INCORPORATION OF POLAR COMONOMERS INTO HIGH DENSITY POLYETHYLENE WITH A CYCLOPENTADIENYL-AMIDO TITANIUM CATALYST

by

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ABSTRACT

The purpose of this research was to synthesize the constrained geometry catalyst Ti[(C$_5$Me$_4$)SiMe$_2$(^{t}BuN)]Cl$_2$ (**1**) with MAO as a cocatalyst for ethylene homopolymerization and copolymerizations with 1-TMSO-alkenes to produce a copolymer with polar functionality. Three 1-alkenols of varying length were purchased and derivatized and used for the copolymerization experiments: 2-propen-1-ol, 3-buten-1-ol and 9-decen-1-ol. Several variables were tested to determine their effects on comonomer incorporation such as temperature, equivalents of comonomer, equivalents of MAO and two different solvents. Higher catalytic activities were correlated with fewer equivalents of polar comonomer, lower temperatures, and no fewer than 1000 equivalents of MAO. Toluene was found to be a far more effective reaction solvent than dichloromethane, as polymer yields were on average thirteen times higher.

All polymer samples were analyzed by high temperature ^{1}H NMR spectroscopy and selected samples were analyzed by DSC and IR spectroscopy. DSC determined that the polyethylene produced by **1** was substantially linear HDPE with long chain branching and that comonomer incorporation reduced the T_c and T_m, probably due to increased short chain branching. 1-TMSO-9-Decene was the most effective comonomer, as it had the highest incorporation rates (8.0 mol%) of all three of the polar comonomers. The two shorter comonomers exhibited no incorporation at all. This confirmed the hypothesis that polar comonomers with longer chains would be less prone to poisoning the electrophilic catalyst.

ACKNOWLEDGEMENTS

STATEMENT OF ORIGINALITY

The research discussed in this thesis was carried out by the author in the Department of Chemistry at Queen's University under the supervision of Dr. Michael C. Baird.

All of the syntheses were performed by the author except for the preparation of 3-buten-1-ol and 2-propen-1-ol by Heidi Murray. She also performed the dimethylzirconocene tests for 1-TMSO-3-butene and 1-TMSO-2-propene. The drying and degassing of the NMR solvents C_6D_6 and toluene-d_8 were performed by former PhD students from the Baird lab. All of the ethylene polymerizations and copolymerizations with the **1**/MAO system and product characterizations were performed by the author.

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LIST OF SYMBOLS AND ABBREVIATIONS

^{t}Bu	*tert*-butyl
Cp	cyclopentadienyl (η^5-$C_5H_5^-$)
d	doublet
dd	doublet of doublets
ddt	doublet of doublets of triplets
dt	doublet of triplets
DSC	differential scanning calorimetry
Et	ethyl
equiv.	equivalents
g	gram
GPC	gel permeation chromatography
η	hapticity
h	hour
HDPE	high density polyethylene
IR	infrared
J	coupling constant
Kg	kilogram
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
m	multiplet
MAO	methylaluminoxane
Me	methyl

MHz	megahertz
mmol	millimole
mol	mole
mol%	mole percentage
MW	molecular weight
NMR	nuclear magnetic resonance
PE	polyethylene
Ph	phenyl
ppm	parts per million
R	alkyl group
s	singlet
t	triplet
TCE-d_2	1,1,2,2-tetrachloroethane-d_2
T_c	crystallization temperature
T_g	glass transition temperature
T_m	melting temperature
TMA	trimethylaluminum
TMS	trimethylsilyl
TMSO	trimethylsiloxy
Trityl	triphenylmethyl

CHAPTER 1: INTRODUCTION

1.1 Introduction

Polymers have become an important part of modern life and polyolefins are a multi-billion dollar business thanks to the discovery of heterogeneous ethylene catalysis by Karl Ziegler in the 1950s.[1] Polyethylene has one of the simplest repeating units and its feedstock is the small molecule ethylene (ethene). Even though polyethylene is synthesized from a small and simple molecule, it is a very versatile polymer. Its versatility comes from the fact that polyethylene with different microstructures can be produced by several different methods to produce polymers with a wide range of physical and mechanical properties. Polyethylene is resistant to most solvents and chemical degradation because of the strength of the saturated C-H bond. These properties have made polyethylene a leading choice for many applications such as packaging, containers, piping, coatings, landfill linings, etc. Since polyethylene is such an important polymer in contemporary life, this thesis aimed to improve the properties of polyethylene through copolymerization with a protected polar alkenol using a constrained-geometry Group 4 catalyst.

1.2 Common Types of Polyethylene

Polyethylene is classified by density by convention, as polymer density tends to be correlated to the physical and mechanical properties of polyethylene. While there are many kinds of polyethylene, the main types are high density polyethylene (HDPE), low

density polyethylene (LDPE) and linear low density polyethylene (LLDPE) as shown in Figure 1.
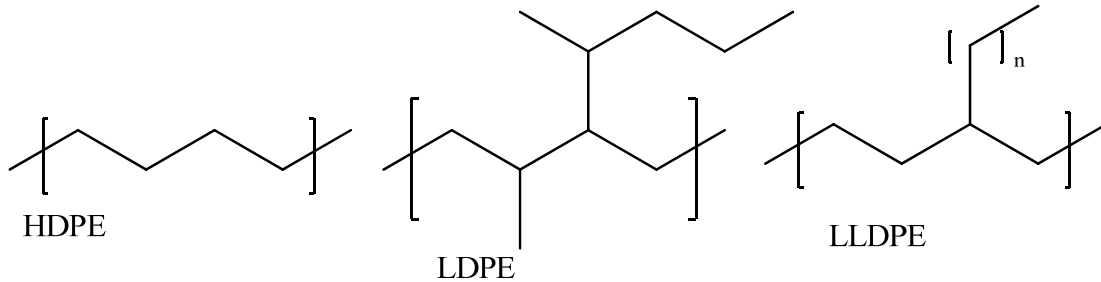
Figure 1. Structure of different types of polyethylene.

HDPE is defined as polyethylene with a density of at least 0.941 g/cm^3. HDPE is produced industrially using Phillips, Ziegler-Natta or metallocene catalysis. This type of polyethylene tends to have little branching and high molecular weights. Since the polymer chains are predominantly linear they readily form a crystalline packing arrangement to maximize Van der Waals interactions. These properties make HDPE relatively strong with high T_m and T_g values and hardness.

LDPE is a highly branched polymer with relatively low molecular weights, usually produced industrially by a free radical process. LDPE is defined as polyethylene with density between 0.910–0.940 g/cm^3. LDPE tends to have many branches of random length, so it is unfavourable for LDPE polymer chains to pack together tightly to maximize intermolecular interactions. This lack of crystallinity means that LDPE tends to have low T_g and T_m (100-120 ºC) values.[2]

LLDPE is a predominantly linear random copolymer with a controlled degree of short branches of a specified length. LLDPE has a density between 0.915–0.925 g/cm^3. It is typically produced by copolymerizing a 1-alkene with ethylene, usually using a

metallocene or Ziegler-Natta catalysis. Some systems can produce the 1-alkene *in situ*

from ethylene by means of tandem catalysis. A chemist can tailor the polymer by

varying the length and concentration of the comonomer to impart greater or lesser

crystallinity to the polymer. LLDPE has greater shear strength and flexibility than

LDPE.[3]

1.3 Ziegler-Natta Catalysis

Ziegler-Natta catalysis was the result of an accidental discovery by Karl Ziegler in

1953. While studying the Aufbau reaction (shown in Scheme 1), which creates 1-alkenes

from ethylene using a trialkylaluminum catalyst, he unexpectedly produced nearly pure

1-butene because an autoclave was contaminated by a colloidal nickel catalyst.[4]
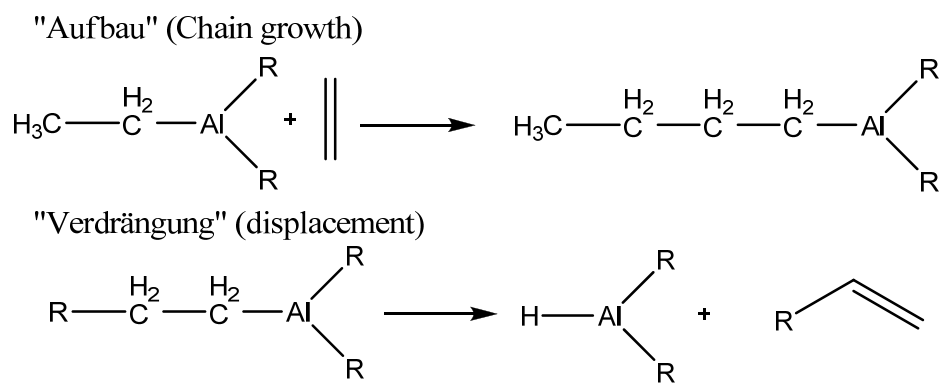
Scheme 1. Aufbau reaction.

Ziegler investigated the catalytic effects of other transition metals and he

discovered that $TiCl_3$ produced high molecular weight linear polyethylene, a previously

unknown substance.[5] His discovery of the first commercial process to produce HDPE

caused a huge change in the world of polyethylene polymerization chemistry. Before

Ziegler's breakthrough, the only type of polyethylene was LDPE, which was produced industrially by a high temperature and high pressure radical process. Giulio Natta's research into the structures of polypropylene led to the discovery of the concept of stereoregularity in polymers and its causes in Ziegler-Natta catalysis, earning both men a shared Nobel Prize in 1963.[6] Polymers of higher olefins can be syndiotactic (alternating R groups), isotactic (*meso* symmetry) or atactic (shown in Figure 2), or have characteristics of all three. Ziegler-Natta polymerization produced isotactic polypropylene, which was not previously possible.

| Syndiotactic | Isotactic | Atactic |
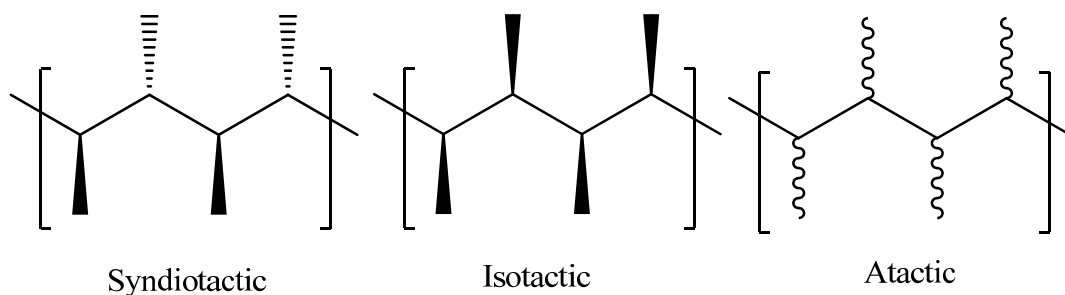
Figure 2. Examples of tactivity in polypropylene.

Crystalline $TiCl_3$ was used as a catalyst for Ziegler-Natta polymerization. Ziegler-Natta polymerization follows the Cossee-Arlman mechanism, shown in Scheme 2.[7] $TiCl_3$ adopts an octahedral configuration within the crystal lattice, but the titanium atoms on the crystal surface have fewer than six ligands, i.e. surface titanium atoms have empty coordination site(s). A large excess (~1000 equiv.) of an alkyl aluminum, typically TMA or $AlEt_2Cl$, initiates polymerization by activating the $TiCl_3$ catalyst. The alkyl on an aluminum atom will undergo ligand substitution with the titanium to replace a chloride. A relatively weak ligand, such as an alkene, may bind to titanium at the "empty

site". A migratory 1,2-insertion occurs and the alkyl chain increases in length by two carbons.
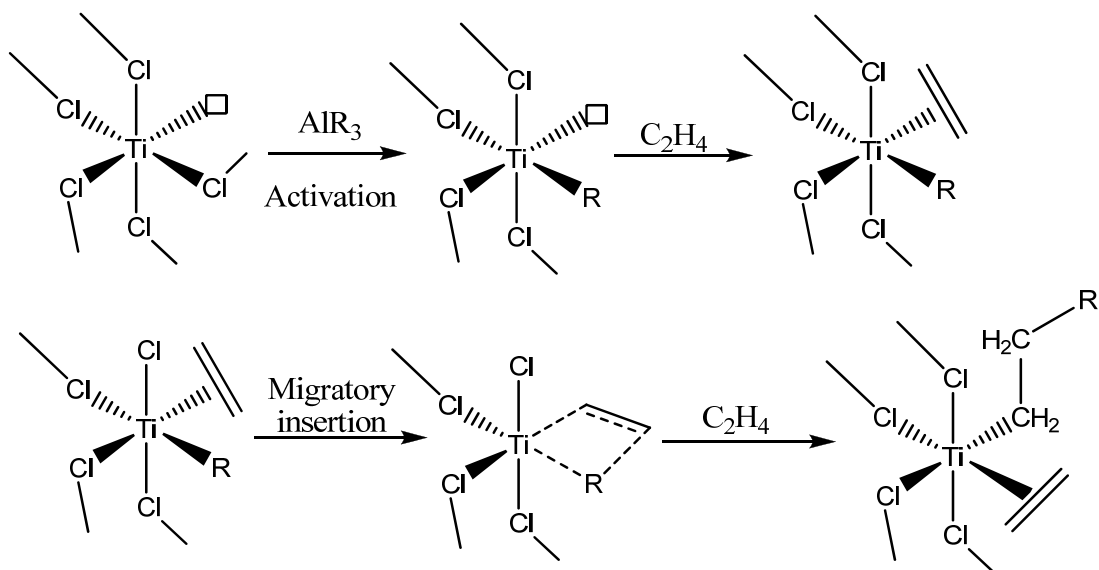
Scheme 2. Cossee-Arlman mechanism of Ziegler-Natta polymerization.

A growing polymer chain will cease propagation if it undergoes hydrolysis, β-hydride elimination or chain transfer to aluminum. When the reaction mixture is quenched to end polymerization, any polymer chains bonded to aluminum or titanium will be hydrolyzed to become saturated polymers. Ziegler-Natta catalysis can produce polyethylene with such high molecular weights that it can become impractical to process for most commercial applications, so hydrogen may be added as a chain transfer agent to reduce the molecular weight.

1.4 Homogeneous Group 4 Metallocene Catalysts

A major breakthrough in the field of polyolefin catalysis was the discovery of highly active Group 4 metallocene (shown in Figure 3) catalysts by Walter Kaminsky in 1980.[8] The compounds referred to as "metallocenes" are *bis*-cyclopentadienyl metal chlorides. Metallocene catalysts are single-site homogeneous catalysts that are known to polymerize olefins. Homogeneous metallocene catalysts can achieve greater catalytic activities than heterogeneous Ziegler-Natta catalysts because each metal atom is potentially catalytically active, instead of only the atoms on the surface of a crystal. Even so, Group 4 metallocene catalysts were not considered to be active enough for commercial use until the discovery of methylaluminoxane (MAO) cocatalysts.[9]

M = Ti, Zr, Hf
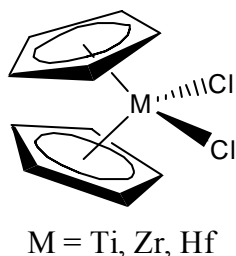
Figure 3. Group 4 metallocene precatalyst.

The most important property of metallocene catalysts is the ability to "tune" them by functionalizing the cyclopentadienyl groups. Polymer properties such as tacticity, branching and molecular weight can all be controlled by selecting the appropriate metallocene catalyst.

Metallocene catalysts polymerize olefins via a mechanism that is analogous to Ziegler-Natta catalysis. The dichloride precatalyst is activated with an aluminum cocatalyst, in this case MAO. MAO reacts with the precatalyst to sequentially abstract

one chloride ligand and exchange another chloride ligand with a methyl group (Scheme 3) to give the catalytically-active cationic species.

M = Ti, Zr, Hf

Weakly-coordinating anion
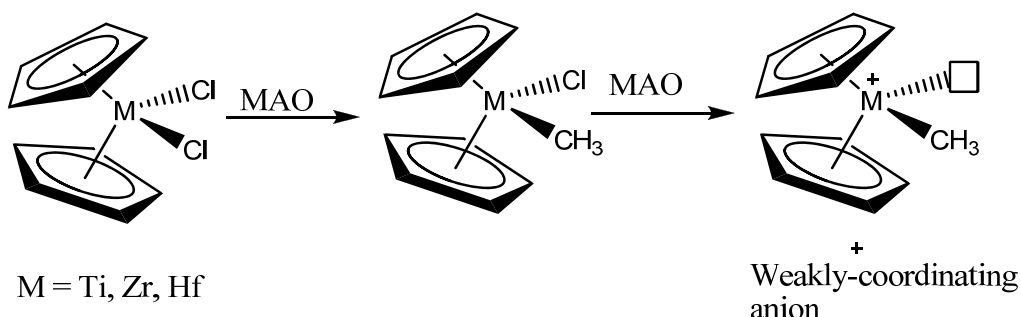
Scheme 3. Activation of a Group 4 metallocene catalyst by MAO.

Weak ligands such as alkenes are able to coordinate to the "activated" metal centre. A 1,2-migratory insertion occurs when an alkene is coordinated to the metal centre, increasing the polymer chain by two carbons and creating an "empty site" where the alkyl used to be (Scheme 4). The orientation of the R group on the alkene (and by extension the tacticity of the polymer) is influenced by the steric effects of the ligand. The polymerization process may be repeated many times until a termination reaction occurs.

M = Ti, Zr, Hf
R = H, $(CH_2)_n OTMS$
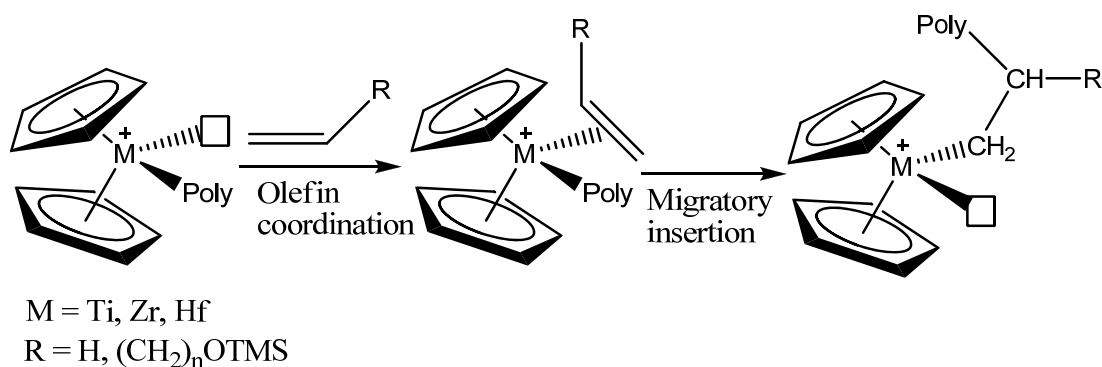
Scheme 4. Mechanism of polymer chain growth with a metallocene catalyst.

There are several ways by which polymer termination can occur (Scheme 5). One termination reaction is hydrolysis, which is fast and irreversible. A protic species would nucleophilically attack the Group 4 metal on the catalyst to irreversibly deactivate the catalyst and protonate the alkyl chain to create a saturated polymer or alkane. β-Hydride elimination is a chain transfer pathway whereby the metal centre abstracts a β-hydride from the polymer chain, creating a terminal olefin. The terminal olefin can be displaced by a monomer or the hydride can reinsert at either the 1 or 2 positions. If polymerization resumes after this step, then a new branch is formed. Cocatalysts also play an important part in the termination reactions. The titanium catalyst can undergo transmetallation with the alkyl aluminum cocatalyst and exchange an alkyl group for the polymer chain.[10]
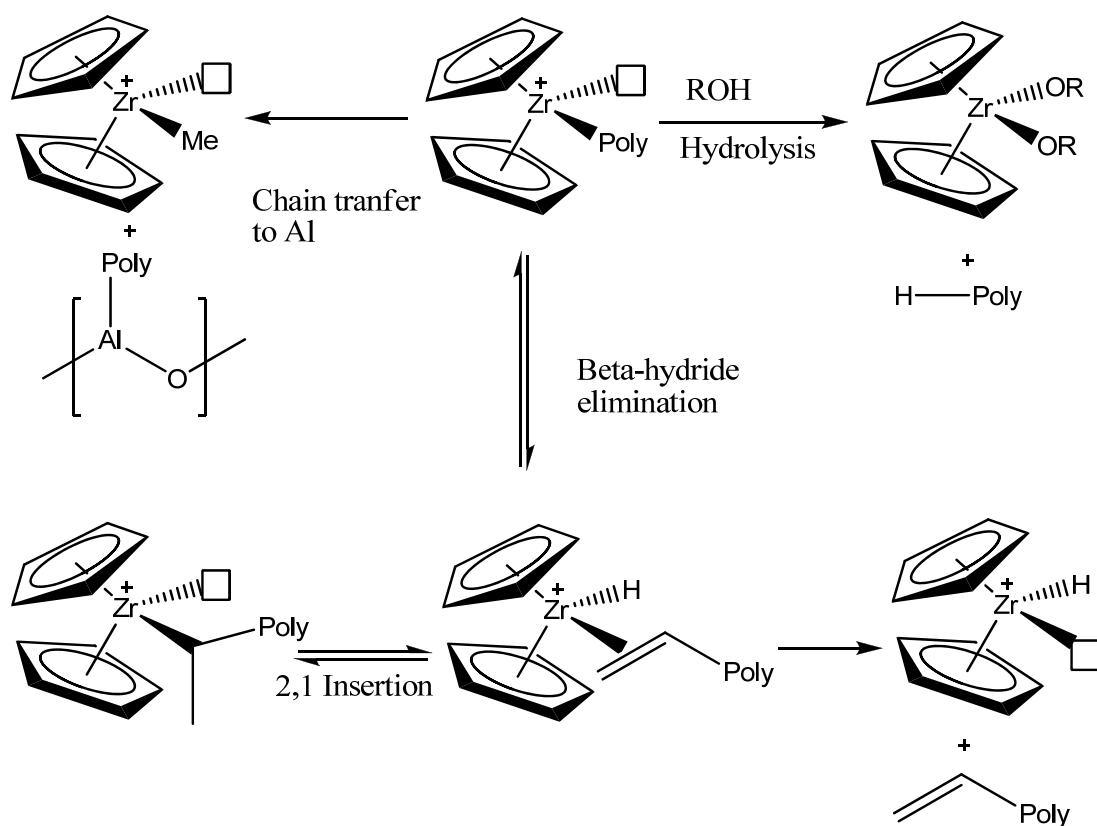
Scheme 5. Chain termination and transfer of metallocene-catalyzed olefin polymerization.

MAO is known to react with homogeneous Ziegler-Natta catalysts to reduce titanium(IV) to a catalytically inactive titanium(III) through a bimolecular process (shown in Scheme 6).[11]

$$2 \ Cp_2TiCl(CH_2CH_2Poly) \cdot AlRCl_2 \longrightarrow 2 \ Cp_2TiCl \cdot AlRCl_2 + CH_2CHPoly + CH_3CH_2Poly$$

Scheme 6. Group 4 metallocene catalyst reduction by an alkyl aluminum dichloride.

CHAPTER 2: LITERATURE REVIEW

$Ti[(C_5Me_4)SiMe_2(^tBuN)]Cl_2$ (**1**), which is shown in Figure 4, was chosen as a catalyst for copolymerization studies after a literature review. The polymerizations that were done over the course of this thesis were performed at atmospheric pressure because the selected catalyst was expected to be sufficiently active at 1 atm that high pressure polymerizations were not necessary. Kaminsky reported that **1** had an activity of 960 kg polymer/(mol · hour) at 3 bar for 1 h in 200 mL of toluene at 30 ºC.[12] Frediani *et al.* also reported activity of 570 kg/mol for **1** when it was polymerized in 200 mL of toluene with 1400 equivalents of MAO, 3 bar of ethylene pressure and 1 hour of reaction time.[13] Unfortunately there were no comparable values for ethylene polymerization at 1 bar with **1** in the Scifinder Scholar database. In addition, each apparatus is different so ethylene homopolymerizations had to be performed for each set of conditions for comparison.

(1)
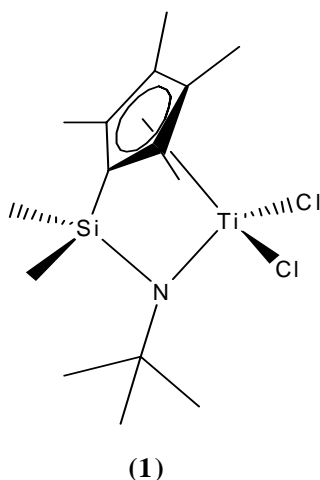
Figure 4. Structure of Ti[(C$_5$Me$_4$)SiMe$_2$(^{t}BuN)]Cl$_2$.

Incorporation rates of polar comonomers into polyethylene were expected to vary with the size of the comonomers and the kinetics of catalyst inhibition. Since **1** has a sterically open active site, it readily incorporates 1-alkenes and unsaturated macromonomers into growing polyethylene chains.[14] For example, Soga achieved 56.4% molar incorporation of 1-octene into polyethylene.[15] Long chain branching in polymers with a narrow molecular weight distribution gives the polymer desirable physical properties with good processability.[16]

1 has also been the subject of tandem catalysis research. Kaminsky discovered a system involving **1** and an (imino)pyridyl Co(II) catalyst (Figure 5) which creates LLDPE from ethylene.[17] In this system, the cobalt catalyst oligomerized ethylene into 1-alkenes, while the titanium catalyst concurrently copolymerized the 1-alkenes with ethylene. Tandem catalysis has the novel benefit of producing LLDPE from only ethylene feedstock instead of adding a comonomer. **1** has also been successfully used as a tandem catalyst with zirconium, titanium and hafnium compounds.[18,19,20]

X = Halide
R = BT, ET, Ph
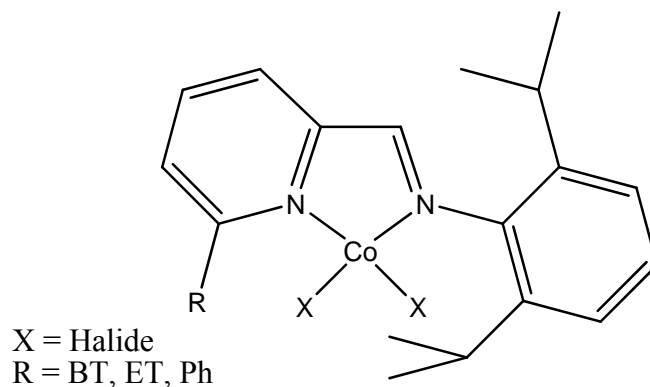
Figure 5. Co(II) pyridyl catalyst used in tandem catalysis of LLDPE.

Direct copolymerization of functional monomers with ethylene is impossible with Zieger-Natta catalysts because of titanium's high affinity for the Lewis basic functionality of the comonomers.[21] Hakala found that long spacers between the alkenyl group and the oxygen atom of a polar comonomer gave increased incorporation, as he achieved up to 0.7 mol% incorporation of 10-undecen-1-ol into polyethylene using a bridged zirconocene catalyst.[22] On the other hand, increased spacer groups did not affect the deactivating effect of the polar comonomer upon the catalyst.[23] Various researchers have had success by pre-treating and/or masking the functional groups of the polar comonomers before copolymerizing with homogeneous Ziegler-Natta catalysts. Pre-treated 5-hexen-1-ol has been incorporated up to 50 mol% into polyethylene and polypropylene and 36.7 mol% 10-undecen-1-ol has been incorporated into polyethylene.[24,25]

2.1 Aluminum Cocatalysts

Since the unexpected discovery of Ziegler-Natta catalysis, alkyl aluminum compounds developed an important role as cocatalysts with transition metal catalysts (examples are shown in Figure 6).
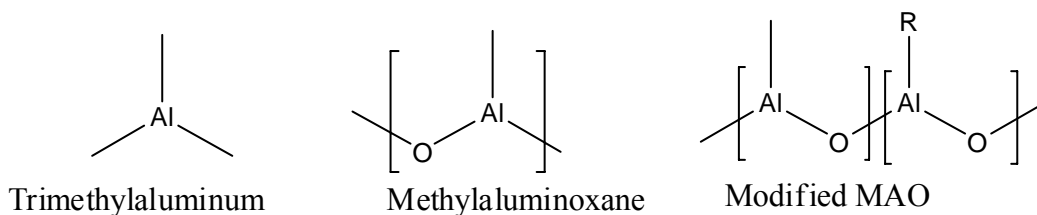
Figure 6. Alkyl aluminum cocatalysts.

Researchers discovered that a small amount of water contamination during polymerization with trimethylaluminum (TMA) significantly improved polymer yields.[26] A controlled hydrolysis of TMA created an aluminum compound known as MAO, which has a commonly accepted stoichiometric formula of $AlOCH_3$. The structure of MAO cannot be directly determined by X-ray crystallography because the different oligomers of MAO cannot be isolated and crystallized.[27] Computational and NMR studies have suggested that MAO adopts a variety of cyclic, fused rings or oligomeric structures.[28] A significant amount of research in the 1980s revealed that MAO was a far superior cocatalyst than TMA for metallocene catalysts because its oligomeric structure stabilized the negative charge after activating the titanium precatalyst, making it a very weak nucleophile in its aluminate form.[29] Another advantageous property of MAO is its high solubility in aromatic solvents, such as toluene.

MAO typically has limited solubility in aliphatic solvents, so scientists developed modified MAO. This variation of MAO has a fraction of the methyl groups replaced by

longer alkyl chains. Modified MAO additionally has a longer shelf-life than
conventional MAO, as it will remain in solution for a longer period of time. MAO is
currently industrially produced by firms such as Akzo-Nobel for polymer production.

2.2 Polar Comonomers

1-Alkenols were used as the polar comonomers that were copolymerized with
ethylene for this thesis. They were chosen because of their commercial availability, ease
of silylation (which is discussed in section 2.3) and the large body of research on
copolymerizing 1-alkenes with ethylene. It was expected that properly protected 1-
alkenol comonomers would behave similarly to 1-alkenes with respect to
copolymerization with ethylene. Group 4 catalysts are highly oxophilic and therefore
susceptible to nucleophilic attack from a 1-alkenol that would deactivate the catalyst, as
shown in Scheme 7. [30]
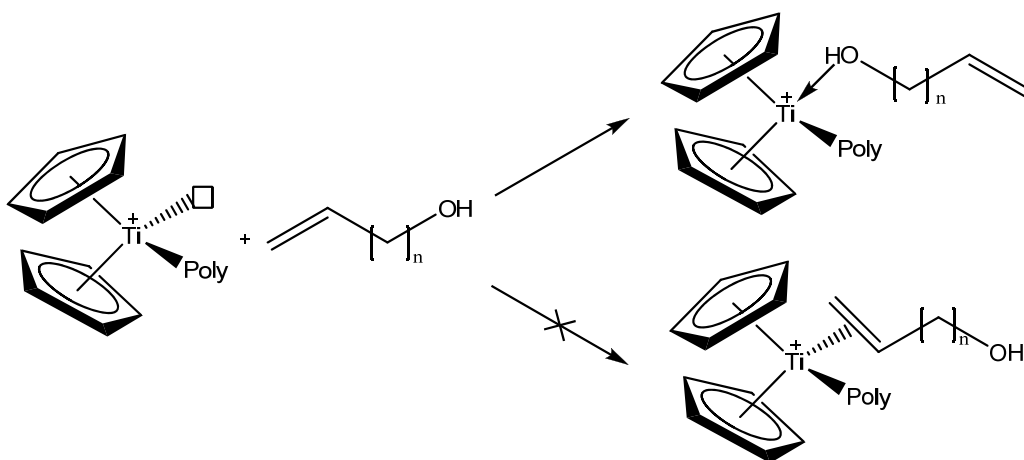
Scheme 7. Catalyst deactivation by a Lewis base.

The alcohol moiety of the 1-alkenols was protected to try to prevent catalyst deactivation during the course of copolymerization. Even so, it was expected that high concentrations of the masked polar comonomer would have an inhibitory effect. 9-Decen-1-ol was the first comonomer that was investigated in the course of this thesis, since it was the subject of previous research in our lab and was already stocked in the laboratory. 9-Decen-1-ol was expected to be an effectively incorporated comonomer because of its relatively long spacer between the polar moiety at one end and the alkene group on the other end, as mentioned in the literature review. To support this hypothesis, two short-chain 1-alkenols, 3-buten-1-ol and 2-propen-1-ol, were used as polar comonomers to study the effectiveness of **1** incorporating short polar comonomers into the polymer. The structures of the three 1-alkenols that were protected and used in copolymerization studies are shown in Figure 7.

9-Decen-1-ol

3-Buten-1-ol

2-Propen-1-ol (allyl alcohol)
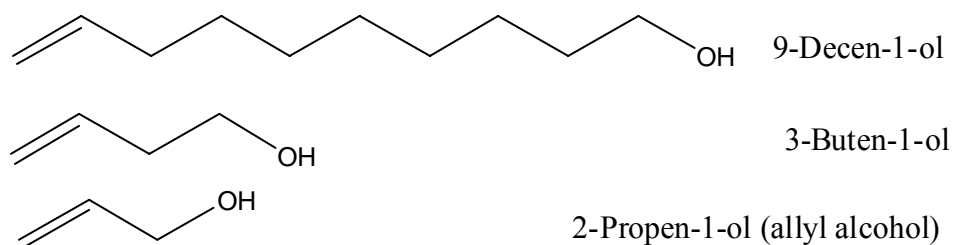
Figure 7. 1-Alkenols that were used as polar comonomers.

2.3 Masking Groups for Polar Comonomers

A previous graduate student in the Baird lab studied methyl, benzyl, trityl, triphenylsilyl, and trimethylsilyl moieties as masking groups for 9-decen-1-ol to reduce the deactivation of early transition metal catalysts.[31] Goran Stojcevic's copolymerization

studies found that the trimethylsilyl (TMS) moiety was the most effective masking agent for 1-alkenols.

TMS substitution reduced catalyst inhibition by the comonomer through both steric and electronic effects. The TMS group is large enough that steric interference reduces the rate at which oxygen coordinated to the metal to deactivate the catalyst. Some of the electron density on the oxygen's lone pairs was donated to silicon's empty d-orbitals through hyperconjugation, reducing the nucleophilicity of the silyl ether.[32] The TMS group was also easier to hydrolyze during polymer work-up than some of the other masking groups that Stojcevic explored. Silyl ethers are typically easier to remove by acid hydrolysis than ether groups.

2.4 Ethylene/1-TMSO-Alkene Copolymers

2.4.1 Properties of Ethylene/1-TMSO Copolymers

Incorporating 1-TMSO-alkenes into polyethylene adds trimethylsiloxy functional groups (which are hydrolyzed to hydroxyl groups) to the otherwise saturated hydrocarbon polymer, shown in Figure 8. Adding hydroxyl groups was expected to increase intermolecular attraction between polymer chains by introducing hydrogen bonding.
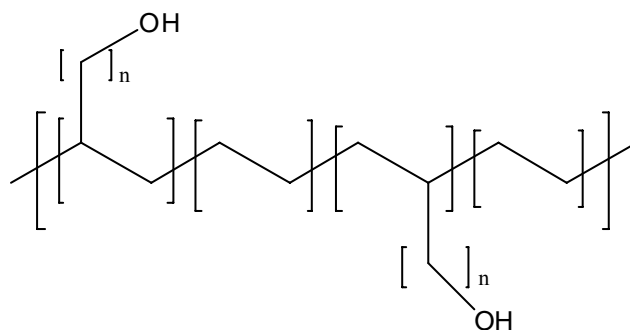
Figure 8. Example structure of a poly(ethylene-*co*-1-alkenol).

Hydrogen bonding was expected to make this copolymer tougher than comparable polyethylene while the controlled branching of the copolymer was expected to also give it physical and melt properties similar to LLDPE. Increasing the polarity of the polymer may create some new advantageous properties with respect to mixing, adhesion, strength, and other chemical or physical properties.

Copolymerizing ethylene with a polar comonomer is one strategy to increase the polarity of a polyethylene surface. There is a large body of research into incorporating polar comonomers in polyethylene by a free radical process.[33] More recently, there has been research into copolymerizing polar comonomers such as ethers and esters with ethylene using late transition metal catalysts, such as a Ni-diimine Brookhart-type catalyst (Figure 9).[34]

M = Ni, Pd
X = halide
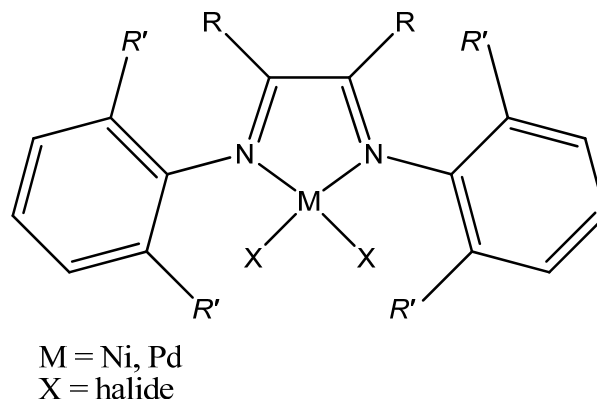
Figure 9. Brookhart-type precatalyst.

2.4.2 Applications of Ethylene/1-TMSO-Alkene Copolymers

There are some applications for which polyethylene performs poorly, but a copolymer of ethylene and a 1-TMSO-alkene was expected to have superior performance. Improving the adhesion properties of polyethylene would make printing on polyethylene surfaces with water-soluble inks easier, since polyethylene is normally non-polar and non-porous. Ink applied to an untreated polyethylene surface beads and smudges easily.[35] Current techniques for printing on a polyethylene surface require adding a surfactant to the ink or subjecting the polyethylene surface to corona discharge treatment. The understanding of the mechanism of corona discharge is currently controversial, but it is hypothesized that the electrical discharge creates carbon radicals that either react with the air to form hydroxyl groups or with adjacent carbon radicals to form unsaturated carbon-carbon bonds.[36] This process is essentially uncontrollable and poorly understood.

Polyethylene lacks miscibility with polar polymers, such as polyamides or polyesters, because of its non-polar nature. Dissolution is entropy-driven, but polymers

are very large molecules so the entropy gain of mixing two polymers is small. If a polar

polymer and polyethylene were melted and mixed together the product would become

phase separated.[37] Increasing dipole-dipole interactions between the different types of

polymer is expected to improve miscibility. This copolymer may have applications for

surface modifying materials such as silica or ceramics, better packaging, etc.

2.5 Cyclopentadienyl-Fluorenyl Zirconium Catalysts

Ewens developed a family of stereospecific polyethylene catalysts in 1988 (Figure

10) to produce syndiotactic polypropylene.[38] Zenk published the *tert*-butyl

functionalized catalyst $Zr[(Cp)CPh_2(2,7-^tbutylfluorene)]Cl_2$ (Figure 10) in 1996 and

explored its properties to produce stereospecific polypropylene.[39] Kaminsky's further

research showed that $Zr[(Cp)CPh_2(2,7-^tbutylfluorene)]Cl_2$ effectively produced

syndiotactic polypropylene because of its large steric bulk and the precatalyst's C_2

symmetry. He also discovered that it effectively incorporated long chain 1-alkenes into

polyethylene and polypropylene.[40] Baird initially chose this catalyst to investigate its

ability to incorporate 1-alkenol derivatives.

R= H, *t*-Bu, etc.   **(2)**
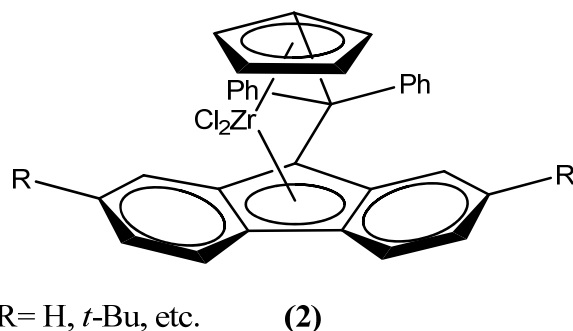
Figure 10. Bridged fluorenyl zirconocene precatalyst.

It was hypothesized that a TMS-masked long chain 1-alkenol would have similar incorporation rates to the 1-alkenes. Catalyst deactivation by the polar comonomer was not expected to be significant because of the steric bulk of the ligand and protected polar comonomer. Due to difficulties preparing this compound, further research was devoted to the catalyst in section 2.6.

2.6 Cyclopentadienyl-Amido Titanium Catalyst

$Ti[(C_5Me_4)SiMe_2(^tBuN)]Cl_2$ (**1**) was synthesized to catalyze ethylene homopolymerization and copolymerization with 1-alkenol derivatives. The cyclopentadienyl-amido ligand was first published by Bercaw in 1988 as a ligand for a scandium catalyst for olefin polymerization.[41] The titanium analogue was developed and patented by Dow and Exxon in the late 1980's because it had relatively high activity at low levels of aluminum cocatalyst and the catalyst copolymerized 1-alkenes with olefins to make high molecular weight polymers.[42]

This catalyst was chosen for this thesis project because it readily incorporates 1-alkenes and macromonomers into growing polymer chains, creating substantially linear polyethylene with long branches.[43] The ability to incorporate long chains into a polymer made this attractive, since if the polar comonomer is sufficiently protected it should behave similarly to 1-alkenes.

The catalyst has a single, sterically open active site because of the constrained geometry of the mono-cyclopentadienyl ligand. This openness reduces steric hindrance from coordinated ligands and increases the Lewis acidity of the titanium centre.[44] Group 4 metals in the +4 oxidation state have no d-electrons; therefore there is no π-back

bonding.[45] The lack of π-back bonding takes electron density away from the ethylene

ligand, making it more electrophilic and weakening the Ti-C_2H_4 bond. On the other

hand, the open active site and high Lewis acidity makes the catalyst highly vulnerable to

nucleophilic contaminants. Cyclopentadienyl-amido titanium catalysts are more stable at

higher temperatures and produce higher molecular weight polymers than *bis*-

cyclopentadienyl catalysts, but are more sensitive to oxygen-containing contaminants.[46]

2.7 Aim of Thesis

The physical properties of polyethylene, such as crystallinity, melting point, glass

transition point, etc. originate from the molecular structure and molecular weight of the

polymer. Recent advances in chemistry are leading to new and improved varieties of

polyethylene through new catalysts, cocatalysts and copolymers.

A series of experiments was performed to determine conditions and reagents that

will balance polar comonomer incorporation with catalytic activity. The variables that

were tested are temperature, equivalents of MAO, equivalents of comonomer, and the use

of dichloromethane and toluene as solvents. The polymer samples were analyzed by

NMR spectroscopy, IR spectroscopy, and DSC in an attempt to understand how the

reaction parameters affect the characteristics of the polymer and to test the hypothesis

that **1** can effectively copolymerize ethylene with 1-TMSO-alkenes to produce

copolymers with improved properties.

CHAPTER 3: EXPERIMENTAL

3.1 Chemical Materials and Reagents

Most of the starting materials and reagents were supplied by Sigma Aldrich. These chemicals include 1,1,1,3,3,3-hexamethyldisilylazane 97%, $LiClO_4$ 95+%, $TiCl_4$ 99.9%, *tert*-butylamine 98%, 3-buten-1-ol 96%, allyl alcohol 99+%, chlorobenzene 99%, 1.6 M methyllithium, 10% methylaluminoxane and 2.5 M *n*-butyllithium. Mixed isomers of tetramethylcyclopentadiene 90+% were ordered from Alfa Aesar. Dichlorodimethylsilane 99%, and *bis*(cyclopentadienyl)zirconium(IV) chloride 99% were provided by Strem. Fischer Scientific provided hydrochloric acid, methanol and silica. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories. These chemicals were all used as-is unless otherwise noted.

3.1.1 Reaction Solvents

Reaction solvents were 99.8% pure and degassed, supplied by Sigma Aldrich in pressurized kegs. The solvents were passed through a nitrogen pressurized alumina solvent purification system to remove trace amounts of moisture. Toluene that was used as a polymerization solvent, ethyl ether, and dichloromethane were further dried by storing them in a Schlenk flask over activated 3 Å molecular sieves. The moisture content of the solvents from the solvent system was measured by Karl-Fischer titration. These titrations were performed monthly by fellow graduate students Kevin Fowler and

Andrew Fraser. The molecular sieves were heated overnight at 300 ºC under vacuum to activate them.

3.1.2 NMR Solvents

Some of the compounds in this project were air and/or moisture sensitive, so the deuterated NMR solvents used for these moisture-sensitive chemicals had to be degassed and dried. The deuterated solvent was added to a Schlenk tube containing calcium hydride connected to a Schlenk line. The solvent was degassed by three freeze-pump-thaw cycles and then the solvent was stirred over calcium hydride overnight to remove traces of moisture. The deuterated solvent was vacuum transferred into an empty Schlenk flask for storage in the glove box. The purification of the deuterated solvents was performed by several different fourth-year students and Baird lab M.Sc student Heidi Murray.

1,1,2,2-Tetrachloroethane-d_2 (b.p. 146.5 ºC) and $CDCl_3$ (b.p. 61 ºC) were only treated with activated 3 Å molecular sieves to remove water. Further purification of those solvents was not necessary as they were used for air and moisture-stable compounds.

3.1.3 Glassware

Glassware was cleaned in a KOH/iPrOH bath, rinsed with water, dipped in an acid bath, rinsed again with water and dried overnight in an oven at 160 ºC. Glass frits were cleaned with an acid bath and aqua regia when necessary.

Hot glassware was either brought into the glove box to be assembled or it was assembled and attached to the Schlenk line to be placed under an argon atmosphere. All of the reactions were performed under an argon atmosphere using standard Schlenk line techniques unless otherwise specified.

3.2 Analytical Methods

3.2.1 IR Spectroscopy

IR spectroscopy samples were prepared by depositing chlorobenzene smears on a NaCl plate. This method avoids interference in the alkyl stretch region from media such as Nujol or Fluorolube.

Approximately 20 mg of polymer was dissolved in about 0.5 mL of hot chlorobenzene in a small vial. After the polymer had completely dissolved, three or four drops of the hot solution were placed onto a NaCl plate. The plate was placed on top of a drying oven at 40 ºC for 20-30 minutes to evaporate the solvent. The spectrum was acquired using a Perkin Elmer IR Spectrum One FT-IR instrument (resolution = 4 cm^{-1}) with 4 scans and an automatic baseline correction procedure was performed.

3.2.2 DSC

A measured polymer sample of no more than 5 mg was placed into a small aluminum DSC pan, the aluminum cover was placed on top and the two halves were

crimped together. An empty aluminum DSC pan was used as a reference. The DSC scans were acquired on a Perkin Elmer DSC 7 instrument.

The same program was used for all of the polymer samples. The sample was held at 30 ºC for 1 min, and then it was heated at a rate of 5 ºC/min to 140 ºC. The temperature was held at 140 ºC for 1 min and then the sample was cooled to 30 ºC. Three cycles were performed consecutively, but only the data from the second run were analyzed.

3.2.3 NMR Spectroscopy

NMR spectroscopy was the main analytical technique for the compounds that were synthesized in the course of this project. All of the NMR spectra were acquired on a 400 or 500 MHz Bruker instrument at the Queen's Department of Chemistry. The instruments were manually shimmed and 16 scans were acquired with a d1 value of 1 s. NMR spectra of polymer samples in TCE-d_2 were run at 120 ºC in the 400 MHz Bruker instrument due to the insolubility of the polymer at ambient temperature.

3.2.4 Dimethylzirconocene Tests

Dimethylzirconocene readily reacts with protic Lewis bases, such as a residual 1-alkenol, to liberate methane gas. Dimethylzirconocene also has distinct ^{1}H NMR signals that can be easily integrated and compared. This makes dimethylzirconocene an ideal reagent to measure protic impurities. High purity polar comonomers were required because compound **1** was very sensitive to Lewis bases. The appearance of methane

(0.21 ppm), and/or oxo-bridged zirconocene (-0.02 ppm) peaks or the change in the integration of the Zr-Me peak (-0.14 ppm) in a ^{1}H NMR spectrum would indicate a reaction with dimethylzirconocene.[47]

Dimethylzirconocene tests were performed to detect unreacted 1-alkenols in the 1-TMSO-alkenes. Approximately 3 mg of dimethylzirconocene was dissolved into a 0.4 mL C_6D_6 or C_7D_8 NMR sample. A ^{1}H NMR spectrum was acquired and then the sample was returned to the glove box. A weighed amount of 5-15 equivalents of masked polar comonomer was added to the same NMR sample by syringe and then another ^{1}H NMR spectrum was acquired.

No significant changes to the intensities of the Zr-Me or the Zr-Cp peaks were observed in any of the ^{1}H NMR spectra after the addition of 5-15 equivalents of polar comonomers. Therefore all three 1-TMSO-alkenols were over 99% pure from these tests. This level of purity was considered to be acceptable, as the masked polar comonomers were effectively pretreated with MAO during polymerizations, which was expected to scavenge residual protic species.

Figure 11 is a ^{1}H NMR spectrum of a dimethylzirconocene test performed on 1-TMSO-2-propene performed by Murray. In this spectrum the integrations of the Cp-Zr and the Me-Zr peaks were unaffected by the presence of a large excess of the polar comonomer, indicating the absence of protic impurities.
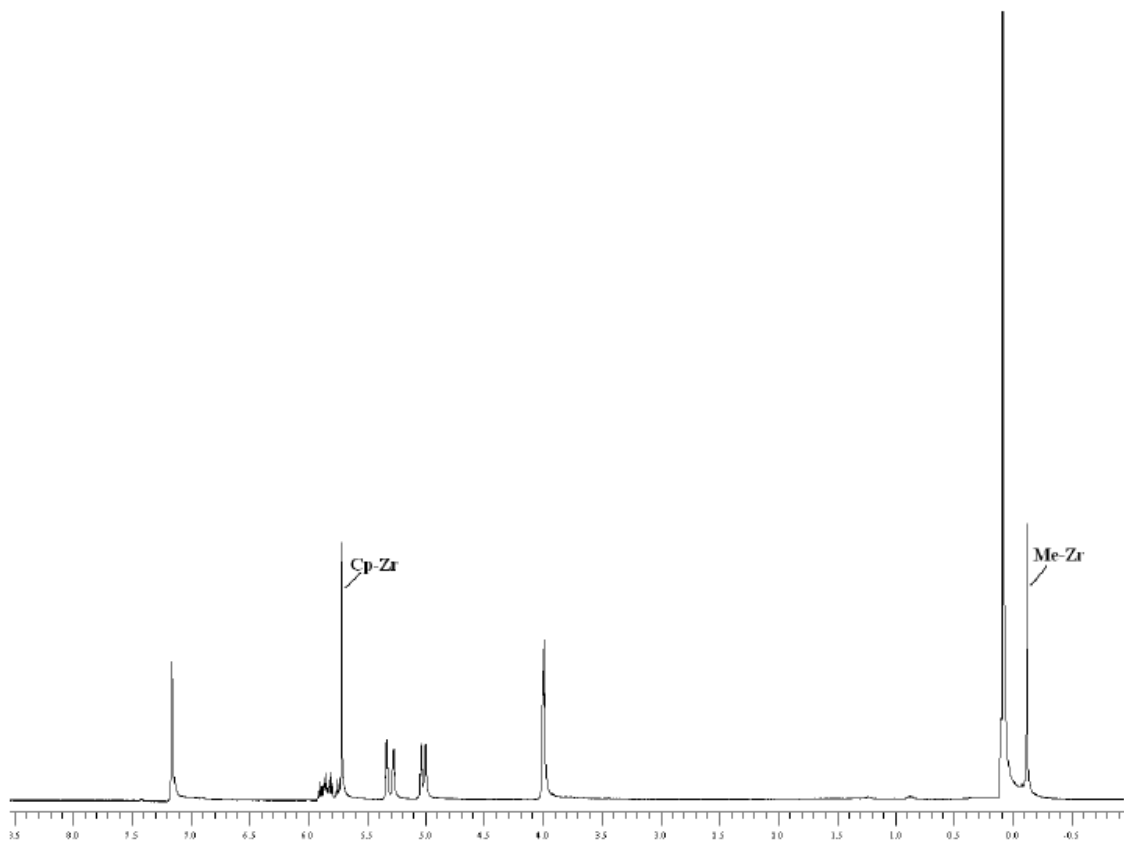
Figure 11. ^{1}H NMR spectrum (300 MHz, C$_6$D$_6$) of 1-TMSO-2-propene with dimethylzirconocene.

3.3 Syntheses

3.3.1 Dimethylzirconocene

A Schlenk flask was charged with 40 mL of ethyl ether, cooled to -78 ºC by a dry ice bath and 4.78 g (0.164 mol) of dichlorozirconocene was added. A slight excess of 1.6 M methyllithium (0.0368 mol, 2.24 equiv.) in ethyl ether solution was added to the stirred reaction mixture slowly by syringe. The solution was slowly warmed to room temperature and it continued stirring overnight. The solvent was removed *in vacuo* and

the residue was dissolved in 40 mL of hexanes. The mixture was filtered through a short

Celite™ column to remove LiCl and the filtrate was reduced by vacuum and cooled with

a dry ice bath to crystallize the product. The product was recrystallized from hexanes,

yielding 1.77 g (0.0704 mol, 43%) of white crystals. The dimethylzirconocene crystals

were vacuum-dried and stored in the glove box freezer at -35 ºC. This is a known

compound that was characterized by ^{1}H NMR (C_6D_6) δ 5.70 (Cp-H, s, 10H) -0.12 (CH_3,

s, 6H).[48]
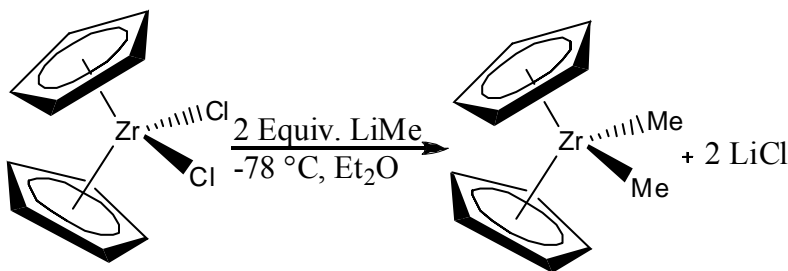
Scheme 8. Synthesis of dimethylzirconocene.

3.3.2 1-TMSO-9-Decene

9-Decen-1-ol was silylated with hexamethyldisilazane (HMDS) by a variation of

the Saidi method (shown in Scheme 9) used on the other two 1-alkenols.[49] This

procedure gave high yields and had a simple work-up because the only by-product was

ammonia and the catalyst was insoluble.
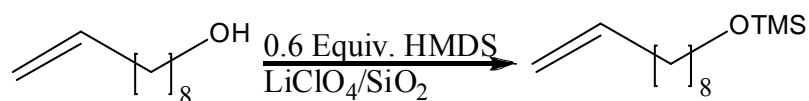
Scheme 9. Silica-supported LiClO$_4$-catalyzed silylation of 9-decen-1-ol.

The LiClO$_4$-SiO$_2$ catalyst was prepared by adding approximately 0.5 g of LiClO$_4$ and 1 g of silica to a Schlenk flask. The flask was sealed with a rubber septum and backfilled with argon from the Schlenk line. 30 mL of ethyl ether was added to the Schlenk flask and the mixture was stirred for 30 min to evenly distribute the LiClO$_4$ on the silica particles. The solvent was removed *in vacuo* and the Schlenk tube was refilled with argon. The Schlenk tube was charged with 36 mL of dry dichloromethane, 10.5 mL of 9-decen-1-ol (9.2 g, 0.058 mol) and 7 mL of hexamethyldisilazane (5.4 g, 0.034 mol, 0.57 equiv.) and then the reaction mixture was stirred overnight. The mixture was filtered through a short silica column to separate the LiClO$_4$-coated silica catalyst and a small amount of hexanes was added to flush the residual TMSO-1-alkene through the column. The solvent and unreacted hexamethyldisilazane were removed by vacuum. The 1-TMSO-9-decene was stirred over sodium metal overnight to react with any residual starting material. The polar comonomer was vacuum distilled to separate the sodium and sodium alkoxides, yielding 3.94 g (0.017 mol, 30.0%) of clear and colourless liquid. The product was a known compound that was characterized by ^{1}H NMR (CDCl$_3$) δ 5.81 (ddt, 1H , alkene CH) 4.99 (dd, 1H, *trans* alkene CH$_2$) 4.92 (dd, 1H, *cis* alkene CH$_2$), 3.56 (t, 2H, CH$_2$OSi), 2.04 (m, 2H, **CH$_2$**CH$_2$O), 1.52 (m, 2H, CH$_2$) 1.37 (m, 2H, CH$_2$), 1.29 (m, 8H, CH$_2$), 0.11 (s, 9H, SiMe$_3$).[50]

3.3.3 1-TMSO-3-Butene

This compound was synthesized according to the literature procedure by Heidi Murray.[51] To a mixture of hexamethyldisilazane (15.0 mL, 0.07 mol) and LiClO$_4$ (5.60 g, 0.05 mol) was added the 3-buten-1-ol (8.9 mL, 0.1mol), and then the mixture was

stirred at room temperature (21 ºC) for 24 hrs. CH_2Cl_2 was then added, $LiClO_4$ was removed by filtration through a short silica column and the excess HMDS and the CH_2Cl_2 were removed under reduced pressure. The resulting product was purified by eluting it through a short alumina column with ethyl ether, which was subsequently removed under reduced pressure. The reaction yielded 10.7 g of a clear liquid (74%).

1-TMSO-3-butene was identifiable only by boiling point (lit. 118-120 ºC) as there was no published ^{1}H NMR spectrum for 1-TMSO-3-butene in the Scifinder Scholar database.[52] ^{1}H NMR ($CDCl_3$) δ 5.82 (ddt, $^3J = 6.2$, $^3J(trans) = 16.8$, $^3J(cis) = 10.2$ Hz, 1H, -CH=), 5.07 (dd, $^2J(geminal) = 2.1$, $^3J(trans) = 16.8$ Hz, 1H), 5.03 (dd, 1H, $^2J(geminal) = 2.1$, $^3J(cis) = 10.2$ Hz, CH_2), 3.64 (t, 7.0 Hz, 2H, CH_2O), 2.29 (dt, $^3J = 6.9$, 6.2 Hz, 2H, CH_2), 0.12 (s, 9H, $SiMe_3$).

3.3.4 1-TMSO-2-Propene

This compound was synthesized by Heidi Murray according to the literature procedure.[53] To a mixture of hexamethyldisilazane (6.02 mL, 28 mmol) and $LiClO_4$ (2.24 g, 20 mmol) was added allyl alcohol (2.75 mL, 40 mmol), and then the mixture was stirred at room temperature for 24 hrs. CH_2Cl_2 was then added and $LiClO_4$ was removed by filtration. The excess HMDS and the CH_2Cl_2 were removed under reduced pressure. The resulting product was purified, eluting through a short alumina chromatograph column with ethyl ether, which was subsequently removed under reduced pressure. The reaction yielded 4.70 g of a clear and colourless liquid (90 %). The product was a known compound that was characterized by ^{1}H NMR ($CDCl_3$) δ 5.85 (m, 1H, alkene CH), 5.16 (m, 2H, alkene CH_2) 4.15 (m, 2H, CH_2), 0.18 (s, 9H, $SiMe_3$).[54]

3.3.5 (C$_5$Me$_4$H)SiMe$_2$(^{t}BuNH)

The constrained geometry cyclopentadienyl-amido ligand for the titanium catalyst was prepared according to literature; the only change was the substitution of hexanes for pentane as a reaction solvent.[55] First, 4.99 g of 1,2,3,4-tetramethylcyclopentadiene (0.408 mol) was dissolved in 150 mL of hexanes. 16.5 mL of 2.5 M *n*-butyllithium in hexanes (0.0413 mol, 1.01 equiv.) was added to the solution over 1 h and the solution was stirred overnight as a white precipitate formed. Next 35.0 mL of dichlorodimethylsilane (0.253 mol, 6.20 equiv.) was added over 30 min. After stirring the reaction solution for 24 h, the solvent and unreacted dichlorodimethylsilane were removed by vacuum to yield a viscous yellow liquid. The Schlenk flask was refilled with argon and the liquid was dissolved in hexanes. 9 mL (0.0853 mol, 2.09 equiv.) of *tert*-butylamine was added to the reaction mixture over 10 min, and then the mixture was stirred for 24 h. The hydrochloride salt was filtered off with a glass frit, and then the solvent was removed from the filtrate by vacuum to isolate (C$_5$Me$_4$H)SiMe$_2$(^{t}BuNH) (2.20 g, 0.00875 mol, 21.4% yield). This is a known compound that was characterized by ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.81 (s, 1H, C$_5$Me$_4$H), 1.95 (s, 6H, Cp-Me), 1.79 (s, 6H, Cp-Me), 1.12 (s, 9H, C(CH$_3$)$_3$), 0.45 (brs, 1H, NH), 0.01 (s, 6H, Si-Me).[56]
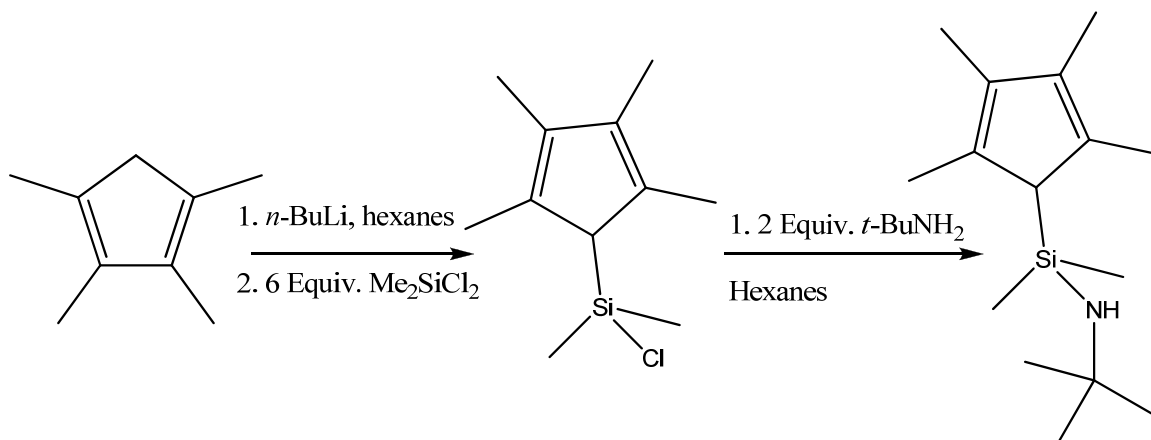
Scheme 10. Synthesis of $(C_5Me_4H)SiMe_2(^tBuNH)$.

3.3.6 Ti[(C$_5$Me$_4$)SiMe$_2$(^{t}BuN)]Cl$_2$

The ligand $(C_4Me_4H)SiMe_2(^tBuNH)$ (2.20 g, 0.00875 mol) was dissolved in 90 mL of ethyl ether in a Schlenk flask cooled to -78 ºC by an acetone/dry ice bath. Two equivalents (7.0 mL, 0.0175 mol) of 2.5 M *n*-butyllithium in hexanes were added drop-wise over 30 min, and then the solution continued stirring while it warmed to room temperature over 20 h. Titanium(IV) chloride (1.47 g, 0.00775 mol, 0.89 equiv.) was dissolved in 40 mL of hexanes and added to the reaction mixture drop-wise over 30 min at -78 ºC, and the mixture was stirred for another 16 h as it slowly warmed to room temperature. The reaction mixture was filtered with a glass frit to remove LiCl, reduced in volume to 30 mL by vacuum, and then cooled to -78 ºC to crystallize the product. The supernatant was carefully removed by syringe and the crystals were washed with a small amount of chilled hexanes. The supernatant was concentrated to recover another crop of crystals. The yield was 1.63 g (0.0044 mol, 57.1% yield) of yellowish-green crystals that were identified by ^{1}H NMR (C$_6$D$_6$) δ 2.00 (s, 6H, β Cp-Me), 1.99 (s, 6H, α Cp-Me), 1.42

(s, 9H, C(CH$_3$)$_3$), 0.43 (s, 6H, Si-Me).[57] The overall yield for the preparation of the

precatalyst was 12.2%.
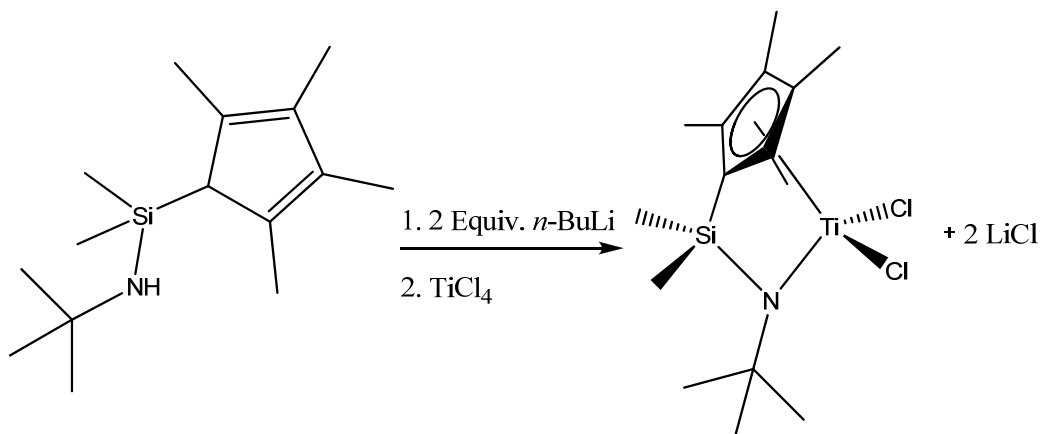
Scheme 11. Metathesis of constrained-geometry catalyst by deprotonation and

coordination of (C$_5$Me$_4$)SiMe$_2$(^{t}BuN) to TiCl$_4$.

3.4 Polymerization

3.4.1 Ethylene Polymerization

The polymerization procedure was derived from the procedures used by

Waymouth.[58] The reaction Schlenk flask contained a Teflon-coated magnetic stir bar,

while another, smaller Schlenk flask had a measured amount of precatalyst. A needle

flowing argon from the Schlenk line was inserted through the Sure-Seal™ of the 10%

MAO solution bottle to prevent air contamination. A measured volume of MAO solution

was drawn out of the bottle by syringe and added to the larger Schlenk flask. Sufficient

toluene was syringed into the Schlenk flask to dilute the MAO solution to 50 mL. 10 mL

of toluene was added to a small Schlenk tube to dissolve 5-10 mg of precatalyst. The

large flask containing the MAO solution was placed in a temperature-controlled oil bath or ice bath for at least 10 min before beginning the reaction if the polymerization was to be performed at an elevated or depressed temperature. Ethylene was bubbled through the stirred MAO solution for 5 minutes to saturate the solution before commencing the reaction. An exhaust needle connected to an oil bubbler was attached to the flask as it was disconnected from the argon line. The precatalyst solution in toluene was added by syringe to the reaction flask to initiate the reaction. After 30 minutes of polymerization, the ethylene and exhaust needles were withdrawn and the flask was opened to air. Methanol acidified with hydrochloric acid was slowly added to the reaction mixture to hydrolyze the alkyl aluminum and the trimethylsilyl ether, precipitate the polymer and quench the catalyst. The methanol/polymer mixture was transferred to an Erlenmeyer flask and stirred overnight to ensure the complete dissolution of the aluminum by-products and precipitation of the polymer. The mixture was vacuum-filtered and washed with methanol. The dried polymer was scraped into a weighed vial and placed overnight in a vacuum oven at 80 ºC to remove traces of solvent or any other volatile compounds.

3.4.2 General Procedure for Ethylene/TMSO-Alkene Copolymerization

The procedure for copolymerization was similar to the procedure for ethylene homopolymerization, except the measured amount of polar comonomer was injected into the large Schlenk after adding the MAO solution, but before initiating the reaction. MAO was expected to scavenge any residual 1-alkenols.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

A total of 102 homo- and co- polymerizations were performed over the course of this thesis project. Temperature, ratio of polar comonomer, amount of precatalyst, solvent, and ratio of MAO were all tested to determine their effects on polymerization and in-depth analyses of the polymers were performed to determine the effects of the different experimental variables on catalytic activity and the polymers' physical properties. The mass of each polymer sample was recorded and each sample was analyzed by ^{1}H NMR and IR spectroscopy. Selected samples were analyzed by DSC to determine the effects of copolymerization and temperature on T_m, T_g and T_c.

The lack of reproducibility of the results of the polymerization experiments was a major concern for this thesis. Stojcevic encountered similar reproducibility issues with an early transition metal catalyst when he was copolymerizing ethylene with masked polar comonomers using early transition metal catalysis.[59] **1** was known to be highly oxophilic and more sensitive to functional monomers and contaminants than metallocene-type catalysts.[60] Contamination may have been present as traces of moisture on the surfaces of glass Schlenk tubes, in the reaction solvent, in the syringes, etc. Minute traces of air may have entered the reaction vessel through rubber septa that may not have sealed properly when punctured or air may have been present in the ethylene line. Ethylene concentration may not have been constant throughout the reaction, as the ethylene needle was susceptible to partial or complete plugging. All of these factors may have reduced the accuracy and precision of the results, thereby limiting some of the conclusions that can be drawn from them.

In light of the aforementioned problems, at least two polymerization runs (usually three, but as many as six) were performed for each set of reaction conditions in order to ensure the results were reliable. Implementing a 30 minute flush of the ethylene line after regeneration and immediately before a set of polymerizations dramatically improved polymer yields. Sixty two of the 102 polymerization experiments were considered acceptable as not all of the polymerizations followed the refined procedure.

4.2 Ti[(C$_5$Me$_4$)Si(Me$_2$)(^{t}BuN)]Cl$_2$

Precatalyst preparation was successful, though the overall yield of 12.2% was below expectations. (C$_5$Me$_4$H)Si(Me)$_2$(^{t}BuNH) was prepared with a 21.4% yield (2.20 g, 8.75 mmol), and the metathesis reaction of the dilithium salt of the ligand with TiCl$_4$ had a 57.1% yield (1.63 g, 4.43 mmol). The overall yields reported by literature for the preparation of Ti[(C$_4$Me$_5$)SiMe$_2$(^{t}BuN)]Cl$_2$ by way of a metathesis reaction are considered low (20-40%).[61]

The low yield for the precatalyst synthesis may be partly the result of impurities in the starting materials, though it was difficult to determine which reagents were responsible since the ligand intermediates were not isolated.

An alternative preparation for **1** was a templated synthesis that had a reported yield of 53.4% for the coordination of the ligand to titanium, but the templated preparation involved additional steps and the use of toxic lead salts.[62] The step-wise synthesis was chosen because the laboratory was stocked with most of the reagents and the synthesis required fewer steps and fewer toxic chemicals.
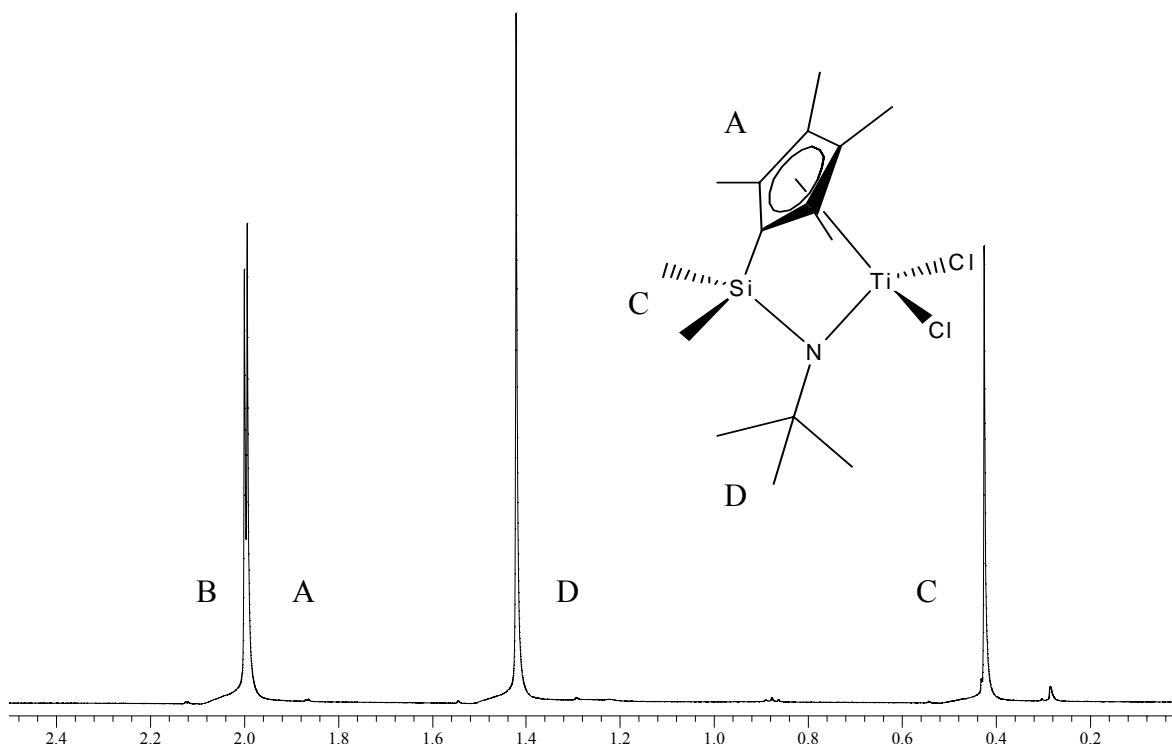
Figure 12. ^{1}H NMR (400 MHz, C_6D_6) spectrum of $Ti[(C_5Me_4)SiMe_2(^tBuN)]Cl_2$.

The ^{1}H NMR spectrum in Figure 12 was in accordance with the literature values for **1**. The two Cp-Me peaks were close together because little difference is expected between Cp substitution in the 1 and 2 positions, as well as being downfield from an alkane peak. The *tert*-butyl amine peak was a singlet, as expected. The trimethylsilyl peak appears upfield, as silyl groups are electron-donating. This spectrum does not contain any residual free ligand or other significant impurities.

4.3 1-Trimethylsiloxy-Alkenes

Preparations of the masked polar comonomers were generally successful. The yield of 1-TMSO-9-decene was low at 30%, though there was no published yield for the LiClO$_4$-SiO$_2$ catalyzed Saidi preparation.[63] The 90% 1-TMSO-2-propene yield that Murray achieved was only slightly below the literature yield of 95% that Saidi achieved

with his LiClO$_4$-SiO$_2$ catalyzed method.[64] 1-TMSO-3-butene was prepared with a 74.3%

yield, though there was no published yield for the LiClO$_4$-catalyzed Saidi method.
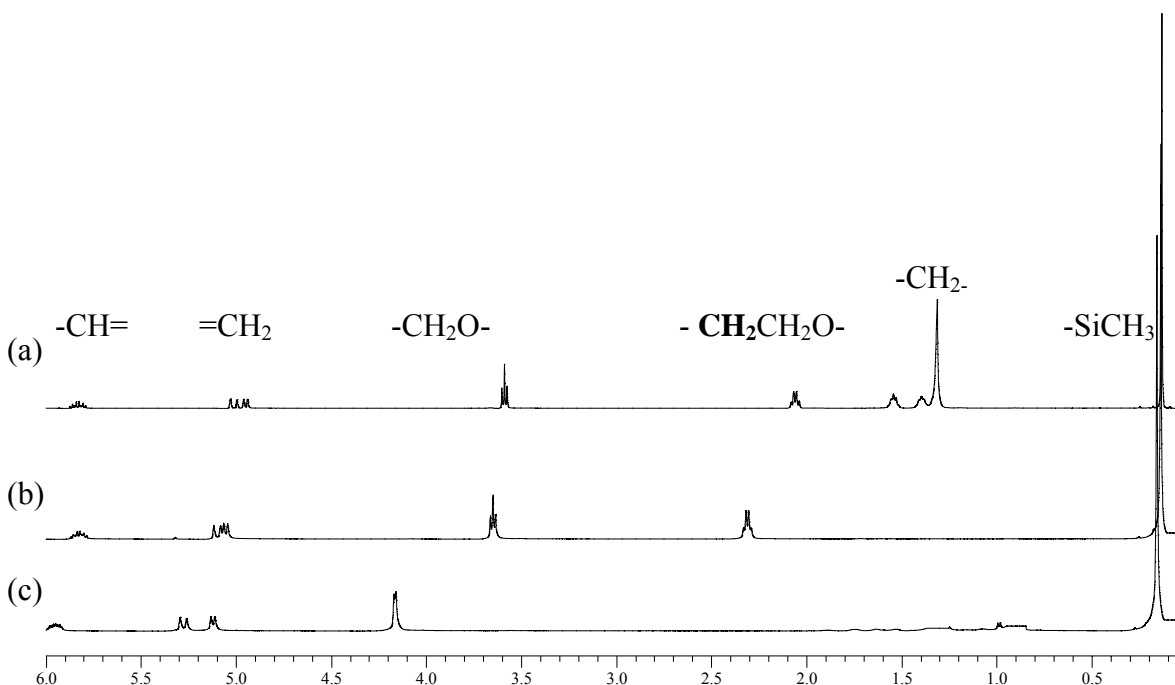
Figure 13. Overlaid ^{1}H NMR (500 MHz, CDCl$_3$) spectra of (a) 1-TMSO-9-decene, (b)

1-TMSO-3-butene and (c) 1-TMSO-2-propene. Hexanes and silicone grease peaks were

removed for clarity.

The ^{1}H NMR spectra of all three 1-TMSO-alkenes were consistent with their

structures (shown in Figure 13). All of the spectra had a TMS peak near 0.2 ppm, a

CH$_2$O peak between 3.6 and 4.2 ppm, and three alkene peaks between 5 and 6 ppm. 1-

TMSO-3-butene and 1-TMSO-9-decene have a methylene quintet that is β to the oxygen.

Lastly, 1-TMSO-9-decene has additional methylene peaks between 1.0 and 1.5 ppm.

4.4 Ethylene Homopolymers

4.4.1 NMR Spectroscopy of Polyethylene

Each polyethylene sample was analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of polyethylene shown in Figure 14 below is typical of PE produced by **1**/MAO. As shown in Figure 1, saturated PE with long chain branching has three proton environments: methyl, methylene and methine. The integral of the methyl triplet at 0.89 ppm was calibrated to 1. The large methylene singlet at 1.40 ppm had an integral between 30 and 200. The small methine peak overlaps with the methylene peak. The chemical shifts of the polyethylene NMR signals corresponded to literature values.[65]
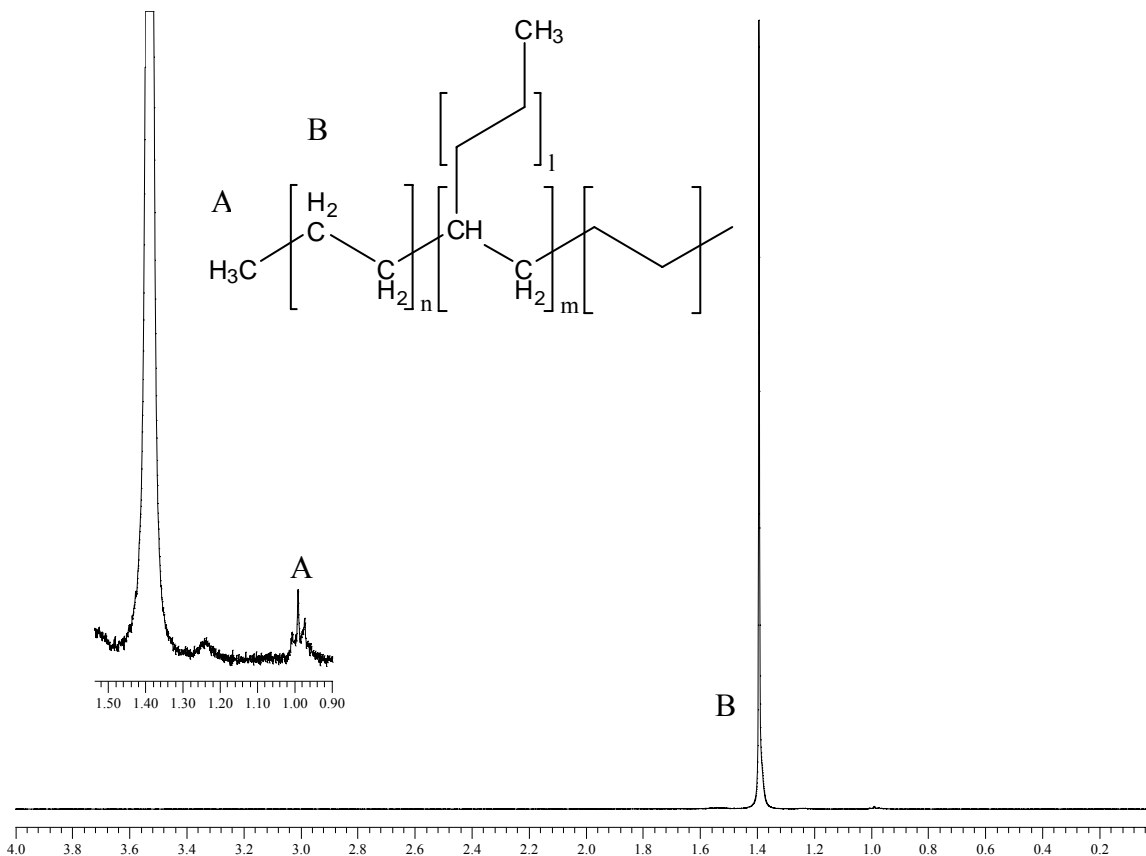
Figure 14. ^{1}H NMR spectrum (400 MHz, TCE-d$_2$) of polyethylene with long chain branching at 120 ºC.

Branching was determined from ^{1}H NMR spectra by dividing the number of (terminal) methyl groups by the total number of carbons, and then converting that number into branches/1000C. The formula for approximating branching is shown in the appendix. The degree of branching for the polyethylene produced by the author varied from 3-20 branches/1000C. Literature and ^{1}H NMR spectroscopy agree on the presence of long chain branching within the polyethylene produced by **1**.[66]

4.4.2 IR Spectroscopy of Polyethylene

Representative IR spectra of polyethylene samples were acquired for comparison with IR spectra of copolymers or attempted copolymers. IR spectra of the polymers were obtained to qualitatively demonstrate incorporation of polar comonomers. An IR spectrum of PE should have no peaks above 3000 cm^{-1} (aside from an artefact at 3584 cm^{-1}); therefore the presence of hydroxyl groups in a copolymer should be immediately apparent. IR spectra of blank NaCl plates showed a small amount of absorbed moisture (as the background signal was not entirely flat in that region), but this was distinguished from comonomer O-H stretching by peak width and intensity.
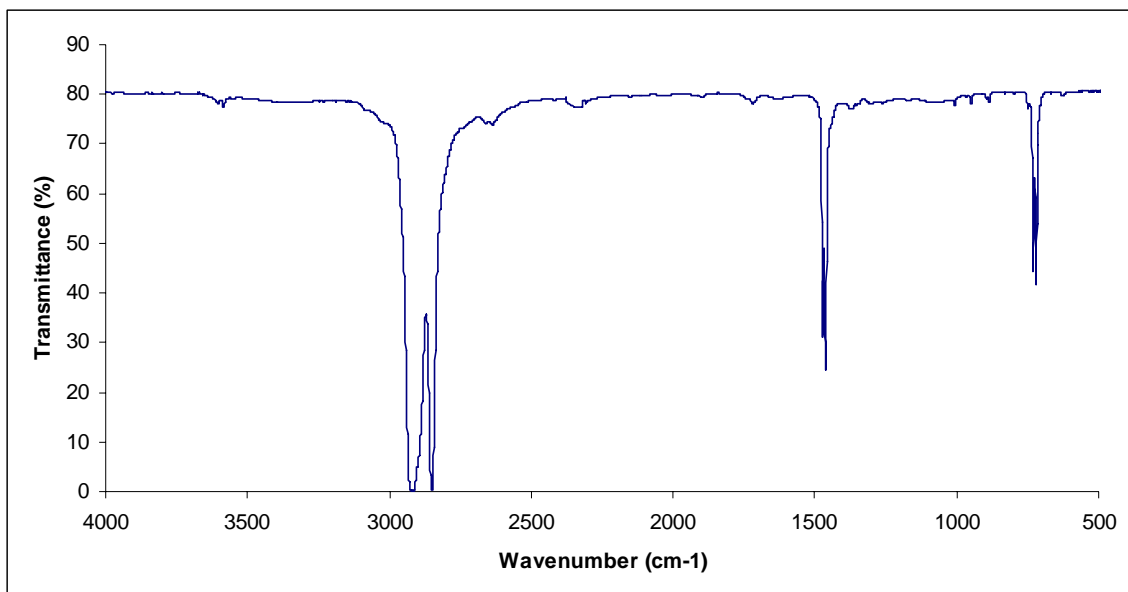
Figure 15. IR spectrum of a polyethylene sample produced at room temperature.

All of the polyethylene samples that were analyzed by IR spectroscopy were very similar in both peak intensity and peak position. Figure 15 shows an IR spectrum of a typical polyethylene sample produced with **1**/MAO. There was a strong intensity asymmetric C-H stretching peak at 2918 cm^{-1}, a strong symmetric C-H stretching peak at 2849 cm^{-1}, a medium intensity C-H bending peak at 1473 cm^{-1}, a medium intensity C-H scissoring peak at 1463 cm^{-1}, and a C-H rocking peak at 729 cm^{-1}. The IR assignments were confirmed by literature.[67]

4.4.3 Ethylene Homopolymerization Results

Ethylene homopolymerization experiments were performed so that direct
comparisons could be made with the copolymers. The activity and branching values in
Table 1 are highly variable due to variations in temperature, mixing, trace contamination,
etc. In Table 1 catalytic activity was highest and branching lowest for polymerizations
performed at room temperature, with a maximum activity of 170 kg/(mol·h·atm).
Catalytic activity and branching are correlated because the reactions that cause branching
and chain propagation are competitive, so the degree of branching was determined by the
relative rates. Also, the catalyst may decompose at elevated temperatures, which may
explain the lower activity rates for ethylene homopolymerizations performed at 60 and 80
ºC. Overall the catalytic activity and polymer branching values were highly variable.

Table 1. Ethylene polymerized with 1000 equivalents of MAO.

Run	Temperature (ºC)	Activity (kg/(mol Ti•h•atm))	Branching (/1000C)
29	0	10	20
30	0	21	16
31	0	32	8
20	21	170	3
21	21	131	5
22	21	112	4
23	60	3	13
24	60	1	54
25	60	26	9
26	60	64	23
27	60	15	7
28	60	50	8
32	80	44	9
37	80	25	8
38	80	7	15

The number of equivalents of MAO had an effect on catalytic activity; polymerizations that used only 500 equivalents of MAO (data in Table 2) had far lower catalytic activities than ethylene polymerizations performed with 1000 equivalents of MAO.

Table 2. Ethylene polymerizations performed with 500 equivalents of MAO.

Run	Temperature (ºC)	Activity (kg/(mol Ti•h•atm))	Branching (/1000C)
39	21	1	19
40	21	30	6
41	21	1	40

4.4.4 DSC Results for Polyethylene

The T_m value was determined by measuring the highest point of the upward peak. The T_c was determined by measuring the lowest point of the DSC trace as the sample cooled. The T_g values were not determined and as they were far below 40 ºC.

DSC traces of the polymers were obtained to determine the effects of copolymerization and reaction conditions on the T_m and T_c. The DSC results revealed a small degree of variation in the T_m for the different polymers.

Figure 16 is a DSC trace of a polyethylene sample that was produced at 0 ºC. This sample had a T_m value of 132 ºC and a T_c value of 121 ºC. These results were consistent with reported T_m values of approximately 130 ºC for polyethylene with long chain branching produced by metallocene catalysts.[68] The T_c values were lower than the T_m values because of the relatively fast rate of cooling.
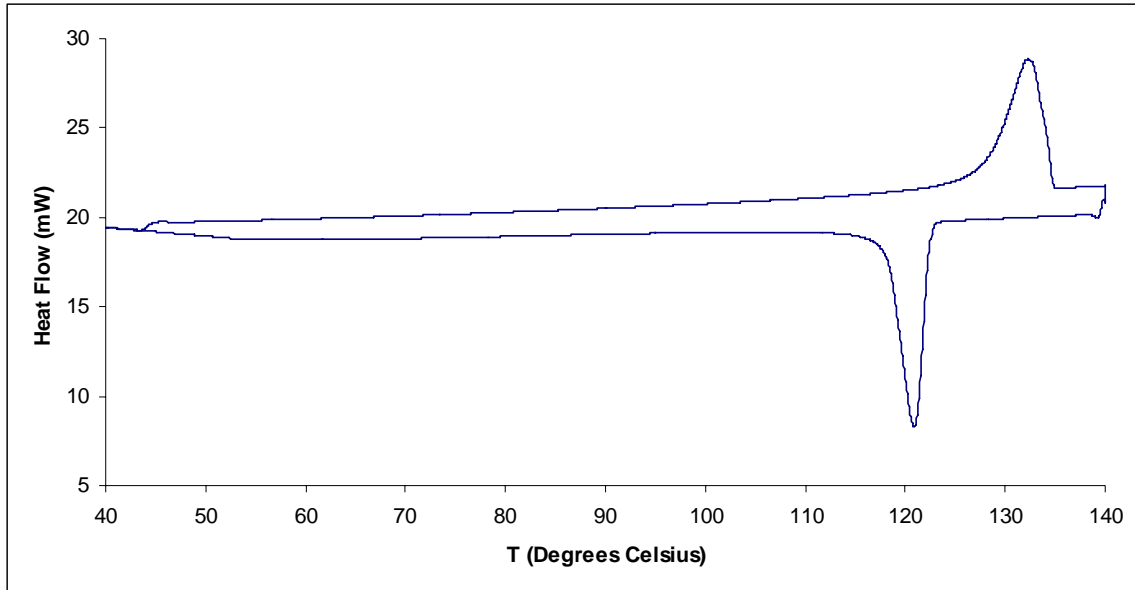
Figure 16. DSC trace of polyethylene sample 30 that was produced at 0 ºC.

Figure 17 is the DSC trace of a polyethylene sample produced at 21 ºC. This sample had a T_m value of 134 ºC and a T_c value of 121 ºC.
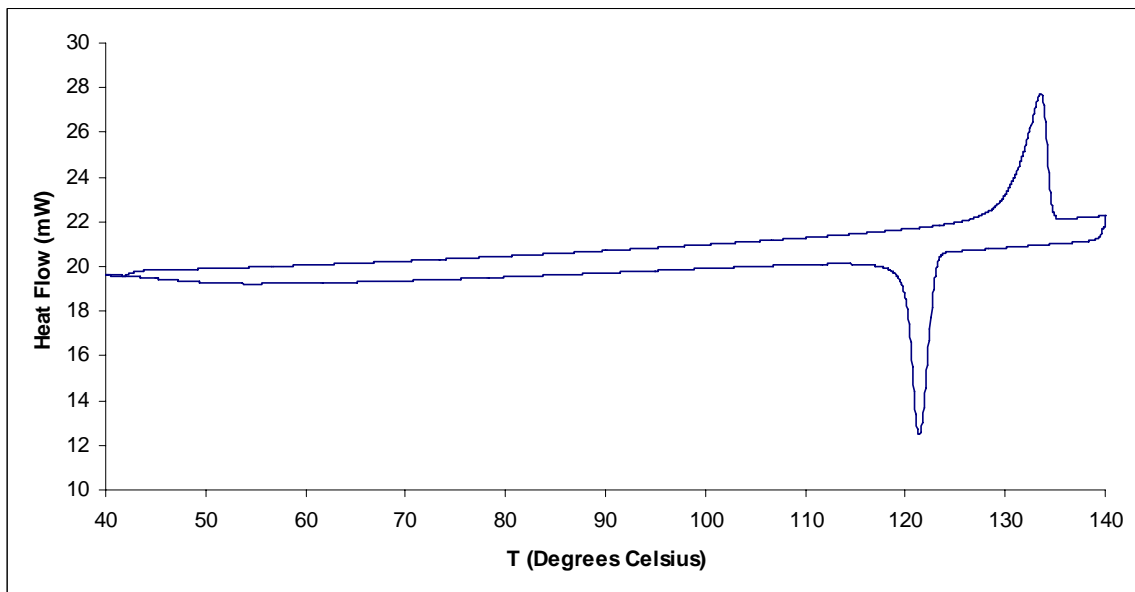
Figure 17. DSC trace of polyethylene sample 21 that was produced at room temperature.

Figure 18 is the DSC trace of a polyethylene sample that was produced at 60 ºC has a T_m of 131 ºC and T_c value of 121 ºC. Polymerizations performed between 0 and 60 ºC had little effect on the melt characteristics of polyethylene.
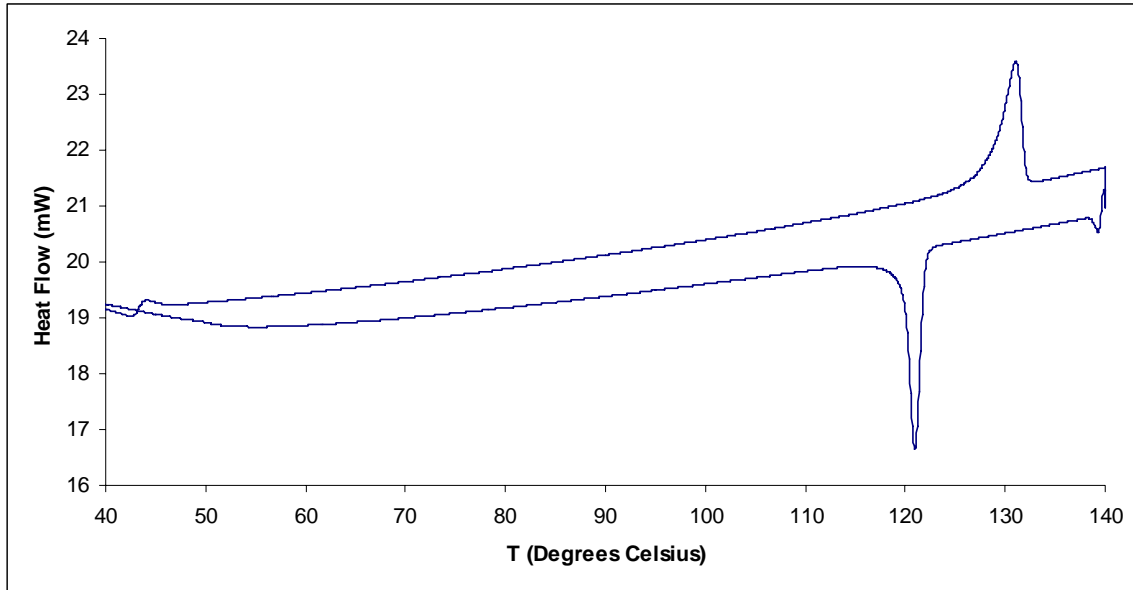
Figure 18. DSC trace of polyethylene sample 28 that was produced at 60 ºC.

Figure 19 is the DSC trace of a polyethylene sample produced at 80 ºC. This sample had a much broader and smaller melting peak than the other polyethylene samples. Additionally, there appears to be a very small and very broad peak during the heating of the polymer sample around 114 ºC. This polymer sample has a T_m of 125-126 ºC and a T_c of 115 ºC. Both of those values are lower than the respective values of the other polyethylene samples. This is because polymers produced at higher temperatures have lower MW and greater branching.[69]
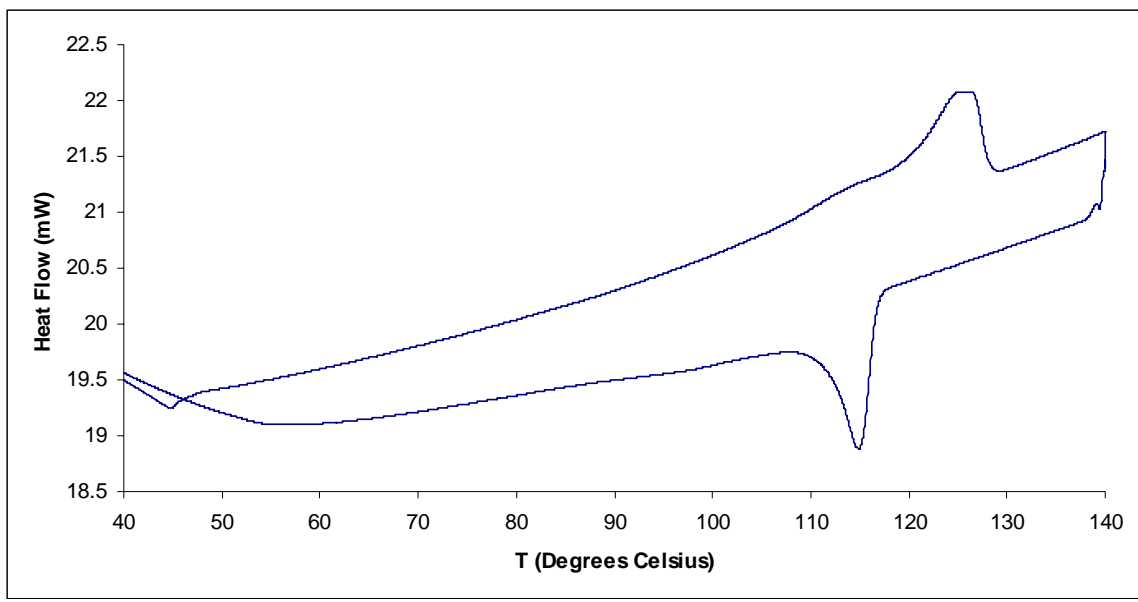
Figure 19. DSC trace of polyethylene sample 38 that was produced at 80 ºC.

Ethylene homopolymers had T_m values between 126-133 ºC determined by measuring the highest point of the highest peak. Polyethylene produced at higher temperatures had slightly lower T_m values, presumably due to greater branching and lower MW. T_g values of the polymers were not measured and they were well below 40 ºC.

4.5 Poly(ethylene-*co*-9-decen-1-ol)

4.5.1 NMR Spectroscopy of Poly(ethylene-*co*-9-decen-1-ol)
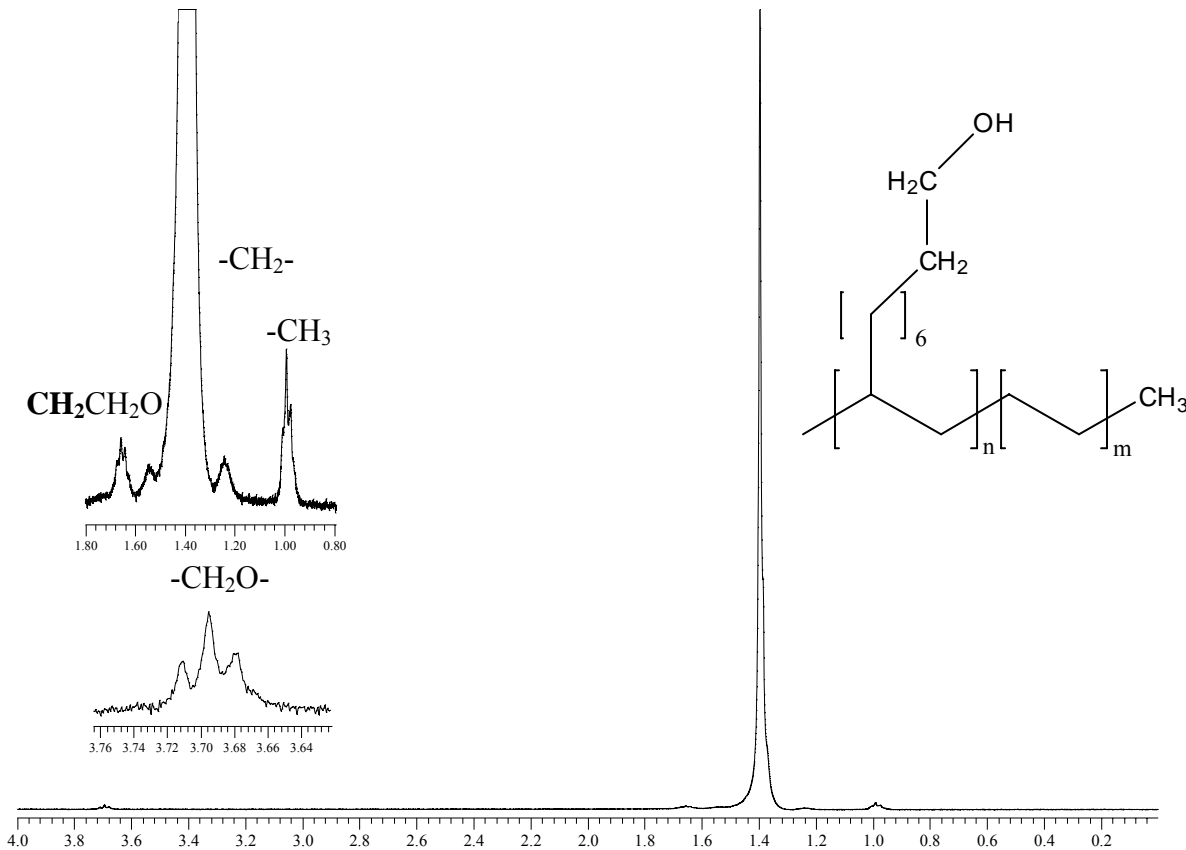
Figure 20. ^{1}H NMR (400 MHz, TCE-d$_2$) spectrum of poly(ethylene-*co*-9-decen-1-ol) that was polymerized at 60 ºC with 16.1 equivalents of 1-TMSO-9-decene (0.85 mol%).

The ^{1}H NMR spectrum of poly(ethylene-*co*-9-decen-1-ol) in Figure 20 exhibited two more resonances than that of polyethylene. These signals corresponded to the methylene groups α and β to the hydroxyl groups on the comonomer side branches. The α-methylene proton appeared as a triplet at 3.7 ppm. The β-methylene protons appeared as a quintet at 1.66 ppm. Both of these methylene protons signals had the same coupling constant of 6.4 Hz. The resonances of methylene protons more than three bonds away

from the hydroxyl groups were indistinguishable from these of the methylene protons in the polymer backbone. The alcoholic proton could not be detected under the conditions used for high temperature NMR. The ^{1}H NMR assignments were confirmed by literature.[70]

The mol% incorporation of all three attempted copolymers was quantitatively determined by ^{1}H NMR spectroscopy. The value of the integral of the methylene protons α to primary alcohol groups on the comonomer side chains (which were expected to be within 3-4 ppm) relative to the integral of the methylene backbone was used to determine the degree of 1-alkenol incorporation. See the appendix for the formula that was used to calculate mol% incorporation of polar comonomers. It was not possible to determine whether the copolymers have alternating or random structures from ^{1}H NMR spectra, though a random copolymer is expected due to the low incorporation.

4.5.2 IR Spectroscopy of Poly(ethylene-*co*-9-decen-1-ol)
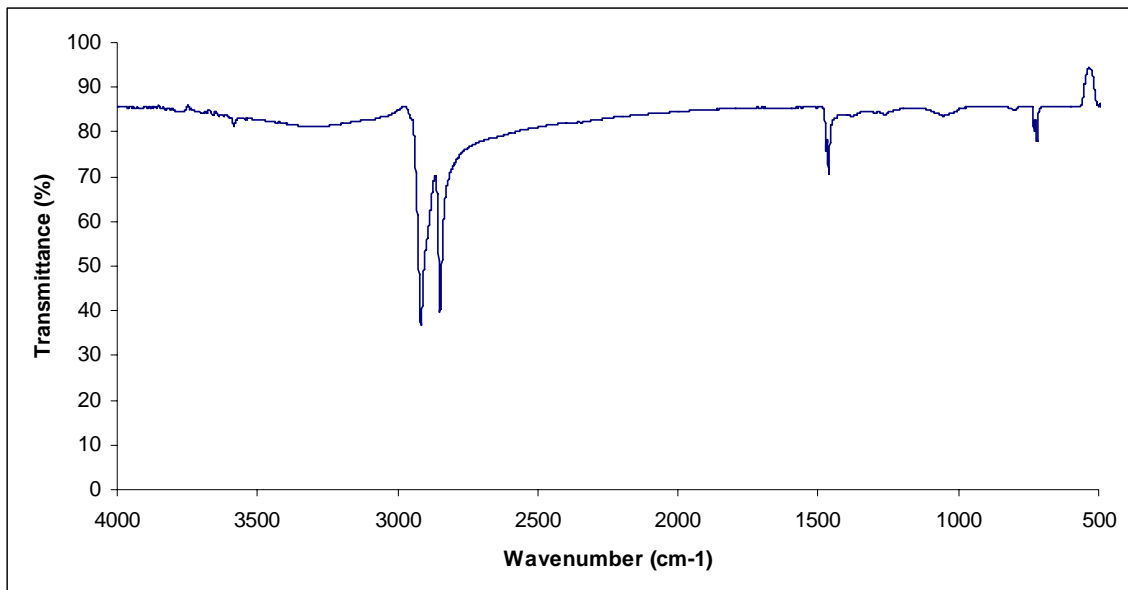
Figure 21. IR spectrum of poly(ethylene-*co*-9-decen-1-ol) produced at 0 °C with 13.7 equivalents of 1-TMSO-9-decene (1.75 mol%).

IR spectra were acquired for every copolymer sample. The IR spectrum of poly(ethylene-*co*-9-decen-1-ol) in Figure 21 exhibited two more peaks than the polyethylene IR spectrum in Figure 15. The copolymer had a broad O-H stretching peak at ~3370 cm^{-1} and a small C-O stretching peak at 1054 cm^{-1}. Polymer samples with high degrees of polar comonomer incorporation had medium intensity O-H stretching peaks and small C-O stretching peaks; conversely polymer samples from attempted copolymerizations (no incorporation by ^{1}H NMR spectroscopy) had negligible or no O-H and C-O stretching peaks. This confirms that there is 9-decen-1-ol incorporation.

4.5.3 Results of Attempted 1-TMSO-9-Decene Copolymerization with Ethylene

Poly(ethylene-*co*-9-decen-1-ol) samples had significant degrees of comonomer incorporation, as determined by ^{1}H NMR spectroscopy. High temperature copolymerizations produced copolymers with very low rates of incorporation and polymerizations with high ratios of 1-TMSO-9-decene to catalyst had the highest degrees of incorporation. The data in Table 3 suggests that increased concentrations of 1-TMSO-9-decene decreased catalytic activity. On the other hand, copolymerizations at 0 ºC had slightly lower degrees of incorporation than the copolymerizations performed at 21 ºC, when adjusted for the slightly different ratio of comonomer to catalyst.

Table 3. Copolymerization attempts with ethylene and 1-TMSO-9-decene with 1000 equivalents of MAO.

Run	Temperature (ºC)	Equiv. of Comon.	Activity (kg/(mol•h))	Branching (/1000C)	Mol% Incorp.
25	0	13.7	10	21	1.8
26	0	15.2	2	28	2.8
27	0	16.2	7	27	2.3
20	21	9.8	35	16	0.8
19	21	11.4	10	21	2.3
21	21	11.5	26	17	0.7
17	21	18.2	9	36	4.7
15	21	20.3	2	30	3.6
13	21	21.4	1	40	7.0
16	21	22.0	3	35	5.1
18	21	22.4	7	37	5.0
14	21	24.1	1	20	2.7
10	21	52.1	1	51	8.0
12	21	60.0	1	31	4.0
11	21	78.1	1	34	4.0
23	60	16.1	77	15	0.9
24	60	18.5	6.4	53	7.3
22	60	19.4	23	27	2.9
29	80	8.5	101	7	0.0
30	80	12.9	62	8	0.0
28	80	14.4	1	10	0.0

Copolymerizations performed with reduced equivalents of MAO in Table 4 resulted in dramatically lower catalytic activity and no polar comonomer incorporation at all. The activities were far lower than the corresponding activities for ethylene homopolymerizations performed with 500 equivalents of MAO. This suggests that MAO or TMA formed an adduct with 1-TMSO-9-decene that has less catalytic inhibition. More data is required to confirm and quantify this effect.

Table 4. Copolymerization attempts with ethylene and 1-TMSO-9-decene with 500 equivalents of MAO.

Run	Temperature (ºC)	Comonomer Equiv.	Activity (kg/(mol•h))	Branching (/1000C)	Mol%
1	21	11.6	1	11	0.0
2	21	13.5	1	22	0.0
3	21	12.9	1	16	0.0

Poly(ethylene-*co*-9-decen-1-ol) had increased branching with higher degrees of incorporation. This trend was consistent with the fact that polar comonomer incorporation directly introduced branching (as each polar comonomer subunit is a branch) as well as inhibited chain propagation, which increases the relative rate of β-hydride elimination.

4.5.4 Poly(ethylene-*co*-9-decen-1-ol) DSC Results

The polymer samples from 1-TMSO-9-decene copolymerization attempts with ethylene had different DSC traces than polyethylene. T_m and T_c were determined in the same manner as for polyethylene in section 4.4.4.

Figure 22 is the DSC trace of poly(ethylene-*co*-9-decen-1-ol) produced at 0 ºC (7.34 mol%), which has a broad peak at 114 ºC as well as a somewhat sharper upward peak at 127-130 ºC. The copolymer sample also has two downward peaks; one sharp peak at 119 ºC and a broad one at 106 ºC.
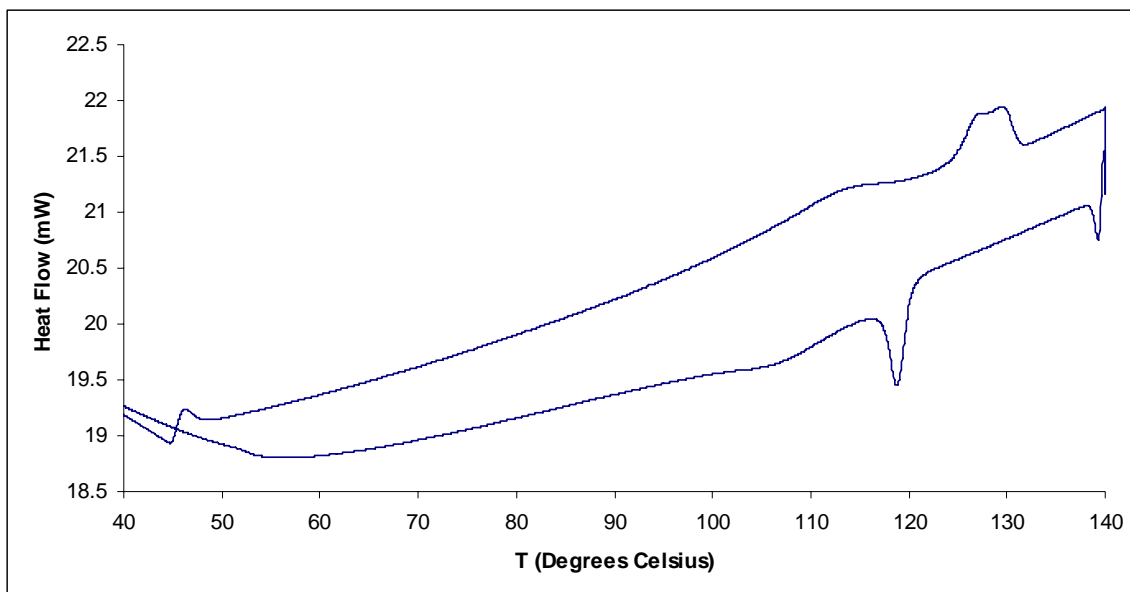
Figure 22. DSC trace of poly(ethylene-*co*-9-decen-1-ol) sample 25 produced at 0 ºC

with 13.7 equivalents of 1-TMSO-9-decene (1.75 mol%).

Poly(ethylene-*co*-9-decen-1-ol) produced at 21 ºC (2.27 mol%) had a T_m value of

126 ºC and a T_c of 116 ºC. There were no broad, secondary peaks in Figure 23.
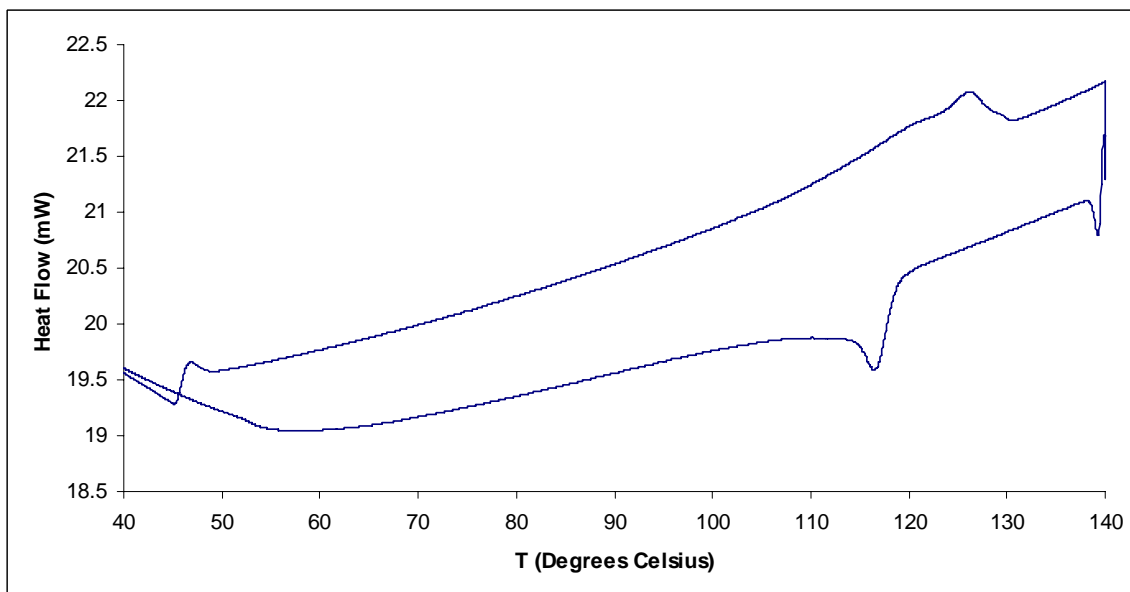
Figure 23. DSC trace of poly(ethylene-*co*-9-decen-1-ol) sample 19 produced at room

temperature. with 11.4 equivalents of 1-TMSO-9-decene (2.27 mol%).

In general, the DSC traces of poly(ethylene-*co*-9-decen-1-ol) had broader, smaller peaks at lower temperatures than polyethylene samples produced at the same temperatures. The DSC results suggest that 9-decen-1-ol incorporation into the polymer reduced crystallinity through greater branching.

4.6 Poly(ethylene-*co*-3-buten-1-ol)

4.6.1 NMR Spectroscopy of Attempted Copolymers of Ethylene and 1-TMSO-3-Butene

The ^{1}H NMR spectrum in Figure 24 is virtually identical to that of polyethylene. There are no peaks in the alcohol region (3-4 ppm) that would be indicative of CH_2O protons from incorporated 3-buten-1-ol. Neither is there a peak at 1.8 ppm that would indicate the presence of CH_2CH_2O protons. The only peaks in the spectrum are the ones that correspond to the methyl and methylene protons.

4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2
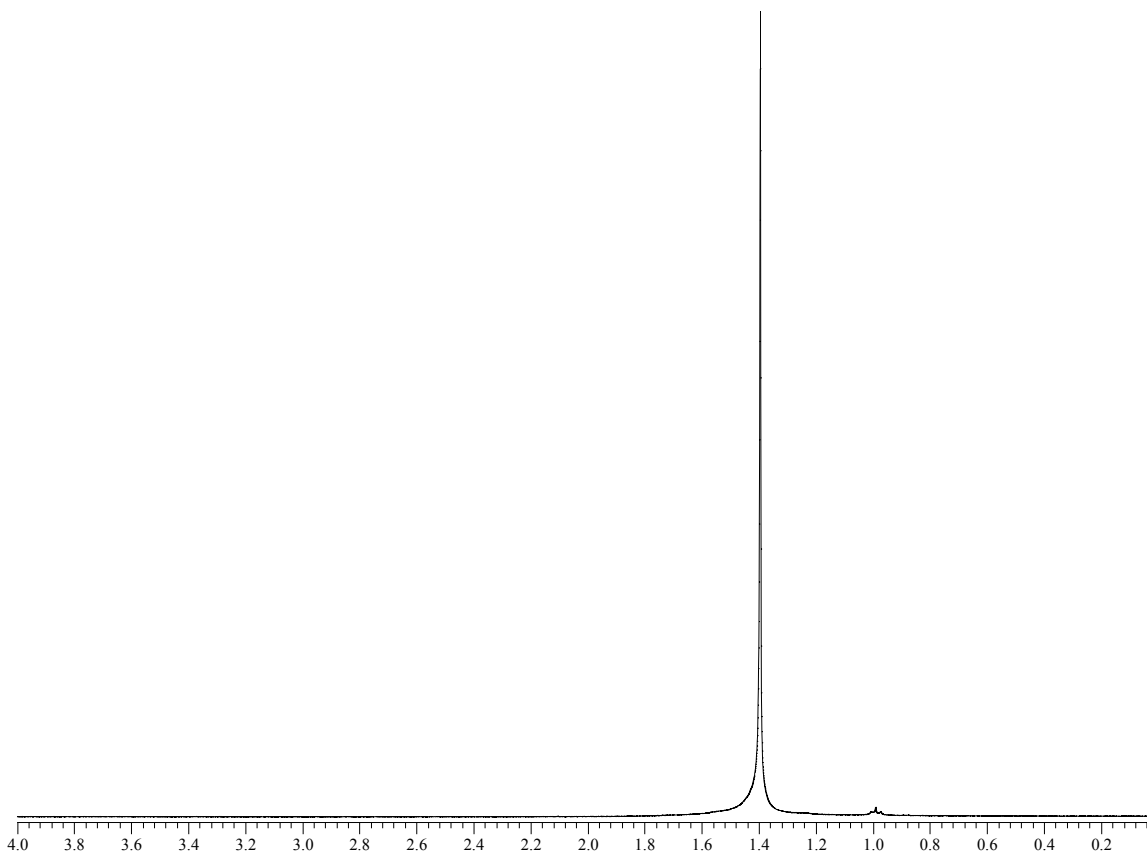
Figure 24. ^{1}H NMR spectrum (400 MHz, TCE-d$_2$) of polymer produced at room

temperature. with 41 equivalents of 1-TMSO-3-butene at 120 ºC.

4.6.2 IR Spectroscopy of Attempted Copolymers of Ethylene and

1-TMSO-3-Butene

The attempted copolymer samples showed no signs of incorporation in the IR

spectra. There was no C-O stretching peak at ~1050 cm^{-1}, and neither was there a broad

O-H stretching peak ~3300 cm^{-1}. Otherwise the IR spectrum in Figure 25 was identical

to that of polyethylene.
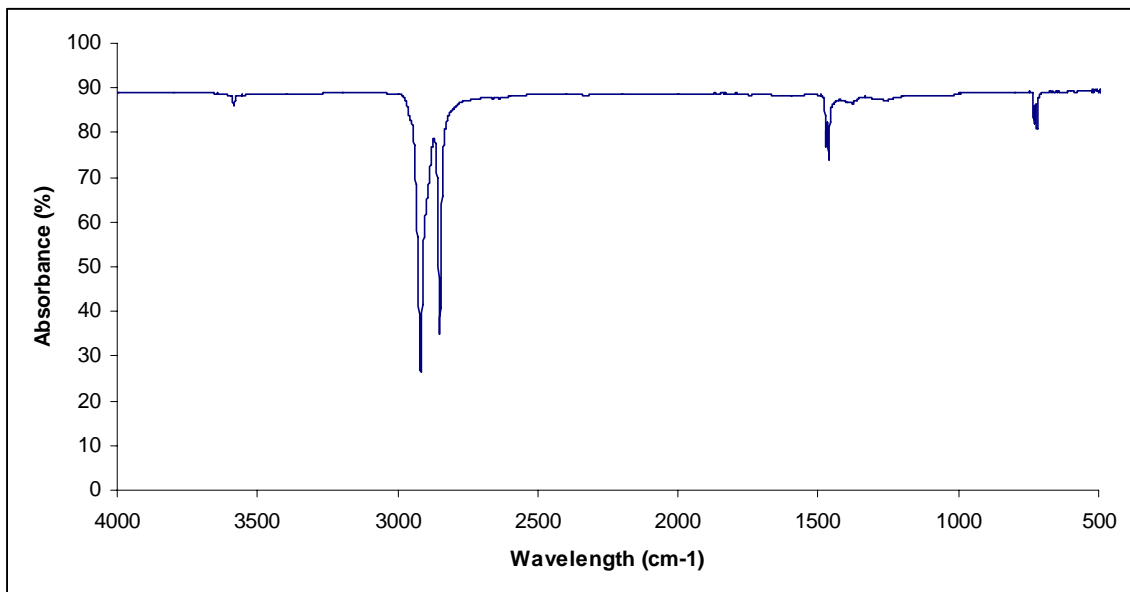
Figure 25. IR spectrum of polymer produced at room temperature. with 20.7 equivalents of 1-TMSO-3-butene.

4.6.3 Attempted 1-TMSO-3-Butene Copolymerization with Ethylene Results

Table 5 contains data from 1-TMSO-3-butene copolymerization attempts with ethylene under the conditions specified in section 3.4.2. The activity data was highly variable, though the values were consistently lower than the activities for ethylene homopolymerization. There was also no measurable comonomer incorporation in any of the attempted copolymerizations, as determined by ^{1}H NMR spectroscopy. The presence of 1-TMSO-3-butene in the polymerization solution reduced catalytic activity without any corresponding incorporation. The branching values were too inconsistent to draw

any conclusions about the effects of attempted copolymerization on the degree of branching.

Table 5. Copolymerization attempts of ethylene and 1-TMSO-3-butene with 1000 equivalents of MAO.

Run	Temperature (ºC)	Comonomer Equiv.	Activity (kg/(mol Ti•h•atm))	Branching (/1000C)	Mol%
7	21	13.0	25	58	0.0
8	21	9.9	10	81	0.0
9	21	20.4	10	29	0.0
10	21	20.7	2	42	0.0
1	21	24.0	8	17	0.0
2	21	24.3	11	14	0.0
3	21	27.6	7	17	0.0
4	21	41.0	1	46	0.0
5	21	43.7	3	24	0.0
6	21	49.8	3	26	0.0
11	60	28.3	90	25	0.0
12	60	23.4	38	65	0.0

4.6.4 DSC Results of Attempted Copolymers of Ethylene and 1-TMSO-3-Butene

The polymer sample that was analyzed by DSC had a trace (Figure 26) that was virtually identical to that of polyethylene. Therefore the presence of 1-TMSO-3-butene did not seem to significantly affect the microstructure of the polymer to any appreciable degree. The presence of 1-TMSO-3-butene only reduced catalytic activity and slightly increased branching.
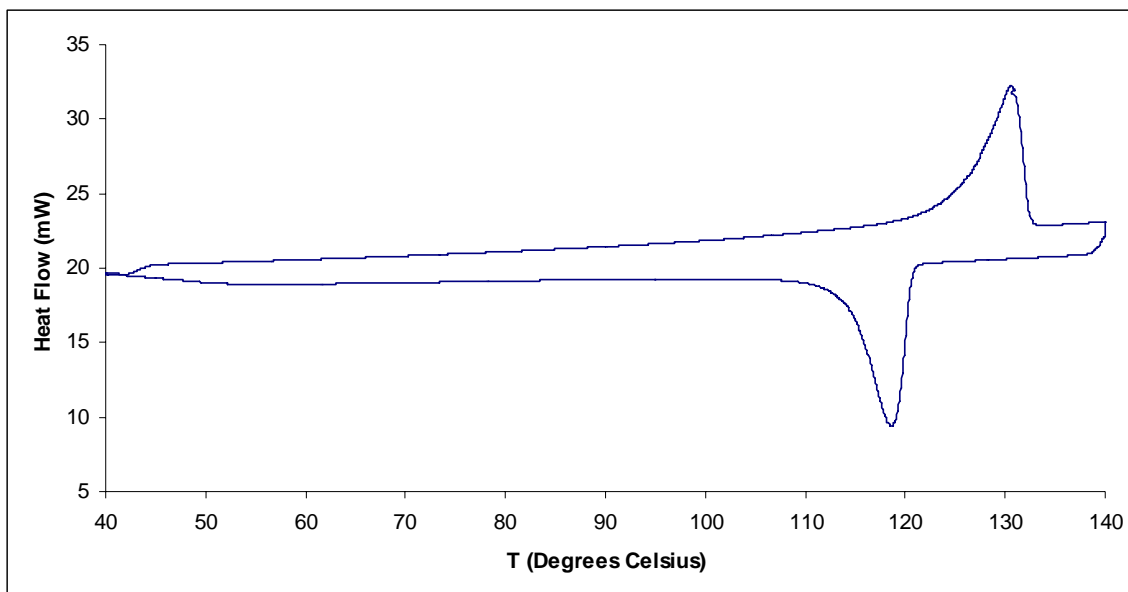
Figure 26. DSC trace of polymer produced at 60 ºC with 23.4 equivalents of 1-TMSO-3-butene.

4.7 Poly(ethylene-*co*-2-propen-1-ol)

4.7.1 NMR Spectroscopy of Attempted Copolymers of Ethylene and 1-TMSO-2-Propene

The ^{1}H NMR spectrum in Figure 27 of a polymer sample produced during an attempted copolymerization of ethylene and 1-TMSO-2-propene has no peaks that would suggest that any polar comonomer was incorporated. There are no peaks in the alcohol region (3-4) ppm that would come from CH_2O protons if there was polar comonomer incorporation. This spectrum is identical to that of polyethylene, as it has only methyl and methylene proton peaks. Therefore poly(ethylene-*co*-2-propen-1-ol) was not produced during the attempted copolymerizations.
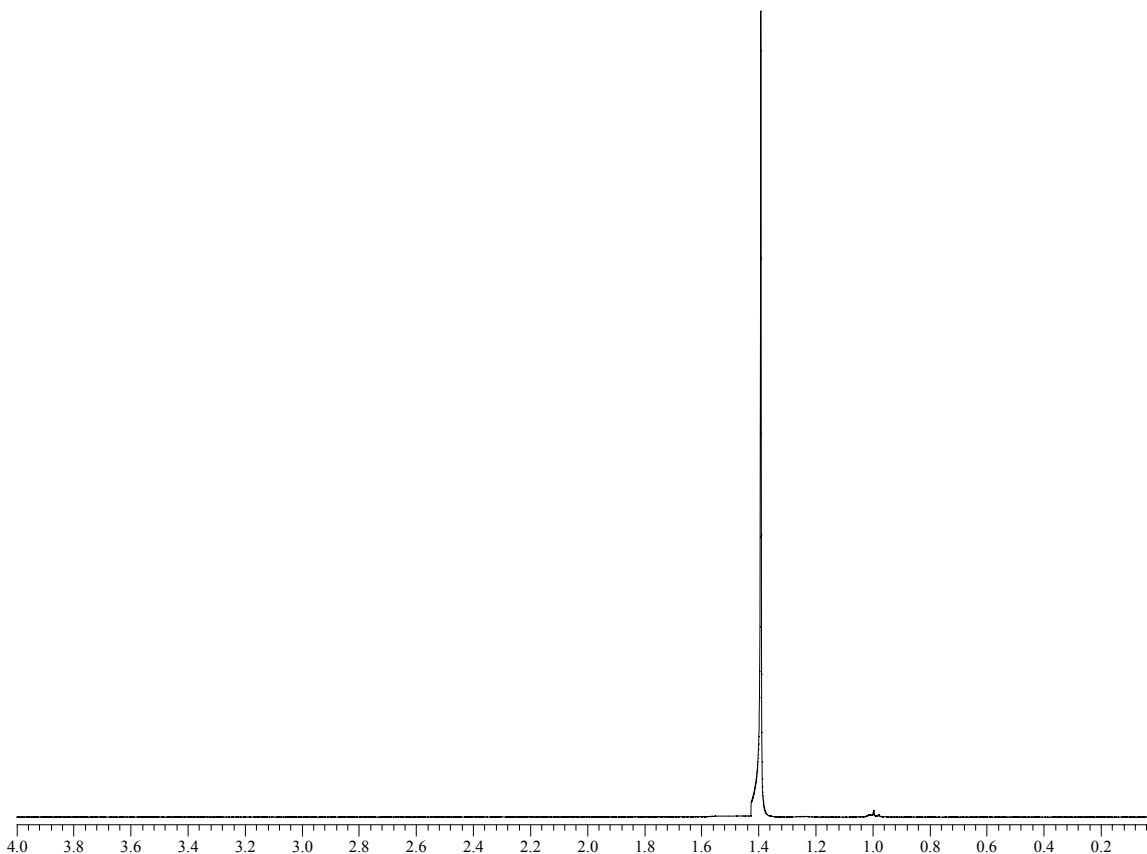
Figure 27. ^{1}H NMR spectrum (400 MHz, TCE-d$_2$) of polymer produced at 60 ºC with 25.5 equivalents of 1-TMSO-2-propene at 120 ºC. The H$_2$O peak at 1.6 ppm was removed for clarity.

4.7.2 IR Spectroscopy of Attempted Copolymers of Ethylene and 1-TMSO-2-Propene

The polymer samples produced in attempted copolymerizations of ethylene and 1-TMSO-propene had IR spectra that were no different than polyethylene and lacked the peaks of the IR spectra of poly(ethylene-*co*-9-decen-1-ol). There was no C-O stretching peak around 1050 cm^{-1}, nor was there a broad O-H stretching peak at 3300 cm^{-1}.
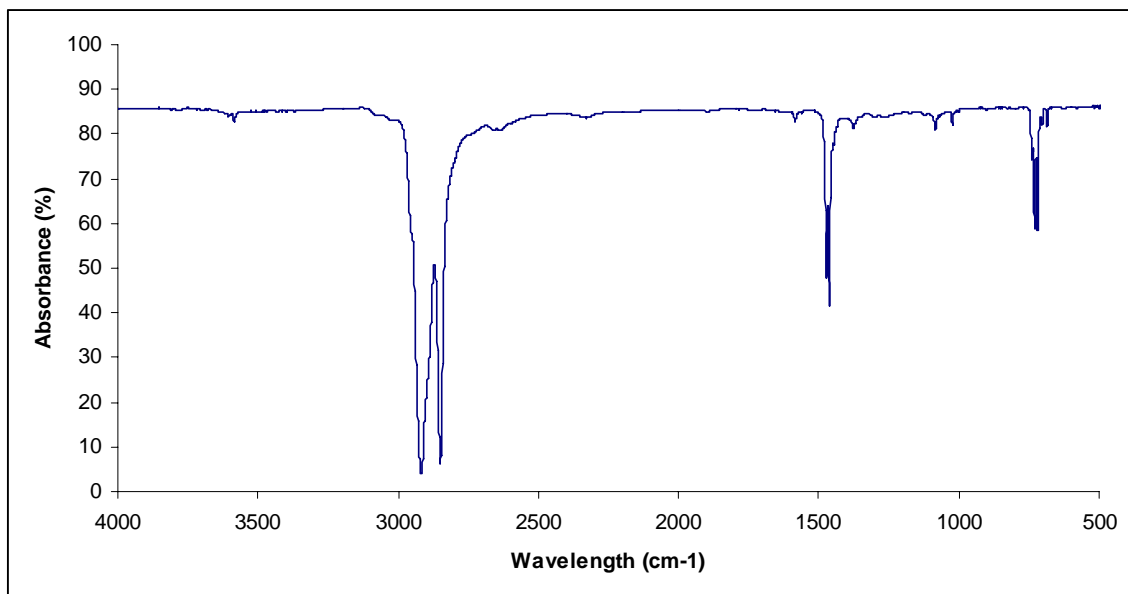
Figure 28. IR spectrum of polymer produced at room temperature. with 36.9 equivalents of 1-TMSO-2-propene.

4.7.3 Attempted 1-TMSO-2-Propene Copolymerization with Ethylene Results

Table 6 contains data from 1-TMSO-2-propene copolymerization attempts with ethylene under the conditions specified in section 3.4.2. The activity data was erratic and lower on average than the activity values for ethylene homopolymerization. There was also no measurable comonomer incorporation in any of the attempted copolymerizations, as determined by ^{1}H NMR spectroscopy. The presence of 1-TMSO-2-propene in the polymerization solution reduced catalytic activity without any corresponding incorporation. The branching values were higher on average than those of the PE samples produced at room temperature in section 4.4.3.

Table 6. Copolymerization attempts of ethylene and 1-TMSO-2-propene with 1000 equivalents of MAO.

Run	Temperature (ºC)	Comon. Equiv.	Activity (kg/(mol Ti•h•atm))	Branching (/1000C)	Mol%
1	21	10.9	34	83	0.0
2	21	11.3	45	53	0.0
3	21	16.7	27	63	0.0
4	21	36.9	9	69	0.0
5	21	32.0	14	56	0.0
6	21	76.4	1	87	0.0
7	60	25.5	29	16	0.0
8	60	25.1	26	12	0.0

4.7.4 DSC Data of Attempted Copolymers of Ethylene and 1-TMSO-2-Propene

The product of the attempted copolymerization of ethylene and 25 equiv. of 1-TMSO-2-propene produced at 60 ºC was analyzed by DSC (shown in Figure 29). The T_m value was determined to be 131 ºC and the T_c value was 119 ºC, which are very similar to the values of the polyethylene sample produced at 60 ºC. Therefore attempted copolymerization of ethylene and 1-TMSO-2-propene had little effect on the properties of the product.
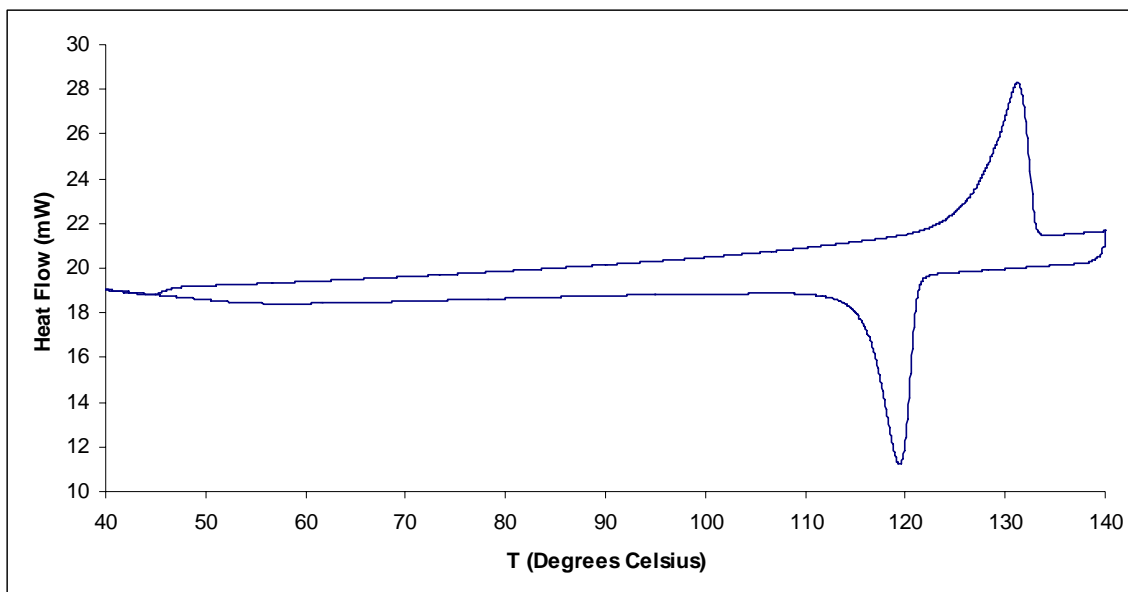
Figure 29. DSC trace of polymer sample 8 produced at 60 ºC with 25.1 equivalents of 1-TMSO-2-propene.

4.8 Conclusions

The experimental results for this thesis only permit relatively modest conclusions to be drawn. Poly(ethylene-*co*-9-decen-1-ol) was successfully produced at lower rates of catalytic activity than anticipated and there was no success copolymerizing either 1-TMSO-3-butene or 1-TMSO-2-propene with ethylene. Consistent with literature, longer chain length was associated with greater incorporation, but all of the polar comonomers reduced catalytic activity.

9-Decen-1-ol incorporation was affected to some extent by polymerization temperature, and MAO ratio. Copolymers produced at higher temperatures had lower incorporation rates than poly(ethylene-*co*-9-decen-1-ol) produced at room temperature. On the other hand, copolymerizations performed at 0 ºC did not have significantly different degrees of incorporation than the copolymerizations performed at room

temperature. 1-TMSO-9-decene copolymerizations performed with 500 equivalents of MAO had no incorporation at all and significantly lower activities than the corresponding ethylene polymerizations performed with 1000 equivalents of MAO.

Activities were on average far higher for polyethylene homopolymerization than for any of the copolymerizations. The catalytic activity for ethylene homopolymerizations performed at room temperature averaged 138 kg/(mol Ti·h·atm), which is six times higher than the average activity of 23 kg/(mol Ti·h·atm) for poly(ethylene-co-9-decen-1-ol) at room temperature. The yields of the 1-TMSO-3-butene copolymerizations were the lowest, averaging only 8.60 kg/(mol Ti·h·atm) and the polymer activities for 1-TMSO-2-propene copolymerizations averaged 25.64 kg/(mol Ti·h·atm).

The DSC data indicated that 9-decen-1-ol incorporation slightly lowered T_m and T_c values. Polymers from attempted copolymerizations with 1-TMSO-3-butene and 1-TMSO-2-propene had slightly lower T_m and T_c values than polyethylene samples prepared at the same temperatures. Catalytic activity was highly sensitive to the concentration of trimethylsilylated 1-alkenol. Increased chain length mitigated silyl ether coordination to titanium(IV) as expected.

Further research into this project should devote greater effort to the characterization of the polymer samples to determine if this class of copolymers indeed has novel properties. High temperature GPC should be performed to determine the molecular weight and polydispersity index of the polymers to achieve a better understanding of the effects of copolymerization. The tensile strength of the polymers should also be determined to corroborate the hypothesis that hydrogen bonding from

polar comonomer incorporation would increase the strength of the polymer and affect its elasticity. The hydrophilicity of the copolymer surface should be measured to determine the extent polar comonomer incorporation increases wettability and the application of water-soluble inks.

Copolymers of 1-alkenes (analogous to the three polar comonomers used in this thesis) should be prepared with similar degrees of incorporation. These LLDPE samples can be compared to 1-alkenol copolymers to quantify the effects of hydrogen bonding and other effects the polar comonomer might have on polymerization.

Alternative constrained geometry catalysts could be explored to improve polar comonomer incorporation, as well as copolymerizing with masked tertiary alkenols.

APPENDIX

The integration values from ^{1}H NMR spectra were used to determine mol%
incorporation. Firstly, it was assumed that the total number of 9-decen-1-ol subunits of a
copolymer sample was proportional to the integration of the CH_2O triplet at 3.7 ppm.
The number of ethylene subunits in the polymer sample is proportional to the integration
of the CH_2 signal at 1.37 ppm minus the methylene groups present in the comonomer side
branches. From these values, the mol% can be calculated.

$$mol\% = \frac{nDecenol}{nC_2H_4 + nDecenol}$$

$$nDecenol = \frac{A_{CH_2O}}{2}$$

$$nC_2H_4 = \frac{A_{CH_2} - 7A_{CH_2O}}{4}$$

Subsitute

$$mol\% = \frac{\left(\dfrac{A_{CH_2O}}{2}\right)}{\left(\dfrac{A_{CH_2O}}{2}\right) + \left(\dfrac{A_{CH_2} - 7A_{CH_2O}}{4}\right)}$$

$$mol\% = \frac{2A_{CH_2O}}{A_{CH_2} - 5A_{CH_2O}}$$

The degree of branching was approximated by ^{1}H NMR spectroscopy. The
number of termini in a polymer was assumed to be equal to the number of branches. This
assumes that the molecular weight of the polymer is relatively high. The number of
termini was proportional to the integrations of the methyl and CH_2O signals (terminal
vinyl groups would be included if they were observed the ^{1}H NMR spectra).

$$Branching = \frac{\left(A_{CH_3}/3\right) + \left(A_{CH_2O}/2\right)}{\left(A_{CH_2}/2\right) + \left(A_{CH_3}/3\right) + \left(A_{CH_2O}/2\right)} \times \frac{1000}{1000C}$$

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