โฮโม และ โคพอลิเมอไรเซชันของ 1-เฮกซีนกับ 1,5-เฮกซะไดอีนโดยใช้ตัวเร่งปฏิกิริยาเซอร์โคโนซีน

นายสุพจน์ พันธุ์จินดาวรรณ

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HOMO- AND COPOLYMERIZATION OF 1-HEXENE AND 1,5-HEXADIENE BY ZIRCONOCENE CATALYSTS

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A Thesis Submitted in Partial Fulfillment of the Requirements
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สุพจน์ พันธุ์จินดาวรรณ : โฮโม และโคพอลิเมอไรเซชันของ 1-เฮกซีนกับ 1,5-เฮกซะไดอีน ใช้ตัวเร่งปฏิกิริยาเซอร์โคโนซีน (HOMO- AND COPOLYMERIZATION OF 1-HEXENE AND 1,5-HEXADIENE BY ZIRCONOCENE CATALYSTS) อ. ที่ปรึกษา : รศ.ดร. วิมลรัตน์ ตระการพฤกษ์; 109 หน้า. ISBN 974-17-3647-9

ในงานวิจัยนี้ ได้ทำปฏิกิริยาโฮโม- และโคพอลิเมอไรเซชันของ 1- เฮกซีน 1,5-เฮกซาไดอีน โดยใช้ตัวเร่งปฏิกิริยาเซอร์โคโนซีน: *rac*-Et(Ind)$_2$ZrCl$_2$ (**Cat 1**) และ Cp$_2$ZrCl$_2$ (**Cat 2**) ใช้เมทิลอะลูมินอกแซน (MAO) และสารประกอบโบรอน [Ph$_3$C][B(C$_6$F$_5$)$_4$] เป็นตัวเร่งปฏิกิริยาร่วม ศึกษาผลของปริมาณตัวเร่งปฏิกิริยา สัดส่วนโดยโมลของ Al/Zr และอุณหภูมิพอลิเมอไรเซชัน ต่อประสิทธิภาพในการเร่งปฏิกิริยา ภาวะที่เหมาะสมสำหรับปฏิกิริยาพอลิเมอไรเซชันของ 1-เฮกซีน คือ ที่อุณหภูมิ 60 °ซ เวลา 24 ชั่วโมง ปริมาณตัวเร่งปฏิกิริยา 2.5 ไมโครโมล สัดส่วนโดยโมลของ Al/Zr เท่ากับ 4000 ที่ภาวะเดียวกัน **Cat 1** มีประสิทธิภาพในการเร่งปฏิกิริยาใกล้เคียงกับ **Cat 2** สำหรับ พอลิเมอไรเซชันของ 1,5-เฮกซาไดอีน ภาวะที่เหมาะสมสำหรับ **Cat 1** คือ ที่อุณหภูมิ 30 °ซ เวลา 5 ชั่วโมง ปริมาณตัวเร่งปฏิกิริยา 2.5 ไมโครโมล สัดส่วนโดยโมลของ Al/Zr เท่ากับ 4000 ที่ภาวะเดียวกัน **Cat 1** มีประสิทธิภาพในการเร่งปฏิกิริยามากกว่า **Cat 2** เมื่อเปรียบเทียบตัวเร่งปฏิกิริยาร่วมที่ต่างกัน พบว่าประสิทธิภาพของระบบ **Cat 1**/MAO สูงกว่า **Cat 1**/[Ph$_3$C][B(C$_6$F$_5$)$_4$] นอกจากนี้ภาวะที่เหมาะสมสำหรับโฮโมพอลิเมอไรเซชันของ 1- เฮกซีน 1,5-เฮกซาไดอีน คือ ที่ 30 °ซ เวลา 5 ชั่วโมง 50 %โมลของ 1,5-เฮกซาไดอีน ปริมาณตัวเร่งปฏิกิริยา 2.5 ไมโครโมล และสัดส่วนโดยโมลของ Al/Zr เท่ากับ 4000 พอลิเมอร์ที่ได้ทั้งหมดถูกวิเคราะห์โครงสร้างด้วย FT-IR และ ^{13}C-NMR สเปกโทรสโคปี อุณหภูมิสภาพแก้ววิเคราะห์ด้วย DSC และวัดน้ำหนักโมเลกุลด้วย GPC สำหรับโฮโมพอลิเมอไรเซชัน พอลิเฮกซีนที่เตรียมด้วย **Cat 1** มีโครงสร้างแบบไอโซแทคทิค ขณะที่ใช้ **Cat 2** เป็นแบบอะแทคทิค ผลิตภัณฑ์ที่ได้จากพอลิเมอไรเซชันของ 1,5-เฮกซาไดอีนเป็นไซโคลพอลิเมอไรเซชันของไดอีน มีโครงสร้างทั้งแบบ ทรานส์-ไอโซแทคทิค และซิส-อะแทคทิค ส่วนโคพอลิเมอไรเซชัน พบว่า โมโนเมอร์ทั้งสองชนิดเกิดรวมกันในโครงร่างโคพอลิเมอร์ โดยสัดส่วนขึ้นอยู่กับสัดส่วนของโมโนเมอร์ที่ผสม

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... **ลายมือชื่อนิสิต**.................................

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#4472459823 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORD: 1-HEXENE/1,5-HEXADIENE/POLYMERIZATION/ZIRCONOCENE

SUPOJ PHANJINDAWAN : HOMO- AND COPOLYMERIZATION OF 1-HEXNE AND 1,5-HEXADIENE BY ZIRCONOCENE CATALYSTS. THESIS ADVISOR: ASSOCIATE PROFESSOR WIMONRAT TRAKARNPRUK, Ph.D. 109 pp. ISBN 974-17-3647-9

In this work, homo- and copolymerizations of 1-hexene, 1,5-hexadiene were performed using zirconocene catalysts: *rac*-Et[Ind]$_2$ZrCl$_2$ (**Cat 1**) and Cp$_2$ZrCl$_2$ (**Cat 2**) methylaluminoxane (MAO) and boron compound ([Ph$_3$C][B(C$_6$F$_5$)$_4$]) as cocatalyst, the influences of catalyst amount, Al/Zr mole ratio and polymerization temperature on the catalytic activity were evaluated. The optimum condition for 1-hexene polymerization was at 60^o C, 24 hrs, 2.5 μmol catalyst and Al/Zr mole ratio of 4000. At the same condition, **Cat 1** gave comparable activity to **Cat 2**. For 1,5-hexadiene polymerization, the optimum condition for **Cat 1** was at 30^o C, 5 hrs, 2.5 μmol catalyst and Al/Zr mole ratio of 4000. At the same condition, **Cat 1** gave higher activity than **Cat 2**. Comparing different cocatalyst, the activities for **Cat 1**/MAO were higher than **Cat 1**/[Ph$_3$C][B(C$_6$F$_5$)$_4$] system. Furthermore, the optimum condition for 1-hexene and 1,5-hexadiene copolymerization was found at 30^o C, 5 hrs, 50 %mol 1,5-hexadiene, 2.5 μmol catalyst and Al/Zr mole ratio of 4000. All the resulting polymers were structurally analyzed by FT-IR and ^{13}C-NMR spectroscopies. Glass transition temperature was determined by DSC and the molecular weights were measured with GPC. For the homopolymerization, the polyhexene prepared with **Cat 1** was isotactic while with **Cat 2**, it was atactic. The product obtained from the polymerization of 1,5-hexadiene was cyclopolymerization of the diene, exist in both *trans*-isotactic and *cis*-atactic. For the copolymerization, it was found incorporation of both monomers in the copolymer backbone, the ratio depended on the monomer ratios.

Field of study Petrochemistry and Polymer science. **Student's signature**..............................

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LIST OF SCHEMES

LIST OF ABBREVIATIONS

$AlMe_3$	Trimethylaluminium
Al/Zr	Aluminium per zirconium mole ratio
n-BuLi	Butyl lithium
^{o}C	Degree Celsius
$CDCl_3$	Deuterochloroform
cm^{-1}	Unit of wave number
^{13}C-NMR	Carbon-13 nuclear magnetic resonance
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
DEPT	Distortionless enhancement of polarization transfer spectroscopy
DVB	Divinylbenzene
Flu	1-Fluorenyl
Hex	1-Hexene
HD	1,5-Hexadiene
MAO	Methylaluminoxane
Me	Methyl
MeCp	3-Methyl-cyclopentadienyl
M_n	Number average molecular weight
M_w	Weight average molecular weight
MWD or M_w/M_n	Molecular weight distribution
m/z	Mass per charge
PMCP	Poly(methylene-1,3-cyclopentane)
PO	Poly(α-olefin)
rac-EBI	Racemic-ethylenebis(indenyl)
TIBA	Triisobutylaluminium
T_p	Polymerization temperature
T_g	Glass transition temperature
t_p	Polymerization time
δ	Chemical shift

CHAPTER I

INTRODUCTION

Polyolefin plastics are nowadays in their mature phase, with a consumption of about 40 million tons per year, and could therefore be appropriately defined as “commodity”. These materials have been discovered and now produced all over the world. Polymer-based materials such as plastic, fibers, elastomers were consumed. In the portion of markets, polyolefins was majority. The production and consumption of polyolefins will proportionally increase with the increasing population number.

Such an exceptional expansion is mainly due to the following factors: [1]

1. A great versatility in terms of properties, that makes them suitable to the most diverse application;
2. The environmental aspects (polyolefins are absolutely non-toxic and friendly to the environment)
3. The superior saving in energy costs, both at production and application levels with respect to other conventional materials;
4. The low costs due to the plentiful availability of raw materials;
5. The possibility of adopting low cost, very versatile and non-polluting processes.

Metallocene-based catalysts, including the so-called “single-site” catalysts have become an important technology for the global polymer industry. Although it is true that free radical initiated high pressure polyethylene polymerization was the foundation for the polyolefin industry, advances in coordination Ziegler-Natta catalysis during the past 40 or so years have been responsible for most of the growth in production volume in polyolefin plastics.

While polyethylene and polypropylene dominate in terms of production volumes in the polyalkene industry, polymers of higher α-alkenes find use due to their special physical properties. In catalytic alkene polymerization the molecular weights of the produced polyalkenes and reaction rates decrease in order: propylene > 1-butene >1-pentene > 1-hexene.[2]

Especially to the low commercial interest with the higher α-olefin polymers, studies on the polymerization and polymer characterization of higher poly(α-olefin) (PO) have not been carried out actively. Products derived from the longer, straight chain, α-olefins can be used in principle as base materials for lubricating oil formulation (low molecular weight) or as pour point depressants and drag-reducers (high molecular weight).

In general, all higher α-olefins can be polymerized by the various classes of Ziegler-Natta catalysts to mainly isotactic polymer. The polymerization rate decreased with increasing steric requirements, that is, both more chain length in straight-chain olefins leads to decrease, as does branching near to the double bond. Chiral *ansa*-metallocene catalysts have also been studied for the homogeneous polymerization of higher α-olefins (C_4-C_{18}) in order to get high molecular weight polymer with high polymerization rate. The *ansa*-metallocene catalysts are single-site catalysts that show high activity coupled with high stereospecificity and narrow molecular weight distributions.

The polymerization of 1-hexene in the presence of complex catalysts was first carried out by Natta. Further works showed the possibility of the formation of oligomers (M_w = 400-1000) or rubber-like amorphous polymers with molecular weights of 50,000-60,000.[3] The use of titanium(IV) complex catalysts led to the synthesis of poly(1-hexene) with a M_w of 26,000-31,000. Based on the results, it might be assumed that the increase in the M_w value is probably due to decrease for the degree of chain transfer reaction by $AlMe_3$.[4] The application of poly(1-hexene) is used for plastic bag industry.

The polymerization of 1, 5-hexadiene was carried out using titanium tetrachloride with triisobutylaluminum yielded poly(methylene-cyclopentane), which is a white, tough, rubbery polymer. It finds application in medical and optical materials.

When two different types of monomers were joined in the same polymer chain, the polymer is called a “copolymer”. Copolymer of olefins and diolefins were found to have more properties and useful than homopolymer. For example, poly(styrene-butadiene-styrene) (SBS rubber) was used for the soles of shoes and for tire treads Acrylate copolymer was used as a binder or a hair fixative and styrene-divinylbenzene (DVB) copolymer beads are plastic spheres that are converted into ion exchangers and adsorbents. These tough, plastic beads act like plastic ball bearings and function as a lubricant in well drilling applications.

Ethylene copolymer of higher *α*-olefins such as 1-butene, 1-hexene and 1-octene are industrially important materials. In 1996, worldwide production of ethylene/α-olefin copolymers exceeded 24 million metric tons of approximately 30% of the market share of polymer products from ethylene. Control over the incorporation and distribution of α-olefins in ethylene/α-olefin copolymers is industrially important for the control of polymer properties such as melting point, glass-transition temperature, tensile strength, flexibility, and processability. In general, the short-chain branching introduced into polyolefins by α-olefin comonomers results in lower melting point, lower crystallinity, and lower density, making these polymer films more flexible and processable.[5]

The aim of this thesis is to study homopolymerization and copolymerization of 1-hexene and 1,5-hexadiene in using two types of zirconocene in combination with two kinds of cocatalyst: MAO and boron compound, the copolymerization between 1-hexene and 1,5-hexadiene has never been reported. The various reaction parameters, which may influence the catalytic efficiency of zirconocene catalysts for olefin homopolymerization and copolymerization have been investigated.

1.1 The objectives of the thesis

1.1.1 To synthesize zirconocene catalysts.

1.1.2 To utilize the zirconocene catalysts for homo- and copolymer of 1-hexene and 1,5-hexadiene.

1.1.3 To determine the optimum conditions for polymerization.

1.1.4 To compare efficiency of two zirconocene catalysts for homo- and copolymerizations of 1-hexene and 1,5-hexadiene.

1.2 The scope of the thesis

1.2.1 To synthesize and characterize zirconocene catalysts: Bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2) and *rac*-ethylene-bis(indenyl)zirconium dichloride (*rac*-$Et(Ind)_2ZrCl_2$).

1.2.2 To homopolymerize 1-hexene monomer and 1,5-hexadiene monomer.

1.2.3 To copolymerize 1-hexene monomer/1,5-hexadiene monomer.

1.2.4 To investigate the parameters affecting polymerization: polymerization temperature, concentration of the catalyst and catalyst/cocatalyst mole ratio.

1.2.5 To characterize the obtained products from the polymerization reactions.

CHAPTER II

THEORY

To really understand the importance of the so-called “single-site” catalyst, it is necessary to look at the difference between these catalysts and the “multi-site” Ziegler-Natta type catalysts. In the Ziegler-Natta catalysts, which are heterogeneous, the active metal center occupies a position on the surface of the crystal. Polymerization at the active site is influenced by the electronic and steric environment of the crystal lattice. Because the active centers can occupy a wide variety of lattice sites, they tend to give products with a broad molecular weight distribution (MWD) and also, for example, non-homogeneous comonomer distribution in olefin copolymer.

The example of the Ziegler-Natta catalyst system $MgCl_2$-$TiCl_4/AlR_3$ is endowed with a very high activity in ethylene polymerization. In the case of the propylene polymerization, the high activity is combined with a low stereospecificity (40-50%).[1]

Bis(cyclopentadienyl)group IV metal complexes are currently introduced in industry as a new generation of Ziegler-Natta catalysts for the polymerization of olefins. Ziegler-Natta catalysis means the rapid polymerization of ethylene and α-olefins with the aid and in the coordination sphere of a metal catalyst, operating at low pressures (up to 30 atm) and low temperatures (less than $120^{o}C$). The group IV metallocene catalysts make polymers accessible which cannot be produced by conventional Ziegler-Natta catalysts.

From 1984, when the stereoselective polymerization of propylene with zirconocene catalysts was first reported, the synthetic, structural, mechanistic and applied research on metallocene catalysts has been highly visible in organometallic chemistry. A central piece of work in zirconocene catalyzed polymerizations of α-olefins was the elucidation of ligand effects, the correlation of the steric situation at the Cp-ligand with the polymer parameters, such as molar mass, molar mass distribution, comonomer insertion and distribution, and especially the tacticity. With metallocene catalysts the polymer parameters can be tailored through a rational ligand design at the transition metal center.

The zirconocene complexes are not catalytically active by themselves but require the action of a cocatalyst. The cocatalyst is methylaluminoxane, abbreviated as MAO. The novelty of metallocene *versus* classical Ziegler-Natta catalysis is best summarized in the word ‘single-site catalyst’. This means that the active catalytic sites in the molecular zirconocene species are almost identical, whereas classical Ziegler-Natta catalysts are heterogeneous not just by the phase (as solid state catalysts) but also by having active sites with different environments at corners and edges on the solid surface. Metallocene catalysts are sometimes also termed ‘homogeneous’ referring both to their solubility and to their single-site character.

The most important differences between classical Ziegler-Natta and metallocene catalysts can be summarized as follows:

1. Metallocenes are organometallic compounds that can be completely characterized, both from the chemical and the structural point of view.
2. They are soluble in aliphatic and aromatic solvents.
3. The electronic and steric surrounding of the catalytic center can be much more easily modified in the case of metallocene based catalyst.
4. The chain growth mechanism implies two coordination sites in the case of metallocene based catalyst, while only one is available for the titanium anchored on the $MgCl_2$ surface.
5. The homogeneity of the catalytic centers, in the case of metallocene based catalyst (single-center catalysts), allows the preparation of polymers with narrow molecular weight distribution and chemical composition[1].

Metallocenes offer several advantages over traditional Ziegler-Natta catalysts. In contrast to Ziegler-Natta catalysts, metallocene systems give narrow molecular weight distributions, high comonomer incorporation, and narrow compositional distributions.[6] In addition, the relationship between copolymerization behavior and catalyst structure is more readily investigated with metallocene catalysts and can provide insight into the mechanism of olefin polymerization.

2.1 Metallocene based catalyst

Metallocenes are organometallic compounds in which one or two carbocyclic ligands or substituted carbocyclic ligands such as cyclopentadienyl ring, substituted cyclopentadienyl ring or derivatives of cyclopentadienyl ring (for example, fluorenyl, indenyl, etc.) are π-bonded to the metal center atom.

The typical chemical structure of metallocene catalyst is shown in Figure 2.1. M is the group IVB, VB or VIB transition metals, generally in group IVB (Ti, Zr and Hf). R is a σ-homoleptic hydrocarbyl such as H, alkyl, or hydrocarbon groups and X represents chlorine or other halogens or an alkyl group.

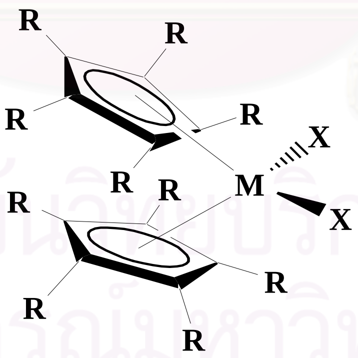


Figure 2.1 Typical chemical structure of a metallocene catalyst.

The central transition metal atom, cyclopentadienyl (or cyclopentadienyl derivatives) ligands, bridging atom and halides modified by variation and / or substitutions some of these parts can result in variation of the catalytic activity, polymer structure, molecular weight and molecular weight distribution.

The structures or compositions of metallocene catalysts have many varieties. Types of catalysts are divided by different structures or compositions. When the two cyclopentadienyl (Cp) rings on either side of the transition metal are unbridged, (Figure 2.2), this metallocene is nonstereorigid, it has C_{2v} symmetry.

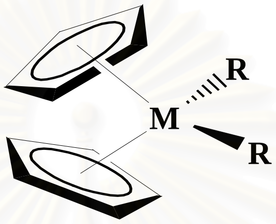


Figure 2.2 Non-bridging C_{2v} symmetric metallocene catalyst.

When the two cyclopentadienyl ligands which are bonded to the metal atom, are connected by bridging atom or bridging molecule (Figure 2.3), the metallocene is stereorigid compound, called "*ansa*-metallocene" (ansa means handle).

The rotation of Cp ligands can be prevented by bridging which connects them together, to give a rigid and stereoselective ligands framework. It shows C_1, C_2 or C_s symmetry, depending on the substituents on two Cp rings and the structure of the bridging unit.

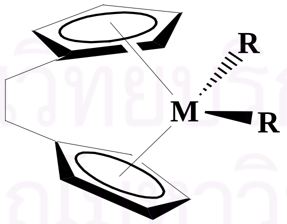


Figure 2.3 Ethylene bridged cyclopentadienyl metallocene catalyst.

The use of metallocene as homogeneous polymerization catalysts has dramatically improved the understanding of mechanistic features such as the nature of the active sites and the influence of ligand structure on the regio- and stereoselectivity. One of the many advantages is the controlling of activity, molecular weight, polydispersity and microstructure of the resulting polyolefins by structurally well-defined and on the molecular level modifiable metal complexes.

2.2 Half-metallocene catalyst

It is well known that the many advantages of the metallocene systems generally associated with the bis(cyclopentadienyl) ligand systems, however, occasionally turn into a disadvantage: the characteristic and highly consistent electronic and steric situation within the bent metallocene unit has long been recognized to cause substantial steric blocking of the metal-centered reaction site.

Enhancement of reactivity is observed when the two ring ligands are “tied back” by a dimethylsilanediyl link as in many Brintzinger-type *ansa*-metallocene complexes. In order to alleviate this steric constraint of the metallocenes, one could utilize, in place of two cyclopentadienyl ligands, one cyclopentadienyl ligand that contains an additional coordinating site X or L tethered to the periphery of the five-membered ring *via* a bridge Z, where X and $X^{/}$ donate a one-electron, L and $L^{/}$ are two-electron ligands (using the neutral ligand formalism), and Z is a covalent bridge of appropriate length (Figure 2.4). Such bidentate ligands may form chelate complexes in which the cyclopentadienyl group and the additional donor group X or L are both interacting with one metal center.

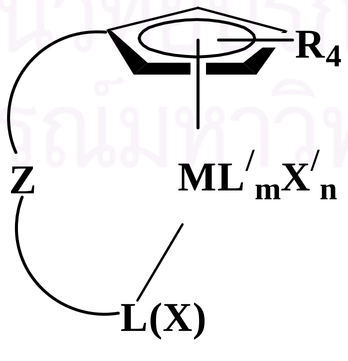


Figure 2.4 General formula for a metal complex containing a bifunctional cyclopentadienyl ligand.

The replacement of one cyclopentadienyl moiety in a bridged bis(cyclopentadienyl) ligand by an amido ligand NR$^{/}$, connected *via* a bridge Z, results in ligand systems that form complexes differing from both *ansa*-metallocenes and the simple half-sandwich complexes without the link Z (Figure 2.5). The amido group is a three-electron ligand, in contrast to the five-electron L_2X-type cyclopentadienyl ligand.

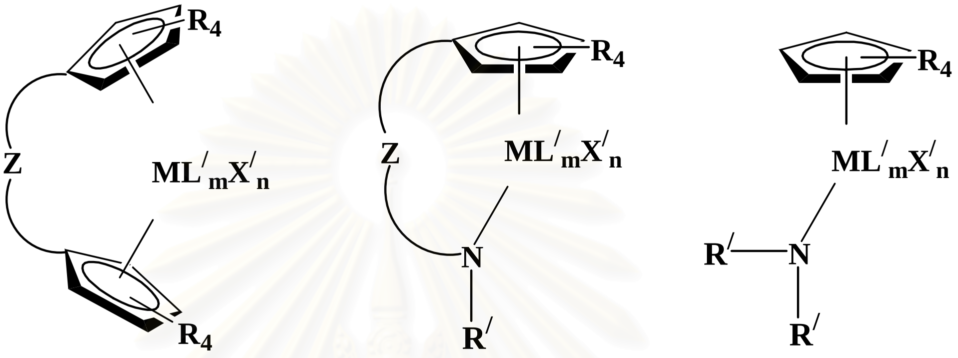


Figure 2.5 Relationship between *ansa*-metallocenes, linked amido-cyclopentadienyl, and half-sandwich amido complexes.

2.3 Non-metallocene catalyst

More recently, some new complexes with non-Cp ligands are also claimed as the catalysts for olefin polymerization. The advances in the design and synthesis of well-defined transition-metal complexes have spurred the rapid development of highly active olefin polymerization catalysts. Thus, quite a few highly active olefin polymerization catalysts based on both early- and late-transition-metal complexes have been developed. Notable examples are nickel complexes with diimine ligands[7] or phenoxy-imine ligands[8], iron or cobalt complexes with diimined-pyridine ligands[9], titanium complexes with diamide ligands[10], phosphine-imide ligands[11], zirconium complexes with diamide ligands[12] or bis(phenoxy)-amine ligands[13], and tantalum complexes with amide-pyridine ligands. These complexes display activities comparable to those of the group IV metallocene catalysts. These complexes are considered to have more space like constrained geometry catalyst for the monomer coordination as compared with ordinary metallocenes. These complexes may be thus of interest also for the synthesis of copolymers of olefinic monomers.

2.4 Cocatalyst and initiating step in polymerization

Cocatalysts are the key to the activity of the metallocene. They can be classified into 2 main groups; aluminum- and boron-compound cocatalysts.

2.4.1 Aluminum-compound cocatalyst

Methylaluminoxane (MAO) is the famous cocatalyst in this group. It is the product of a careful reaction between trimethylaluminum and water (from a hydrated inorganic salt; $Al_2SO_4.16H_2O$, $CuSO_4.5H_2O$, $FeSO_4.7H_2O$). From many different analytical investigations, cryoscopic measurements, GPC and NMR analysis, one can hypothesize that the MAO structure is composed of a mixture of linear or cyclic oligomers of MeAlO units or a metallocene in a host-guest complex as in Figure 2.6. It is generally accepted that MAO is an oligomer compound with a molecular weight between 1,000 and 1,500 g/mol.

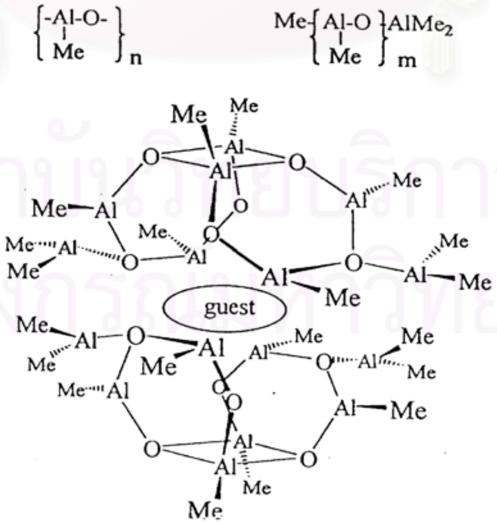
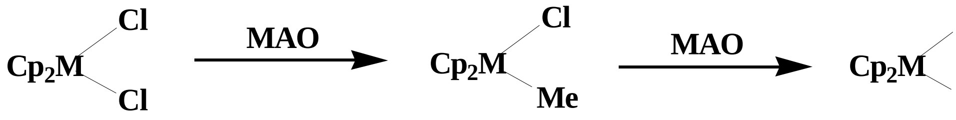


Figure 2.6 The postulated MAO structure.

The first function of the MAO is the alkylation of the halogenated metallocene complex. Monomethylation takes place within seconds, and an excess of MAO leads to dialkylated species. The formation of active species are proposed following equation 2.1.



(2.1)

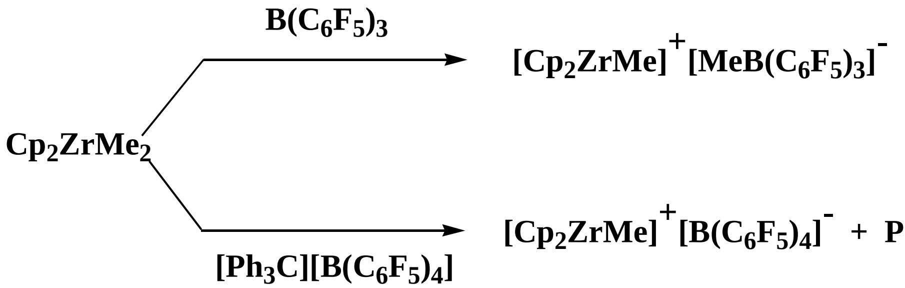
It would appear as if the MAO complex can seize a methyl anion, a Cl^- or an OR^- from the metallocene, forming an AlL_4^- anion which can distribute the electron over the whole cage, thus stabilizing the charged system. The formation of active species are proposed following these equation 2.2. The formed cationic $L_2M(Me)^+$ is generally regarded as the active center in olefin polymerization.

(2.2)

A further function of MAO is the reactivation of inactive complexes formed by hydrogen transfer reactions. In solution, the combination of MAO and metallocene leads to fast complexation and methylation, followed by the evolution of methane and a catalytically inactive M-CH_2-Al complex. This complex reacts with MAO to form Zr-CH_3^+ and Al-CH_2-Al structure, which explains why a large excess of MAO is required.

2.4.2 Boron-compound cocatalyst

Other bulky anionic complexes which show weak co-ordination, such as borane {$B(C_6F_5)_3$} and borates ($[Ph_3C][B(C_6F_5)_4]$, $[PhNMe_2H][B(C_6F_5)_4]$), play an increasing role too. This is evidenced by the formation of highly metallocene catalysts when using anionic counterions such as tetraphenyl borate $(C_6H_5)_4B^-$, carborane or fluorinated borate. Typically cation metallocene complexes can be formed by reactions of perfluorinated triphenylborane {$B(C_6F_5)_3$} or trityltetrakis (pentafluorophenyl)borate($[Ph_3C][B(C_6F_5)_4]$). The formation of active species are proposed following equations 2.3 and 2.4.



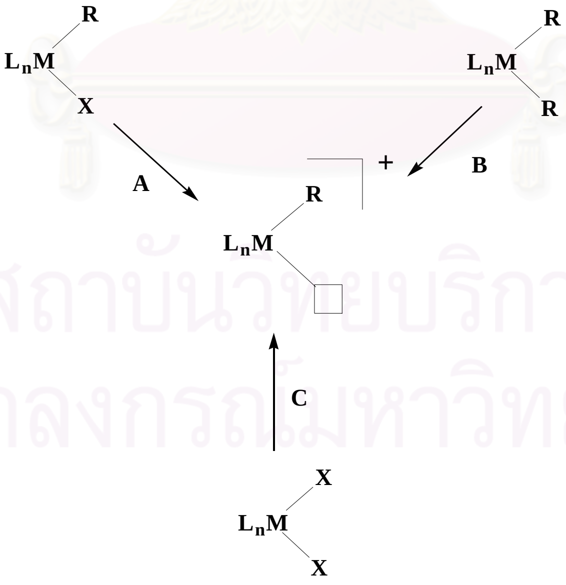
$$Cp_2ZrMe_2 \xrightarrow{B(C_6F_5)_3} [Cp_2ZrMe]^+[MeB(C_6F_5)_3]^- \quad (2.3)$$

$$Cp_2ZrMe_2 \xrightarrow[{[Ph_3C][B(C_6F_5)_4]}]{} [Cp_2ZrMe]^+[B(C_6F_5)_4]^- + Ph_3CMe \quad (2.4)$$

Whereas the ratio of MAO to metallocene needs to be around 5,000:1 for active catalyst systems, the ratio of borate to metallocene is 1:1. On the other hand, the borate system is very sensitive to poisons and decomposition and must be stabilized by small amounts of aluminum alkyls.

2.5 The active site

It is generally agreed that the catalytically active species in olefin polymerization is a coordinatively unsaturated cationic alkyl complex $[L_nMR]^+$. To generate such species several methods can be employed; three different routes (A, B and C) are shown in Scheme 2.1.



Scheme 2.1 Three different routes to the catalytical acitive species $[L_nMR]^+$

□ represents the site of coordinative unsaturation.

Route A involves the abstraction of an anionic ligand (e.g. a halide) and its substitution for a “noncoordinating” anion by a salt elimination. Common reagents are $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ or silver salts such as $AgBF_4$ or $AgOSO_2CF_3$ (AgOTf) for the late transition metals.

Route B involves the abstraction of an alkyl ligand or, more strictly, an alkyl anion. Reagents used for these ligands are, for example $[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2][B(C_6F_5)_4]$, $[H(OEt_2)_2][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ or $B(C_6F_5)_3$. Whereas the trityl reagent is an abstracting agent, the anilinium salt and the acid remove the alkyl ligand by protonation. In the case of $B(C_6F_5)_3$ the alkyl ligand is only partly abstracted leading to “cation-like” catalytic species.

Route C is a combined alkylation and abstraction process, which can be achieved by treating a dihalide procatalyst first with an alkylating species and then with one of the aforementioned alkyl-abstracting agents, for example a trialkylaluminum compound followed by $B(C_6F_5)_3$. Some reagents can perform both processes, for example, alkylaluminoxane (MAO).

2.6 Polymerization machanisms

2.6.1 Initiation step

The nature and the information of the true active catalytic species are not yet fully elucidated. But, for group IVB metallocene polymerization catalysts are generally accepted that metallocene catalysts combined with MAO consist of cationic complexes formed by reaction of a metallocene with MAO. The formation of active species are proposed following equation 2.5.

$$\mathbf{Cp_2MX_2} + \mathbf{MAO} \xrightleftharpoons[\mathbf{M = Ti,\ Zr\ and\ Hf}]{} \mathbf{[Cp_2MMe]^+[MAO\text{-}X_2]^-} \qquad \mathbf{(2.5)}$$

MAO methylated and abstracted ligands on metallocene catalyst to show Lewis acidity. The use of a large excess of MAO is necessary because of the low value of the equilibrium constant.

2.6.2 Propagation step

There are three basic mechanisms suggested for the insertion of olefin into a transition metal alkyl bond in metallocene catalyst[14], shown in Figures 2.7-2.9. These mechanism are:

1. The direct insertion mechanism proposed by Cossee and Arlman.
2. The metathesis mechanism proposed by Green and Rooney.
3. The modified Green-Rooney mechanism proposed by Brookhart and Green.

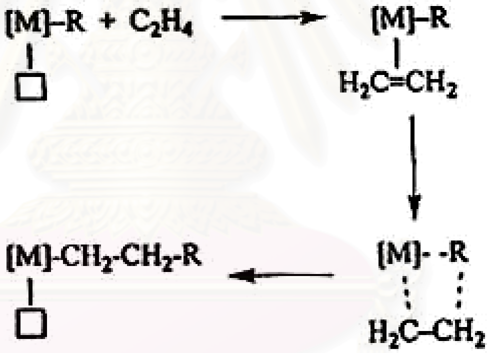


Figure 2.7 Direct insertion mechanism (□ is vacant coordination site).

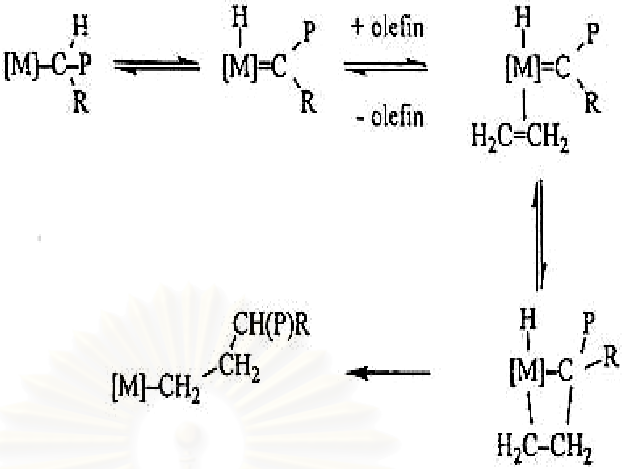


Figure 2.8 Metathesis mechanism.

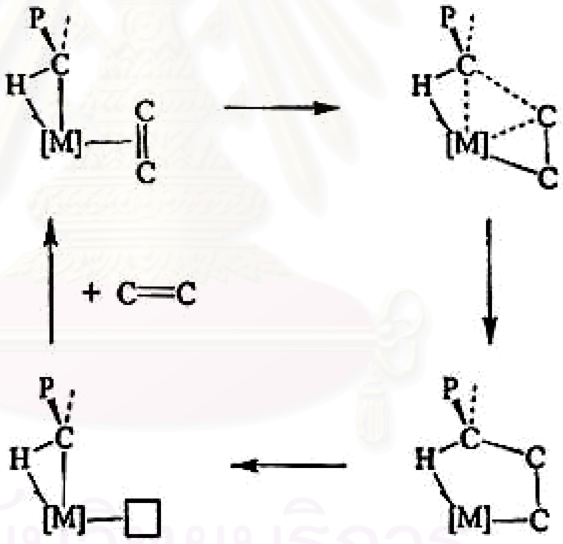
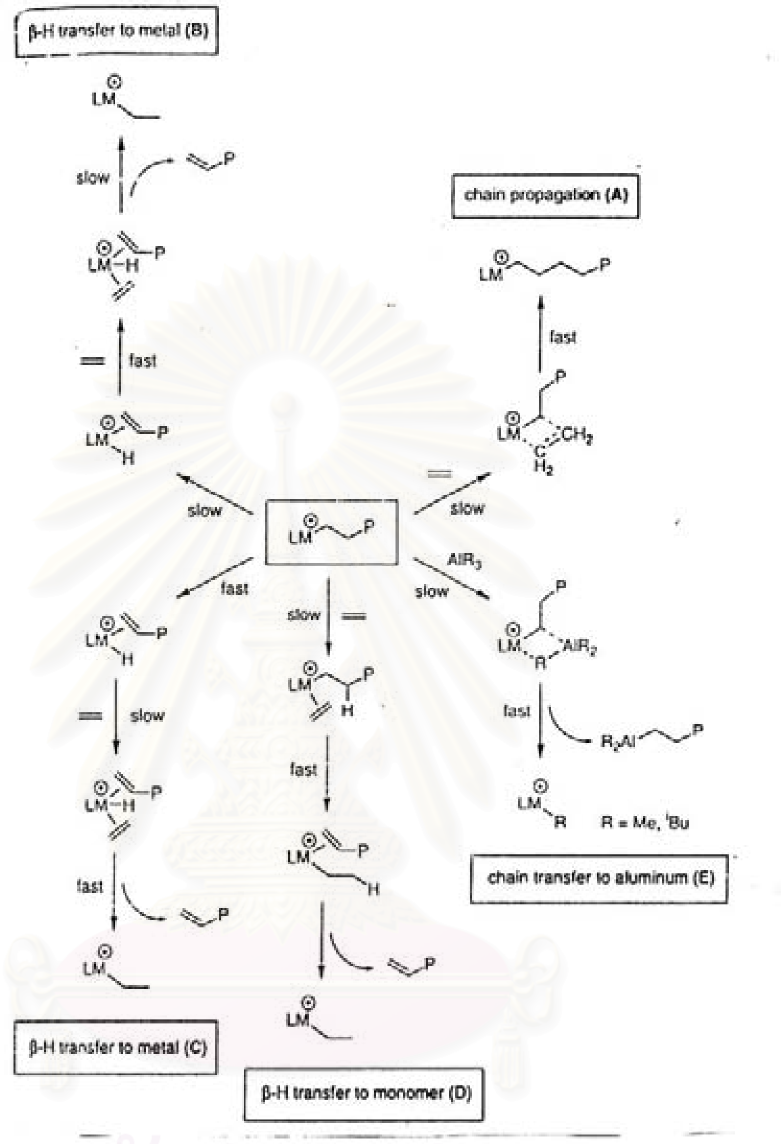


Figure 2.9 Modified Green-Rooney mechanism.

2.6.3 Chain transfer and termination steps

Scheme 2.2 shows the polymerization mechanism, that is, the chain propagation and the possible chain-transfer pathways.



Scheme 2.2 Possible chain propagation and transfer pathways.

In pathway **A**, a Cossee-type propagation mechanism is assumed, involving migratory insertion of ethylene into a metal alkyl bond, whereby the rate has a first-order dependence upon the ethylene concentration.

Four different chain-transfer pathways can be distinguished. Two involve kinetically distinct β-H transfer to metal processes (**B** and **C**), a third β-H transfer to monomer (**D**), and a fourth chain transfer to aluminum (**E**).

β-H transfer to metal of type **B** is a common chain-transfer process, especially for late transition metal catalysts. This β-H elimination reaction is unimolecular, that is, independent of monomer concentration, provided that the subsequent step, the associative displacement of the polymer chain by monomer, is fast and therefore is not the rate-determining step.

If this is not the case, this chain-transfer process becomes a β-H transfer to metal of type **C**, which is kinetically indistinguishable from β-H transfer to monomer (**D**). These chain-transfer pathways are both bimolecular, that is, first order in monomer, and the latter (**D**) has been postulated previously for certain metallocene catalysts.

The fourth, less common chain-transfer reaction is chain transfer to aluminum (**E**). This process has also been observed for Ziegler-Natta systems, group 4B metallocenes, and lanthanocenes and is dependent upon the alkyl aluminum concentration. This pathway involves formation of an alkyl-bridged M-Al species, which allows the growing polymer chain to be exchanged for a new alkyl group, while a vacant site is still available at the metal center.

In general, β-H-transfer reactions, to the metal (**B** and **C**) or the monomer (**D**), give one unsaturated chain end per polymer chain (vinyl end groups), whereas chain transfer to aluminum (**E**) results in fully saturated polymer chains.

2.7 Copolymerization

When a polymer is made by linking only one type of small molecule, or monomer, together, it is called a “homopolymer”. When two different types of monomers are joined in the same polymer chain, the polymers is called a “copolymer”.

When the two monomers are arranged in an alternating fashion, the polymer is called an *alternating copolymer*:

—A—B—A—B—A—B—A—B—A—B—A—B—A—B—

alternating copolymer

In a *random copolymer*, the two monomers may follow in any order:

—A—A—B—A—B—B—A—B—A—A—B—B—B—A—

random copolymer

In a *block copolymer*, all of one type of monomer are grouped together, and all of the others are grouped together. A block copolymer can be thought of as two homopolymers joined together at the ends:

—A—A—A—A—A—A—A—B—B—B—B—B—B—B—

block copolymer

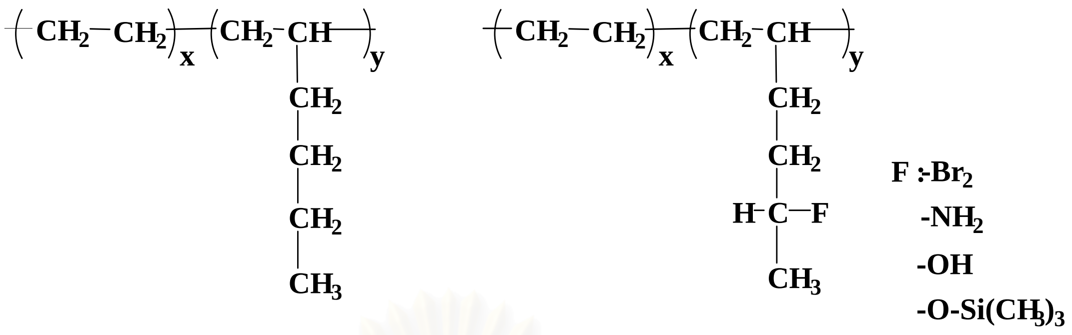
Studies of metallocene-catalyzed copolymerization of ethylene with α-olefins ranging from C_3-C_{18} have been reported by several groups. Incorporation of α-olefin comonomers has been studied as a function of ligand substitution pattern, interannular bridge, and metal. One common observation from these studies is that *ansa*-metallocenes with one- or two-membered bridges between the ligands incorporate α-olefin comonomers better than unbridged metallocenes.[5]

The lack of functional (reactive) groups in polyolefins has significantly limited many of their end uses, particularly those in which adhesion, dyeability, paintability, printability, or compatibility with other polymers is paramount. It has long been a scientific challenge in exploring the route to functionalize polyolefins, especially polyethylene and polypropylene. These functionalized polyolefins can serve as interfacial modifiers to improve their adhesion to and compatibility with other materials.

In general, there are two routes to the functionalization of polymers, including direct copolymerizations with functional monomers and chemical modifications of preformed polymers. Unfortunately, Ziegler-Natta catalysts used in the preparation of polyolefins are normally incapable of incorporating functional group-containing monomers because of catalyst poisoning. In the past few years, borane monomers was be copolymerized with α-olefins in Ziegler-Natta polymerization. Many polyolefins with a broad range of compositions have been obtained with many desirable physical properties.

On the other hand, modification reactions of polyolefins are usually accompanied by some undesirable side reactions, such as cross-linking and degradation of the polymer backbone. In addition, the control of functional group concentration and homogeneity in the polyolefin backbone is usually very difficult. Recently, there have been several successful examples of unsaturated polymers, with the double bonds at the chain ends or pendant along the polymer backbone, as the “reactive” prepolymers for subsequent modification reactions resulting in functionalized products.

A two-step approach involving (i) the preparation of unsaturated polyethylene, resulting from a copolymerization reaction of ethylene and 1,4-hexadiene using *rac*-$Et(Ind)_2ZrCl_2$/MAO catalyst and (ii) subsequent functionalization by borane chemistry was adapted. The unique combination of comonomers, single-site catalyst, and borane reagents provides the route to prepare functionalized polyethylene with a broad range of concentrations and composition of functionalized polyethylene(LLDPE-f) is structurally similar to that of linear low-density polyethylene(LLDPE) is shown in Figure 2.10.



LLDPE LLDPE-f

Figure 2.10 Functionalized polyethylene(LLDPE-f) and linear low-density polyethylene(LLDPE)

It is very interesting to note the advantages of 1,4-hexadiene as a comonomer.[15]

(i) The low boiling offers the possibility of using gas phase copolymerization processes.

(ii) The unsymmetrical diene provides selective copolymerization at the α-olefin group. Therefore, a high concentration of diene comonomer can be incorporated into the PE structure without cross-linking reactions.

(iii) The internal double bonds in PE result in desirable borane moieties, containing secondary C-B bonds in the side chain of PE, after hydroboration reaction. The secondary C-B bond can be quantitatively converted to various functional groups. The complete interconversion of borane groups to other functionalities is essential to obtain processible PE products.

Two approaches can be envisioned for the synthesis of a functionalized poly-α-olefins:[16]

1. Modification of the preformed polyolefin and direct copolymerization of an olefin with a functionalized monomer. Free-radical grafting reaction (with maleic anhydride for example) is a common approach to introducing functionality into polyolefins; however, this poorly controlled reaction often leads to polymer degradation, cross-linking, and nonuniform incorporation of the desired functionality. Other methods

include ionic treatment (both anionic and cationic), plasma induced modification, treatment with ionizing radiation, oxidation (acidic treatment), and halogenation.

2. Functionalized poly(α-olefin) synthesis consists of the direct copolymerization of functionalized olefins. An example of this method is the free radical copolymerization of ethylene with acrylic acid to yield the ionomer Surlyn (DuPont, 1964). Unfortunately, this rather effective technique is limited to monomers without R-hydrogens (e.g.: ethylene, styrene, acrylic acid, etc.) due to rapid chain-transfer reactions for monomers that contain allylic hydrogens. This disadvantage can be overcome by using coordination-type catalysts. Copolymerization of ethylene and propylene with alkyl acrylates using palladium(II) catalysts, for example, gave high molar mass polymers under mild and controlled conditions.

A well-known limitation of conventional Ziegler-Natta catalyst systems is their intolerance to most functional groups (ethers, esters, amines, alcohols, and carboxylic acids). Previous attempts to directly homo-or copolymerize various functionalized R-olefin monomers met with limited success due to a severe loss of activity caused by catalyst deactivation. On the other hand, zirconocene/methylalumoxane (MAO) catalysts were to a certain extent successful in copolymerizing ethylene and propylene with 1-hydroxy-10-undecene[17],[18], 1-chloro-10-undecene, *N*,*N*-bis(trimethylsilyl)-1-amino-10-undecene, silsesquioxane-functionalized decene[19], an *o*-heptenylphenol derivative[20], and borane-functionalized R-olefins[21],[22].

The direct synthesis of cationic, group 4 metallocene complexes has led to catalysts which show some tolerance for Lewis basic solvents.[23]-[25] Furthermore these catalysts made possible the polymerization of olefins in the absence of alkylaluminum cocatalysts in solvents such as anisole, *N*,*N*-dimethylaniline, and chlorobenzene.[26],[27] The homopolymerization of R-olefins containing silyl-protected alcohols and different tertiary amines was studied.[28],[29] Copolymerization of 5-*N*,*N*-diisopropylamino-1-pentene with 1-hexene and 4-methyl-1-pentene using cationic group 4 metallocenes was described.

A class of dimethylmonocyclopentadienyl zirconium acetamidinates, $Cp^{*}ZrMe_2[NR^1C(Me)NR^2]$ (Cp^{*} = η^5-pentamethylcyclopentadienyl) is catalyst precursors for the living Ziegler-Natta polymerization of α-olefins upon activation by a borate cocatalyst. By manipulating the steric bulk of the two *N*-acetamidinate substituents, R^1 and R^2, and most importantly, by going from C_s to C_1 symmetry as exemlified by compounds **1** and **2** is shown in Figure 2.11, the stereospecific living polymerization of 1-hexene has been achieved to provide highly isotactic, high molecular weight materials possessing low polydispersities. With all the possibilities for materials engineering that living polymerization processes provide, this new class of Ziegler-Natta catalyst precursor should make available, for the first time, a large number of new stereoregular polyolefins possessing desirable physical properties.[30]

1 **2**

Figure 2.11 Dimethylmonocyclopentadienyl zirconium acetamidinates

2.8 Catalyst activities

Catalyst activities are highly dependent upon the precise reaction conditions, including stirring rate and the configuration of the reactor. Also, often little or no information is given about the kinetic profile or lifetime of the catalyst. Information about the catalyst's kinetic profile is very useful in allowing the most appropriate operating conditions to be chosen. For example, solution-phase catalysts generally require shorter reactor residence time than for a supported gas-phase catalyst.

The activity available in the literature is in units of g mmol^{-1}h^{-1}bar^{-1} and the rating of activity ranging from very low to very high, as shown in Table 2.1.

Table 2.1 Rating of catalyst activity

Rating	Activity [g mmol^{-1}h^{-1}bar^{-1}]
very low	less than 1
low	1-10
moderate	10-100
high	100-1000
very high	more than 1000

CHAPTER III

LITERATURE REVIEWS

3.1. Historical development of metallocene research

Metallocene-based catalysts, the so-called “single-site” catalysts have become important for the polymer industry. The evolution of the metallocene catalyst for olefin polymerization is shown in Table 3.1.

Table 3.1 Timetable and historical development of metallocene research[31]

1952	Development of the structure of ferrocene (Fisher and Wilkinson)
1955	Metallocene as component of Ziegler-Natta catalysts, low activity with common aluminium alkyls
1973	Addition of small amount of water to increase the activity ($Al:H_2O$ = 1:0.05 up to 1:0.3) (Reichert, Meyer and Breslow)
1975	Unusual increase in activity by adding water at the ratio $Al:H_2O$ = 1:2 (Kaminsky, Sinn and Motweiler)
1977	Using separately prepared methylaluminoxane (MAO) as cocatalyst for olefin polymerization (Kaminsky, Sinn)
1982	Synthesis of *ansa*-metallocenes with C_2 symmetry (Brintzinger)
1984	Polymerization of propylene using a *rac/meso* mixture of *ansa*-titanocenes leading to partially isotactic polypropylene (Ewen)
1984	Chiral *ansa*-zirconocene producing highly isotactic polypropylene(Kaminsky and Brintzinger)

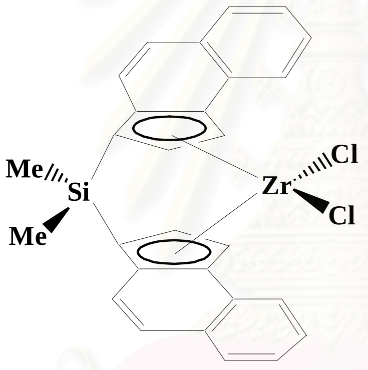
3.2. 1-Hexene polymerization

Asanuma, T. *et al.*[32] studied polyolefins having syndiotactic structure obtained by using 1-methyl-1-ethylidene-（cyclopentadienyl-1′-fluorenyl）zirconium dichloride and methylaluminoxane as a catalyst. 1-Butene and 4-methyl-1-pentene gave crystalline polymers having syndiotactic structure, while 1-pentene, 1-hexene and 1-octene gave non-crystalline polymers having syndiotactic structure. The identification of syndiotactic and isotactic polyolefins was made by ^{13}C NMR, X-ray diffraction and differential scanning calorimetry.

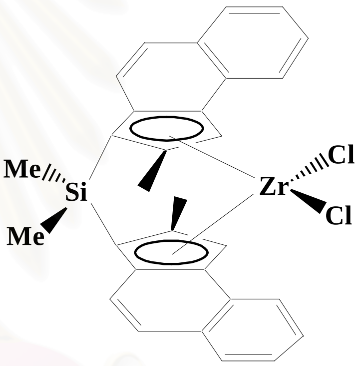
Sukhova, T. A. *et al.* [3] studied $TiCl_4$-alkylaluminium systems fixed on graphite and other inorganic supports and used in 1-hexene polymerization. Kinetic studies showed a decreasing polymerization rate from high initial values. High conversions (up to 99%) were reached, although retardation by a diffusion process was observed above 60%. The polymers have high molecular weights (up to 10^7) and high isotacticity (up to 98.5%). The effects of the nature of the components (carrier, alkylaluminium), and their concentration on the polymerization kinetics and the molecular structure of the polymer were discussed. The linear chain has one alkyl group (the alkylaluminium) and one unsaturation at the chain ends. Despite the high tacticity, the polymers are amorphous and rubber-like.

Babu, G. N. *et al.* [33] polymerized of 1-hexene with *rac*-ethylenebis(1-η^5-indenyl)zirconium dichloride in the presence of triphenylcarbenium tetrakis(pentafluorophenyl)borate ($[Ph_3C][B(C_6F_5)_4]$). The ratio of the total proton NMR intensity to the olefinic end group intensity corresponds to the GPC-determined number-average molecular weight. The chemical shift and intensity of the α-CH_2 at 34.4 ppm in the ^{13}C NMR spectrum indicate a highly isotactic microstructure for the poly(1-hexene). The ^{13}C NMR spectra contain minor resonances due to a variety of 1,2-disubstituted and 1,1,2-trisubstituted vinylene and vinylidene end groups.

Stehling, U. *et al.*[34] synthesized the dimethylsilyl-bridged zirconocene complexes: $(CH_3)_2$(benz[*e*]indenyl)$_2ZrC1_2$ (**I**) and $(CH_3)_2Si$(2-methylbenz[*e*]indenyl)$_2$ $ZrCl_2$ (**II**), which used in polymerization of propylene and γ-branched olefins: 3-methyl-1-butene and 3-methyl-1-pentene in the presence of MAO as cocatalyst. The isotactic polymers obtained with 2-methyl-substituted complex, (**II**) have molar mass about 4 times higher than produced with the analogous complex (**I**). An increase in the molar mass of product was reported earlier for *ansa*-zirconocenes with an additional α-substituent appending to the C_5 moiety. Mechanistic investigations revealed that the additional α-substituent in (**II**) blocks chain terminations that arise from chain transfer to a coordinated monomer molecule, also explaining the higher molar mass of the polymers obtained with (**II**).

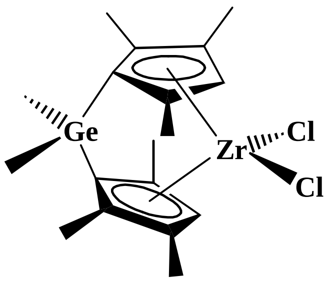


I

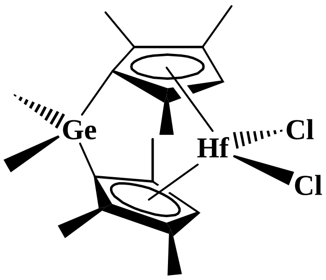


II

Yamaguchi, Y. *et al.*[35] study stereospecific polymerization of 1-hexene under high pressure (up to 1000 MPa) using *rac*-[$Me_2Ge(\eta^5$-C_5H-2,3,5-$Me_3)_2MCl_2$] (M = Zr, ***rac*-4a**; M = Hf, ***rac*-4b**) catalysts in the presence of MAO. It was found that high pressures induced enhancement of the catalytic activity and the molecular weight of the polymer in most of the catalysts. The maximum of both the catalytic activity and the molecular weight of the polymer were mostly observed at 100-500 MPa in each catalyst, although the enhanced ratio was smaller than that observed for nonbridged metallocene. Isospecificity of the C_2-symmetric *ansa*-metallocene catalysts was essentially maintained even under high pressure. Highly isotactic polyhexene ([mmmm] = 91.6%) with very high molecular weight (M_w = 2360000) was achieved by ***rac*-4b** under 250 MPa.

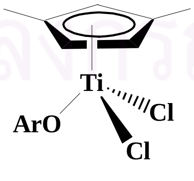


***rac*-4a**

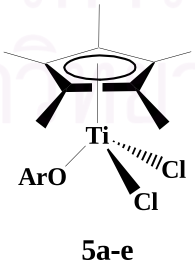


***rac*-4b**

Nomura, K. *et al.*[36] studied effect of substituents on cyclopentadienyl group for catalytic activity in 1-hexene and 1-octene polymerization with a series of $Cp'TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$[Cp′ = Cp (1a), $^tBuC_5H_4$ (**2a**), 1,3-$Me_2C_5H_3$ (**3a**) , 1,3-$^tBu_2C_5H_3$ (**4a**) and C_5Me_5 (**5a**)]-MAO catalysts. It was found that the activity increased in the order: **4a** (kg polymer/mol Ti·h) < **1a** (63) < **2a** (89) < **3a** (184) < **5a** (728). The catalytic activity in 1-hexene polymerization with the series of $Cp^*TiCl_2(OAr)$ [OAr = 2,6-$^iPr_2C_6H_3$(**5a**), 2,4,6-$Me_3C_6H_2$ (**5b**) , 2,6-$Me_2C_6H_3$ (**5c**), 2-^tBu-4,6-$Me_2C_6H_2$ (**5d**) , 4-MeC_6H_4 (**5e**)]-MAO catalysts increased in the order: **5a** 728 kg polymer/mol Ti·h > **5d** (694) > **5c** (76) > **5e** (48) > **5b** (39). These orders are somewhat different from those in ethylene polymerization, and these differences observed here would be due to the steric bulk of monomer used as well as of substituents on both cyclopentadienyl and aryloxy groups. Although **4a** showed the lowest catalytic activity for polymerization of both 1-hexene and 1-octene, **4a** exhibited the significant activity for copolymerization of ethylene with 1-hexene, resulting in copolymer with relatively high 1-hexene contents (20.2-36.5 mol%) with relatively narrow molecular weight distributions.



1-4a



5a-e

R^1, R^2 = H, H (1); ^tBu, H (2); Me, Me (3); ^tBu, ^tBu (4)

Ar = 2,6-$^iPr_2C_6H_3$ (a); 2,4,6-$Me_3C_6H_2$ (b); 2,6-$Me_2C_6H_3$ (c);

2-^tBu-4,6-$Me_2C_6H_2$ (d); 4-MeC_6H_4(e)

Kissin, Y. V. *et al.*[37] discovered a new type of cocatalyst which is capable of activating metallocene complexes in olefin polymerization reactions. This cocatalyst has two components: (a) a haloorganoaluminum compound $Al_nR_mX_{n-m}$, (for example, $AlEt_2Cl$, $AlMe_2Cl$, $Al_2Et_3Cl_3$, $AlEt_2F$, *etc.*) and (b) a dialkylmagnesium compound MgR'_2 (R′ = butyl, hexyl *etc.*). These compounds were used at a molar [Al]:[Mg] ratio of greater than alkylaluminium. When polymerization of 1-hexene with zirconocene: bis(*n*-butylcyclopentadienyl) zirconium dichloride, $(n\text{-BuCp})_2ZrCl_2$; *rac*-ethylenebis(1-indenyl)zirconium dichloride, $C_2H_4(Ind)_2ZrCl_2$; *rac*-dimethylsilylbis(1-indenyl)zirconium dichloride, $Me_2Si(Ind)_2ZrCl_2$; and dimethylsilyl(cyclopentadienyl)(9-fluorenyl)zirconium dichloride, $Me_2Si(Cp)(Flu)ZrCl_2$ on support dibutyl magnesium ($MgBu_2$), which suggests cocatalyst structure that the most propable reaction is:

$$\mathbf{2\,AlMe_2Cl \;+\; MgBu_2 \longrightarrow MgCl_2 \;+\; 2\;AlMe_2\mathit{n}\text{-}Bu}$$

It was found that an [Al]:[Mg] molar ratio from 2 to 5 was needed for a catalytic effect; the same combinations at the [Al]:[Mg] ratio less than dialkylaluminum chlorides were virtually inactive. In the case of ethylene copolymerization reactions, polymer yields ranged from 2500 to 10000. Comparison with MAO as a cocatalyst it was shown that $AlR_2Cl\text{-}MgR'_2$ combinations were 5-10 times less active. The results poly(1-hexene) with metallocene complexes which activated with AlR_2Cl and MgR'_2 have relatively broad molecular weight distributions, with M_w/M_n values in the range of 10-15. However, ethylene/α-olefin copolymers prepared with these catalysts have relatively narrow compositional distributions, an important indicator of single-site catalysis.

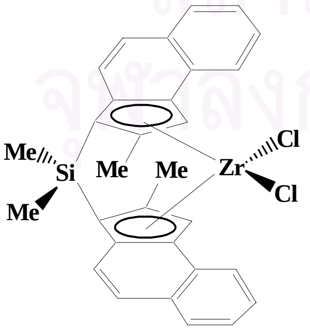
Chain growth reactions with $AlR_2Cl\text{-}MgR'_2$-activated metallocene complexes proceed in the same manner as over MAO-activated metallocenes complexes. The principal chain termination reaction is β-hydrogen elimination. In the case of ethylene/1-hexene copolymerization reactions (products prepared with a $Cp_2ZrCl_2\text{-}AlEt_2Cl\text{-}MgBu_2$ system in toluene at 85 °C), it produces two chain-end double bonds: vinyl bonds when the last monomer unit in the chain is ethylene and vinylidene bonds when the last monomer unit in the chain is 1-hexene unit. Comparison of the chain-end composition with the overall copolymer composition (by IR) shows that the probability of the second reaction is ca. 20 times higher.

$$\mathrm{Zr^{+}\!-\!CH_2\!-\!CH_2\!-\!R \longrightarrow Zr^{+}\!-\!H \;+\; H_2C{=}CH\!-\!R}$$

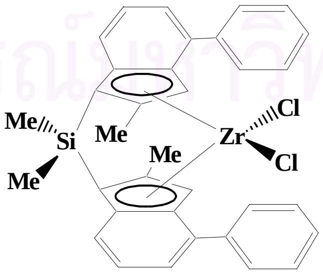
$$\mathrm{Zr^{+}\!-\!CH_2EnDash\!-\!CH_2(C_4H_9)H\!-\!R \longrightarrow Zr^{+}\!-\!H \;+\; H_2C{=}C(C_4H_9)\!-\!R}$$

In the case of zirconocene complexes, each of the components, if used alone, does not produce an olefin polymerization catalyst. However, when these components are mixed, they readily activate metallocene complexes for polymerization reactions.

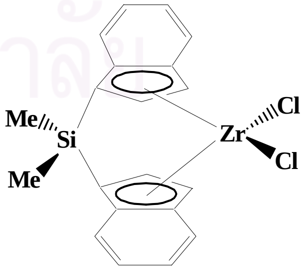
Vathauer, M. *et al.*[38] studied the polymerization of 1-butene and 1-pentene with three different metallocenes: dimethylsilylbis(2-methyl-4,5-benzoindenyl)zirconium dichloride [$Me_2Si(2\text{-}Me\text{-}4,5\text{-}BzoInd)_2ZrCl_2$] (**1**), dimethylsilylbis(2-methyl-4-phenylindenyl) zirconium dichloride [$Me_2Si(2\text{-}Me\text{-}4\text{-}PhInd)_2ZrCl_2$] (**2**), and dimethylsilylbis- (indenyl)zirconium dichloride [$Me_2Si(Ind)_2ZrCl_2$] (**3**). The polymerizations were conducted with the *rac*-isomers of the metallocenes and mixtures of the *rac*-and *meso*-systems for **1** and **2** and with the *meso*-form of catalyst **3** combined with MAO. It was shown that the activities in the polymerization of the α-olefins of the *meso*-isomers of **1** and **2** were much higher than those of the *rac*-metallocenes, while a *vice versa* behavior was observed for catalyst **3**. Additionally, reaction profiles of **1** and **2** were recorded which underlines that the stability of their *meso*-compounds are much higher than that of the *rac*-systems for the polymerization of the investigated monomers.



I



II

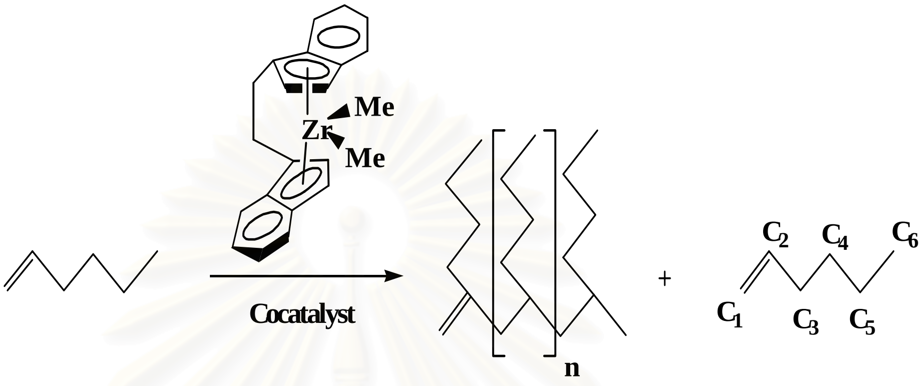


III

Liu, Z. *et al.*[39] reported the application of quenched-flow kinetics, active site counting, polymer microstructure analysis, and molecular weight distribution analysis to the determination of fundamental rate laws for initiation, propagation, and termination for the polymerization of 1-hexene in toluene solution as catalyzed by the contact ion−pair, [*rac*-(Et(1-Ind)$_2$)ZrMe][MeB(C$_6$F$_5$)$_3$] over the temperature range of -10 to 50°C. It was found that highly isotactic (>99% *mmmm*) poly-1-hexene is produced with no apparent enchained regioerrors. Initiation and propagation processes are first order in the concentrations of 1-hexene and [*rac*-(Et(1-Ind)$_2$)ZrMe][MeB(C$_6$F$_5$)$_3$] but independent of excess borane or the addition of the contact ion-pair [PhNMe$_3$][MeB(C$_6$F$_5$)$_3$].

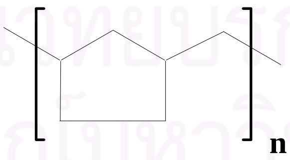
Pedeutour,J. N. *et al*.[40] studied the activation process by methylaluminoxane (MAO) of various zirconocene precursors of the type *rac*-Et(Ind)$_2$ZrX$_2$, with different extractable X ligands (X = Cl, Me, NMe$_2$, CH$_2$Ph) through 1-hexene polymerization kinetics. The different elementary steps yielding olefin polymerization active species, i.e. methylation and cationization of the transition metal could be readily discriminated. Unlike *rac*-Et(Ind)$_2$ZrCl$_2$ precursor for which high amount of MAO (Al/Zr = 2000) is required to form catalytic species active towards olefin polymerization, the complete activation of other *rac*-Et(Ind)$_2$ZrX$_2$ tested (with X = Cl, Me, NMe$_2$, CH$_2$Ph) is readily achieved at relatively low Al/Zr ratios (Al/Zr = 40-50). The corresponding zirconocenium species exhibit different catalytic activity according to the nature of the extracted X ligand, showing the important role of the formed [MAO-X]$^-$ counter-anion in the activation process and more particularly, its ability to still coordinate with the metal center and compete with the incoming olefin.

Landis, C. R. *et al.*[41] studied the first determination of empirical and computed ^{12}C/^{13}C kinetic isotope effects(KIE) for polymerization of 1-hexene using *rac*-(Et(1-Indenyl)$_2$)ZrMe$_2$ by various cocatalysts. Experimental KIE values demonstrate that the transition state in which 1-hexene is committed to irreversible insertion into the growing polymer does not vary significantly with the cocatalyst. The advantage of the KIE as a kinetic probe is its insensitivity to active site concentration. Computations support reversible 1-hexene association at the catalysts followed by irreversible migratory insertion, although a concerted process cannot be eliminated. Assuming a two-step process, the dramatic effect of cocatalyst on reaction rate arises from the effect of the counterion on the alkene association equilibrium constant.



3.3. 1,5-Hexadiene cyclopolymerization

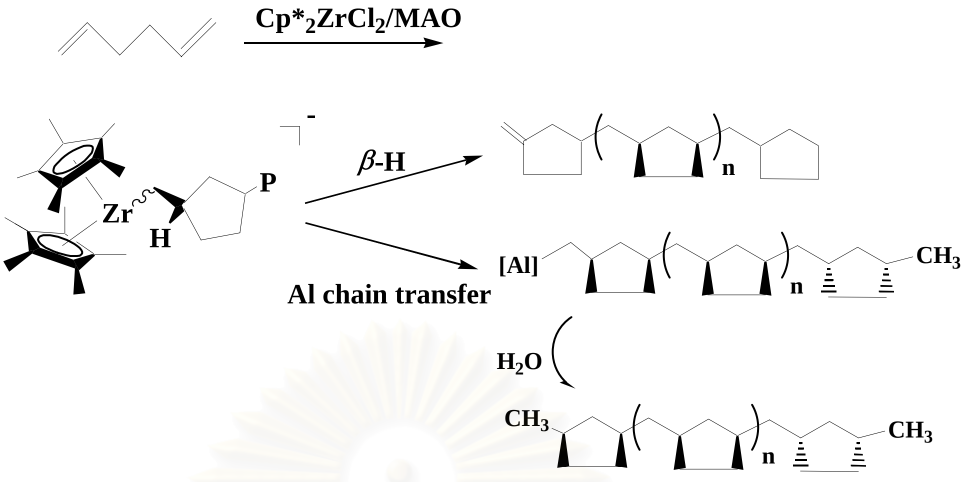
Marvel,C. S. *et al.* [42] cyclopolymerized of 1,5-hexadiene with a catalyst formed of triisobutylaluminum and titanium tetrachloride to obtain poly(methylene-cyclopentane),which is a white, tough, rubbery polymer, about 40% of which was soluble in benzene. The best conversion to a soluble polymer was obtained by using a 3:1 catalyst ratio at room temperature with a high ratio of polymerization solvent to monomer. The most probable structure for the principal recurring unit of this polymer is resulting from the intermolecular-intramolecular polymerization mechanism.



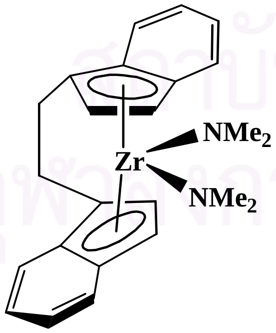
Resconi, L. *et al.* [43] cyclopolymerized of 1,5-hexadiene in the presence of Cp_2ZrX_2 derivatives (X=Cl, Me) or $Cp^*_2ZrCl_2$ catalysts and methylaluminoxane. Using Cp_2ZrCl_2 or Cp_2ZrMe_2, the reaction proceeded with conversions of 11 and 25% after 1 h to give a solid polymer (M_w = 21000 and 20000; Mw/Mn = 2.2 and 2.1, respectively). It was found that metallocene derivatives Cp_2ZrX_2（X = Cl, Me）have an unprecedented *trans* selectivity in the cyclopolymerization of 1,5-hexadiene, which the more sterically hindered $Cp^*_2ZrCl_2$ a high-*cis* polymer is obtained. Under the same conditions, polymerization of 1-hexene with Cp_2ZrMe_2 proceeded with similar conversion of monomer but yielded only low-molecular-weight oligomers (Dp= 6). Thus, under similar conditions, 1,5-hexadiene produces a much higher molecular weight polymer than 1-hexene. The polymerization of 1,5-hexadiene demonstrates higher molecular weight due to a lower termination rate, which explained by the higher strain energy of the liberated olefin (methylenecyclopentane end-groups).

Kesti, M. R. *et al.* [44] studied cyclopolymerization of 2-methyl-1,5-hexadiene by Cp^*ZrMe_2 in the presence of MAO and $B(C_6F_5)_3$ as cocatalyst. It was found that $Cp^*ZrMe_2/B(C_6F_5)_3$ system produces a solid polymer (M_w = 18175), while Cp^*ZrMe_2/MAO system afforded oligomers of lower molecular wieght (M_w = 619). In both cases the selectivity for cyclopolymerization is extremely high. The propagation species of $Cp^*ZrMe_2/B(C_6F_5)_3$ system would eliminate the possibility of chain transfer to aluminium because it contains no β-hydrogens. Both β-CH_3 elimination and chain transfer to aluminium occur in the Cp^*ZrMe_2/MAO system.

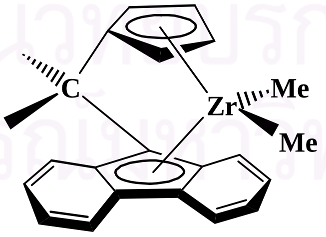
Mogstad, A.-L. *et al.*[45] cyclopolymerized 1,5-hexadiene with $Cp^*_2ZrCl_2$/ MAO. It was found that at room temperature oligomeric PMCP with an average molecular weight M_w =700 was obtained where approximately 70% of the carbocyclic rings are *cis*. At -25 °C the polymerization yields a completely saturated solid polymer ($M_w > 4000$). The absence of olefin end groups indicates that β-H elimination does not occur under these conditions. These results indicate that, chain transfer occurs both by β-H elimination and chain transfer to aluminum. Because β-H elimination is a unimolecular process and chain transfer to aluminum is bimolecular, a temperature dependence on the ratio of these two processes might be expected.



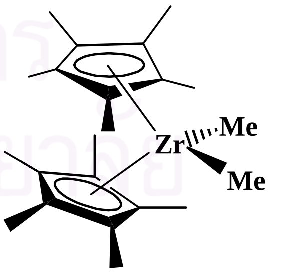
Kim, I. *et al.*[46] cylopolymerized 1,5-hexadiene at various temperature in toluene by using three different stereospecific metallocene catalysts: isospecific *rac*-(EBI)Zr(NMe$_2$)$_2$; **Cat 1**, syndiospecific Me$_2$C(Cp)(Flu)ZrMe$_2$; **Cat 2** and aspecific Cp*$_2$ZrMe$_2$; **Cat 3** in the presence of Al(*i*-Bu)$_3$ and [Ph$_3$C][B(C$_6$F$_5$)$_4$]. It was found that the resulted polymer is poly(methylene-1,3-cyclopentane)(PMCP). The activities of catalysts decrease in the following order: **Cat 1** > **Cat 2** > **Cat 3**. PMCPs produced by **Cat 1** are not completely soluble in toluene, but PMCPs by **Cat 2** and **Cat 3** are soluble. *trans*-Diisotactic rich PMCPs are produced by **Cat 1** and **Cat 2** , and *cis*-atactic PMCP by **Cat 3**. The *cis*/*trans* ratio PMCP by **Cat 1** and **Cat 2** is relatively insensitive to the polymerization temperature, but that by **Cat 3** is highly sensitive to the polymerization temperature. Melting temperatures of PMCP produced increase with the *cis* to *trans* ratio of rings



Cat 1



Cat 2



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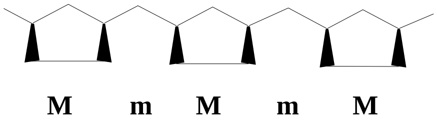
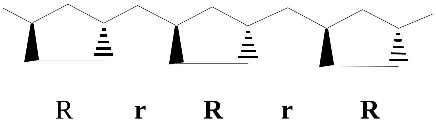
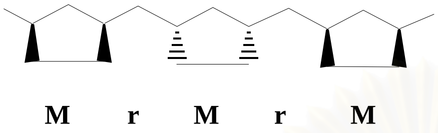


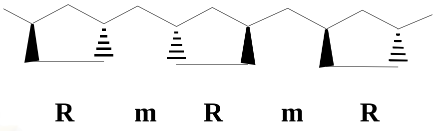
***cis*-diisotactic**



***trans*-diisotactic**



***cis*-disyndiotactic**



***trans*-disyndiotactic**

3.4. Copolymerization of 1-hexene and 1,5-hexadiene with other monomer

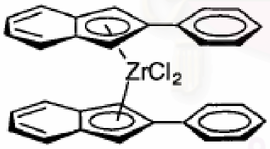
3.4.1. 1-Hexene copolymerization

Stehling, U. M. *et al.*[16] studied metallocene/borate catalysts, generated from zirconocene dimethyl compounds, L_nZrMe_2, and anilinium borate, $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$, were used to copolymerize 5-*N*,*N*-diisopropylamino-1-pentane with 1-hexene and 4-methyl-1-pentene. The selected zirconocenes, bis(pentamethylcyclo pentadienyl) zirconium(IV) dimethyl ($Cp^*_2ZrMe_2$) and *rac*-ethylenebis(4,5,6,7-tetra hydroindenyl)zirconium(IV) dimethyl (*rac*-EB(THI)$ZrMe_2$), provided atactic and isotactic materials, respectively. The isotactic polymers produced were amorphous or crystalline depending of the monomer. The polymerization of 1-hexene in the presence of the saturated 1-*N*,*N*-diisopropylaminopentane with *rac*-EB(THI)$ZrMe_2$/borate was compared with analogous copolymerizations of 1-hexene/5-*N*,*N*-diisopropylamino-1-pentene. The aminopentene was more effective than the aminopentane in inhibiting the rate of total monomer conversion, implicating both intra- and intermolecular mechanisms for inhibition by the amine. Copolymers of 4-methyl-1-pentene/5-*N*,*N*-diisopropylamino-1-pentene produced with *rac*-ethylenebisindenyl zirconium(IV) dimethyl (*rac*-EBI$ZrMe_2$) /borate have higher decomposition temperatures with increasing amounts of aminopentene.

Lehmus, P. *et al.*[47] investigated the influence of siloxy substitution of ethylene-bridged bis(indenyl)- and bis (tetrahydroindenyl)zirconium dichlorides on ethylene/1-hexene copolymerization. Ethylene was copolymerized with 1-hexene over *rac*-[ethylenebis(1-(*tert*-butyldimethylsiloxy)-3-indenyl)]zirconium dichloride(**1**), *rac*-[ethylenebis(1-(*tert*-butyldimethylsiloxy)-4,5,6,7-tetrahydro-3-indenyl)] zirconium dichloride(**H1**), *rac*-[ethylenebis(2-(*tert*-butyldimethylsiloxy)-1-indenyl)] zirconium dichloride(**2**) and *rac*-ethylenebis(1-indenyl)zirconium dichloride(**EBI**) using MAO as cocatalyst. 1-Siloxy substitution was found to improve the copolymerization ability and 2-siloxy substitution enhances the polymerization activity of ethylenebis(indenyl) zirconium dichlorides. Optimum copolymerization condition was observed at a vary low Al(MAO) concentration(= 500), which for **2** could be reduced to a level of 0.2 mmol/dm^3 by using a small amount of triisobutylaluminium. The 1-siloxy-substituted metallocene catalysts **1** and **H1**(hydrogenated 1) revealed decreasing comonomer incorporation and increasing induction times with increasing Al(MAO) concentration, which indicates the presence of unfavorable interactions betweens these metallocenes and MAO. Chain termination occurred mainly by chain transfer to the monomer and β-hydrogen transfer to the metal for catalysts with indenyl and tetrahydroindenyl ligands, respectively.

Stehling, U. M. *et al.*[48] copolymerized 5-*N*,*N*-diisopropylamino-1-pentene with 1-hexene using zirconocene/borate catalysts $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$. The selected zirconocenes: bis(pentamethylcyclopentadienyl)zirconium(IV) dimethyl ($Cp^*_2ZrMe_2$) and *rac*-ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium(IV) dimethyl (*rac*-EB(THI) $ZrMe_2$), provided atactic and isotactic materials, respectively. It was found that the isotactic polymers produced were amorphous or crystalline depending of the monomer. The calculated reactivity ratios for the copolymerization of 5-*N*,*N*-diisopropylamino-1-pentene with 1-hexene and metallocene *rac*-EB(THI)$ZrMe_2$ indicate that this system approximates an ideal azeotropic copolymerization with r_1 = 1.11 and r_2 = 0.87. Estimates for the reactivity ratios for the copolymerization of 5-*N*,*N*-diisopropylamino-1-pentene with 4-methyl-1-pentene were r_1 = 3 and r_2 = 1 for *rac*-EB(THI)$ZrMe_2$ and r_1 = 5 and r_2 = 0.5 for $Cp^*_2ZrMe_2$. The polymerization of 1-hexene in the presence of the saturated 1-*N*,*N*-diisopropylaminopentane with *rac*-EB(THI)$ZrMe_2$/borate was compared with analogous copolymerizations of 1-hexene/5-*N*,*N*-diisopropylamino-1-pentene. The aminopentene was more effective than the aminopentane in inhibiting the rate of total monomer conversion, implicating both intra- and intermolecular mechanisms for inhibition by the amine. Copolymers of 4-methyl-1-pentene/5-*N*,*N*-diisopropylamino-1-pentene produced with *rac*-ethylenebis(indenyl) zirconium(IV) dimethyl (*rac*-EBIZrMe$_2$)/borate have higher decomposition temperatures with increasing amounts of aminopentene.

Reybuck, S. E. *et al.*[5] studied the copolymerization of ethylene and 1-hexene with a variety of unbridged indenylmetallocenes(**1-3**) and compared to unbridged bis(indenyl)zirconium dichloride(**5**) and bis(cyclopentadienyl)zirconium dichloride(**6**) as well as *ansa*-bridged *rac*-ethylenebis(indenyl)zirconium dichloride (EBIZrCl$_2$)(**4**). The unbridged bis(2-phenylindenyl)zirconium dichloride(**1**) showed higher selectivity for the incorporation of 1-hexene than **4** and much higher 1-hexene incorporation than **5** and **6**. Both ligands appear to be important since the 1-hexene incorporation of the mixed ligand compound (cyclopentadienyl)(2-phenylindenyl)zirconium dichloride(**2**) is much lower than **1**. For unbridged bis(indenyl)metallocenes, the nature of the substituent in the 2-position plays an important role in comonomer selectivity:



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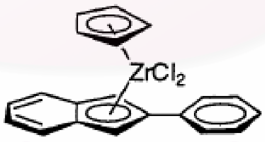

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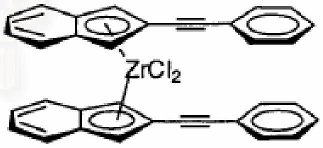

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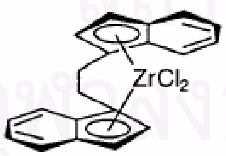

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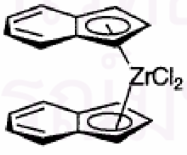

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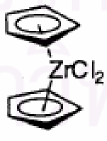

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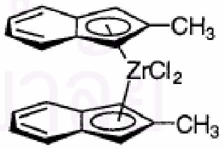


7

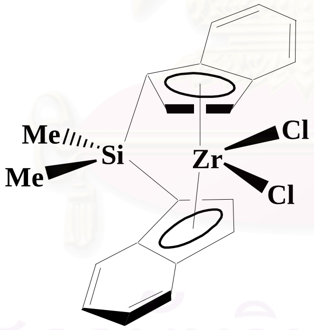
3.4.2. 1,5-Hexadiene copolymerization

Chung, T. C. *et al.*[15] studied the synthesis of poly(ethylene-co-1,4-hexadiene) copolymers, which are useful intermediates for the preparation of functionalized linear low-density polyethylene (LLDPE-f). Three catalyst systems, including one heterogeneous catalyst ($TiCl_4$.AA/Et_2AlCl) and two homogeneous metallocene catalysts (Cp_2ZrCl_2 and $Et(Ind)_2ZrCl_2$ with MAO), were used in the copolymerization reaction between ethylene and 1,4-hexadiene. In general, the homogeneous catalysts are much more effective than their heterogeneous counterparts in the incorporation of diene monomers in PE structure. Especially, the single-site $Et(Ind)_2C1_2$/MAO catalyst with a strained geometry provides unsaturated PE with narrow molecular weight distribution and controllable diene concentration.

Bergemann, C. *et al.*[49] investigated the copolymerization of ethylene and 1,5-hexadiene under high pressure of 1500 bar using dimethylsilylbis(tetrahydroindenyl) zirconium dichloride in the presence of MAO. It was found that the activity of catalyst is high when the concentration of diene is below 20 %mol in the feed, but lower than in the homopolymerization of ethylene. The analysis of the resulting copolymers shows a decrease of the molecular weight, the melting point and the crystallinity with increasing concentration of the comonomer in the feed, which was expected. The selectivity for cyclization depends on the polymerization conditions. It improves with decreasing concentration of 1,5-hexadiene. At high concentrations of the diene the competitive reaction, the 1,2-polymerization of 1,5-hexadiene, is favoured.

Pietikainen, P. *et al.*[50] studied copolymerization of ethylene with 1,5-hexadiene(HD) by Cp_2ZrCl_2/MAO system at 90°C. According to the results, HD formed five-member rings to polyethylene, even though selectivity towards cyclization has been reported to decrease when HD concentration in the reactor increases over 50 %mol. HD addition had almost no effect on the molar mass. The conversion of HD decreased when the diene concentration in the reactor was increased.

Naga, N. *et al.*[51] copolymerized of propene with 1,5-hexadiene with isospecific *rac*-dimethylsilylenebis(indenyl)zirconium dichloride(**1**) and syndiospecific diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride(**2**) combined with MAO. Microstructures of the copolymers were determined by ^{1}H-NMR, ^{13}C-NMR and DEPT spectroscopies. Incorporation of 1,5-hexadiene in the copolymer was higher with **2** than with **1**. Intramolecular cycloaddition of the 1,5-hexadiene proceeded regardless of the catalysts. Stereoselectivity in cycloaddition of 1,5-hexadiene was investigated based on the structures of isolated methylene-1-cyclopentane units. It was found that 1,5-hexadiene was inserted stereospecifically by enantiomorphic site control with both catalysts. The diastereoselectivity of the cyclization step of 1,2-inserted 1,5-hexadiene was, however, found to be independent of stereospecificity of the catalyst. **1** gave the copolymers with higher selective in cyclization than **2**. Decrease of cyclization selectivity was observed with the increases of 1,5-hexadiene concentration in copolymerization. Propene insertion could disturb the cyclization of 1,2-inserted dienes, which declined the cyclization selectivity of the copolymers, except propene/1,5-hexadiene copolymerization with **2**.



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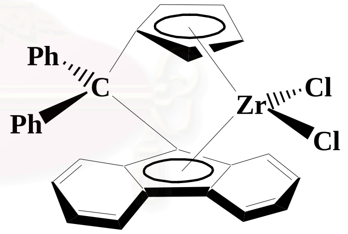


2

Pietikainen, P. *et al.*[52] studied copolymerization of ethylene with 1,5-hexadiene(HD) by Cp_2ZrCl_2/MAO system at several temperatures from 20 to 80°C. Polymerization conditions had a dramatic effect on the degree of crosslinking of the product. At polymerization temperatures from 20 to 65°C the copolymer of ethylene and HD were nearly totally crosslinked, whereas at 80°C the degree of crosslinking was under 10%.

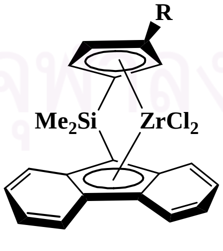
Kim, I. *et al.*[53] copolymerized propylene with 1,5-hexadiene (HD) with isospecific *rac*-1,2-ethylenebis(1-indenyl)Zr(NMe_2)$_2$, [*rac*-(EBI)Zr(NMe_2)$_2$] and syndiotactic isopropylidene(cyclopentadienyl)(9-fluorenyl)ZrMe_2 [*i*-Pr(Cp)(Flu)ZrMe_2] compounds combined with Al(*i*-Bu)$_3$/[Ph_3C][B(C_6F_5)$_4$] as a cocatalyst. The isospecific *rac*-(EBI)Zr(NMe_2)$_2$/Al(*i*-Bu)$_3$/[Ph_3C][B(C_6F_5)$_4$] catalyst showed much higher polymerization rate than *i*-Pr(Cp)(Flu)ZrMe_2/Al(*i*-Bu)$_3$/[Ph_3C][B(C_6F_5)$_4$] system, however, the latter system showed higher incorporation of HD than the former system. The high value of r_p x r_{HD} far above *rac*-(EBI)Zr(NMe_2)$_2$ demonstrated that the copolymers obtained by both catalysts are blocky.

Britto, M. L. *et al.*[54] copolymerized ethylene and 1-hexene in hexane at 60°C by using ethylenebis(indenyl)zirconium dichloride/MAO in the presence of triisobutylaluminium(TIBA). The influence of the alkylaluminum concentration and Al/Zr molar ratio on the catalyst activity and comonomer incorporation were evaluated. Increasing the TIBA concentration, MAO solubility is increased, as well as the catalyst activity and the comonomer incorporation. Increasing the Al/Zr molar ratio, catalyst activity becomes higher, while comonomer incorporation remained constant at around 8 %wt for molar ratios between 0 to 5000. For Al/Zr molar ratios higher than 5000 comonomer incorporation increased gradually. Under the same conditions dimethylsilylbis(indenyl)zirconium dichloride showed higher thermal stability and led to higher comonomer incorporation.

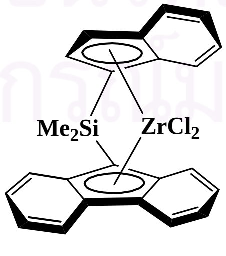
Kim, I. *et al.*[55] copolymerized ethylene and 1,5-hexadiene(HD) with *rac*-1,2-ethylenebis(1-indenyl)Zr(NMe_2)$_2$ [*rac*-(EBI)Zr(NMe_2)$_2$] and isopropylidene (cyclopentadienyl)(9-fluorenyl)ZrMe_2 (^{i}Pr(Cp)(Flu)ZrMe_2) compounds combined with Al(*i*-Bu)$_3$/[Ph_3C][B(C_6F_5)$_4$] as a cocatalyst system. It was found that the isospecific *rac*-(EBI)Zr(NMe_2)$_2$/Al(*i*-Bu)$_3$/[Ph_3C][B(C_6F_5)$_4$] catalyst showed much higher polymerization activity than syndiospecific ^{i}Pr(Cp)(Flu)ZrMe_2/Al(*i*-Bu)$_3$/[Ph_3C] [B(C_6F_5)$_4$] catalyst, however, the latter catalyst showed much higher comonomer reactivity. The 1,2-inserted HD led to cyclic backbones by the intramolecular reaction. The intramolecular cyclization was independent of the polymerization temperature.

Detailed investigation on the structure of copolymers by ^{13}C-NMR and DEPT spectroscopy showed that alternating structural units become predominant as the amount of HD incorporated into the copolymer increased.

Choo, T. N. *et al.*[56] copolymerized ethylene with 1-hexene or 1,5-hexadiene using several zirconocene catalysts(**1-5**) in the presence of MAO as cocatalyst. The result of copolymer composition reveals that 1,5-hexadiene and 1-hexene are readily copolymerized with ethylene in the presence of metallocenes **1**, **3**, and **4**. Under these conditions ([HD] < 2.0 M), 1,5-hexadiene cyclopolymerizes almost exclusively to give methylene-1,3-cyclopentane units in the copolymers, with only traces of uncyclized 1,2-inserted hexadiene. The diastereoselectivity of the cyclocopolymerization favors the formation of *trans*-1,3-cyclopentane rings for metallocenes **1**, **3**, and **4** (74% trans, 81% trans, and 66% trans respectively). For metallocenes **1** and **4**, the E/H and E/HD copolymerization yielded copolymers with similar comonomer compositions and sequence distributions over a range of feed ratios. This result suggests that for catalysts derived from **1** and **4**, the copolymerization behavior of 1,5-hexadiene is similar to that of 1-hexene, even though the nature of the propagating polymer chain end after the insertion of the α-olefin is slightly different (i.e. a butyl branch *vs* a 1,3-cyclopentane unit). In contrast, the E/H and E/HD copolymers derived from metallocene **3** show very different compositions and sequence distributions over the range of feed ratios investigated. At comparable feed ratios, the E/HD copolymers obtained were enriched in the hexadiene comonomer and deficient in ethylene when compared to the corresponding E/H copolymers.



1 **R = H**
2 **R = Me**



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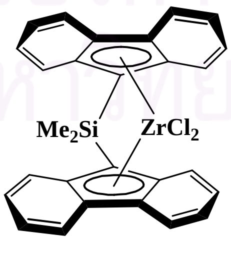

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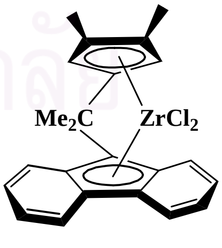

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CHAPTER IV

EXPERIMENT

In the present study of homo- and copolymerization of 1-hexene and 1,5-hexadiene with zirconocene catalysts, the experiment was divided as follows:

1. Synthesis and characterization of zirconocene catalysts.
2. 1-Hexene polymerization with the prepared zirconocene catalysts and characterization of poly(1-hexene) product.
3. 1,5-Hexadiene polymerization with the prepared zirconocene catalysts and characterization of poly(1,5-hexadiene) products.
4. 1-Hexene and 1,5-hexadiene copolymerization with the prepared zirconocene catalysts and characterization of products.

The details of the experiments were explained in the following.

4.1. Operation and equipments

The experiments were done in an inert atmosphere, prepurified nitrogen, using standard Schlenk technique. All equipments used in the catalyst preparation and polymerization are listed as follows:

4.1.1. Schlenk line

Schlenk line consists of nitrogen and vacuum lines. The vacuum line was equipped with the solvent trap and pump, respectively. The nitrogen line was connected to the moisture trap (purified nitrogen gas by passing through molecular sieve, NaOH and P_2O_5, respectively.) and the oil bubbler that contained enough oil to provide a seal from the atmosphere. The Schlenk line was shown in Figure 4.1.

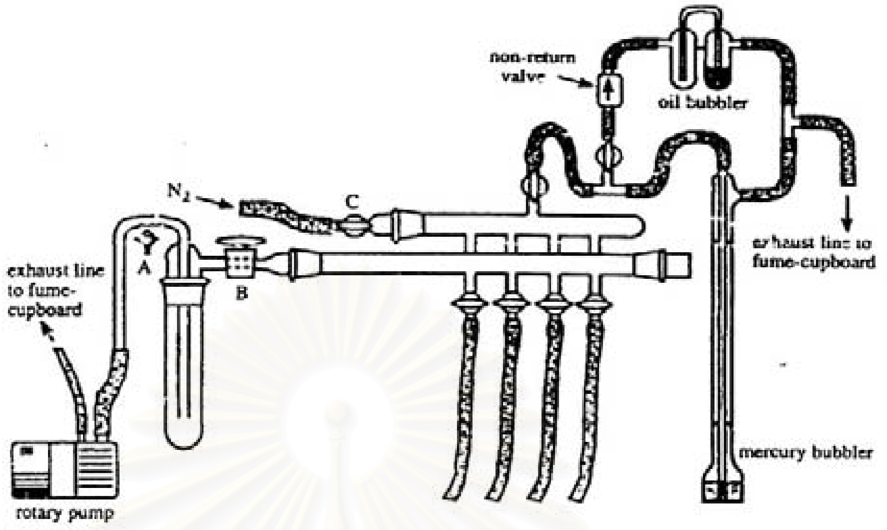


Figure 4.1 Schlenk line.

4.1.2. Schlenk flask

A flask with a side-arm for use with inert gas. It has a side-arm to connect to the Schlenk line manifold. Some typical models are shown in Figure 4.2.

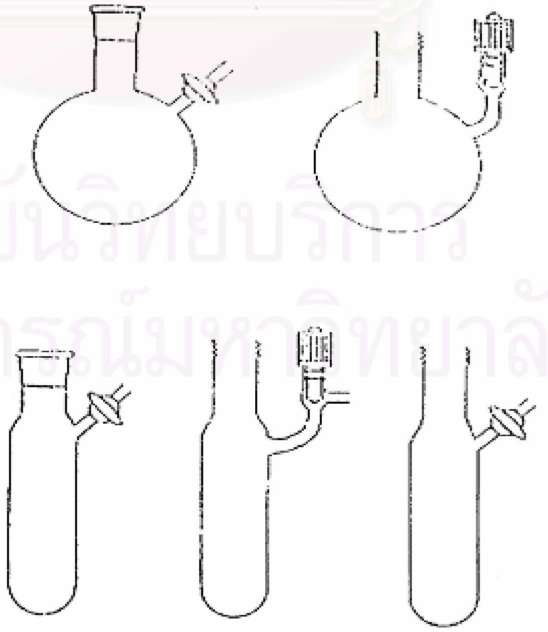


Figure 4.2 Round-bottomed and tube Schlenk flasks.

4.1.3 Vacuum pump

A pressure of $10^{-3} – 10^{-1}$ mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

4.1.4 Heating bath

The heating oil bath with thermometer was used to hold the temperature of polymerization reaction.

4.1.5 Inert gas supply

Ultra high purity nitrogen gas was purified by passing through three columns packed with molecular sieve 4^{o}A, NaOH and P_2O_5, respectively. The inert gas was used to feed in the nitrogen line of the Schlenk line and polymerization reactor.

4.1.6 Syringe and needle

The syringes with volume of 50, 10, 5, 2, 1 and 0.5 ml. Needles No. 19, 20, and 22 were used.

4.1.7 Glove bag

Glove bag is a moderate-volume gas-tight container from which air or moisture are excluded. The glove bag has a way to connect to the Schlenk line, which can be evacuated and then filled with nitrogen gas.

4.2 Chemicals

The chemicals used in this experiment are analytical grade, except critical materials are specified as follows:

Table 4.1 Chemical reagents and suppliers

Chemicals	Suppliers
1. Ultra high purity nitrogen gas (99.999%)	Thai Industry Gas Co.,Ltd., Thailand
2. Toluene	Lab Scans Co., Ltd., Ireland
3. Tetrahydrofuran	Lab Scans Co., Ltd., Ireland
4. Dichloromethane	Merck, Germany
5. Methanol	Lab Scans Co., Ltd., Ireland
6. Diethyl ether	Lab Scans Co., Ltd., Ireland
7. Petroleum ether	J. T. Baker Inc., U.S.A.
8. Chloroform	Lab Scans Co., Ltd., Ireland
9. Xylene	Lab Scans Co., Ltd., Ireland
10. Butyl lithium(*n*-BuLi)	Merck, Germany
11. Zirconium tetrachloride, $ZrCl_4$	Fluka Chemie A.G., Switzerland
12. Dicyclopentadiene	Fluka Chemie A.G., Switzerland
13. Indene	Fluka Chemie A.G., Switzerland
14. Dibromoethane	Fluka Chemie A.G., Switzerland
15. 1-Hexene	Fluka Chemie A.G., Switzerland
16. 1,5-Hexadiene	Fluka Chemie A.G., Switzerland
17. Sodium sulfate anhydrous	Merck, Germany
18. Ammonium chloride	Merck, Germany
19. Methylaluminoxane (MAO) has Al 9%w/v	Donated from Japan Advanced Institute of Science and Technology (JAIST), Japan
20. Triisobutylaluminium, TIBA	Donated from Japan Advanced Institute of Science and Technology (JAIST), Japan
21. Triphenylcarbenium tetrapentafluorophenyl borate, $[Ph_3C][B(C_6F_5)_4]$	Donated from Japan Advanced Institute of Science and Technology (JAIST), Japan

In this work, several reagents react violently with water and ignite spontaneously in air (by reaction with oxygen and/or moisture). So they were handled safely using inert atmosphere techniques (Schlenk and glove bag techniques). Also, the chemicals and solvents were dried before use with following methods:

1. Non - halogenated solvent was purified by refluxing over sodium /benzophenone and distilled under nitrogen atmosphere.
2. Dichloromethane was purified by refluxing with calcium hydride before use.
3. Diethyl ether was dried by storing over molecular sieve.
4. 1-Hexene was dried over calcium hydride and distilled before use.
5. 1,5-Hexadiene was dried over calcium hydride and distilled before use.

In many low temperature reactions, the mixture of dry ice-acetone was used for temperature of –78^{o}C and dry ice-carbon tetrachloride was used for -20^{o}C.

4.3 Characterization methods

The methods used to characterize catalyst and polymer products are specified in the following:

4.3.1 Fourier transform infrared spectrometry (FT-IR)

Fourier transform infrared spectra of the polymers and complexes were recorded on Nicolet FT-IR Impact 410 Spectrophotometer at Department of Chemistry, Chulalongkorn University. The liquid samples were coated on NaCl cells. The solid samples were prepared by pressing the sample with KBr. Infrared spectra were recorded between 400 cm^{-1} to 4,000 cm^{-1} in transmittance mode.

4.3.2 Nuclear magnetic resonance spectroscopy (NMR)

^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker ACF 200 MHz at Department of Chemistry, Chulalongkorn University. The NMR spectra were measured in chloroform-d at room temperature. Broad-band decoupling was used to remove the ^{13}C-^{1}H coupling. The center peak of chloroform-d was used as the internal reference (^{1}H-NMR at 7.2 ppm and ^{13}C-NMR at 77.0 ppm).

For copolymer products, ^{13}C-NMR spectra were obtained on JNM-A500 MHz operated at 125.65 MHz in the pulse Fourier transform mode at the Scientific and Technological Research Equipment Centre (STREC), Chulalongkorn University. ^{13}C-NMR spectra were run using inverse-gated decoupling technique. Spectra were taken with a flip angle 45°, an acquisition time of 0.5 s, and a delay of 2.0 s. The NMR spectra were measured in chloroform-d at room temperature.

4.3.3 Differential scanning calorimetry (DSC)

The melting temperature (T_m) and the glass-transition temperature (T_g) of the polymers were determined by a NETZSCH DSC 200 at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. The analyses were performed at the heating rate of 10^{o}C/min. in the temperature range of 25 – 300^{o}C. The heating cycle was run twice. In the first scan, polymer products were heated and then cooled down to room temperature. In the second scan, samples were reheated at the same rate, only the last scan was recorded because the first scan was influenced by the mechanical and thermal history of samples.

4.3.4 Gel permeation chromatography (GPC)

GPC curves of polymers were determined on a Waters 150-CV GPC at the National Metal and Materials Technology Center (MTEC), the National Science and Technology Development Agency (NSTDA). The molecular weight and molecular weight distribution of the polymer was measured at room temperature using THF as an eluent solvent at a flow rate of 1 mL/min by Waters 150-C column (column TL gel 10 μm mixed B 2 column, reflextive index detector and injection volumn 100 μL). Polystyrene standard molecular weights in range of 500 to 1,000,000 were used for calibration.

4.4 Procedures for zirconocene catalysts synthesis

4.4.1 *rac*-Ethylenebis(indenyl)zirconium dichloride : *rac*-Et(Ind)$_2$ZrCl$_2$[57]

Into a 100 mL three-necked flask equipped with dropping funnel and a magnetic bar, indene (0.049 mol, 5.67 g) was added dropwise in the THF 30 mL. Add dropwise of *n*-BuLi (0.049 mol, 19.5 mL) at -78°C over a period of one hour. The solution turned red. After that it was warmed up to room temperature and stirred for another hour. Add dropwise of 1,2-dibromoethane (0.024 mol, 4.5 g) dissolved in THF 5 mL *via* the dropping funnel slowly. Then stir for two hours at room temperature. Cool the reaction mixture to 0°C, quench with saturated solution of ammonium chloride. Transfer the contents of the flask to a separatory funnel and add 20 mL petroleum ether to dilute the organic phase. Discard the aqueous phase and wash the organic phase with 20 mL distilled water, dried with anhydrous sodium sulphate. Separate the sodium sulphate by filtration, reduce solvent to obtain white crystals.

A solution of diindenylethane (0.01 mol, 2.584 g) in 100 mL of dry THF was treated with a solution of *n*-BuLi in hexane (0.02 mol, 8.44 mL of 2.4 M) at -78°C. The mixture was warmed to room temperature and after 1 h an orange-red solution of the dianion was obtained. Then it was added into $ZrC1_4$ (0.01 mol, 4.77 g) dissolved in 50 mL of THF in a separate flask, with vigorous stirring. The orange-yellow solution was stirred overnight at room temperature. Then, the solution was cooled to 0°C and a yellow solution was obtained. The solvent was reduced *in vacuo* until yellow precipitate had separated (2.18 g, 52 %yield).

^{1}H-NMR(CDCl$_3$): δ (ppm) 7.1-7.6 (m, C_6 ring), 6.57 (d, C_5 ring(α)), 6.19 (d, C_5 ring (β)), 3.74 (s, C_2H_4 bridge)

ref.[57] 7.1-7.6 (m, C_6 ring), 6.57 (d, C_5 ring(α)), 6.19 (d, C_5 ring (β)), 3.74 (s, C_2H_4 bridge)

^{13}C-NMR(CDCl$_3$): δ (ppm) 126.7, 126.6, 125.7, 121.8, 121.4, 113.9, 110.8, 29.1

FT-IR (NaCl): ν (cm^{-1}) 2918(w), 1634(s), 1459(d), 1264(s), 1097(s), 801(s), 739(s)

4.4.2 Bis(cyclopentadienyl) zirconium dichloride : Cp_2ZrCl_2[58]

Cyclopentadiene (0.05 mol, 4.12 g) was reacted with finely divided sodium (0.05 mol, 1.15 g) in THF 10 mL. The mixture was stirred at room temperature, the resulting orange solution of cyclopentadienyl sodium was cooled and was injected slowly into zirconium tetrachloride ($ZrCl_4$) (0.017 mol, 3.96 g). After stirring the reaction for 3 hours, the solvent was removed by vacuum. The residue was then extracted with chloroform, cooled in a dry ice-acetone bath and the crystals separated by filtration. The resulting colorless crystal is bis(cyclopentadienyl) zirconium dichloride (2.5 g, 30 %yield). This compound was identified by comparing its ^{1}H-NMR spectrum with that reported in the literature.[58]

^{1}H-NMR($CDCl_3$): δ (ppm) 6.40-6.51 (m, C_5 ring)

^{13}C-NMR($CDCl_3$): δ (ppm) 116.1 (s, C_5 ring)

FT-IR (NaCl): ν (cm^{-1}) 2922(w), 1443(s), 1018(s), 922(s), 805(s)

4.5 Preparation of catalyst solution

4.5.1 *rac*-Et(Ind)$_2$ZrCl$_2$ catalyst stock solution

rac-Et(Ind)$_2$ZrCl$_2$, yellow-brownish solid 0.0836 g (2.0×10^{-4} mol) was dissolved in 50 mL distilled toluene.

4.5.2 Cp_2ZrCl_2 catalyst stock solution

Cp_2ZrCl_2, white solid 0.0407 g (1.39×10^{-4} mol) was dissolved in 50 mL distilled toluene.

4.6 Polymerization procedure

4.6.1 Polymerization of 1-hexene

Polymerization of 1-hexene was carried out under dry nitrogen atmosphere in a 100 ml round bottomed Schlenk flask with a magnetic bar. Zirconocene catalyst solution and MAO solution were stirred at room temperature for 1 h, then equilibrate to the desired temperature for 30 minutes, 1-hexene monomer was injected to start the polymerization. Finally, the polymerization was terminated by adding 5% aqueous hydrochloric acid. The organic layer was separated, dried over Na_2SO_4 and the polymerization product was obtained after evaporation of the solvent.

4.6.2 Polymerization of 1,5-hexadiene

Polymerization of 1,5-hexadiene was carried out under dry nitrogen atmosphere in a 100 ml round bottomed Schlenk flask with a magnetic bar. Zirconocene catalyst solution and MAO solution was stirred at room temperature for 1 h, then equilibrate to the desired temperature for 30 minutes, 1,5-hexadiene monomer was injected at 0 °C to start the polymerization. Finally, the polymerization was terminated by adding methanol. The organic layer was separated, dried over Na_2SO_4 and the polymer was obtained after evaporation of the solvent.

In the case of boron compound as cocatalyst, catalyst solution was mixed with triisobutylaluminium (TIBA) and stirred at room temperature for 30 minutes. After that, a boron cocatalyst solution was added and stirred for 30 minutes. After the reaction mixture was equilibrated to the desired temperature for 30 minutes. The next steps were the same as in MAO.

4.6.3 Copolymerization of 1-hexene and 1,5-hexadiene

Copolymerization of 1-hexene and 1,5-hexadiene was carried out under dry nitrogen atmosphere in a 100 ml round bottomed Schlenk flask with a magnetic bar. Zirconocene catalyst solution, MAO solution was stirred at room temperature for 1 h, then equilibrate to the desired temperature for 30 minutes, 1-hexene and 1,5-hexadiene monomer was injected. The next steps were the same as in section 4.6.1.

In the case of boron compound as cocatalyst, zirconocene catalyst solution, 1,5-hexadiene monomer was mixed with triisobutylaluminium (TIBA) and stirred at room temperature for 30 minutes. After the reaction mixture was equilibrated to the desired temperature for 30 minutes. 1-hexene monomer and boron cocatalyst solution was injected to start the polymerization. The next steps were the same as in MAO.

4.7 Characterization of polymer and copolymer

Poly(1-hexene), poly(1,5-hexadiene) and copolymer products were characterized by the following methods.

1. Fourier transform infrared spectrometry (FT-IR)

   The FT-IR technique was used to characterize a polymer functional group.

2. Nuclear magnetic resonance spectroscopy (NMR)

   Nuclear magnetic resonance spectroscopy was used to determine tacticity of polymer. The samples were dissolved in chloroform-d, run at room temperature. The chemical shift in ^{13}C-NMR spectra determined the tacticity of the polymer.

   For ^{13}C-NMR spectra of copolymer used to integrate amount of monomer in copolymer.

3. Differential scanning calorimetry (DSC)

   Differential scanning calorimetry was used to determine the thermal properties of polymer products such as melting temperature (T_m) and glass-transition temperture (T_g).

4. Gel permeation chromatography (GPC)

   Gel permeation chromatography was used to determine weight average molecular weight (M_w), number average molecular weight (M_n) and molecular weight distribution (MWD).

4.8 Activity

Activity in this experiment can be calculated by the equation

Activity = kilograms of polymer / mole of catalyst

4.9 % Conversion

% Conversion in this experiment can be calculated by the equation

$$\%\ \text{Conversion} = \frac{[(\text{grams of initial monomer})\text{-grams of product}] \times 100}{\text{grams of initial monomer}}$$

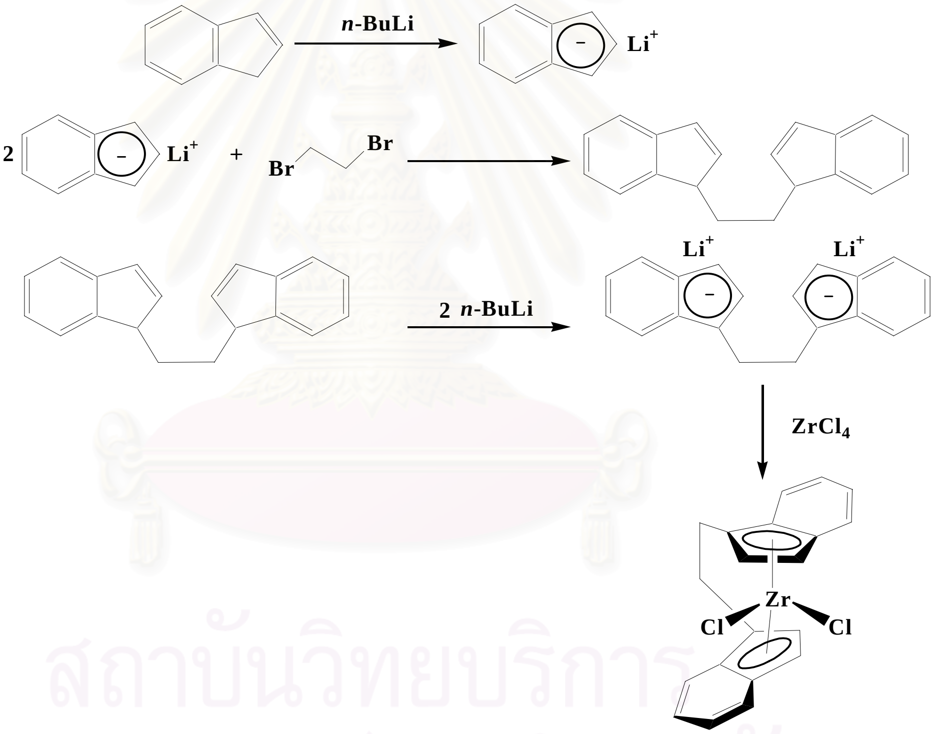
CHAPTER V

RESULTS AND DISCUSSION

5.1 Synthesis of zirconocene catalysts

5.1.1 *rac*-Ethylene-bis(indenyl)zirconium dichloride; *rac*-Et[Ind]$_2$ZrCl$_2$

The synthesis of *rac*-ethylene-bis(indenyl)zirconium dichloride was followed as in Scheme 5.1.



Scheme 5.1 Synthesis of *rac*-ethylene-bis(indenyl)zirconium dichloride.

The *rac*-ethylene-bis(indenyl)zirconium dichloride was prepared as follows: indene was firstly lithiated with *n*-BuLi at -78°C to indenyllithium. Two equivalents of indenyllithium were reacted with 1,2-dibromoethane at room temperature to obtain diindenylethane. Then it was further lithiated with two equivalents of *n*-BuLi at -78°C to yield diindenyllithium ethane, which was reacted with zirconium tetrachloride, resulted in *rac*-ethylene-bis(indenyl)zirconium dichloride as yellow-brownish crystals (52% yield).

The ^{1}H-NMR, ^{13}C-NMR and FT-IR spectra of *rac*-ethylenebis(indenyl) zirconium dichloride were shown in Figures 5.1-5.3. The assignments of peaks are in Tables 5.1-5.3.

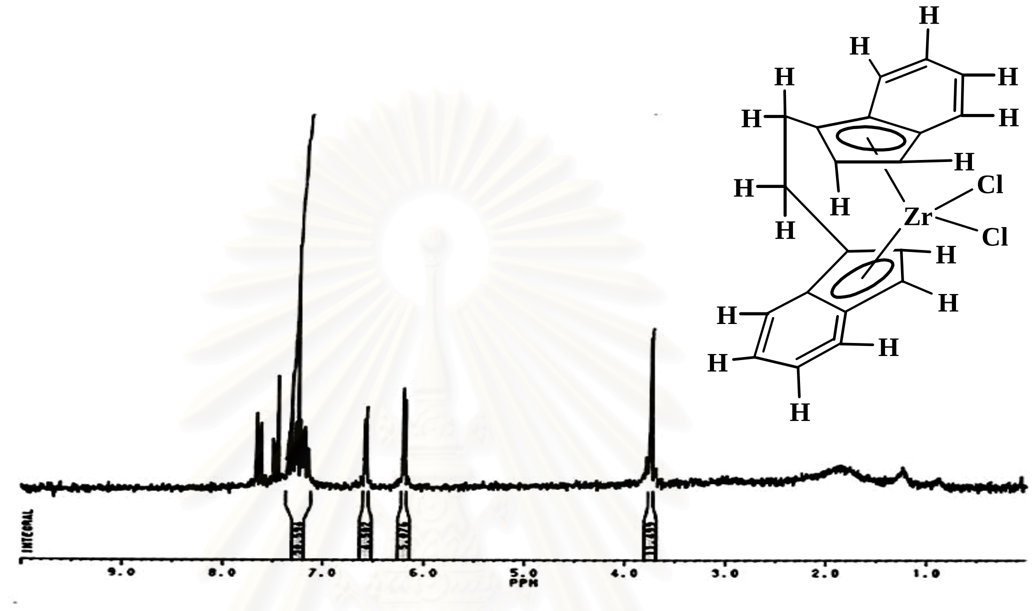


Figure 5.1 ^{1}H-NMR ($CDCl_3$) spectrum of *rac*-ethylene-bis(indenyl)zirconium dichloride.

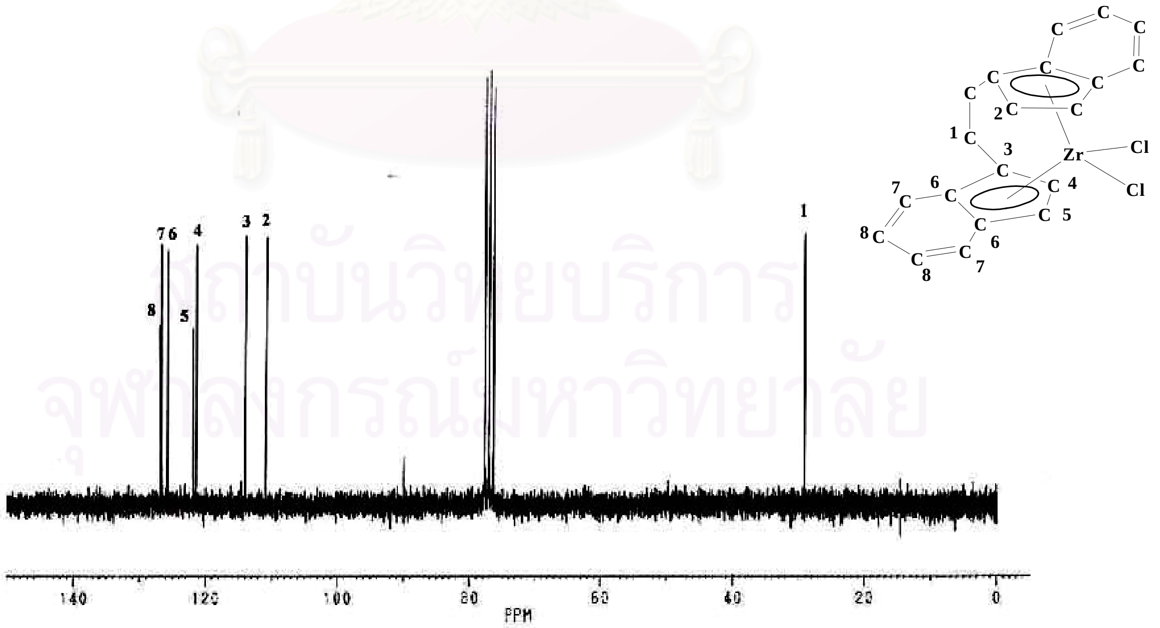


Figure 5.2 ^{13}C{H}-NMR ($CDCl_3$) spectrum of *rac*-ethylene-bis(indenyl)zirconium dichloride.

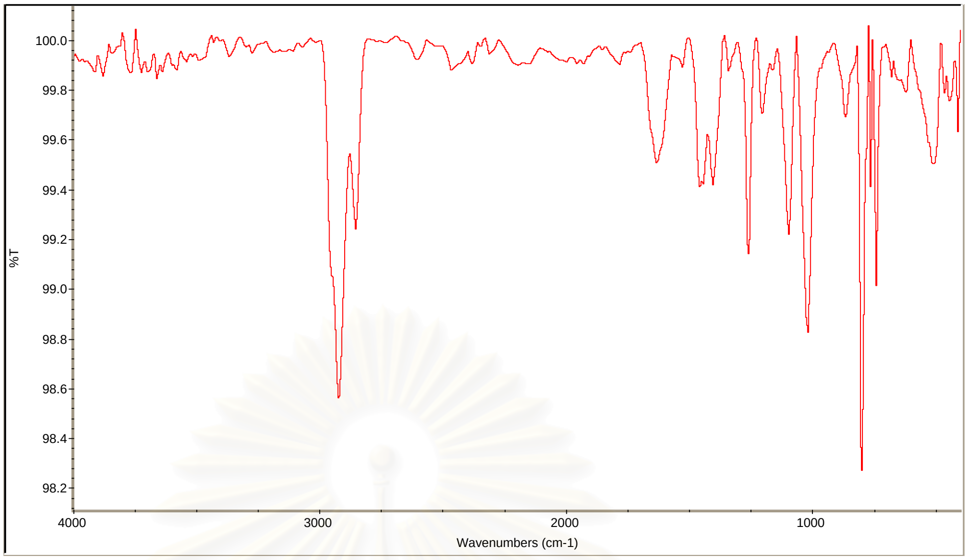


Figure 5.3 FT-IR spectrum of *rac*-ethylene-bis(indenyl)zirconium dichloride.

Table 5.1 ^{1}H-NMR data of *rac*-ethylene-bis(indenyl)zirconium dichloride

Chemical shift (ppm)	Multiplicity	Number of protons	Assignment
7.40	multiplet	8H	C_6H_4
6.57	doublet	2H	C_5H_2 (α)
6.19	doublet	2H	C_5H_2 (β)
3.74	singlet	4H	C_2H_4

The ^{1}H-NMR of *rac*-ethylene-bis(indenyl)zirconium dichloride showed a multiplet peak at 7.40 ppm that is assigned to aromatic ring protons. A doublet peak at 6.57 is assigned to cyclopentadienyl ring protons (α). A doublet peak at 6.19 is assigned to cyclopentadienyl ring protons (β). A singlet peak at 3.74 ppm is assigned to ethylene protons.[57]

Table 5.2 ^{13}C-NMR data of *rac*-ethylene-bis(indenyl)zirconium dichloride

Chemical shift (ppm)	Assignment
126.7	C^8
126.6	C^7
125.7	C^6
121.8	C^5
121.4	C^4
113.9	C^3
110.8	C^2
29.1	C^1

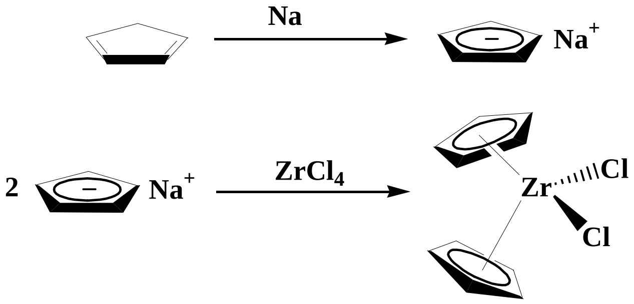
Table 5.3 FT-IR data of *rac*-ethylene-bis(indenyl)zirconium dichloride

Wave number(cm^{-1})	Assignment
2918	C-H aromatic stretching
1634	C=C stretching
1459	-CH_2 stretching
1264, 1097	C-H bending
801, 739	out-of-plane C-H bending

The ^{13}C-NMR spectrum of *rac*-ethylene-bis(indenyl)zirconium dichloride consisted of indenyl ring carbons at 126.7, 126.6, 125.7, 121.8, 121.4, 113.9 and 110.8 ppm, ethylene-bridge carbons at 29.1 ppm. The FT-IR spectrum showed C-H stretching at 2918 cm^{-1}, C=C stretching at 1634 cm^{-1} and –CH_2 stretching at 1459 cm^{-1}.

5.1.2 Bis(cyclopentadienyl) zirconium dichloride; Cp_2ZrCl_2

The synthesis of bis(cyclopentadienyl) zirconium dichloride was followed as in Scheme 5.2.



Scheme 5.2 Synthesis of bis(cyclopentadienyl) zirconium dichloride.

The bis(cyclopentadienyl) zirconium dichloride was prepared from the reaction between cyclopentadienylsodium and zirconium tetrachloride. First, cyclopentadiene was reacted with divided sodium to yield cyclopentadienylsodium. Then the reaction of cyclopentadienylsodium with zirconium tetrachloride at room temperature resulted in bis(cyclopentadienyl) zirconium dichloride as colorless crystals (30% yield).

The ^{1}H-NMR, ^{13}C-NMR and FT-IR spectra of bis(cyclopentadienyl) zirconium dichloride were shown in Figures 5.4-5.6. The assignments of peaks are in Table 5.4.

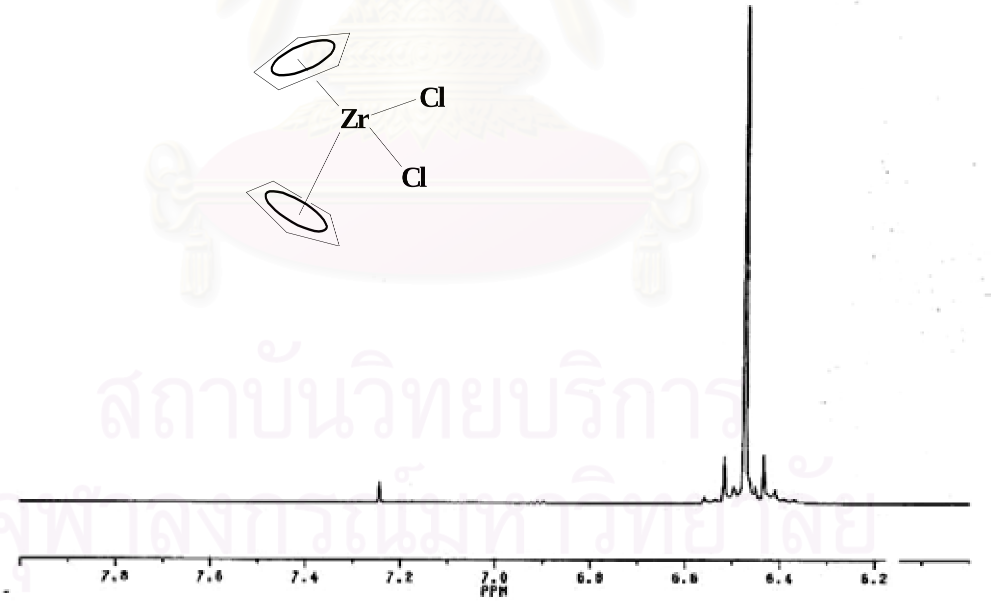


Figure 5.4 ^{1}H-NMR ($CDCl_3$) spectrum of bis(cyclopentadienyl) zirconium dichloride.

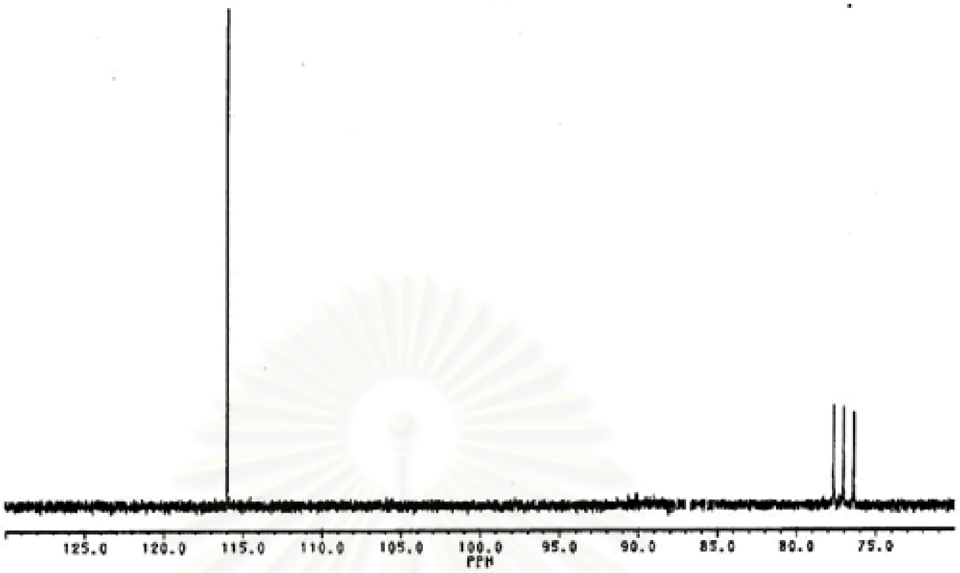


Figure 5.5 $^{13}C\{H\}$-NMR ($CDCl_3$) spectrum of bis(cyclopentadienyl) zirconium dichloride.

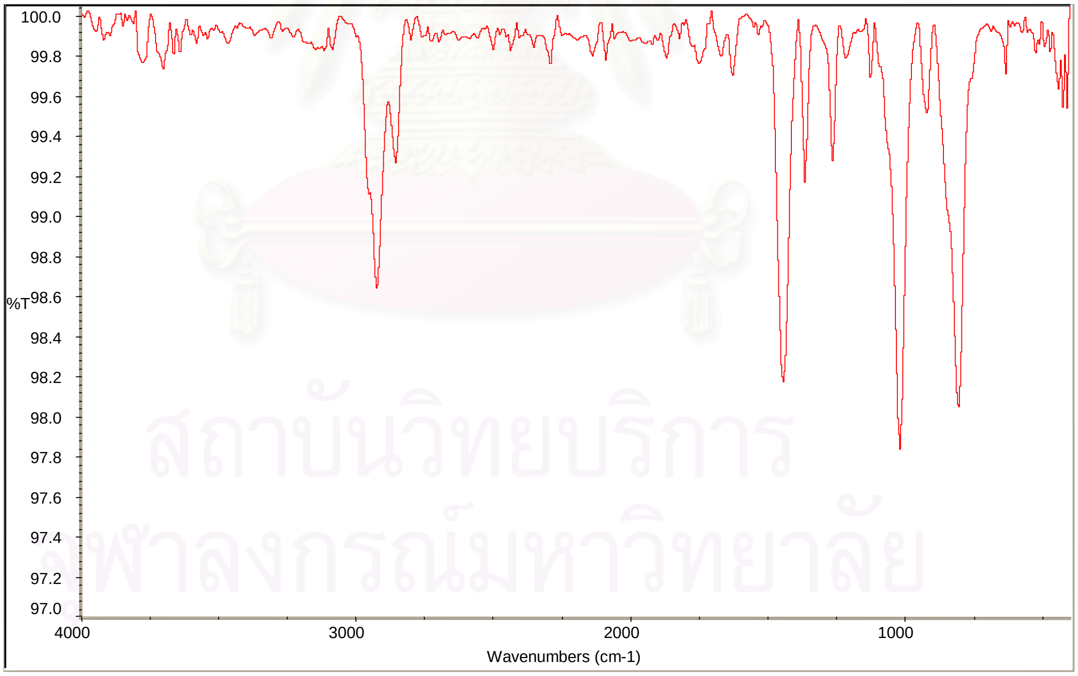


Figure 5.6 FT-IR spectrum of bis(cyclopentadienyl) zirconium dichloride.

The ^{1}H-NMR spectrum of bis(cyclopentadienyl) zirconium dichloride showed a singlet peak at 6.48 ppm which was assigned to cyclopentadienyl ring protons. The ^{13}C-NMR spectrum of bis(cyclopentadienyl) zirconium dichloride presented a peak at 116.1 ppm, assigned to cyclopentadienyl ring carbons.[58]

Table 5.4 FT-IR data of bis(cyclopentadienyl) zirconium dichloride

Wave number (cm^{-1})	Assignment
2922	C-H aromatic stretching
1443	C=C stretching
1018	C-H bending
922, 805	out-of-plane C-H bending

The FT-IR spectrum showed C-H stretching at 2922 cm^{-1} on the cyclopentadienyl ring.

5.2 Polymerization of 1-hexene

5.2.1 Using *rac*-Et[Ind]$_2$ZrCl$_2$(**1**) catalyst

The effects of the amount of catalyst, Al/Zr mole ratio and polymerization temperature(t$_p$) were investigated by varying the catalyst concentration from 1.0x10^{-6} to 5.0x10^{-6} mol, Al/Zr mole ratio of 2000 and 4000 and polymerization temperature at 0°C, 30°C and 60°C. The experimental results were shown in Table 5.5.

Table 5.5 Polymerization of 1-hexene using *rac*-Et[Ind]$_2$ZrCl$_2$(**1**)/MAO

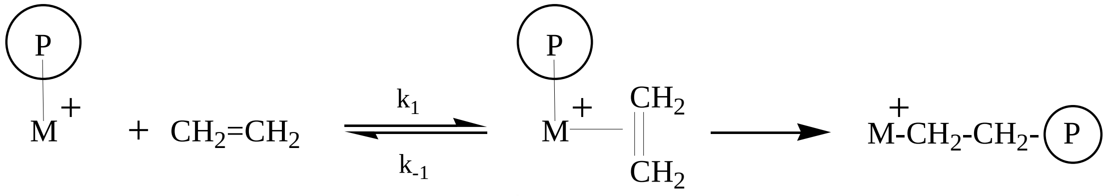
Entry	Amount of catalyst (μmol)	Al/Zr mole ratio	Temp. (°C)	Yield (g)	Activity (kg/mol)	% Conversion
1	1	4000	60	0.0354	35	3
2	2.5	4000	0	0.0082	8	1
3	2.5	4000	30	0.6595	264	49
4	2.5	4000	60	0.9725	389	72
5	2.5	2000	60	0.0616	25	5
6	5	4000	60	0.8854	177	66

1-Hexene 2 mL (15.99 mmol, 1.346 g), t_p 24 hrs.

Comparing the entries 1, 4 and 6, the results showed that the highest catalytic activity was obtained at 2.5 μmol of catalyst. Increasing amount of catalyst caused the decreasing in the activity. This might be caused by the decreasing of active species due to the dimerization of catalyst forming inactive species.[59] This result agreed with that reported using other metallocene catalyst systems. Additionally, it might also be explained that the activity was decreased because of the increase of termination rate (that is β-H transfer to metal) when the excess amount of catalyst was used. It is well-known that β-H transfer to metal is a common chain-transfer process, especially for late-transition metal catalysts.[9]

A comparison between entries 4 and 5 showed that Al/Zr mole ratio at 4000 gave higher activity. The reason of using excess amount of MAO in this work is that usually high amount of MAO was used and seems to be necessary since it can stabilize the cation active species and also acts as an impurity scavenger.

The influence of polymerization temperature that was investigated from entries 2-4 showed that the temperature at 60°C gave the highest activity. An increasing in temperature results in higher propagation rate. These results can be explained by a widely accepted mechanism of propagation which involves the initial formation of a π-complex of an olefin with the catalyst metal, followed by chain migratory insertion.



When π-olefin coordinated with metal center to form the ∏-olefin complex, this complex is more stable at low temperature. Therefore, it is difficult for the complex to go on the propagation step by insertion process. This affects to the increase of activity with increasing polymerization temperature.

This result was in good agreement with that reported by other groups, on 1-hexene polymerization with *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst/MAO system. The polymerization condition was 15.99 mmol 1-hexene, 2.5 μmol catalyst and Al/Zr mole ratio of 5000. It was found that at high temperature (60°C) gave higher %yield than at low temperature (0°C).[59]

5.2.2 Using Cp$_2$ZrCl$_2$(**2**) catalyst

The polymerization was performed using the optimum condition found for the *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst (amount of catalyst 2.5 μmol, Al/Zr mole ratio 4000). The effect of polymerization temperature was investigated by varying polymerization temperature at 0^{o}C, 30^{o}C and 60^{o}C. The experimental results were shown in Table 5.6.

Table 5.6 Polymerization of 1-hexene using Cp_2ZrCl_2(**2**)/MAO

Entry	Temp. (°C)	Yield (g)	Activity (kg/mol)	% Conversion
1	0	0.5883	138	44
2	30	0.6713	269	50
3	60	0.7986	319	60

1-Hexene 2 mL (15.99 mmol, 1.346 g), amount of catalyst 2.5 μmol, Al/Zr mole ratio = 4000 and t_p 24 hrs.

The results showed that higher catalytic activity was obtained at higher temperature, similar to that of 1-hexene polymerization by *rac*-Et$[Ind]_2ZrCl_2$ catalyst.

It can be seen that 1-hexene polymerization using Cat **1** and Cat **2** catalysts gave similar catalytic activity at the same condition (264 and 269, respectively). Again, this result is in good agreement with that reported using the same catalysts in the polymerization condition: 15.99 mmol 1-hexene, 2.5 *μ*mol catalyst, Al/Zr mole ratio of 5000 and polymerization temperature at 45°C (479 and 463, respectively).[59]

5.3 Characterization of products

5.3.1 Infrared spectroscopy (IR)

The infrared spectroscopy is an effective method to determine the microstructure of polymer. It is sufficient to characterize the functional groups of polymer in the wave number of 400-4000 cm^{-1}. The FT-IR spectra of products obtained from *rac*-Et$[Ind]_2$ $ZrCl_2$ and Cp_2ZrCl_2 were shown in Figures 5.7-5.8. The identification of the spectra was summarized in Tables 5.7-5.8.

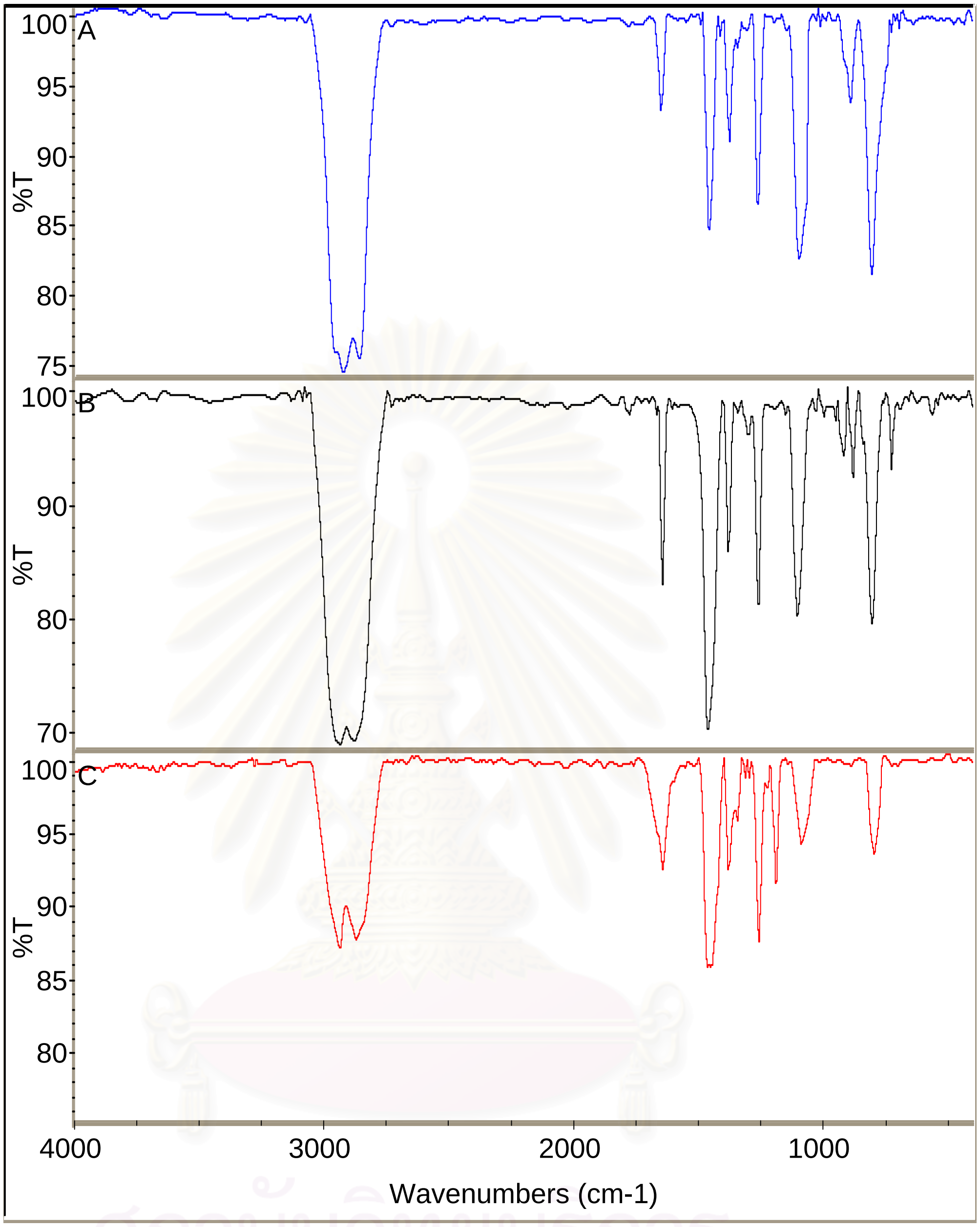


Figure 5.7 FT-IR spectra of the poly(1-hexene) obtained with *rac*-Et[Ind]$_2$ZrCl$_2$.

(2.5 μmol)

A. Al/Zr 4000, 60°C

B. Al/Zr 4000, 30°C

C. Al/Zr 2000, 60°C

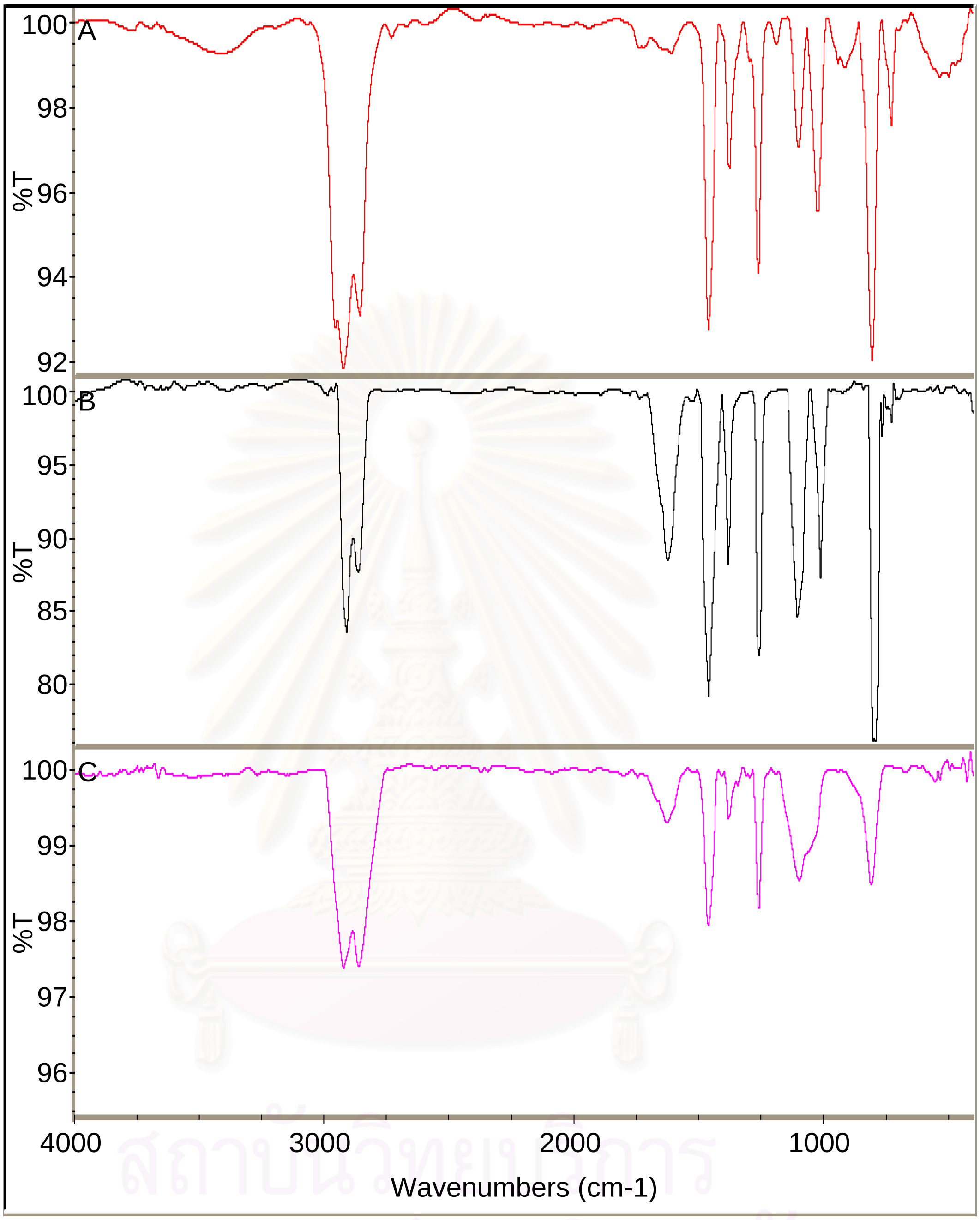


Figure 5.8 FT-IR spectra of the poly(1-hexene) obtained with Cp$_2$ZrCl$_2$.(2.5μmol)

A. Al/Zr 4000, 0°C

B. Al/Zr 4000, 30°C

C. Al/Zr 4000, 60°C

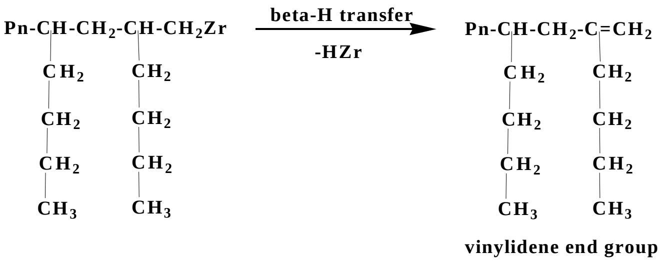
Table 5.7 FT-IR data of the product from 1-hexene polymerization by *rac*-Et[Ind]$_2$ZrCl$_2$

Wave number (cm^{-1})	Ref.[60]	Assignment
2959	2962	-CH$_3$ stretching
2859	2850	-CH$_2$ stretching
1459	1460	C=C stretching of vinylidene
1372	1370	C=C stretching of internal double bond
1000-1200	1000-1200	C-H bending
800-900	800-900	out-of-plane C-H bending

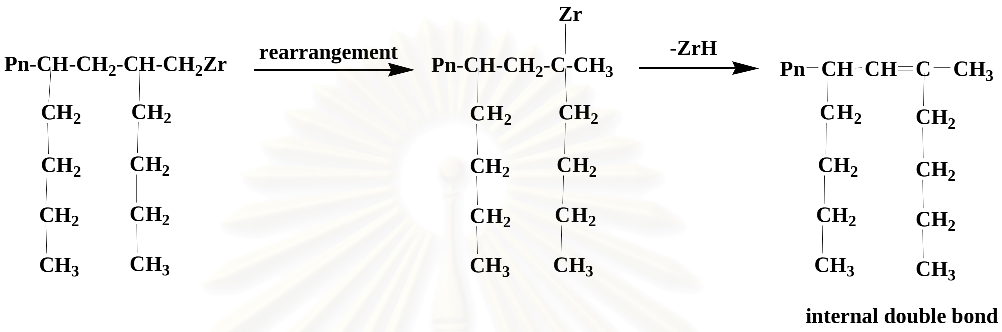
Table 5.8 FT-IR data of the product from 1-hexene polymerization by Cp$_2$ZrCl$_2$

Wave number (cm^{-1})	Ref.[60]	Assignment
2959	2962	-CH$_3$ stretching
2856	2850	-CH$_2$ stretching
1461	1460	C=C stretching of vinylidene
1376	1370	C=C stretching of internal double bond
1000-1200	1000-1200	C-H bending
800-900	800-900	out-of-plane C-H bending

From Tables 5.7-5.8, the peak at 2959 cm^{-1} is assigned to –CH$_3$ stretching. The peak at 2856 is –CH$_2$ stretching. The lower wave number range gives the information on the end groups of the polymer. The signals in range of 1000-1200 are C-H in-plane bending and those at 800-900 cm^{-1} are C-H out-of –plane bending. In the spectra, there are two kinds of C=C stretching vibrations, a relatively strong vibration at 1459 cm^{-1} corresponding to vinylidene end groups and a weak one at 1372 cm^{-1} corresponding to internal double bonds. This result indicated that in both systems (*rac*-Et[Ind]$_2$ZrCl$_2$ catalyst and Ind$_2$ZrCl$_2$ catalyst) the termination process occurred by β-H transfer as well as rearrangement of double bond (shown in equations 5.1-5.2). This result was consistent with the result of 1-hexene polymerization catalyzed by *rac*-Me$_2$Si(1-C$_5$H$_2$-2-CH$_3$-4-^{t}Bu)$_2$Zr(NMe$_2$)$_2$/TIBA /[Ph$_3$C][B(C$_6$F$_5$)$_4$]. [60]

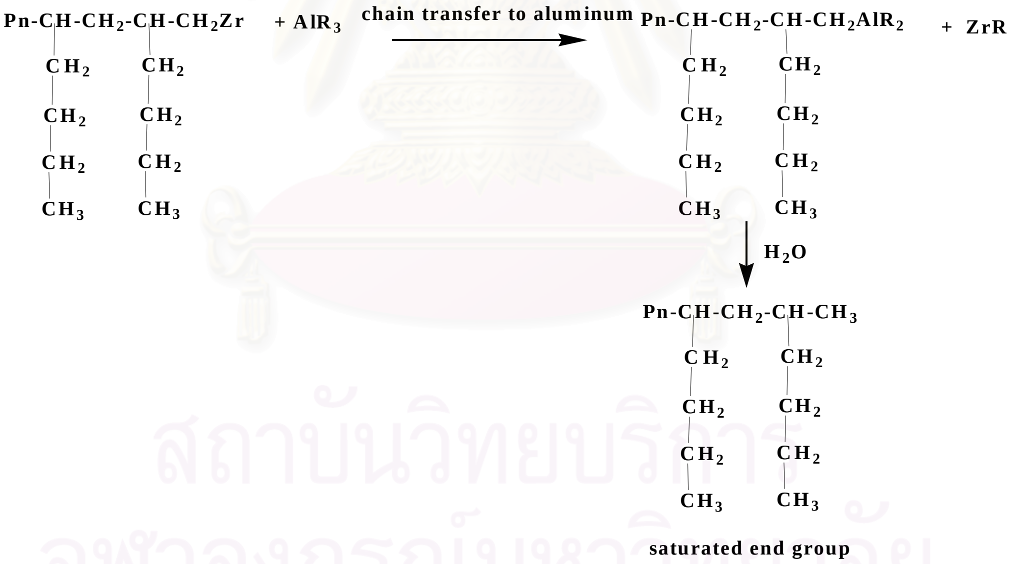


$$\text{Pn-CH-CH}_2\text{-CH-CH}_2\text{Zr} \xrightarrow[\text{-HZr}]{\text{beta-H transfer}} \text{Pn-CH-CH}_2\text{-C=CH}_2 \qquad (5.1)$$



$$\text{Pn-CH-CH}_2\text{-CH-CH}_2\text{Zr} \xrightarrow{\text{rearrangement}} \text{Pn-CH-CH}_2\text{-}\overset{\text{Zr}}{\text{C}}\text{-CH}_3 \xrightarrow{\text{-ZrH}} \text{Pn-CH-CH=C-CH}_3 \qquad (5.2)$$

In addition, from the spectra was found saturated end group, which resulted from chain transfer to aluminum (shown in equation 5.3).



$$\text{Pn-CH-CH}_2\text{-CH-CH}_2\text{Zr} + \text{AlR}_3 \xrightarrow{\text{chain transfer to aluminum}} \text{Pn-CH-CH}_2\text{-CH-CH}_2\text{AlR}_2 + \text{ZrR} \qquad (5.3)$$

$$\text{Pn-CH-CH}_2\text{-CH-CH}_2\text{AlR}_2 \xrightarrow{H_2O} \text{Pn-CH-CH}_2\text{-CH-CH}_3$$

5.3.2 Carbon-13 nuclear magnetic resonance spectroscopy (^{13}C-NMR)

Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy is a tool for molecular structure analysis. The ^{13}C-NMR spectra of products obtained with *rac*-Et $[\text{Ind}]_2\text{ZrCl}_2$ and Cp_2ZrCl_2 are shown in Figures 5.9-5.10. The assignments of the chemical shifts are shown in Tables 5.9-5.10.

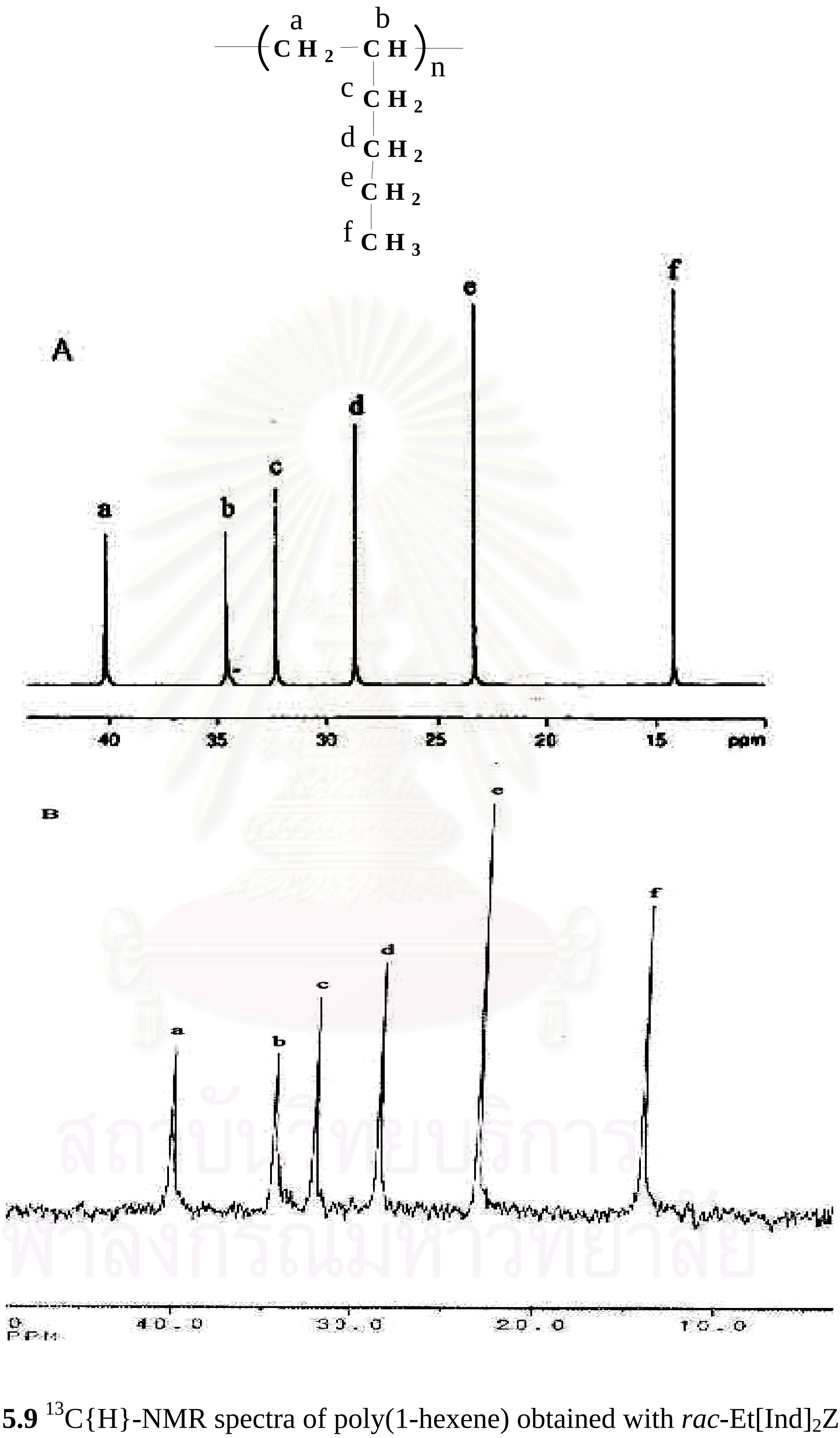


Figure 5.9 $^{13}C\{H\}$-NMR spectra of poly(1-hexene) obtained with *rac*-Et[Ind]$_2$ZrCl$_2$.

A) isotactic poly(1-hexene) reference[59]

B) isotactic poly(1-hexene) from *rac*-Et[Ind]$_2$ZrCl$_2$

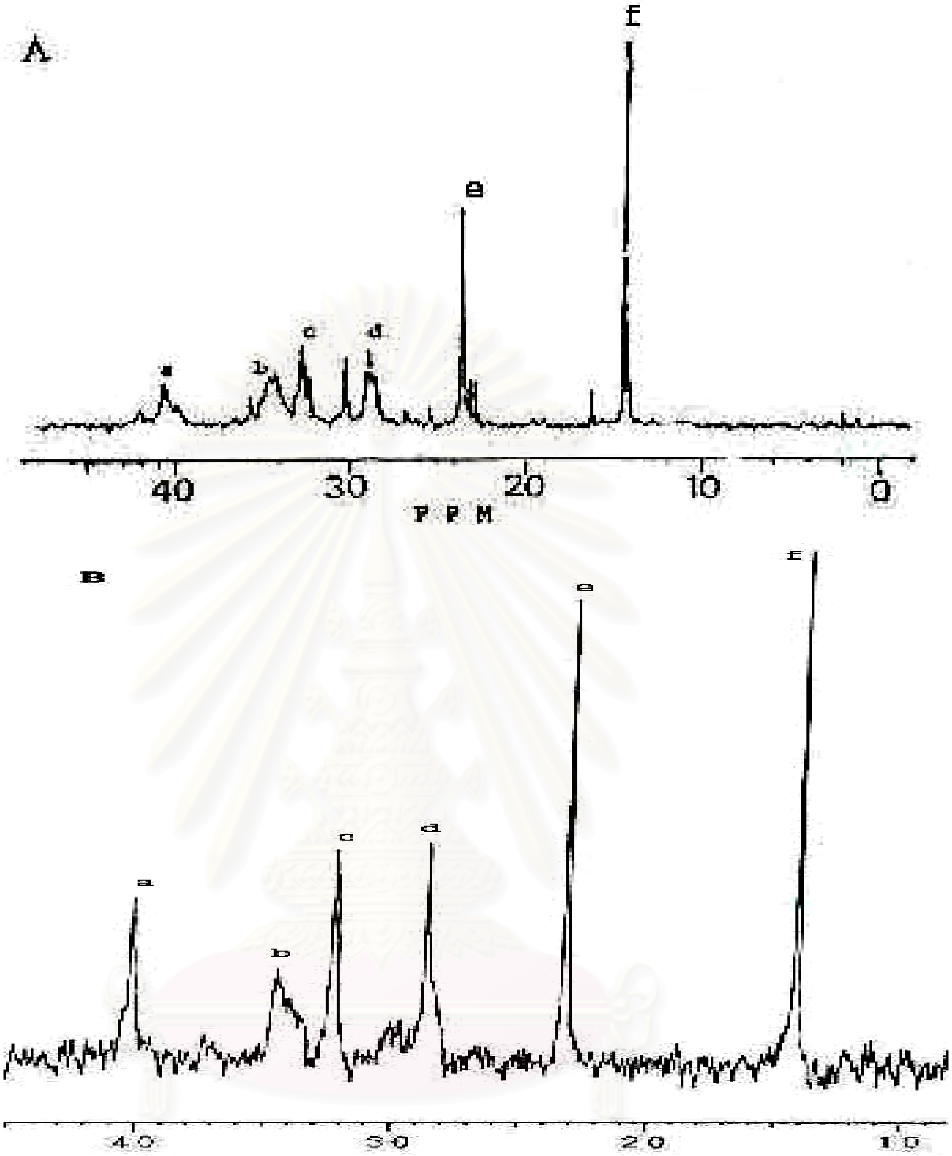


Figure 5.10 $^{13}C\{H\}$-NMR spectra of poly(1-hexene) obtained with Cp_2ZrCl_2.

A) atactic poly(1-hexene) reference[61]

B) atactic poly(1-hexene) from Cp_2ZrCl_2

Table 5.9 ^{13}C-NMR data of poly(1-hexene) obtained with *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst

Chemical shift (ppm)		Assignment
Sample	Isotactic poly(hexene) [59]	
40	40	C_a
35	35	C_b
32	32	C_c
29	29	C_d
23	23	C_e
14	14	C_f

Table 5.10 ^{13}C-NMR data of poly(1-hexene) obtained with Cp$_2$ZrCl$_2$ catalyst

Chemical shift (ppm)		Assignment
Sample	Atactic poly(hexene) [61]	
41	41	C_a
35	35	C_c
32	32	C_b
29	29	C_d
23	23	C_e
14	14	C_f

White rubber-like products obtained with *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst are found to be isotactic poly(1-hexene). This was identified by the comparison of ^{13}C-NMR spectra of the products and isotactic poly(1-hexene) reference in Figure 5.9. It was reported that this zirconium catalyst produced isotactic poly(1-hexene).[35]

Viscous colorless liquid obtained with Cp$_2$ZrCl$_2$ catalyst is found to be atactic poly(1-hexene). This result was identified by the comparison of ^{13}C-NMR spectra with atactic poly(1-hexene) reference in Figure 5.10.

It might be noticed that ^{13}C-NMR spectra of atactic and isotactic poly(1-hexene) showed the same chemical shift, however the appearance of peaks were different. Atactic poly(1-hexene) showed broad and multiplet peaks while the isotactic poly(1-hexene) showed sharp singlet peak.

5.3.3 Glass-transition temperature (T_g)

The glass-transition temperature (T_g) of poly(1-hexene) from *rac*-Et[Ind]$_2$ZrCl$_2$ and Cp$_2$ZrCl$_2$ catalysts has been determined. DSC curves of the poly(1-hexene) were shown in Figures 5.11-5.12.

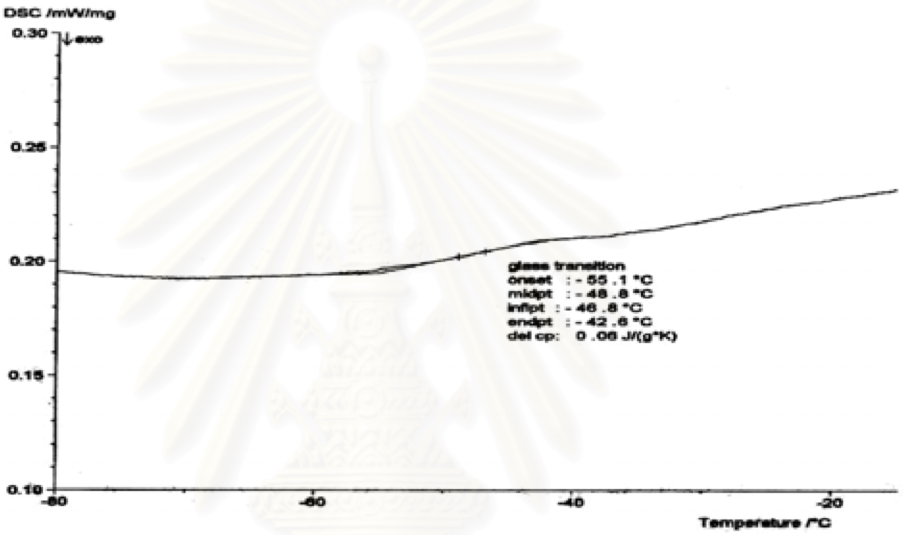


Figure 5.11 DSC curve of poly(1-hexene) produced by *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst.

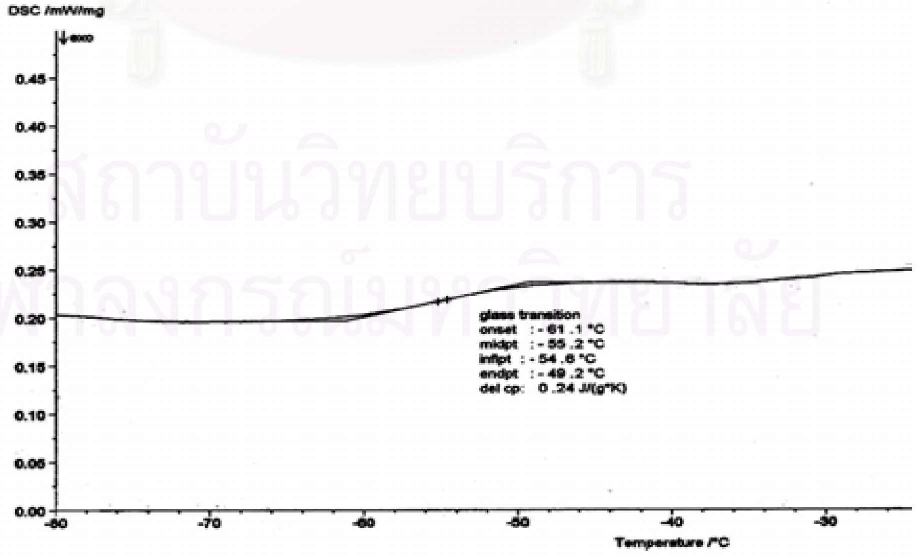


Figure 5.12 DSC curve of poly(1-hexene) produced by Cp$_2$ZrCl$_2$ catalyst.

The glass-transition temperature (Tg) for polymer produced using *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst was observed at –48^{o}C which was corresponded to the value for isotactic polyhexene. In the case of Cp$_2$ZrCl$_2$ catalyst, the glass-transition temperature (Tg) was observed at –55^{o}C that was close to the value for atactic polyhexene. [35]

5.3.4 Molecular weight (Mw) and molecular weight distribution (MWD)

The molecular weight and molecular weight distribution of poly(1-hexene) produced with *rac*-Et[Ind]$_2$ZrCl$_2$ and Cp$_2$ZrCl$_2$ were investigated. The results were shown in Figures 5.13-5.14.

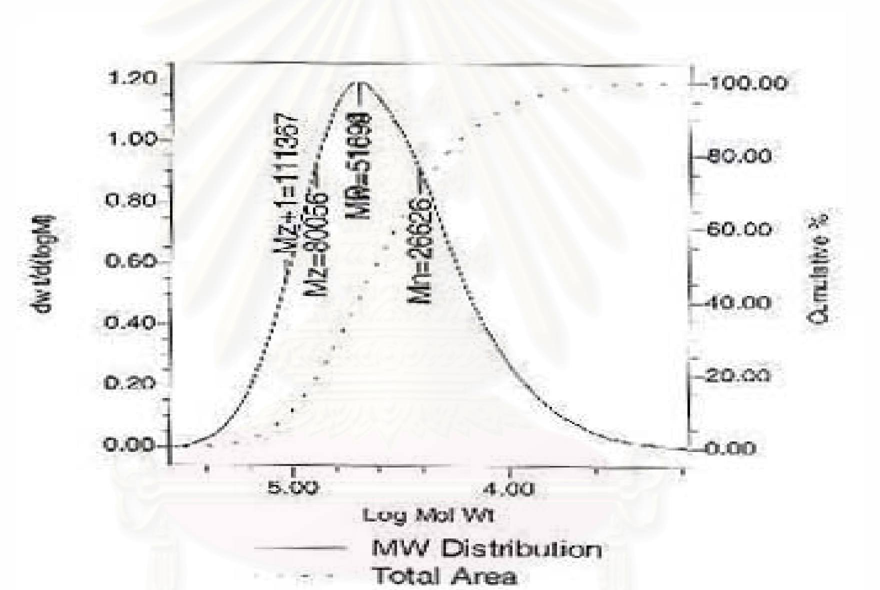


Figure 5.13 GPC curve of poly(1-hexene) from *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst.

Figure 5.13 showed that *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst produced poly(1-hexene) with Mw of 51099, Mn of 26626 and exhibited molecular weight distribution of 1.92.

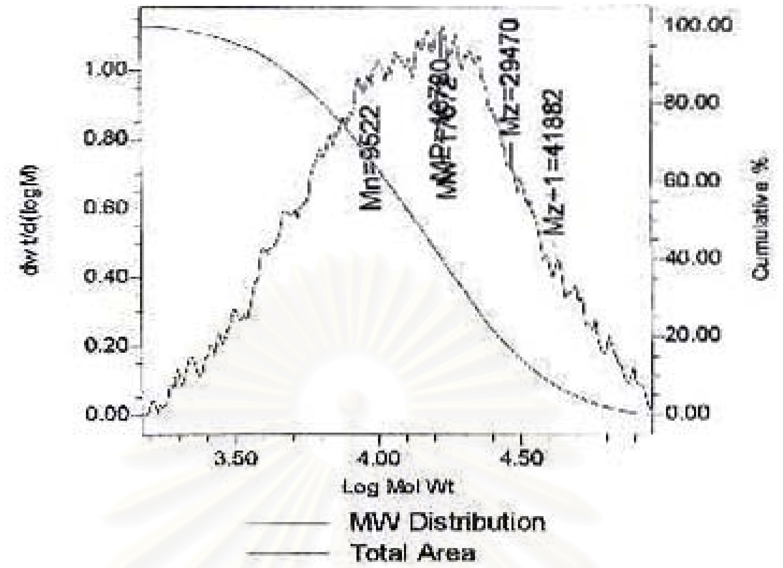


Figure 5.14 GPC curve of poly(1-hexene) from Cp_2ZrCl_2 catalyst.

Figure 5.14 showed that Cp_2ZrCl_2 catalyst produced poly(1-hexene) with Mw of 9942, Mn of 4111 and exhibited molecular weight distribution of 2.41.

The above result suggested that the presence of a bridging group in *rac*-Et$[Ind]_2ZrCl_2$ has a significant effect on the ability to incorporate monomer. It was reported that *rac*-Et$[Ind]_2ZrCl_2$ catalyst gave higher molecular weight of poly(1-hexene) than Cp_2ZrCl_2 catalyst (19500 and 850, respectively)(hexene 15.99 mmol, catalyst 2.5 μmol, Al/Zr mole ratio of 5000 and polymerization temperature at 30°C.[59]

5.4 Polymerization of 1,5-hexadiene

5.4.1 Using MAO as cocatalyst

Using the optimum condition found in 1-hexene polymerization (amount of catalyst 2.5 μmol). The effects of Al/Zr mole ratio (2000 and 4000), polymerization temperature, polymerization time (0°C, 30°C and 60°C) and type of catalyst (*rac*-Et[Ind]$_2$ZrCl$_2$(**1**) and Cp$_2$ZrCl$_2$(**2**)). The experimental results were summarized in Table 5.11.

Table 5.11 Polymerization of 1,5-hexadiene using *rac*-Et[Ind]$_2$ZrCl$_2$(**1**) and Cp$_2$ZrCl$_2$(**2**)/ MAO

Entry	Cat.	Al/Zr mole ratio	Temp. (^{o}C)	Time (hr)	Yield (g)	Activity (kg/mol)	% Conversion
1	**1**	2000	30	5	0.0147	6	1
2	**1**	4000	30	5	1.2751	510	92
3	**1**	4000	30	3	0.5536	221	40
4	**1**	4000	60	5	0.5737	230	41
5	**2**	4000	30	3	0.4221	169	30

1,5-Hexadiene 2 mL (16.9 mmol, 1.388 g), amount of catalyst 2.5 μmol

The results from Table 5.11 presented that Al/Zr mole ratio at 4000 gave higher activity than at 2000. The polymerization temperature investigated in this work was focused at 30°C, which is usually performed in other works. It should be mentioned that 1,5-hexadiene polymerization was reported to give low yield at 0°C.[46] The activity at 60°C was found to be lower since boiling point of 1,5-hexadiene is 56°C, causing the volatization of 1,5-hexadiene during the polymerization.

Comparing Cat **1** and Cat **2** in the same condition, Cat **1** gave higher activity than Cat **2** (221 and 169, respectively). This suggested that bridged metallocene incorporated α-olefin monomer more readily than unbridged metallocene. This was proposed that the bridging ethylene caused the bite angle bigger, and so more open up for the incorporation of monomer.[5] This result was supported by previously reported 1,5-hexadiene polymerization with *rac*-Et[Ind]$_2$Zr(NMe$_2$)$_2$ and Cp$_2$ZrMe$_2$ catalysts using [Ph$_3$C][B(C$_6$F$_5$)$_4$] as cocatalyst. It was found that *rac*-Et[Ind]$_2$Zr(NMe$_2$)$_2$ catalyst gave higher activity than Cp$_2$ZrMe$_2$ catalyst due to ethylene bridged in *rac*-Et[Ind]$_2$ Zr(NMe$_2$)$_2$.[46]

5.4.2 Using boron compound as cocatalyst

The polymerization was performed using the optimum condition *rac*-Et[Ind]$_2$ ZrCl$_2$/MAO (Section 5.4.1). The influence of polymerization temperature on 1,5-hexadiene polymerization was studied by varying temperature. Using *rac*-Et[Ind]$_2$ZrCl$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] in the presence of TIBA (Al/Zr mole ratio = 400). The experimental results were shown in Table 5.12.

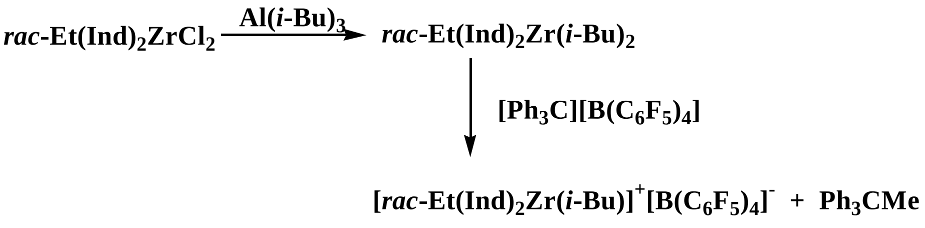
Table 5.12 Polymerization of 1,5-hexadiene using *rac*-Et[Ind]$_2$ZrCl$_2$(**1**)/[Ph$_3$C][B (C$_6$F$_5$)$_4$]/ TIBA

Entry	Temp. (°C)	Yield (g)	Activity (kg/mol)	% Conversion
1	0	0.1563	62	11
2	50	0.5013	200	36

1,5-Hexadiene 2 mL (16.9 mmol, 1.388 g), amount of catalyst 2.5 μmol, Al/Zr mole ratio = 400, [Ph$_3$C][B(C$_6$F$_5$)$_4$] 1.1 equivalent and t$_p$ 3 hrs.

The results from Table 5.12 showed that the temperature at 50°C gave higher activity. This result was supported by 1,5-hexadiene polymerization with *rac*-Et[Ind]$_2$Zr(NMe$_2$)$_2$ catalyst using TIBA/[Ph$_3$C][B(C$_6$F$_5$)$_4$] as cocatalyst. The polymerization condition was 1,5-hexadiene 88 mmol, 0.975 μmol catalyst and Al/Zr mole ratio of 80. It was found that high temperature (70°C) gave higher activity than low temperature (0°C) (0.9841 g > 0.4775 g, respectively).[46]

The role of TIBA is an alkylating agent, to change *rac*-Et[Ind]$_2$ZrCl$_2$ to *rac*-Et[Ind]$_2$Zr(*t*-Bu)$_2$. The role of boron compound ([Ph$_3$C][B(C$_6$F$_5$)$_4$]) is to create cationic form which is active species. The formation of active species is demonstrated in equation 5.4.



$$\begin{tikzcd} \textbf{\textit{rac}-Et(Ind)}_2\textbf{ZrCl}_2 \arrow[r, "\textbf{Al(\textit{i}-Bu)}_3"] & \textbf{\textit{rac}-Et(Ind)}_2\textbf{Zr(\textit{i}-Bu)}_2 \arrow[d, "{[\textbf{Ph}_3\textbf{C}][\textbf{B(C}_6\textbf{F}_5)_4]}"] \\ & {[\textbf{\textit{rac}-Et(Ind)}_2\textbf{Zr(\textit{i}-Bu)}]^+[\textbf{B(C}_6\textbf{F}_5)_4]^- + \textbf{Ph}_3\textbf{CMe}} \end{tikzcd} \quad (5.4)$$

active species

Comparing different cocatalyst studied in this work, boron compound ($[Ph_3C][B(C_6F_5)_4]$) and aluminium compound or MAO, in the same condition MAO showed higher activity (221 and 159, respectively). It was believed that MAO not only functions as an alkylating agent but also acts as an impurity scavenger. This result was supported by polymerization of 2-methyl-1,5-hexadiene by Cp^*ZrMe_2 in the presence of MAO and $B(C_6F_5)_3$ as cocatalyst. It was found that MAO cocatalyst gave higher activity than $B(C_6F_5)_3$ cocatalyst.[44]

5.5 Characterization of 1,5-hexadiene polymerization

5.5.1 Infrared spectroscopy (IR)

The FT-IR spectra of products obtained from *rac*-$Et[Ind]_2ZrCl_2$ by MAO and $[Ph_3C][B(C_6F_5)_4]$ and Cp_2ZrCl_2/MAO were shown in Figures 5.15-5.17. The identification of the spectrum was summarized in Tables 5.13-5.15.

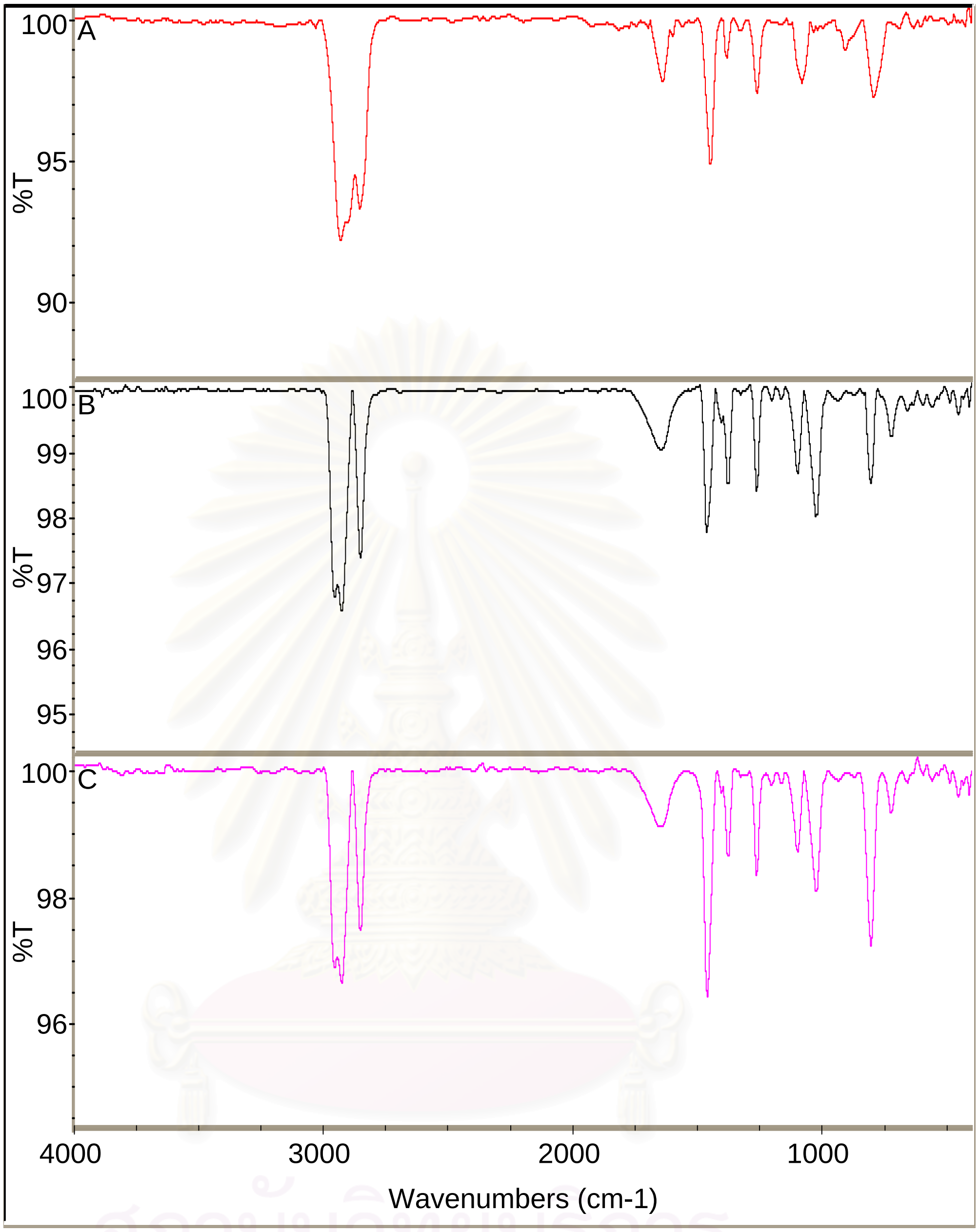


Figure 5.15 FT-IR spectra of the poly(1,5-hexadiene) obtained with *rac*-Et[Ind]$_2$ZrCl$_2$/MAO.(2.5 μmol)

A. Al/Zr 4000, 30°C

B. Al/Zr 4000, 60°C

C. Al/Zr 2000, 30°C

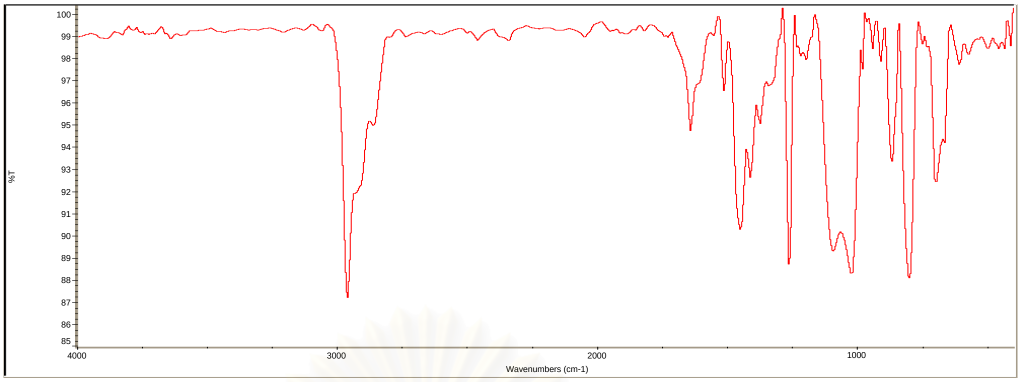


Figure 5.16 FT-IR spectrum of the poly(1,5-hexadiene) obtained with *rac*-Et[Ind]$_2$ZrCl$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$].(2.5 μmol, Al/Zr 200, 30°C)

Figure 5.17 FT-IR spectrum of the poly(1,5-hexadiene) obtained with Cp$_2$ZrCl$_2$.

Table 5.13 FT-IR data of the products from 1,5-hexadiene polymerization by *rac*-Et [Ind]$_2$ZrCl$_2$/MAO

Wave number (cm^{-1})	Ref.[46]	Assignment
2922	2926	asymmetric -CH$_2$ stretching
2852	2850	symmetric -CH$_2$ stretching
1459	1460	C=C stretching of vinylidene
1373	1370	C=C stretching of internal double bonds
1000-1200	1000-1200	C-H bending
800-900	800-900	out-of-plane C-H bending

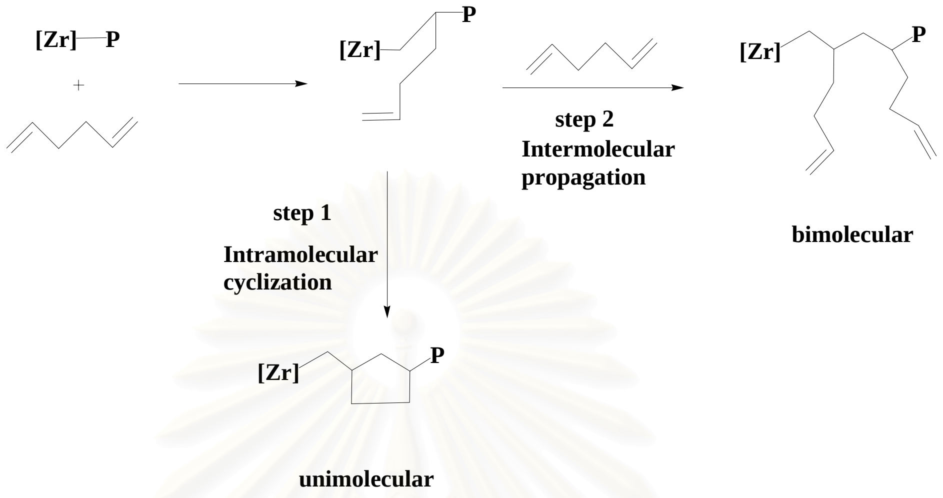
Table 5.14 FT-IR data of the product from 1,5-hexadiene polymerization by *rac*-Et $[Ind]_2ZrCl_2/[Ph_3C][B(C_6F_5)_4]$

Wave number (cm^{-1})	Ref.[46]	Assignment
2922	2926	asymmetric $-CH_2$ stretching
2860	2850	symmetric $-CH_2$ stretching
1460	1460	C=C stretching of vinylidene
1370	1370	C=C stretching of internal double bonds
1200-1000	1200-1000	C-H bending
900-800	900-800	out-of-plane C-H bending

Table 5.15 FT-IR data of the product from 1,5-hexadiene polymerization by Cp_2ZrCl_2/MAO

Wave number (cm^{-1})	Ref.[46]	Assignment
2922	2926	asymmetric $-CH_2$ stretching
2856	2850	symmetric $-CH_2$ stretching
1459	1460	C=C stretching of vinylidene
1373	1370	C=C stretching of internal double bonds
1200-1000	1200-1000	C-H bending
900-800	900-800	out-of-plane C-H bending

From Tables 5.13-5.15, a peak at 2922 cm^{-1} is assigned to the asymmetric vibration of $–CH_2$-. The peak at 2860 is the symmetric vibration of $–CH_2$-. The lower wave number range gives the information on the end groups of the polymers. The signals in range of 1200-1000 are C-H bond bending and those at 900-800 cm^{-1} are out-of-plane C-H bending. There are two kinds of C=C stretching vibrations, a relatively strong vibration at 1459 cm^{-1} corresponding to vinylidene end groups and a weak one at 1373 cm^{-1} corresponding to internal double bonds. This result was explained by the mechanism shown in Scheme 5.3. First, olefin was inserted into active species and then underwent cyclization[46] (step 1). In addition, the competitive intermolecular propagation reaction was also occurred (step 2).



Scheme 5.3 Mechanism of cyclopolymerization of 1,5-hexadiene.

From Table 5.15, FT-IR spectrum of product from 1,5-hexadiene polymerization catalyzed by Cp_2ZrCl_2 also showed vinylidene end group at 1461 cm^{-1} and internal double bond at 1376 cm^{-1}, similar to the result obtained by *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst.

5.5.2 Carbon-13 nuclear magnetic resonance spectroscopy (^{13}C-NMR)

The ^{13}C-NMR spectra of products obtained with *rac*-Et[Ind]$_2$ZrCl$_2$/MAO, *rac*-Et[Ind]$_2$ZrCl$_2$/[Ph_3C][$B(C_6F_5)_4$] and Cp_2ZrCl_2/MAO are shown in Figures 5.18-5.19. The assignments of the chemical shifts are shown in Tables 5.16-5.17.

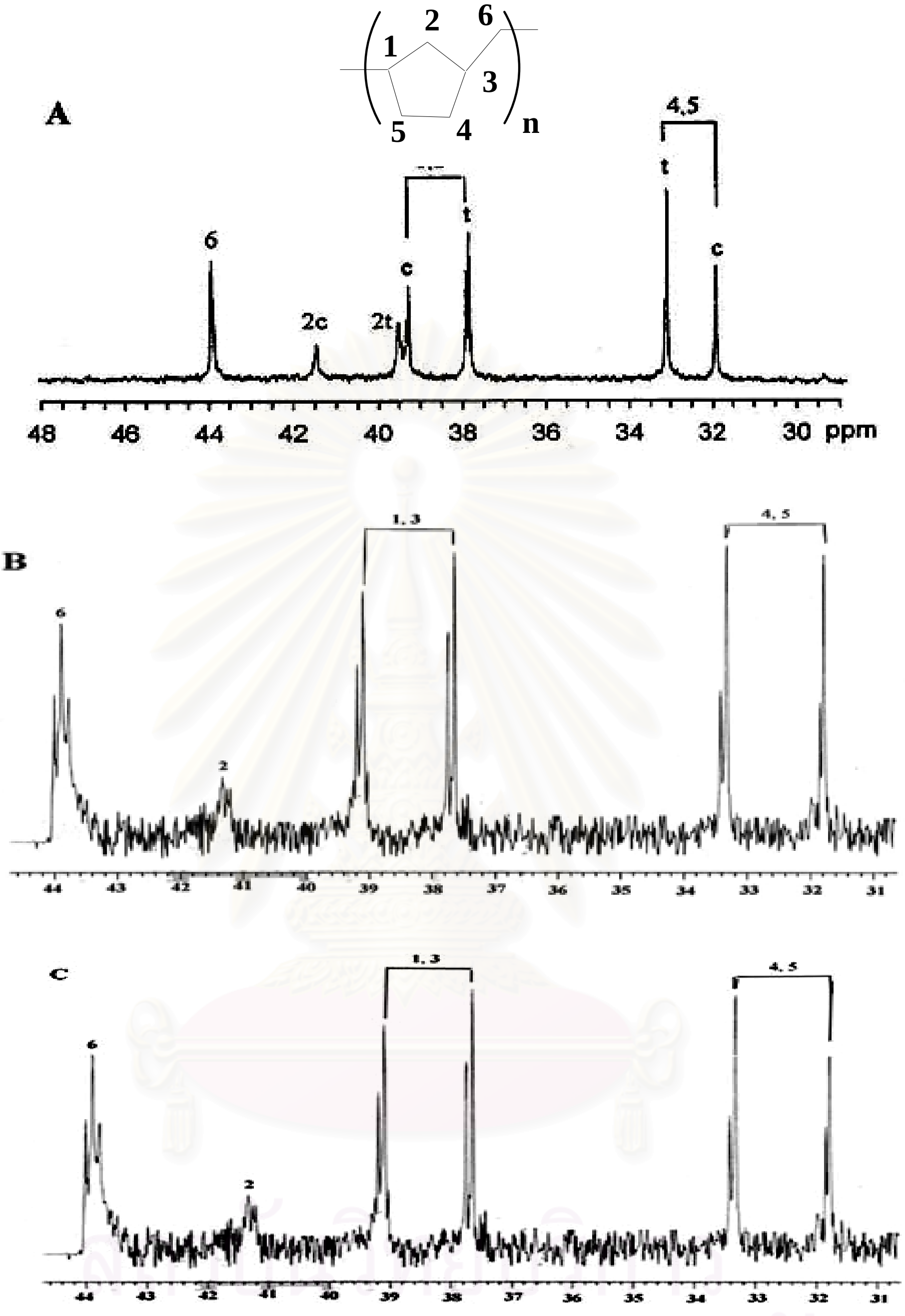


Figure 5.18 $^{13}C\{H\}$-NMR spectra of PMCP obtained with *rac*-Et[Ind]$_2$ZrCl$_2$.

A) *trans*-isotactic PMCP reference[46]

B) *trans*-isotactic PMCP from *rac*-Et[Ind]$_2$ZrCl$_2$/MAO

C) *trans*-isotactic PMCP from *rac*-Et[Ind]$_2$ZrCl$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$]

c: *cis*-, t: *trans*-

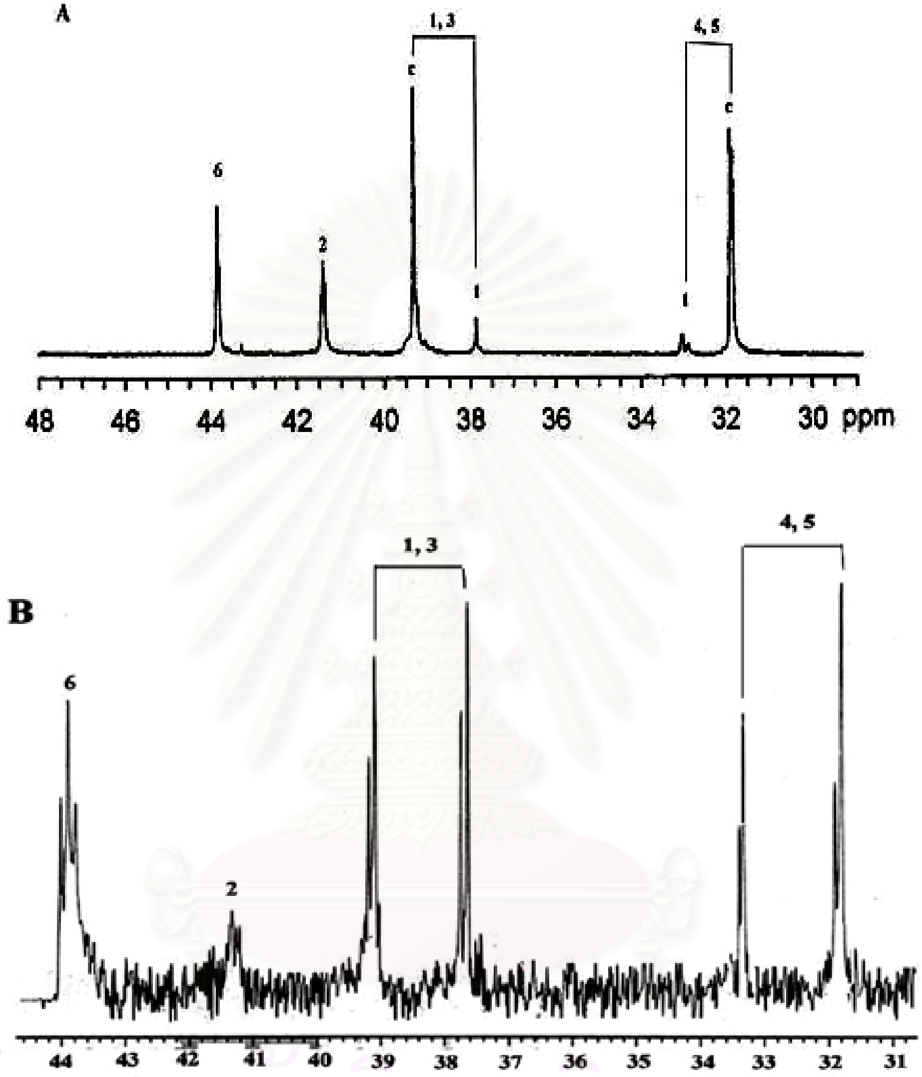


Figure 5.19 ^{13}C{H}-NMR spectra of PMCP obtained with Cp_2ZrCl_2.

A) *cis*-atactic PMCP reference[46]

B) *cis*-atactic PMCP from Cp_2ZrCl_2/MAO

Table 5.16 ^{13}C-NMR data of poly(methylene-1,3-cyclopentane) obtained with *rac*-Et[Ind]$_2$ZrCl$_2$/MAO system and *rac*-Et[Ind]$_2$ZrCl$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] system

Chemical shift (ppm)			Assignment
Sample using MAO cocatalyst	Sample using [Ph$_3$C][B(C$_6$F$_5$)$_4$] cocatalyst	Isotactic poly(methylene-1,3-cyclopentane) [46]	
44	44	44	C$_6$
41	41	41	C$_2$
38, 39	38, 39	38, 39	C$_{1, 3}$
32, 33	32, 33	32, 33	C$_{4, 5}$

Table 5.17 ^{13}C-NMR data of poly(methylene-1,3-cyclopentane) obtained with Cp$_2$ZrCl$_2$/ MAO system

Chemical shift (ppm)		Assignment
Sample	Atactic poly(methylene-1,3-cyclopentane) [46]	
44	44	C$_6$
41	41	C$_2$
38, 39	38, 39	C$_{1, 3}$
32, 33	32, 33	C$_{4, 5}$

Compared with ^{13}C-NMR data from reference 46, it was confirmed that white rubber-like product obtained with *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst is isotactic poly(methylene-1,3-cyclopentane) or PMCP.

By the comparison of ^{13}C-NMR spectrum of sample with reference atactic poly(methylene-1,3-cyclopentane) in Figure 5.19, the polymer obtained with Cp$_2$ZrCl$_2$ catalyst is atactic poly(methylene-1,3-cyclopentane). ^{13}C-NMR resonances at 32 and 33 ppm, indicating *cis* and *trans* rings, respectively.[46] This result was consistent with one presented by Waymouth and coworkers who investigated the effect of metallocene geometry on the diastereoselectivity (selectivity of *cis*- and *trans*-cyclization) in the 1,5-hexadiene homopolymerization and concluded that diastereoselectivity was affected by the steric effect of ligand and bite angle associated with the metallocene catalyst precursors.[43-45]

Since poly(methylene-1,3-cyclopentane) can exist in many forms (Figure 5.20), the *cis/trans* ratio of the polymer was determined by the integration of ^{13}C-NMR resonances at 32 and 33 ppm, indicating *cis* and *trans* rings, respectively.[46]

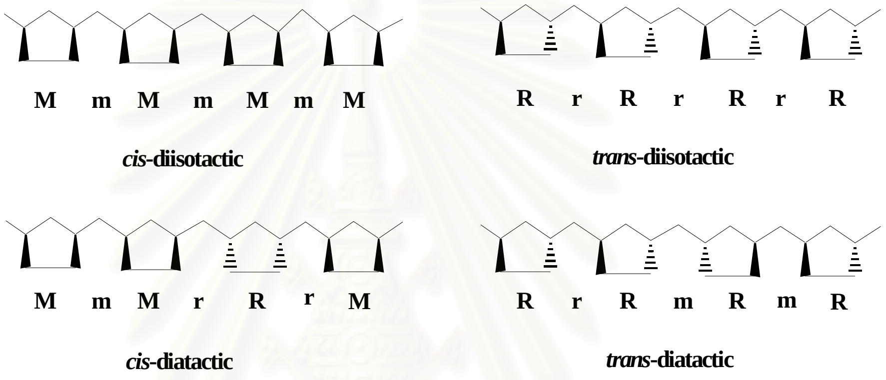


Figure 5.20 Microstructures of PMCP

5.5.3 Glass-transition temperature (T_g)

The glass-transition temperature (T_g) of PMCP from *rac*-Et[Ind]$_2$ZrCl$_2$/MAO system has been determined. DSC curve of the PMCP was shown in Figure 5.21.

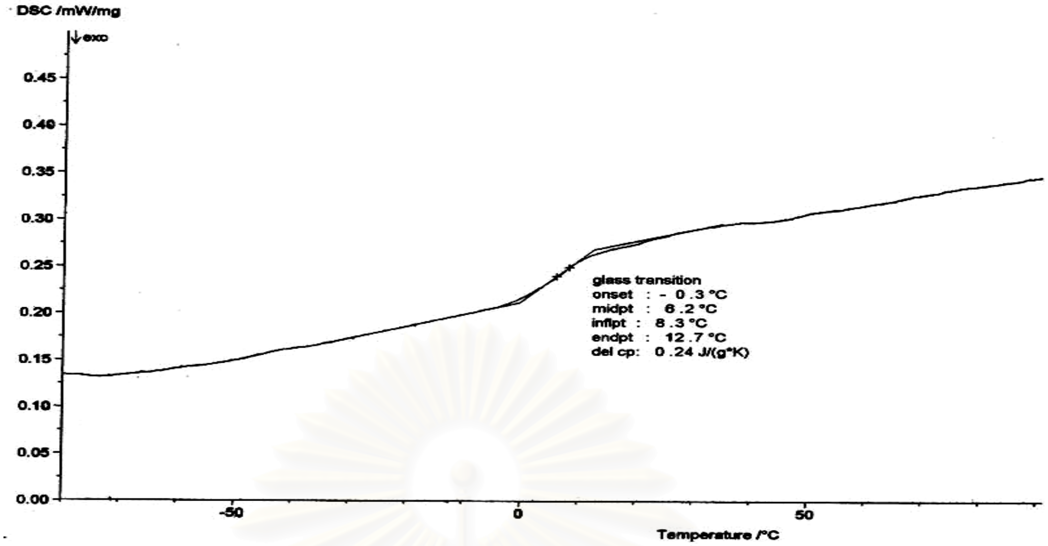


Figure 5.21 DSC curve of PMCP produced by *rac*-Et[Ind]$_2$ZrCl$_2$/MAO system.

The glass-transition temperature (Tg) was observed at 6^{o}C of *rac*-Et[Ind]$_2$ZrCl$_2$/MAO system which was corresponded to the value for *trans*-isotactic PMCP.[62]

5.5.4 Molecular weight (Mw) and molecular weight distribution (MWD)

The molecular weight and molecular weight distribution of PMCP produced with *rac*-Et[Ind]$_2$ZrCl$_2$/MAO system was investigated. The result was shown in Figure 5.22.

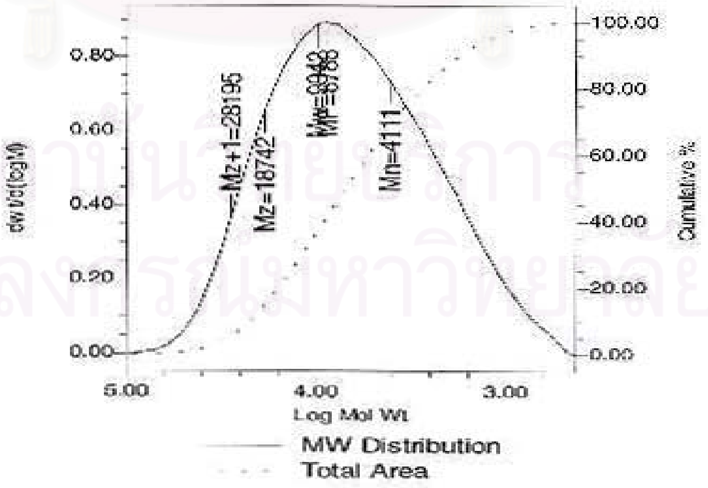


Figure 5.22 GPC curve of PMCP from *rac*-Et[Ind]$_2$ZrCl$_2$/MAO system.

Figure 5.22 showed that *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst produced PMCP with Mw of 17672, Mn of 9522 and exhibited molecular weight distribution of 1.86.

5.6 Copolymerization of 1-hexene and 1,5-hexadiene

5.6.1 Using MAO as cocatalyst

The optimum condition found in 1-hexene polymerization (Section 5.2.1) was used except that polymerization temperature was at 30°C and 50°C. The volume ratio of 1-hexene to 1,5-hexadiene was varied as shown in Table 5.18. The %mol 1,5-hexadiene was varied from 0, 9, 17, 50 and 100. The experimental results were shown in Tables 5.19-5.20.

Table 5.18 The volume ratio and %mol of 1-hexene, 1,5-hexadiene

Volume (mL)		%Mol 1-hexene	%Mol 1,5-hexadiene
1-Hexene	1,5-Hexadiene		
2	0	100	0
1.8	0.2	91	9
1.7	0.3	83	17
1	1	50	50
0	2	0	100

Table 5.19 Copolymerization of 1-hexene and 1,5-hexadiene using *rac*-Et[Ind]$_2$ZrCl$_2$ /MAO

Entry	%Mol 1,5-hexadiene	Amount of catalyst (μmol)	Temp. (^{o}C)	Yield (g)	Activity (kg/mol)
1[a]	0	2.5	30	0.6595	264
2	9	2.5	30	0.9711	388
3	17	2.5	30	1.0805	432
4	50	2.5	30	1.3135	525
5	50	2.5	50	1.2540	502
6[b]	100	2.5	30	1.2751	510

Copolymerization time 24 hrs., Al/Zr mole ratio = 4000

[a]: polymerization time 24 hrs., [b]: polymerization time 5 hrs.

The influence of polymerization temperature that was investigated from entries 3 and 4 presented that the temperature at 30°C gave the highest catalytic activity similar to that of 1,5-hexadiene polymerization.

The influence of %mol 1,5-hexadiene that was investigated from entries 1-3 and 5 showed that at 50 %mol 1,5-hexadiene gave the highest catalytic activity. The catalyst activity increased when the concentration of diene increased. Similar results were reported for copolymerization of ethylene and 1,5-hexadiene.[63]

Table 5.20 Copolymerization of 1-hexene and 1,5-hexadiene using Cp_2ZrCl_2/MAO

Entry	%Mol 1,5-hexadiene	Amount of catalyst (μmol)	Temp. (^{o}C)	Yield (g)	Activity (kg/mol)
1[a]	0	2.5	30	0.6713	269
2	17	2.5	30	0.8270	331
3	50	2.5	30	1.0902	437
4[b]	100	2.5	30	0.4221	169

Copolymerization time 24 hrs., Al/Zr mole ratio = 4000, copolymerization temperature 30 ^{o}C,

[a]: polymerization time 24 hrs., [b]: polymerization time 3 hrs.

The results from Table 5.20 showed that 50 %mol 1,5-hexadiene gave the highest catalytic activity that is similar to the copolymerization of 1-hexene and 1,5-hexadiene by Cat **1**.

Copolymerization of 1-hexene and 1,5-hexadiene using Cat **1** gave higher catalytic activity than Cat **2** at the same condition (525 and 437, respectively) which is the same as polymerization of 1,5-hexadiene by Cat **1** and Cat **2**.

5.6.2 Using boron compound as cocatalyst

Using the optimum condition in 1,5-hexadiene polymerization (Section 5.4.2). The effects of %mol 1,5-hexadiene and polymerization temperature were investigated. The experimental results were shown in Table 5.21.

Table 5.21 Copolymerization of 1-hexene and 1,5-hexadiene using *rac*-Et[Ind]$_2$ZrCl$_2$/ [Ph$_3$C][B(C$_6$F$_5$)$_4$] / TIBA

Entry	%Mol 1,5-hexadiene	Temp. (^{o}C)	Yield (g)	Activity (kg/mol)
1	17	30	0.2742	110
2	50	30	0.6874	275
3[a]	100	30	0.3965	159

Amount of catalyst 2.5 μmol, [Ph$_3$C][B(C$_6$F$_5$)$_4$] 1.1 equivalent.,
Al/Zr mole ratio = 200, copolymerization time 24 hrs.,
[a]: polymerization time 3 hrs.

Comparison between boron compound and MAO of *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst for 1-hexene and 1,5-hexadiene copolymerization under the same condition, it was found that MAO gave higher activity than boron compound ([Ph$_3$C][B(C$_6$F$_5$)$_4$]) (525 and 275, respectively).

5.7 Characterization of 1-hexene and 1,5-hexadiene copolymerization

5.7.1 Infrared spectroscopy (IR)

The FT-IR spectra of copolymer obtained from *rac*-Et[Ind]$_2$ZrCl$_2$ by MAO and [Ph$_3$C][B(C$_6$F$_5$)$_4$] and Cp$_2$ZrCl$_2$/MAO were shown in Figures 5.23-5.25. The identification of the spectra was summarized in Table 5.22.

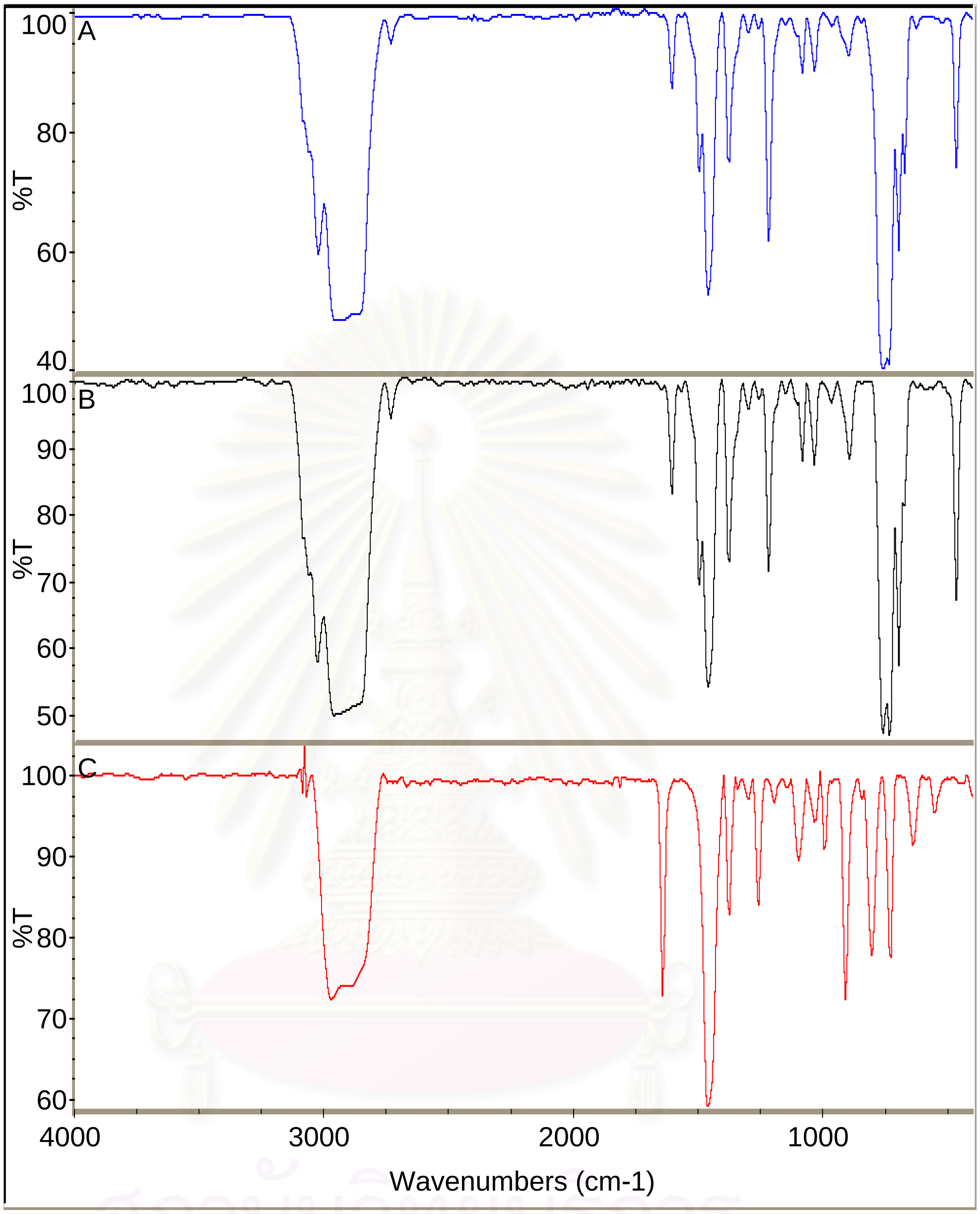


Figure 5.23 FT-IR spectra of the copolymer obtained with *rac*-Et[Ind]$_2$ZrCl$_2$/MAO.

A) 9 %mol 1,5-hexadiene

B) 17 %mol 1,5-hexadiene

C) 50 %mol 1,5-hexadiene

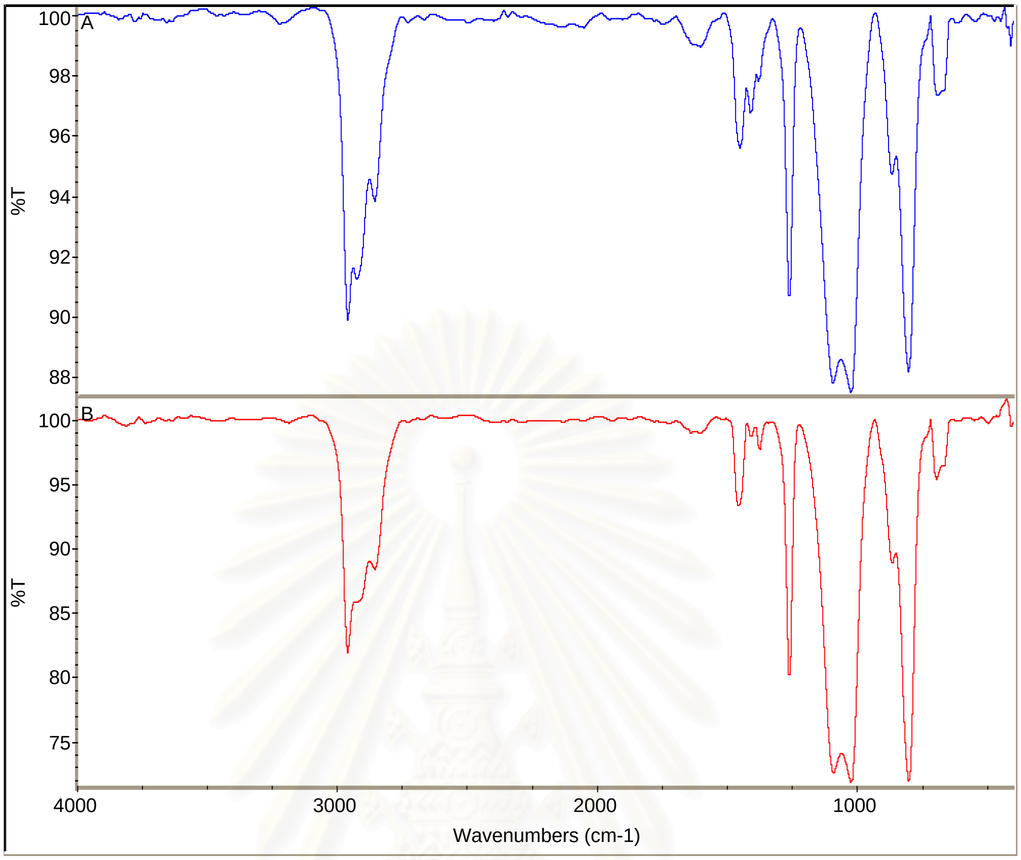


Figure 5.24 FT-IR spectra of the copolymer obtained with *rac*-Et[Ind]$_2$ZrCl$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$].

A) 17 %mol 1,5-hexadiene

B) 50 %mol 1,5-hexadiene

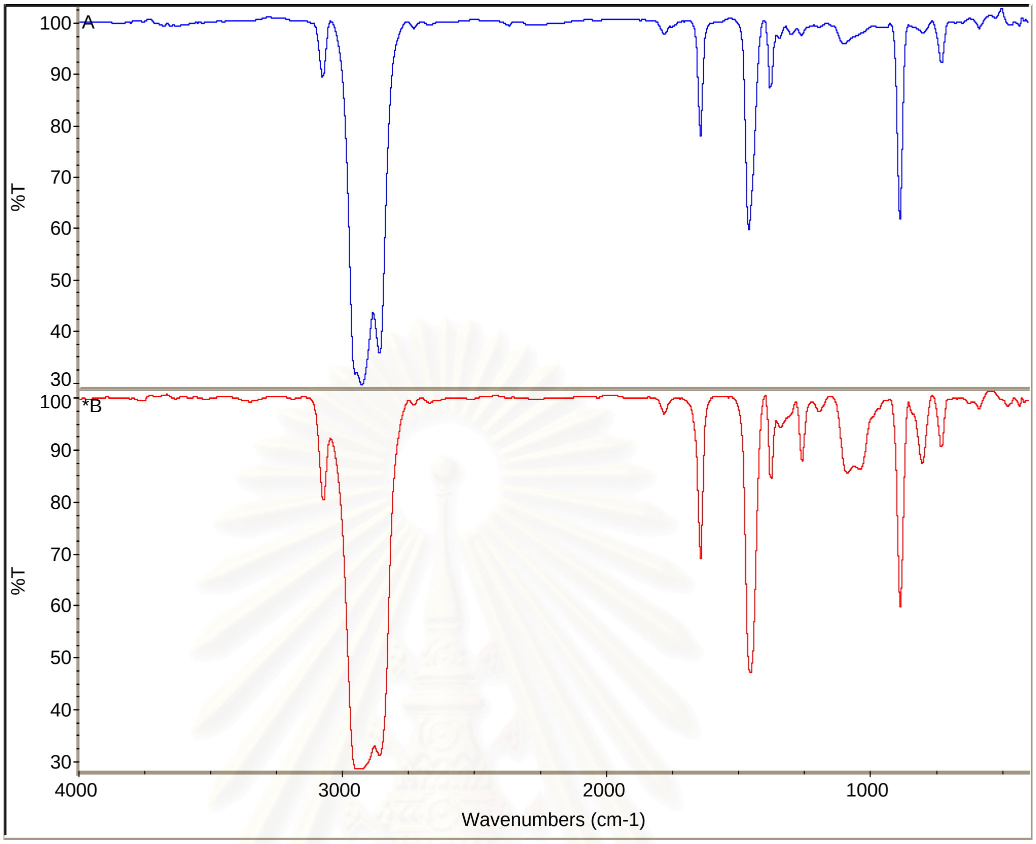


Figure 5.25 FT-IR spectra of the copolymer obtained with Cp_2ZrCl_2/MAO system.

A) 17 %mol 1,5-hexadiene

B) 50 %mol 1,5-hexadiene

Table 5.22 FT-IR data of the products from 1-hexene and 1,5-hexadiene copolymerization by *rac*-Et[Ind]$_2$ZrCl$_2$/MAO and [Ph$_3$C][B(C$_6$F$_5$)$_4$] system and Cp$_2$ZrCl$_2$/MAO system

Wave number (cm^{-1})			Assignment
rac-Et[Ind]$_2$ZrCl$_2$/MAO	*rac*-Et[Ind]$_2$ZrCl$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$]	Cp$_2$ZrCl$_2$/MAO	
2960	2960	2960	-CH$_3$ stretching
2922	2922	2922	asymmetric -CH$_2$ stretching
2852	2852	2852	symmetric -CH$_2$ stretching
1459	1459	1459	C=C stretching of vinylidene
1377	1377	1377	C=C stretching of internal double bond
1000-1200	1000-1200	1000-1200	C-H bending
800-900	800-900	800-900	out-of-plane C-H bending

From Table 5.22, the peak at 2960 cm^{-1} is assigned to -CH$_3$ stretching. The peak at 2922 cm^{-1} is the asymmetric of -CH$_2$ stretching. The peak at 2852 cm^{-1} is the symmetric of -CH$_2$ stretching. The signals in range of 1000-1200 are C-H bending and those at 800-900 cm^{-1} are out-of–plane C-H bending. The peaks at 1377 and 1459 cm^{-1} are C=C stretching. The peaks at 1377 and 1459 cm^{-1} are C=C stretching(corresponding to internal double bonds and vinylidene end groups, respectively)

FT-IR spectra in Figures 5.23-5.24 presented three types of end groups of copolymer when using *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst with MAO or [Ph$_3$C][B(C$_6$F$_5$)$_4$] cocatalyst; -CH$_3$ end group at 2960 cm^{-1}, vinylidene end group at 1459 cm^{-1} and internal double bond at 1377 cm^{-1}. As a result, it can be concluded according to the results obtained in this work that the 1-hexene and 1,5-hexadiene copolymerize to copolymer with different end group.

The possible structure of the copolymer was proposed to result from the competitive insertion of 1-hexene and diene, yielding copolymer with both monomers in the backbone. It should be noted that in the copolymerization of propylene and 1,5-hexadiene catalyzed by *rac*-(EBI)Zr(NMe$_2$)$_2$/TIBA/[Ph$_3$C][B(C$_6$F$_5$)$_4$], it was found that copolymerization occurred through insertion of both monomers with some cyclization of diene in polymer backbone as shown in Figure 5.26.

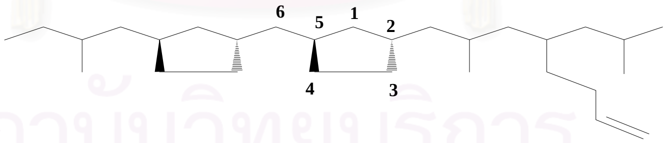
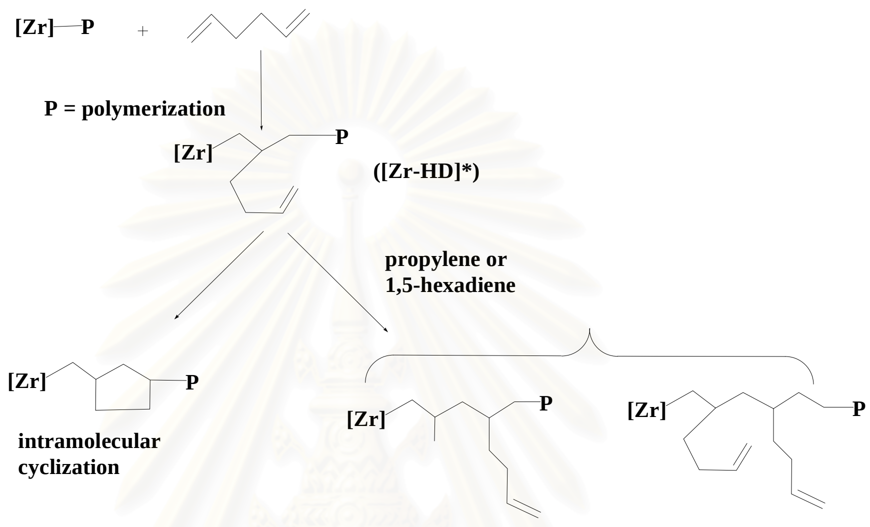


Figure 5.26 1,2-Added 1,5-hexadiene

The 1,5-hexadiene cyclization could occur intramolecularly while intermolecular propagation reaction might also occur as shown in Scheme 5.4. In the first step, only one 1,5-hexadiene double bond is involved, to form [Zr-1,5-hexadiene]* active species. The active species can either yield a cyclic structure, by reacting intramolecularly with the residual double bond, or attacking one of the double bonds of another 1,5-hexadiene. Another way is, instead of forming a cyclic structural unit, the unsaturated linear structural units is left behind in the growing chain. It was studied and reported that intramolecular cyclization of 1,5-hexadiene was unimolecular and occur with 1,2-insertion whereas the intermolecular propagation was bimolecular.[53]



Scheme 5.4 Mechanism of copolymerization of propylene or 1,5-hexadiene.

FT-IR spectrum of copolymer using Cp_2ZrCl_2 catalyst in Figure 5.25 also showed three types of end group; $-CH_3$ end group, vinylidene end group and internal double bond, similar to that of *rac*-$Et[Ind]_2ZrCl_2$ catalyst.

5.7.2 Carbon-13 nuclear magnetic resonance spectroscopy (^{13}C-NMR)

The ^{13}C-NMR spectra of products obtained with *rac*-$Et[Ind]_2ZrCl_2$ and Cp_2ZrCl_2 by MAO as cocatalyst were shown in Figures 5.27-5.28. The assignments of the chemical shifts were shown in Table 5.23.

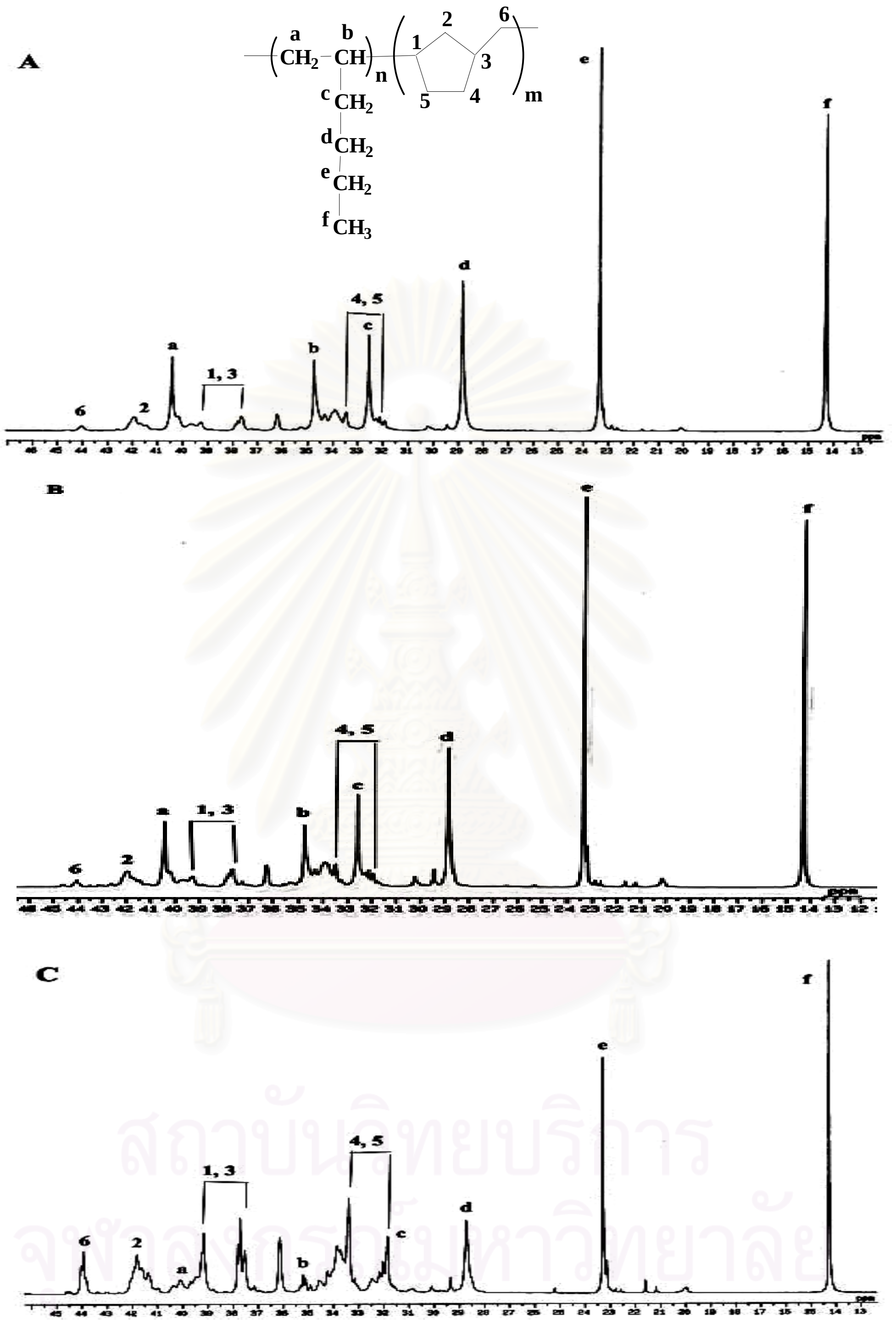


Figure 5.27 ^{13}C{H}-NMR spectra of copolymer obtained with *rac*-Et[Ind]$_2$ZrCl$_2$/MAO.

A) 9 %mol 1,5-hexadiene

B) 17 %mol 1,5-hexadiene

C) 50 %mol 1,5-hexadiene

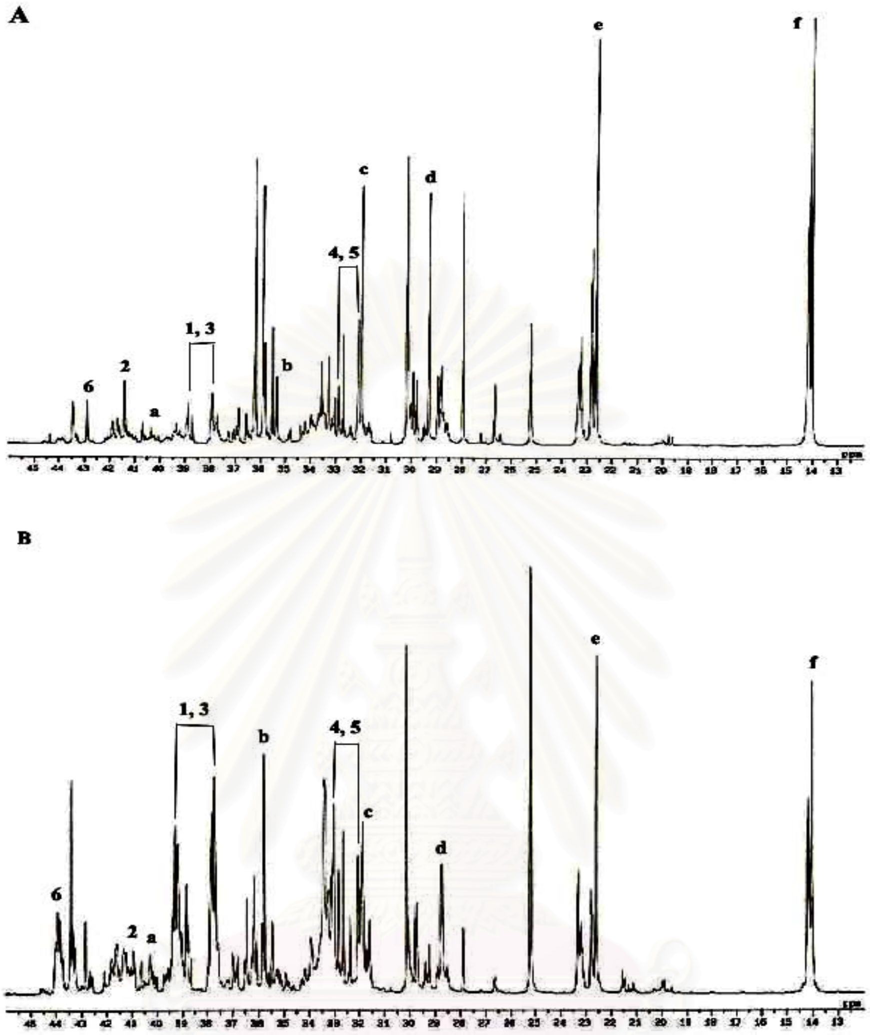


Figure 5.28 $^{13}C\{H\}$-NMR spectra of copolymer obtained with Cp_2ZrCl_2/MAO.

A) 17 %mol 1,5-hexadiene

B) 50 %mol 1,5-hexadiene

Table 5.23 ^{13}C-NMR data of copolymer obtained with *rac*-Et[Ind]$_2$ZrCl$_2$ and Cp$_2$ZrCl$_2$/MAO

Chemical shift (ppm)		Assignment
rac-Et[Ind]$_2$ZrCl$_2$	Cp$_2$ZrCl$_2$	
44	44	C_6
41	41	C_2
40	40	C_a
38, 39	38, 39	$C_{1,3}$
35	35	C_b
32, 33	32, 33	$C_{4,5}$
32	32	C_c
29	29	C_d
23	23	C_e
14	14	C_f

White rubber-like copolymer obtained using *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst was characterized by ^{13}C-NMR. The resonances at 14 ppm is assigned to C_f of 1-hexene and 44 ppm to C_6 of 1,5-hexadiene. These two peaks were chosen to represent two monomers in the copolymer obtained in order to measure their incorporation by measuring the integration (area) of these two peaks in the ^{13}C-NMR spectra.

When increasing %mol 1,5-hexadiene in the feed, amount of 1,5-hexadiene in the polymer structure was found to increase accordingly. For example, the copolymerization performed with 50 %mol of 1,5-hexadiene gave higher incorporation of 1,5-hexadiene in copolymer. The peak integration results might be concluded that the incorporation of 1,5-hexadiene in the copolymer backbone are: 27 % and 3 %, when using 50 % and 9 %mol 1,5-hexadiene in feed, respectively.

In addition, *cis/trans* ratio of the methylene-1,3-cyclopentane units in copolymer was determined by the integration of ^{13}C –NMR resonances at 32.1 and 33.3 ppm, which were reported to represent *cis* and *trans* configuration, respectively. It was concluded that by using *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst, *trans*-MCP units were obtained (in Figure 5.27) while *cis*-MCP units were obtained by using Cp_2ZrCl_2 catalyst (in Figure 5.28). These results are similar to those observed for the homopolymerization of 1,5-hexadiene. As mentioned before, it seems that diastereoselectivity was affected by the steric effect of ligand and bite angle associated with the metallocene catalyst precursors.[43-45]

5.5.1.3 Glass-transition temperature (T_g)

The glass-transition temperature (T_g) of copolymer obtained from *rac*-Et[Ind]$_2$ZrCl$_2$/MAO system has been determined. DSC curves of the copolymer were shown in Figure 5.29. The glass-transition temperature (T_g) of copolymers was shown in Table 5.24.

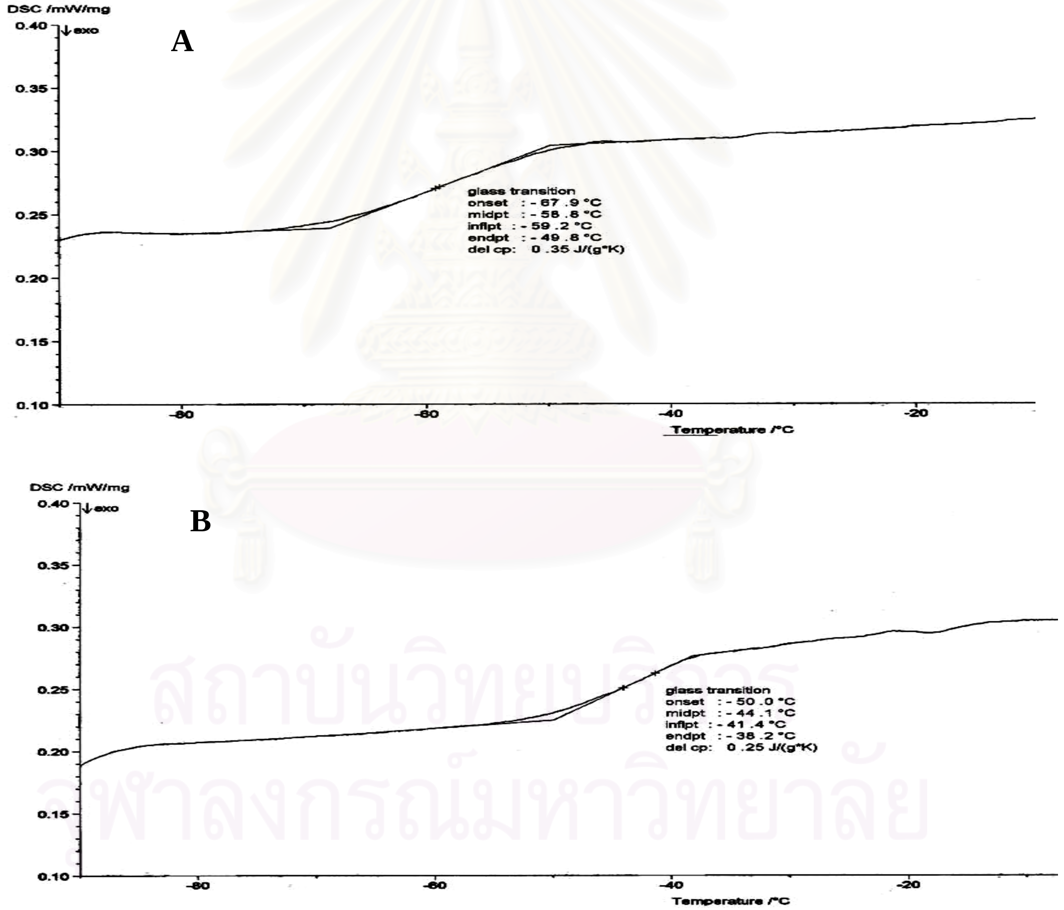


Figure 5.29 DSC curves of copolymer produced by *rac*-Et[Ind]$_2$ZrCl$_2$/MAO system.

A) 9 %mol 1,5-hexadiene

B) 50 %mol 1,5-hexadiene

Table 5.24 The glass-transition temperature (Tg) of copolymer using *rac*-Et[Ind]$_2$ZrCl$_2$/MAO

% Mol of 1,5-hexadiene	T$_g$ (°C)
9	-59
50	-44

5.7.4 Molecular weight (Mw) and molecular weight distribution (MWD)

The molecular weight and molecular weight distribution of copolymer produced with *rac*-Et[Ind]$_2$ZrCl$_2$ and Cp$_2$ZrCl$_2$/MAO system was investigated. The result was shown in Figure 5.30-5.31.

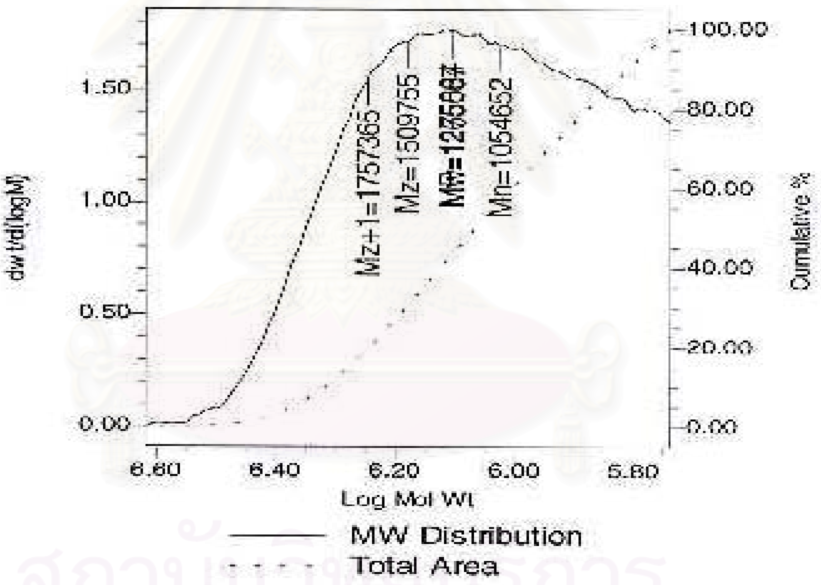


Figure 5.30 GPC curve of copolymer from *rac*-Et[Ind]$_2$ZrCl$_2$/MAO system.

Figure 5.30 showed that *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst produced copolymer with Mw of 1265037, Mn of 1054652 and exhibited molecular weight distribution of 1.20.

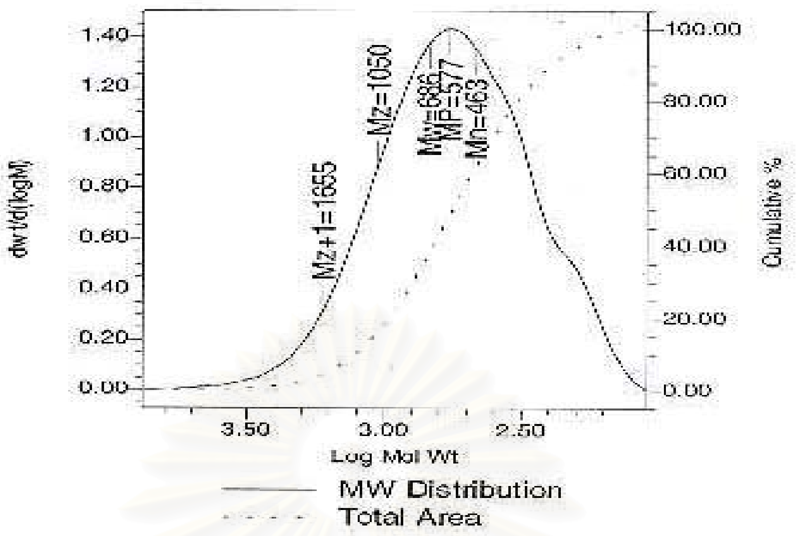


Figure 5.31 GPC curve of copolymer from Cp_2ZrCl_2/MAO system.

Figure 5.31 showed that Cp_2ZrCl_2 catalyst produced copolymer with Mw of 686, Mn of 463 and exhibited molecular weight distribution of 1.48.

Comparison between *rac*-Et[Ind]$_2$ZrCl$_2$ and Cp_2ZrCl_2 catalysts from Figures 5.28-5.29, *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst showed higher molecular weight of copolymer.

CHAPTER VI

CONCLUSION AND SUGGESTION

6.1 Conclusion

To study homo- and copolymerizations of 1-hexene and 1,5-hexadiene by zirconocene catalysts, *rac*-$Et[Ind]_2ZrCl_2$ (**Cat 1**) and Cp_2ZrCl_2 (**Cat 2**) were prepared and characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR. For the polymerization of 1-hexene by zirconocene catalysts in the presence of MAO as cocatalyst, it was found that the catalyst concentration, Al/Zr mole ratio and polymerization temperature affected the polymerization. The optimum condition for 1-hexene polymerization was at 60°C, 24 hrs, 2.5 μmol catalyst and Al/Zr mole ratio of 4000. The activities of **Cat 1** and **Cat 2** for 1-hexene polymerization were similar. The information from ^{13}C-NMR, DSC, GPC techniques identified that **Cat 1** produced isotactic poly(1-hexene) with molecular weight (Mw) of 51099, molecular weight distribution (Mw/Mn) of 1.92 and glass-transition temperature (T_g) at –48°C, while **Cat 2** produced atactic poly(1-hexene) with molecular weight (Mw) of 9942, molecular weight distribution (Mw/Mn) of 2.41 and glass-transition temperature (T_g) at –55°C. These results confirmed the ability of zirconocene catalysts in controlling the polymer structure: the isospecific zirconocene (**Cat 1**) yields isotactic poly(1-hexene), while the aspecific zirconocene (**Cat 2**) yields atactic poly(1-hexene).

For 1,5-hexadiene polymerization using MAO cocatalyst, the optimum condition for **Cat 1** was at 30°C, 5 hrs, 2.5 μmol catalyst and Al/Zr mole ratio of 4000. At the same condition, **Cat 1** gave higher activity than **Cat 2**. A difference in activity of **Cat 1** in 1,5-hexadiene polymerization using different cocatalysts: MAO and $[Ph_3C][B(C_6F_5)_4]$ were revealed. The activities for **Cat 1**/MAO gave higher than **Cat 1**/$[Ph_3C][B(C_6F_5)_4]$ system. For **Cat 1**/$[Ph_3C][B(C_6F_5)_4]$ system, the condition used at 50°C, 3 hrs, 2.5 μmol catalyst, Al/Zr mole ratio = 400 and $[Ph_3C][B(C_6F_5)_4]$ 1.1 equivalent. The information from ^{13}C-NMR, DSC, GPC techniques identified that **Cat 1** produced *trans*-isotactic poly(methylene-1,3-cyclopentane) with molecular weight (Mw) of 17672, molecular weight distribution (Mw/Mn) of 1.86 and glass-transition temperature (T_g) at 6°C, while **Cat 2** produced *cis*-atactic poly(methylene-1,3-cyclopentane). The difference in structure of polymer obtained was controlled by stereochemistry of zirconocene catalysts.

For copolymerization of 1-hexene and 1,5-hexadiene by MAO cocatalyst, condition used was at 30°C, 5 hrs, 50 %mol 1,5-hexadiene, 2.5 μmol catalyst and Al/Zr mole ratio of 4000. At the same condition, **Cat 1** gave higher activity than **Cat 2**. Copolymerization of 1-hexene and 1,5-hexadiene by **Cat 1**/$[Ph_3C][B(C_6F_5)_4]$ cocatalyst was at 50°C, 24 hrs, 2.5 μmol catalyst, Al/Zr mole ratio = 200 and $[Ph_3C][B(C_6F_5)_4]$ 1.1 equivalent. The activity for **Cat 1**/MAO was higher than **Cat 1**/$[Ph_3C][B(C_6F_5)_4]$ system. Based on the result from ^{13}C-NMR, DSC, GPC techniques, it was found more incorporation of diene produced by **Cat 2** when increasing diene momomer. This type of copolymer is expected to find application in raw material for transparent plastic.

6.2 Suggestion

Copolymerization of 1-hexene and other dienes *e.g.* conjugated-diene should be attempted using the *rac*-$Et[Ind]_2ZrCl_2$ catalyst, the product is expected to possess different properties.

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