เคมีของตัวกำจัดสิ่งปนเปื้อนต่อสมรรถนะของตัวเร่งปฏิกิริยาเมทัลโลซีนบนตัวรองรับ

นางสาวโสวดี สายโสภา

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THE CHEMISTRY OF SCAVENGER ON THE PERFORMANCE OF THE SUPPORTED METALLOCENE CATALYST

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A Thesis Submitted in Partial Fulfillment of the Requirements
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ในวิทยานิพนธ์ฉบับนี้ได้ทำการศึกษาเกี่ยวกับชนิดและความเข้มข้นของหมู่อะคิลอะลูมินัมที่ใช้เป็นตัวกำจัดสิ่งปนเปื้อนมาจากสารที่ใช้กันโดยทั่วไปในกระบวนการผลิตพอลิโอเลฟินโดยจะศึกษาถึงผลกระทบต่อความว่องไวของตัวเร่งปฏิกิริยาเมทัลโลซีนบนตัวรองรับและสมบัติของผลิตภัณฑ์ หมู่อะคิลอะลูมินัมถูกแบ่งเป็น 2 ชนิด คือ ไตรเอทิลอะลูมินัม และ ไตรอัลโซบิวทิลอะลูมินัมที่ใช้ในการศึกษา การเติมหมู่อะคิลอะลูมินัมเพื่อกำจัดสิ่งปนเปื้อนมีความสำคัญและจำเป็นในกระบวนการพอลิเมอไรเซชันนี้เพราะเมื่อไม่มีหมู่อะคิลอะลูมินัมกำจัดสิ่งปนเปื้อนส่งผลให้เกิดการเสื่อมของตัวเร่งปฏิกิริยาอย่างรวดเร็ว ที่ความเข้มข้นที่ให้ความว่องไวมากที่สุดคือ 0.7 และ 1.2 mmol/L in hexane และให้ค่าความว่องไว 6.027 และ 8.603 kg.PE/g Cat.*h ของ ไตรเอทิลอะลูมินัม และ ไตรอัลโซบิวทิลอะลูมินัม ตามลำดับ ในปฏิกิริยาเอทิลีนพอลิเมอไรเซชัน แต่อย่างไรก็ตามที่ความเข้มข้นของตัวกำจัดสิ่งปนเปื้อนมากเกินพอ ส่งผลให้ค่าความว่องไวลดลง เนื่องจากเกิดสารประกอบเชิงซ้อนเฮททัลโลไดนิวเคลียร์ ซึ่งอาจยับยั้งหรือลดประสิทธิภาพของตัวเร่งปฏิกิริยา สันนิษฐานว่าไตรเอทิลอะลูมินัมสะดวกต่อการเกิดสารประกอบเชิงซ้อนเฮททัลโลไดนิวเคลียร์มากกว่าไตรอัลโซบิวทิลอะลูมินัมเนื่องจากเหตุผลของความเกะกะทางโครงสร้าง นอกจากนี้ไตรเอทิลอะลูมินัมเป็นตัวรีดิวซ์ที่แรงกว่าไตรอัลโซบิวทิลอะลูมินัมในการลดสถานะของเซอร์โคเนียมจากเซอร์โคเนียมสถานะสี่เป็นเซอร์โคเนียมสถานะสามซึ่งเป็นสถานะที่มีความว่องไวต่ำในปฏิกิริยาเอทิลีนพอลิเมอไรเซชัน ความเข้มข้นของตัวกำจัดสิ่งปนเปื้อนไม่ส่งผลต่ออุณหภูมิหลอมเหลวและความเป็นผลึกของพอลิเมอร์ สำหรับเอทิลีนและวันเฮกซีนโคพอลิเมอไรเซชัน พบว่าการแทรกตัวของวันเฮกซีนไม่ขึ้นกันความเข้มข้นของหมู่อะคิลอะลูมินัม ผลกระทบของไฮโดรเจนแสดงการลดลงของค่าความว่องไวเนื่องจากสารประกอบเชิงซ้อนเมทัลไฮไดรด์ไปลดอัตราของปฏิกิริยาขั้นแผ่ขยาย

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....
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KEYWORDS: ALKYLALUMINUM / SCAVENGER / SYSTEM SUPPORTED METALLOCENE CATALYST / EFFECT OF HYDROGEN

SOWADEE SAISOPA: THE CHEMISTRY OF SCAVENGER ON THE PERFORMANCE OF THE SUPPORTED METALLOCENE CATALYST. ADVISOR: ASSOC. PROF. BUNJERD JONGSOMJIT, Ph.D., 104 pp.

In this study, the effect of the various types and concentrations of alkylaluminum acting as scavenge impurities which contaminate in materials commonly used in polyolefin processes was studied on catalytic activity of supported metallocene catalyst and product properties. Alkylaluminum was divided into 2 types including triethylaluminum (TEA) and triisobutylaluminum (TiBA) used to investigate. The addition of alkylaluminum as scavenger is important and necessary in this polymerization process because without alkylaluminum to scavenge impurities rapid deactivation occurs. The concentration which reached maximum catalytic activity was found at 0.7, 1.2 mmol/L in hexane and 6.027, 8.603 kg.PE/g Cat.*h of TEA and TiBA, respectively in ethylene homopolymerization. Nevertheless, with excess concentration of scavenger, the catalytic activity is depressed. This is due to heterodinuclear complexes form which may inhibit or lower the catalytic efficiency. TEA can be presumed that facile the formation of heterodinuclear complexes than TiBA due to steric effect (or hindrance). Furthermore, TEA is a stronger reducing agent than TiBA to reduce Zr(IV) to Zi(III) states, which is inactive for ethylene polymerization. The melting temperature and the crystallinities of the polymers are, therefore, unaffected by the concentration of scavenger. For ethylene and 1-hexene copolymerization, the 1-hexene incorporation was not a function of the trialkylaluminum concentration. The effects of hydrogen have shown a decrease catalytic activity due to metal hydride complex formed leading to a lower propagation rate.

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

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CHAPTER I

INTRODUCTION

Polyethylene (PE) is one kind of polymers that is very popular in the world and its use accounts for one third of the total plastic markets. PE is usually used to produce many products such as shampoo bottles, soap bottles, tail lamps, children toys, grocery bags, little electrical parts components and other products. PE is the least costly of the major synthetic polymer. Because, it has excellent chemical resistance and can be processed in a variety of way including film blowing, pipe extrusion, blow molding and injection molding into myriad shapes and devices. The global polyethylene demand is forecast to increase in next 5 years and the consumption is also continued. Thus, an important in polyethylene properties and polymerization process is crucial for industrial plastics.

The discovery of metallocene catalysts for the olefin polymerization has opened a frontier in the field of organometallic chemistry, polymer synthesis, and processing. New tailor-made polymers can be synthesized by metallocene catalysts. The metallocene catalyst was uncovered by Ernst O. Fischer and Geoffrey Wilkinson in 1952 [1-2]. Highly active metallocene catalysts for the olefin polymerization have enabled for the production of linear, polyethylene with narrow molecular weight distribution and good mechanical properties.

Aluminum alkyls are often added to the reactor in slurry or gas-phase polymerization with supported metallocene/MAO and conventional Ziegler-Natta catalysts to scavenge impurities. In conventional Ziegler-Natta systems, aluminum alkyls also serve as cocatalysts to generate catalytic active sites. There are many reports on the use of aluminum alkyls as cocatalyst in the ethylene polymerization and copolymerization with α-olefins using supported metallocene catalysts [4-7]. In this study, we paid attention only to investigate the effect of aluminum alkyls on the catalytic activity and properties of polymer. Others have reported that the activator is affect on molecular weight, activity, stereoregularity and comonomer incorporation [[3, 8-12]. As a result, an optimum amount of aluminum alkyl is desired in the polymerization reactor, such as an amount that is enough to scavenge impurities, but not excessive to inhibit the catalytic activity. However, the effect of aluminum alkyls in polymerization behavior are different depending on the used catalyst and the polymerization conditions.

This study was divided into three parts. The first part was investigated the effect of an amount of aluminum alkyl in ethylene polymerization with supported metallocene catalyst. The effect of different types of aluminium alkyl activators on catalytic activity and properties of polymer was also studied.

The second part of this work was investigated how the different type of aluminum alkyls would affect on the kinetic behavior, catalytic activity and polymer properties for ethylene and 1-hexene copolymerization with supported metallocene catalyst.

The final part was studied the effect of H_2 on catalytic activity and polymer properties for ethylene homopolymerization.

The obtained polymer and copolymer was characterized by means of scanning electron microscope (SEM) to observe polymer morphology, where thermal properties was observed by differential scanning calorimetry (DSC). Molecular weight (MW) and molecular weight distribution (MWD) were characterized by gel permeation chromatography (GPC). The insertion of 1-hexene in the obtained copolymer was evaluated by Fourier-transform infrared spectroscopy (FT-IR).

1.1 Objectives

The objective of this research is to study the effect of type and concentration of alkylaluminum on catalytic activity and properties of polymer in ethylene was homo and copolymerization with 1-hexene. In addition, it also investigated an effect of H_2 on catalytic activity and properties of polymer in ethylene homopolymerization.

1.2 Research scopes

- Studied the effect of alkylaluminum based on scavenge impurity by varying type of alkylaluminum such as triethylaluminum (TEA) and triisobuthylaluminum (TIBA).

- Varied concentration of alkylalumiunm as scavenger for 0.3, 0.5, 0.7, 1.0, 1.2 mmol/L of triethylauminum (TEA) and triisobuthylaluminum (TIBA) for 0.7, 1.0, 1.2, 1.5, 1.7 mmol/L.
- Studied the effect of alkylaluminum on catalytic activity in ethylene homopolymerization and copolymerization with 1-hexene in 2 L reactor.
- Characterized obtained polymer by means of SEM, DSC, GPC, bulk density and FTIR
- Studied the effect of H_2 in ethylene homopolymerization 2 L reactor by flow H_2 continue for 4 ml/min and characterized polymer properties by using SEM, DSC, GPC, bulk density.

1.3 Research

The research methodology is shown in flow diagram as Figure1.1

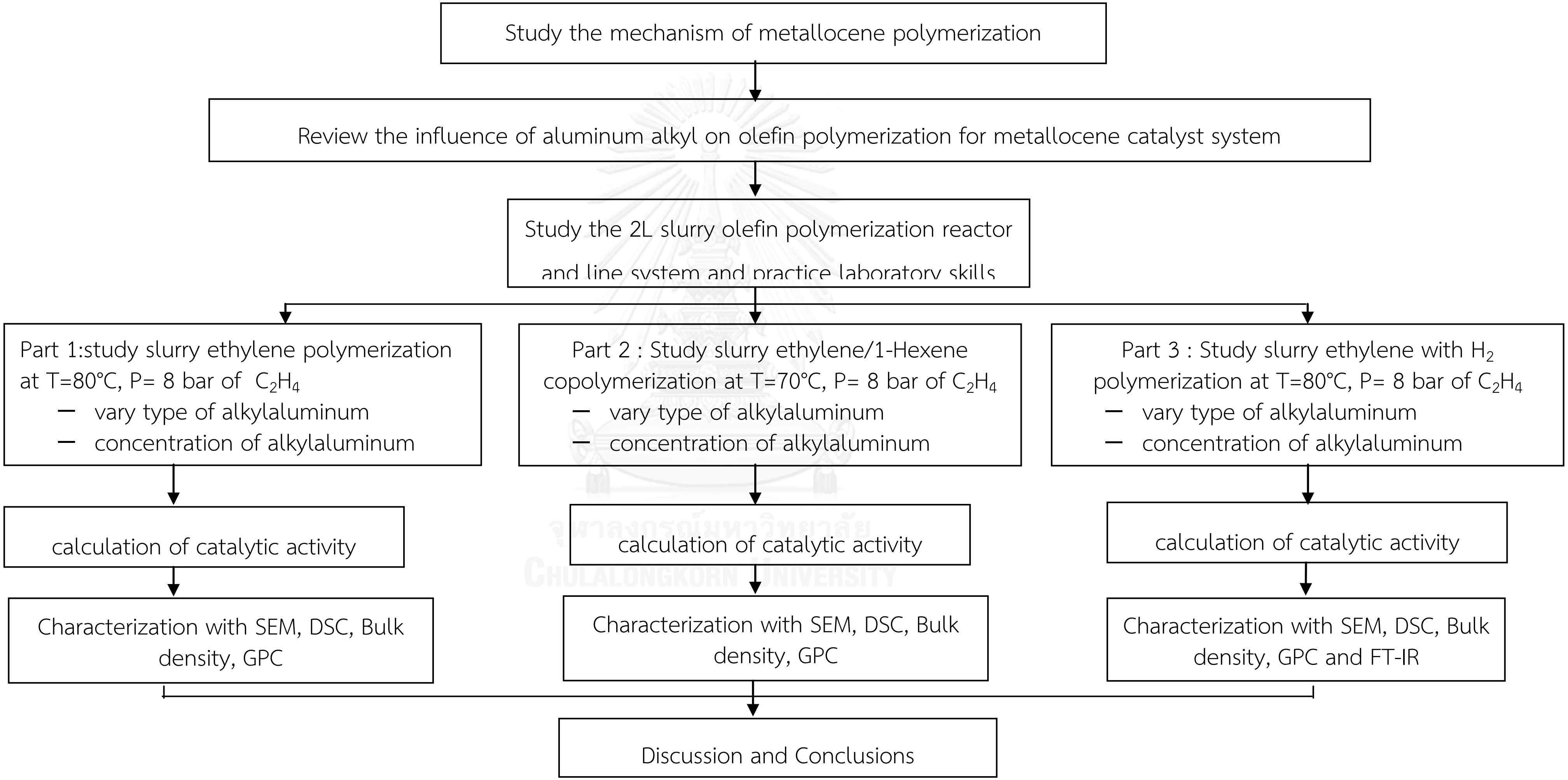


Figure 1. 1 Flow diagram research methodology

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Polyethylene classification

Ethene (IUPAC) or ethylene molecules as we know includes of C atom and H atom with $CH_2{=}CH_2$ or C_2H_4. Ethylene has a simple structure as illustrated in Figure 2.1. One monomer of ethylene is connected with other with a hundred monomers and form polyethylene.

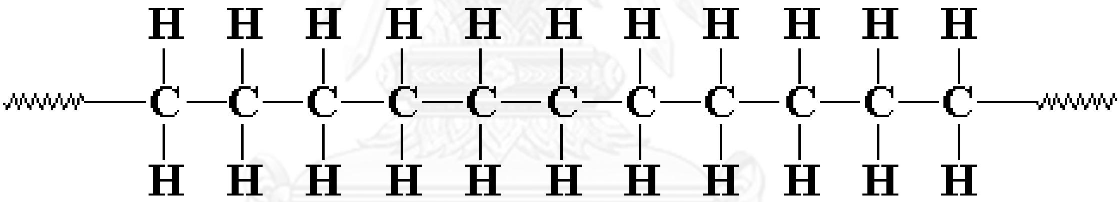


Figure 2. 1 Polyethylene

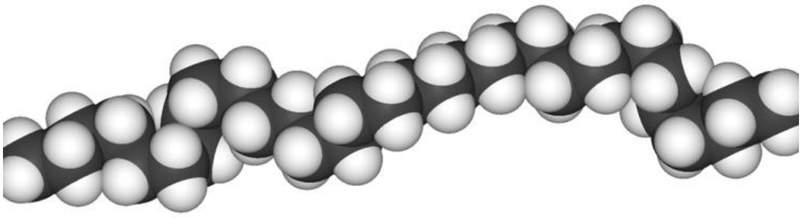


Figure 2. 2 Chain of polyethylene

Industrial polyethylene

The early period, polyethylene synthetical industrially practices was discovered by Eric Fawcett and Reginald Gibson at ICI Chemicals in 1933. In 1935, Michael Perrin who is another ICI chemist started to develop a reproducible industrial synthesis for low density polyethylene (LDPE)

In 1951 Robert Banks and John Hogan at Phillips Petroleum discovered chromium trioxide based catalyst. In 1953, the German chemist Karl Ziegler developed a catalytic system based on titanium halides and organoaluminium compounds that worked at even milder conditions than the Phillips catalyst.

2.2 Produced polyethylene [13]

Polyethylene both in laboratory and industrially is produced by polymerization process. This process connects monomer or a mixture of monomer become together by reaction that results in a chain form called polymer. They are three methods involved in producing polyethylene in polymerization process

1. Radical polymerization
2. Anionic polymerization
3. Cationic polymerization

The SPI or Society of the Plastic Industry which an industry trade association founded in 1937, divides three main groups of polyethylene based on density:

- Low density : 0.910-0.925 g/cm^3
- Medium density : 0.926-0.940 g/cm^3

- High density : 0.941-0.965 g/cm^3

Later, the American Society for Testing and Material (ASTM) has also defined various types of polyethylene. An ASTM publication entitled “Standard Terminology Relating to Plastics” (ASTM D 883-00) provides the following classifications based upon density :

- High density polyethylene(HDPE): $>$0.941 g/cm^3
- Linear medium density polyethylene (LMDPE): 0.926-0.940 g/cm^3
- Medium density polyethylene (MDPE): 0.926-0.940 g/cm^3
- Linear low density polyethylene(LLDPE): 0.919-0.925 g/cm^3
- Low density polyethylene (LDPE): 0.910-0.925 g/cm^3

Furthermore, SPI and ASTM classification do not provide more detail such as molecular weight or comonomer employed to describe the extensive range of polyethylene available in the industry. An overview of many classification of polyethylene in common use in industry is provided below :

- Very Low Density Polyethylene (VLDPE) : also called ultra low density polyethylene (ULDPE) by some manufactures, is produced primarily with Ziegler Natta catalysts using α-olefin comonomers, density range from about 0.885 to 0.915 g/cm^3. Select grades of VLDPE produced with single site catalyst are known as polyolefin plastomers (POP) and polyolefin elastomers (POE) because products display both thermoplastic and elastomeric properties. Densities of POP fall in the VLDPE range, but densities of POE are in the range 0.855 to 0.885 g/cm^3. A major application is in food packing.

- Low Density Polyethylene (LDPE): the primeval polyethylene, is produced only by free radical polymerization of ethylene initial by organic peroxides or other reagents that readily depose into free radicals. Density is typically 0.915-0.930 g/cm^3 LDPE is the most easily processed of major type of polyethylene and is often blended with linear low density polyethylene and high density polyethylene to improve processability. LDPE is highly branched and contains relatively high amorphous content which results in outstanding clarity in film for food packing, a major application.

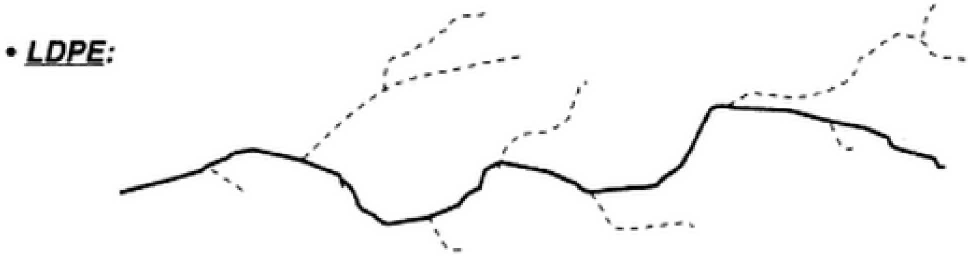


Figure 2. 3 Low density polyethylene

- High Molecular Weight High Density Polyethylene [HMW-HDPE (or HMWPE)] : density range 0.94-0.96 g/cm^3. HMW-HDPE grade are typically produced in a dual reactor configuration which results in bimodal molecular weight distribution with comonomer incorporated in high molecular weight fraction. Key applications are pipe, grocery sacks and automotive fuel tanks.

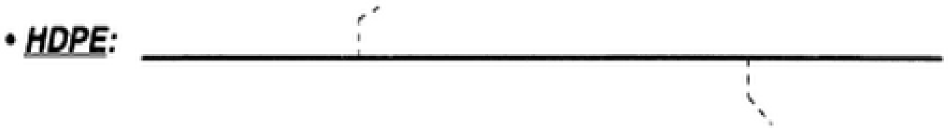


Figure 2. 4 High density polyethylene

- Ultrahigh Molecular Weight Polyethylene (UHMWPE) :

  Molecular weights range from about 3,000,000 to 7,000,000 amu. UHMWP has a amazingly low density ~0.94 g/cm^3, most likely owing to crystalline defect and lamellar effects caused by the vastly long chains. UHW\MWPE shows good properties such as excellent impact strength and abrasion-resistance. UHMWPE is used to make porous battery separator films.

Microstructures of polyethylene depend upon type of catalyst, polymerization conditions, comonomers used, etc. Polyethylene and copolymers produced by free radical polymerization include short chain and long chain branching and higher amorphous content relative to LLDPE and HDPE. HDPE contains little short chain branching because comonomers are used in low quantities.

2.3 Heterogeneous catalyst for olefin polymerization

Polyolefins illustrate approximate 50% by weight of all commodity polymer, which amount to about 90% by weight of the global polymer production. Ziegler-Natta catalysts has significant role for producing polyethylene and polypropylene more than 50 years [14]. Karl Ziegler and Giulio Natta, who discovered the Ziegler-Natta catalyst. In 1953, Ziegler discovered $TiCl_4/AlEt_3$ and Natta discovered $TiCl_3/AlEt_3$ in 1954 and their won the Nobel Prize in 1963 [15]. During 60 years of development of Ziegler–Natta (Z-N) catalysts, they have been produced many industrially polymeric materials such as polyethylene, polypropylene(PP), polybutadiene(PBd), polyisoprene (PI) and ethylene-co-propylene copolymer. Especially, a capacity of polyethylene and polypropylene has accounted for more than 60% of all industrial polymers in the world and most important constituent in the polyolefin family [16]. It results that have been the continue to development of Ziegler–Natta (Z-N) catalysts show in Table 2.1. The most widely $MgCl_2$ is used for support of Ziegler–Natta (Z-N) catalysts moreover, SO_2, metal oxides such as ZnO, Al_2O_3, Fe_2O_3, CrO_3 and CuO, carbon nanotubes [17, 18] and various polymers is used [19, 20].

The main advantages of supported Z-N catalysts are as follows:

- Supported Ziegler–Natta catalysts give the possibility of high activity catalytic systems without reactor fouling.
- A lower ratio of co-catalyst/catalyst to provide a maximum activity than a homogeneous catalysts.

- The molecular weight and molecular weight distribution of the polymers is varied more easily with good processability.

Table 2. 1 Revolutionary development of Ziegler–Natta catalysts Year Composition

Generation	Year	Composition
1st	1957–1970	$TiCl_3/AlCl_3/AlEt_2Cl$
2nd	1970-1978	$TiCl_3/AlE_{t2}Cl$
3rd	1978-1980	$TiCl_4$/esters/$MgCl_2$ +AlR_3/ester
4th	1980-	$TiCl_4$/diesters/$MgCl_2$ +AlR_3/silane $TiCl_4$/diethers/$MgCl_2$ +$AlEt_3$

2.4 Metallocene catalysts

The structure of metallocenes, so called “sandwich compounds” in which a π-bonded metal atom is situated between two aromatic ring systems, was uncovered by Ernst O. Fischer and Geoffrey Wilkinson in 1952. They were both awarded the Nobel Prizein 1973 for this accomplishment [21, 22]. Metallocene compounds are molecules that have two cyclic ligands bonded to a metal center which show that in Figure2.5. Metallocene catalysts are soluble in hydrocarbons, show only one type of active site and their chemical structure can be easily changed. New tailor-made polymers can be synthesized by metallocene catalysts. A wide variety of metallocenes are used for olefin polymerization today. These properties of the resulting polyolefins by knowing the structure of the catalyst used during their manufacture and to control the resulting molecular weight and distribution, comonomer content and tacticity by careful selection of the appropriate reactor conditions.

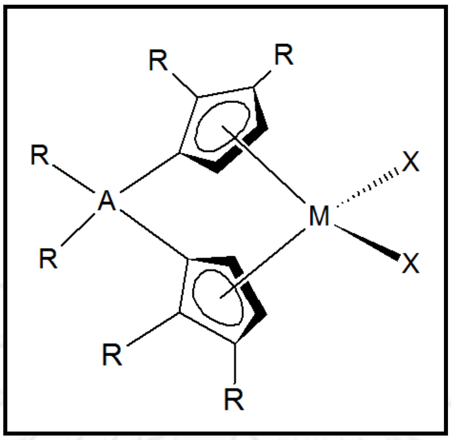


Figure 2. 5 Basically structure of metallocene catalyst

M = transition metal e.g. Ti, Zr or Hf

X = halogen(7A) e.g. Cl or alkyl group

R = alkyl group(C_nH_{2n+1}), H or other hydrocarbon groups

A = optional bridging atom(s) e.g. ethylene, dimethylsilyl


= Cyclopentadienyl, Indenyl, Fluorenyl (Substituted & Unsbstituted)

Attractive of Metallocene Catalysts

- The homogeneous nature of these catalysts provides active sites for every molecule in solution and explains their great activity.
- High activity of metallocene catalyst 100 times more active than conventional Ziegler-Natta or Phillips catalysts.

- Their potential to polymerize prochiral olefins, such as propylene, to give stereospecific polymers (isotactic, syndiotactic, hemitacticpolypropylene) [23-25]. This variety opens the door to polyolefin elastomers
- Very uniform and narrow weight distribution (MWD < 2.5)
- Their capability as so-called “single site” catalysts to produce polyolefins with narrow molecular weight distributions ($Mw/Mn \approx 2$).
- Uniform comonomer incorporation
- Significantly reduced low molecular weight fractions (low solvent extractables)

2.5 The Role of the Cocatalyst

Metallocenes are not active by themselves for polymerization. Usually, a cocatalyst is required to activate the metallocene, which are organoalumoxanes especially methylalumoxane, that provides maximum activity [26-30]. Methylaluminoxane (MAO) or borate compounds are used to activate the metallocene. The activation reaction is contained of first the methylation of the central metal and second a carbanion abstraction to produce a metallocenemonomethylcation as the actual catalytic species [31-33] . This theory is supported by the fact that strong Lewis acids, e.g. $B(C_6F_5)_3$, abstract a methyl anion from dimethylated complexes of the type $Cp_2MMe_2$to form a cationic species Cp_2MMe^+ that is the actual catalyst for the polymerization of olefins [34-36] .

2.6 Alkylaluminum [37]

The term of alkylaluminum is meant to include any compound that contains an alkylaluminum grouping and encompasses R_3Al, R_2AlCl, $R_3Al_2Cl_3$ (the so - called sesquichlorides), $RAlCl_2$, R_2AlOR', and R_2AlH. Among commercially available alkylaluminums, R is typically a C_1– C_4 alkyl. Alkylaluminums are important components for Metal-Catalyzed Olefin Polymerization.

Alkylaluminums have been produced commercially since 1959 using technology originally licensed by Nobel prestigious Karl Ziegler [38]. Alkylaluminums are pyrophoric (reactive materials can ignite spontaneously or react violently on contact with air) and violently reactive with water [39, 40].

Owing to these properties, it is distinguished that millions of pounds of alkylaluminums are produced each year and have been supplied to the polyolefin industry worldwide for half a century. Major alkylaluminums available in the merchant market (and their common acronyms) are show in Table 2.2.

Table 2. 2 Major commercially available alkylaluminums

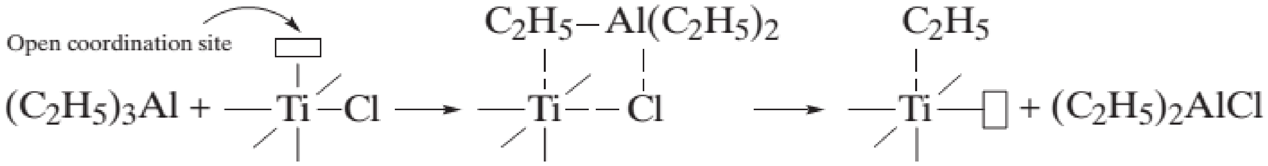
Product	Acronym	Formula	Theoretical wt% Al
Trimethylaluminum	TMAL	$(CH_3)_3Al$	37.4
Dimethylaluminum chloride	DMAC	$(CH_3)_2AlCl$	29.2
Methylaluminum sesquichloride	MASC	$(CH_3)_3Al_2Cl_3$	26.3
Triethylaluminum	TEAL	$(C_2H_5)_3Al$	23.6
Diethylaluminum chloride	DEAC	$(C_2H_5)_2AlCl$	22.4
Diethylaluminum iodide	DEAI	$(C_2H_5)_2AlI$	12.7
Ethylaluminum sesquichloride	EASC	$(C_2H_5)_3Al_2Cl_3$	21.8
Ethylaluminum dichloride	EADC	$C_2H_5AlCl_2$	21.3
Isobutylaluminum dichloride	MONIBAC	$i\text{-}C_4H_9AlCl_2$	17.4
Tri - n- butylaluminum	TNBAL	$(C_4H_9)_3Al$	13.6
Triisobutylaluminum	TIBAL	$(i\text{-}C_4H_9)_3Al$	13.6
Diisobutylaluminum hydride	DIBAL - H	$(i\text{-}C_4H_9)_2AlH$	19.0
Tri-n-hexylaluminu m	TNHAL	$(C_6H_{13})_3Al$	9.6
Tri-n-octylaluminum	TNOAL	$(C_8H_{17})_3Al$	7.4
Di-n-octylaluminum iodide	DNOAI	$(C_8H_{17})_2AlI$	7.1
" isoprenylaluminum "	IPRA	Not available	Not available

Product	Acronym	Formula	Theoretical wt% Al
Diethylaluminum ethoxide	DEAL-E	$(C_2H_5)_2AlOC_2H_5$	20.7
Ethylpropoxyaluminum chloride	EPAC	$(C_2H_5)(C_3H_7O)AlCl$	17.9
Diisobutylaluminum butylated oxytoluene	DIBAL - BOT	$(i\text{-}C_4H_9)_2AlO[C_6H_2(CH_3)(t\text{-}C_4H_9)_2]$	7.5

Basically, aluminum alkyls have different effects on homogeneous metallocene mediated olefins polymerization:

- they can alkylate catalyst precursor L_2MX_2, whereX¼Cl, NMe_2; M¼Zr, Ti, before its activation by borate reagents and even operate as a cocatalyst [41, 42]
- scavenge traces of impurities which are always present in the monomer or in solvents [43, 44]
- act as a chain transfer agent [45]
- trap of free TMA admixtures in MAO [41]
- act as a reducing agent for the titanium compound [46]

Transition metal compound was reduced by alkylaluminum (called "alkylation") to produce active centers for polymerization, as illustrated in Equation (1) with triethylaluminum (TEAL) and $TiCl_3$.

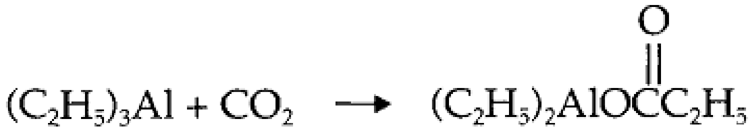


…Eq. (1)

Alkylaluminums also act the target of scavenging catalyst poisons such as H_2O, O_2, CO_2 , CO , alcohols, acetylenics, dienes, sulfur-containing compounds and other protic and polar contaminants. Poisons reach as parts-per-million (ppm) contaminants in materials commonly used in polyolefin processes for example monomer, comonomer, solvents, and chain transfer agents. Reaction of the aluminum alkyl with contaminants generates alkylaluminum derivatives that are not as damaging to catalyst performance. For example, water reacts with TEAL to produce small amounts of ethylaluminoxane, as show in Equation (2):

$$(C_2H_5)_3Al + \frac{1}{2} O_2 \rightarrow (C_2H_5)_2AlOC_2H_5$$

$$2\ (C_2H_5)_3Al + H_2O \rightarrow (C_2H_5)_2Al\text{-}O\text{-}Al(C_2H_5)_2 + 2\ C_2H_6 \uparrow$$



$$(C_2H_5)_3Al + CO_2 \longrightarrow (C_2H_5)_2AlO\overset{\overset{O}{\|}}{C}C_2H_5$$

Eq….(2)

Typical properties of commercially available alkylaluminums are concluded as follow:

- Alkylaluminums are usually clear, colorless liquids at ambient temperature and are miscible in all proportions with aliphatic hydrocarbons (HCs). Large quantities of aluminum alkyls are supplied as solutions in HCs, because solutions are perceived to be safer.

- R_3Al compounds (R = ethyl or higher) contain small amounts of R_2AlH. Hydride content is showed as AlH_3 by tacit convention among major suppliers and normally ranges from about 0.02 wt% in TEAL to about 0.5 wt% in triisobutylaluminum (TIBAL).

R_3Al compounds also commonly contain small amounts of other trialkylaluminum compounds (R'_3Al). This is usually a resultant of the purity of beginning materials or of side reactions during manufacture, such as addition of an ethylaluminum moiety in TEAL across ethylene to produce an n-butylaluminum group (Figure 2.6).

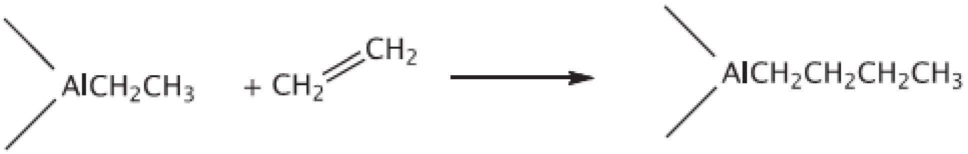


Figure 2. 6 Insertion of ethylene into an ethyl group – aluminum bond to form butylaluminum.

R'_3Al contents are low, often <0.5 wt%. An exception is TEAL where n-butylaluminum content is typically ∼5 wt%. In the various majority of transition metal polyolefin catalyst systems, hydride content and the presence of small amounts of other trialkylaluminum compounds (R'_3Al) are not damaging to performance.

Alkylaluminums also contain ppm amounts of aluminoxanes and alkoxides resulting from reaction with water, similar show in Equation 2. Water and oxygen reach as contaminants (typically <5 ppm) in process materials, such as nitrogen, ethylene, and hydrogen. Aluminoxanes and alkoxides are usually undetectable (below 500 ppm) and, at these quantity, cause no problems in polyolefin catalyst systems.

R_3Al are reactive with CO_2 [47]. In fact, reaction of trimethylaluminum (TMAL) with CO_2 has been used to produce methylaluminoxane cocatalysts for SSCs. The R_3Al/CO_2 reaction is easily controlled and has been used to passivate alkylaluminum waste streams. However, R_3Al are unreactive with CO. Alkylaluminums containing halogen or oxygen (DEAC, DEAL-E, etc.) are not reactive with CO_2.

Most trialkylaluminum compounds are associated as dimers, except when steric bulk of alkyl groups such as t-butyl, isobutyl prevents association. For instance, TMAL associates via three center – two electron bonding (also called " electron - deficient " bonding [48]) as illustrate in Figure 2.7.

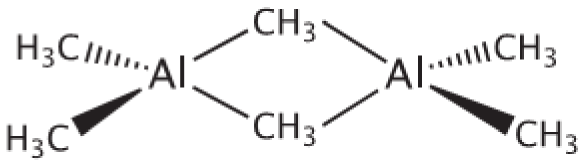


Figure 2. 7 Trimethylaluminum dimer

Alkylaluminums has a moderate to great thermal stability, depending on ligands. Thermal stability of alkylaluminums is especially important for used in solution processes for polyethylene since these often operate at temperature >190 °C. Thermal decomposition data of selected alkylaluminum compounds as show in Table .2.3.

Example of AlR_3 and structure

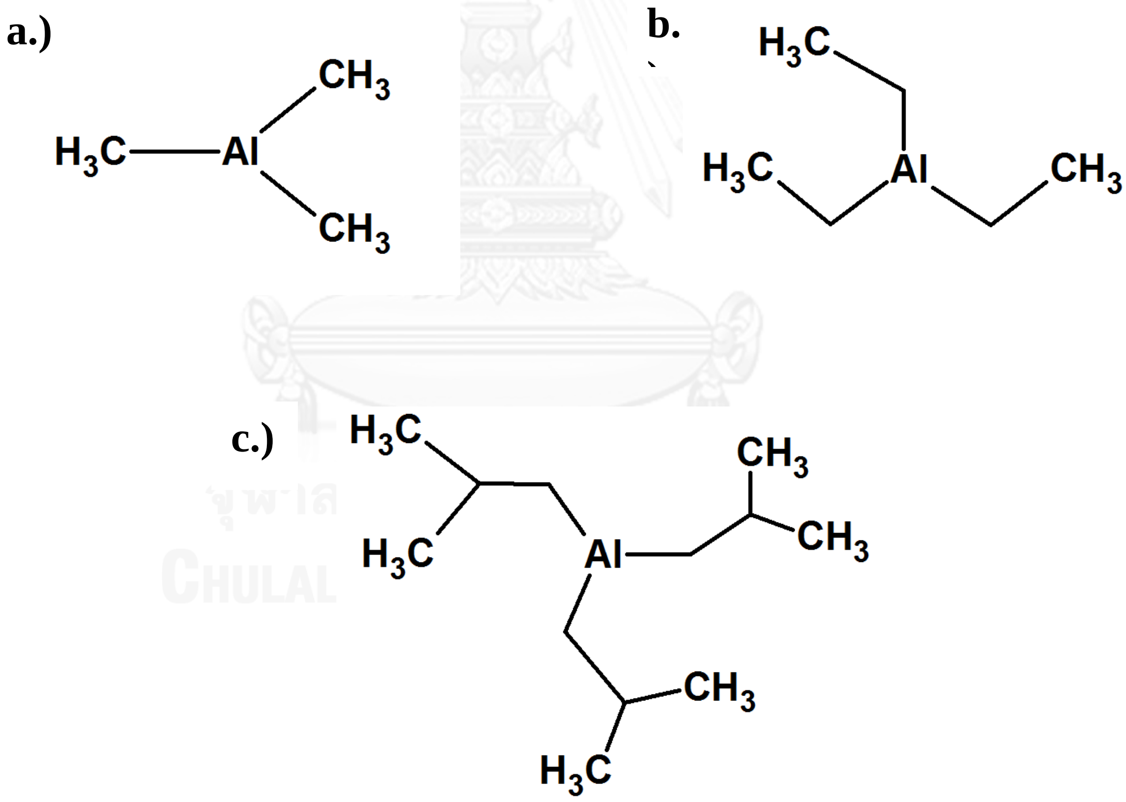


Figure 2. 8 structure ofAlR_3 a.) Trimethyaluminum (TMA) b.) Triethylaluminum (TEA) c.) Triisobutylaluminum (TIBA)

Lower R_3Al's decompose slowly at raised temperatures, but thermal stability decreases as chain length or branching enhance. Thermal decomposition of alkylaluminums usually occurs by β-hydride elimination, for example TIBAL show in Figure 2.9. From the Table 2.3 expressed alkylaluminums that include ligands with halogen or oxygen are more stable thermally than the R_3Al compounds. While TEAL starts to decompose at temperature 120 °C but DEAC is stable up to temperature at 174 °C and DEAL-E up to temperature at 192°C.

Table 2. 3 Thermal decomposition data of selected alkylaluminum compounds [49]

Product	Decomposition Temperature (°C)[a]	% Decomposed (3 h at 180 °C)
Triethylaluminum	120	64
Tri-n-butylaluminum	100	87
Triisobutylaluminum	50	92
Tri-n-octylaluminum	60	90
Diethylaluminum chloride	174	2
Diisobutylaluminum chloride	165	4
Diethylaluminum ethoxide	192	0

[a] Estimated temperature at which decomposition is first observed in inert atmosphere.

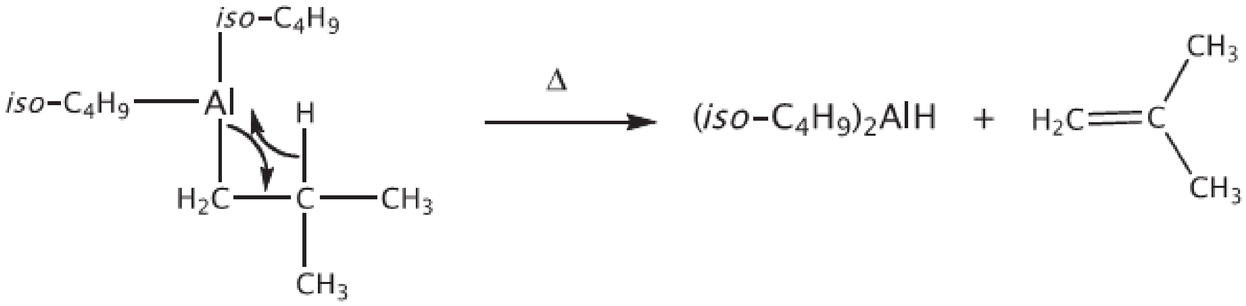


Figure 2. 9 Decomposition of triisobutyaluminum

In the previous region of Ziegler–Natta (ZN) catalysts, alkylaluminums compose of chlorinated for example DEAC and EASC were the most important and functioned as both cocatalysts and reducing agents. They were easily available and relatively inexpensive and performed well with first - generation ZN catalysts. Nevertheless, in the 1970s supported ZN catalysts was developed, TEAL replaced DEAC and EASC because TEAL worked better. TEAL remains today the largest volume alkylaluminum result in many millions of pounds are sold every year to the global polyolefin industry.

As normal, cost is a preliminary consideration in selecting an alkylaluminum. The currently, a commercial prices for alkylaluminum range about \$5-\$10 per pound. However, for specialty products can be higher than commercial prices for example TMAL, DEAI , and isoprenylaluminum (IPRA).

Even though DEAC and EASC remain cheaper than TEAL, they are unpopular used with supported catalysts because they perform inferior. For illustrate, they may cause lower catalyst activity or reduced stereoregularity in polypropylene. They also release chloride - containing residues in the polymer that can corrode equipment or degrade the polymer.

As selection of alkylaluminum as cocatalyst is usually commanded, by cost. Nevertheless, in other cases, benefit of an alternative cocatalyst overcomed the price factor. Due to an alternative cocatalyst gives preferable process performance such as higher catalytic activity, enhanced kinetic profile and improved polymer properties. For example, use of TMAL act as cocatalyst instead of TEAL in a gas - phase process to produce linear low-density polyethylene or LLDPE product with lower extractables and improved film tear strength. Use of isoprenylaluminum (IPRA) as cocatalyst can result in ultrahigh molecular weight polyethylene (PE) with broader molecular weight distribution (MWD). IPRA is a complex composition, is used to cocatalyst bring about ultrahigh molecular weight polyethylene (PE) with broader molecular weight distribution (MWD) [50]. Improved Enhanced properties can change into superior polymer performance and such resins command higher prices, therefore defeating the enlarged cost of cocatalyst.

2.7 Methylaluminoxane (MAO)

Methylaluminoxane (MAO) is the reaction product of the careful partial hydrolysis of trimethylaluminum(TMA) according to the reaction given in Equation (3) and investigated by Sinn and Barron [30, 51], it consists mainly of units of the basic structure [$Al_4O_3Me_6$], which contains four aluminium, three oxygen atoms and six methyl groups.

$$x(CH_3)_3\,Al + xH_2O \rightarrow\sim (CH_3AlO)_x \sim + 2xCH_4 \uparrow \qquad \text{Eq....(3)}$$

The use of water, or water acquired from emulsified water vapor, from water-saturated nitrogen vapor or from the surface of deeply cooled ice, can offset the problem of salts remaining in MAO, but care is needed since the risk of runaway reactions has to be taken into account [52]. As the aluminium atoms in this structure are co-ordinatively unsaturated, the basic units (mostly four) join together forming clusters and cages show in Figure 2.10. Published data on MAO isolated from toluene have shown a wide range of molecular weights (MWs) 300 – 3000 amu, primarily using cryoscopic methods. MAO is often called as a black box due to the lack of a deep understanding of its structure. Moreover, the structure of MAO remains too complex, although it has been investigated by cryoscopic, IR, UV, and NMR spectroscopic measurements and other methods. MAO has become a very important cocatalyst for metal-catalyzed olefin polymerization. Very extensive research has been carried out in both academia and industry [53].

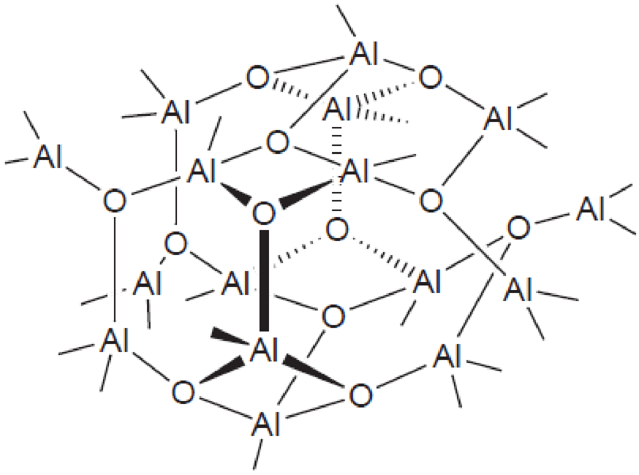
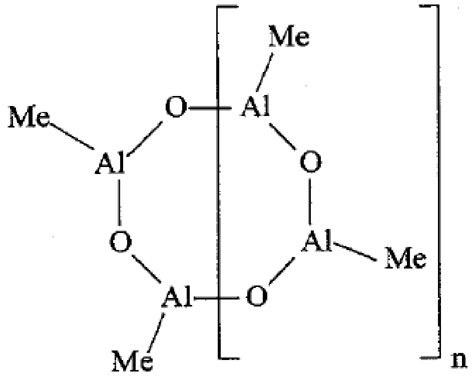


Figure 2. 10 Suggestion of a structure for methylaluminoxane clusters by Sinn [28]

chain

Double chain “ladder”



ring

Figure 2. 11 Early MAO structure models

The structure of MAO can hardly be elucidated directly because of the multiple equilibria present in MAO solutions, and residual trimethylaluminum in MAO solutions appears to participate in equilibria that interconvert various MAO oligomers. There are two types of TMA present in typical MAO solutions: “free” TMA and “associated” TMA show in Equation 4.

$$\text{-[Al(Me)O]}_n\text{-}\bullet x\,\text{AlMe}_3 \rightleftharpoons \text{-[Al(Me)O]}_n\text{-}\bullet(x\text{-}y)\text{AlMe}_3 + y\text{AlMe}_3 \qquad (\text{.....}\textbf{Eq.}4)$$

“associated” “free”

It is generally assumed that some of the Al centers in MAO have an exceptionally high propensity to abstract a Cl from $Cp_2ZrMeCl$ or a CH_3^- from in-situ formed Cp_2-$ZrMe_2$ and to form ion-paired structures such as $Cp_2\text{-}ZrMe^+Cl[\text{-}Al(Me)O\text{-}]_n^-$ or $Cp_2ZrMe^+Me[Al(Me)O\text{-}]_n^-$ for active species in olefin polymerization as shown in Equation 5 and Figure 2.12 .

$$Cp_2Zr(CH_3)_2 + [Al(CH_3)O]_n \rightleftarrows Cp_2Zr(CH_3)^+Me[Al(CH_3)O]^-_n \quad (......\textbf{Eq}.5)$$

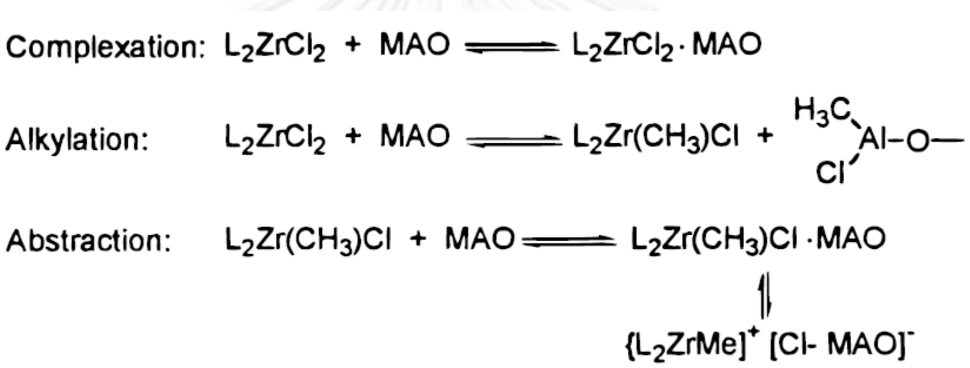
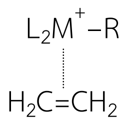


Figure 2. 12 Activation of metallocene with methylaluminoxane (MAO)

2.8 Ethylene polymerization

There are three different commercial olefin polymerization processes where metallocene catalysts can be used. They are the: solution, gas phase and slurry processes. Homogeneous or heterogeneous catalysts are used in the Solution process. Understanding the mechanisms and kinetics involved in the polymerization process enables one to predict the structure of the polymer formed. Propagation and termination rates determine molecular weight, molecular weight distribution.

Table 2. 4 Steps of ethylene polymerization

Reaction	Reaction pathway
1.Activation	$L_2MCl_2 + MAO \longrightarrow L_2M^+{-}CH_3 + [MAO\text{-}Cl_2]^-$
2.Propagation	 $\underset{H_2C=CH_2}{L_2M^+{-}R}$ $+ CH_2{=}CH_2 \longrightarrow L_2M^+{-}\ CH_2CH2CH_2CH_2R$
3.Chain transfer reaction	
- Chain transfer to monomer	$M^+{-}CH_2CH_2R + CH_2{=}CH_2 \longrightarrow M^+{-}CH_2CH_3 + CH_2{=}CHR$
- β-H elimination	$M^+{-}CH_2CH_2R \longrightarrow M^+{-}H + CH_2{=}CHR$
- Chain transfer to aluminum	$M^+{-}CH_2CH_2R + AlR'_3 \longrightarrow M^+{-}R' + R'2AlCH_2CH_2R$
- Chain transfer to hydrogen	$M^+{-}CH_2CH_2R + H2 \longrightarrow M^+{-}H + CH_3CH_2R$
- σ-bond metathesis	$M^+{-}CH_2CH_2R + CH_2{=}CH_2 \longrightarrow M^+{-}CH{=}CH_2 + CH_3CH_2R$

2.9 Copolymerization

Copolymers formed of ethylene and higher α-olefins are important commercial products. A comonomer incorporation is highly uniform distribution and copolymers produced with metallocenes have unique and competitive properties when compared to those obtained by Zieglar-Natta catalysts. Ethylene is copolymerized with α-olefins to produce copolymers with lower densities. It is commonly observed that the addition of a comonomer generally increases the polymerization rate significantly. This comonomer effect is sometimes related to the reduction of diffusion limitations by producing a lower crystallinity polymer or to the activation of catalytic sites by the comonomer [7, 54, 55]. The polymer molecular weight often decreases with comonomer addition, possibly because of a transfer to comonomer reactions. Finally, the polymerization rate are maximum as the ratio of aluminum to transition metal increases. The exact location of this maximum value depends on the catalyst type and whether the polymerization system is homogeneous or heterogeneous. Heterogeneous polymerizations tend to be less sensitive to changes in the aluminum/transition metal ratio. Chain transfer to aluminum is also favored at high aluminum concentrations. This increase in chain transfer would reasonable produce a polymer with lower molecular weight. However, some researchers have observed decreases and some others have observed no changes in the molecular weight with increasing aluminum concentration.

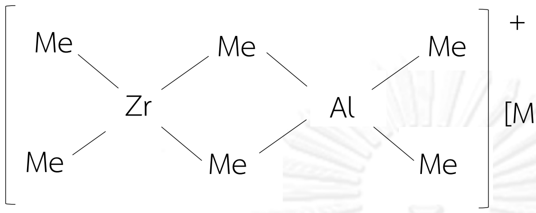
2.10 Literature reviews

Irina V. Vasilenko et al. [56], studied the effect of the addition of different aluminum alkyls [(TEA, trihexylaluminum (THA), TIBA)] to a zirconocene (L_2ZrCl_2)/MAO catalytic system, where L_2ZrCl_2 was rac-$EtInd_2ZrCl_2$ (1) and rac-$(CH_3)_2CInd_2ZrCl_2$ (2).

During the activation of metallocene precatalyst by MAO at high Al/Ti ratio ≥ 500 is presented below.

the species $L_2ZrMe^{+} \leftarrow MeMAO^{-}$ (A)

and



$[MeMAO]^{-}$ (B) (dormant active species)

When polymerization higher α-olefin via replacement of part of MAO with linear aluminum alkyls (TEA, THA) act as a poison for metallocene catalyst forming stable heteronuclear complexes with cationic species[similar to (B)] that strongly depressed the catalytic activity and as a chain transfer agent. On the contrary, the replacement of part of MAO by bulky triisobutylaluminum leads to an increase in the catalyst activity as well as in molecular weight and isotacticity of polymers. It should be noted that TIBA can react with MAO to form a mixed aluminoxane containing isobutyl groups. The increase in the size of alkyl groups in aluminoxane makes the active cationic ion pair ($L_2ZrR^{+}\cdots MAO^{-}$) looser, this can lead to an increase of the catalyst activity.

H. Hammawa et al. [57], investigated the effects of aluminum alkyls on the kinetic behavior and polyolefin properties for gas-phase ethylene and ethylene/1-hexene polymerization with different porous polymeric supported $(n\text{-}BuCp)_2ZrCl_2$/MAO. Activities were generally higher for copolymerization than homopolymerization due to the comonomer synergism. Residual aluminum alkyls in the reactor significantly suppressed the initial polymerization activity. However, the broadening of the activity profiles due to the presence of aluminum alkyls often led to higher average activities for 1-h runs. The effectiveness of the aluminum alkyls in inhibiting the initial polymerization activity decreases with increasing size of the alkyl group, i.e., TEA > TIBA > TNOA. Aluminum alkyls affect polymerization systems differently depending on the catalyst used and the polymerization conditions.

Il Kim et al. [58], studied an effectiveness of AlR_3 and MAO cocatalysts for the ethylene polymerizations by using a metallocene diamide compound, $Cp^*_2Zr(NMe_2)_2$ ($Cp^* = C_5Me_5$) and investigated the effects of the type and the amount of AlR_3 on the catalytic activity and the properties of polymer. Zirconocene amide complex $Cp^*_2Zr(NMe_2)_2$ showed high activity when combined with either MAO or common alkylaluminum cocatalysts such as $AlEt_3$, $Al(i\text{-}Bu)_3$, and $Al(i\text{-}Bu)_2H$. The induction period becomes longer at higher alkyl aluminum concentrations. On the contrary, the negligible induction period MAO cocatalyzed system but rapid deactivation. The $AlMe_3$ cocatalyzed system showed no activity due to the formation of stable and heterodinuclear $[Cp^*_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ cations. These results indicate that intermediate adducts derived from the reaction of $Cp^*_2Zr(NMe_2)_2$ with various alkylaluminums are different. The bulkier ethyl or isobutyl could result dissociation of the intermediate complexes to the active monomeric $[Cp^*_2ZrR]+$ species, facilitating the access of ethylene monomers to the active sites once the active species form and ,resulting rapid rise to the maximum rate of polymerization. However, the long induction periods of the bulky alkyl aluminum cocatalyzed systems demonstrated that the alkylation followed by dissociation is a somewhat slow process.

V.N. Panchenko et al [59], determined the affects when treat typical supported SiO_2/MAO/SBIZrCl_2 catalyst with TIBA solubilizes on properties of polyethylene (PE) product and catalytic activity of ethylene polymerization by supported SiO_2/MAO/SBIZrCl_2 catalysts in the presence of TIBA and absence TIBA. The homogeneous MAO/SBIZrCl_2/TIBA systems has high maximum activity, but short-lived activity and the properties of their PE product, while polymerization with the catalyst SiO_2/MAO/SBIZrCl_2 treated TIBA has long-lived. The results that TIBA interacts with the MAO and the zirconocene species on the surface of SiO_2/MAO/SBIZrCl_2 catalysts and is thus capable to transfer substantial parts of these catalyst components into heptane solution. Polymerization of ethylene proceeds both on the solid catalyst surface and in solution.

Qing Wu et al. [60], studied the effect of free alkylaluminium in the catalyst system on the polymerization. The free alkylaluminium plays an important role in styrene polymerizations with titanocene catalyst. By addition of external alkylaluminium, TMA or triisobutylaluminium (TIBA), into the catalyst system with the MAO initially containing less retained TMA, the styrene polymerization was more efficiently raised than without the external alkylaluminium. The result is contrary to the case of ethylene polymerization in which high content of retained TMA in MAO decreased the catalytic activity. The difference in the effect of alkylaluminium on the catalytic activity between ethylene and styrene polymerization may be concerned with the dissimilarity in the oxidation state of the catalytic species for these polymerizations. It has been suggested that the Ti^{3+} species are active for styrene syndiotactic polymerization, whereas the active species for ethylene polymerization are Ti^{4+} (or $Zr^{4+)}$. Based on this consideration, a higher concentration of free alkylaluminium, which is a strong reducing agent in the catalyst system, favors the reduction of Ti^{4+} to Ti^{3+}, resulting in an enhanced catalytic activity in the styrene polymerization.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

The chemicals used in this study were specified as following detail :

1. Ethylene gas was supplied from Thai Polyethylene Co., Ltd.
2. Nitrogen gas was supplied from Thai Polyethylene Co., Ltd.
3. Ultra high purity of argon (99.999%) was purchased from Thai Industrial Gas Co., Ltd.
4. Ultra high purity of hydrogen (99.999%) was purchased from Thai Industrial Gas Co., Ltd
5. Triethylaluminum (TEA) diluted in hexane solution 200 mmol/l was supplied from Thai Polyethylene Co., Ltd
6. Triisobutylaluminum (TIBA) diluted in hexane solution 200 mmol/l was supplied from Thai Polyethylene Co., Ltd
7. 1-hexene comonomer was supplied from Thai Polyethylene Co., Ltd. and further purified by molecular sieve
8. Commercial grade of n-hexane was supplied from Thai Polyethylene Co., Ltd.
9. A commercial metallocene catalyst was supplied from Thai Polyethylene Co.,Ltd.

3.2 Polymerization reaction

3.2.1 Ethylene polymerization

Ethylene polymerization was performed in 2-L stainless steel reactor equipped with propeller motor, temperature control, mass flow meter and data acquisition systems. Purification the reactor and all feed lines by purging nitrogen gas at 75 °C for 1 hours before polymerization was used to avoid side effect of impurity such as moisture and oxygen. The desired amount of supported metallocene catalyst (25 mg) and n-hexane was loaded into the schlenk tube inside the glovebox. After purified the system at high temperature, the reactor was cooled down to room temperature and then, n-hexane 850 ml was charged in reactor and 150 ml of n-hexane was added in hexane bomb for flushing catalyst. The desired type and amount of aluminum alkyl was filled in reactor under nitrogen atmosphere to allow scavenging of the impurities. After that, finished catalyst in n-hexane was pipeted into bomb catalyst, which connected to the reactor. Nitrogen gas was vented, followed by feeding ethylene gas 3 bar to replace inert gas for 3 times. Ethylene gas 3 bars were saturated into n-hexane solutions in 2L reactor system. The reactor was gradually heated to the polymerization temperature of 80°C. Catalyst was flushed with ethylene 8 bar, and the reactor pressure was maintained for 2 hours by continuous ethylene feed to replenish the amount consumed in the reactor.

3.2.2 Ethylene/1-hexene copolymerization

The desired amount of finished catalyst (25 mg) and n-hexane was loaded into the schlenk tube inside the glove box. After purified the system at high temperature, the reactor was cooled down to room temperature and then, it was fed n-hexane 850 ml into reactor and 150 ml hexane into bomb for flushing catalyst. The desired aluminum alkyl and 1-hexene were filled in reactor under nitrogen atmosphere to allow scavenging of the impurities. The supported metallocene catalyst in hexane was pipeted into catalyst bomb, which connected to the reactor. After the reactor was vented nitrogen gas followed by feeding ethylene gas 3 bar to replace inert gas for 3 times. Ethylene gas was saturated in n-hexane solutions in 2L reactor. The reactor was gradually heated to the polymerization temperature of 70°C. Catalyst was flushed with ethylene at 8 bar, and the reactor pressure was maintained at 8 bar for 2 hours by continuous ethylene feed to replenish the amount consumed in the reactor.

3.3 Instruments for characterization

3.3.1 Scanning electron microscope (SEM)

JEOL model JSM-6510 LV was used to characterization to investigate the morphology of polyethylene and ethylene and l-hexene, copolymers. The polymer samples for SEM analysis was coated with gold particles by ion sputtering device to provide electrical contact to the specimen.

3.3.2 Differential scanning calorimetry (DSC)

The melting temperature (T_m) and crystallinity (X_c) of homo and copolymers were determined by Perkin-Elmer diamond DSC revealed. The characterizations were performed at a heating rate of 20 °C min^{-1} in the temperature range of 50–170 °C. The samples were heated and cooled to room temperature in the first scan. Then, it was heated again at the same rate. The results of the second scan were only reported due to avoidance of any impurities in samples of first scan. The crystallinity of polymers were calculated by the heat of fusion parameter as shown in the Equation 3.1;

$$Xc = \frac{H_f}{H_f^0} \times 100 \qquad \textbf{(Eq.}\ 3.1)$$

Where, H_f is the enthalpy of tested samples

H^0_f is the enthalpy of a totally crystalline polyethylene, was assumed to be 269.9 J/g [61]

X_c is the percent crystallinity of the samples

3.3.3 ^{13}Carbon nuclear magnetic resonance spectroscopy (^{13}C NMR)

The ^{13}C-NMR spectrum was recorded by JEOL JNM-A500 at 125°C operating at 125 MHz. The sample was prepared by using 1,1,2,2-tetrachloroethane-d_2 as solvent and for internal lock.

3.3.4 Fourier-transform infrared spectroscopy (FT-IR)

Fourier Transform Infrared Spectrometer (FT-IR) performed by Bruker Tensor 37 was used to evaluated the amount of 1-hexene in the copolymer. The measurement wavelength were restricted in 1378.1-1377.9 cm^{-1} region. Sample was scan with 16 scans at resolution of 4 cm^{-1}.

3.3.5 Gel Permeation Chromatography (GPC)

A high temperature GPC (Waters) equipped with a viscometric detector was used to determine the molecular weight (MW) of the polyethylene and ethylene and l-hexene copolymers. The solvent for GPC was 1,2,4- trichlorobenzene the temperature for characterization was 140 °C.

3.3.6 Density

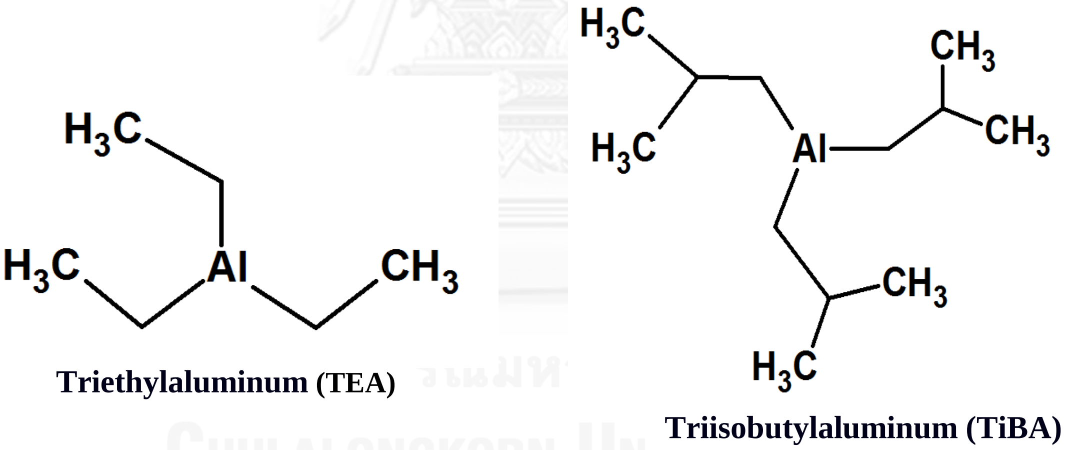
The density of polymer were investigated by Density measuring system of Shibayama scienctific with 6 column and maintained temperature 23°C in bath. The glass cylinder has length 1010 mm and an external diameter of 48 mm with a resolution 1 mm. The procedure testing followed by ASTM D 1505-03, ASTM 2839-02, MPC METHOD NO.HZ-F-0109 and ISO 1183-2.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of alkylaluminum as scavenger in ethylene homopolymerization

In the first part, the effect of alkylaluminum on the catalytic activities and properties of polymer for ethylene homopolymerization were investigated. Alkylaluminum was divided into 2 types including triethylaluminum (TEA), triisobutylaluminum (TiBA). The molecular structures of alkylaluminum are shown in Figure 4.1.



Triethylaluminum (TEA)

Triisobutylaluminum (TiBA)

Figure 4. 1 Molecular structures of different types of alkylaluminum

Alkylaluminum is used to scavenge impurities such as O_2, H_2O, and other protic impurities in this system before feeding the supported metallocene catalysrt and ethylene gas to polymerization. Moreover, many reports reveal that alkylaluminum can be used as a cocatalyst, an alkylate catalyst precursor, a chain transfer agent and a reducing agent in the ethylene polymerization using supported metallocene catalyst which affectimg on polymerization process and obtained polymer. Thus, we were also interested in the effect of different types and concentrations of alkylaluminum on catalytic activity and properties of polymer.

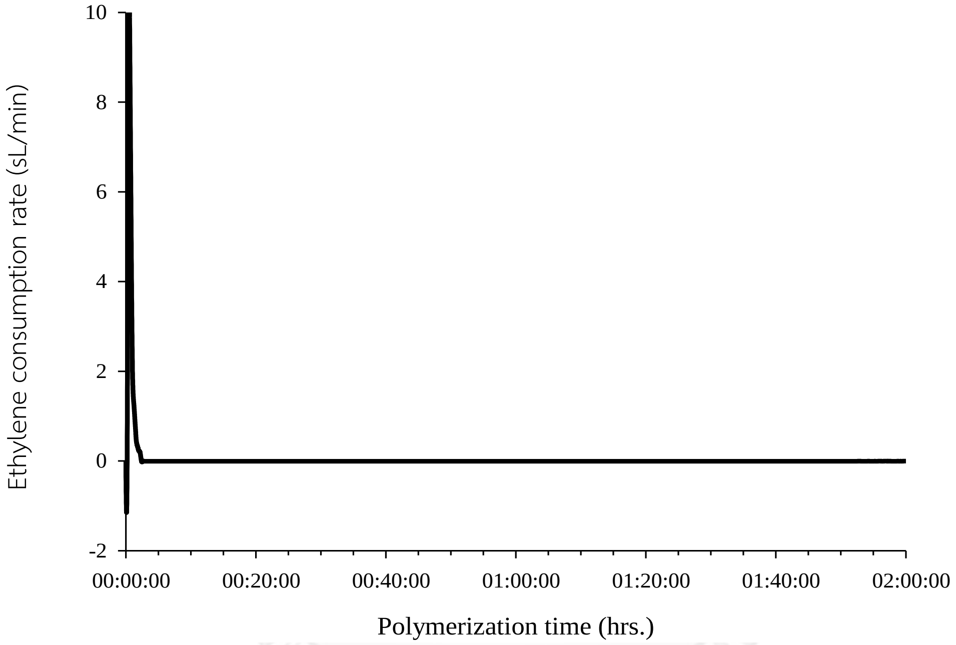


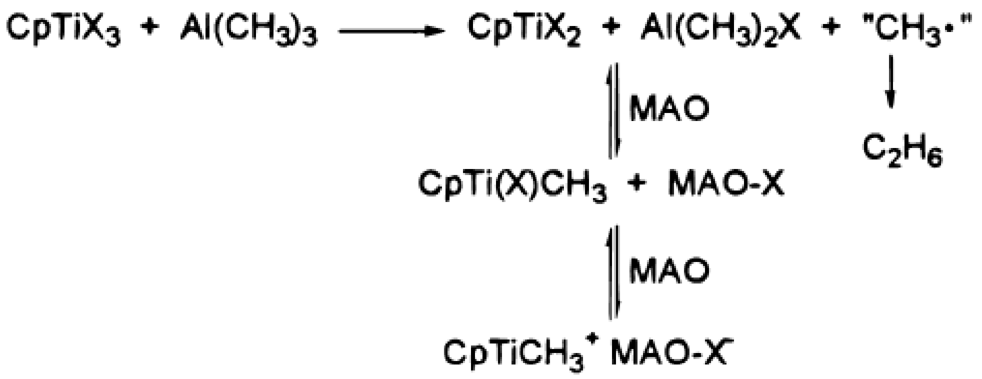
Figure 4. 2 . Ethylene consumption rate profile of ethylene polymerization without alkylaluminum as scavenger

The ethylene homopolymerization activity profile without alkylaluminum to scavenge impurities is shown in Figure 4.2. The system without alkylaluminum to scavenge impurities exhibits rapid deactivation resulting in low polymer yield. Therefore, adding alkylaluminum as scavenger is important and necessary in this polymerization process. This supported metallocene catalyst performed differently depending on the alkylaluminum compounds and their concentrations.

4.1.1. Effect of triethylaluminum (TEA) as scavenger

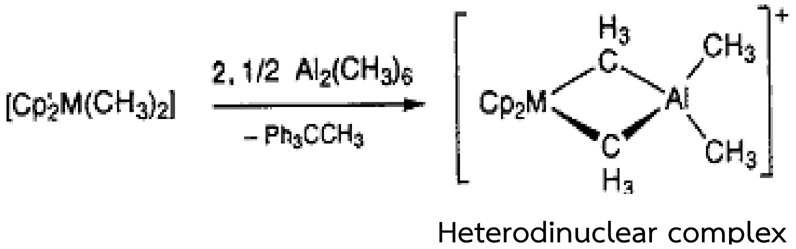
After that, the concentration of triethylaluminum (TEA) was varied including 0.3, 0.5, 0.7, 1.0, 1.2 mmol/L in hexane. The catalytic activity of ethylene polymerization for these concentrations of TEA is shown in Figure 4.3. At lower concentration of TEA, it shows low catalytic activity (Figure4.3) because it does not have enough amount to scavenge impurities. At the higher concentration of TEA the catalytic activity increases and reaches the maximum (6.027 kgPE•gcat^{-1}h^{-1} as shown in Table 4.1) at the concentration of 0.7 mmol/L in hexane. However, too much TEA concentration of 1.0 and 1.2 mmol/L in hexane results in the depression of catalytic activity.

Alkylaluminum not only acts as a scavenger, but it can be a reducing agent. The assumption for this phenomenon is with the excess of TEA. The decreasing catalytic activity may be concerned with the oxidation state of the catalytic species for ethylene polymerization. The active species for ethylene polymerization are Zr^{4+} (or Ti^{4+}) [62, 63]. Based on this consideration, a higher concentration of TEA, which is a strong reducing agent in the catalyst system, favors the reduction of Zr^{4+} to Zr^{3+}, resulting in reduction of catalytic activity in the ethylene polymerization [60]. Then, reduction of metal complex is probably caused by the free trimethylaluminum (TMA) contained in MAO, and addition of external of triethylaluminum (TEA) as scavenger, since alkylaluminums are more effective reducing agents than alumoxanes, as illustrated in Scheme 1.



Scheme 1 Alkylaluminums are more effective reducing agents than alumoxanes [2]

Moreover, in the presence of excess TEA, metallocene cations form heterodinuclear complexes $[Cp'_2M(\mu\text{-}Me)_2AlMe_2]^+$ (M = Zr, Ti, Hf), which are coordinatively saturated and lack a vacant orbital suitable for binding the olefinic substrate and may inhibit or lower the catalytic efficiency as shown in the Scheme 2 [2, 64].



Scheme 2 The reaction between excess alkylaluminum and metallocene catalyst

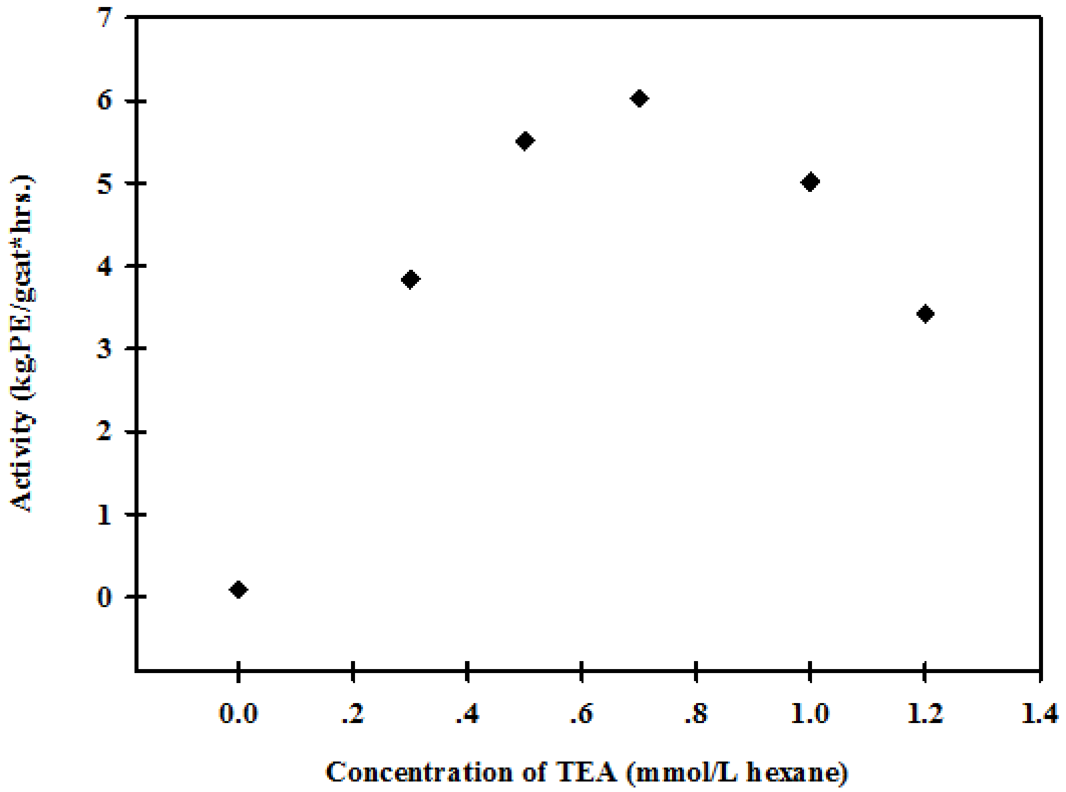


Figure 4. 3 Dependence of the catalyst activity versus the concentration of TEA for ethylene polymerization with supported metallocene catalyst

4.1.2. Effect of triisobuthylaluminum (TiBA) as scavenger

Ethylene polymerization in this part was carried out with various concentrations of triisobuthylaluminum (TiBA) including 0.7, 1.0, 1.2, 1.5, 1.7 mmol/L in hexane. Figure 4.4 shows the trend of catalytic activity with different concentrations of alkylaluminum using the supported metallocene catalyst.

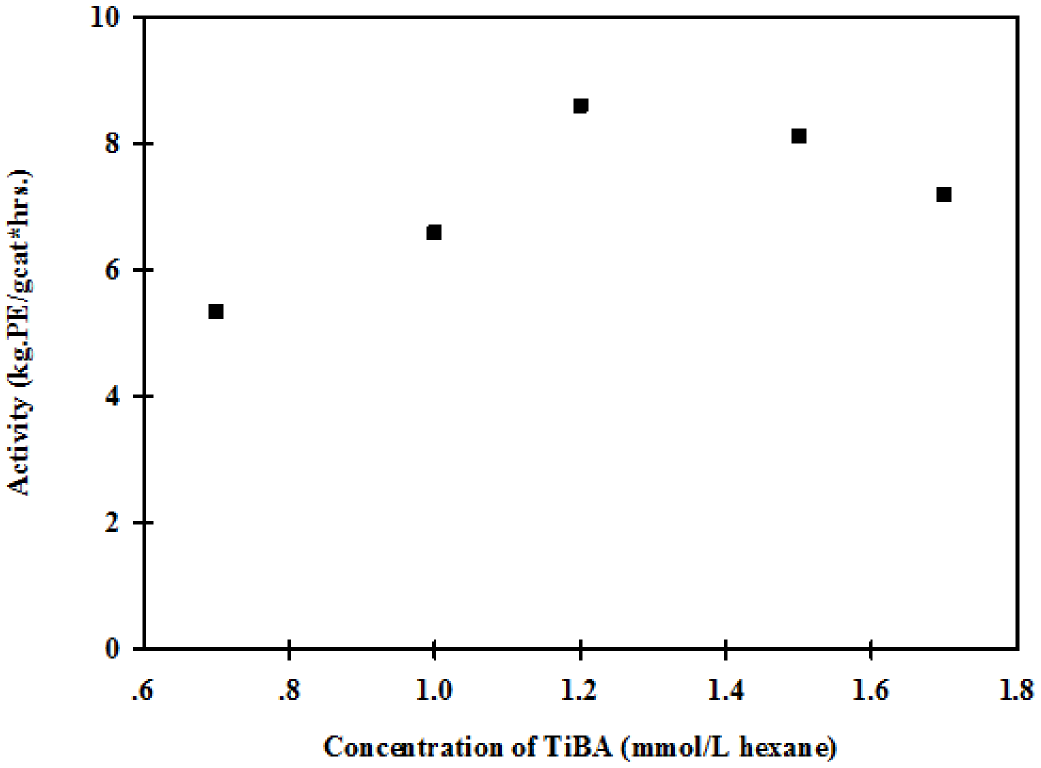


Figure 4. 4 Dependence of the catalyst activity versus the concentration of TiBA for ethylene polymerization with supported metallocene catalyst

The catalytic activity for ethylene polymerization with TiBA at 1.2 mmol/L in hexane is the optimum concentration owing to the highest catalytic activity. The lower concentrations of TiBA show the decreasing of catalytic activity because of too low concentration to scavenge impurities leading to deactivation of active species. Nevertheless at higher concentration, the activity of the catalysts was lower due to the reduction of active species from Zr^{4+} to Zr^{3+} which was not active form for ethylene polymerization [62, 63]. In addition to the decreasing of catalytic activity maybe due to it forms heterodinuclear complexes from adding excess of TiBA with similar as shown in Scheme 2, but it is difficult occured with steric reasons.

4.1.3. Comparison effect of alkylaluminum (TEA, TiBA) as scavenger

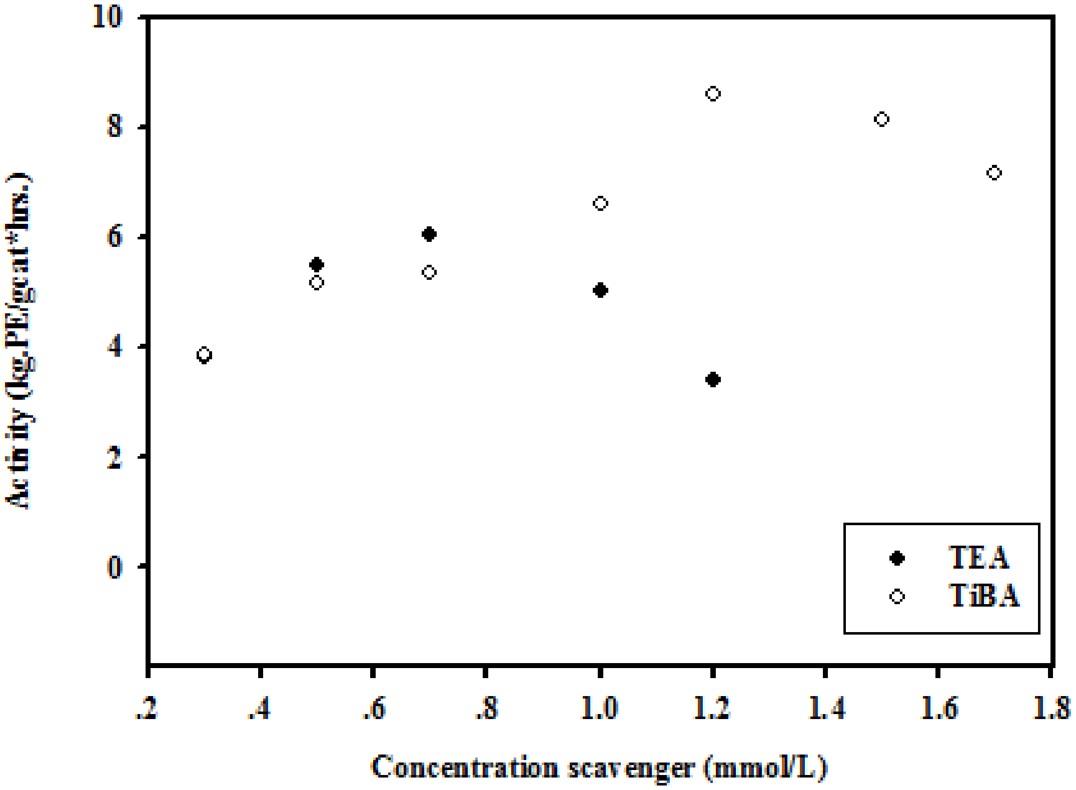


Figure 4. 5 Dependence of the catalyst activity versus the concentration of scavenger (i.e. TEA, TiBA) for ethylene polymerization with supported metallocene catalyst

The different types of alkylaluminum influenced on catalytic activity. The concentration of TEA 0.7 mmol/L in hexane which optimum concentration of the system exhibited slightly higher catalytic activity than TiBA (as shown in Figure 4.5 and Table 4.1). However, with higher concentration of scavenger, the catalytic activity of TiBA is higher than TEA since TEA is stronger alkylating and reducing agent than TiBA. TEA could cause the reducing of the metallocene compound resulting in an inactive species [60].

At low concentration of alkylaluminum, the catalytic activity of TEA system was higher than that of TiBA system. This is because TEA has stronger alkylating and reducing agent than TiBA, resulted in alkylating metallocene complex to form active species and interacting with impurity faster than TiBA [58].

High concentration of alkylaluminum results in higher catalytic activity of TiBA system than that of TEA system due to the fact that TIBA can react with MAO to form a mixed aluminoxane containing isobutyl groups [65, 66]. The increase in the size of alkyl groups in aluminoxane makes the active cationic ion pair $(L_2ZrR^{+}\cdots\cdots MAO^{-})$ looser, this can lead to an enhance of the catalyst activity [65]. Furthermore, the presence of bulkier alkyl ligands may prevent aluminum atoms in the oligomeric MAO chain from reaching a more stable four coordination number, which reduces cocatalyst activity. Moreover, the bulkier isobutyl ligands render the chain-chain coordination sterically unfavorable, affording good polymerization activity in aliphatic solvents [67].

Moreover, deactivation of catalytic activity at high concentration of TEA can be presumed that facile the formation of heterodinuclear complexes than TiBA. The inhibition of the metallocenes also decreases for steric reasons in the sequence TMA>TEA>TIBA [41].

Table 4. 1 Effect of the alkylaluminum on the catalytic activity with supported metallocene catalyst for ethylene homopolymerization[a]

Type of Alkylaluminum	Concentration (mmol/L in hexane)	Yield PE (g)	Activity[b] (kg•PE/g Cat•h)
-	-	4.47	0.089
TEA	0.3	192.07	3.841
TEA	0.5	275.36	5.507
TEA	0.7	301.36	6.027
TEA	1.0	250.58	5.012
TEA	1.2	170.87	3.417
TiBA	0.7	267.20	5.344
TiBA	1.0	329.32	6.586
TiBA	1.2	430.15	8.603
TiBA	1.5	405.63	8.113
TiBA	1.7	359.05	7.181

[a] Fixed supported metallocene catalyst at 25 mg

[b] Slurry ethylene polymerization was performed at temperature : 80 °C and ethylene pressure : 8 bar for 2 hours

Table 4. 2 Effect of the alkylaluminum on properties of polymer with supported metallocene catalyst for ethylene homopolymerization[a]

Type of Alkylaluminum	Concentration (mmol/L in hexane)	Mw (g/mol)[b]	MWD[c]	T_m(°C)[d]	$\%\chi_c$[e]
TEA	0.3	173,014	3.81	133.95	41.30
TEA	0.5	183,299	4.43	133.69	44.99
TEA	0.7	207,130	4.04	134.63	35.76
TEA	1.0	218,990	4.21	134.05	47.82
TEA	1.2	213,488	4.05	134.64	46.09
TiBA	0.7	N/A	N/A	129.37	42.96
TiBA	1.0	N/A	N/A	129.13	39.91
TiBA	1.2	N/A	N/A	129.78	39.44
TiBA	1.5	N/A	N/A	129.42	42.44
TiBA	1.7	N/A	N/A	129.74	41.66

[a] Fixed supported metallocene catalyst at 25 mg.

[b] Molecular weight of polymer was characterized by GPC.

[c] *Mw/Mn* or MWD as determined by GPC.

[d] Melting temperature as determined by DSC.

[e] Crystallinity: $Xc(\Delta H_f/\Delta H_f^0)\times100$, where ΔH_f^0 is 269.9 J/g and ΔH_f is the melting heat of the sample, as determined by DSC [61]

N/A = Not Available

From the Table 4.2 it shows the melting temperature of obtained polymer for ethylene polymerization with various concentrations [TEA about 133-134 °C, which is in the range of high density polyethylene (HDPE) [68] and crystallinity of 35-48%]. Furthermore, the results of a melting temperature of 129-130 °C and crystallinity of 39-43% for the process which various concentrations of TiBA were obtained.

From Figure 4.6 (a,b) it shows that the average melting temperature is 134.19 °C and the average crystallinity is 43.19 %, respectively. The melting temperature and the crystallinities of the polymers are, therefore, unaffected by the addition of TEA, as illustrated in Figure 4.6. (a,b). It can be seen that the melting temperature and crystallinity unchanged the concentration of TiBA, as illustrated in Figure 4.7 (a.b).

The trend of molecular weight for ethylene polymerization with difference of TEA concentrations was small changes and the average molecular weight distribution is 4.11 (from Table 4.2). Molecular weight was slightly increased when more TEA added. This result might be due to the residual TEA, which was occurred after TEA scavenge impurity in system completely and act as a reducing agent for metallocene complex to form inactive species as well as act as a chain transfer agent. From the result in Table 4.2, it was showed that the effect of TEA in terms of reducing agent was higher than that in terms of chain transfer agent, thus leading to depressed catalytic activity whereas molecular weight slightly increased.

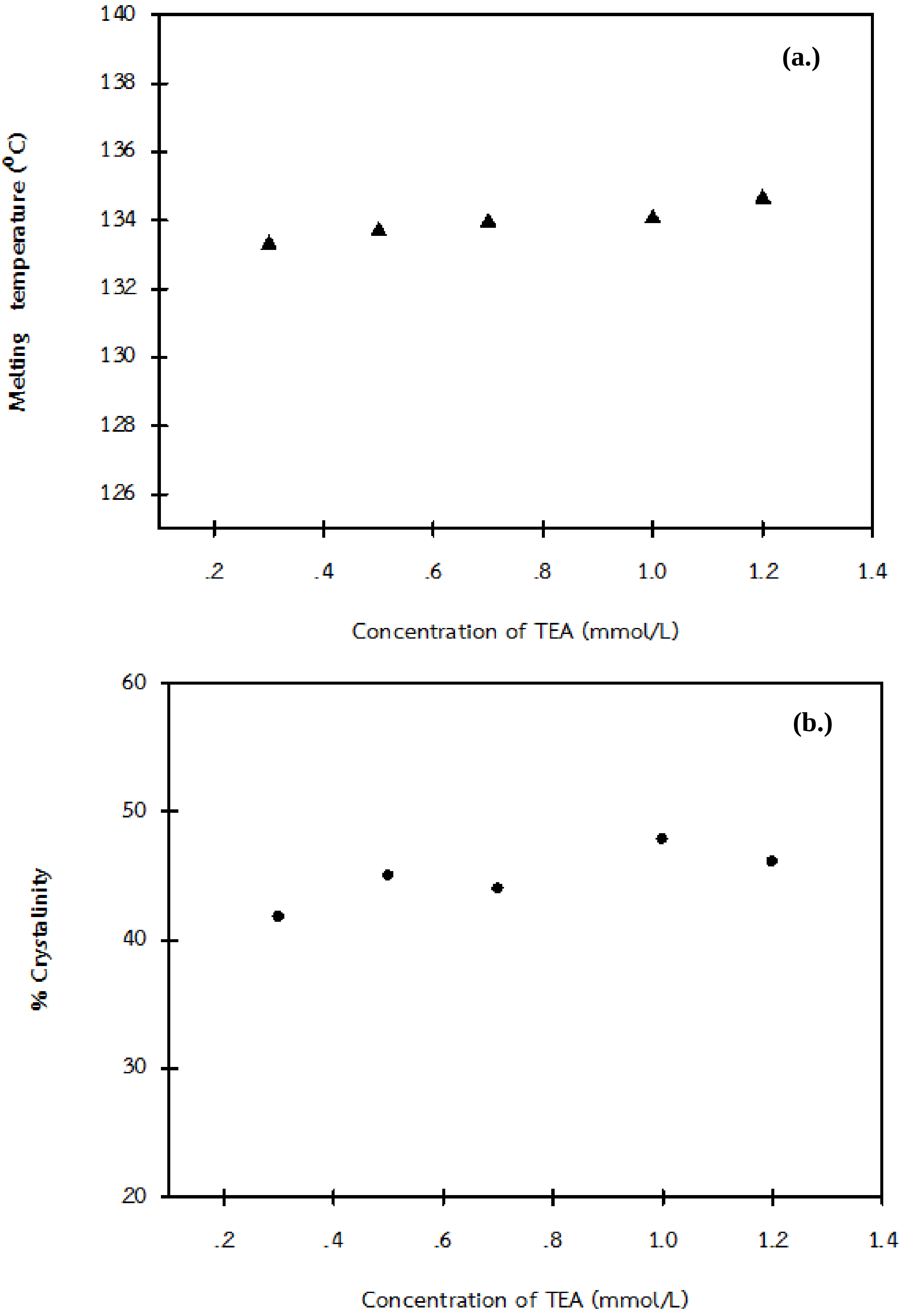
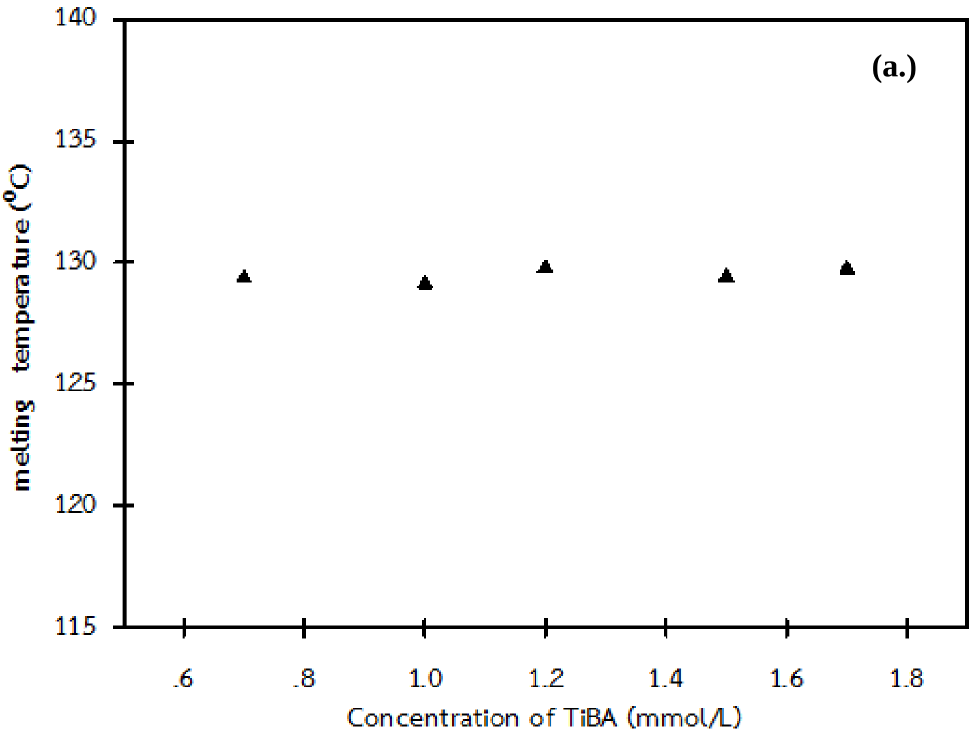


Figure 4. 6 (a) melting point, and (b) crystallinity versus the concentration of TEA for ethylene polymerization with supported metallocene



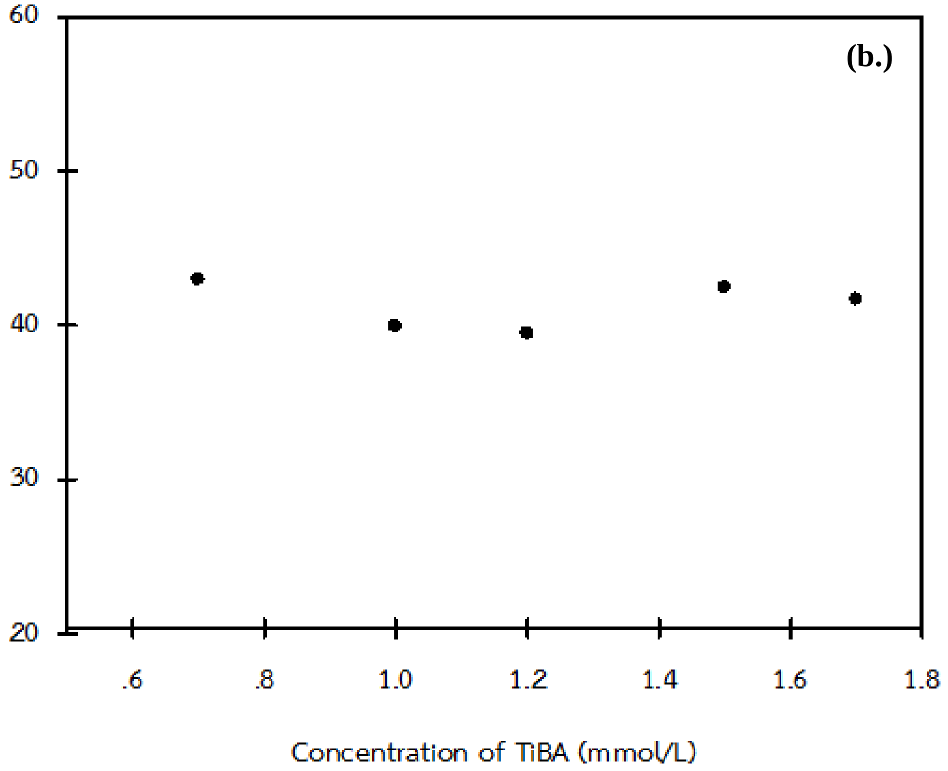


Figure 4. 7 (a) melting point, and (b) crystallinity versus the concentration of TiBA for ethylene polymerization with supported metallocene

In general, the ability to a chain transfer increased with decreasing the bulkiness of the corresponding aluminum alkyls. So, polymer produced by TEA exhibited lower molecular weight than that with TiBA. However, in this study different behavior for alkylaluminums results were perhaps not representative of all samples. The samples were analyzed by GPC to determine the molecular weight (MW), had but it the problem of melting sample.

Normally, molecular weight distribution (MWD) of polyethylene for ethylene polymerization by metallocene catalyst is narrow but MWD of polyethylene for this system broadening likely resulted from the interactions between the metallocene and the support, which leads to the formation of active sites differently in electronic and steric character [69].

4.2 Effect of alkylaluminum as scavenger in ethylene and 1-hexene copolymerization

In the second part, we intended to investigate the effect of alkylaluminum on the catalytic activities and properties of polymer for ethylene and 1-hexene copolymerization.

The ethylene and 1-hexene (30 ml) copolymerization activity profile without alkylaluminum to scavenge impurities is shown in Figure 4.8. The system without alkylaluminum to scavenge impurities results in decrease catalytic activity immediately and trace of copolymer.

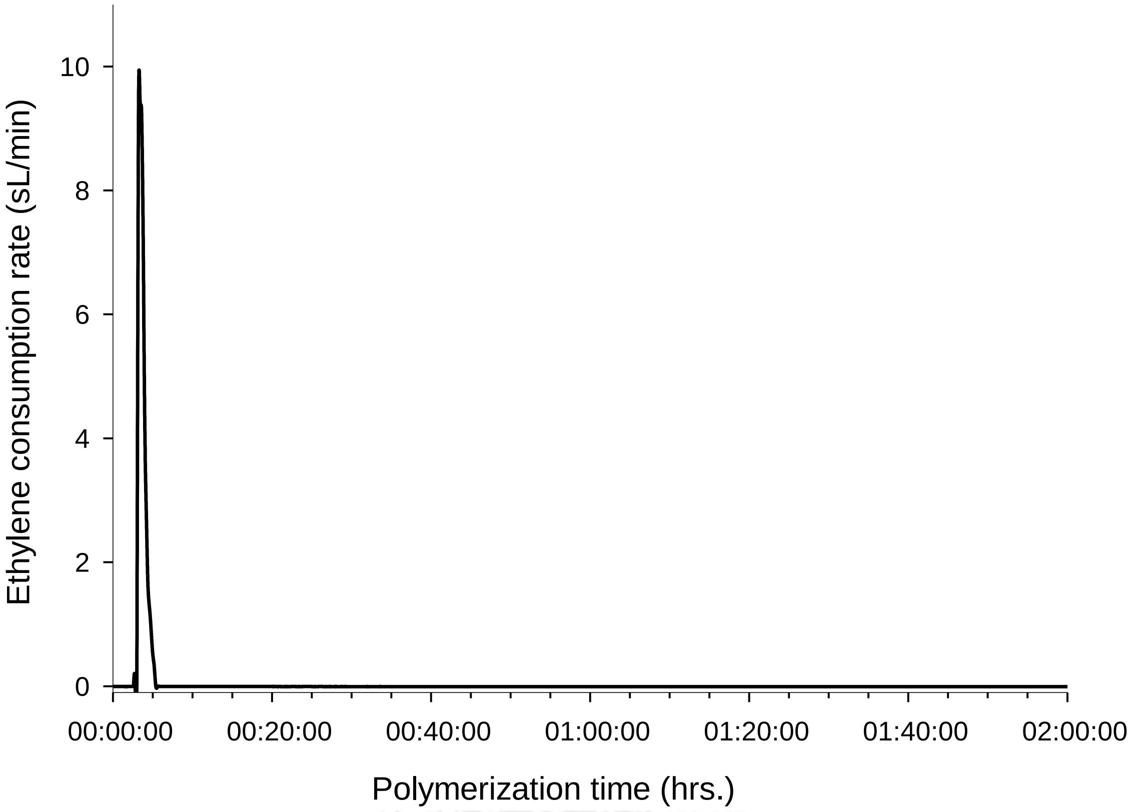


Figure 4. 8 Ethylene consumption rate profile of ethylene and 1-hexene copolymerization without alkylaluminum as scavenger

4.2.1. Effect of triethylaluminum (TEA) as scavenger

The ethylene and 1-hexene copolymerization in this part with various concentrations of TEA including 0.3, 0.5, 07, 1.0, 1.2 mmol/L in hexane and 30 ml of 1-hexene as comonomer were used in this process.

Table 4. 3 Effect of the triethylaluminum (TEA) on the catalytic activity with supported metallocene catalyst for ethylene and 1-hexene copolymerization[a]

Type of Alkylaluminum	**Concentration (mmol/L in hexane)**	**Yield (g)**	**Activity[b] (kg.Powder/g Cat.*h)**
-	-	trace	0.020
TEA	0.3	223.93	4.479
TEA	0.5	308.44	6.169
TEA	0.7	253.85	5.077
TEA	1.0	240.32	4.806
TEA	1.2	170.19	3.404

[a] Fixed supported metallocene catalyst at 25 mg.

[b] Slurry ethylene and 1-hexene of 30 ml copolymerization was performed at temperature : 70 °C and ethylene pressure : 8 bar for 2 hours.

TEA is a scavenger, which may help in reducing the amount of impurities in the system thereby leading to an increase catalytic activity than the system without alkylaluminum as scavenger. Moreover, polymerization can proceed for two hours without deactivation before. At concentration of TEA 0.5 mmol/L proceed, it resulted in the highest catalytic activity of 6.169 kg.PE/g Cat*h, as illustrated in Table 4.3. However, at higher concentrations of TEA of 0.7, 1.0, 1.2 mmol/L in hexane, it led to a decreased catalytic activity. Furthermore, TEA is an alkylating and reducing agent, it could cause the reduction of the metallocene compound resulting in an inactive species [60]. It may also compete with MAO into the metallocene catalyst as a complexing ligand and TMA is also able to inhibit certain functions of MAO leading to a catalyst with lower polymerization activity [69]. Therefore, the addition of TEA has both advantages and disadvantages to catalytic activity.

Table 4. 4 Effect of the triethylaluminum (TEA) on properties of polymer with supported metallocene catalyst for ethylene and 1-hexene copolymerization[a]

Type of Alkylaluminum	Concentration (mmol/L in hexane)	Mw[b] (g/mol)	MWD[c]	T_m(°C)[d]	$\%\chi_c^e$	1-Hexene[f] insertion	
						(%wt.)	(%mol)
TEA	0.3	220,601	4.63	113.39	24.33	4.11	1.42
TEA	0.5	205,666	4.18	116.77	27.19	4.40	1.52
TEA	0.7	211,052	4.13	117.11	24.67	3.97	1.37
TEA	1.0	178,166	3.95	116.15	25.32	4.12	1.42
TEA	1.2	181,002	4.12	113.83	23.43	3.70	1.27

[a] Fixed supported metallocene catalyst at 25 mg.

[b] Molecular weight of polymer was characterized by GPC.

[c] *Mw/Mn* or MWD as determined by GPC.

[d] Melting temperature as determined by DSC

[e] Crystallinity: $Xc(\Delta H_f/\Delta H_f^0)\times 100$, where ΔH_f^0 is 269.9 J/g and ΔH_f is the melting heat of the sample, as determined by DSC [61].

[f] Concentration of incorporated 1-hexene, as determined by FTIR.

Molecular weight slightly diminished when higher concentration of TEA was added. This might result from increasing the chance of the chain transfer to alkylaluminum reaction leading to termination of copolymer chain. However, chain transfer to TEA might not be the major chain transfer reaction in this system since only a small change in Mw resulted even when more TEA was added, as shown in Table 4.4. Then, the Table 4.4 show molecular weight distribution (MWD) of obtained copolymer were broad than for the normally analogous homogeneous system likely resulted from the interactions between the metallocene and the support, which leads to the formation of different active species [69].

Figure 4.9 and Table 4.4 show that the incorporation of 1-hexene in copolymer is more or less constant with the TEA concentration. The average incorporation of 1-hexene is 4.06 %wt or 1.4 %mol as shown in Table 4.4. The average melting temperature is 115.45 °C, and the average crystallinity is 24.99% as shown in Table 4.4. The copolymers were produced in copolymerization of ethylene and 1-hexene having lower melting temperature and lower crystallinities than the homopolymerization because of the short branching from the incorporated 1-hexene [70].

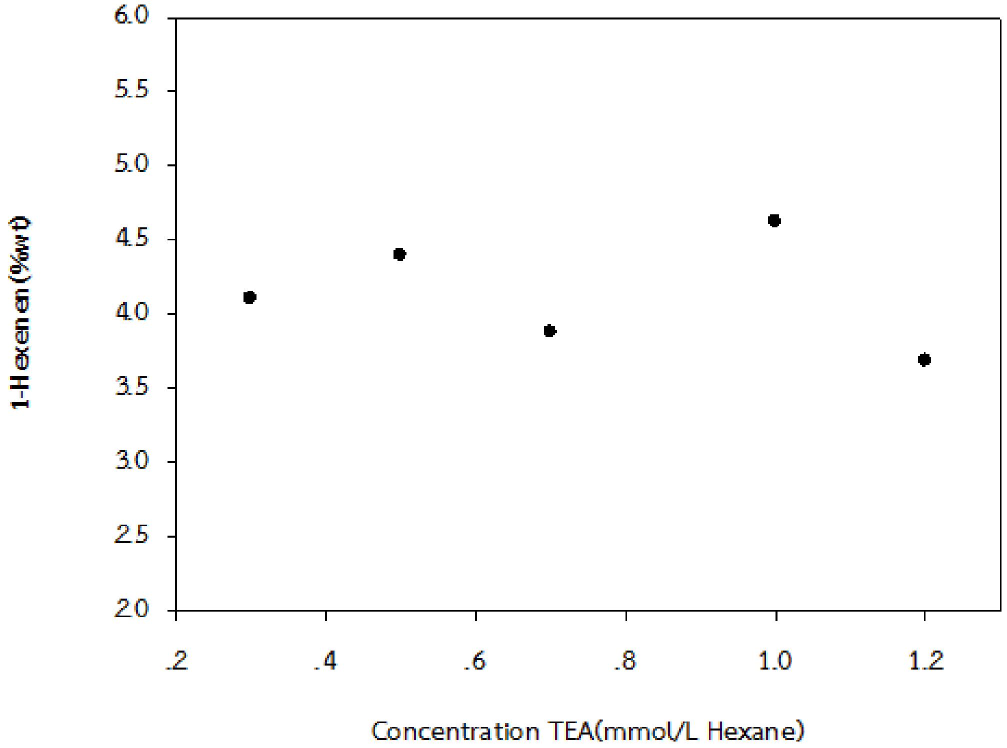


Figure 4. 9 Amount of 1-hexene in the copolymer as functions of TEA

The melting temperature and the crystallinities of the copolymers are, therefore, unaffected by the addition of TEA, as illustrated in Table 4.4. However, the 1-hexene incorporation is, as mentioned, unchanged upon TEA addition [71].

4.2.2. Effect of triisobuthylaluminum (TiBA) as scavenger

For this case, the ethylene and 1-hexene (10 ml) copolymerization by various concentrations of TiBA including 0.7, 1.0, 1.2, 1.5, 1.7 mmol/L in hexane was investigated.

Table 4. 5 Effect of the triisobuthylaluminum (TiBA) on the catalytic activity with supported metallocene catalyst for ethylene and 1-hexene copolymerization[a]

Type of Alkylaluminum	Concentration (mmol/L in hexane)	Yield (g)	Activity[b] (kg.Polymer/gCat.*h)
-	-	trace	0.020
TiBA	0.7	394.46	7.889
TiBA	1.0	481.82	9.636
TiBA	1.2	492.68	9.854
TiBA	1.5	521.98	10.439
TiBA	1.7	449.40	8.988

[a] Fixed supported metallocene catalyst at 25 mg.

[b] Slurry ethylene and 1-Hexene 10 ml copolymerization was performed at temperature : 70 °C and ethylene pressure : 8 bar for 2 hours.

The effect of TiBA concentration on catalytic activity for ethylene and 1-hexene (10ml) copolymerization is shown in Table 4.5. Comparison of run without alkylaluminum and run with alkylaluminum as scavenger shows that catalytic activity for run with alkylaluminum was about vary much higher than the catalytic activity for run without alkylaluminum. The lower catalytic activity for low concentration of TiBA was likely due to deactivation of some of the catalyst by residual impurities in the reactor. Comparison concentration of TiBA 0.7 to 1.5 mmol/L in hexane in Table 4.5, it reveals that increasing the concentration of TiBA in the reactor systematically increased the catalytic activity and rised the yield of copolymer. The maximum catalytic activity (10.439 kg.Polymer/g Cat.*h as shown in Table 4.5) of this part reaches at concentration of TiBA 1.5 mmol/L in hexane. In contrast, excess TiBA concentration (1.7 mmol/L hexane) reduced the catalytic activity perhaps caused by heterodinuclear complexes similar as shown in Scheme 2 which species are coordinatively saturated and lack a vacant orbital suitable for binding the olefinic substrate [64].

Table 4. 6 Effect of the triisobuthylaluminum (TiBA) on properties of polymer with supported metallocene catalyst for ethylene and 1-hexene copolymerization[a]

Type of Alkylaluminum	Concentration (mmol/L in hexane)	T_m(°C)[b]	$\%\chi^{c}_{e}$	1-Hexene insertion[d]	
				(%wt.)	(%mol)
TiBA	0.7	126.97	27.81	2.61	0.90
TiBA	1.0	126.96	27.79	2.46	0.84
TiBA	1.2	126.97	30.62	1.60	0.54
TiBA	1.5	127.99	30.75	2.59	0.89
TiBA	1.7	126.97	31.50	1.69	0.57

[a] Fixed supported metallocene catalyst 25 mg.

[b] Melting temperature as determined by DSC.

[c] Crystallinity: $X_c(\Delta H_f/\Delta H_f^0)\times 100$, where ΔH_f^0 is 269.9 J/g and ΔH_f is the melting heat of the sample, as determined by DSC [61].

[d] Concentration of incorporated 1-hexene, as determined by FTIR.

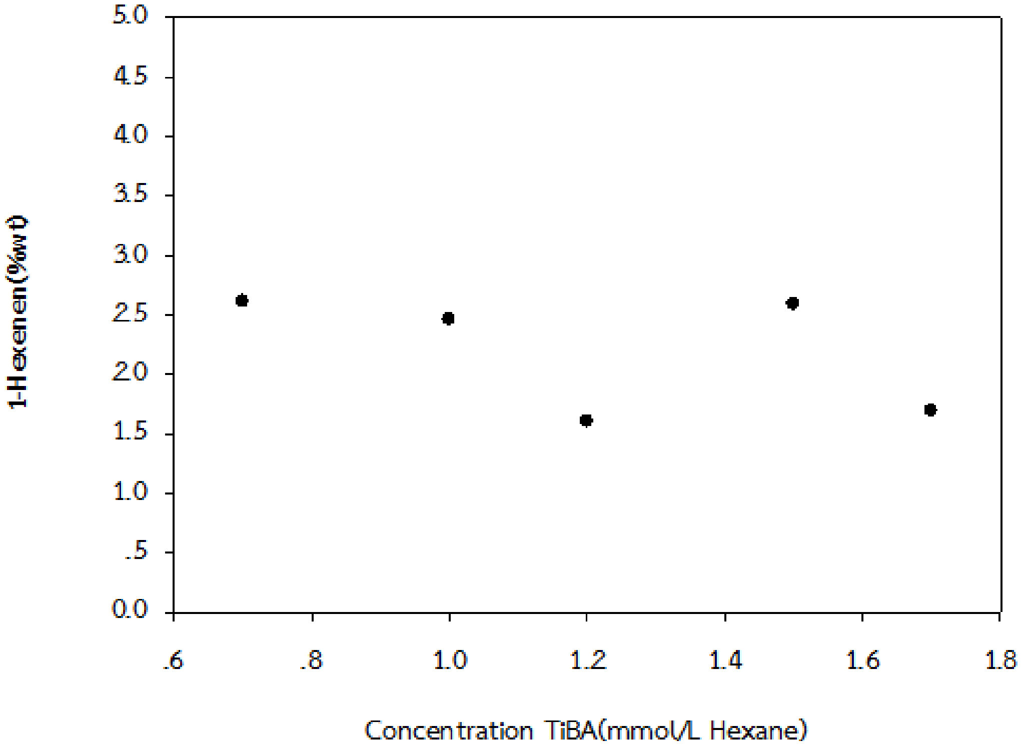


Figure 4. 10 Amount of 1-hexene in the copolymer as functions of TiBA concentration

The trend of 1-hexene copolymerization with difference of TiBA concentrations changes insignificantly, as illustrated in Table 4.6. The incorporation of 1-hexene in copolymer as shown in Figure 4.10 and Table 4.6 is up or down with the TiBA concentration. The average incorporation of 1-hexene is 2.19 %wt or 0.75 %mol as shown in Table 4.6. Table 4.6 shows that the average melting temperature and average crystallinity of the copolymers are 127.17°C and 29.69%, respectively. The melting temperature and crystallinities of copolymer are lower than polyethylene due to the incorporated 1-hexene leads to the short chain branching [70].

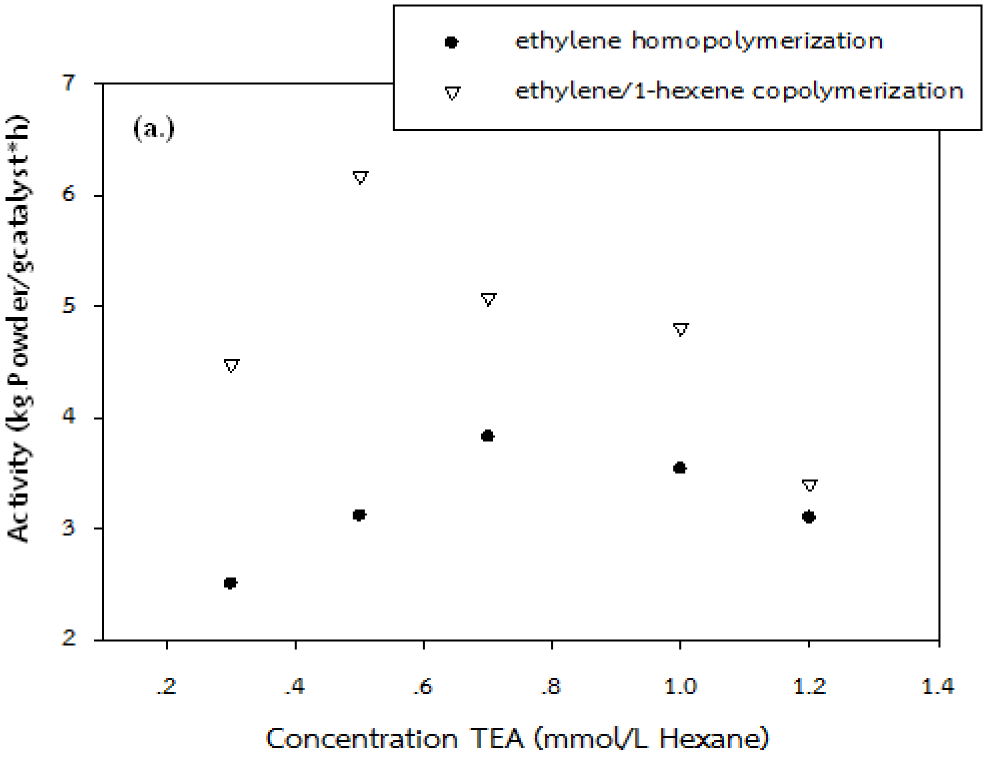
Moreover, the melting temperature and the crystallinities of the copolymers are independent on concentration of TiBA. Furthermore, the 1-hexene incorporation was not a function of the TiBA concentration.

4.2.3. Comparison ethylene homopolymerization and ethylene/1-hexene copolymerization with alkylaluminum (TEA, TiBA) as scavenger [67, 68, 70, 71]

From the Figure 4.11 it shows that the catalytic activity of ethylene/1-hexene copolymerization with alkylaluminum as scavenger for both TEA and TiBA is more higher than the catalytic activity of ethylene homopolymerization. Normally, in olefin polymerization adding of small amounts of comonomer such as 1-hexene to ethylene polymerization system results in an enhance in the ethylene consumption rate in comparison to a homopolyethylene run. This phenomena has several reasons both in chemical and physical nature. It has been proposed to account for the ‘‘comonomer effect’’.

For reasons in term of chemical effects such as modification of the catalytic sites and increase in the number of active centers. The copolymerization kinetics in the presence of the comonomer effect can be rationalized on the issue of the formation, stability, and behavior of the active centers. Karol et al. [72] have proposed that α-olefins can be operation as ligands. By coordination to the active center, α-olefin can alter the charge density on the cationic zirconocenium ion. Metal centers with higher mobility, lower steric interference, and higher electrophilicity are believed to form stronger ion pairs. Monomers that cause a greater separation between the cationic metal centers and the MAO aggregates can enhance the activity of the catalyst.

For reasons in terms of physical effects such as catalyst particle fragmentation and diffusion phenomena. The presence of α-olefin in the reaction as comonomer makes the polymer product more amorphous or less crystalline polymer and soluble and, therefore increases the diffusivity of ethylene to the active center during copolymerization than in homopolymerization. In another factor, in the supported catalyst, an observation of earlier precipitation of the polymer during homopolymerization than in copolymerization was observed, which could contribute to the rate improvement during the copolymerization. For this reason, there would be more facile monomer diffusion to the active centers during copolymerization than homopolymerization, thus promoting the production of a larger amount of polymer [73].



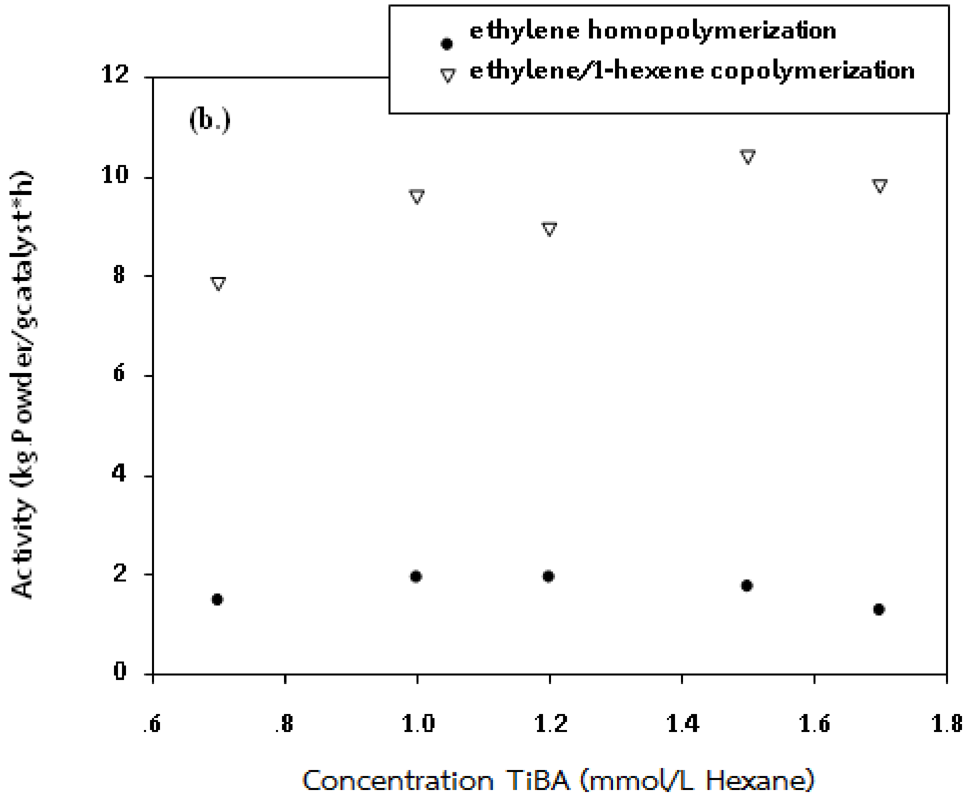


Figure 4. 11 Dependence of the catalyst activity versus the concentration of scavenger (a.) TEA, (b.) TiBA for ethylene polymerization and ethylene/1-hexene copolymerization with supported metallocene catalyst

4.3 Effect of alkylaluminum as scavenger in ethylene polymerization with H_2

The final part was investigated the effect of H_2 on catalytic activity and polymer properties for ethylene homopolymerization using supported metallocene catalysts by feeding H_2 rate of 4 ml/min during polymerization.

4.3.1. Effect of triethylaluminum (TEA) as scavenger

For the ethylene homopolymerization with H_2 at feed rate of 4 ml/min continuously, the concentrations of TEA were varied at 0.3, 0.5, 07, 1.0 and 1.2 mmol/L in hexane, respectively.

The catalytic activity increases with increasing the concentration of TEA, as shown in the Table 4.7 and Figure 4.12. The explanation for the observed increase in the catalysis activity is that, it scavenged the impurity in the system such as monomer, solvents and chain transfer agents. However, when adding excess concentration of TEA (1.0, 1.2 mmol/L in hexane) it results in much lower catalytic activity. The decrease in catalytic activity can be explained by taking into account that when increasing TEA concentration in the polymerization, TEA and metallocene cations can form heterodinuclear complexes which are similar to complexs in Scheme 2. In addition to decreased catalytic activity, TEA can reduce the transition metal Zr(IV) to Zr(III) specie which is inactive species in ethylene polymerization[2, 53, 60, 74].

Table 4. 7 Effect of the triethylaluminum (TEA) on the catalytic activity with supported metallocene catalyst for ethylene and H_2 polymerization[a]

Type of Alkylaluminum	Concentration (mmol/L in hexane)	Yield PE (g)	Activity[b] (kg.PE/g Cat.*h)
TEA	0.3	140.38	2.8076
TEA	0.5	228.38	4.5676
TEA	0.7	264.29	5.2858
TEA	1.0	92.99	1.8598
TEA	1.2	97.69	1.9538

[a] Fixed supported metallocene catalyst at 25 mg and H_2 feed rate of 4 ml/min continuously

[b] Slurry ethylene polymerization with H_2 was performed at temperature : 80 ℃, ethylene pressure : 8 bar and feed continue H_2 flow rate 4 ml/min for 2 hours

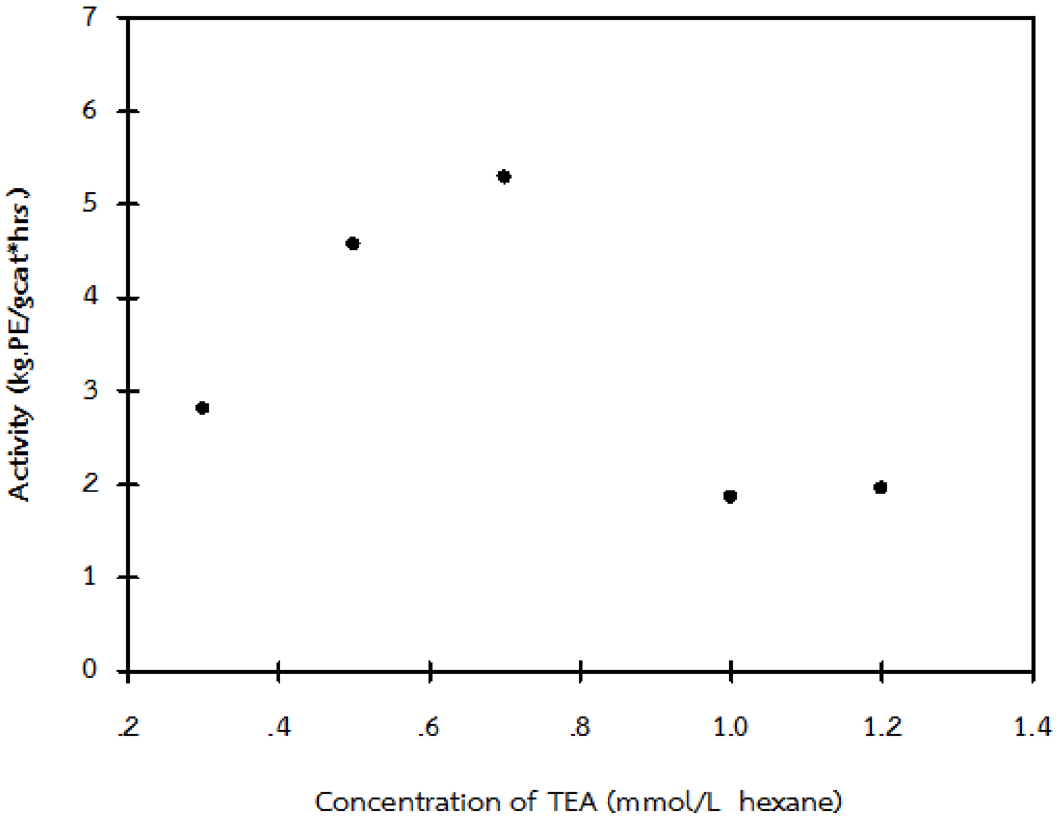


Figure 4. 12 Dependence of the catalyst activity versus the concentration of TEA for ethylene polymerization with H_2 using supported metallocene catalyst

Table 4. 8 Effect of the triethylaluminum (TEA) on properties of polymer with supported metallocene catalyst for ethylene and H_2 polymerization[a]

Type of Alkylaluminum	Concentration (mmol/L in hexane)	Mw (g/mol)[b]	MWD[c]	T_m(°C)[d]	$\%\chi_c$[e]
TEA	0.3	109,839	14.02	133.09	60.14
TEA	0.5	114,834	14.61	133.35	59.18
TEA	0.7	91,442	7.21	133.61	55.22
TEA	1.0	60,069	9.12	132.67	67.34
TEA	1.2	60,136	8.48	131.69	61.43

[a] Fixed supported metallocene catalyst at 25 mg. and H_2 feed rate of 4 ml/min continuously

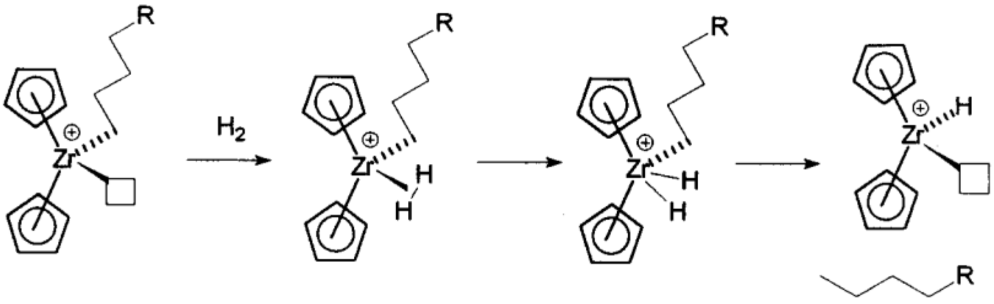
[b] Molecular weight of polymer was characterized by GPC

[c] *Mw/Mn* or MWD as determined by GPC.

[d] Melting temperature as determined by DSC

[e] Crystallinity: $X_c(\Delta H_f/\Delta H_f^0)\times100$, where ΔH_f^0 is 269.9 J/g and ΔH_f is the melting heat of the sample, as determined by DSC [[61].

The molecular weight (Mw) and molecular weight distribution (MWD) of polyethylene for ethylene polymerization is carried out in the presence of hydrogen determined by gel permeation chromatography (GPC), which the polymers were filtered with 1,2,4 trichlorobenzene at 140 °C to protect the equipment from block with polymer. From the Table 4.8, it shows that the molecular weight of polymer decreases gradually with increasing concentration of TEA. The reasons of decreasing molecular weight can be explained in terms of chain transfer reaction to aluminum. Apart from decrease in molecular weight, hydrogen is an efficient chain transfer agent when used with metallocene catalysts and chain transfer to hydrogen is shown in Scheme 3. TEA remains after scavenger bring about decreasing molecular weight obviously at high concentration of TEA, as shown in the Table 4.8, and Figure 4.12. In the system with presence hydrogen, due to the fact that size of hydrogen is smaller than TEA, thus it can easily react with metal to form metal hydride resulted in a decrease in catalytic activity compared to an absence of hydrogen. Remain of TEA after trapping impurity, it would act as a reducing agent to form inactive specie and act as chain transfer agent. For the hydrogen system, active species would react with hydrogen and form metal hydride, thus leading to remain of TEA which acts as a chain transfer to aluminum. Therefore, the lower molecular weight of polymer was observed in these systems. Average melting temperature is about 132.88 °C with different concentration of TEA so the amount of TEA does not affect on the melting temperature of obtained polymer. Molecular weight distributions of polymer at different concentrations of TEA were broader than the molecular weight distributions of the system with the absence of hydrogen as shown in Table 4.8 and Table 4.2 due to hydrogen effect on the metallocene catalyst. From the Table 4.8, it shows that the crystallinity of polymer for the ethylene polymerization with the presence of hydrogen is higher than the crystallinity of polymer for the run with the absence of hydrogen. For the reason of these, the effect of hydrogen on chain transfer reaction leads to low molecular weight of polymer. Relatively short polymer chains form crystals more facile than long chains, because the long chains tend to be more disturbed.



Scheme 3 Propoed reaction of the catalyst with hydrogen **[1]**

4.3.2. Comparison the catalyst activity for ethylene polymerization with the presence and absence of H_2 using supported metallocene catalyst by using TEA as scavenger

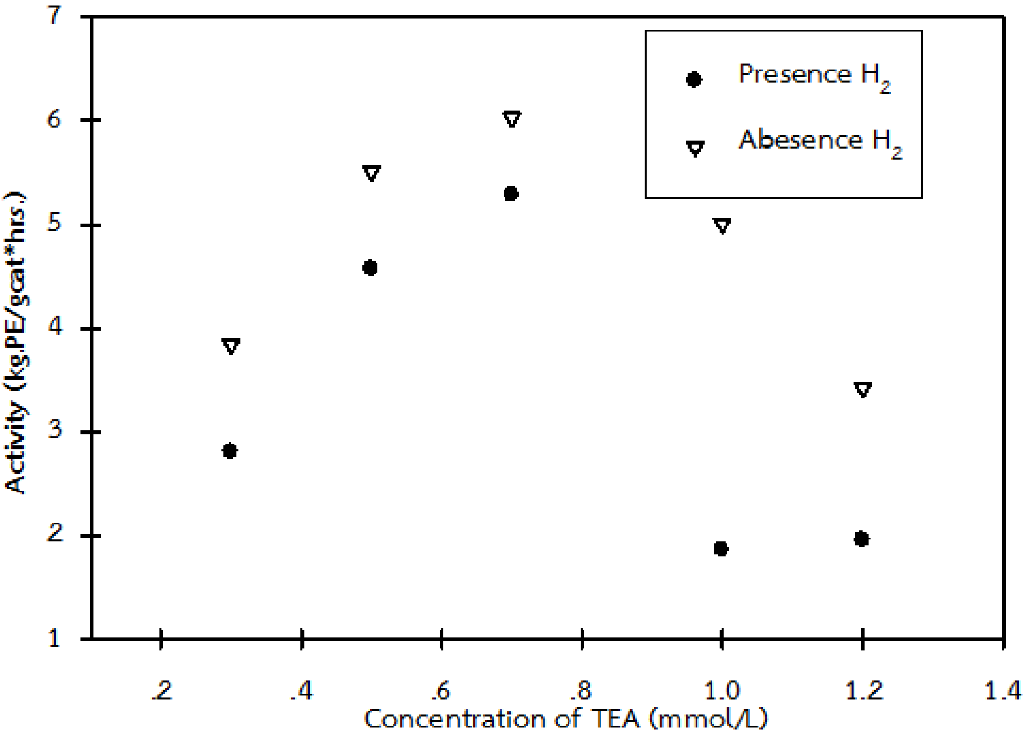


Figure 4. 13 Dependence of the catalyst activity versus the concentration of TEA for ethylene polymerization with the presence and absence using supported metallocene catalyst

From the Figure 4.13 it shows the catalytic activity of the polymerization with the absence hydrogen is higher than the catalytic activity obtained from run with the presence of hydrogen for with all concentrations of TEA on the studied range. So hydrogen affects on the catalytic activity.

This phenomena on may be caused by coordination of hydrogen and metal. Hydrogen may coordinate to the metal atom to form more metal hydride complexes in competition with an ethylene as monomer and stabilize it [75]. As a result, the total propagation rate comes to down, which leads to lower polymerization activity. Moreover, it can cause reduction of ethylene concentration around active sites because of its characteristics, which is hydrogenation of olefin monomer [75-77].

4.3.3. Effect of triisobuthylaluminum (TiBA) as scavenger

The concentrations of TiBA were varied at 07, 1.0, 1.2, 1.5, and 1.7 mmol/L in hexane, respectively for investigation of ethylene polymerization with the presence of hydrogen.

Table 4. 9 Effect of the triisobuthylaluminum (TiBA) on the catalytic activity with supported metallocene catalyst for ethylene and H_2 polymerization[a]

Type of Alkylaluminum	Concentration (mmol/L in hexane)	Yield (g)	Activity[b] (kg.PE/g Cat.*h)
TiBA	0.7	314.91	6.298
TiBA	1.0	344.92	6.898
TiBA	1.2	353.64	7.073
TiBA	1.5	270.13	5.403
TiBA	1.7	174.82	3.496

[a] Fixed supported metallocene catalyst at 25 mg. and H_2 feed rate of 4 ml/min continuously

[b] Slurry ethylene polymerization with H_2 was performed at temperature : 80 °C, ethylene pressure : 8 bar and feed continue H_2 flow rate 4 ml/min for 2 hours

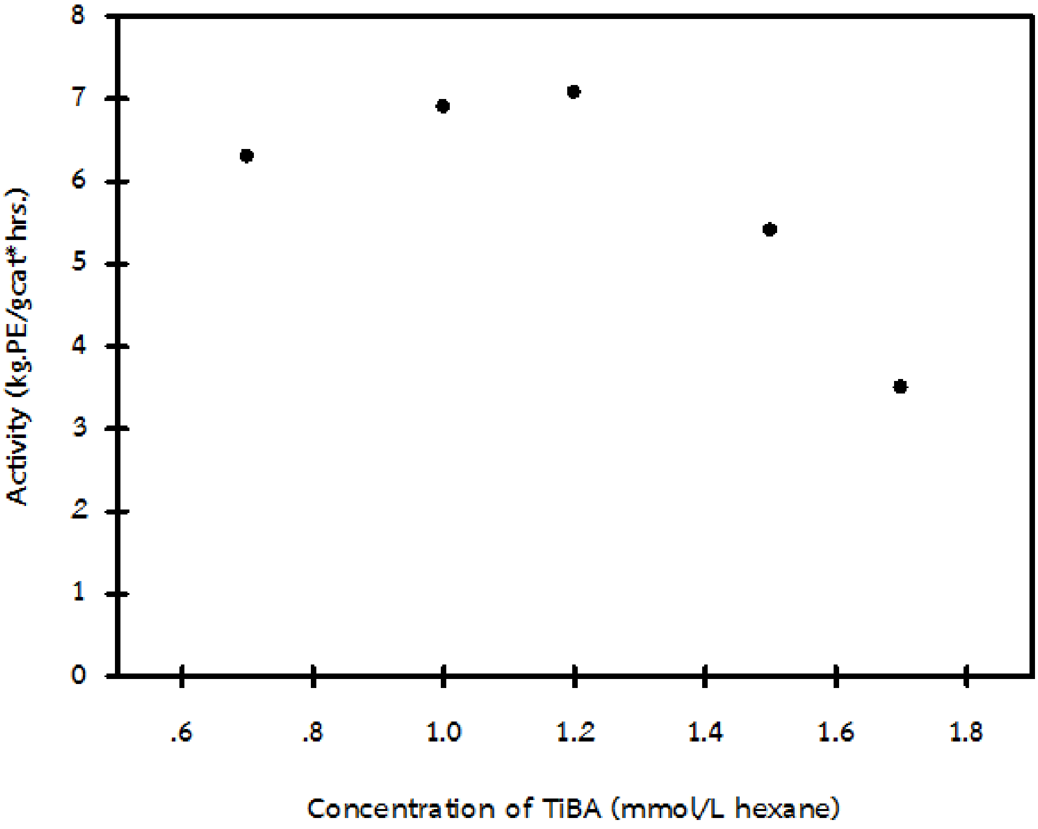


Figure 4. 14 Dependence of the catalyst activity versus the concentration of TiBA for ethylene polymerization with H_2 using supported metallocene catalyst

From the Table 4.9 and Figure 4.14, it shows that the higher catalytic activity with increasing the concentration of TiBA as sufficient amount of TiBA to eliminate impurity was observed. On the other hand, the lower catalytic activity observed for low concentration of TiBA at 0.7, 1.0 mmol/L in hexane was likely due to deactivation of some of the catalyst by the residual impurities in the reactor. Furthermore, when addition excess concentration of TiBA at 1.5, 1.7 mmol/L in hexane, it results in a decrease of catalytic activity. As a result of the system with presence of excess trialkylaluminum (TiBA), trialkylaluminum and metallocene cations adducts to heterodinuclear complexes form, which are similar to complexs in scheme 2. Moreover, the other reasons for the decrease in catalytic activity with time may be the reduction of Zr(IV) to Zi(III) states with TiBA, which is inactive for ethylene polymerization [2, 53, 60, 74]

The results from gel permeation chromatography (GPC) technique provided the molecular weight (Mw) and molecular weight distribution (MWD) of polyethylene. The obtained polymers were filtered with 1,2,4 trichlorobenzene at high temperature (140 °C) in order to prevent blocking of polymer into the column GPC before analyze sample by GPC technique. At higher concentration of TiBA, it was observed reduction in molecular weight, probably due to chain transfer reaction to alkylaluminum (as shown in Scheme 4.) during the polymerization reaction, as shown in the Table 4.10.

Table 4. 10 Effect of the triisobuthylaluminum (TiBA) on properties of polymer with supported metallocene catalyst for ethylene and H_2 polymerization[a]

Type of Alkylaluminum	Concentration (mmol/L in hexane)	Mw (g/mol)[b]	MWD[c]	T_m(°C)[d]	$\%\chi_c$[e]
TiBA	0.7	111,353	11.55	133.74	51.15
TiBA	1.0	128,472	8.21	133.08	52.61
TiBA	1.2	132,249	7.7	133.27	56.37
TiBA	1.5	117,961	8.73	132.29	48.20
TiBA	1.7	95,348	10.02	133.42	56.71

[a] Fixed supported metallocene catalyst at 25 mg and and H_2 feed rate of 4 ml/min continuously

[b] Molecular weight of polymer was characterized by GPC.

[c] *Mw/Mn* or MWD as determined by GPC.

[d] Melting temperature as determined by DSC.

[e] Crystallinity: $Xc(\Delta H_f/\Delta H_f^0)\times 100$, where ΔH_f^0 is 269.9 J/g and ΔH_f is the melting heat of the sample, as determined by DSC [61].

$$Mt-CH_2-\overset{CH_3}{\overset{|}{CH}}-P \xrightarrow{AlR_3} Mt-R + R_2-Al-CH_2-\overset{CH_3}{\overset{|}{CH}}-P$$

Scheme 4 Chain transfer reaction to alkylaluminum : Mt = metal, and P = polymer chain [3]

In addition to decreasing of molecular weight, the catalyst is influenced by the presence of hydrogen in the system as chain transfer agent and mechanism as shown in the Scheme 3. The molecular weight distributions of polymer with different concentrations of TiBA were broader than molecular weight distributions of polymer in the run with the absence of hydrogen as shown in the Table 4.2. Owing to Influence from hydrogen, the shape of MWDs changes from unimodal to bimodal [76]. From the Figure 4.10 it shows the melting temperature at different concentrations of TiBA and average melting temperature of polymer in this part is 133.16 °C. Moreover, the average crystallinity of polymer is 53.01% and higher than average crystallinity of polymer in the run with the absence of hydrogen (Table 4.2). Owing to increasing rate of chain transfer by H_2, the system has more short polymer chains to form crystals easier than long polymer chains, because the long polymer chains can be liable more tangled. From the results, melting temperature and crystallinity of polymer are independent with the concentration of TiBA.

4.3.4. Comparison the catalyst activity for ethylene polymerization with presence and absence of H_2 using supported metallocene catalyst by using TiBA as scavenger

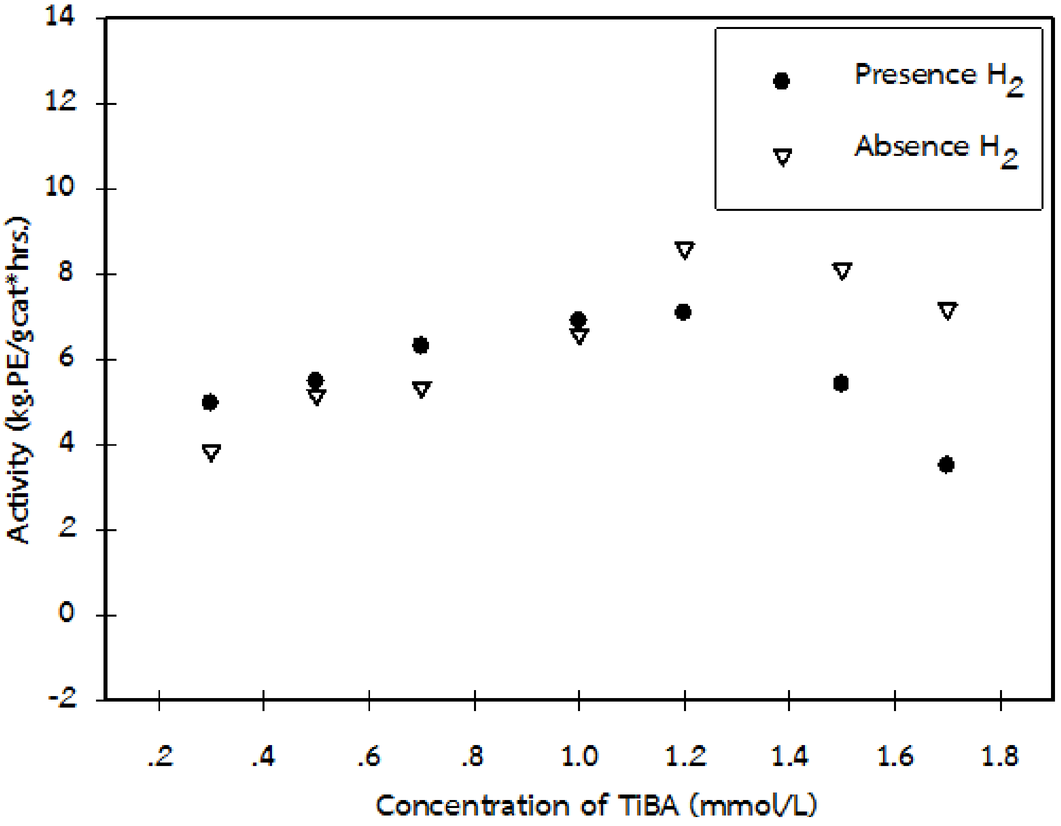


Figure 4. 15 Dependence of the catalyst activity versus the concentration of TiBA for ethylene polymerization with the presence and absence of H_2 using supported metallocene catalyst

From the Figure 4.15, it shows that the catalytic activity in both with the presence of hydrogen and absence of hydrogen at low concentrations of TiBA (0.3, 0.5, 0.7, 1.0 mmol/L in hexane) very slight difference in catalytic activity, therefore, unaffected by the addition of hydrogen. On the other hand, the previous studied from Zakharov et al. [78], they reported the increase of catalytic activity of the system with presence of hydrogen. Based on FT-IR studies of inorganic supported transition metal catalysts, they investigated the system with the presence of hydrogen, the surface metal hydride formed on the inorganic support that can be correlated with an increase in the number of active sites leading to increase in catalytic activity. However, at high concentration of TiBA (1.2, 1.5, 1.7 mmol/L in hexane), it was observed the lower catalytic activity by effect of hydrogen. Hydrogen might be coordinate to the metal atom and make metal hydride complexes in competition with ethylene monomer and stabilizes the metal hydride complexes resulting in a lower propagation rate, which bring about in depressed catalytic activity of polymerization. Furthermore, the metallocene are good hydrogenation catalyst as compared with conventional Ziegler-Natta catalysts and hydrogenate olefinic monomers that can cause reduction of ethylene concentration around active species. These might be the reasons for the low catalytic activity of polymerization in the presence of hydrogen [75-77].

4.3.5. Comparison the catalyst activity for ethylene polymerization with the presence of H_2 for supported metallocene catalyst by using trialkylaluminum (TEA, TiBA) as scavenger

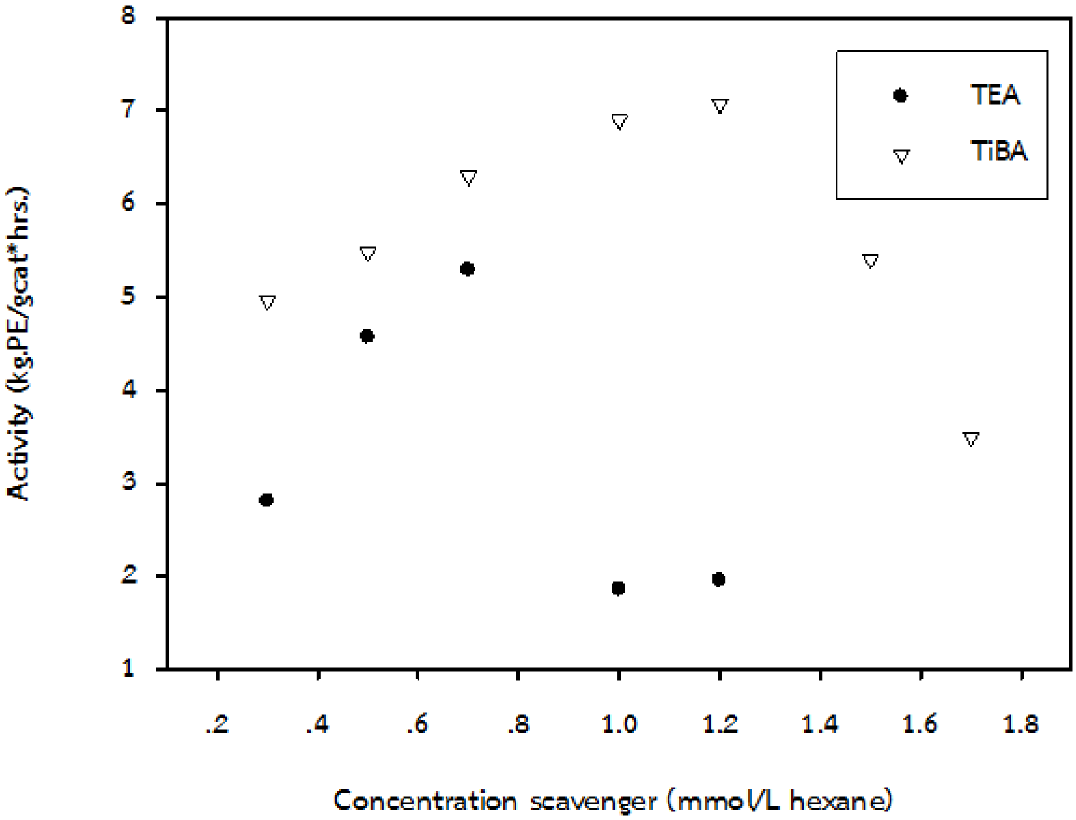


Figure 4. 16 Dependence of the catalyst activity versus the concentration of scavenger for ethylene polymerization with the presence of H_2 using supported metallocene catalyst

From the Figure 4.16, it shows that the type of alkylaluminum as scavenger in ethylene polymerization with the presence of H_2 affects on the catalytic activity obviously. The catalytic activity of the system that used TiBA as scavenger was higher than the catalytic activity of the system that used TEA as scavenger for all ranges of concentrations studied. The reason of this phenomenon may be caused by looser of the active cationic ion pair. TIBA can react with MAO to form a mixed aluminoxane containing isobutyl groups [56, 65]. The increase in the size of alkyl groups in aluminoxane makes the active cationic ion pair (L_2ZrR^+·····MAO^-) looser. This can bring about an improve in catalyst activity [56]. Moreover, the reduction of catalytic activity by the presence of TEA might be stronger effect of hydrogen, which decreases the catalytic activity by metal hydride complexes form resulting in a lower propagation rate than [75-77] the presence of TiBA due to steric bulk of alkyl groups in trialkylaluminum reason. In addition, TEA is stronger reducing agent than TiBA to reduce Zr(IV) to Zi(III), which is inactive for ethylene polymerization resulting in depression of catalytic activity [2, 53, 60].

Table 4. 11 Effect of trialkylaluminum (TEA,TiBA) as scavenger on properties of polymer with supported metallocene catalyst for ethylene and H_2 polymerization[a]

Type of Alkylaluminum	Concentration (mmol/L in hexane)	Mw (g/mol)[b]	MWD[c]	T_m(°C)[d]	%χ_c[e]
TEA	0.7	91,442	7.21	133.61	55.22
TiBA	0.7	111,353	11.55	133.74	51.15
TEA	1.0	60,069	9.12	132.67	67.34
TiBA	1.0	128,472	8.21	133.08	52.61
TEA	1.2	60,136	8.48	131.69	61.43
TiBA	1.2	132,249	7.7	133.27	56.37

[a] Fixed supported metallocene catalyst at 25 mg. and H_2 feed rate of 4 ml/min continuously

[b] Molecular weight of polymer was characterized by GPC.

[c] *Mw/Mn* or MWD as determined by GPC.

[d] Melting temperature as determined by DSC.

[e] Crystallinity: Xc($\Delta H_f/\Delta H_f^0$)×100, where ΔH_f^0 is 269.9 J/g and ΔH_f is the melting heat of the sample, as determined by DSC [61]

A different behavior for alkylaluminum in the molecular weight of polymer is shown in Table 4.11. For polymerization with presence of hydrogen with TiBA, it resulted in increase molecular weight, while polymerization with TEA resulted in decreases molecular weight of polymer at the same concentration. The ability to a chain transfer decreased with increasing the bulkiness of the corresponding alkylaluminums. In fact, small size alkylaluminum (TEA) diminished the molecular weight strongly, while bulky TIBA noticeably increased the molecular weight of the polymers obtained [56, 57]. Moreover, the addition of TEA increased the crystallinity of polymer higher than addition of TiBA at the same concentration. Due to lower molecular weight by addition TEA, this runs has more short polymer chains to form crystals easier than long polymer chains. However, the type of alkylaluminum did not have a significant effect on melting temperature of product.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research aims to investigate the effect of alkylaluminum acts as scavenge impurities such as O_2, H_2O and other protic impurities which contaminate in materials commonly used in polyolefin processes such as monomer, comonomer, solvents, and chain transfer agents. The results focused on the catalytic activity and properties of product obtained. Alkylaluminum was divided into 2 types including triethylaluminum (TEA) and triisobutylaluminum (TiBA). The concentrations of TEA and TiBA were varied at 0.3, 0.5, 07, 1.0, 1.2 and 07, 1.0, 1.2, 1.5, 1.7 mmol/L in hexane, respectively. The addition of alkylaluminum as scavenger is important and necessary in this polymerization process because without alkylaluminum to scavenge impurities it has rapid deactivation. For ethylene homopolymerization trend of catalytic activity with different concentrations of alkylauminum, they are similar in both TEA and TiBA. The increase of catalytic activity with increased concentration of alkylaluminum was observed. At lower concentration of alkylaluminum, it shows low catalytic activity because it is not enough to scavenge impurities. At the concentration, which reached maximum catalytic activity is at 0.7, 1.2 mmol/L in hexane and 6.027, 8.603 kg.PE/g Cat.*h for TEA and TiBA, respectively. However, with higher concentration of scavenger, the catalytic activity is lower due to heterodinuclear complexes formed, which are coordinatively saturated and lack of a vacant orbital suitable for binding the olefin substrate when excess of alkylaluminum is used in the system. Moreover, higher deactivation of catalytic activity at higher concentration of TEA than TiBA can be presumed that facile the formation of heterodinuclear complexes than TiBA. . In addition TEA is stronger reducing agent than TiBA to reduce Zr(IV) to Zi(III), which is inactive for ethylene polymerization resulting in depression of catalytic activity. The melting temperature and the crystallinities of the polymers are, therefore, unaffected by the concentration of scavenger. For ethylene and 1-hexene copolymerization, it reached maximum catalytic activity at concentrations of 0.5, 1.5 mmol/L in hexane and 6.169, 10.439 kg.powder/g Cat.*h of TEA and TiBA , respectively. Furthermore, the 1-hexene incorporation was not a function of the trialkylaluminum concentration. The catalytic activity of ethylene/1-hexene copolymerization with alkylaluminum as scavenger for both TEA and TiBA is much higher than the catalytic activity of ethylene homopolymerization. From the results it has many reasons to propose that account for the ‘‘comonomer effect’’ such as modification of the catalytic sites, increase in the number of active centers, catalyst particle fragmentation and diffusion phenomena. For effect of trialkylaluminum as scavenger in ethylene polymerization with H_2, it was similar to the effect of trialkylaluminum in ethylene homopolymerization. However, catalytic activity and properties of polymer were influenced by hydrogen. Hydrogen might coordinate to the metal atom and make more metal hydride complexes in competition with ethylene monomer and stabilizes the metal hydride complexes resulting in a lower propagation rate leading to in depressed catalytic activity of polymerization. The decreasing of molecular weight with increased concentration of scavenger maybe because of chain transfer reaction to alkylaluminum during the polymerization reaction. In addition to decreasing of molecular weight, catalyst is influenced by the presence of hydrogen in system acting as chain transfer agent.

5.2 Recommendations

1. It is ambiguity of molecular weight and molecular weight distribution in the part of ethylene homopolymerization because the results from GPC were not representative of all samples. Then, the other characterization methods should be discussed to confirm accurate data.
2. In order to prove the proposal that TiBA reacts with MAO to form a mixed aluminoxane containing isobutyl groups leading to improve activity, the mixed aluminoxane containing isobutyl groups should be characterized by ^{1}H NMR [79]. Then, the other characterization methods should be discussed to confirm the discussion and support our data as we reported in Chapter IV.
3. The polymerization with other trialkylaluminums as scavenger should be further studied in more detail.
4. The effect of H2 on catalytic activity is less well understood than that in the case of Ziegler-Natta catalysts. This occurrence is still open discussion and should be considered in the further study.

Method to feed hydrogen such as continue, batch, semi-batch differently affects on catalytic activity and properties of product. This occurrence is still open discussion and should be considered in the further study.

REFERENCES

[1] Alt, H.G. and Köppl, A. Effect of the nature of metallocene complexes of group IV metals on their performance in catalytic ethylene and propylene polymerization. Chemical Reviews 100(4) (2000): 1205-1222.

[2] Chen, E.Y.-X. and Marks, T.J. Cocatalysts for metal-catalyzed olefin polymerization: activators, activation processes, and structure-activity relationships. Chemical Reviews 100(4) (2000): 1391-1434.

[3] Naga, N. and Mizunuma, K. Chain transfer reaction by trialkylaluminum (AIR< sub> 3</sub>) in the stereospecific polymerization of propylene with metallocene—AIR< sub> 3</sub>/Ph< sub> 3</sub> CB (C< sub> 6</sub> F< sub> 5</sub>)< sub> 4</sub>. Polymer 39(21) (1998): 5059-5067.

[4] Ribeiro, M.R., Deffieux, A., and Portela, M.F. Supported metallocene complexes for ethylene and propylene polymerizations: preparation and activity. Industrial & engineering chemistry research 36(4) (1997): 1224-1237.

[5] Hlatky, G.G. Heterogeneous single-site catalysts for olefin polymerization. Chemical Reviews 100(4) (2000): 1347-1376.

[6] Fink, G., Steinmetz, B., Zechlin, J., Przybyla, C., and Tesche, B. Propene polymerization with silica-supported metallocene/MAO catalysts. Chemical Reviews 100(4) (2000): 1377-1390.

[7] Przybyla, C., Tesche, B., and Fink, G. Ethylene/hexene copolymerization with the heterogeneous catalyst system SiO2/MAO/rac‐Me2Si [2‐Me‐4‐Ph‐Ind] 2ZrCl2: The filter effect. Macromolecular rapid communications 20(6) (1999): 328-332.

[8] Soga, K. and Kaminaka, M. Copolymerization of olefins with SiO2‐, Al2O3‐, and MgCl2‐supported metallocene catalysts activated by trialkylaluminiums. Macromolecular Chemistry and Physics 195(4) (1994): 1369-1379.

[9] Michiels, W. and Muñoz‐Escalona, A. Mixed cocatalyst systems in metallocene ethylene polymerization. in Macromolecular Symposia, pp. 171-183: Wiley Online Library, 1995.

[10] Soga, K. and Kaminaka, M. Polymerization of propene with the heterogeneous catalyst system Et [IndH4] 2ZrCl2/MAO/SiO2 combined with trialkylaluminium. Die Makromolekulare Chemie, Rapid Communications 13(4) (1992): 221-224.

[11] Forlini, F., Fan, Z.Q., Tritto, I., Locatelli, P., and Sacchi, M.C. Metallocene‐catalyzed propene/1‐hexene copolymerization: Influence of amount and bulkiness of cocatalyst and of solvent polarity. Macromolecular Chemistry and Physics 198(8) (1997): 2397-2408.

[12] Maciejewski Petoff, J.L., Myers, C.L., and Waymouth, R.M. Influence of trialkylaluminum reagents on the propylene polymerization behavior of bridged and unbridged 2-arylindene metallocene polymerization catalysts. Macromolecules 32(24) (1999): 7984-7989.

[13] Malpass, D.B. Introduction to industrial polyethylene: properties, catalysts, and processes. Vol. 45: John Wiley & Sons, 2010.

[14] Chadwick, J.C., Garoff, T., and Severn, J.R. Traditional Heterogeneous Catalysts. Tailor-Made Polymers: Via Immobilization of Alpha-Olefin Polymerization Catalysts (2008): 43-78.

[15] Jiang, X. and He, A. Stereospecific polymerization of olefins with supported Ziegler– Natta catalysts. Polymer International 63(2) (2014): 179-183.

[16] Albizzati, E., Giannini, U., Collina, G., Noristi, L., and Resconi, L. Chapter 2: Catalysts and Polymerizations in Polypropylene Handbook, ed. by Moore EP. Hanser, Munich (1996): 11.

[17] Choi, B., et al. Generation of Ultra-High-Molecular-Weight Polyethylene from Metallocenes Immobilized onto N-Doped Graphene Nanoplatelets. Macromolecular rapid communications 34(6) (2013): 533-538.

[18] Park, H.-J., Kim, J., Seo, Y., Shim, J., Sung, M.-Y., and Kwak, S. Wear behavior of in situ polymerized carbon nanotube/ultra high molecular weight polyethylene composites. Macromolecular Research 21(9) (2013): 965-970.

[19] DiMaio, A.-J., Meverden, C.C., and Becker, P.D. Polymer-supported catalyst for olefin polymerization. 2001, Google Patents.

[20] Bedell, S.A., Coleman III, W.M., and Howell Jr, W.R. Polymer supported Ziegler-Natta catalysts. 1986, Google Patents.

[21] Wilkinson, G. and Birmingham, J. Bis-cyclopentadienyl compounds of Ti, Zr, V, Nb and Ta. Journal of the American Chemical Society 76(17) (1954): 4281-4284.

[22] FISCHER, E. Uber Cyclopentudien-Komplexe
des Eisens und Kobalts. Angewandte Chemie International Edition in English 64(22) (1952): 620.

[23] Brintzinger, H.H., Fischer, D., Mülhaupt, R., Rieger, B., and Waymouth, R.M. Stereospecific olefin polymerization with chiral metallocene catalysts. Angewandte Chemie International Edition in English 34(11) (1995): 1143-1170.

[24] Ewen, J.A., Jones, R.L., Razavi, A., and Ferrara, J.D. Syndiospecific propylene polymerizations with Group IVB metallocenes. Journal of the American Chemical Society 110(18) (1988): 6255-6256.

[25] Razavi, A., et al. The geometry of the site and its relevance for chain migration and stereospecificity. in Macromolecular symposia, pp. 345-367: Wiley Online Library, 1995.

[26] Andresen, A., et al. Halogen-Free Soluble Ziegler Catalysts for the Polymerization of Ethylene. Control of Molecular Weight by Choice of Temperature. Angewandte Chemie International Edition in English 15(10) (1976): 630-632.

[27] Barron, A.R. A new understanding of the co-catalytic activity of alumoxanes: The opening of a black box! in Macromolecular symposia, pp. 15-25: Wiley Online Library, 1995.

[28] Harlan, C.J., Bott, S.G., and Barron, A.R. Three-coordinate aluminum is not a prerequisite for catalytic activity in the zirconocene-alumoxane polymerization of ethylene. Journal of the American Chemical Society 117(24) (1995): 6465-6474.

[29] Mason, M.R., Smith, J.M., Bott, S.G., and Barron, A.R. Hydrolysis of tri-tert-butylaluminum: the first structural characterization of alkylalumoxanes [(R2Al) 2O] n and (RAlO) n. Journal of the American Chemical Society 115(12) (1993): 4971-4984.

[30] Sinn, H. Proposals for structure and effect of methylalumoxane based on mass balances and phase separation experiments. in Macromolecular symposia, pp. 27-52: Wiley Online Library, 1995.

[31] Eisch, J.J., Piotrowski, A.M., Brownstein, S.K., Gabe, E.J., and Lee, F.L. Organometallic compounds of Group III. Part 41. Direct observation of the initial insertion of an unsaturated hydrocarbon into the titanium-carbon bond of the soluble Ziegler polymerization catalyst Cp2TiCl2-MeAlCl2. Journal of the American Chemical Society 107(24) (1985): 7219-7221.

[32] Jordan, R.F., Bajgur, C.S., Willett, R., and Scott, B. Ethylene polymerization by a cationic dicyclopentadienyl zirconium (IV) alkyl complex. Journal of the American Chemical Society 108(23) (1986): 7410-7411.

[33] MORRIS, M.J. Cyclopentadienyl Complexes of Chromium, Molybdenum and Tungsten. Vanadium and Chromium Groups 5 (1995): 393.

[34] Hlatky, G.G., Turner, H.W., and Eckman, R.R. Ionic, base-free zirconocene catalysts for ethylene polymerization. Journal of the American Chemical Society 111(7) (1989): 2728-2729.

[35] Sishta, C., Hathorn, R.M., and Marks, T.J. Group 4 metallocene-alumoxane olefin polymerization catalysts. CPMAS-NMR spectroscopic observation of cation-like zirconocene alkyls. Journal of the American Chemical Society 114(3) (1992): 1112-1114.

[36] Bochmann, M., Lancaster, S.J., Hursthouse, M.B., and Malik, K.A. Synthesis of Base-Free Cationic Zirconium Methyl and Benzyl Complexes. The Crystal and Molecular Structure of {C5H3 (SiMe3) 2-1, 3} 2ZrMe (. mu.-Me) B (C6F5) 3. Organometallics 13(6) (1994): 2235-2243.

[37] Malpass, D.B. Commercially available metal alkyls and their use in polyolefin catalysts. Handbook of transition metal catalysts. Wiley, Hoboken (2009).

[38] Ziegler, K. American Chemical Society Monograph No. 147. Organometallic Chemistry. New York: Van Nostrand Reinhold. Company, 1960.

[39] Wilkinson, G., Stone, F.G.A., and Abel, E.W. Comprehensive organometallic chemistry. 1 (1982): 368.

[40] Malpass, D., Fannin, L., and Ligi, J. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 16. 1981, Wiley, New York.

[41] Kleinschmidt, R., Van der Leek, Y., Reffke, M., and Fink, G. Kinetics and mechanistic insight into propylene polymerization with different metallocenes and various aluminium alkyls as cocatalysts. Journal of Molecular Catalysis A: Chemical 148(1) (1999): 29-41.

[42] Panin, A., Sukhova, T., and Bravaya, N. Triisobutylaluminum as cocatalyst for zirconocenes. I. Sterically opened zirconocene/triisobutylaluminum/perfluorophenylborate as highly effective ternary catalytic system for synthesis of low molecular weight polyethylenes. Journal of Polymer Science Part A: Polymer Chemistry 39(11) (2001): 1901-1914.

[43] Chien, J.C., Song, W., and Rausch, M.D. Effect of counterion structure on zirconocenium catalysis of olefin polymerization. Macromolecules 26(12) (1993): 3239-3240.

[44] Beck, S., Brintzinger, H.-H., Suhm, J., and Mülhaupt, R. Propene polymerization with rac‐Me2Si (2‐Me‐Benz [e] Ind) 2ZrX2 [X= Cl, Me] using different cation‐generating reagents. Macromolecular rapid communications 19(5) (1998): 235-239.

[45] Po, R., Cardi, N., and Abis, L. Effect of aluminium alkyls on the synthesis of syndiotactic polystyrene with titanium complexes/methylaluminoxane catalytic systems. Polymer 39(4) (1998): 959-964.

[46] Schellenberg, J. and Newman, T.H. Effect of phenylsilane on the syndiospecific polymerization of styrene in the presence of half-sandwich metallocenes. European polymer journal 37(9) (2001): 1733-1739.

[47] Ziegler, K. American Chemical Society Monograph No. 147
Organometallic Chemistry. New York: Van Nostrand Reinhold. Company
1960

[48] Ziegler, K. American Chemical Society Monograph No. 147. Organometallic Chemistry. New York: Van Nostrand Reinhold. Company, 1960.

[49] Sakharovskaya, G., Korneev, N., and Smirnov, N. A. F. Popov.“Thermal Decomposition of Alkylalurninurns”. J. Gen. Chem. USSR 44 (1974): 560-564.

[50] Ehlers, J. and Walter, J. Process for the preparation of ultrahigh molecular weight polyethylene having a high bulk density. 1996, Google Patents.

[51] Koide, Y., Bott, S.G., and Barron, A.R. Alumoxanes as cocatalysts in the palladium-catalyzed copolymerization of carbon monoxide and ethylene: genesis of a structure-activity relationship. Organometallics 15(9) (1996): 2213-2226.

[52] Winter, H., Schnuchel, W., and Sinn, H. The preparation of aluminoxane from trimethylaluminium at a defined surface of deeply cooled ice. in Macromolecular symposia, pp. 119-125: Wiley Online Library, 1995.

[53] Pedeutour, J.-N., Radhakrishan, K., Cramail, H., and Deffieux, A. Reactivity of metallocene catalysts for olefin polymerization: influence of activator nature and structure. Macromolecular rapid communications 22(14) (2001): 1095-1123.

[54] Jüngling, S., Koltzenburg, S., and Mülhaupt, R. Propene homo‐and copolymerization using homogeneous and supported metallocene catalysts based on Me2Si (2‐Me‐Benz [e] lnd) 2ZrCl2. Journal of Polymer Science Part A: Polymer Chemistry 35(1) (1997): 1-8.

[55] Suhm, J., Schneider, M., and Mülhaupt, R. Temperature dependence of copolymerization parameters in ethene/1‐octene copolymerization using homogeneous rac‐Me2Si (2‐MeBenz [e] Ind) 2ZrCl2/MAO catalyst. Journal of Polymer Science Part A: Polymer Chemistry 35(4) (1997): 735-740.

[56] Vasilenko, I.V., Kostjuk, S.V., Kaputsky, F.N., Nedorezova, P.M., and Aladyshev, A.M. Effect of Different Aluminum Alkyls on the Metallocene/Methylaluminoxane Catalyzed Polymerization of Higher α‐Olefins and Styrene. Macromolecular Chemistry and Physics 209(12) (2008): 1255-1265.

[57] Hammawa, H., Mannan, T., Lynch, D., and Wanke, S. Effects of aluminum alkyls on ethylene/1‐hexene polymerization with supported metallocene/MAO catalysts in the gas phase. Journal of applied polymer science 92(6) (2004): 3549-3560.

[58] KIM, I. CSH Polymerization of ethylene with (C5Me5) 2Zr (NMe2) 2 cocatalyzed by common alkyl aluminums. Journal of Molecular Catalysis A-Chemical, Elsevier 210(1-2) (2004): 47-52.

[59] Panchenko, V., Echevkaya, L., Zakharov, V., and Matsko, M. Influence of triisobutylaluminum on the polymerization of ethylene by SiO< sub> 2</sub>-supported< i> ansa</i>-zirconocene catalysts. Applied Catalysis A: General 404(1) (2011): 47-53.

[60] Wu, Q., Ye, Z., and Lin, S. Syndiotactic polymerization of styrene with cyclopentadienyltribenzyloxytitanium/methylaluminoxane catalyst. Macromolecular Chemistry and Physics 198(6) (1997): 1823-1828.

[61] Quijada, R., Dupont, J., Miranda, M.S.L., Scipioni, R.B., and Galland, G.B. Copolymerization of ethylene with 1-hexene and 1-octene: correlation between type of catalyst and comonomer incorporated. Macromolecular Chemistry and Physics 196(12) (1995): 3991-4000.

[62] Longo, P., Proto, A., and Zambelli, A. Syndiotactic specific polymerization of styrene: driving energy of the steric control and reaction mechanism. Macromolecular Chemistry and Physics 196(9) (1995): 3015-3029.

[63] Chien, J.C., Salajka, Z., and Dong, S. Syndiospecific polymerization of styrene. 3. Catalyst structure. Macromolecules 25(12) (1992): 3199-3203.

[64] Bochmann, M. and Lancaster, S.J. Monomer–Dimer Equilibria in Homo-and Heterodinuclear Cationic Alkylzirconium Complexes and Their Role in Polymerization Catalysis. Angewandte Chemie International Edition in English 33(15-16) (1994): 1634-1637.

[65] Wang, W., Fan, Z., Zhu, Y., Zhang, Y., and Feng, L. Effects of cocatalyst on structure distribution of propylene polymers catalyzed by< i> rac</i>-Me< sub> 2</sub> Si (Ind)< sub> 2</sub> ZrCl< sub> 2</sub>/aluminoxane. European polymer journal 38(8) (2002): 1551-1558.

[66] Bhriain, N.N., Brintzinger, H.-H., Ruchatz, D., and Fink, G. Polymeryl Exchange between a nsa-Zirconocene Catalysts for Norbornene-Ethene Copolymerization and Aluminum or Zinc Alkyls. Macromolecules 38(6) (2005): 2056-2063.

[67] Zimnoch Dos Santos, J.H., et al. Effects of ethylene polymerization conditions on the activity of SiO2-supported zirconocene and on polymer properties. Journal of Polymer Science Part A: Polymer Chemistry 37(13) (1999): 1987-1996.

[68] Schmacke, S. Investigations of Polyethylene Materials by Means of X-ray Diffraction. (2011).

[69] Chao, C., Praserthdam, P., Khorbunsongserm, S., and Rempel, G.L. Effects of TMA and MAO on Ethylene–Propylene Copolymer Using Supported Zirconocene Catalysts. Journal of Macromolecular Science, Part A 40(2) (2003): 181-192.

[70] Galland, G.B., Seferin, M., Mauler, R.S., and Dos Santos, J.H.Z. Linear low-density polyethylene synthesis promoted by homogeneous and supported catalysts. Polymer International 48(8) (1999): 660-664.

[71] Bruaseth, I., Bahr, M., Gerhard, D., and Rytter, E. Pressure and trimethylaluminum effects on ethene/1-hexene copolymerization with methylaluminoxane-activated (1, 2, 4-Me3Cp) 2ZrCl2: Trimethylaluminum suppression of standard termination reactions after 1-hexene insertion. Journal of Polymer Science Part A: Polymer Chemistry 43(12) (2005): 2584-2597.

[72] Karol, F.J., Kao, S.C., and Cann, K.J. Comonomer effects with high-activity titanium-and vanadium-based catalysts for ethylene polymerization. Journal of Polymer Science Part A: Polymer Chemistry 31(10) (1993): 2541-2553.

[73] Awudza, J.A. and Tait, P.J. The “comonomer effect” in ethylene/α-olefin copolymerization using homogeneous and silica-supported Cp2ZrCl2/MAO catalyst systems: Some insights from the kinetics of polymerization, active center studies, and polymerization temperature. Journal of Polymer Science Part A: Polymer Chemistry 46(1) (2008): 267-277.

[74] Cam, D., Sartori, F., and Maldotti, A. Reduction of bis (η5-cyclopentadienyl) zirconium dichloride in the presence of methylalumoxane. Macromolecular Chemistry and Physics 195(8) (1994): 2817-2826.

[75] Han, T.K., Choi, H.K., Jeung, D.W., Ko, Y.S., and Woo, S.I. Control of molecular weight and molecular weight distribution in ethylene polymerization with metallocene catalysts. Macromolecular Chemistry and Physics 196(8) (1995): 2637-2647.

[76] Chu, K.J., Soares, J.B., and Penlidis, A. Effect of hydrogen on ethylene polymerization using in-situ supported metallocene catalysts. Macromolecular Chemistry and Physics 201(5) (2000): 552-557.

[77] Ahn, T.O., Hong, S.C., Huh, W.S., Lee, Y.C., and Lee, D.H. Modification of a Ziegler-Natta catalyst with a metallocene catalyst and its olefin polymerization behavior. Polymer Engineering & Science 39(7) (1999): 1257-1264.

[78] Zakharov, V., Nesterov, G., Vasnetsov, S., and Thiele, K. Active Centers of the Supported Organic and Hydride Transition Metal Catalysts for Ethylene Polymerization. in Transition Metals and Organometallics as Catalysts for Olefin Polymerization, pp. 91-100: Springer, 1988.

[79] Bryliakov, K.P., Semikolenova, N.V., Panchenko, V.N., Zakharov, V.A., Brintzinger, H.H., and Talsi, E.P. Activation of rac-Me2Si (ind) 2ZrCl2 by

Methylalumoxane Modified by Aluminum Alkyls: An EPR Spin-Probe, 1H NMR, and Polymerization Study. Macromolecular Chemistry and Physics 207(3) (2006): 327-335.

APPENDIX

APPENDIX A

CALCULATION FOR SCAVENGER PREPARATION

A. Calculation of stock solution (a solution alkylaluminum as scavenger)

A.1. Calculation of a solution alkylaluminum as scavenger loading

A.1.1 For this research, vary concentrations of TiBA including 0.7, 1.0, 1.2, 1.5, 1.7 mmol/L in hexane.

For example : calculation of TiBA loading for 0.7 mmol/L in hexane

Reagent : stock solution of TiBA 200 mmol/L hexane

$$\text{stock solution loading} = \frac{\text{concentrations required} \times 1\ \text{L (solution in reactor)}}{\text{concentration of stock solution}}$$

$$= \frac{0.7\ \text{mmol/L in hexane} \times 1\ \text{L}}{200\ \text{mmol/L}}$$

$$= 3.5\ \text{ml}$$

A.1.2 On the one part, vary concentrations of TEA including 0.3, 0.5, 0.7, 1.0, 1.2 mmol/L in hexane.

For example : calculation of TEA loading for 0.3 mmol/L in hexane

Reagent : stock solution of TEA 200 mmol/L hexane

$$\text{stock solution loading} = \frac{\text{concentrations required} \times 1\ \text{L (solution in reactor)}}{\text{concentration of stock solution}}$$

$$= \frac{0.3\ \text{mmol/L in hexane} \times 1\ \text{L}}{200\ \text{mmol/L}}$$

$$= 1.5\ \text{ml}$$

APPENDIX B

CALCULATION OF CATALYTIC ACTIVITY

B. Calculation of catalytic activity

The can be calculated as follows: catalytic activity =

$$\text{catalytic activity} = \frac{y}{t\ (\text{hrs.}) \times m\ (\text{g})}$$

where

y = yield polymer (g)

t = quantity of catalyst added (hrs.)

m = the time for polymerization (g)

APPENDIX C

CALCULATION OF POLYMER PROPERTIES

C.1 Calculation of crystallinity of polyethylene

The percentage of crystallinity of polyethylene was determined by differential scanning calorimeter (DSC). The overall crystallinity of polymers is calculated from the following equation.

$$\% X_C = (H_m/H_p)*100$$

where $\% X_C$ is the percentage of crystallinity of polyethylene

H_m is the enthalpy of the sample

H_p is the enthalpy of a totally crystalline polyethylene 269.9 J/g [61]

C.2 Calculation of 1-Hexene conversion in ethylene and 1-hexene copolymerization

The conversion of reactant is performance of catalyst then, there is used demonstrated for olefin polymerization.

The 1-Hexene conversion is assigned that weight of 1-hexene converted with respect to 1-hexene in feed:

$$\text{1-Hexene conversion (\%)} = \frac{[\text{weight of 1-Hexene in feed} - \text{weight of 1-Hexene}] \times 100}{\text{weight of 1-Hexene in feed}}$$

$$\text{1-Hexene in polymer} = \frac{\text{\% 1-Hexene insertion} \times \text{yield product}}{100}$$

For example : 1-Hexene feed 30 ml, yield product 223.93 g, 1-Hexene insertion (by FTIR technique) 4.11 % wt.

Density of 1-Hexene = 0.678 g/ml

$$\text{1-Hexene in polymer} = \frac{4.11 \times 223.93}{100}$$

$$= 9.20 \text{ g}$$

1-Hexene in feed = 30 ml

$$\text{From} \quad D = \frac{m}{V}$$

where D is the density (g/ml),

m is mass of material (g)

V is volume (ml)

1-Hexene in feed = 0.678 g/ml × 30 ml

= 20.34 g

1-Hexene conversion (%) = 20.34 g - 9.20 g

$$= \frac{[\,20.34\ \text{g} - 9.20\ \text{g}] \times 100}{20.34\ \text{g}}$$

1-Hexene conversion = 54.77 %

APPENDIX D

LIST OF PUBLICATION

Sowadee Saisopa, Saovalak Sripothongnak, Bunjerd Jongsomjit and Piyasan Praserthdam "The chemistry of scavenger on the catalyst performance based on supported matallocene catalyst" (The proceeding of the 2nd Pure and Applied Chemistry International Conference (PACCON 2014), Khon Kaen, Thailand.

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