

ABSTRACT

Title of Dissertation / Thesis: **ETHYLENE POLYMERIZATION USING A ZIRCONIUM AMIDINATE SUPPORTED CATALYST**

Andrea Elise Young, Master of Science, 2004

Dissertation / Thesis Directed By: **Professor Lawrence R. Sita, Inorganic Division, Department of Chemistry and Biochemistry**

A series of W. R. Grace Davison IOLA™, methylaluminoxane-silica (MAO/Silica) and MAO/IOLA support materials were used to activate and immobilize a zirconium amidinate single site catalyst of the formula $Cp^*ZrMe_2[tBuNC(Me)NCEt]$. Ethylene homo-polymerizations and co-polymerizations with 1-hexene were conducted in heptane and compared. The catalysts activity was investigated under varying condition such as pre-catalyst loading, pressure, temperature, co-monomer incorporation and additives. The catalyst supported on the MAO/IOLA B support material proved to be more active than the IOLA and m-IOLA support activators, and the MAO/Silica and MAO/IOLA A support materials. A difference in activity of as much as $1015 \text{ g}_{PE}/\text{g}_{cat}\cdot\text{h}^{-1}$ was noted. The catalyst sensitivity to varying ethylene polymerization conditions such as temperature and pressure were investigated for the MAO/IOLA B supported catalyst. Catalyst activities of more than $2100 \text{ g}_{PE}/\text{g}_{cat}\cdot\text{h}^{-1}$ were achieved. Homo-polymer and co-polymer samples were characterized and compared with respect to their melting temperature, molecular weights and polydispersities.

**ETHYLENE POLYMERIZATION USING A ZIRCONIUM AMIDINATE
SUPPORTED CATALYST**

By

Andrea Elise Young, Master of Science, 2004

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Advisory Committee:
Dr. Lawrence Sita, Chair
Dr. Brian Eichhorn
Dr. Jeffery Davis

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Chapter 1: Introduction

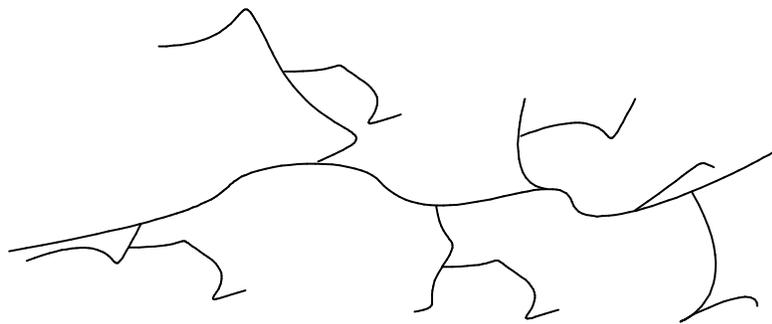
In the mid 1950's, Karl Ziegler and Giulio Natta reported the first stereoregular polymerization of ethylene¹⁻². These discoveries spear headed the synthesis of a host of new materials and revolutionized the polyolefin industry. Polyethylene is now one of the most common plastics in the world. It is used to make grocery bags, bottles, children's toys and a host of other everyday items. Polyethylene is of great industrial importance, and is produced in millions of tons each year. Its versatility combined with its physical and chemical properties makes it an attractive commodity to produce. Of most interest to industry is linear low density polyethylene (LLDPE), which is actually an ethylene and α -olefin co-polymer. The production of this ethylene material has the greatest growth rate of 11.2% per year, and is believed will replace other plastics on the market in the future³⁻⁴.

The polyethylene molecule of itself is simple. It is a long chain of carbon atoms with two hydrogens to each carbon. When there is no branching off the main backbone of the polymer, the polymer is called linear polyethylene or high density polyethylene (HDPE). When branching occurs off the backbone of the main polymer chain, the branched polymer is called low density polyethylene (LDPE)⁵. The average molecular weight for HDPE is in the range of 200,000 to 500,000. Polyethylene with molecular weights in the millions, is referred to as ultra-high molecular weigh polyethylene or UHMWPE. This material is used to manufacture fibers of such high tensile strength, that they can replace Kevlar, typically used in bulletproof vests.

Figure 1-1. HDPE or Linear Polyethylene



Figure 1-2. LDPE or Branched Polyethylene



The introduction of co-monomers into the polyethylene molecule allows for a wider range of products with different physical properties. The most common co-monomers being used today are octene, butene and 1-hexene⁶. Polyethylene by nature is semi-crystalline. The incorporation of α -olefin co-monomers to the polymer's side chains reduces its crystallinity⁷. This significantly impacts polymer performance, which is improved as the side chain branching is lengthened. By controlling the amount of side chain branching that occurs, manufactures are able to produce various polyethylene grades for different applications.

The leading developer of polyethylene reactor and catalyst technology today is Dow. Dow's reactor technology, which polymerizes ethylene in solution is not licensed out. However, Univation's (Dow and Exxon Mobil) Unipol reactor technology is the

world's most licensed polyethylene process technology. Another significant process is the Innovene technology, developed by BP chemicals and Dow. Both Unipol and Innovene are gas-phase processes^{7, 8}.

The most commonly used coordination catalysts in industry are Ziegler-Natta and Phillips type catalyst⁹. Typically, heterogeneous Ziegler-Natta catalysts consist of a metal alkyl or hydride, of the transition metals of Groups IV to VII. The most common of which are aluminum alkyls, such as diethylaluminum chloride, and titanium (IV) chloride. The catalyst system affects the polymerization behavior, polymer structure and morphology. However, homogeneous metallocene single site catalysts, unlike their heterogeneous Ziegler-Natta counterparts allow manufactures to control the composition and polydispersity of the polymer more closely, thereby improving polymer properties. Metallocene single site catalysts are characterized by the fact that their metal centers behave alike during polymerization. On the other hand, for industrial purposes, it is not always possible to employ homogeneous catalysts for some applications such as loop and gas phase processes. One way to surmount this problem is to convert the homogeneous catalyst systems to heterogeneous ones, by immobilizing them on solid support material^{10, 11}.

Single site catalysts must be activated by an organometallic Lewis Acid in order to create a cationic metal center. Typically used compounds, such as methylaluminoxane (MAO) are pyrophoric and must be used in large stoichiometric amounts. In an effort to avoid the use of these materials, the development of alternative activators and co-catalyst like borates, and boranes have been developed. Although these compounds are not themselves pyrophoric, they require pyrophoric materials for their synthesis and are

expensive to prepare. This adversely affects the development of the heterogeneous analogs of the single site catalysts in terms of cost, performance, stability and handling⁹.

The application of the catalyst and the resulting polymer must also be taken into consideration. The catalyst can affect the polymer properties by influencing molecular weight, density, cross-linking, crystallinity and branching. However, the polymerization process of the catalyst controls the presence of low molecular weight impurities, the presence of catalyst residues and cost.

The overall efficiency of a single site catalyst is determined not only by the properties of the product, but also by the activity of the system, the catalyst cost of use and the product conversion per unit time and yield. The stability and ease of handling of the catalyst is also a major factor when it comes to catalyst choice for industry. It is generally known that the majority of Ziegler-Natta and metallocene catalyst become deactivated when exposed to air. Coordination catalysts must be shielded from air and moisture during preparation, storage and use. This adds to production costs and makes use of the catalyst problematical.

Another factor to be considered for the use of single site coordination catalysts is the employment of the catalyst in a heterogeneous state. The advantages of using heterogeneous catalysts in slurry processes are quite significant. Slurry polymerizations can be carried out in a reactor where the monomer, catalyst and solvent can be added directly to the reactor. The polymer produced does not go into solution, but is solid (polymer fluff), and is allowed to drop out of the solvent before being removed. With this type of polymerization process, factors other than activity and selectivity of the catalyst come into play⁹. For slurry processes, it is necessary to have a supported catalyst that

produces high bulk density material. If the bulk density of a polymer is too low, it is not commercially practical to use. In addition, it is advantageous to have polymer material of uniform spherical particles with minimal fines. It is possible for fines to have large bulk densities, but they do not settle well, and the use of them in processing leads to trouble in handling.

A key difference between slurry processes and solution processes is that solution processes require high reaction temperatures of more than 130 °C and pressures of over 450 psi. This yields lower molecular weight polymer as a result of rapid chain termination under such harsh conditions. Reducing the reaction conditions, or altering the metallocene catalyst can produce polymer of higher molecular weight, but it is not possible to use the polymer in downstream equipment because of high solution viscosity. Slurry processes are able to surmount these issues simply by operating at milder reaction conditions (temperatures less than 100 °C). The polymers produced from these reactions are typically of high molecular weight and possess uniform particle size and morphology. The advantages of using slurry polymerization processes are motives to create new single site heterogeneous catalyst.

There were four main objectives for this research. The first was to determine whether our already existing homogeneous zirconium amidinate catalyst could perform ethylene polymerizations. Secondly, to create a working heterogeneous single site catalyst, by immobilizing the zirconium amidinate on solid support material. The third objective was to produce polyethylene material with good morphology and catalyst activity under industrially relevant conditions, and finally, to make LLDPE material with desirable 1-hexene incorporation.

Chapter 2: Homogeneous Polymerization

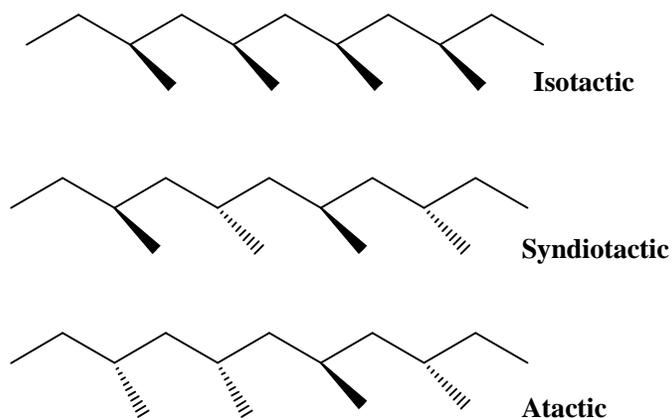
Introduction

The first homogeneous Ziegler-Natta catalyst reported was by Breslow and Natta¹²⁻¹⁵. The catalyst was a metallocene complex of formula Cp_2TiCl_2 , activated by an Et_3Al or Et_3AlCl co-catalyst. Another group Sinn and Kaminsky discovered that partially hydrolyzed Me_3Al , methylaluminoxane (MAO) could activate group IV metallocenes and polymerize α -olefins^{16,17}.

There have been many proposed Ziegler-Natta mechanisms over the past years. However, most agree that chain growth is a result of multiple insertions into a metal-carbon bond. In order for insertions to occur, there must be a cis relationship between the olefin double bond and the growing polymer chain. The olefin double bond opens and the growing polymer chain migrates to the olefin (chain migratory insertion)¹⁸. When the insertions occur on the same enantioface of the olefin, a polymer with isotactic stereochemistry is produced. Insertions on alternating enantiofaces result in syndiotactic polymer. Random insertions result in polymer of irregular tacticity called atactic polymer (see Figure 2-1). Because of the structure of the ethylene molecule, stereochemistry is not an issue.

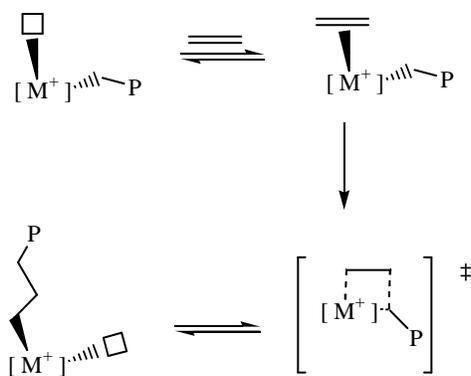
The generally accepted Ziegler-Natta mechanism is one proposed by Cossee¹⁹⁻²¹. It involves the binding of the olefin to an empty coordination site at the metal center, followed by chain migratory insertion of the growing polymer chain to the olefin double bond.

Figure 2-1. Polymer Stereochemistry



This proceeds via a metallocyclobutane transition state with 1,2 cis olefin insertion. A new vacant site is provided for monomer and the polymer chain is continued. (See Scheme 2-1).

Scheme 2-1. Cossee Mechanism for Ziegler-Natta polymerization



In 2000, our lab reported the first living homogeneous Ziegler-Natta catalyst capable of stereoselective living polymerization of 1-hexene²². The pre-catalyst, a

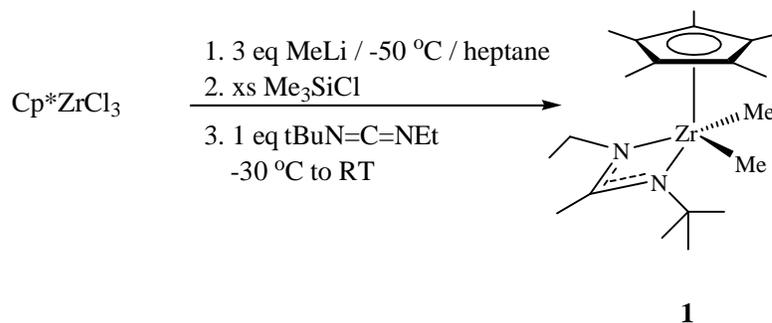
dimethylmonocyclopentadienyl zirconium amidinate of the formula $\text{Cp}^*\text{Zr}(\text{Me}_2)[\text{tBuNC}(\text{Me})\text{NEt}]$ was successfully activated by a borate co-catalyst $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_4)_4]$ to produce isotactic poly(1-hexene) with polydispersities (PDI) less than 1.03. The first goal of this research was to determine whether the catalyst could in fact polymerize ethylene.

Experimental

The synthesis of the zirconium amidinate pre-catalyst involves the addition of 3 eq. of methyl lithium (MeLi) to the 1 eq. of monocyclopentadienylzirconium trichloride (Cp^*ZrCl_3) in heptane. This reaction was previously performed only in diethyl ether. However, because this research was conducted at an industrial lab, a substitute for diethyl ether, because of its potentially hazardous nature, was sought. This diversion led to the realization that the pre-catalyst could be successfully synthesized from heptane. Although the solvent proved more difficult to remove with longer reaction times and small heptane peaks are visible in the ^1H NMR spectra, was not affected. This was confirmed by comparing 1-hexene polymerizations of the catalyst made in diethyl ether with the heptane version.

The heptane and Cp^*ZrCl_3 solution was cooled to $-50\text{ }^\circ\text{C}$ and the MeLi added via syringe. The solution became cloudy and was allowed to stir for 2 hrs before the reaction was quenched with chlorotrimethylsilane (TMS-Cl). The t-butyl, ethyl carbodiimide was then added via cannula to the solution and the reaction continued for another 2.5 hours. Volatiles were removed in vacuo and the product; a light yellow to cream solid, was re-crystallized from heptane. The average yield for this reaction was 75 %.

Scheme 2-2. Synthesis of Cp*Zr(Me)₂[tBuNC(Me)NEt]



Two different homogeneous ethylene polymerizations were performed with pre-catalyst **1**. The first was done in chlorobenzene (see Table 2-1, entry 1) and the second in toluene (entry 2). The zirconium amidinate pre-catalyst was prepared by dissolving it completely in solvent and adding it to the borate co-catalyst already in solution. A lime green color was observed and a stream of ethylene was bubbled through the solution via syringe. All of the polymerizations were performed at RT in an argon atmosphere dry box. The reaction was quenched with methanol and the polymer filtered and washed with acetone and heptane. It was then dried overnight in a vacuum oven.

Results

The polymers obtained from these homogeneous polymerization reactions were white and film like in appearance. There was no significant affect of solvent on the catalyst activity. There was however a noticeable difference in the molecular weight and polydispersities. The polymer from the chlorobenzene solution had a PDI that was 1.74 units less than the polymer from the toluene solution. (See Table 2-1.)

Table 2-1. Homogeneous Polymerization from Pre-catalyst 1

Entry	Solvent	Yield PE (g)	Cat. Act. ^a	Zr Act. ^b	Mw	Mn	PDI
1	Chlorobenzene	1.75	35.0	307	43,400	18,520	2.35
2	Toluene	1.73	34.6	304	61,200	14,900	4.11

a. $(g_{PE}/g_{cat}).h^{-1}$, b. $(g_{PE}/g_{Zr}).h^{-1}$

This difference could be a result of solubility issues with the borate co-catalyst in toluene.

These results confirmed our belief that the zirconium amidinate could polymerize ethylene and moved to convert the homogeneous pre-catalyst **1** to a heterogeneous catalyst by immobilizing it on solid support material.

Chapter 3: Heterogeneous Polymerization

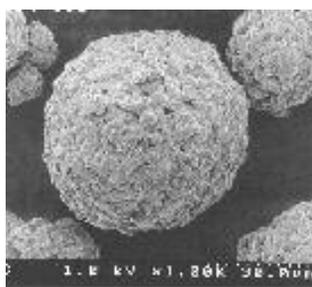
IOLA™ Support Activator

Introduction

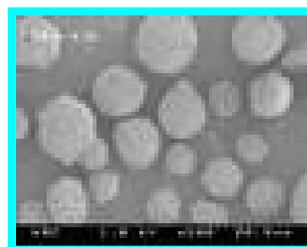
To carry out heterogeneous polymerizations with our zirconium amidinate pre-catalyst **1**, it was necessary to immobilize it on solid support material. The first solid support investigated was the W. R. Grace IOLA™ support activator (S/A).

IOLA support activator is an inorganic oxide, possessing Lewis Acid properties. This facilitates it being a good activator as well as support material. The IOLA material itself is a clay and silica agglomerate. It is made by spray drying a mixture of clay particles and silica gel. The particle is spherical in appearance and porous in nature. IOLA is considerably less expensive to produce compared to traditional Ziegler-Natta activators such as MAO. The IOLA can be easily disposed of, is environmentally friendly, non-hazardous and air stable (see Fig. 3-1).

Figure 3-1. IOLA Material



**W. R. Grace IOLA
Support Activator**

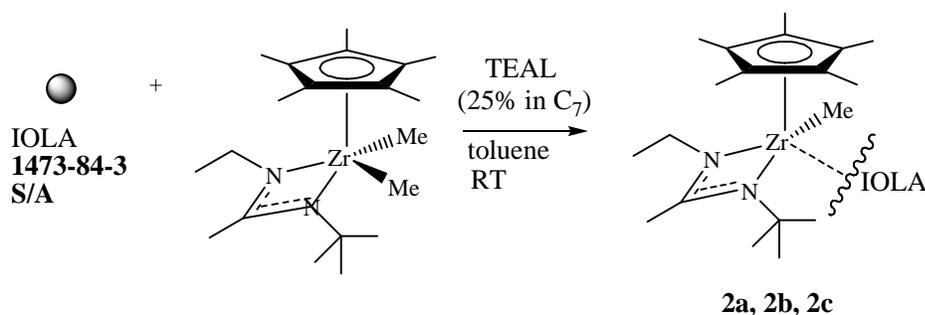


**W. R. Grace IOLA
Support Activator
Particles**

Experimental

For research purposes, only two IOLA™ support activators were tested. IOLA 1473-84-5 and IOLA 1473-84-3. IOLA support activator 1473-84-3 was prepared by calcining it in a furnace for 5 hours at 400 °C. The material was calcined at high temperature to remove any volatiles. For catalyst **2a**, **2b**, and **2c** 0.010 g of pre catalyst **1** was combined with 1.0 g of IOLA support activator in toluene to form a brown colored slurry. Triethylaluminum (TEAL) was added to the slurry in varying amounts for alkylation purposes. Alkylation was necessary to treat the surface of the IOLA material to minimize the presence of any poisons to the Zr metal center. The slurry was agitated for 2 hours before removing the volatiles in vacuo, to produce a sandy colored catalyst. Catalyst **2a**, **2b** and **2c** were produced in approximately 100% yield based on the pre-catalyst.

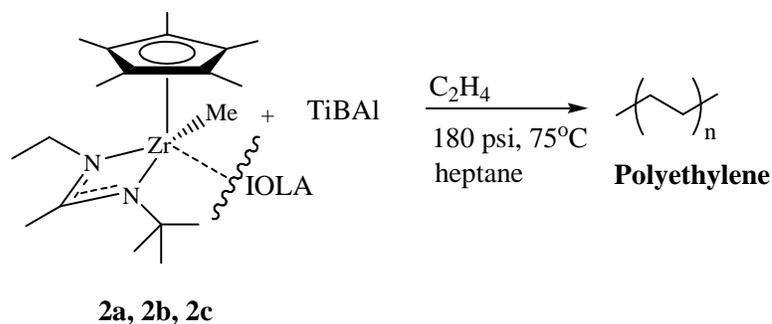
Scheme 3-1. Activation of 1 with IOLA™ Support Activator



The catalysts were prepared for polymerization by adding them to a solution of heptane and triisobutylaluminum (TiBAI) in a pressurized pop bottle. TiBAI is added as a scavenger to remove poisons in the polymerization reactor. All polymerizations were

done under controlled conditions in a polymerization reactor at 180 psi and 75 °C with 500 μ l of TiBAI for 1 hour.

Scheme 3-2. Polymerization of 2a, 2b and 2c Supported Catalyst



Results

The polymer from the IOLA™ supported catalyst was off white in color and had a flaky morphology. The activity of **2a-2c** decreased as the amount of TEAL added to the reaction was decreased (See Table 3-1). Catalyst activity dropped from 26.4 g/g.h⁻¹ with 0.5 mLs of TEAL (25% in heptane) to no activity at all when no TEAL was added. The kinetic profile of catalyst **2b** shows that activity spiked at the start of the reaction, then dropped. (See Figure 3-2). The lack of activity was interpreted to be an indication that more alkylation of the IOLA™ support activator's surface was needed, and as a result, the preparation of the catalysts was altered and the surface of the IOLA™ material was alkylated with TEAL before reacting with pre-catalyst **1**. This 'modified' IOLA material was called m-IOLA support activator.

Table 3-1 Polymerization from IOLA™ Supported Catalyst 2a, 2b and 2c

Entry	Catalyst	TEAL (mL)	Yield PE (g)	Cat. Act. ^a	Zr Act. ^b	Zr Act. ^c
1	2a	0.50	1.32	26.4	1.21×10^4	9.00
2	2b	0.10	0.640	13.6	6.23×10^3	4.64
3	2c	0.0	0.0	0.0	0.0	0.0

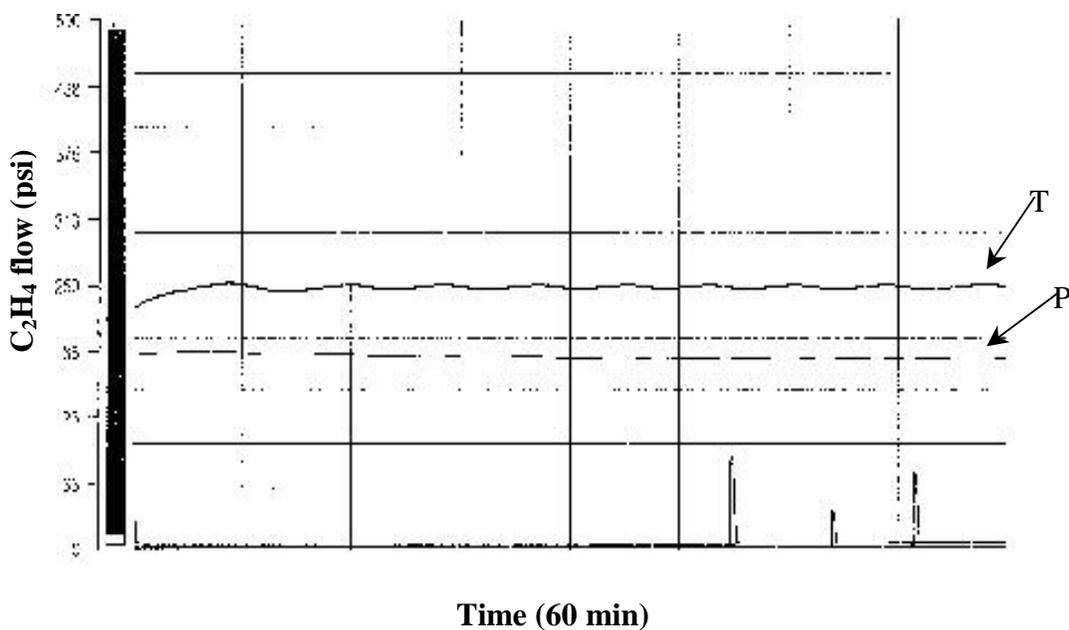
a. $(g_{PE}/g_{cat}).h^{-1}$, b. $(g_{PE}/g_{Zr}).h^{-1}$, c. $(g_{PE}/mmol_{Zr}).h^{-1}.atm^{-1}$

Figure 3-2. Polymerization Kinetic Profile of 2a @ 180 psi, 75 °C

Legend

T Temperature

P Pressure

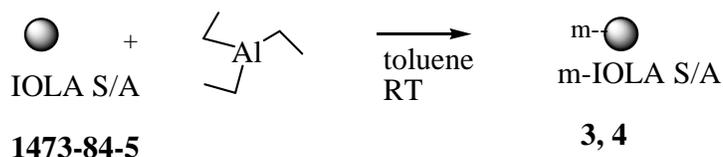


m-IOLA™ Support Activator

Experimental

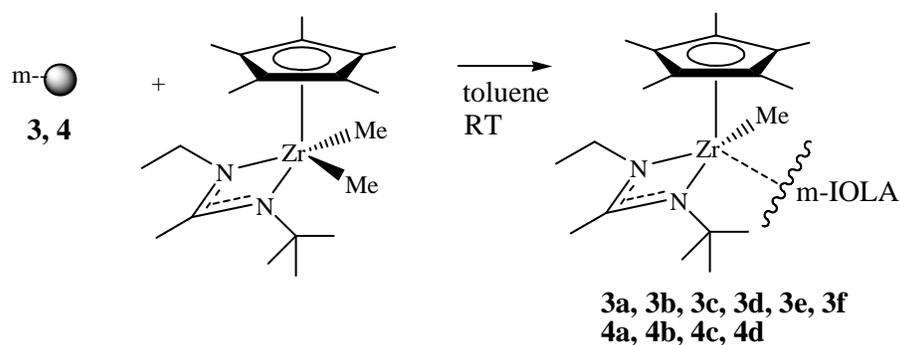
The IOLA™ support activator 1473-84-5 was calcined in two batches. The first batch was calcined at 500 °C and the other at 250 °C for 5 hours each. These two IOLA support activators (10.0 g each) were then combined with the 5.0 mLs of the alkylating agent, TEAL (25% in heptane) in a toluene solution and allowed to agitate for 2 hours at RT before removing the volatiles in vacuo.

Scheme 3-3. Preparation of m-IOLA™ Support Activator

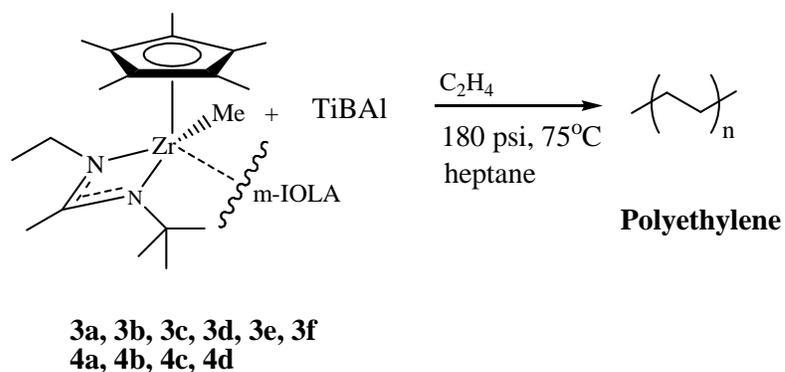


The material calcined at 500 °C was called m-IOLA support activator 3 and material calcined at 250 °C became m-IOLA support activator 4. Catalysts **3a-3f** and **4a-4d** were prepared by combining 1.0 g of the respective mIOLA support activator with pre-catalyst **1** at varying loading levels in a toluene solution. The resulting slurry was brick red in color, and was allowed to agitate for 2 hours before removing volatiles in vacuo. The catalysts were pink in color and obtained in yields of approximately 100 % based on the pre-catalyst.

Scheme 3-4. Activation of 1 with m-IOLA™ Support Activator 3 and 4



Scheme 3-5. Polymerization of m-IOLA™ Supported Catalyst



All polymerizations of catalyst **3a-3f** and **4a-4d** were performed under controlled conditions in a polymerization reactor at 180 psi and 75 °C with 500 μ L of TiBAI for 1 hour with 0.050 g of catalyst.

Results

The polymers made from catalyst **3a-3f** and **4a-4d** were white and had no defined morphology. They were a mix of powdery, and fluffy polymer. There was also

considerable reactor fouling: meaning that there was a film of melted polymer on the blades and wall of the reactor. The trend noticed for catalysts made from m-IOLA™ support activator **3** was that as pre-catalyst **1** loading was increased, the polymerization activities decreased (see Table 3-2). The catalyst with the highest loading **3f** (0.075 g of **1**) had the lowest activity of 53 g/g.h⁻¹, while the catalyst with the lowest pre-catalyst loading had the highest activity of 196 g/g.h⁻¹. The only deviation from this trend was noticed with catalyst **3d**. The activity for catalyst **3d** was 26 g/g.h⁻¹, which was lower than the activity for catalysts **3e** and **3f**; both of which had a higher pre-catalyst loading. This deviation from the trend is attributed to the fact that 0.5 mLs of TEAL was added to the catalyst preparation.

Table 3-2. Polymerization Results of Catalysts Prepared from m-IOLA™ S/A 3

Entry	Catalyst	Cat. 1 (g)	Yield (g)	Cat. Act ^a	Zr Act ^b	Zr Act ^c
1	3a	0.010	9.78	196	8.63x10 ⁴	600
2	3b	0.020	9.78	196	4.48x10 ⁴	300
3	3c	0.025	6.51	130	2.33x10 ⁴	177
4*	3d	0.030	1.30	26.0	3.88x10 ³	29.5
5	3e	0.050	2.91	58.2	4.09x10 ³	39.6
6	3f	0.075	2.66	53.2	3.74x10 ³	24.1

a. (g_{PE}/g_{cat}).h⁻¹, b. (g_{PE}/g_{Zr}).h⁻¹, c. (g_{PE}/mmol_{Zr}).h⁻¹.atm⁻¹

*Catalyst **3d** was prepared with 0.50 mLs of TEAL

For catalysts **4a-4d**, there was no distinguishable trend. The kinetic profile of the catalyst **4a** shows that there was no activity. The reason behind this is not completely known at

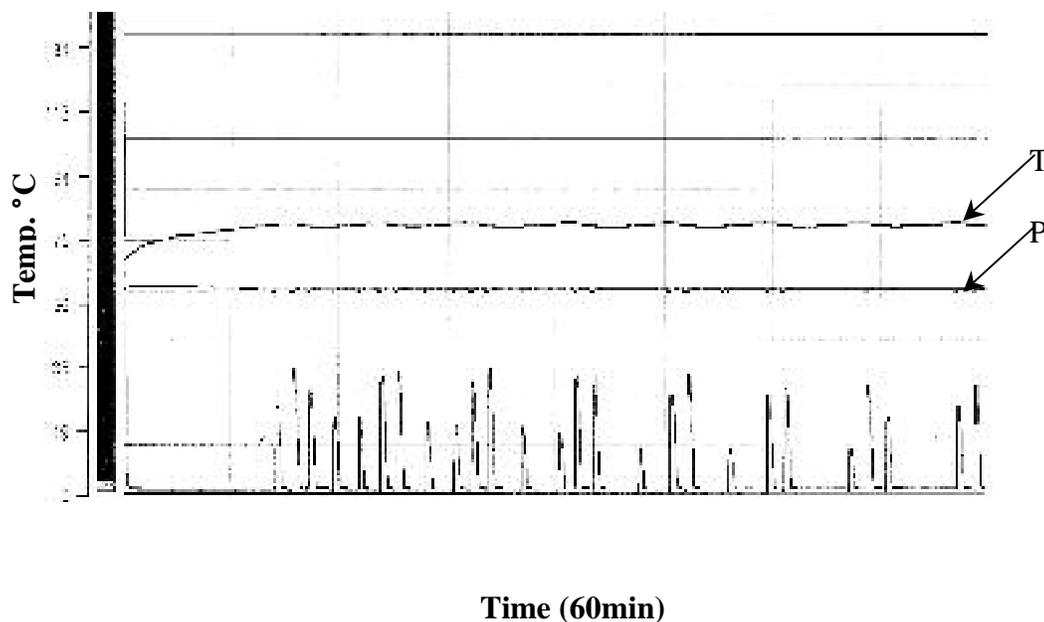
this time. Due to the response of the m-IOLA™ support activator, no further experimentation was done.

Table 3-3. Polymerization of Catalyst Prepared from m-IOLA™ S/A 4

Entry	Cat.	Cat. 1 (g)	Yield (g)	Cat. Act. ^a	Zr. Act. ^b	Cat. Act. ^c
1	4a	0.010	4.79	95.8	6.73×10^3	327
2	4b	0.025	8.66	173	1.22×10^4	237
3	4c	0.050	4.75	95.0	6.67×10^3	64.7
4	4d	0.075	5.33	107	7.49×10^3	48.5

a. $(g_{PE}/g_{cat}).h^{-1}$, b. $(g_{PE}/g_{Zr}).h^{-1}$, c. $(g_{PE}/mmol_{Zr}).h^{-1}.atm^{-1}$

Figure 3-3. Polymerization Kinetic Profile of Catalyst 4a @ 180 psi, 75 °C



MAO/Silica and MAO/IOLA™ Support Material

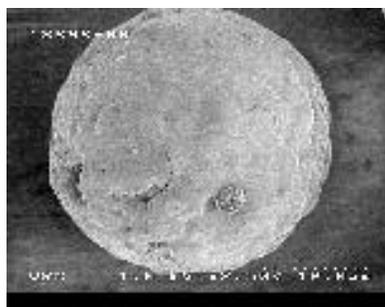
Introduction

Methylaluminoxane (MAO) supported on an inorganic oxide such as silica, accounts for the bulk of supported materials used in immobilizing single site catalysts. Silica is the support of choice for supporting metallocene catalyst, and can influence polymer morphology and catalyst activity. Its surface chemistry, in particular hydroxyl groups and siloxane bridges, are used for immobilizing reagents. In addition, silica controls the amount of fragmentation that occurs during the polymerization process, resulting in the creation of uniform polymer particles with high bulk densities and narrow particle size distribution. The second group of supports to be investigated was a MAO/Silica and MAO/IOLA support material produced at W. R. Grace. (See Fig. 3-4).

Figure 3-4. W. R. Grace Support Materials



**W. R. Grace MAO/IOLA B
Support Material**



**W. R. Grace MAO/Silica A
Support Material**

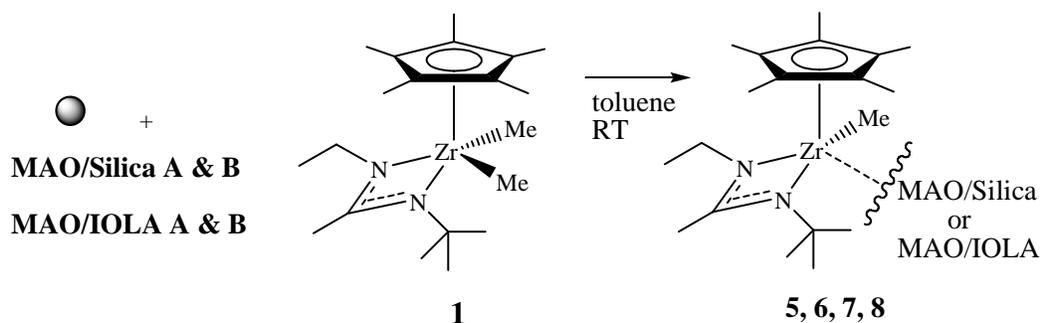
The support material is prepared by reacting either silica or IOLA support particles with a MAO solution in toluene. The MAO/Silica supports used were made with Silica A, which was an advanced 4th generation silica (MAO/Silica A) and Silica B, which is W. R.

Grace's Sylopol® 948 (MAO/Silica B). The two MAO/IOLA™ support materials used were MAO/IOLA A made from IOLA A and MAO/IOLA B prepared from IOLA B.

Experimental

The first supported catalysts prepared were made from 0.020 g of pre-catalyst **1** and 1.0 g of the MAO/Silica and MAO/IOLA support materials. MAO/IOLA A and B were used as the support for **5** and **6** respectively, while MAO/Silica A and B were used for **7** and **8** respectively. The MAO/Silica and MAO/IOLA support materials were prepared by using dehydrated silica or IOLA material and excess MAO in a hot toluene solution. The pre-catalyst **1** was added to slurry mixture of the support and toluene, and gently agitated for 2 hours. A yellow color was observed. The slurry was then filtered and the volatiles removed in vacuo. The dried catalysts were light to dark yellow in color and obtained in 100 % yield based on the pre-catalyst.

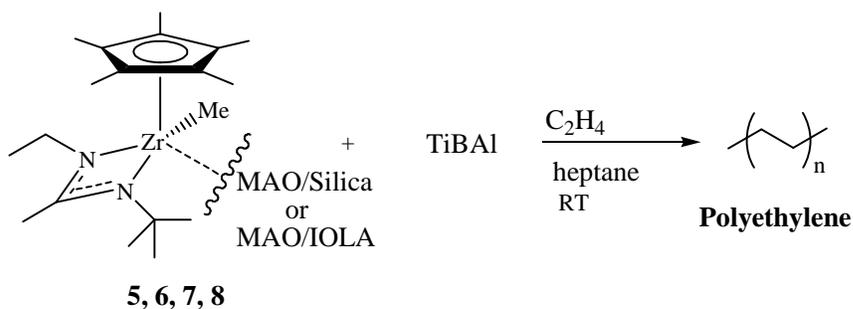
Scheme 3-6. Activation of 1 with MAO/Silica and MAO/IOLA™ Support



Preliminary polymerizations of catalyst **5**, **6**, and **7** were done in the dry box at RT before putting into the reactor. The catalysts were prepared in a glass vial with toluene and 200 μ l of TiBAI added to the desired vials (see Table 3-4-2). A stream of ethylene was bubbled through the solution (approximately 3-5 psi) and within 30 min, the solution became thick and viscous. Agitation became a problem and the reaction was stopped. The polymer was filtered and washed with acetone and heptane, then dried over night in a vacuum oven.

Scheme 3-7. MAO/Silica and MAO/IOLA™ Support Material

Polymerizations in Dry Box



After the preliminary catalyst testing in the dry box, the catalysts were remade with 0.050 g pre-catalyst **1** loading and tested in the polymerization reactor. The catalysts were prepared for polymerization by adding 0.050 g of the catalyst to a pop bottle with approximately 300 mLs of heptane. TiBAI was added to the solution at this time if necessary. The polymerizations were carried out in a polymerization reactor under controlled conditions at 180 psi and 75 °C for 1 hour.

Results

The polymers from the dry box reactions were white in color and had a fluffy like morphology. All the support results were promising, especially MAO/IOLA™ B support material (see Table 3-4-2, entry 2), polymerized with TiBAI, which appeared to be the most active with an activity of 44 g/g.h⁻¹.

Table 3-4-1. MAO/Silica and MAO/IOLA Support Comparison without TiBAI

Entry	Cat.	Support	Yield PE (g)	Cat. Act. ^a	Zr Act. ^b	Mn	PDI
1	5	MAO/IOLA A	0.27	13.5	1,244	5,600	5.59
2	6	MAO/IOLA B	0.40	20.0	1,843	28,200	4.38
3	7	MAO/Silica A	0.65	32.5	2,995	242,600	2.62

a. (g_{PE}/g_{cat}).h⁻¹, b. (g_{PE}/g_{Zr}).h⁻¹

Table 3-4-2. MAO/Silica and MAO/IOLA Support Comparison with TiBAI

Entry	Cat.	Support	Yield PE (g)	Cat. Act. ^a	Zr Act. ^b	Mn	PDI
1	5	MAO/IOLA A	0.39	19.5	1,797	177,800	5.54
2	6	MAO/IOLA B	0.88	44.0	4,055	288,200	4.10
3	7	MAO/Silica A	0.27	13.5	1,244	217,100	3.46

a. (g_{PE}/g_{cat}).h⁻¹, b. (g_{PE}/g_{Zr}).h⁻¹

The results from the reactor polymerizations of catalyst **5**, **6**, **7** and **8** (Table 3-5) confirmed the results seen in the dry box polymerizations. An activity of 1110 g/g.h⁻¹ was achieved for catalyst **6** from MAO/IOLA B support. Consequently, MAO/IOLA B support material was singled out, and used to prepare a series of supported catalysts

differing by pre-catalyst loading, using the method described above. A series of homo- and co-polymerizations were carried out on the resulting catalysts from MAO/IOLA™ B support material at various conditions in order to determine the best polymerization conditions for MAO/IOLA B support material.

Table 3-5. MAO/Silica and MAO/IOLA™ Support Comparison

Entry	Cat.	Support	Yield PE (g)	Cat. Act. ^a	Zr Act. ^b	Zr Act. ^c
1	5	MAO/IOLA A	10.1	201	1.85×10^4	4.48×10^6
2	6	MAO/IOLA B	22.2	1.11×10^3	9.87×10^4	2.38×10^7
3	7	MAO/Silica A	18.1	361	3.32×10^4	8.02×10^6
4	8	MAO/Silica B	6.80	136	8.30×10^3	2.00×10^6

a. $(g_{PE}/g_{cat}).h^{-1}$, b. $(g_{PE}/g_{Zr}).h^{-1}$, c. $(g_{PE}/mmol_{Zr}).h^{-1}.atm^{-1}$

Polymerization Variables

Pre-catalyst Loading

The first variable to be manipulated was pre-catalyst loading. This was necessary in order to determine which catalyst had the most effective metal activity. Catalysts **6a-6d** were prepared in toluene with 1.0 g of MAO/IOLA B support material according to the method described previously for the preparation of the MAO/IOLA supported catalyst. All the MAO/IOLA B supported catalysts were yellow in appearance and obtained in 96% yield based on the pre-catalyst. The polymerization reactions were run under controlled conditions in a polymerization reactor at 180 psi, 75 °C with 500 μL of TiBAI for 1 hour with 0.050 g of catalyst.

Scheme 3-8. Polymerization of 6a, 6b, 6c, 6d and 6

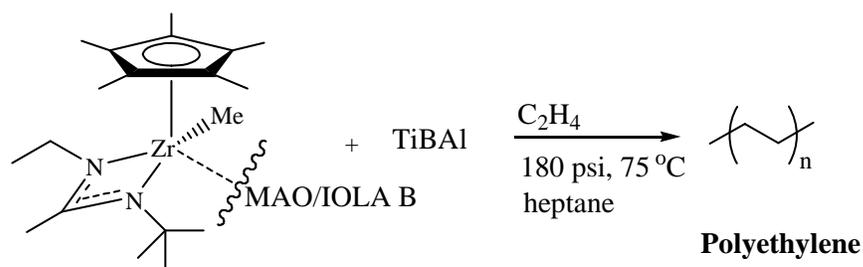


Table 3-6. Effect of Pre-catalyst Loading with Support MAO/IOLA B

Entry	Catalyst	Cp* (g)	Yield PE (g)	BD (g/cc)	Cat. Act. ^a	Zr Act. ^b	Zr Act. ^c
1	6a	0.010	4.25	n/a	85.0	3.89x10 ⁴	1.04x10 ⁷
2	6b	0.020	9.47	n/a	189	4.34x10 ⁴	1.16x10 ⁷
3	6c	0.025	12.6	n/a	251	4.60x10 ⁴	1.11x10 ⁷
4	6	0.050	48.1	0.29	962	8.81x10 ⁴	2.13x10 ⁷
5	6d	0.075	75.9	0.36	1520	9.28x10 ⁴	2.24x10 ⁷

a. (g_{PE}/g_{cat}).h⁻¹, b. (g_{PE}/g_{Zr}).h⁻¹, c. (g_{PE}/mmol_{Zr}).h⁻¹.atm⁻¹

From the polymerization results (Table 3-6), catalyst **6d** prepared with 0.075 g of pre-catalyst **1** proved to be the most active with an activity of 1519 g/g.h⁻¹ and a metal activity of 9.28x10⁴g/g.h⁻¹ (see entry 5). The polymer was white and made up of uniform granular particles. The bulk density of this material was 0.36 g/cc, which is fairly good by industrial standards. Particle size distribution measurements showed that the majority of the particles, 89.3 % were 250 microns in size. This material had a PDI of 2.81 and a molecular weight of 198,200.

TiBAI Effects

The next variable to be investigated was the effect of TiBAI on the polymerization activities. TiBAI is added to the polymerization reaction as a scavenger. It serves the purpose of reacting with any undesirable side reactions that may occur during the polymerization process and reduce activity. All polymerizations were conducted with 0.050 g of supported catalyst **6d**. Polymerization conditions were maintained at 75 °C and 180 psi for 1 hour.

Scheme 3-9. Polymerization of **6d** with Varying Amounts of TiBAI

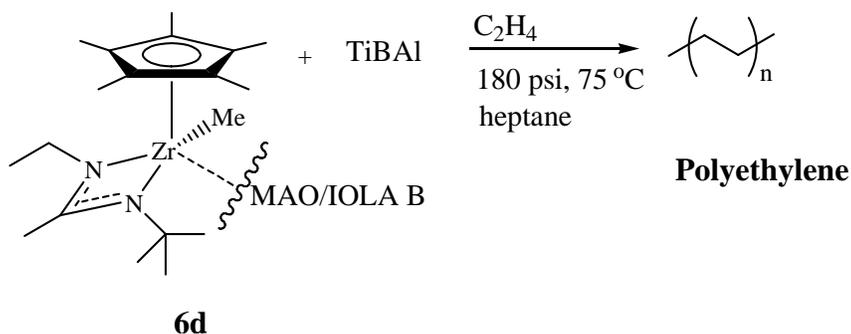


Table 3-7 Effect of TiBAI on Polymerization at 75 °C and 180 psi with **6d**

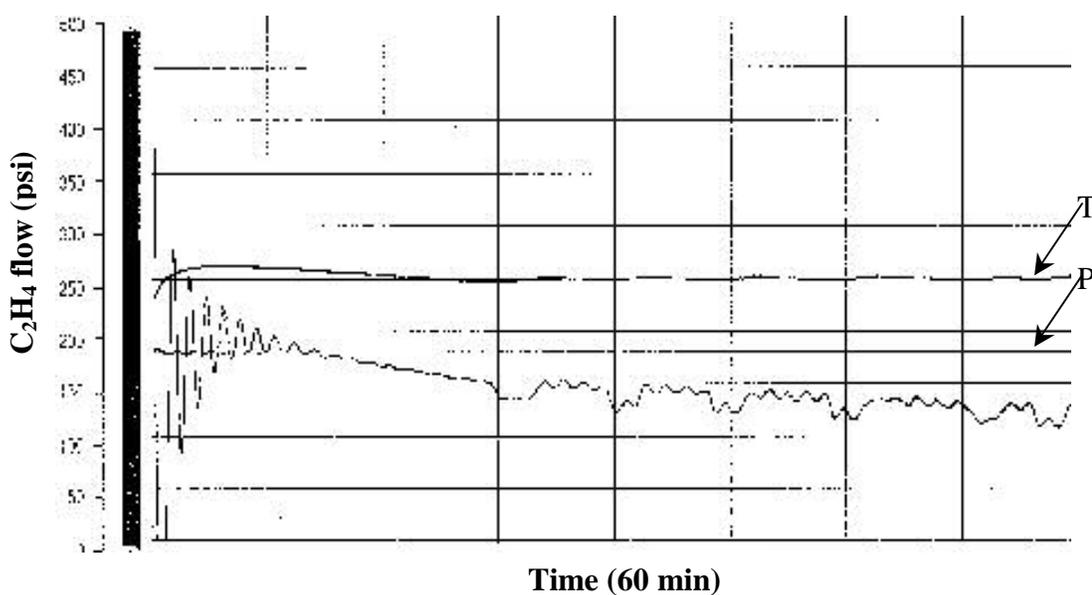
Entry	TiBAI (uL)	Yield PE (g)	BD (g/cc)	Cat. Act. ^a	Zr Act. ^b	Zr Act. ^c
1	500	75.97	0.36	1519	9.28x10 ⁴	2.24x10 ⁷
2	300	86.96	0.34	1739	1.06x10 ⁵	2.56x10 ⁷
3	200	99.73	0.34	1995	1.22x10 ⁵	2.94x10 ⁷
4	180	85.67	0.37	1713	1.05x10 ⁵	2.52x10 ⁷
5	175	90.97	0.38	1819	1.11x10 ⁵	2.68x10 ⁷
6	150	99.61	0.38	1992	1.22x10 ⁵	2.93x10 ⁷

Entry	TiBAI (uL)	Yield PE (g)	BD (g/cc)	Cat. Act. ^a	Zr Act. ^b	Zr Act. ^c
7	100	96.03	0.31	1921	1.17×10^5	2.83×10^7
8	0	53.08	0.36	1062	6.48×10^4	1.56×10^7

a. $(g_{PE}/g_{cat}).h^{-1}$, b. $(g_{PE}/g_{Zr}).h^{-1}$, c. $(g_{PE}/mmol_{Zr}).h^{-1}.atm^{-1}$

The polymers made from these reactions were all white in color and differed in morphology. The polymers made from 500 μ L (see Table 3-7, entry 1) and no TiBAI (entry 8) were more similar than the others. They were fine uniform particles and their bulk densities were identical 0.36 g/cc. Entry 3 and entry 6 which had the best catalyst activities of 1994 and 1992 $g/g.h^{-1}$ had higher bulk densities and the polymer particles were larger. Particle size distribution showed that 40 % and 50 % of the particles were 500 to 250 microns in size respectively. This experiment helped us to narrow down the balance of TiBAI, to activity and morphology. This was determined to be between 200 and 100 μ L of TiBAI.

Figure 3-5. Polymerization Kinetic Profile of 6d at 180psi, 75 °C and 200 μ L TiBAI



Hydrogen Effects

Hydrogen was added in small amounts (4-5 psi) directly into the reactor during the polymerization process. This was done because of the high molecular weights being achieved. The hydrogen was added in an attempt to reduce molecular weights by encouraging termination/hydride elimination. GPC results indicated that polymer with molecular weights of over 1,000,000 were being produced. Melting point index data could not be recorded for any of the polymers due to the fact that they could not be melted (because of high molecular weight). Polymerizations were conducted with 0.050 g of catalyst **6** at 200 psi and 80°C with 300 μ L of TiBAI.

Scheme 3-10. Polymerization of **6** with Hydrogen

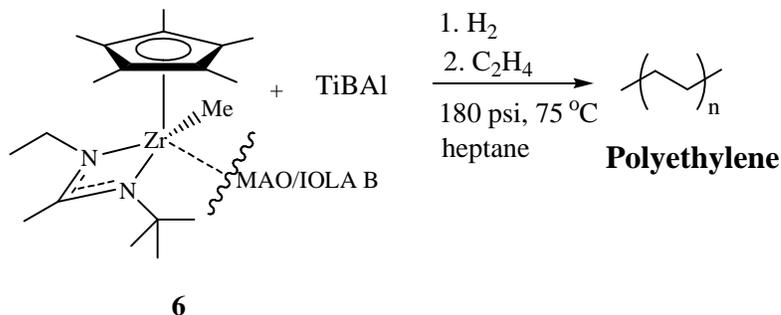


Table 3-8. Hydrogen Effects with Catalyst 6

Entry	C ₂ H ₄ (psi)	H ₂ (psi)	Yield PE (g)	Cat. Act. ^a	Zr Act. ^b	Zr Act. ^c	Mn	Mw	PDI
1	196	4	12.83	256.6	2.35x10 ⁴	6.17x10 ⁶	6,800	90,500	13.3
2*	195	5	14.36	287.2	2.63x10 ⁴	6.87x10 ⁶	6,000	29,600	4.93

* 10 mLs of 1-hexene

a. (g_{PE}/g_{cat}).h⁻¹, b. (g_{PE}/g_{Zr}).h⁻¹, c. (g_{PE}/mmol_{Zr}).h⁻¹.atm⁻¹

The polymer from these reactions had a fluffy quality. Hydrogen had the effect of dramatically reducing the catalyst activity of **6** compared to polymerizations without hydrogen (see Table 3-6). Although the molecular weight of the polymer was decreased, the reported PDI was 13.3 and the activity dropped from 962 g/g.h⁻¹ (Table 3-6, entry 4) to 256.6 g/g.h⁻¹ when 4 psi of hydrogen was added to the reactor. The activity of the polymerization with 1-hexene was not much better, even though the reported PDI had a lower value of 4.93.

Polymerization conditions

In an effort to determine the conditions at which the catalyst was most sensitive, the activity of the most active catalyst (**6d**) was tested at various polymerization conditions. The catalyst (0.050 g) was prepared in 300 mLs of heptane with 150 μL of TiBAI. The temperature and pressure of the polymerization reactions were varied.

Scheme 3-11. Polymerization of **6d** at Varying Temperature and Pressure

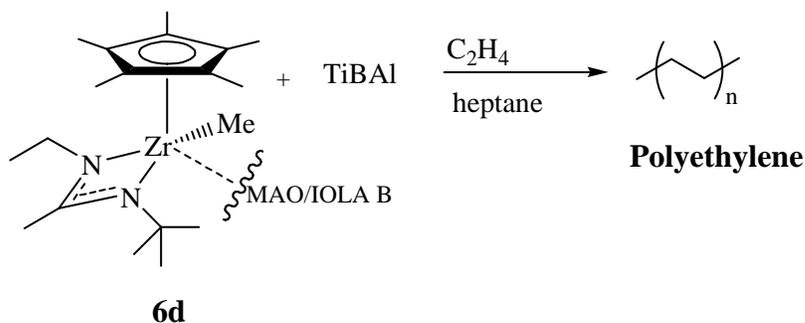


Table 3-9. Catalyst **6d at Varying Temperature and Pressure**

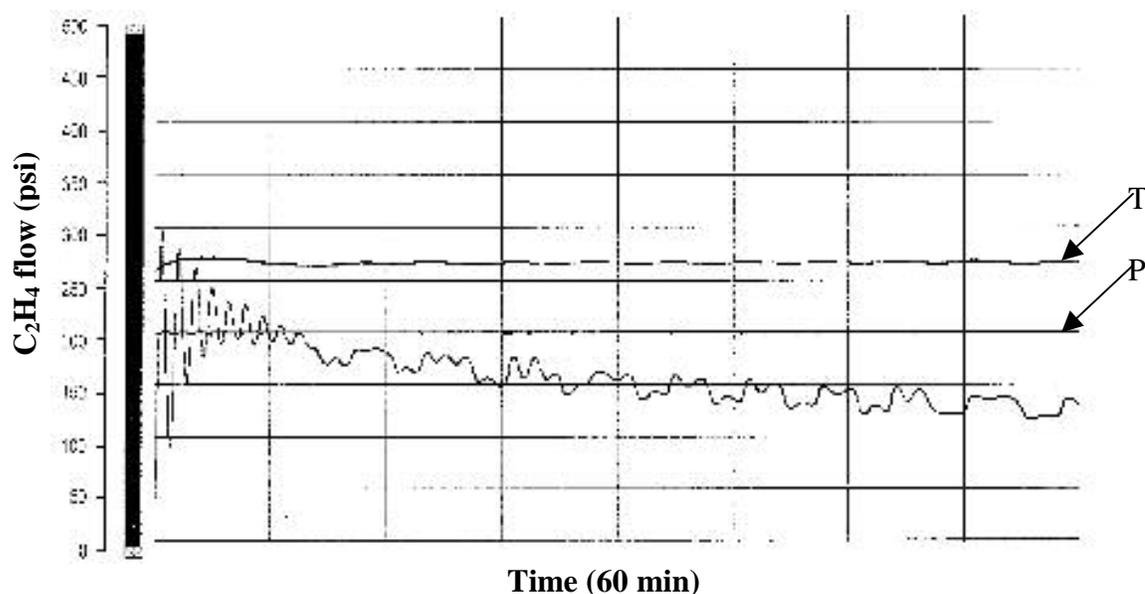
Entry	C ₂ H ₄ (psi)	Temp (°C)	Yield PE (g)	BD (g/cc)	Cat. Act. ^a	Zr Act. ^b	Zr Act. ^c
1	180	75	99.61	0.38	1992	1.22x10 ⁵	2.93x10 ⁷

Entry	C ₂ H ₄ (psi)	Temp (°C)	Yield PE (g)	BD (g/cc)	Cat. Act. ^a	Zr Act. ^b	Zr. Act. ^c
2	180	80	92.14	0.37	1843	1.12x10 ⁵	2.71x10 ⁷
3	200	80	107.6	0.37	2153	1.31x10 ⁵	3.52x10 ⁷

a. (g_{PE}/g_{cat}).h⁻¹, b. (g_{PE}/g_{Zr}).h⁻¹, c. (g_{PE}/mmol_{Zr}).h⁻¹.atm⁻¹

The catalyst activity of **6d** was most favorable at 200 psi, 80 ° C with 150µL of TiBAI (see Table 3-9, entry 3). The polymer produced from this reaction had good morphology (no clumping and few fines) with no reactor fouling. The activity of 2153 g/g.h⁻¹ was higher than the last reported activity of 1995 g/g.h⁻¹ when catalyst **6d** was polymerized at 180 psi and 75° C with 200 µL of TiBAI (see Table 3-7). This material had a molecular weight of 239,000, a PDI of 2.25 and melting point of 135 °C.

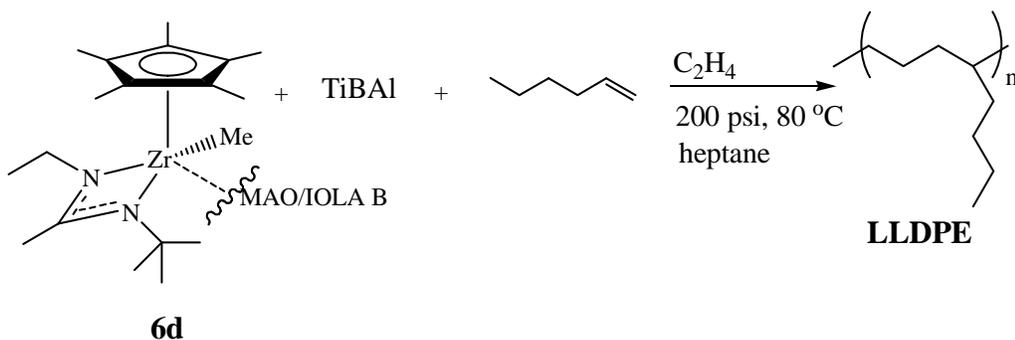
Figure 3-6. Polymerization Kinetic Profile of 6d at 200 psi, 80 ° C and 150 uL TiBAI



Ethylene and 1-Hexene Co-polymerizations

The efficiency of catalyst **6d** was tested on its capability to produce ethylene and 1-hexene co-polymer material. Two methods of 1-hexene additions to the polymerization reaction were investigated. The first involved adding 1-hexene directly to the pop bottle with the catalyst and heptane solution. The second method involved adding the co-monomer directly to the reactor vessel under pressure before adding the catalyst and heptane solution. All polymerizations were run at 80 °C, 200 psi with 150 μL of TiBAI and 0.05 g of catalyst.

Scheme 3-12. Co-polymerization of Ethylene and 1-hexene (Method 1)



Scheme 3-13. Co-polymerization of Ethylene and 1-hexene (Method 2)

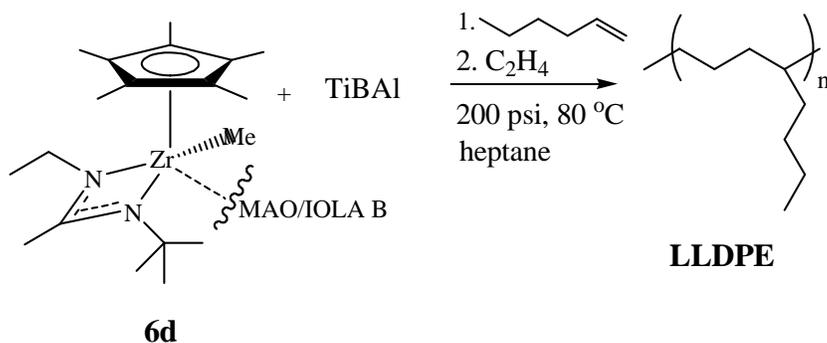


Table 3-10. Polymerization Results of Co-polymerizations with 6d

Entry	1-Hex (mLs)	Yield PE (g)	Cat. Act. ^a	Zr Act. ^b	Zr Act. ^c	Mn	Mw	PDI
1	10.0	78.66	1573	9.60x10 ⁴	2.32x10 ⁷	262,000	561,800	2.14
2*	10.0	22.79	455.8	2.78x10 ⁴	7.46x10 ⁶	355,500	1,049,000	2.95
3	5.00	86.65	1733	1.06x10 ⁵	2.84x10 ⁷	509,600	1,377,500	2.70
4*	5.00	74.84	1497	9.14x10 ⁴	2.45x10 ⁷	465,000	1,154,000	2.48
5	2.50	88.46	1769	1.08x10 ⁵	2.96x10 ⁷	488,000	1,220,500	2.50
6*	2.50	88.05	1761	1.07x10 ⁵	2.88x10 ⁷	586,700	1,372,000	2.34

a. (g_{PE}/g_{cat}).h⁻¹, b. (g_{PE}/g_{Zr}).h⁻¹, c. (g_{PE}/mmol_{Zr}).h⁻¹.atm⁻¹

* Method 2

There was a visible difference between the polymer materials produced by the two different methods. The polymer produced from Table 3-10, entry 1 with 10 mLs of 1-hexene was a mix of granular and clumpy particles, while the polymer produced by the alternate method (entry 2) was one large clump of polymer. Polymers with 5 and 2.5 mLs of 1-hexene reacted the similarly. The polymer material from the first method remained more granular while the polymer from the other method was clumpier. Nothing could be clearly determined from GPC data. DSC results showed that the average melting point for the homo-polymers was 135 °C, while the melting point of the co-polymers was 131 °C (some 1-hexene incorporation).

NMR data was very difficult to obtain. Samples had to be heated in an oven for up to 4 hours at 140 °C in order to get the polymer melted and into solution. ¹H NMR and ¹³C NMR for the homo-polymer closely resembled NMR data for UHMWPE (see Fig. 3-7 and 3-8)²³. For the ¹H NMR of the homo-polymer a resonance appeared at 1.5 ppm and 30 ppm for ¹³C NMR. Preliminary ¹³C NMR from the co-polymer, indicated that there

was less than 0.15% wt incorporation of 1-hexene at 10 mLs for the polymer made by method 1. ^{13}C NMR for the polymer made via Method 2 at 10 mLs (entry 2) was not obtained. The material could not be melted.

Figure 3-7. ^1H NMR of Homo-polymer in Trichlorobenzene @ 140 °C

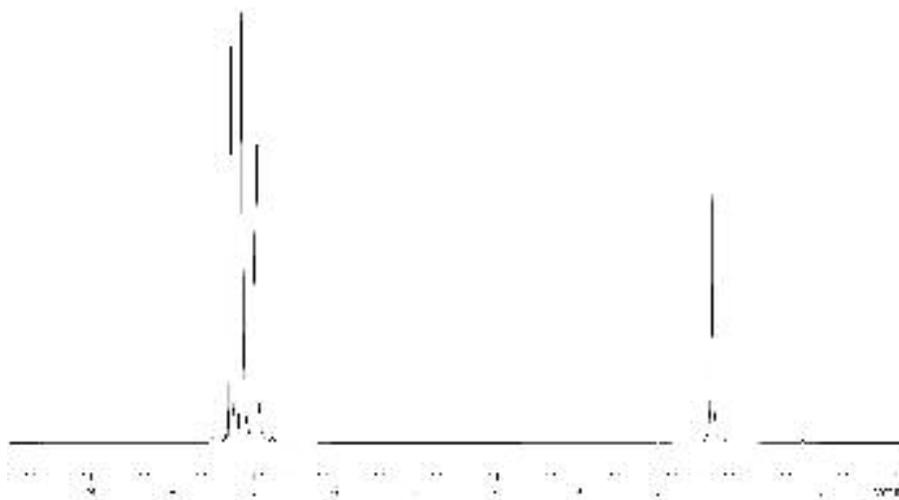
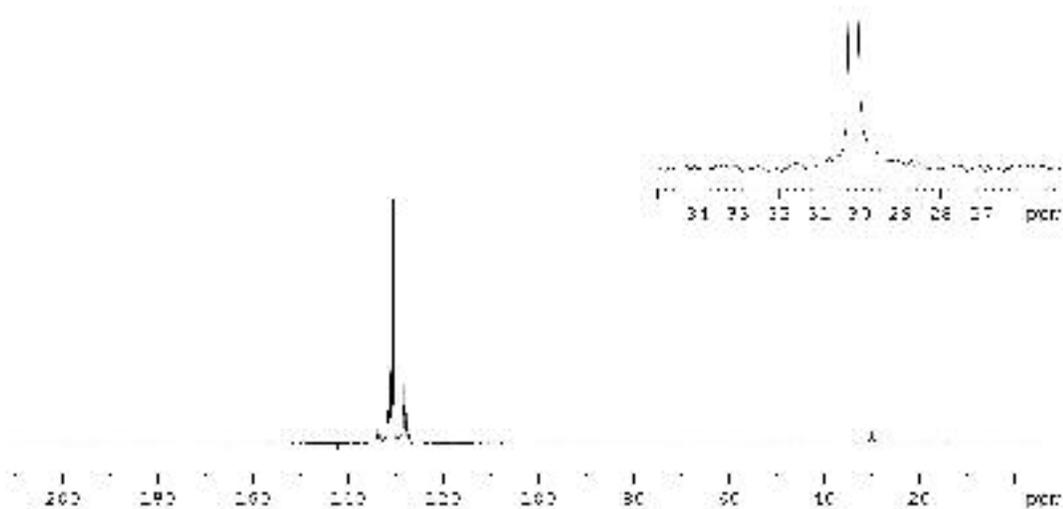


Figure 3-8. ^{13}C NMR of Homo-polymer in Trichlorobenzene @ 140 °C



Chapter 4: Conclusion

The initial homogeneous polymerizations of the zirconium amidinate catalyst proved to us that the system was capable of ethylene polymerization and encouraged us to attach it to a solid support.

The first support tested for ethylene polymerizations, the W. R. Grace IOLA™ support activator was not successful in producing polymer with good morphology and activity. Activities ranged from 26.4 $\text{g}_{\text{PE}}/\text{g}_{\text{cat}}\cdot\text{h}^{-1}$ to 0, and the polymer was flaky in appearance. The IOLA support activator was then modified with TEAL in an attempt to increase activity. This new support activator was called m-IOLA material and was used to activate the zirconium amidinate pre-catalyst. The m-IOLA support activator's performance was not much better than the IOLA support activator. The polymer produced had poor morphology and activities ranging from 173 $\text{g}/\text{g}\cdot\text{h}^{-1}$ to 53 $\text{g}/\text{g}\cdot\text{h}^{-1}$. There was also considerable reactor fouling associated with the support activator.

The next supports tested were the MAO/Silica A and B, and MAO/IOLA A and B support materials. From preliminary ethylene polymerizations in the dry box, MAO/IOLA B support material proved to be superior to the others. This was even more evident when the support was tested on the polymerization reactor and produced polymer with uniform particles, minimal fines, good bulk density, no reactor fouling and activities of 1100 $\text{g}/\text{g}\cdot\text{h}^{-1}$. The next best activity of 361 $\text{g}/\text{g}\cdot\text{h}^{-1}$ was achieved by support material MAO/Silica A.

MAO/IOLA™ B support material was then singled out and various manipulations carried out on the catalyst and polymerization conditions. In order for the catalysts to be truly successful it was necessary to determine the best pre-catalyst loading level. A series

of catalyst were prepared ranging in pre-catalyst **1** loading from 0.010 g to 0.075 g. The catalyst **6d** prepared with 0.075 g of pre-catalyst was the most active, producing polymer with good morphology at relatively mild industrial conditions (180 psi, 75 °C) and activity of 1519 g/g.h⁻¹.

GPC and NMR data of the polymer proved to be difficult to obtain due to the extremely high molecular weights of the polymers being reported. In an attempt to solve this problem, a small amount of hydrogen was added to the polymerization reactions to reduce the molecular weights. As a result of this, the catalyst activity dropped to 257 g/g.h⁻¹ and the molecular weights were greatly decreased.

The sensitivity of the most promising catalyst **6d** was investigated at varying temperature and pressure polymerization conditions. The amount of TiBAI added to the reaction was also investigated. Catalyst **6d** performed the best with 150 uL of TiBAI, at 200 psi and 80 °C. Polymer produced at these conditions had good morphology, no reactor fouling and an activity of 2153 g/g.h⁻¹, the highest activity achieved so far with MAO/IOLA™ B support material.

Ethylene and 1-hexene co-polymerizations were carried out with catalyst **6d**. The 1-hexene was added to the reaction using two different methods. ¹³C NMR data showed that there was less than 0.15 % wt of 1-hexene incorporation when 10 mLs of 1-hexene was added to the reaction with the catalyst in solution. DSC results also show that the melting point of the homo-polymer was 135 °C and 131 °C for the co-polymer, indicating there is some degree of 1-hexene incorporation. More co-polymer research and characterization with the catalyst is needed.

At every pre-catalyst loading level, the MAO/IOLA™ B support material was more active than the IOLA support activator. The exact reason as to why the MAO/IOLA support material out performed the IOLA and m-IOLA support activators, and MAO/Silica support materials is not known. A head to head comparison of the various supports is shown in Table 4-1.

Table 4-1. Comparison of Solid Supports at 180 psi and 75 °C

Entry	Support	Cat.	Cp* (g)	Yield PE (g)	Cat. Act ^a	Zr Act ^b	Zr Act ^b
1	MAO/IOLA B	6a	0.010	4.25	85.0	3.89x10 ⁴	1.04x10 ⁷
2	IOLA	2a	0.010	0.680	26.4	6.23x10 ³	9.00
3	m-IOLA™ 3	3a	0.010	9.78	196	8.63x10 ⁴	600
4	m-IOLA™ 4	4a	0.010	4.79	95.8	6.73x10 ³	326
5	MAO/IOLA B	6c	0.025	12.6	251	4.60x10 ⁴	1.11x10 ⁷
6	m-IOLA™ 3	3c	0.025	6.51	130	2.33x10 ⁴	177
7	m-IOLA™ 4	4b	0.025	8.66	173	1.22x10 ⁴	236
8	MAO/IOLA B	6	0.050	22.2	1.11x10 ³	9.87x10 ⁴	2.38x10 ⁷
9	m-IOLA™ 3	3e	0.050	2.91	58.2	4.09x10 ³	39.7
10	m-IOLA™ 4	4c	0.050	4.75	95.0	6.67x10 ³	64.8
11	MAO/IOLA B	6d	0.075	99.7	1.99x10 ³	1.22x10 ⁵	2.94x10 ⁷
12	m-IOLA™ 3	3f	0.075	2.66	53.2	3.74x10 ³	24.2
13	m-IOLA™ 4	4d	0.075	5.33	106	7.49x10 ³	48.5

a. (g_{PE}/g_{cat}).h⁻¹, b. (g_{PE}/g_{Zr}).h⁻¹, c. (g_{PE}/mmol_{Zr}).h⁻¹.atm⁻¹

It is believed however, that MAO/IOLA™ B support material performed better than the other MAO/Silica and MAO/IOLA support materials because it was more porous and therefore allowed for more access to the metal's active site (see Fig. 3-4).

The results of the MAO/IOLA B support material with the zirconium amidinate pre-catalyst exceeded all expectations. The supported catalyst **6d** was able to produce polymer with good morphology, acceptable industrial standard bulk density of 0.37 g/cc and polymer activities of over 2100 g/g.h⁻¹. The fact that the catalyst was able to polymerize ethylene without any reactor fouling was another desirable quality it possessed. However, there is still a lot of research to be done with respect to characterization of the homo-polymer and co-polymer. As mentioned earlier, GPC results recorded cannot be completely trusted, due to the extremely high molecular weights being produced. Future work with this catalyst system would include investigating the activity of the cyclopentadienyl version of the amidinate catalyst verses the cyclopentamethyldienyl version used in this research. In addition it is more than likely that changing the amidinate ligand would also have an effect on the catalyst activity. This zirconium amidinate catalyst supported on MAO/IOLA B support material has not only proven that it can successfully polymerize ethylene to industry standards, but with more research has the potential to become a true player in the industrial world of supported Ziegler-Natta polymerization catalyst.

Experimental

Dry, oxygen-free solvents and standard Schlenk line and glove box techniques were used throughout. Heptane (JT Baker) was dried over molecular sieves calcined at 300 °C and degassed in an argon pressurized POPE tank before use. Toluene (Aldrich 99.8% anhydrous) was dried over molecular sieves calcined at 300 °C. 1-Hexene (Aldrich, 97 %) and chlorobenzene (Aldrich 99.9 %) were distilled over appropriate drying agents. Diethyl ether (99.9% anhydrous in sure seal bottle), methyl lithium, chlorotrimethylsilane, and 1-t-butyl, 3-ethylcarbodiimide were obtained from Aldrich and used without further purification. Cyclopentadienylzirconium trichloride (Cp^*ZrCl_3) and N,N-Dimethylaniliniumtetra(pentafluoro-phenyl)borate $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ were obtained from Strem and used as received. All GPC data was collected on a Viscotek HighTemperature Chromatogram Series PL-GPC-220 with precision detectors PD 2040 & Viscotek viscometer 220R and 4 PLgel 20 μm MIXED-ALS (300x7.5mm) columns. The eluent used was 1,2,4 trichlorobenzene and 0.00125% BHT as a stabilizer and a flow rate of 1.0ml/min. All ^1H and ^{13}C NMR was collected on a 400 MHz Bruker instrument using a solution of 1,2,4 trichlorobenzene and d-benzene. NMR polymer samples had to be heated in sealed tubes at 140 °C in oven. DSC data was performed on a Perkin-Elmer DSC-7 instrument. IOLATM and MAO/Silica and MAO/IOLA support materials were obtained from Grace Davison at Curtis Bay, MD and calcined before use in a Lindberg Blue box furnace between 300 °C and 500 °C for 5 hours.

Synthesis of Pre-catalyst 1

To a solution of 1.00 g (3.09 mmols) of Cp*ZrCl₃ in 70 mLs of heptane cooled to -50 °C, 7.49 mLs (10.19 mmols) of MeLi was added. An additional 10 mLs of Et₂O was added to the solution and allowed to stir for 2 hours. The reaction was quenched with 0.5 mLs of TMS-Cl and allowed to stir for 10 min. A solution of 0.37 g (2.93 mmols) 1-t-butyl,3-ethylcarbodiimide in 10 mLs of Et₂O was added to the solution at -30 °C and allowed to stir for 3 hours. The volatiles were removed in vacuo and the product recrystallised from heptane at -15 °C. Yield was 78%. ¹H NMR (400 MHz, C₆D₆): δ 0.25 (s, 6H), 0.91 (t, 3H, J=7.1 Hz), 1.17 (s, 9H), 1.70 (s, 3H), 2.02 (s, 15H), 2.86 (q, 2H, J=7.1 Hz).

IOLA™ Supported Catalyst 2a, 2b and 2c

IOLA 1473-84-3 S/A calcined at 400 °C (1.00 g), was placed in a 100 ml round bottom flask and 19.5 mLs of toluene added. For catalyst **2a** and catalyst **2b** 0.50 mLs (0.063 mmols) and 0.10 mLs (3.15 x 10⁻⁴ mmols) of triethylaluminum (TEAL) were added respectively via syringe to the flask while swirling. Pre-catalyst **1** (0.010g, 0.0251 mmols) was dissolved in 0.50 mLs of toluene and added to the solution while swirling. The flask was attached to a rotary evaporator (spinning only) for 2 hours. The volatiles were removed in vacuo. The average yield was 100 %.

Preparation of m-IOLA Support Activator 3 and 4

IOLA 1473-84-5 support activator, calcined at 500 °C for **3** (10.0g) and IOLA 1473-91 calcined at 250 °C for **4** (10.0 g) was placed in a 100 mL round bottom flask and 33 mLs of toluene added. Using a syringe the TEAL (5.0 mLs, 0.028 mmols) was added to the

flask while swirling. The flask was attached to a rotary evaporator (spinning only) for 2 hours. The solution was then filtered in a medium frit and washed with heptane. The catalyst was dried in vacuo for 3 to 4 hours. The average yield was 100 %.

Synthesis of Catalyst 3a-3f

m-IOLA™ support activator **3** (1.00 g) was placed in a 100 mL round bottom flask and 19.5 mLs of toluene added. For catalyst **3a-3f**, 0.010 g, (0.0250 mmols), 0.020g (0.050 mmols), 0.025 (0.0628 mmols), 0.030 g (0.075 mmols), 0.050 g (0.125 mmols) and 0.075g (0.188 mmols) of pre- catalyst **1** was dissolved respectively in 0.5 mLs of toluene and added to the solution while swirling. The flask was attached to a rotary evaporator (spinning only) for 2 hours. The solution was then filtered in a medium frit and washed with heptane. The catalyst was dried in vacuo for 3 hours. The average yield was 100 %.

Synthesis of Catalyst 4a-4d

m-IOLA S/A **4** (1.00 g) was placed in a 100 mL round bottom flask and 19.5 mLs of toluene added. For catalyst **4a-4d**, 0.010 g, (0.0250 mmols), 0.025 (0.0628 mmols), 0.050 (0.125 mmols) and 0.075 g (0.188 mmols) of pre-catalyst **1** was dissolved respectively in 0.5 mLs of toluene and added to the solution while swirling. The flask was attached to a rotary evaporator (spinning only) for 2 hours. The solution was then filtered in a medium frit and washed with heptane. The catalyst was dried in vacuo for 3 hours. The average yield was 100 %.

Preparation of MAO/Silica and MAO/IOLA™ Supported Catalyst 5, 6, 7 and 8

MAO/Silica A support material (1.00 g) was placed in a 100 mL round bottom flask and 20 mLs of toluene added. Pre-catalyst **1** (0.050g, 0.125 mmols) was dissolved in 0.5 mLs of toluene and added to the round bottom flask. The flask was placed on a shake table for 2 hrs. The solution was then filtered in a medium frit and washed with heptane. Catalyst **5** was dried in vacuo for 3 hours. The same procedure using support materials MAO/IOLA B, MAO/Silica A, and MAO/Silica B was used to prepared catalyst **6, 7** and **8** respectively. Average yield was 100 %.

Preparation of MAO/IOLA B Supported Catalyst 6a-6e

MAO/IOLA B support material (1.00 g) was placed in a 100 mL round bottom flask and 19.5 mLs of toluene added. For catalyst **6a-6e**, 0.010 g, (0.0250 mmols), 0.020g (0.050 mmols), 0.025 (0.0628 mmols), 0.050 g (0.125 mmols) and 0.075g (0.188 mmols) of pre-catalyst **1** was dissolved respectively in 0.5 mLs toluene and added to the round bottom flask. The flask was attached to a rotary evaporator (spinning only) for 2 hours. The solution was then filtered in a medium frit and washed with heptane. The catalyst was dried in vacuo for 3 hours. Average yield was 100 %.

Polymerization Procedure

Homogeneous Polymerization procedure

The catalyst was prepared by adding a solution of 0.050 g (0.125 mmols) of **1** in 4 mLs of chlorobenzene to 0.10 g (0.125 mmols) of [PhNMeH₂][B(C₆F₅)₄] in 6 mLs of chlorobenzene. After 10 min, a stream of ethylene gas (approx. 3-5 psi) was bubbled

through the solution. At the desired time the polymerization was quenched with 6-7 mLs of methanol. The polymer was filtered and washed with acetone and heptane. It was then allowed to dry overnight in a vacuum oven.

Heterogeneous Polymerization procedure

To a pop bottle, approx. 300 mLs of heptane was added. TiBAI if needed, was added at this time. The catalyst was then weighed and added to the pop bottle while swirling. The bottle was removed from the dry box and solution injected into the reactor set at desired conditions.

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