ผลกระทบของตัวเร่งปฏิกิริยาฟีนอกซีอิมีนแบบมีตัวรองรับและไม่มีตัวรองรับที่มีต่อความว่องไวของตัวเร่งปฏิกิริยาและคุณลักษณะของพอลิโอเลฟินสำหรับการทำโฮโม และโคพอลิเมอร์ไรเซชันของเอทิลีนกับแอลฟาโอเลฟิน

นางสาวสุภาภรณ์ ขอบุญส่งเสริม

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THE EFFECT OF SUPPORTED AND UNSUPPORTED PHENOXY-IMINE CATALYSTS ON CATALYTIC ACTIVITIES AND POLYOLEFIN CHARACTERISTICS FOR HOMO- AND CO-POLYMERIZATION OF ETHYLENE AND α-OLEFIN.

Miss Supaporn Khaubunsongserm

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
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Thesis Title	THE EFFECT OF SUPPORTED AND UNSUPPORTED PHENOXY-IMINE CATALYSTS ON CATALYTIC ACTIVITIES AND POLYOLEFIN CHARACTERISTICS FOR HOMO- AND CO-POLYMERIZATION OF ETHYLENE AND α-OLEFIN
By	Miss Supaporn Khaubunsongserm
Field of Study	Chemical Engineering
Thesis Advisor	Professor Piyasan Praserthdam, Dr.Ing.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Doctoral Degree

……………………………………………….Dean of the Faculty of Engineering
(Professor Bundhit Eua-Arporn, Ph.D.)

THESIS COMMITTEE

……………………………………………….Chairman
(Assistant Professor Anongnat Somwangthanaroj, Ph.D.)

……………………………………….……Thesis Advisor
(Professor Piyasan Praserthdam, Dr.Ing.)

……………………………………………….Examiner
(Associate Professor ML. Supakanok Thongyai, Ph.D.)

……………………………………………….Examiner
(Assosiate Professor Bunjerd Jongsomjit, Ph.D.)

……………………………………………….External Examiner
(Pimpa Hormnirun, Ph.D.)

สุภาภรณ์ ขอบุญส่งเสริม : ผลกระทบของตัวเร่งปฏิกิริยาฟีนอกซีอิมีนแบบมีตัวรองรับและไม่มีตัวรองรับที่มีต่อความว่องไวของตัวเร่งปฏิกิริยาและคุณลักษณะของพอลิโอเลฟินสำหรับการทำโฮโม และโคพอลิเมอร์ไรเซชันของเอทิลีนกับแอลฟาโอเลฟิน (THE EFFECT OF SUPPORTED AND UNSUPPORTED PHENOXY-IMINE CATALYSTS ON CATALYTIC ACTIVITIES AND POLYOLEFIN CHARACTERISTICS FOR HOMO- AND CO-POLYMERIZATION OF ETHYLENE AND α-OLEFIN) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ศ.ดร. ปิยะสาร ประเสริฐธรรม, 110 หน้า

งานวิจัยนี้มุ่งเน้นถึงการสังเคราะห์ตัวเร่งปฏิกิริยาฟีนอกซีอิมีนจำนวนสองชนิดทั้งแบบมีตัวรองรับและไม่มีตัวรองรับ และศึกษาถึงผลกระทบต่างๆของตัวเร่งปฏิกิริยาฟีนอกซีอิมีนที่มีต่อความว่องไวของตัวเร่งปฏิกิริยา และคุณสมบัติของพอลิเมอร์สำหรับการทำโฮโม- และโค-พอลิเมอร์ไรเซชันของเอทิลีน กับแอลฟาโอเลฟิน ตัวเร่งปฏิกิริยาฟีนอกซีอิมีนที่สังเคราะห์ขึ้นมาสองชนิดคือตัวเร่งปฏิกิริยาฟีนอกซีอิมีนที่มีหมู่แทนที่เป็นไซโคลอัลคิล(สารประกอบเชิงซ้อน 1) และตัวเร่งปฏิกิริยาฟีนอกซีอิมีนที่มีหมู่แทนที่เป็นฮาโลเจน(สารประกอบเชิงซ้อน 2) จากการประเมินประสิทธิภาพของตัวเร่งปฏิกิริยาทั้งสองชนิดสำหรับการทำโฮโม- และโค-พอลิเมอร์ไรเซชัน พบว่าตัวเร่งปฏิกิริยาฟีนอกซีอิมีนทั้งสองชนิดจะให้ความว่องไวของตัวเร่งปฏิกิริยาที่สูงสำหรับการผลิตพอลิเอททิลีน นอกจากนี้ สารประกอบเชิงซ้อน 2 จะผลิตพอลิเอทิลีนที่มีน้ำหนักโมเลกุลสูงกว่าสารประกอบเชิงซ้อน 1 (มากกว่าสองเท่า) อย่างไรก็ตาม สารประกอบเชิงซ้อน 2 สามารถผลิตโคพอลิเมอร์ของเอทิลีนกับ 1- เฮกซีน และเอทิลีนกับ 1- ออกทีนที่มีการรวมตัวกับโคมอโนเมอร์ที่สูงกว่าสารประกอบเชิงซ้อน 1 ที่สังเคราะห์โคพอลิเมอร์ของเอทิลีนกับ 1- เฮกซีน และเอทิลีนกับ 1- ออกทีนที่มีความสามารถในการรวมตัวกับโคมอโนเมอร์ได้น้อยมาก จากการทดสอบประสิทธิภาพของตัวเร่งปฏิกิริยาทั้งสองชนิดที่ยึดติดบนตัวรองรับของแมกเนเซียมไดคลอไรด์ และซิลิกาสำหรับการทำเอทิลีนพอลิเมอ์ไรเซชัน พบว่า ตัวเร่งปฏิกิริยาแบบมีตัวรองรับทั้งสองชนิดสามารถสังเคราะห์พอลิเอทิลีนที่มีสัณฐานวิทยาที่ดี และตัวเร่งปฏิกิริยาทั้งสองชนิดที่ยึดติดบนตัวรองรับแมกเนเซียมไดคลอไรด์จะให้ความว่องไวของตัวเร่งปฏิกิริยาที่สูงกว่าตัวเร่งปฏิกิริยาทั้งสองชนิดที่ยึดติดบนตัวรองรับซิลิกาเนื่องจากการเกิดอันตรกิริยาเกี่ยวกับอิเลคตรอนระหว่างเฮทเทอโรอะตอมในตัวเร่งปฏิกิริยาฟีนอกซีกับตัวรองรับแมกเนเซียมไดคลอไรด์

ภาควิชา.....วิศวกรรมเคมี.......	ลายมือชื่อนิสิต......................................
สาขาวิชา....วิศวกรรมเคมี.......	ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก.....................
ปีการศึกษา...2556................	ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์ร่วม.................

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KEYWORDS : PHENOXY-IMINE COMPLEX / UHMWPE / ETHYLENE POLYMERIZATION / SUPPORT / COPOLYMERIZATION / HMWPE

SUPAPORN KHAUBUNSONGSERM: THE EFFECT OF SUPPORTED AND UNSUPPORTED PHENOXY-IMINE CATALYSTS ON CATALYTIC ACTIVITIES AND POLYOLEFIN CHARACTERISTICS FOR HOMO- AND CO-POLYMERIZATION OF ETHYLENE AND α-OLEFIN ADVISOR: PROF. PIYASAN PRASERTHDAM, Dr. Ing., 110 pp.

This research focused on supported and unsupported two phenoxy-imine catalyst synthesis and studied in the effects of phenoxy-imine (FI) catalyst on catalytic activity and polymer properties for homo- and co-polymerization of ethylene and alpha-olefin. Two synthesized phenoxy-imine catalysts were the phenoxy-imine catalyst having cycloalkyl substituent (complex 1) and the phenoxy-imine catalyst containing halogen substituent (complex 2). In the evaluation of both catalyst efficiency for homo- and co-polymerization, it was found that both catalysts showed highly catalytic activity for polyethylene production. In addition, complex 2 can produce polyethylene having higher molecular weight (> 2 times) than that produced by complex 1. However, complex 2 can produce copolymer of ethylene/1-hexene and ethylene/1-octene having higher comonomer incorporation than that obtained by complex 1 synthesizing copolymer of ethylene/1-hexene and ethylene/1-octene being capable of the small amount of comonomer incorporation. Based on the performance test of both catalysts immobilized on magnesium dichloride and silica for ethylene polymerization, it was found that both supported catalysts can synthesize polyethylene with good morphology. Both catalysts immobilized on magnesium dichloride exhibited higher catalytic activity than those immobilized on silica because of electronic interaction between hetero atom in phenoxy-imine catalyst with magnesium dichloride.

Department:……Chemical Engineering…. Student's Signature……………………

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Abbreviations

DSC	Differential scanning calorimeter
SEM	Scanning electron microscopy
NMR	Nuclear magnetic resonance
GPC	Gel permeation chromatography
HDPE	High density polyethylene
UHMWPE	Ultra high molecular weight polyethylene
E	Ethylene
H	1-hexene
O	1-octene
MAO	Methylaluminoxane
MMAO	Modified methylaluminoxane
NMR	Nuclear magnetic resonance
PE	Polyethylene
PDI	Polydispersity
TEA	Triethylaluminium
T*n*HAl	Tri-*n*-hexylaluminum
TIBA	Triisobuthylaluminium
TMA	Trimethylaluminium
T*n*OAl	Tri-*n*-octylaluminum
FI	Phenoxy-imine

Symbols

[Al]	Aluminium concentration
[Ti]	Titanium concentration
[M]	Monomer concentration
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
t	Polymerization time
T_m	melting temperature
Y	Polymer yield

CHAPTER I

INTRODUCTION

Recently, the Middle East builds Petrochemicals plants for producing polyolefin with the tremendous capacity. This increases the supply in the commodity plastic market rapidly. It has an effect on polyolefin producers in Europe, America and Japan which cannot export polyethylene and polypropylene to contribute in Asia market having high potential consumption due to high feedstock cost and high operating cost comparable with those in Middle East. Consequently, the market of commodity plastic has a severe competition in issue of sales, profit, operation and transportation cost. Polyolefin producer want to solve this problem by researching and investigating the novel catalyst and new process or improve original technology for producing the new and value-added products instead of other materials having special properties such as glass, stainless steel, metal, aluminium, etc. for increasing the value of the better product properties. Most Polyolefinic materials as well-known are produced using transition metal catalyzed olefin polymerization technology.

The development of $MgCl_2$-Supported $TiCl_4$ catalysts beginning in the late 1960s by Mitsui Petrochemical and Montecatini has had impact on the polyolefin industry. [1, 2] These catalysts contribute to the enormous growth of polyolefin production and help to reduce effectively the cost by cutting the step of de-ashing out of process. Additional, these catalysts exhibited two order magnitude greater activities for ethylene polymerization than the original Ziegler-Natta catalyst ($TiCl_4$/alkylaluminum catalysts). [3] The Ziegler-Natta catalyst is efficiently high activity, but the nature of these catalysts is multi-site. It is difficult to control the polyolefin microstructure having a well-defined polymer chain and molecular weight distribution.

Next, Sinn and Kaminsky [4] discover the new catalytic system based on metallocenes with alkylaluminonoxane for making polyethylene and polypropylene. These catalysts are single-site, so they can be tailored to produce polyolefin with special stereoregularity, a high degree of tacticity and narrow molecular weight distribution depending on the ligand structure of metallocenes.

Recently, the metallocene catalysts are impregnated on the various supports such as SiO_2, Al_2O_3 etc. for controlling morphology of polymer and preventing the reactor fouling from using homogeneous catalyst system. For these advantages of single-site catalyst, there are development of novel catalysts such as "constrained geometry catalyst(CGC)", post metallocene catalyst, etc. for achieving a variety of new or differentiated polyolefin such as copolymer, block copolymer, functional polymer, etc. Especially, post metallocene catalysts immobilized on $MgCl_2$/alcohol adduct/alkylaluminum showed highly catalytic activity for ethylene polymerization without using MAO as cocatalyst. For these reasons, it is interesting to research and develop the novel post metallocene based on synthesized method to give high yield and raw materials being available in commercial.

In this present study, unsupported and supported post metallocene at least two types will be synthesized for producing value-added polyolefin in new application. Post metallocene consist of phenoxy-imine ligand or halogenated phenoxy-imine ligand and 4 group transition metals formed in bidentated complexes. Two types of catalyst are used to polymerize in homogeneous and heterogeneous catalyst systems for finding the optimum conditions such as temperature, pressure, catalyst and cocatalyst concentration, etc. Additionally, both catalyst systems will be performed copolymerization of ethylene with higher α-olefin. From all above statement, it will be to summarize as follow.

1. The effect of unsupported post metallocene structure on homogeneous polymerization

Post metallocene catalyst will be prepared from two types of ligand, one is cycloalkylated phenoxy-imine ligand and the other one is halogenated phenoxy-imine ligand. Post metallocene catalyst is composed of bidentated ligand with group 4 transition metal. The halogen in phenoxy-imine ligand is electron-withdrawing group due to higher electronegativity; this substituent in FI catalyst effect on catalytic behavior and polyolefin properties in homo- and co-polymerization.

2. The effect of unsupported and supported two post metallocene with various cocatalysts on catalytic behavior and polyolefin properties.

Unsupported post metallocene with various cocatalysts will be polymerized in homogeneous system. While supported post metallocene with various cocatalysts will be polymerized in heterogeneous system. To study the polyolefins obtained with unsupported post metallocene by comparing with those made from supported post metallocene in issue of morphology and molecular weight distribution including catalytic activity. Additionally, it will be to investigate both catalysts in capable of temperature stability and lifetime.

3. The effect of various supported post metallocene on catalytic behavior and polyolefin properties in heterogeneous polymerization.

To investigate post metallocene supported on $MgCl_2$ and SiO_2 carrier for ethylene polymerization and ethylene copolymerization with higher α-olefin such as 1-hexene or 1-octene. Additionally, the resultant polyolefin obtained with both catalysts will be characterized for comparing in morphology, molecular weight distribution and chemical composition in microstructure.

1.1 Objective

1.11. To synthesize *ortho*-fluorinated bis[phenoxy-imine]titanium catalyst and cycloalkylated bis(phenoxy-imine)titanium catalyst and study the influence of these catalysts on homo- and co-polymerization of ethylene and higher α-olefin including catalytic activities.

1.12. To investigate the effect of various supports such as SiO_2, $MgCl_2$ modified with various cocatalysts such as TEA, TIBA, MAO, etc. immobilized with FI catalyst system for ethylene polymerization on catalytic behavior and polymer characteristics.

1.13. To examine the optimum conditions such as temperature, catalyst concentration, etc. for homo- and co-polymerization with unsupported and supported catalyst.

1.2. Scopes

1.21. Preparation of *ortho*-fluorinated bis[phenoxyimine]titanium catalyst and bis(phenoxyimine)titanium catalyst.

1.22. Characterization of ligand and catalyst complexes by ^1H NMR and elemental analyzer.

1.23. Preparation of modified various support with using in preparation of in situ supported *ortho*-fluorinated bis[phenoxyimine]titanium catalyst and cycloalkylated bis(phenoxyimine)titanium catalyst by treating with various cocatalysts such as TIBA, TEA, MAO, etc. for ethylene polymerization.

1.24. Polymerization of ethylene with using homogeneous catalyst and heterogeneous catalyst with various cocatalysts.

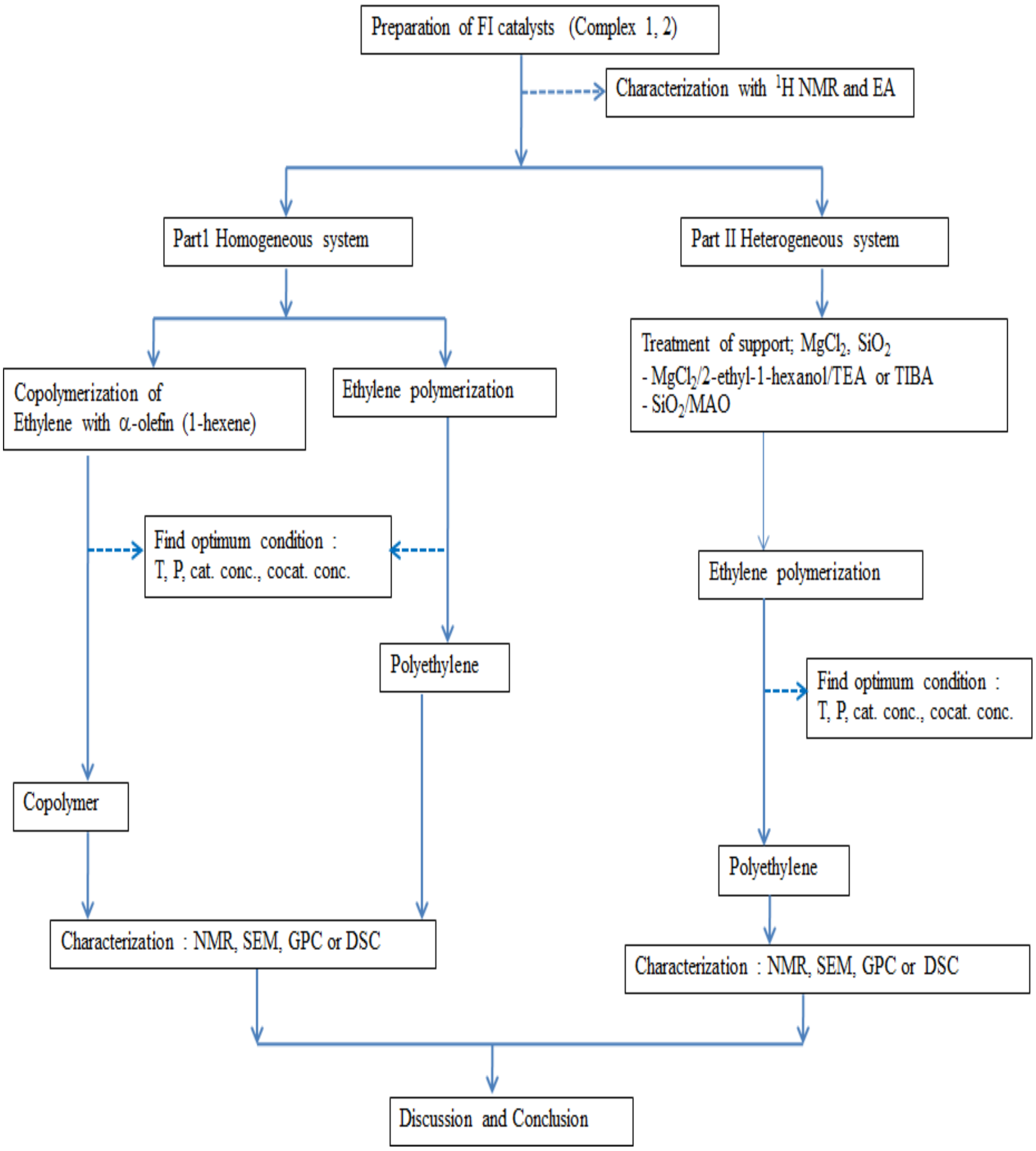
1.25 Copolymerization of ethylene with higher α-olefins such as 1-hexene and 1-octene with using homogeneous catalyst in presence of MAO.

1.26. Determination of the optimum polymerization conditions with unsupported and supported FI catalyst.

1.27. Investigation on the effect of unsupported and supported FI catalyst on catalytic activity.

1.28. Characterization of polyethylene and copolymer of ethylene with higher α-olefin by SEM, ^{13}C NMR, GPC, and DSC.

1.3 Research methodology



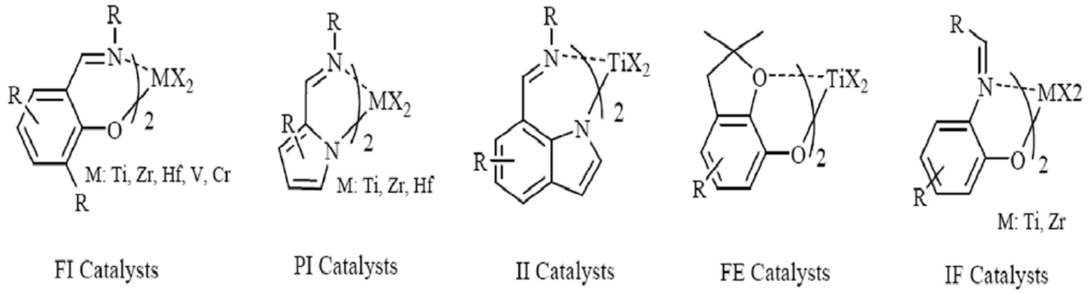
CHAPTER II

LITERATURE REVIEW

2.1 Introduction

The discovery of metallocene complexes as single site catalysts are explored the high performance catalyst for improving the catalytic behavior and polymer properties in aspects of molecular structure, higher alpha-olefin comonomer incorporation, molecular weight distribution. For this reason, these single site metallocene catalysts can produce the differentiated resultant polymers such as linear low density polyethylene (LLDPE), elastomers, isotactic and syndiotactic polypropylenes and syndiotactic polystyrene. Due to the demand in the creation of polymers with new composition and molecular characteristic, the researchers have an effort to develop the new single-site catalysts based on both early and late transition metal based on various ligand environments by focusing on the design concept of ligand orientation to provide higher catalyst efficiency and greater control over polymer microstructure. In the mid-1990s, the nickel catalyst systems based on late transition metals in Shell Higher Olefin Process (SHOP) is potential to polymerize ethylene. The highly active nickel di-imine catalyst can produce linear or highly branched polyethylene depending on the ligand structure and reaction conditions. [5] In the late 1990s, the iron based on catalyst was capable to polymerize ethylene with high active which has not been previously reported in olefin polymerization. Fujita at Mitsui chemicals [6] present the salicyladimine(phenoxy-imine) early transition metal complexes for olefin insertion polymerization, while Johnson at Dupont [7] and Grubbs at Caltech [8-9] introduce salicyladimine(phenoxy-imine) late transition metal complexes in the same year.

The concept of ligand oriented design emphasizing the flexible electronic nature was used to develop and discover the high performance catalyst complexes for olefin polymerization which represent the examples of phenoxy-imine ligated early transition metal complexes (FI catalysts), pyrrolide-imine ligated group 4 transition metal complexes (PI catalysts), imine-phenoxy ligated group 4 transition metal complexes (IF catalysts), phenoxy-ether ligated titanium complexes (FE catalysts), and indolide-imine ligated ligated titanium complexes (II catalysts) as shown in Figure 3.1[10, 11, 12-16]



FI Catalysts PI Catalysts II Catalysts FE Catalysts IF Catalysts

Figure 2.1 Highly active single-site catalyst complexes for ethylene polymerization. [11]

2.2 Ligand oriented catalyst design

Generally, Olefin polymerization catalyst consists of a metal center, ancillary ligand, a growing polymer chain, a coordinated olefin and a cocatalyst, as shown in Figure 3.2. The process of ethylene polymerization involve with intense electron exchange between a ligand and a metal. The ligands must be electronically flexible properties for receiving electrons from the coordinating olefin through metal and releasing electrons to expedite the olefin insertion. During the research of olefin polymerization with metallocene catalysts, these catalysts having a small energy gap between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) of ligand show higher activities. These results indicate that the electronic properties of a ligand play an important role in catalytic activity.

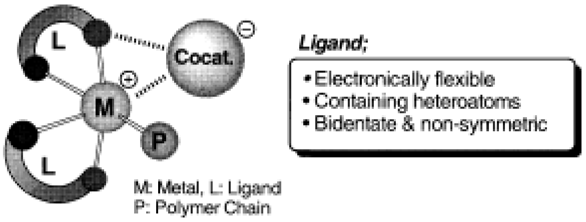


Figure 2.2 Ligand oriented catalyst design concept. [17]

Generally, the requirements for a highly active polymerization catalyst must have olefin-insertion ability, two available *cis*-located sites for polymerization and being stable enough under usual polymerization conditions. [18] For this reason, the basic strategy used to design the ligand oriented catalyst concept for developing highly active catalysts are summarized as shown in Figure 2.3.

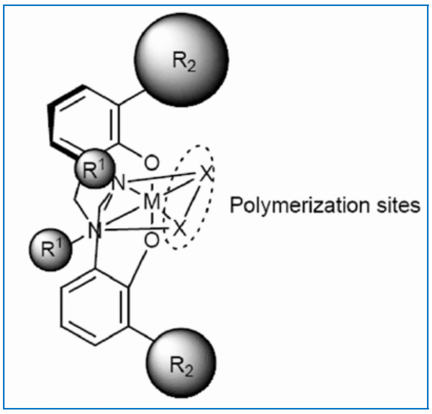


Figure 2.3 Molecular structure of FI catalyst. [23]

With respect to requirement in olefin insertion ability, the ligand should have some properties such as moderate electron-donating properties which were estimated by several calculations, a chelating structure to meet a demand for thermal stability and electron counting that fulfills the metal's requirement to form a complex of 16 electrons or less. Therefore, the ligand of non-symmetric chelating structure was designed for olefin polymerization catalysts

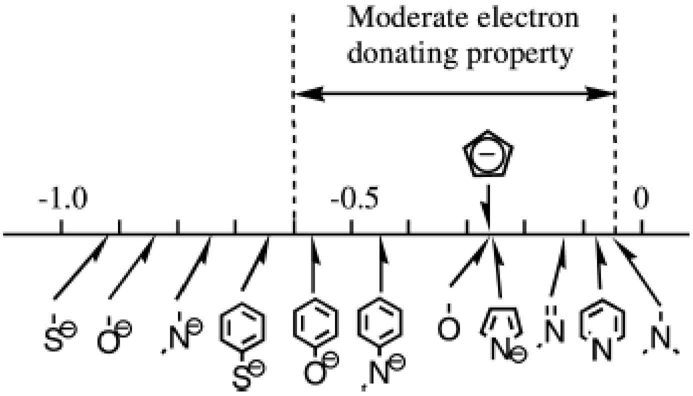


Figure 2.4 Moderate electron-donating ligands calculated by PM_3/MNDPO. [20]

Examples of non-symmetric and electrically flexible ligands as shown in Figure 3.5 consist of neutral ligand having HOMO/LUMO energy gap approximately < 8.5eV, and anionic ligands having HOMO/LUMO energy gap approximately < 7.0eV, calculated by PM_3-MNDO.

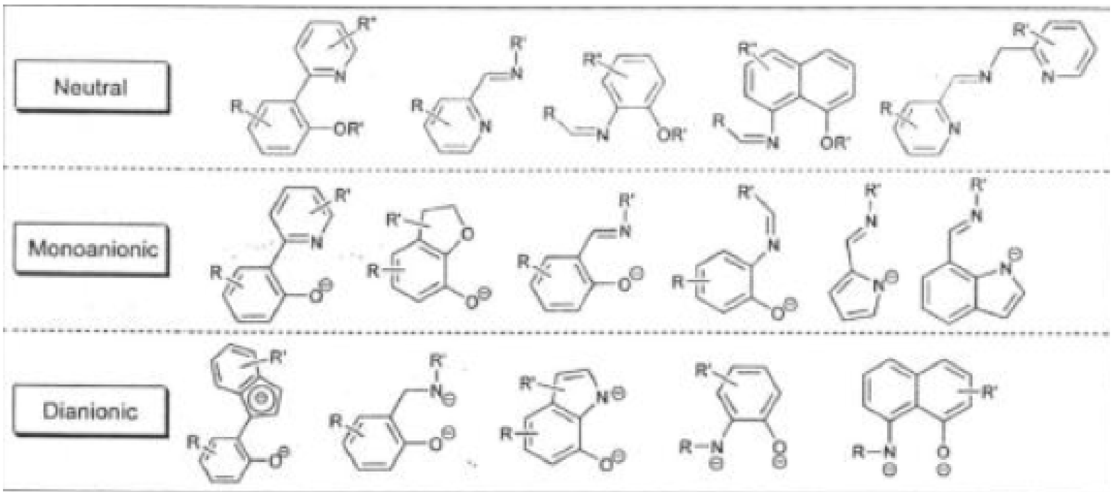


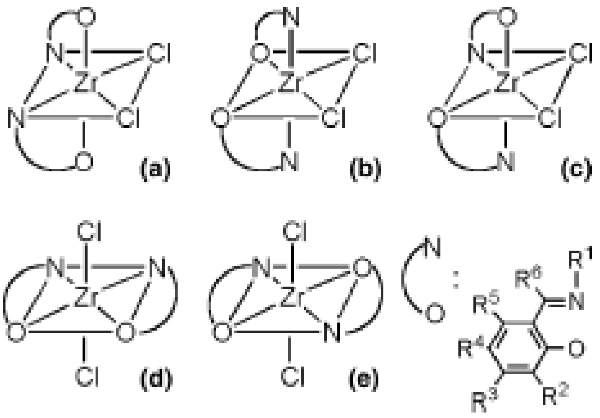
Figure 2.5 Ligand obtained from concept of ligand-oriented design. [21]

The ligands having phenoxy, pyridine and a conjugated imine moiety was considered due to surplus electron donation for sufficiently stabilizing the transition metal leading to olefin insertion. Regarding to the requirement of two available *cis*-located sites for polymerization and being stable enough under usual polymerization conditions, multidentate ligands is capable to forming five-or six–membered ring by chelation which formed with the transition metals to generate catalyst complexes having two available *cis*-located sites and provide the stable catalyst.

Hence, the catalyst comprising of transition metal complexes with multidentate and non-symmetric ligands having moderate electron donating were considered as the efficient and potential post metallocene or non-metallocene which was obtained from ligand oriented catalyst design. In this work, I am focused on the phenoxy-imine complexes for olefin polymerization.

2.3 Structure of FI catalyst

FI catalysts have a wide range of catalyst design possibilities such as ligand structure having various substituents including O, S, N, P and halogen-based functional groups and various transition metals to form complexes which are the most important characteristic of FI. FI catalyst contains an early or late transition metal and two bidentated non-symmetric ligand such as phenoxy-imine, pyrrolide-imine, indolide-imine, phenoxy ether, phenoxy-pyridine, imine-pyridine and phenoxy-imine pyridine. Generally, FI catalyst has potentially five isomers in an octahedral configuration depending on geometry of ligand coordination as shown in scheme 2.1. Normally, FI catalyst exists as a mixture of predominant isomer A in form of C_2 symmetry with *trans*-O, *cis*-N and *cis*-Cl arrangement and isomer B in C_1 symmetry with *cis*-O, *cis*-N and *cis*-Cl arrangement.



Scheme 2.1 Possible FI catalyst isomers [22]

DFT calculations were performed in order to gain information about the source of the very high activity observed with Zr-FI catalyst. Calculations for an ethylene-coordinated methyl cationic complex generated from Zr-FI catalyst and MAO suggest that the cationic complex assumes a distorted octahedral geometry with a *trans*-O, *cis*-N and *cis*-Me/coordinated-ethylene (angle: 74.6°) arrangement (Figure 2.6). This is potentially significant for achieving high activity, because a critical requirement for a high-efficiency catalyst is that it possesses a pair of *cis*-located sites for polymerization.

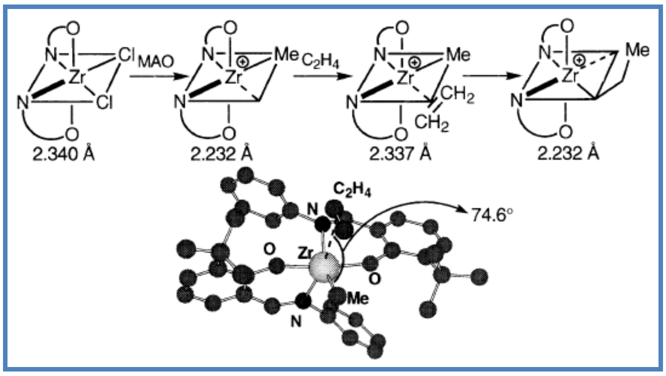


Figure 2.6 Calculated structure of active species from Zr-FI catalyst. [17]

Interestingly, the DFT calculations also indicate that the Zr-N bonds that lie in the same plane as the polymerization sites expand and contract according to the reaction coordinate of the ethylene insertion(2.23-2.34 °A) while, conversely, the Zr-O bond length remains virtually unchanged. Based on these results, it can be concluded that this variable Zr-N bond length which mean a smooth and flexible electron exchange between metal and ligands, and the *cis*-located active sites, as well as the electronically flexible nature of the phenoxy-imine ligands are probably responsible for the high polymerization activities of FI catalyst.[17]

As seen in Scheme 2.1, FI catalyst displays five isomers which have three isomers with *cis*-located polymerization site. For this reason, FI catalysts can produce the multimodal behavior of polymer simultaneously in polymerization reaction. Moreover, fluxional isomerization between two enantiomers (Λ/Δ racemization) for the C_2 symmetric FI catalysts was proposed by theoretical calculations.in propylene polymerization with Ti-FI catalysts.

As the C_2 symmetric FI catalyst structure, two imines (N) and two *cis*-located X ligands are located at the backside of the X-M-X moiety. R^1 substituents on the imine are located on the backside of the X-M-X moiety, whereas the R^2 substituents ortho to the phenoxy are located at the lower and upper of an X-M-X plane in Figure 2.7. These R^1 and R^2 substituents are an important and potential position to provide the polymerization behavior of FI catalysts after activation of FI catalysts because two X sites are transformed into the olefin polymerization sites.

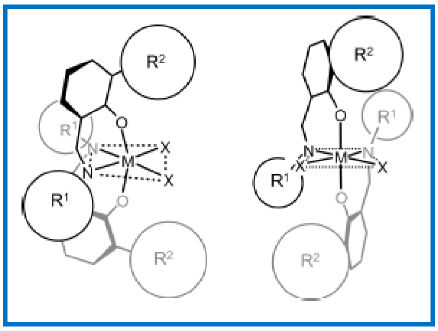
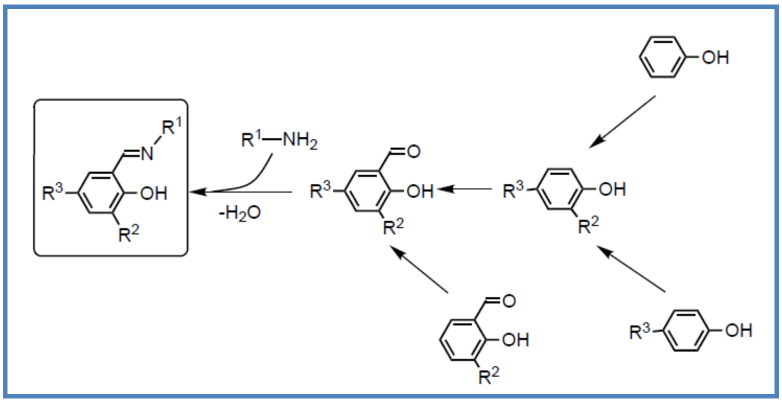


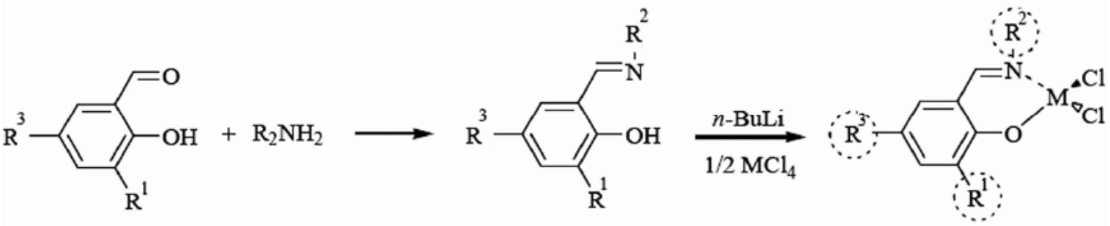
Figure 2.7 Molecular structures of the FI catalysts. [19]

Phenoxy-imine catalysts (FI catalysts) consist of phenoxy-imine ligand and transition metal complexes. The phenoxy-imine ligands have the advantageous properties of diversity and tunability. There are three easily changeable substituents which will sterically and electronically affect polymerization reactions (R^1 to R^3, Scheme 2.2). Phenoxy-imine ligands can be prepared from primary amines and phenol derivatives. The desired substituents on phenols can be introduced by electrophilic aromatic substitutions with electrophiles such as alcohols, olefins and silyl halides. Formylation at the 2-position of phenols can be performed using paraformaldehyde with many established methods in high yields (70-80%). Salicylaldehydes and primary amines are condensed into Schiff bases under standard condensation conditions as shown in Scheme 2.6. Generally, the overall synthesis requires fewer steps and gives higher yields than those for metallocene. [20]



Scheme 2.2 Synthesis of phenoxy-imine ligand [20]

FI catalysts are readily synthesized by forming the FI ligands with the transition metal to complexes. A synthetic route of phenoxy imine catalysts was shown in Figure 2.3



Scheme 2.3 FI catalyst route synthesis [10]

2.4 Electronic features of FI catalysts

FI catalysts have heteroatom [O$^-$, N] having high electron withdrawing property coordinated with transition metal. After activation, the cationic active species of FI catalyst possess a highly electrophilic nature relative to the active species derived from metallocene catalysts having cyclopentadienyl-based on ligand. For this reason, FI catalysts exhibit the high efficiency for olefin polymerization and high performance for incorporation of olefin with a high nucleophilic nature such as norbornene. In addition, [O^-, N] on ligand linking with the metal-ligand bonding promoted the FI catalysts have more ionic and polarized character.

Due to this ionic and polarized feature, FI catalysts are strongly adsorbed on the surface of inorganic support such as $MgCl_2$, Clays because of chemical interactions. Attractive noncovalent interactions, such as hydrogen bonding and electrostatic attraction, play an important role to achieve controlled catalysis with high productivity and selectivity. Although repulsive interaction between the ligand and other components in the catalyst system as shown in Figure 2.8 play a key role in enhancing the stereoregularity and molecular weight of the resulting polymers. Attractive interactions are tunable and are more versatile than repulsive interaction. For this reason, it is expected that attractive interactions provide precise control over catalytic properties such as catalytic activity, polymer molecular weight, polymer stereoregularity and comonomer incorporation. [24]

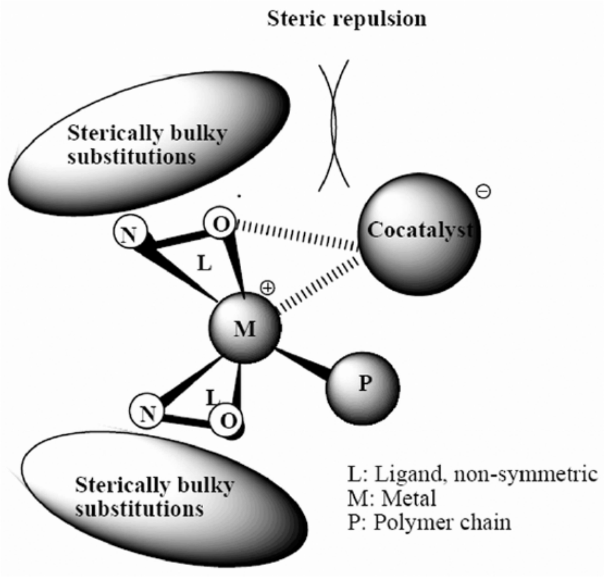
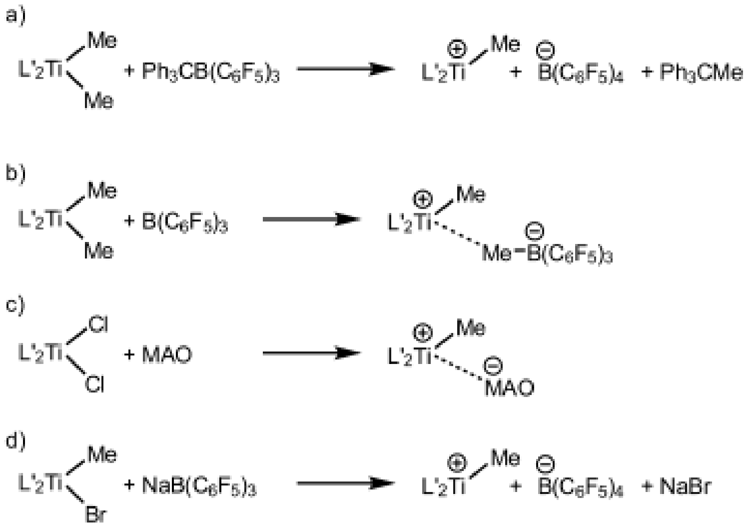


Figure 2.8 Polymerization components. [10]

Additionally, FI catalyst immobilized on $MgCl_2/R'_nAl(OR)_{3-n}$, hetero-poly compounds/R_3Al and Clay/R_3Al are highly active supported catalyst for olefin polymerization. [17, 25-28] For FI catalyst in combination with $MgCl_2/R'_nAl(OR)_{3-n}$, R'$_n$Al(OR)$_{3-n}$ can act as an alkylating agent for FI catalyst and $MgCl_2$ works as an activator and as a support for FI catalyst in simultaneous.[25]

2.5 Activation methods and active species.

Like metallocene complexes, FI catalysts (L'$_2$MX$_2$) activated with various cocatalysts was transformed into coordinatively and electronically unsaturated monoalkyl cationic complexes (L'$_2$M$^+$-R) as shown in Scheme 2.4. [19] When FI catalysts are activated with triisobutylaluminum (iBu$_3$Al) and $Ph_3CB(C_6F_5)_4$ instead of MAO, a new active species is generated in situ because the imine is reduced to an amine by iBu$_3$Al with the concurrent formation of isobutene. [17, 20] The resulting phenoxy-imine complexes showed various interesting polymerization characteristic owing to their unusual iBu$_3$Al-N donors, which will be bulkier and weaker as donors than the imine-N's.



Scheme 2.4 FI catalyst activated with various cocatalysts [19]

FI catalysts consist of a pair of nonsymmetric phenoxy-imine ligands which results in enormous structural diversity of ligands which can be modified by changing substituent, isomers arising from ligand coordination arrangements in an octahedral configuration and potential fluxionality among these isomers. Phenoxy-imine ligands also prepare FI catalysts with highly electrophilic, chemically absorbable, and functional group presumably due to the existing heteroatoms and the M-L' bonding feature. In addition, the in situ ligand modification can be obtained by selecting the cocatalyst type for activation because of the high reactivity of imine moiety. From the above mentioned reason, FI catalysts having a distinctive feature are associated in the production of unique and novel polymer.

2.6 Supported FI catalyst

Effective $MgCl_2$-based activators for single-site catalysts have also been obtained starting from adduct of $MgCl_2$ and 2-ethyl-1-hexanol. Activation of Ti-based FI catalysts using $MgCl_2/Al(i\text{-}Bu)_n(OR)_{3-n}$, obtained in situ via reaction of Al(i-Bu)3 with a solution of $MgCl_2$ and 2-ethylhexanol, resulted in catalyst activities comparable with those obtained using MAO. This approach also gave very high activities with zirconium- and vanadium-based FI catalysts and resulted in well-defined polymer particle morphology. In the case of V-FI catalysts, stable ethylene polymerization kinetics are obtained even at 75 ^{o}C, in contrast to the frequently observed rapid decay in activity of vanadium-based catalysts in olefin polymerization.

V-FI catalyst with $MgCl_2/Et_mAl(OEH)_{3-m}$ which is a thermally robust single-site V catalyst for ethylene polymerization, copolymerize ethylene with propylene at elevated temperature of 75 ^{o}C in the presence of H_2(as a chain transfer agent) and forms a high molecular weight amorphous copolymer[Mw 697000, Mw/Mn 4.72, propylene content 21.3 mol% (^{13}C NMR). [29] GPC-IR analysis revealed that the copolymer has a unique comonomer distribution (Figure 2.9). Thus, the longer copolymer chains possess higher propylene content, which is rather unexpected but should have beneficial effects on the properties of materials.

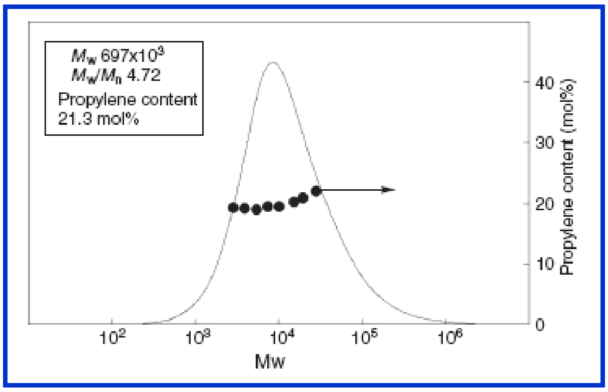


Figure 2.9 GPC-IR chart of the ethylene-propylene copolymer. [17]

2.6.1 Supports or carrier

The support or carrier used in impregnation with Ziegler-Natta, metallocene and non-metallocene or post metallocene catalyst must have high surface area, good mechanical strength, appropriated pore size, pore volume and thermal stability including good morphology.

Most catalyst preparations using silica/alumina based supports involve a thermal pre-treatment, chemical pretreatment or both, in order to remove residual water or hydroxy groups which can deactivate the metallocene active sites. The optimum pre-treatment depends on the silica type and the metallocene complex to be used

2.6.1.1. Silica

Silica is used widely as support in heterogeneous single-site catalyst preparation. Silica has many phases but the phase most commonly used to prepare supported catalysts is the amorphous form such as anhydrous amorphous silica and surface-hydroxylated amorphous silica. Typically, silicas are usually unmodified and fully hydroxylated forms. The surface on its form is saturated in silanol groups. Three diffrent hydroxyl groups can be distinguished isolated (I), germinal (II) and vicinal (III) as shown in Figure 2.10.

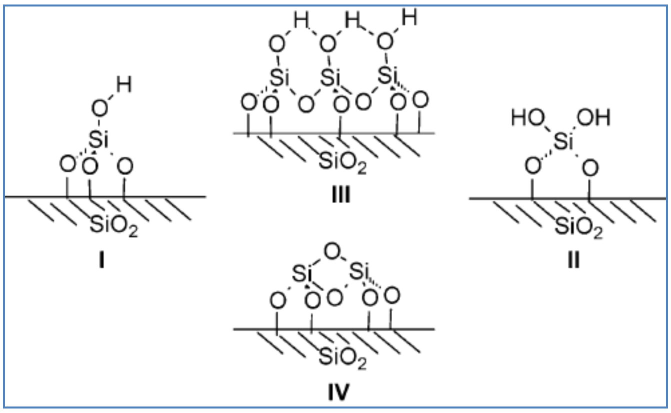


Figure 2.10 Surface hydroxyl species of silica. [30]

The reactions of MAO and its component species (e.g. TMAL) with silica surface have been studies by several groups employing a variety of analytical, spectroscopic and theoretical techniques, or a combination of these. For example, Bartam et al. proposed a chemisorption model for the interaction of MAO with a silica surface based on Si-Me and Al-Me population ratios. [31] In the surface model, a monomethylaluminum complex and methyl groups bound to silicon atom are proposed to be the predominant surface species at room temperature as shown in Figure 2.11. It should be noted that the surface aluminum species are 3-coordinate, and should in principle be highly reactive lewis acids, with the potential to abstract a leaving group from a single-site catalyst and generate an active catalyst.

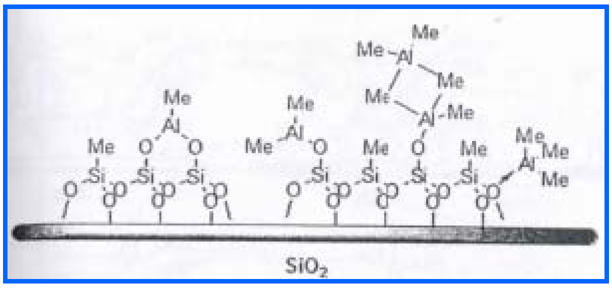


Figure 2.11 model of silica treated with MAO. [32]

2.6.1.2 Magnesium chloride

Magnesium chloride is a widely used support in conventional Ziegler-Natta catalysts. It used for support in single-site catalyst less than silica support. Recently, there has been a notable increase in research on single site catalyst immobilization and activation using $MgCl_2$-based systems. This interest stems partly from the development of controlled-morphology $MgCl_2$ supports for Ziegler-Natta catalysts. Spherical supports having controlled particle size can be produced by cooling emulsions of molten $MgCl_2.nROH$ in paraffin oil, thus obtaining almost perfectly spherical supports, which are then converted into Ziegler-Natta catalysts by reaction with $TiCl_4$ and other components. Porous support materials can be prepared by partial dealcoholation of a $MgCl_2.3EtOH$ adduct, followed by reaction with AlR_3 or MAO, and such supports have been used in conjunction with zirconocenes for ethylene homo-and copolymerization. $MgCl_2/AlEt_n(OEt)_{3-n}$ support have been used in the absence of MAO for the immobilization and activation of titanium-based single-site catalysts leading to polyethylene having narrow molecular weight distribution and spherical particle morphology.

Magnesium chloride can function as a catalyst activator even in the absence of any additional cocatalyst, as a result of its lewis acidity. Marks show that $MgCl_2$ is able to activate $(C_5Me_5)_2ThMe_2$ by the abstraction of a methide anion, generating a catalytically active actinide center $[(C_5Me_5)_2ThMe_2]^+$, as illustrated in Figure 2.12.

[33] The formation of Mg-CH_3 species and the insertion of ethylene into the Th-CH_3 bond is demonstrated using ^{13}C cross-polarization/magic angle spinning(CP/MAS) NMR spectroscopy, which also reveal that approximately 50% of the Th in this system is catalytically active. [66]

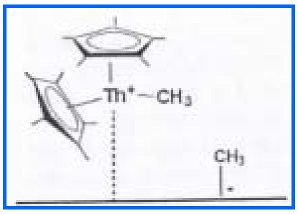


Figure 2.12 Generation of active species by CH_3- transfer to a lewis acidic surface site on $MgCl_2$ [32]

Taking into account the widespread development and utilization of silica/MAO based systems for the immobilization of metallocenes and other single-site catalysts; it is not surprising that a variety of efforts have been made to use $MgCl_2$-immobilized catalysts together with MAO catalyst, or to immobilize the aluminoxane itself on a magnesium chloride support. $MgCl_2$-supported metallocene with MAO as cocatalyst in ethylene polymerization involve a support prepared by the reaction of $MgBu_2$ with *t*-BuCl in the presence of diisoamyl ether in hexane, followed by treatment with Cp_2ZrCl_2. [34] This support has a spheroidal morphology with narrow particle size distribution and PE obtained from this supported catalyst is also narrower molecular weight distribution (MWD).

The preparation and use of supports obtained by partial dealcoholation of $MgCl_2$ adducts and ethanol having spherical particle morphology has also been described. [35] The reaction of these supports with an aluminum alkyl gives rise to the formation of products having a composition $MgCl_2/AlEt_n(OEt)_{3-n}$, followed by impregnation with a toluene solution containing the complex of *rac*-Et(Ind)$_2$ZrCl$_2$. This supported catalyst with MAO activation exhibit in ethylene polymerization in hexane slurry at 75°C, giving yield of 2 kg PE/g cat.

Recently, The preparation and use of an adduct of magnesium chloride and ethanol is also described in a Equistar patent application. [36] Firstly, $MgCl_2.2.5EtOH$ is treated with MAO and then with a mixture of MAO and a zirconocene complex containing an indenoindolyl ligand. The resulting catalyst has higher ethylene polymerization activity than that obtained using either anhydrous $MgCl_2$ or calcined SiO_2 as support materials.

$MgCl_2$-based supports having relatively high contents of MAO have been obtained by the dealcoholation of a spherical adduct $MgCl_2.2.6EtOH$ at 250 ^oC, followed by treatment with a solution of MAO in toluene and a crosslink agent such as glycol, glycerol or triethanolamine. [37] The incorporation of the crosslink agent increased the Al content in the support up to around 12 wt%. These $MgCl_2$/MAO supports are mixed with *rac*-Et(Ind)$_2$ZrCl$_2$ and used in ethylene polymerization, giving a spherical polyethylene morphology and activities of up to 2320 KgPE/mol/bar/h at 80^{o}C.

Recently, Magnesium chloride support in combination with borate activators is reports by a few researchers. The main challenge is to develop an effective method for effective coordination or tethering of the activator on the support. A recent example of such an approach is the synthesis and use the borate $[Ph_3C][B(C_6F_5)_3(C_6H_4NMe_2)]$. [38] Here, use is made of the ability of the amine to coordinate strongly to magnesium chloride, leading to immobilization of the borate activator. Impregnation of a chemically activated $MgCl_2$ support with this borate, followed by treatment with a toluene solution of the product of reacting *rac*-Me$_2$Si(1-indenyl)$_2$ZrCl$_2$ with $AliBu_3$, gave an immobilized catalyst used in ethylene and propylene homopolymerization and in ethylene/1-butene copolymerization. An ethylene polymerization activity of approximately 1700 Kg/mol/bar/h is obtained at 60^{o}C, without reactor fouling.

The use of magnesium chloride in combination with a simple aluminum alkyl cocatalyst such as $AlEt_3$ or $AliBu_3$ has the desirable advantage of avoiding the use of a more expensive and more complicated aluminoxane or borate activator. Supports obtained by reacting an aluminum trialkyl with solid $MgCl_2$/ethanol adducts having a spherical particle morphology have been shown to be effective for the immobilization and activation of a wide range of early-transition metal catalysts, including titanium-,vanadium- and chromium-based systems. [39, 40, 41, 42, 43]

2.6.2 Cocatalyst

2.6.2.1 Methylaluminaoxane(MAO)

MAO is the most important cocatalyst which activates the group 4 metallocenes in homogeneous and heterogeneous single-site catalyst such as metallocene, post-metallocene and non-metallocene catalyst. Before the discovery of the MAO cocatalyst, the homogeneous metallocene catalyst Cp_2TiCl_2 is activated with alkyaluminum chloride which leads to poor catalytic activity. The use of MAO cocatalyst with metallocene raised the catalytic activity by several order magnitude. There are some other aluminoxanes such as ethylaluminoxanes (EAO) and isobutylaluminoxane (iBAO), but MAO is much more effective than EAO and iBAO.

MAO is formed by hydrolysis of trimethylaluminum (TMA). The controlled hydrolysis of TMA is first performed by the reaction of TMA with crystal water of $CuSO_4.5H_2O$. Later, $Al_2(SO_4)_3$ hydrates are chosen as the water source for the reaction in order to prevent the contamination of MAO from Cu(I) alkyl compounds.

MAO is an oligomer with 6-20 [-O-Al(Me)-] repeat units. A higher degree of oligomerization of MAO provides a beneficial effect to the catalyst activity. The exact structure of MAO remains a puzzle. MAO might exist in a linear and/or a cyclic form as Figure 2.13. [44]

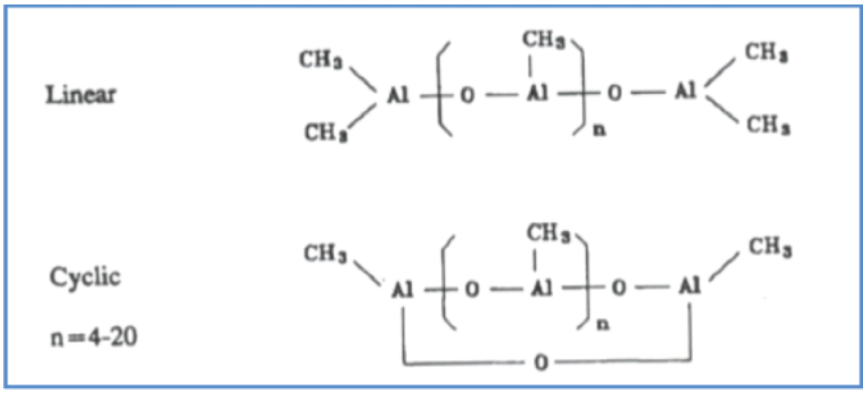


Figure 2.13 Possible structures of MAO [44]

MAO undoubtedly acts as a methylating agent and an impurity scavenger. [45] Other simple alkyl aluminum compounds can also alkylate metallocene chlorides and scavenge impurities, but they do not lead to high catalyst activities. MAO not only produces the cationic active species but also stabilizes the anion by formation of a "crown-aluminoxane complex" analogous to crown-ether complexes of cations for preventing termination process in cationic polymerization. The metallocene is probably surrounded by MAO even in the outer-sphere and thus prevents catalyst deactivation by bimolecular processes between two metallocene molecules. [47]

2.6.2.2 Alkylaluminum

Alkylaluminums such as trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-*n*-hexylaluminum and tri-*n*-octylaluminum are mostly used as cocatalyst for generating some ZN catalyst system, metallocene and non-metallocene catalyst system to active form. Alkylaluminum is an alkylating agent and impurity scavenger. [46]

2.7 Olefin polymerization with FI catalysts

2.7.1 Catalyst efficiency

FI ligands having electronically flexible nature are an important factor with influencing on the remarkably high ethylene polymerization activities of FI catalysts. [15, 17] From ethylene polymerization, phenoxy-imine catalysts requires sterically bulky group *ortho* to the phenoxy-O to achieve highly catalytic activity. [24, 48] Additionally, the steric encumbered groups also promote to afford the steric protection toward the anionic phenoxy-O donors from coordination with Lewis acidic compounds such as MAO or from the active cationic species which is highly electrophillic and the inducement of effective ion separation between the cationic active species and an anionic cocatalyst, resulting in the increase of catalytic activity. Moreover, Covallo and co-workers have proposed a site inversion mechanism that can explain that the steric bulky substituent *ortho* to the phenoxy-oxygen in bis(phenoxy-imine)Ti complexes with C_2 Symmetry play a crucial role in syndiospecific olefin polymerization. [49, 50] As shown the FI catalyst structure in Figure 2.14, the increase of the steric bulky R^1 substituent of FI catalysts results in the enhancement of the catalytic activity and polymer molecular weight. [51] The increased catalytic activity may be attributed to the effective ion separation providing more space for polymerization and the increased degree of unsaturation associated with the cationic active species.

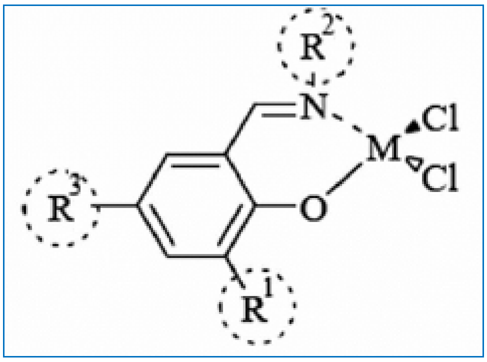


Figure 2.14 FI catalyst structure. [23]

The steric encumbered R^2 substituent in Figure 2.14 has a significant influence on the catalytic performance of FI catalyst which different from R^1 substitutent. For Ti based FI catalyst, the increase of steric bulky R^2 substituent resulted in the deleterious effects on the catalytic activity and polymer molecular weight. In case of introducing R^2 substituent with alkyl group, the activity of FI catalyst decrease because of the increased steric congestion in close proximity to the active site which hindered the ethylene reacting to active site and/or growth of the polymer chain. However, the molecular weight trend of the Zr-based FI catalysts is inversed, for eample: the attachment of methyl or i-propyl to the R^2 position highly increases the molecular weight of polymer. [52, 53] In addition, the catalytic activity of FI catalysts can also be increase by electronically controlling the active sites such as changing the R^2 substituent to electron-withdrawing substituent. [17, 20]

While the R^3 substituent of FI catalyst has a small effect of both catalytic activity and polymer molecular weight due to the location of R^3 substituent far from the polymerization center. [18, 53] Additionally, R^3 substituent has an influence on the thermal stability of FI catalyst, For example: the introduction of an electron donating methoxy group at R^3 substituent of FI catalyst for polymerization at higher temperature. [17, 20]

Ionic feature of the active species obtained from FI catalyst with various cocatalysts have an impact on catalytic activity according to information in section of 2.5 activation method.

2.7.2 Catalyst Deactivation

FI catalyst is deactivated with MAO by ligand transferred to trimethylaluminum in MAO, yielding an Al-FI complex ($L'AlMe_2$), a methane molecule and inactive group 4 metal compounds with one FI ligand as shown in Figure 2.15. [54-56] The deactivation way can be effectively blocked by the large bulky R^2 substituents which is consistent with the catalytic activity depending on the R^2 group size. For living Ti-FI catalyst for polymerization, the ligand transfer reaction for deactivation is extremely retarded when the metal-bound alkyl group is a polymeryl group. [54] The observed intramolecular 1,2-migratory insertion of M-benzyl to the electrophilic moiety is detrimental to olefin polymerization catalysis. [57] In addition, the highly electrophilic L'_2Ti^+-Me coexist with neutral L'_2TiX_2 leads to the formation of dinuclear complex as an inactive dormant species. **[58]**

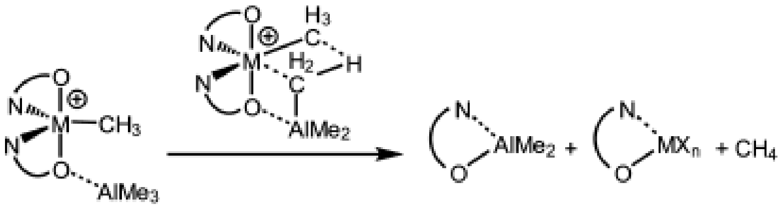


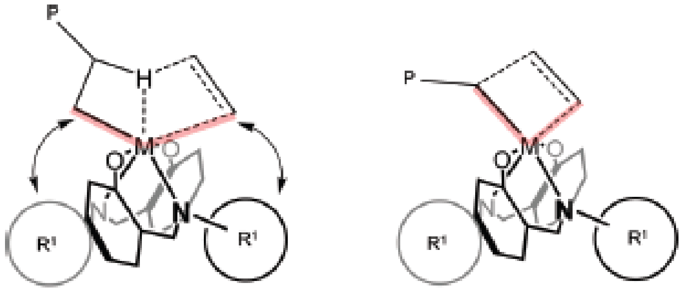
Figure 2.15 Catalyst deactivation. [58]

2.7.3 Control of Molecular weight

The average molecular weight of polymers is statistically determined by the ratio of the chain growth and the chain-terminating reaction. Therefore, it is essential to understand chain transfer reactions for controlling the molecular weight of polymers. FI catalysts with various ligand structures possess an unusual wide range of molecular weight from 10^3 to 10^7 without adding the chain transfer agents due to responsible in the R^1 substituents. [15, 17, 20]

On DFT calculatuions, the large bulky R^1 substituents located at the backside of the polymerization site would destabilize a sterically bulky six-centered transition state for β-hydrogen transfer to a coordinating ethylene to a greater extent than the compact four-centered transition state for ethylene insertion as shown in Scheme 2.5. The X-ray structure result of FI catalyst exhibited narrower Cl-Zr-Cl bonding angle as the larger size of R^2 group. [15]

When the sterically encumbered R^1 groups help to inhibit the reaction of β-H transfer, therefore a chain transfer to alkyl aluminum can be prominent. For example FI-Zr catalysts having R^1 substituent as 2-isopropylphenyl group afford an alkylaluminum-terminated PE with molecular weight of 1000-720,000 and polydispersity of 2.0-2.6 depending on activation with MAO/trimethylaluminum. [15]



β-H transfer to monomer monomer insertion

Scheme 2.5 Six-centered or four-centered transition state for ethylene polymerization. **[19]**

It is well known that living polymerization can be to control polymerization degree, chain end structures, stereochemistry and molecular weight of polymer. FI catalyst bearing at least one fluorine located in 2,6-positions of phenyl group as R^2 substituent displayed high activity for living olefin polymerization because electron withdrawing fluorines increase the electrophilicity and consequently the reactive of active centers. The effect of *ortho*-fluorine substituent represents a novel strategy to develop or modify the transition complexes for living olefin polymerization. [20]

2.7.4 Control of comonomer consumption

FI catalysts having R^1 substituent located at an appropriated position in the presence of MAO can produce the E/P copolymer which is capable of controlling propylene incorporation. As the previous described, the R^1 substituent *ortho* to phenoxy–O in FI catalyst also has an influence on activity. This substituent plays an important dual role in olefin polymerization. [17, 20] A striking characteristic of a large bulky R^1 substituent induces greatly high selectivity for ethylene which is unachievable with metallocene catalysts. FI catalyst having R^1 substituent as a cumyl is more reactive approximately 30 times to ethylene relative to propylene with evaluation from the monomer molar ratio in medium and in comonomer composition. This unusual and special feature resulted in the production of ultra-high molecular weight polyethylene and PE-based multiblock copolymers. [15]

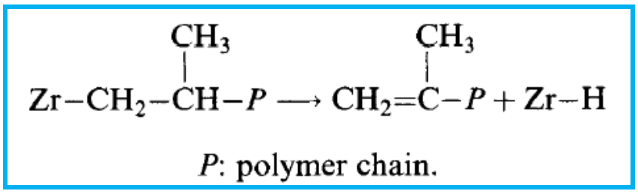
In addition, FI catalyst having the sterically unencumbered R^1 substituent exhibits the higher propylene incorporation in copolymer. However, the results of FI catalyst bearing R^1 substituent as phenyl group provide a sterically more open active site than that as *tert*-butyl group due to rotating to evade steric congestion. [59] For this reason, FI catalyst with phenyl substituent at R^1 position can produce highly efficiency for the copolymerization of ethylene with cyclic olefins or polar monomers, as well as higher α-olefin.

Norbornene is a more nucleophilic feature than ethylene and α-olefin, while FI catalyst active species possess higher electrophilicity than a metallocene active species. For this reason, FI catalyst has a high potential to produce the copolymer of ethylene and norbornene.

2.8 Mechanism for single-site catalyst polymerization

As in heterogeneous ZN catalyst systems, Polymer chain growth process has 3 steps including chain initiation, propagation and termination reactions. Polymer chain growth is terminated by chain transfer reactions in homogeneous metallocene-based catalyst systems. Several types of transfer reactions which may occur in the homogeneous and heterogeneous single-site systems too are listed as follows.

β-Hydrogen Elimination - The metal center abstracts a H atom bonded to the β-C of the growing polymer chain, forming M-H bond (M=transition metal) and leaving a polymer with an unsaturated end.

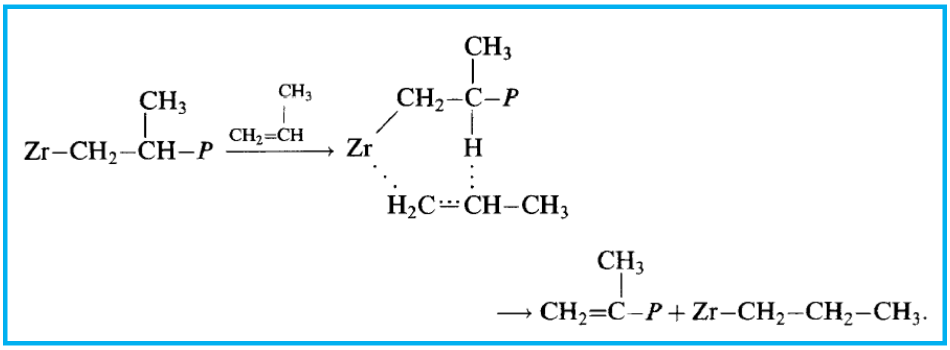


$$\mathrm{Zr{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}}P \longrightarrow \mathrm{CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}}P + \mathrm{Zr{-}H}$$

P: polymer chain.

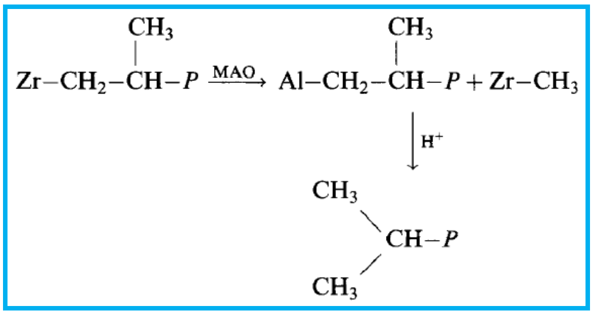
Scheme 2.6 β-Hydrogen Elimination

Chain transfer by monomer - β-hydrogen elimination and olefin monomer insertion at the active center take place simultaneously without forming the M-H bond.



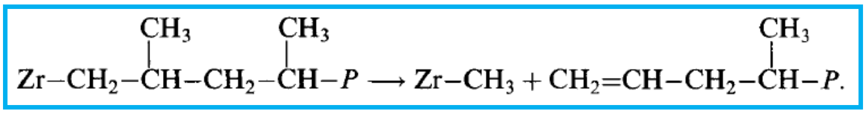
Scheme 2.7 Chain transfer by monomer

Chain transfer to MAO - The growing polymer chain attached to an active center exchanges with the methyl group of a MAO molecule, if MAO is used to activate catalyst, forming the M-CH_3 bond in the active center and the Al-terminated polymer chain.



Scheme 2.8 Chain transfer to MAO

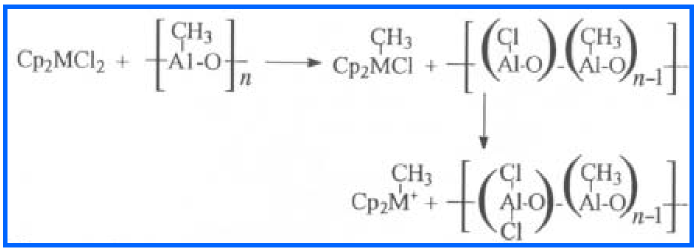
β-CH_3 Elimination- This is a newly discovered chain transfer mechanism in the polymerization of propylene. The metal center abstracts a CH_3-group, instead of an H atom, at β-C of the growing chain, thus forming a M-CH_3 bond at the active center and leaving a polymer with an allyl end.



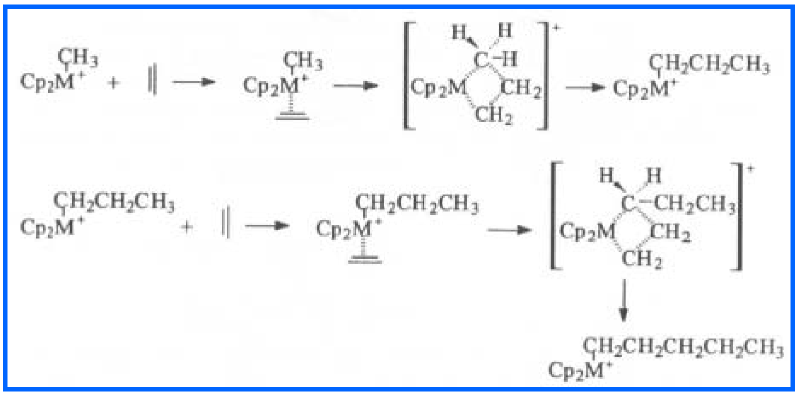
$$Zr-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2-\overset{CH_3}{\overset{|}{C}}H-P \longrightarrow Zr-CH_3 + CH_2{=}CH-CH_2-\overset{CH_3}{\overset{|}{C}}H-P.$$

Scheme 2.9 β-CH_3 Elimination

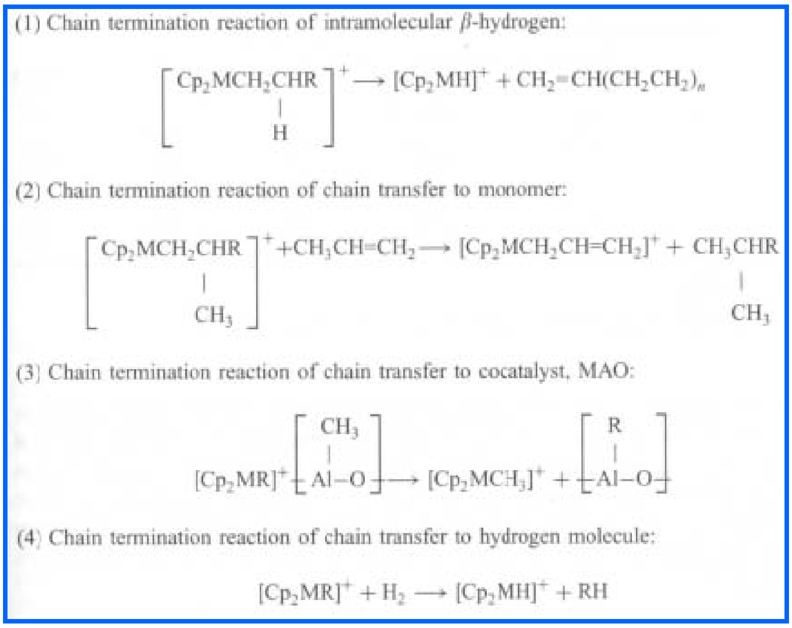
The mechanism coinsides with the chain polymerization process comprising of chain initiation, propagation and termination reactions in the polymerization of olefin monomers via metallocene catalysts. For example, the processes of metallocene (Cp_2TiCl_3/MAO) catalytic ethylene polymerization are shown in Scheme 2.12-2.14. [60]



Scheme 2.10 Chain initiation reactions. [60]



Scheme 2.11 Chain propagation reactions. [60]



(1) Chain termination reaction of intramolecular *β*-hydrogen:

(2) Chain termination reaction of chain transfer to monomer:

(3) Chain termination reaction of chain transfer to cocatalyst, MAO:

(4) Chain termination reaction of chain transfer to hydrogen molecule:

$$[Cp_2MR]^+ + H_2 \longrightarrow [Cp_2MH]^+ + RH$$

Scheme 2.12 Chain termination reactions. [60]

2.9 Living olefin polymerization

The goal of all chemical synthesis is to precisely control microstructure products as requirement. Likely polymer synthesis, it would like to control precisely and select the architecture of macromolecules microstructure in order to required material properties. One of the powerful methods which are capable for producing polymer architecture is living polymerization with catalyst system.

Living polymerization has seven criteria as follow.

1. Polymerization proceeds to complete monomer conversion, chain growth depend on monomer addition.
2. Number average molecular weight (M_n) of the polymer enhance linearly as function of monomer conversion
3. Number of active sites remains constant for the duration of the polymerization process.
4. Molecular weight of polymer can be precisely controlled through stoichiometry.
5. Polymers have narrower molecular weight distribution (M_w/M_n 1).
6. Block copolymer can be prepared by sequential monomer addition.
7. End-functionalized polymer can be synthesized. [61, 62]

The development of living olefin polymerization catalysts has been notably slower. Recently, It was found that unprecedented living olefin polymerization catalysts (fluorinated Ti-Fi catalysts), which allow for the preparation of a variety of precisely controlled polyolefinic materials including monomer-disperse polymers, end-functionalized polymers, and block copolymers from ethylene, propylene and higher α-olefins.

2.10 Polyolefin and copolymer of ethylene and higher α-olefin obtained from unsupported and supported FI catalysts.

Mullen et al. [63] investigated bis[*N*-(3-*t*-butylsalicylidene)cycloheptylaminato]titanium(IV) dichloride immobilized on various polystyrene latex support composition in presence of dried MAO for ethylene polymerization. It was found that these catalyst systems are highly active for producing ultra-high molecular weight polyethylene (UHMWPE) and narrow polydispersity. Besides, these supported catalysts based on latex containing PEO and pyridine as nucleophilic groups attributed to stabilize environment of catalytic active center providing constantly long polymerization time without a decrease in activity. Molecular weight of obtained polyethylene with supported Ti-FI complex depend on temperature only, not affected from ethylene pressure.

Bis(phenoxyimine)titanium complexes activated with MAO for ethylene polymerization were investigated in the temperature range of 30-70 ^{o}C. The different structure substituent at the imine and phenoxy group in FI catalyst had an influence on the catalytic activity and polymer properties. The perfluorophenyl substituent at the imine of FI catalyst showed very active for ethylene polymerization due to electron donating effect of fluorine to provide increasing the electrophilicity of titanium species and resulting in the decrease of activation energy in ethylene insertion. [64]

Jones, R.L., and Armoush M. [65] presented the type of catalyst such as ZN catalyst, metallocene and non-metallocene for producing UHMWPE. The ZN catalyst based on silica or magnesium chloride support having multiple reactive sites afforded a mixture of different polymer chains with broad polydispersity. Whereas, the metallocene and non-metallocene single-site catalysts have identical ligand environments resulting in the polymer chains with the similar length. The main chain transfer reaction of ethylene polymerization was β-hydride elimination and chain transfer to aluminum. When the catalyst systems help to suppress β-hydride elimination, it can produce UHMWPE.

Wang et al. [66] present the method for trapping free TMA existing in MAO as cocatalyst by adding a sterically hindered phenol such as tBu2Ph-OH for improving performance of MAO. Phenoxyimine titanium complex activated with the improved MAO is higher active than that activated with original MAO for producing polypropylene.

Bryliakov et al. [67] presented o-F-substituted and nonsubstituted bis(enolatoimine) titanium complexes activated with MAO for ethylene polymerization. The o-F substituented bis(enolatoimine) titanium complexes displayed highly active in living ethylene polymerization and afforded polyethylene with high molecular weight and narrow polydispersity, wheareas nonsubstituted bis(enolatoimine) titanium complexes showed nonliving feature. The results may be cause to favor the interaction of o-F substituents with the metal center resulting in suppression of chain transfer and of β-hydrogen transfer processes.

Choi and Soares [68] investigated nickel diimine complexes supported on $MgCl_2$/alcohol adduct/alkylaluminum and SiO_2 capable to produce polyethylene. The polymer particles made with both SiO_2- and $MgCl_2$-based supported catalysts resulted in free flowing particles.

Hu et al. [69] investigated the different phenoxyketimine zirconium complexes activated MAO with highly activity for ethylene polymerization. The phenoxyketimine catalyst having substituent in the ortho-aniline with fluorine showed high activity for producing polyethylene compared with that with alkyl group due to the increase of metal positive charge caused by fluorine having strong electron-withdrawing. Likewise, bis(phenoxyketimine) zirconium complex bearing the electron-withdrawing group in the carbon atom of imine double bond exhibited higher activity and higher molecular weight of polyethylene. Additionally, the catalytic activity decrease with the increase of temperature because of the catalyst decomposition in high temperature.

Non-fluorinated phenoxyimine catalysts with 5-position of the salicylaldiminato ring as electron–withdrawing group are highly active in ethylene polymerization because of the increase of a more electrophilic titanium center. Additionally, this paper is shown the influence of catalyst concentration, temperature, pressure and catalyst and cocatalyst molar ratio on catalyst behavior. [70]

Fujita and coworkers [71] reported fluorinated bis(phenoxy-imine)titanium complexes impregnated with $MgCl_2/i\text{-}Bu_nAl(OR)_{3-n}$ capable to produce syndiotactic polypropylene with narrow molecular weight distribution. These supported catalysts are the first MAO- and borate-free living catalysts displayed highly stereoselectivity.

Weiser and Mulhaupt [72] presented the new phenoxyimine catalyst of Bis-(N-(3,5-diiodo-salicylidene)-2,6-difluoroaniline)-titanium(IV)-dichloride) activated MAO exhibited highly active catalyst for producing polyethylene with ultra-high molecular weight, polypropylene and block copolymer of ethylene and propylene in living fashion.

Living olefin polymerization offers a new synthetic approach for the preparation of block copolymers which might be useful as compatibilizers in polymer blends for tailoring mechanical properties and the synthesis of new materials.

Sullivan et al. [73] investigated the Ziegler-Natta catalyst and phenoxy-imine catalyst activated with alkyl aluminum or MAO for producing UHMWPE and copolymer. $TiCl_3$ Ziegler-Natta catalyst has low activity for producing UHMWPE compared with Mg/Si supported titanium catalyst having excellent activity and molecular weight as well. Phenoxy-imine titanium catalysts (Ti-FI) are highly active catalysts for UHMWPE and copolymer having various molecular weights depending on the ligand structure on Ti-FI catalyst.

Bulychev et al. [74] reported the influence of organoaluminum activator on catalytic behavior of non-fluorinated and fluorinated phenoxy-imine zirconium complexes in ethylene polymerization. Non-fluorinated Zr-FI catalyst activated with MAO is higher active than that with TIBA and TMA and no active when activated with dried MAO. While fluorinated Zr-FI catalyst in presence of MAO, dried MAO and TIBA displayed a highly active catalyst for producing polyethylene including copolymer of ethylene and 1-hexene or propylene with low comonomer content.

New fluorinated phenoxyimine zirconium complexes bearing different halogen in the *ortho* and *para* positions on phenoxy ring activated with various co-catalysts for α-olefin polymerization were introduced by Pellechia et al. [75] the complexes bearing chlorine and bromine in the *ortho*- and *para*- phenolate ring showed higher activity for propylene polymerization than the analogous complex with alkyl substitution due to halogen as strong electron-withdrawing group which increase the electrophilic character of active species. Both halogenated complexes can produce steroirregular, syndiotactic polypropylene and poly(1-hexene), including copolymer of ethylene and 1-hexene with different properties depending on the appropriated choice of cocatalysts such as MAO and $Al(iBu)_3/Ph_3CB(C_6F_5)_4$.

Sandaroos and coworkers [76] introduced two FI Zr catalysts of bis[*N*-(3,5-dicumylsalicylidene)-napthylaminato]zirconium(IV) dichloride and bis[*N*-(3,5-dicumylsalicylidene)-anthracylaminato]zirconium(IV) dichloride activated with MAO for ethylene polymerization. FI Zr complex bearing three aromatic fused rings on N atom demonstrated lower activity for ethylene polymerization than that bearing two aromatic fused rings due to the increase steric hindrance of catalyst. The activities of both complexes were increased with increasing the monomer and [MAO]/Zr ratio. Both catalysts in presence of MAO showed living behavior in ethylene polymerization as seen in linear relations of polymerization time and molecular weight.

Ahmadjo et al. [77] reported bis[N-(3,5-dicumylsalicylidene)-2′,6′-fluoroanilinato]zirconium(IV) dichloride activated with MAO for ethylene polymerization. This catalyst exhibited moderate activity and give polyethylene with high molecular weight due to the suppression of β-hydride chain transfer reaction by the influence of the *ortho*-F substituted phenyl ring on N atom in catalyst. The catalytic activity and molecular weight of polyethylene is slightly sensitive to hydrogen concentration.

Fujita et al. [78] synthesized vinyl- and Al-terminated polyethylene with using phenoxyimine zirconium complexes(FI-Zr) activated with dried methyaluminoxane (DMAO) or DMAO/trimethylaluminum(TMA) and changed vinyl-terminated PEs to end-funtionalized PEs and PE/polyethylene glycol(PEG) hybrid materials. The sterically bulkier substituents on the imine-N in catalyst resulted in the increase of molecular weight product and catalytic activity. The FI-Zr complexes bearing cycloalkyl group on the imine-N give higher degree of unsaturated vinyl-terminated PEs compared with those bearing acyclic alkyl groups because of less steric congestion to active sites.

CHAPTER III

EXPERIMENTAL

3.1 Materials

All manipulations were performed under an inert atmosphere (Nitrogen or Argon) with using a standard Schlenk line and a glove box. Dried solvents [tetrahydrofuran (THF), toluene, hexane, heptane and dichloromethane (DCM)] were purified by solvent purification unit from M Braun and Innovative Technology, stored in Schlenk tube with molecular sieve 4 Å and bubbled in nitrogen gas before use. Diethyl ether was purchased from Merck and use as received. Anhydrous $MgCl_2$, 1.6 M *n*-butyl lithium in hexanes, 2 M *n*-butyl lithium (*n*-BuLi) in cyclohexanes, cycloheptyl, cyclooctyl, 2,6-difluoroaniline, dibromosalicylaldehyde, 2-*tert*-butyl phenol, 3.0 M EtMgBr in diethyl ether, paraformaldehyde, triethylamine, Magnesium sulfate, 2-ethyl-1-hexanol and titanium tetrachloride were purchased from Aldrich and used without purification. Silica Sylopol 2229 supplied by Grace Davision, was heated under vacuum at 400 °C for 6 h before use. Ultra high purity Nitrogen and Argon (99.999%) was obtained from Thai Industrial Gas Company. Ethylene gas was supplied from Praxair Technology Inc. 1-hexene and 1-octene were purchased from Aldrich and distilled with calcium hydride prior to use.

Methylaluminoxane (MAO) (10 wt. % in toluene), tri-*n*-octylaluminum (T*n*OAl; 25 wt% in hexanes), triethylaluminum (TEA; 1 M in hexane) and trimethylaluminum (TMA; 2 M in hexane) were obtained from Aldrich and used without further purification. Tri-n-hexylaluminum (T*n*HAl; 0.4 M in hexanes) and Triisobutylaluminum (TIBA; 1.1 M in toluene) was supplied from Acros Organics used as received. Modified methylaluminoxane (MMAO; 7wt% in heptane) was purchased from Akzo Nobel. All other chemicals are commercially available and were used as supplied unless otherwise stated.

3.2 Ligand Synthesis

The phenoxy-imine ligand was developed by ligand oriented design concept. Two ligands combined with transition metal show high performance catalyst for olefin polymerization. [10-24] The phenoxy-imine ligand was synthesized in the similar route according to the published paper [20] depending on the raw material of phenol or salicylaldehyde derivatives.

3.2.1 Synthesis of N-(3-tert-butylsalicylidene)cyclooctylamine (L1)

2-tert-butyl phenol (10 g, 66.57 mmol) was dissolved in THF (40 ml) at 0^oC and 3.0 M EtMgBr in diethyl ether (66.57 mmol) was slowly added in this solution at 0^oC with continuously stirring for 2 h. After removal of the solvent, paraformaldehyde (166.43 mmol) and triethylamine (99.86 mmol) in toluene (50ml) were added and stirred continuously to obtain the yellow solution. The mixture is refluxed for 2 h at 95^oC and cool down to room temperature. Hydrochloric acid (1N, 250 ml) was added to the mixture. The resulting solution was separated by funnel flask and kept the toluene filtrate as organic phase. While, the water filtrate was extracted with diethyl ether (200x3ml), and then collected the toluene and diethyl ether filtrate together. After removal of the residue water with $MgSO_4$, the combined organic phase solution was evaporated under vacuum to obtain yellow viscous liquid and then purified by distillation under reduced pressure to obtain the product of 3-tert-butylsalicylidehyde as a slightly yellow clear liquid in 65% yield (12.44 g). Cyclooctylamine (1.38 g, 10.89 mmol) was added to the solution of 3-tert-butylsalicylidehyde (1.94 g, 10.89 mmol) in ethanol (20 ml) and stirred continuously for 3 h at room temperature. After removal of the solvent, the resultant was concentrated in vacuo to obtain the yellow liquid of N-(3-tert-butylsalicylidene)cyclooctylamine in 97.76% yield (3.06).

^{1}H NMR data (500.13 MHz, $CDCl_3$, δ): 14.22(brs, 1H, OH), 8.32 (s, 1H, NCH), 7.31-7.24(d, 4JHH = 2.36, 2H, ArH), 7.12-7.07 (dd, 4JHH = 2.36, 2H, ArH), 6.80-6.77 (m, 1H, ArH), 3.40(m, 1H, cyclooctyl-H), 1.60-1.82(m, 14H, cyclooctyl-CH_2), 1.44(s, 9H, t-Bu)

3.2.2 Synthesis of N-(3,5-dibromosalicylidene)-2′,6′-difluoroaniline (L2)

3,5-dibromosalicylaldehyde (2.00 g, 7.14 mmol) in ethanol (20 ml) was added to 2,6-difluoroaniline (0.92 g, 7.14 mmol) and formic acid (2-3 drops) at room temperature. The mixture was stirred continuously for 3 h. The resultant was formed in orange solid and then filtered and concentrated in vacuo to obtain *N*-(3,5-dibromosalicylidene)-2′,6′-difluoroaniline in 98% yield (2.74 g).

^{1}H NMR data (500.13 MHz, $CDCl_3$, 298 K): δ 13.91 (s, 1H, OH), 8.34 (s, 1H, NCH), 7.63 (d, 4JHH = 2.4, 1H, ArH), 7.48 (d, 4JHH = 2.4, 1H, ArH), 7.24-7.16 (m, 1H, ArH), 7.05-6.98 (m, 2H, ArH)

3.3 Phenoxy-imine complex synthesis

To take the cycloalkylated phenoxy-imine ligand as L1 and fluorinated phenoxy-imine ligand as L2 reacting with early transition of Ti which is cheap and easily available in commercial. The synthesis route of phenoxy-imine (FI complexes) is similar to the published paper of FI catalyst. [23]

3.3.1 Synthesis of bis[*N*-(3-*tert*-butylsalicylidene)cyclooctylamine]titanium dichloride(1)

N-(3-*tert*-butylsalicylidene)cyclooctylamine (3.06 g, 10.64 mmol) was dissolved in tetrahydrofuran (THF). The resulting solution was cooled down to 0°C. A 10.64 mmol solution of *n*-BuLi was added dropwise in the solution at 0°C. The mixture is stirred for 1 h at room temperature. Then, the solution of $TiCl_4$ (5.32 mmol) or $TiCl_4.2THF$ (5.32 mmol) in THF 20 ml was added dropwise to the resulting mixture at temperature 0°C. The mixture was stirred continuously overnight at room temperature, and then removed the solvent under vacuum to afford crude solid. The crude solid was dissolved in dichloromethane and LiCl was precipitated out of liquid. The resulting mixture was filtered to remove LiCl and the organic resultant filtrate was evaporated in vacuo to yield red brown solid. The solid was recrystallized with toluene/hexane mixture to give the product of bis[*N*-(3-*tert*-butylsalicylidene)cyclooctylamine]titanium dichloride in 78% yield (2.87 g).

^{1}H NMR data (500.13 MHz, $CDCl_3$, δ): 8.14 (s, 2H, NCH), 7.62-7.57(dd, 4JHH = 2.4, 2H, ArH), 7.28-7.21 (d, 4JHH = 2.4, 2H, ArH), 6.96-6.93 (m, 2H, ArH), 4.05(m, 2H, cyclooctyl-CH), 1.63(m, 18H, t-Bu), 1.43-1.17(m, 28H, cyclooctyl-CH_2)

Elemental analysis of $C_{38}H_{56}Cl_2N_2O_2Ti$: calc. C=65.99 %, N=4.05%, H=8.16%. Found C=65.70%, N=3.94%, H=8.59%

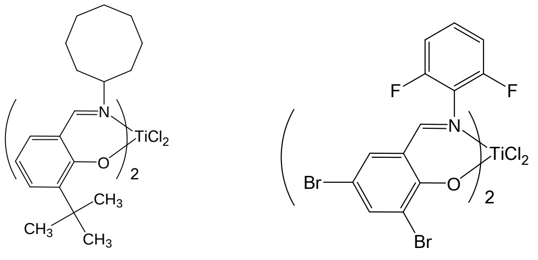
3.3.2 Synthesis of bis[*N*-(3,5-dibromosalicylidene)-2′,6′-difluroanilinato]titanium(IV) dichloride (2)

The *N*-(3,5-dibromosalicylidene)-2′,6′-difluoroaniline ligand (3.00 g, 7.67 mmol) was dissolved in THF (40 mL) and then *n*-butyl lithium (1.6 M solution in hexanes, 4.79 mL, 7.67 mmol) was dropwise added into the solution at 0°C. The solution was stirred at room temperature for 1 h. Then, a solution of $TiCl_4$ (1.0 M solution in DCM, 3.84 mL, 3.84 mmol) was added dropwise to the resulting solution at 0°C. The reaction mixture was stirred at room temperature for 24 h. After removal of the solvent, the product was extracted with DCM. LiCl was isolated by filtration, followed by removal of the filtrate to obtain a dark red solid. The solid was recrystallized from a mixture of toluene and hexane (4:1) at -20 °C to give complex 2 as orange crystals in 48% yield (1.67 g).

^{1}H NMR data (500.13 MHz, $CDCl_3$, δ): 8.20 (s, 2H, NCH), 7.79 (d, 4JHH = 2.5, 2H, ArH), 7.48 (d, 4JHH = 2.5, 2H, ArH), 7.28-7.00 (m, 4H, ArH), 6.56-6.47 (m, 2H, ArH)

Elemental analysis for $C_{26}H_{12}Br_4Cl_2F_4N_2O_2Ti$: calc. C=34.75%; H=1.35%; N=3.12%. Found C= 34.84%; H=1.40%; N= 2.84%.

The structure of synthesis phenoxy-imine titanium complexes is shown as follows.

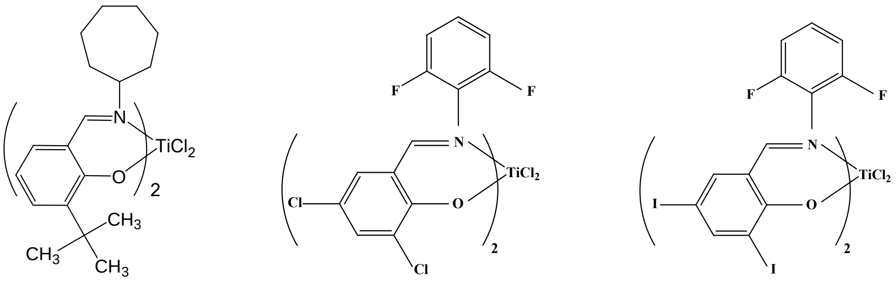


(1) (2)

Scheme 3.1 Structure of synthesized phenoxy-imine titanium complexes

3.3.3 Reference phenoxy-imine complexes

The reference complexes of bis[*N*-(3-*tert*-butylsalicylidene)cycloheptylamine]titanium dichloride (ref.1), bis[*N*-(3,5-dichlorosalicylidene)-2′,6′-difluroanilinato]titanium(IV) dichloride (ref.2) and Bis[*N*-(3,5-diiodosalicylidene)-2′,6′-difluroanilinato]titanium(IV) dichloride (ref.3) was donated by PTT public company for comparison.



(Ref. 1) (Ref.2) (Ref.3)

Scheme 3.2 Structure of reference phenoxy-imine titanium complex

3.4 Preparation of supports

The magnesium dichloride support was used to the development on Ziegler-Natta catalyst [1-2] to control morphology and increase activity, including metallocene [32-43] and FI catalyst as well. [17, 25-29] Then, silica was used widely as a support in the single-site catalyst preparation by removing OH-group on silica surface before use. [31-32] Therefore, it is interesting to investigate the effect of various supports on catalyst behaviors and polymer properties.

3.4.1 $MgCl_2$/2-ethyl-1-hexanol adduct preparation

2-ethyl-1-hexanol (117.2 ml, 900 mmol) was slowly added into anhydrous $MgCl_2$ (28.56 g, 300 mmol) in *n*-decane (145.5ml). The mixture was stirred and refluxed at 140 ^{o}C for 4 h and cooled down to room temperature. The solution of $MgCl_2$/2-ethyl-1-hexanol adduct had a concentration of 1.00 M at a molar ratio of $MgCl_2$/2-ethyl-1-hexanol = 1/3

3.4.2 SiO_2 support preparation

SiO_2 Grace Davison sylopol 2229 was dried at 400^{o}C under vacuum for 6 h and cooled down to room temperature and stored in bottle under nitrogen atmosphere before use.

3.5 Ethylene Polymerization

3.5.1 Homogeneous ethylene polymerization

The polymerization was performed in a glass reactor size of 0.5-2 L equipped with an agitator. The reactor was evacuated and purged with N_2 several times at 120 ^{o}C for removing of oxygen and moisture in this system. Then, the reactor was cooled down to room temperature. The toluene 250-750 ml was added into the reactor, thermostated to a desired polymerization temperature and saturated with ethylene gas. Then, various desired co-catalyst (MAO, TEA, TIBA, TMA, T*n*HAl, T*n*OAl) and desired catalyst complexes were added respectively with stirring at 450 rpm under ethylene pressure at 1 bar. The polymerization temperature was kept constant during the specified reaction time. After finished the polymerization, the residue ethylene gas was released out of reactor and the polymer slurry was quenched with acidic ethanol. The polymer was filtrated, washed with ethanol and dried in vacuum oven at 45-75^{o}C overnight.

3.5.2 In-situ heterogeneous ethylene polymerization

Ethylene polymerization was carried out under atmospheric pressure in toluene in a 500-mL glass reactor or 2 L stainless steel reactor equipped with a mechanical stirrer. The reactor was removed oxygen and moisture by evacuating and purging with N_2 several times at 120^{o}C. Toluene (250-750 mL) was introduced into the nitrogen-purged glass or stainless steel reactor, stirred at 450 rpm and saturated with ethylene gas. The desired $MgCl_2$/2-ethyl-1-hexanol adducts or SiO_2 support and co-catalyst (TEA, TMA, MAO, MMAO, TIBA, T*n*HAl, T*n*OAl) was added respectively into the reactor and treated for 20s, followed by specified catalyst complexes. After a prescribed time, the ethylene gas feed was stopped and ethanol/HCl was added to terminate the polymerization. The polymer was filtered, washed with ethanol, and dried in vacuo at 45-75°C overnight.

3.6 Characterization of support, catalyst complex and polymer

Nuclear Magnetic Resonance (NMR) spectroscopy of Bruker model Advance 500 MHz was used to investigate the structure of ligand, catalyst complexes and comonomer incorporation. The elemental analysis of phenoxy-imine ligand and catalyst complex was determined by LECO TrueSpec® micro-elemental analyzer. The melting temperature (T_m) was determined by differential scanning calorimeter model DSC 204 F1 Phoenix® from Netzsch at heating rate of 10°C/min and used the reheating results in the second time for eliminating thermal and mechanical history of polymer. Molecular weights (M_w, M_n) and polydispersities (PDI) of polymers were measured at 160°C with gel permeation chromatography of Polymer Laboratories model PL-GPC-220. The polystyrene was used as a standard reference and 1,2,4-trichlorobenzene at flow rate of 1 ml/min was used as a mobile phase. Polyethylene was dissolved in 1,2,4-trichlorobenzene with using sample preparation machine at 160°C about 2-3 hr. Morphology of PE powder was determined by Apple mini ipad and scanning electron microscope (SEM) from FEI Company model Inspect S50.

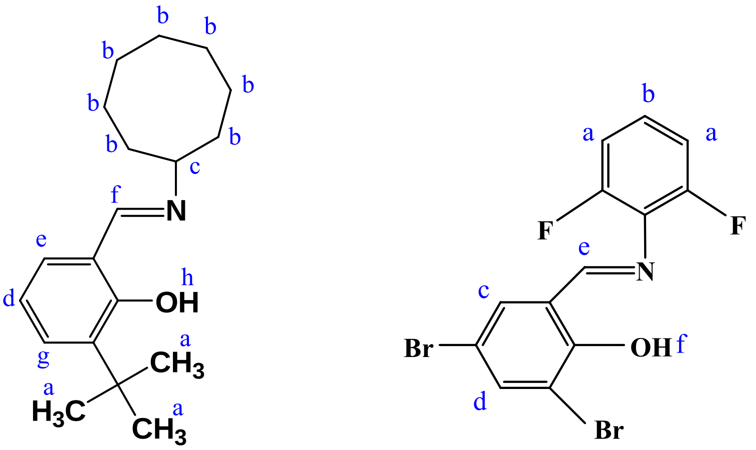
CHAPTER IV

RESULT & DISCUSSION

4.1. Phenoxy-imine titanium complexes characterization

4.1.1 Characterization of haloginated and cycloalkylated phenoxy-imine ligand.

To characterize two type of synthesized phenoxy-imine ligand which was developed by ligand oriented design concept[5-24] as seen in Scheme 4.1, one is haloginated phenoxy-imine ligand as *N*-(3-*tert*-butylsalicylidene)cyclooctylamine (L1) and another one is cycloalkylated phenoxy-imine ligand as *N*-(3,5-dibromosalicylidene)-2′,6′-difluoroaniline (L2) with using the nuclear magnetic resonance spectroscopy. The ^{1}H NMR results of two ligands are shown in Table 4.1 and 4.2 and Figure 4.1 and 4.2, respectively.



L1 L2

Scheme 4.1 The chemical structure of *N*-(3-*tert*-butylsalicylidene)cyclooctylamine (L1) and *N*-(3,5-dibromosalicylidene)-2′,6′-difluoroaniline (L2).

Table 4.1 ^{1}H NMR data of *N*-(3-*tert*-butylsalicylidene)cyclooctylamine (L1).

Chemical shift (δ, ppm)	multiplicity	Position of proton	Number of protons	Coupling constant (J, Hz)
1.44	singlet	a (*t*-Bu)	9	-
1.60-1.82	multiplet	b (cyclooctyl-CH_2)	14	-
3.40	multiplet	c (cyclooctyl-H)	1	-
6.80-6.77	triplet	d (ArH)	1	-
7.12-7.07	doublet	g(ArH)	1	2.36
7.31-7.24	double doublet	e(ArH)	1	2.36
8.32	singlet	f (NCH)	1	-
14.22	broaden singlet	h (OH)	1	-

Table 4.2 ^{1}H NMR data of *N*-(3,5-dibromosalicylidene)-2′,6′-difluoroaniline (L2)

Chemical shift (δ, ppm)	multiplicity	Position of proton	Number of protons	Coupling constant (J, Hz)
6.98-7.05	multiplet	a (ArH)	2	-
7.16-7.24	multiplet	b (ArH)	1	-
7.48	doublet	c (ArH)	1	2.4
7.63	doublet	d (ArH)	1	2.4
8.84	singlet	e (NCH)	1	-
13.91	singlet	f (OH)	1	-

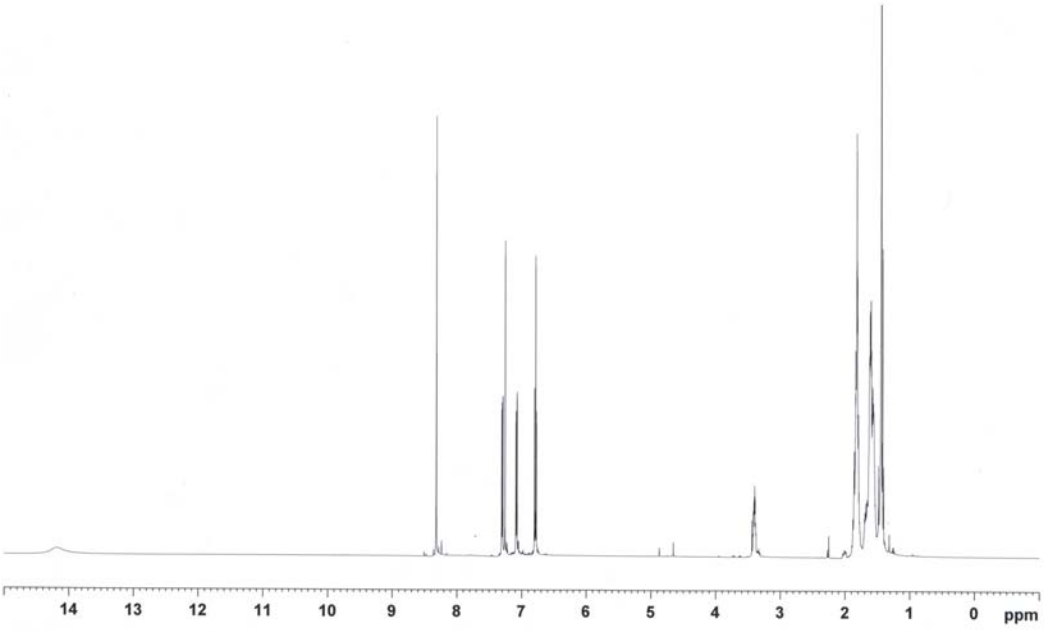


Figure 4.1 ^{1}H NMR spectrum of *N*-(3-*tert*-butylsalicylidene)cyclooctylamine (L1)

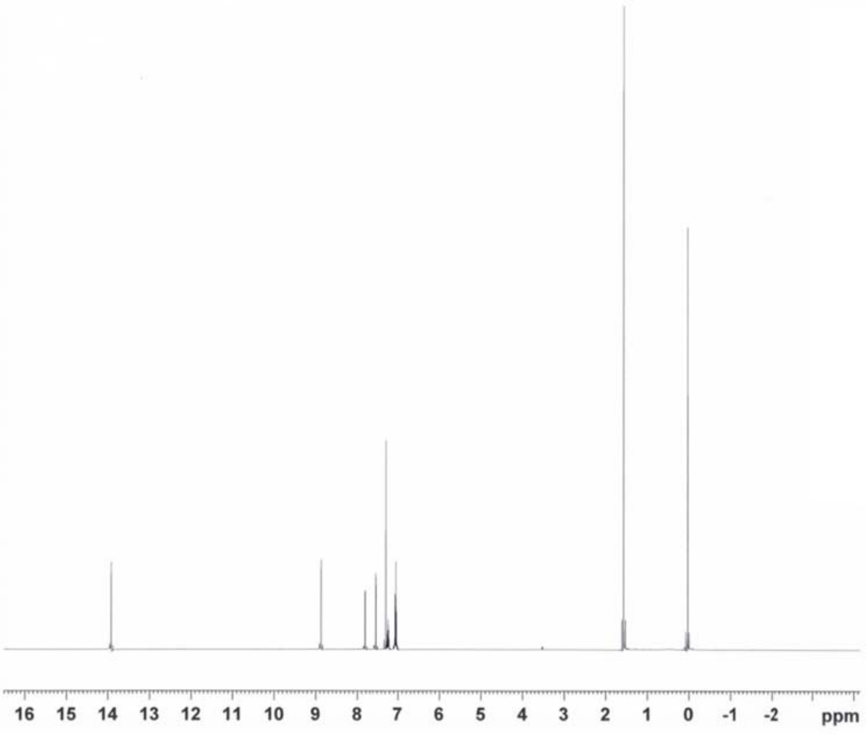
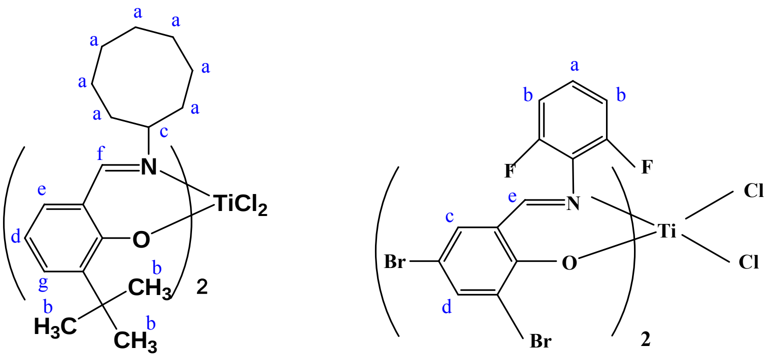


Figure 4.2 ^{1}H NMR spectrum of *N*-(3,5-dibromosalicylidene)-2′,6′-difluoroaniline (L2)

4.1.2 Characterization of two phenoxy-imine titanium complexes

Post metallocene catalyst complexes were prepared from two types of ligand, one is cycloalkylated phenoxy-imine ligand and another one is halogenated phenoxy-imine ligand. Post metallocene catalysts are composed of bidentated ligand with group 4 transition metal. In my research, the catalyst complex 1 of bis[*N*-(3-*tert*-butylsalicylidene)cyclooctylamine]titanium dichloride(1) having a formula in $C_{38}H_{56}Cl_2N_2O_2Ti$ as a cycloalkylated phenoxy-imine titanium catalyst and complex 2 of bis[*N*-(3,5-dibromosalicylidene)-2′,6′-difluroanilinato]titanium(IV) dichloride (2) having a formula of $C_{26}H_{12}Br_4Cl_2F_4N_2O_2Ti$ as a halogenated phenoxy-imine titanium catalyst were synthesized according to the procedure of previous chapter III as shown the structure complexes in Scheme 4.2. The complex 1 and 2 were confirmed the chemical structure by NMR spectroscopy and shown the results in Table 4.3 and 4.4 and seen spectrum in Figure 4.3 and 4.4, respectively.



Complex 1 **Complex 2**

Scheme 4.2 The chemical structure of bis[*N*-(3,5-dibromosalicylidene)-2′,6′-difluroanilinato]titanium(IV) dichloride (2).

Table 4.3 ^{1}H NMR data of bis[*N*-(3-*tert*-butylsalicylidene)cyclooctylamine]titanium dichloride (1)

Chemical shift (δ, ppm)	multiplicity	Position of proton	Number of protons	Coupling constant (J, Hz)
1.17-1.43	multiplet	a (cyclooctyl-CH_2)	28	-
1.63	singlet	b (*t*-Bu)	18	-
4.05	multiplet	c (cyclooctyl-CH)	2	-
6.93-6.96	triplet	d (ArH)	2	-
7.21-7.28	doublet	g (ArH)	2	2.4
7.57-7.62	double doublet	e(ArH)	2	2.4
8.14	singlet	f (NCH)	2	-

Table 4.4 ^{1}H NMR data of bis[*N*-(3,5-dibromosalicylidene)-2′,6′-difluroanilinato]titanium(IV) dichloride (2)

Chemical shift (δ, ppm)	multiplicity	Position of proton	Number of protons	Coupling constant (J, Hz)
6.47-6.56	multiplet	a (ArH)	2	-
7.00-7.28	multiplet	b (ArH)	4	-
7.51	doublet	c (ArH)	2	2.5
7.82	doublet	d (ArH)	2	2.5
8.20	singlet	e (NCH)	2	-

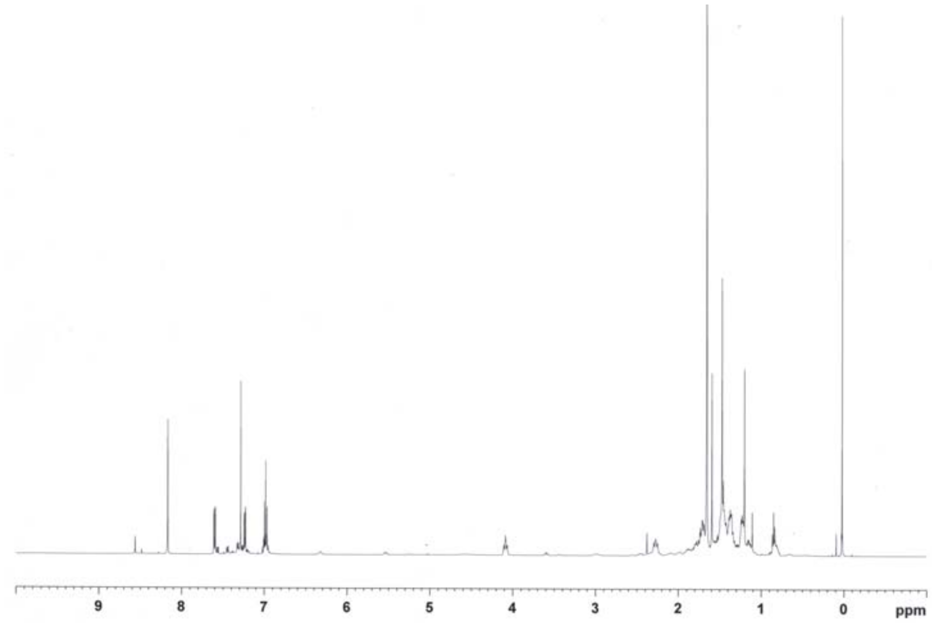


Figure 4.3 ^{1}H NMR spectrum of bis[*N*-(3-*tert*-butylsalicylidene)cyclooctylamine]titanium dichloride (1)

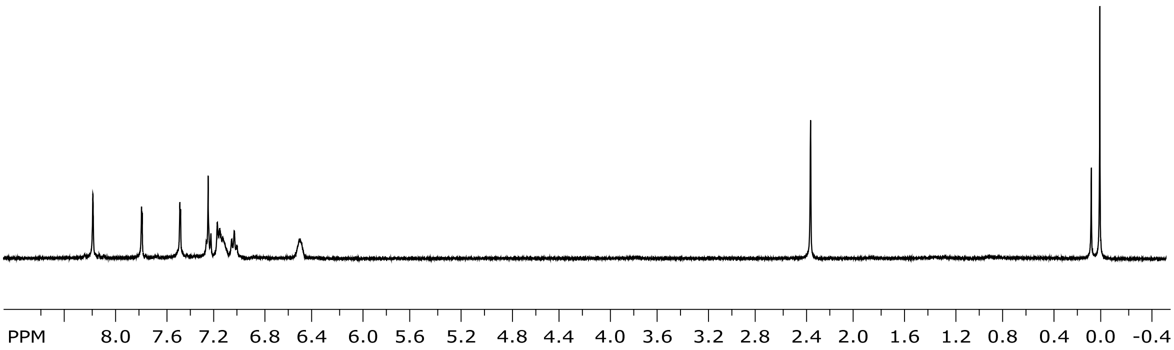


Figure 4.4 ^{1}H NMR spectrum of bis[*N*-(3,5-dibromosalicylidene)-2′,6′-difluroanilinato]titanium(IV) dichloride (2)

Additionally, both complexes were investigated the element composition with using elemental analyzer. The result are shown in Table 5

Table 4.5 Element composition of complex 1 and 2

Complex	Formula	Calculation			Elemental Analysis		
		%C	%H	%N	%C	%H	%N
1	$C_{38}H_{56}Cl_2N_2O_2Ti$	65.99	4.05	8.16	65.70	3.94	8.59
2	$C_{26}H_{12}Br_4Cl_2F_4N_2O_2Ti$	34.75	1.35	3.12	34.84	1.40	2.84

From the above results, it is confirmed that both (phenoxy-imine)titanium complexes are produced correctly as considered from the amount of each element in catalyst composition of complex 1 and 2 measured with elemental analysis machine are closely to that calculated from formula of both complexes.

4.2. The effect of different unsupported post metallocenes on catalytic activity in homogeneous polymerization

Phenoxy-imine titanium complexes were dissolved in toluene under inert atmosphere (Nitrogen or Argon) with concentration 0.001 M [1 μmol = 1 ml]. Then, to investigate the influences of various complexes, catalyst concentrations, co-catalyst/catalysts (Al/Ti) ratio, polymerization time and ethylene pressure on the catalyst behavior in the ethylene polymerization as follow.

4.2.1 Ethylene polymerization using phenoxy-imine complex 1 compared with ref.1 in the presence of MAO

4.2.1.1 The effect of various temperatures in ethylene polymerization on the activities of complex 1 and ref.1

Complex 1 and ref.1 activated MAO was carried out ethylene polymerization in toluene 250 ml under ambient pressure at different temperatures (10, 20, 30, 40, and 50 °C) for 20 minutes with using reactor size 500 ml equipped with magnetic stirrer.

It is interesting to study the catalytic behavior of complex 1 and ref 1, whose substituents on nitrogen atom of phenoxy-imine titanium complexes were different.

Both complexes activated with MAO were employed for the ethylene polymerization in slurry process under ambient pressure with various temperatures. Complex 1 having cyclooctyl on the nitrogen atom of phenoxy-imine ligand exhibited higher catalytic activity than complex ref .1 containing cycloheptyl-imine over the temperature between 20-50°C. This result is similar to phenoxy-imine zirconium complex containing different substituents on *N*-phenoxy-imine ligand affecting on the catalytic activity of ethylene polymerization [52-53, 79]. Additionally, the steric bulky groups on the *N*-phenoxy-imine complexes have an influence on the catalytic activity and polymer properties [80]. However, polyethylene obtained from complex 1 showed molecular weight lower than that obtained from complex ref.1 in the presence of MAO over this temperature range. This result is opposite to the previous published research, which demonstrated that the sterically encumbered substituent (cyclohexyl) on N-phenoxyimine complex displayed molecular weight higher than the small bulky substituents (cyclopentyl, cyclobutyl) on N-phenoxyimine complexes [78, 80]. It is presumably that the steric bulky substituent on N-imine ligand of FI complex should be an appropriated size for increasing the molecular weight of polymer. [64] The results of ref. 1 catalyst activated with MAO exhibited UHMWPE and narrow polydispersity as similar to the results of ref.1 supported on polystyrene latex with dried MAO in ethylene polymerization. [63]

From Table 4.6, the catalytic activity of complex 1 enhanced with increasing the polymerization temperature from 20 to 30°C. While the polymerization temperature was increased over 30°C, the catalytic activity decreased moderately. It means that the increase of temperature results in deactivation of the catalyst complex 1. This result corresponds to the catalytic activity of non-salicyladimine or phenoxyketimine titanium and zirconium complexes, which moderately decrease with increasing the polymerization temperature due to catalyst decay. [13, 32, 69] Additionally, the deactivation process due to the poor stability of the cationic center of FI-Ti complexes activated with MAO for ethylene polymerization was reported by Sun et al. as well. [70] The trend of polymerization temperatures and catalytic activity of both complexes (ref.1, 1) is similar excepting in case of ref.1 when the temperature over 40°C apparently resulted in the decrease of activity. The molecular weight of PE obtained from both complexes decreases with increasing the polymerization temperature. This result corresponds to the fluorinated FI zirconium-based catalyst activated with MAO as co-catalyst employed for ethylene polymerization. [77] The increase of polymerization temperature affects on the decrease of polymer molecular weight because of β-hydride chain transfer. [70, 77] The complex 1 can synthesize polyethylene with the highest activity (11.82 kg PE/mmolcat.h) at the temperature of 30°C, while the complex ref.1 can produce polyethylene with the highest activity (9.10 kg PE/mmolcat.h) at 40°C. Polyethylene obtained from these complexes have narrow polydispersity [1.52-1.75] and have the melting temperature in the range of 126.5-128°C. Complex 1 can produce the high molecular weight polyethylene (HMWPE) under ambient pressure with various temperatures in the presence of MAO. However, complex ref.1 activated with MAO can synthesize the ultra-high molecular weight polyethylene (UHMWPE, M_W more than 2,000,000) under atmospheric pressure at the temperature about 20 - 30°C and produce the high molecular weight polyethylene (HMWPE) over 30°C.

Table 4.6 Results of ethylene polymerization with complexes **1**/MAO at various temperatures compared with ref. 1/MAO[a]

Entry	Complex	Temp (°C)	Yield (g)	Activity kg PE/mmol cat·h	M_w[b] ($\times10^{-6}$)	M_n[b] ($\times10^{-6}$)	M_w/M_n[b]	T_m[c] (°C)
1	**1**	20	3.43	10.03	1.97	1.14	1.72	128
2	**1**	30	3.94	11.82	1.80	1.05	1.71	127.4
3	**1**	40	3.23	9.70	1.69	0.97	1.73	127.6
4	**1**	50	3.01	9.03	1.34	0.81	1.64	127.7
5	**1**	60	2.60	7.80	1.11	0.70	1.57	127.5
6	**ref.1**	20	2.82	8.47	2.33	1.38	1.68	127.7
7	**ref.1**	30	2.85	8.54	2.18	1.36	1.59	127.5
8	**ref.1**	40	3.03	9.10	1.95	1.27	1.52	127.6
9	**ref.1**	50	2.96	8.87	1.65	0.94	1.75	126.5
10	**ref.1**	60	2.69	8.07	1.23	0.75	1.63	127.2

[a] Conditions: complex (1 μmol), cocatalyst MAO (1.25 mmol), 1 atm, toluene 250 mL. [b] Determined by GPC using polystyrene calibration. [c] Melting temperature of synthesized polyethylene determined by DSC.

4.2.1.2 The effect of catalyst concentration on the catalytic activity of complex 1

Complex 1 is highly efficient for HMWPE production with the highest activity at temperature of 30°C under ambient pressure. Therefore, we are interesting to investigate the effect of catalyst concentration, co-catalyst/catalyst (Al/Ti) ratio, polymerization time and ethylene pressure on the catalytic behavior of complex 1 in the ethylene polymerization. Table 4.7 illustrates the influence of catalyst concentration on catalytic activity and polymer properties in term of molecular weights, polydispersities and melting temperatures. When the catalyst concentration of complex 1 increase, the catalytic activity decreases moderately, including the reduction of PE molecular weight as well. The catalyst concentration of 1 μmol yields the highest activity at 11.43 kg PE/mmolcat.h for ethylene polymerization due to easily reacting monomer onto the catalyst active site. While the catalyst concentration of 6 μmol exhibits the lowest activity at 4.16 kg PE/mmolcat.h for ethylene polymerization because the bimolecular process of catalyst occurs as inactive site for ethylene polymerization. [70] Polyethylenes produced from complex 1 have narrow polydispersities (< 2) and melting temperature of 126.8-127.5°C.

Table 4.7 Results of ethylene polymerization with various complex 1 concentrations[a]

Run	**Catalyst (μmol)**	**Yield (g)**	**Activity kg PE/mmolcat.h**	**M_w[b] ($x10^{-6}$)**	**M_n[b] ($x10^{-6}$)**	**PDI[b]**	**T_m[c] (°C)**
1	1	3.81	11.43	1.84	1.06	1.72	128.1
2	2	6.05	9.08	1.77	1.06	1.67	127.5
3	3	7.79	7.79	1.65	1.13	1.45	127.2
4	4	8.14	6.10	1.58	0.91	1.72	127.3
5	5	8.91	5.35	1.47	0.82	1.78	127.1
6	6	8.32	4.16	1.32	0.72	1.83	126.8

[a]Condition : Toluene 250 ml, ethylene pressure 1 bar, polymerization time 20 min., temperature 30°C, MAO 1.25 mmol, [b] Determined by GPC using polystyrene calibration. [c]Melting temperatures of obtained polyethylene measured by DSC.

4.2.1.3 The effect of various MAO cocatalysts on the catalytic activity of complex 1 in ethylene polymerization

From the result in Table 4.7, the catalyst concentration is 1 μmol to give the highest activity. For this reason, in the next experiment, the concentration of catalyst was fixed at 1 μmol and the amount of MAO as co-catalyst was varied under atmospheric ethylene pressure in 250 ml toluene. Table 4.8 shows that the catalytic activity of complex 1 enhances with increasing the MAO/catalyst ratios upto 1650, and then the catalytic activity decreases when MAO/catalyst ratio is over 1650 due to catalyst deactivation. [54-58] At the ratios of MAO/catalyst between 1450 and 1650, the catalytic activity obtained from complex 1 reaches the maximum value because MAO completely changes the catalyst into active forms and eliminates impurities in this system [70]. Additionally, MAO also has a function as a chain transfer agent. It has an effect on the molecular weight of the synthesized PE, which decreases with increasing the MAO/catalyst ([Al]/[Ti]) ratios over 1650. Polyethylene produced from complex 1 have narrow polydispersities and melting temperatures is in the range of 127.1-127.8°C.

Table 4.8 Results of ethylene polymerization with complex 1 activated with various MAO[a]

Run	MAO (mmol)	[Al]/[Ti]. ratio	Yield (g)	Activity kg PE/mmolcat.h	M_w[b] ($x10^{-6}$)	M_n[b] ($x10^{-6}$)	PDI[b]	T_m[c] (°C)
1	1.25	1250	3.00	9.00	1.80	1.00	1.80	127.6
2	1.45	1450	3.22	9.66	1.82	1.18	1.53	127.8
3	1.65	1650	3.21	9.65	1.93	1.20	1.60	127.8
4	1.85	1850	3.18	9.56	1.90	1.19	1.59	127.7
5	2.05	2050	3.17	9.52	1.82	1.18	1.60	127.1

[a]Condition : Toluene 250 ml, ethylene pressure 1 bar, polymerization time 20 min., temperature 30°C, catalyst 1μmol, [b] Determined by GPC using polystyrene calibration, [c] Melting temperature of obtained polyethylene measured by DSC.

4.2.1.4 The effect of polymerization time on the catalytic activity of complex 1

As seen in Table 4.9, the ethylene polymerization is performed at the catalyst concentration of 1 μmol, MAO/catalyst ratios 1450 and temperature of 30°C with various polymerization times to study the catalytic activity and polyethylene properties. The polymerization times of 10 min exhibits the highest catalytic activity at 11.03 kg PE/mmolcat.h because of better monomer diffusion. Then, when the polymerization time increases, the catalytic activity of complex 1 essentially decreases. This is due to monomers diffuse slowly and more difficult to react with active sites covered with polymer. Additionally, the molecular weight of polyethylene obtained from complex 1 can be increased with increasing the reaction time as seen in Figure 4.5. It is implied that the catalyst complex 1 can synthesize polyethylene in the living polymerization. Surprisingly, the cycloalkyl group on the *N*-phenoxy-imine ligand in complex 1 exhibits the same living fashion as the 2,6 difluorinated aromatic group on the *N*- phenoxy-imine ligand in the complex according to the published articles [82, 22]. Polyethylenes produced from complex 1 have narrow polydispersity value less than 2 and high molecular weight in the range of 1,650,000-2,010,000 g/mole and melting temperature (T_m) in the range of 127.4-128°C. As shown in Figure 4.5, UHMWPE having molecular weight higher than 2,000,000 g/mol can be produced at polymerization time over 60 minutes.

Table 4.9 Results of ethylene polymerization with complexes 1 in various polymerization times[a]

Run	**Time (min.)**	**Yield (g)**	**Activity kg PE/mmol cat.h**	**M_w[b] ($x10^{-6}$)**	**M_n[b] ($x10^{-6}$)**	**PDI[b]**	**T_m[c] (°C)**
1	10	1.83	11.03	1.65	0.97	1.70	128
2	20	3.19	9.59	1.82	1.12	1.62	128
3	30	4.13	8.27	1.91	1.14	1.67	128.3
4	40	4.72	7.09	1.93	1.19	1.61	127.8
5	50	5.60	6.72	1.95	1.25	1.55	127.4
6	60	6.08	6.08	2.01	1.30	1.53	127.6

[a]Condition : Toluene 250 ml, ethylene pressure 1 bar, catalyst 1 μmol, polymerization temperature 30°C, MAO 1.45 mmol, [b] Determined by GPC using polystyrene calibration, [c] Melting temperature of obtained polyethylene measured by DSC.

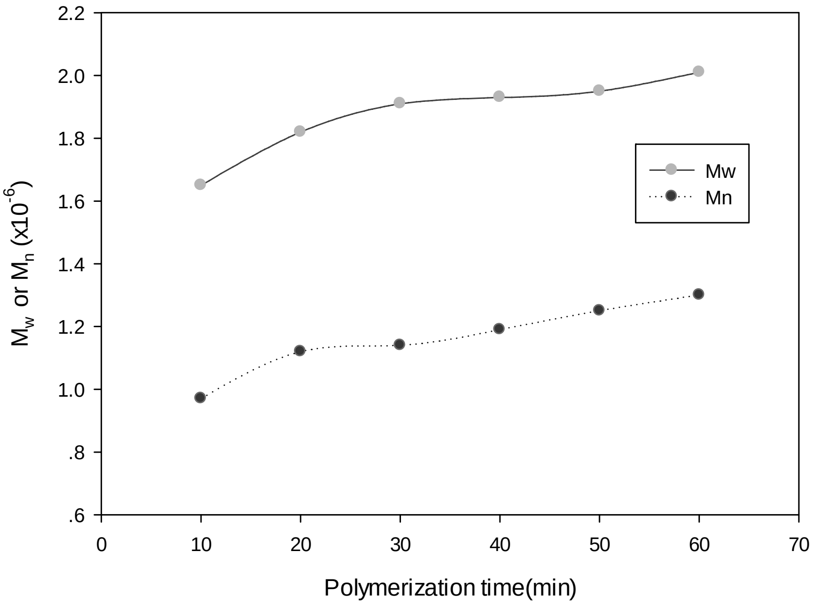


Figure 4.5 Relation of polymerization time and M_w or M_n

4.2.1.5 The effect of various ethylene pressures on the catalytic activity of complex 1

The ethylene polymerization was carried out under various ethylene pressures in toluene of 750 ml, catalyst concentration of 3 μmol, MAO as co-catalyst of 4.35 mmol and resident times 20 minutes. As seen in Figure 4.6, the catalytic activity of FI-titanium complex 1 enhances moderately with increasing the ethylene pressure because of the increase of monomer solubility in toluene. These results are similar to those produced from three FI-Ti type catalysts, [70] two FI-Zr type catalysts, [76] and phenoxy-imine based Zr complexes [81] in case of the higher monomer pressure. Thus, higher catalytic activity is observed in ethylene polymerization due to high monomer concentration close to catalyst active sites. [76, 81] Polyethylenes synthesized from complex 1 activated with MAO have high molecular weight in the range of 1,940,000-2,060,000 g/mole, narrow polydispersity (1.61-1.68) and melting temperature in the range of 127.3-127.9°C.

Table 4.10 Result of ethylene polymerization of various ethylene pressure[a]

Run	**Ethylene (bar)**	**Yield (g)**	**Activity kg PE/mmolcat.h**	$\boldsymbol{M_w}$[b] **(x10^{-6})**	$\boldsymbol{M_n}$[b] **(x10^{-6})**	**PDI**[b]	$\mathbf{T_m}$[c] **(^{o}C)**
1	1	9.20	9.20	2.06	1.27	1.61	127.7
2	2	11.21	11.21	1.94	1.17	1.65	127.3
3	3	13.84	13.84	1.94	1.19	1.63	127.7
4	4	19.62	19.62	2.13	1.28	1.65	127.5
5	5	22.50	22.50	2.00	1.18	1.68	127.9

[a]Condition : Toluene 750 ml, polymerization time 20 min., temperature 40^{o}C, catalyst 3 μmol, , MAO 4.35 mmol, [b] Determined by GPC using polystyrene calibration, [c] Melting temperature of obtained polyethylene measured by DSC.

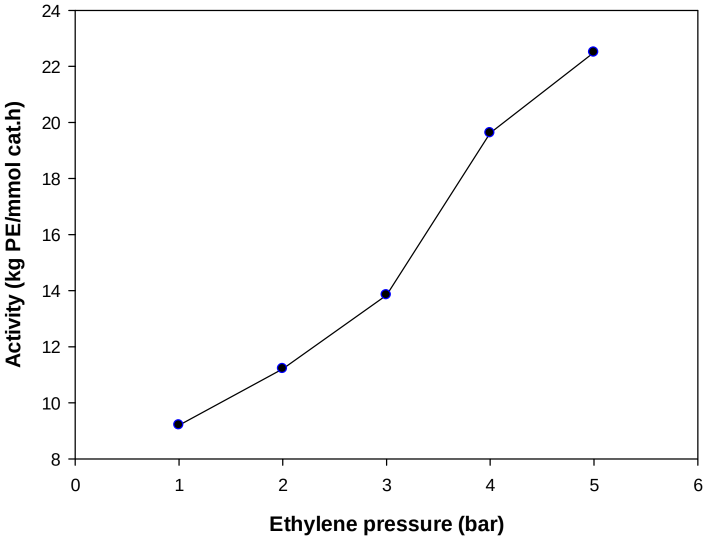


Figure 4.6 Relationship between ethylene pressure and catalytic activity obtained from complex 1

4.2.2 Ethylene polymerization using halogenated (phenoxy-imine) titanium [Ti-FI] complex 2 compared with complexes ref.2 and 3 in the presence of MAO

4.2.2.1 The effect of various temperatures in ethylene polymerization on the activity of complex 2

Complex 2, ref.2 and ref.3 as halogenated Ti-FI catalysts in presence of MAO was performed on ethylene polymerization in toluene 250 ml under atmospheric pressure at different temperatures (10, 20, 30, 40, and 50 °C) for 20 minutes by reactor size 500 ml equipped with a magnetic stirrer.

Table 4.11 Results of ethylene polymerization with halogenated complexes **2**/MAO at various temperatures compared with ref. 2-3/MAO[a]

Entry	Complex	Temp (°C)	Yield (g)	Activity kg PE/mmol cat·h	M_w[b] ($\times10^{-6}$)	M_n[b] ($\times10^{-6}$)	M_w/M_n[b]	T_m[c] (°C)
1	**2**	10	2.54	3.81	4.17	3.65	1.08	127.7
2	**2**	20	4.62	6.93	4.07	3.56	1.14	127.2
3	**2**	30	5.50	8.25	4.27	3.87	1.05	127.3
4	**2**	40	0.97	1.45	2.58	1.46	1.77	128.2
5	**2**	50	0.53	0.80	1.86	0.89	2.07	128.0
6	**ref.2**	10	2.31	3.46	3.98	3.52	1.13	127.9
7	**ref.2**	20	2.89	4.33	4.20	3.77	1.11	127.1
8	**ref.2**	30	2.55	3.82	4.11	3.71	1.10	127.6
9	**ref.2**	40	1.00	1.50	3.61	3.09	1.17	127.3
10	**ref.2**	50	0.39	0.58	1.75	0.74	2.34	128.3
11	**ref.3**	10	3.42	5.13	3.88	3.37	1.15	125.5
12	**ref.3**	20	4.74	7.11	4.21	3.89	1.08	125.8
13	**ref.3**	30	3.20	4.80	3.59	3.09	1.16	126.1
14	**ref.3**	40	2.07	3.10	3.47	2.71	1.27	125.7
15	**ref.3**	50	1.64	2.47	3.45	2.74	1.26	127.3

[a] Conditions: complex (2 μmol), cocatalyst MAO (1.25 mmol), 1 atm, toluene 250 mL. [b] Determined by GPC using polystyrene calibration. [c] Melting temperature of synthesized polyethylene determined by DSC.

As shown in Table 4.11, halogenated three complexes of complex 2, ref.2 and ref.3 are active catalysts for ethylene polymerization and produce ultra-high molecular weight polyethylene (UHMWPE) under the given conditions in living character. The results corresponding to the different fluorinated phenoxy-imine complexes activated with MAO reported by Weiser and Mulhaupt [72], and Jones et al. [73] exhibited highly active catalyst for producing UHMWPE in living fashion. The polyethylene obtained from these complexes exhibit the T_m values in the range of 125.5-128.3 °C. The constancy of the melting temperature with increasing the polymerization temperature was also reported by Weiser and coworkers. [83] Plots of the catalytic activities of above-mentioned three complexes versus the polymerization temperatures are illustrated in Figure 4.7. In the case of ref 2, the catalytic activity enhances from 3.46 kg PE/mmol cat·h at 10 °C to 4.33 kg PE/mmol cat·h at 20 °C.

Above 20 °C, the activity gradually decreases and at 50 °C, the lowest activity of 0.58 kg PE/mmol cat·h is observed. When the polymerization temperature increases, the catalytic activity also increases, causing the increase of the propagation rate of transferring the monomer to the active metal center. [77, 84] However, at high temperature, the chain transfer reactions are promoted and the solubility of ethylene in the solvent decreases, it is attributed to the decrease of the propagation reaction. [85] Additionally, the catalyst may be also deactivated at higher polymerization temperature resulting in the decrease of activity. The molecular weight of polyethylene formed with ref.2 increase with changing the temperature from 10 to 20 °C due to the increase of the propagation rate. While, the molecular weight is slightly decreased when increasing the temperature from 20 to 40 °C, suggesting that no significant effect of termination reaction operated in this temperature range. In addition, the molecular weight distributions of the resulting polymers obtained from 10 to 40 °C are relatively narrow which indicate the living nature of ref. 2. However, a significant decrease in molecular weight and the broadening of the molecular weight distribution were observed (Mw = 1.75 × 10^{-6}, M_w/M_n = 2.34) at 50 °C. These results suggest that the catalyst decomposition occurs at this temperature.

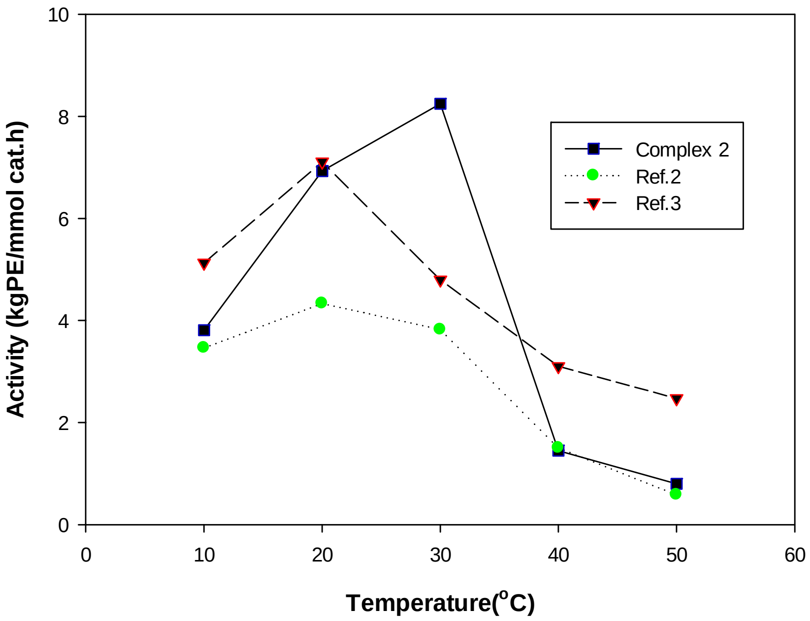


Figure 4.7 Relationship between the polymerization temperature and the polymerization activity using complexes 2, ref. 2 and ref. 3.

Changing of the *ortho* chlorine substituent in the phenoxy-oxygen (ref.2) to bromine (complex 2) results in the enhancement of the catalytic activity in ethylene polymerization from the temperatures 10 to 30 °C. The optimum polymerization temperature of this complex is observed at 30 °C with the highest activity of 8.25 kg PE/mmol cat·h. Comparing with ref.2, the enhancement of the catalytic activity using complex 2 may arise from an effective ion-pair separation between the cationic active species and an anionic cocatalyst by the *ortho* R substituent situated closely to the metal center. [48-51, 86] In addition, FI catalyst having the different steric bulky R^1 substitutent *ortho* to phenoxy-O in FI catalyst has an influence on catalytic activity. [59] At the temperatures above 30 °C, the catalytic activity decrease significantly and hence the decrease of molecular weight is observed. The observed molecular weight distribution is broadening at elevated temperatures (entries 4 and 5, Table 4.11). These results suggest that the chain transfer termination process [60] have a significant increase.

In the case of ref. 3 with the *ortho* iodine substituent, the highest catalytic activity of 7.11 kg PE/mmol cat·h is observed at temperature of 20 °C. Although the catalytic activity of ref.3 decreases at the temperature above 20 °C similar to that of ref.2, the molecular weights of obtained polyethylene are relatively unchanged and the molecular weight distributions are narrow ($M_w/M_n < 1.3$). These results suggest that the bulkier size of the substituent at the *ortho* position of the phenoxy rings leads to the increase of the steric congestion at the metal center, and hence decreasing in the catalytic activity. However, the chain transfer termination processes are diminished due to the steric protection at the active site from the *ortho* bulky size substituent.

As the complex 2 activated with MAO displays a high efficiency for producing UHMWPE with the highest activity at 30 °C compared with the ref. 2 and 3/MAO systems at the same condition, we, therefore, investigate the catalytic behavior of this catalyst in more details. The effects of the catalyst concentration, the cocatalyst/catalyst ratio, ethylene pressure and the polymerization time on catalyst performance in ethylene polymerization are investigated in order to find the optimum condition for producing UHMWPE.

4.2.2.2 The effect of catalyst concentration on the catalytic activity of complex 2

From the above Table 4.11, complex 2 with MAO can produce polyethylene with the highest activity (8.25 kg PE/mmol cat.h) at the temperature 30°C. Therefore, to study the effect of catalyst concentration on catalytic activity in this further experiment is fixed a polymerization condition at temperature 30°C. The brominated complex 2 can polymerize polyethylene under ethylene pressure 1 bar, polymerization time 20 min and MAO as co-catalyst 2.5 mmol in toluene 500 ml. The highest catalytic activity is observed at catalyst concentration 2 μmol because the catalyst reacts with sufficient MAO to change completely in active site form. When, the catalyst concentrations increase more than 2 μmol, the catalytic activity decrease moderately because of the bimolecular reaction of catalyst. The polyethylene obtained from complex 2 with various catalyst concentrations has molecular weight in the range of 3.5x10^6-4.1x10^6 and narrow polydispersity. It is shown that complex 2 can synthesize UHMWPE with independent on catalyst content in the temperature 30°C.

Table 4.12 Results of ethylene polymerization with complex **2**/MAO at various catalyst concentrations[a]

Entry	Complex (μmol)	[Al]/[Ti]	Yield (g)	Activity kg PE/mmol cat·h	M_w[b] ($\times10^{-6}$)	M_n[b] ($\times10^{-6}$)	M_w/M_n[b]	T_m[c] (°C)
1	**2** (1.0)	2500	3.43	10.31	4.01	3.64	1.10	127.1
2	**2** (2.0)	1250	7.85	11.77	3.95	3.53	1.11	126.8
3	**2** (3.0)	833	10.36	10.36	3.90	3.43	1.13	127.2
4	**2** (4.0)	625	13.24	9.93	3.72	3.20	1.16	127.3
5	**2** (5.0)	500	13.39	8.03	3.68	3.11	1.18	127.1
6	**2** (6.0)	417	13.75	6.87	3.57	2.87	1.24	127.1

[a] Conditions: cocatalyst MAO (2.50 mmol), 1 atm, toluene 500 mL, time 20 min, temperature 30°C. [b] Determined by GPC using polystyrene calibration. [c] Melting temperature of synthesized polyethylene determined by DSC.

MAO does not only act as a cocatalyst in homogeneous polymerization, but also can functioned as a potential chain transfer agent which is the drawback of the living polymerization system, including as the impurity scavenger in the system. [66]

In general, a large amount of MAO is used in the ethylene polymerization, but this can be affected on the catalytic activity. Therefore, in this study, the effect of the cocatalyst-catalyst concentration ratio on catalyst behavior and polymer properties was investigated. Table 4.12 illustrates the results of ethylene polymerization using complex **2** activated with MAO at different catalyst concentrations. The highest catalytic activity was observed when the concentrations of catalyst and cocatalyst were 2.0 μmol and 2.5 mmol, respectively ([Al]/[Ti] = 1250, entry 2, Table 4.12) due to catalyst formed completely in active site. Further enhancing the catalyst concentration resulted in decreasing the catalytic activity in ethylene polymerization and polyethylene molecular weight. On the other hand, the activity and the molecular weight of the resulting polymer increase (entries 3-6, Table 4.12) with increasing the Al/Ti concentration ratio upto [Al]/[Ti] = 1250. These results were also observed in the bis(pheneoxyimine)titanium catalyst containing pentafluoroaniline group by Rastogi and coworkers.[85] The enhancement in the polarity of the medium with increasing MAO concentration results in a better ion-pair separation, affording a higher polymerization rate. At the high Al/Ti concentration ratio (entry 1, Table 4.12), the decrease of catalytic activity may be attributed to the result of heterogenization of the system due to the high concentration of MAO. In this system, decreasing of the catalytic activity and molecular weight of obtained PE due to chain transfer to aluminum seem not to be an important reason. [87] This was supported by the observed narrow molecular weight distribution in the range of 1.10-1.24, indicating the living nature of this catalyst system.

4.2.2.3 The effect of various MAO cocatalysts in ethylene polymerization on the catalytic activity of complex 2

From the previous experiment, the polymerization condition to get the highest activity is catalyst concentration of 2 μmol and temperature at 30°C. For this reason, the further experiment to study the effect of MAO on catalytic activity of complex 2 is fixed at this condition. As shown in Table 4.13, the highest catalytic activity is observed at cocatalyst/catalyst ratio of 1825 due to the catalyst complex changing from inactive to active form completely. With increasing the cocatalyst/catalyst ratio from 1025 to 1825, the catalytic activity enhances moderately, while molecular weight of the resulting polymer slightly decreases because MAO have also a function as chain transfer agent. [44] However, the activity decrease moderately with the increase of MAO/catalyst ratio over 1825 because overdose MAO as co-catalyst deactivated the catalyst to inactive form for ethylene polymerization. [54-58]

As seen in Table 4.13, the optimum condition for producing UHMWPE with the highest activity is the use of catalyst concentration of 2 μmol with the Al/Ti ratio of 1825 at 30 °C (entry 5, Table 4.13).

Table 4.13 Results of ethylene polymerization with complex **2**/MAO at various MAO concentrations [a]

Entry	**MAO (mmol)**	**[Al]/[Ti]**	**Yield (g)**	**Activity kg PE/mmol cat·h**	**M_w[b] ($x10^{-6}$)**	**M_n[b] ($x10^{-6}$)**	**PDI**	**T_m[c] (^oC)**
1	2.05	1025	5.73	8.60	3.84	3.31	1.15	127.3
2	2.45	1225	6.14	9.21	3.71	3.21	1.15	126.8
3	2.85	1425	6.33	9.49	3.55	3.00	1.18	126.5
4	3.25	1625	7.37	11.06	3.43	2.33	1.47	127.1
5	3.65	1825	7.76	11.65	3.25	2.19	1.48	126.9
6	4.05	2025	6.90	10.35	3.15	2.08	1.50	127.0

[a] Conditions: complex (2 μmol), ethylene pressure 1 atm, toluene 500 mL, time 20 min, temperature 30°C. [b]Determined by GPC using polystyrene calibration. [c]Melting temperature of synthesized polyethylene determined by DSC.

4.2.2.4 The effect of polymerization time on catalytic activity of complex 2

To further investigate the complex **2** activated MAO in living fashion, the polymerizations at 10, 20, 30, 40, 50, and 60 min were carried out under ethylene pressure 1 bar, toluene of 500 ml, catalyst content 2 μmol and MAO 3.65 mmol. The results are summarized in Table 4.14. The residence times in ethylene polymerization are in the range of 10-20 min to observe the high activity because of monomer diffusion easily. Then, the polymerization time increases, the catalytic activity of complex 2 decreases because monomer diffuse slowly and difficultly to react into active site having a covered polymer for ethylene polymerization. The increase of the polymer yield as a function of polymerization time indicates that the complex **2**/MAO catalyst system has a catalytic life time of at least 60 min as shown in Figure 4.8. The broaden molecular weight distribution caused by the non-homogenity of the ethylene polymerization system due to excess polymer precipitation was not observed. The living nature [61-62] of ethylene polymerization was therefore demonstrated by the observed narrow polydispersities (PDI < 1.4). The molecular weight of polyethylene is in the range of 3.5×10^6-3.8×10^6, it classify in UHMWPE. The melting temperature of UHMWPE is in the range of 126.5-127.1 °C.

Table 4.14 Results of ethylene polymerization with complex **2**/MAO at various polymerization times[a]

Entry	Time (min)	Yield (g)	Activity kg PE/mmol cat·h	M_w[b] ($\times10^{-6}$)	M_n[b] ($\times10^{-6}$)	PDI[b]	T_m[c] (°C)
1	10	6.03	9.05	3.56	2.60	1.37	126.5
2	20	12.17	9.13	3.60	2.91	1.23	127.1
3	30	13.95	6.97	3.69	3.09	1.19	127.0
4	40	13.46	5.05	3.80	3.28	1.15	127.0
5	50	14.43	4.33	3.88	3.42	1.13	127.0
6	60	15.53	3.88	4.03	3.66	1.10	127.1

[a] Conditions: complex (2 µmol), cocatalyst MAO (3.65 mmol), [Al]/[Ti] = 1825, 1 atm, toluene 500 mL, temperature 30°C. [b] Determined by GPC using polystyrene calibration. [c] Melting temperature of synthesized polyethylene determined by DSC.

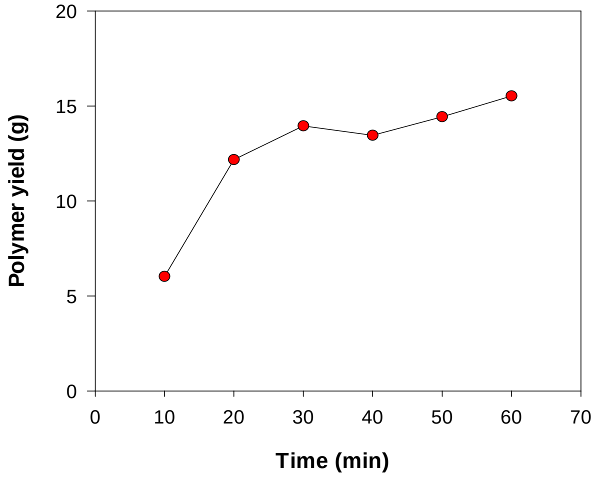


Figure 4.8 Relationship between the polymerization time and the polymer yield obtained with complex **2**/MAO. Conditions: complex (2 µmol), cocatalyst MAO (3.65 mmol), [Al]/[Ti] = 1825, 1 atm, toluene 500 mL, temperature 30°C.

4.2.2.5 The effect of ethylene pressure on catalytic activity of complex 2

To study the influence of ethylene pressure on catalytic activity of complex 2 activated MAO by operating at the catalyst concentration of 2 µmol, [Al]/[Ti] ratio of 1825, the polymerization temperature and time of 30°C and 30 minute, respectively in toluene media 250 ml. The catalytic activity of complex 2 increases with the increase of ethylene pressure from 1 to 5 bar due to increase a monomer solubility in toluene as shown in Table 4.15. These results correspond to the phenoxy-imine zirconium complex in ethylene polymerization. The enhancement of activity is observed from the increase of ethylene pressure because of high monomer close to active sites of catalyst. [76]

Table 4.15 Results of ethylene polymerization with complex 2/MAO at various ethylene pressures[a]

Entry	**Pressure (bar)**	**Yield (g)**	**Activity kg PE/mmol cat·h**	M_w[b] ($\times10^{-6}$)	M_n[b] ($\times10^{-6}$)	***PDI***[b]	T_m[c] (°C)
1	1	12.17	9.13	3.99	3.48	1.14	127.4
2	2	13.84	10.38	3.73	3.21	1.16	127.1
3	3	14.77	11.08	3.59	2.85	1.25	127.0
4	4	15.86	11.90	3.52	2.58	1.36	127.0
5	5	16.75	12.56	3.52	2.50	1.40	127.6

[a] Conditions: complex 2 (2 μmol), cocatalyst MAO (3.65 mmol), [Al]/[Ti] = 1825, toluene 500 mL, temperature 30°C, time 30 min.

4.2.3 The effect of various phenoxy-imine titanium complexes activated with various co-catalysts on the catalytic activity

The complexes (1, ref.1, 2) activated with various co-catalysts (TEA, TIBA, TMA, T*n*HAl, T*n*OAl, MAO and MMAO) were performed on ethylene polymerization at temperature 25°C under atmospheric ethylene pressure for 20 minutes. The results are summarized in Table 4.16.

Table 4.16 Comparison of ethylene polymerization with various FI catalyst and cocatalyst[a].

Entry	**Complex**	**Cocatalyst**	**Yield (g)**	**Activity (kg PE/ mmol cat h)**	**M_w[b] ($\times 10^{-6}$)**	**M_n[b] ($\times 10^{-6}$)**	**PDI[b]**	**T_m[c] (^oC)**
1	**1**	TMA	1.15	3.45	1.20	0.72	1.66	126.4
2	**1**	TEA	0.11	0.33	0.10	0.03	2.75	124.6
3	**1**	TIBA	1.02	3.06	0.93	0.53	1.73	127.1
4	**1**	T*n*HAl	0.25	0.75	0.28	0.12	2.28	127.7
5	**1**	T*n*OAl	0.29	0.87	0.37	0.20	1.85	126.1
6	**1**	MAO	2.91	8.73	1.60	0.90	1.76	128.0
7	**1**	MMAO	2.83	8.49	1.50	0.85	1.74	127.9
8	**Ref.1**	TMA	0.99	2.96	1.24	0.87	1.42	127.0
9	**Ref.1**	TEA	trace	-	-	-	-	-
10	**Ref.1**	TIBA	0.90	2.70	0.77	0.52	1.47	127.1
11	**Ref.1**	T*n*HAl	0.23	0.69	0.31	0.19	1.61	126.2
12	**Ref.1**	T*n*OAl	0.21	0.63	0.42	0.18	2.29	127.4
13	**Ref.1**	MAO	2.52	7.56	2.27	1.45	1.55	127.8
14	**Ref.1**	MMAO	2.20	6.6	2.20	1.59	1.38	127.1
15	**2**	TMA	No polymer	-	-	-	-	-
16	**2**	TEA	No polymer	-	-	-	-	-
17	**2**	TIBA	No polymer	-	-	-	-	-
18	**2**	T*n*HAl	No polymer	-	-	-	-	-
19	**2**	T*n*OAl	No polymer	-	-	-	-	-
20	**2**	MAO	2.23	6.69	3.96	3.15	1.25	126.6
21	**2**	MMAO	0.04	0.12	1.16	0.22	5.23	127.7

[a] Conditions : Toluene (250 ml), ethylene pressure (1 bar), polymerization time (20 min), complex (1 μmol), cocatalyst (1.25 mmol), polymerization temperature (25 °C).
[b] Determined by GPC using polystyrene calibration.
[c] Melting temperature of synthesized polyethylene determined by DSC.

The aluminum alkyls (AlR_3) used as cocatalysts were active to generate the active species of **1** (entries 1-5, Table 4.16) and **ref. 1** (entries 8-12, Table 4.16) in the ethylene polymerizations. In contrast, the complex **2** activated with various aluminum alkyls were virtually inactive (entries 15-19) for ethylene polymerization. Complex 1 in the presence of TMA (entry 1) and TIBA (entry 3) exhibited high catalytic activities and produced high molecular weight PEs with narrow PDIs. However, the catalytic activities of complex 1 in ethylene polymerizations using TEA (entry 2), T*n*HAl (entry 4) and T*n*OAl (entry 5) were found to be relatively low and yielded the low molecular weight of polyethylenes. When MAO was used as a cocatalyst, the highest activity of 8.73 kg PE/mmol cat h was observed and the obtained polyethylene had high molecular weight of 1.60 x 10^6 and narrow PDI (PDI = 1.76). The similar observed activity and molecular weight were observed when MMAO was employed as a cocatalyst (entry 7). In the case of **ref.1**, the effect of various cocatalysts on the catalytic activities was similar to that of **1**; *i.e*. the activity decreases in the order TMA > TIBA >> T*n*HAl ≈ T*n*OAl >> TEA. The high catalytic activities were observed when TMA and TIBA were used as cocatalyst (entries 8 and 10, respectively), whereas the low activities were detected by using TEA, T*n*HAl, and T*n*OAl (entries 9, 11, and 12, respectively). The polymerizations using ref.1 activated with MAO (entry 13) disclosed slightly higher activity than that of activated with MMAO (entry 14). However, Complex 2 activated with MAO (entry 20) displayed high catalytic activity and gave an ultrahigh molecular weight PE with a narrow PDI value which was opposite to that using MMAO (entry 21). The results are similar to the fluorinated phenoxyimine zirconium complexes activated with MAO and MMAO which exhibited highly active for ethylene polymerization while those activated with alkylaluminum showed inactive. [74]

A comparison of the data in Table 4.16 disclosed that the use of aluminum alkyls as co-catalysts comparing with MAO, displayed low catalytic activity and low molecular weight PEs. The chain transfer process with aluminum alkyls may be accounted for this observation. In addition, the sterically encumbered cycloalkyl group on the N-imine ligand (cyclooctyl group for **1** and cycloheptyl group for ref.**2**) had an effect on both catalytic activity and molecular weight of the resulting polyethylene. The results suggested that the sterically bulkier cyclooctyl group was prone to produce higher catalytic activity because of the steric protection at the metal active site, resulting in the elimination of chain transfer process [80]. From the above results, it is implied that the different catalysts have an effect on the catalytic activity and polyethylene molecular weight, including the different of co-catalysts influencing on both activity and polymer molecular weight as well. In term of polymer morphology, the polymers produced from all three complexes have ill-defined structure. Therefore the immobilization and activation processes of **1, ref.2 and 2** on $MgCl_2$- and SiO_2-based supports in order to improve polymer morphology were carried out.

4.3. The effect of phenoxy-imine titanium complexes immobilized on in-situ $MgCl_2$/2-ethyl-1-hexanol adduct and silica-based support on heterogeneous polymerization

4.3.1 The effect of various cocatalysts in ethylene polymerization with complexes 1, 2 and ref.1 immobilized on $MgCl_2$-based and SiO_2-based supports[a]

The in-situ $MgCl_2/AlR_n(OEH)_{3-n}$ [R = CH_3, C_2H_5, i-Bu; OEH = 2-ethyl-1-hexoxy] supports used in the research were prepared according to the published procedure [26]. Typically, $MgCl_2$ treated with 3.0 equivalent of 2-ethyl-1-hexanol in decane at 140 ºC to form a $MgCl_2$/2-ethyl-1-hexanol adduct solution. Subsequently, aluminum alkyl (AlR_3) was used in dealcoholysis process to yield a mixture of $MgCl_2$, AlR_3, and $AlR_n(OEH)_{3-n}$. The in-situ supported catalyst with various co-catalysts for ethylene polymerization was performed in heptane 250 ml, the amount of $MgCl_2$/2-ethyl-1-hexanol adduct with 2 ml or SiO_2 sylopol 2229 content 0.2 g, specified co-catalysts such as TIBA, TEA, etc. and catalyst complex to initiate the reaction under ambient pressure at 25°C for 30 min. The results of ethylene polymerization with the $MgCl_2$-and SiO_2-based supported catalysts are collected in Table 4.17.

Ethylene polymerization with bis(phenoxy-imine) titanium complexes 1, 2 and ref.1 were carried out with using the $MgCl_2/AlR_n(OEH)_{3-n}$, where R = methyl, ethyl, and i-butyl), as an activator. Alkyl aluminum 2-ethyl-1-hexoxides are expected to act as in situ alkylating agents for the titanium complexes as well as impurity scavengers in a polymerization system, and $MgCl_2$ has a function as Lewis acid to generate a cationic active species from the alkylated complex. [26, 27, 68, 71]

The complexes immobilized on $MgCl_2/AlR_n(OEH)_{3-n}$ exhibited the catalytic activities in the range of 0.51-5.37 kg PE/(mmol cat h) depending on the ligand structure. In contrast to the homogenous polymerization system, complex 2 immobilized on $MgCl_2$/2-ethyl-1-hexanol adduct with aluminum alkyl as a cocatalyst in ethylene polymerization was virtually active. The highest catalytic activity was obtained from 1 immobilized on $MgCl_2$/2-ethyl-1-hexanol adduct treated with TMA as the co-catalyst (entry 1) whereas the lowest catalytic activity was observed from 2 impregnated with $MgCl_2$-based support and TEA (entry 10). The result corresponds to $MgCl_2$-supported half-metallocene activated with TMA giving also highly activity because of the effect of bulkiness of alkyl-aluminum on the performance of support catalyst system [53].

Table 4.17 Results of ethylene polymerization with complexes **1,** ref.1 and 2 immobilized on $MgCl_2$-based and SiO_2-based supports in the presence of various cocatalysts.[a]

Entry	**Complex**	**Support**	**Cocatalyst**[c]	**Yield (g)**	**Activity (kg PE/ mmol cat h)**	M_w[c] (× 10^{-6})	M_n[c] (× 10^{-6})	**PDI**[c]	T_m[d] (°C)
1	**1**	$MgCl_2$/2-ethyl-1-hexanol	TMA	8.06	5.37	2.10	1.23	1.69	127.1
2	**1**	$MgCl_2$/2-ethyl-1-hexanol	TEA	2.20	1.46	1.75	0.93	1.87	127.6
3	**1**	$MgCl_2$/2-ethyl-1-hexanol	TIBA	2.61	1.74	0.19	0.12	1.62	128.9
4[b]	**1**	SiO_2 Sylopol 2229	MAO	0.89	0.89	1.78	1.00	1.76	128.1
5	**Ref.1**	$MgCl_2$/2-ethyl-1-hexanol	TMA	6.16	4.10	2.10	1.23	1.69	127.2
6	**Ref.1**	$MgCl_2$/2-ethyl-1-hexanol	TEA	1.92	1.28	1.73	0.64	2.70	128.0
7	**Ref.1**	$MgCl_2$/2-ethyl-1-hexanol	TIBA	2.93	1.95	0.28	0.15	1.86	128.5
8[b]	**Ref.1**	SiO_2 Sylopol 2229	MAO	0.59	0.59	1.90	1.19	1.59	128.8
9	**2**	$MgCl_2$/2-ethyl-1-hexanol	TMA	1.16	0.77	4.38	3.83	1.14	128.1
10	**2**	$MgCl_2$/2-ethyl-1-hexanol	TEA	0.77	0.51	2.22	1.18	1.88	123.9
11	**2**	$MgCl_2$/2-ethyl-1-hexanol	TIBA	0.82	0.54	2.88	2.03	1.41	127.8
12[b]	**2**	SiO_2 Sylopol 2229	MAO	0.55	0.55	5.34	5.12	1.04	128.0

[a] Conditions : Toluene (250 ml), ethylene pressure (1 bar), polymerization time (30 min), complex (3 μmol), cocatalyst (6.6 mmol), polymerization temperature (25 °C), 1.0 M $MgCl_2$/2-ethyl-1-hexanol adduct solution (2 mL), SiO_2 (0.2 g).

[b] complex (2μmol), MAO (2.50 mmol), Al/Ti ratio 1250.

[c] Determined by GPC using polystyrene calibration.

[d] Melting temperature of synthesized polyethylene determined by DSC.

In general, complex 1 immobilized on the $MgCl_2$-based support has the higher activity than $MgCl_2$-supported complexes ref.1 and 2, respectively, which is the same trend as for the homogeneous catalytic system. Additionally, the catalytic activity of the supported Ti complexes in ethylene polymerization was found to depend strongly on the type of aluminum alkyls used for modification of the support. The activity of all complexes decreases in the order TMA > TiBA > TEA. From the above experiment, phenoxy-imine titanium complex activated with $MgCl_2/R_mAl(OR)_n$ was high performance, it may be related to the complex having O and N heteroatom in ligand capable to electronically interacting with $MgCl_2$ as well [89].

As shown in Table 4.17, The GPC data displayed narrow molecular weight distributions with PDI values < 2.0 except the polymer produced by $MgCl_2$-supported complex with TEA as a cocatalyst (entry 6, PDI = 2.70). This indicates that Ti-FI catalysts can maintain single-site behavior after immobilization [33]. Furthermore, the high molecular weight of polyethylene was prepared when TMA was used as a cocatalyst (entries 1, 5 and 9).

The use of SiO_2 as a support for Ti-FI catalysts 1-3 were also investigated (Table 2, entries 4, 8, and 12). The ethylene polymerization with Ti-FI catalyst immobilized on silica treated with MAO was carried out at [Al/Ti] ratio of 1250 under pressure 1 bar for 30 min. The highest catalytic activity of 0.89 kg PE/mmol cat h was observed for $1/SiO_2/MAO$ system (entry 4) whereas the $2/SiO_2/MAO$ system displayed the lowest activity of 0.55 kg PE/mmol cat h (entry 12). It can be seen that the highest molecular weight PE of 5.34×10^6 with remarkably narrow PDI value of 1.04 was produced by complex 2 immobilized on SiO_2 with MAO as a cocatalyst (entry 12). The single-site characteristic was also demonstrated in this heterogeneous system as evidenced by the observed narrow PDI values (< 1.76). The results in Table 4.17 also shows that the melting point of the polyethylene obtained from supported Ti-FI catalyst is similar to that obtained from the unsupported catalyst (Tm = 126-128 ^{o}C).

4.3.2 Effect of catalyst loading on the support

For ethylene polymerization, the catalytic activity of **2** attached on $MgCl_2/AlR_n(OEH)_{3-n}$ were practically low comparing with 1 and ref.1 immobilized on $MgCl_2/AlRn(OEH)_{3-n}$ because of the different ligand structure. In the next experiment, to investigated the effect of three complexes loading on $MgCl_2/AlMe_n(OEH)_{3-n}$ when TMA was used as a cocatalyst on the polymerization activity. The results are summarized in Table 4.18.

Table 4.18

Effect of catalyst concentration in complexes **1** and ref.1 immobilized on a $MgCl_2$-based support.[a]

Entry	complex	Amount of complex (μmol)	Yield (g)	Activity (kg PE/ mmol cat h)	M_w[b] ($\times 10^{-6}$)	M_n[b] ($\times 10^{-6}$)	PDI[b]	T_m[c] (^oC)
1	**1**	1	2.08	4.16	1.77	0.92	1.91	127.5
2	**1**	3	8.06	5.37	2.10	1.23	1.69	127.1
3	**1**	5	8.10	3.24	2.01	1.13	1.77	127.2
4	**1**	7	8.87	2.53	1.55	0.78	1.97	126.9
5	**1**	10	12.76	2.55	1.51	0.62	2.41	126.0
6	**Ref.1**	1	1.24	2.49	1.77	0.92	1.91	127.7
7	**Ref.1**	3	6.16	4.11	2.02	1.09	1.84	127.0
8	**Ref.1**	5	8.03	3.21	1.95	0.98	1.97	127.3
9	**Ref.1**	7	8.72	2.49	1.77	0.82	2.14	127.1
10	**Ref.1**	10	12.19	2.43	1.76	0.81	2.17	127.1
11	**2**	1	0.87	1.74	4.26	3.58	1.18	127.3
12	**2**	3	1.16	0.77	4.38	3.83	1.14	128.4
13	**2**	5	1.97	0.79	4.11	3.44	1.19	128.4
14	**2**	7	2.84	0.81	3.95	3.17	1.24	128.2
15	**2**	10	5.74	1.14	3.69	2.83	1.30	127.9

[a] Conditions: Toluene (250 ml), ethylene pressure (1 bar), polymerization time (30 min), polymerization temperature (25 °C), 1.0 M $MgCl_2$/2-ethyl-1-hexanol adduct solution (2 mL), TMA (6.6 mmol).
[b] Determined by GPC using polystyrene calibration.
[c] Melting temperature of synthesized polyethylene determined by DSC.

As shown in Table 4.18, the polymerization activity of both complexes of 1 and ref.1 increased as the catalyst loading on the support was increase from 1 μmol to 3 μmol. Then the activity decreased when the amount of catalyst loading was enhanced (from 5 μmol to10 μmol). Plots of the catalytic activities of complexes 1 and ref.1 vesus the amount of catalyst loading are shown in Figure 4.9. The increase of the activity as the loading is decreased was also found in other systems, for example, in $(RCp)_3ZrCl_2/MgCl_2.AlEt_n(OEt)_{n-3}$ system [90] and $MgCl_2/TiCl_4$ Ziegler-Natta catalyst system [88]. These results suggested that $MgCl_2$-based supports contain relatively low proportions of surface coordination sites for effective catalyst activation [90]. In this work, the molar ratio of Ti-FI catalyst: $MgCl_2$/2-ethyl-1-hexanol:TMA at the optimum polymerization condition at atmospheric pressure and 25 °C for both complexes **1** and **ref.1** is 0.0015:1.0:3.3. As a result, subsequent experiments were performed with this condition. The highest activity of 5.37 kg PE/mmol cat h (entry 2) was observed for **1**/ $MgCl_2/AlMe_n(OEH)_{3-n}$ and the highest activity of 4.11 kg PE/mmol cat h was observed for **2** $MgCl_2/AlMe_n(OEH)_{3-n}$ (entry 7).

In the case of complex 2 impregnated on $MgCl_2/AlMe_n(OEH)_{3-n}$, the catalytic activity increased with the increase of catalyst concentration from 3 to 10 μmol while the concentration about 1 μmol gave the highest activity due to strong propagation rate. Additionally, the resultant polyethylene displayed ultrahigh molecular weight and narrow polydispersity. However, the polydispersity of PEs obtained from three complexes had a similar decreased trend with the increase of catalyst concentration. Besides, PEs obtained from supported complex 2 had moderately higher molecular weight than that from supported complex 1 and ref.1.

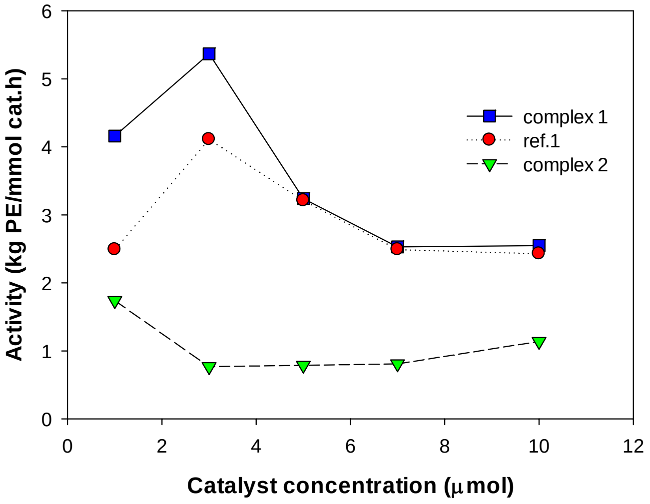


Figure 4.9 Relationship between the catalyst concentration and the polymerization activity.

4.3.3 Effect of polymerization time

To further examine the living fashion of Ti-FI complexes **1**, **ref.1 and 2** in combination with $MgCl_2/AlMe_n(OEH)_{3-n}$, the polymerizations at different time were carried out under ethylene pressure 1 bar. The molar ratio of Ti-FI catalyst: $MgCl_2$/2-ethyl-1hexanol:TMA was fixed at 0.0015:1.0:3.3. The results in ethylene polymerization are shown in Table 4.19. The increase of the polymer yield as a function of polymerization time indicates that the $MgCl_2$-based Ti-FI catalysts have a catalytic life time at least 120 min, as seen in Figure 4.10. In addition, the molecular weight of PEs produced with **1**/$MgCl_2/AlMe_n(OEH)_{3-n}$, ref.1/ $MgCl_2/AlMe_n(OEH)_{3-n}$ and **2**/ $MgCl_2/AlMe_n(OEH)_{3-n}$ increased with increasing polymerization time, as shown in Figure 4.10. For example, the M_w of polyethylene prepared with **1**/ $MgCl_2/AlMe_n(OEH)_{3-n}$ in 30 min was 1.38×10^6 (entry 1) while the M_w of polyethylene prepared in 120 min was 1.76×10^{-6} (entry 4). The living nature of the catalyst system was also demonstrated by the observed narrow PDI values (< 2.2), essentially PDI of PEs obtained from complex 2/ $MgCl_2/AlMe_n(OEH)_{3-n}$ close to 1 because of interaction of o-F substituents on FI catalyst with the growing polymer chain to induce living polymerization via chain transfer and β-hydrogen transfer suppression. [67]

Table 4.19

Effect of time in ethylene polymerization using complexes **1** and **2** immobilized on a $MgCl_2$-based support.[a]

Entry	complex	Time (min)	Yield (g)	Activity (kg PE/mmol cat h)	M_w[b] ($\times 10^{-6}$)	M_n[b] ($\times 10^{-6}$)	PDI[b]	T_m[c] (^oC)
1	**1**	30	9.51	2.11	1.38	0.63	2.18	123.6
2	**1**	60	11.94	1.32	1.64	0.81	2.01	126.8
3	**1**	90	15.29	1.13	1.68	0.84	1.99	126.5
4	**1**	120	20.07	1.11	1.76	0.88	1.98	125.4
5	**Ref.1**	30	6.82	1.51	1.60	0.76	2.09	123.6
6	**Ref.1**	60	10.92	1.21	2.20	1.28	1.70	123.7
7	**Ref.1**	90	12.53	0.92	2.45	1.47	1.66	123.6
8	**Ref.1**	120	12.90	0.71	2.88	1.91	1.50	123.6
9	**2**	30	4.67	1.03	3.25	2.40	1.35	122.7
10	**2**	60	5.29	0.58	3.82	3.18	1.20	123.9
11	**2**	90	7.46	0.55	3.89	3.30	1.17	127.1
12	**2**	120	9.89	0.54	3.96	3.43	1.15	123.6

[a] Conditions: Toluene (750 ml), ethylene pressure (1 bar), polymerization temperature (25 °C), complex (9 μmol), 1.0 M $MgCl_2$/2-ethyl-1-hexanol adduct solution (6 mL), TMA (19.8 mmol).

[b] Determined by GPC using polystyrene calibration.

[c] Melting temperature of synthesized polyethylene determined by DSC.

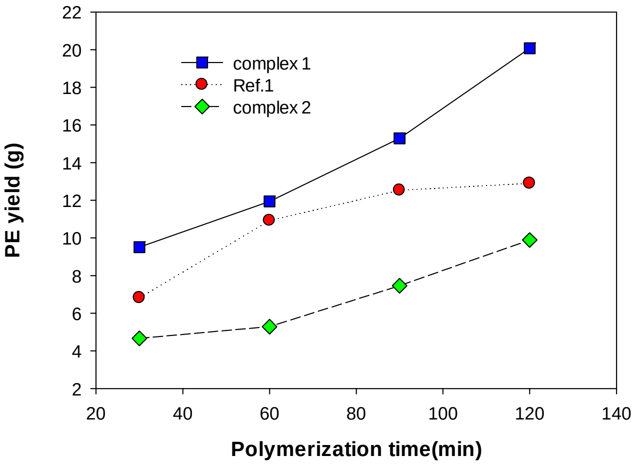


Figure 4.10 Relationship between the polymerization time and the polymer yield obtained by complexes **1** ref.1 and **2** immobilized on a $MgCl_2$-based support.

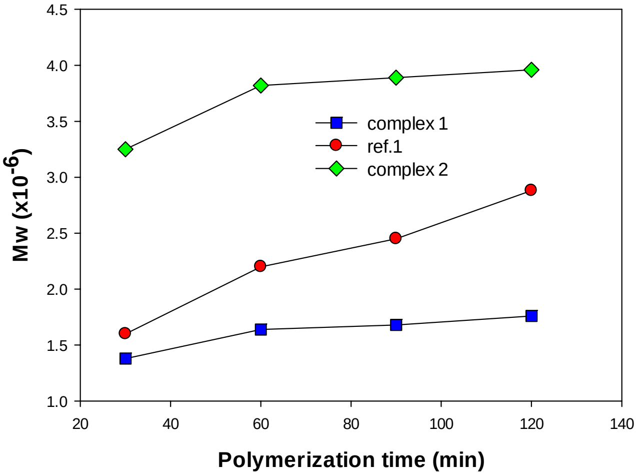


Figure 4.11 Relationship between the polymerization time and the M_w obtained by complexes **1**, ref.1 and **2** immobilized on a $MgCl_2$-based support.

4.3.4 Effect of polymerization pressure

In order to investigate the influence of pressure on the polymerization activity, the ethylene pressure was varied from 1 to 5 bar and the polymerization results are summarized in Table 4.20. The increase of the polymerization pressure was found to have an impact on the polymerization activity. As shown in Figure 4.12, the catalytic activity of three Ti-FI complexes impregnated on $MgCl_2/AlMe_n(OEH)_{3-n}$ enhanced with increasing the ethylene pressure because of the increase of monomer solubility. The highest catalytic activity of 5.21 kg PE/mmol cat h was produced with **1**/$MgCl_2/AlMe_n(OEH)_{3-n}$ (entry 5) while the highest activity of 3.50 kg PE/mmol cat.h was obtained from **ref.1**/$MgCl_2$/$AlMe_n(OEH)_{3-n}$ (entry 10). In case of 2/$MgCl_2$/$AlMe_n(OEH)_{3-n}$, the highest activity was observed at 1.98 kg PE/mmol cat.h (entry 15).

Table 4.20

Effect of pressure in ethylene polymerization using complexes **1** and **2** immobilized on a $MgCl_2$-based support.[a]

Entry	complex	Pressure (bar)	Yield (g)	Activity (kg PE/mmol cath)
1	**1**	1	9.51	2.11
2	**1**	2	13.87	3.08
3	**1**	3	17.54	3.89
4	**1**	4	20.74	4.61
5	**1**	5	23.44	5.21
6	**Ref.1**	1	6.82	1.51
7	**Ref.1**	2	8.38	1.86
8	**Ref.1**	3	10.50	2.33
9	**Ref.1**	4	12.55	2.79
10	**Ref.1**	5	15.76	3.50
11	**2**	1	4.67	1.03
12	**2**	2	5.23	1.16
13	**2**	3	6.26	1.39
14	**2**	4	7.98	1.77
15	**2**	5	8.93	1.98

[a] Conditions: Toluene (750 ml), polymerization temperature (25 °C), polymerization time (30 min), complex (9 μmol), 1.0 M $MgCl_2$/2-ethyl-1-hexanol adduct solution (6 mL), TMA (19.8 mmol).
[b] Determined by GPC using polystyrene calibration.
[c] Melting temperature of synthesized polyethylene determined by DSC.

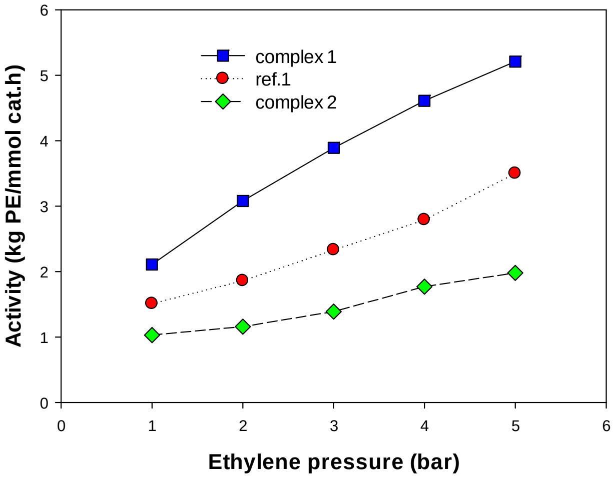


Figure 4.12 Relationship between the polymerization pressure and the activity obtained by complexes **1, ref.1** and **2** immobilized on a $MgCl_2$-based support.

4.4 Characterization of support and PE particles obtained from unsupported and in-situ supported catalyst of two complexes (ref.1 and 1)

From the polymer particle photograph as shown in Figure 4.13, PE particle powder obtained from unsupported catalyst complex 1 and ref.1 with TMA as a cocatalyst displayed some polymer aggregation because homogeneous catalyst system mostly produced polyolefin with irregular shapes in picture (a) to (b).

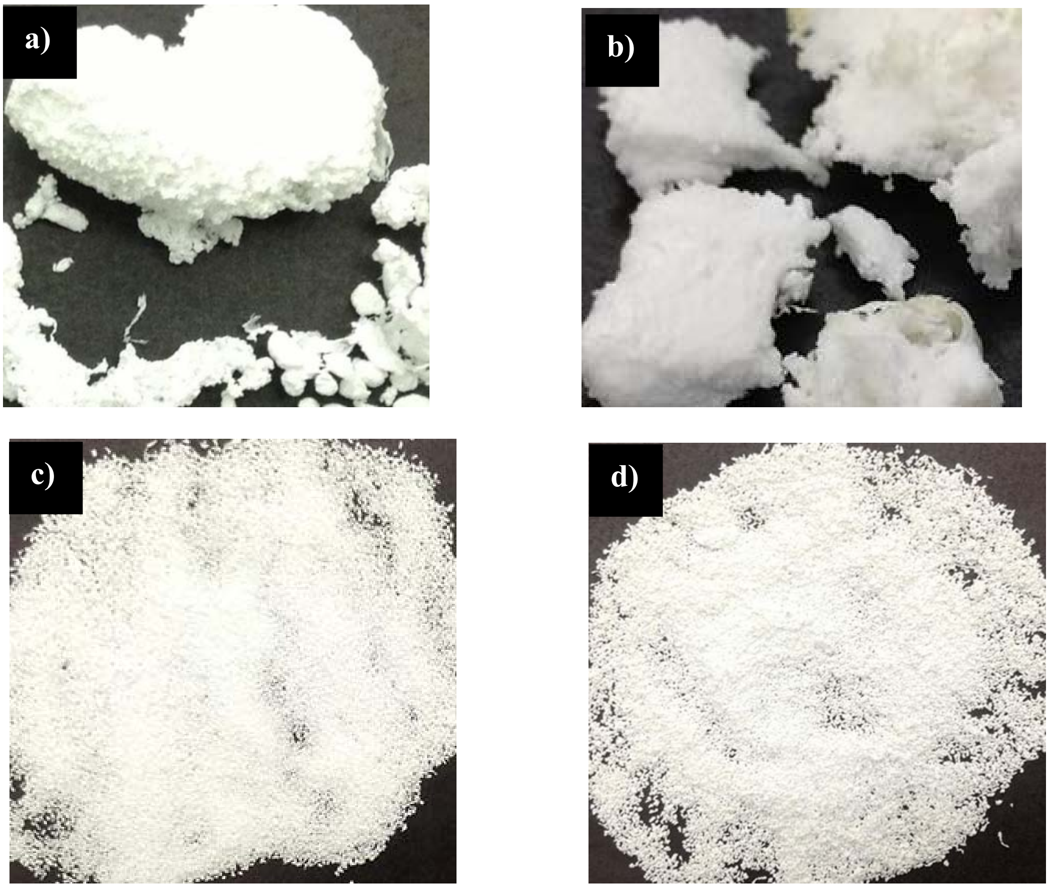


Figure 4.13 Photograph of PEs produced with a) ref.1/TMA; b) 1/TMA; c) $MgCl_2$/1-ethyl -2-hexanol/TMA/ref.1; d) $MgCl_2$/1-ethyl -2-hexanol/TMA/1

In case of supported catalyst system, complex 1 and ref.1 immobilized on $MgCl_2$/2-ethyl-1-hexanol adduct/TMA can produce polyethylene with well-defined and non-coherent particles as seen in Figure 4.13 of (c) and (d). The above results are corresponding to different bis(phenoxy-imine) titanium complexes or nickel diimine complexes in presence of $MgCl_2$-based activators produced well-defined polyethylene particles. It is shown that $MgCl_2/R_mAl(OR)_{3-n}$ can act as a good support and activator for FI catalysts without MAO and borate compound as co-catalysts. (12, 20, 68)

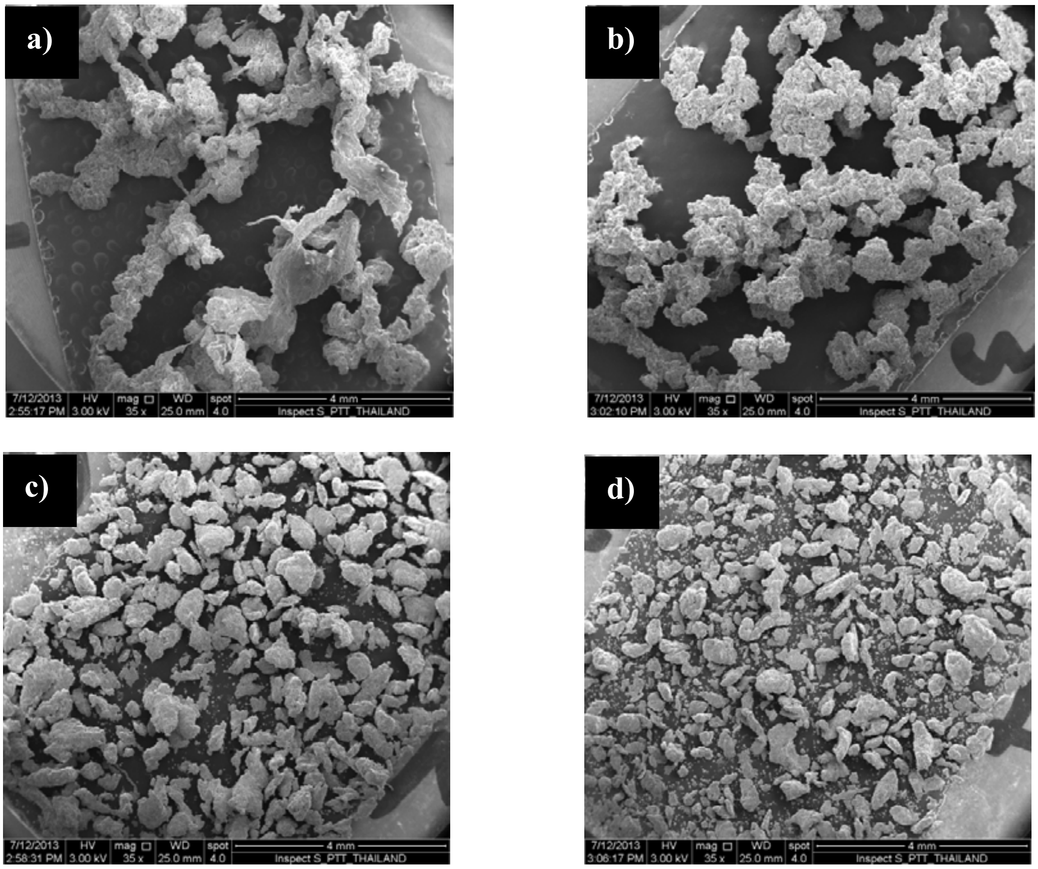


Figure 4.14 SEM Micrographs of PEs produced with a) ref.1/MAO; b) 1/MAO; c) SiO_2/MAO/ref.1; d) SiO_2/MAO/1

Scanning electron micrographs of the polymer particles produced with Ti-Fi catalyst/MAO and Ti-Fi catalyst/SiO_2/MAO and with Ti-Fi catalyst/TMA and Ti-Fi catalyst/$MgCl_2/AlMe_n(OEH)_{3-n}$ are compared in Figures 4.14 and 4.15, respectively. It can be seen that the polyethylenes produced with $MgCl_2$-based supported and SiO_2-based supported catalysts display well-defined morphologies with noncoherent polymer particles, whereas those prepared with the MAO and TMA activation systems exhibit ill-defined morphologies with irregular shape. These observations suggest that the Ti-Fi catalysts **1** and **2** are immobilized on the surface of both solid supports, SiO_2/MAO and $MgCl_2/AlMe_n(OEH)_{3-n}$, and hence the ethylene polymerization takes place on the solid [25]. The well-defined polymer morphology is an important factor for the commercial gas-phase and slurry polymerization systems.

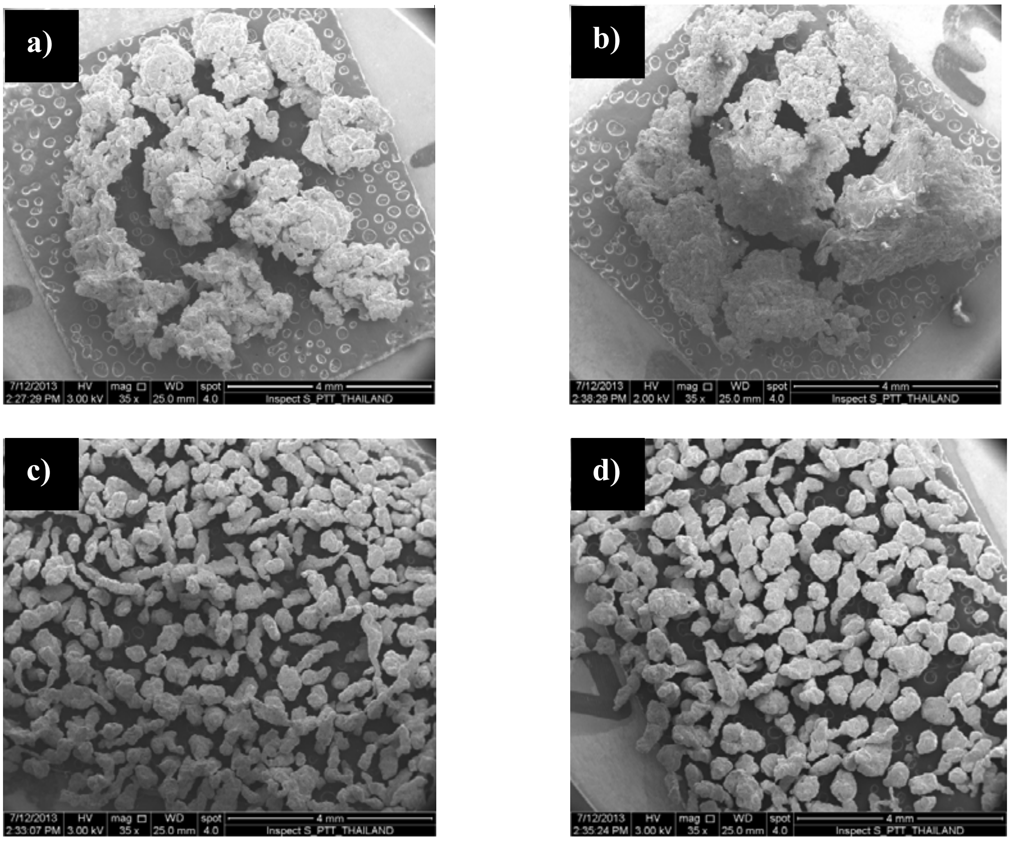


Figure 4.15 SEM Micrographs of PEs produced with a) ref.1/TMA; b) 1/TMA; c) $MgCl_2$/1-ethyl -2-hexanol/TMA/ref.1; d) $MgCl_2$/1-ethyl -2-hexanol/TMA/1

4.5 Copolymerization of ethylene and higher alpha-olefins

4.5.1 The effect of comonomer content on catalytic activity of three Ti-FI complexes (1, ref.1 and 2) with MAO for the copolymerization

To further investigate the effect of comonomer content on catalytic activity of three Ti-FI complexes (1, ref.1 and 2) with MAO for the copolymerization. The copolymerization of ethylene and 1-hexene or 1-octene was performed at 25^{o}C for 30 min under ethylene pressure 1 bar. The copolymerization data are collected in Table 4.21. As seen in Figure 4.16 and 4.17, the catalytic activity of both complexes (1, 2) activated with MAO decrease with increasing the amount of comonomer (1-hexene or 1-octene) for the copolymerization of ethylene and 1-hexene or 1-octene, respectively. In addition, the molecular weight of ethylene/1-hexene copolymer produced with both complexes (1, 2) decrease with the increase of the amount of 1-hexene comonomer as seen in Figure 4.18. This result was the same trend as the molecular weight of ethylene/1-octene copolymer prepared with both complexes (1, 2). The single site characteristic of these catalyst systems with MAO for copolymerization was illustrated by the observed narrow PDI value less than 1.65. These results correspond to fluorinated FI-Ti catalyst for living copolymerization of ethylene/1-octene. The decrease molecular weight of E/O copolymer was observed with the enhancement of 1-octene content in feed. This could be attributed to slower propagation rate more than the chain transfer to 1-octene due to the obtained copolymer having narrow polydispersity. While the catalytic activity of fluorinated FI-Ti catalyst activated with DMAO for copolymerization decreased with increasing the amount of comonomer in feed because of steric hindrance to the insertion of ethylene monomer. [91] The melting temperature of both copolymers with complex 1 is in the range of 118.4-121.5. While, the melting temperature of both copolymers with complex 2 is in the range of 41.4-91.2 which is lower than that with complex 1.

Table 4.21 Copolymerization of ethylene and higher α-olefin obtained from various catalysts in presence of MAO with various the amount of comonomer

Entry	complex	comonomer content	Yield (g)	Activity (kg PE/mmol cat h)	M_w [b] (× 10^{-6})	M_n [b] (× 10^{-6})	PDI[b]	T_m [c] (°C)
1	**1**	1-octene (5 ml)	2.24	2.24	1.01	0.61	1.65	121.5
2	**1**	1-octene (10 ml)	1.54	1.54	0.61	0.39	1.55	120.1
3	**1**	1-octene (15 ml)	1.20	1.20	0.58	0.36	1.58	119.6
4	**1**	1-octene (20 ml)	1.01	1.01	0.52	0.34	1.54	119.1
5	**1**	1-octene (25 ml)	0.81	0.81	0.39	0.26	1.50	117.7
6	**1**	1-hexene (5 ml)	2.00	2.00	0.79	0.51	1.55	121.4
7	**1**	1-hexene (10 ml)	1.21	1.21	0.56	0.36	1.55	119.8
8	**1**	1-hexene (15 ml)	1.03	1.03	0.43	0.27	1.57	118.4
9	**1**	1-hexene (20 ml)	0.81	0.81	0.35	0.22	1.59	118.4
10	**1**	1-hexene (25 ml)	0.78	0.78	0.31	0.19	1.60	118.7
11	**2**	1-octene (5 ml)	3.88	3.88	3.57	2.72	1.31	91.2
12	**2**	1-octene (10 ml)	3.42	3.42	3.40	2.41	1.40	77.5
13	**2**	1-octene (15 ml)	2.65	2.65	3.30	2.19	1.50	64.5
14	**2**	1-octene (20 ml)	1.83	1.83	3.27	1.99	1.64	55.6
15	**2**	1-octene (25 ml)	1.74	1.74	3.05	1.57	1.93	39.9
16	**2**	1-hexene (5 ml)	2.54	2.54	3.72	2.98	1.24	90.8
17	**2**	1-hexene (10 ml)	2.32	2.32	3.60	2.73	1.31	70.3
18	**2**	1-hexene (15 ml)	1.85	1.85	3.52	2.35	1.49	53.3
19	**2**	1-hexene (20 ml)	1.76	1.76	3.42	2.11	1.61	48.5
20	**2**	1-hexene (25 ml)	1.01	1.39	2.80	1.70	1.64	41.4

[a]Condition: Temperature 25 °C, polymerization time 30 min, catalyst 2 μmol, MAO as cocatalyst 2.32 ml, Al/Ti 2000; [b] Determined by GPC using polystyrene calibration.; [c] Melting temperature of synthesized polyethylene determined by DSC.

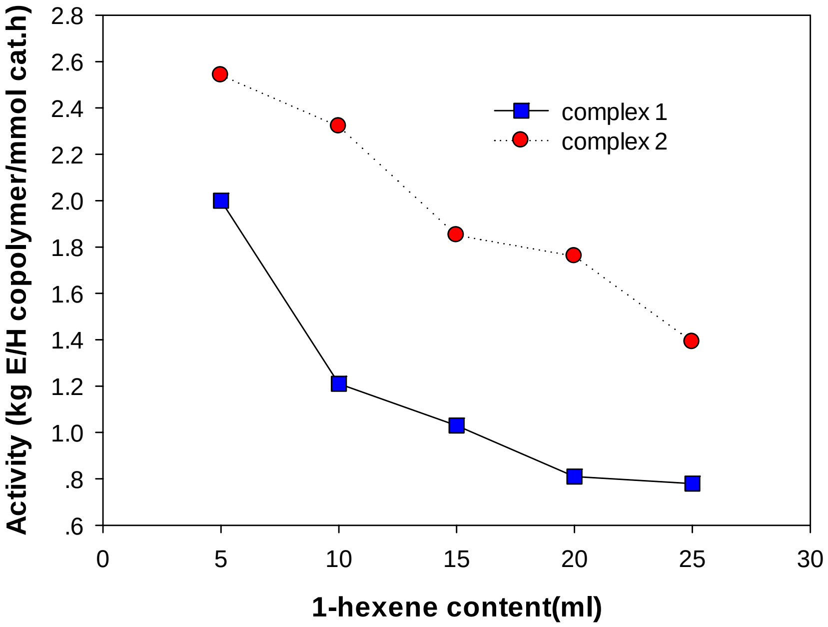


Figure 4.16 Relationship of 1-hexene content and catalytic activity of Ethylene/1-hexene copolymer obtained from various phenoxy-imine catalysts

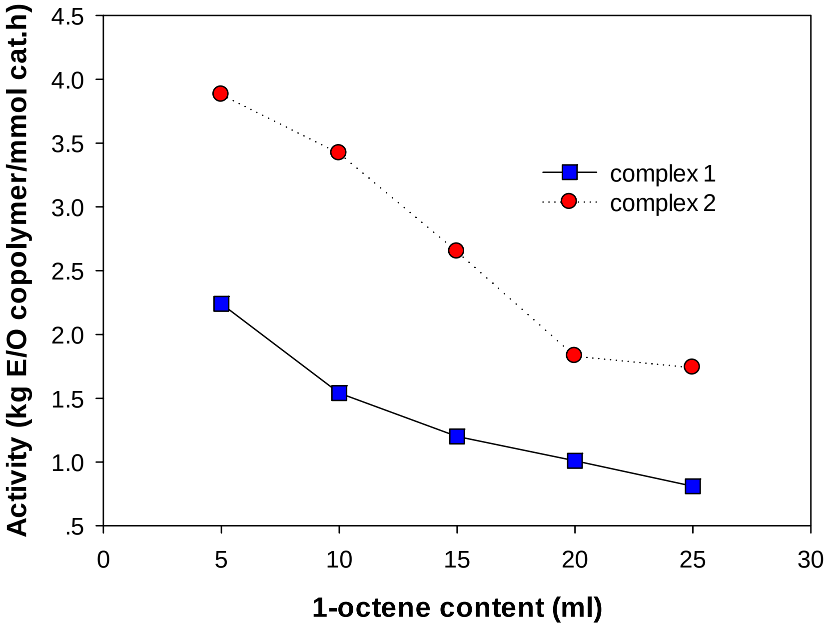


Figure 4.17 Relationship of 1-octene content and catalytic activity of Ethylene/1-octene copolymer obtained from various phenoxy-imine catalysts

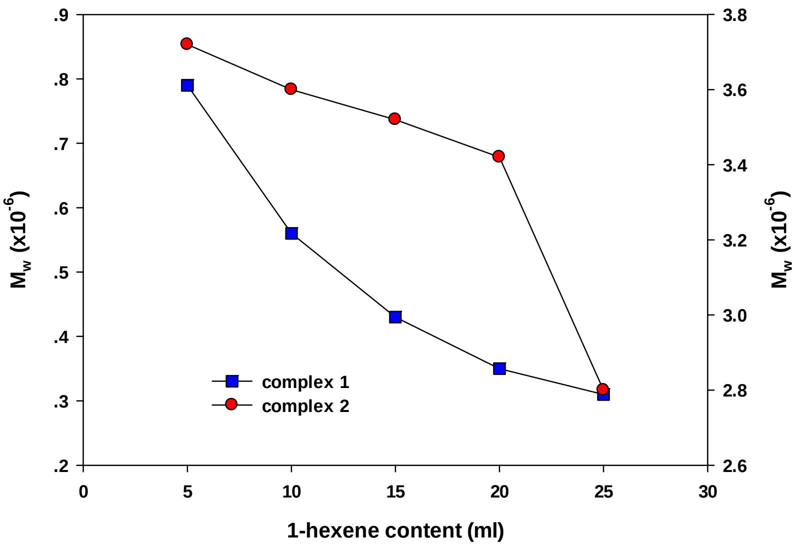


Figure 4.18 Relationship of 1-hexene content and molecular weight of Ethylene/1-hexene copolymer obtained from various phenoxy-imine catalysts

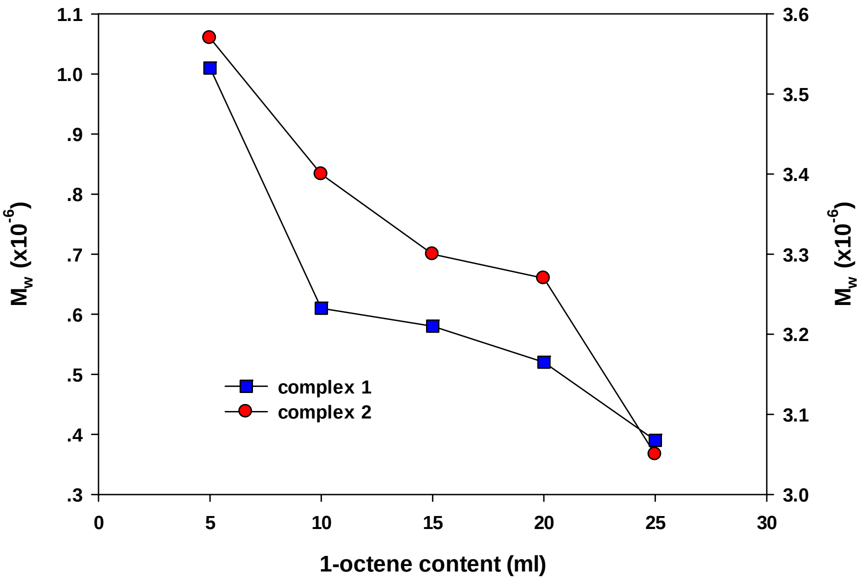


Figure 4.19 Relationship of 1-octene content and molecular weight and PDI of Ethylene/1-hexene copolymer obtained from various phenoxy-imine catalysts

4.5.2 The effect of polymerization time on catalytic activity of Ti-FI complex/MAO for the copolymerization

In order to study the effect of residence time on the activity of both Ti-FI complexes (1, 2) activated with MAO for copolymerization of ethylene and higher α-olefin. The experiment of both copolymerizations was carried out at temperature of 25 °C, catalyst 2 μmol, and Al/Ti ratio of 2000 under ethylene pressure 1 bar. The results are collected in Table 4.22. Yield of E/H copolymer increased with increasing the polymerization time as shown in Figure 4.20, whereas the catalytic activity of both complexes (1, 2) activated with MAO decreased with increasing the polymerization time for copolymerization of ethylene and 1-hexene due to active sites covered with polymer. Likewise, the activity of both complexes in the presence of MAO decreased with the enhancement of residence time for the copolymerization of ethylene and 1-octene but E/O copolymer yield enhanced with the increase of the residence time as seen in Figure 4.21. In addition, the molecular weight of the E/H copolymer produced with both complexes (1, 2) activated with MAO increase with increasing the polymerization time. Plot of polymerization time and the molecular weight of the E/O copolymer prepared with both complexes (1, 2) activated with MAO was observed as the same trend in that of E/H copolymer as shown in Figure 4.22 and 4.23 respectively. The single site characteristic of both complexes in the presence of MAO for copolymerization of ethylene and higher a-olefins (1-hexene, 1-octene) was demonstrated by the observed narrow polydispersity less than 1.65. The melting temperature of E/H copolymer obtained from complex 2 is in the range of 70.3-71.2 which is lower than that with complex 1. In the same way, the melting temperature of E/O copolymer prepared with complex 2 is lower than that with complex 1 as shown in Table 4.22, entry 9-12 and 1-4 respectively.

Table 4.22 Copolymerization of ethylene and higher α-olefin obtained from various catalysts in presence of MAO with various polymerization times.

Entry	complex	comonomer	time	Yield (g)	Activity (kg PE/mmol cat. h)	M_w[b] ($\times 10^{-6}$)	M_n[b] ($\times 10^{-6}$)	PDI[b]	T_m[c] (°C)
1	**1**	1-octene	30	1.54	1.54	0.69	0.45	1.65	119.7
2	**1**	1-octene	60	3.09	1.54	0.78	0.53	1.58	120.3
3	**1**	1-octene	90	4.30	1.34	0.87	0.62	1.54	119.8
4	**1**	1-octene	120	5.35	1.33	0.93	0.68	1.50	119.8
5	**1**	1-hexene	30	1.21	1.21	0.56	0.36	1.55	119.2
6	**1**	1-hexene	60	2.32	1.16	0.71	0.47	1.51	119.3
7	**1**	1-hexene	90	3.01	1.00	0.82	0.54	1.50	119.3
8	**1**	1-hexene	120	4.04	1.01	0.84	0.56	1.49	118.8
9	**2**	1-octene	30	3.42	3.42	3.40	2.41	1.40	76.4
10	**2**	1-octene	60	4.35	2.17	3.82	3.00	1.27	76.9
11	**2**	1-octene	90	4.67	1.55	3.93	3.15	1.24	77.4
12	**2**	1-octene	120	5.44	1.36	4.16	3.40	1.22	76.4
13	**2**	1-hexene	30	2.32	2.32	3.60	2.73	1.31	70.3
14	**2**	1-hexene	60	2.93	1.46	3.93	3.12	1.25	70.0
15	**2**	1-hexene	90	4.03	1.35	4.01	3.37	1.18	70.2
16	**2**	1-hexene	120	4.78	1.18	4.19	3.62	1.15	71.2

[a]Condition: Temperature 25 °C, catalyst 2 μmol, MAO as cocatalyst 2.32 ml, Al/Ti 2000, heptane 250 ml; comonomer 10 ml [b]Determined by GPC using polystyrene calibration. ; [c]Melting temperature of synthesized polyethylene determined by DSC.

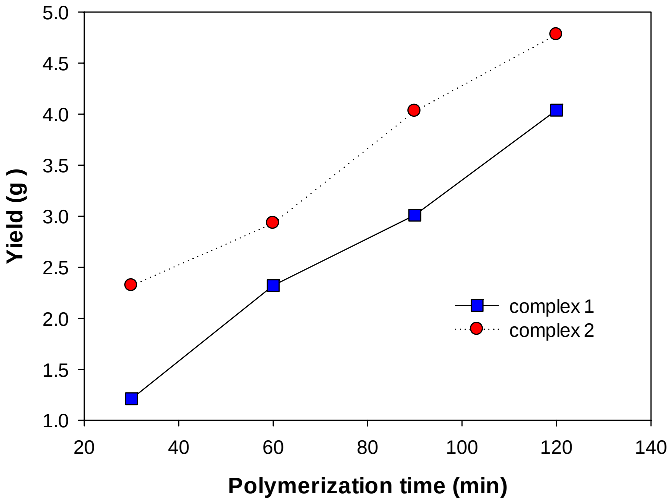


Figure 4.20 Relationship of polymerization time and yield of Ethylene/1-hexene copolymer obtained from various phenoxy-imine catalysts

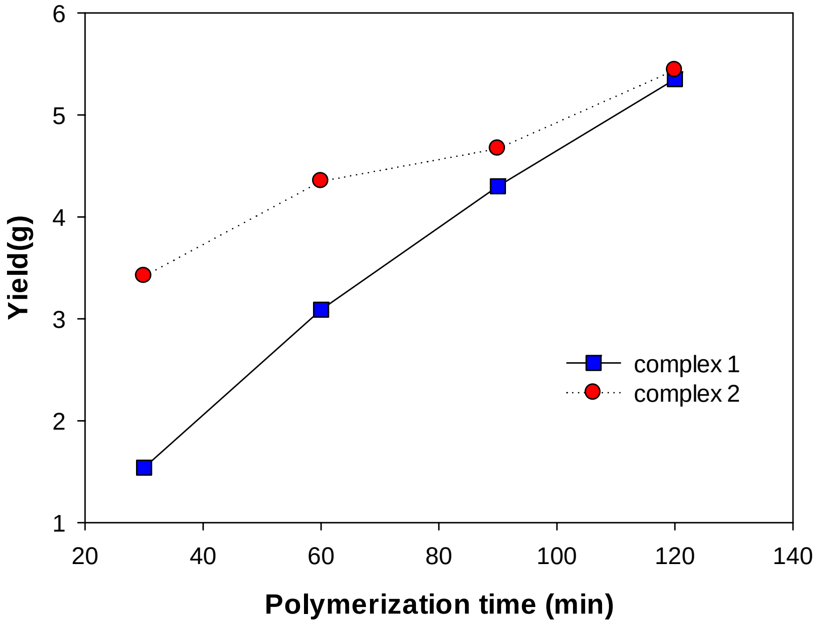


Figure 4.21 Relationship of polymerization time and yield of Ethylene/1-octene copolymer obtained from various phenoxy-imine catalysts

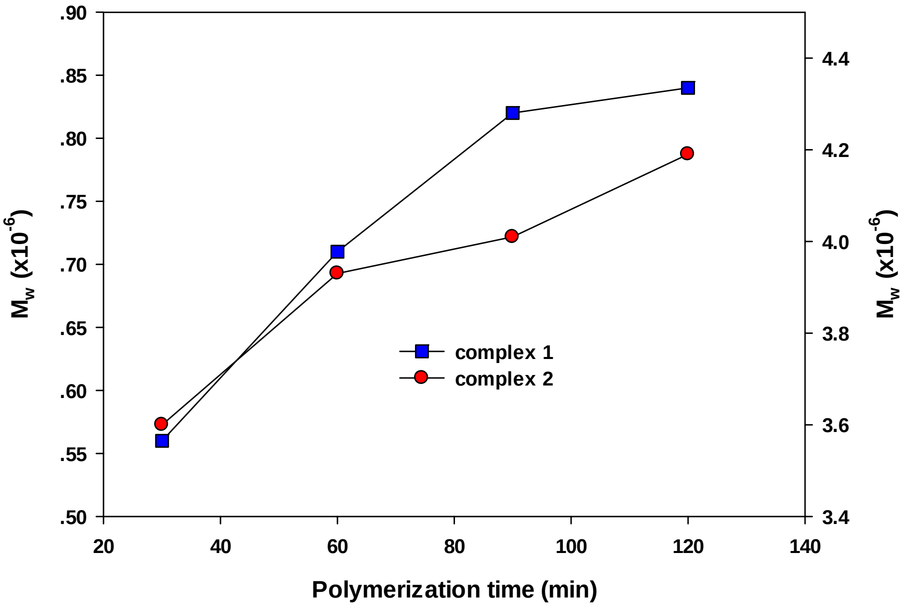


Figure 4.22 Relationship of polymerization time and molecular weight of Ethylene/1-hexene copolymer obtained from various phenoxy-imine catalysts

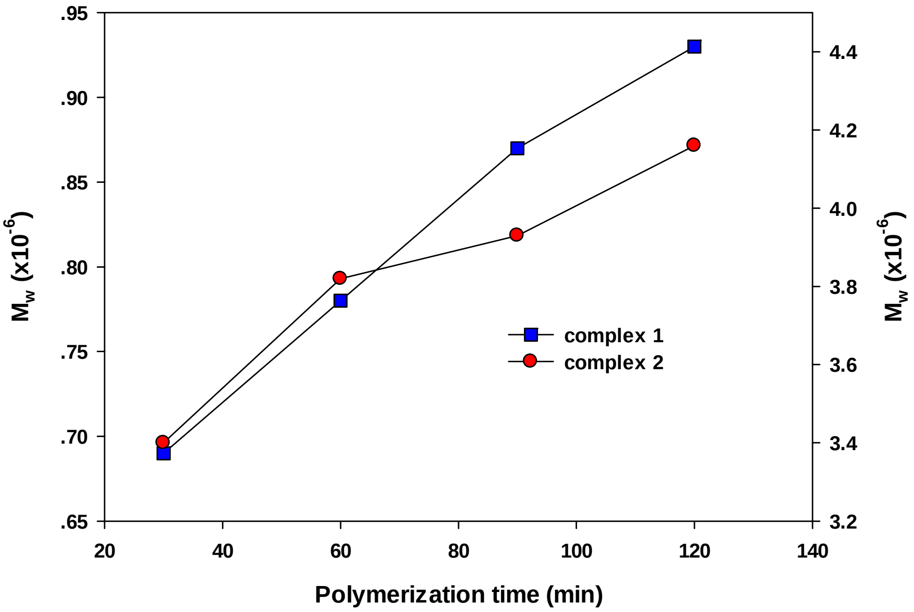


Figure 4.23 Relationship of polymerization time and molecular weight of Ethylene/1-octene copolymer obtained from various phenoxy-imine catalysts

4.5.3 The effect of Al/Ti ratio on catalytic activity of both complexes in copolymerization

The data in Table 4.23 reveal that the catalytic activity of complex 1 and 2 increase as the increase of Al/Ti ratio from 1000 to 5000 and 6000, respectively for the copolymerization of ethylene and 1-octene as shown in Figure 4.26. Additionally, the activity of complex 1 and 2 in copolymerization of ethylene and 1-hexene enhanced with the increase of Al/Ti ratio from 1000 to 4000 and 5000, respectively similar to E/O copolymerization as seen in Figure 4.25. Plot of molecular weight of E/H copolymers prepared with both complexes and the Al/Ti ratio as shown in Figure 4.26 have the same trend with that between activities of both catalysts and the Al/Ti ratio because of catalyst deactivation by overdose MAO. For copolymerization of ethylene and 1-octene, the molecular weight of copolymer obtained from complex 1 decreased with increasing the Al/Ti ratio as seen in Figure 4.27 due to steric hindrance of 1-octene comonomer resulting in the slower rate of ethylene insertion and the chain transfer to β-hydrogen elimination. However, the molecular weight of copolymer obtained from complex 2 increased with the enhancement of the Al/Ti ratio due to attractive interaction between o-F on catalyst and growing polymer chain resulting in β-hydrogen suppression.

Table 4.23 Copolymerization of ethylene and higher α-olefin obtained from various catalysts in presence of MAO with various Al/Ti ratios

Entry	**complex**	**comonomer**	**Al/Ti ratio**	**Yield (g)**	**Activity (kg PE/mmol cat. h)**	M_w[b] (× 10^{-6})	M_n[b] (× 10^{-6})	**PDI**[b]	T_m[c] (°C)
1	**1**	1-octene	1000	1.42	1.42	0.67	0.46	1.44	120.5
2	**1**	1-octene	2000	1.54	1.54	0.61	0.39	1.55	120.2
3	**1**	1-octene	3000	1.63	1.63	0.60	0.36	1.64	120.3
4	**1**	1-octene	4000	1.79	1.79	0.59	0.35	1.66	119.9
5	**1**	1-octene	5000	1.83	1.83	0.58	0.33	1.75	120.3
6	**1**	1-octene	6000	1.89	1.89	0.58	0.29	1.99	120.5
7	**1**	1-octene	7000	1.87	1.87	0.56	0.27	2.04	121.3
8	**1**	1-hexene	1000	1.14	1.14	0.55	0.35	1.57	119.1
9	**1**	1-hexene	2000	1.21	1.21	0.56	0.36	1.55	118.9
10	**1**	1-hexene	3000	1.36	1.36	0.57	0.40	1.44	119.8
11	**1**	1-hexene	4000	1.52	1.52	0.61	0.44	1.36	119.2
12	**1**	1-hexene	5000	1.45	1.45	0.59	0.41	1.41	119.6
13	**1**	1-hexene	6000	1.32	1.32	0.56	0.39	1.43	119.4
14	**1**	1-hexene	7000	1.31	1.31	0.54	0.36	1.49	119.7
15	**2**	1-octene	1000	1.90	1.90	3.20	2.22	1.44	78.5
16	**2**	1-octene	2000	3.42	3.42	3.40	2.41	1.40	76.6
17	**2**	1-octene	3000	4.01	4.01	3.41	2.61	1.30	76.5
18	**2**	1-octene	4000	4.47	4.47	3.61	3.70	1.30	74.8
19	**2**	1-octene	5000	4.65	4.65	3.70	2.90	1.27	77.4
20	**2**	1-octene	6000	4.31	4.31	4.01	3.37	1.19	77.7
21	**2**	1-octene	7000	4.07	4.07	4.12	3.53	1.16	76.9
22	**2**	1-hexene	1000	1.15	1.15	3.32	2.05	1.62	72.1
23	**2**	1-hexene	2000	2.32	2.32	3.60	2.73	1.31	70.1
24	**2**	1-hexene	3000	2.61	2.61	3.87	3.11	1.24	70.3
25	**2**	1-hexene	4000	3.40	3.40	3.96	3.25	1.21	71
26	**2**	1-hexene	5000	3.84	3.84	4.09	3.28	1.18	70.5
27	**2**	1-hexene	6000	3.83	3.83	4.02	3.45	1.23	70.9
28	**2**	1-hexene	7000	3.70	3.70	3.91	3.25	1.26	70.4

[a] Condition: Temperature 25 °C, catalyst 2 μmol, heptane 250 ml, polymerization time 30 min, comonomer 10 ml

[b] Determined by GPC using polystyrene calibration.

[c] Melting temperature of synthesized polyethylene determined by DSC.

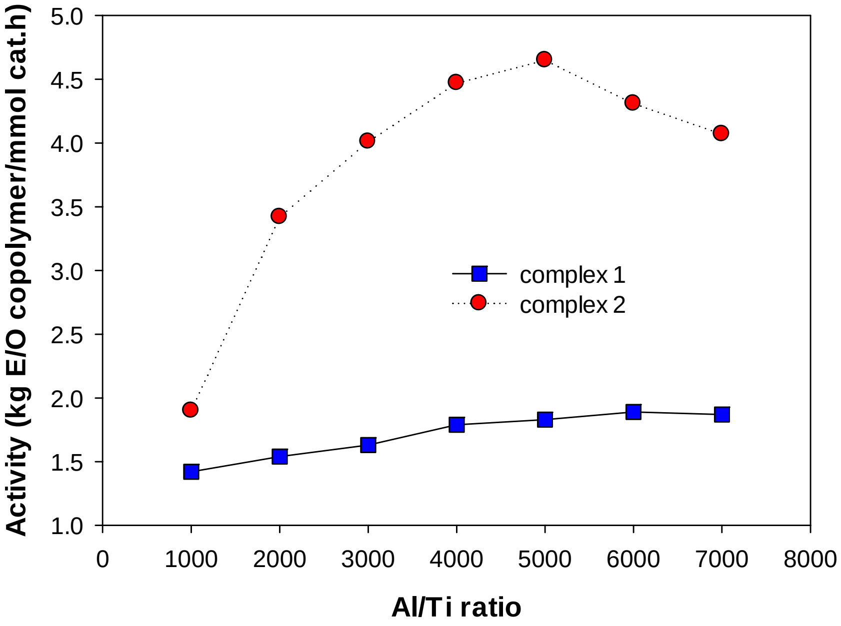


Figure 4.24 Relationship of Al/Ti ratio and catalytic activity of Ethylene/1-octene copolymer obtained from various phenoxy-imine catalysts

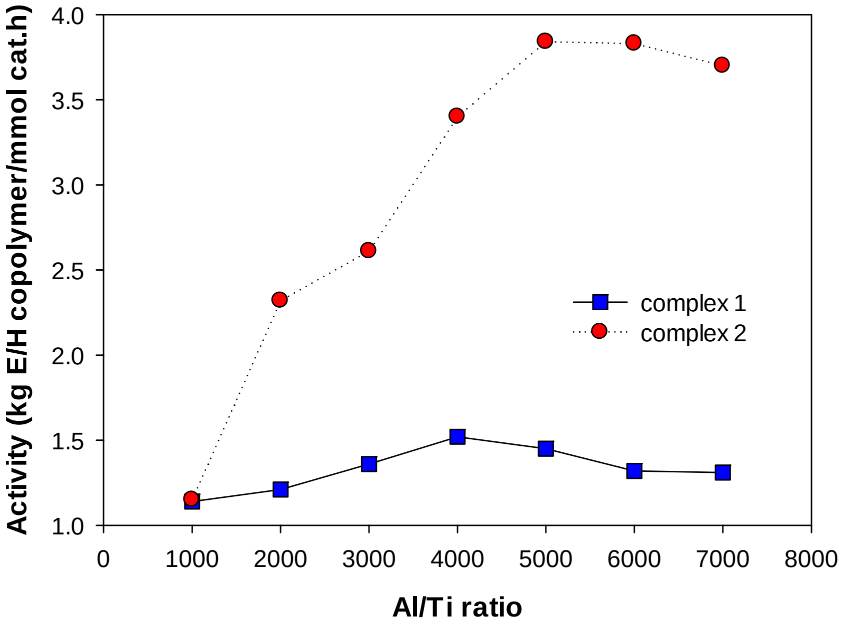


Figure 4.25 Relationship of Al/Ti ratio and catalytic activity of Ethylene/1-hexene copolymer obtained from various phenoxy-imine catalysts

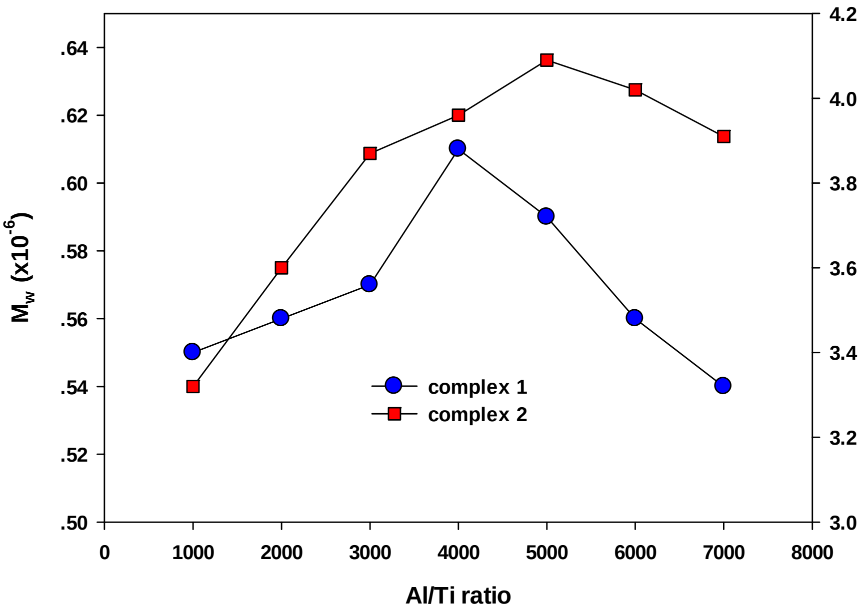


Figure 4.26 Relationship of Al/Ti ratio and molecular weight of Ethylene/1-hexene copolymer obtained from various phenoxy-imine catalysts

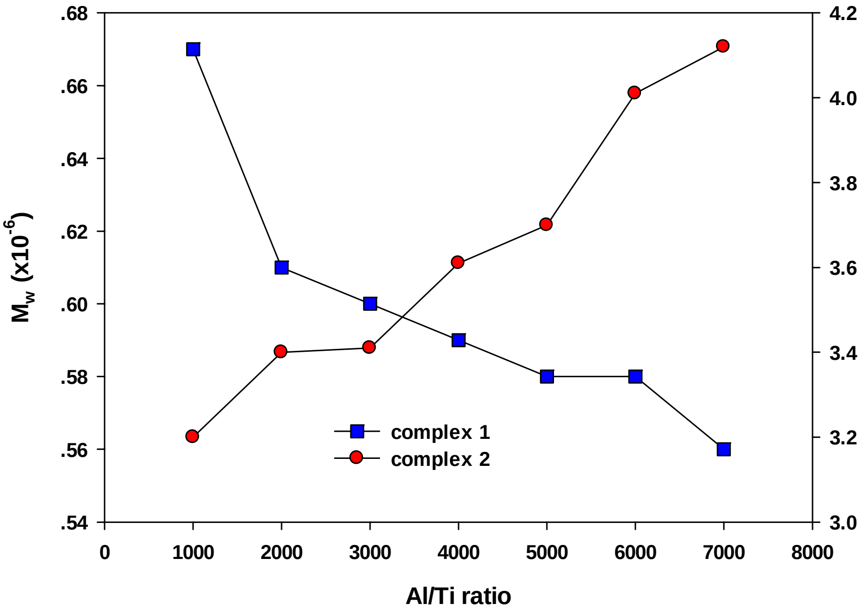


Figure 4.27 Relationship of polymerization time and molecular weight of Ethylene/1-octene copolymer obtained from various phenoxy-imine catalysts

4.5.4 Characterization of E/H copolymer and E/O copolymer with ^{13}C NMR spectroscopy.

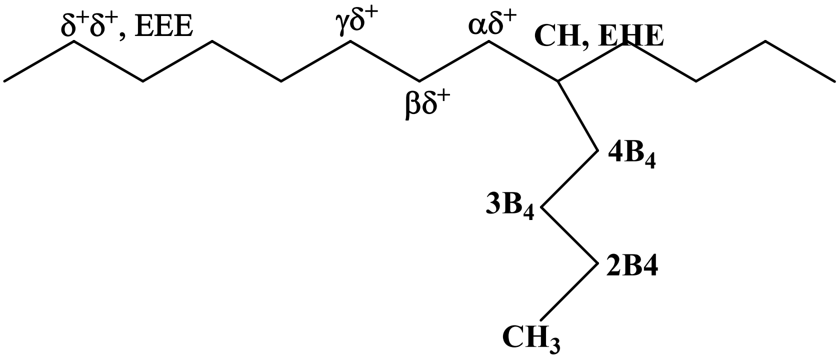
4.5.4.1. Characterization of E/H and E/O copolymer obtained with complex 2/MAO

Ethylene/1-hexene copolymer composition and sequence distribution was determined with using ^{13}C- NMR spectroscopy. The method calculated the comonomer incorporation and nomenclature about monomer unit sequence within copolymer chain suggested by Randall were employed. The results of comonomer contents and monomer sequence distribution in E/H copolymer were compiled in Table 4.24. The amount of comonomer incorporation in E/H copolymer increased with the increase of comonomer content added in copolymerization reaction with complex 2/MAO. While, ethylene content within E/H copolymer decrease with enhancing of comonomer contents used in the copolymerization system. From the Table 4.24, the sequence of HEH was observed in E/H copolymer chain when used the 1-hexene contents in the copolymerization not less than 15 ml. In addition, the monomer sequences of EHH, EHE and HEE in E/H copolymer enhanced with increasing of 1-hexene content in polymerization process contrasted to the EEE sequences decreased moderately and no sequence of HHH was observed. At 1-hexene content in the reaction of 25 ml, the E/H copolymer consists of 1-hexene insertion about 12.92 mol % and ethylene content of 87.08 mol %. For the above results, the complex 2 activated with MAO can produce copolymer of ethylene and 1-hexene having different 1-hexene incorporation depending on the comonomer contents feeding in the polymerization system. The results corresponding to the fluorinated phenoxy-imine zirconium and titanium complexes activated with MAO exhibited highly active for copolymerization of ethylene and 1-hexene and gave copolymer with higher 1-hexene incorporation. [65, 75]

Table 4.24 Triads distribution based on ^{13}C NMR spectra for E/H copolymer prepared with complex 2/MAO

Run	Comonomer (ml)	[HHH]	[EHH]	[EHE]	[EEE]	[HEH]	[HEE]	%E	%H
1	Hexene (5)	0	0.0026	0.0131	0.9555	0	0.0288	98.43	1.57
2	Hexene (10)	0	0.0074	0.0373	0.8734	0	0.0819	95.53	4.47
3	Hexene (15)	0	0.0360	0.0584	0.7537	0.0009	0.1510	90.56	9.44
4	Hexene (20)	0	0.0457	0.0686	0.7058	0.0032	0.1765	88.56	11.44
5	Hexene (25)	0	0.0555	0.0737	0.6706	0.0028	0.1974	87.08	12.92

The microstructure characteristic of the E/H copolymer prepared with complex 2/MAO was investigated based on the ^{13}C NMR results. General features of the different E/H copolymer spectra have been reported in many published research. The nomenclature of carbon atoms was typically used for the description of the monomer sequence distribution in copolymer of ethylene and 1-hexene as shown in Scheme 4.3



Scheme 4.3 Nomenclature of chain structures for ethylene/1-hexene copolymers.

The ^{13}C NMR spectra of E/H copolymer produced with complex 2/MAO in various comonomer contents in feed were shown in Figure 4.28. The ^{13}C NMR signals of E/H copolymer were assigned on the basis of the published research. The results of chemicals shift assignments for each peak in the ^{13}C NMR spectra were summarized in Table 4.25. The ethylene/1-hexene copolymer prepared with complex 2/MAO contained the different monomer sequence distribution of EHE, EEE, HEE, EHEE, HEEE, EHEH and etc. depending on the 1-hexene incorporation. The signals at 29.98 ppm were assigned to the $\delta^+\delta^+$ carbon in the ethylene sequence of copolymer.

The signals at 23.38, 29.57 and 34.21 ppm were assigned to the $2B_4$, $3B_4$ and $4B_4$ carbon, confirming the chain branching of 1-hexene formed in the polymer. While, the signals at 33.57 ppm assigned to HHH triad sequences was not observed, indicating the 1-hexene unable to form long sequences in E/H copolymer. For run 4 and 5, the observed signals at 24.58 and 30.93 ppm was assigned to EHEHE and HEEH in which 1-hexene units were separated by one or two ethylene units, respectively. As a result, the complex 2/MAO can produce the E/H copolymer with uniform 1-hexene incorporation because of the isolated H units in polymer chain.

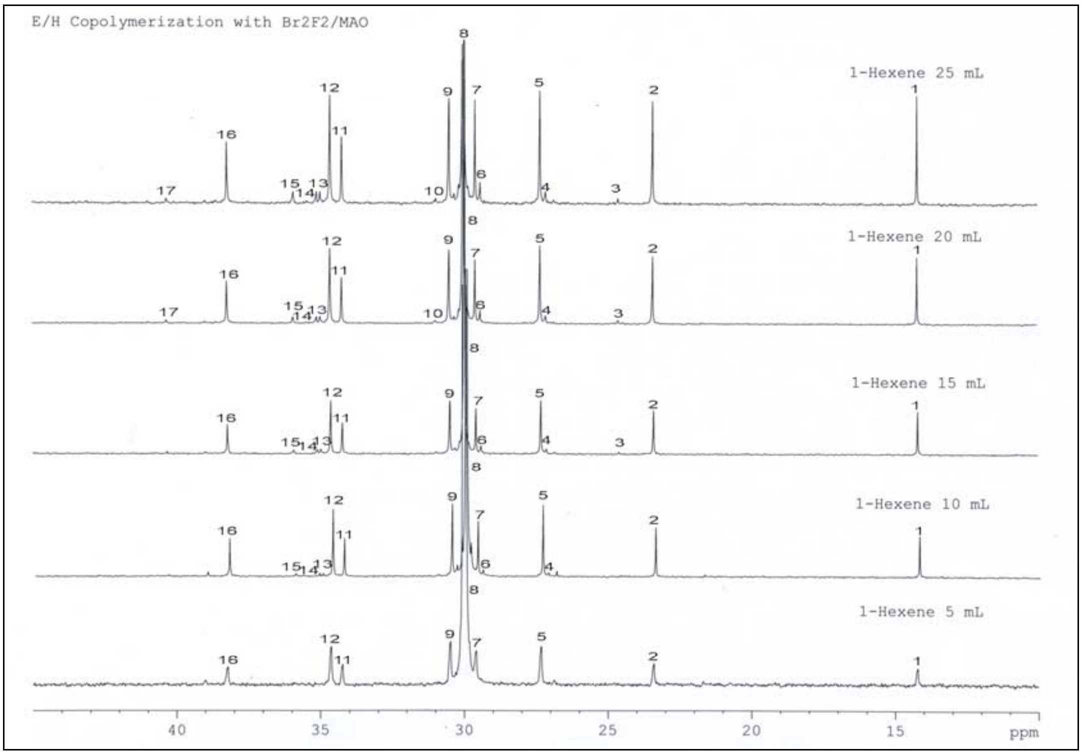


Figure 4.28 ^{13}C NMR spectrum of E/H copolymer at 125 °C in 1,1,2,2-tetraethylchloroethane

Table 4.25 The observed signal assignment in ^{13}C NMR spectra of copolymer of ethylene and 1-hexene.

Peak No.	Carbon type	Monomer sequence	Chemicals shift (ppm)				
			Run 1	Run 2	Run 3	Run 4	Run 5
1	CH_3	EHE+EHH+HHE+HHH	14.21	14.20	14.20	14.20	14.20
2	$2B_4$	EHE+EHH+HHE+HHH	23.39	23.39	23.38	23.38	23.38
3	ββ	EHEHE			24.58	24.58	24.59
4	βδ+	HHEE+EEHH		27.11	27.11	27.11	27.11
5	βδ+	EHEE+EEHE	27.31	27.31	27.30	27.31	27.30
6	$3B_4$	EHH+HHE		29.40	29.39	29.39	29.39
7	$3B_4$	EHE	29.58	29.58	29.57	29.57	29.57
8	$\delta^+\delta^+$	(EEE)n	29.97	29.98	29.97	29.98	29.97
9	γδ+	HEEE+EEEH	30.47	30.47	30.47	30.47	30.47
10	γγ	HEEH				30.93	30.93
11	4B4	EHE	34.22	34.22	34.21	34.21	34.21
12	αδ+	EHEE+EEHE	34.62	34.61	34.61	34.61	34.61
13	αδ+	HHEE+EEHH		34.96	34.96	34.96	34.96
14	αγ	HHEH+HEHH		35.08	35.08	35.08	35.08
15	CH	EHH+HHE		35.91	35.90	35.90	35.90
16	CH	EHE	38.21	38.21	38.21	38.21	38.21
17	αα	EHHE				40.31	40.31

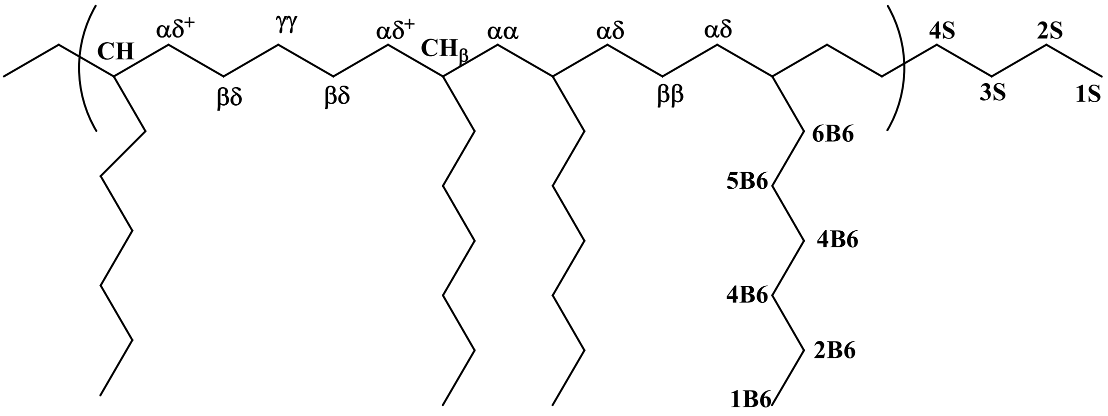
The composition and monomer sequence distribution of E/O copolymer were analyzed by ^{13}C NMR spectroscopy. The calculation method to find the comonomer incorporation and nomenclature of monomer sequences within E/O copolymer chain suggested by Randall were employed. The results of comonomer contents and monomer sequence distribution in E/O copolymer were summarized in Table 4.26. The amount of comonomer incorporation in E/O copolymer increased with the increase of comonomer contents feeding in polymerization reaction with complex 2/MAO. While, ethylene content within E/O copolymer decrease with enhancing of comonomer contents used in the copolymerization system. The results of E/O copolymer were the same trend as those of E/H copolymer. From the Table 4.27, the sequence of OEO and OOO was observed in E/O copolymer chain when used the 1-octene contents in the copolymerization not less than 25 ml. In addition, the monomer sequences of EOE, and OEE in E/O copolymer increase with increasing of 1-hexene content in polymerization process contrasted to the EEE sequences decreased moderately. At 1-hexene content in the reaction of 25 ml, the E/H copolymer consists of 1-hexene insertion about 7.23 mol % and ethylene content of 92.77 mol %. From the above results, the complex 2 activated with MAO can produce copolymer of ethylene and 1-octene having different 1-octene incorporation depending on the comonomer contents feeding in the polymerization system. However, the E/O copolymer prepared with 2/MAO having 1-octene incorporation of 7.23 mol %, whereas the E/H copolymer produced with 2/MAO having 1-hexene incorporation of 12.92 mol % under the same comonomer contents in the polymerization. The results are corresponding to ziroconocene aluminohydride complexes supported on SiO_2 in the presence of MAO for copolymerization of ethylene and alpha-olefins. At high comonomer additions, propylene comonomer showed the highest incorporation, followed by 1-butene, 1-hexene and 1-octene, respectively. The level of comonomer incorporation has been related to the steric hindrance produced by the alpha-olefins in the copolymerization reactions. [92]

In addition to corresponding with bis(β-enaminoketonato) titanium complexes with MMAO as cocatalyst, the comonomer (1-hexene, 1-octene) incorporation increased along with increasing the comonomer concentration.[93] The tendency of incorporation was 1-hexene > 1-octene, which agreed with the results of metallocene catalyst. [94] The bulkier steric hindrance of 1-octene comparing with that of 1-hexene may be disturbed olefin coordination or insertion according to the literature of Randall et al. [95, 96]

Table 4.26 Triads distribution based on ^{13}C NMR spectra for E/O copolymer prepared with complex 2/MAO

Run	Comonomer (ml)	[OOO]	[EOO]	[EOE]	[EEE]	[OEO]	[OEE]	%E	%O
1	Octene (5)	0	0	0.0103	0.9640	0	0.0257	98.97	1.03
2	Octene (10)	0	0	0.0229	0.9260	0	0.0511	97.72	2.28
3	Octene (15)	0	0	0.0412	0.8629	0	0.0959	95.88	4.12
4	Octene (20)	0	0	0.0571	0.8224	0	0.1204	94.29	5.71
5	Octene (25)	0.0029	0	0.0694	0.7639	0.0035	0.1602	92.77	7.23

The microstructure characteristic of the E/O copolymer produced with complex 2/MAO was investigated based on the ^{13}C NMR results. General features of the different E/O copolymer spectra have been reported in many published paper. The nomenclature of carbon atoms was typically used for the description of the monomer sequence distribution in copolymer of ethylene and 1-octene as shown in Scheme 4.4.



Scheme 4.4 Nomenclature of chain structures for ethylene/1-octene copolymers.

The ^{13}C NMR spectra of E/O copolymer prepared with complex 2/MAO in various comonomer contents in feed were illustrated in Figure 4.29. The ^{13}C NMR signals of E/H copolymer were assigned on the basis of the published research. The results of chemicals shift assignments for each peak in the ^{13}C NMR spectra were collected in Table 4.27. The ethylene/1-octene copolymer produced with complex 2/MAO contained the different monomer sequence distribution of EOE, EEE, OEE, EOEE, OEEE, EOEO and etc. depending on the 1-octene incorporation. The signals at 29.98 ppm (peak no.7) were assigned to the $\delta^+\delta^+$ carbon in the ethylene sequence of copolymer. The signals at 22.90, 32.22, 29.97, 27.77 and 34.61 ppm were assigned to the $2B_6$, $3B_6$, $4B_6$, $5B_6$ and $6B_6$ carbon, confirming the chain branching of 1-octene formed in the polymer. While, the signals at 40.33 ppm assigned to OOO triad sequences was only observed in the copolymerization reaction with 1-octene comonomer content of 25 ml in feed. As a result, the complex 2/MAO can produce the E/O copolymer with different 1-octene incorporation.

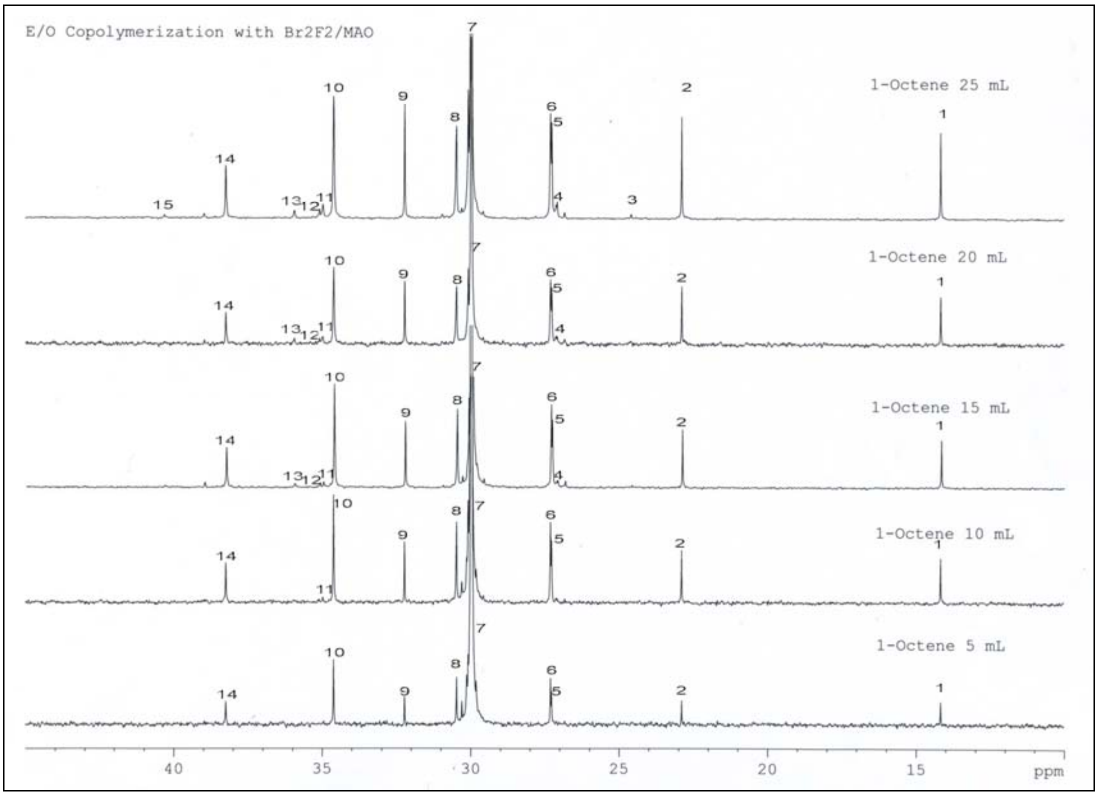


Figure 4.29 ^{13}C NMR spectrum of E/O copolymer at 125 ^{o}C in 1,1,2,2-tetraethylchloroethane

Table 4.27 The observed signal assignment in ^{13}C NMR spectra of copolymer of ethylene and 1-hexene.

Peak No.	Carbon type	Monomer sequence	Chemicals shift (ppm)				
			Run 1	Run 2	Run 3	Run 4	Run 5
1	1S+1B$_6$	EOE+OOE+OOO	14.17	14.17	14.17	14.17	14.17
2	2S+2B$_6$	EOE+OOE+OOO	22.90	22.90	22.90	22.89	22.89
3	Bβ	OEO					24.58
4	$\beta\delta^+$	OOEE			27.12	27.12	27.08
5	5B$_6$	EOE+OOE+OOO	27.27	27.27	27.27	27.26	27.26
6	$B\delta^+$	OEE	27.30	27.30	27.30	27.30	27.30
7	$\delta^+\delta^+$+4B$_6$	(EEE)n	29.97	29.98	29.98	29.97	29.98
8	γδ+	OEEE	30.47	30.47	30.47	30.47	30.47
9	3S+3B$_6$	EOE+OOE+OOO	32.22	32.22	32.22	32.22	32.22
10	αδ+6B$_6$	EOEE+EOE	34.61	34.61	34.61	34.61	34.61
11	αγ	EOEO		34.98	34.98	34.98	34.97
12	αδ+6B$_6$	EEOO+EOO			35.09	35.08	35.08
13	CH	OOE			35.94	35.94	35.93
14	CH	EOE	38.24	38.24	38.24	38.24	38.24
15	αα	EOOE					40.31

4.5.4.2. Characterization of E/H and E/O copolymer obtained with complex 1/MAO

Ethylene/1-hexene copolymer composition and monomer sequence distribution was analyzed with using ^{13}C- NMR spectroscopy. The ^{13}C-NMR spectrum of Ethylene/1-hexene copolymer prepared with complex 1/MAO was showed in Figure 4.30. The calculation method determining the comonomer incorporation and nomenclature about monomer unit sequence within copolymer chain suggested by Randall were used. The results of comonomer contents and monomer sequence distribution in E/H copolymer were collected in Table 4.28.

Table 4.28 Triads distribution based on ^{13}C NMR spectra for E/H copolymer prepared with complex 1/MAO

Run	Comonomer (ml)	[HHH]	[EHH]	[EHE]	[EEE]	[HEH]	[HEE]	%E	%H
1	Hexene (5)	0	0	0	1.0	0	0	100	0
2	Hexene (10)	0	0.0001	0	0.9997	0	0.0001	99.99	0.01
3	Hexene (15)	0	0.0020	0.0012	0.9923	0	0.0044	99.68	0.32
4	Hexene (20)	0	0.0008	0.0019	0.9925	0	0.0047	99.72	0.28
5	Hexene (25)	0	0	0.0011	0.9967	0	0.0022	99.89	0.11

As the results for copolymerization of ethylene and 1-hexene in Table 4.28, it was found that polymer prepared with complex 1/MAO has the extremely small amount of 1-hexene incorporation within polymer chain. In addition, when increasing the comonomer content from 5 to 20 ml into polymerization reaction, this catalyst system is unable to polymerize 1-hexene incorporated with ethylene, comparing with complex2/MAO. It is implied that the catalyst structure have an influence on comonomer content in polymer backbone.

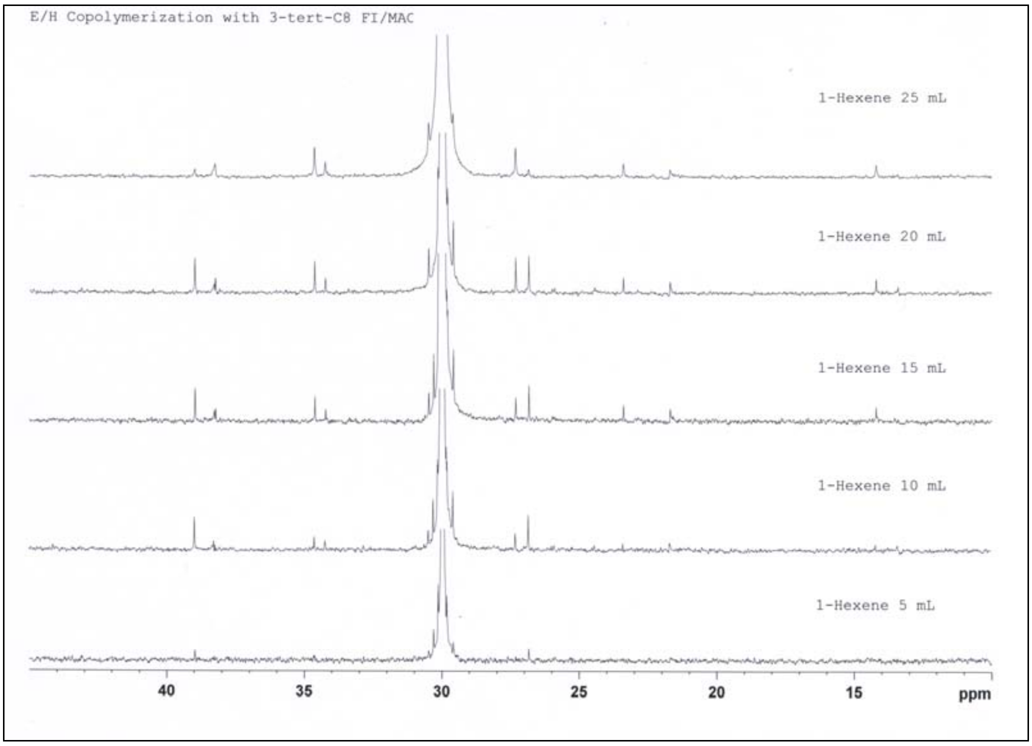


Figure 4.30 ^{13}C NMR spectrum of E/H copolymer at 125 ^{o}C in 1,1,2,2-tetraethylchloroethane

The composition and monomer sequence distribution of E/O copolymer were investigated by ^{13}C NMR spectroscopy. The results of ^{13}C NMR spectrum are shown in Figure 4.31. The calculation method to find the comonomer incorporation and nomenclature of monomer sequences within E/O copolymer chain suggested by Randall were used. The results of comonomer contents and monomer sequence distribution in E/O copolymer were summarized in Table 4.29.

Table 4.29 Triads distribution based on ^{13}C NMR spectra for E/O copolymer prepared with complex 2/MAO

Run	Comonomer (ml)	[OOO]	[EOO]	[EOE]	[EEE]	[OEO]	[OEE]	%E	%O
1	Octene (5)	0	0	0.0003	0.9996	0	0.0001	99.97	0.03
2	Octene (10)	0	0	0.0020	0.9958	0	0.0022	99.80	0.20
3	Octene (15)	0	0	0.0025	0.9943	0	0.0032	99.75	0.25
4	Octene (20)	0	0	0.0020	0.9933	0	0.0048	99.80	0.20
5	Octene (25)	0	0	0.0027	0.9927	0	0.0046	99.73	0.27

As the results for copolymerization of ethylene and 1-octene in Table 4.29, it was found that polymer prepared with complex 1/MAO has the extremely small amount of 1-octene incorporation within polymer chain as similar to the results of ethylene and 1-hexene copolymers. Additionally, when increasing the 1-octene comonomer content from 5 to 25 ml into polymerization reaction, this catalyst system is unable to polymerize 1-octene incorporated with ethylene, comparing with complex2/MAO. It is implied that the catalyst structure have an influence on comonomer content in polymer backbone.

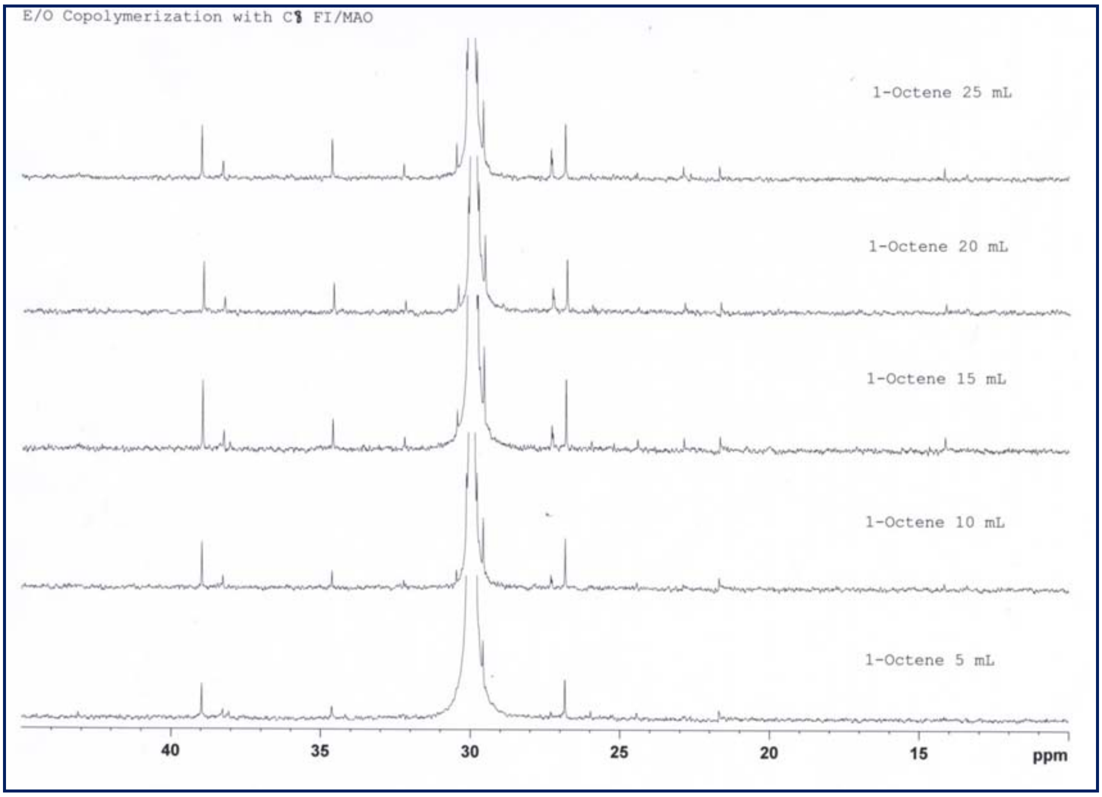


Figure 4.31 ^{13}C NMR spectrum of E/O copolymer at 125 °C in 1,1,2,2-tetraethylchloroethane

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Bis [*N*-(3-*tert*-butylsalicylidene)cyclooctylamine] titanium dichloride can produce HMWPE and UHMWPE with narrow molecular weight distribution. This complex can polymerize ethylene in the living fashion as same as the *ortho*-fluorinated aromatic ring on N-substituent of phenoxyimine complex. The higher catalyst concentration has an effect on the catalytic activity because of bimolecular process. Additionally, MAO/catalyst [Al/Ti] ratio has an influence on the catalytic activity as well because MAO can act as a scavenger for removing of impurities in the system, an activator for changing the catalyst to active form and a charge transfer agent for terminating the polymer chain. Changing the cycloalkyl groups on the N-substituent of phenoxyimine complex has an effect on the activity. It is demonstrated that the bulkier group of cyclooctyl in complex 1 exhibits higher activity than that of the cycloheptyl in analogous complex 2. Besides, the increased ethylene pressure results in the dramatic increase of catalytic activity because of higher monomer concentration near active sites. The polyethylene obtained from complex 1and 2 have molecular weight in the range of 1,230,000-2,330,000 g/mole and melting temperature between 126.5 and 128^{o}C.

Three fluorinated bis(phenoxy-imine) titanium complexes bearing halide substituents on the *ortho* position of the phenoxy rings have been synthesized and tested as precatalysts for ethylene polymerization in the presence of MAO as a cocatalyst. All complexes are active toward ethylene polymerization and produce ultra-high molecular weight polyethylene (UHMWPE). The polymerization activities are affected by the *ortho* halide substituents on the phenoxy rings. Complex **2** with *ortho* bromo substituents was found to have the highest activity at 30 °C and under atmospheric pressure. In accordance with previous studies, the presence of a fluorine atom adjacent to the imine nitrogen in the ligand is the requirement for living polymerization through the suppression of β-hydrogen transfer. The living nature of all complexes is demonstrated by the observed narrowed molecular weight distributions.

Bis[*N*-(3-*tert*-butylsalicylidene)cyclooctylamine]titanium dichloride (1) and Bis[*N*-(3-*tert*-butylsalicylidene)cycloheptylamine]titanium dichloride (Ref.1) activated with MAO were effectively active catalysts for ethylene polymerization comparing with those with various cocatalysts (TIBA, TEA, TMA and MMAO). Additionally, polyethylene obtained from complex 1 and 2 activated with alkylaluminum have molecular weight lower than those obtained from MAO and MMAO because of alkylaluminum as good chain transfer agent. While, bis-[*N*-(3,5-dibromosalicylidene)-2′,6′-difluroanilinato]titanium(IV) dichloride (2) was highly active for producing polyethylene having ultrahigh molecular weight (3,292,775) in presence of MAO only. These behavior exhibited that different catalyst activated various cocatalysts have an influence on catalytic activity and polyethylene properties. The complex 1 immobilized on $MgCl_2$/2-ethyl-1-hexanol adduct treated with TMA as activator give the highest activity for ethylene polymerization compared with that treated with TIBA and TEA, as the same trend with Ref.1 and 2. The three complexes immobilized on in situ SiO_2/MAO support give lower catalytic activity than that on in situ $MgCl_2$/2-ethyl-1-hexanol/TMA support whereas the PE molecular weight prepared with complexes 1 and ref.1 attached on both support are slightly different but the PE molecular weight obtained with complex 2 impregnated on SiO_2/MAO give extremely higher molecular weight than that on $MgCl_2$/2-ethyl-1-hexanol/TMA. Polyethylene obtained from silica-based and $MgCl_2$ -based supported catalysts showed morphologies characterized by well-defined particles and narrow polydispersities.

Bis-[*N*-(3,5-dibromosalicylidene)-2′,6′-difluroanilinato]titanium(IV) dichloride (2) activated with MAO can produce the E/H copolymer and E/O copolymer with high comonomer incorporation in contrasted to complex 1 as bis[*N*-(3-*tert*-butylsalicylidene)cyclooctylamine]titanium dichloride activated with MAO to give both copolymer with a small amount of comonomer incorporation. Complex 2 /MAO showed highly active for copolymerization of ethylene and higher α-olefin (1-hexene or 1-octene) and gave both copolymers with greatly high molecular weight and narrow polydispersities, comparing with complex 1. In addition, the comonomer content within copolymer chain increased with increasing the amount of comonomer in feed of the reaction system. The different structure of catalyst has an impact on the catalytic activity, comonomer insertion and polymer properties.

5.2 Recommendations

In the preliminary study on the effect of various catalysts on catalytic activity and polymer properties, we have attempted on testing in ethylene polymerization and ethylene/higher α-olefin copolymerization. The results showed interestingly for the case of bis-[*N*-(3,5-dibromosalicylidene)-2′,6′-difluroanilinato]titanium(IV) dichloride (complex 2) in the presence of MAO producing UHMWPE and copolymer of ethylene and 1-hexene or 1-octene with highly active. Whereas, bis[*N*-(3-*tert*-butylsalicylidene)cyclooctylamine]titanium dichloride (1) activated with MAO displayed highly active for ethylene polymerization and gave HMWPE with narrow polydispersity. In addition, both complexes immobilized on in situ $MgCl_2$/2-ethyl-1-hexenol/TMA exhibited highly active for ethylene polymerization and showed well-defined morphology.

For the above results, the unsupported and supported catalysts having different ligand structure with various cocatalysts have an influence on catalytic activity and polymer properties for homo- and co-polymerization. In the future, it is recommended that to solve the complex 2 supported on $MgCl_2$/2-ethyl-1-hexenol/TMA with various catalyst concentration again because the results was moderately different from complex 1 and Ref.1. Additionally, the catalytic activity of $MgCl_2$/2-ethyl-1-hexenol/TMA supported complex 2 reduced extremely when comparing with that of the homogeneous complex 2/MAO. Additionally, complex 1 having cyclooctyl on *N*-amine showed higher catalytic activity than ref.1 having cycloheptyl on *N*-amine but molecular weight of PE obtained from complex 1 was lower than that from ref.1 in contrast to the previous published paper about phenoxy-imine catalyst bearing bulkier substituent on *N*-amine capable to give higher activity and PE molecular weight. In addition, complex 1 show higher catalytic activity than complex 2 for ethylene polymerization but it wasn't apparent the evidence that the bulky cyclooctyl substituents on *N*-amine of phenoxy-imine catalyst was more significantly important than the bulky bromine substituent on ortho-phenoxy of phenoxy-imine catalyst in aspect of ion separation between the cationic active species and anionic MAO to open more space for the ethylene monomer insertion. Hence, it should be to investigate the substituent on *N*-amine of phenoxy-imine catalyst and the substituent on *ortho*-phenoxy of phenoxy-imine catalyst in aspects of the size and electronic feature, including the distance of space for olefin insertion influencing on catalytic activity and polymer properties for homo- and co-polymerization of ethylene and alpha-olefin.

In case of copolymerization of complex 1, the results of comonomer content in polymer chain was fluctuated, it should be to characterize ^{13}C NMR again with using probe size 10 mm for analyzing the specific polymer. Additionally, the supported complex 1 and 2 based on $MgCl_2$ without MAO as cocatalyst should be investigated for copolymerization of ethylene and higher α-olefin comparing with the unsupported complexes 1 and 2 in aspects of catalytic behavior, polymer properties and morphology.

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APPENDIX

APPENDIX

^{13}C NMR SPECTRA OF ETHYLENE/ α-OLEFIN COPOLYMER

Polymer microstructure and also traid distribution of monomer can be calculated according to the Randall in the list of reference. The detail of calculation for ethylene/ α-olefin copolymer was interpreted as follow.

Ethylene/1-hexene copolymer

The integral areas of ^{13}C-NMR spectra in the specified range of E/H copolymer are listed as follows.

T_A = 39.5 - 42 ppm
T_B = 38.1 ppm
T_C = 33 - 36 ppm
T_D = 28.5 - 31 ppm
T_E = 26.5 - 27.5 ppm
T_F = 24 - 25 ppm
T_G = 23.4 ppm
T_H = 14.1 ppm

Triad distribution was calculated as the followed formula.

$k[HHH] = 2T_A+T_B-T_G$
$k[EHH] = 2(T_G-T_B-T_A)$
$k[EHE] = T_B$
$k[EEE] = 0.5(T_A+T_D+T_F-2T_G)$
$k[HEE] = 2(T_G-T_A-T_F)$
$k[HEH] = T_F$

The factor k in the above equations is the NMR constant, which is later removed through normalization.

$\%E = [EEE] + [EEH] + [HEH]$
$\%C = [HHH] + [HHE] + [EHE]$

Ethylene/1-Octene copolymer

The integral areas of ^{13}C-NMR spectra in the specified range of E/O copolymer are listed as follows.

T_A = 39.5 - 42 ppm
T_B = 38.1 ppm
T_C = 36.4 ppm
T_D = 33 – 36 ppm
T_E = 28.5 - 31 ppm
T_F = 25.5 - 27.5 ppm
T_G = 24 - 25 ppm
T_H = 22 - 23 ppm
T_I = 14 – 15 ppm

Triad distribution was calculated as the followed formula.

$k[OOO] = T_A - 0.5T_C$
$k[EOO] = T_C$
$k[EOE] = T_B$
$k[EEE] = 0.5T_F - 0.25T_E - 0.25T_G$
$k[OEE] = T_G - T_E$
$k[OEO] = T_H$

The factor k in the above equations is the NMR constant, which is later removed through normalization.

$\%E = [EEE] + [EEO] + [OEO]$
$\%C = [OOO] + [OOE] + [EOE]$

VITA

Supaporn Khaubunsongserm was born on November 25, 1969 in Bangkok, Thailand. After graduated from Benjamarachalai School in 1987, she spent for 4 years at Kasetsart University, Faculty of science, Department of Chemistry to earn a Bachelor Degree of Science in Chemistry. In 1991, she worked at Service Science Department and Electricity Generating Authority of Thailand (EGAT), respectively for 4 years. Thereafter, she studied at Department of Chemical Engineering and joined catalysis and catalytic reaction engineering research group to receive the Master Degree of Chemical Engineering. Then, she worked at Bangkok Polyethylene Company Limited for 5 years and has changed her jobs to PTT Public Company limited until to present. Simultaneously, she studied again at Department of Chemical Engineering and joined catalysis and catalytic reaction engineering research group in Doctoral degree of Chemical Engineering under part time course in 2008-2013. This research was published in the international journal two papers: firstly, Fluorinated bis(phenoxy-imine)titanium complexes with methylaluminoxane for the synthesis of ultrahigh molecular weight polyethylene, Polymer, 54 (2013), 3217-3222 and secondly, Bis[*N*-(3-*tert*-butylsalicylidene)cyclooctylamine] titanium dichloride activated with MAO for ethylene polymerization, European Polymer Journal, 49 (2013) 1753-1759. Additionally, the paper in title of $MgCl_2$-supported and SiO_2-supported bis(phenoxy-imine)titanium complexes for ethylene polymerization sent to the Editor of Polymer Journal two months ago and now is ongoing to investigate by committee in Polymer Journal.