.84, H: 11.55, N: 0.00.

**Ethyl tricosa-1,22-diene-12-sulfonate (4).** 11.78 grams of undec-10-en-1-yl trifluoromethanesulfonate (2) was added after each deprotonation. Yield: 6.79 grams, 40%. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 5.85-5.74 (m, 2H), 5.01-4.91 (m, 4H), 4.31-4.24 (q, 2H), 2.98-2.94 (p, 1H), 2.07-1.97 (q, 4H), 1.95-1.85 (m, 4H), 1.74-1.62 (m, 4H), 1.54-1.28 (br, 27H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) 139.2, 114.1, 71.9, 65.3, 61.2, 33.8, 29.5, 29.4, 29.3, 29.1, 28.9, 28.9, 26.6, 15.2. HRMS (ESI) \((m/z)\): (M+NH\textsubscript{4})\textsuperscript{+} calcd for C\textsubscript{13}H\textsubscript{24}O\textsubscript{3}S 278.1784; found 278.1786. Elemental Analysis: calcd for C\textsubscript{13}H\textsubscript{24}O\textsubscript{3}S, C: 59.96, H: 9.29, N: 0.00; found C: 60.23, H: 9.42, N: 0.00.

**Polymerization Procedures**

Monomer solutions in DCM (2.0M) were inserted into dry Schlenk tubes and subjected to freeze-pump-thaw cycles until gas evolution failed to appear during thaw cycles. A final freeze was performed and while under argon purge, 1 mol\% of Grubbs' first generation catalyst was added. The Schlenk was then equipped with a reflux condenser and argon flow adapter. The apparatus was lowered into an oil bath at the appropriate temperature to maintain the reflux of DCM. Polymerizations were continued for the times specified individually below, after which samples cooled and a solution of ethyl vinyl ether in toluene (1:10) was added. The polymers were then precipitated from methanol at around -18 °C and subsequently filtered, collected, and dried under high vacuum.

**SO\textsubscript{3}Et8U.** 1.0 gram of ethyl undeca-1,10-diene-6-sulfonate (3). Polymerization proceeded for 72 hours. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 5.45-5.33 (br, 2H), 4.30-4.23 (q, 4H), 3.01-2.93 (p, 1H), 2.08-1.94 (m, 4H), 1.93-1.84 (m, 4H), 1.78-1.45 (m, 4H), 1.43-
1.34 (t, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 130.1, 129.6, 65.5, 60.9, 32.3, 28.4, 27.0, 26.4, 15.3. FT-IR (ATR) v in cm$^{-1}$ 2935, 2866, 1459, 1391, 1341, 1163, 1097, 1002, 970, 909, 763, 701, 627. GPC (THF, Polystyrene Standards): $M_n =$ 6,600 g/mol; $M_n =$ 13,500 g/mol (PDI = 2.05).

**SO$_3$Et$_20U – 33K.** 2.0 grams of ethyl tricosa-1,22-diene-12-sulfonate (4).
Polymerization proceeded for 72 hours. $^1$H NMR (300 MHz, CDCl$_3$) δ 5.39-5.34 (br, 2H), 4.31-4.23 (q, 2H), 2.98-2.94 (p, 1H), 2.02-1.85 (m, 4H), 1.73-1.61 (m, 4H), 1.49-1.24 (br, 27H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 130.3, 65.3, 61.2, 32.6, 29.7, 29.5, 29.5, 29.5, 29.3, 29.2, 28.9, 26.6, 15.2. FT-IR (ATR) v in cm$^{-1}$ 2922, 2852, 1645, 1464, 1342, 1167, 1095, 1005, 967, 912, 768, 721, 628. GPC (THF, Polystyrene Standards): $M_n =$ 33,300; $M_n =$ 73,600 (PDI = 2.21).

**SO$_3$Et$_20U – 19K.** 2.0 grams of ethyl tricosa-1,22-diene-12-sulfonate (4).
Polymerization proceeded for 24 hours. $^1$H NMR (300 MHz, CDCl$_3$) δ 5.39-5.34, 4.28-4.23 (q, 2H), 2.98-2.92 (p, 1H), 2.01-1.85 (m, 4H), 1.73-1.61 (m, 4H), 1.49-1.26 (br, 27H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 130.3, 65.3, 61.2, 32.6, 29.7, 29.5, 29.5, 29.5, 29.3, 29.2, 28.9, 26.6, 15.2. FT-IR (ATR) v in cm$^{-1}$ 2922, 2852, 1464, 1342, 1167, 1095, 1005, 967, 912, 768, 721. GPC (THF, Polystyrene Standards): $M_n =$ 19,800; $M_n =$ 48,500 (PDI = 2.45).

**SO$_3$Et$_20U – 6K.** 2.0 grams of ethyl tricosa-1,22-diene-12-sulfonate (4).
Polymerization proceeded for 12 hours. $^1$H NMR (300 MHz, CDCl$_3$) δ 5.39-5.34 (br, 2H), 4.28-4.23 (q, 2H), 2.98-2.92 (p, 1H), 2.01-1.85 (m, 4H), 1.73-1.61 (m, 4H), 1.49-1.26 (br, 27H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 130.3, 65.3, 61.2, 32.6, 29.7, 29.5, 29.5, 29.5, 29.3, 29.2, 28.9, 26.6, 15.2. FT-IR (ATR) v in cm$^{-1}$ 2915, 2849, 1468, 1342, 1262, 1163,
1100, 1004, 914, 796, 773, 719, 701, 627. GPC (THF, Polystyrene Standards): $M_n = 6,900$; $M_n = 15,100$ (PDI = 2.19).

**SO$_3$EtCoU.** 1.664 grams of ethyl undeca-1,10-diene-6-sulfonate (3) and 1.328 grams of 1,9-decadien were polymerized for 72 hours. $^1$H NMR (300 MHz, CDCl$_3$) δ 5.48-5.530 (br, 4H), 4.31-4.24 (q, 2H), 3.02-2.96 (p, 1H), 2.17-1.86 (br, 8H), 1.78-1.61 (br, 4H), 1.59-1.45 (m, 4H), 1.42-1.25 (br, 11H).$^{13}$C NMR (75 MHz, CDCl$_3$) δ 131.5, 130.3, 128.9, 65.3, 61.0, 32.6, 32.3, 29.6, 29.0, 28.3, 27.2, 26.4, 15.2. FT-IR (ATR) ν in cm$^{-1}$ 2923, 2852, 1457, 1342, 1166, 1004, 966, 912, 763, 703. GPC (THF, Polystyrene Standards): $M_n = 2,200$; $M_n = 3,200$ (PDI = 1.45).

**Hydrogenation Procedures**

Dry unsaturated polymer samples (1.0 g) were dissolved in 30-50 mL of dry toluene in a round bottom flask and degassed with a steady argon flow for a minimum of 24 hours. Next, 0.5 mol% of Wilkinson’s Catalyst (tris(triphenylphosphine)rhodium chloride) was added and immediately the flasks were sealed in a Parr bomb rated for 2000 psi of hydrogen gas. The vessel was purged three times with hydrogen. On the final fill, a pressure of 500 psi of hydrogen was added and the vessel was lowered into an oil bath at 90 °C for 5 days. NMR was performed to confirm complete saturation before the polymers were precipitated from methanol at around -18 °C and subsequently filtered, collected, and dried under high vacuum.

**SO$_3$Et8.** $^1$H NMR (300 MHz, CDCl$_3$) δ 4.31-4.23 (q, 2H), 2.99-2.93 (p, 1H), 1.96-1.84 (m, 4H), 1.73-1.61 (m, 4H), 1.46-1.24 (br, 11H).$^{13}$C NMR (75 MHz, CDCl$_3$) δ 65.3, 61.1, 29.5, 29.2, 28.9, 26.6, 15.3. FT-IR (ATR) ν in cm$^{-1}$ 2921, 2852, 1638, 1464, 1340, 1261, 1164, 1096, 1003, 910, 767, 701, 628.
SO$_3$Et$_2$O $-$ 33K. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.31-4.24 (q, 2H), 2.96-2.94 (p, 1H), 1.95-1.85 (m, 4H), 1.72-1.62 (m, 4H), 1.48-1.25 (br, 35H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 65.3, 61.1, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 28.9, 26.6, 15.2. FT-IR (ATR) $\nu$ in cm$^{-1}$ 2916, 2849, 1467, 1342, 1165, 1099, 1003, 913, 772, 720.

SO$_3$Et$_2$O $-$ 19K. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.32-4.25 (q, 2H), 2.96-2.94 (p, 1H), 1.94-1.83 (m, 4H), 1.72-1.62 (m, 4H), 1.48-1.25 (br, 35H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 65.4, 61.0, 29.8, 29.7, 29.6, 29.5, 29.5, 29.3, 28.9, 26.6, 15.2. FT-IR (ATR) $\nu$ in cm$^{-1}$ 2915, 2848, 1467, 1340, 1164, 1099, 1003, 912, 772, 710.

SO$_3$Et$_2$O $-$ 6K. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.30-4.25 (q, 2H), 2.97-2.94 (p, 1H), 1.92-1.81 (m, 4H), 1.72-1.62 (m, 4H), 1.48-1.25 (br, 35H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 65.4, 61.0, 29.8, 29.7, 29.6, 29.5, 29.5, 29.3, 28.9, 26.6, 15.2. FT-IR (ATR) $\nu$ in cm$^{-1}$ 2915, 2849, 1467, 1343, 1165, 1100, 1003, 914, 772, 719.

SO$_3$EtCo. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.28-4.21 (q, 2H), 2.95 -2.91 (p, 1H), 1.90-1.82, (m, 4H), 1.68-1.61 (m, 4H), 1.44-1.33 (t, 3H), 1.29-1.06 (br, 24H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 13C NMR (75 MHz, cdcl3) $\delta$ 65.2, 61.1, 34.3, 29.6, 29.4, 29.3, 28.8, 26.5, 15.2. FT-IR (ATR) $\nu$ in cm$^{-1}$ 2917, 2849, 1463, 1342, 1262, 1167, 1096, 1005, 912, 768, 729, 720.

Deprotection

Dry saturated polymer samples (800 mg) were suspended in 10-15 mL of 200 proof ethanol in a round bottom flask. 5 mL of a 25 wt. % sodium methoxide in methanol solution was added to the mixture and the reaction was allowed to reflux for 72 hours under argon. The reactions were then cooled and concentrated. Flasks were then flooded with cold deionized water and the polymers filtered, washed with water twice.
more with water, collected, and dried under high vacuum to yield the sodium sulfonate salt precision polymers.

\( \text{SO}_3\text{Na}_8 \). FT-IR (ATR) \( \nu \text{ in cm}^{-1} \) 2923, 2853, 1686, 1436, 1169, 1046, 881, 842, 802, 721, 628.

\( \text{SO}_3\text{Na}_{20} – 33\text{K} \). FT-IR (ATR) \( \nu \text{ in cm}^{-1} \) 3424, 2916, 2849, 1688, 1466, 1436, 1167, 1139, 1051, 880, 842, 803, 723, 631.

\( \text{SO}_3\text{Na}_{20} – 19\text{K} \). FT-IR (ATR) \( \nu \text{ in cm}^{-1} \) 3440, 2916, 2849, 1693, 1467, 1168, 1049, 841, 802, 721, 631.

\( \text{SO}_3\text{Na}_{20} – 6\text{K} \). FT-IR (ATR) \( \nu \text{ in cm}^{-1} \) 3443, 2916, 2849, 1693, 1467, 1165, 1047, 719, 631.

\( \text{SO}_3\text{NaCo} \). FT-IR (ATR) \( \nu \text{ in cm}^{-1} \) 3433, 2917, 2850, 1688, 1466, 1170, 1047, 843, 802, 720, 631.

**Acidification**

Sodium sulfonate polymer samples (400 mg) were suspended in 5-10 mL of 200 proof ethanol and 5 mL of 12 molar hydrochloric acid was added dropwise while stirring. The mixtures were allowed to reflux for 24 hours under argon. After the reactions were cooled and concentrated. The flasks were then flooded with a cold 2 molar hydrochloric acid solution. Polymers were filtered, washed twice more with the acid solution, and the sulfonic acid polymers were collected and dried under vacuum.

\( \text{SO}_3\text{H}_8 \). FT-IR (ATR) \( \nu \text{ in cm}^{-1} \) 3381, 2923, 2853, 2337, 1646, 1466, 1147, 1034, 714, 629, 606.

\( \text{SO}_3\text{H}_{20} – 33\text{K} \). FT-IR (ATR) \( \nu \text{ in cm}^{-1} \) 2916, 2849, 1700, 1467, 1128, 1034, 851, 805, 719, 628.
SO₃H₂O – 19K. FT-IR (ATR) ν in cm⁻¹ 2917, 2849, 1700, 1467, 1128, 1031, 917, 719.

SO₃H₂O – 6K. FT-IR (ATR) ν in cm⁻¹ 2916, 2849, 1700, 1467, 1120, 1032, 804, 719.

SO₃HCo. FT-IR (ATR) ν in cm⁻¹ 2916, 2849, 1668, 1466, 1156, 1035, 912, 718.

**Results and Discussion**

Precise synthesis of protected ester monomers is the most intensive step of the entire route due to the stringent reaction conditions and reagent preparations. Previous literature reported a 30% yield of monomer (Figure 2-3). However, repeated attempts to reproduce this reaction were not successful to the extent of 30%. Thus, alternatives to the published synthesis were investigated. As noted in this chapter’s introduction, alternative syntheses were not successful, and the ethyl sulfonate ester appeared to be the simplest monomer in terms of synthetic steps and reagent preparations. Therefore, the ethyl protecting group was our starting point.

An evaluation of the published monomer reaction conditions was first conducted. Via carbon–carbon bond formation using lithium diisopropylamide (LDA), the optimum monomer synthesis is one-step using commercially available reagents. LDA is added to the ethyl methanesulfonate, resulting in deprotonation of the methyl directly attached to sulfur. The resulting carbanion can then perform a nucleophilic attack on the alkyl bromide of choice; repeating this process will give the α,ω-diene monomer.

Confirmation of ethyl methanesulfonate’s deprotonation was scrutinized first, as this is the initial mechanistic step of the reaction. Deprotonation indeed was occurring and confirmed by ¹H NMR. After ethyl methane sulfonate was deprotonated with LDA, the reaction was quenched with deuterium oxide. This process suppressed the methyl
peak after deuteration, thus confirming a proton exchange took place with LDA. Since deprotonation was occurring, the substitution reaction was being hindered by some other phenomenon.

Figure 2-3. Previously reported monomer synthesis published by Opper et al.\textsuperscript{55}

Initially, it was speculated that lithium cations from LDA were bound tightly to the deprotonated methane sulfonate species, preventing bromide displacement and resulting in low yields. However, low yields were observed when alternative counterions, such as potassium, and crown ethers, were employed in an attempt to free the carbanion for nucleophilic attack on the alkyl halide. The only plausible explanation left was leaving group ability. In fact, success was found when the bromide was abandoned for the triflate leaving group. The monomer yield was improved from 1-3\% to 40\% and 45\% simply by opting for a better leaving group. This new, higher yielding synthetic scheme is shown in Figure 2-4.

Triflates 1 and 2 were synthesized by the reaction of commercially available terminal alkene-containing alcohols with trifluoromethanesulfonic anhydride and pyridine. Reagent addition order is key: the reaction between trifluoromethanesulfonic anhydride and pyridine must take place before the alcohol is added, or side reactions
result in isomerization of the double bond; isomerization will lead to an imprecise material defeating the purpose of ADMET. The triflates were passed through silica plugs and following structural confirmation were kept inert before use in the next step.

![Chemical reaction diagram]

Figure 2-4. Precision sulfonic acid and sodium salt polymer synthetic route. The new protected sulfonic acid monomer route using triflate leaving groups is faster and results in higher yields.

Although monomer synthesis conditions were altered, LDA remained the base of choice. Purification and preparation of LDA starting materials is quite simple, and titration of the base is trivial. A substoichiometric amount (39 mmols) of LDA was used to deprotonate 40 mmols of ethyl methane sulfonate, followed by the addition of the appropriate triflate. Typically, excesses of such bases and reagents would be used to account for residual moisture and enhance yields. However, the use of excess of LDA and triflate reagents resulted in undetectable amounts of trialkylated monomers. These triene (trifunctional) species were in one case carried through purification and even
passed elemental and NMR analysis. Resulting polymers from these hidden triene species were crosslinked and consequently imprecise. Consequently, substoichiometric amounts of LDA and triflate were used to avoid triene species formation.

Care was also essential when adding triflates to deprotonated ethane methanesulfonate, which is in tetrahydrofuran (THF). The triflate must be added to the reaction in solution due to its reactivity, yet THF is the wrong solvent choice. Even at low temperature, the triflate was found to cationically ring-open THF, as observed by previous researchers.\textsuperscript{68} Dry heptane was instead found to be the ideal solvent for the triflate solution addition, but the temperature was held at -78 °C as a precaution due to the reactivity of triflates.

Monomers were purified via column chromatography and characterization was consistent with published results for the ester protected monomer. \textsuperscript{1}H NMR of monomer 4 is shown in Figure 2-5A. Clearly, the external olefins are intact and isomerization-free at 5.85-5.74 ppm (internal -CH=C-) and 5.01-4.91 (external -C=CH\textsubscript{2}). After exposure to ADMET conditions, where the monomers are refluxed in DCM along with Grubbs’ first generation catalyst, conversion to polymer is unquestionable. External double bonds are transformed into a single internal olefin signal which resonates at 5.39-5.34 ppm (internal -CH=CH-) with no end-groups detectible via NMR, an indication of high-polymer (Figure 2-5B). Gel permeation chromatography (GPC) results are consistent with this finding. Number-average molecular weights of up to 33,300 g/mol were achievable after 72 hours of polymerization, at which time solutions were highly viscous with stir bars were locked into place.
Figure 2-5. NMR spectra overlay of protected sulfonic acid synthetic route. A) $^1$H NMR of monomer 4, ethyl tricosa-1,22-diene-12-sulfonate in CDCl$_3$ B) $^1$H NMR of unsaturated ethyl protected polymer $\text{SO}_3\text{Et}_{21}\text{U} - 33\text{K}$ in CDCl$_3$ C) $^1$H NMR of completely saturated ethyl protected polymer $\text{SO}_3\text{Et}_{21} - 33\text{K}$ in CDCl$_3$.

Polymerizations in the bulk under high vacuum previously reached number-average molecular weights in the 20,000 g/mol range.$^{55}$ By refluxing sulfonate monomers in DCM, molecular weights were improved significantly proving the ability of a refluxing ADMET solution polymerization to provide high molecular weights.
Figure 2-6. Sulfonic polymer IR spectra overlay for each stage of the synthesis A) $\text{SO}_3\text{Et}_{21}\text{U} - 33K$, B) $\text{SO}_3\text{Et}_{21} - 33K$, C) $\text{SO}_3\text{Na}_{21} - 33K$, and D) $\text{SO}_3\text{H}_{21} - 33K$ representing each step of polymer transformation.

Catalytic hydrogenation was achieved with Wilkinson’s catalyst at 500 psi of hydrogen gas and proceeded to completion for each polymer. Complete olefin conversion is apparent for $\text{SO}_3\text{Et}_{21} - 33K$ in Figure 2-5C, where no signals are present between 5 and 6 ppm. However, to further substantiate quantitative saturation, Fourier
transform infrared spectroscopy (FT-IR) was performed. Figure 2-6A and 2-6B show IR spectra for \( \text{SO}_3\text{Et}_2\text{U} – 33K \) and \( \text{SO}_3\text{Et}_2 – 33K \), respectively. \( \text{SO}_3\text{Et}_2\text{U} – 33K \) exhibits an olefinic C-H wag at 967 cm\(^{-1}\), which is clearly not present in \( \text{SO}_3\text{Et}_2 – 33K \).

All polymers exhibit polyethylene-like character evidenced by \( \text{CH}_2 \) scissoring (1464 cm\(^{-1}\)) and \( \text{CH}_2 \) rocking (721 cm\(^{-1}\)) modes in the IR spectra. \( \text{SO}_3\text{Et}_2\text{U} – 33K \) and \( \text{SO}_3\text{Et}_2 – 33K \) each possess asymmetric O=S=O (1342 cm\(^{-1}\)) and symmetric O=S=O (1167 cm\(^{-1}\)) stretches. The ester protecting group in \( \text{SO}_3\text{Et}_2\text{U} – 33K \) and \( \text{SO}_3\text{Et}_2 – 33K \) is definitively represented at 1005 cm\(^{-1}\) and 912 cm\(^{-1}\), with both signals indicative of S-O-C stretches.

Initially, deprotection was successful using a sodium hydroxide/DMSO solution for ester hydrolysis. The ester-protected polymer was suspended in DMSO, a poor solvent for the organic polymer. Upon the addition of sodium hydroxide pellets at 80 °C, polymers were eventually reacted into solution as the esters were hydrolyzed. It was hypothesized that keeping the ester in solution ensured complete deprotection. This method was promising and worked well, but was abandoned due the difficulty of removing DMSO completely. Also, higher molecular weight species were not found to dissolve even after ester hydrolysis.

Alternatively, refluxing sodium methoxide and ethanol were found to deprotect all ester-protected polymers. Although the esters were not completely soluble, the reaction proceeded to completion. Sodium methoxide was chosen here, because a methoxide nucleophilic attack on the ether ester would produce methoxyethane, which boils at 7.4 °C and can be driven off easily at ~80 °C to force the reaction to complete. The reaction is essentially a Williamson ether synthesis, in which the sulfonate moieties of the
polymer are the leaving groups. After a 72-hour period, the sodium salt polymers were isolated. Figure 2-6C (SO$_3$Na$^{2-}$3K) contains no trace of sulfonate ester stretches at either 1005 cm$^{-1}$ or 912 cm$^{-1}$, strong evidence that this method results in complete deprotection. Further, SO$_3$Na$^{2-}$3K exhibits a distinct S-O stretch (631 cm$^{-1}$) which is common of organic sulfonate compounds. After drying at elevated temperatures (~100 °C) and high-vacuum, O-H stretching (3440 cm$^{-1}$) and O-H scissoring (1690 cm$^{-1}$) signals are present. These signals are not indicative of moisture, for which signals would be much broader. We believe these signals result from interactions between sulfonates and possible some sulfonic acids which may have already formed prior to acid treatment.

After sulfonate acidification with 12M hydrochloric acid in refluxing ethanol, the sulfonic acid polymer was isolated. SO$_3$Na$^{2-}$3K and SO$_3$H$^{2-}$3K show similar features via IR, but differ as follows (1) the S-O stretch associated with sulfonates (SO$_3^-$) is not present in the IR of the acid: (2) the sulfonic stretch at 1123 cm$^{-1}$ lacks the intensity of the sodium sulfonate stretch; (3) O-H stretching and O-H scissoring differ slightly from acid to sodium salt. The different intensities associated with the acid stretching and bending are similar to that of previous carboxylic and phosphonic precision systems where 1:1 acid interactions where found between lamellae. Based on this preliminary IR data, we expect the same 1:1 acid behavior but this will require X-ray analysis as did the previous studies. The greater intensity of the sodium sulfonate stretch is caused by the stronger dipole-ion interactions occurring, which are not present in the sulfonic acid samples.
Semicrystallinity is observed in the DSC thermograms of \( \text{SO}_3\text{Et21U} – 33\text{K} \), \( \text{SO}_3\text{Et21} – 33\text{K} \), and \( \text{SO}_3\text{H21} – 33\text{K} \) (Figure 2-7). Saturation of the internal olefins increases the \( T_m \) by 30 °C and the \( \Delta H_m \) by 17 J/g. Post-hydrogenation, such an increase is commonly observed and established in the literature for precision ADMET polymers. The lower melting points of unsaturated polymers are attributed to the existence of both cis and trans conformations, which disrupt crystallinity. \( \text{SO}_3\text{Na21} – 33\text{K} \) isolated after the alkali deprotection step does not appear semicrystalline and exhibits no melt. Acidification of the sulfonates (R-\( \text{SO}_3^- \)) to sulfonic acids (R-\( \text{SO}_3\text{H} \)) results in reversion to the previous crystalline nature but higher in melting point than the ethyl esters (65 °C for \( \text{SO}_3\text{H21-33K} \) compared to 36 °C for \( \text{SO}_3\text{Et21-33K} \)).

Figure 2-7. DSC thermogram overlay of \( \text{SO}_3\text{Et21U} – 33\text{K} \), \( \text{SO}_3\text{Et21} – 33\text{K} \), \( \text{SO}_3\text{Na21} – 33\text{K} \), and \( \text{SO}_3\text{H21} – 33\text{K} \) representing each step of polymer transformation. Samples were heated/cooled at 10 °C/min. Vertical scale is offset for clarity.
Similar salt-to-acid behavior was noted by Baughman. Precision acrylic acid copolymers with a carboxylic acid placed every 21st melt at 45°C, while the corresponding zinc carboxylate copolymer did not melt before decomposition.35

![Graph A](image1.png)

**Figure 2-8.** DSC comparison of sodium sulfonate polymers vs. sulfonic acid polymers A) DSC thermogram overlay of sodium sulfonate polymers B) DSC thermogram overlay of sulfonic acid polymers. Samples were heated/ cooled at 10 °C/min. Vertical scales are shifted for clarity.

As mentioned above, sodium sulfonate polymers (all carbon spacings, random and precise) do not exhibit semicrystallinity (Figure 2-8A). However, upon acidification to the acid analog of each sample, crystallinity in longer run-length samples is regained. This coincides exactly with trends displayed by precision carboxylic and carboxylate samples prepared and characterized by Baughman and Seitz. The carboxylics have layered structures with hydrogen bonds between the carboxyl groups on adjacent layers; while the anions have ordered ionic cluster morphologies. These results suggest that the sulfonic polymers exhibit the same layered acid and ordered ionic cluster morphologies.35, 37

Each polymer containing a sulfonic acid on every 21st carbon displays a fairly clear melt (Figure 2-8B). As molecular weight is increased, melting temperatures are
increased slightly (SO$_3$H$_{21} - 6K$<SO$_3$H$_{21} - 33K$<SO$_3$H$_{21} - 33K$). The random copolymer SO$_3$HCo containing an identical carbon to acid ratio melts over a broad range, indicating precision has a profound effect on the crystalline nature of the materials. SO$_3$H9 exhibits no distinct thermal transitions because the short run-lengths between acid groups prevent crystallization.

Figure 2-9. TGA comparison of sodium sulfonate polymers vs. sulfonic acid polymers. A) TGA thermogram overlay of sodium sulfonate polymers. B) TGA thermogram overlay of sulfonic acid polymers. Samples were heated at 10 °C/min.

Thermogravimetric analysis of all samples provides evidence of thermal stability to temperatures of around 200 °C. Sodium sulfonate (Figure 2-9A) and sulfonic acid (Figure 2-9B) polymer samples appear to decompose within the same range as other sulfonated materials (~280 °C).$^{72}$ The initial weight losses correspond to desulfonation, known to occur first in sulfonated materials, followed by the degradation of the polyethylene backbone, typical in PE and other ADMET analogs.

Most of these precision sodium salts are clearly retaining more mass than their acid counterparts above 400 °C, indicating the formation of ionic by-products from the sodium sulfonate. All samples exhibit good thermal stability and do not begin significant
degradation until above 200 °C, a temperature below which most potential applications will take place.

**Conclusion**

For the first time, precision sulfonic acid polymers and precision sodium sulfonate polymers have been synthesized. This completes the precision acid library containing precision carboxylic, phosphonic, boronic, and now sulfonic acids. During the preparation process of these new precision acid materials, the monomer synthesis was significantly improved: decreased reaction time (hours instead of days) and higher yield. If the precision sulfonic acids are found to be applicable, such synthetic improvements will make production more commercially feasible.

Quantitative deprotection utilizing sodium methoxide provided precision sodium sulfonates, which thermal data suggest are amorphous. On the contrary, sulfonate protonation leads to semicrystallinity for lower concentration precision acids. IR and thermal data provide substantial confirmation of deprotection and suggest different morphologies for acid and basic materials. Comparing the DSC data for these materials and other precision acids, it is likely that the sulfonic materials form layers in the acid form and well-defined clusters in the anion form. These highly ordered, strong-acid materials may in fact, possess better conductivity than existing commercial materials due to their precise nature.

Further characterization, including solid state NMR and X-ray scattering, of these newly synthesized structures will help clarify their properties and possible applications. Most important, conductivity will be investigated to determine viability for conducting applications.
CHAPTER 3
SULFITES

Introduction

This chapter reports the synthesis and characterization of unsaturated polymers containing precisely placed sulfite groups within a polyethylene-like backbone. Polymers containing a sulfite after every 8th, 14th, and 20th carbon are displayed in Figure 3-1. These polysulfites are new, not just in terms of precision, but to polymer chemistry in general. To the best of our knowledge, even conventional polymerization techniques have not been used to produce such structures. Further, these are the first polymers which possess an incorporated oxidized sulfur functionality, as opposed to the pendent moieties typically produced by our research group.

Figure 3-1. Sulfite-containing polymers synthesized with a sulfite precisely placed every 8th, 14th, and 20th carbon.

Recently, our group has turned to precision placement of more polar functionalities including carboxylic acids, phosphonic acids, sulfonates, ionomers, and...
and now even sulfonic acids mentioned in Chapter 2. Incorporation of polar functionalities into and on polyethylene backbones at precisely known spacings allows for sophisticated structures, new morphologies, and potential applications (e.g., ion transport). In the present work, our attention has shifted to sulfite ester incorporation. Organic sulfites (sulfite esters) are polar oxidized sulfur groups similar to sulfurous acid, and have been used as synthetic intermediates, insecticides, plasticizers,\textsuperscript{74, 75} oxidative inhibitor additives,\textsuperscript{76} and even for lithium ion battery applications.\textsuperscript{77}

The intention of this study is to incorporate the sulfite functionality into the polyolefin backbone, essentially creating a sulfurous acid ester polyolefin, and to investigate the effect of sulfite concentration on properties and morphology. Exploiting the distinctive precise nature of ADMET, the sulfite concentration effect is an isolated variable from which morphological trends may be elucidated.

**Experimental**

**Materials and Instrumentation**

All chemicals and materials were used as received and purchased through Sigma Aldrich unless otherwise stated. Dry solvents were obtained from a solvent purification system. Grubbs’ 1st generation catalyst was graciously donated by Materia, Inc. and used as received. Flash chromatography was performed using SiliCycle SiliaFlash® P60, 40-63 μm, 60 Å silica. \textsuperscript{1}H NMR and \textsuperscript{13}C NMR was performed on a Varian Mercury-300 NMR Spectrometer using VNMRJ software. IR spectroscopy was performed on a PerkinElmer FT-IR Spectrum One with ATR attachment using Spectrum Software for data analysis. Molecular weights were obtained in THF at 40 °C relative to polystyrene standards using an Agilent 1100 GPC with a refractive index detector. Thermogravimetric Analysis (TGA) was performed on a TA Instruments Q5000 using a
temperature ramp of 10 °C/min under nitrogen atmosphere. Differential Scanning Calorimetry (DSC) was performed on a TA Instruments Q1000 DSC. DSC samples were equilibrated at -80 °C and subsequently heated at 10 °C/min until final temperature was reached. Cooling was also performed at 10 °C/min to -80 °C. Three heat/cool cycles were performed for each sample. Samples for X-ray scattering were prepared by annealing under vacuum at 80°C for 3 days to remove any residual solvent or moisture. Samples were loaded into capillary tubes which were then flame-sealed and aged for 3 days at room temperature. X-ray scattering was performed at the Multiangle X-ray Scattering (MAXS) Facility at the University of Pennsylvania by Trigg and Winey. Details of the MAXS Facility can be found in Buitrago et. al. Data reduction and analysis were performed using Datasqueeze software.

Alcohol Synthesis

According to a literature procedure, sodium acetate (2.0 eq.) was dissolved in DMF in a round-bottom flask at room temperature. The appropriate alkenyl bromide was added and subsequently the temperature was raised to 80 °C for 14 hours with stirring. The mixture was extracted twice with diethyl ether and washed with water. Ether was then evaporated, 1M sodium hydroxide and methanol was added and stirred 2 hours. The reaction was extracted with ether and the organic layer was dried over MgSO₄, filtered, and the solvent removed under reduced pressure to yield a colorless oil. Alcohols were purified by column chromatography.

Pent-4-en-1-ol (7). 5.0 g (33.6 mmols) of 5-bromo-1-pentene, 5.5 g (67.1 mmols) of NaOAc, 70 mL of DMF. 70 mL of 1 M NaOH and 400 mL of MeOH were added for hydrolysis; Yield = 76%; Rf = 0.50 (dichloromethane); ¹H NMR (300 MHz, CDCl₃) δ 5.89
(m, 1H), 5.01 (m, 2H), 3.65 (t, 2H), 2.68 (q, 2H), 2.16 (p, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 137.4, 115.3, 61.8, 31.2, 29.9.

**Oct-7-en-1-ol (8).** 4.5 g (23.5 mmols) of 8-bromo-1-octene, 3.86 g (47.0 mmols) of NaOAc, 50 mL of DMF. 50 mL of 1 M NaOH and 400 mL of MeOH were added for hydrolysis; Yield = 86%; R\(f\) = 0.32 (hexanes:EtOAc, 5:2); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.83 (m, 1H), 4.98 (m, 2H), 3.65 (t, 2H), 2.08 (q, 2H), 1.57 (br, 8H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 139.1, 114.4, 62.8, 33.8, 32.3, 28.9, 25.7.

**Monomer Synthesis**

Following protocol outlined by Kiaset et. al.,\(^8\) anhydrous sodium sulfite (1.5 eq.) and dry thionyl chloride (1.5 eq.) were added to a flame-dried round-bottom flask under argon purge. A solution of the appropriate alkenyl alcohol in dichloromethane (1 mmol/5 mL) was added dropwise to the flask and stirred at room temperature for 2 hours. Upon completion observed by TLC, the reaction mixture was filtered and washed with dichloromethane. The solids were discarded, and the filtrate was collected and condensed to yield the crude dialkenylsulfite. The crude products were purified by column chromatography.

**Di(pen-4-en-1-yl) sulfite (10).** 4.39 g (34.8 mmols, 1.5 eq.) \(\text{Na}_2\text{SO}_3\), 2.53 mL (34.8 mmols, 1.5 eq.) SOCl\(_2\), 2.0 g (23.2 mmols) pent-4-en-1-ol (7), 80 mL DCM; Yield = 84% light yellow oil, R\(f\) = 0.32 (hexane:DCM, 2:1); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.78 (m, 2H), 5.02 (m, 4H), 3.98 (m, 4H), 2.15 (q, 4H), 1.78 (p, 4H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 137.2, 115.7, 61.6, 29.9, 28.7. FT-IR (ATR) \(\nu\) in cm\(^{-1}\) 3078, 2929, 1740, 1641, 1465, 1370, 1215, 945, 779, 740. HRMS (ESI) (m/z): [M+H]\(^+\) calcd for C\(_{10}\)H\(_{18}\)O\(_3\)S 219.1049; found 219.1005. Elemental Analysis: calcd for C\(_{10}\)H\(_{18}\)O\(_3\)S, C: 55.02, H: 8.31, N: 0.00 S: 14.69; found: C: 55.15, H: 8.15, N: 0.00, S: 14.64.
**Bis(oct-7-en-1-yl) sulfite (11).** 3.7 g (29.2 mmols, 1.5 eq.) Na$_2$SO$_3$, 2.1 mL (29.2 mmols, 1.5 eq.) SOCl$_2$, 2.5 g (19.5 mmols) oct-4-en-1-ol (8), 60 mL DCM; Yield = 74% light yellow oil, $R_f = 0.21$ (hexane:DCM, 2:1); $^1$H NMR (300 MHz, CDCl$_3$) δ 5.79 (m, 2H), 4.95 (m, 4H), 3.96 (m, 4H), 2.04 (q, 4H), 1.68 (m, 4H), 1.36 (br, 12H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 138.9, 114.4, 62.4, 33.7, 29.6, 28.8, 28.7, 25.7. FT-IR (ATR) ν in cm$^{-1}$ 3078, 2928, 1741, 1641, 1465, 1372, 1214, 945, 778, 741. HRMS (ESI) ($m/z$): [M+H]$^+$ calcd for C$_{16}$H$_{30}$O$_3$S 320.2254; found 320.2248. Elemental Analysis: calcd for C$_{16}$H$_{30}$O$_3$S, C: 63.53, H: 10.00, N: 0.00 S: 10.60; found: C: 63.76, H: 10.01, N: 0.00, S: 10.43.

**Bis(undec-10-en-1-yl) sulfite (12).** 22.2 g (176 mmols, 1.5 eq.) Na$_2$SO$_3$, 12.8 mL (176 mmols, 1.5 eq.) SOCl$_2$, 20 g (117 mmols) undec-10-en-1-ol (9), 400 mL DCM; Yield = 54% light yellow oil, $R_f = 0.22$ (hexane:DCM, 2:1); $^1$H NMR (300 MHz, CDCl$_3$) δ 5.80 (m, 2H), 4.95 (m, 4H), 3.96 (m, 4H), 2.05 (q, 4H), 1.67 (m, 4H), 1.29 (br, 24H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 139.3, 114.3, 62.5, 34.0, 29.7, 29.6, 29.4, 29.3, 29.1, 26.0. FT-IR (ATR) ν in cm$^{-1}$ 3078, 2928, 2857, 1641, 1466, 1212, 992, 939, 908, 722. HRMS (ESI) ($m/z$): [M+H]$^+$ calcd for C$_{22}$H$_{42}$O$_3$S 387.2927; found 387.2883. Elemental Analysis: calcd for C$_{22}$H$_{42}$O$_3$S, C: 68.34, H: 10.90, N: 0.00 S: 8.13; found: C: 68.60, H: 10.96, N: 0.00, S: 8.05.

**Polymerization Procedures**

The liquid α,ω-dienesulfite monomer was added to a flame-dried argon purged Schlenk tube. The monomer was degassed with a steady flow of bubbling argon at room temperature for 24 hours prior to catalyst addition. After degassing, 1 mol% Grubbs’ 1st generation catalyst was added to the monomer, and the vessel was subjected to vacuum (~10^-3 torr) with stirring. The Schlenk tube was then lowered into
an oil bath maintained at 50 °C. After three days, the reaction mixture was dissolved in
10 mL of toluene containing 1% (v/v) of ethyl vinyl ether. The polymer solution was then
slowly precipitated into ice-cold methanol. The polymer was filtered, collected and dried
before characterization.

Polymerization of di(pen-4-en-1-yl) sulfite (SO₃8U). ¹H NMR (300 MHz, CDCl₃) δ 5.43 (m, 2H), 3.93 (m, 4H), 2.08 (q, 4H), 1.73 (p, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 129.8, 129.3, 61.6, 29.4, 29.3, 28.6, 23.4. FT-IR (ATR) ν in cm⁻¹ 2942, 2848, 1447, 1384, 1202, 905, 712. GPC data (THF vs. polystyrene standards): Mn = 7,300
g/mol, Mw = 12,800 g/mol, (PDI = 1.75).

Polymerization of di(oct-7-en-1-yl) sulfite (SO₃14U). ¹H NMR (300 MHz, CDCl₃) δ 5.38 (m, 2H), 3.93 (m, 4H), 1.96 (q, 4H), 1.67 (p, 4H), 1.34 (br, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 129.6, 61.6, 31.79, 28.8, 28.7, 28.0, 25.0. FT-IR (ATR) ν in cm⁻¹ 2930, 2856, 1740, 1466, 1376, 1210, 968, 708. GPC data (THF vs. polystyrene
standards): Mn = 7,600 g/mol, Mw = 19,100 g/mol, (PDI = 2.51).

Polymerization of di(undec-10-en-1-yl) sulfite (SO₃20U). ¹H NMR (300 MHz, CDCl₃) δ 5.38 (m, 2H), 3.95 (m, 4H), 1.97 (q, 4H), 1.67 (p, 4H), 1.28 (br, 24H). ¹³C NMR (75 MHz, CDCl₃) δ 130.4, 62.4, 32.7, 29.7, 29.6, 29.5, 29.4, 29.2, 25.8. FT-IR (ATR) ν in cm⁻¹ 3081, 2923, 2853, 1643, 1468, 1375, 1205, 917, 775, 721. GPC data (THF vs.
polystyrene standards): Mn = 21,400, Mw = 40,500 (PDI = 1.89).

Results and Discussion

The synthesis of precision sulfite monomers is easy, accomplished in two steps.
Symmetrical α,ω-diene sulfite-containing monomers 10,11, and 12 in Figure 3-2 of
varying lengths were synthesized from an appropriate alkenyl alcohol and thionyl
chloride along with sodium sulfite in dichloromethane. Synthesis of the starting alcohols
7, 8, and 9 was dictated by the commercial availability of each. Alcohols 7 and 8 were synthesized by acetoxylation of the respective alkenyl bromides 5 and 6, followed by hydrolysis of the acetate, according to a literature procedure, while 9 was purchased directly. Alcohols were purified via column chromatography before use to ensure that no mono-olefin or mixed-length alkyl species would be present in symmetrical monomers 10, 11, and 12. Monomers were synthesized according to a mild literature procedure by the reaction of alcohols 7, 8, and 9 with thionyl chloride and sodium sulfite in dichloromethane at room temperature. The technique varies somewhat from typical procedures that use harsher conditions such as refluxing thionyl chloride. Milder methods prevent alkene side reactions, because such byproducts would be carried through to polymerization, ultimately inhibiting polymerization reactions and reducing molecular weights.

![Chemical diagram](image)

Figure 3-3. Synthesis of precision poly(unsaturated sulfites) with known spacing lengths via ADMET. $SO_3$ denotes the sulfite group and the following number denotes carbon spacing. For example, $SO_38$ corresponds to a sulfite precisely located after 8 carbons. U denotes the unsaturation.
Monomers were all purified by column chromatography and purity was confirmed by mass spectrometry, elemental analysis, and NMR before proceeding to polymerization. The $^1$H NMR spectrum of monomer 11 in Figure 3-3A shows the olefin resonances at around 5.0 ppm (external olefin) and 5.8 ppm (internal olefin). After polymerization using common ADMET conditions (Grubb's 1st generation catalyst and high vacuum at 50 °C), conversion to polymer $\text{SO}_3\text{14}$ is apparent in Figure 3-3B, which shows only the internal olefins at 5.4 ppm; no end-group olefins are observed. The molecular weight and thermal data for each polymerization are summarized in Table 3-1.

![Diagram](image)

Figure 3-3. A) Sulfite monomer 11 $^1$H NMR with labeled peaks. B) Polysulfite $\text{SO}_3\text{14}$ $^1$H NMR after polymerization displaying no detectable end-groups from sulfite monomer 11.
Number-average molecular weights ranged from 7,300 to 21,400 g/mol for the poly(unsaturated sulfites), with the lower-concentration sulfite $SO_3^{20}$ possessing the highest molecular weight. We suspect that proximity of the sulfite functionality to the catalysis site may be affecting the mechanism and somewhat inhibiting ADMET reactions for monomers with short methylene spacer lengths. Considering the thermal data for the same polymers (Table 3-1), a decrease in sulfite concentration leads to a noticeable increase in crystallinity. As sulfite content is increased from 63 per 500 carbons ($SO_3^{8}$) to 36 per 500 carbons ($SO_3^{14}$) polymers are no longer amorphous, but are low melting semicrystalline substances. However, increasing the melting temperature above room temperature requires a smaller sulfite to carbon ratio ($SO_3^{20}$, 25 sulfites per 500 carbons). Nevertheless, the melting temperatures and heats of fusion are slightly lower than those of a 100% alkene-containing carbon backbone, presumably due to the rotational flexibility accompanying sulfite incorporation. All three sulfite polymers display thermal degradation temperatures between 225 and 310 °C at 5% decomposition (Figure 3-4). Increasing the carbon content not only increases the degree of crystallinity, but also improves the thermal stability of the sulfite-containing polymers.

<table>
<thead>
<tr>
<th>Sulfite Polymer</th>
<th>$M_n \times 10^3$ (g/mol)$^a$</th>
<th>Sulfite per 500 carbons</th>
<th>Tm (°C)</th>
<th>$\Delta$Hm (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SO_3^{8}$U</td>
<td>7.3 (1.75)</td>
<td>63</td>
<td>Amorphous</td>
<td>-</td>
</tr>
<tr>
<td>$SO_3^{14}$U</td>
<td>7.6 (2.51)</td>
<td>36</td>
<td>7</td>
<td>49</td>
</tr>
<tr>
<td>$SO_3^{20}$U</td>
<td>21.4 (1.89)</td>
<td>25</td>
<td>37</td>
<td>63</td>
</tr>
</tbody>
</table>

$^a$Weight-average molecular weight obtained by GPC using THF at 40 °C compared to polystyrene standards (g/mol).

$^b$Polydispersity index ($M_w/M_n$).
In addition to thermal analysis, X-ray scattering provided insight on sulfite-sulfite interactions and how crystallinity is affected by sulfite functionalization. The following data and analysis was provided by a collaboration with Professor Karen Winey’s research group at the University of Pennsylvania. X-ray scattering data for SO$_3$20U, SO$_3$14U, and SO$_3$8U are presented in Figure 3-5, along with ADMET PE for comparison. The X-ray scattering confirms SO$_3$20 is semicrystalline at room temperature, while SO$_3$14 and SO$_3$8 are amorphous (note, scattering experiments were performed at room temperature, above the $T_m$ of SO$_3$14 and SO$_3$8). Clearly, increased sulfite incorporation disrupts chain order and crystallization while longer methylene spacings are necessary for semicrystallinity. SO$_3$20 exhibits a peak at $q = 0.5$ nm$^{-1}$ with
an intensity of approximately 13 nm indicating smaller crystallites than those found in PE synthesized by ADMET (q = 0.17 nm\(^{-1}\), l \(\sim\) 37 nm). \textbf{SO}\textsubscript{20} also exhibits a sharp peak at \(q = 13.9\) nm\(^{-1}\), which provides additional evidence that a well-ordered crystalline structure exists. While the PE by ADMET exhibits scattering indicative of a typical orthorhombic structure, \textbf{SO}\textsubscript{20} peaks at \(q > 13\) nm\(^{-1}\) are quite different from PE.

Figure 3-5. X-ray scattering of \textbf{SO}\textsubscript{8}, \textbf{SO}\textsubscript{14}, \textbf{SO}\textsubscript{20}, and ADMET PE collected at room temperature. Data and analysis provided by Professor Karen Winey's research group at the University of Pennsylvania. Inter-crystallite correlation peaks are present at low \(q\) for PE and \textbf{SO}\textsubscript{20} only. Sulfite correlation peaks are indicated with inverted triangles. Crystal diffraction peaks are present at high \(q\) for PE and \textbf{SO}\textsubscript{20} only. Data is rescaled and shifted vertically for clarity.

Peaks at 13.9 nm\(^{-1}\) and 16.6 nm\(^{-1}\) are both evidence of a monoclinic PE-like crystal structure.\textsuperscript{82} The less intense feature at approximately 15 nm\(^{-1}\) may indicate the co-existence of an orthorhombic crystal structure. No features are present at low \(q\) values for \textbf{SO}\textsubscript{8} and \textbf{SO}\textsubscript{14} and only broad peaks at 14 nm\(^{-1}\) exist. This data would
corroborate thermal evidence of amorphous morphologies for $SO_{38}$ and $SO_{314}$ at room temperature.

The inverted triangles in Figure 3-5 indicate the sulfite correlation peaks. Polymer $SO_{320}$ has three peaks at relative positions $q^* : 2q^* : 3q^*$, indicating 1-dimensional periodicity. This suggests that the sulfite groups form layers within the crystal structure, driven by favorable polar interactions between precisely spaced sulfite groups. The periodicity of this layered structure is 1.9 nm, while the calculated all-trans length of the polymer repeat unit is 2.8 nm. This difference illustrates the sulfite layers are, in fact, tilted relative to the chain axis, in contrast to precise poly(ethylene-co-phosphonic acid) wherein the acid layers are perpendicular to the alkyl spacers. These layered morphologies have previously been observed in longer run-length semicrystalline precision polymers as well.

The shorter run-length $SO_{38}$ and $SO_{314}$ show single broad peaks indicating disordered or liquid-like arrangements of sulfite groups, either isolated or as small aggregates of the functional groups. Precise poly(ethylene-co-1-methylimidazolium bromide), precise poly(ethylene-co-acrylic acid), and precise poly(ethylene-co-phosphonic acid) display similar morphological trends. These polymers contain short hydrocarbon segments and are amorphous regardless of precision, because the higher functionalization impedes polyethylene crystallization.

**Conclusion**

In summary, we have demonstrated the ability of ADMET to provide unique functionalized polyolefins containing sulfite functionalities at precisely spaced intervals. By systematically and precisely altering the run-length between sulfite groups, the sulfite effect was isolated from conventional polymerization defects allowing for further
investigation. Higher carbon content poly(unsaturated sulfites) possess greater thermal stability and are semicrystalline, whereas increasing the concentration of sulfite moieties results in an amorphous polymer. X-ray scattering data for the semicrystalline polymer supports the existence of sulfite layers and interactions similar to those of other precision materials synthesized via ADMET. This study demonstrates and reiterates ADMET’s practicality in producing diverse structures with morphological trends not observed using other polymerization techniques.
CHAPTER 4
SULFONES

Introduction

For almost three decades ADMET polymerization has created functionalized polymers with distinct well-defined architectures not possible by other techniques.\(^2, 84, 85\) Polar functionality incorporation into non-polar backbones has expanded to include a variety of materials such as precise phosphonic acids,\(^41\) carboxylic acids,\(^35\) halogens,\(^86,\) \(^87\) alcohols,\(^26, 88\) and many others.\(^89\) Recently, oxidized sulfur functionalities have received attention. Sulfonate esters,\(^33, 55\) sulfonic acids, sodium salts, and sulfites\(^90\) have been made. Our sulfone work started when sulfones were used as protection for thiol-Michael produced monomers, preventing premature catalyst death by sulfur chelation and others side reactions by van Hensbergen et al.\(^49\) Sulfone-ADMET compatibility led us to produce linear, aliphatic polysulfones.

The term polysulfone is typically synonymous with aryl sulfones. Commercial polysulfones are known for their excellent chemical and thermal stability. Possessing a superior service temperature range (150-200 °C) and good mechanical properties, these thermoplastic materials find many high-end applications in the aerospace, medical, and automotive industries, as well as in consumer goods and machine parts.\(^91\) Faye et al. used ADMET to study the crystalline nature of aromatic etherethersulfone copolymers.\(^92\) Polysulfones often are used when polycarbonates and other engineering plastics cannot withstand conditions required for use. Sulfone functionalities add a polar feature to polymers and, unlike polyesters, polysulfones are resistant to acid and base hydrolysis.\(^93\) Random aliphatic polysulfones are not as prevalent as their amorphous, rigid-rod, aromatic counterparts. Aliphatic sulfone copolymers are produced through
free-radical polymerization of SO$_2$ and olefins, and the resulting polymers are stable to temperatures of around 200-225 °C. However, applications are limited due to the cost of production and structural defects, such as uncontrollable branching incurred during free-radical polymerization. On the other hand, ADMET polymerization yields precise structures, which may produce a more viable material. Polymers synthesized via ADMET exhibit better crystalline and thermal properties as a result. We now have precise aliphatic polysulfones which exhibit a unique melt pattern compared with all other precise polymers we have produced in 25 years.

\[
\text{Figure 4-1. Sulfone-containing polymer structures synthesized with a sulfone placed after every 8th, 14th, and 20th methylene unit.}
\]

This paper describes the application of ADMET precision to polysulfone chemistry. We report the synthesis and characterization of precisely spaced sulfone functionalized polyolefins to examine the effect of sulfone concentration on polymer morphology. Figure 4-1 displays the structures of the three target polymers of this investigation, with sulfone functionalities precisely placed after every 8th, 14th, and 20th carbon. These three structures were chosen to study polyethylene-like character
exhibited by high-sulfone concentration materials with precision not possible using free-radical polymerization.

**Experimental**

**Materials and Instrumentation**

All chemicals, materials, and solvents were purchased through Sigma Aldrich unless otherwise noted. Dry solvents where obtained from a solvent purification system when needed. Monomers were purified using SiliCycle SiliaFlash® P60, 40-63 μm, 60 Å silica. Grubbs’ 1st generation catalyst was donated by Materia, Inc. and used as received.

IR spectroscopy and data analysis was performed using a PerkinElmer FTIR Spectrum One with ATR attachment and Spectrum Software. A Varian Mercury-300 NMR Spectrometer was used to obtain both ¹H NMR and ¹³C NMR spectra using VNMRJ software. Due to the insolubility of polymers in most solvents, DOSY NMR was performed on a Varian-500 NMR Spectrometer in deuterated tetrachloroethane at 25 °C using a procedure similar to that outlined by Chen et al.⁹⁵ Elemental analysis was performed by Atlantic Microlabs and mass spectroscopy was performed by the Mass Spec labs in the University of Florida’s Chemistry Department.

A TA Instruments Q5000 was used for Thermogravimetric Analysis (TGA) at a heating rate of 10 °C/min under nitrogen. DSC was performed using a TA Instruments Q2000 calibrated for temperature transitions and enthalpy changes using an indium standard. All measurements were performed under helium purge. In the DSC, samples were heated to above the melting point and equilibrated for 5 minutes to erase thermal history. They were then cooled to -80°C followed by a second heating to above the
melting point. All heating and cooling rates were 10°C/min. The DSC profile was recorded for the second heating ramp.

For X-ray scattering analysis, samples were loaded into capillary tubes and dried under vacuum above the melting point for 2-4 hours to remove any residual moisture or solvent. The samples were slowly cooled and then removed from vacuum and sealed with hot glue inside a glove box filled with nitrogen to prevent any exposure to atmospheric moisture. X-ray scattering was performed at the Multiangle X-ray Scattering (MAXS) Facility at the University of Pennsylvania by Winey and Trigg. Details of the MAXS Facility can be found in Buitrago et al. Data reduction and analysis were performed using the Datasqueeze software. X-ray curves were re-scaled such that all intensities were equal at \( q = 10.0 \text{ nm}^{-1} \), where no peaks are present, so that peak intensities could be compared.

**Synthetic Procedures**

**Bis(undec-10-en-1-yl)sulfide (16).** According to a literature procedure, 105 g (0.437 mols, 1.47 eq.) sodium sulfide nonahydrate was dissolved in 95 mL of 200 proof ethanol (~0.2 mL/mmol of sodium sulfide nonahydrate) in a 500 mL round bottom flask. Then, 70 g of 11-bromo-1-undecene (0.300 mols, 1.0 eq.) was added and the reaction was refluxed for 72 hours. After the allowed time, the flask was flooded with distilled water, stirred, and the product was allowed to separate from the aqueous layer. The organic layer was removed and washed twice with a 5% sodium hydroxide solution, and once with water. The product was isolated as a slightly yellow viscous oil, dried under vacuum and used without further purification. Yield: 50.52 g, 99.5%. 

\(^1\text{H NMR (300 MHz, CDCl}_3\): } \delta \text{ (ppm) 5.70-5.84 (m, 2H)}, 4.87-4.99 (m, 4H), 2.49 (t, 4H), 1.96-2.03 (m, 4H), 1.74-1.84 (m, 4H), 1.17-1.43 (m, 24H); \text{ \textsuperscript{13}C NMR (75 MHz, CDCl}_3\): } \delta 139.3, 114.3, 77.6,
77.2, 76.8, 34.0, 32.4, 29.9, 29.7, 29.5, 29.3, 29.2, 28.9. Elemental Analysis: calcd for C_{22}H_{42}S, C: 78.03, H: 12.50, N: 0.00, S: 9.47; found C: 78.19, H: 12.55, N: 0.00, S: 9.58.

The procedure described above was used, with pertinent alkenyl bromide, for the synthesis of both bis(oct-7-en-1-yl)sulfide and bis(pent-4-en-1-yl)sulfide as well. All sulfides were consistent with published spectra.

**Bis(oct-7-en-1-yl)sulfide (17).** Yield: 80%. \(^1\)H NMR (300 MHz, CDCl\(_3\)): δ (ppm) 5.73-5.86 (m, 2H), 4.91-5.02 (m, 4H), 2.49 (t, 4H), 1.99-2.07 (m, 4H), 1.57-1.62 (m, 4H), 1.26-1.43 (m, 12H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ (ppm) 139.2, 114.4, 77.7, 77.2, 76.8, 33.9, 32.3, 29.9, 29.0, 28.9. Elemental Analysis: calcd for C\(_{16}\)H\(_{30}\)S, C: 75.52, H: 11.88, N: 0.00, S: 12.60; found C: 75.49, H: 11.84, N: 0.00, S: 12.67.

**Bis(pent-4-en-1-yl)sulfide (18).** Yield 85%. \(^1\)H NMR (CDCl\(_3\)): δ (ppm) 5.77-5.87 (m, 2H), 4.94-5.08 (m, 4H), 2.49-2.57 (t, 4H), 2.17-2.25 (q, 4H), 1.81-1.76 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)): δ (ppm) 29.03, 31.63, 33.06, 115.31, 138.03. Elemental Analysis: calcd for C\(_{10}\)H\(_{18}\)S, C: 70.52, H: 10.65, N: 0.00, S: 18.82; found C: 70.49, H: 10.70, N: 0.00, S: 18.73.

**Monomer Synthesis**

**Bis(undec-10-en-1-yl)sulfone (19).** To a 50 mL round bottom flask 15.0 g (0.044 mols) of bis(undec-10-en-1-yl)sulfide, 10 mL of distilled water, and 1.5 g (0.1 eq.) of hexachlorophosphazene were added and stirred at 0 °C. A 13 mL (0.130 mols) aliquot of 30% hydrogen peroxide was added dropwise and the reaction was allowed to warm to room temperature. The reaction was stirred for 30 mins, at which point a white solid had formed. The reaction was extracted with ethyl acetate (4x25 mL). The organic layer was dried over magnesium sulfate before removal of the solvent. The crude
sulfone was recrystallized from ethanol and subsequently passed through a silica plug using a hexanes:ethyl acetate (9:1) eluent. Yield: 15.77 g, 96%. $^1$H NMR (300 MHz, CDCl3): δ (ppm) 5.70-5.84 (m, 2H), 4.87-4.99 (m, 4H), 2.89 (t, 4H), 1.96-2.03 (m, 4H), 1.74-1.84 (m, 4H), 1.17-1.43 (m, 24H); $^{13}$C NMR (75 MHz, CDCl3) δ (ppm) 139.4, 114.4, 77.7, 77.2, 76.8, 52.9, 34.0, 29.6, 29.4, 29.3, 29.1, 28.7, 22.2. HRMS (ESI) (m/z): (M+H)$^+$ calcd for C$_{22}$H$_{42}$O$_2$S 371.2978; found 371.2983. Elemental Analysis: calcd for C$_{22}$H$_{42}$O$_2$S, C: 71.29, H: 11.42, N: 0.00, S: 8.65; found C: 71.58, H: 11.48, N: 0.00, S: 8.50. The procedure described above was used, with pertinent sulfide, for the synthesis of both bis(oct-7-en-1-yl)sulfone and bis(pent-4-en-1-yl)sulfone as well.

**Bis(oct-7-en-1-yl)sulfone (20).** Yield 79%. $^1$H NMR (300 MHz, CDCl3): δ (ppm) 5.68-5.82 (m, 2H), 4.89-4.99 (m, 4H), 2.91 (t, 4H), 1.97-2.07 (m, 4H), 1.74-1.85 (m, 4H), 1.27-1.46 (m, 12H); $^{13}$C NMR (75 MHz, DMSO) δ (ppm) 139.4, 115.4, 52.2, 40.7, 40.5, 40.2, 39.9, 39.6, 39.4, 33.7, 28.7, 28.2, 21.9. HRMS (ESI) (m/z): (M+H)$^+$ calcd for C$_{16}$H$_{30}$O$_2$S 287.2039; found 287.2037. Elemental Analysis: calcd for C$_{16}$H$_{30}$O$_2$S, C: 67.08, H: 10.56, N: 0.00, S: 11.19; found C: 65.42, H: 10.33, N: 0.00, S: 10.82.

**Bis(pent-4-en-1-yl)sulfone (21).** Yield 92%. $^1$H NMR (300 MHz, CDCl3): δ (ppm) 5.69-5.82 (m, 2H), 5.03-5.11 (m, 4H), 2.93 (t, 4H), 2.18-2.25 (m, 4H), 1.74-1.85 (m, 4H); $^{13}$C NMR (75 MHz, CDCl3) δ (ppm) 135.8, 116.1, 76.9, 76.5, 76.1, 51.6, 31.7, 20.6. HRMS (ESI) (m/z): (M+H)$^+$ calcd for C$_{10}$H$_{18}$O$_2$S 203.1100; found 203.1101. Elemental Analysis: calcd for C$_{10}$H$_{18}$O$_2$S, C: 59.37, H: 8.97, N: 0.00, S: 15.85; found C: 59.28, H: 9.06, N: 0.00, S: 15.59.

**Polymerization Procedures**

**Polymerization of Bis(undec-10-en-1-yl)sulfone (SO$_2$20U).** To a dry 50 mL Schlenk tube containing a stir bar was added a 2M solution of 1.0 g of monomer (2.7...
mmols) in dichloromethane. The solution was subjected to multiple freeze-pump-thaw cycles until no visible gases were expelled from the solution. Before the final thaw, 1 mol% Grubbs’ First Generation catalyst was added to the flask, and the vessel was equipped with a reflux condenser and argon flow adapter. The apparatus was evacuated and purged with argon before refluxing for 72 hours. After the allotted polymerization time, the polymer precipitated from solution. Ethyl vinyl ether and tetrachloroethane were added to quench the polymerization and dissolve the polymer. The polymer was precipitated from cold methanol, filtered, collected, and dried under vacuum before characterization. $^1$H NMR (300 MHz, C$_2$D$_2$Cl$_4$) δ (ppm) 5.89-5.76 (m, 2H), 5.40-5.30 (m, 2H), 5.03-4.92 (m, 4H), 2.94-2.89 (t, 4H), 2.05-1.93 (m, 4H), 1.84-1.69 (m, 4H), 1.46-1.28 (m, 24H); $^{13}$C NMR (75 MHz, C$_2$D$_2$Cl$_4$) δ 139.1, 130.2, 129.8, 114.2, 52.5, 33.6, 32.5, 29.5, 29.2, 29.1, 28.9, 28.3, 27.1, 21.8. FT-IR (ATR) ν in cm$^{-1}$ 2918, 2847, 1461, 1414, 1327, 1274, 1248, 1225, 1123, 1098, 964, 909, 774, 724, 603.

**Polymerization of Bis(oct-7-en-1-yl)sulfone (SO$_2$14U).** $^1$H NMR (300 MHz, C$_2$D$_2$Cl$_4$) δ (ppm) 5.44-5.37 (m, 2H), 2.95-2.89 (t, 4H), 2.00-1.95 (m, 4H), 1.84-1.71 (m, 4H), 1.47-1.25 (m, 12H); $^{13}$C NMR (75 MHz, C$_2$D$_2$Cl$_4$) δ (ppm) 130.5, 74.5, 74.2, 73.8, 52.9, 32.6, 29.4, 28.6, 22.2. FT-IR (ATR) ν in cm$^{-1}$ 2918, 2849, 1459, 1412, 1326, 1274, 1249, 1203, 1122, 1082, 965, 773, 727, 668, 602.

**Polymerization of Bis(pent-4-en-1-yl)sulfone (SO$_2$8U).** $^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 5.53-5.38 (m, 2H), 3.01-2.87 (t, 4H), 2.26-2.14 (m, 4H), 1.95-1.82 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 131.4, 75.6, 75.2, 74.9, 53.4, 32.4, 22.9. FT-IR (ATR) ν in cm$^{-1}$ 2942, 2860, 1451, 1412, 1321, 1275, 1235, 1119, 1078, 1017, 965, 841, 774, 742, 703.
Hydrogenation of Unsaturated Polysulfones

SO$_2$20. Similar to a literature procedure, 250 mg of SO$_2$20U was suspended in 20 mL of anhydrous $m$-xylene. Next, 0.9 g (3 eq.) of p-toluenesulfonylhydrazide (TSH) and 1 mL of tripropylamine (TPA) was added to the flask. The reaction was allowed to reflux for 3.5 hours, after which an additional 3 eq. TSH and TPA was added. The reaction was again refluxed for 3.5 hours and then condensed to half the original volume before being precipitated into cold methanol. The polymers were filtered and dried under high vacuum. $^1$H NMR (300 MHz, C$_2$D$_2$Cl$_4$) $\delta$ (ppm) 2.95-2.89 (t, 4H), 1.78-1.74 (m, 4H), 1.61 (m, 4H), 1.41-1.18 (m, 24H); FT-IR (ATR) $\nu$ in cm$^{-1}$ 2916, 2846, 1462, 1413, 1327, 1292, 1270, 1246, 1216, 1123, 1092, 774, 724.

SO$_2$14. $^1$H NMR (300 MHz, C$_2$D$_2$Cl$_4$) $\delta$ (ppm) 2.95-2.89 (t, 4H), 1.81-1.66 (m, 4H), 1.61 (m, 4H), 1.44-1.26 (m, 12H); $^{13}$C NMR (75 MHz, C$_2$D$_2$Cl$_4$) $\delta$ (ppm) 52.9, 29.8, 29.5, 28.7, 22.2. FT-IR (ATR) $\nu$ in cm$^{-1}$ 2916, 2846, 1461, 1413, 1326, 1300, 1267, 1239, 1197, 1123, 1072, 988, 802, 774, 742, 725.

SO$_2$8. $^1$H NMR (300 MHz, C$_2$D$_2$Cl$_4$) $\delta$ (ppm) 2.95-2.90 (t, 4H), 1.85-1.75 (m, 4H), 1.48 (m, 4H), 1.46-1.32 (m, 4H); $^{13}$C NMR (75 MHz, C$_2$D$_2$Cl$_4$) $\delta$ (ppm) 75.6, 75.3, 74.9, 54.0, 30.1, 29.7, 23.2. FT-IR (ATR) $\nu$ in cm$^{-1}$ 2936, 2846, 1459, 1412, 1324, 1271, 1224, 1193, 1120, 1011, 775, 745, 728.

Results and discussion

Aliphatic sulfone-containing $\alpha,\omega$-diene monomers 19, 20, and 21 were synthesized in a similar fashion to that of other ADMET monomers by alkylation of a functionality with a terminal alkene substrate. Our monomer synthesis is remarkably simple. Typically, harsh and sensitive reagents are required in the production of ADMET monomers with a carbon center, including the use of LDA and even potassium metal for
nitrile reductions. The monomer reactions here were all performed with exposure to atmospheric conditions with readily available and cost-effective reagents, thus simplifying the procedures and increasing the scalability. Beginning with commercially available sodium sulfide nonahydrate and alkenyl bromides 13, 14, and 15 in Figure 4-2, simple substitution reactions were performed according to a literature procedure, providing the thioethers in excellent yield. Product 18 was isolated at a 99% yield and high purity directly from the flask, with elemental analysis performed upon isolation.

![Figure 4-2. Synthesis of precision aliphatic polysulfones via ADMET. Our polymer structure notation is as follows: SO$_2$ denotes the sulfone functionality, U denotes unsaturation, and the number corresponds to the total number of carbons in the polymer repeat unit. We must emphasize the ease of this reaction by noting the simple workup: after 72 hours the flask was flooded with water and the virtually pure product was separated from the aqueous layer. A highly efficient and selective oxidation method published by](image_url)

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Bahrami et al.\textsuperscript{98} was utilized to convert thioethers \textbf{16, 17}, and \textbf{18} to the α,ω-diene sulfone monomers \textbf{19, 20}, and \textbf{21}. Again, fairly mild conditions were used open to air, resulting in high yields (96\% and above). Purification by column chromatography was performed to ensure that any long-chain, non-polar chain-stoppers were not present. Purities and structures were confirmed by NMR, elemental analysis, and mass spectrometry prior to polymerization. No prior ADMET monomers have been so easy to synthesize.

The polymerization of sulfone monomers was carried out in dry dichloromethane (DCM) under reflux until the polymerization was complete, often within 24 hours, as evidenced by precipitation of the polymers. Typically, ADMET is carried out under high vacuum (10\(^{-3}\) torr) at 50 °C to remove the ethylene condensate and drive the equilibrium to polymer product.\textsuperscript{3} ADMET bulk polymerization is possible in most cases because in monomers are liquids and most unsaturated ADMET products remain in the melt below 50 °C, but sulfone monomers \textbf{19, 20}, and \textbf{21} are solid at lower temperature. Thus, solution polymerization was selected. For aliphatic polysulfones, refluxing serves as an appropriate ethylene removal technique, while dichloromethane, which has been cited as the best solvent for ADMET reactions, boils at 39 °C, keeping catalyst decomposition and side reactions to a minimum.\textsuperscript{99}
Figure 4-3. A) Sulfone monomer 20 \(^1\)H NMR with labeled signals (CDCl\(_3\)). B) Unsaturated polysulfone SO\(_{214}U\) after ADMET polymerization (C\(_2\)D\(_2\)Cl\(_4\)). C) Final saturated aliphatic polysulfone SO\(_{214}\) (C\(_2\)D\(_2\)Cl\(_4\)).
Post-polymerization, warm tetrachloroethane was the only solvent found to
dissolve the sulfone polymer samples. Thus, NMR investigation of the polymers was
performed in C\textsubscript{2}Cl\textsubscript{4}D\textsubscript{2}. Figure 2 displays the \textsuperscript{1}H NMR spectra for sulfone monomer 20,
unsaturated polymer SO\textsubscript{2}14U, and saturated polymer SO\textsubscript{2}14. The monomer contained
internal and external olefin protons whose signals appeared at 5.68-5.82 and 4.89-4.99
ppm, respectively. After 24 hours of subjection to ADMET conditions, no external olefin
signals were detectable, with only a single resonance at 5.44-5.37 ppm. Although, SO\textsubscript{2}8U presented a similar signal pattern in the olefin region, SO\textsubscript{2}20U displayed signals
indicative of olefin end groups, and molecular weight data show the polymer was one
third the size of SO\textsubscript{2}8 and SO\textsubscript{2}14. It is plausible that the longer aliphatic run-lengths
caused SO\textsubscript{2}20U to precipitate prematurely from the polymerization ultimately halting the
reaction. Since, the polymers are C\textsubscript{2}Cl\textsubscript{4}D\textsubscript{2} soluble, diffusion ordered NMR spectroscopy
(DOSY) was performed as an alternative to gel permeation chromatography (GPC)
according to literature procedures.\textsuperscript{95} Weight-average molecular weights, obtained from
DOSY experiments using PS standards for comparison, are presented in Table 4-1.
Molecular weights are lower than those typically found for ADMET and other step-
condensation polymerizations. This premature precipitation is attributed to the strong
intermolecular interactions between polymer chains resulting from incorporation of the
sulfone functionality. These interactions are presumably the culprit for precipitation from
DCM during polymerization. However, the favorable properties of these materials
discussed below show that precise polysulfones potentially possess practical utility and
outweigh polymerization shortcomings.
Table 4-1. Molecular Weight and Thermal Properties of Poly(aliphatic sulfones) by ADMET polymerization.

<table>
<thead>
<tr>
<th>Sulfone Polymer&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$\bar{M}_w$ (g/mol)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Sulfone per 500 carbons</th>
<th>$T_m$ (°C)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>$\Delta H$ (J/g)</th>
<th>$T_{95%}$ (°C)&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;8U</td>
<td>13,800</td>
<td>62</td>
<td>113</td>
<td>32.5</td>
<td>302</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;14U</td>
<td>15,800</td>
<td>35</td>
<td>125</td>
<td>27.6</td>
<td>325</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;20U</td>
<td>4,800</td>
<td>25</td>
<td>131</td>
<td>37.7</td>
<td>345</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;8</td>
<td>-</td>
<td>62</td>
<td>175</td>
<td>49.1</td>
<td>260</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;14</td>
<td>-</td>
<td>35</td>
<td>167</td>
<td>47.9</td>
<td>290</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;20</td>
<td>-</td>
<td>25</td>
<td>147</td>
<td>91.4</td>
<td>277</td>
</tr>
</tbody>
</table>

<sup>a</sup>Unsaturated polymers provided by ADMET polymerizations of 24 hr duration. Saturated polymers subjected to hydrogenation conditions.

<sup>b</sup>Molecular weights determined by DOSY in C<sub>2</sub>Cl<sub>4</sub>D<sub>2</sub>.

<sup>c</sup>$T_m$ obtained from DSC at 10 °C/min. 

<sup>d</sup>5% decomposition determined from TGA at 10 °C/min.

To our surprise hydrogenation of the unsaturated polymers results in a further increase in the melting temperatures, as shown in Table 4-1. As functional group proximity increases, the melting point increases. We have never observed such behavior in precision systems. Successful reduction was accomplished using p-toluenesulfonylhydrazide in refluxing m-xylene (Figure 4-2). While only partially soluble in m-xylene at 140 °C, the reaction proceeded to completion. Complete internal olefin removal was confirmed by NMR, as shown in Figure 4-3C, where no olefin signals are present. Further, FT-IR data for all polymers before and after hydrogenation show disappearance of the olefin C-H wag at 965 cm<sup>-1</sup> upon saturation, conclusive evidence of complete saturation.
Figure 4-4. DSC thermograms of the saturated and unsaturated sulfone polymers. Data are shifted vertically for clarity.

All precision polysulfones (saturated and unsaturated) exhibit semicrystalline behavior as seen in the DSC thermogram overlay presented in Figure 4-4 and represented in Table 4-1. Slight variations in the structure result in drastic differences in melting temperatures and enthalpies of melting. Such thermal behavior differences are attributed to the concentration of sulfone groups and the concentration of double bonds only. SO$_2^{8}$U, SO$_2^{14}$U, and SO$_2^{20}$U all melt well above 100 °C, a most important factor when considering applications. The $T_m$ decreases with increasing concentration of both sulfone groups and C=C double bonds (SO$_2^{8}$U<SO$_2^{14}$U< SO$_2^{20}$U). The depressed $T_m$ of the unsaturated polymers is attributed to defects arising from the presence of both
trans and cis carbon-carbon double bonds. The lower enthalpies are attributed to these same structural defects in addition to the cis confirmation polymer that is excluded from the crystallites. This trend of double bond lowering is well documented and observed in ADMET.\textsuperscript{71}

Polymer melting points are increased significantly after saturation, especially in the case of SO\textsubscript{2}8 which melts at 175 °C, while SO\textsubscript{2}8U melts at 113 °C, a difference of 62 °C. This is a first. It is also quite favorable from a potential utility point of view. For the saturated polymers, T\textsubscript{m} increases with increasing concentration of sulfone groups, a phenomenon opposite the trend observed for unsaturated materials. Favorable hydrogen bonding interactions between sulfone groups and α-hydrogens within the crystal structure are responsible for the T\textsubscript{m} increase.

X-ray scattering data were acquired to further investigate the nature of these interactions and the effects of sulfone concentration on polymer morphology (Figure 4-5 and Table 4-2). X-ray data and interpretation was provided by Professor Karen Winey and her group at the University of Pennsylvania. X-ray scattering performed at room temperature substantiates the DSC evidence and confirms semicrystalline behavior in all saturated and unsaturated and precision aliphatic polysulfones. Single, sharp peaks at approximately 15 nm\textsuperscript{-1} are observed for each of the six polysulfones: an indication of crystallinity. These peaks correspond to the [110] peak typical of an orthorhombic crystal structure possessed by polyethylene. Conversely, no peaks are present around 17 nm\textsuperscript{-1} (the [200] peak), suggesting a defective orthorhombic crystal, the crystals are small in comparison, or a hexagonal crystal structure exists. Although melting temperatures for these polysulfones exist over a range of approximately 62 °C,
semicrystallinity is still clearly evident through interpretation of the room temperature X-ray scattering (Figure 4-5). This trend is atypical of other ADMET polymers.

Figure 4-5. X-ray scattering of the saturated and unsaturated precision aliphatic polysulfones. Peaks arising from the sulfone layers (in the ratio 1:2:3:4) are marked with inverted triangles. Traces are shifted vertically for clarity. Provided by Professor Karen Winey’s group at the University of Pennsylvania

Each of these polysulfones exhibit layered morphologies, in addition to semicrystallinity. The low q regions in Figure 4-5 show the presence of scattering peaks in the ratio 1:2:3:4, which is evidence for layer existence. As the repeat unit increases in length, the space between layers increases. This increase in space between layers is indicated by lower q peaks for polymers with longer repeat units and provides evidence that layers of sulfone are separated by crystallized methylene segments. The spacing between sulfone layers is 76% ± 2% of the calculated all-trans length of the polymer repeat unit in all six polymers (Table 4-2), suggesting that the vector normal to the sulfone layer plane is tilted by approximately 40° relative to the chain direction.
Previously synthesized ADMET precision polymers including poly(ethylene-co-acrylic acid) (pnAA), poly(ethylene-co-1-methylimidazolium bromide) (pnImBr), and poly(ethylene-co-sulfite) (pnSO₃) are also known to possess such layered morphologies. However, these previously studied saturated polymers all have lower melting temperatures than linear polyethylene, while these new aliphatic polysulfones melt quite high in comparison. Additionally, continuous methylene segments of at least 14, 15, and 21 are required for crystallization in pnSO₃, pnImBr, and pnAA, respectively. The layered morphologies in the precise sulfone polymers are unique because (1) the saturated polymers show much higher melting temperatures than linear polyethylene; and (2) crystallinity is present when the alkane segment is only 8 carbons long.

Table 4-2. Layer spacing (from X-ray scattering) and comparison with calculated all-trans length of the polymer repeat unit.

<table>
<thead>
<tr>
<th>Sulfone Polymer</th>
<th>Layer Spacing [nm]</th>
<th>Ratio of layer spacing to d_{all-trans}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂20U</td>
<td>2.20</td>
<td>0.78</td>
</tr>
<tr>
<td>SO₂20</td>
<td>2.23</td>
<td>0.78</td>
</tr>
<tr>
<td>SO₂14U</td>
<td>1.59</td>
<td>0.77</td>
</tr>
<tr>
<td>SO₂14</td>
<td>1.59</td>
<td>0.76</td>
</tr>
<tr>
<td>SO₂8U</td>
<td>0.97</td>
<td>0.75</td>
</tr>
<tr>
<td>SO₂8</td>
<td>0.97</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Sulfone functional group geometry plays an important role in these unique properties. Sulfones are more closely related to a methylene in regards to size, when compared to previously studied groups. The smaller size of a sulfone (compared to other groups by ADMET) is more readily accommodated within the aliphatic crystals.
than larger groups. Additionally, sulfones lack tactility, whereas the pnAA and pnImBr precision polymers are atactic, resulting in disruption of crystallinity. Here we compare these precision aliphatic sulfone polymers to nylons, which display similar behavior. Both polar amides (no tacticity) and non-polar methylene run-lengths are present in nylons. The polar amide functional groups arrange into layers as well. Nylons can even crystallize when their methylene run-lengths are short, and nylons also exhibit higher thermal transitions as polar functionalization increases in the repeat unit.¹⁰¹

Unsaturated polysulfone exhibit broader and lower-intensity X-ray scattering peaks than the corresponding saturated polysulfones (Figure 4-5). The unsaturated polymers also display fewer peaks linked with the layered morphology (indicated with inverted triangles in Figure 4-5). Along with lower melting temperatures and enthalpies, we can state the unsaturated polysulfones form smaller or more defective crystallites. Furthermore, peaks around 15nm⁻¹ shift to lower q for the unsaturated polymers, indicative of lattice expansion, no doubt a by-product of disrupted chain packing.

X-ray scattering provides strong evidence that all six polysulfones studied possess the same morphology type. The wide range of thermal behaviors observed via DSC are yielded by the concentration of sulfone groups and the concentration of carbon-carbon double bonds. Strong sulfone interactions result in an increasing melting temperature, while increasing double bond concentration leads to a lower melting point through disruption of the crystal structure. Melting temperatures increase with increasing sulfone concentration when the backbone is hydrogenated and temperatures decrease with increasing carbon-carbon double bond concentration when unsaturated. Possessing similar morphologies, these precision aliphatic sulfones may be easily
adjusted to provide any desired melting point within a broad range of 113°C to 175°C, and possibly well above 200 °C. The capability to perform such structural tailoring will be most important when considering applications.

**Conclusion**

A simple, yet elegant and efficient, synthetic procedure for aliphatic polysulfones via ADMET has been developed. The essence of the synthetic work is one of simplicity. The resulting polymers are high-melting materials, all of which are semicrystalline and whose properties are enhanced by precise sulfone functionalization. Polysulfones produced via ADMET provide a completely new trend compared to other precision systems, for which properties are enhanced as functionalization is increased. X-ray scattering confirms the crystalline nature and also provides evidence that all of the polymers exist in ordered layers. This study is a testament to ADMET’s ability to provide unique materials not possible through conventional methods.
CHAPTER 5
MICROWAVE-ASSISTED ADMET POLYMERIZATION

Introduction

In an attempt to overcome the issue of polymer precipitation from polymerizations of sulfone monomers discussed in Chapter 4, we began exploring new techniques for performing ADMET polymerizations. Microwave devices attracted us to attempt solid state polymerization of the sulfones, which could be irradiated and mixed without the need for a solvent. Unfortunately, reactions of sulfone monomers only achieved dimers. However, the technique has been explored further and expanded as a method of improvement over conventional ADMET polymerizations.

Enhancing ADMET Chemistry with Microwave Techniques

Figure 5-1. Graphical representation of microwave-assisted ADMET polymerization.

As previously mentioned, ADMET materials are synthesized in a precise manner in which functional groups are placed in exact locations along polymer backbones. Precision results from the selective ADMET reaction of symmetrical α,ω-diene monomers using tolerant and robust catalysts. Effective control of polymerization conditions eliminates unintentional side reactions and defects, yielding precision materials. This chapter details the expansion of ADMET’s versatility, using microwave irradiation, a technique synonymous with control.\textsuperscript{102}

Microwave usage for chemical synthesis has grown over the past two decades with the emergence of new devices. These devices allow for easy and accurate management of energy regulation, much more so than conventional laboratory heating techniques.\textsuperscript{103} Efficiency is the key. Polymerization under microwave irradiation is becoming more common; examples are the synthesis of polyesters,\textsuperscript{104, 105} biodegradable polymers,\textsuperscript{106} as well as polymers made via RAFT\textsuperscript{107} and ring-opening polymerization.\textsuperscript{108} Microwaves often provide enhancement of the polymerization by increasing reactions rates and decreasing reaction times.\textsuperscript{109, 110}

Herein we investigate the use of microwave irradiation to promote ADMET chemistry. The intention of this investigation has been to provide proof-of-concept data, and to determine the best conditions for ADMET using highly-controlled microwave techniques for efficient polymerizations.

**Experimental**

**Materials and Instrumentation**

The 1,9-decadiene monomer was purchased from Sigma-Aldrich and purified either by potassium mirror or by passing through a silica plug using
hexanes as the solvent, followed by rotary evaporation. Monomers tricosa-1,22-diene-12-ol and undecyl-1,10-diene-6-ol were prepared by previously reported methods. Methylene chloride was obtained from a solvent system; 1,2-dichlorobenzene (Fisher) was stored over alumina for at least 24 hours prior to use.

A CEM Discover S-Class microwave reactor was used with 10 mL heavy-walled sample tubes. Proton- and $^{13}$C NMR were acquired using a Gemini-300 MHz operating under VNMR6.1C software, using CDCl$_3$ as the solvent. Molecular weights were obtained using an Agilent 1100 series GPC with a refractive index detector, using THF as the solvent and polystyrene standards for calibration. Thermogravimetric Analysis (TGA) was performed on a TA Instruments Q5000 using a temperature ramp of 20 °C/min with nitrogen as the purge gas. A TA Instruments Q1000 DSC was used for Differential Scanning Calorimetry with helium as the purge gas. The sample was heated from -80 °C to 250 °C at 10°C/min, then cooled to -80 °C at 10°/min. This heat/cool sequence was repeated twice and the data from the third heating ramp were used for analysis.

**Polymerization Procedures**

The procedure for a typical polymerization in 1,2-dichlorobenzene is given. Other reaction conditions, including catalyst types and mole percentages, are specified in Table 5-1 and Table 5-2. Catalyst was weighed and placed in a 10-mL heavy-walled microwave reaction tube with small magnetic stir bar. The tube was sealed with a septum equipped with two 21 gauge needles (12 cm for Ar entry and 3.8 cm for Ar escape), and the tube was flushed with Ar for several minutes. The tube was weighed, 1,2-dichlorobenzene (1.5-1.7g) was added by
syringe, and the tube was weighed again. Then approximately 0.6 mL monomer was added by syringe, and the tube was reweighed, so that the exact weight of monomer was known (0.45-0.50 g; 3.2-3.6 mmol for 1,9-decadiene (a); 0.63-0.68 g; 3.9-4.2 mmol for undecyl-1,10-diene-6-ol) (b). The tube was then connected to the Ar supply and placed in the microwave reactor, which was programmed as specified in Table 5-1 and Table 5-2. For most of the reactions, the reaction mixture was irradiated for several hours, and the reaction tube was removed several times to obtain samples for GPC and NMR analysis. The times specified in the tables are total irradiation times. The polymer d was dissolved in 5-6 mL of toluene: ethyl vinyl ether, 10:2, v:v, and precipitated by dropwise addition into ~500 mL cold methanol. The solid was filtered and kept in a vacuum desiccator. For polymer e, the solvent was THF: ethyl vinyl ether, 10:2, v:v, and the product was precipitated from cold hexanes.

**Results and Discussion**

A non-polar diene, 1,9-decadiene (a) (Figure 5-2), was first selected for investigation. Polar monomers were also investigated for comparison. Simple alcohol-containing dienes, such as undecyl-1,10-diene-6-ol (b) and tricosa-1,22-diene-12-ol (c), were chosen to provide polarity, in addition to altering concentration of polarity in polymer structures. Note that monomer b will result in a polymer e containing a much higher concentration of polar functionalization than polymer f (specifically, 125 alcohols per 1000 carbons for e versus approximately 48 alcohols per 1000 carbons for f).
Figure 5-2. Polymerization of polar and non-polar α,ω-dienes utilizing microwave-assisted ADMET polymerization.

We chose the CEM Discover S-Class microwave reactor, which is capable of either fixed-power with a specified maximum temperature, $T_{\text{max}}$, or fixed-temperature operation. Here, the fixed-power mode is referred to as “pulsed.” In pulsed mode the reactor irradiates the sample at the specified microwave power until the maximum temperature is reached; subsequently, the microwave power (at one-half the specified wattage) is applied intermittently to sustain $T_{\text{max}}$. In the fixed temperature mode, the programmed power (100 W) is applied until the preset temperature is reached. Then, the temperature is maintained by continuous irradiation at very low power (<5 W). The reactor also can be programmed for maximum pressure, sealing the reaction chamber; in this work the reaction vessel remains open for the removal of ethylene driving the reaction forward to polymer product.
Confirmation of microwave success is provided by $^1$H-NMR evidence, where progress of the reaction is monitored in the 5-6 ppm region (Figure 5-3). The internal and external proton resonances of the terminal double bond in monomer a are well separated at about 5 ppm (=CH$_2$) and 5.8 ppm (=CH–), while those for internal alkenes occur at 5.4 ppm. Thus, during polymerization the multiplets at 5 and 5.8 ppm gradually disappear as the polymer resonance at 5.4 ppm grows, indicative of high-molecular weight polymer formation.

Table 5-1 provides the conditions and results for the polymerization of non-polar monomer a producing polymer d. The table presents a variety of microwave and sample conditions for consideration. Contrary to conventional ADMET procedures, continuous vacuum operation was not feasible. Instead, other methods of ethylene removal were tested. Entry 1 was performed with
pulsed irradiation, which was ceased periodically to apply vacuum for ethylene removal, followed with an argon purge prior to restarting the microwave reactor. Pausing for vacuum removal of ethylene results in an a weight-average molecular weight of 11,000 g/mol. Obtaining higher molecular weight required continuous removal of generated ethylene. In addition, a solvent was used to facilitate ethylene removal (1,2-dichlorobenzene, Entry 2). Ethylene was removed by flushing the solution with a continuous stream of argon, similar to a degassing procedure. Methodology described in Entry 2 effectively tripled the molecular weight of the polymer observed with Entry 1 conditions. For the sake of comparison, Entry 7 displays conditions used to mimic conventional ADMET methods. In Entry 7, monomer a was subjected to the same temperature of 60 ºC and argon flow in a heated oil bath, instead of microwaves. The heated oil bath resulted in a molecular weight almost one-third lower than found for microwave procedure ($\bar{M}_w = 12000$ g/mol), under similar conditions over the same time period. Without question, microwave irradiation enhances ADMET polymerization significantly in comparison with conventional heating methods.

Both the pulsed mode and continuous low power operation provide an absolute advantage over the oil bath heat source. The continuous low power run yielded slightly lower molecular weight (Entry 3, $\bar{M}_w = 22,000$ g/mol) than pulsed power in the same solvent, 1,2-dichlorobenzene (Entry 2, $\bar{M}_w = 31,000$ g/mol). These data provide clear evidence that the increased power (150 Watts) of the pulsed mode has a positive effect on polymer molecular weight in contrast to the low-power (<5 Watts) of fixed-temperature experiments. The continuous low-power mode was also employed to investigate another ethylene removal
technique: refluxing. By using a continuous power of less than 5 Watts, the temperature was maintained at 50°C allowing for the removal of ethylene by refluxing in dichloromethane (DCM) blanketed with argon (Entry 4). This technique provides the ethylene an escape route through the gaseous bubbles of solvent formed. Molecular weights in refluxing DCM are comparable to those in 1,2-dichlorobenzene.

Table 5-1: Microwave Polymerization of 1,9-decadiene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample Conditions</th>
<th>Microwave Setting</th>
<th>Reaction Time (h)</th>
<th>$\bar{M}_n$ (g/mol)</th>
<th>$\bar{M}_w$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5% Grubbs G1 Periodic Vacuum (10³ torr)</td>
<td>150 W, Pulsed $T_{\text{max}} = 60$ ºC</td>
<td>12</td>
<td>5600</td>
<td>11000</td>
</tr>
<tr>
<td>2</td>
<td>1% Grubbs G1 o-C₆H₄Cl₂ w/Ar flow</td>
<td>150 W, Pulsed $T_{\text{max}} = 60$ ºC</td>
<td>22</td>
<td>16000</td>
<td>31000</td>
</tr>
<tr>
<td>3</td>
<td>1% Grubbs G1 o-C₆H₄Cl₂ w/Ar flow</td>
<td>Fixed $T = 60$ ºC, Power &lt; 5 W</td>
<td>16</td>
<td>9800</td>
<td>22000</td>
</tr>
<tr>
<td>4</td>
<td>1% Grubbs G1 CH₂Cl₂, reflux</td>
<td>Fixed $T = 50$ ºC, Power &lt; 5 W</td>
<td>24</td>
<td>12200</td>
<td>26400</td>
</tr>
<tr>
<td>5</td>
<td>1% Grubbs G2 o-C₆H₄Cl₂ w/Ar flow</td>
<td>100 W, Pulsed $T_{\text{max}} = 60$ ºC</td>
<td>22</td>
<td>6500</td>
<td>22100</td>
</tr>
<tr>
<td>6</td>
<td>1% Hoveyda-Grubbs G1 o-C₆H₄Cl₂ w/Ar flow</td>
<td>100 W, Pulsed $T_{\text{max}} = 60$ ºC</td>
<td>22</td>
<td>8200</td>
<td>20900</td>
</tr>
<tr>
<td>7ᵃ</td>
<td>1% Grubbs G1 o-C₆H₄Cl₂ w/Ar flow</td>
<td>Oil Bath, 60 ºC</td>
<td>22</td>
<td>5400</td>
<td>12000</td>
</tr>
</tbody>
</table>

ᵃ Reaction performed for comparison. Molecular weights were obtained by GPC using THF as the solvent at 40 ºC. G1 = 1ˢᵗ Generation, G2 = 2ⁿᵈ Generation

Additional Grubbs catalysts were employed using 1,2-dichlorobenzene as the solvent. Results with Grubbs 2ⁿᵈ Generation and Hoveyda-Grubbs 1ˢᵗ Generation catalysts also provided excellent, useful step polymerization molecular weights in a similar period of time (Table 5-1 Entries 5 and 6, respectively). No discernable advantage was evident: Entries 5 and 6 illustrate
that different catalysts are compatible under the defined experimental conditions. Investigation of techniques, conditions, and catalyst choice makes apparent that this series of microwave methods provides the polymer chemist with efficient and distinct advantages over orthodox ADMET polymerization techniques.

Table 5-2 summarizes the reaction conditions and molecular weight data for the polymerization of polar monomer b using the pulsed power mode at $T_{\text{max}} = 60 \, ^\circ\text{C}$, which previously yielded the best results with a non-polar substrate in Table 5-1. Entries 8-12 describe polymerizations that resulted in highly viscous reaction media. Viscosity plays an important role in any polycondensation reaction, leading to lower molecular weights in all cases. Slightly less viscous solution polymerizations provided higher molecular weights over neat polymerizations. Observing such high viscosity for all entries in Table 5-2 indicates that the endpoint of polymerization is approached early, making ethylene gas diffusion difficult and resulting in lower molecular weights.

**Table 5-2: Microwave Polymerization of Undecyl-1,10-diene-6-ol. Molecular weights were obtained by GPC using THF as the solvent at 40 °C.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample Conditions</th>
<th>Microwave Setting</th>
<th>Reaction Time (h)</th>
<th>$\bar{M}_n$ (g/mol)</th>
<th>$\bar{M}_w$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1% Grubbs G1 Bulk w/Ar flow</td>
<td>100 W, Pulsed $T_{\text{max}} = 60 , ^\circ\text{C}$</td>
<td>8</td>
<td>1900</td>
<td>2500</td>
</tr>
<tr>
<td>9</td>
<td>1% Grubbs G1 Bulk w/Ar flow</td>
<td>100 W, Pulsed $T_{\text{max}} = 60 , ^\circ\text{C}$</td>
<td>6</td>
<td>1300</td>
<td>2700</td>
</tr>
<tr>
<td>10</td>
<td>1% Grubbs G1 $\sigma$-C$_6$H$_4$Cl$_2$ w/Ar flow</td>
<td>100 W, Pulsed $T_{\text{max}} = 60 , ^\circ\text{C}$</td>
<td>22</td>
<td>1500</td>
<td>2000</td>
</tr>
<tr>
<td>11</td>
<td>1% Grubbs G1 $\sigma$-C$_6$H$_4$Cl$_2$ w/Ar flow</td>
<td>100 W, Pulsed $T_{\text{max}} = 60 , ^\circ\text{C}$</td>
<td>44</td>
<td>7800</td>
<td>17500</td>
</tr>
<tr>
<td>12</td>
<td>1% Grubbs G1 $\sigma$-C$_6$H$_4$Cl$_2$ w/Ar flow</td>
<td>100 W, Pulsed $T_{\text{max}} = 60 , ^\circ\text{C}$</td>
<td>46</td>
<td>6000</td>
<td>12300</td>
</tr>
</tbody>
</table>
The longer carbon run-length alcohol, tricosa-1,22-diene-12-ol (c), was polymerized under similar conditions in 1,2-dichlorobenzene as non-polar monomer a. After the same time required for high molecular weight with the diene a, polymerization of c was analyzed. Preliminary tests with DOSY (diffusion-ordered NMR spectroscopy) indicated a weight-average molecular weight of about 4000 g/mol (100 W, Pulsed, \( T_{\text{max}} = 60^\circ\text{C} \)). At this average chain size the solution was also highly viscous, enough to lock the stir bar in place. The polymerization of both b and c alcohol-containing monomers provided a challenge that may possibly be overcome with the incorporation of mechanical stirring into the reactor, requiring a more complex reactor design.

![Figure 5-4. Representative DSC thermograms for polymers prepared from 1,9-decadiene and undecyl-1,10-diene-6-ol.](image-url)
Thermal properties of polymers from both Table 5-1 and Table 5-2 were characterized by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Typical DSC thermograms are shown in Figure 5-4. Polyoctenamer \( d \) melted at around 19 °C, within the range of structurally similar polyolefins. Alcohol-containing polymer \( e \) displayed a much higher melting temperature at 107 °C. The stark contrast in melting temperatures is attributed to hydrogen-bonding of pendent alcohols. This phenomenon is presumably causing higher polymerization viscosities as well. TGA thermograms are shown in Figure 5-5. The TGA results showed good thermal stability, with only 5% loss at temperatures up to 354 °C for \( e \) and 390 °C for \( d \).

**Conclusion**

Microwave irradiation enhances ADMET polymerization of \( \alpha,\omega \)-dienes by shortening the time required to produce high molecular weight polymers of the
step variety. Microwave settings of both pulsed and continuous low power modes were useful in obtaining high molecular weights. The pulsed mode, which used higher power, provided a slight advantage. A variety of solvents, catalysts, and ethylene removal techniques can be used to synthesize polyolefins in a microwave reactor. No perceptible difference in reaction enhancement was observed for alcohol monomers; microwave reactors are viable for polymerizing both non-polar and polar substrates. Without question, microwave-assisted ADMET chemistry offers an advantage over the typical oil bath-heated polymerizations by essentially tripling molecular weights in the same time period.
Ethyl undeca-1,10-diene-6-sulfonate

$^1$H NMR (CDCl$_3$):

$^{13}$C NMR (CDCl$_3$):
Ethyl tricosa-1,22-diene-12-sulfonate

$^1$H NMR (CDCl$_3$):

$^{13}$C NMR (CDCl$_3$):
SO₃Et₈U

¹H NMR (CDCl₃):

¹³C NMR (CDCl₃):
IR (ATR):

SO$_3$Et$_8$

$^1$H NMR (CDCl$_3$):
$^{13}$C NMR (CDCl$_3$):

IR (ATR):
SO$_3$Na$_8$

IR (ATR):

SO$_3$H$_8$

IR (ATR):
SO₃Et₂0U – 33K

¹H NMR (CDCl₃):

¹³C NMR (CDCl₃):
IR (ATR):

SO$_3$Et$_2O$ – 33K

$^1$H NMR (CDCl$_3$):
$^{13}$C NMR (CDCl$_3$):

IR (ATR):

Wavenumber cm$^{-1}$

% Transmittance
**SO$_3$Na$_20$ – 33K**

IR (ATR):

![IR Spectra of SO$_3$Na$_20$](image1)

**SO$_3$H$_20$ – 33K**

IR (ATR):

![IR Spectra of SO$_3$H$_20$](image2)
SO$_3$EtCoU

$^1$H NMR (CDCl$_3$):

$^{13}$C NMR (CDCl$_3$):
IR (ATR):

$\text{SO}_3\text{EtCo}$

$^1\text{H NMR (CDCl}_3)$:
$^{13}$C NMR (CDCl$_3$):

IR (ATR):

![Graph showing 13C NMR spectrum for CDCl$_3$]

![Graph showing IR spectrum (ATR)]
SO$_3$NaCo

IR (ATR):

SO$_3$HCo

IR (ATR):
Bis(pen-4-en-1-yl)sulfite (10)

$^1$H NMR (CDCl$_3$):

$^{13}$C NMR (CDCl$_3$):
IR (ATR):

Bis(oct-7-en-1-yl)sulfite (11)

$^1$H NMR (CDCl$_3$):
$^{13}$C NMR (CDCl$_3$):

IR (ATR):

[Graphs of NMR and IR spectra]
Bis(undec-10-en-1-yl)sulfite (12)

$^1$H NMR (CDCl$_3$):

$^{13}$C NMR (CDCl$_3$):
IR (ATR):

\[ \text{SO}_{38U} \]

\[^1\text{H NMR (CDCl}_3\text{):}\]

...
$^{13}\text{C NMR (CDCl}_3\text{)}$:

IR (ATR):

[Graphs of NMR and IR spectra are shown here.]
SO$_3$14U

$^1$H NMR (CDCl$_3$):

$^{13}$C NMR (CDCl$_3$):
IR (ATR):

SO$_{2}$20U

$^1$H NMR (CDCl$_3$):
$^1$H NMR (CDCl$_3$):

IR (ATR):

% Transmittance

Wavenumber cm$^{-1}$
Bis(pen-4-en-1-yl)sulfone

$^1$H NMR (CDCl$_3$):

$^1$H NMR (CDCl$_3$):

$^1$3 NMR (CDCl$_3$):
Bis(oct-7-en-1-yl)sulfone

$^1$H NMR (CDCl$_3$):

$^{13}$C NMR (CDCl$_3$):
Bis(undec-10-en-1-yl)sulfone

$^{1}H$ NMR (CDCl$_3$):

$^{13}C$ NMR (CDCl$_3$):
SO$_2$8U

$^1$H NMR (CD$_2$Cl$_4$):

$^1$3 NMR (CD$_2$Cl$_4$):
IR (ATR):

![IR Spectrum]

\( \text{SO}_2 \text{S} \)

\( ^1\text{H NMR (CD}_2\text{Cl}_4) \):

![NMR Spectrum]
$^{13}$C NMR (CD$_2$Cl$_4$):

IR (ATR):

SO$_2$14U

$^1$H NMR (CD$_2$Cl$_4$):

$^{13}$C NMR (CD$_2$Cl$_4$):
IR (ATR):

\[ \text{SO}_2 \text{I} \]

\[ \text{H NMR (CD}_2\text{Cl}_4): \]

[Chemical structure image]

[1H NMR spectrum image]
$^{13}$C NMR (CD$_2$Cl$_4$):

IR (CD$_2$Cl$_4$):
SO$_2$20U

$^1$H NMR (CD$_2$Cl$_4$):

$^{13}$C NMR (CD$_2$Cl$_4$):
IR (ATR):

SO$_2$20

$^1$H NMR (CD$_2$Cl$_4$):
IR (ATR):
APPENDIX B
DSC & TGA THERMOGRAMS

SO$_3$Et$_9$U
SO₃Et₉
$\text{SO}_3\text{H}_9$

![Thermogravimetric Analysis (TGA) graph showing weight loss as a function of temperature. Peaks at 203.7°C and 375.9°C are indicated.}

![Differential Scanning Calorimetry (DSC) graph showing heat flow as a function of temperature. A baseline shift is observed.]
SO$_3$Et$_2$U – 33K

[Chemical structure image]

[Graph image 1]

[Graph image 2]
SO$_3$Et$_21$ – 33K

![Diagram of SO$_3$Et$_21$ structure]

![Graph showing weight loss with temperature]

![Graph showing heat flow with temperature]
SO₃Na₂₁ – 33K

O⁻ Na⁺

O=SO₂=O

n

120

80

60

40

20

0

0

200

400

600

800

Temperature (°C)

84.43°C 95.00%

234.83°C 90.00%

Weight (%)

0.8

0.6

0.4

0.2

0.0

-0.2

-0.4

-0.6

-100

-50

0

50

100

150

200

Temperature (°C)

76.69°C (II)

75.39°C

80.89°C

Exo/Endo

Heat Flow (W/g)
SO₃H₂₁ – 33K

[Chemical structure image]

[Graph with temperature and weight percentage]

[Graph with temperature and heat flow]
SO$_3$Et$_2$U – 19K
SO$_3$Na$^{2-}$ – 19K

Graph showing weight percentage vs. temperature.

Graph showing heat flow vs. temperature.

Chemical structure diagram.
SO₃H₂₁ – 19K

---

157
SO$_3$Et$_{21}$ – 6K

- Chemical structure:

- Thermal analysis graphs:
  - Weight (%): Temperature (°C)
  - Exo-Endo: Heat Flow (W/g) vs. Temperature (°C)
SO$_3$Na$_2$1 – 6K

![Graph showing weight loss as a function of temperature.]

- 352.11°C, 95.90%
- 374.78°C, 80.60%

![Graph showing heat flow as a function of temperature.]

---

159
SO₃H₂₁ – 6K
SO₃EtCo
SO₃NaCo

\[ \text{Diagram of SO₃NaCo structure} \]

\[ \text{Graph showing temperature vs. weight loss} \]

\[ \text{Graph showing temperature vs. heat flow} \]
$SO_3HCo$
SO$_2$14U

[Graph of weight percentage vs. temperature with a peak at 324.5°C and 95.09%]

[Another graph of heat flow vs. temperature with peaks at 124.7°C and 114.93°C, labeled 27.5 J/g]
SO$_2$14

- Weight % vs. Temperature (°C)
- Heat Flow (mW/g) vs. Temperature (°C)

Legend:
- 288.66°C, 95.00%
- 181.68°C, 47.84 kg
- 167.34°C
LIST OF REFERENCES


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BIOGRAPHICAL SKETCH

Taylor Gaines was born in Hickory, NC in 1989. He was resided in Hudson, NC for 9 years before moving to Florence, SC. Taylor attended West Florence High School and graduated in 2007. In 2007, he enrolled in the University of South Carolina (Columbia, SC). He performed undergraduate research under the advisement of Professor Brian C. Benicewicz. Taylor’s research emphasis was polybenzimidazole membrane fabrication and testing for high-temperature fuel cell applications. He graduated from the University of South Carolina in May of 2011, soon after which, he joined Professor Kenneth B. Wagener’s research group at the University of Florida (Gainesville, FL) for graduate studies. Upon completion of the Ph.D. requirements in the fall of 2015, Taylor relocated to Chandler, AZ, where he is currently employed by Intel Corporation.