

SINGLE SITE CATALYST FOR NOVEL ETHYLENE/ PROPYLENE POLYOLEFINS

By

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A THESIS PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

UNIVERSITY OF FLORIDA

2016

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To my father, my mother, my wife, and my son

ACKNOWLEDGMENTS

I am grateful to many people for assistance, advice, and encouragement. It was Prof. Abdul-Aziz Al-Suhybany and Prof. Abdul-Aziz Al-Wassil who have first inspired me to pursue a higher education; therefore I am thankful for their support and communication along with my graduate experience.

I would like to thank Prof. Miller who gives me a chance to join his group and for his support and guidance. Also, I would like to thank my committee members, Prof. Grenning and Prof. Smith for their supports and encouragements.

I would like to thank all of Miller unit who have shared time and knowledge with me, more precisely Ha Nguyen for being a productive mentor and being there for discussion and ideas.

Also I would like to thank my employer "SABIC" for funding my higher education. Also, I would like to thank Dr. Abdul-Aziz Al-Humydi and Dr. Khalid Al-Bahily for their support and encouragement and all of my colleagues at SABIC.

I am entirely grateful to my parents, my wife, and my sibling who have supported and encouraged me.

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LIST OF ABBREVIATIONS

C	Celsius
Cat.	Catalyst
Cp	Cyclopentadiene
DSC	Differential Scanning Calometry
EPM	Ethylene/propylene rubber
Equiv.	Equivalent
g	Grams
HDPE	High density polyethylene
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MAO	Methylaluminoxane
mL	Milliliter
mol.	Moles
NMR	Nuclear magnetic resonance
PE	Polyethylene
PP	Polypropylene
r_e	Reactivity ratio of ethylene monomer
r_p	Reactivity ratio of propylene monomer
T_g	Glass transition temperature
T_m	Melting temperature
X_e	Mole fraction of ethylene
X_p	Mole fraction of propylene
η	Hapticity

Abstract of Thesis Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Master of Science

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May 2016

Chair: Stephen A. Miller
Major: Chemistry

Both the performance and properties of ethylene/propylene copolymer-rubber EPM depend on the monomer distribution along the polymer chain. EPM was synthesized using different metallocene systems: (A) Oct-Cp catalyst, (B) Ewen catalyst, (C) Cp_2ZrCl_2 catalyst, and (D) Brintzinger catalyst (Figure 1.3). As a result, the EPM made from the metallocene catalyst (A) having Oct ligand has tendency to form long sequences of α -olefin vs. ethylene. This was seen by the relative amount between the comonomer as $r_e r_p > 1$. Moreover, the copolymer shows a dramatic increase of r_p compared to r_e (reactivity ratio of ethylene and propylene, respectively). It has been noticed that the nature of the Oct ligand has influence on the copolymerization selectivity to incorporate more α -olefin than ethylene, the overall activity, and on the stereochemistry. Moreover, this particular copolymer almost bears no EEE sequences (ethylene triad sequences), which might lead to better thermal properties as it shows tendency for the T_g to be as high as $-13\text{ }^\circ\text{C}$. The sequence distributions of EPM copolymers was analyzed by ^{13}C NMR as described by Randall. The polymerizations were conducted at $20\text{ }^\circ\text{C}$ in a liquid propylene with a constant overpressure of ethylene, or condensed ethylene.

CHAPTER 1

MOTIVATION AND TARGETS

1.1 Introduction

Polymer was found to make us live in a modern world. They are easy to make and easy to process, which has contributed heavily to the facile development and use of polymers. Example of polymer goods include: rubber, milk bottles, shopping bags, dispensing bottles, piping, wire and cable insulation, food packages, disposable dippers, etc.¹ A major type of polymer is polyolefin material, exemplified by polyethylene, polypropylene, and ethylene/ α -olefin copolymer. About 60% of the world's thermoplastic materials are homopolymers or copolymers containing ethylene and/or propylene.² Polyolefin materials are various polymers using the same monomer with different type of heterogeneous catalysts activated by aluminum alkyls, or homogeneous catalysts activated by MAO, or via radical chemistry. However, the largest scale chemical processes are by heterogeneous catalysts, which produces roughly 99% of the world's polyethylene and polypropylene.³ Polyethylene can have different microstructures due to density variation (Figure 1-1). The branching has a large effect on the crystallinity of the polymer.³ Polyethylene including linear low density polyethylene (LLDPE) is produced from ethylene and α -olefin; low density polyethylene (LDPE) is commercialized using free radical process at high temperature and pressures, and high density polyethylene (HDPE) is typically formed by Ziegler catalyst or supported chromium oxide catalyst.⁴ Also polypropylene architectures depend heavily on the relative configuration of the methyl groups along the polymer chain to produce isotactic polypropylene, syndiotactic polypropylene, or atactic polypropylene (Figure 1-2).⁴ These polymers have different performance and properties from each

other, which leads to a variety of applications. Therefore, LLDPE is used for plastic bags. On the other hand, HDPE is used for milk bottles.

A combination of the ethylene monomer and the propylene monomer is called copolymer, which are resistant to heat, oxidation, ozone, weather and electrical resistor for having a saturated backbone.⁴ The performance and properties of the copolymer depend on the content distribution of ethylene and propylene in the polymer chain. As a result, ethylene-propylene copolymer (EPM) exhibits lower crystallinity and higher impact strength than isotactic polypropylene with a small amount of ethylene. In contrast, amorphous rubbery materials are produced with larger amount of ethylene than propylene.⁵ Therefore, the synthesis of the EPM copolymer would be controlled via reactivity ratio (r_{ethylene} , $r_{\text{propylene}}$) of the monomers content. Interestingly, the relative amount of $r_{\text{e/p}}$ is an indicator of the type of the copolymer. As a result, $r_{\text{e/p}} = 1$ indicates a random copolymer, $r_{\text{e/p}} < 1$ indicates an alternating copolymer, and $r_{\text{e/p}} > 1$ indicates the tendency to form long sequences of at least one of the comonomer.⁵ However, as it noted in the following reference,⁵ the reactivity ratio r_{e} and r_{p} for most heterogeneous and homogeneous catalysts have the tendency to form longer ethylene sequences (Table 1-1).⁵ However, our catalyst containing the Oct ligand (Oct = Octamethyloctahydrodibenzofluorenyl) was used to synthesize copolymer of ethylene and α -olefin “except propylene”, is found to be more reactive to incorporate α -olefins than it does for ethylene.¹ Keep in mind that ethylene and propylene has a tremendous impact in business field. Herein, we explore our metallocene system catalyst (A) (Figure 1-3) to see if it will also be more selective toward propylene than it does toward ethylene. Copolymer with more propylene incorporation than ethylene would result in a

different microstructure which could form a novel polyolefin with better properties and broaden applications.

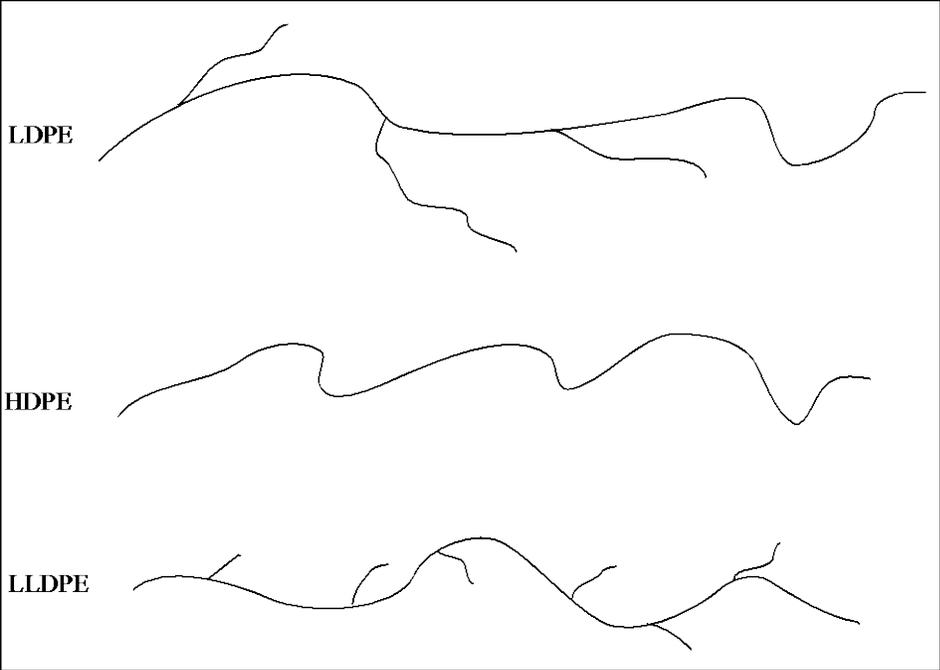


Figure 1-1. Selections of polyethylene microstructures

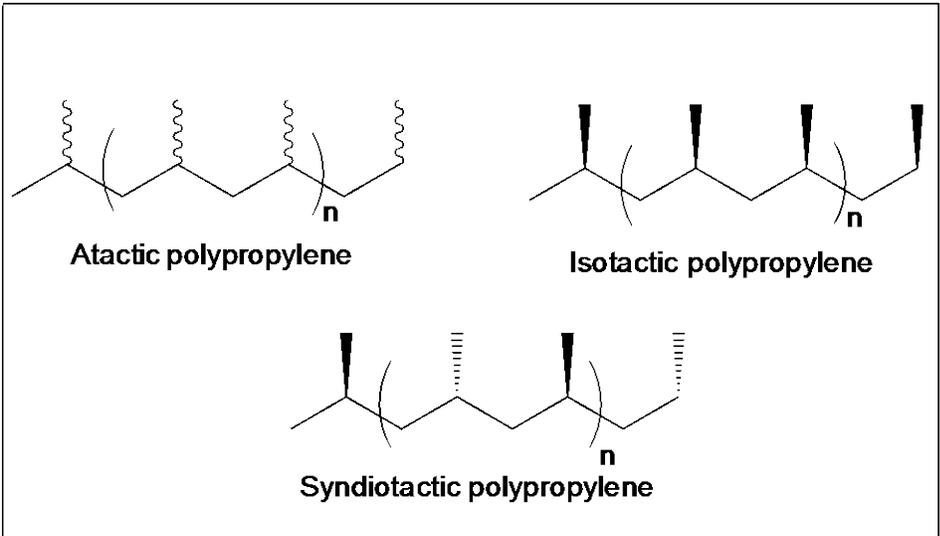


Figure 1-2. Major tacticity of polypropylene microstructures

Table 1-1. Reactivity ratios for ethylene/propylene copolymer ⁵

Catalyst	T, °C	r _e	r _p	r _e r _p	ref
δ- TiCl ₃ - Al(C ₂ H ₅) ₂ Cl	70	11.6	0.35	4.1	12
δ- TiCl ₃ - Al(C ₂ H ₅) ₃	40	7.3	0.76	5.5	13
MgCl ₂ /TiCl ₄ /ethyl Benzoate-Al(C ₂ H ₅) ₃	70	5.5	0.36	2.0	12
VCl ₃ – Al(n-C ₆ H ₁₃) ₃	25	5.6	0.15	0.81	14
Cp ₂ TiCl ₂ /MAO	30	15.7	0.009	0.14	15
Cp ₂ Ti=CH ₂ /MAO	50	24	0.0085	0.204	16
Cp ₂ ZrCl ₂ /MAO	30	16	0.025	0.4	15
Cp* ₂ ZrCl ₂ /MAO	50	250	0.002	0.5	16
Me ₂ SiCp ₂ ZrCl ₂ /MAO	50	24	0.029	0.7	16
Cp ₂ HfCl ₂ /MAO	30	20.6	0.074	1.5	15
EBIZrCl ₂ /MAO	50	6.61	0.06	0.4	17
EBIZrCl ₂ /MAO	25	6.26	0.11	0.69	17
EBIZrCl ₂ /MAO	0	5.2	0.14	0.73	18
Me ₂ C(Cp)(Flu)ZrCl ₂ /MAO	25	1.3	0.2	0.26	18

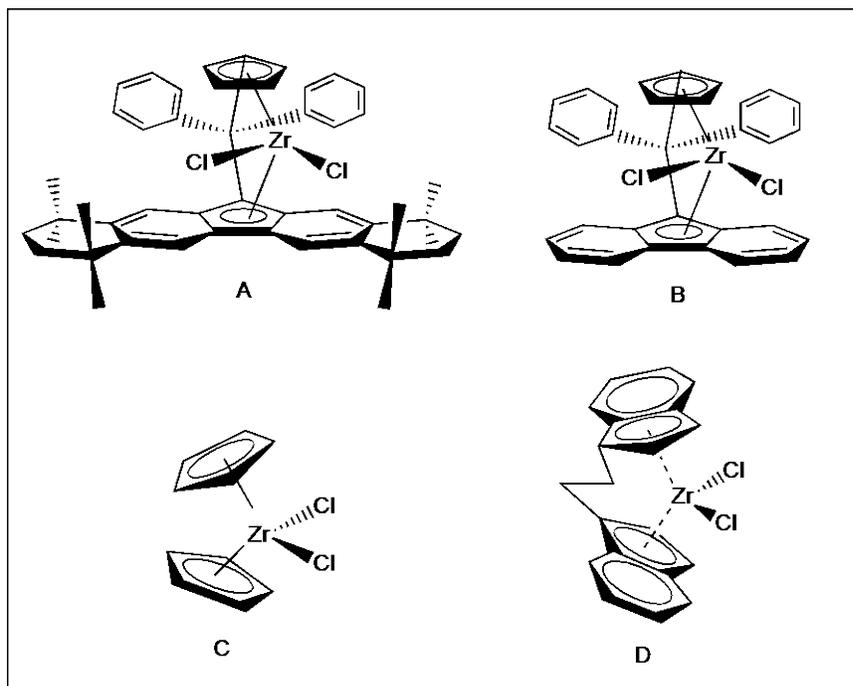


Figure 1-3. Selective structures of metallocene catalysts

1.2 Catalyst Design

1.2.1 Catalyst A

The syntheses of these compounds are known, and has been accomplished by Miller et al.⁶

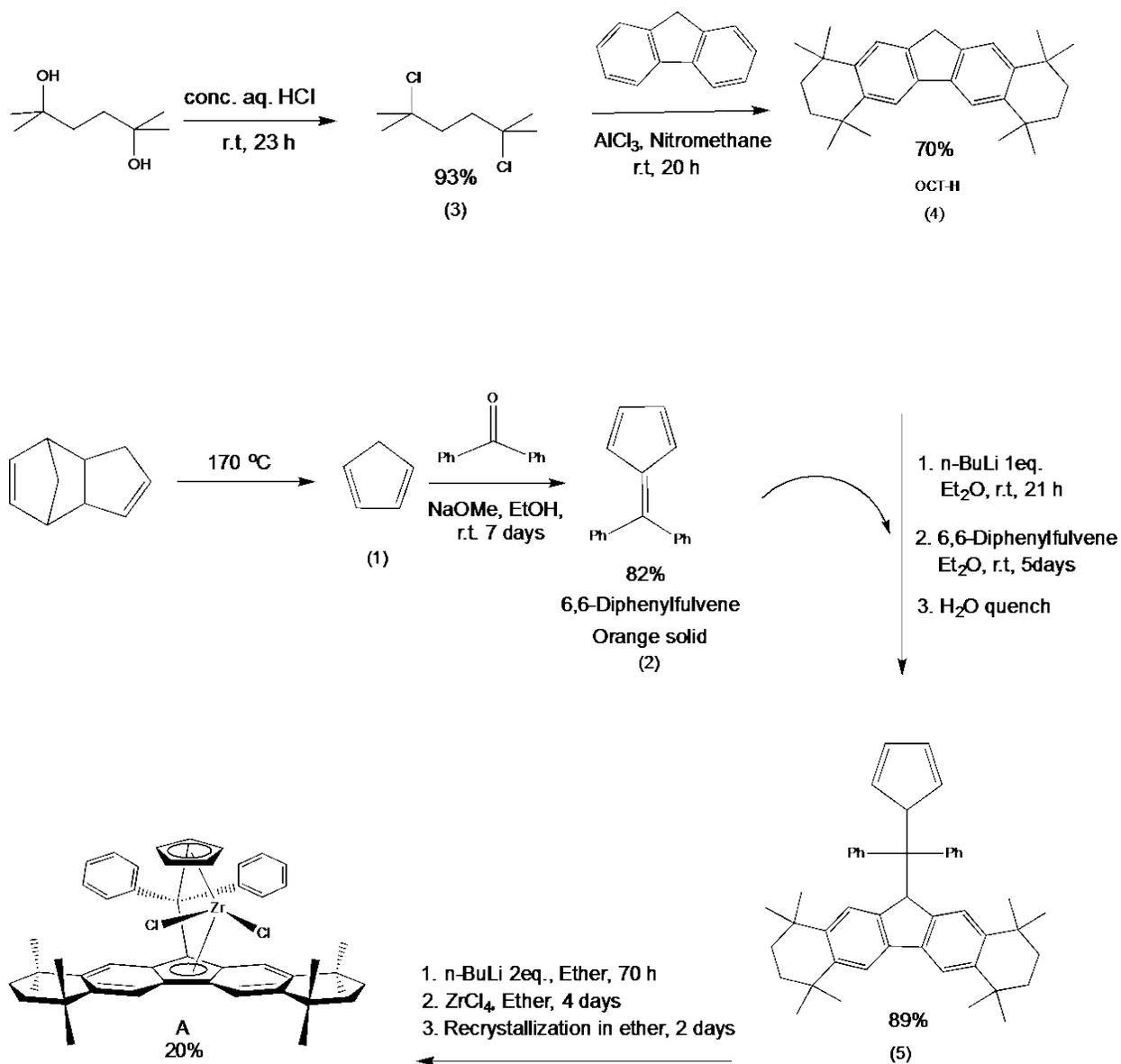


Figure 1-4. Synthesis of Oct-Cp metallocene catalyst (A)

1.2.2 Catalyst B

The syntheses of these compounds are known, and have been accomplished by Ewen et al.¹¹

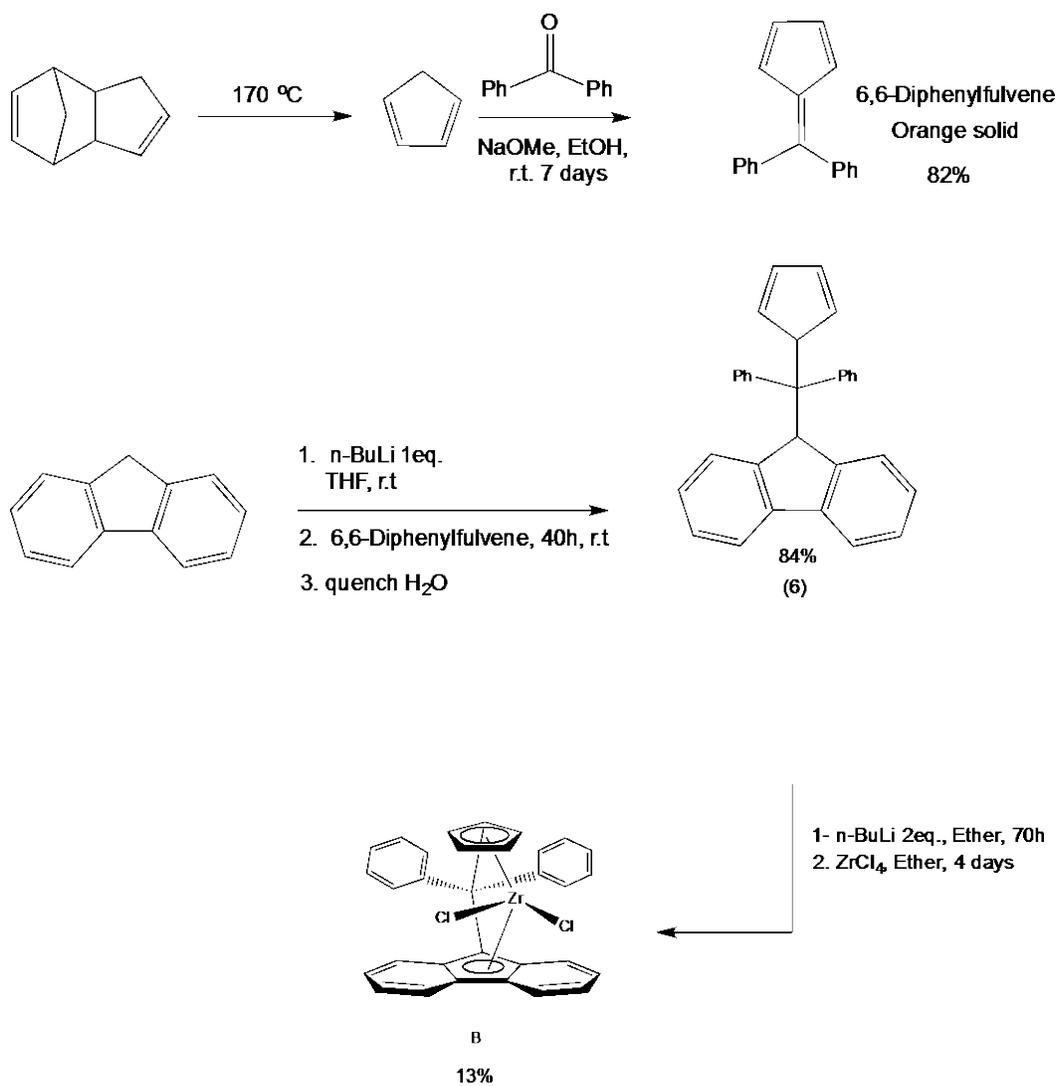


Figure 1-5. Synthesis of Ewen catalyst (B)

1.3 Polymerization Results, Characterization, and Discussion

1.3.1 Results

Homopolymerization was run first to demonstrate the fact that Oct-Cp catalyst system is more reactive and stereoselective than Ewen catalyst is. (Table 1-2).

Table 1-2. Polypropylene polymerization results

entry	Cat. (mg)	MAO (equiv)	T _p (°C)	C ₃ H ₆ (mL)	time (min)	Yield (g)	Reactivity (Kg/mol.hr)
1	A (1.0)	2000	20	30	10	1.00	3300
2	B (1.0)	2000	20	30	10	1.09	1550

Ethylene-propylene copolymerization was carried out at 20°C (water bath) in 20 mL of toluene, liquid propylene, and liquid ethylene/ or constant overpressure of ethylene. All copolymerizations were employed MAO as a co-catalyst; for overall pressure, temperature, and stirring speed limit, see Table 1-2, and Table 1-3 for copolymerization results.

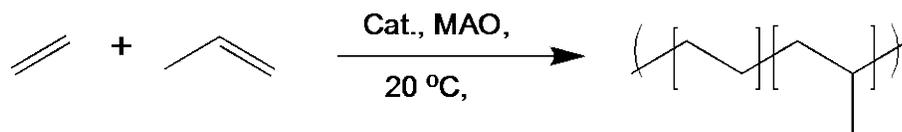


Figure 1-6. Ethylene-propylene copolymer (EPM)

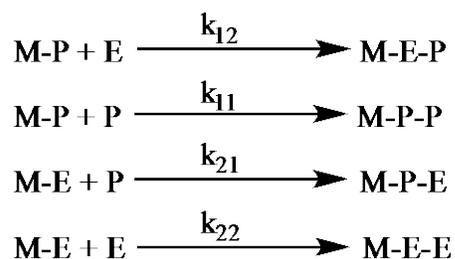
1.3.2 Discussion and Characterization

Metallocene catalysts show an interest to control the selectivity of incorporation of the comonomer due to their well-defined kinetic behavior.² Recently, our group has shown that Oct ligand has influenced the catalyst to be more active toward α -olefin than

it is for ethylene due to the steric demands and the electron donation of the tertiary alkyl groups of Oct ligand.¹

The electron richness of the Oct ligand allow the ring slip to 1η ; therefore, further metallocene bending creates more room for the approaching monomer to incorporate. More interestingly, A/MAO also behaves similarly with ethylene-propylene copolymerization, where propylene as a comonomer is found to be faster toward the electron deficient metal center of the catalyst than it does ethylene.

The first order Markov model is given by four equations as follows:



Where r_e and r_p can be simplified to $r_e = k_{22}/k_{21}$ and $r_p = k_{11}/k_{12}$. M-P indicates the active center with last propylene and M-E indicates the active center with the last ethylene.

Our point view is having a more electron rich comonomer would facilitate the insertion with catalyst (A), which is in this case the propylene comonomer.

The Oct-Cp catalyst influences on the reactivity ratio and the overall reactivity compared to Ewen catalyst (B) that bears fluorenyl group. Table 1-3 shows that despite the copolymerizations were run with identical conditions, Oct-Cp (A) produced significant higher activity ratio of propylene than the Ewen catalyst (B); also this observation was correlated with the results of entry 1 and 2 (Table 1-3) where the former has greater r_p than the later.

Table 1-3. Ethylene-propylene copolymerization results with continuous ethylene flow at 20 °C

entry	Cat. (mg)	MAO (equiv)	X_e/X_p (feed mol%)	Time (min)	T_g (°C)	T_m (°C)	r_e	r_p	$r_e r_p$
1	A (1.0)	2000	0.22	1	-7	110	1.00	1.90	1.90
2	B (1.0)	2000	0.21	2	-11	120	1.09	1.23	1.34
3	A (0.5)	1000	0.21	2	-22	116	0.51	1.13	0.57
4	B (0.5)	1000	0.21	8	-15	118	-	-	-

Table 1-4. Ethylene-propylene copolymerization results with condensed ethylene at 20 °C

entry	Cat. (mg)	MAO (equiv)	X_e/X_p (feed mol%)	Time (min)	T_g (°C)	T_m (°C)	r_e	r_p	$r_e r_p$
1	A (0.5)	1000	0.26	1	-43	104	1.6	0.75	1.19
2	B (0.5)	1000	0.26	10	-41	n.o.	1.68	0.16	0.27
3	A (0.25)	1000	0.26	7	-37	n.o.	-	-	-

Table 1-5. EP copolymerization with Oct-Cp (A) with continuous ethylene flow at 20 °C

entry	Cat. (mg)	MAO (equiv)	X_e/X_p (feed mole%)	Time (min)	T_g (°C)	T_m (°C)	r_e	r_p	$r_e r_p$
1	1.0	2000	0.22	1	-7	110	1.00	1.90	1.19
2	0.5	1000	0.21	2	-22	116	0.50	1.13	0.57
3	0.25	1000	0.21	7	-37	n.o.	-	-	-

The results were analyzed by the ^{13}C NMR spectra obtained; (Figure 1-7) and (Figure 1-8). The Oct-Cp catalyst shows less integration of EEE sequences than the Ewen catalyst (B).

Also, it was noticed that Table 1-4 shows no dramatic increase change on the T_g and T_m of the produced polymer, which is an advantage for elastomeric material to have lower T_g . However, we are lacking the tools to control the composition and the

conversion percentage of propylene comonomer, which might be the reason behind that. The reported activity from (Table 1-1) assumed the conversion is 10% from the propylene. As it has mentioned earlier, the Oct-Cp catalyst is more active than Ewen catalyst; therefore we assumed that the conversion with catalyst (A) is higher than 10% with such a highly active catalyst. This clearly can be seen from the reaction time through the data mentioned earlier leading to the same yield of the produced polymer. Thus, different amounts of Oct-Cp (A) were loaded into the copolymerization (Table 1-5); the catalyst has more control of the reactivity ratio with lower loading, which is correlated to what was mentioned earlier about the conversion of the propylene comonomer.

The sequence distribution of the copolymer produced by A/MAO revealed a tendency to increase PP dyad and diminish the EEE triad sequence (Figure 1-10) and (Figure 1-11).

The copolymer composition was investigated by ^{13}C NMR as has been accomplished by Carman and coworkers and Randall.^{7,8} The carbon positions were given by S, T, and P refer respectively to the secondary (methylene), tertiary (methine), and primary (methyl) carbons, and used Greek letters to assign the distance from that carbon to methine, as it is assumed the δ letter is indicator of four or more carbons away from the methine (Figure 1-9).

Moreover, Kakugo and coworkers;⁹ accomplished a way to calculate the mole percent of monomers in EP copolymers and reactivity ratios of monomers (Table 1-4). However, in our case X_e/X_p is the mole feed fraction ratio of ethylene and propylene in the liquid phase.

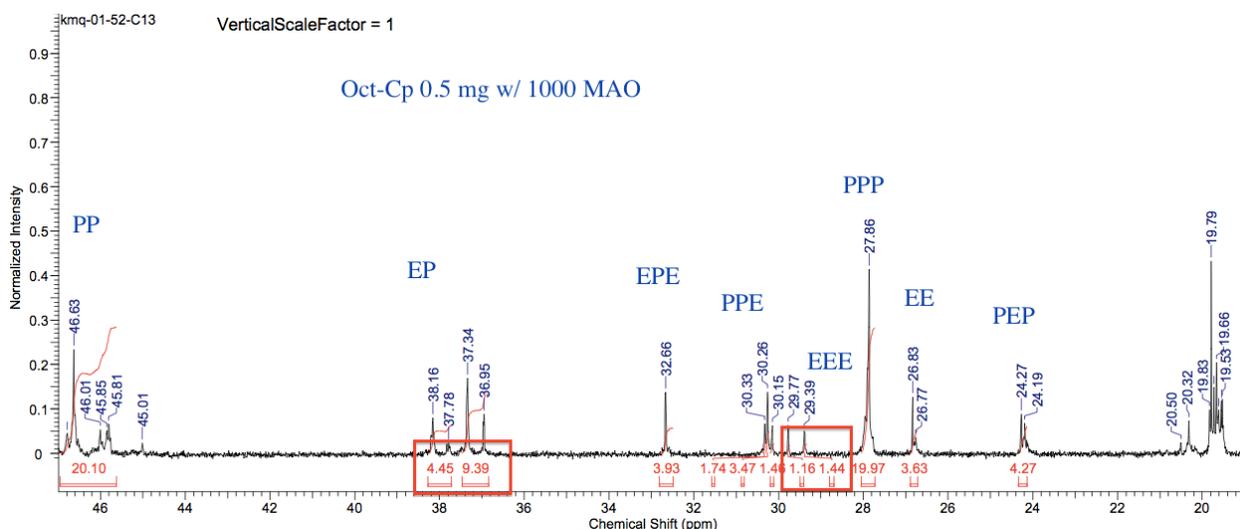


Figure 1-7. ¹³C NMR of EP copolymer synthesized using Catalyst A

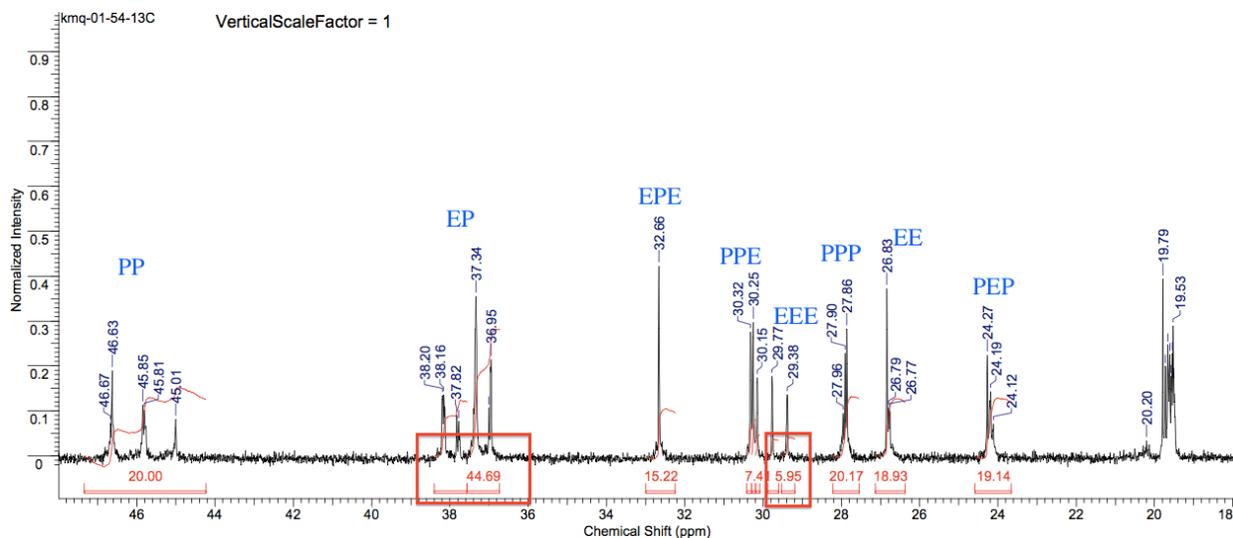


Figure 1-8. ¹³C NMR of EP copolymer synthesized using Catalyst B

Table 1-6. Monomer distributions and reactivity ratios⁹

Dyad & Triad distributions:	Mole % of monomer in copolymer:
<p>Dyad:</p> $PP = S_{\alpha\alpha}$ $EP = S_{\alpha\gamma} + S_{\alpha\delta}$ $EE = \frac{1}{2}(S_{\beta\delta} + S_{\delta\delta}) + \frac{1}{4}(S_{\gamma\delta})$ <p>Triad:</p> $PPP = T_{\beta\beta}$ $PPE = T_{\beta\delta}$ $EPE = T_{\delta\delta}$ $PEP = S_{\beta\beta} = \frac{1}{2}(S_{\alpha\gamma})$ $EEP = S_{\alpha\delta} = S_{\beta\delta}$ $EEE = \frac{1}{2}(S_{\delta\delta}) = \frac{1}{4}(S_{\gamma\delta})$	<p>Dyad:</p> $E = EE + \frac{1}{2}(EP)$ $P = PP + \frac{1}{2}(EP)$ <p>Triad:</p> $E = EEE + EEP + PEP$ $P = PPP + PPE + EPE$ <p>Ethylene & propylene reactivity ratio:</p> $r_{e/p} = \frac{EE[PP/(PE/2)^2]}{r_e = (EE/E)/\{[1-EE/E]^* [X_e/X_p]\}}$ $r_p = (PP/P)^* [X_e/X_p]/[1-PP/P]$

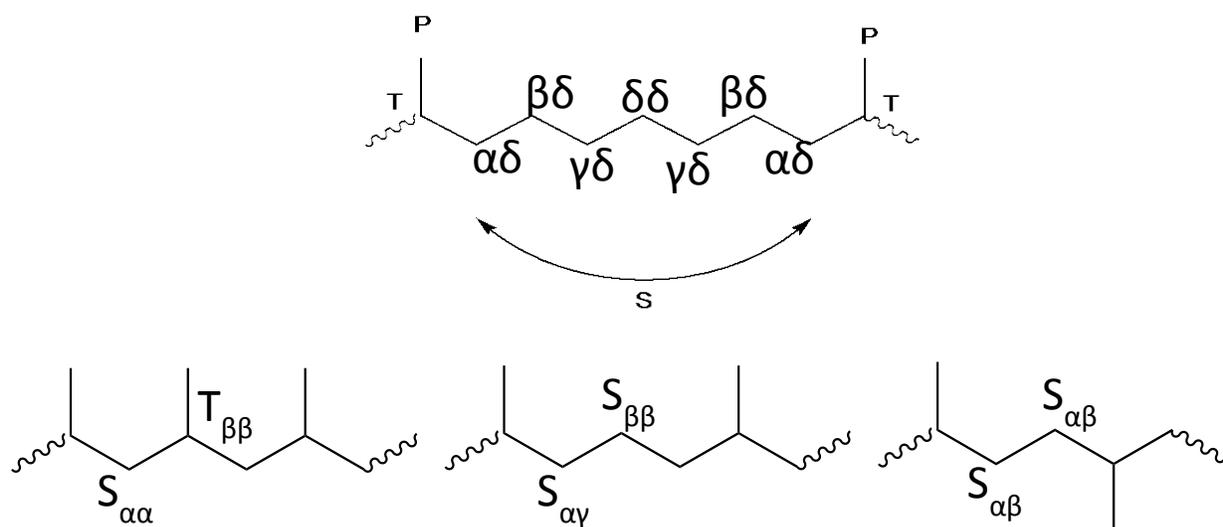


Figure 1-9. Peak assignment for ethylene-propylene copolymer (EPM)^{7,8}

Table 1-7. Monomer distributions and reactivity ratios for Oct-Cp (A)

Dyad & Triad distributions:	Mole % of monomer in copolymer:
<p>Dyad:</p> <p>PP = 0.55 EP = 0.38 EE = 0.08</p> <p>Triad:</p> <p>PPP = 0.48 PPE = 0.08 EPE = 0.09 PEP = 0.10 EEP = 0.22 EEE = 0.02</p>	<p>Dyad:</p> <p>$E = 0.08 + \frac{1}{2}(0.38) = 0.27$ $P = 0.55 + \frac{1}{2}(0.38) = 0.74$</p> <p>Triad:</p> <p>$E = 0.02 + 0.22 + 0.10 = 0.34$ $P = 0.48 + 0.08 + 0.09 = 0.65$</p> <p>Ethylene & propylene reactivity ratio: $r_{ep} = 0.08[0.55/(0.38/2)^2] = 1.19$ $r_e = (0.30)/\{[1-0.30]*[0.26]\} = 1.6$ $r_p = (0.74)*[0.26]/[1-0.74] = 0.75$</p>

Table 1-8. Monomer distributions and reactivity ratios for Ewen (B)

Dyad & Triad distributions:	Mole % of monomer in copolymer:
<p>Dyad:</p> <p>PP = 0.21 EP = 0.65 EE = 0.14</p> <p>Triad:</p> <p>PPP = 0.17 PPE = 0.11 EPE = 0.13 PEP = 0.17 EEP = 0.38 EEE = 0.04</p>	<p>Dyad:</p> <p>$E = 0.14 + \frac{1}{2}(0.65) = 0.465$ $P = 0.21 + \frac{1}{2}(0.65) = 0.535$</p> <p>Triad:</p> <p>$E = 0.04 + 0.38 + 0.17 = 0.59$ $P = 0.17 + 0.11 + 0.13 = 0.41$</p> <p>Ethylene & propylene reactivity ratio: $r_{ep} = 0.14[0.21/(0.65/2)^2] = 0.27$ $r_e = (0.30)/\{[1-0.30]*[0.26]\} = 1.68$ $r_p = (0.39)*[0.26]/[1-0.39] = 0.16$</p>

Table 1-9. Monomer distributions and reactivity ratios for Oct-Cp (A)

Dyad & Triad distributions:	Mole % of monomer in copolymer:
<p>Dyad:</p> <p>PP = 0.80 EP = 0.18 EE = 0.02</p> <p>Triad:</p> <p>PPP = 0.72 PPE = 0.08 EPE = 0.04 PEP = 0.07 EEP = 0.09 EEE = 0.00</p>	<p>Dyad:</p> <p>$E = 0.02 + \frac{1}{2}(0.18) = 0.11$ $P = 0.80 + \frac{1}{2}(0.18) = 0.89$</p> <p>Triad:</p> <p>$E = 0.00 + 0.09 + 0.07 = 0.16$ $P = 0.72 + 0.08 + 0.04 = 0.84$</p> <p>Ethylene & propylene reactivity ratio: $r_{eP} = 0.02[0.80/(0.18/2)^2] = 1.90$ $r_e = (0.18)/\{[1-0.18]*[0.22]\} = 1.00$ $r_p = (0.89)*[0.22]/[1-0.89] = 1.90$</p>

Table 1-10. Monomer distributions and reactivity ratios for Ewen (B)

Dyad & Triad distributions:	Mole % of monomer in copolymer:
<p>Dyad:</p> <p>PP = 0.71 EP = 0.26 EE = 0.03</p> <p>Triad:</p> <p>PPP = 0.64 PPE = 0.08 EPE = 0.05 PEP = 0.10 EEP = 0.13 EEE = 0.00</p>	<p>Dyad:</p> <p>$E = 0.03 + \frac{1}{2}(0.26) = 0.16$ $P = 0.71 + \frac{1}{2}(0.26) = 0.84$</p> <p>Triad:</p> <p>$E = 0.00 + 0.13 + 0.10 = 0.23$ $P = 0.64 + 0.08 + 0.05 = 0.77$</p> <p>Ethylene & propylene reactivity ratio: $r_{eP} = 0.03[0.71/(0.26/2)^2] = 1.34$ $r_e = (0.19)/\{[1-0.19]*[0.22]\} = 1.09$ $r_p = (0.84)*[0.22]/[1-0.84] = 1.23$</p>

Table 1-11. Monomer distributions and reactivity ratios for Oct-Cp (A)

Dyad & Triad distributions:	Mole % of monomer in copolymer:
<p>Dyad:</p> <p>PP = 0.71</p> <p>EP = 0.28</p> <p>EE = 0.02</p> <p>Triad:</p> <p>PPP = 0.63</p> <p>PPE = 0.12</p> <p>EPE = 0.04</p> <p>PEP = 0.09</p> <p>EEP = 0.13</p> <p>EEE = 0.00</p>	<p>Dyad:</p> <p>$E = 0.02 + \frac{1}{2}(0.28) = 0.16$</p> <p>$P = 0.71 + \frac{1}{2}(0.28) = 0.85$</p> <p>Triad:</p> <p>$E = 0.00 + 0.13 + 0.09 = 0.22$</p> <p>$P = 0.63 + 0.12 + 0.04 = 0.79$</p> <p>Ethylene & propylene reactivity ratio:</p> <p>$r_{e/p} = 0.02[0.71/(0.28/2)^2] = 0.57$</p> <p>$r_e = (0.13)/\{[1-0.13]*[0.22]\} = 0.51$</p> <p>$r_p = (0.84)*[0.22]/[1-0.84] = 1.13$</p>

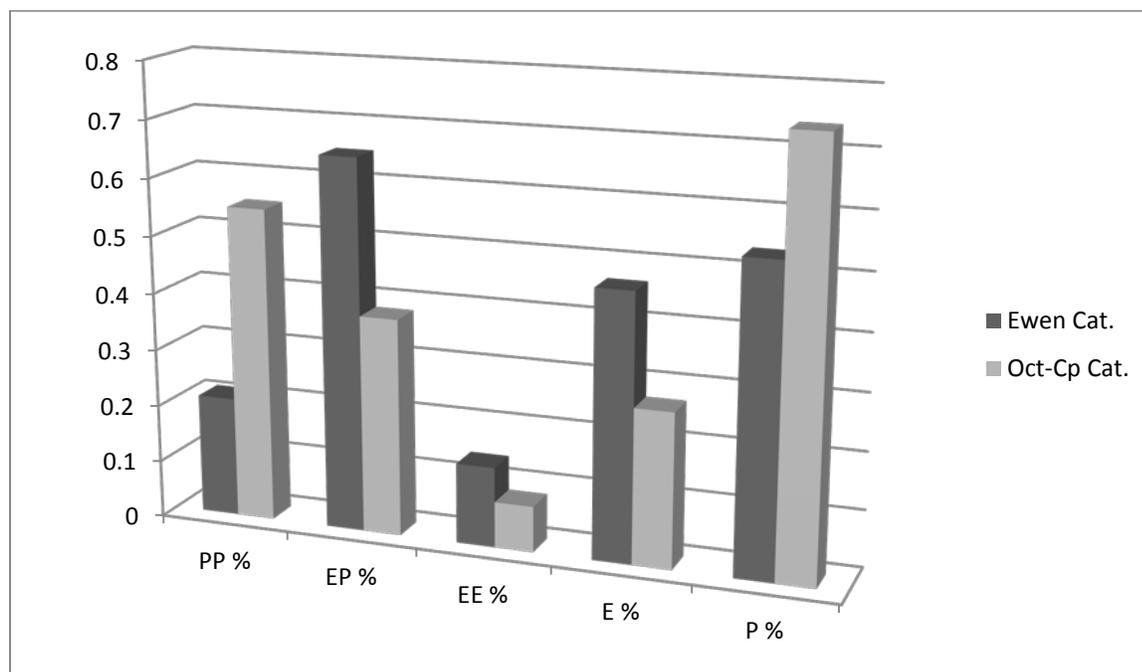


Figure 1-10. Dyad distribution of ethylene-propylene copolymer; synthesized using a continuous ethylene

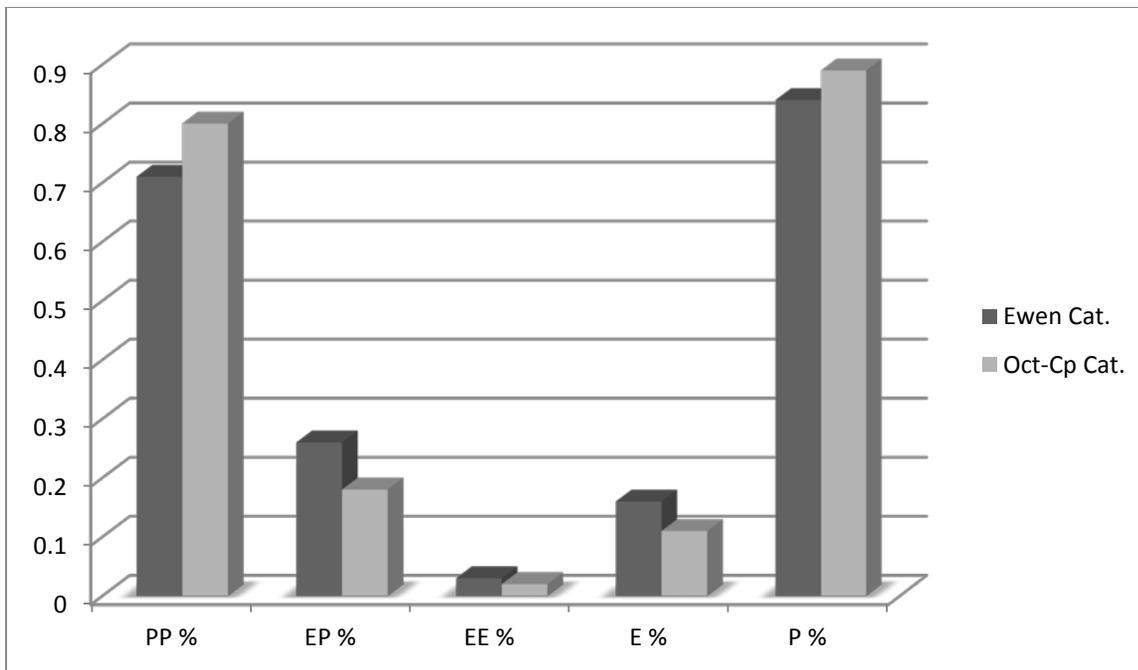


Figure 1-11. Dyad distribution of ethylene-propylene copolymer; synthesized using a continued flow of ethylene

CHAPTER 2 EXPERIMENTAL PROCEDURES

2.1 General Considerations

Most of the reaction procedures have been carried out under an atmosphere of argon or nitrogen using standard glove box, and Schlenk line techniques. The following were purchased from Aldrich and used as received: n- butyllithium (1.6 M in hexanes); zirconium tetrachloride (99.5%); aluminum chloride (99.99%); 2,5-dimethyl-2,5-hexanediol (99%); and benzophenone (99%). The following were purchased from Acros and used as received; fluorene (98%); dicyclopentadiene (95%); and nitromethane (96%). Benzene- d_6 was dried over calcium hydride and isolated by vacuum transfer.

2.2 Polymer Characterization:

Polymer glass transition temperatures and melting temperatures were obtained by the Differential Scanning Calometry (TA – DSC – Q1000). Samples were scanned from -80°C to 200°C at 10°C/min.

The reactivity ratios of ethylene and propylene were calculated based on the ^{13}C NMR spectra obtained by NMR 125 MHz at 124 °C in tetrachloroethane- d_2 . A 90° pulse and a delay time of 3s, acquisition time of 4s and a minimum of 1300 scans were used

2.3 Synthesis of Catalysts

The syntheses of A and B were accomplished similar to the literature procedure.³

2.3.1 Preparation of Catalyst (A)

2.3.1.1 Cyclopentadiene (1)

A 180 mL of dicyclopentadiene was charged in a 250 ml vessel connected to a distillation apparatus. After it was heated up to 160 °C using oil bath, the internal temperature reach at 40 °C to allow the retro Diels-Alder reaction to occur. At the end,

114 mL of cyclopentadiene is collected in a 250 mL vessel and stirred in an ice bath and used immediately after being distilled.

2.3.1.2 6,6-diphenylfulvene (2)

Sodium methoxide (21.00 g, 380.0 mmol), ethanol (570 mL), and benzophenone (142.50 g, 782.0 mmol) were poured into a 1 L vessel. Cyclopentadiene (114.0 mL, 677 mmol) was poured in cold, which gives a red solution. After stirring for 7 days, the orange precipitate was collected by filtration and rinsed with 50 mL ethanol. The solid was refluxed in 200 mL methanol for 2 hour. Upon cooling the solid was collected, rinsed with 75 mL methanol, and dried in vacuo, to provide the product as an orange powder: 147.28 g (81.7%).

2.3.1.3 2,5-dichloro-2,5-dimethylhexane (3)

A 1 liter argon purged vessel was charged with 2,5-dimethyl-2,5-hexanediol (53.77 g, 0.368 mol) and concentrated aqueous hydrochloric acid (269 mL, 10.8 mol HCl) was poured in. The white slurry was shaken and stirred for 19 hours. The white solid was collected by filtration lightly vacuumed and rinsed with 630 mL water. The solid was dissolved in diethyl ether, the water layer was removed, and the organic layers was dried over MgSO_4 . The solvent was removed; precipitate was collected by the filtrate and washed with 50 mL of ethanol. The white crystalline solid was dried in vacuum to provide the product: 59.78 g (88.7%).

2.3.1.4 Octamethyloctahydrodibenzofluorene (4)

A 2 liter argon purged vessel was charged with fluorene (26.32 g, 158.37 mmol) and 2,5-dichloro-2,5-dimethylhexane (58.5.00 g, 319.5 mmol). The solids were dissolved in 438 mL nitromethane and the vessel was equipped with an addition funnel which was charged with AlCl_3 (28.12 g, 210 mmol) dissolved in 50 mL nitromethane.

The solution was added over 10 minutes and the purple reaction was stirred for 48 hours before it was slowly poured into 500 mL of ice water. The precipitate was collected by filtration and refluxed in 500 mL ethanol for 2 hours. Upon cooling, the solid was collected by filtration and this was refluxed in 300 mL hexanes for 2 hours. After cooling, the solid was collected by filtration and dried in vacuo, giving the product as a white powder: 40.1 g (65.5%)

2.3.1.5 Ph₂C(C₅H₄)(C₂₉H₃₆)H₂ (5)

A 500 mL flask was charged with octamethyloctahydrodibenzofluorene (12.00 g, 31.04 mmol), equipped with a 180° needle valve, evacuated and charged with diethyl ether (120 mL) by vacuum transfer. At 0°C, n-butyllithium (21.0 mL, 33.6 mmol, 1.6 M in hexanes) was syringed in over 3 minutes, giving much yellow precipitate. After 21 hours, the solvent was removed and 6,6-diphenylfulvene (7.148 g, 31.04 mmol) was added. Diethyl ether (150 mL) was condensed in and the reaction stirred at room temperature for five days before 60 mL aqueous NH₄Cl were added slowly at 0°C. The organic layer was isolated and the aqueous layer was extracted with diethyl ether (4 x 100 mL). The combined organic layers were dried over MgSO₄, filtered and rotavapped to provide the crude product in quantitative yield 89.4% (17.12 g)

2.3.1.6 Ph₂C(C₅H₄)(C₂₉H₃₆)ZrCl₂ (A)

A 250 mL flask equipped with a swivel frit was charged with (5) (3.00 g, 4.9 mmol), then diethyl ether (35 mL) was condensed in at -78°C, and n-BuLi (6.1 mL, 9.73 mmol) was added before the cold bath was removed. The reaction was warmed up and stirred for 45 hours, solvent was removed and ZrCl₄ (1.134 g, 4.9 mmol) was added. Diethyl ether (35 mL) was condensed in at -78°C and the cold bath was removed. After

47 hours, the swivel frit flipped upside down. The volume was reduced to 20 mL, and kept stirring overnight. Then, the pink material was collected and dried in vacuo: 0.6 g (20.0%).

2.3.2 Prepration of Catalyst (B)

2.3.2.1 Ph₂C(C₅H₄)(C₁₃H₈)H₂ (6)

A 500 mL flask was charged with fluorene (14.43 g, 86.8 mmol), equipped with a 180° needle valve, evacuated, and 180 mL of diethyl ether were transferred in. n-butyllithium (55.0 mL, 87.1 mmol, 1.6 M in hexanes) was syringed in over ten minutes at 0°C. After 19 hours, all solvent was removed and 6,6-diphenylfulvene (20.00 g, 86.7 mmol) was added and 100 mL diethyl ether was condensed in. After stirring for six days, the vessel was cooled to 0°C and 60 mL water were very slowly added, followed by 30 mL aqueous NH₄Cl solution. The slurry was suction filtered and the crude product was dissolved in Chloroform and dried over MgSO₄. This was filtered hot through a celite layer and the slurry was rotovapped before crystal solid was collected and dried (28.78 g, 83.6%).

2.3.2.2 Ph₂C(C₅H₄)(C₁₃H₈)ZrCl₂ (B)

A 250 mL flask equipped with a swivel frit was charged with (6) (3.00 g, 7.56 mmol) and diethyl ether (35 mL) was condensed in at -78°C and n-BuLi (7.3 mL, 15.2 mmol) was added before the cold bath was removed. The reaction was warmed up and stirred for 48 hours, solvent was removed and ZrCl₄ (1.77 g, 7.6 mmol) was added. Petroleum ether (35 mL) was condensed in at -78°C and the cold bath was removed. After 47 hours, The volume was reduced to 20 mL, and kept stirring overnight. Then, the orange material was collected and dried in vacuo: 0.4 g (13 %).

2.4 Copolymerization Procedure

CAUTION: All polymerizations need to be done behind the blast shield during the polymerization. All polymerization reaction preparation were carried out in nitrogen atmosphere (glove box). Methylaluminoxane (MAO) was purchased in toluene solution from Sigma Aldrich and was used as a powder after removal of all volatiles. Toluene was collected from M-Braun purification system and dried according to standard procedures and it was further purified over sodium; finally degased using the Schlenk line. Ultra high pure propylene from Matheson Gases (99.99%) and Ethylene from AirGas (UHP grade) were used following drying through a Matheson 6410 drying system equipped with an OXYSORB column.

All polymerizations were carried out in a fume hood using a 3 oz. Lab Crest glass high-pressure reaction vessel and stirred by a magnetic stirrer bar. The vessel was filled with MAO and toluene in the glove box before propylene was condensed over several minutes at 20 °C. The vessel was then kept equilibrated at 20 °C over 10 minutes. In case of copolymerization, ethylene then was condensed at -5 °C using an ice bath and NaCl. After that, the vessel was warmed up for 10 minutes to 20 °C in a water bath before the injection of the catalyst in a toluene solution via a 2 mL Hamilton gastight syringe. After the desired time, polymerization reactions were vented and quenched with a small volume of methanol/concentrated HCl (10:1), and kept stirring overnight. The polymer was collected by filtration. Finally, the residual amounts of toluene and methanol were removed by vacuum to obtain a dry polymer.

CHAPTER 3 CONCLUSION

In conclusion, a series of ethylene-propylene copolymers was synthesized using different types of catalysts. It was found that the Oct-Cp catalyst system with MAO has influenced the reactivity ratio of propylene vs. ethylene. Moreover, the Oct-Cp catalyst system is capable of producing elastomeric material of EP copolymer.

These results demonstrated the influence of Oct-H ligand in metallocene catalysts, which enhance the ring slip to be more facile than Fluorene ligand; therefore the dominant factor is electronic rather than steric. As a result, the more electron rich “ α -olefins” would polymerize much faster than the less electron rich “ethylene”.

The distribution of comonomers in the produced copolymer was analyzed using ^{13}C NMR. The sequence distributions of the copolymer are correlated with the larger ^{13}C NMR intensity peaks.

Finally, the impact of the Oct-Cp ligand can be on stereochemistry, reactivity, and selectivity to control the sequence distribution between ethylene and α -olefin.

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BIOGRAPHICAL SKETCH

Khalid Alqahtani was born in 1989 in Riyadh, Saudi Arabia. After high school, he studied chemistry at the King Saud University where he obtained his bachelor's degree in chemistry in June 2011. After graduation, he worked for SABIC (Saudi Arabia Basic Industries Corporation). Then, he got nominated for a master's program at the University of Florida in 2013. In Fall 2014, Khalid joined Miller research group in the Organic Division of the Chemistry Department at the University of Florida. Under the guidance supervision by Prof. Stephen Miller, his research focuses on the synthesis of polyolefin polymers. Khalid obtained his Master of Science degree from UF in May 2016.