

Development of Late Transition Metal Catalysts and Advanced Polyolefins

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DEDICATION

To my late Grandfather, Walter Fricker

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ABSTRACT

This dissertation describes advances made within the Long Research Group to design single-site catalysts for olefin polymerizations, and for the synthesis of thermally cross-linkable polyolefins. We have 1) designed thermally robust Ni-based catalysts for ethylene polymerization, 2) expanded this thermal stability enhancement strategy to Co-based catalysts, and 3) developed thermally cross-linkable polyethylene that is facilitated by the rearrangement of a co-monomer.

Catalysts employing late transition metals have been heavily studied for olefin polymerizations but their implementation in industry remains limited due to a variety of drawbacks. One specific limitation is the general thermal instability of these catalysts at temperatures commonly used for industrial polymerizations. We will herein demonstrate that the precatalyst bis[(2,6-dibenzhydryl-4-methylimino)acenaphthene] nickel(II) dibromide can be used to dramatically enhance the thermal stability of this family of Ni-based catalysts. This precatalyst proved to be thermally robust for ethylene polymerizations at temperatures as high as 90 °C and showing living polymerization behavior at temperatures as high as 75 °C.

This bulky ligand was further expanded to sterically demanding Fe- and Co-based olefin polymerization catalysts bearing 2,6-bis(biphenylmethyl)-4-methylaniline substituted bis(imino)pyridine ligands were synthesized and evaluated for ethylene polymerization. The extreme ligand bulk mitigated detectable chain-transfer to aluminum and associative chain-transfer events. These bulky Co catalysts display great thermal

stability up to 80 °C and show enhanced thermal stability at 90 °C. These observations are attributed to the extreme steric demand by which the ligand mitigates catalyst transfer, deactivation, and decomposition.

Lastly, materials that are accessible using catalysts currently employed in Industry. Industrial methods to cross-linked polyethylene are polymer irradiation and the incorporation of peroxides. These methods suffer from lack of control over cross-link bond formation and can result in a tacky polymer. We developed a thermally cross-linkable polyethylene that utilizes benzocyclobutene as a co-monomer. After polymerization, non-cross-linked films were formed and cross-linked by increasing the temperature to promote the thermal rearrangement of benzocyclobutene. These co-monomers can undergo cycloaddition with other activated benzocyclobutene co-monomers leading to covalently linked polyethylene chains. It will be demonstrated that cross-linking at temperatures above 200 °C yield cross-linked PEX films that show up to 82 % gel percent content.

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LIST OF ABBREVIATIONS

BCB	3-allylbicyclo[4.2.0]octa-1,3,5-triene
PVC	polyvinylchloride
PE	polyethylene
PEX	cross-linked polyethylene
GPC	gel permeation chromatography
NMR	nuclear magnetic resonance spectroscopy
<i>I</i> Pr*	2,6-bis(diphenylmethyl)-4-methylaniline
TOF	turnover frequency
Đ	polymer dispersity
LC-MS	liquid-chromatography mass spectrometry
PMAO-IP	performance methylaluminoxane
M_n	number average molecular weight
T_m	transition melting temperature
T_g	transition glass temperature
T_{rxn}	temperature of reaction
Å	angstrom
MHz	megahertz
RI	refractive index
DCM	dichloromethane
μ	micro

HRMS high resolution mass spectrometry

DSC differential scanning calorimetry

CBC Constrained Geometry Catalyst

PDI pyridine bis(imine)

psi pounds per square inch

B branches / 1000 Carbons

NUMBERING SCHEME FOR THE COMPOUNDS

- 1a** (N,N-bis(2,6-isopropylphenyl)butadione-1,2-diimine) nickel dibromide
- 1b** (N,N-bis(2,6-isopropylphenyl)butadione-1,2-diimine) palladium methyl chloride
- 2a** (N,N-bis(2,6-isopropylphenyl)acenaphthylene-1,2-diimine) nickel dibromide
- 2b** (N,N-bis(2,6-isopropylphenyl)acenaphthylene-1,2-diimine) palladium methyl chloride
- 3a** 2,6-(cyclophaneaniline)acenaphthylene-1,2-diimine) nickel dibromide
- 3b** 2,6-(*i*Pr)₂C₆H₃-N=C(R)-C(R)=N-2,6-(*i*Pr)₂C₆H₃ (R=Camphyl) nickel dibromide
- 4a** 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl-pyridine iron (II) dichloride
- 4b** 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl-pyridine cobalt (II) dichloride
- 5** 3-allylbicyclo[4.2.0]octa-1,3,5-triene
- 6** co-polyethylene-co-3-polybicyclo[4.2.0]octa-1,3,5-triene
- 7** 3-allyl-1,3-Cyclohexadiene-5,6-bis(methylene)
- 8** co-polyethylene-co-3-polybicyclo[4.2.0]octa-1,3,5-triene-[4+2]cycloaddition cross-link
- 9** co-polyethylene-co-3-polybicyclo[4.2.0]octa-1,3,5-triene-[2+2]cycloaddition cross-link
- 10** (N,N-bis(2,6-diisopropyl-4-methylphenyl)acenaphthylene-1,2-diimine) nickel dibromide
- 11** (N,N-bis(2,6-dibenzhydryl-4-methylphenyl)acenaphthylene-1,2-diimine) nickel dibromide

- 12** 2,6-bis(diphenylmethyl)-4-methylaniline
- 13** N,N-bis(2,6-dibenzhydryl-4-methylphenyl)acenaphthylene-1,2-diimine-aminoalane
- 14** (N,N-bis(2,6-dibenzhydryl-4-methylphenyl)acenaphthylene-1,2-diimine
- 15** 2,6-Bis[1-(2,6-bis(diphenylmethyl)-4-methylaniline)] pyridine iron (II) chloride
- 16** 2,6-Bis[1-(2,6-bis(diphenylmethyl)-4-methylaniline)] pyridine cobalt(II)bromide
- 17** 2,6-Bis[1-(2,6-bis(diphenylmethyl)-4-methylaniline)] pyridine
- 18** [(*t*-butylamido)(tetramethylcyclopentadienyl)-dimethylsilane] titanium dichloride

Chapter 1

Introduction

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Mitchell NE, Long BK. Recent Advances in Thermally Robust, Late Transition Metal Catalyzed Olefin Polymerization. *Polymer International*. **2018**. *Under review*.

I conducted the research and writing for this article. The work was advised by Dr. Brian Long.

1.1. Introduction to Polyolefins

1.1.1 Evolution of Olefin Polymerization Catalysts

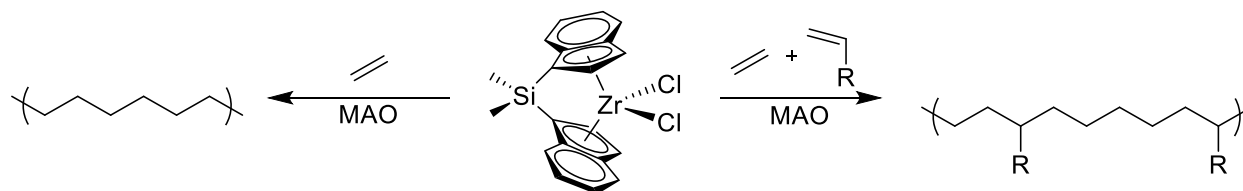
Over the last century, polymeric materials have pervaded almost every aspect of modern human life. This is in part due to their plethora of accessible thermal, mechanical, rheological, and even optical properties, which may be fine-tuned by tailoring a polymer's composition, architecture, and pendant functionality. Of the many materials that we encounter each and every day, such as grocery bags, prescription bottles, hard hats, hula hoops, packaging materials, etc., many are constructed from a class of polymers known as polyolefins.¹⁻² Polyolefins are polymeric materials derived from readily available and low-cost olefinic starting materials, such as ethylene, propylene, and higher α -olefins. Because of this, polyolefins have become the most widely produced polymers in the world, and have found wide-spread utility as inexpensive, lightweight, and durable alternatives to traditional materials such as wood, metal, and glass.

Olefin polymerizations were first discovered in the early 1950's by the groups of Ziegler and Natta, and Hogan and Banks, independently. Both group's developed catalytic systems that were heterogeneous in nature and utilized early transition metals such as Cr, Ti, and V.³⁻⁴ While these systems perform well, and are still used today, they proved difficult to study due to their heterogeneous nature and the presence of multiple distinct active sites that can each display their own kinetic rate constant, stereoselectivity, and rates of chain transfer and termination.³ Furthermore, because detailed mechanistic

studies are often extremely difficult to perform on heterogeneous species, our understanding of the nature of the active site, mechanism of olefin polymerization, and source of tacticity control remained limited. This gap in fundamental knowledge eventually inspired the development of homogenous, metallocene-based catalysts that were soluble in many common organic solvents allowing them to be easily studied through various solution-state techniques.⁴⁻⁶

Early efforts to develop highly active metallocene-based olefin polymerization catalysts proved difficult as only low molecular weight polymers and low catalyst activities were commonly observed when these catalysts were activated using traditional alkyl aluminum activators, such as triethylaluminum and diethylaluminum chloride. However, this situation changed dramatically when Kaminsky and coworkers discovered that partially hydrolyzed trimethylaluminum, commonly referred to as methylaluminoxane (MAO), is a remarkably potent activator for metallocene catalyzed olefin polymerizations, leading to highly active catalysts and high molecular weight polyolefins.^{5, 7-8} The development of these homogeneous, single-site catalysts reinvigorated olefin polymerization catalysis research and included numerous detailed mechanistic and kinetic investigations that provided unparalleled insight into the olefin polymerization process.⁹ These catalysts could create linear polyethylene from an ethylene feedstock, and incorporate non-polar higher α -olefin co-monomers to create different polyethylene architecture types with more branching than the ethylene only counterpart. (Scheme 1.1)

Scheme 1.1. Early transition metal based metallocene catalysts able to produce linear ethylene or branched polyethylene using higher α -olefins.



Through detailed studies of metallocene catalyzed olefin polymerizations, it quickly became apparent that the identity of the active metal site, as well as its surrounding ligand both play vital roles in dictating an individual catalyst's activity, reactivity, and selectivity. Soon thereafter, researchers expanded their ligand library to non-metallocene-based catalysts to further advance the fundamental study of polyolefin catalysts. These so-called post-metallocene catalysts employ a variety of early transition metal complexes bearing ligands such as diamides, iminopyrrolides, β -diketiminates, alkoxides/aryloxides, and bis(phenoxy)imine ligands, just to name a few.¹⁰⁻¹¹ Detailed investigations of these post-metallocene catalysts have provided further fundamental insight into the initiation, propagation, and termination steps of olefin polymerization, as well as informing the development of numerous unique catalyst/ligand architectures.¹²⁻¹⁵

Though the development of metallocene and post-metallocene catalysts pervaded olefin polymerization research in the 1980's and 1990's, these catalyst classes were somewhat limited in that they traditionally employed early transition metals such as Ti, Zr, Hf, V, and Cr. It was not until 1995 when the first examples of late transition metal

catalyzed olefin polymerizations were reported by Brookhart and coworkers.⁸ They demonstrated that Ni- and Pd-based catalysts bearing α -diimine ligands (**1-2**) (Figure 1.1.) could produce high molecular weight polyolefins. These catalysts were activated using MAO and it was determined that sterically bulky ligands were required to block the axial coordination sites of the active metal center and to prevent deleterious chain transfer events, such as associative displacement of the growing polymer chain by monomer.⁷⁻⁸

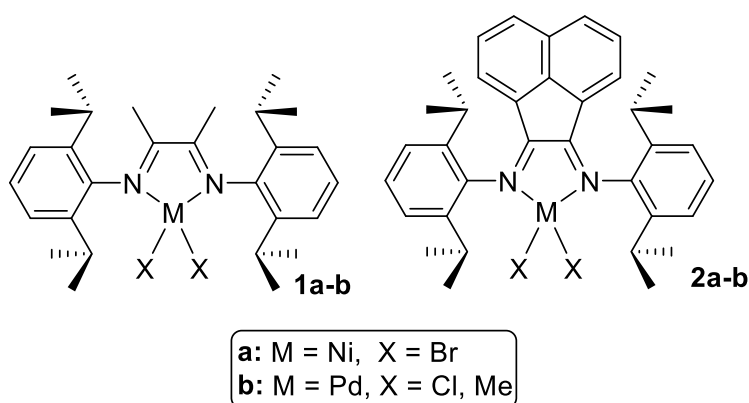


Figure 1.1. Structure of Ni and Pd α -diimine catalysts **1-2** for olefin polymerizations.⁸

1.1.2. Introduction to the Chain-Walking Mechanism

A unique feature of catalysts **1-2** is their ability to produce branched polyethylene microstructures (1.2 to 300 branches/1000 carbons) when using ethylene as a sole monomer feedstock. This is in contrast to most group 4 catalysts that require copolymerization of ethylene and higher α -olefins to yield similar branched materials. These branched polyolefins are produced via a process known as “chain-walking,” which

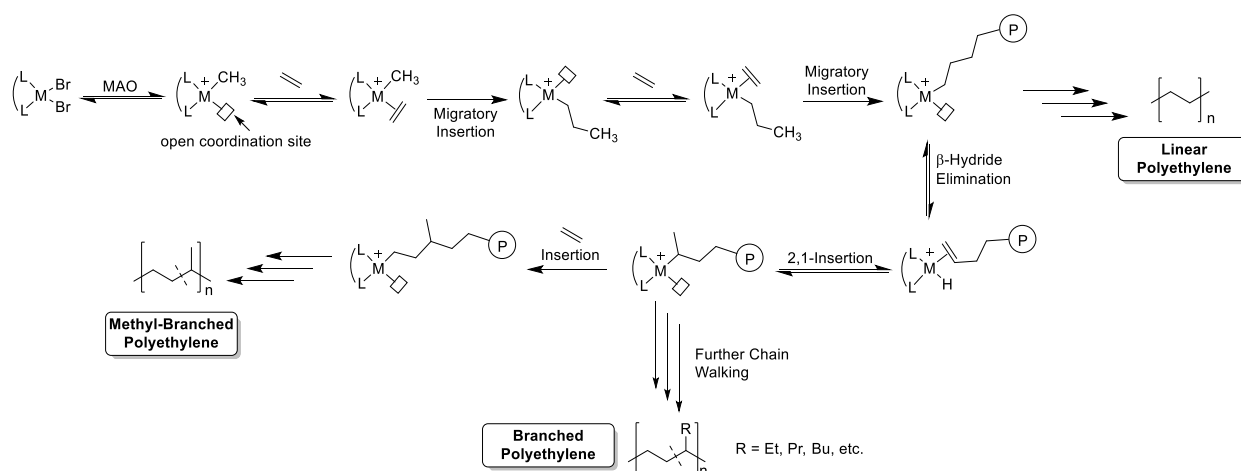


Figure 1.2. Overview of coordination-insertion and chain-walking mechanisms of olefin.

Note: agostic interactions were omitted for clarity and simplicity.

occurs through a repeated series of β -hydride eliminations and subsequent reinsertions that allow the active catalyst to migrate along the growing polymer chain (Figure 1.2.).^{9,}

13, 15-16

If at any point during that chain-walking process, a monomer is coordinated and inserted, a branch point is created. These branches can include both long and short alkyl branches, as well as the possibility to produce branch-on-branch structures. It was also discovered that the degree of branching in these polymers could be modulated by altering the polymerization temperature, ethylene feed pressure, activator concentration, and even ligand sterics and electronics.¹⁷⁻²⁴ For example, increasing ethylene feed pressure has been shown to increase the rate of chain propagation relative to that of the chain-walking process, thereby producing polyethylene with a more linear microstructure. This ability to control the relative rates of chain propagation to chain-walking has led to myriad

investigations over the past decades, and has provided numerous pathways by which polymeric microstructure may be finely tuned while only using a single inexpensive monomer source, ethylene.

Despite the numerous enticing characteristics of Ni-, Pd-, Fe-, and Co-based olefin polymerization catalysts, late transition metal catalysts have seen limited industrial use for the production of high molecular weight polyolefins. A significant limitation is that these late transition metal catalysts are often thermally unstable, and thus not be suitable for many industrially used polyolefin synthetic processes, such as fluidized bed reactors (Figure 1.3.), which may operate at temperatures as high as 70-110 °C.²⁵

1.2. Thermally Robust Catalysts

1.2.1 α -Diimine Ligands

Nickel and palladium α -diimine catalysts have been a staple of late transition metal olefin polymerization catalysis research since their introduction to the field in 1995 (Figure 1.1.). The most common method to increase their thermal stability has been to restrict rotation of the ligand's *N*-aryl moieties, about the C–N bond, relative to the imine containing ligand backbone plane (see Figure 1.4.). By restricting *N*-aryl rotations, it has been hypothesized that catalyst deactivation is minimized by disfavoring transition state conformations that facilitate unwanted side-reactions, such as C-H activation of the ligand

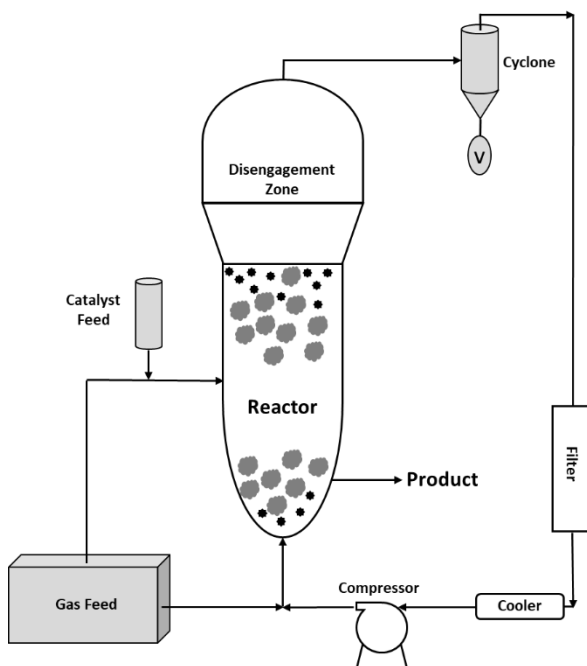


Figure 1.3. Schematic diagram of a fluidized bed reactor for gaseous olefin polymerizations.²⁵ Adapted with permission from *Ind. Eng. Chem. Res.* **1998**, 37, 3414.

by the active metal site. Catalyst deactivation via C-H bond activation has been shown by Brookhart and coworkers when using Pd α -diimine catalysts.²⁶⁻²⁸

To restrict these *N*-aryl rotations, two main methods have historically been employed: 1) the utilization of *N*-aryl moieties containing sterically demanding or conformationally locked substituents, or 2) the utilization of bulky diimine backbone structures that also restrict *N*-aryl rotations through steric repulsions (see Figure 1.4.). Prior to 2010, these methods were successfully employed by the groups of Guan, Rieger, and Wu to enhance the stability of their catalytic systems.²⁹⁻³³ Two examples of these modified α -diimine catalysts can be seen in Figure 1.4. in which cyclophane-derived Ni

catalyst **3a** was shown to be thermally stable for the polymerization of ethylene at temperatures up to 70 °C for ten minutes before losing activity,³¹ whereas catalyst **3b** bearing a camphor-based diimine backbone was shown to polymerize ethylene at temperatures up to 80 °C, but which deactivated slowly over the course of the polymerization (Figure 1.4.).^{29, 34} Although these catalysts were reported before 2010 and will not be discussed at length herein, they serve as important landmarks to reference in the quest to develop thermally stable, late transition metal olefin polymerization catalysts.

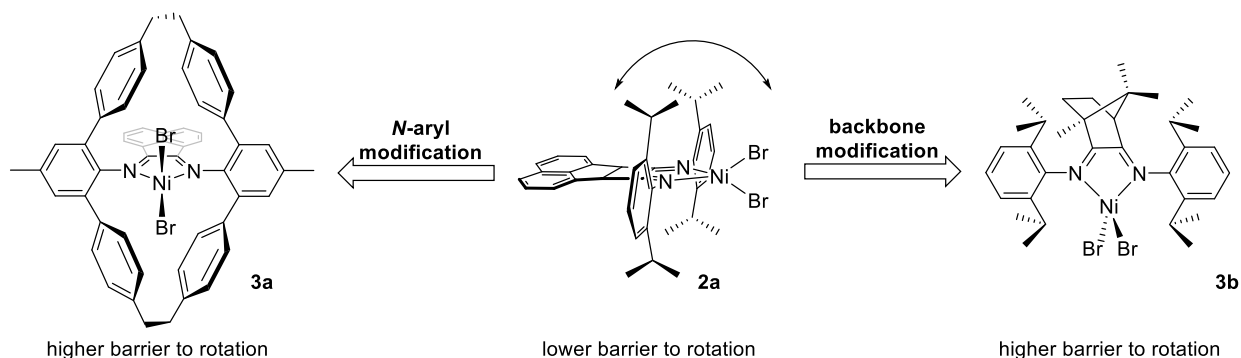


Figure 1.4. Examples in which *N*-aryl rotations have been restricted via *N*-aryl group modifications (catalyst **3a**),²⁹ and via α -diimine ligand backbone modifications (catalyst **3b**).³¹

Following the reports of catalysts **3a** and **3b**, the development of thermally robust olefin polymerization catalysts remained somewhat dormant, while investigations into topics such as ligand electronic effects, higher α -olefin incorporation, and polar

comonomer incorporation flourished for Ni and Pd α -diimine catalysts bearing either symmetrically or asymmetrically substituted ligands.^{4, 7, 35-41}

1.1.2. Fe and Co based Polyolefin Catalysts

Following the success of group 10 transition metal catalysts, catalysts bearing group VIII and IX transition metals were also highly sought after due to the earth abundance and low cost of transition metals such as Fe and Co. Highly active catalysts employing both Fe and Co were independently reported in 1998 by the groups of Brookhart, Gibson, and DuPont.⁴²⁻⁴⁴ Each of these catalyst systems utilized tridentate, coordinating ligand frameworks and were found to produce high molecular weight, highly linear polyethylene.⁴³⁻⁴⁹ In similarity to the Ni and Pd catalysts described above, sterically bulky ligands were also required to block the active metal site's axial coordination positions and to avoid undesirable chain transfer events that could limit attainable molecular weights.⁵⁰ By far, the most commonly utilized Fe- or Co-based catalysts are those that employ the bis(imino)pyridine ligand framework (**4a-b**), which provides ample opportunity to modulate ligand sterics and electronics through facile substitution of their *N*-aryl moieties (Figure 1.5.). These catalysts are most commonly activated using MAO, and high activities can be achieved that under certain conditions begin to rival commonly employed metallocene-based catalysts.⁵¹⁻⁵²

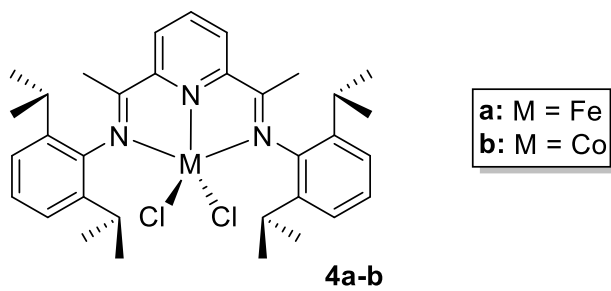


Figure 1.5. Structure of bis(imino)pyridine ligated Fe and Co catalysts.

1.2.3. Bis(imino)pyridine Ligands

Fe and Co are both inexpensive, earth abundant metals that have intrigued researchers in the field of olefin polymerization catalysis. Depending on the identity of their coordinating ligand, catalysts containing these metals have proven to produce polyolefins and α -olefin oligomers;^{47, 50, 53} however, only those that produce polyolefins will be discussed in this review. These catalysts are typically activated using MAO, which yields highly active species that can produce linear, high molecular weight polyethylene.^{46, 53} Generally speaking, it is not uncommon for Fe-based catalysts to exhibit faster activity than their Co counterparts, though this is not always true.⁴⁶ In similarity to the Ni and Pd catalysts described above, most Fe and Co catalysts also suffer from poor thermal stability. To address this, several recent reports have shown that the thermal stability of Fe- and Co-based catalysts may be enhanced using various ligand-tuning-based strategies. Many of those recent reports will be discussed below, while a more comprehensive review can be found in the literature.^{46, 52-53}

Tridentate bis(imino)pyridine ligands are, by far, the most prevalent ligand framework for Fe- and Co-based catalysts (Figure 1.5.). They are synthesized via the condensation of substituted aniline derivatives onto 2,6-diacetylpyridine. These ligands are then metallated using an appropriate Fe or Co metal precursor, such as Fe and Co halides.^{43-44, 47} In similarity to the Ni- and Pd-based catalysts described above, researchers discovered that bulky ligand frameworks are required to prevent premature chain transfer events and to access high molecular weight polymers.⁵⁴⁻⁵⁶ Catalysts **4a**

and **4b** are prototypical examples of these bis(imino)pyridine catalysts and were shown to polymerize ethylene at temperatures as high as 90 and 125 °C, producing polymers with modest molecular weights (9 – 17.4 kg/mol). While the temperature tolerance of these catalysts is impressive, it wasn't until two decades later that the time-resolved thermal stability of these catalysts would be evaluated. These studies showed that catalyst **4b** decomposes rapidly even at 80 °C, as evidenced by plots of its polyethylene productivity vs time.^{45, 57}

Motivated by the desire to develop thermal robust bis(imino)pyridine Fe and Co catalysts, researchers have found that incorporating steric bulk around the active metal site often leads to enhanced thermal stability. This methodology is directly analogous to those used for Ni- and Pd-based catalysts, and is typically accomplished via two routes: 1) increasing steric bulk through *N*-aryl group modifications, or 2) increasing steric bulk and restricting *N*-aryl rotations through ligand backbone modifications. As a note, while the most commonly employed method to date has been to modify *N*-aryl moieties with bulky asymmetric or symmetric ligands, an upward trend of adding bulk via backbone modification has been seen in the past few years.

1.3. Discussion of Cross-Linking for Polyolefins

Lower α -polyolefins have shown to have a wide variety of uses in everyday life due to their ability to create plastics with varying chemical and mechanical properties from cheap, readily available starting monomers. Polyethylene is especially used in a variety

of applications because differing polymerization conditions can result in a thermoplastic or thermoset polymer from the same starting lower α -olefin. However, in many households, polyvinylchloride (PVC), or copper, is being replaced by cross-linked polyethylene plastic for use in household plumbing or use for the insulation of electrical wires due to the polymers natural electrical resistance.⁵⁸⁻⁵⁹ Research has been previously performed to cross-link polyethylene by multiple procedures to give thermoset plastics. This cross-linked polyethylene has similar mechanical properties to PVC or copper which makes it useful for replacing these materials while having the advantage of excellent flexibility. Drawbacks arise with the current industrial methods performed to cross-link polyethylene either *in situ* or via post-polymerization modification. Currently, there are two industrial standards, use of irradiation or peroxides that have the capability to cross-link polyethylene. Irradiation of a polyethylene plastic with a low branching content will produce a cross-linked polyethylene. The irradiation energy used depends upon the thickness of the material needing to be cross-linked. The thicker the polyethylene sample, the larger the energy needed to penetrate the surface to give a cross-linked material. Problems occur pertaining to the thickness of the material due to the need for extremely high energy, dangerous radiation to cross-link polyethylene with a relatively low percent yield for the reaction.

Another industrial procedure to cross-link polyethylene with a chemical initiator was with the use of peroxides to generate radicals on branches which can combine with another radical on a different branch to produce cross-linked polyethylene.⁵⁹ This

process, however, is costly and needs to be run with as little oxygen present as possible to prevent side radical reactions with atmospheric oxygen which can result in the deformation of the surface and give the polymer an overall tacky type feel unsuitable for use. With both methods proving inefficient and costly, a need is present to be able to efficiently cross-link polyethylene with as little to no *in situ* or post-modification as possible to maximize the mechanical and chemical properties of cross-linked polyethylene while keeping over-head cost low. However, a new route to cross-linked polyethylene will be discussed in later chapters with the thermal rearrangement of co-monomer addition leading to cross-linking (Figure 1.6.).

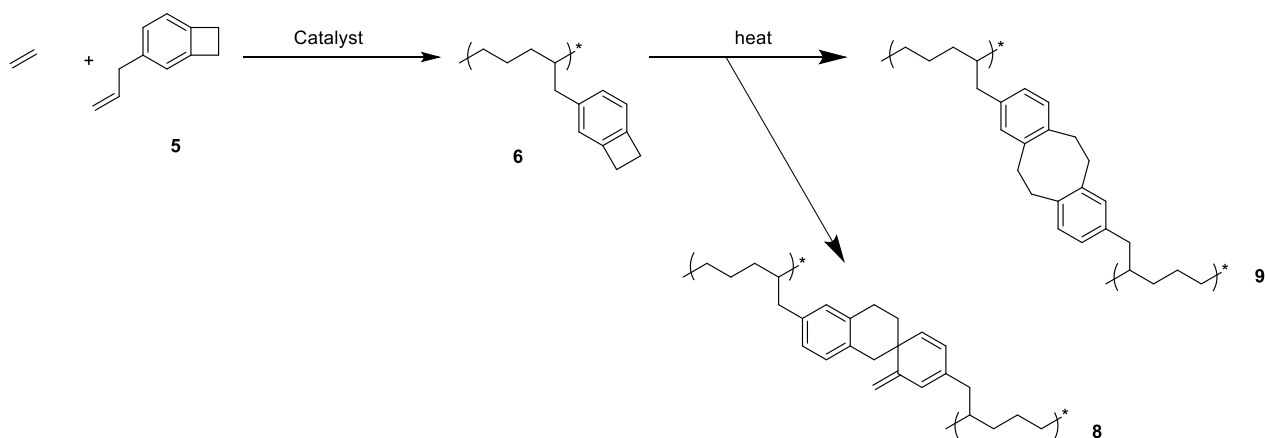


Figure 1.6. Cross-linking of polyethylene with BCB by two routes.

1.4. Research Objectives

This dissertation serves to address two distinct points of interest: 1) gaining fundamental insight into how late transition metal-based catalyst ligand structure may be manipulated to enhance catalyst thermal stability and to improve industrial appeal, and 2)

utilizing the thermal rearrangement of benzocyclobutene as a method of accessing cross-linked polyethylene (PEX) in a manner that does not require problematic irradiation or peroxides.

In Chapter 2, a detailed catalytic study of a Ni α -diimine catalysts bearing a sterically demanding ligand is used to enhance time-resolved thermal stability during polymerization. In depth studies show that these catalysts are thermally stable up to temperatures as high as 90 °C, and that living polymerization conditions are maintained up to 75 °C.

In Chapter 3, a bulky *N*-aryl group was condensed onto a bis(imino)pyridine backbone to yield a tridentate ligand. This ligand was metallated using either an Fe or Co metal precursor and evaluated for its thermal stability at elevated temperatures. The Co-based variant was shown to be stable up to 80 °C and that deleterious chain transfer events were mitigated.

In Chapter 4, a benzocyclobutane derivative is incorporated into a polyethylene backbone and its cross-linking efficacy and efficiency studied in detail. Multiple benzocyclobutane incorporation ratios were synthesized and evaluated at a plethora of cross-linking temperatures. Under optimal conditions, these benzocyclobutane modified polymers can yield cross-linking efficiencies greater than 80 % after thermal rearrangement of the incorporated co-monomer.

Following these chapters are the corresponding references. Presentation of supplementary experimental data for chapter 2 can be found in appendix A, data for

chapter 3 can be found in appendix B, and data for chapter 4 can be found in appendix C. These include detailed synthetic schemes, general methods and materials, representative gel permeation chromatographs, differential scanning calorimetry traces, mass spectrometry data, ^1H NMR, and ^{13}C NMR data.

Chapter 2

Enhancing α -Diimine Catalysts for High-Temperature Ethylene Polymerization

Reproduced in part with permission from:

Rhinehart, J. L.; Mitchell, N. E.; Long, B. K., Enhancing α -Diimine Catalysts for High-Temperature Ethylene Polymerization. *ACS Catalysis* **2014**, 8, 2501-2504. Copyright © 2014, American Chemical Society DOI: 10.1021/cs500694m

I conducted the synthesis and characterization of the ligands used. The catalyst and resulting polymerization trials were performed by Dr. Jenn Rhinehart. The work was advised by Dr. Brian Long.

Reproduced in part with permission from:

Brown, L. A.; Jr, W. C. A.; Mitchell, N. E.; Gmernicki, K. R.; Long, B. K., High Temperature, Living Polymerization of Ethylene by a Sterically-Demanding Nickel(II) α -Diimine Catalyst. *Polymers* **2018**, 10, 41. DOI: 10.3390/polym10010041

I conducted all polymer characterization by gel permeation chromatography and data analysis. Synthesis, purification of catalyst, and polymerization trials were run by the Dr. Lauren Brown and Dr. Curtis Anderson. The work was advised by Dr. Brian Long.

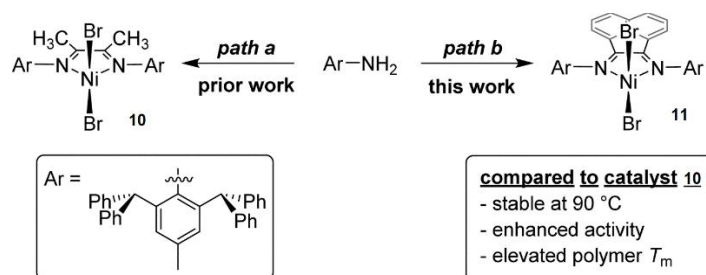
2.1. Introduction

Annually, polyolefins account for over 50% of the polymers produced within the United States, providing affordable alternatives to traditional materials, such as wood, metal, and glass.⁶⁰ Ziegler and Natta originally pioneered the field of olefin polymerization with the development of heterogeneous group IV catalysts; however, the development of homogeneous, single-site catalysts has since revolutionized the field, enabling researchers to gain greater mechanistic understanding, to enhance catalytic control, and to produce designer polyolefins.^{4-5, 61-62} During this period, perhaps one of the most pivotal advancements were the development of late-transition metal based catalysts by Brookhart and co-workers. These Ni- and Pd-based catalysts permitted the incorporation of polar comonomers⁶³⁻⁶⁵ and have facilitated the production of high-molecular-weight polyethylene with topologies ranging from highly linear to hyperbranched.^{9, 18, 66-67}

One of the most widely studied classes of Ni- and Pd-based catalysts is those bearing α -diimine ligands, and despite their numerous potential advantages, a major impediment to their commercialization has been their poor thermal stability at the elevated temperatures required for industrially used gas-phase polymerizations (70–110 °C).⁶⁸ To address this, many studies have been published concerning the elucidation of α -diimine derived catalyst's decomposition pathways; however, their full extent is not completely understood.⁶⁹⁻⁷⁰ As an example, cationic Pd-based catalysts are known to rapidly undergo C–H activation of their ligand substituents, potentially hindering further polymerization.²⁶

Advancements in Ni and Pd α -diimine catalysts' thermal stability have been reported through various modifications of ligand backbone and *N*-aryl substituents.^{32, 34,}
⁷¹ For example, catalysts bearing camphorquinone-derived ligands have shown moderate stability up to 80 °C,³¹ whereas *N*-aryl modifications, such as the use of cyclophane-based ligands, have resulted in catalysts with high turnover frequencies and enhanced thermal stability.⁷²⁻⁷³ More recently, benzhydryl-derived ligand frameworks were investigated,^{67,}
⁷⁴⁻⁷⁶ and in an effort to further advance this area, we have previously reported the use of Ni-based catalyst **10**, which demonstrated exceptional thermal stability (Scheme 2.1.).⁷⁷
 This catalyst was readily synthesized from inexpensive, commercial starting materials, demonstrated impeccable thermal stability up to 90 °C, and produced polyethylene molecular weights exceeding 500 kg/mol. At the time, this catalyst represented the most thermally stable α -diimine-based catalyst, as there is room for debate it what constitutes a thermally stable catalyst.

Scheme 2.1. Development of sterically encumbered precatalysts.



2.2. Synthesis of Catalysts

2.2.1. Synthesis of N,N-bis(2,6-dibenzhydryl-4-methylphenyl)acenaphthylene-1,2-diimine (12)

To a solution of 2,6-bis(diphenylmethyl)-4-methylaniline (805.0 mg, 1.8 mmol) in toluene, trimethylaluminum (0.9 mL, 2.0 M in toluene) was added dropwise. The reaction was heated to 100 °C for 2 h and then cooled to room temperature. A toluene solution of acenaphthenequinone (170.8 mg, 0.9 mmol) was then added dropwise and heated to 100 °C for an additional 20 h. The reaction mixture was then cooled to room temperature and 10 mL of 1 M NaOH was added. The mixture was extracted using ethyl acetate (3 X 10 mL) and the combined organic layers were dried with MgSO₄ and filtered. The solvent was removed *in vacuo* and purified via flash column chromatography. Yield 9.7% (91.2 mg). ¹H NMR (CDCl₃, 500 MHz): δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.12 (m, 12H), 7.07 (m, 8H), 6.91 (s, 4H), 6.85 (m, 10H), 6.64 (m, 1H), 6.11 (d, *J* = 7.0 Hz, 2H), 5.69 (s, 4H), 2.29 (s, 6H). ¹³C NMR (CDCl₃, 75 MHz): δ 163.81, 160.80, 146.89, 144.09, 142.83, 132.83, 131.74, 129.98, 129.72, 128.78, 128.20, 127.98, 126.78, 126.16, 125.89, 124.51, 51.60, 21.73. Anal. Calcd for C₇₈H₆₀N₂•CH₂Cl₂: C 85.46, H 5.63, N 2.52. Anal found for C₇₈H₆₀N₂•CH₂Cl₂: C 84.64, H 5.71, N 2.46.

2.2.2. Synthesis of (N,N-bis(2,6-dibenzhydryl-4-methylphenyl)acenaphthylene-1,2-diimine) nickel dibromide (**11**)

A solution of **14** (102.5 mg, 0.09 mmol) in methylene chloride (5 mL) was added to nickel(II) dibromide dimethoxyethane adduct (30.0 mg, 0.09 mmol) in a Schlenk flask and stirred overnight at 40 °C. Under an inert atmosphere, the reaction was filtered through a pad of celite and the solvent removed *in vacuo*. Precatalyst **11** was used without further purification. Yield 22% (27.0 mg). ¹H NMR (CD₂Cl₂, 300 MHz) (paramagnetic): δ 32.23, 22.57, 21.50, 15.89, 8.35, 7.05, 6.80, 6.10, 4.32. Anal. Calcd for C₇₈H₆₀Br₂N₂Ni: C 75.32, H 4.86, N 2.25. Anal found for C₇₈H₆₀Br₂N₂Ni: C 74.64, H 5.25, N 2.32.

2.3. Results and Discussion

Encouraged by these results, we began to further investigate the effects that ligand backbone structure have on this class of sterically encumbered catalysts, placing emphasis on enhancing polyethylene melting temperatures and mechanical properties, improving catalytic activity, and increasing or maintaining thermal stability. To accomplish this, we sought to utilize the popular acenaphthene-based backbone; however, we were unable to successfully condense 2 equiv of 2,6-bis(diphenyl-methyl)-4-methylaniline onto acenaphthenequinone using common synthetic methodologies. More recently, we have discovered that conversion of this bulky aniline derivative into an aminoalane intermediate provides a useful strategy to overcome this limitation.³¹ Thus, we herein report the synthesis, activity, and stability of bis[(2,6-dibenzhydryl-4-methylimino)-

acenaphthene]dibromo nickel(II) (**11**) for the polymerization of ethylene at elevated temperatures (Scheme 2.1.).

Initial strategies to condense 2 equiv of aniline derivative **12** onto acenaphthenequinone via acid-catalyzed routes yielded only monocondensed products, which was consistent with previous literature reports.^{74, 78} Attempts using the “template method” of Rosa and co-workers also exclusively formed singly condensed monoimine product.⁷⁹ Ultimately, the synthesis of diimine ligand **14** was realized in ~10% yield via reaction of **12** with trimethylaluminum to form aminoalane **13**, followed by subsequent addition of acenaphthenequinone (Scheme 2.2.). This methodology relies on the thermodynamic driving force of Al–O bond formation and has been previously used for the formation of α -diimine ligands bearing electron-deficient *N*-aryl substituents, as well as with sterically encumbered diamine backbones.^{31, 80} Last, ligand **14** was metalated using nickel(II) dibromide dimethoxyethane adduct to form precatalyst **11**.

Scheme 2.2. Synthesis of precatalyst **11**.

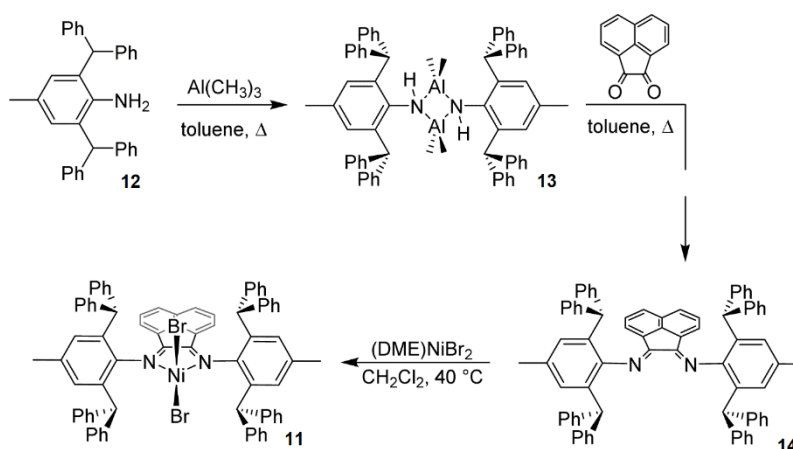


Table 2.1. Low pressure ethylene polymerizations using catalyst **11**.^a

	$T_{\text{rxn.}}$	Yield	TOF ^b	M_n^c		T_m^d
entry	(°C)	(mg)	(h ⁻¹)	(kg/ mol)	$\bar{D}^c$	(°C)
1	-40 ^e	64	463	74	1.27	127
2	-20	31	901	35	1.33	112
3	0	29	843	58	1.13	92
4	20	82	2352	85	1.10	83
5	40	181	5198	78	1.17	74
6	60	151	4340	85	1.11	67
7	80	287	8256	102	1.33	54
8	100	193	5557	64	1.32	53

^aPolymerization conditions: [cat] = 5 μmol , 100 mL toluene, 15 psi, 15 min. ^bTurnover frequency (TOF) = mol ethylene/(mol cat. $\cdot$ h). ^cDetermined using gel permeation chromatography at 145 °C in 1,2,4-trichlorobenzene. ^dDetermined by differential scanning calorimetry, second heating. ^e60 min

Ethylene polymerizations with precatalyst **11** were performed using polymethylaluminoxane-improved performance (PMAOIP) (a product of Akzo Nobel) as an activator. Initial studies using low ethylene pressure (15 psi) revealed that high-molecular-weight material could be obtained with consistently low molecular weight distributions across a wide range of temperatures ($\bar{M}_w = 1.11\text{--}1.33$) (Table 2.1.). Low-temperature polymerizations (Table 2.1., entry 1) produced highly linear polyethylene, as evidenced by differential scanning calorimetry measurements ($T_m = 127\text{ }^\circ\text{C}$), and as the reaction temperature was increased, the resultant polyethylene showed a correlated and expected decrease in the melting temperature due to the increased extent of chain-walking.

To further investigate catalyst stability at elevated temperatures and ethylene pressures, polymerizations were conducted from 80–100 $^\circ\text{C}$ at 100 psi of ethylene pressure (Table 2.2.). The molecular weight of the resultant polymers reached ~ 500 kg/mol, with the highest molecular weights observed at 80 and 90 $^\circ\text{C}$ after 20 min of polymerization (Table 2.2., entries 4 and 8). Similar to catalyst **10**, polymerization reactions beyond 20 min were performed; however, precipitation of polymer from solution became problematic, thus hindering the reproducibility and making TOF/productivity calculations unreliable. The molecular weight distributions observed were relatively narrow ($\bar{M}_w \leq 1.82$) and the polymers displayed higher melting transitions than those obtained with catalyst **10** (58–67 $^\circ\text{C}$ vs 37–46 $^\circ\text{C}$), suggesting a decrease in branching content. This was quantitatively confirmed by NMR spectroscopy, which showed that

polymers produced using catalyst **11** contained 43–60 branches per 1000 carbons as opposed to catalyst **10**, which produced 63–75 branches per 1000 carbons. In addition, the polymers produced using catalyst **11** contained mostly methyl branches (Figure 2.1. and Figure 2.2.), which is consistent with results obtained using catalyst **10**, although Figure 2.2. does show some ethyl branching which appears at 11 ppm.^{77, 81}

Unlike catalyst **10**, which produced polyethylene with molecular weights up to 600 kg/mol,⁷⁷ lower molecular weight material was obtained using catalyst **11** at 90 °C (491 kg/mol). This strongly indicated that although still catalytically active, chain transfer may have occurred to a greater extent, thereby limiting ultimate molecular weights. This hypothesis was further supported by the observation of moderately broadened molecular weight distributions as compared with those obtained when using catalyst **10**. This result was not surprising because catalysts bearing alkyl backbones have been shown to produce higher-molecular-weight polymers, and it is consistent with previous investigations into backbone effects on polymerization activity and behavior.^{31, 69}

The plot of turnover frequency (TOF) versus time for catalyst **11** clearly indicates that at 100 °C, the catalyst begins to decompose, showing a 15% decrease in turnover frequency after just 10 min (Figure 2.3.). To ensure accuracy, polymerizations were run in triplicate and averages were used with standard deviations reported in the plots. However, the activity of catalyst **11** remained constant at 80 and 90 °C and displayed TOFs ~1.4 times greater than those observed for catalyst **10**. Similarly, a plot of productivity versus time (Figure 2.3.b) showed a linear increase in productivity at 80 and

90 °C, whereas after only 10 min at 100 °C, the productivity of catalyst **11** decreases, as evidenced by its decreased slope. These data clearly indicate that the acenaphthyl-based catalyst **11** does indeed demonstrate higher TOFs while maintaining thermal stability up to 90 °C. In addition, higher polyethylene melting temperatures and lower branching content was observed for catalyst **11** than was witnessed using catalyst **10**.

Table 2.2. High-temperature ethylene polymerizations using catalyst **11**.^a

entry	T _{rxn.} (°C)	t (min)	Yield (mg)	TOF ^b (h ⁻¹)	M _n ^c (kg/ mol)	<i>D</i> ^c	T _m (°C)	branches/ 1000 carbons ^e
1	80	5	327	97	287	1.25	66	43
2	80	10	740	105	392	1.43	67	43
3	80	15	1063	105	514	1.59	66	47
4	80	20	1481	111	534	1.70	63	45
5	90	5	442	132	269	1.41	62	49
6	90	10	779	116	409	1.56	64	46
7	90	15	1086	108	489	1.56	62	61
8	90	20	1633	123	491	1.71	60	53
9	100	5	453	135	260	1.45	59	52
10	100	10	904	135	314	1.66	60	56
11	100	15	1203	119	329	1.78	58	56
12	100	20	1520	114	354	1.82	58	51

^aPolymerization conditions: [**11**] = 1.4 μmol, 100 mL of toluene, 100 psi, and 400 equiv of PMAO-IP. ^bTurnover frequency (TOF)

= mol of ethylene/(mol of cat. × h). ^cDetermined using gel permeation chromatography at 145 °C in 1,2,4-trichlorobenzene.

^dDetermined by differential scanning calorimetry, second heating. ^eDetermined using ¹H NMR spectroscopy.

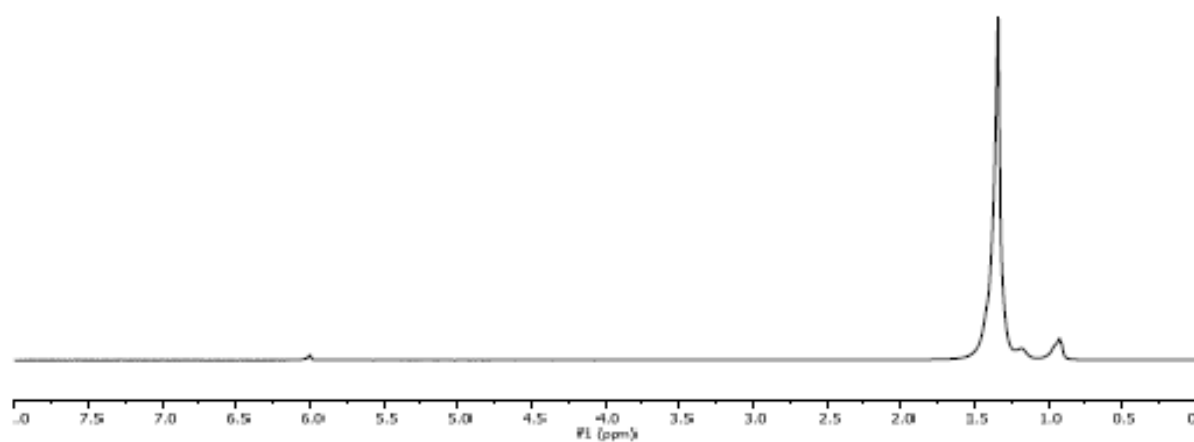


Figure 2.1. Representative ^1H NMR of polymer made using catalyst **11** (Table 2.2, entry 4).

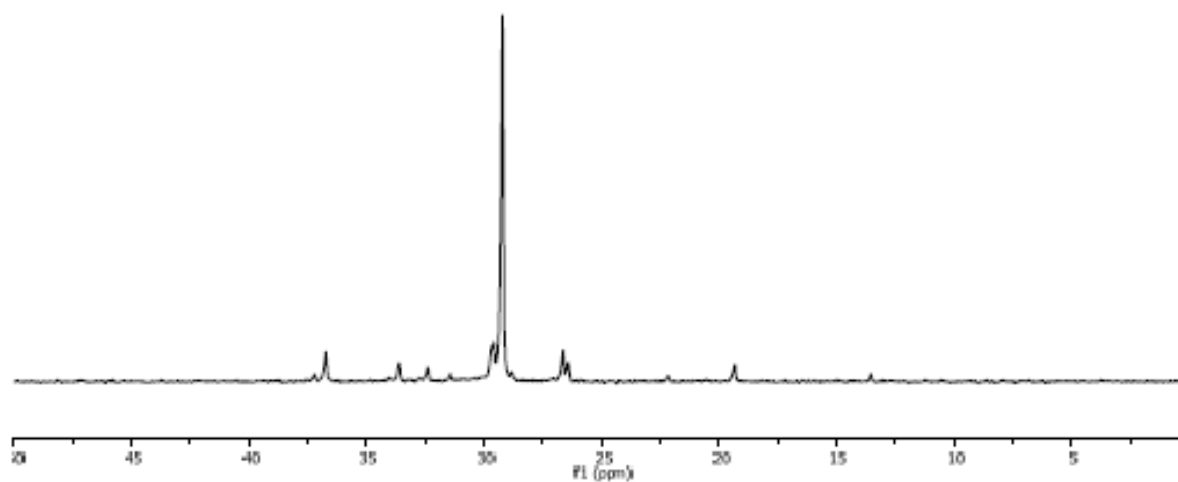


Figure 2.2. Representative ^{13}C NMR of polymer made using catalyst **11** (Table 2.2, entry 4).

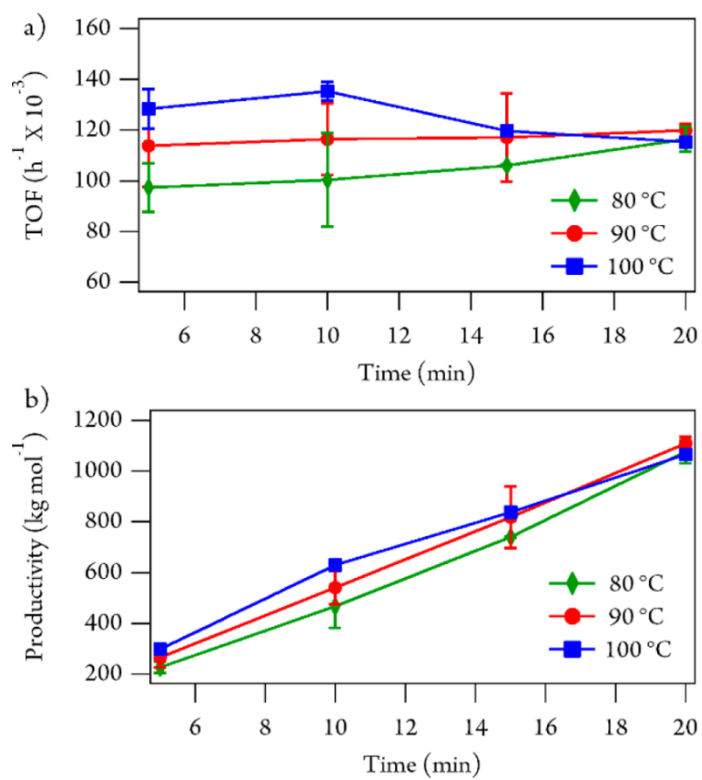


Figure 2.3. Plots of (a) turnover frequency (TOF) versus time and (b) productivity versus time for catalyst **11** at varying temperatures.

2.4. Living Polymerization of Ethylene

While catalyst **11** was previously reported to be thermally stable up to 90 °C, in part to the bulk *N*-aryl moiety and sterically hindering acenaphthenequinone backbone, it was noted in the work that a small, high molecular weight shoulder resulted in polymers having dispersities ($\bar{D}$) broader than what is typically encountered for living polymerizations. Although still relatively low when compared to commonly employed olefin catalysts (Table 2.2.)⁷⁷, further research was conducted to elucidate details about why the high molecular weight shoulder was appearing in gel permeation chromatography traces (Figure 2.4). It was determined that a catalyst impurity was present that was not detectable by ¹H NMR spectroscopy, but was detectable by liquid-chromatography-mass spectrometry (LC-MS). The impurity present was an asymmetric analogue of the ligand in which only three benzhydryl *N*-aryl moieties are present (Figure A.4.) However, the impurity which resulted during the Friedel-Crafts alkylation of *p*-toluidine using benzhydrol and ZnCl₂ was removed after recrystallization in isopropanol was performed in quadruplicate (Figure A.5.).

After removal of the catalyst impurity, ethylene polymerization trials were conducted between 70-80 °C using catalyst **11**, 100 eq. of PMAO-IP, and time trials over one hour (Table 2.3.). When compared to trials conducted in Table 2.2., the decrease in dispersity ($\bar{D}$) when comparing the impure and pure catalysts remarkable. At 70 °C, catalyst **11** polymerizes ethylene for over 60 min with a consistent decrease in dispersity (1.35 to 1.17 $\bar{D}$, Table 2.3., entry 1-4) while average number molecular weight (M_n)

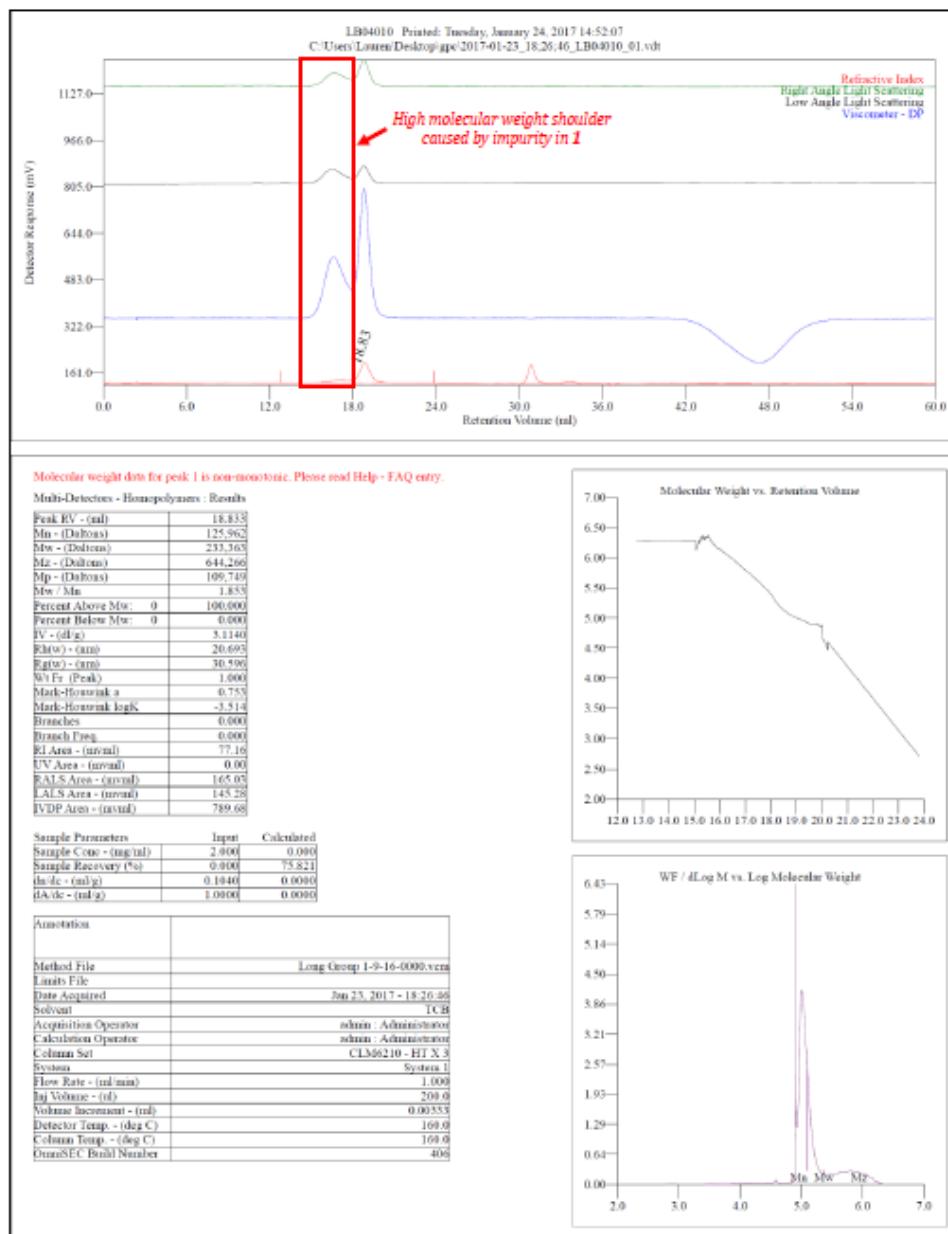


Figure 2.4. Representative GPC of polyethylene produced using complex **11** prior to rigorous ligand purification.

Table 2.3. Ethylene polymerizations using pure ligand **14** to synthesize catalyst **11**.

	t	T _{rxn.}	Yield	TOF ^b	M _n ^c	$\bar{D}^c$	B^d
Entry	(min)	(°C)	(g)	(h ⁻¹)	(kg/mol)		
1	10	70	0.16	6900	44	1.35	47
2	15	70	0.22	6300	50	1.22	48
3	30	70	0.49	7000	128	1.14	48
4	45	70	0.77	7300	164	1.18	48
5	60	70	0.96	6900	244	1.17	47
6	10	75	0.17	7300	40	1.37	48
7	15	75	0.23	6600	67	1.20	47
8	30	75	0.49	7000	155	1.17	49
9	45	75	0.85	8100	191	1.14	47
10	60	75	1.07	7600	253	1.15	50
11	15	80	0.30	8600	70	1.10	46
12	30	80	0.61	8700	114	1.17	48
13	45	80	0.72	6900	162	1.24	49
14	60	80	0.93	6600	193	1.33	50

^aEthylene polymerization conditions: 5.0 μ mol of catalyst **11**, 15 psi of ethylene, 98 mL of toluene, 2 mL of dichloromethane, and 100 equiv of PMAO-IP; ^bTurnover frequency (TOF) = mol of ethylene/(mol of cat. $\cdot$ h); ^cDetermined using triple detection gel permeation chromatography at 160 °C in 1,2,4-trichlorobenzene. ^dBranches per 1000 total carbons determined via ¹H NMR.

increases linearly throughout the same time (44 to 244 kg/mol). A similar trend is seen for 75 °C which is indication of a living polymerization as the $\bar{D}$ decreases and M_n increases in a linear fashion as the time increases. The turnover frequency (TOF) entries 6-10 of Table 2.3. also are important to note: as the polymerization proceeds from 10 to 60 minutes, the TOF remains relatively unchanged and is a strong indicator that the pure catalyst **11** still maintains its thermal stability at elevated temperatures while having living polymerization characteristics.

2.5. Conclusion

In conclusion, the use of synthetically simple dibenzhydryl as ortho *N*-aryl substituents on nickel(II) α -diimine catalysts **10** and **11** has been shown to impart remarkable thermal stability. Similarly to catalyst **10**, catalyst **11** displayed impeccable thermal stability up to 90 °C. However, in contrast, catalyst **11** does exhibit TOFs 1.4 times greater than catalyst **10**, produced polyethylene with melting temperatures increased by ~20 °C, and yielded fewer branches per 1000 carbons than polymers made with catalysts bearing alkyl substituted backbones. Upon further purification of the bulk ligand (**14**) for catalyst **11**, it shows living polymerization behavior for ethylene at 75 °C as M_n shows a linear increase and $\bar{D}$ sees a decrease with an increase in time. This purified catalyst also maintains its thermal stability up to 75 °C at 60 minutes before degrading at higher temperatures.

Chapter 3

Mitigating Chain-Transfer of Co-based Olefin Polymerizations

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Mitchell, N.E.; Anderson, W.C.; Long, B.K. Mitigating Chain-Transfer and Enhancing the Thermal Stability of Co-based Olefin Polymerization Catalysts through Sterically Demanding Ligands. *J. Poly. Sci. A*. **2017**, 55, 3990. © 2017, John Wiley and Sons. DOI: 10.1002/pola.28783

I conducted the synthesis and characterization of all compounds, and performed all polymerization trials and interpreted them. The crystallography and structure refinement were performed by W.C. Anderson. The work was advised by Dr. Brian Long.

3.1. Introduction

The development of well-defined, homogeneous olefin polymerization catalysts remains a vital area of research within industry and academia alike. In particular, homogeneous single-site catalysts have enabled researchers to gain tremendous insight into the mechanistic underpinnings of olefin polymerization and the identity of their catalytically active species.^{3, 5, 7, 18, 62} This information has enabled researchers to intimately examine how ligand sterics, ligand electronics, and transition metal choice influence overall catalytic activity, reactivity, and selectivity, which has in turn lead to enhanced polymerization control.^{3, 7, 30, 41, 71, 82-83}

For many years, researchers focused heavily on single-site catalysts that use early transition metals such as Ti, Zr, and Hf.³ However, in the late 1990s, it was discovered that late transition metal catalysts using metals such as Ni, Pd, Fe, and Co were also capable of producing high-molecular-weight polyolefins.⁸ This capability was enabled through careful ligand design and use of sufficiently bulky substituents that effectively block the axial sites of the active metal center and prevent undesirable associative displacement of the growing polymer chain by monomer.⁷⁻⁸

Despite their appeal, late transition metal-based catalysts often suffer from many limitations that can include: (1) poor thermal stability, which is well documented for many Ni and Pd-based α -diimine catalysts and (2) a notable propensity to undergo deleterious chain transfer events, which has been well-documented for Fe- and Co-based bis(imino)pyridine catalysts.^{26, 29, 31, 84-85} Recent work by our group has addressed a

portion of these issues by demonstrating that Ni(II) α -diimine catalysts bearing sterically demanding 2,6-dibenzhydryl-4-methylaniline moieties exhibit greatly enhanced thermal stability (at temperatures as high as 90 °C) and virtually no detectable chain transfer events.^{77, 86} Furthermore, these moieties have also been used to enhance Pd(II) α -diimine and Ni(II) salicylaldimine catalysts as well.⁸⁷⁻⁸⁹

The enhanced performance of these, Ni catalysts are believed to arise due to restricted *N*-aryl rotations within the ligand, which in turn mitigates deleterious catalyst decomposition and deactivation reactions.^{26, 70, 85, 90-95} We hypothesized that such sterically demanding dibenzhydryl moieties may also enhance the performance of related Fe and Co bis(imino)pyridine catalysts **4a** and **4b** (Figure 3.1.).⁴⁵⁻⁴⁶

Late transition metal precatalysts **4a** and **4b** drew considerable attention as they use earth abundant and inexpensive metal precursors.^{52, 96} They are known to produce highly linear polyethylene at low ethylene feed pressures, which is in stark contrast to their Ni- and Pd-based counterparts that often produce branched polyethylene via a chain-walking mechanism.⁹ However, despite these advantages, precatalysts **4a** and **4b** are limited in that they often produce lower molecular weight polyethylene due to their propensity to undergo chain transfer to aluminum. The presence of these aluminum species stems from the use of methylaluminoxane (MAO), which is required for the activation of **4a** and **4b**.⁴⁵ Furthermore, although these catalysts have been reported to be active at elevated temperatures, no systematic determination of their time-resolved thermal stability has ever been reported, to the best of our knowledge.

Toward this goal, herein, we describe the synthesis and polymerization behavior of symmetric, dibenzhydryl-substituted precatalysts **15** and **16**. We will show that precatalyst **16** is highly active for ethylene polymerization, while **15** is virtually inactive. Furthermore, we will compare the susceptibility of precatalysts **4b** and **16** to chain-transfer to aluminum as well as evaluate their time-resolved thermal stability.

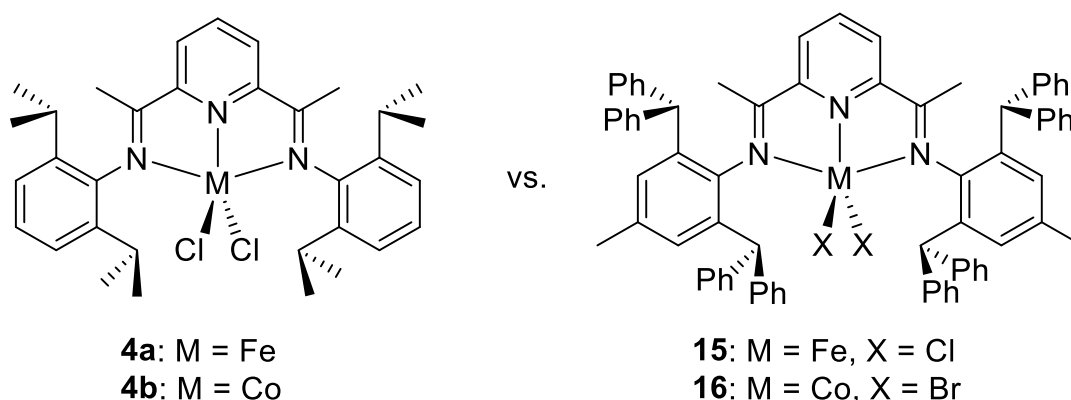


Figure 3.1. Comparison of previously reported Co and Fe precatalysts **4a-b** and the symmetrically substituted Co and Fe precatalysts **15** and **16** bearing dibenzhydryl moieties.

3.2. Results and Discussion

3.2.1 Synthesis and Characterization of Complexes

The well-known cobalt precatalyst **4a-b** were synthesized as reported previously.⁴⁵ Precatalysts **15** and **16** were synthesized according to Scheme 3.1. in which 2,6-

dibenzhydryl-4-methylaniline was synthesized as described previously via electrophilic aromatic substitution of p-toluidine using benzhydrol and catalytic ZnCl_2 .^{77, 86} This substituted aniline was condensed onto 2,6-diacetylpyridine to provide the target ligand 2-[1-(2,6-dibenzhydryl-4-methyl-phenyl-imino)ethyl]-6-[1-arylimino)eth-yl]-pyridine (**17**) in good overall yield (69.5%). Ligand **17** was metallated using the appropriate Co or Fe precursor in THF to provide precatalysts **15** and **16**.

NMR spectroscopy confirmed that both precatalysts **15** and **16** display paramagnetic behavior, which was expected for high-spin Fe and Co complexes. Single crystals of precatalyst **16** suitable for X-ray diffraction analysis were obtained by vapor diffusion of hexanes into a saturated dichloromethane (DCM) solution (Figure 3.4.). Complex **16** displayed a distorted square-pyramidal geometry in which the Co center is pushed out of the chelating [N,N,N]-ligand plane. This observation is believed to be due to ligand sterics, which has also been noted for analogous complexes.^{45, 84-85} As a note, we were unable to obtain suitable crystals of **15** for analysis by X-ray diffraction.

3.2.2. Ethylene Polymerizations

Both precatalysts **4a** and **4b** are known to be highly active for ethylene polymerization, and have been detailed in the literature.⁴⁵ In contrast, initial ethylene polymerizations quickly revealed that while **16** is active for ethylene polymerization, precatalyst **15** is essentially inactive, yielding only trace amounts of polymer. Although we are not certain of the origins of inactivity of **15**, it agrees strongly with related studies by

Sun and coworkers and may potentially be due to the instabilities of the MAO activated Fe species.^{52, 84-85} Because of the inactivity of **15**, the remainder of this work will only focus on the cobalt containing precatalysts **4b** and **16** so as to make a direct comparison of the effects of ligand sterics on catalytic behavior.

To evaluate the catalytic behavior of **16**, ethylene polymerizations were conducted at temperatures ranging from 20 to 100 °C (Table 3.1.). It was found that each polyethylene sample produced was highly linear, as evidenced by their high T_m (121.9–134 °C), and a decreasing trend in T_m was observed as a function of increasing temperature (Table 3.1., entries 1–6). For comparison, perfectly linear polyethylene is generally regarded to have a $T_m = 137$ °C.⁹⁷ Similarly, molecular weight was also found to decrease as a function of increasing temperature (33 to 3 kg/mol) which can be attributed to either the decreased solubility of ethylene gas in the reaction solvent (toluene) or increased rates of chain transfer at elevated temperatures (Table 3.1., entries 1–6).^{19, 69, 98} However, we will provide evidence in the following sections of this work that ethylene solubility is the likely cause. Finally, polymerizations conducted at or below 60 °C yielded polymer dispersity values ($\bar{D}$) that are significantly broader than those obtained at higher polymerization temperatures. This is due to the presence of a high-molecular-weight shoulder in their respective GPC chromatograms (Figures B.17. to B.58.), but which is virtually eliminated for all polymerizations conducted at or above 80 °C.

Polymerizations conducted under an ethylene feed pressure of 30 psi (Table 3.1., entries 1–6) show a steady increase in polyethylene productivity as polymerization

Table 3.1. Expanded ethylene polymerization results for prectalyst **16**.

entry	T_{rxn} (°C)	Yield (mg)	prod. ^b		$\bar{D}^c$	T_m^d (°C)	Branches (per 1000C)
			(kg/ mol)	M_w^c (kg/mol)			
1	20	75	14.9	33	4.72	134.0	6
2	40	139	27.8	23	3.09	133.9	7
3	60	211	42.2	13	3.62	130.5	8
4	80	271	54.1	10	1.23	129.5	9
5	90	312	62.4	4.3	1.47	127.8	11
6	100	282	56.5	3.0	1.30	121.9	17
7 ^e	40	757	151	55	1.95	133.4	9
8 ^e	80	1240	247	29	2.84	132.0	7
9 ^e	100	707	141	10	1.84	130.6	7

^aPolymerization conditions: [**16**] = 5 μ mol, 50 mL toluene, 30 psi ethylene, 300 equiv MAO, 30 min. ^bProductivity = kg of ethylene/ mol cat. ^cDetermined using gel permeation chromatography at 145 °C in 1,2,4-trichlorobenzene. ^dDetermined via differential scanning calorimetry, second heating cycle. ^ePolymerizations performed at 100 psi of ethylene.

temperature is increased, reaching a maximum of 62.4 kg/mol at 90 °C (Table 3.1., entry 5). However, further increasing the polymerization temperature to 100 °C resulted in a slight drop in productivity suggesting that some degree of catalyst decomposition or deactivation may be occurring at this temperature (Table 3.1., entry 6). This drop in productivity at 100 °C was also observed for polymerizations conducted at higher ethylene feed pressure (100 psi) (Table 3.1., entries 7–9), which partially suggests that catalyst **16** may potentially be thermally unstable at this temperature. Additionally, polymerizations conducted at 100 psi of ethylene feed pressure produced polymers with significantly higher molecular weights and increased melting temperatures relative to those conducted at 30 psi. We attribute both of these observations to increased monomer concentration in solution, which increases polymerization rates and decreases the propensity of the catalyst to undergo any chain-walking events.⁹

It was noted that the productivity of catalyst **16** was consistently lower than observed when using catalyst **4b** under identical conditions (62.4 kg/mol versus 264 kg/mol, respectively). We attribute the decreased productivity of **16** to the greatly increased ligand sterics surrounding the open coordination site of the activated Co center, which thereby hinders ethylene coordination and insertion. Polymerizations conducted at 100 psi of ethylene feed pressure showed that productivity of **16** can be greatly enhanced (54.1 to 247 kg/mol) by increasing ethylene feed pressure (Table 3.1., entries 4 and 8). This suggests that rate of chain propagation of catalyst **16** is heavily dependent on ethylene concentration.

3.2.3. Comparing the Effects of [Al] for **4b** and **16**

As mentioned previously, the ratio of MAO activator to catalyst (Al:cat) can have a strong influence on the activity of the propagating catalyst, particularly in regards to polymer yield, molecular weight (M_w), and molecular weight dispersity ($\mathcal{D}$). This is particularly true for precatalyst **4b** and its Fe-based analogue, which are known to produce lower molecular weight polymers when using high Al:cat ratios. This effect has been directly attributed to chain transfer to Al during polymerization.⁴⁵ Therefore, to evaluate the propensity of precatalyst **16** toward chain transfer to Al, varying ratios of Al:cat were screened and compared with analogous polymerizations using **4b** (Table 3.2.).

As expected, polymerizations using catalyst **4b** showed a slightly increasing trend in productivity as a function of increasing Al:cat ratio. However, a corresponding notable decrease in M_w was also observed (23 to 5.6 kg/mol) (Table 3.2., entries 1–5) as the Al:cat ratio was increased, which supports previous reports that **4b** undergoes deleterious chain transfer from cobalt to aluminum. Furthermore, analysis of these samples via ^1H NMR spectroscopy also revealed the presence of olefinic end groups (Figures B.12. and B.13.) that is indicative of β -hydride transfer events, which may result due to β -hydride elimination followed by dissociation or chain-transfer to monomer (Table 3.2.).

In contrast to catalyst **4b**, the productivity of catalyst **16** was found to increase steadily up to an Al:cat ratio of 1000:1, reaching a maximum productivity of 260 kg/mol (Table 3.2., entry 9). Further increasing the Al:cat ratio to 1500:1 resulted in a decrease

Table 3.2. Evaluating the effects of [Al] for precatalysts **4b** and **16**.

entry	cat.	Al:cat	Yield (mg)	Prod. ^b (kg/ mol)	M_w^c (kg/mol)	$\bar{D}^c$
1	4b	100:1	4383	876	23	1.3
2	4b	300:1	5160	1032	10	1.4
3	4b	500:1	4868	973	9.1	1.9
4	4b	1000:1	5879	1176	6.7	1.2
5	4b	1500:1	6263	1253	5.6	1.9
6	16	100:1	295	59	39	3.4
7	16	300:1	774	155	57	4.1
8	16	500:1	764	153	61	3.2
9	16	1000:1	1302	260	62	2.3
10	16	1500:1	1068	214	69	2.0

^aPolymerization conditions: [cat] = 5 μ mol, 50 mL toluene, 100 psi, 40 °C, 30 min.

^bProductivity = kg ethylene/mol cat. ^cDetermined using gel permeation chromatography at 145 °C in 1,2,4-trichlorobenzene.

in productivity; however, it did not alter the molecular weight of the resultant polyethylene (Table 3.2., entry 10). The absence of associative chain transfer events is further supported by the lack of olefinic end groups via ^1H NMR spectroscopy (Figures. C.14. and C.15.).

These observations suggest that while activity of catalyst **16** is directly dependent on Al:cat ratio, it is not readily susceptible to deleterious chain transfer to Al events, as is observed for catalyst **4b**. We hypothesize that chain transfer to Al is avoided due to the extreme steric bulk of the dibenzhydryl substituted ligand and effective steric congestion of the active Co-center's axial coordination sites.

3.2.4. Evaluating the Thermal Stability of **4b** and **16**

To evaluate the thermal stability of precatalysts **4b** and **16**, ethylene polymerizations were conducted at 80, 90, and 100 °C under constant ethylene feed pressure (30 psi). Although catalyst **16** displays optimal productivity when using an Al:cat ratio of 1000:1, a lower ratio of 300:1 was chosen for this study so that chain-transfer to aluminum is minimized when studying comparative polymerizations using precatalyst **4b**. Furthermore, although the exact deactivation pathways for Fe- and Co-based bis(imino)pyridine catalysts are not fully known,⁵¹ we suspected that chain transfer to aluminum could be a potential source of catalyst deactivation and ultimately complicate a direct comparison between the temporal thermal stability profiles of catalyst **4b** and **16**.

To study the temporal thermal stability of precatalysts **4b** and **16**, polyethylene productivities were monitored as a function of time. In these studies, a linear increase in productivity versus time is expected if the catalyst is stable at a given temperature. Each reaction was equilibrated at the desired temperature (80, 90, or 100 °C) and ethylene pressure (30 psi) before being activated by injection of 300 equivalents of MAO. The polymerizations were stopped at the prescribed time interval by injecting methanol into the polymerization reactor, and the polymer samples were stirred in acidic methanol for 24 h to dissolve any polymeric MAO-based contaminants before being isolated and dried before analysis.

The results of this study are shown in Figure 3.2., where catalyst **4b** clearly shows little or no polyethylene productivity after the first 20 min of polymerization, which clearly suggests deactivation of the catalyst. This same result was observed at each elevated temperature studied (80, 90, and 100 °C), and in each case catalyst **4b** was virtually inactive after just 30 min of polymerization time. Polymer molecular weights decreased as temperature was increased; however, no observable trends in polymer dispersity or molecular weight were observed as a function of time, which was expected for this non-living polymerization catalyst. In contrast, polymerizations using catalyst **16**, which bears sterically demanding dibenzhydryl moieties, shows a perfectly linear increase in productivity as a function of time at 80 °C (Figure 3.3.). This suggests that catalyst **16** is thermally stable at 80 °C for the entire time studied (70 min). Ethylene polymerizations at

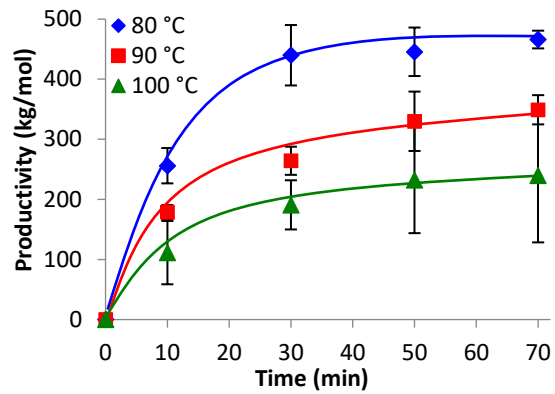


Figure 3.2. Plot of polyethylene productivity versus time for precatalyst **4b**.

Polymerization conditions: [**4b**] = 5 μ mol, 30 psi ethylene, 50 mL toluene, 300 equiv MAO.

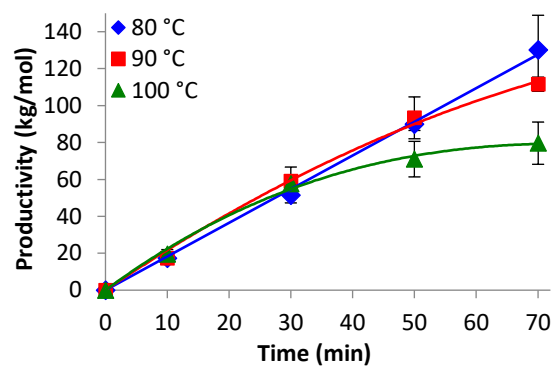


Figure 3.3. Plot of productivity versus time for precatalyst **16**. Polymerization conditions: **[16]** = 5 μ mol, 30 psi ethylene, 50 mL toluene, 300 equiv MAO.

even higher temperatures revealed that polyethylene productivity deviates from linearity at 90 °C and shows significant deviation from linearity at 100 °C, which we attribute to decomposition or deactivation of the active catalytic species. Although catalyst **16** is not perfectly stable at 90 °C, it shows only slightly diminished productivity after 1 h of polymerization and is far more stable at this temperature than catalyst **4b** which is virtually inactive after 50 min. In similarity to catalyst **4b**, polymer molecular weights generally decreased as temperature was increased; however, no observable trends in polymer dispersity or molecular weight were observed as a function of time, which again was expected for this non-living polymerization catalyst.

Although the detailed decomposition pathways of bis(imino)-pyridine-ligated Fe- and Co-based catalysts are not fully understood, we attribute the enhanced thermal stability of catalyst **16** (at 80 °C and 90 °C), relative to **4b**, to the bulky dibenzhydryl *N*-aryl moieties of the ligand backbone. We hypothesize that the extreme steric demand of **16** ligand severely inhibits *N*-aryl rotations and rigidifies the catalyst structure. This rigid ligand effectively blocks the axial coordination sites of the active Co metal center and prevents deleterious reactions that lead to the premature deactivation or decomposition of catalyst **16**.^{31, 77}

Finally, several structural parameters have been previously proposed to influence catalyst thermal stability. These include the presence of short metal to nitrogen bond lengths, and the presence of a firm/rigid ligand framework.⁴⁵ Catalyst **16** clearly

represents a complex in which ligand rigidity is enhanced due to steric constraints, and based upon the trends presented herein support those hypotheses.

3.3. Conclusions

In sum, we synthesized and evaluated the ethylene polymerization behavior of catalysts **15** and **16**. Upon activation with MAO, catalyst **15** was found to be essentially inactive for ethylene polymerizations while catalyst **16** showed good polymerization activity and was used for the fundamental studies presented herein. Specifically, the time resolved thermal stability of catalyst **16**, and its sensitivity to Al:cat ratio were investigated relative to the extensively studied catalyst **4b**. Through these investigations, it was found that catalyst **16** displays virtually no deleterious chain transfer to Al events, which is in stark contrast to the results obtained for **4b**.

Furthermore, catalyst **16** demonstrates near perfect time resolved thermal stability at 80 °C and greatly enhanced thermal stability at 90 °C as compared to catalyst **4b**. We attribute this enhancement in thermal stability and decrease in deleterious chain transfer to Al events to sterically demanding dibenzhydryl substituted ligand framework of catalyst **16**. These bulky substituents are proposed to restrict *N*-aryl rotations and effectively block the axial coordination sites of the active metal center. We hypothesize that this steric protection mitigates any unwanted reactions that lead to premature catalyst transfer, deactivation, and/or decomposition.

3.4. Experimental Details

3.4.1. General Methods and Materials

All reactions were performed under an inert nitrogen atmosphere using an MBraun UniLab glovebox or using standard Schlenk techniques, unless otherwise noted. All solvents were dried using an Innovative Technologies PureSolv Solvent Purification System and degassed via three freeze–pump–thaw cycles. CDCl_3 was dried over activated molecular sieves (4 Å). The compounds 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]-pyridine, 2,6-bis[1-(2,6-diisopropylphenyl-imino)ethyl]pyridine cobalt(II)bromide, 2,6-bis-(diphenylmethyl)-4-methylaniline, and **15** were prepared as reported previously.^{45, 77, 85, 99} MAO was received as a gift from Albemarle Corp. and used as received. All other reagents were purchased from commercial vendors and used without further purification. ^1H and ^{13}C spectra were recorded at ambient temperature on a Varian VNMRs 500 MHz narrow-bore broadband system. ^1H and ^{13}C NMR chemical shifts were referenced to residual solvent. Gel permeation chromatography was performed at 145 °C in 1,2,4-trichlorobenzene at 1.0 mL/min on Malvern Viscotek HT-GPC equipped with refractive index, viscometer, and two-angle light-scattering detectors. Polymer melting transition temperatures (T_m 's) were measured on a TA Instruments Q2000 differential scanning calorimeter on the second heating cycle at a heating rate of 10 °C/min. High resolution mass spectrometry was obtained using a

direct inject, positive ion mode with an electrospray ionization onto a Thermo Scientific Exactive Plus Orbitrap mass spectrometer.

3.4.2. Synthesis of 2,6-Bis[1-(2,6-bis(diphenylmethyl)-4-methylaniline)] pyridine (17)

To a solution of 2,6-diacetylpyridine (185 mg, 1.14 mmol) in absolute ethanol (20 mL) was added 2,6-bis(diphenylmethyl)-4-methylaniline (1.00 g, 2.28 mmol). A few drops of glacial acetic acid were added and the solution was refluxed overnight. Upon cooling to room temperature, the product crystallized from the ethanol solution. The product was washed with ethanol and dried under vacuum overnight to give an off-white solid (787.2 mg) in 69.5% yield.

^1H NMR (CDCl_3 , 500 MHz): δ 8.12 (d, 2 H), δ 7.78 (t, 1 H), δ 7.26–7.02 (m, 40 H), δ 6.71 (d, 4 H), δ 5.30 (s, 4 H), δ 2.19 (s, 6 H), δ 0.91 (s, 6 H). ^{13}C NMR (CDCl_3 , 75 Hz) 170.1, 154.8, 146.0, 143.8, 142.6, 136.4, 132.2, 131.6, 129.8, 129.4, 128.6, 127.9, 126.0, 121.9, 121.9, 77.2, 76.7, 51.9, 21.3, 16.8. HRMS $\text{C}_{75}\text{H}_{63}\text{N}_3$ (H^+ adduct) = 1006.5056 m/z ; HRMS^{expt} $\text{C}_{75}\text{H}_{63}\text{N}_3$ (H^+ adduct) = 1006.5076 m/z .

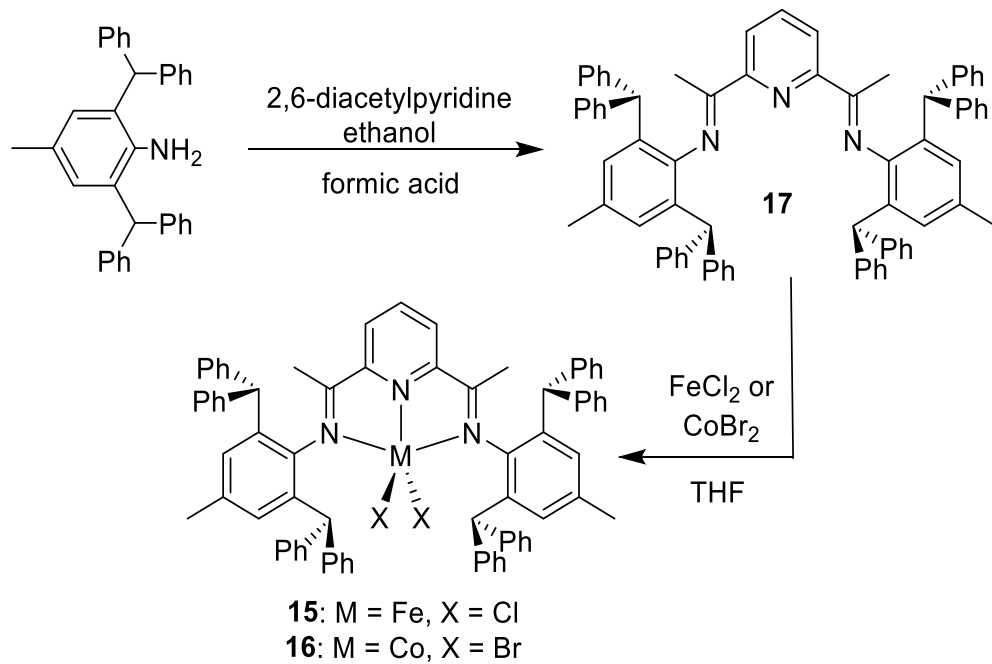
3.4.3. Synthesis of 2,6-Bis[1-(2,6-bis(diphenylmethyl)-4-methylaniline)] pyridine cobalt(II)bromide (16)

A solution of **17** (400 mg, 0.40 mmol) in tetrahydrofuran (20 mL) was added to cobalt(II) dibromide hydrate (83.1 mg, 0.38 mmol) in a Schlenk flask and stirred overnight

at room temperature. Diethyl ether (10 mL) was then added to the reaction to precipitate the complex and the resulting solids were filtered in air, washed using diethyl ether and pentane, and dried in vacuo to yield complex **16** as a brown powder (268.8 mg) in 67.2% yield.

^1H NMR (DMSO- d_6 , 500 MHz) δ 8.18 (d, 2 H), δ 7.98 (m, 1 H), δ 7.27–6.95 (m, 40 H), δ 6.64 (s, 4 H), δ 5.21 (s, 4 H), δ 2.21 (s, 6 H), δ 0.80 (s, 6 H). HRMS_{calc} $\text{C}_{75}\text{H}_{63}\text{N}_3\text{Br}_2\text{Co}$ (H^+ adduct) = 1224.2700 m/z ; HRMS^{expt} $\text{C}_{75}\text{H}_{63}\text{N}_3\text{Br}_2\text{Co}$ (H^+ adduct) = 1224.5700 m/z .

Scheme 3.1. Synthesis of precatalysts **15** and **16**.



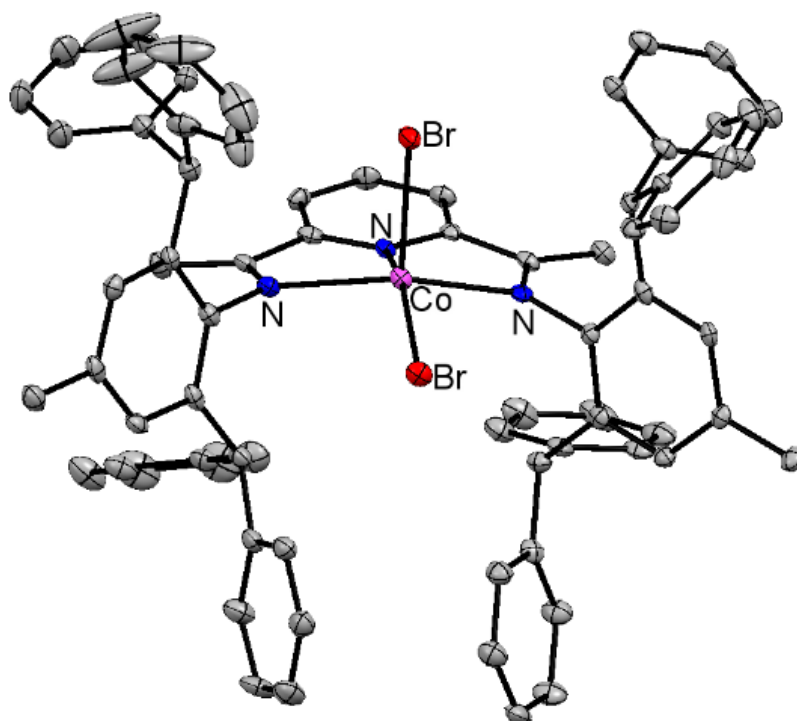


Figure 3.4. An ORTEP representation of precatalyst **16** with thermal ellipsoids drawn at 30% probability. Hydrogens are omitted for clarity.

Chapter 4

Thermal Rearrangement of Benzocyclobutene for Cross-Linking of Polyethylene

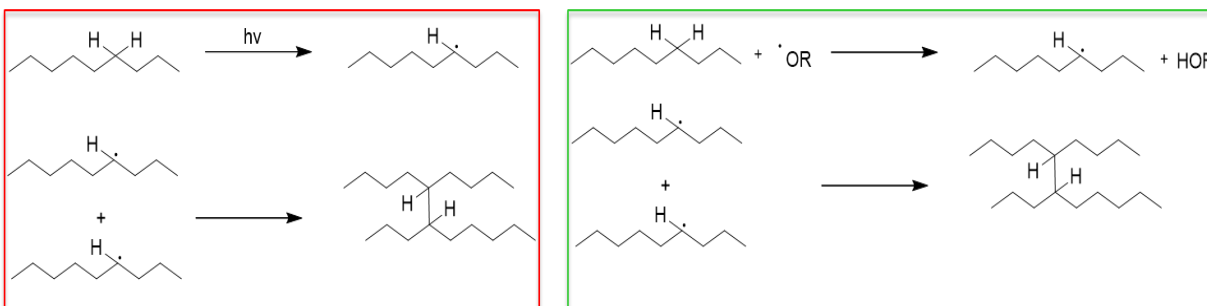
4.1. Introduction

Broadening the use of these polymers begins with widening the synthetic scope available to scientists in producing polyolefins to suit the specific needs of society. From cheap, readily available starting materials, a wide variety of chemical and mechanical properties can be achieved from the humble beginnings of α -olefin monomers.^{2, 100-102} Polyethylene is specifically used in a variety of applications because of its unique ability to be a thermoplastic or thermoset polymer depending on the physical conditions, and/or co-monomers, during the polymerization.

More recently, another area that polyolefins have looked to replace more expensive metals or specialty plastics is the replacement of household plumbing and insulation of electrical wires. However, the polyolefin material that mechanically suits these needs is cross-linked polyethylene (PEX) which has natural electrical resistance, can be bent, and is more cost effective than the metal or specialty plastic alternatives. When compared to high-density polyethylene (HDPE), PEX shows superior properties in a few different ways. After cross-linking, PEX displays increased environmental stress crack resistance, increased resistance to slow crack growth, increased creep resistance to improved long-term stability under pressure and loads, and increased chemical resistance over HDPE.^{101, 103} These particular advantages have stimulated a rapidly expanding use of PEX for hot and cold water supply piping. Current industrial methods to produce PEX at a high cross-linking percentage are either *in situ* or post-polymerization methods. Use of irradiation or peroxides are the current industrial standards. Irradiation

of a polyethylene plastic with low branching content will produce PEX, but any irradiation is thickness dependent, has dangerous and expensive lasers involved, and cannot produce consistent results because of the previous facts listed.^{101, 104-106} (Scheme 4.1.) Peroxides, the other industrial method to synthesize PEX, allows for radicals to be created on branches that naturally occur in polyethylene and can be done post-polymerization, but has natural drawbacks as well. Peroxide technique involves the use of expensive materials, residual stickiness in the final polymer, and uncontrollable cross-linking density and Scheme 4.1. outlines the synthetic routes to PEX.⁵⁹

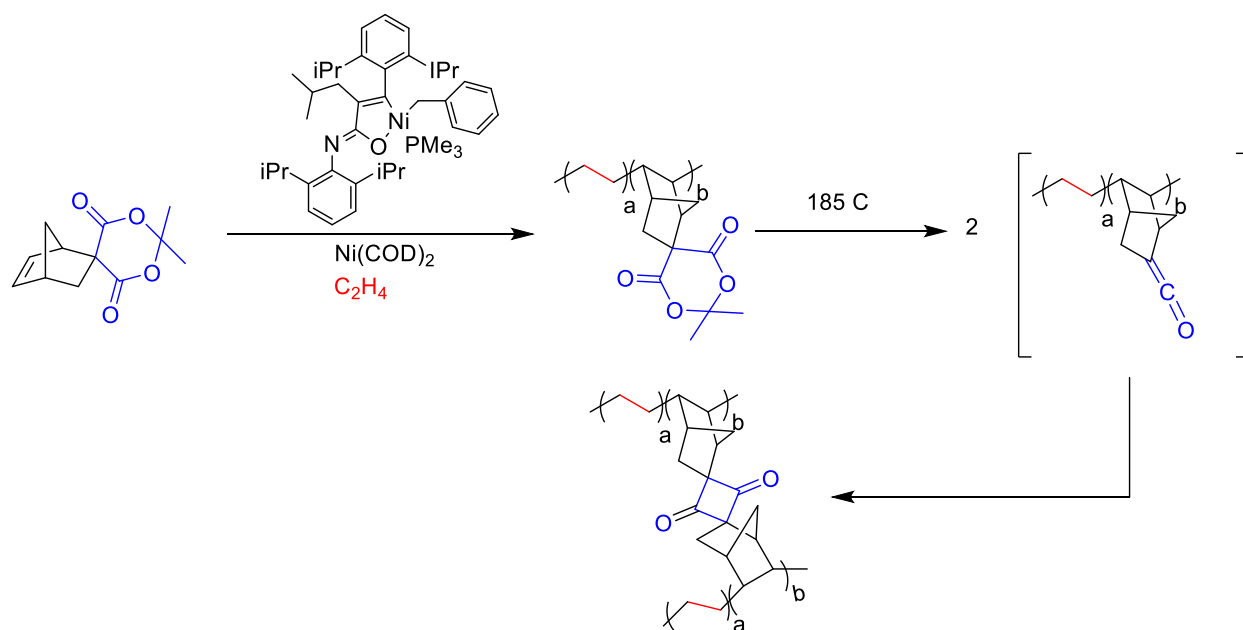
Scheme 4.1. Cross-linking of polyethylene by irradiation (red box) or by peroxide usage (green box).



A possible route around these drawbacks laid out above is the *in situ* cross-linking of polyethylene by using a group that can undergo activation by an outside stimuli and react to produce cross-links. Preferably, the monomer must be able to incorporate into olefin coordination insertion polymerization, and have an easily accessible activation from the external stimulus. Some work previously done by Hawker utilized the thermal rearrangement of ketene's in a polyethylene-polynorbornene block co-polymer.¹⁰⁷ The

polymer is initially synthesized with a Meldrum's acid functional group on the norbornene monomer. After polymerization with a late transition metal catalyst, rearrangement occurs above 185 °C to give the ketene functional group which undergoes cross-linking with another ketene, resulting in cross-linking efficiencies over 90% (Scheme 4.2.).

Scheme 4.2. Thermal rearrangement of ketene for co-polymerization of norbornene and ethylene.

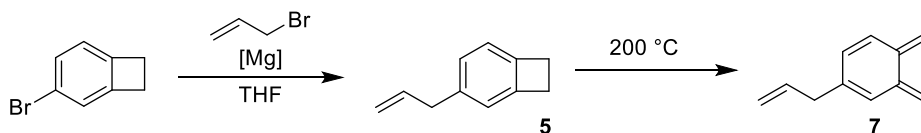


However, the norbornene incorporation eliminates mechanical properties of the polyethylene and late transition metal catalysts are not widely used industrial production. Chung *et al.* also utilized thermal rearrangement mechanisms to produce a cross-linked polypropylene with the use of divinyl styrene based monomers with success, but not for

ethylene.¹⁰⁸ One of the most attractive areas for this kind of chemistry has been benzocyclobutene (BCB) research. Synthesized first in 1910, the monomer consisting of a highly strained four-member ring can crack open into reactive diene bonds when temperatures are increased high enough.¹⁰⁹⁻¹¹⁰ This monomer scope has been previously employed by DOW chemical company in their patent literature, but no academic studies have been performed for polyethylene to the authors knowledge.¹¹¹⁻¹¹² Torkleson *et al.* did show the rearrangement of BCB after incorporation into a polystyrene polymer results in cross-linking, but this monomer was never used for polyethylene production.¹¹³⁻¹¹⁴

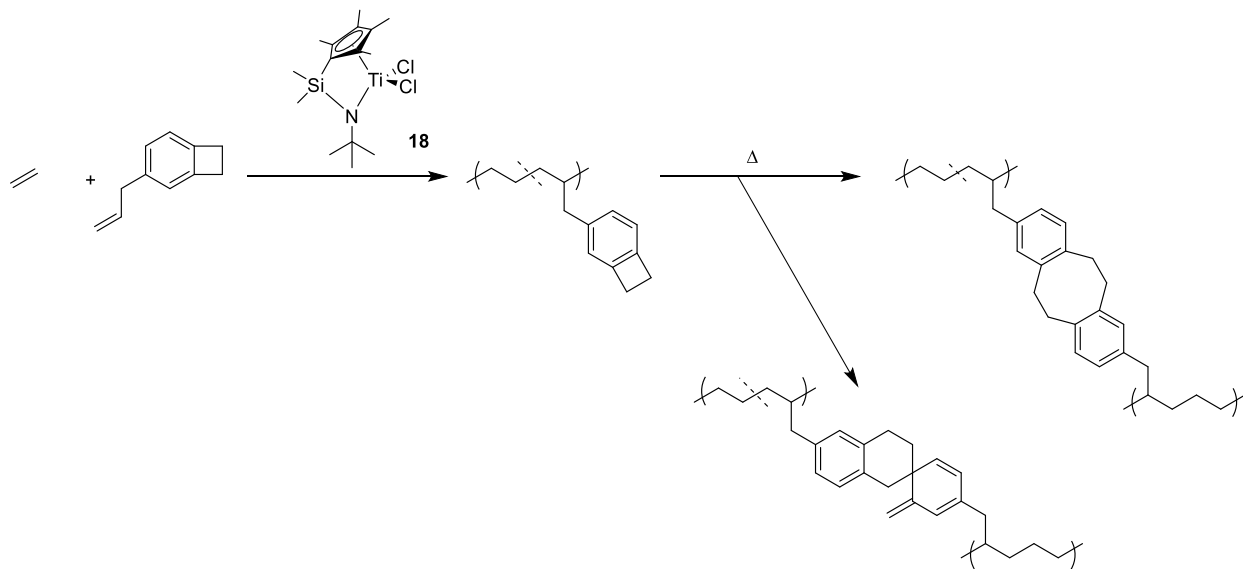
In order to cross-link polyethylene in a cheap and effective way, we propose to covalently cross-link polyethylene by the incorporation of 3-allylbicyclo[4.2.0]octa-1,3,5-triene (BCB) (**5**) into the polyethylene backbone. Previous work has proven that the strained cyclobutene ring in BCB will open at or above 200 °C (Scheme 4.3.).¹¹⁵⁻¹¹⁶ BCB incorporation into the polyethylene chain by co-polymerization with ethylene occurring at the reactive allylic carbons produces compound **6** (Scheme 4.4.). Further heating of **5** past 200 °C would allow for the opening of the BCB moiety, result in **7**, (Scheme 4.4.) and allow cross-linking to occur between polymer chains. The ring-opening reaction of polymer **6** can then precede through two different routes (Scheme 4.4.), a [4+2]

Scheme 4.3. Ring-opening of benzocyclobutene.



cycloaddition results in **8**, or the less favored [4+4] addition which results in **9**, which is subsequently the structure of cross-linked polyethylene. It is important to note that [4+2] cycloaddition is favored in this reaction, but with the formation of **8** or **9**, the covalent cross-linking of polyethylene is achieved.²⁴ A relatively small amount of BCB (1-2%) is needed for the complete cross-linking of all polyethylene chains and this synthetic route would eliminate the need for high energy, expensive radiation or the necessity to use peroxides that tend to form defects in the final polymer product.

Scheme 4.4. Cross-linking rearrangement for BCB derivative with polymerization of ethylene.



4.2. Results and Discussion

In this dissertation, a radical and siloxane free method for the cross-linking is presented for the formation of PEX, containing several BCB units incorporated into the polymer backbone. The monomer was synthesized through a series of organic steps (Scheme C.1.) to obtain **5**, which could be used in the polymerization of ethylene. Although difficult to synthesize organically, **5** is an ideal co-monomer to incorporate into α -olefin polymer backbones as it is: 1) non-polar in nature and 2) structurally similar to the styrene unit. The former is important due to group IV metal catalysts consistently used in industrial ethylene polymerizations do not tolerate polar co-monomers and will result in a deactivation of the catalyst due to chelating effects from the polar co-monomer. Incorporation of a non-polar, all carbon and hydrogen co-monomer gives an advantage that catalyst selection for the polymerization becomes easier due to the wide variety of catalysts available for incorporating α -olefin type co-monomers. To the later point above, structural similarity to a widely used and widely known polymerization procedure of styrene is advantageous because the selection of catalyst becomes simpler. While other methods look to include polar co-monomers, the transition to a late transition metal that is needed can have drawbacks on the polymerizations molecular weight, and is not industrially viable due to their low thermal stability when compared to industrial temperatures.

The catalyst chosen, **18**, is a group IV metal constrained geometry catalyst (CGC) that is known to polymerize both ethylene and styrene to high molecular weights with an

extremely linear backbone that contains little to no branching. Two other advantages of this known Ti-based catalyst are as follows: a) **18** is currently employed in industrial settings, which eases the transition from academic study to industrial viability and b) it is also known to readily incorporate non-polar co-monomers into a polyethylene backbone.¹¹⁷ As seen in Table 4.1., entry 1, an initial screening was performed for the polymerization of ethylene under mild, room temperature conditions. The catalyst, **18**, was charged in a Fisher Porter bottle with toluene and placed under 15 PSI of ethylene feed. After injection of the activator, MAO, at room temperature the polymerization was conducted for 1.5 h and produced 4.03 g of polymer after filtration and drying. Also of note is the T_m of 133.3 °C, which falls around the generally accepted $T_m = 137$ °C that is seen for linear polyethylene, indicating there is little to no branching content.⁹⁷

After determining the catalyst chosen would produce polyethylene to high enough molecular weight for film formation, evaluation of **5** incorporation into the polymer backbone needed to be tested and proven. Initially, for Table 4.1., entry 2-5, the polymerization proceeded as outlined above, however, the incorporation of **5** was included when the flask was charged with toluene and catalyst. Through varying incorporation amounts based off molarity, yield drastically drops (4.03 g to 0.99 g) with the increasing addition of **5** into the polymerization.

Of the most importance, though, is the T_m of each polymer and the T_m (x-link) column seen in Table 4.1. For initial trials, DSC was used as an effective way to determine if **5** could be incorporated into the polymer backbone, and subsequently cross-linked to

form PEX. After drying *in vacuo* at 75 °C overnight of polymer samples (Table 4.1., entry 2-5), a DSC test was performed. The ring-opening of **5** should theoretically occur at or above 200 °C, and this theory was tested as seen in Figure 4.1. After the initial melt,

Table 4.1. Initial trials for the incorporation of **5** into polyethylene.

	[BCB]	Yield	M _n		mol %	T _m	T _m (x-link)
entry	(mmol)	(g)	(kg/mol)	<i>Đ</i>	BCB	(°C)	(°C)
1	0	4.03	70	5.81	-	133.3	-
2	10	1.70	125	2.07	ND	130.8	128.8
3	15	1.23	36	2.60	1.1	126.4	123.5
4	20	1.05	35	2.63	1.3	124.7	119.6
5	30	0.99	32	1.81	2.3	120.8	108.8

^a10 μmol cat, [Al]/[Ti] = 1000, 30 mL Toluene, T_{rxn} = 20 °C, t_{rxn} = 1.5 h

which is not pictured, a T_m was obtained for each sample and recorded. For the third melt, however, the temperature was taken well above 200 °C to ensure all rings in **5** would be opened and subsequently cross-link. The disruption of crystallinity in the polyethylene backbone lowers T_m, and provides an exotherm which can be seen in the representative

trace in Figure 4.1. The theory was proven correct, as the third melts all showed a decrease in T_m temperature, which is routinely seen when cross-linking materials.

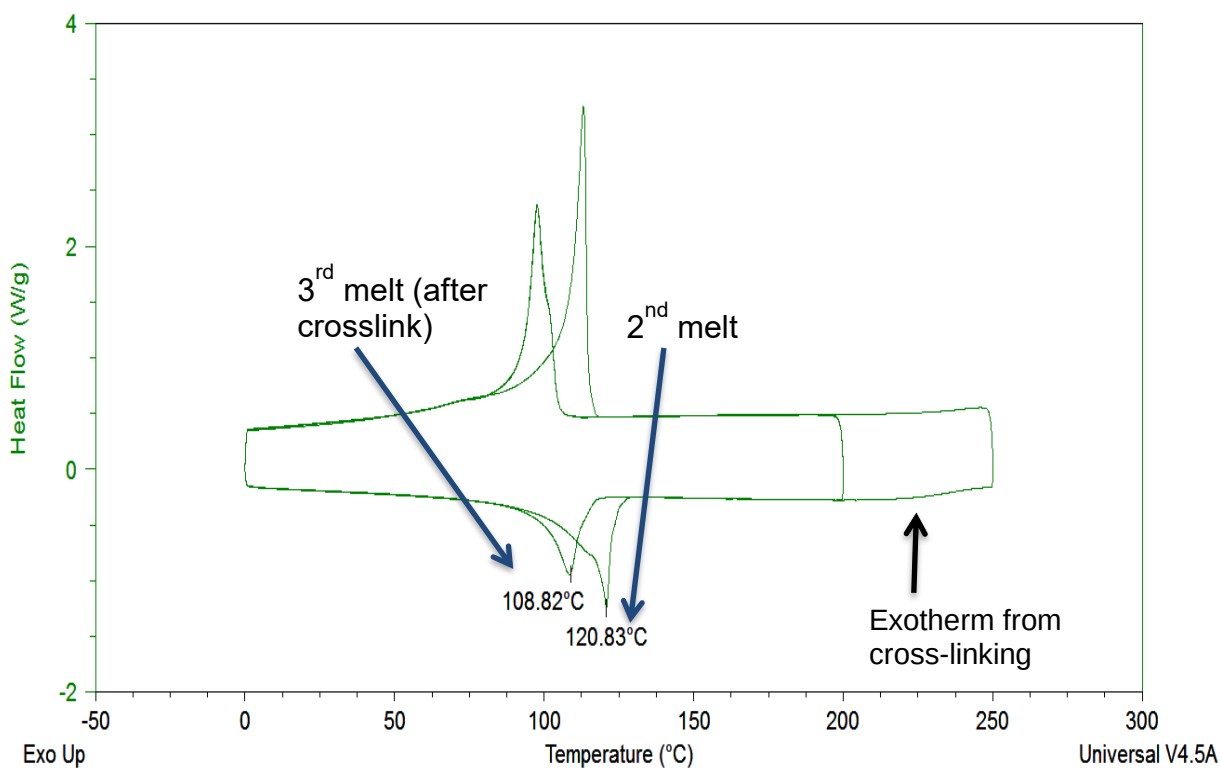


Figure 4.1. Initial DSC testing for cross-linking after thermal rearrangement with 10 mmol of BCB added to the polymerization trial (Table 4.1., entry 2).

While adequate for initial testing, further tests needed to be performed to ensure the incorporation of **5** into the polymer backbone, to ensure the ring-opening reaction occurs, and subsequent cross-linking to form covalent bonds, and to investigate how the varying percent incorporations would affect the temperature and time needed to cross-link polyethylene. The NMR results for Table 4.1., entry 2-5 were encouraging, as the

peaks of **5** are unique and can be identified readily (Figure C.7. - C.9.). Incorporation of Table 4.1., entry 3 (15 mmol) of **5** yielded a 1.1 % incorporation, entry 4 (20 mmol) yielded a 1.3 % incorporation, and entry 5 (30 mmol) gave 2.3 % incorporation of **5** into the polyethylene backbone. The three distinct olefinic shifts at 2.5 and 3.3 ppm correspond to the closed ring protons on **5**, and two protons on the allylic bridge, while the shifts at 7.0 ppm are aromatic and again an identifying factor in the incorporation of **5**.

Polyethylene films, especially linear ones, proved difficult to solution cast with any amount of reproducible nature and was abandon for the more favorable film formation method using a Carver Press. After incorporation was confirmed via NMR, the sample of dry powder was placed between two metal plates at 150 °C, and then pressed with 5000 lbs of force for 7 min. The temperature chosen was to ensure that cross-linking did not occur, while also remaining above the T_m for each polymer to help with film formation. Films produced at lower temperatures were brittle, porous, and often times produced an uneven surface. After film formation, **6** was subjected to temperatures that met or exceeded the 200 °C for ring-opening reactions to occur while under vacuum in a polymer oven. To reduce yellowing of the films from oxidation from the atmosphere, upon introduction to the polymer vacuum, the oven was refilled with inert nitrogen three times with vacuum introduced between each turn. The films could then be tested at various times and temperatures, followed by gel percentage testing, to determine the exact amount of cross-linking seen for the polymer samples.

Table 4.2. Polymerization results for longer time to obtain a higher polymer yield.

	[BCB]	Yield	M _n		mol %	T _m	T _m (x-link)
entry ^a	(mmol)	(g)	(Da)	Đ	BCB	(°C)	(°C)
1 ^b	0	4.03	70,406	5.81	-	133.3	-
2	10	10.1			0.4	129.8	129.2
3	30	7.45			1.2	121.9	113.6

^a10 μmol cat., [Al/Ti] = 1000 equiv., 60 mL toluene, RT, 6 h. ^b10 μmol cat, [Al]/[Ti] = 1000, 30 mL Toluene, T_{rxn} = 20 °C, t_{rxn} = 1.5 h

Gel content, or gel percentage, is an informative metric to determine when examining cross-linking reactions, and is also a simple to perform. It is determined by first cross-linking the polymer film under a prescribed set of conditions. Then, that sample is subjected to a series of vigorous solvent extractions. Following those extractions, the insoluble polymer fraction is isolated, dried, and massed to determine what percentage of the original material was insoluble and what percentage was extracted into the solvent. This insoluble polymer fraction is a direct result of polymer cross-linking to form an insoluble network, or gel, whereas the solubilized fraction represents non-cross-linked or only very lightly cross-linked material. Specific to our project, gel percentage was determined via vigorous solvent extraction in xylenes for 5 h to remove the soluble fraction of polymer. After this time, the remaining insoluble film was recovered using forceps, and

the entire extraction process was then repeated two additional times. After the last extraction, and film recovery, the insoluble polymer was dried *in vacuo* overnight at 75 °C and re-weighed. The final mass was then divided by the films initial mass ($\times 100\%$) to provide the gel percentages described below.

Initial results (Table 4.1.), however, did not produce enough polymer to continue with an adequate number of cross-linking tests and were therefore unable to give a complete set of gel percentage data points that would be performed in triplicate for accuracy. A new set of polymerizations were run, as seen in Table 4.2., where the polymerization time and solvent volume were increased to increase the yield of each

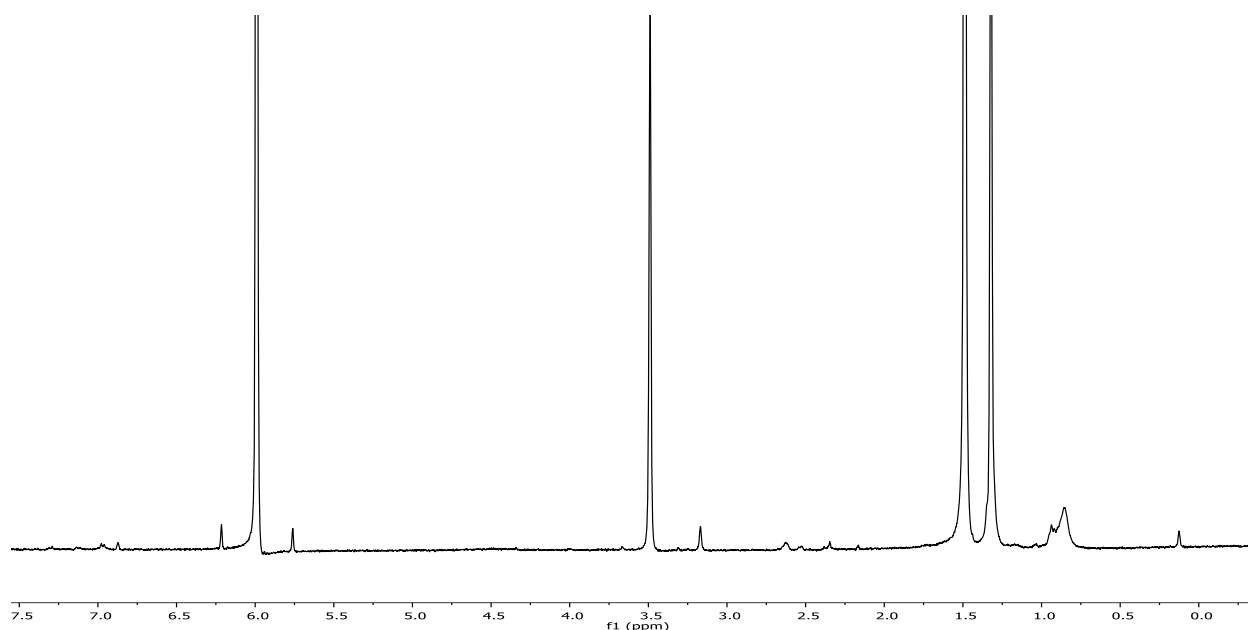


Figure 4.2. NMR of polyethylene-BCB with 10 mmol of BCB added (Table 4.2, Entry 2).

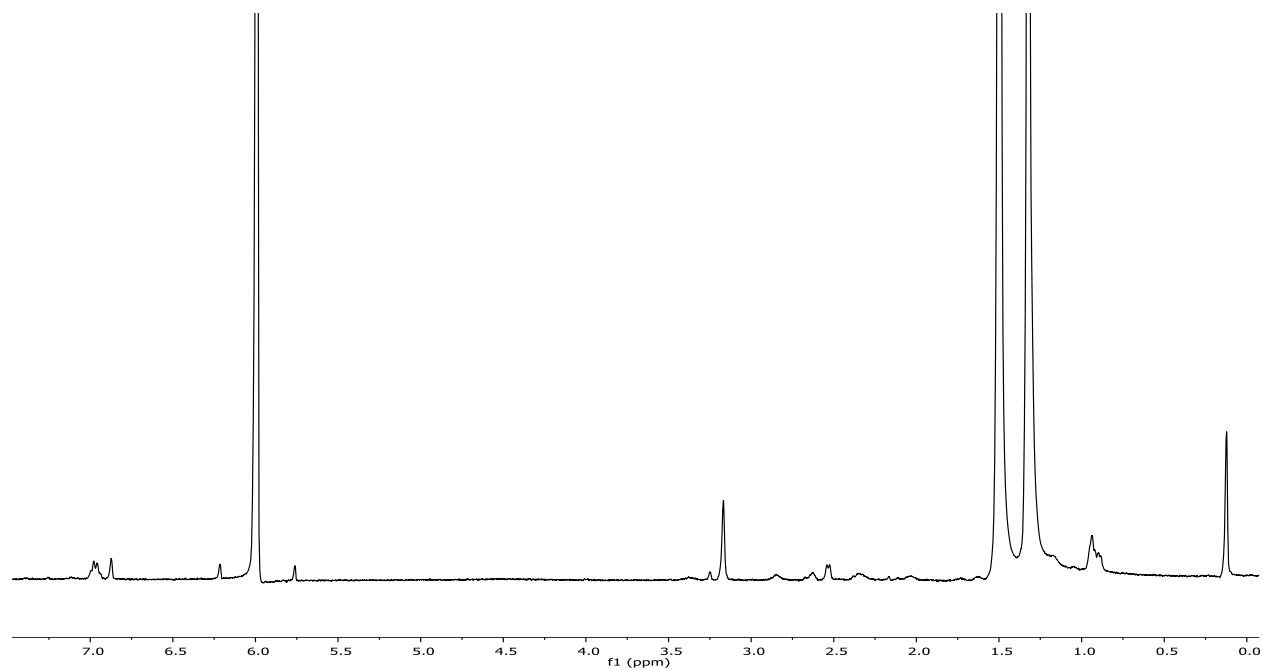


Figure 4.3. NMR of polyethylene-BCB with 30 mmol of BCB added (Table 4.2, Entry 3).

polymer, giving enough to produce multiple films and do a variety of cross-link testing on films of the same incorporation percentage. Unfortunately, at the current time high temperature GPC was not available to the author to determine M_n or $\bar{M}_w$ value's, but this data gap will be filled in imminently and the formation of films suitable for gel percent testing is a strong indicator M_n is at or above previous trials. The polymers do form films upon pressing, and Figure(s) 4.2. and 4.3. illustrate the successful incorporation of **5** into the polyethylene chain as can be seen from the NMR. In both Figure 4.2. and Figure 4.3., successful incorporation of **5** into the polyethylene backbone can be seen with magnetic shifts at 2.5, 3.2, and 6.9-7.0 ppm for the ^1H NMR spectrum. The broader shift at 2.5 ppm in both figures corresponds to the two methyl-bridged protons seen between the BCB unit and polyethylene backbone. The sharp singlet peak at 3.2 ppm corresponds to the four protons present in the strained butene ring as further proof of BCB incorporation. Finally, the two aromatic peaks seen at 6.9-7.0 ppm in both Figures correlates to the three aromatic protons in the BCB unit. As incorporation of BCB is increased, the signal of these BCB proton shifts also increases and becomes more apparent.

Figure 4.4. is the film formed and tested from Table 4.2., entry 3, and shows how gel percentage (or cross-linking percentage) can vary with time at a given temperature. With temperature remaining constant at 230 °C, and incorporation constant at 2.3 %, the gel percentage increases with increasing time. It is interesting that there appears to be an induction period for the cross-linking of these films, as all data collected for five minutes resulted in a gel percent of 0 %, indicating no cross-linking has occurred. It is

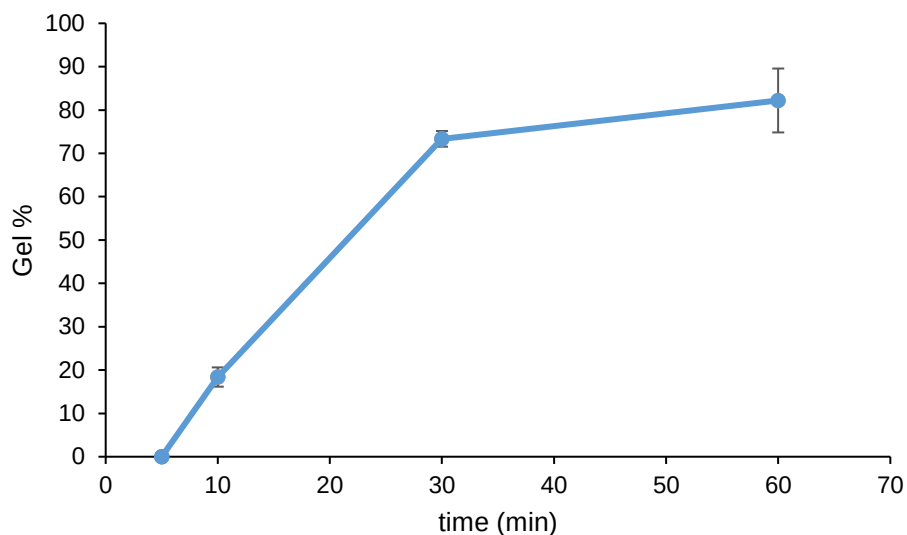


Figure 4.4. Gel percentage for 30 mmol incorporation trial, measured at a constant temperature of 230 °C over varying times.

hypothesized the time needed for the ring-opening and subsequent cross-linking reaction to occur does not happen below the 5-min mark. As time is increased to 10, 30, and 60 min respectively, however, a maximum average cross-linking efficiency of 82.2 % at the 60-min time point. Continuing to Figure 4.5. which shows gel percentage as a function of temperature, but a consistent time of 60 min. As expected, the lowest temperature of 200 °C shows the lowest gel percentage for both Table 4.2., entry 2 (10 mmol) and entry 4 (30 mmol), with a subsequent increase corresponding to increased temperature. Throughout the temperature trials, Table 4.4., entry 3 consistently shows higher gel percentage, which is expected as the percent incorporation of **5** is seen and increases the number of cross-link formations that can occur.

Also, important to study is how incorporation percentage relates to gel percentage over various times. As seen in Figure 4.6., the expected trend of longer exposure to cross-linking conditions leads to an increase in gel percentage holds true. Gel percentage consistently increases as time is increased for both 0.4 and 1.2 % incorporation of **5**, while reaching a maximum of 82.2 %.

4.3. Conclusion

The linear polymer **6**, containing flexible and thermally activated benzocyclobutene moieties, has been prepared by polymerization with **18**. The resulting polymer can be heat pressed at elevated temperatures, and thermally cross-linked at temperatures above 200 °C and longer than 5-min via [4+2] or [4+4] cycloaddition reactions. Clearly, even a small amount of **5** incorporation into the polymer can cross-link to high yields to produce PEX. As time is increased, as well as cross-linking temperature and incorporation percentage, gel percentage increases accordingly to a current maximum of 82.2%. At this time, more tests are being performed with higher incorporation percentages of **5**, in hopes of reducing the time and temperature needed to obtain a fully cross-linked material as efficiently as possible.

4.4. General Methods and Materials

All reactions were performed under an inert nitrogen atmosphere using an MBraun UniLab glovebox or using standard Schlenk techniques, unless otherwise noted. All

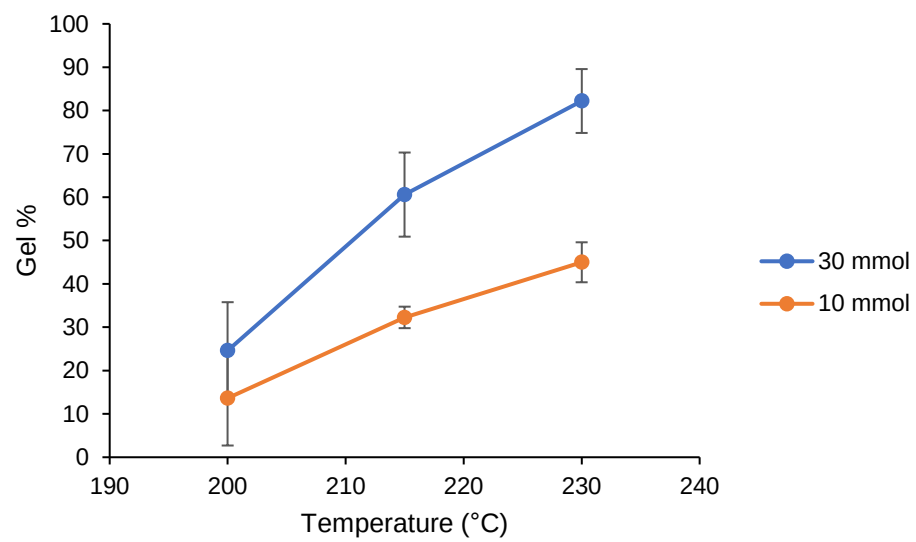


Figure 4.5. Gel percentage for 10 and 30 mmol trials, with a constant time of 60 min at varying temperatures.

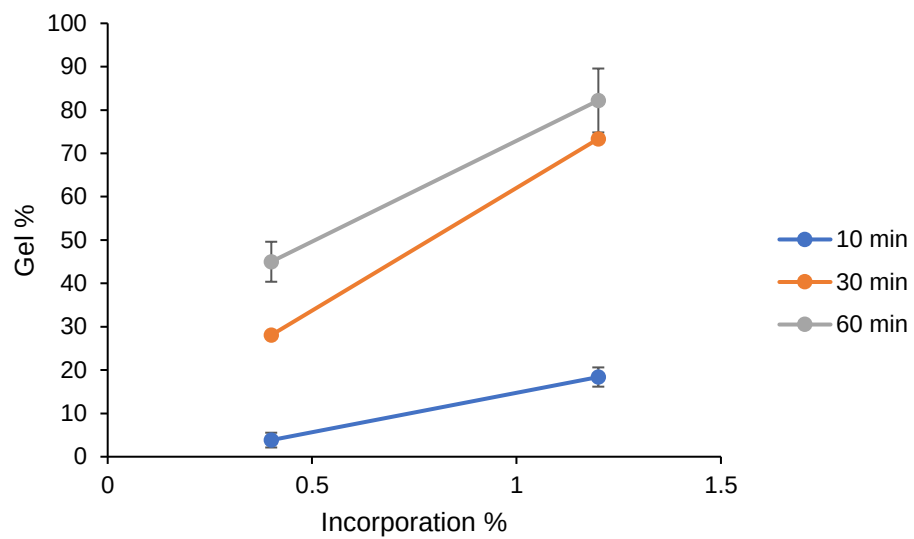


Figure 4.6. Gel percentage for varying time trials with constant temperature of 230 °C and multiple BCB incorporation percentages.

solvents were dried using an Innovative Technologies PureSolv Solvent Purification system and degassed via three freeze-pump-thaw cycles. CDCl_3 was dried over activated molecular sieves (4 Å). MAO was received from Albemarle Corp. and used as received. All other reagents were purchased from commercial vendors and used without further purification.

^1H and ^{13}C spectra were recorded at ambient temperature on a Varian VNMRS 500 MHz narrow-bore broadband system. Polymer ^1H spectra for polymer were taken on a Bruker VNMRS 400 MHz at 100 °C. ^1H and ^{13}C NMR chemical shifts were referenced to residual solvent. Gel permeation chromatography was performed at 160 °C in 1,2,4-trichlorobenzene at 1.0 mL/min on a Malvern Viscotek HTGPC equipped with refractive index, viscometer, and two-angle light-scattering detectors. Polymer melting transition temperatures (T_m) were measured on a TA Instruments Q2000 differential scanning calorimeter on the second heating cycle at a heating rate of 10 °C/min.

4.4.1. General Polymerization Procedure.

In a typical polymerization, pre-catalyst was added to a flame dried Fischer Porter bottle, charged with toluene (60 mL) and BCB, and sealed in a nitrogen filled glove box. The polymerization reactor was then removed from the glove box and flushed and back-filled three times with ethylene gas. The reactor was allowed to equilibrate at the desired temperature for 10 min under constant ethylene pressure (15 psi) before MAO solution (1000 equivalents) was injected *via* syringe with stirring. The reactions were terminated

by adding methanol and then stirred overnight in acidic methanol (5% HCl in CH₃OH). The resultant polymer was collected by filtration and dried *in vacuo* at 75 °C overnight.

4.4.2. Formation of Films

After drying overnight *in vacuo* at 75 °C, the polymer was crushed in a mortar and pestle to ensure an even particle distribution. In a Carver Heat Press polymer (2.5 g) was distributed evenly in a circle between two layers of Kapton film. The press was set to 150 °C and films were pressed with 5000 lbs of force and let sit for 7 mins. After the time was up, the press heat was turned off, pressure released, and films removed from the machine when the temperature was 70 °C.

4.4.3. Evaluation of Cross-Linking Efficiency.

A polymer oven was preheated to the desired temperature before cut strips of film were placed in it. As films were placed in, vacuum was pulled and then re-filled with N₂ (3x) to prevent yellowing due to oxygen. The PE-BCB films were then boiled in xylenes for 5 h after cross-linking and then filtered. This was repeated two more times using fresh xylenes each time. Polymers were then re-dried at 75°C overnight and weighed. The difference in weight from pre and post xylene treatment was used to determine gel content of the films.

4.4.4. Evaluation of Benzocyclobutene Incorporation Percentage

NMR peaks from BCB were integrated accordingly for a single BCB molecule, and then integration was performed for polyethylene peaks. This number was used for the formula:

$$(1 \text{ BCB unit} / ((\# \text{ Hydrogen Protons from integration}) / 2 / 2)) \times 100 = \% \text{ BCB incorporation}$$

The hydrogen protons were divided by two to account for four hydrogens per ethylene repeat unit to only two hydrogens per carbon. The value was again divided by two to account for two hydrogens reduced to a single carbon, giving one BCB unit per number of carbons. This was multiplied by 100 to obtain a percentage.

Chapter 5

Conclusions and Future Work

5.1. Conclusions

This dissertation is focused on two main subjects: 1) Advancing late transition metal catalysts thermal robustness *via* enhancement of ligand bulk around the metal center, and 2) Formation of the advanced material, PEX, through thermal rearrangement of a non-polar co-monomer (BCB).

In Chapter 2, the bulky *i*Pr* framework is applied to an acenaphthenequinone backbone and metallated with Ni (II). Once formed, catalyst **11** underwent ethylene polymerization trials at elevated temperatures to determine its thermal stability and gain further insight into these catalyst systems. The catalyst, **11**, remained robust and active at polymerization temperatures up to 90 °C with consistent activity and linearly increasing productivity. Although slower than **10**, the bulkier backbone in **11** helped contribute to the enhanced thermal stability, and also led to an increase in T_m 's from a more linear polymer. Later, this catalyst was also found to polymerize ethylene in a living fashion at temperatures up to 75 °C after an impurity was removed.

Chapter 3 extends the bulk framework of the *i*Pr* ligand to more earth abundant and cheaper group X metals of Fe and Co. While catalyst **15** was seen to be inactive, with its bulky PDI backbone, this was confirmed by other literature and no further polymerization trials were conducted. However, **16** showed thermal stability over 60-min trials at 80 °C, and did not see signs of decomposition or chain transfer until the tail end of this time trial at 90 °C. When comparing Al:cat ratios for **16** and **4b**, the bulkier former

catalyst shows no deleterious chain-transfer events while the latter sees a decrease of M_n with increasing ratio.

Chapter 4 highlights the use of a BCB like co-monomer, **5**, which can be incorporated into the polyethylene during polymerization. Upon incorporation with a CGC catalyst, thermal rearrangement of the co-monomer can occur which forms cross-link units when two of the moieties encounter one another. Various cross-linking conditions, such as varying temperature, time, and incorporation, were studied and a maximum gel percentage of 82 % was seen for this particular system. Whether by [4+4] or [4+2] addition, heating past 200 °C allows for the ring-opening of **5** and subsequent cross-linking. It was seen that as exposure time is increased, the gel percentage increases for all incorporation ratios, and as incorporation ratios increase, gel percentage also increases. This method of thermal rearrangement could be industrially viable and avoids the use of harmful peroxides and irradiation typically used in the synthesis of PEX. With an added advantage that cross-linking percentage can be controlled by tuning the properties of time, temperature, and incorporation.

5.2. Future Work

A few recommendations for future work are made by looking at the larger picture obtained from this dissertation. Moving forward with the α -diimine Ni-based catalyst, and Co-based catalyst, both bearing bulky *i*Pr* ligand framework would be to further work to enhance thermal stability. In order to achieve this goal, a few synthetic modifications can

be employed. First, linking two ligands together to give a dinucleating species during polymerization is shown to enhance thermal stability over time, and also increase the molecular weight of the resulting polymer. Second, further bulk can be incorporated into the ligand by the introduction of naphthene groups, instead of phenyl, at the *ortho*-position of the *N*-aryl moiety. Finally, α -diimine and PDI based catalysts are only two of the many catalyst structures employed in late transition metal olefin catalysis. Recent work performed by Sun and co-workers has shown the stability of 2-(arylimino)benzylidene-9-arylimino-5,6,7,8-tetrahydrocycloheptapyridyl backbones for Co-based catalysts, and introduction of the *i*Pr* ligand would be worth investigation. Another backbone modification to make would be the condensation of *i*Pr* onto the bulkier dibenzobarrelene backbone previously seen in ethylene polymerization by Long *et al.*

Preliminary work into the formation of PEX by thermal rearrangement of two BCB co-monomers has proven encouraging, and although high gel percentage is seen, continued work incorporating 60 mmol of BCB needs to be done. Once a maximum percent of **5** incorporation can be determined, efforts can be put forth to produce the highest gel percent possible with minimal heating and time. Also, the specific tuning of incorporation, time, and temperature could be used to tailor cross-linking percentage for the formation of PEX, something not seen in industry currently. Finally, mechanical properties, such as tensile strength and modulus, testing needs to be performed to ensure that the thermally rearranged formation of PEX still meets industry standards and holds the same mechanical values even with the co-monomer BCB incorporation.

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Appendices

APPENDIX A

Supporting Information for Chapter 2

General Methods and Materials

All reactions were performed under an inert nitrogen atmosphere using an MBraun UniLab glovebox or using standard Schlenk techniques, unless otherwise noted. All solvents were dried using an Innovative Technologies PureSolv Solvent Purification System and degassed via three freeze-pump-thaw cycles. CD_2Cl_2 was dried over activated molecular sieves ($4\text{\AA}$) and degassed by three freeze-pump-thaw cycles prior to use. 2,6-bis(diphenylmethyl)-4-methylaniline was prepared as previously reported.⁷⁷ PMAO-IP was purchased from Akzo Nobel. All other reagents were purchased from commercial vendors and used without further purification. ^1H and ^{13}C NMR spectra were recorded at ambient temperature on a Varian Mercury 300 MHz or Varian VNMRS 500 MHz narrow-bore broadband system. Polyethylene ^1H and ^{13}C NMR spectra were recorded at $135\text{ }^\circ\text{C}$ on a Bruker 400 MHz. ^1H and ^{13}C NMR chemical shifts were referenced to residual solvent. Elemental microanalyses were carried out by Atlantic Microlab, Inc. (Norcross, GA). Gel permeation chromatography was performed at $145\text{ }^\circ\text{C}$ in 1,2,4-trichlorobenzene at 1.0 mL/min on a Polymer Labs GPC220 equipped with refractive index and two-angle light-scattering detectors (Precision Detectors). Weight average molecular weights (M_w) were obtained from GPC light scattering data and molecular weight distributions ($\mathcal{D}$) were obtained from GPC refractive index data relative to polystyrene standards. Number average molecular weights (M_n) were calculated using M_w , obtained from light scattering, and molecular weight distributions ($\mathcal{D}$) obtained from RI. Polymer melting transition temperatures (T_m) were measured on a TA Instruments

Q1000 differential scanning calorimeter on the second heating cycle at a heating rate of 10 °C/min.

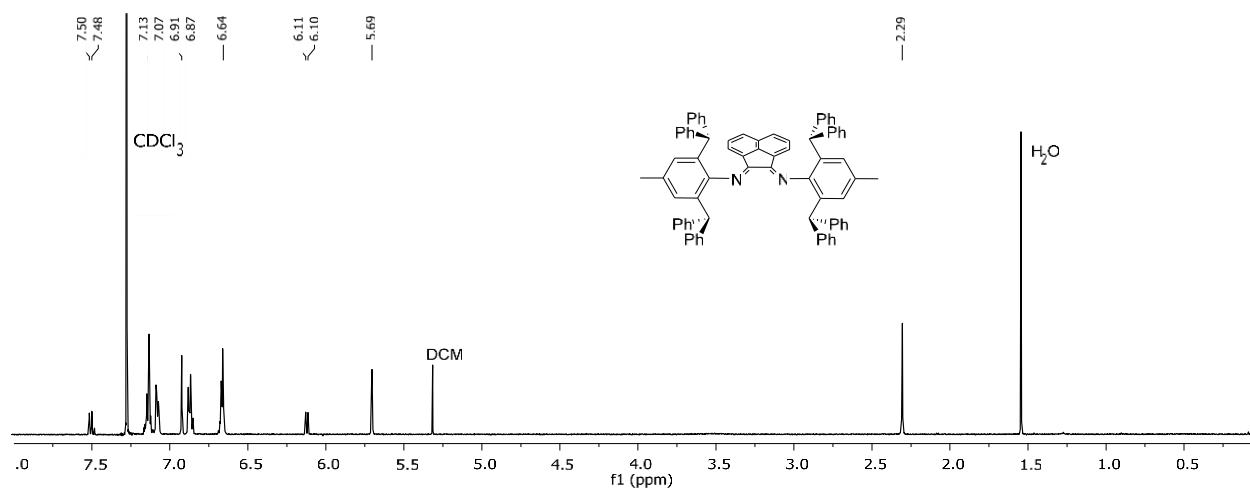


Figure A.1. ¹H NMR of **14** in CDCl₃.

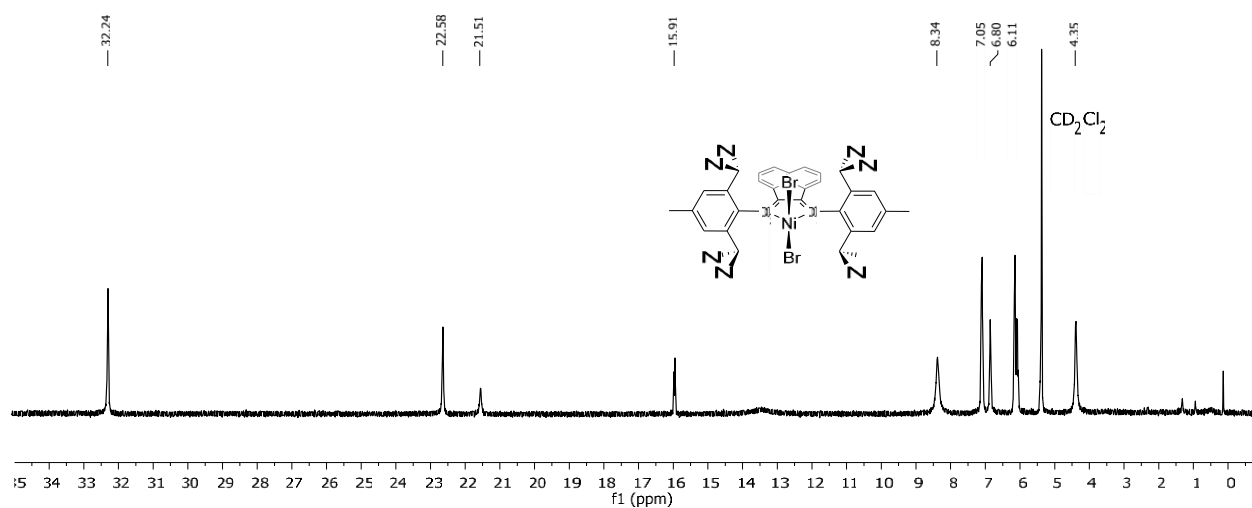


Figure A.2. ¹H NMR of **11** in CD₂Cl₂.

Table A.1. Results for ethylene polymerizations with **11** at 80 °C.

	t	Yield	TOF ^b	Prod ^c
entry	(min)	(mg)	(h ⁻¹)	(kg/mol)
1	5	326.9	97682	227
2	5	293.2	87612	204
3	5	356.8	106617	248
4	10	739.7	110516	514
5	10	785.1	117300	545
6	10	654.4	97772	454
7	10	506.2	75630	352
8	15	1063.4	105496	738
9	15	1070.5	106200	743
10	15	1069.1	106062	742
11	20	1554.0	116793	1079
12	20	1480.8	111291	1028
13	20	1612.5	121190	1120

^aPolymerization conditions: [**11**] = 1.4 μmol, 100 mL toluene, 100 psi and 400 eq. PMAO-IP. ^bTurnover frequency (TOF) = mol ethylene/(mol cat.*h). ^cProductivity = yield polyethylene/mol catalyst.

Table A.2. Results for ethylene polymerizations with **11** at 90 °C.

	t	Yield	TOF ^b	Prod ^c
entry	(min)	(mg)	(h ⁻¹)	(kg/mol)
1	5	442.3	132166	307
2	5	360.2	107633	250
3	5	339.2	101358	236
4	10	778.9	116373	541
5	10	684.5	102269	475
6	10	874.5	130657	607
7	15	1086.5	107788	755
8	15	1070.6	106210	743
9	15	1382.9	137192	960
10	20	1591.0	119574	1105
11	20	1633.2	122745	1134
12	20	1562.0	117394	1085

^aPolymerization conditions: [**11**] = 1.4 μ mol, 100 mL toluene, 100 psi and 400 eq. PMAO-IP. ^bTurnover frequency (TOF) = mol ethylene/(mol cat.*h). ^cProductivity = yield polyethylene/mol catalyst.

Table A.3. Results for ethylene polymerizations with **11** at 100°C.

	t	Yield	TOF ^b	Prod ^c
entry	(min)	(mg)	(h ⁻¹)	(kg/mol)
1	5	453.1	135393	315
2	5	434.0	129685	301
3	5	401.0	119825	278
4	10	904.7	135169	628
5	10	882.0	131777	613
6	10	931.0	139098	647
7	10	122.3	121260	849
8	15	1203.7	119415	836
9	15	1191.7	118224	828
10	15	1520.1	114245	1056
11	20	1566.1	117702	1088
12	20	1514.5	113824	1052
13	20	1612.5	121190	1120

^aPolymerization conditions: [**11**] = 1.4 μ mol, 100 mL toluene, 100 psi and 400 eq. PMAO-IP. ^bTurnover frequency (TOF) = mol ethylene/(mol cat.*h). ^cProductivity = yield polyethylene/mol catalyst.

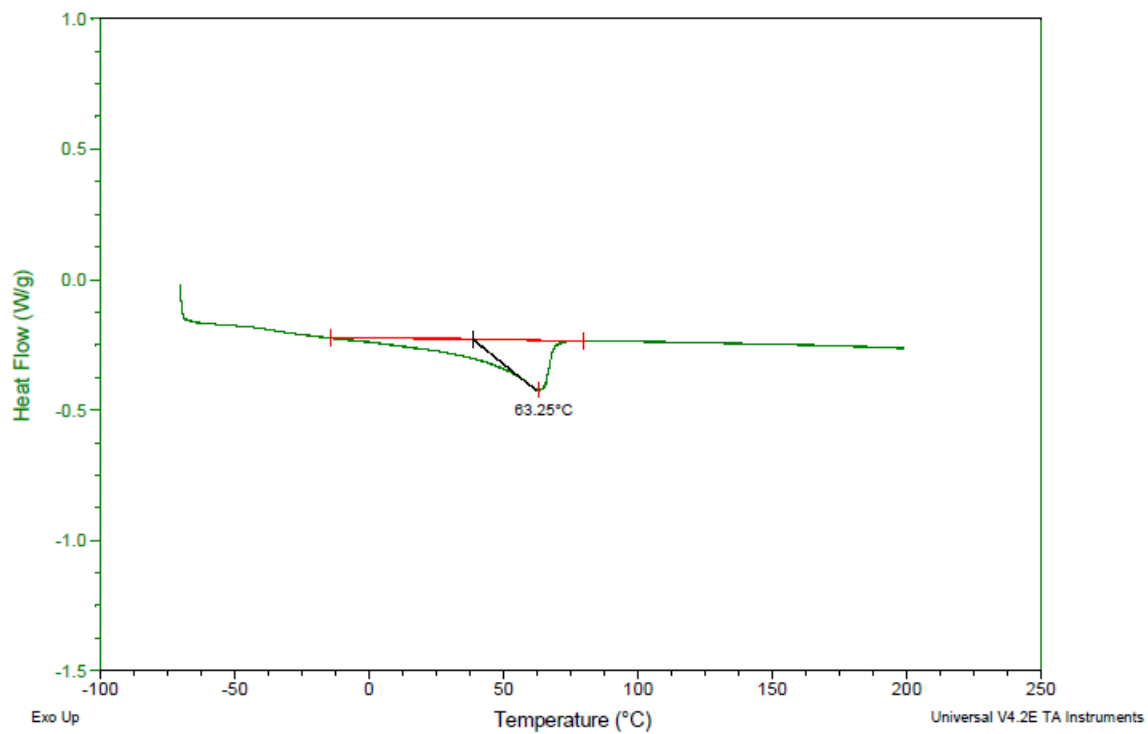


Figure A.3. Representative DSC of polymer made using catalyst **11** (Table 2.2., entry 4)

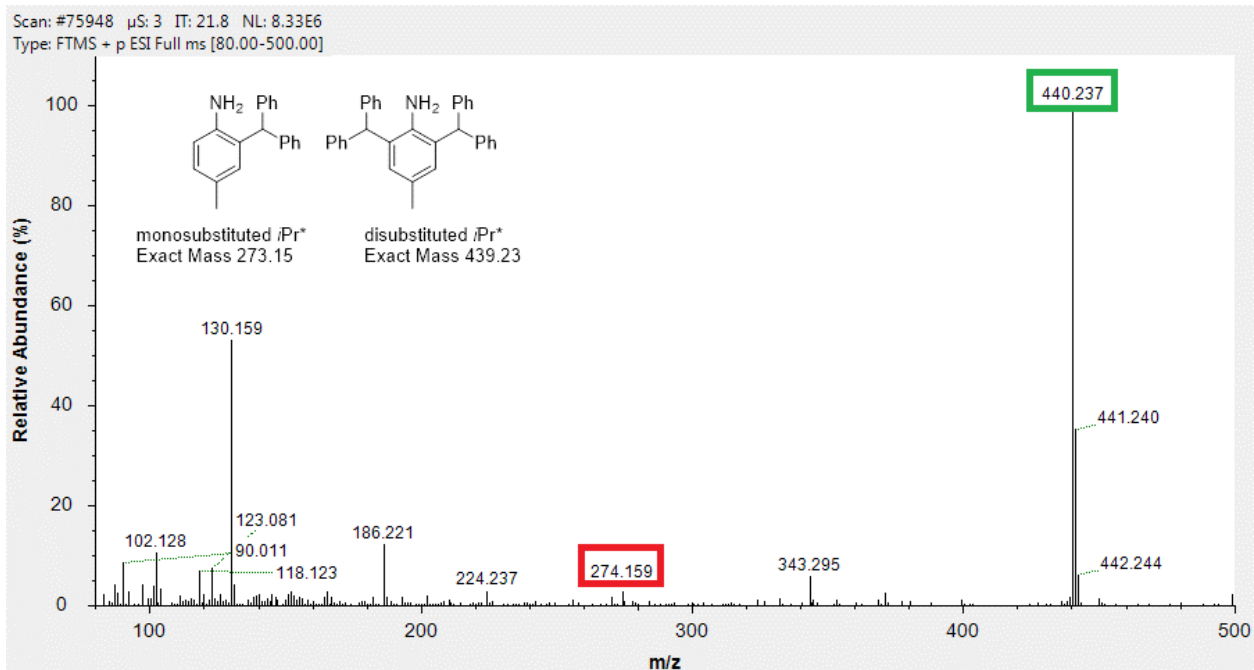


Figure A.4. LC-MS of bulky aniline (**14**) in DCM prior to purification.

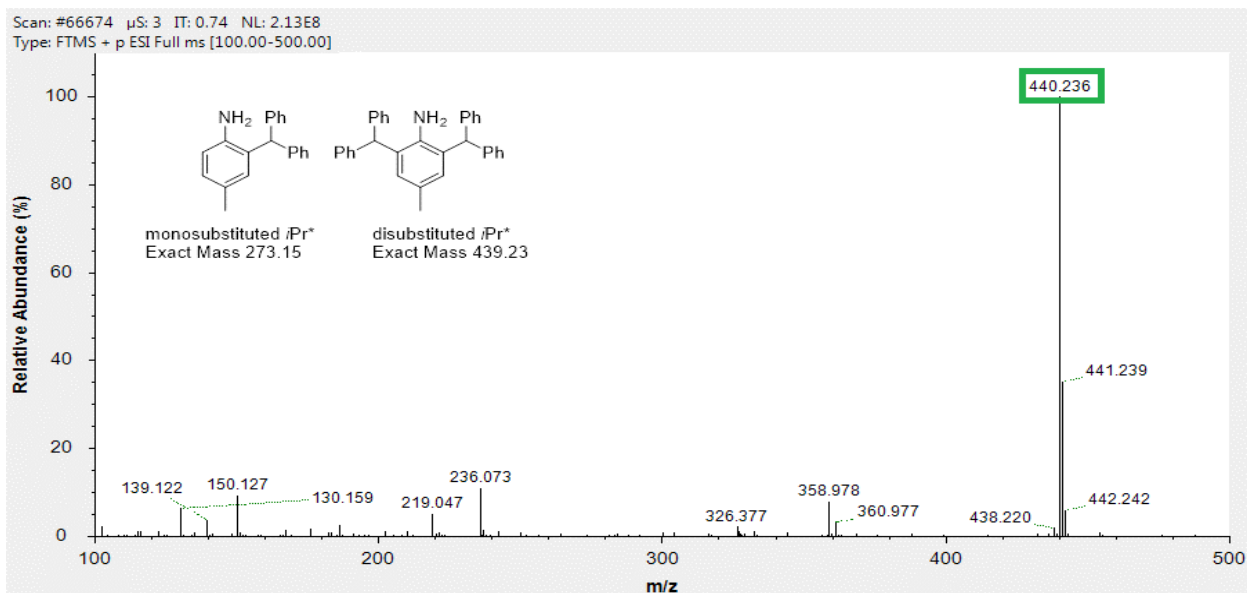


Figure A.5. LC-MS of bulky aniline (**14**) in DCM prior to purification.

APPENDIX B

Supporting Information for Chapter 3

General Methods and Materials

X-ray diffraction measurements were performed on single crystals coated with Paratone oil and mounted on glass fibers. Each crystal was frozen under a stream of N₂ and data were collected at 100(2) K using a Bruker SMART APEX diffractometer (MoK α radiation, $\lambda = 0.71073 \text{ \AA}$) 1 $\text{\AA}$ matrix scan using at least 12 centered reflections was used to determine initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT 4.05. Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS,¹ if necessary. Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structure. The structures were solved by intrinsic phasing method and were refined using SHELXTL 5.0 ² software package. Subsequent difference Fourier calculations and full-matrix least-squares refinement against F² were performed with SHELXL-2014 ² using OLEX2.3. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed as standard riding atoms with refined isotropic displacement parameters. Compound **16**, had a large solvent accessible volume (total solvent accessible volume / cell = 5375.6 $\text{\AA}^3$ [19.8 %], total electron count/cell = 1129.0) and was successfully masked using OLEX2.3. The A-alert (THETM01_ALERT_3_A The value of $\sin(\theta_{\text{max}})/\text{wavelength}$ is less than 0.550 Calculated $\sin(\theta_{\text{max}})/\text{wavelength} = 0.5049$) was generated due to the nature of the crystal (large cell with lots of disordered

solvent giving rise to weak diffractions) and the selected data crystal was the best of several examined, no diffraction was observed above the reported $\theta(\text{max})$.

Synthesis of 2,6-bis[1-(2,6-bis(diphenylmethyl)-4-methylaniline)]pyridine iron(II)chloride (15**)**

A solution of ligand **17** (400 mg, 0.40 mmol) in tetrahydrofuran (20 mL) was added to iron(II) dichloride hydrate (83.1 mg, 0.38 mmol) in a Schlenk flask and stirred overnight at room temperature. Diethyl ether (10 mL) was then added to the reaction to precipitate the complex and the resulting solids were filtered in air and washed using diethyl ether and pentane and dried *in vacuo* to yield complex **15** as a blue powder (254.3 mg) in 63.6% yield. ^1H NMR (CDCl_3 , 500 MHz) δ 8.18 (d, 2 H), δ 7.98 (m, 1 H), δ 7.27-6.95 (m, 40 H), δ 6.64 (s, 4 H), δ 5.21 (s, 4 H), δ 2.21 (s, 6 H), δ 0.80 (s, 6 H). HRMS_{calc} $\text{C}_{75}\text{H}_{63}\text{N}_3$ (H^+ adduct) = 1132.3782 m/z ; HRMS^{expt} $\text{C}_{75}\text{H}_{63}\text{N}_3$ (H^+ adduct) = 1132.3740 m/z .

General Polymerization Procedure

In a typical polymerization, pre-catalyst was added to a flame dried Fischer Porter bottle, charged with toluene (50 mL), and sealed in a nitrogen filled glove box. The polymerization reactor was then removed from the glove box and flushed and back-filled three times with ethylene gas. The reactor was allowed to equilibrate at the desired temperature for 10 min under constant ethylene pressure (30 psi) before MAO solution (300 equivalents) was injected *via* syringe with stirring. The reactions were terminated by

adding methanol and then stirred overnight in acidic methanol (5% HCl in CH₃OH). The resultant polymer was collected by filtration and dried *in vacuo* at 75 °C overnight.

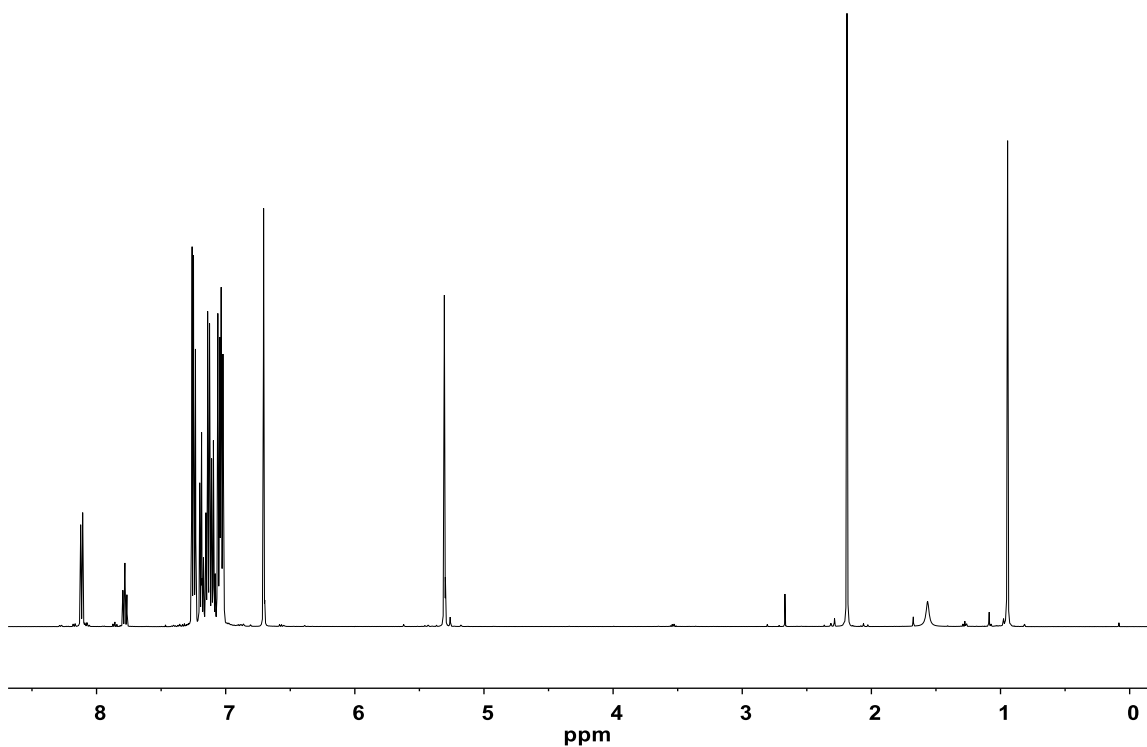


Figure B.1. ¹H NMR spectrum of ligand **17** in CDCl₃.

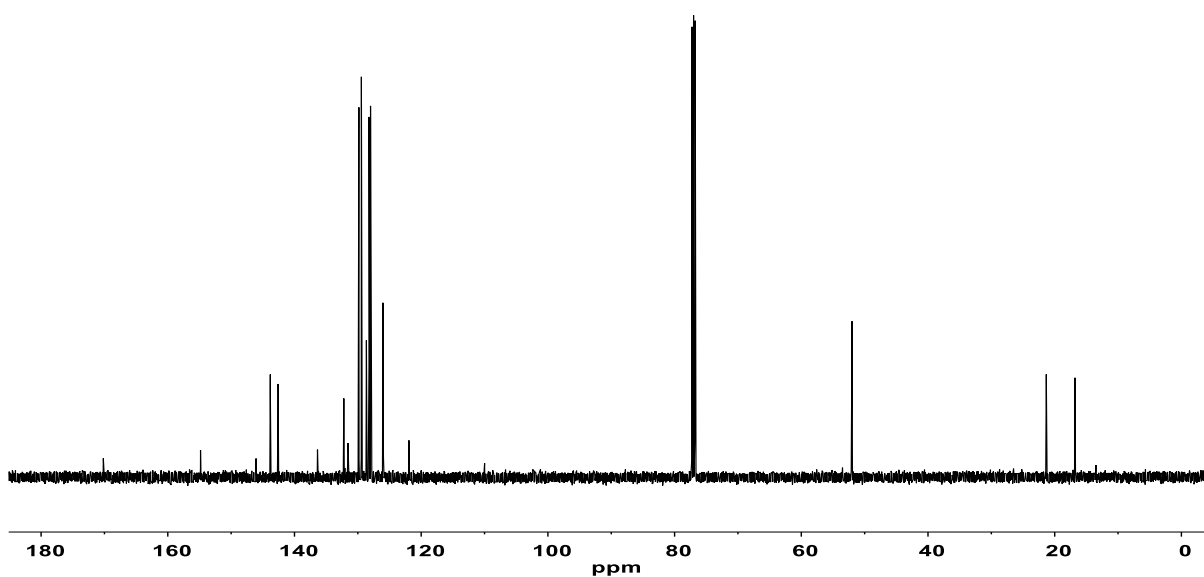


Figure B.2. ^{13}C NMR spectrum of ligand **17** in CDCl_3 .

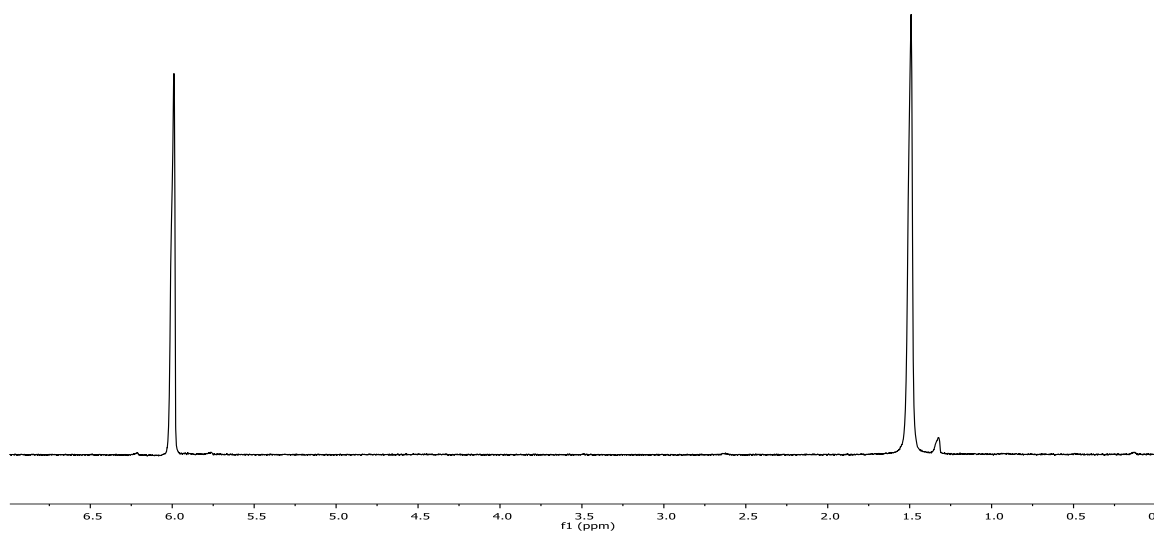


Figure B.3. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.1., entry 1).

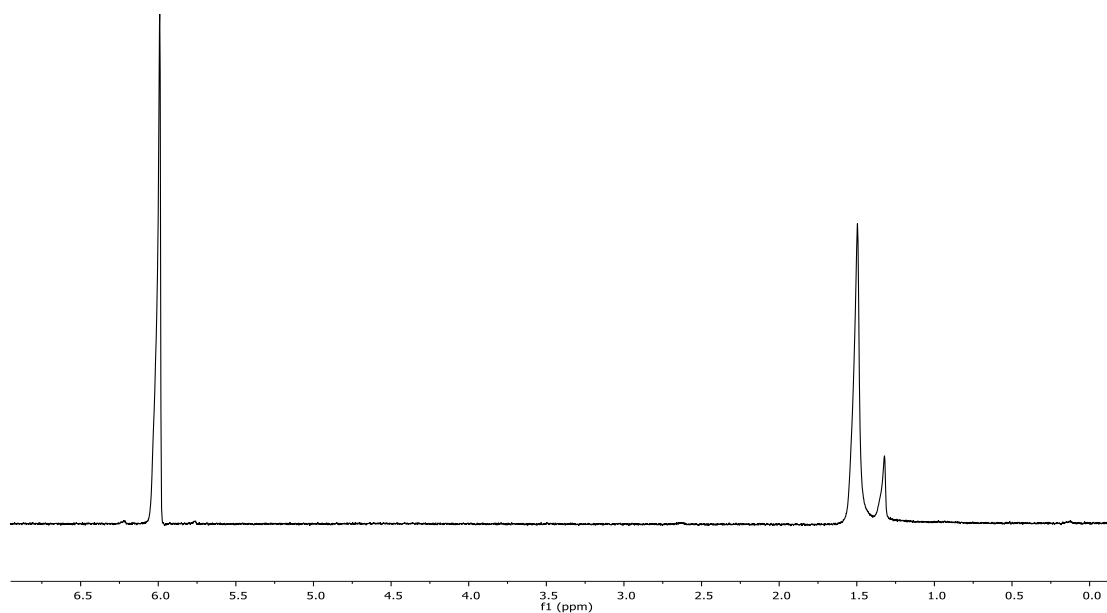


Figure B.4. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.1., entry 2).

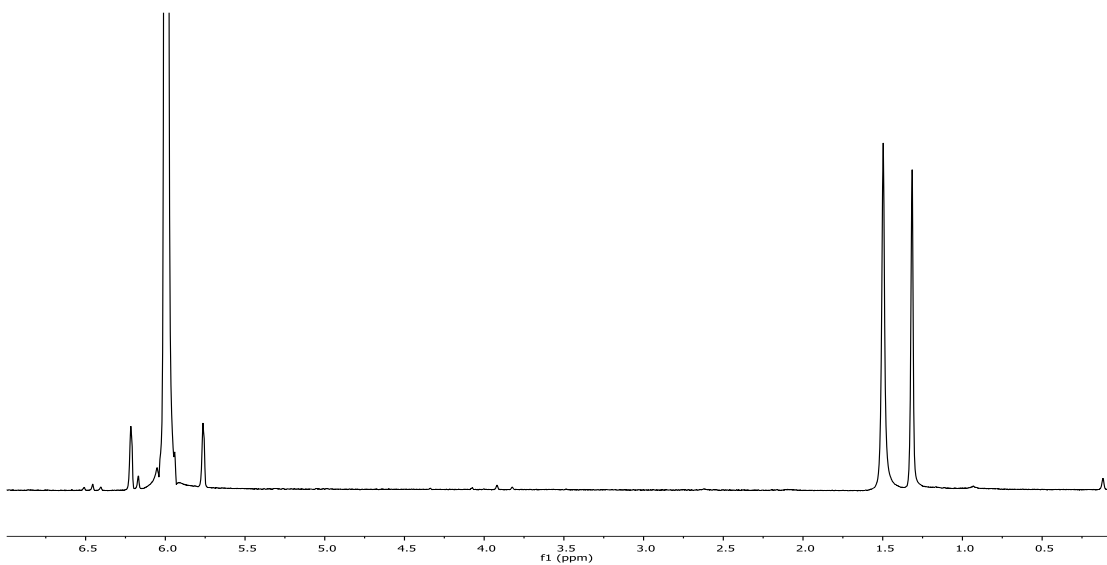


Figure B.5. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.1., entry 3).

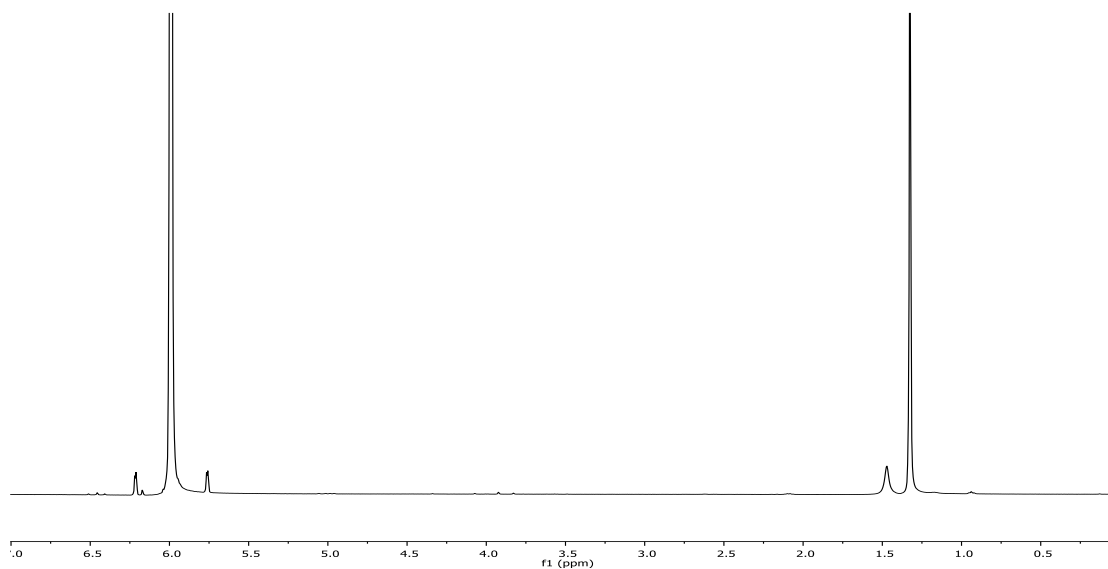


Figure B.6. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.1., entry 4).

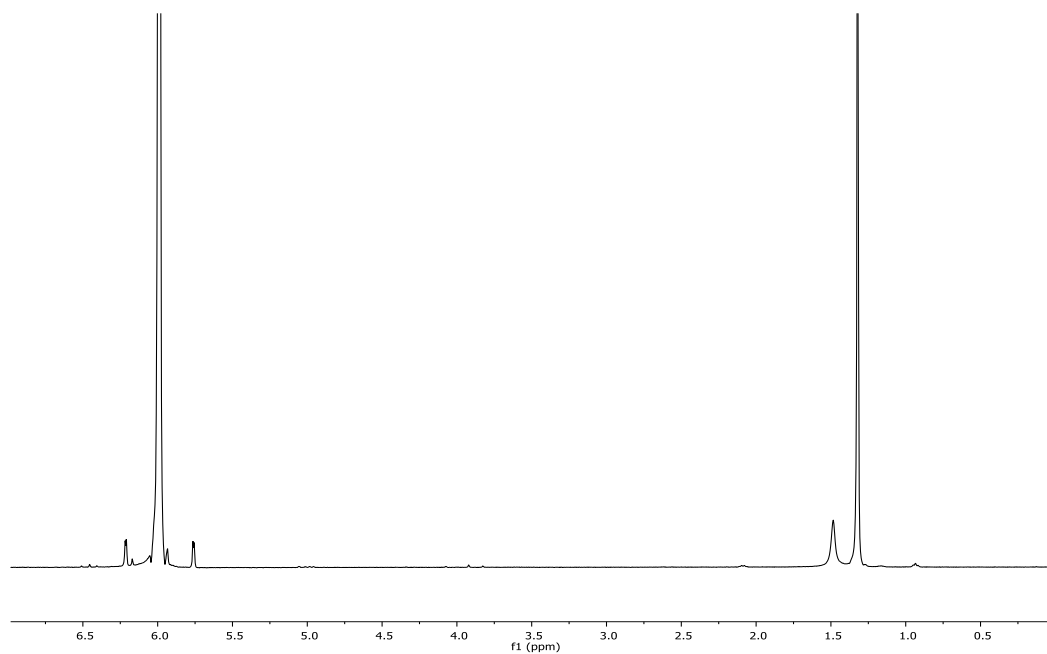


Figure B.7. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.1., entry 5).

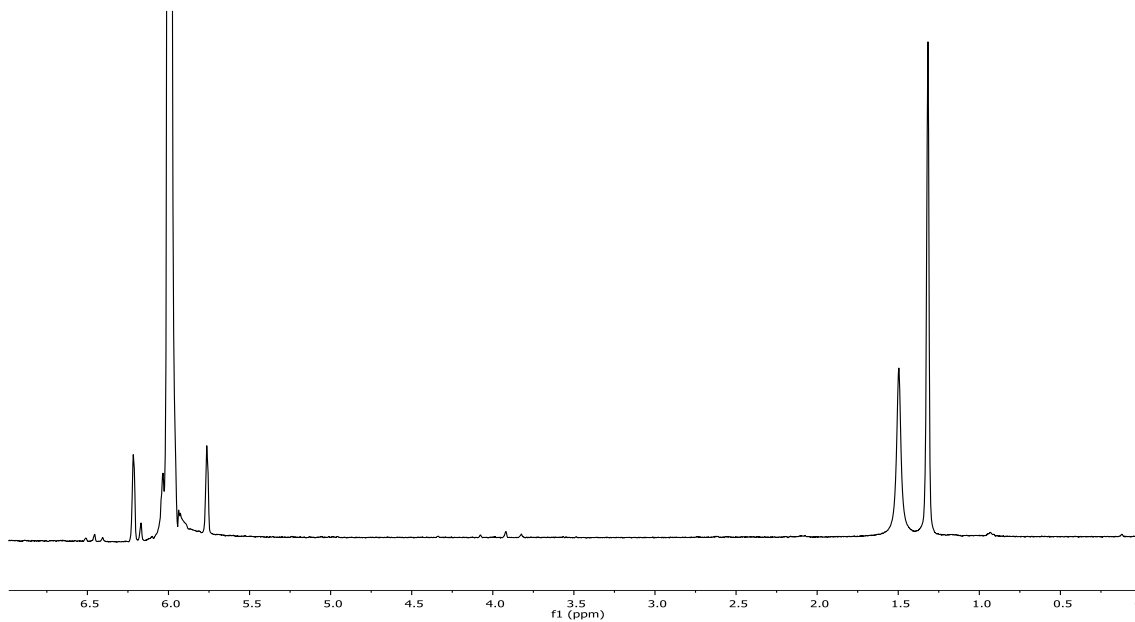


Figure B.8. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.1., entry 6).

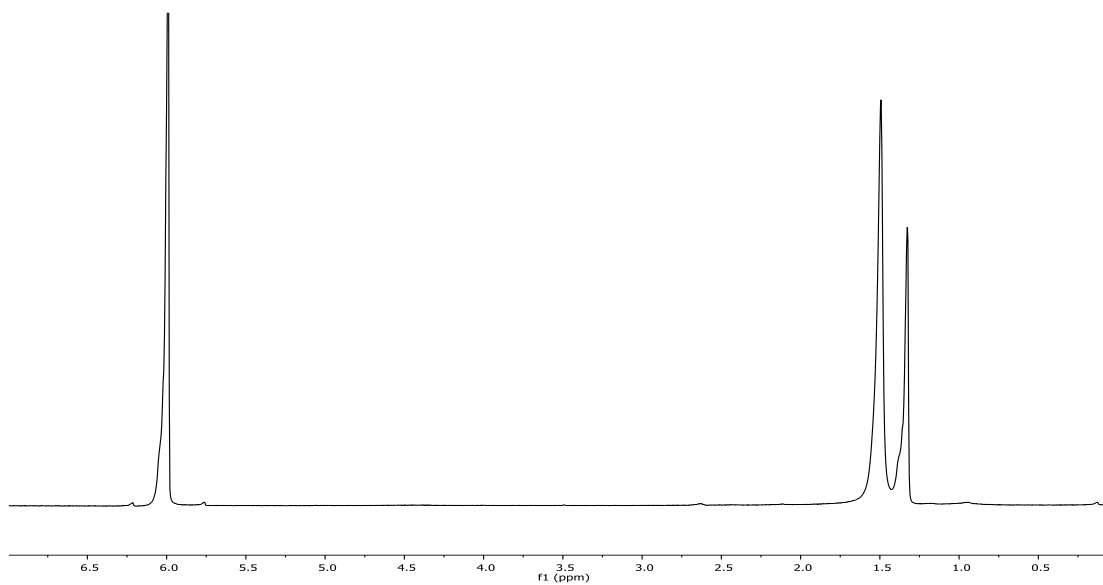


Figure B.9. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.1., entry 7).

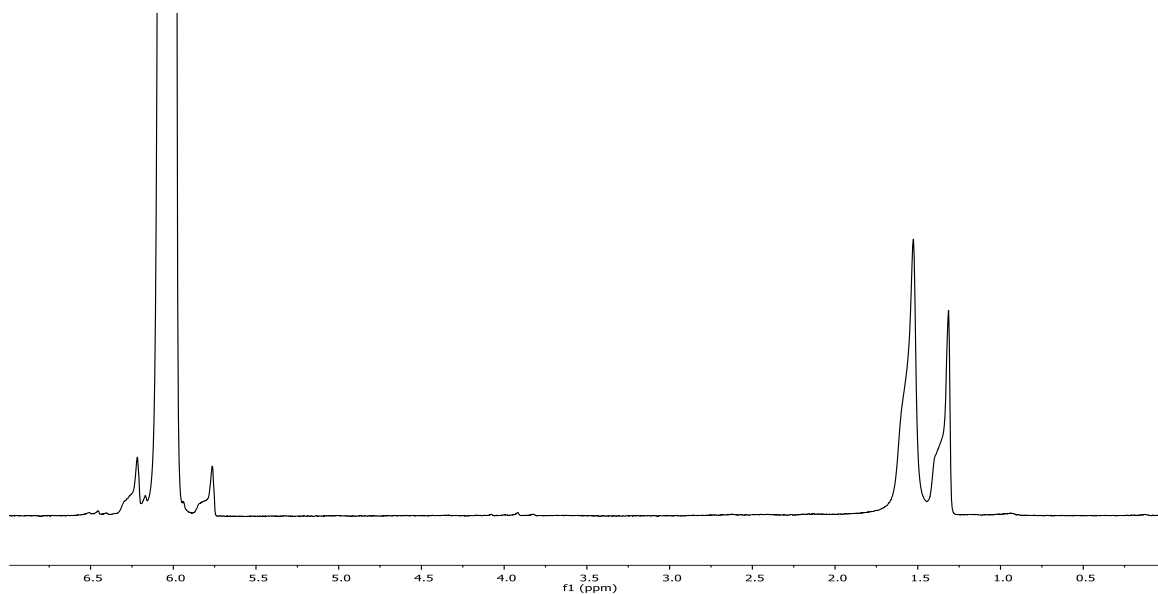


Figure B.10. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.1., entry 8).

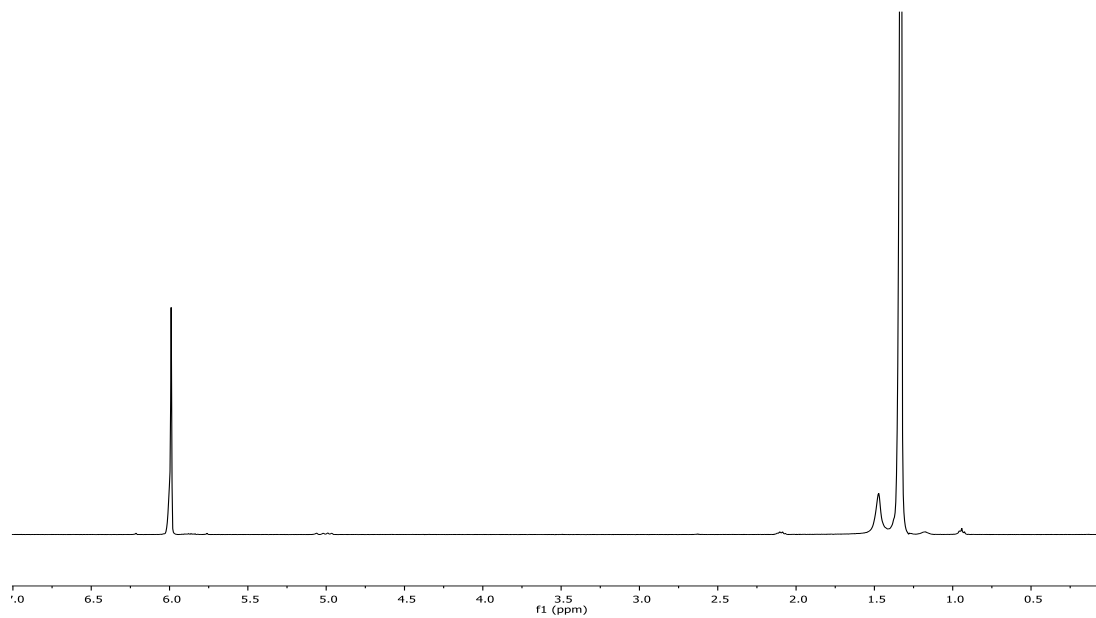


Figure B.11. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.1., entry 9).

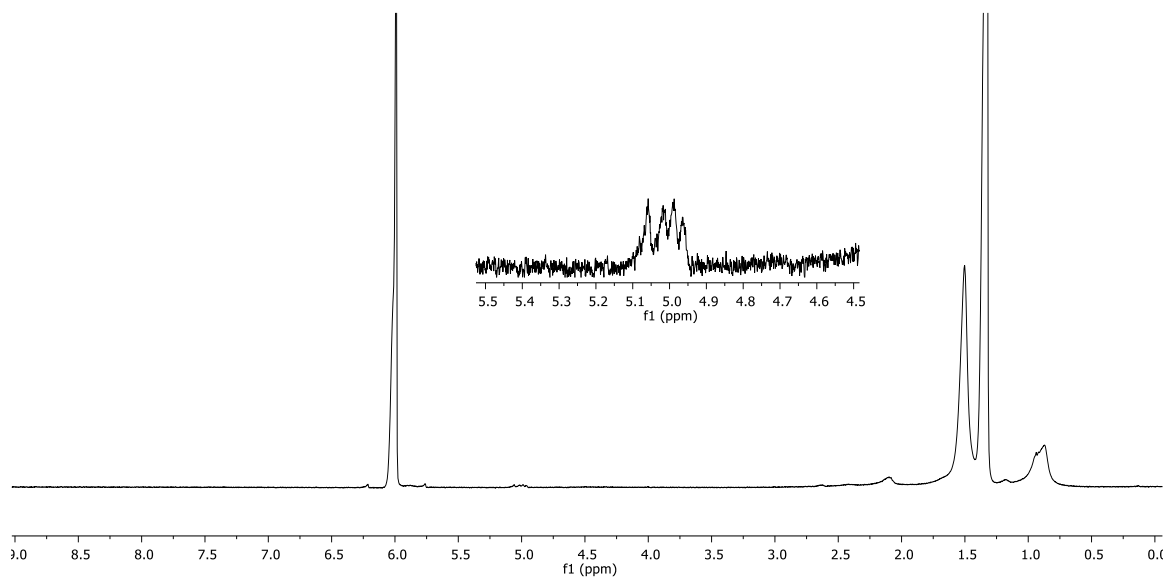


Figure B.12. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.2., entry 3). Inset shows the presence of signals corresponding to olefinic end-groups.

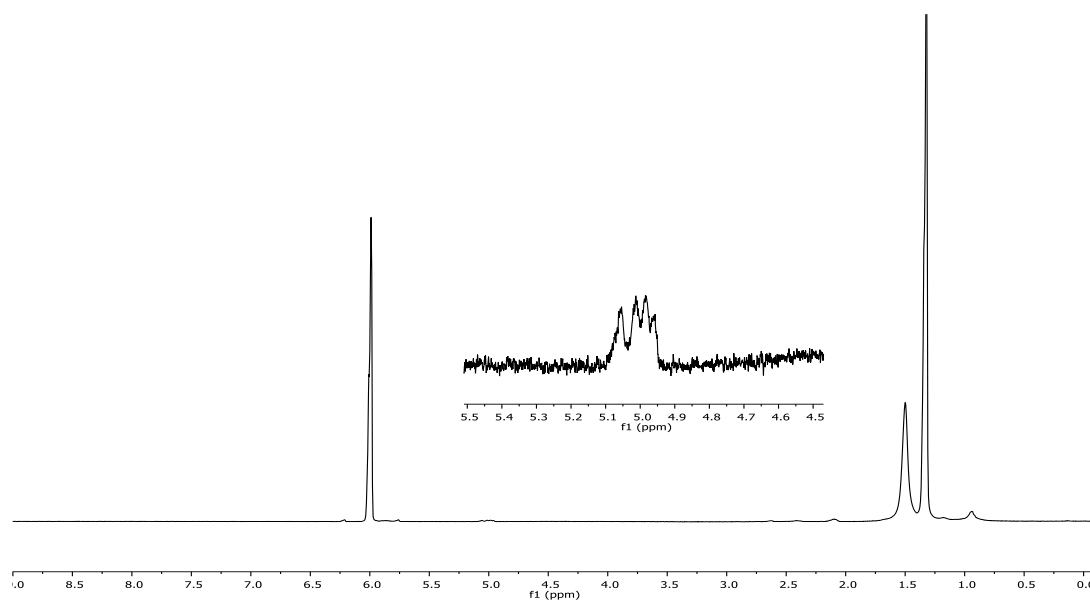


Figure B.13. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.2., entry 5). Inset shows the presence of signals corresponding to olefinic end-groups.

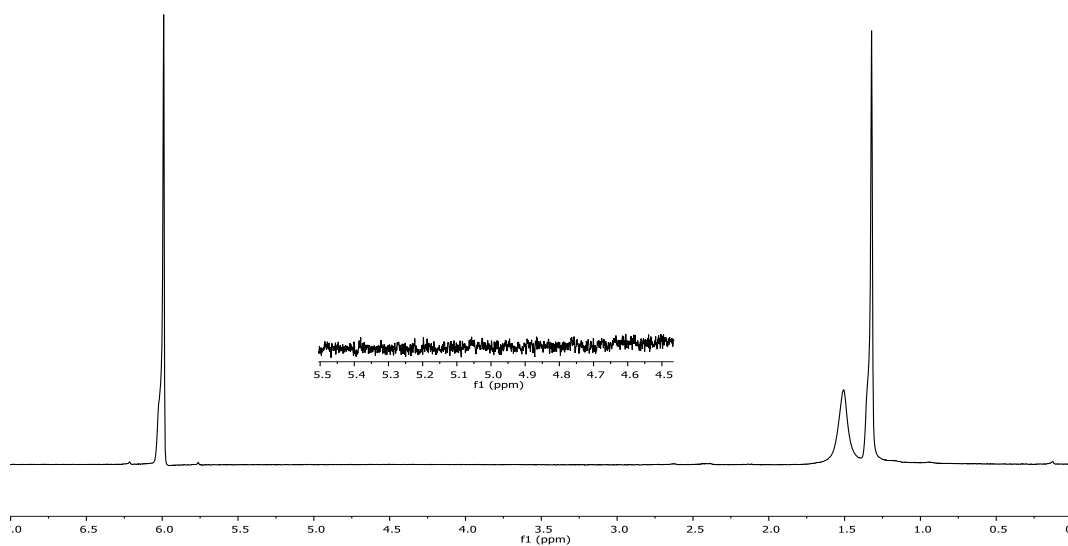


Figure B.14. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.2., entry 6). Inset shows the presence of signals corresponding to olefinic end-groups.

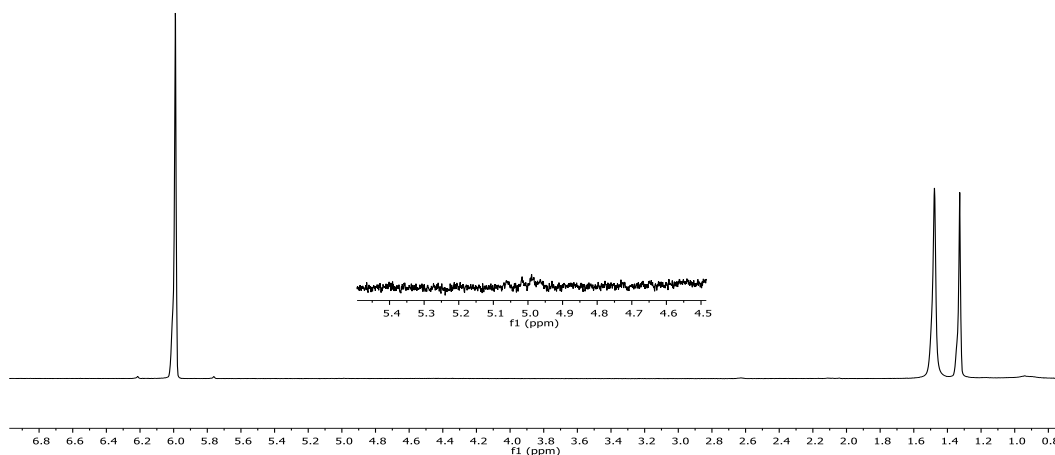


Figure B.15. ^1H NMR spectrum of polyethylene in d_2 -tetrachloroethane (Table 3.2., entry 7). Inset shows the presence of signals corresponding to olefinic end-groups.

Table B.2. High temperature ethylene polymerization results for catalyst **16**.

	T_{rxn}	t	Yield	TOF	Productivity ^b
entry	(°C)	(min)	(mg)	(h ⁻¹) ^a	(kg/mol)
1	80	10	86.5	3700	17.3
2	80	10	84.6	3620	16.9
3	80	10	86.9	3720	17.4
4	80	30	268.5	3829	53.70
5	80	30	233.0	3323	46.60
6	80	30	270.6	3859	54.12
7	80	50	455.2	3895	91.04
8	80	50	464.0	3970	92.80
9	80	50	430.5	3683	86.10
10	80	70	748.9	4577	149.8
11	80	70	641.0	3917	128.2
12	80	70	561.3	3430	112.2
13	90	10	85.0	3636	17.0
14	90	10	91.1	3897	18.2
15	90	10	82.7	3538	16.5
16	90	30	311.9	4448	62.38
17	90	30	250.6	3573	50.12
18	90	30	322.2	4595	64.44

Table B.2. Continued.

	T_{rxn}	t	Yield	TOF	Productivity ^b
entry	(°C)	(min)	(mg)	(h ⁻¹) ^a	(kg/mol)
20	90	50	481.4	4119	96.28
21	90	50	404.1	3457	80.82
22	90	70	580.0	3545	116.0
23	90	70	548.0	3349	109.6
24	90	70	545.5	3334	109.1
25	100	10	98.1	4190	19.6
26	100	10	84.3	3606	16.9
27	100	10	109.5	4684	21.90
28	100	30	282.3	4026	56.46
29	100	30	309.9	4419	61.98
30	100	30	274.0	3907	54.80
31	100	50	310.0	2652	62.00
32	100	50	405.8	3472	81.16
33	100	50	348.7	2983	69.74
34	100	70	456.4	2789	91.28
35	100	70	396.2	2421	79.24
36	100	70	341.9	2089	68.38

Table B.2. Continued.

Polymerization conditions: [**16**] = 5.0 μ mol, 50 mL toluene, 30 psi, 300 eq. MAO. ^a TOF = mol ethylene/(mol cat.*h). ^bProductivity = yield polyethylene/mol cat.

Table B.3. High temperature ethylene polymerization results for catalyst **4b**.

entry	T_{rxn} (°C)	t (min)	Yield (mg)	TOF ($\times 10^{-3}$ h ⁻¹)	Productivity (kg/mol)
1	80	10	1208.5	51.700	241.70
2	80	10	1449.4	62.006	289.88
3	80	10	1182.7	50.596	236.54
4	80	30	1956.8	27.904	391.36
5	80	30	2183.1	31.131	436.62
6	80	30	2458.8	35.063	491.76
7	80	50	2143.1	18.336	428.62
8	80	50	2083.0	17.822	416.6
9	80	50	2458.7	21.037	491.74
10	80	70	2398.4	14.657	479.68
11	80	70	2340.0	14.300	468.00
12	80	70	2252.1	13.763	450.42
13	90	10	850.7	36.39	170.1
14	90	10	934.9	40.00	187.0

Table B.3. Continued.

	T_{rxn}	t	Yield	TOF	Productivity
entry	(°C)	(min)	(mg)	($\times 10^{-3} \text{ h}^{-1}$)	(kg/mol)
15	90	10	929.3	39.76	185.9
16	90	30	1188.2	16.944	237.64
17	90	30	1367.1	19.495	273.42
18	90	30	1408.8	20.089	281.76
19	90	50	1768.3	15.129	353.66
20	90	50	1365.9	11.686	273.18
21	90	50	1815.4	15.532	363.08
22	90	70	1884.7	11.518	376.94
23	90	70	1659.0	10.139	331.80
24	90	70	1693.2	10.348	338.64
25	100	10	783.0	33.49	156.6
26	100	10	620.7	26.55	124.1
27	100	10	267.6	11.45	53.52
28	100	30	1167.7	16.651	233.54
29	100	30	935.4	13.34	187.0
30	100	30	759.8	10.83	151.9
31	100	50	1607.8	13.756	321.56
32	100	50	722.7	6.183	144.5

Table B.3. Continued.

	T_{rxn}	t	Yield	TOF	Productivity
entry	(°C)	(min)	(mg)	($\times 10^{-3} \text{ h}^{-1}$)	(kg/mol)
33	100	50	1154.2	9.8755	230.84
34	100	70	968.7	5.920	193.7
35	100	70	793.9	4.851	158.8
36	100	70	1833	11.20	366.6

Polymerization conditions: [**4b**] = 5.0 μmol , 50 mL toluene, 30 psi, 300 eq. MAO. ^a TOF = mol ethylene/(mol cat.*h). ^bProductivity = yield polyethylene (g)/mol cat.

Table B.4. High temperature ethylene polymerization results for selected polymers from Table B.2. and Table B.3.

table	catalyst	entry	Mw ^a (kg/mol)	$\bar{D}^a$
S2	4b	1	5.7	4.5
		4	6.6	2.7
		7	8	2.2
		11	11	1.3
		13	3.9	2.0
		16	4.4	1.5
		20	34	4.7
		23	10	1.9
		25	2.1	3.1
		28	3	1.3
		32	3	1.8
		34	2.1	1.6
S3	16	1	8.6	1.3
		5	5.9	1.6
		7	4.3	3.8
		14	4.9	1.6
		17	5.3	1.6
		19	3.6	3.0
		23	8	1.0
		26	4	1.3
		30	4	2.3
		33	4.3	2.0
		36	2.9	7.0

^aDetermined using gel permeation chromatography at 145 °C in 1,2,4-trichlorobenzene

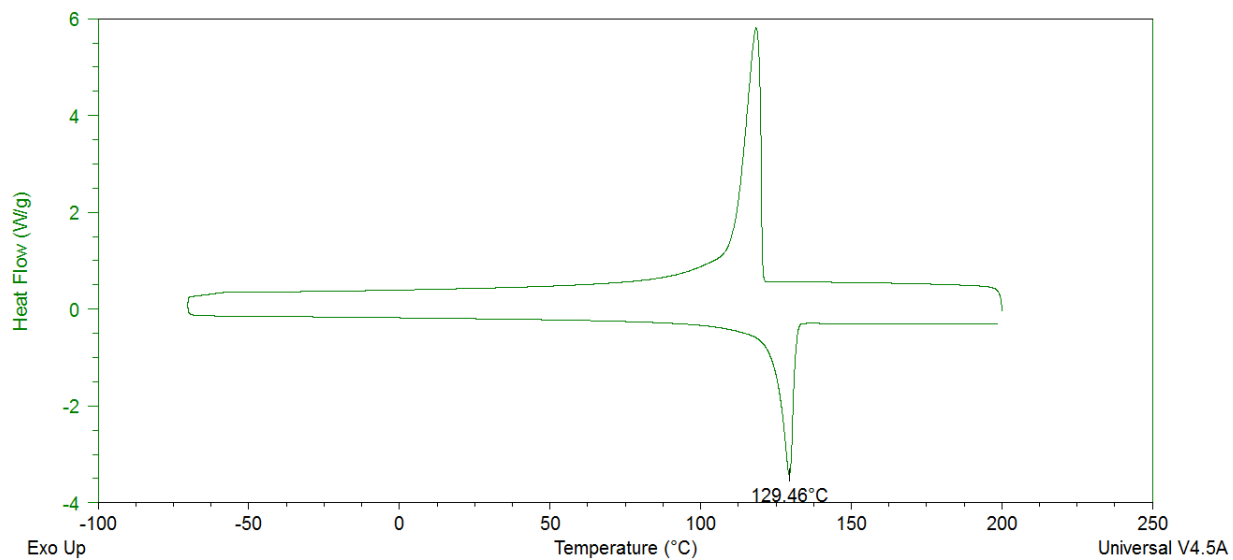


Figure B.16. Representative DSC trace of polyethylene (Table 3.1., entry 9). Second heating cycle.

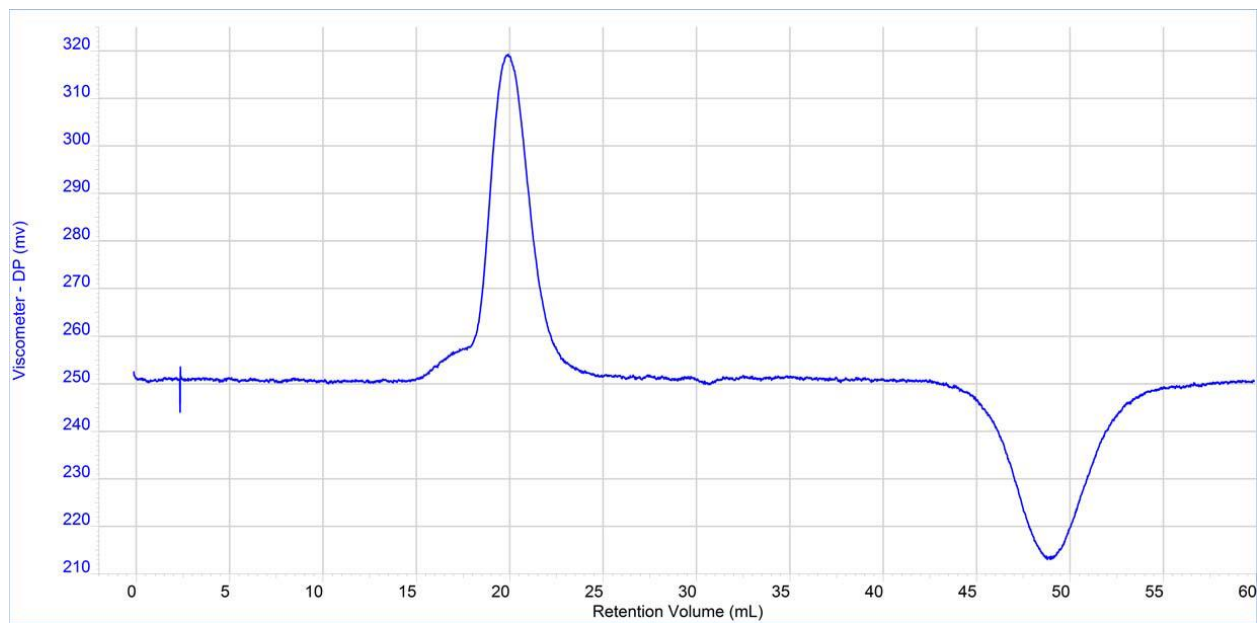


Figure B.17. GPC analysis of polyethylene (Table 3.1., entry 1).

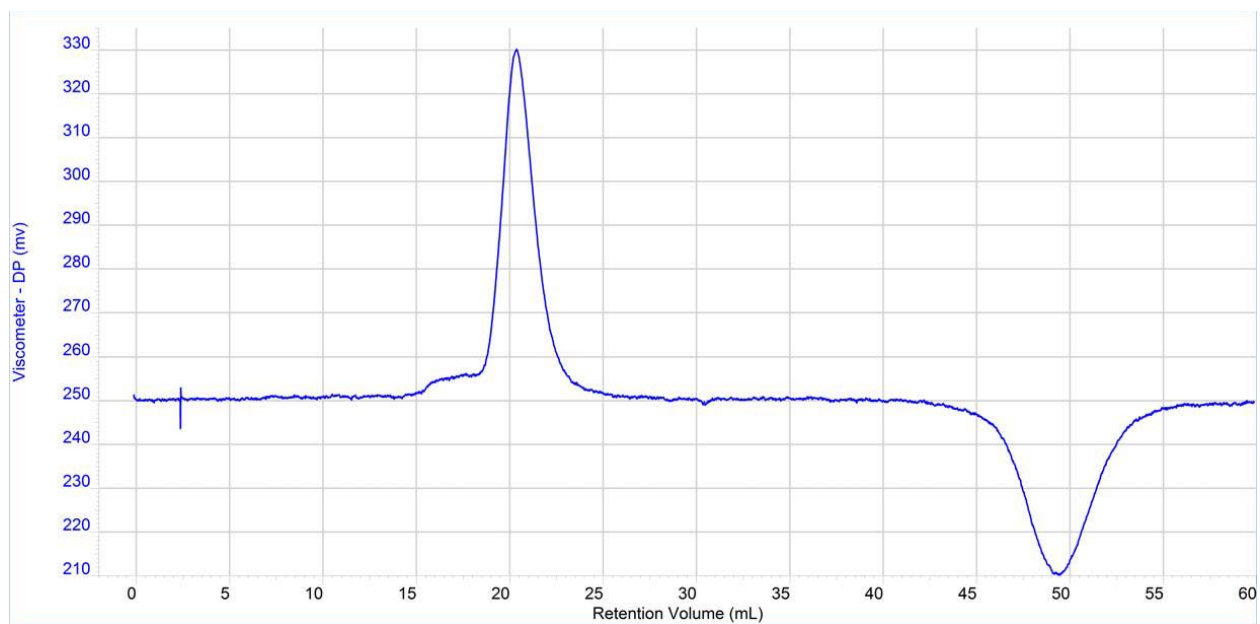


Figure B.18. GPC analysis of polyethylene (Table 3.1., entry 2).

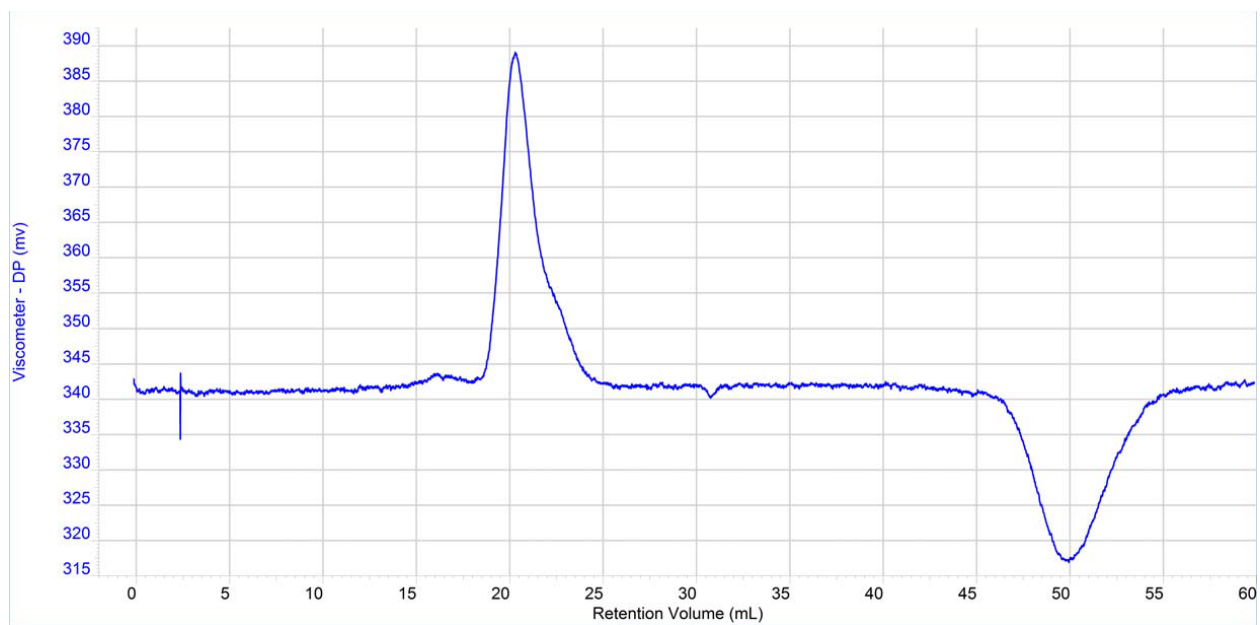


Figure B.19. GPC analysis of polyethylene (Table 3.1., entry 3).

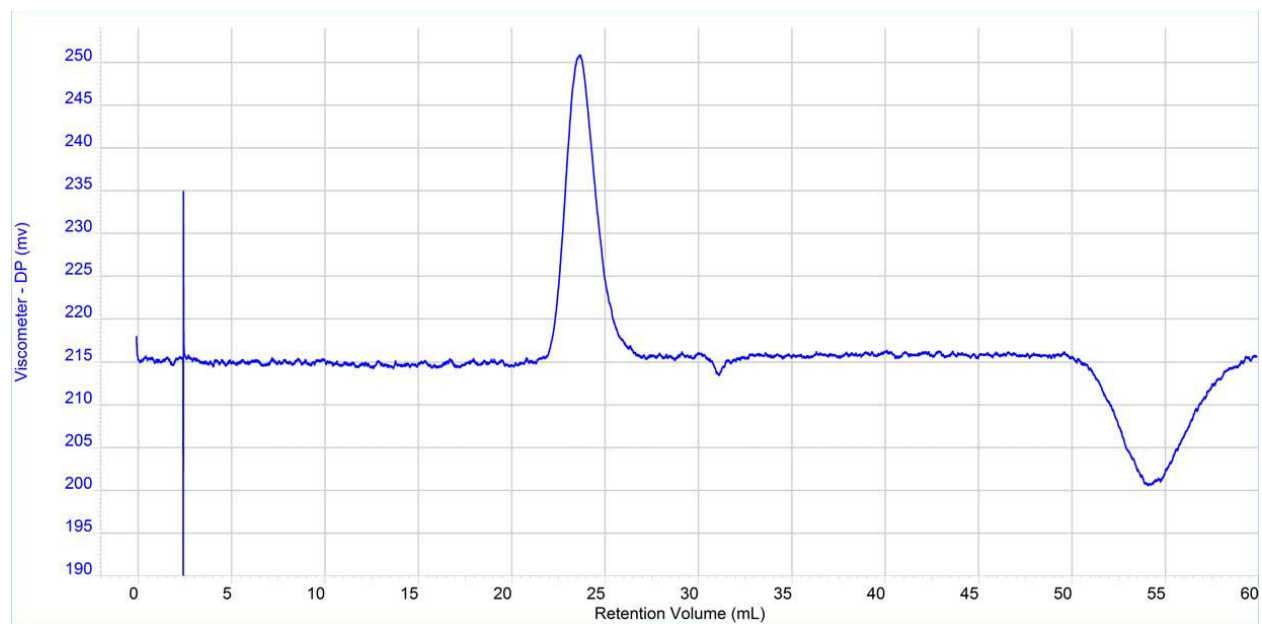


Figure B.20. GPC analysis of polyethylene (Table 3.1., entry 4).

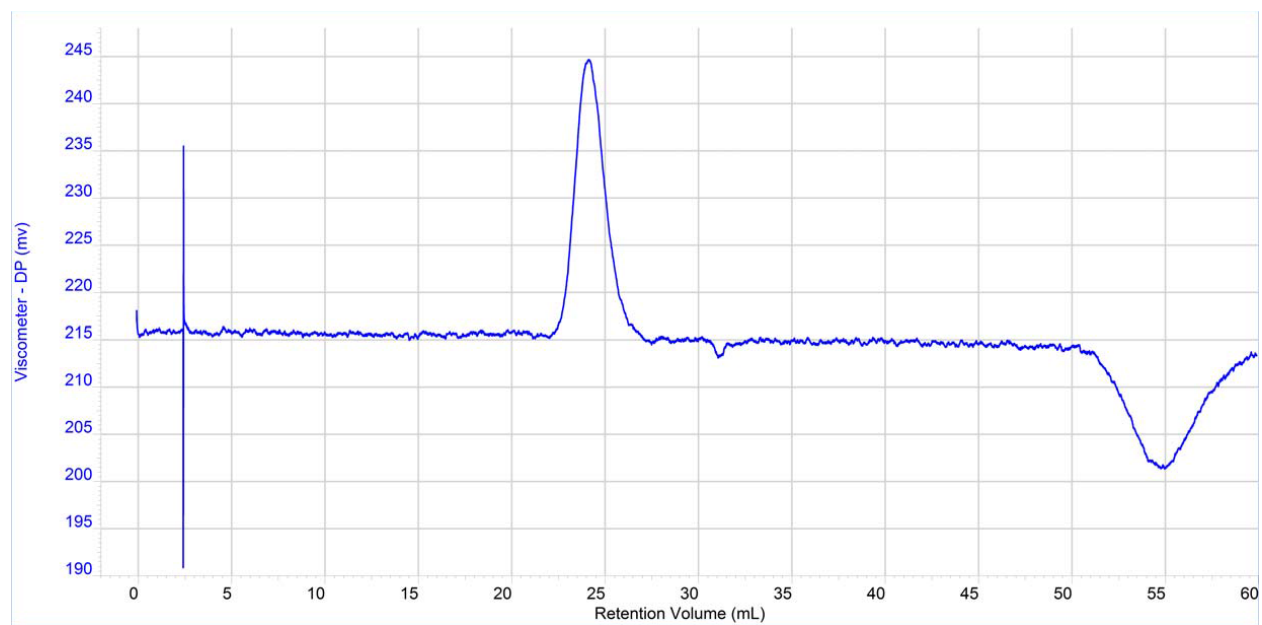


Figure B.21. GPC analysis of polyethylene (Table 3.1., entry 5).

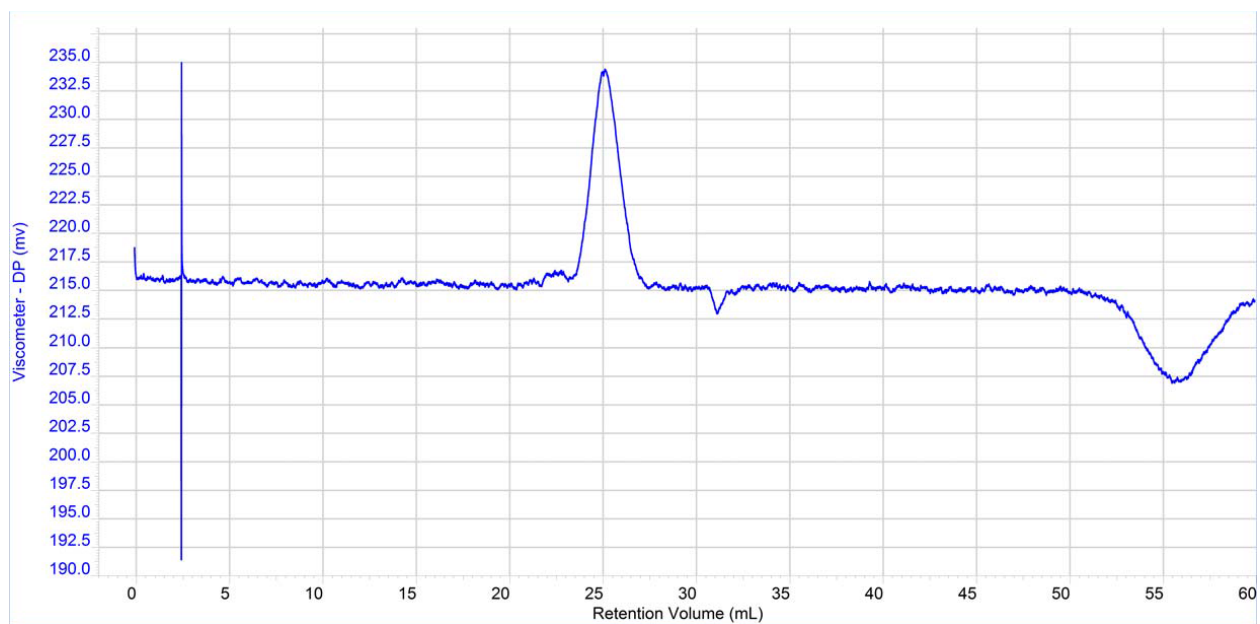


Figure B.22. GPC analysis of polyethylene (Table 3.1., entry 6).

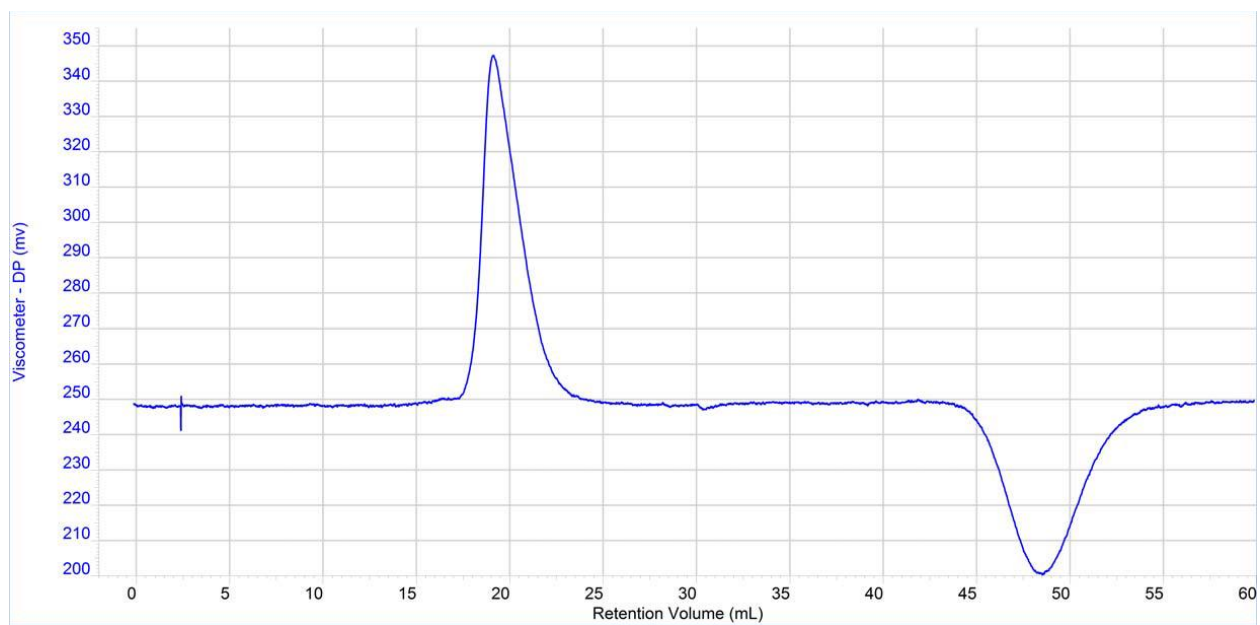


Figure B.23. GPC analysis of polyethylene (Table 3.1., entry 7).

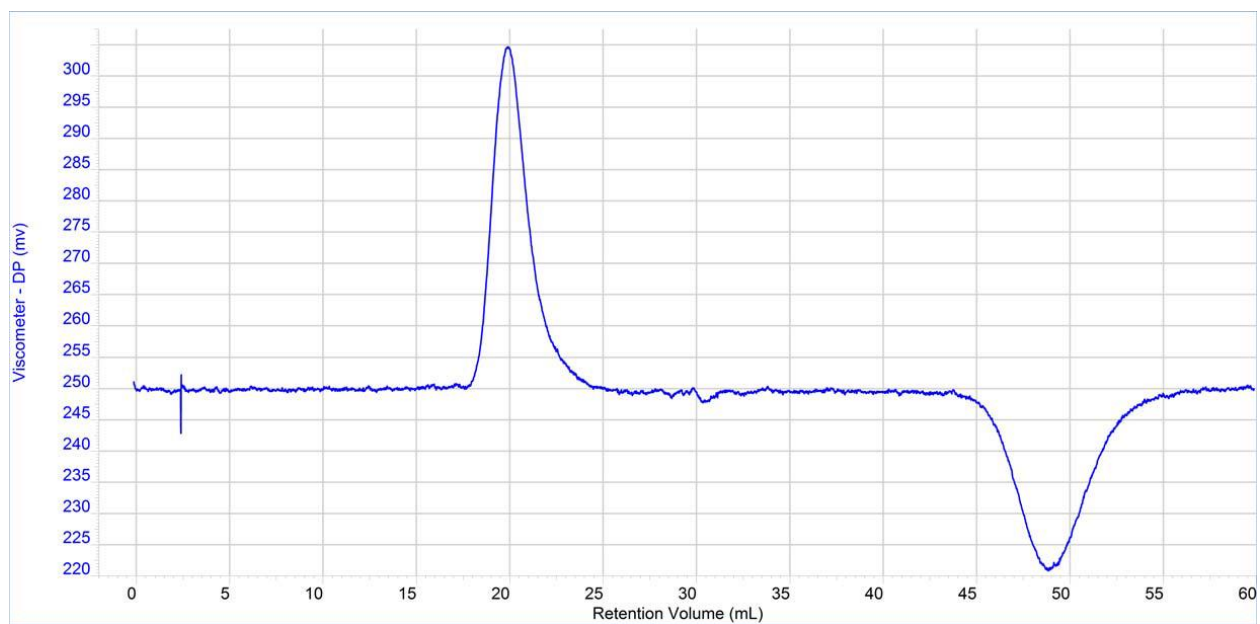


Figure B.24. GPC analysis of polyethylene (Table 3.1., entry 8).

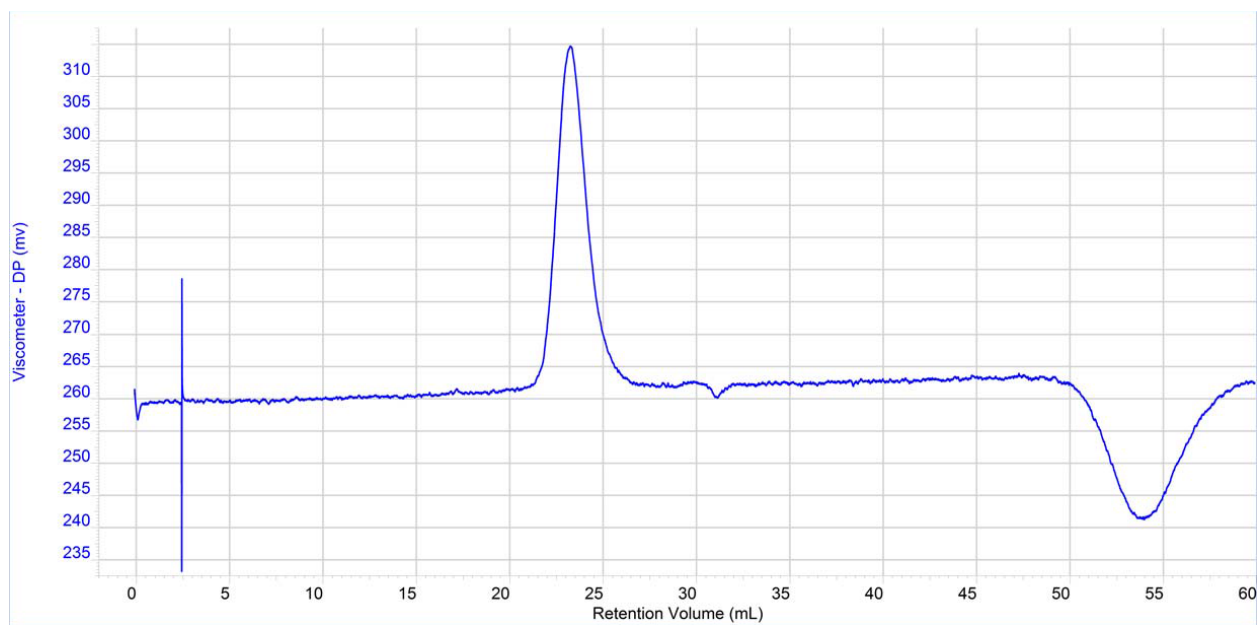


Figure B.25. GPC analysis of polyethylene (Table 3.1., entry 9).

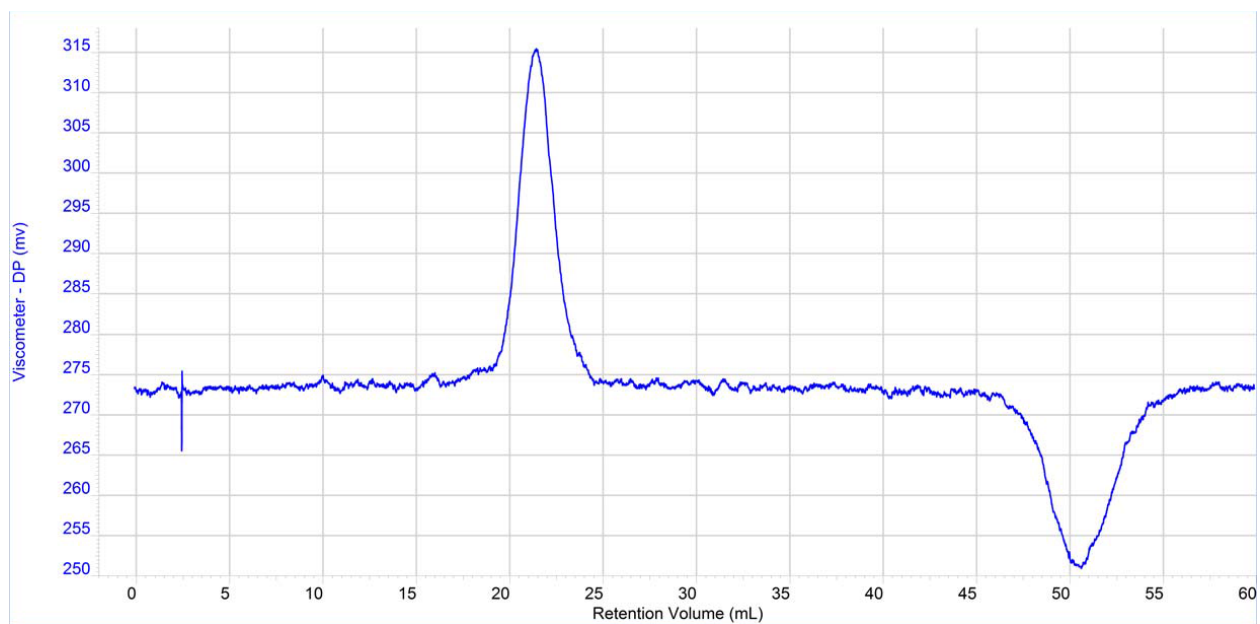


Figure B.26. GPC analysis of polyethylene (Table 3.2., entry 1)

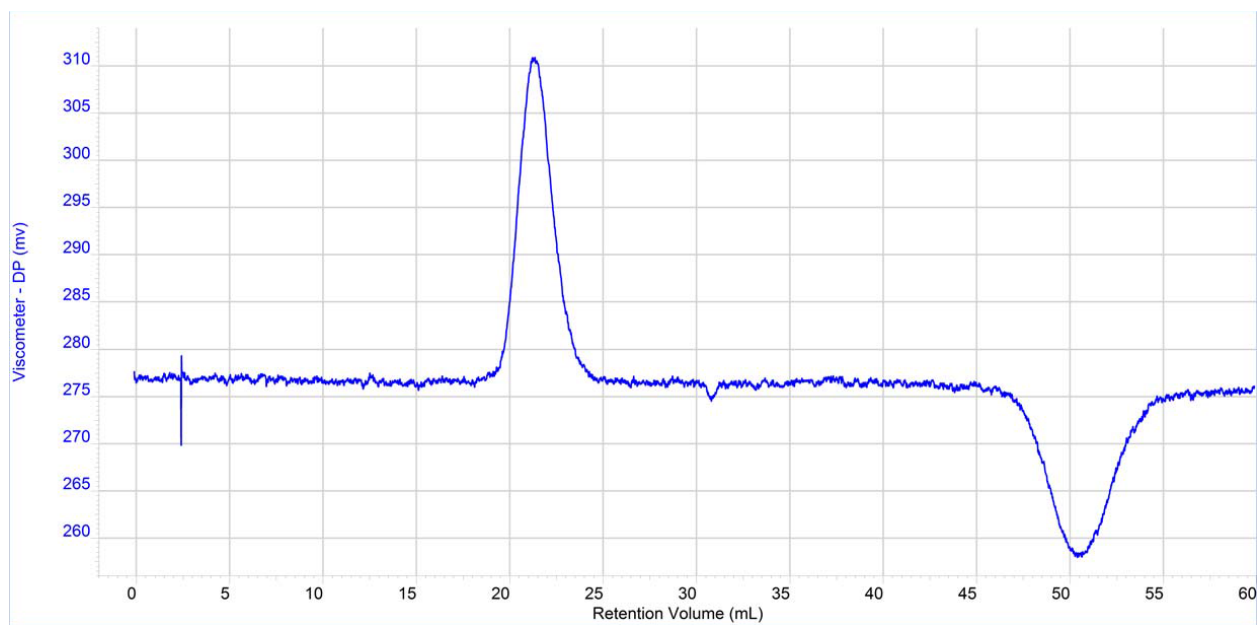


Figure B.27. GPC analysis of polyethylene (Table 3.2., entry 2)

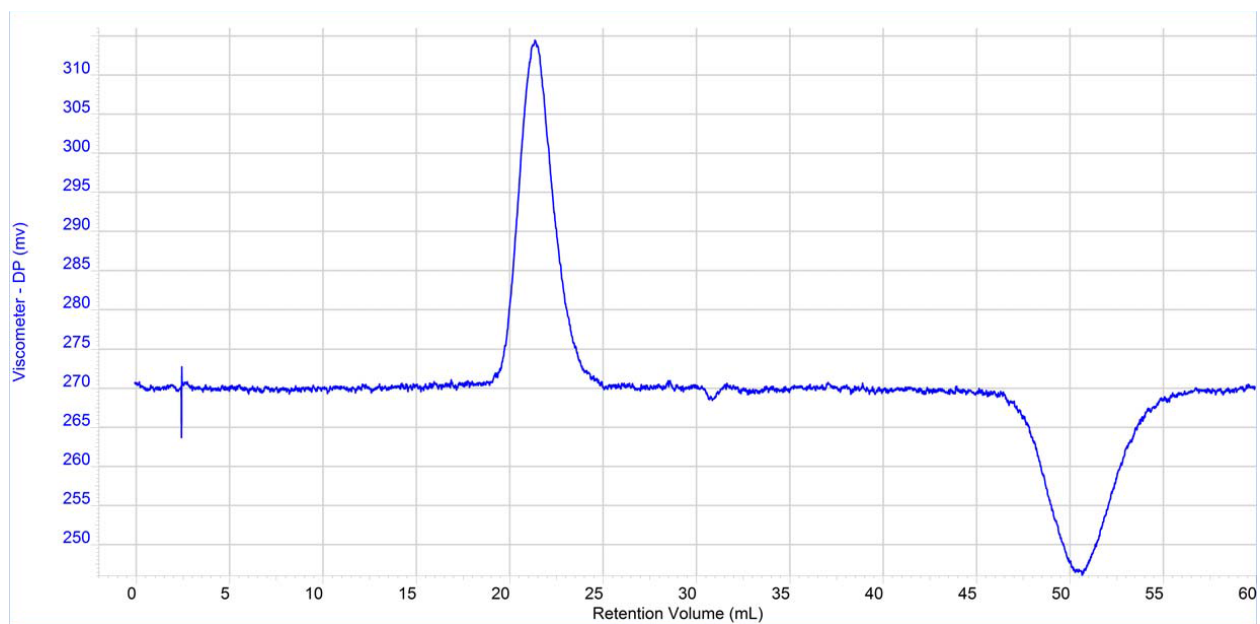


Figure B.28. GPC analysis of polyethylene (Table 3.2., entry 3)

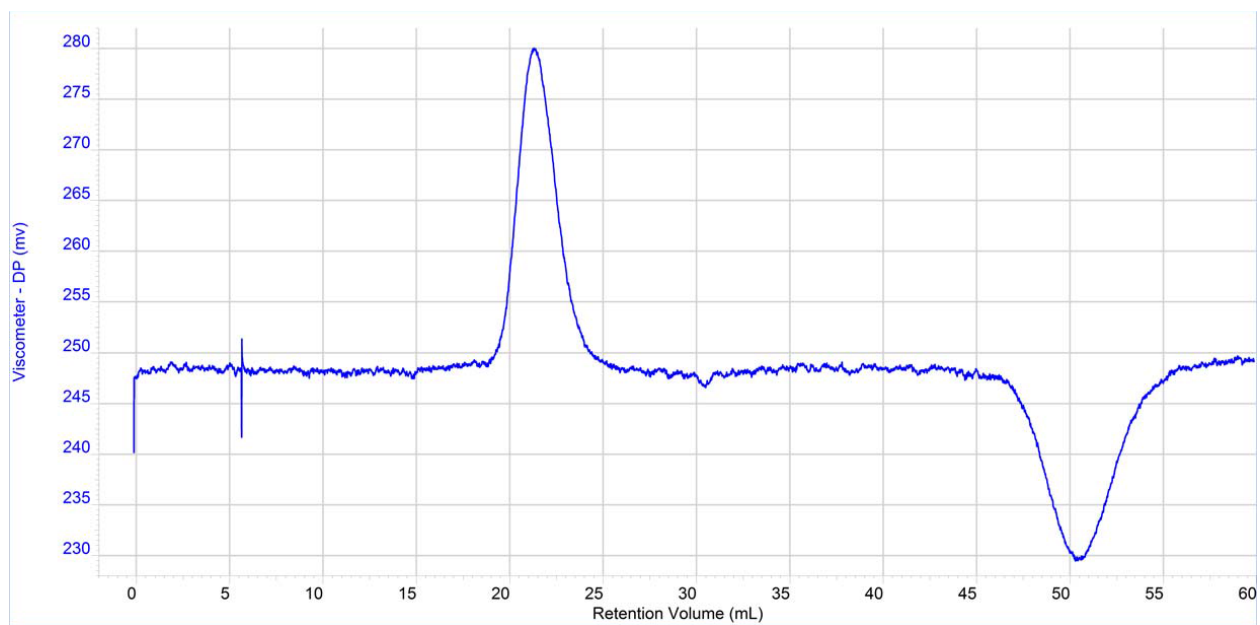


Figure B.29. GPC analysis of polyethylene (Table 3.2., entry 4)

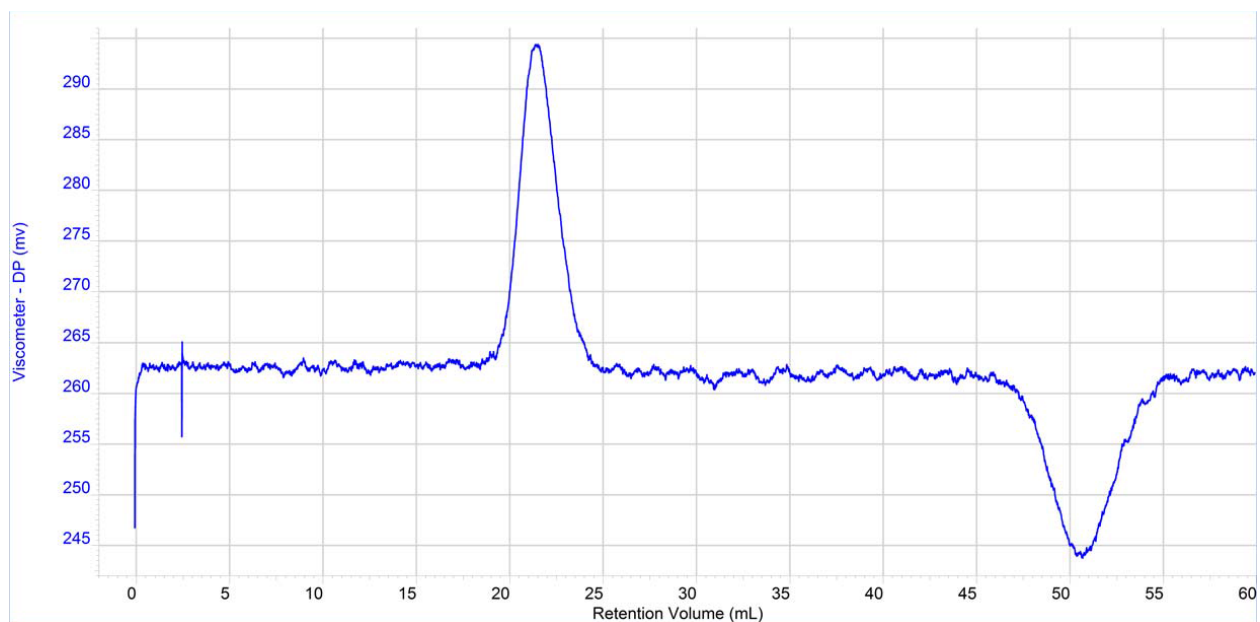


Figure B.30. GPC analysis of polyethylene (Table 3.2., entry 5)

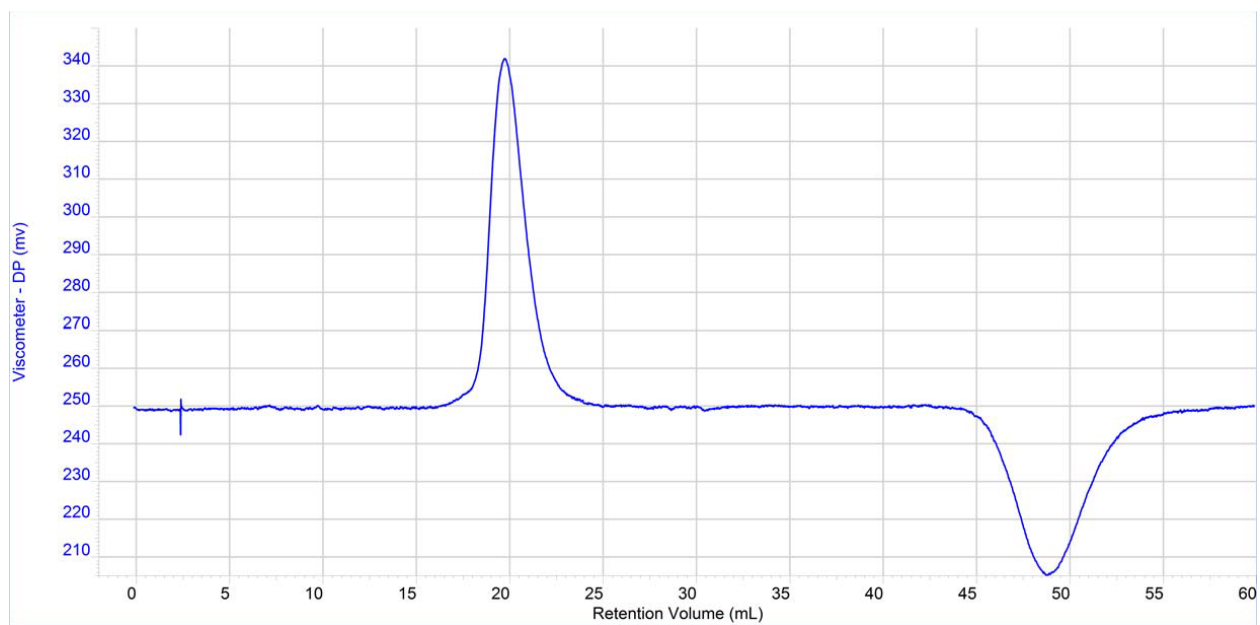


Figure B.31. GPC analysis of polyethylene (Table 3.2., entry 6).

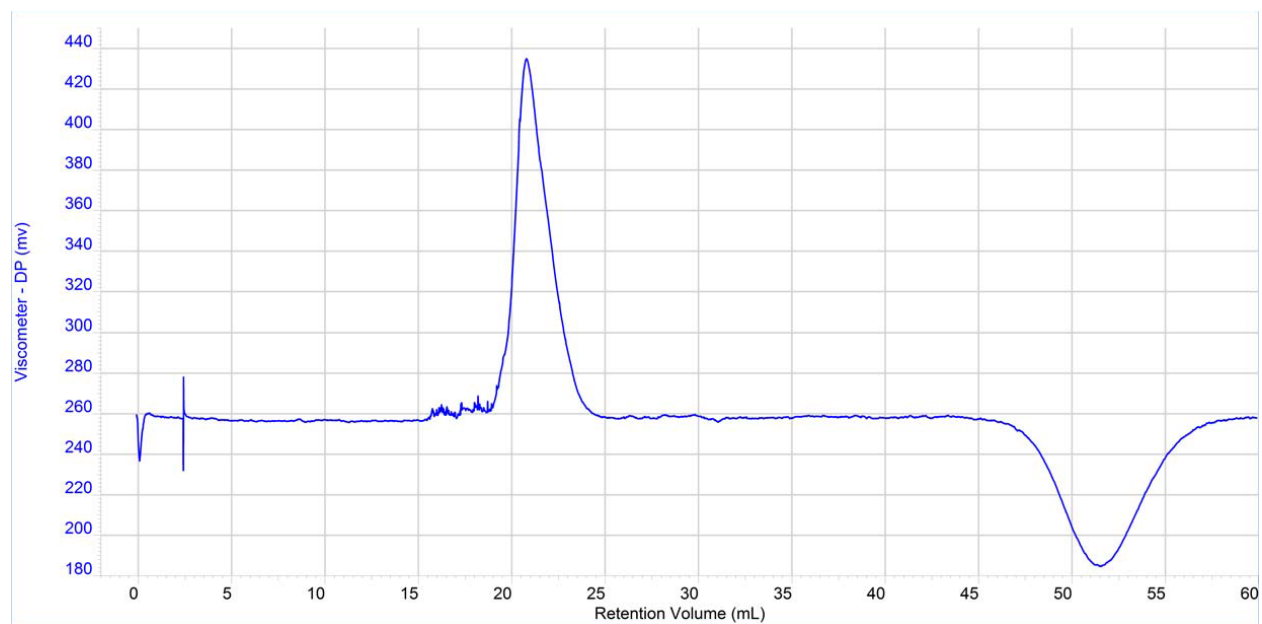


Figure B.32. GPC analysis of polyethylene (Table 3.2., entry 7).

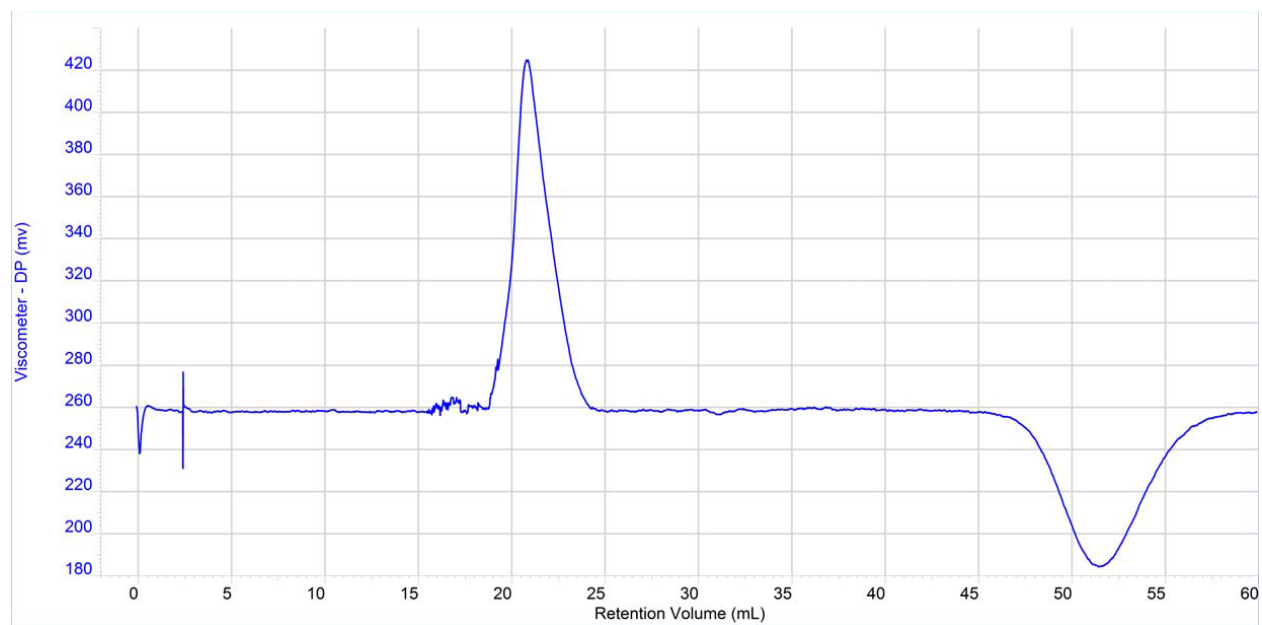


Figure B.33. GPC analysis of polyethylene (Table 3.2., entry 8).

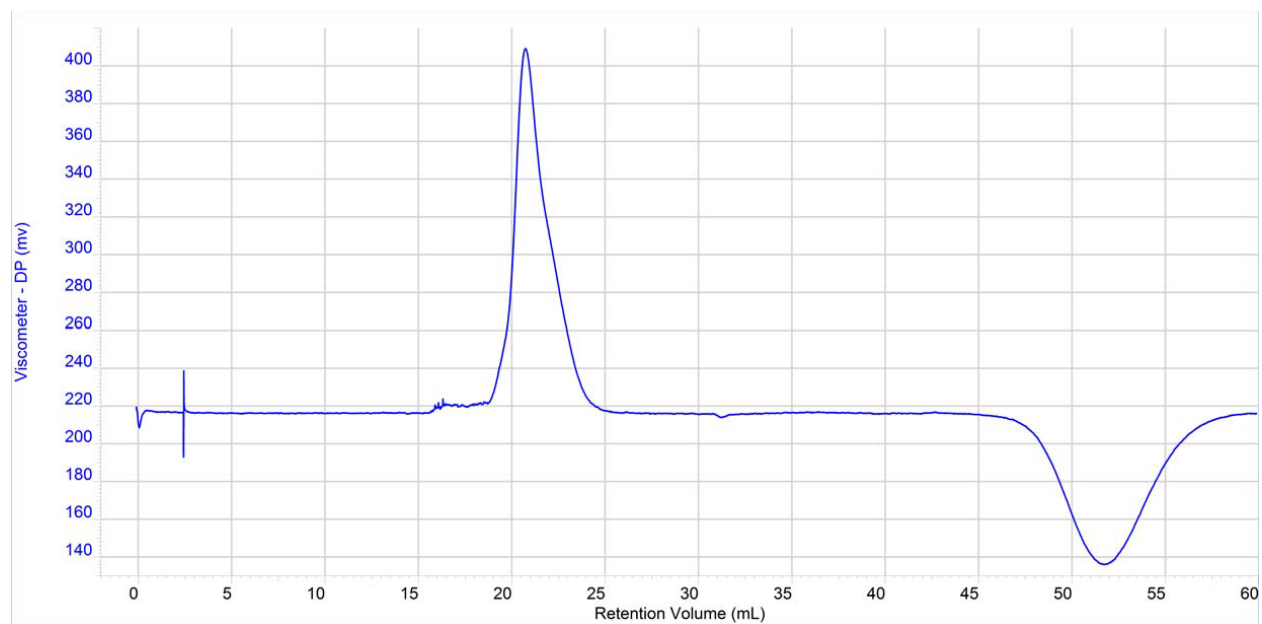


Figure B.34. GPC analysis of polyethylene (Table 3.2., entry 9).

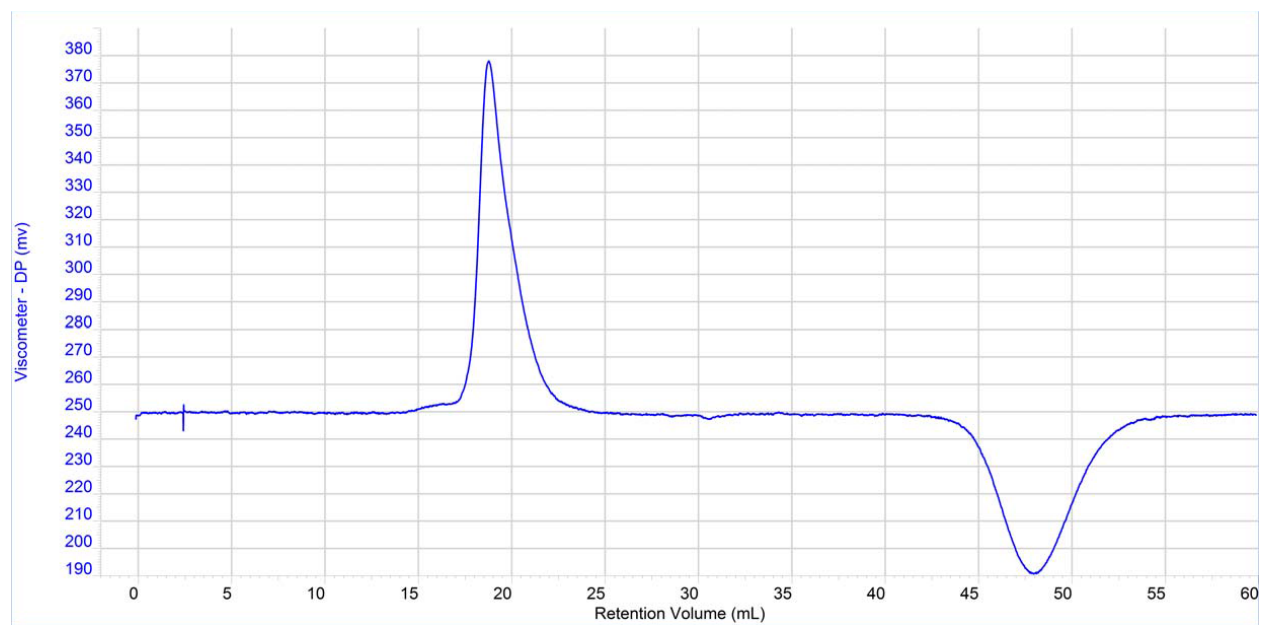


Figure B.35. GPC analysis of polyethylene (Table 3.2., entry 10).

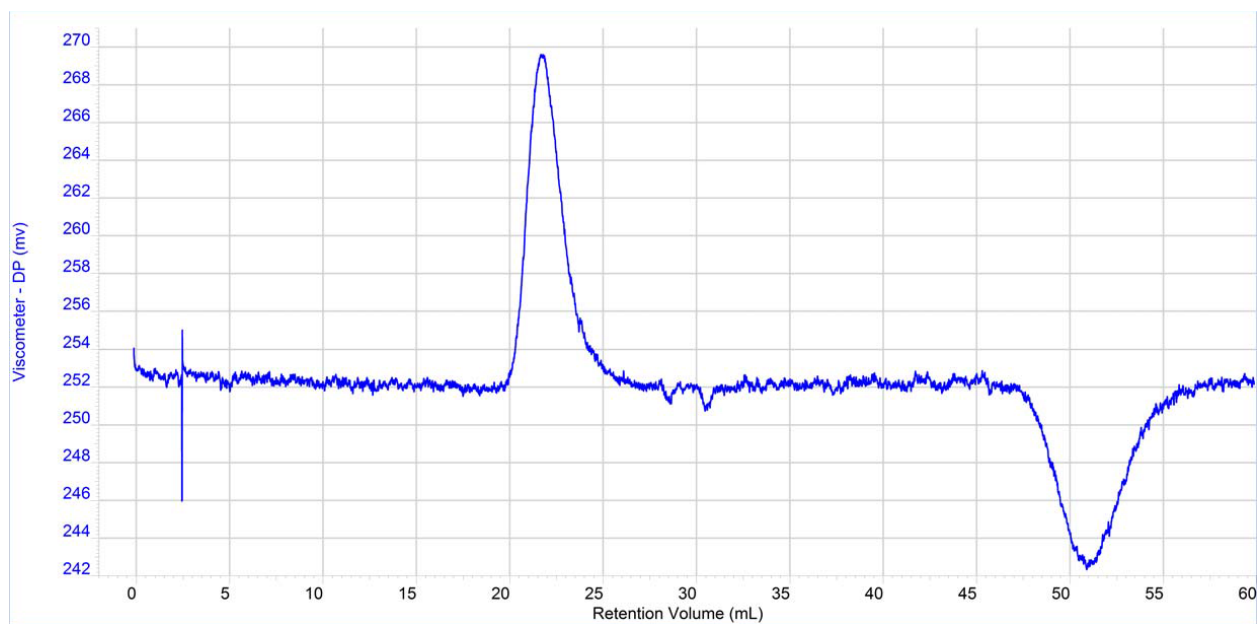


Figure B.36. GPC analysis of polyethylene (Table B.1., entry 1).

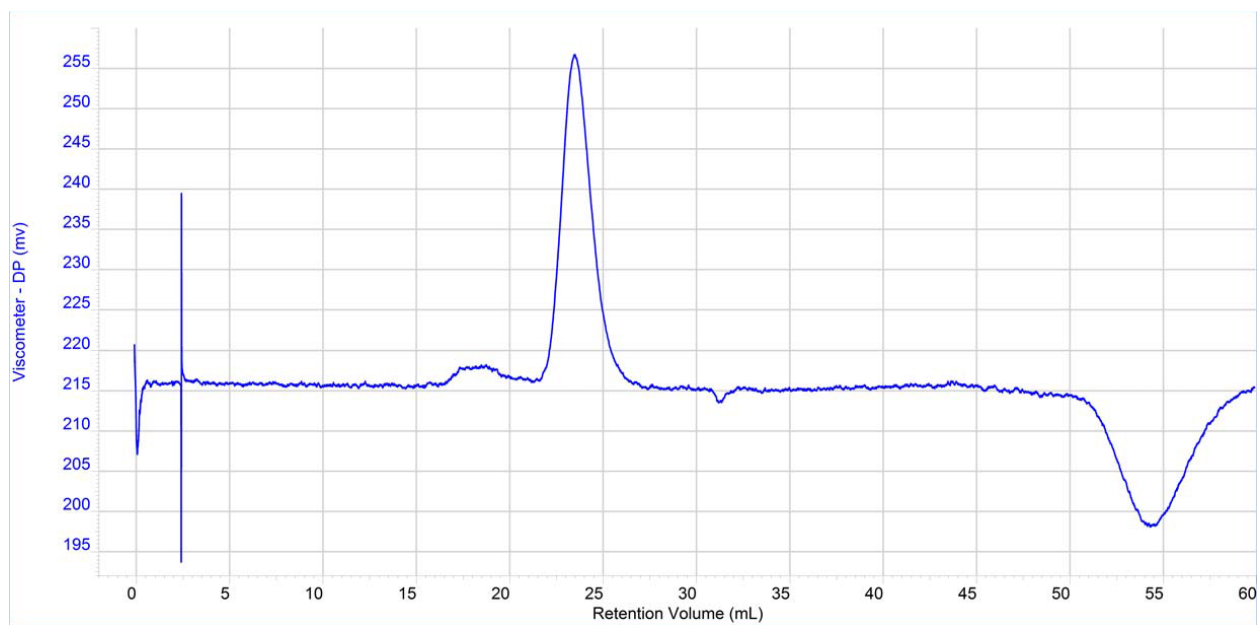


Figure B.37. GPC analysis of polyethylene (Table B.1., entry 4).

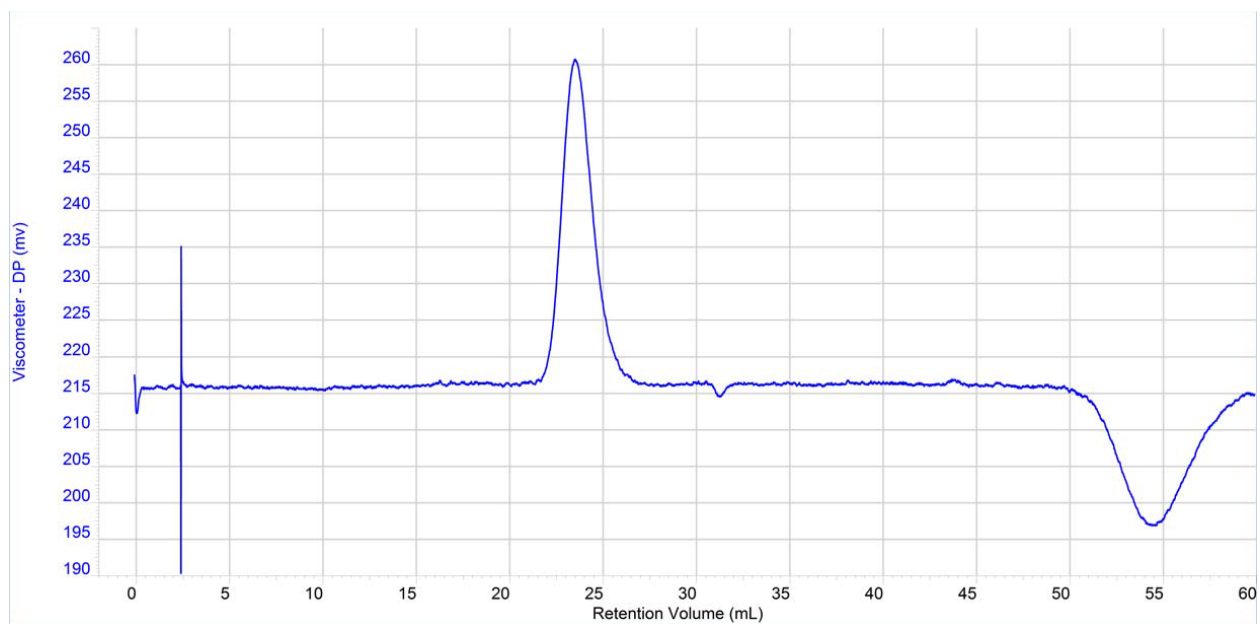


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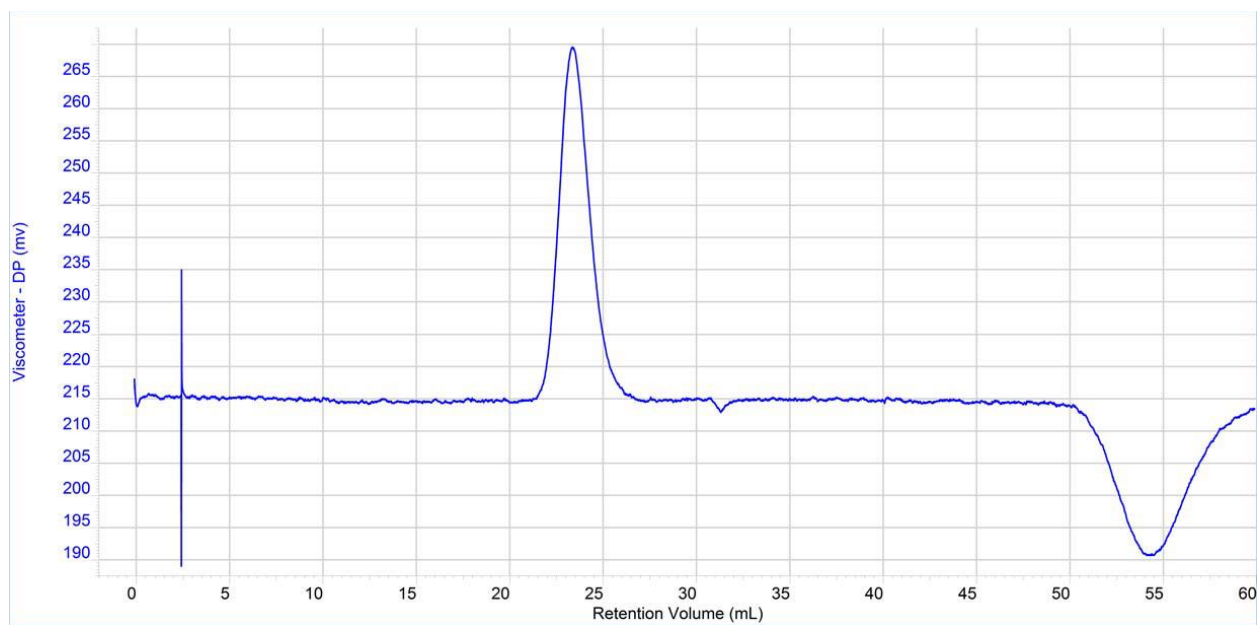


Figure B.39. GPC analysis of polyethylene (Table B.1., entry 11).

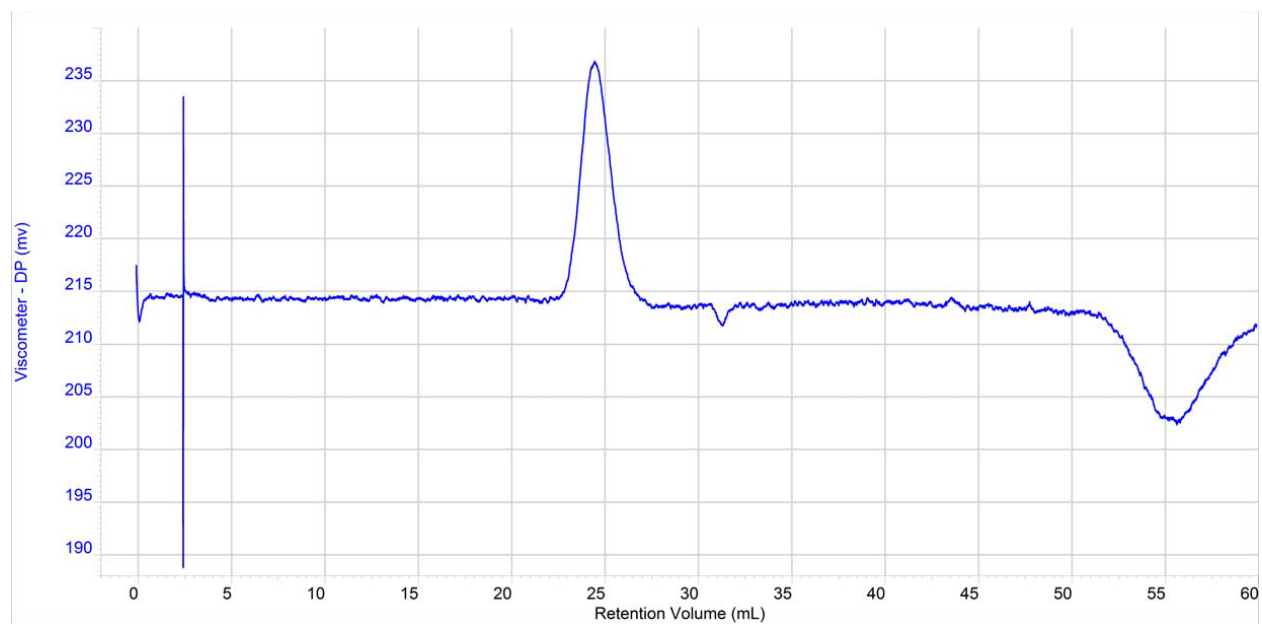


Figure B.40. GPC analysis of polyethylene (Table B.1., entry 13).

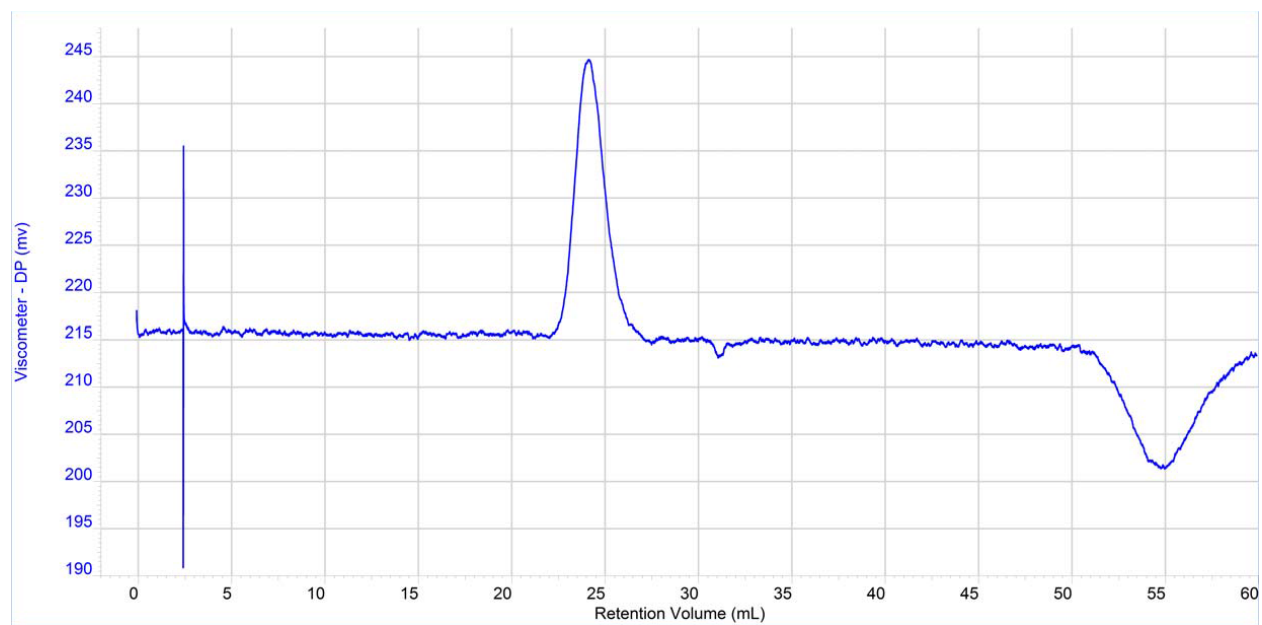


Figure B.41. GPC analysis of polyethylene (Table B.1., entry 16).

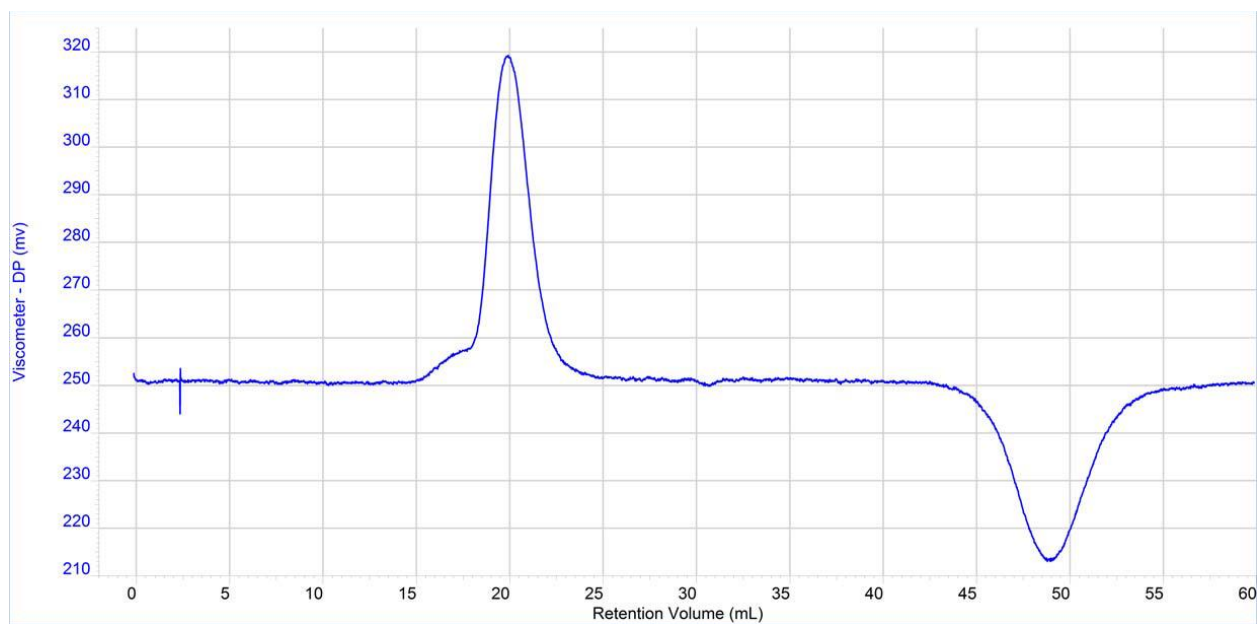


Figure B.42. GPC analysis of polyethylene (Table B.1., entry 20).

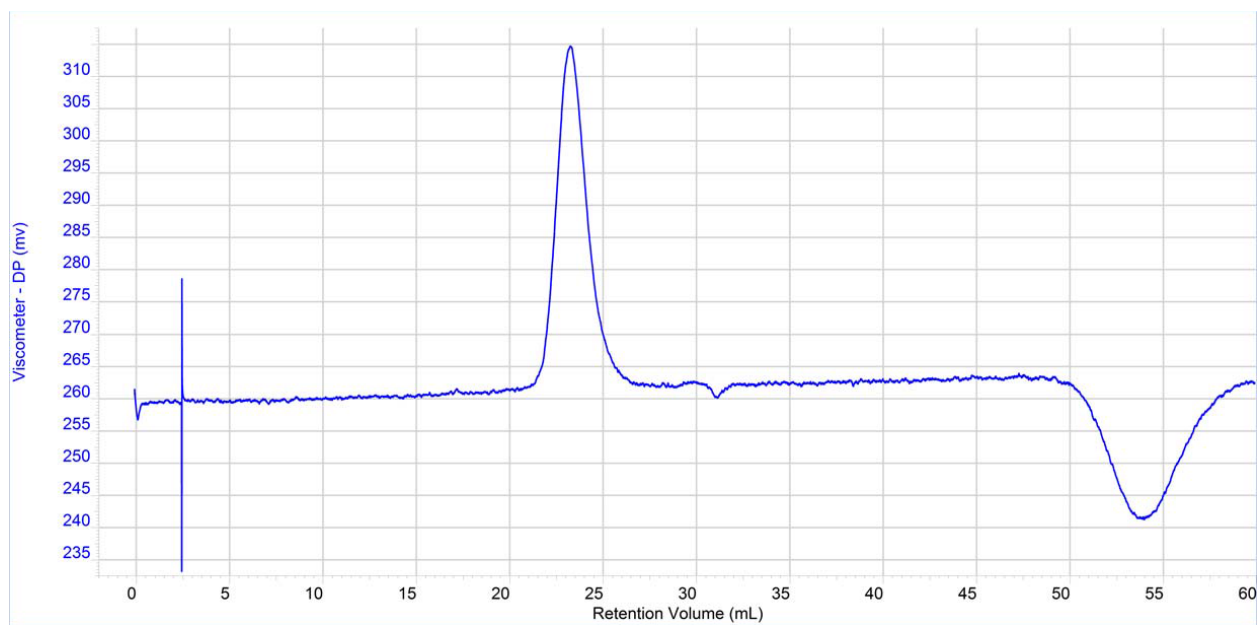


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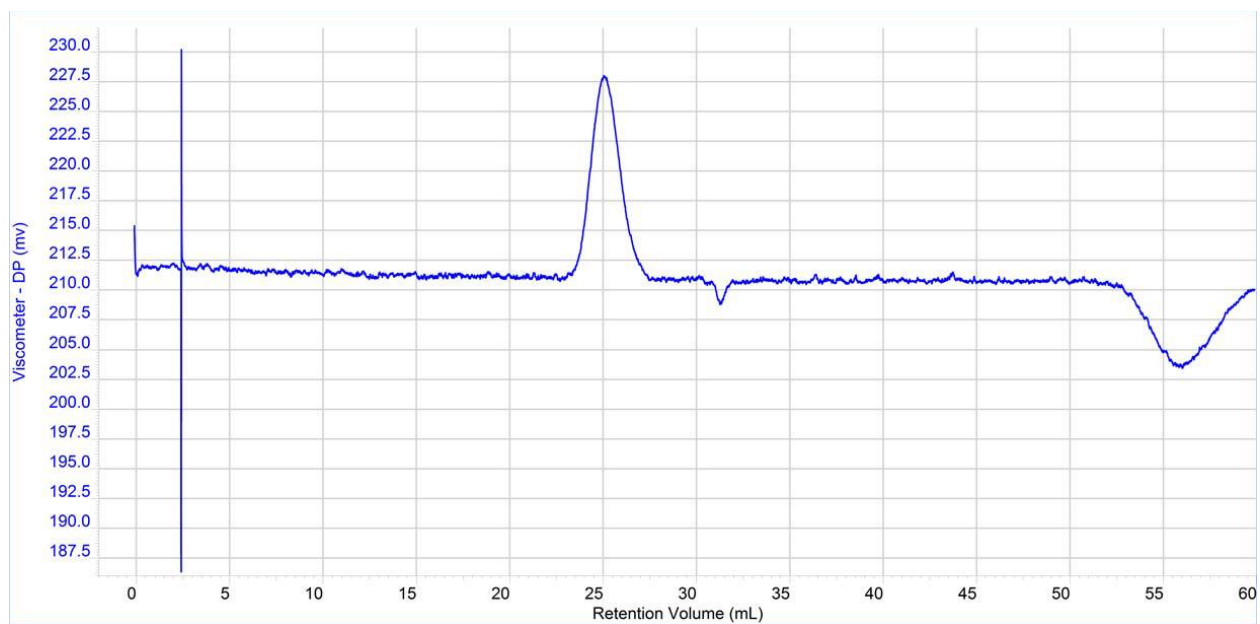


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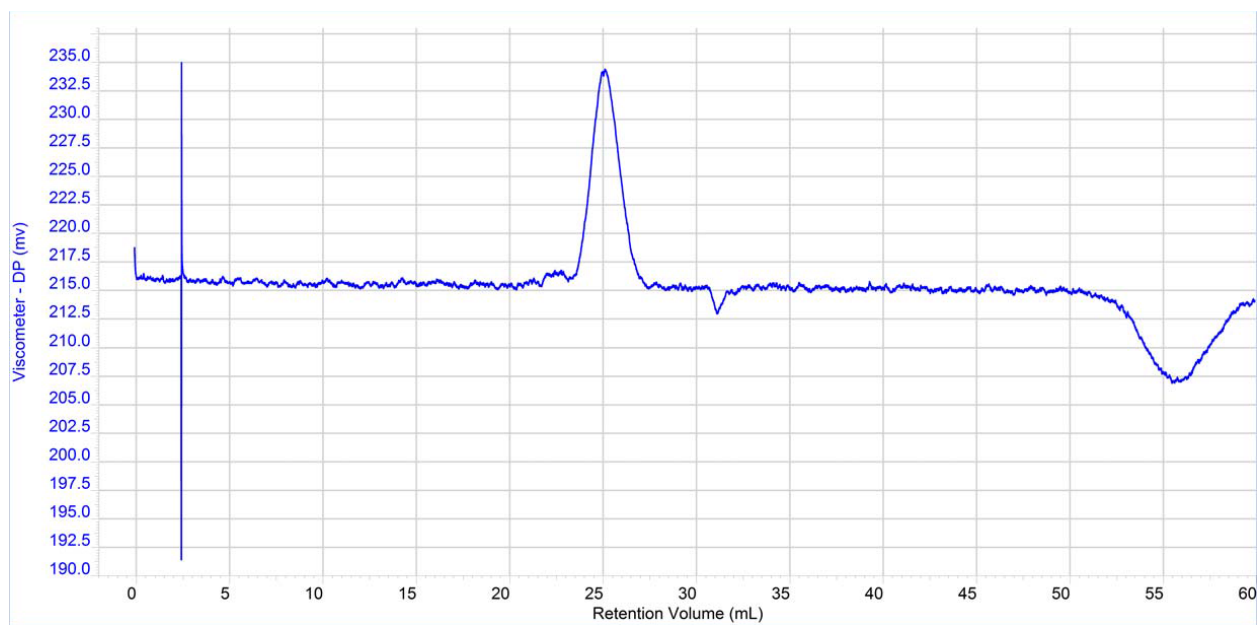


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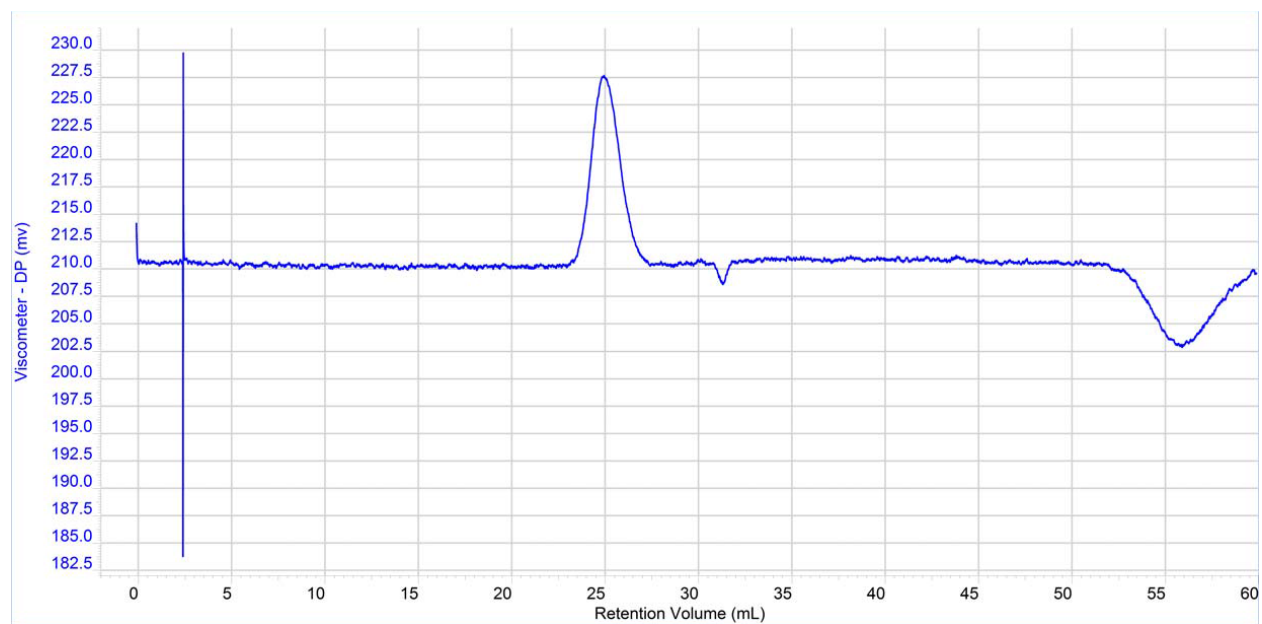


Figure B.46. GPC analysis of polyethylene (Table B.1., entry 32).

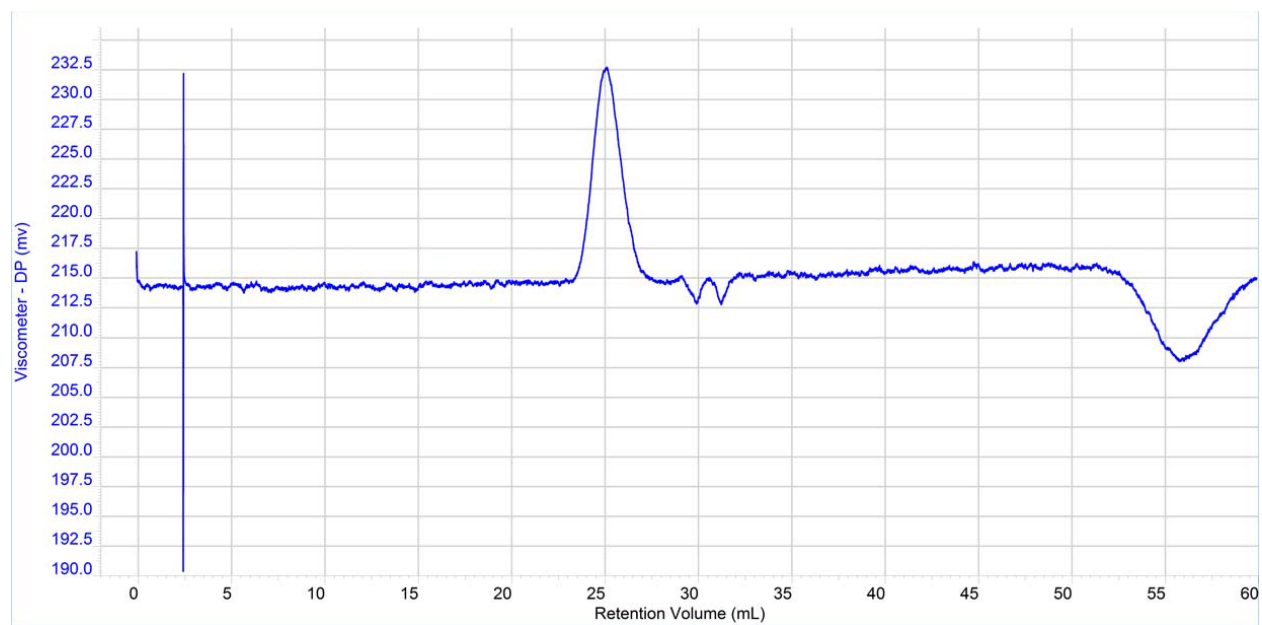


Figure B.47. GPC analysis of polyethylene (Table B.1., entry 34).

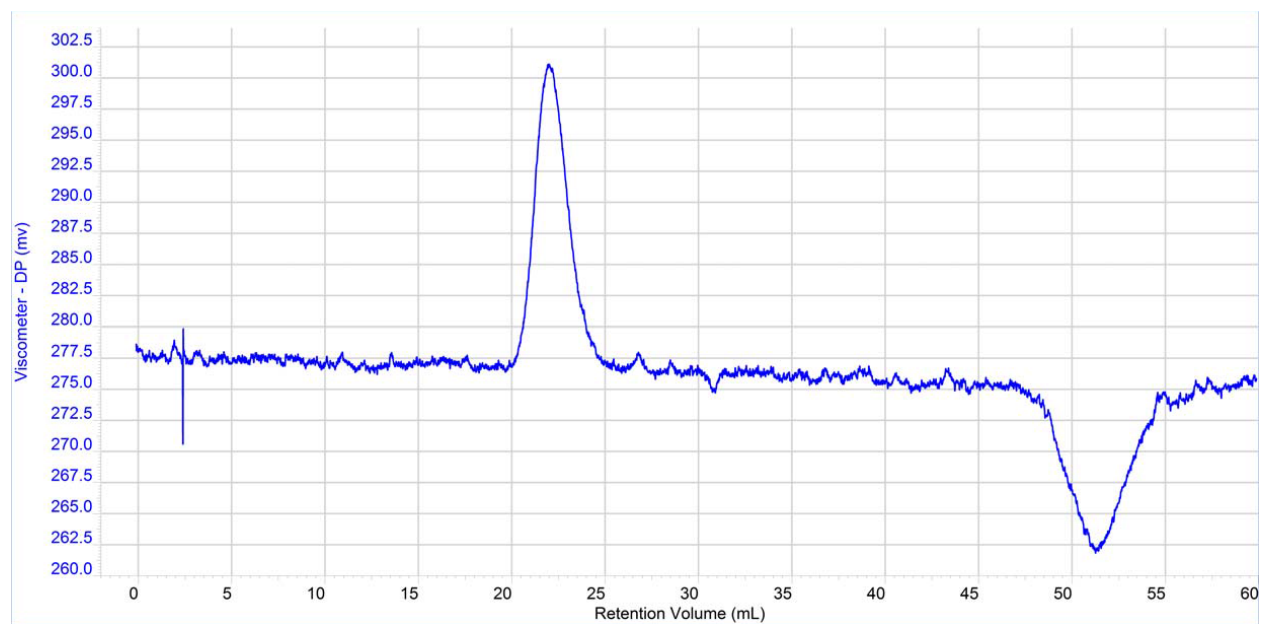


Figure B.48. GPC analysis of polyethylene (Table B.2., entry 1)

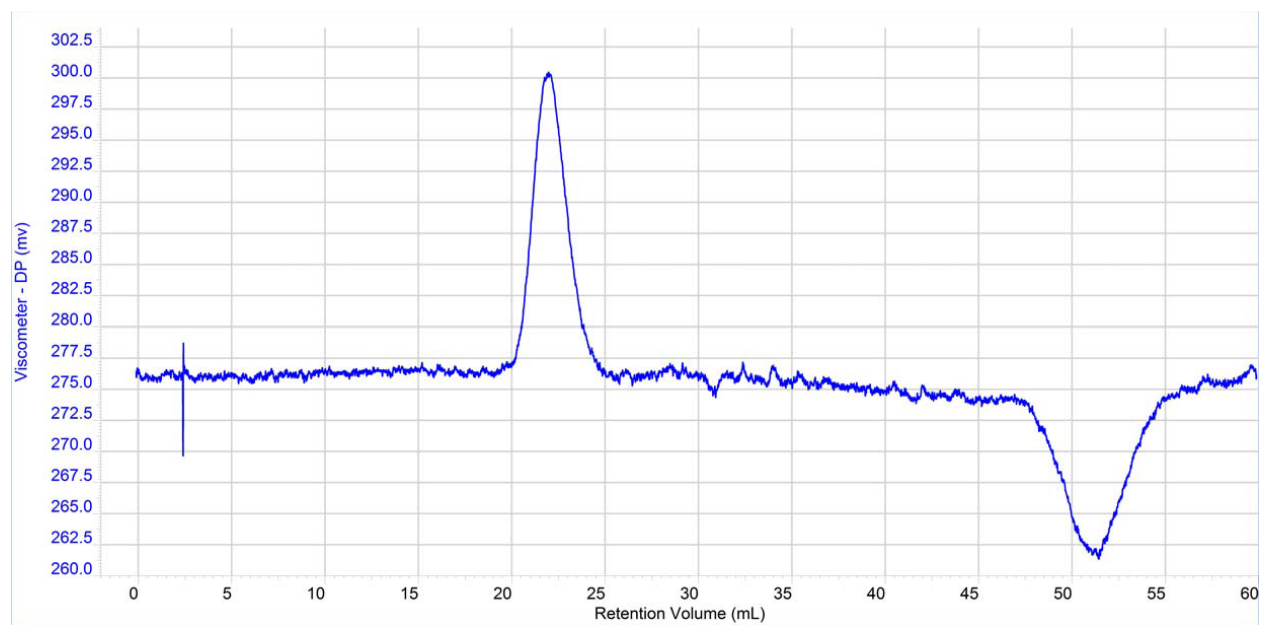


Figure B.49. GPC analysis of polyethylene (Table B.2., entry 5)

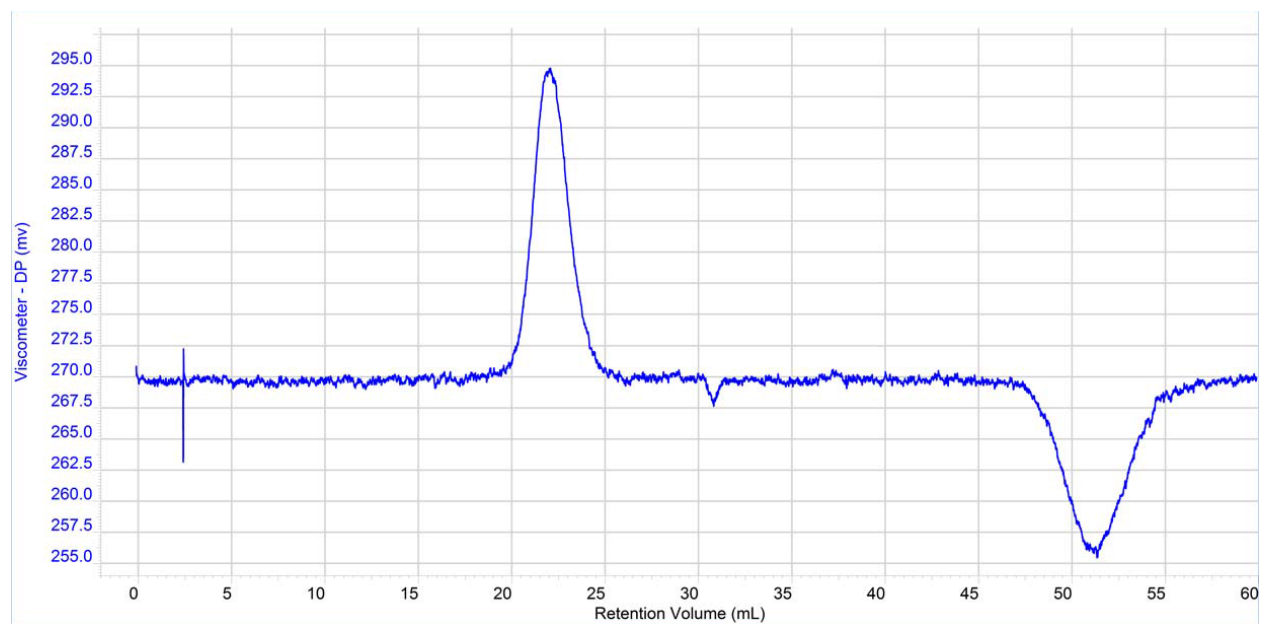


Figure B.50. GPC analysis of polyethylene (Table B.2., entry 7)

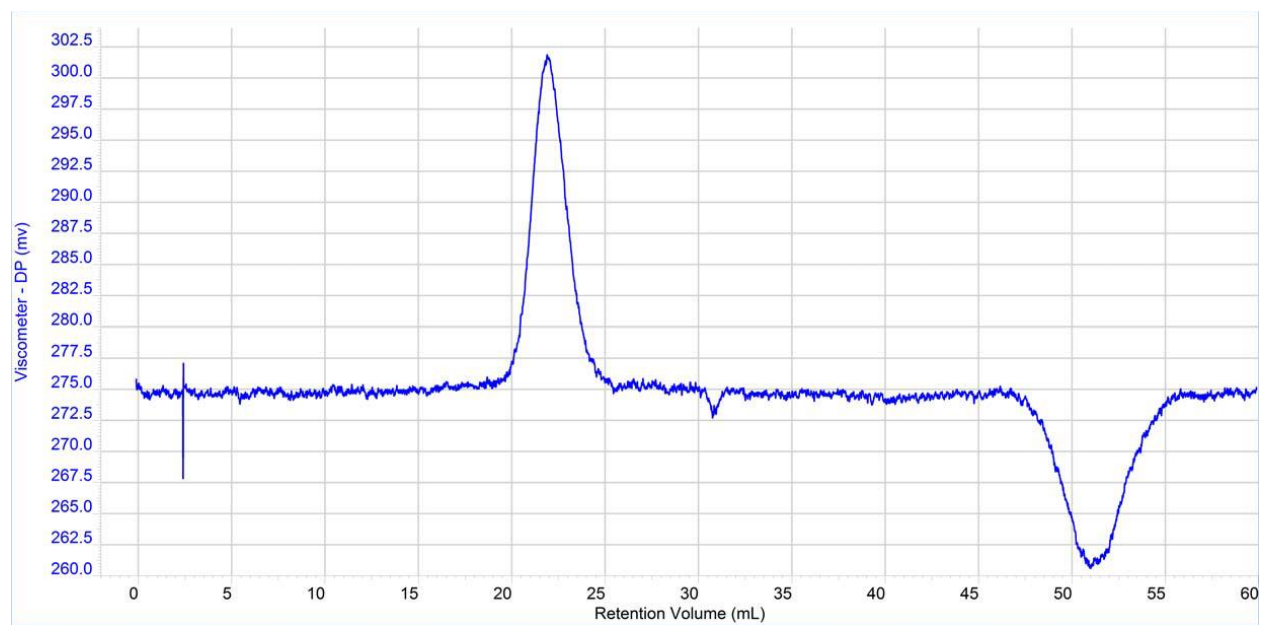


Figure B.51. GPC analysis of polyethylene (Table B.2., entry 11)

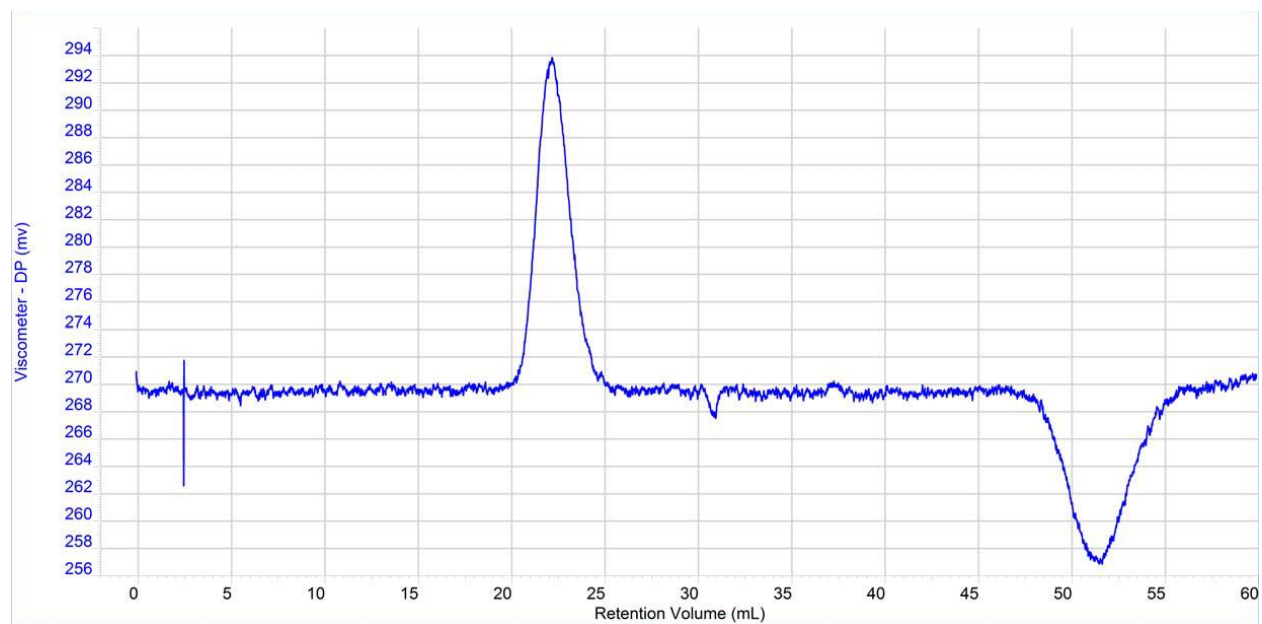


Figure B.52. GPC analysis of polyethylene (Table B.2., entry 14)

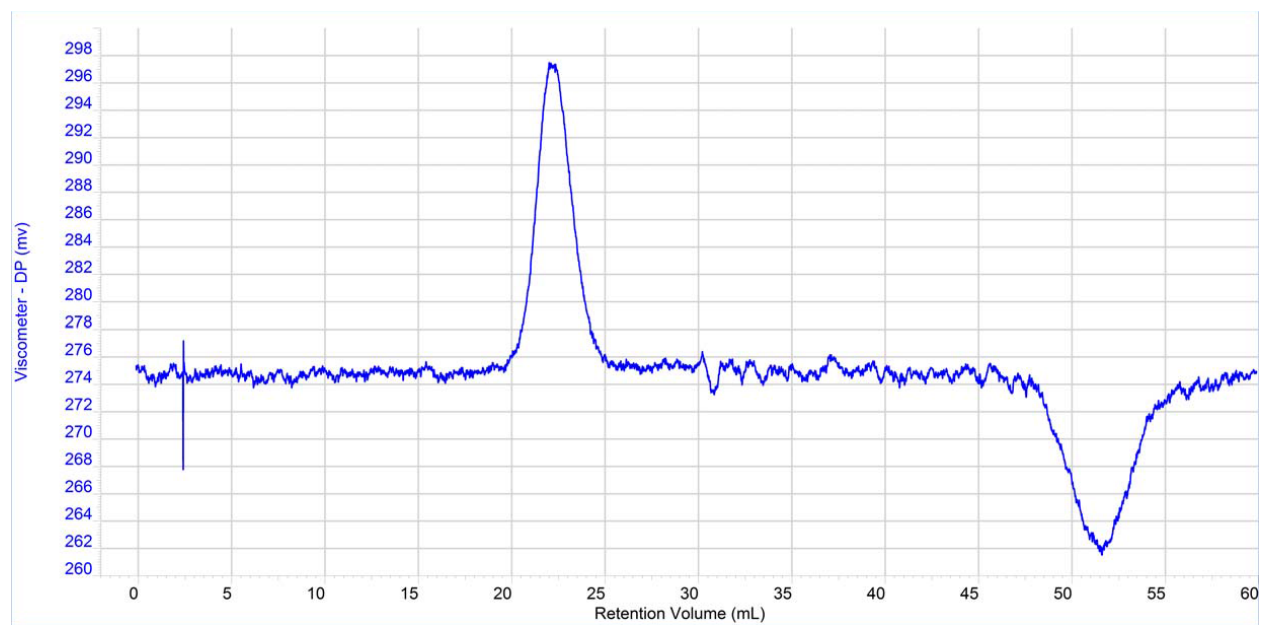


Figure B.53. GPC analysis of polyethylene (Table B.2., entry 17)

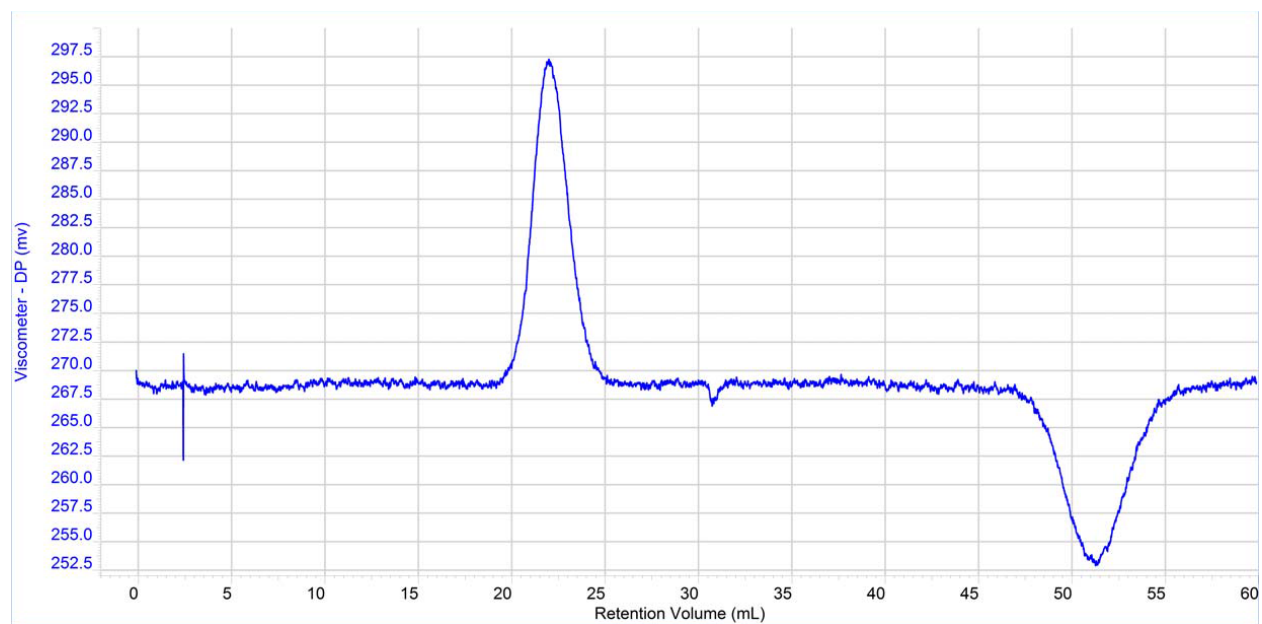


Figure B.54. GPC analysis of polyethylene (Table B.2., entry 19)

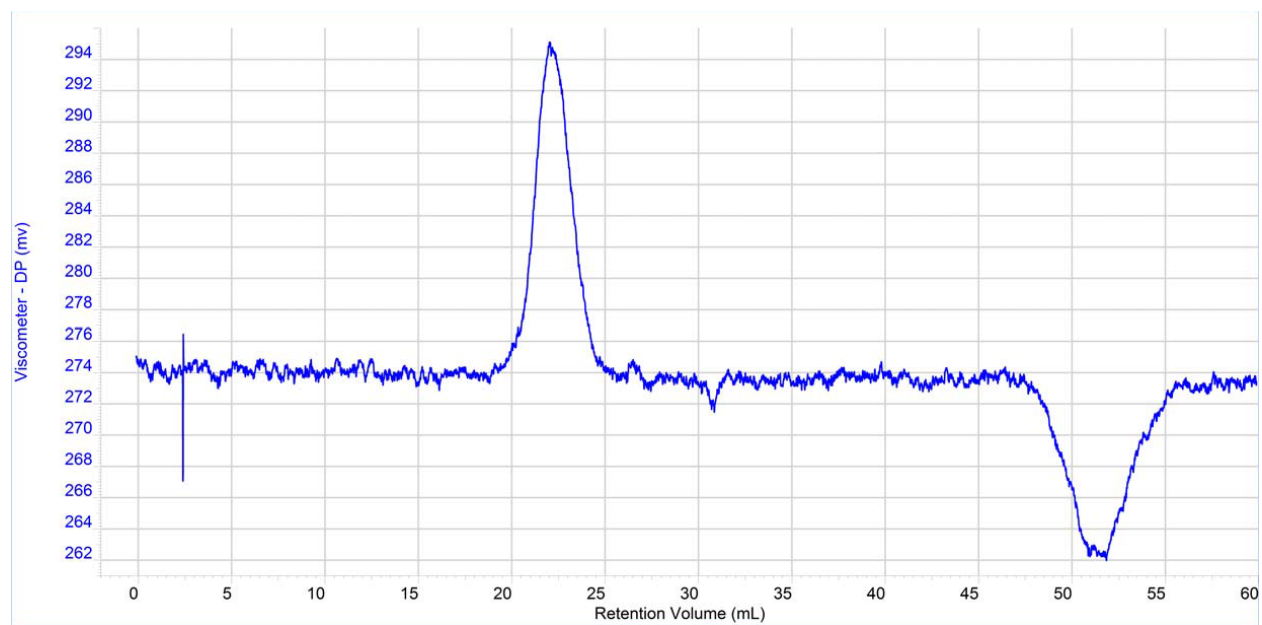


Figure B.55. GPC analysis of polyethylene (Table B.2, entry 23)

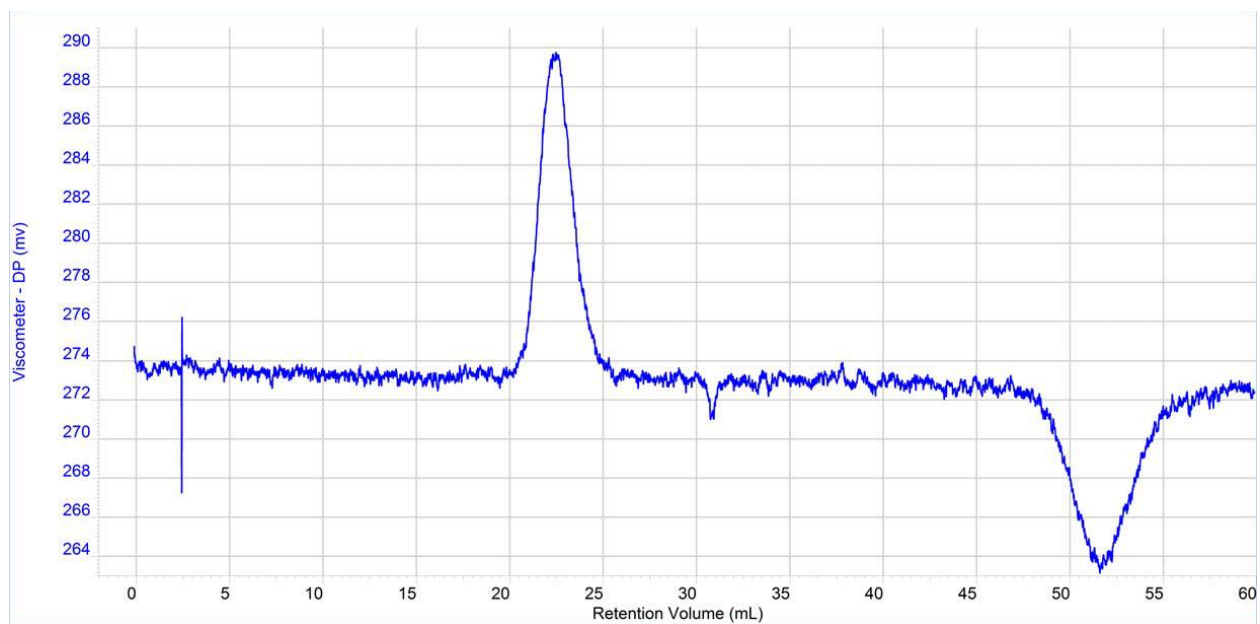


Figure B.56. GPC analysis of polyethylene (Table B.2., entry 26)

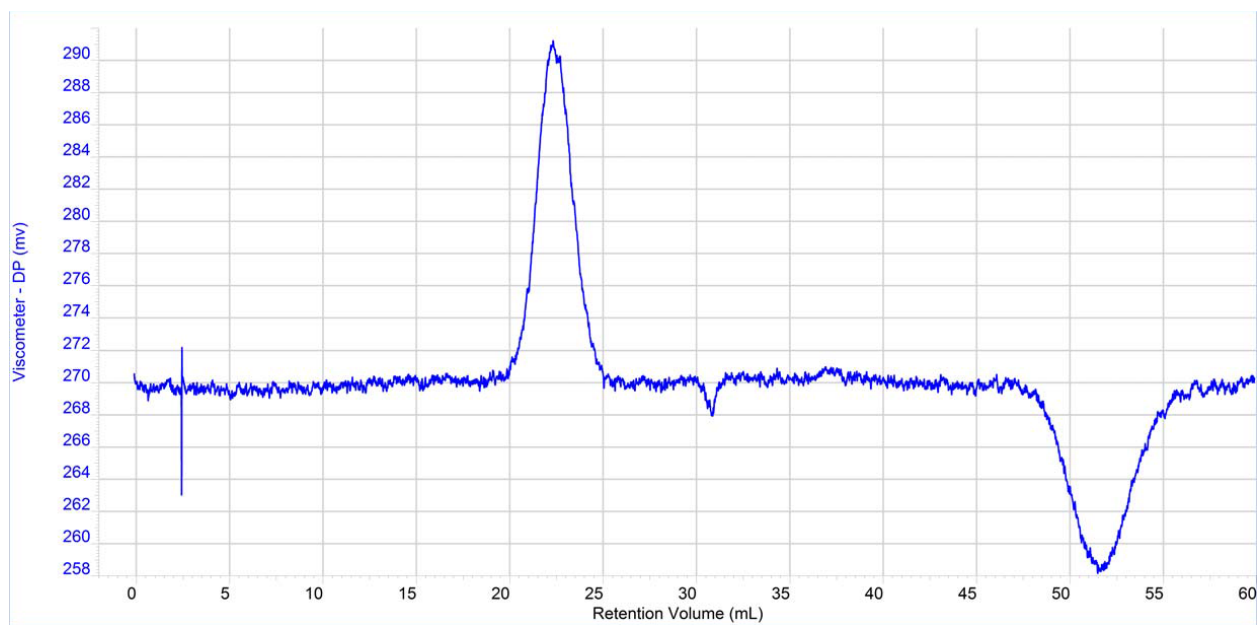


Figure B.57. GPC analysis of polyethylene (Table B.2., entry 30)

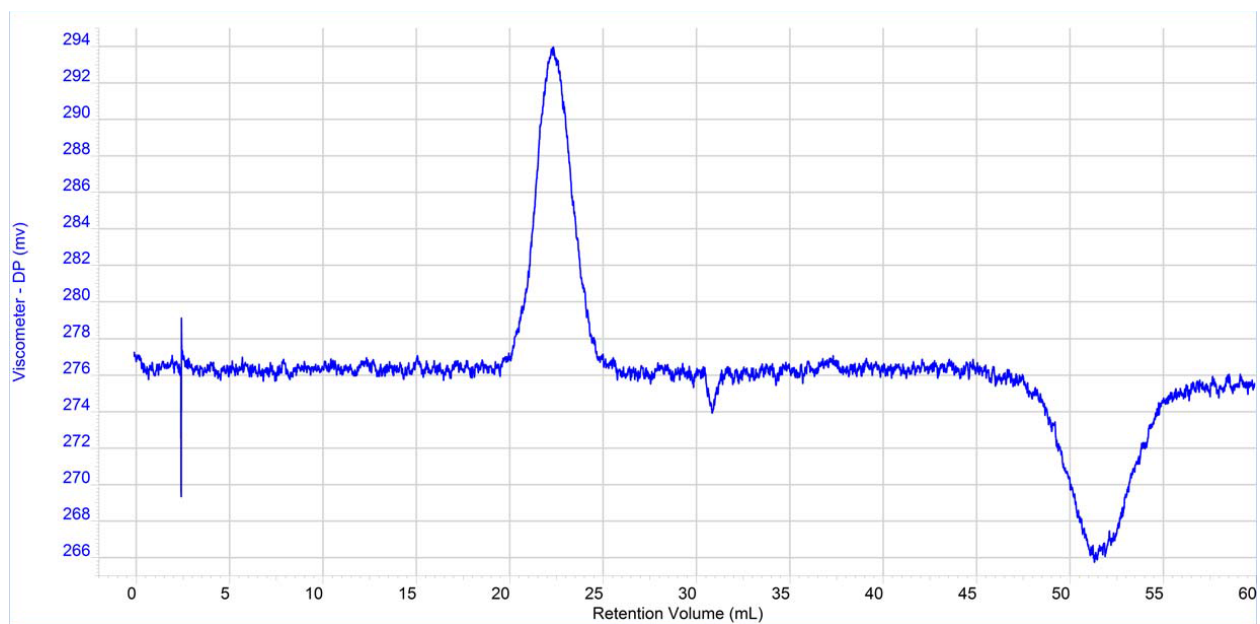


Figure B.58. GPC analysis of polyethylene (Table B.2., entry 33)

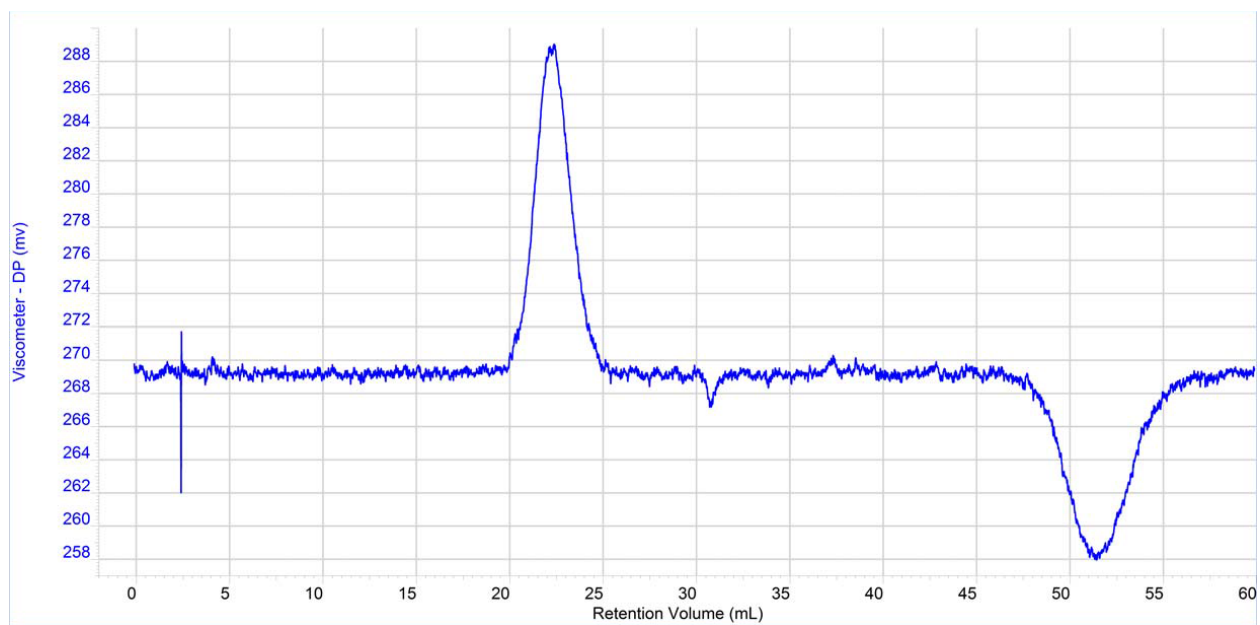


Figure B.59. GPC analysis of polyethylene (Table B.2., entry 36)

Additional References

- 1) Rhinehart, J. L.; Brown, L. A.; Long, B. K. *J Am Chem Soc* **2013**, *135*, 16316.

APPENDIX C

Supporting Information for Chapter 4

Synthesis of 2-(2-bromophenyl)ethanol.

Added to a 1000 mL three neck round bottom flask was 2-bromophenylacetic acid (50 g, 116 mmol) and condenser attached. After vacuum and refilling with N₂ three times, dry tetrahydrofuran (THF) (500 mL) was canula transferred into the flask and then borane dimethylsulfide (14.8 mL, 302 mmol) was slowly added to the flask until bubbling stopped. The reaction was stirred 2 hours at RT, 1 h at 100 °C, and then cooled back to RT and stirred overnight. After, a H₂O/THF mixture (200 mL) was added slowly to the reaction to quench excess borane. The THF was stripped by rotary evaporator, then the residual was dissolved in diethyl ether. Organic layer was washed with Na₂CO₃ (200 mL, 3x), NaHCO₃ (200 mL, 3x), and brine (200 mL, 3x). Organic layers were dried with MgSO₄, filtered, and evaporated to yield 2-(2-bromophenyl)ethanol. Yield: 90.2 %, ¹H NMR (CDCl₃, 500 MHz) δ 7.58 (m, 4 H), δ 3.86 (t, 2 H), δ 3.0 (t, 2 H)

Synthesis of toluene-4-sulfonic acid 2-(2-bromophenyl)ethyl ester.

A 500 mL round bottom flask charged with pyridine (200 mL) and 2-(2-bromophenyl)ethanol (50 g, 248.7 mmol) then cooled to 0 °C. p-toluenesulfonylchloride (98 g, 497.4 mmol) was added as small portions over ten minutes. Once added, the reaction mixture changed to yellow, was capped, and placed in the fridge overnight. The next day, the generated salt was filtered and the filtrate was poured into 800 mL of water, then extracted with methylene chloride (DCM) (250 mL, 3x). The organic layer was the washed with hydrochloric acid (HCl) (1 M) until all pyridine was removed, washed with Na₂CO₃ (250 mL, 3x), and brine (250 mL, 3x). Organic layers were dried with MgSO₄,

filtered, and evaporated. Yield: 89.2 %, ^1H NMR (CDCl_3 , 500 MHz) δ 7.7-7.10 (m, 8 H), δ 4.3 (t, 2 H), δ 3.1 (t, 2 H), δ 2.45 (s, 3 H)

Synthesis of 1-bromo-2-(2-bromoethyl)benzene.

A 500 mL round bottom flask was charged with acetone (300 mL), toluene-4-sulfonic acid 2-(2-bromophenyl)ethyl ester (60 g, 170 mmol), and LiBr (29.71 g, 340 mmol). A condenser was attached, and under N_2 , the mixture was refluxed overnight. After cooling the next day, the salt was filtered and acetone was stripped. The residual product was dissolved in ether and washed with Na_2CO_3 (200 mL, 3x), and brine (200 mL, 3x). Organic layers were dried with MgSO_4 , filtered and stripped of solvent. The crude product was purified by column filtration with n-hexane as the eluent. Yield: 82.1 %, ^1H NMR (CDCl_3 , 500 MHz) δ 7.60-7.13 (m, 4 H), δ 3.63 (t, 2 H), δ 3.32 (t, 2 H).

Synthesis of (bicyclo[4.2.0]octa-1,3,5-triene).

A 50 mL round bottom flask was flame dried and charged with 1-bromo-2-(2-bromoethyl)benzene (4 g, 15.15 mmol), THF (10 mL), and cooled in a methanol/liquid nitrogen bath for 20 mins. When cooled, n-butyl lithium (2.6 M in hexanes, 4.8 mL) was slowly syringed into the flask. After 15 mins, the flask was removed from the cold bath and stirred overnight at RT. The next day, the mixture was poured into 150 mL of water, extracted with diethyl ether (100 mL, 3x), and the organic layer was washed with brine (100 mL, 3x). The ether solution was dried with MgSO_4 , filtered, and stripped of solvent. For purification, the organic layers of multiple reactions were combined and distilled under

vacuum to yield benzocyclobutene. Yield: 52.1 %, ^1H NMR (CDCl_3 , 500 MHz) δ 7.12-7.08 (m, 4 H), δ 3.23 (s, 4 H).

Synthesis of 3-bromo-bicyclo[4.2.0]octa-1,3,5-triene.

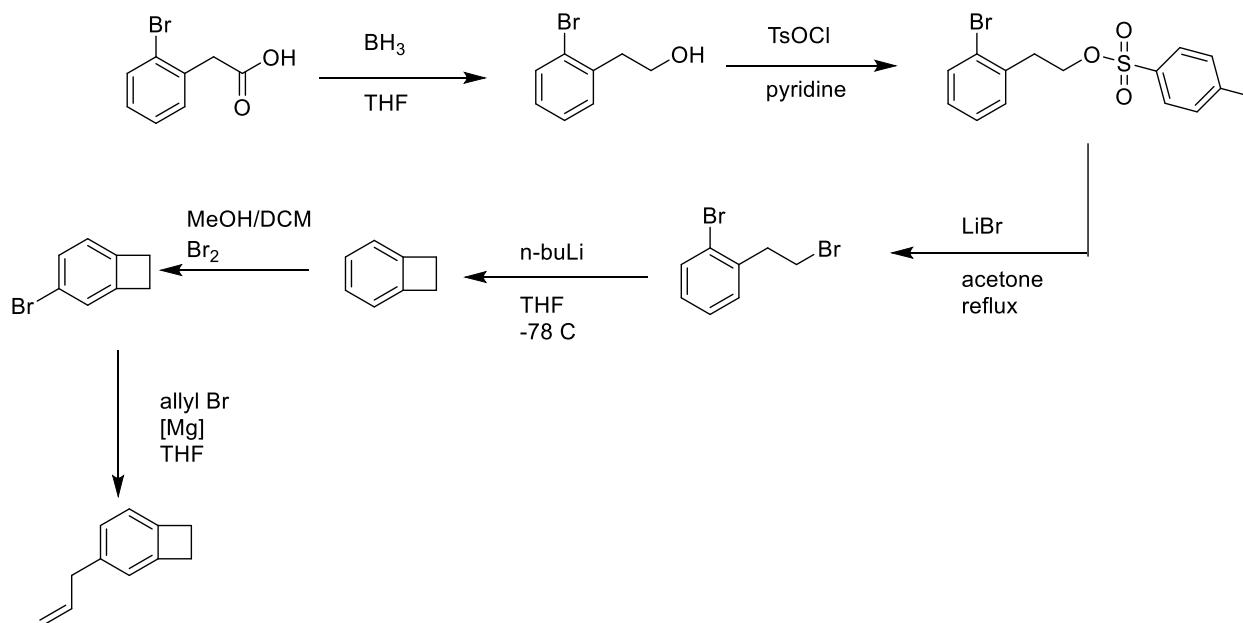
A 50 mL round bottom flask was charged with BCB (4.47 g, 42.92 mmol), methanol (4.5 g), and dichloromethane (DCM) (18.0 g) and cooled in an ice bath. Bromine (2.61 mL, 51.50 mmol) was dropwise added slowly by syringe. After 2 h of stirring, bromine (1.20 mL) was again added slowly at 0 °C and the reaction was stirred overnight warming to RT. The next day, the mixture was poured into a sodium bisulfate (100 mL, 1 M) to quench excess bromine and then extracted with diethyl ether (100 mL, 3x). The organic layers were combined, washed with brine (100 mL, 3x), dried with MgSO_4 , filtered, and stripped. The crude product was columned in n-hexane (R_f = 0.65), and then distilled under vacuum for purification and final product. Yield: 59.1 %, ^1H NMR (CDCl_3 , 500 MHz) δ 7.3-7.2 (m, 2 H), δ 6.90 (m, 1 H), δ 3.21 (m, 4 H).

Synthesis of BCB (3-allyl-bicyclo[4.2.0]octa-1,3,5-triene) (5).

A flame dried 250 mL round bottom flask was charged with magnesium shavings (500 mg, 20.65 mmol), dry THF (50 mL), and 3-bromobenzocyclobutene (2.5 g, 13.77 mmol). The mixture was immersed in an ice bath and left to stir 8 h. After the mixture turned grey, allyl bromide (2.40 mL, 27.54 mmol) was slowly dropwise added to the flask. When done, the flask was heated to 50 °C for two hours, then cooled to RT and let to stir overnight. The next day the mixture was poured into water (250 mL) and then extracted with diethyl ether (100 mL, 2x), then the organic layers were washed with brine (100 mL,

2x), dried with MgSO_4 , filtered, and stripped of solvent. The crude product was columned in n-hexane ($R_f = 0.80$) and collected to yield 3-allyl-benzocycobutene. Yield: 54.0 %, ^1H NMR (CDCl_3 , 500 MHz) δ 7.28-6.99 (m, 2 H), δ 6.94 (s, 1 H), δ 6.0 (m, 1 H), δ 5.11 (m, 2 H), δ 3.41 (d, 2 H), δ 3.20 (s, 4 H).

Scheme C.1. Synthetic route to obtain **5** for the addition to ethylene polymerization.



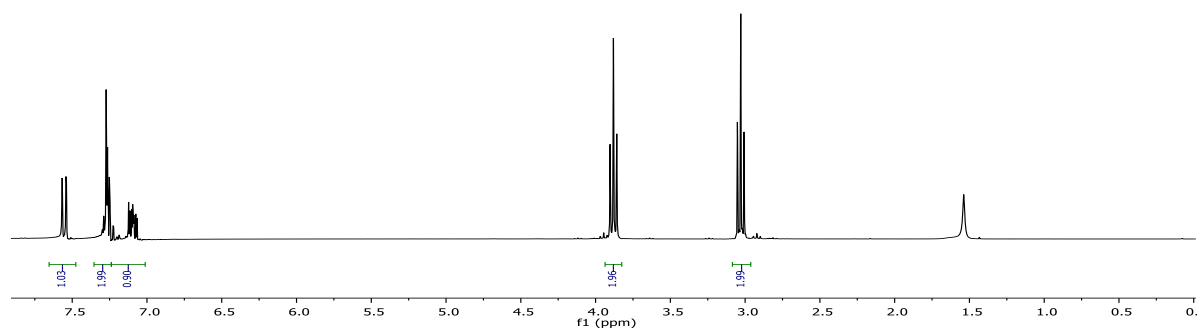


Figure C.1. ^1H NMR of 2-(2-bromophenyl) ethanol.

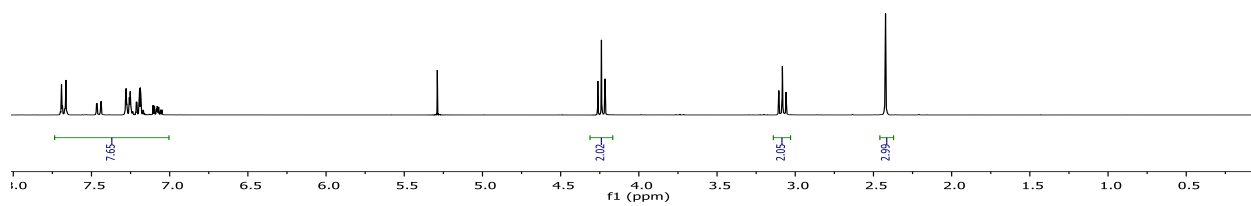


Figure C.2. ^1H NMR of toluene-4-sulfonic acid 2-(2-bromophenyl) ethyl ester

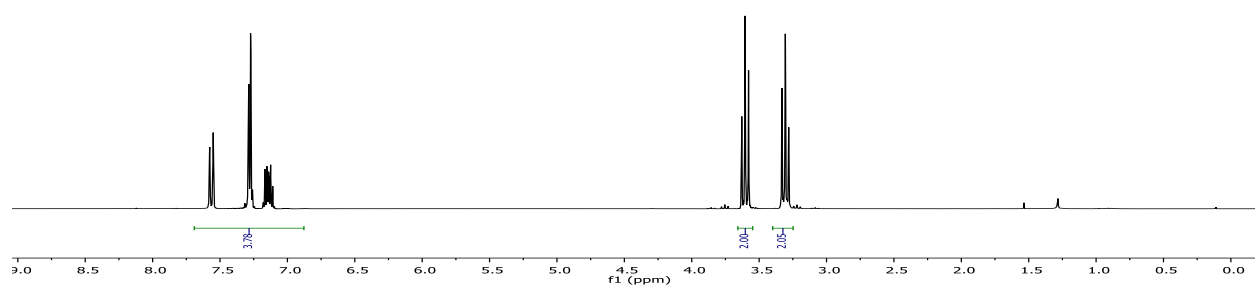


Figure C.3. ¹H NMR of 1-bromo-2-(2-bromoethyl) benzene

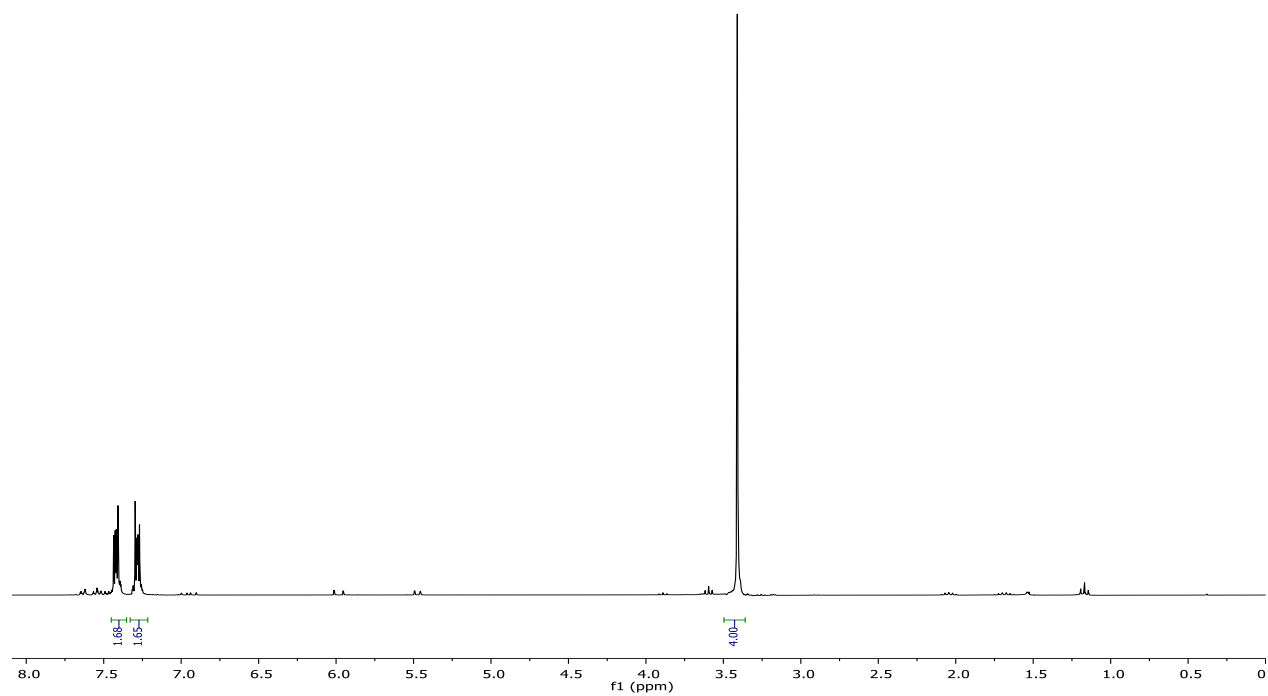


Figure C.4. ¹H NMR of bicyclo[4.2.0]octa-1,3,5-triene.

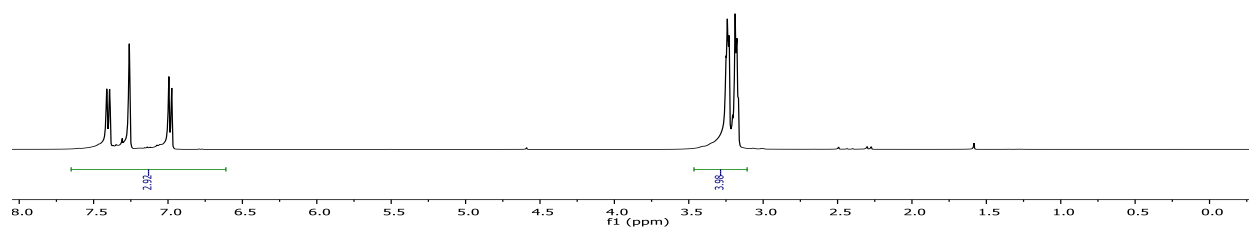


Figure C.5. ^1H NMR of 3-bromo-bicyclo[4.2.0]octa-1,3,5-triene.

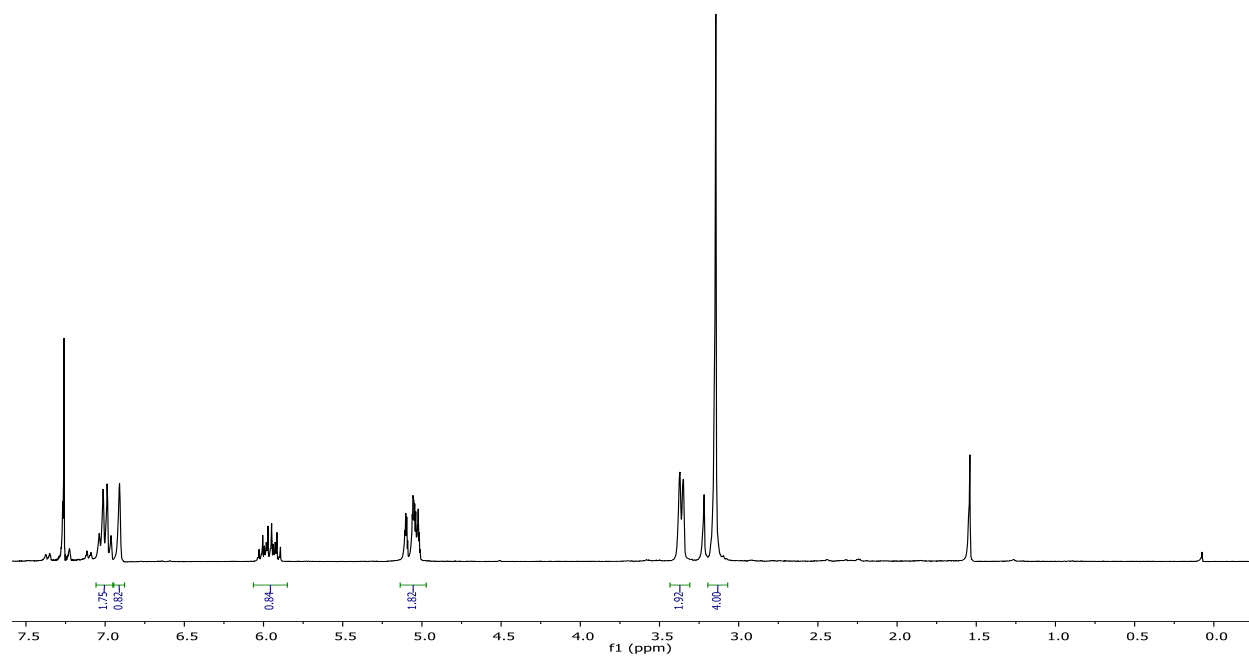


Figure C.6. ^1H NMR of BCB (3-allyl-bicyclo[4.2.0]octa-1,3,5-triene).

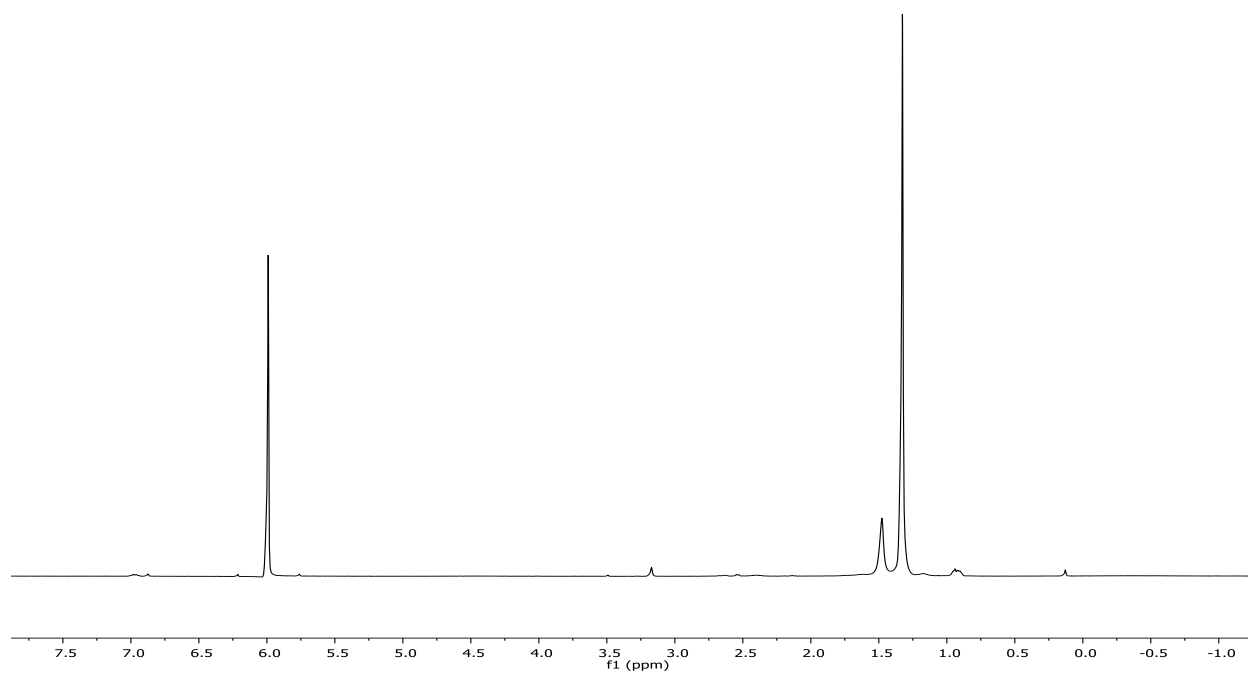


Figure C.7. NMR of Table 4.1., entry 3 bearing **5** peaks at 7.0, 2.5, and 3.3 ppm.

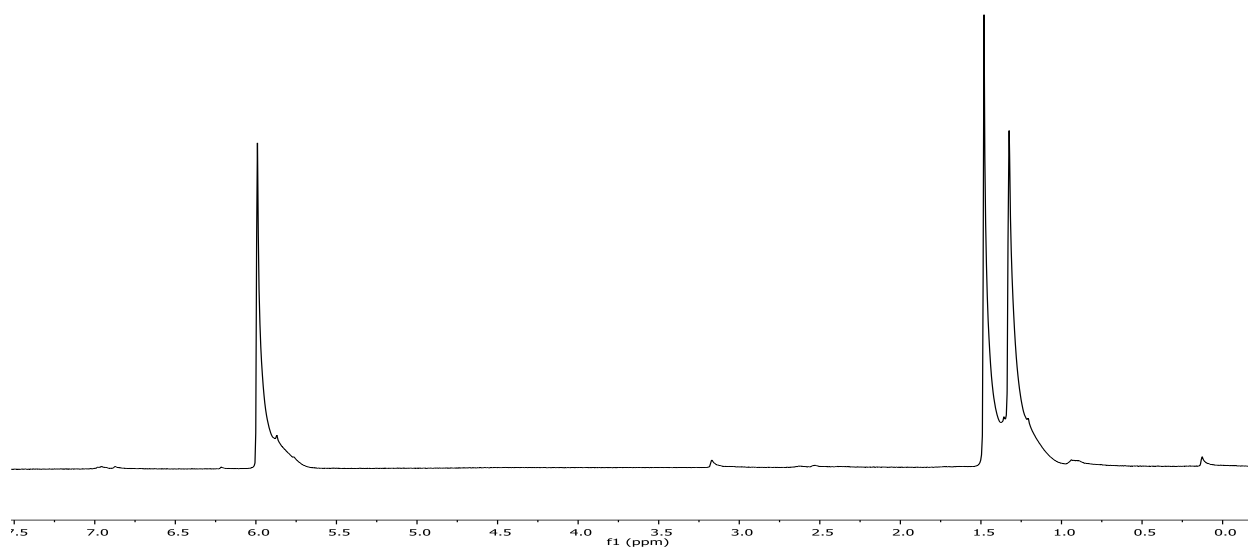


Figure C.8. NMR of Table 4.1., entry 4 bearing **5** peaks at 7.0, 2.5, and 3.3 ppm.

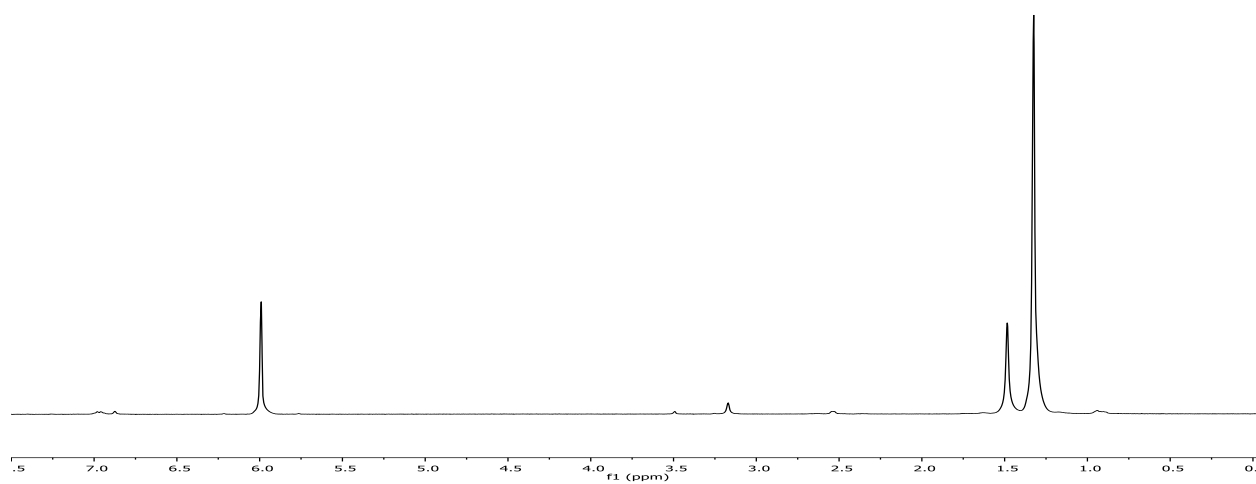


Figure C.9. NMR of Table 4.1., entry 5 bearing 5 peaks at 7.0, 2.5, and 3.3 ppm.

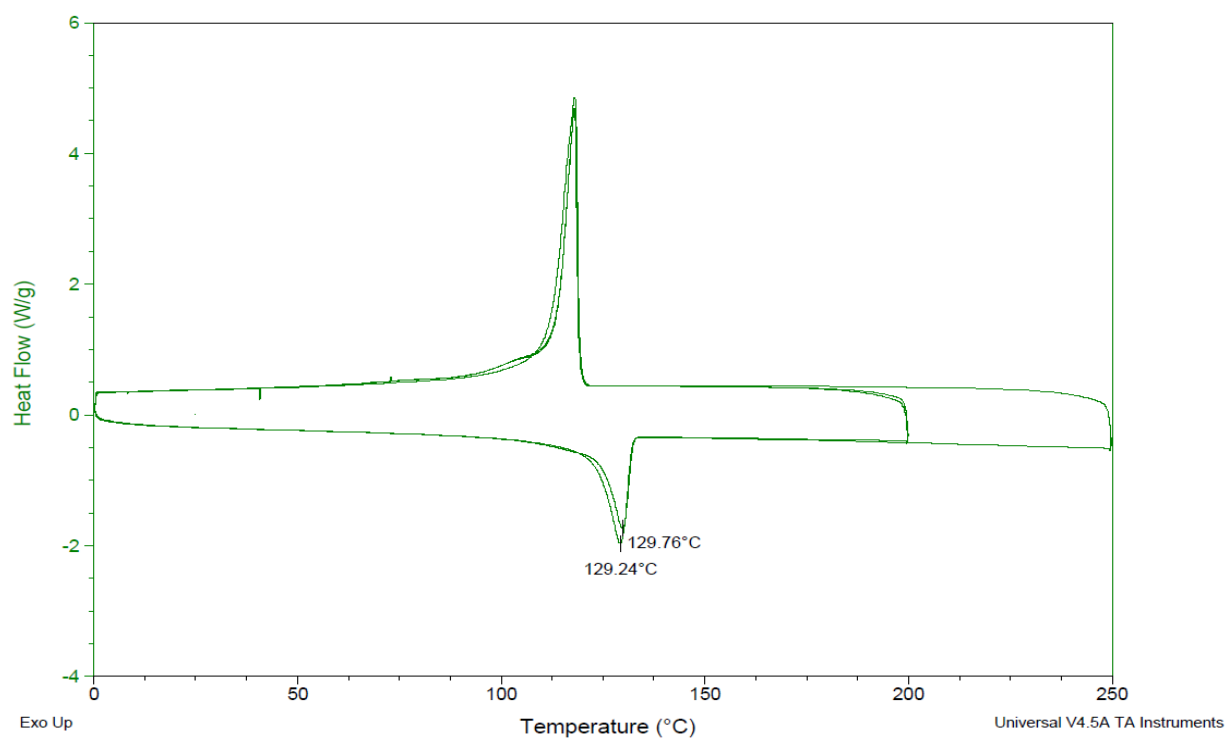


Figure C.10. DSC trace of Table 4.2., entry 2.

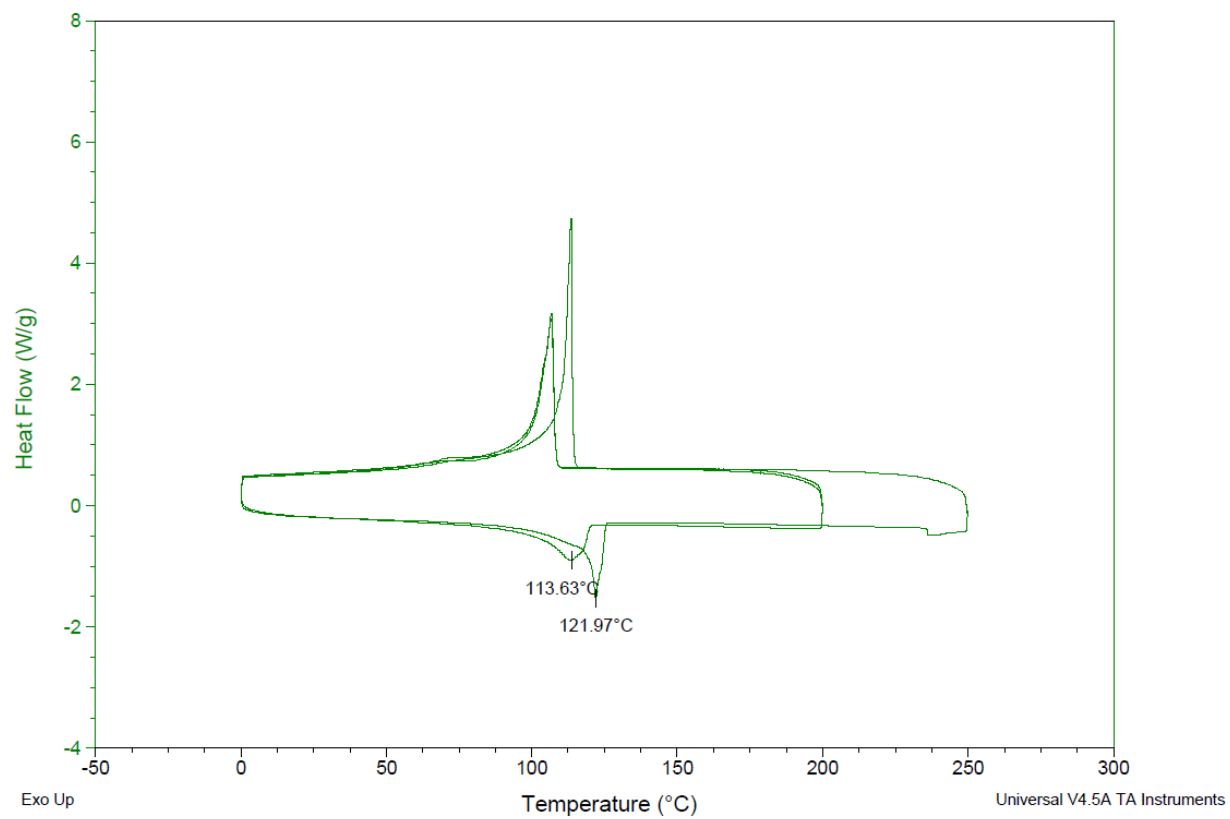


Figure C.11. DSC trace of Table 4.2., entry 3.

VITA

Nolan Evan Mitchell grew up in Rocky River, OH to Mello and Mary Jo Mitchell. His adolescent education was through the Rocky River School system. Following graduating high school in 2009, he enrolled in The Ohio State University (Columbus, OH). He graduated in December of 2012 with a B.S. degree in Chemistry. Nolan conducted undergraduate research with Prof. Jon Parquette on the synthesis of sulfonated carboxylic acids. He began his Ph.D studies in polymer chemistry at the University of Tennessee (Knoxville, TN) in July 2013 with Prof. Brian Long studying olefin polymerization catalysis and functional polyolefins.