Stereoselective Propylene Polymerization with Supported Titanium Catalysts

by

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Abstract

Titanium FI (Ti-FI) catalysts catalyze polymerizations that exhibit “living,” or ideal, behavior in homogeneous (soluble-phase) reactions. The polymers produced have high molecular weights, low polydispersities, and high syndiotacticity. However, Ti-FI catalysts cannot be used in industrial polymerizations. In industrial slurry reactors, homogeneous catalysts cause “fouling”: the formed polymer is deposited at the reactor walls, which impairs the reactor’s efficiency and clogs its feed lines. In order for Ti-FI catalysts to be usable in industrial reactors, it is necessary that they be immobilized.

Three methods of immobilizing a Ti-FI catalyst were investigated. The goal of the first two methods was to synthesize a self-immobilizing catalyst by attaching a vinyl or an allyl functional group to one of its ligands. The synthesis of the vinyl ligand was successful, but the attempts to attach it to a catalyst failed. The synthesis of the allyl ligand catalyst was successful, and this catalyst was used to polymerize polypropylene. The polypropylene produced was compared to polypropylenes produced by homogenous catalysts, but no evidence of immobilization of the catalyst was verifiable. The third immobilization method involved immobilizing two different Ti-FI catalysts onto silica. When compared to control polymers, the polypropylene produced by some of the silica-immobilized catalysts proved to have higher molecular weights, and similar PDIs. The immobilized catalysts produced a mixture of 65% syndiotactic and 35% isotactic polypropylenes, compared to the highly syndiotactic polypropylenes produced by the control homogeneous Ti-FI catalysts.
Introduction

Plastics are versatile materials with applications in all aspects of modern life. Plastics are polymers: long-chain macromolecules made up of many repeating small molecules, or monomers. In the year 2001, the worldwide consumption of polyolefins, or polymers made from alkene monomers such as styrene, ethylene, propylene, etc. was 83 million tons. Consumption is expected to increase by 5% over the next 10 years.\(^1\) With desirable properties such as low density, high strength, resistance to chemical attack, and cost-effectiveness, polyolefins are used in packing materials, films, molded parts, toys, appliances, fibers, foam, automotive and electrical components, and more.

The physical properties of a polymer not only depend on the composition of its monomers and its molecular weight, but also on the polymerization method used to generate it. There are many mechanisms that lead to the formation of a polymer. Free radical, cationic, and anionic polymerizations use radical, electrophilic, and nucleophilic attack, respectively, to link small molecules together. The problem with these polymerization methods is that it is often hard to control the molecular structure of the resulting polymer. In the 1950s, researchers discovered that transition metals can act as polymerization catalysts. Catalytic polymerization proceeds by a more controlled mechanism, known as the Cossee-Arlman mechanism.\(^2\) The metal (M) coordinates both the growing polymer chain (CH\(_2\)R) and the monomer, and inserts the monomer onto the end of the polymer via migratory insertion: the polymer chain leaves its coordination site, migrates over to the monomer, and forms a carbon-carbon bond.
Catalytic coordination-insertion polymerizations produce useful polymers because they allow control over the microstructure, and thus the physical properties, of the polymers. The discovery and development of highly active, transition metal-based, olefin polymerization catalysts accounts for much of the success realized in the synthesis of polyolefinic materials today.

Our group has been working with a family of titanium-centered olefin polymerization catalysts with phenoxy-imine ligands called FI catalysts. (The letters FI stand for the Japanese pronunciation of Fenoxy-Imine ligands.) These catalysts are highly active and give a great deal of control over the polymers they create. However, because they are soluble in the polymerization solvent, they cannot be used in modern industrial reactors. Soluble, or homogeneous, catalysts produce light, poorly-formed polymer particles that clog reactors, whereas supported, or heterogeneous, catalysts support spherical particles that stay at the bottom of the reactor. Our objective is to attach a titanium FI catalyst to a solid in order to make it insoluble, and thus applicable to modern industrial processes, while retaining the desirable features of the homogeneous catalyst.
History of Polymerization Catalysts

Ziegler and Natta launched the polyolefin industry in the 1950s when they used titanium chloride in combination with alkyl aluminum (TiCl$_3$/AlR$_3$) as a catalyst to prepare high density polyethylene and isotactic polypropylene.\textsuperscript{3-6} The reaction conditions for this type of polymerization were mild compared to the high pressure and high temperature conditions needed for the free-radical polymerizations previously in use. The classic Ziegler-Natta catalyst is heterogeneous, that is, insoluble in the polymerization solvent. It is also multisite, meaning it has several coordination sites for monomers and polymer chains.\textsuperscript{7} This leads to inconsistencies in the process and makes it difficult to control the properties of the resulting polymer.

In 1968, scientists at Mitsui Petrochemical and Montecatini independently discovered that TiCl$_4$ catalysts supported on magnesium chloride (MgCl$_2$) were two orders of magnitude more active than the Ziegler-Natta catalysts, and that they also gave high control of the morphologies of the resulting polymers.\textsuperscript{8-10} The high efficiency and isospecificity of these MgCl$_2$-supported catalysts made removal of atactic polypropylene, and catalyst or cocatalyst metal impurities, from the polymers unnecessary.\textsuperscript{7} These catalysts made possible the commercial production of high-performance high density polyethylenes, linear low density polyethylenes, highly isotactic polypropylenes, and polyolefinic elastomers.\textsuperscript{1}

Metallocenes, or metals sandwiched between two cyclopentadienyl ligands, were first characterized and used as olefin polymerization catalysts in combination with alkylaluminum cocatalysts in the late 1950s. The metallocene catalysts were single-site and homogeneous, or soluble in the polymerization solvent.\textsuperscript{11-14} Because of
their low activity, they were not considered important at that time. However, in 1980, Sinn and Kaminsky combined group 4 metallocenes with methylaluminoxane (MAO), and discovered that, when paired with this new cocatalyst, the metallocenes displayed activities rivaling those of the Ziegler-Natta catalysts.\textsuperscript{15-16}

![Figure 2. A metallocene pre-catalyst.](image)

The Sinn-Kaminsky metallocene catalysts became important because they possessed single, well-defined active sites that could be studied and modified. When the three phases of the polymerization process (activation, propagation, and termination) were better understood in relation to catalytic polymerizations, researchers could fine-tune the catalyst’s structure in order to give control over the polymer’s microstructure. The polymerization catalyst’s activity and stereoselectivity, and the produced polymer’s molecular weight, microstructure, and physical properties could be controlled.\textsuperscript{1}

From the 1990s onward, researchers have been using their knowledge about polymerization catalyst active sites for the rational design of new catalysts that will promote longer chain lengths, eliminate $\beta$-hydride termination and chain-transfer, and copolymerize different olefins. The new catalysts are known as the post-metallocene catalysts. They use different metal centers, such as Ni, Fe, and Co, different ligands, such as diimines, diamides, and diiminopyridines, and different cocatalysts, such as
MgCl₂, borates, and modified alkyl aluminas.¹ Many of the post-metalloocene catalysts are expensive to make, but are valuable nonetheless because they produce high-performance polymers.⁷

**Methylaluminoxane (MAO)**

Methylaluminoxane is a cocatalyst that is used with many post-metalloocene catalysts. It is prepared by the controlled partial hydrolysis of trimethylaluminum, Al(CH₃)₃. Using different hydrolysis procedures to prepare MAO affects the activity of the polymerization it cocatalyzes. The structure of MAO, and the structure of the catalyst-cocatalyst complex, is not well understood. Studies show that most of the aluminum in MAO is coordinated to four other atoms. Proposed structures of MAO include linear chains, cyclic rings, and many different 3-D structures.¹⁷

![Figure 3. A proposed 3-D cage structure of MAO](image)

MAO has many roles in a polymerization reaction. First, some of the residual trimethylaluminum, which is always left in an MAO solution, alkylates the catalyst (L₂TiCl₂). An MAO aluminum metal center then abstracts a chloride ion, leaving an empty coordination site.¹⁷

Alkylation: L₂TiCl₂ + MAO → L₂Ti(CH₃)Cl + [Cl-Al-O]ₙ

Abstraction: L₂Ti(CH₃)Cl + MAO → [L₂Ti(CH₃)]⁺[Cl-MAO]⁻
During the polymerization, the MAO anion interacts with the catalyst to form an ion pair. MAO also reactivates inactive complexes such as \( \text{L}_2\text{M-CH}_2\text{-AlR}_2 \) that are formed by hydrogen-transfer reactions.\(^{18}\)

There are a few disadvantages associated with using MAO as a cocatalyst. First, the ratio of MAO to catalyst required for good polymerization activity is very high. This makes polymerizations more costly, and gives the resulting polymer higher ash (\( \text{AlO}_x \)) content. Second, MAO as a cocatalyst gives little control over the polymer’s morphology. Third, the active species, or the actual interaction between MAO and the catalyst, is difficult to characterize. However, MAO as a cocatalyst gives such extremely high activity that all of these considerations become unimportant. Researchers have been able to make modifications to the system that lessen these undesirable effects.\(^{17}\)

**Current Goals of Polymerization Catalyst Design: Living Behavior and Tacticity**

Some of the goals of catalyst designers today are to synthesize catalysts that (1) exhibit living behavior, and (2) produce polymers with highly controlled tacticity. These features improve the uniformity and physical properties of the polymers produced.

A ‘living’ polymerization is a polymerization in which chain transfer and chain termination are absent. In a living polymerization, the degree of polymerization varies linearly with time: the chain length grows at a constant rate. ‘Living’ polymerization catalysts are highly desirable because they offer excellent control over the forming polymer. The polymers produced by such a polymerization have uniform
molecular weights. The polymer molecular weight is measured in two ways: $M_n$, the number average molecular weight, counts the number of molecules at each weight ($M_n = \Sigma N_i M_i / \Sigma N_i$). $M_w$, the weight average molecular weight, measures the weight fraction of each species times its molecular weight ($M_w = \Sigma N_i M_i^2 / \Sigma N_i M_i$). The ratio $M_w/M_n$ is the polydispersity, and is often defined as less than 1.2 for a living polymerization. Living polymerization catalysts have the ability to produce block copolymers: they can start off polymerizing ethylene, for example, and then when propylene gas is introduced, they can switch to polymerizing polypropylene. When the reaction is quenched, there will be a ‘block’ of polyethylene and a ‘block’ of polypropylene in the same chain.

The tacticity of a polymer is the relative stereochemistry of the adjacent chiral centers in the polymer backbone. The degree of tacticity measures how much of the carbon chain displays a regular pattern. The tacticity of a polymer can be determined by the distribution of peaks in its $^{13}$C NMR spectrum. Polymer tacticity is important, because it is related to the polymer’s physical properties, such as crystallinity, strength, elongation, modulus, toughness, melting point, and solubility. Polyethylene is not affected by tacticity, because the polymer chain has no substituents on it. Polypropylene is a long carbon chain with a methyl substituent bonded to every other carbon (assuming that there are no regioerrors in the polymerization). It can be isotactic, syndiotactic, or atactic. Isotactic polypropylene has all of its methyl groups on one side of the chain. A polypropylene chain five carbons long with the three methyl groups on the same side of the chain is known as an $mm$ triad, where $m$ stands for meso. Syndiotactic polypropylene has alternating methyl groups. A
polypropylene chain five carbons long with the three methyl groups on opposite sides of the chain is known as an *rr* triad, where *r* stands for *racemo*. In atactic polypropylene, the methyl groups do not have any pattern.

Figure 4. Isotactic, syndiotactic, and atactic polypropylene.

**Titanium FI Catalysts**

The research of our group at Wesleyan has been focused on the family of post-metallocene catalysts called titanium FI catalysts, invented by Fujita et al in 1998. Centered about a titanium (Ti) atom, Ti-FI catalysts have two chelated, phenoxy-imine ligands. These single-site, homogeneous catalysts catalyze highly active, living polymerizations of ethylene and propylene when combined with cocatalyst MAO. The polypropylene produced by Ti-FI catalysts is highly syndiotactic. Our goal is to modify these catalysts for use in industrial polymerizations.
The Fujita group designed the FI catalysts for high activity by strategically choosing and arranging the ligands’ heteroatoms and bulky substituents. Assuming that a catalyst’s ligands play an active, electron-exchanging role in the olefin polymerization, the Fujita group decided to use phenoxy-imine ligands for their high-activity catalyst. Phenoxy-imines have O and N heteroatoms that can withdraw electrons from the metal center during coordination of the monomer, and can donate electrons to the metal center during insertion. The Fujita group designed their ligand to have a bulky substituent ortho to the phenoxy-oxygen in order to sterically protect the O from electrophilic attack by Lewis acids, as well as to promote ion separation between the cationic metal center and the anionic cocatalyst. They also determined that a small substituent on the imine carbon was important for high activity, because it would leave space for polymer growth.¹

Coates et al. discovered that the fluorination of the ligands affects whether or not titanium FI catalysts demonstrate living behavior. The catalyst is only ‘living’ when the aniline of the ligand has fluorines ortho to the –NH₂ group. Coates et al. synthesized a library of catalysts with ortho- and non-ortho-fluorinated ligands. They

Figure 5. One of the Ti-FI catalysts.
found that the living catalysts had much higher activities than the nonliving catalysts. The Coates group also made some heteroligand catalysts: catalysts with two different ligands attached to the metal center. Their most interesting results were obtained from catalysts that combined one ‘living’ ligand and one ‘nonliving’ ligand. Instead of having activities in between those of the living and the nonliving catalysts, the heteroligand catalyst was actually more active than the ‘living’ homoligand catalysts by a factor of 4. The molecular weights of the polymers produced by the heteroligand catalysts were also unusually high. Our group has been using Coates’ synthesis to make both living homoligand catalysts, and living/nonliving heteroligand catalysts.

FI catalysts are C$_2$-symmetric: when they are rotated 180 degrees about an axis in the plane of the Cl and N substituents, the same molecule results. Usually, C$_2$-symmetric, migratory-insertion polymerization catalysts produce isotactic polypropylene, because the two coordination sites of a catalyst with C$_2$ symmetry are identical. Surprisingly, titanium FI catalysts produce highly syndiotactic polypropylene. Cavallo et al. modeled the system and accounted for this phenomenon by the fact that Ti-FI catalysts are chiral.
Figure 6. The $\Lambda$ and $\Delta$ catalyst complexes, and the $si$ and $re$ orientations of the monomer.

FL catalysts isomerize between the two chiralities: $\Lambda$ and $\Delta$. Propylene can be coordinated to the catalyst’s empty site in two different ways: the $re$ and $si$ orientations. Cavallo et al found that the $\Lambda$ stereocenter energetically favors coordinating the monomer in the $si$ orientation, and the $\Delta$ stereocenter energetically favors coordinating the monomer in the $re$ orientation. This is because for the opposite combinations, ($\Delta$ and $si$, $\Lambda$ and $re$) there is a steric interaction between the methyl group of the coordinated propylene and the $tert$-butyl and aromatic groups of the nearby ligand.

After coordination of the $si$- or $re$- oriented monomer, the catalyst inserts the monomer into the polymer chain, resulting in a $si$- or $re$- coordinated polymer chain. The $si$- or $re$- ending chain then induces a $\Lambda$ or $\Delta$ complex. Suppose that the polymer
chain is a $re$-ending chain. It will energetically favor the formation of a $\Lambda$ catalyst active site. The $\Lambda$ complex then will favor the coordination of a $si$-oriented monomer. The catalyst will insert the newly coordinated $si$-monomer into the chain, giving a $si$-ending chain which will induce the formation of a $\Delta$ active site. The $\Delta$ active site then will favor the coordination and insertion of a $re$-oriented monomer, and this process will continue. The alternating chirality of the catalyst’s active site results in syndiotactic polypropylene!^{20}

Clearly, Ti-FI catalysts could make a significant contribution to the catalytic polymerization industry today. They are remarkable because of their high activity, unique stereospecificity, low polydispersity, living behavior, comparatively high polymerization reaction temperature, and relatively straightforward synthesis. Ti-FI catalysts could potentially be used to make high performance polyethylene and polypropylene. However, in spite of these favorable properties, the Ti-FI catalysts cannot be used in industrial polymerization reactors. The reactors currently in use were designed for heterogeneous catalysts. Using a homogeneous catalyst in this type of reactor causes fouling. It is our group’s objective to immobilize these promising catalysts in order to make them usable in industry.

**Immobilizing Polymerization Catalysts**

One of the main goals in polymerization catalyst research today is to immobilize single-site homogeneous catalysts onto various solids. Typically, industry today uses gas- and slurry-phase reactors, which are designed for heterogeneous catalysts. Homogeneous catalysts cause “fouling” in these reactors: the formed
polymer is deposited at the reactor walls, which reduces the reactor’s efficiency and clogs its feed lines. Immobilizing, or supporting, the catalyst eliminates this problem. Immobilizing the catalyst also allows control of the morphology of the forming polymer: supported catalysts produce polymers that mimic the shape of the catalyst’s support. Immobilizing a catalyst also reduces the amount of cocatalyst MAO necessary for high activity. Important considerations for the immobilization of homogeneous catalysts are: the surface area and chemistry of the support, preventing leaching of the catalyst from the support, homogeneous distribution of the catalyst over the support, and good monomer access to the catalytic centers after the polymerization has begun. Ideally, an immobilized catalyst would retain its high activity, low molecular weight distribution and high stereoselectivity, would not foul industrial reactors, and would gain in morphological control. Unfortunately, because immobilized catalysts are such a different species from their homogeneous counterparts, immobilizing a catalyst often reduces its activity, and changes the qualities of the produced polymer.

Our group has been investigating two different methods of supporting our Ti-FI catalysts. The first method involves attaching a vinyl or an allyl functional group to one of the ligands of the catalyst, and then polymerizing this vinyl or allyl group with styrene. This would incorporate the catalyst into an insoluble polystyrene chain, and the polystyrene/catalyst compound could be used in a heterogeneous propylene polymerization. The second method involves immobilizing the Ti-FI catalyst onto
MAO-impregnated silica. Silica is a commonly used support; however, the Ti-FI catalysts in particular have not yet been immobilized on it.

**Self-Immobilizing Catalysts**

A self-immobilizing catalyst is a catalyst that has an olefin functional group attached to one of its ligands. When used in a polymerization, a self-immobilizing catalyst will not only polymerize the monomer, but it will copolymerize other catalyst molecules and incorporate them into the growing polymer chain. Because the polymer chain is insoluble, this process will generate a heterogeneous catalyst system.

![Figure 7. A self-immobilized catalyst.](image)

The advantage of making a self-immobilizing catalyst over supporting it on an inorganic material is that an active catalyst’s metal center is Lewis acidic, and often is reactive with an inorganic support. This reduces the supported catalyst’s activity. However, this problem is irrelevant in a self-immobilizing catalyst system.

Polymers produced by self-immobilizing catalysts have different properties than polymers produced by homogeneous catalysts. Tiny differences in a catalyst’s structure cause changes in the interactions between the catalyst and the cocatalyst, and the solvent. Alt et al. have found that self-immobilizing catalysts produce polyethylenes with evenly distributed ethyl branches. This gives the polymers higher tensile strength and clarity. Usually, to get this effect, a comonomer such as 1-butene
must be added to the polymerization reactor. Alt et al have successfully designed a self-immobilizing ansa-metallocene catalyst that is currently used to produce Linear Low Density Polyethylene (LLDPE) in slurry loop reactors.\textsuperscript{21}

Jin and Zhang have synthesized self-immobilizing zirconium and titanium FI catalysts by attaching allyl and allyloxy substituents to the imine section of the phenoxy-imine ligands.

![Figure 8. Three of the self-immobilizing catalysts synthesized by Jin and Zhang.](image)

They found that polyethylene produced by these self-immobilizing catalysts had much broader molecular weight distributions (3.5-19.2) compared to the free catalyst (<3.0). They also found that the position of the allyloxy group affected the activity of the catalyst. Catalysts with the allyloxy group \textit{meta} to the imine N had higher activities than catalysts with the allyloxy group \textit{para} to the imine N. Catalysts with titanium centers gave polymers with molecular weights 10 times higher than those with zirconium centers; however, the zirconium centered catalysts were at least 20 times more active. The morphology of the polymers produced by these self-
immobilizing catalysts was much improved: the polyethylene particles were spherical and of regular size. NMR showed that the polyethylene produced by this procedure, like that produced by Alt’s self-immobilizing metallocenes, had regularly spaced butyl branches.\textsuperscript{23}

Our group has been pursuing an approach similar to that of Jin and Zhang: we seek to attach a vinyl or allyl substituent to one of the phenoxy-imine ligands in order to make a self-immobilizing catalyst. The catalysts we synthesize, however, are heteroligand catalysts, where only one ligand has an allyl substituent. Also, we will be using the catalysts to polymerize propylene, rather than ethylene.

**Silica as a Support**

The most popular support for catalyst immobilization is silica, SiO\textsubscript{2}. There are many types of silica used for catalyst supports: granulated, spray-dried, MCM-41 lattices, and more.\textsuperscript{24-25} The silica preparation method determines the shape and pore size of the silica particles, which in turn will determine the morphology of the polymer formed. The surface of silica is saturated with silanol groups, and is thus very hydrophilic: it easily adsorbs moisture from the air. Water can be desorbed by raising the temperature to 100-200°C. After calcination at this temperature, the number of OH groups (silanols) per nm\textsuperscript{2} is about 5.5. The density and number of silanols decreases as the calcination temperature is increased. When calcined at 600-800°C, the silica is almost completely dehydroxylated: there is only one OH group per nm\textsuperscript{2}.\textsuperscript{24}
Figure 9. Different types of silanols.

There are many ways to attach a catalyst to a silica support. Directly reacting the catalyst with the silica does not work because the silica support’s silanol groups decompose the catalyst. A common procedure for supporting a catalyst on silica is calcination of the silica, followed by impregnation of the silica with MAO, and subsequent addition of the catalyst. Catalysts have also been covalently bonded to the silica, which is an effective way of preventing leaching.²⁴

Fink et al. did an extensive study on polymerization with a silica-supported metallocene catalyst and examined the morphology of the resulting polymer. The silica support fragments during the polymerization. During the first few minutes of the polymerization reaction, the most accessible catalytic sites begin polymerizing the olefin, and a polymer layer forms around the outside of the particle. This layer causes a diffusion problem for the monomer, and the rate of polymerization slows for a period of time, which Fink calls the ‘induction period.’ During this period, the slowly forming polymer begins to push deep in the pores of the silica. The forming polymer puts ‘hydraulic’ forces on the inside of the pores, causing the support to fragment. When the particle breaks, it frees up new active sites. As a result, activity increases, and reaches a maximum when the support is completely fragmented and evenly
distributed in the polymer matrix. Poor choice of silica preparation and pore size can result in unevenly fragmented silica trapped in the polymer, which makes the polymer useless. The fragmentation process is the key to the polymer particles mirroring the morphology of the support. To show this, Fink et al. created a system in which the catalyst active centers were attached exclusively to the outside of the particle: there were none in the pores. Fragmentation did not occur, and the resulting polymer had an uncontrolled morphology.\textsuperscript{24}

Chadwick et al. were successful in immobilizing a zirconocene catalyst onto silica. In their study, they used two different types of silica gel and two different calcination temperatures. They also used three different methods of impregnation: (1) contacting the silica with the MAO before adding the catalyst, and stirring this mixture at room temperature, (2) contacting the silica with the MAO before adding the catalyst, and stirring the mixture at elevated temperatures, and (3), preactivating the catalyst with MAO before adding the silica. The second method was more effective than the first: raising the temperature of the immobilization reaction gave a more homogeneous distribution of aluminum throughout the support, which consequently gave higher catalytic activities. The third method, however, gave the highest activities, best morphology, and the least leaching. Because the immobilized catalyst produced polymers with narrow molecular weight distributions, the Chadwick group concluded that it did retain its single-center behavior. They achieved higher molecular weight polymers with the immobilized catalyst than with the free catalyst, perhaps because there was less aluminum present making chain transfer to Al less likely. Chadwick et al. also determined that lower silica calcination
temperatures (250°C) gave higher activities than higher silica calcination temperatures (600°C).\textsuperscript{26}

Our group has been using Chadwick’s second and third procedures for immobilizing our Ti-FI catalysts onto silica. However, we have included an extra control step, to check for leaching of the catalyst.

**Objectives**

The Ti-FI catalysts have great potential to be used in industry because of their high activity, unique stereospecificity, and living behavior. However, they must be immobilized onto some type of solid before they can be used in industry. Hoping to capitalize on the work done by Alt, Jin, and Chadwick, we have used three different methods to immobilize our Ti-FI catalysts.

A phenoxy-imine ligand with a vinyl functional group \textit{para} to the phenol was synthesized. Attempts made to attach this ligand to a heteroligand catalyst, using Coates’ synthesis, were unsuccessful. The ligand was polymerized with polystyrene in order to incorporate it into the chain, and thus immobilize it. However, attempts to attach this immobilized ligand to a catalyst were unsuccessful.

A phenoxy-imine ligand with an allyl functional group \textit{para} to the imine N was prepared using a Claisen rearrangement. This ligand was successfully attached to a heteroligand catalyst using Coates’ synthesis. The catalyst was used to polymerize polypropylene, and the polypropylene produced was analyzed for evidence of immobilization of the catalyst. Attempts were made to polymerize the allyl ligand with polystyrene in order to incorporate it into the polystyrene chain.
Two different Ti-FI catalysts, a homoligand catalyst and a heteroligand catalyst, were immobilized onto silica impregnated with MAO using two of Chadwick’s methods. In the first method, the silica was contacted with MAO before the addition of the catalyst at an elevated temperature. In the second method, the catalyst and MAO were contacted before adding them to the silica. A control step was added to the Chadwick procedure in order to check for leaching of the catalyst. These compounds were used to polymerize polypropylene.

The $^1$H and $^{13}$C NMR spectra, and the GPC data of the polymers produced by the different immobilized catalysts were compared to the NMR and GPC data of polymers produced by homogeneous homoligand and heteroligand catalysts. Thus, these homogeneous catalysts served as the control for this experiment.

Herein are presented the syntheses of the two homogeneous control catalysts and the data for the polypropylene they produced; the synthesis of the vinyl ligand and the results of its polystyrene incorporation; the synthesis of the allyl catalyst, the results of its polystyrene incorporation, and the data for the polypropylene it produced; and the data for the polypropylene produced by the catalysts immobilized on silica.
Results

I. The Control Experiment:
Synthesis of Homogeneous Catalysts, and Data for the Resulting Polypropylene.

In this experiment, three different methods of immobilizing the homogeneous Ti-FI catalysts were attempted. To judge whether an immobilization was successful, the polymers produced by the immobilized catalysts were compared to the polymers produced by the homogeneous catalysts. Thus, the homogeneous catalysts' polymers served as a control.

Two different control catalysts were synthesized. The homoligand catalyst, compound 3, had two identical ligands (compound 1) attached to the titanium center. The heteroligand catalyst, compound 5, had two different ligands (compounds 1 and 2) attached to the titanium center. The syntheses of the homoligand and heteroligand homogeneous catalysts are presented in eqs. 1-5.

Eq. 1
Eq. 2

\[
\begin{align*}
\text{cat. formic acid} & \quad \text{ethanol reflux} \\
\begin{array}{c}
\text{t-Bu} \\
\text{OH} \\
\text{t-Bu} \\
\text{t-Bu}
\end{array}
\quad & \\
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{F} \\
\text{NH}_2
\end{array}
\quad & \\
\begin{array}{c}
\text{t-Bu} \\
\text{OH}
\end{array}
\end{align*}
\]

Eq. 3

1. nBuLi, add at -78 C, warm to r. t. stir 15 min
2. Cool to -78 C, add 1/2 mol equiv TiCl₄, slowly warm to r. t. stir 6h.

Eq. 4

\[
\text{TiCl}_4(\text{THF})_2 \\
\text{THF, add ligand at -78 C}
\]
1. Compound 1 deprotonated with nBuLi in ether
2. Add soln to 4 in ether at -78°C, stir at r.t. 6h
Compound 1, the ligand $L^1$, was synthesized by heating 3,5-di-$t$-butyl-2-hydroxybenzaldehyde and pentafluoroaniline with $P_2O_5$, a catalytic amount of $p$-toluenesulfonic acid, and no solvent. These harsh reaction conditions were necessary for the synthesis of ligands with four and five fluorines attached to the aniline, because the electron-withdrawing fluorines reduce the nucleophilicity of the aniline N. Compound 1 exhibits the $^1H$ NMR spectrum shown below.

![Figure 10. $^1H$ NMR spectrum of 1 in CDCl$_3$.](image)
Compound 2, the ligand $L^2$, was synthesized by refluxing 3,5-tert-butyl-2-hydroxybenzaldehyde with 3,5-difluoroaniline in ethanol with a catalytic amount of formic acid. These reaction conditions could be used for the synthesis of ligands with three or fewer fluorines attached to the aniline. Compound 2 exhibits the $^1$H NMR spectrum shown below.

![Figure 11. $^1$H NMR spectrum of compound 2 in CDCl$_3$.](image-url)
Compound 3, the homoligand catalyst \((L^1)_2\text{TiCl}_2\), where \(L^1\) is compound 1, exhibits the \(^1H\) NMR spectrum shown below. All manipulations were carried out under nitrogen atmosphere, because the product is air-sensitive. Ligand 1 was deprotonated with n-butyl lithium, and then was added to an ether solution of titanium tetrachloride at -78°C. The reaction was stirred at room temperature for 6 hours, and after filtration, yielded a red-brown powder.

![Chemical Structure](image)

**Figure 12.** \(^1H\) NMR spectrum of compound 3, the homoligand catalyst \((L^1)_2\text{TiCl}_2\), in \(C_6D_6\).
Compound 4, the complex $L^2\text{TiCl}_3$(THF), where $L^2$ is compound 2, was synthesized under nitrogen atmosphere by combining $\text{TiCl}_4$(THF)$_2$ and compound 2. This complex is the heteroligand catalyst precursor. It exhibits the $^1\text{H}$ NMR spectrum shown below.

Figure 13. $^1\text{H}$ NMR spectrum of Compound 4, $L^2\text{TiCl}_3$(THF), in $\text{C}_6\text{D}_6$. 
Compound 5, the heteroligand catalyst \( \text{L}^1\text{L}^2\text{TiCl}_2 \) where \( \text{L}^1 \) is compound 1 and \( \text{L}^2 \) is compound 2, was synthesized under nitrogen atmosphere from compounds 1 and 4. 1 was deprotonated with n-butyllithium before it was added to an ether solution of 4 at -78°C. The mixture was stirred for 6 hours, and after filtration, yielded a red-brown powder.

**Figure 14.** 1H NMR spectrum of Compound 5, the heteroligand catalyst \( \text{L}^1\text{L}^2\text{TiCl}_2 \), in C₆D₆.
Toluene solutions of compounds 3 and 5, the homoligand and heteroligand catalysts, were each combined with MAO at 0°C to polymerize propylene as in Eq. 6. The polypropylene produced by both of these catalysts was highly syndiotactic. The $^1$H and $^{13}$C NMR spectra of syndiotactic polypropylene produced by the heteroligand catalyst are displayed below. The spectra of the polypropylene produced by the homoligand catalyst are identical to these. The spectra of the polymers produced by immobilized catalysts later in this experiment were compared to these control spectra.

Eq. 6

Figure 15. $^1$H NMR spectrum of syndiotactic polypropylene produced by compound 5, the heteroligand catalyst. (1,1,2,2-tetrachloroethane-d2)
Figure 16. $^{13}$C NMR spectrum of syndiotactic polypropylene produced by compound 5, the heteroligand catalyst. (1,1,2,2-tetrachloroethane)

GPC spectra of the polypropylene produced by the two catalysts were taken. The results are reported in Table 1. These control data were compared to GPC data of polypropylene produced by immobilized catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (g)</th>
<th>Mn</th>
<th>Mw</th>
<th>Mp</th>
<th>PDI</th>
<th>TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>L$^{1}$TiCl$_2$</td>
<td>1.5</td>
<td>95,000</td>
<td>127,000</td>
<td>109,000</td>
<td>1.34</td>
<td>360</td>
</tr>
<tr>
<td>L$^{1}$L$^{2}$TiCl$_2$</td>
<td>7.3</td>
<td>114,000</td>
<td>147,000</td>
<td>138,000</td>
<td>1.29</td>
<td>1683</td>
</tr>
</tbody>
</table>

Table 1. GPC data of polypropylene produced by compounds 3 and 5.
II. The Self-Immobilizing Vinyl Ligand Catalyst

Our first plan to synthesize a self-immobilizing catalyst involved attaching a vinyl substituent to a phenoxy-imine ligand, and then attaching the ligand to a heteroligand homogeneous catalyst. This ‘vinyl ligand catalyst’ would be used to polymerize styrene. It would incorporate itself, via the vinyl substituent, into the polystyrene chain, and then the polystyrene/catalyst compound could be used as a heterogeneous catalyst to polymerize propylene.

The synthetic route to make the ‘vinyl ligand catalyst’ is shown in eqs. 7-13. All of the synthetic steps worked except for the very last one.

Eq. 7

\[
\begin{array}{c}
\text{t-Bu} \quad \text{OH} \\
\text{t-Bu} \quad \text{OH} \\
\text{t-Bu} \quad \text{CHO} \\
\text{t-Bu} \quad \text{Cl}
\end{array}
\quad \text{KSF-Et}_3\text{N, Toluene, 100°C}
\quad \Rightarrow
\begin{array}{c}
\text{t-Bu} \quad \text{OH} \\
\text{t-Bu} \quad \text{CHO} \\
\text{t-Bu} \quad \text{Cl}
\end{array}
\]

Eq. 8

\[
\begin{array}{c}
\text{t-Bu} \quad \text{OH} \\
\text{OH} \\
\text{t-Bu} \quad \text{CHO}
\end{array}
\quad \text{(CH}_2\text{O)}_n
\quad \Rightarrow
\begin{array}{c}
\text{t-Bu} \quad \text{OH} \\
\text{t-Bu} \quad \text{CHO}
\end{array}
\quad \text{HCl, r.t. 4 days}
\]
Eq. 9

\[
\begin{align*}
7 & \quad \xrightarrow{\text{PPh}_3, \text{benzene, reflux 1h}} \quad 8 \\
& \quad \text{t-Bu} \quad \text{CHO} \quad \text{OH} \quad \text{Cl} \\
\end{align*}
\]

Eq. 10

\[
\begin{align*}
8 & \quad \xrightarrow{\text{HCHO aq. NaOH}} \quad 9 \\
& \quad \text{t-Bu} \quad \text{CHO} \quad \text{OH} \quad \text{CHO} \\
\end{align*}
\]

Eq. 11

\[
\begin{align*}
9 & \quad \xrightarrow{\text{cat. formic acid ethanol reflux}} \quad 10 \\
& \quad \text{t-Bu} \quad \text{OH} \quad \text{NH}_2 \quad \text{F} \\
\end{align*}
\]
Eq. 12

1. Add TiCl$_4$(THF)$_2$ in THF at -78°C to 10.
2. Stir for 6 hours at room temperature.

Eq. 13

1. Add nBuLi to 1 at -78°C in ether, warm to room temperature.
2. Add solution of deprotonated 1 to 11 at -78°C, warm to room temperature, stir for 6 hours.

Vinyl ligand catalyst
Compound 6, 3-\textit{tert}-butylsalicylaldehyde, was synthesized from 2-\textit{tert}-butylphenol and formaldehyde using KSF montmorillonite as a clay catalyst. This reaction produced 3-\textit{tert}-butylsalicylaldehyde in high yield when small amounts were being made, but when the reaction was scaled up, the yields decreased.

\[ \text{t-Bu} \quad \text{OH} \quad \text{C} \quad \text{H} \]

\textbf{Figure 17.} $^1$H NMR of 6 (CDCl$_3$)
Compound 7, 3-tert-butyl-4-chloromethylsalicylaldehyde, was synthesized by stirring 6 and formaldehyde in concentrated HCl. Flash chromatography was used to purify the compound.

Figure 18. $^1$H NMR of compound 7 in CDCl$_3$. 
Compound 8 was synthesized by stirring 7 with triphenylphosphine in toluene until the solid salt precipitated out of solution. This first step of the alkene-forming Wittig reaction produced 8, the triphenylphosphine salt of 4-chloromethylsalicylaldehyde, in high yield.

Figure 19. $^1$H NMR of PPh$_3$ salt 8 in CDCl$_3$
Compound 9, 3-tert-butyl-2-hydroxy-5-vinylbenzaldehyde, was synthesized by combining compound 8 with formaldehyde. This second step of the Wittig reaction produced compound 9 in very low yield.

Figure 20. $^1$H NMR of compound 9 in CDCl$_3$. 
Compound 10, the vinyl ligand L₃, was synthesized from 9 and 3,5-difluoroaniline using the ethanol/formic acid method.

Figure 21. ¹H NMR spectrum of vinyl ligand 10 in CDCl₃.
Compound 11, the \( \text{L}^3\text{TiCl}_3\text{THF} \) complex where \( \text{L}^3 \) is vinyl ligand 10, was synthesized by reacting 10 with TiCl(THF)\(_2\) under a nitrogen atmosphere.

![Compound 11](image)

**Figure 22.** \(^1\text{H} \) NMR spectrum of compound 11, (vinyl ligand)TiCl\(_3\)(THF) in \( \text{C}_6\text{D}_6 \)

Attempts were made to attach a second ligand to compound 11; however, none of them worked. Attempts were also made to attach the vinyl ligand 10 to compound 4, but that did not work either.
As an attempt to immobilize the ligand before attaching it to a catalyst, the vinyl ligand, compound 10, was polymerized in a 20:1 ratio with styrene, using azobisisobutyronitrile (AIBN) as a radical initiator. Some incorporation of the ligand into the polymer chain was observed.

![Diagram of polymerization reaction involving compound 10 and styrene]

**Figure 23.** $^1$H NMR spectrum of compound 10 incorporated into polystyrene.
III. The Self-Immobilizing Allyl Ligand Catalyst

Our second plan to make a self-immobilizing catalyst involved attaching an allyl functional group to one of the ligands of a homogeneous, heteroligand catalyst. Attempts were made to incorporate this allyl ligand L⁴ (compound 14) into a polystyrene chain. No incorporation was observed. The ‘allyl catalyst’ 15 was used to polymerize polypropylene without first attaching it to polystyrene. The ¹H and ¹³C NMR spectra and GPC data of the polymers obtained were recorded. The synthetic route to make the allyl ligand and the allyl ligand catalyst is shown in equations 14-17.

Eq. 14

\[
\text{NH}_2 \quad \text{HN} \\
\begin{array}{c}
\text{2 equiv} \\
\text{DMF, } K_2\text{CO}_3, \text{ 0 C}
\end{array} \\
\rightarrow \quad \text{1 equiv allyl bromide} \\
\text{12}
\]

Eq. 15

\[
\begin{array}{c}
\text{HN} \\
\text{Claisen rearrangement} \\
\text{2 ZnCl}_2, \text{xylene reflux} \\
\end{array} \quad \text{12} \\
\rightarrow \quad \text{13}
\]

Eq. 16

\[
\begin{array}{c}
\text{13} \\
\text{cat. formic acid, ethanol reflux}
\end{array} \quad \text{14}
\]
Eq. 17

1. deprotonate with nBuLi
2. $\text{L}_2\text{TiCl}_3\text{THF}$, ether, add at -78°C
Compound 12, N-allyl-2,6-xylidine, exhibits the $^1$H NMR spectrum shown below. The synthetic plan to make this compound was an $S_N2$ reaction of 2,6-xylidine with allyl bromide. The substitution occurred too readily at high temperatures, resulting in doubly allylated xylidines. Even when the reaction was to be carried out at 0°C, some doubly allylated xylidine resulted, and the products had to be separated by column chromatography.

Figure 24. N-allyl-2,6-xylidine 12 in CDCl$_3$. 
Compound 13 exhibits the $^1$H NMR spectrum shown below. This compound was synthesized by stirring 12 with zinc chloride. This resulted in a Claisen rearrangement, giving compound 13, 4-allyl-2,6-xylidine, with 100% conversion. The multiplets at $\delta$1.0 and $\delta$1.4 ppm are due to the hexane solvent.

Figure 25. $^1$H NMR spectrum of 4-allyl-2,6-xylidine 13 in CDCl$_3$. 
Compound 14, the allyl ligand $L^4$, was synthesized by combining 13 with 3,5-di-tert-butylsalicylaldehyde using the ethanol/formic acid method. It exhibits the $^1H$ NMR spectrum shown below.

Figure 26. $^1H$ NMR spectrum of compound 14, the allyl ligand $L^4$, in CDCl$_3$. 
Compound 15, the catalyst \( \text{L}^2\text{L}^4\text{TiCl}_2 \) where \( \text{L}^2 \) is compound 2 and \( \text{L}^4 \) is compound 14, was synthesized by deprotonating 14 with n-butyllithium, and adding it at \(-78^\circ\text{C}\) to compound 4. After stirring the solution for 6 hours at room temperature, a red-brown powder was collected.

![Figure 27. \(^1\text{H} \) NMR spectrum of Compound 15, \( \text{L}^2\text{L}^4\text{TiCl}_2 \), in C_6D_6.](image-url)
Compound 14, the allyl ligand, was combined with styrene and azobisisobutyronitrile (AIBN), a radical activator, as in Eq. 18, in order to incorporate the ligand into a polystyrene chain. A control radical polymerization of styrene was carried out, as in Eq. 19. The $^1$H NMR spectra of the polymers produced by these two processes were identical; thus, no incorporation was observed.

**Eq. 18**

![Chemical structure of Eq. 18]

**Figure 28.** $^1$H NMR spectrum of products from the radical polymerization of styrene and the allyl ligand 14. (acetone-d6)
Eq. 19

\[ \text{AIBN} \rightarrow \text{polystyrene} \]

Figure 29. \(^1\)H NMR spectrum of polystyrene from a radical polymerization. (acetone-d6)
A toluene solution of the allyl catalyst, compound 15, was combined with MAO in toluene at 0°C to polymerize propylene. The polypropylene produced by the allyl ligand catalyst gave the $^1$H and $^{13}$C NMR spectra, and GPC data below.

Figure 30. $^1$H NMR of polypropylene produced by allyl ligand catalyst 15 (1,1,2,2-tetrachloroethane-d2)
**Figure 31.** $^{13}$C NMR of polypropylene produced by allyl ligand catalyst 15 (1,1,2,2-tetrachloroethane-d2)


d| Catalyst | Yield (g) | Mn | Mw | Mp | PDI | TOF |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>L2L*TiCl2</td>
<td>1.25</td>
<td>4,800</td>
<td>12,000</td>
<td>10,200</td>
<td>2.51</td>
<td>300</td>
</tr>
</tbody>
</table>

**Table 2.** GPC data of the polypropylene produced by compound 15.
IV. Immobilizing the Catalyst on Silica

Our plan for this part of the experiment for the most part followed the procedures of Chadwick et al. for the immobilization of a catalyst on MAO/silica; however, we added a control step to check for leaching. The two procedures were used to immobilize both of the control catalysts (compounds 3 and 5).

The first procedure involved contacting the silica and MAO at an elevated temperature before adding the catalyst. The control step involved stirring the immobilized catalyst in only toluene or a mixture of toluene and MAO for 3 hours in order to mimic polymerization conditions. The solid and liquid were separated, and both fractions were used in a polymerization. The solid fractions from the immobilizations of 3 and 5 polymerized polypropylene and gave the $^1$H NMR spectra below. The singlet at $\delta$1.5 ppm is due to water.

![Figure 32. $^1$H NMR spectrum the polypropylene produced by the homoligand catalyst 3 immobilized using the first method. (1,1,2,2-tetrachloroethane-d2)]
Figure 33. $^1$H NMR spectrum of the polypropylene produced by the heteroligand catalyst 5 immobilized using the first method. (1,1,2,2-tetrachloroethane-d2)
The second procedure involved contacting the catalyst and MAO solutions before adding them to a silica slurry. The mixture was stirred and the solvent was evaporated. In order to mimic polymerization conditions, the immobilized catalyst was stirred in toluene or in a mixture of toluene and MAO for 3 hours. The solid and liquid were separated, and both fractions were used in a polymerization. The solid fraction produced polypropylene. The $^1$H NMR spectrum of the polypropylene produced by compound 3 immobilized on silica is shown below. The polypropylene produced by the heteroligand catalyst 5 immobilized onto silica did not give a clean spectrum; it is not presented in this paper. The singlet at $\delta 1.5$ ppm is due to water.

Figure 34. $^1$H NMR spectrum of polypropylene produced by the homoligand catalyst 3 immobilized on silica/MAO using method 2. (1,1,2,2-tetrachloroethane)
The liquid fractions obtained from the control steps of both of the immobilization methods did not give polypropylene. Usually, no product formed during the polymerizations catalyzed by the liquid fractions. Three polymerizations, two catalyzed by the liquid fraction from method 1, (one of which was stirred with only toluene; the other was stirred with toluene and MAO) and one catalyzed by the liquid fractions from method 2, (which included toluene and MAO) gave a very small amount of white product which was sent to Atlantic Microlabs for elemental analysis. The results are shown below. The C:H ratio for polypropylene is %C = 85.6% and %H = 14.4%.

<table>
<thead>
<tr>
<th>Element</th>
<th>Polypropylene</th>
<th>Method 1, with MAO</th>
<th>Method 1, no MAO</th>
<th>Method 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>85.6%</td>
<td>2.77</td>
<td>83.26</td>
<td>0.42</td>
</tr>
<tr>
<td>H</td>
<td>14.4%</td>
<td>4.77</td>
<td>14.36</td>
<td>4.62</td>
</tr>
</tbody>
</table>

Table 4. Elemental analysis of the white solids produced by polymerizations with the liquid fraction of the control step.

GPC spectra were taken of all of the polymers produced by the silica-immobilized catalysts. The data are shown in Table 3. The TOF was not calculated, because the amount of catalyst added to the reaction was not quantified in this experiment.

<table>
<thead>
<tr>
<th>Catalyst and Method</th>
<th>Yield (g)</th>
<th>Mn</th>
<th>Mw</th>
<th>Mp</th>
<th>PDI</th>
<th>MAO added?</th>
</tr>
</thead>
<tbody>
<tr>
<td>5, method 1</td>
<td>0.10</td>
<td>118,000</td>
<td>220,000</td>
<td>302,000</td>
<td>1.86</td>
<td>no</td>
</tr>
<tr>
<td>3, method 1</td>
<td>0.07</td>
<td>105,000</td>
<td>260,000</td>
<td>314,000</td>
<td>2.48</td>
<td>no</td>
</tr>
<tr>
<td>3, method 2</td>
<td>0.15</td>
<td>188,000</td>
<td>274,000</td>
<td>307,000</td>
<td>1.45</td>
<td>no</td>
</tr>
<tr>
<td>3, method 1</td>
<td>0.14</td>
<td>45,400</td>
<td>134,000</td>
<td>106,000</td>
<td>2.95</td>
<td>no</td>
</tr>
<tr>
<td>3, method 1</td>
<td>0.18</td>
<td>554,000</td>
<td>681,000</td>
<td>772,000</td>
<td>1.23</td>
<td>yes</td>
</tr>
<tr>
<td>3, method 2</td>
<td>0.02</td>
<td>121,000</td>
<td>219,000</td>
<td>256,000</td>
<td>1.81</td>
<td>yes</td>
</tr>
<tr>
<td>5, method 2</td>
<td>0.05</td>
<td>365,000</td>
<td>484,000</td>
<td>507,000</td>
<td>1.33</td>
<td>no</td>
</tr>
</tbody>
</table>

Table 3. GPC data for catalysts immobilized onto silica. Under Catalyst and Method, the numbers 3 and 5 refer to the homoligand and heteroligand catalysts, respectively.
Discussion

I. The Control: Homoligand and Heteroligand Homogeneous Catalysts

The homoligand catalyst (L\textsuperscript{1})\textsubscript{2}TiCl\textsubscript{2} and the heteroligand catalyst L\textsuperscript{1}L\textsuperscript{2}TiCl\textsubscript{2}, where L\textsuperscript{1} is compound 1 and L\textsuperscript{2} is compound 2, were successfully synthesized using Coates’ procedure. The disappearance of the \textsuperscript{1}H NMR hydroxyl peak at δ13 ppm and the relocation of the imine peak from δ8.5 to δ7.5 ppm when comparing the ligand spectra to the product spectra (Figures 10-14) indicated that the ligands had in fact been attached to the titanium metal center. Both of these control catalysts were used in combination with MAO to catalyze homogeneous, 3-hour propylene polymerizations at 0°C.

The polymerizations catalyzed by these two catalysts gave polypropylenes that were highly syndiotactic, according to the \textsuperscript{1}H and \textsuperscript{13}C NMR spectra (Figures 15 and 16). In the \textsuperscript{1}H NMR spectrum, the doublet at δ0.9 ppm corresponds to the methyl protons; the triplet at δ1.2 ppm corresponds to the methylenes; and the multiplet at δ1.7 ppm corresponds to the methines. In the \textsuperscript{13}C NMR spectrum, the peak at δ20 ppm corresponds to the methyl carbons; the peak at δ28.5 ppm corresponds to the methylenes; and the peak at δ46 ppm corresponds to the methines. As shown in Figures 35 and 36, isotactic and atactic polypropylene give peaks at different shifts in both the \textsuperscript{1}H and \textsuperscript{13}C NMR spectra; none of these peaks were observable in the obtained spectra. Thus, the control catalysts were experimentally proven to produce highly syndiotactic polypropylene, in agreement with the literature.
Figure 35. $^{13}$C NMR spectrum of the methyl peaks of isotactic, atactic, and syndiotactic polypropylene.\textsuperscript{27}

Figure 36. $^1$H NMR spectrum of isotactic and syndiotactic polypropylene.\textsuperscript{27}
The polypropylenes produced by the two control catalysts were measured by GPC in ortho-dichlorobenzene at 130°C, and the data was compared to a calibration curve created using polymethylmethacrylate (PMMA) standards. According to the GPC data, the polymers produced by compounds 3 and 5 had $M_n$ values of 95,000 and 114,000 Daltons, respectively. These high molecular weights indicate a high degree of polymerization. These experimental $M_n$ values are three times higher than the $M_n$ value of 28,000 obtained by Coates et al. for the catalyst $(L^1)\text{TiCl}_2$.\textsuperscript{19} This discrepancy probably results from the different calibration standards used: the Coates group calibrated their samples against polyethylene standards. Since polypropylene is chemically more similar to polyethylene than PMMA, which has heteroatom substituents, the Coates group’s values are probably more accurate. The GPC data also showed that the polydispersities (PDI) of the polypropylenes produced by the control catalysts 3 and 5 were 1.34 and 1.29, respectively. Since the PDI is a ratio of $M_w/M_n$, these measured values should be accurate despite the PMMA calibration standards used. The Coates group obtained polymers with PDIs of about 1.06 with the homoligand catalyst, and polymers with PDIs of 1.32 with the heteroligand catalyst.\textsuperscript{19} The experimental values are comparable to these. These low PDI values show that both of the catalysts displayed close to living behavior in these control polymerizations.

The turnover frequency (TOF) of a catalyst is a measure of the activity of a catalyst, and is calculated by dividing the number of moles of propylene reacted by the moles of catalyst used, and by the reaction time, in hours.

$$\text{TOF} = \frac{\text{mol propylene}}{\text{mol catalyst}(\text{hr})}$$
The homoligand catalyst \((L^1)_2TiCl_2\) had a TOF of 360, which is higher than the Coates group’s value of 221. The heteroligand catalyst \(L^1L^2TiCl_2\) had a TOF of about 1600, compared to the Coates group’s value of 1400. According to Coates et al., the heteroligand catalyst’s extreme improvement in activity over the homoligand catalyst is due to the fact that it has one ‘living’ and one ‘nonliving’ ligand.\(^{19}\)

The NMR and GPC data of the polypropylenes produced by the control catalysts showed that indeed, as claimed in the literature, the homogeneous Ti-FI catalysts are highly active, display living behavior, and give highly syndiotactic polypropylene. The NMR and GPC results for the polypropylene produced by these control catalysts were compared to data of the polypropylene produced by the immobilized catalysts.

II. The Self-Immobilizing Vinyl Ligand Catalyst

All of the steps in the synthesis of the vinyl ligand catalyst were successful, except for the very last one. The syntheses of salicyl aldehyde 6 and chloromethyl salicylaraldehyde 7 gave high yields, and the products were separated from the starting materials using flash chromatography. The first step of the Wittig reaction, the formation of triphenyl phosphonium salt 8, gave good conversion and precipitated out of the solution cleanly. The second step of the Wittig reaction gave the vinylsalicylaraldehyde 9 in very low yield. The small amount of 9 recovered was used to make the vinyl ligand 10, and this ligand was successfully attached to the \(\text{TiCl}_4(\text{THF})_2\) complex to obtain compound 11. However, the second ligand was never successfully attached to compound 11 to make the vinyl ligand catalyst. After each
attempt at this last step of the synthesis, a small amount of white solid was collected on the fritted filter disk, rather than the expected red-brown powder. Because this white solid was not soluble in the NMR solvents, no characterization of the compound was possible. It was hypothesized that this solid was a polymer of the vinyl ligand 10; the styrene moiety of this compound is easily polymerized. Because of this assumption, it was decided that a less active olefin should be attached to the catalyst: this led to the synthesis of the allyl ligand catalyst in the next section.

Since the styrene moiety of the vinyl ligand was deemed too active, an attempt was made to pre-immobilize the ligand by incorporating it into a polystyrene chain. The vinyl group would no longer be able to polymerize during the catalyst synthesis reaction. The vinyl ligand 10 was polymerized in a 20:1 ratio with styrene using azobisisobutyronitrile (AIBN) as a radical initiator. The $^1$H NMR of the product (Figure 23) showed that there was some free ligand left in the NMR sample. The doublets at δ5.3 ppm and δ5.8 ppm correspond to the protons of the ligand 10’s unreacted vinyl substituent. The broad peak at δ8.2 ppm corresponds to the imine proton of 10. The integration of this peak is much larger than the integrations of the unreacted vinyl protons. This shows that there is more ligand in the sample than just free ligand: some of it has been incorporated into the polystyrene chain. It is difficult to determine the percent incorporation because of the complexity of the polystyrene NMR spectrum.

An attempt was made to attach the polystyrene-immobilized ligand to the catalyst precursor 4; however, the polystyrene/ligand compound would not go into solution, and no product was obtained.
III. The Self-Immobilizing Allyl Ligand Catalyst

A Ti-FI catalyst with an allyl group attached to one of the ligands was successfully synthesized. Several steps were needed to attach the allyl substituent to a ligand. First, 2,6-xylidene was reacted with allyl bromide to give N-allyl-2,6-xylidene 12. Although this reaction was carried out at 0°C, the substitution occurred too readily, and some doubly allylated xylidene always resulted and had to be separated from 12 using flash chromatography. Next, the compound was reacted with zinc chloride in order to effect a Claisen rearrangement of the allyl group, giving 13. Two molar equivalents of zinc chloride were needed to give a good rate of reaction.

Figure 37. Mechanism of the Claisen rearrangement.

Compound 13 was reacted with 3,5-di-tert-butyl-2-hydroxylbenzaldehyde to give the allyl ligand 14. The allyl ligand was deprotonated with n-butyllithium and added to compound 4 under nitrogen atmosphere to give 15, the allyl ligand catalyst.

Attempts were made to incorporate the allyl ligand 14 into a polystyrene chain using the same method as was used with the vinyl ligand 10. The allyl ligand was combined with styrene and the radical initiator AIBN, and the resulting polymer was analyzed by $^1$H NMR. The $^1$H NMR spectrum of the products of this reaction did not show any incorporation of ligand. The spectrum was identical to that of the control
polystyrene, which was produced by reacting only styrene with AIBN. This is not unexpected, because styrene is highly susceptible to radical polymerization compared to allyl benzene. The polymerization of styrene must have occurred too rapidly for the allyl species to incorporate itself into the chain.

The allyl catalyst 15 was used to polymerize polypropylene at 0°C in toluene with MAO as the cocatalyst. The TOF of this catalyst was calculated to be 300. Though this catalyst is a heteroligand catalyst, its TOF value is more comparable to the homoligand catalyst. There was no observed increase in activity. The polypropylene produced by this reaction gave a $^1$H NMR spectrum that showed highly syndiotactic polypropylene: all of the methyl, methylene, and methine proton peaks matched up exactly with those of the control spectra. There was one small peak at $\delta1.3$ ppm that was at the right shift to correspond to a peak of one of the methylene protons in isotactic polypropylene. (Figure 30). This feature was not borne out in the $^{13}$C spectrum, however. The $^{13}$C NMR spectrum was difficult to interpret. The peaks in it were at the right chemical shifts to be syndiotactic polypropylene, but the methyl and methylene peaks were doublets, and the methine peak resembled a triplet, when all of the peaks should have been singlets (Figure 31). The extra peaks in the $^{13}$C spectrum did not belong to isotactic or atactic polypropylene; they were at the wrong chemical shifts. There was no evidence of branching of the polymer. According to Alt et al. and Jin et al., butyl branches appear in the $^{13}$C NMR spectrum at 39, 34, 32, 30, 29, 23, 22, and 14 ppm.\textsuperscript{23} No such peaks were observed in this experiment; thus, there is not enough evidence from the NMR data that the catalyst was immobilized.
The polypropylene produced by the allyl ligand catalyst 15 was measured by GPC and calibrated against PMMA standards. The results showed that this polypropylene had a much lower molecular weight than the control catalysts’ polypropylenes: the $M_n$ value was found to be 4,800 Da, or 20 times smaller than that of the controls. This indicates a lower degree of polymerization achieved by this catalyst compared to the controls: chain termination was much more frequent. The polydispersity was calculated to be 2.51.

This extreme difference in $M_n$ and PDI values could be explained in two different ways. It could be attributed to self-immobilization of the catalyst. When a catalyst is successfully self-immobilized, it often produces polymers with higher polydispersities and different molecular weights; for example, Jin et al. found that when their self-immobilizing catalysts incorporated themselves into polymer chains, the PDIs ranged from 3-19. However, this extreme difference could also be attributed to the different electronic structure of the catalyst. Since neither of the ligands of the allyl catalyst $L^2L^4TiCl_2$ have fluorine atoms bonded ortho to the $–NH_2$ group, they are both ‘nonliving’ ligands. In Coates’ study, the heteroligand catalysts with two ‘nonliving’ ligands produced polymers with low molecular weights and high polydispersities. Thus, the polymers resulting from the allyl ligand catalyst are not comparable to the control polymers in this experiment, because the allyl catalyst is extremely different, electronically, from the control catalysts.

Before any assumptions can be made about the success of immobilization of the catalyst, or lack thereof, a control homogeneous catalyst must be made that is more comparable to allyl catalyst 15. Further work on this project should include the
synthesis of a control heteroligand catalyst with ligand $L^2$ and ligand $L^4$ modified to have a propyl instead of an allyl substituent. Then any differences in GPC and NMR data of the polymers produced by the allyl catalyst $L^2 L^4 TiCl_2$ and this new control catalyst could only be attributed to the presence of allyl group.

Another way to improve the allyl catalyst could be to replace ‘nonliving’ ligand $L^2$ with ‘living’ ligand $L^1$ to give $L^1 L^4 TiCl_2$. This catalyst would probably have a higher activity and degree of polymerization than $L^2 L^4 TiCl_2$ because it would have a combination of ‘living’ and ‘nonliving’ ligands.

Possible further steps to take with this allyl catalyst might be to attach it to silica covalently. O’Hare et al. immobilized a zirconocene catalyst with an allyl functional group onto silica by first converting the allyl functionality into a chlorosilane using a triphenylphosphine platinum chloride catalyst, and then reacting the chlorosilane with silica. The resulting immobilized catalyst was attached covalently to the silica surface. The allyl functionality turned into a flexible tether that gave the catalyst good access to monomers.

![Immobilization of a zirconocene catalyst with an allyl substituent onto silica.](image)

**Figure 38.** Immobilization of a zirconocene catalyst with an allyl substituent onto silica.
O’Hare et al. found that the polymers formed by this immobilized catalyst had higher molecular weights and formed larger particles than the polymers from the homogeneous catalyst. This method is yet another possible further step that could be taken with the allyl catalyst 15 from this experiment.

IV. Polypropylene Produced by Catalysts Immobilized onto Silica

The NMR and GPC data of the polymers produced by the immobilized catalysts gave clear evidence that the catalysts were successfully immobilized, and produced polymers with no leaching of the catalyst from the silica surface.

The control step to check for leaching was carried out two different ways: some of the silica/MAO/catalyst compounds were stirred in just toluene for 3 hours, and some were stirred in toluene with 1 mmol MAO. The liquids separated from compounds that were stirred without MAO were clear, and polymerizations catalyzed by these liquids usually gave no product. Liquids separated from compounds that were stirred with MAO were slightly yellow, and polymerizations catalyzed by these liquids sometimes produced a very small amount of white solid. This solid was not soluble in NMR solvents; thus it was sent to Atlantic Microlabs for elemental analysis to see if it was polypropylene. The amounts of C and H in polypropylene should be %C = 85.6% and %H = 14.4%. The amounts of C and H determined were very different from these numbers for two of the compounds; thus, the white solid was not polypropylene. The amounts of C and H for one of the solids (Method 1, no MAO) were the same as they should have been for polypropylene: this proves that there was leaching of the catalyst off of the silica for this particular sample. This is probably
due to experimental inconsistencies in preparation of the silica/catalyst/MAO compound. In future research, the immobilization method must be made more consistent, and the amount of leaching of the catalyst must continue to be monitored.

All information on polymer tacticity was acquired from the $^1$H NMR spectra, because none of the polymers produced by silica-immobilized catalysts were soluble enough in any of the NMR solvents to obtain a $^{13}$C NMR spectrum. The $^1$H NMR spectra for all the polymers produced by silica-immobilized catalysts had what looked like a quadruplet at $\delta$0.9 ppm, a triplet at $\delta$1.1 ppm, a small, broad peak at $\delta$1.3 ppm, and a sextet at $\delta$1.65 ppm (Figures 32-34). These spectra were compared to the $^1$H NMR spectra of iso- and syndiotactic polypropylene. The $^1$H NMR spectrum of syndiotactic polypropylene has a doublet at $\delta$0.9 ppm, a triplet at $\delta$1.1 ppm, and a sextet at $\delta$1.65 ppm. The $^1$H NMR spectrum of isotactic polypropylene has a doublet at $\delta$0.95 ppm, a quintet at $\delta$1.3 ppm, and a sextet at $\delta$1.65 ppm (Figure 36). It was determined that there were only two differences between the $^1$H NMR spectrum of syndiotactic polypropylene and those of the polymers produced by the immobilized catalysts. These differences are accounted for by assuming the presence of an amount of isotactic polypropylene in the sample (about 35%). The small, broad peak at $\delta$1.3 is at the exact shift that the quintet would be for isotactic polypropylene, and the quadruplet observed at $\delta$0.9 can be attributed to two overlapping, slightly offset doublets that correspond to the methyl groups of syndiotactic and isotactic polypropylene.

This result is interesting, because it indicates that the catalyst’s stereocontrol was not lost: there are no peaks for atactic PP. The stereospecificity somehow
switched cleanly from syndiotactic to isotactic. An explanation for the phenomenon observed could be that immobilization of the catalyst onto silica might have inhibited isomerization between the Δ and Λ chiralities for some of the catalyst molecules. This would mean that the unique capability of the Ti-FI catalyst to alternate between the re and si oriented monomers would be lost, and, because of its C₂ symmetry, both of its coordination sites would be identical. The catalyst would behave as the majority of C₂-symmetric catalysts do, and produce isotactic polypropylene. Thus, the fact that some isotactic polypropylene was produced is evidence that the catalyst was successfully immobilized onto silica.

The GPC data showed that almost all of the silica-immobilized catalysts produced polymers with Mₙ values of 100,000 or more, which is within in the same order of magnitude as the molecular weights of the polymers produced by the control catalysts. The PDIs of the immobilized catalysts ranged from 1.45 to 2.95. Though the results of all the immobilized catalysts vary greatly, the results of certain runs definitely merit further work with these procedures.

<table>
<thead>
<tr>
<th>Catalyst and Method</th>
<th>Yield (g)</th>
<th>Mₙ</th>
<th>Mₘ</th>
<th>Mₚ</th>
<th>PDI</th>
<th>TOF</th>
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<tbody>
<tr>
<td>1 L₁₂TiCl₂</td>
<td>1.5</td>
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<td>127,000</td>
<td>109,000</td>
<td>1.34</td>
<td>360</td>
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<tr>
<td>2 L₁L₄TiCl₂</td>
<td>7.3</td>
<td>114,000</td>
<td>147,000</td>
<td>138,000</td>
<td>1.29</td>
<td>1683</td>
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<td>3 5, method 1</td>
<td>0.10</td>
<td>118,000</td>
<td>220,000</td>
<td>302,000</td>
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<td>4 3, method 1</td>
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<td>105,000</td>
<td>260,000</td>
<td>314,000</td>
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<tr>
<td>5 3, method 2</td>
<td>0.15</td>
<td>188,000</td>
<td>274,000</td>
<td>307,000</td>
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<tr>
<td>6 3, method 1</td>
<td>0.14</td>
<td>45,400</td>
<td>134,000</td>
<td>106,000</td>
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<tr>
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<td>681,000</td>
<td>772,000</td>
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<tr>
<td>8 3, method 2</td>
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<td>219,000</td>
<td>256,000</td>
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<td>9 5, method 2</td>
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<td>365,000</td>
<td>484,000</td>
<td>507,000</td>
<td>1.33</td>
<td></td>
</tr>
</tbody>
</table>

Table 5. GPC data for the control catalysts (1-2) and the silica-immobilized catalysts (3-9). Under Catalyst and Method, the numbers 3 and 5 refer to compound 3, L₁₂TiCl₂, and compound 5, L₁L₄TiCl₂, respectively.
The second method of immobilizing the catalysts almost consistently gave better results than the first. All of the catalysts immobilized using method 2 had PDIs between 1.3 and 1.8, whereas for the catalysts immobilized using method 1, half of the PDIs were less than 2.0 and half were between 2.5 and 3.0. Chadwick et al. also found that the second method gave better results than the first.26

The very best result in this experiment was obtained from entry 7, using the homoligand catalyst 3 and the first immobilization method. The $M_n$ value for entry 7 was 550,000, which is almost 6 times higher than the control, while the PDI was 1.23, which is even lower than that of the control! Entries 9 and 5, which used method 2 to immobilize catalysts 5 and 3, respectively, also improved on the molecular weight of the control by a factor of 2 or more, while retaining low PDIs. These particular immobilization effects on the polymers are consistent with the results of the Chadwick group; Chadwick et al. found that catalysts immobilized onto silica produced polymers with higher molecular weights and low PDIs.26 The result for entry 6 was the only polymer that had a lower molecular weight than the controls; entries 4 and 6 had molecular weights higher than 2.0. The cause of these poor data points is probably due to experimental inconsistencies in the preparation of the silica/MAO/catalyst compounds.

The exact cause of this improved molecular weight in entries 5, 7, and 9 is unclear. Some feature of immobilizing the catalyst onto silica must inhibit chain termination or chain transfer, resulting in higher molecular weights. Future goals of research in this area will be to determine the cause of this improvement, and also to make these good results more consistent.
Immobilizing the catalysts onto silica resulted in undesired changes in the yields, morphology, and solubility of the polymers produced.

Polymerizations catalyzed by silica-immobilized Ti-FI catalysts produced extremely small amounts of polypropylene, no matter which immobilization method or which type of catalyst was used. The polymerization yield was never more than 0.2 g polypropylene for any of these silica-immobilized catalysts. The average yield of polymerizations catalyzed by the control homogeneous homoligand catalyst \((L_1)_2TiCl_2\) was about 1.25 g polypropylene, while the yield of the control homogeneous heteroligand catalyst \(L_1L_2^1TiCl_2\) was about 7 g polypropylene. Evidently, immobilization of the catalysts using this method drastically reduces their activity. For these immobilization methods to be useful, it will be necessary to improve the polymer yields.

Three explanations for the low yields observed are possible. First, a much smaller amount of catalyst was being used to catalyze the reactions: only the amount of catalyst that could bond to 0.1 g of the silica/MAO compound was added to the reactor. This amount was not calculated in this investigation. In further work, an elemental analysis of each silica/MAO/catalyst complex should be carried out in order to determine the ratio of titanium to silicon atoms in each sample. This would allow investigators to add equal amounts of control catalyst and immobilized catalyst to the control and experimental polymerizations, and thus make a better comparison of the yields. A second explanation for low polymer yield could be that acid sites on the silica surface might have reacted with the catalyst’s metal center and inactivated a
fraction of the already small amount of catalyst in the reactor. One way to correct this might be to calcine the silica at a higher temperature in order to eliminate more of the silanol groups from the surface. A third explanation for low polymer yield could be that the monomer had poor access to the catalytic sites. If this were true, then the polymerization would stop after a polymer shell formed around the silica particle. The silica particles would fail to fragment and open up new catalytic sites. Low access to the catalytic sites could be caused by poor distribution of the catalyst over the silica particle, or perhaps to an unfavorable physical shape of the silica particle itself.

The morphology and solubility of the polymers produced by immobilized catalysts were very different from the polymers produced by the control catalysts. Rather than producing a fine white powder as the control catalysts did, the catalysts immobilized onto silica produced off-white, coarse solids that sometimes had uniform particle sizes, but more often were chunky and misshapen. These solids were more difficult to dissolve in the NMR and GPC solvents than the control polymers. When heated in 1,1,2,2-tetrachloroethane or ortho-dichlorobenzene, these solids would turn brown and sit at the bottom of the vial rather than going cleanly into solution. This unusual consistency and behavior could be explained by the fact that little polymer was produced, and there was a large percentage of metal impurities in the compound. The low solubility could also be due to higher polymer molecular weights, caused by the favorable effects of immobilizing the catalyst. If further work is done using these methods, and the yield is successfully increased, it will be important to observe whether the morphology and solubility of the produced polymers improve.
Conclusion

Titanium FI catalysts are a new family of olefin polymerization catalysts that are promising because of their high activity, living behavior, and controlled tacticity. Before they can be used in industrial polymerization reactors, these catalysts must be immobilized. Three methods of immobilizing this new type of catalyst were investigated.

First, two different homogeneous Ti-FI catalysts were synthesized in order to be used as controls. When used in a polymerization, catalysts 3 and 5 gave highly syndiotactic polymers with high molecular weights of 95,000 and 114,000, respectively, and low polydispersities of 1.34 and 1.29, respectively. The measured $M_n$ values for the polymers were 3 times higher than the $M_n$ values obtained by Coates et al. for the same catalysts. This inaccuracy was attributed to the different types of polymer standards used to calibrate the GPC data: we used PMMA standards, whereas Coates et al. used polyethylene. The heteroligand catalyst, $L_1^1L_2^2\text{TiCl}_2$, was found to have a higher turnover frequency than the homoligand catalyst, $L_1^1\text{TiCl}_2$, which was as expected from Coates’ results. The NMR and GPC data of polymers produced immobilized catalysts in this experiment were compared to these controls.

The first immobilization method was unsuccessful, because the last step of the synthesis of the vinyl ligand catalyst did not work. The vinyl ligand was successfully incorporated into a polystyrene chain; however, this immobilized ligand could not be attached to a catalyst.

The synthesis of the allyl ligand catalyst was successful. Attempts to incorporate the allyl ligand into a polystyrene chain were unsuccessful. The allyl
catalyst was used to polymerize polypropylene. The NMR data of the polypropylene produced showed high syndiotacticity, but did not give evidence of self-immobilization. The GPC data showed that the polymer produced had a much lower $M_n$ value of 4,800 and a higher PDI value of 2.51, compared to the controls. This is probably because the allyl catalyst was too different, electronically, from the control catalysts. In future experiments, it will be necessary to synthesize control catalysts that are more similar to this allyl catalyst. Then any differences between the experimental and control catalyst can be attributed to the presence of the allyl group.

Further work that could be done with this catalyst includes combining the allyl ligand with a ‘living’ ligand, such as $L^1$, in order to increase the TOF, and using O’Hare’s procedure to immobilize the allyl functionality onto silica.

The third method of immobilizing the Ti-FI catalysts was the most successful. The control step for the most part eliminated the possibility of leaching. The NMR data showed that immobilizing the catalyst onto silica gave a mixture of 65% syndiotactic polypropylene and 35% isotactic polypropylene, rather than just syndiotactic polypropylene. The fact that there was a clear mixture of iso- and syndiotactic polymers, with no atactic peaks evident indicates that there was no loss of tacticity: instead, there was a switch. It was hypothesized that immobilizing the catalyst inhibited some of the catalyst molecules from isomerizing between the $\Delta$ and $\Lambda$ chiralities; this would cause the $C_2$-symmetric catalyst to behave as other $C_2$-symmetric catalysts do, and give isotactic polypropylene. The GPC data showed that the second method of immobilizing the catalyst, in which the catalyst was contacted with MAO before adding it to silica, was more consistent than the first method. The
molecular weights of polymers 5, 9, and 7 were higher than those of the control polymers, while the PDIs were lower. These results show that immobilizing the catalyst onto silica inhibits chain termination and chain transfer, resulting in improved polymer quality. The yields of the immobilized catalysts were much lower than those of the controls: silica-immobilized catalysts never produced more than 0.2 g polymer. The morphology of the polymers was chunky and coarse, and the solubility of the polymers was poor. Future goals of research in this area will be to find the ratio of Ti:Si in the silica/catalyst/MAO compound so that the TOFs can be calculated; increase the polymer yield; make the molecular weight and PDI results more consistent; and track any changes in morphology, leaching, and solubility.
Experimental

$^1$H and $^{13}$C NMR spectra were recorded at 300 MHz with a Varian 300 Mercury pulsed field gradient spectrometer. NMR spectra of polypropylene were carried out at 95°C in 1,1,2,2-tetrachloroethane. NMR spectra of catalysts and catalyst precursors were carried out in C$_6$D$_6$ at room temperature. NMR spectra of anilines, aldehydes, and ligands were carried out in CDCl$_3$ at room temperature. Gas chromatography-mass spectrometry (GC-MS) was carried out on a Hewlett-Packard model 5890 spectrometer. Elemental analysis was carried out by Atlantic Microlabs in Atlanta, Georgia. GPC data was obtained from a Waters Alliance GPCV 2000 gel permeation chromatography spectrometer, using ortho-dichlorobenzene as the solvent. Air-sensitive compounds were stored in a glove box and manipulated using Schlenk techniques under nitrogen atmosphere. Solvents for air-sensitive reactions were dried and deoxygenated using an Innovative Technology solvent system. All other reagents were used as obtained from commercial sources.

General Procedures for the Synthesis of Phenoxy-imine Ligands.

1. Fluoro-, difluoro- and trifluoroanilines: EtOH method.

A 1:1 mixture of the chosen salicyl aldehyde and chosen aniline were refluxed with a few drops of formic acid in ethanol until GC analysis showed the reaction to be complete (usually under 1 hour). The solvent was evaporated, and the crude solid was recrystallized from methanol in the freezer overnight, giving yellow crystals.

Compound 2 (L$^2$): Yellow crystals, 87% yield. $^1$H NMR data (CDCl$_3$ 300 MHz):

$\delta$1.3 (s, 9H) tBu; $\delta$1.5 (s, 9H) tBu; $\delta$6.7 (t, 1H, J=9) para ArH; $\delta$6.8 (d, 2H, J=7.8)
ortho ArH; δ7.2 (s, 1H) phenol ArH; δ7.5 (s, 1H) phenol ArH; δ8.6 (s, 1H) imine; δ13.1 (s, 1H) hydroxyl.

Compound 10 (L³): Deep orange crystals. 70% yield. ¹H NMR data (CDCl₃, 300 MHz): δ1.6 (s, 9H) tBu; δ 5.2 (d, 1H, J=11.1) Ar-CH=CH₂; δ5.6 (d, 1H, J=17) Ar-CH=CH₂; δ6.7 (q, 1H, J=7.7) Ar-CH=CH₂; δ6.8 (t, 1H, J=8.9) imine para-H; δ6.9 (d, 2H, J=7.9) imine ortho-H; δ7.3 (s, 1H) phenol ArH; δ7.5 (s, 1H) phenol ArH; δ8.6 (s, 1H) aldehyde; δ 13.4 (s, 1H) hydroxyl.

Compound 14 (L⁴): Yellow crystals. 68% yield. ¹H NMR data (CDCl₃, 300 MHz): δ1.3 (s, 9H) tBu; δ1.5 (s, 9H) tBu; δ2.2 (s, 6H) Ar(CH₃)₂; δ3.3 (d, 2H, J=6.6) ArCH₂CH=CH₂; δ5.1 (m, 2H) ArCH₂CH=CH₂; δ6.0 (m, 1H) ArCH₂CH=CH₂; δ6.9 (s, 2H) imine ArH; δ7.1 (s, 1H) phenol ArH; δ7.5 (s, 1H) phenol ArH; δ8.3 (s, 1H) imine H; δ13.5 (s, 1H) hydroxyl.

2. Tetrafluoro- or pentafluoroaniline: Solventless P₂O₅ method.¹⁹

3,5-Di-tert-butyl-2-hydroxybenzaldehyde, pentafluoroaniline, and dry phosphorous pentoxide were combined in a 1:1:1/3 ratio in a vial with a small stir bar. A few crystals of p-toluenesulfonic acid were added. The mixture was heated to 110°C and stirred for 4 hours. After cooling, the organic materials were extracted with methylene chloride, filtered, and recrystallized from methanol in the freezer overnight to give yellow crystals of the ligand.

Compound 1 (L¹): Yellow crystals, 75% yield. ¹H NMR data (CDCl₃, 300 MHz): δ 1.3 (s, 9H) tBu; δ1.4 (s, 9H) tBu; δ7.2 (s, 1H) phenol ArH; δ7.6 (s, 1H) phenol ArH; δ8.8 (s, 1H) aldehyde; δ12.8 (s, 1H) hydroxyl.
General Procedure for the Synthesis of the Homoligand Catalyst, L\textsuperscript{n}2TiCl\textsubscript{2}\textsuperscript{19}

n-Butyllithium was added by syringe to an ether solution of L\textsuperscript{n} in a 1:1 ratio at -78°C. The yellow solution was warmed to room temperature and stirred for 15 minutes before being transferred via syringe to an ether solution of TiCl\textsubscript{4} (ligand:TiCl\textsubscript{4} 2:1) at -78°C. As the mixture warmed to room temperature, it turned dark red. The mixture was stirred for 6 hours at room temperature. After removing the solvent in vacuo, residues were taken up in CH\textsubscript{2}Cl\textsubscript{2} and filtered through a fritted funnel, giving a clear dark red solution.

Compound 3 (L\textsubscript{1}2TiCl\textsubscript{2}): Red-brown powder. 68% yield. \textsuperscript{1}H NMR data (C\textsubscript{6}D\textsubscript{6} 300 MHz): δ1.2 (s, 18H) overlapping tBu; δ1.4 (s, 18H) overlapping tBu; δ6.9 (s, 1H) phenol ArH; δ7.1 (s, 1H) phenol ArH; δ7.4 (s, 1H) phenol ArH; δ7.6 (s, 1H) phenol ArH.

General Procedure for the Synthesis of L\textsuperscript{n}TiCl\textsubscript{3}(THF)\textsuperscript{19}

A THF solution of ligand L\textsuperscript{n} was added via cannula to a THF solution of TiCl\textsubscript{4} in a 1:1 ratio at -78°C. As the yellow solution was warmed to room temperature, the color changed to deep red. After stirring for 6 hours, the solvent was removed in vacuo to give a brown solid. Hexane was added to the solid and the soluble compounds were filtered away. The insoluble red-brown product was collected and dried.

Compound 4, L\textsuperscript{2}TiCl\textsubscript{3}(THF): Red-brown powder. 63% yield. \textsuperscript{1}H NMR data (C\textsubscript{6}D\textsubscript{6} 300 MHz): δ1.3 (s, 9H) tBu; δ1.5 (s, 9H) tBu; δ1.8 (broad s, 4H) THF; δ4.2 (broad s,
4H) THF; δ6.8 (t, 1H, J=9) para- ArH; δ7.0 (d, 2H, J=8) ortho- ArH; δ7.4 (s, 1H) phenol ArH; δ7.7 (s, 1H) phenol ArH; δ8.2 (s, 1H) imine.

Compound 11, L^3TiCl_3(THF): Red-brown powder, 40% yield. ^1H NMR data (C_6D_6, 300 MHz): δ 1.6 (s, 9H) t-Bu; δ 2.2 (broad, 4H) THF; δ 4 (broad, 4H) THF; δ 5.2 (d, 1H, J=11.1) ArCH=CH_2; δ 5.6 (d, 1H, J=17) ArCH=CH_2; δ 6.5 (m, 1H) ArC=CH_2; δ 6.7 (t, 1H, J=8.9) para- ArH; δ 6.9 (d, 2H, J=7.9) ortho- ArH; δ 7 (s, 1H) ArH; δ 7.1 (s, 1H) ArH; δ 7.5 (s, 1H) N=CH.

**General Procedure for the Synthesis of the Heteroligand Catalyst, L^nL^mTiCl_2**

n-Butyllithium was added by syringe to an ether solution of ligand L^m in a 1:1 ratio at -78°C. After warming the solution to r.t. and stirring for 15 minutes, the solution was transferred via cannula to an ether solution of L^nTiCl_3(THF) at -78°C (ligand: L^nTiCl_3(THF) = 1:1). The dark red mixture was stirred at room temperature for 6 hours. After removing the solvent in vacuo, residues were taken up in CH_2Cl_2 and filtered through a fritted funnel, giving a clear dark red solution.

Compound 5 (L^1L^2TiCl_2) Red-brown powder. 59% yield. ^1H data (C_6D_6, 300 MHz): δ1.3 (s, 18H) 2 tBu; δ1.5 (s, 9H) tBu; δ1.5 (s, 9H) tBu; δ6.3 (t, 1H, J=9) L^2 para- ArH; δ6.7 (d, 2H, J=7.8) L^2 ortho- ArH; δ6.8 (d, 1H, J=1.8) phenol ArH; δ7.0 (d, 1H, J=1.9) phenol ArH; δ7.3 (s, 1H) HC=N; δ7.5 (s, 1H) HC=N; δ7.7 (d, 1H, J=2) phenol ArH; δ7.8 (d, 1H, J=1.9) phenol ArH.

Compound 15 (L^2L^4TiCl_2) Red-brown powder. 24% yield. ^1H data (C_6D_6, 300 MHz): δ1.2 (s, 9H) tBu; δ1.3 (s, 9H) tBu; δ 1.3 (s, 9H) tBu; δ1.4 (s, 9H) tBu; δ1.6 (s, 6H) Ar(CH_3)_2; δ3.3 (d, 2H, J=6) ArCH_2CH=CH_2, δ5.1 (m, 2H) ArCH_2CH=CH_2; δ6.4 (t,
1H, J=9) para-ArH, L^2; δ6.5 (d, 2H, 7.8) L^2 ortho-ArH; δ7.1 (d, 1H) phenol ArH; δ7.2 (d, 1H, J=1.8) phenol ArH; δ7.5 (s, 1H) phenol ArH; δ8.1 (s, 2H) imine Hs.

3-tert-Butyl-2-hydroxybenzaldehyde\textsuperscript{29}

To a 200 ml round bottom flask, 2-tert-butylphenol (100 mmol), paraformaldehyde (400 mmol, 12 g), triethylamine (100 mmol, 10 g), montmorillonite KSF (15 g), 50 ml toluene, and a stir bar were added. The mixture was refluxed in an oil bath at 110°C overnight. The mixture was cooled to room temperature, and the clay was filtered off and washed with methanol. The solvents were removed on a rotary evaporator, and the crude product was purified by flash chromatography using 5:1 hexane/ethyl acetate as the eluant.

Compound 6: Yellow oil. 40% yield. $^1$H NMR data (CDCl$_3$, 300 MHz): δ1.4 (s, 9H) tBu; δ6.9 (t, 1H, J=7.5) ArH; δ7.4 (d, 1H, J=7.8) ArH; δ7.6 (d, 1H, J=7.8) ArH; δ9.8 (s, 1H) aldehyde; δ11.8 (s, 1H) hydroxyl.

3-tert-Butyl-5-chloromethyl-2-hydroxybenzaldehyde\textsuperscript{30}

3-tert-Butyl-2-hydroxybenzaldehyde and paraformaldehyde were stirred in concentrated HCl for 4 days. The mixture was extracted with ether, and the organic phases were washed with saturated aqueous NaHCO$_3$, brine, and then dried over MgSO$_4$. The solvent was evaporated, leaving a yellow, viscous oil.
Compound 7: Yellow oil. 60% yield. $^1$H NMR data (CDCl$_3$ 300 MHz): $\delta$1.4 (s, 9H) tBu; $\delta$4.6 (s, 2H) ArCH$_2$Cl; $\delta$7.4 (s, 1H) ArH; $\delta$7.6 (s, 1H) ArH; $\delta$9.8 (s, 1H) aldehyde; $\delta$11.9 (s, 1H) hydroxyl.

3-tert-Butyl-5-formyl-4-hydroxybenzyl(triphenylphosphonium) Chloride$^{30}$

3-tert-Butyl-5-chloromethyl-2-hydroxybenzaldehyde was stirred in toluene with triphenylphosphine under reflux for 1 day. After cooling the solution to room temperature, the product precipitated and was filtered off, washed with ether, and dried under vacuum, leaving a white powder.

Compound 8: White powder. 70% yield. $^1$H NMR data (CDCl$_3$ 300 MHz): $\delta$1.2 (s, 9H) tBu; $\delta$5.6 (d, 2H, J=13.8) ArCH$_2$; $\delta$6.9 (s, 1H) ArH; $\delta$7.4 (s, 1H) ArH; $\delta$7.7 (m, 15H) PPh$_3$; $\delta$9.7 (s, 1H) aldehyde; $\delta$11.8 (s, 1H) hydroxyl.

3-tert-Butyl-2-hydroxy-5-vinylbenzaldehyde$^{30}$

The phosphonium salt (above) was stirred in 40% aqueous formaldehyde. A solution of 12.5 M NaOH was added dropwise, keeping the reaction temperature below 40°C. After 2 hours, the mixture was cooled with ice and neutralized with 6 M HCl. At pH = 7, the aqueous phase was extracted with benzene. Evaporation of the solvent gave a semisolid that was purified by flash chromatography (ether/acetone 2:1) and distilled under vacuum. The oily product of distillation partially solidified at room temperature, giving a mixture of oil and light yellow crystals.
Compound 9: Yellow oil/crystals. 20% yield. $^1$H NMR data (CDCl$_3$ 300 MHz): $\delta$1.4 (s, 9H) tBu; $\delta$5.2 (d, 1H, J=12) Ar-CH=CH$_2$; $\delta$5.6 (d, 1H, J=15) Ar-CH=CH$_2$; $\delta$6.7 (q, 1H, J=11.1) Ar-CH=CH$_2$; $\delta$7.4 (s, 1H) ArH; $\delta$7.6 (s, 1H) ArH; $\delta$9.8 (s, 1H) aldehyde; $\delta$11.8 (s, 1H) hydroxyl.

N-allyl-2,6-xylidine$^{31-32}$

2,6-xylidine and allyl bromide in a 2:1 molar ratio were heated at 0°C for 5 hrs in DMF with K$_2$CO$_3$. When GC analysis showed maximum conversion, the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed with water, brine, and dried over MgSO$_4$. Removal of the solvent gave a mixture of 2,6-xylidine, N-allyl-2,6-xylidine, and trace N,N-allyl-2,6-xylidine. This mixture was purified by column chromatography with hexane as the eluant.

Compound 12: Yellow oil. 54% yield. $^1$H NMR data (CDCl$_3$ 300 MHz): $\delta$2.4 (s, 6H) Ar(CH$_3$)$_2$; $\delta$3.1 (broad, 1H) N-H; $\delta$3.7 (d, 2H, J=6.6) CH$_2$CH=CH$_2$; $\delta$5.2 (d, 1H, J=10.2) CH=CH$_2$; $\delta$5.4 (d, 1H, J=16.8) CH=CH$_2$; $\delta$6.1 (m, 1H) CH$_2$CH=CH$_2$; $\delta$6.9 (t, 1H, J=8.1) ArH; $\delta$7.1 (d, 2H, J=7.2) ArH.

4-allyl-2,6-xylidine$^{31}$

N-allyl-2,6-xylidine and ZnCl$_2$ in a 1:2 ratio were refluxed in xylene for 2 hours. (100% conversion by GC). The mixture was cooled to room temperature and 10% NaOH was added. The alkaline layer was separated from the amine and extracted with ether. The combined organic layers were washed with a saturated solution of
NaCl and dried. The xylene was separated from the 4-allyl-2,6-xylidine using a column with hexane as the eluant. A yellow oil was collected.

Compound 13: Yellow oil. 67% yield. $^1$H NMR data (CDCl$_3$ 300 MHz): $\delta$2.2 (s, 6H) Ar(CH$_3$)$_2$; $\delta$3.3 (d, 2H, J=6.6) ArCH$_2$CH=CH$_2$; $\delta$3.6 (b, 2H) -NH$_2$; $\delta$5.2 (m, 2H) ArCH$_2$CH=CH$_2$; $\delta$6.0 (m, 1H) ArCH$_2$CH=CH$_2$; $\delta$6.8 (s, 2H) ArH.

**Immobilization of the Catalyst onto Silica.**

**Calcination of Silica.**

1 g of silica was placed in a quartz boat, which was placed in a sealed quartz tube with a nitrogen flow. The temperature was raised from room temperature to 250°C over 25 minutes, held at 250°C for 3 hours, and cooled to room temperature over 25 minutes. The resulting silica was transferred to a glove box and thereafter handled under nitrogen.

**Method 1: Synthesis of the MAO/Silica Support.**

In the glove box, 1 g of the calcined silica was added to a flask with 10 ml toluene. The solution looked like a translucent liquid/gel. 3.12 mmol MAO in 5 mL toluene was slowly added to the slurry. The flask was taken out of the box and was heated in an oil bath to 110°C and stirred at this temperature under nitrogen for 4 hours. The toluene solvent was removed in vacuo, and then 5 mL more toluene was added and the mixture was stirred under nitrogen at 110°C for 45 more minutes. The solid was dried in vacuo, giving a free-flowing white powder.
Method 1: Immobilization of Catalyst onto MAO/Silica Support.\textsuperscript{26}

Each of the catalysts, compounds 3 and 5, (0.033 mol) were dissolved in 5 ml toluene and the resulting solution added to a slurry of 0.1 g MAO/silica support in 10 mL of toluene. The mixture was allowed to sit for one hour, and then the excess solvent was decanted. The catalyst/MAO/silica compound was washed with an additional 30 mL toluene in order to remove any non-immobilized catalyst. The solvent was removed from the solid via filtration with a fritted funnel.

Method 2: Synthesis of the MAO/Silica/Catalyst Compound.\textsuperscript{26}

In the glove box, 0.2 g MAO in 5 mL toluene was contacted with 0.033 mmol catalyst (either compound 3 or 5) in 5 mL toluene for 10 minutes. This mixture was slowly added to a slurry of silica in 15 mL toluene. The slurry was then heated at 100°C in an oil bath under nitrogen for 4 hours. The solvent was then removed in vacuo, leaving a yellow, free-flowing powder.

Control: Check for leaching of the catalyst.

To be sure that the catalyst was not detaching itself from the support during the polymerization, the support/catalyst compounds were stirred with either toluene or 1 mmol MAO in toluene at 0°C for 3 hours. The solvent was separated from the solid on a fritted funnel, and both the solvent and the solid were used in a propylene polymerization.
General Procedure for Propene Polymerization.

Each polymerization utilized between 0.01 and 0.05 mmol catalyst and 150 times more MAO cocatalyst. Stock solutions of 0.165 mmol catalyst in 25 mL toluene and 4.95 mmol MAO in 50 mL toluene were prepared and put in the dry box. The polymerization reactor and a 5-mL and a 10-mL gastight syringe were dried in an oven for at least 5 hours. In the glove box, 10 mL of the MAO solution was added to the polymerization reactor. Toluene was added to the 40 mL mark. The pressure head was attached to the top of the flask, and 5 mL of the catalyst solution was drawn into the 5 mL gastight syringe. The reactor was placed inside a plastic sleeve and placed in an ice bath. The pressure head was connected to a tank of high purity propylene via a quick-release connector, and the pressure in the vessel was raised to 40 psi. The flask was vented and re-filled 3 times. Propylene was allowed to condense in the reactor at 0°C for 30 minutes. Then the 5 mL of catalyst solution was injected into the flask, and the polymerization began. After 3 hours, the polymerization was quenched with 10 mL acidified methanol. The entire reaction mixture was poured into a beaker containing 300 mL acidified methanol and was allowed to stir overnight. The solvent was filtered away and the white polymer dried in vacuo.

Polymerizations with Silica/MAO/Catalyst compound.

In the glove box, 10 mL MAO solution and 0.1 g supported catalyst was added to the reactor. The pressure head was attached to the top of the flask, and the entire apparatus was removed from the box and placed inside the protective sleeve and
immersed in an ice bath. The pressure head was connected to a tank of high purity propylene via a quick-release connector, and the pressure in the vessel was raised to 40 psi. The flask was vented 3 times. After 3 hours, the polymerization was quenched with 10 mL acidified methanol. The reaction mixture was poured into a beaker containing 300 mL acidified methanol, and was allowed to stir overnight. The solvent was filtered away, and the white polymer was collected and dried in vacuo.

**General Procedure for Styrene/Ligand Polymerizations.**

Styrene and ligand were combined in a 20:1 molar ratio in toluene under nitrogen atmosphere. 10 mg AIBN was added to the flask and the mixture was heated to 100°C. The solution was tested every hour for polymer formation by dropping a small amount of the mixture into methanol. After 6 hours, the reaction was deemed complete. 20 mL methanol was added to the flask, and the polymer precipitated out of solution. The solid was filtered and then extracted in acetonitrile in a Soxhlet extractor at 125°C.
References


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