EFFECT OF COCATALYST COMBINATION IN TITANIUM-BASED ZIEGLER-NATTA CATALYST ON OLEFIN POLYMERIZATION

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ผลของการรวมกันของตัวเร่งปฏิกิริยาร่วมในตัวเร่งปฏิกิริยาซีเกลอร์-นัตตาที่มีองค์ประกอบของไทเทเนียมต่อพฤติกรรมพอลิเมอร์ไรเซชันของโอเลฟิน

น.ส.ธันยพร พงษ์จันทร์

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Thesis Title	EFFECT OF COCATALYST COMBINATION IN TITANIUM-BASED ZIEGLER-NATTA CATALYST ON OLEFIN POLYMERIZATION
By	Miss Thanyaporn Pongchan
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ธันยพร พงษ์จันทร์ : ผลของการรวมกันของตัวเร่งปฏิกิริยาร่วมในตัวเร่งปฏิกิริยาซีเกลอร์-นัตตาที่มีองค์ประกอบของไทเทเนียมต่อพฤติกรรมพอลิเมอร์ไรเซชันของโอเลฟิน. (EFFECT OF COCATALYST COMBINATION IN TITANIUM-BASED ZIEGLER-NATTA CATALYST ON OLEFIN POLYMERIZATION) อ.ที่ปรึกษาหลัก : ศ. ดร.บรรเจิด จงสมจิตร

งานวิจัยนี้มุ่งเน้นการศึกษาผลของชนิดตัวเร่งปฏิกิริยาร่วม (TEA TnOA และ TEA+TnOA) บนตัวเร่งปฏิกิริยาซีเกลอร์-นัตตาที่มีองค์ประกอบของไทเทเนียม ในโอเลฟินพอลิเมอร์ไรเซชันทั้งระบบเซอลารี่และแก๊สเฟส โดยงานวิจัยนี้แบ่งออกเป็น 4 ส่วน ได้แก่ การใช้ตัวเร่งปฏิกิริยาไทเทเนียมเชิงพาณิชย์เพื่อศึกษาผลของอุณหภูมิต่อปฏิกิริยาและสถานะออกซิเดชันของไทเทเนียมจากเครื่องวิเคราะห์ ESR บนเซอลารี่เอทิลีนและโพรพิวลีนพอลิเมอร์ไรเซชันในส่วนแรกและส่วนที่สองตามลำดับ ตัวเร่งปฏิกิริยาเชิงพาณิชย์กับ TEA ให้ค่าความว่องไวสูงที่สุดในเอทิลีนพอลิเมอร์ไรเซชัน อย่างไรก็ตาม ไดวาเลนซ์และไตรวาเลนซ์ของไทเทเนียม (Ti^{2+} และ Ti^{3+}) ถูกกระตุ้นในเอทิลีนพอลิเมอร์ไรเซชันเพื่อผลิตพอลิเมอร์มากขึ้น เสถียรภาพของไทเทเนียมบวกสามถูกสาธิตเพื่อช่วยการแทรกของหนึ่ง-เฮกซีน ดังนั้นระบบโพรพิวลีนเกี่ยวกับอุณหภูมิปฏิกิริยาจึงนำมาศึกษาเพื่อดูเสถียรภาพของไทเทเนียม (Ti^{3+}) ผลของการใช้เทคนิค ESR พบว่า TEA+TnOA ที่ 50 องศาเซลเซียสสามารถทำให้สถานะไทเทเนียม (III) เสถียร

งานวิจัยในส่วนที่สามและสี่เป็นการศึกษาเปรียบเทียบความแตกต่างของแหล่งแมกนีเซียมที่เป็นตัวรองรับตัวเร่งปฏิกิริยาในแก๊สเฟสเอทิลีนพอลิเมอร์ไรเซชัน [$MgCl_2$ (Cat A) MgO (Cat B) และ $Mg(OEt)_2$ (Cat C)] การปรับปรุงตัวรองรับตัวเร่งปฏิกิริยาสามารถปรับปรุงประสิทธิภาพของตัวเร่งปฏิกิริยาและพอลิเมอร์ ผลที่ได้พบว่า Cat C หรือ $Mg(OEt)_2$ ทำปฏิกิริยากับ TEA แสดงค่าความว่องไวสูงที่สุดทั้งโฮโมและโคพอลิเมอร์ไรเซชันของเอทิลีน การเติมหนึ่ง-เฮกซีนซึ่งเป็นโคโมโนเมอร์สามารถปรับปรุงความว่องไวและเพิ่มการตอบสนองโคโมโนเมอร์ เรียกว่า “ผลของโคโมโนเมอร์” นอกจากนี้พอลิเมอร์ที่ได้ในกระบวนการแก๊สเฟสมีโครงสร้างดีขึ้นกว่ากระบวนการเซอลารี่อย่างชัดเจน

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KEYWORD: Ziegler-Natta catalyst, olefin polymerization, Cocatalyst types, titanium oxidation state, gas-phase polymerization

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This research focused on effect of cocatalyst types (TEA, TnOA, and TEA+TnOA) on titanium-based Ziegler-Natta catalyst in olefin polymerization both in slurry and gas-phase systems. This study has been divided into four sections. The commercial titanium-based catalyst was selected to investigate effect of reaction temperature and oxidation state of titanium from ESR measurement on slurry ethylene and propylene polymerization in the first and the second parts, respectively. The commercial catalyst with TEA exhibited the highest activity in ethylene polymerization. However, divalent, and trivalent of titanium (Ti^{2+} and Ti^{3+}) was active in ethylene polymerization to produce more polymer. Stability of Ti^{3+} was demonstrated to assist insertion of 1-hexene. Hence, propylene polymerization under different reaction temperatures was conducted to evaluate the titanium oxidation state (Ti^{3+}). The ESR results revealed that TEA+TnOA at $50^{\circ}C$ can stabilize titanium (III) state.

Regarding to the third and fourth parts, different magnesium sources supported-catalyst; $MgCl_2$ (Cat A), MgO (Cat B), and $Mg(OEt)_2$ (Cat C); were compared in gas-phase ethylene polymerization. The modification of supported catalyst could improve the performance of catalyst and polymer. The results presented that Cat C or $Mg(OEt)_2$ reacting with TEA showed the highest catalytic activity for both homo- and co-polymerization of ethylene. The addition of 1-hexene as comonomer could improve the activity and higher comonomer response called as “comonomer effect”. Moreover, the polymer obtained in gas-phase process exhibited remarkably better morphology than in slurry process.

Field of Study: Chemical Engineering Student's Signature ....

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Thanyaporn Pongchan

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INTRODUCTION

1.1 General introduction

Plastic is widely used to make everything, such as packaging, bags, bottle, and so on [1, 2]. The plastic is extremely produced and consumed to tend upward nowadays. Due to its low cost to produce, good chemical and mechanical properties, good processability, excellent electrical insulation properties and flexibility, the plastic is also highly popular. One of the most common plastic or polyolefins used is polyethylene (PE). Its primary use is in food packaging, grocery bags, plastic films, bottles, sheets, pipes, plastic wrap etc. Among many types of polyethylene, linear low-density polyethylene (LLDPE) consisting of ethylene and 1-olefins (1-butene, 1-hexene, etc.) is commonly produced. Moreover, the second-most famous plastic is followed by polypropylene. Its properties are similar to polyethylene, but being harder and more heat resistance [3]. Then, the polypropylene production necessary concerns high purity, rigidity, and strength [4]. For good quality of production, the important factor in produced polymer is catalyst used. One of popular catalysts is Ziegler Natta catalyst [5-7] having the high performance in polymerization of olefins. Ziegler Natta catalyst is also selected as the first optional catalysts and utilized in industrial due to low cost, high productivity, less poison, broad molecular weight distribution (MWD) and chemical composition distribution (CCD) when comparison with other catalysts [8]. The main substitution of its catalyst precursor is transition metal (titanium, vanadium or chromium). One important thing in industrial seriously concern is how to control polymer morphology because it affects the mechanical properties of polymer and transportation in process rule [9]. The support is preferred to improve morphology of polymer and protect fouling in the reactor. Generally, magnesium chloride ($MgCl_2$) support [10, 11] on Ziegler Natta catalyst is well known and commonly used in olefins polymerization industry. Moreover, it is one of the most effective supports in modify the structure on surface catalyst to improve morphology and particle size including high catalytic activity. Besides, there are many ways in preparation of $MgCl_2$ support from magnesium source (magnesium ethoxide; $Mg(OEt)_2$, magnesium powder; MgO, and $MgCl_2$) to increase performance of catalyst and polymer. For example, M-catalyst as commercial catalyst prepared from Mg powder to $MgCl_2$ is commonly chosen in olefins polymerization industries. For the purpose that, its support is to control morphology and enhancement of catalyst performance. In previous study, $MgCl_2$ as support was formed by reaction of MgR_2 and cocatalyst for olefins polymerization. Thus, the approach leads to good dispersion of $MgCl_2$ support in immobilization method [12]. The support is one important factor for improvement of potential catalyst.

Not only the support, but also cocatalyst types influence on catalyst and polymer potentially. So, the cocatalyst types are further significant factor in process. The supported catalyst essentially completed with suitable cocatalyst. The optional alkylaluminum groups, AlR_3 as cocatalyst components assist to reduce titanium on the catalyst oxidation state, increase types of active center distribution, and each cocatalyst exhibits reducing power to different catalyst. As the nature of Ziegler Natta catalyst reacted with triethylaluminum (TEA) having high reducing power and this cocatalyst has been selected. Moreover, difference of activator types affected on catalytic activity and polymer properties along with stability of trivalent titanium and

1-hexene insertion is studied. From many researches, effect of the cocatalyst was studied in ethylene polymerization. It showed that TEA exhibited the highest catalytic activity and followed by tri-iso-butyl aluminum (TIBA) and tri-n-octyl aluminum (TnOA). Moreover, alkylation power of the cocatalyst mixture is still determined [13, 14]. This may be the reason for studying one and mixed cocatalyst both in olefins polymerization. To investigate the change of oxidation state of titanium with different cocatalyst affected on insertion of 1-olefins, it brings to polymerization of propylene for checked titanium state.

In addition, gas-phase ethylene polymerization is simple process design, low operating cost, improve incorporation of 1-hexene and controlled morphology of polymer. The commercial catalyst and synthesized catalyst method using tetrahydrofuran (THF) as low price is compared. THF as Lewis base influences to control of morphology's polymer and decrease activity in this process for limited over heat temperature [15].

In the current study, it researches about effects of cocatalyst activation both single and combination cocatalyst on commercial titanium-based Ziegler Natta catalyst with the behaviors of olefins polymerization process comprise of the change trivalent titanium (Ti^{3+}) state and how to develop 1-hexene incorporation on polyethylene.

1.2 Research objective

1) To investigate different cocatalyst activation on a commercial Ti-based ZN catalyst on the change of Ti^{3+} state to behaviors of ethylene polymerization and ethylene/1-hexene copolymerization.
2) To investigate polymerization temperature with different cocatalyst on propylene polymerization using Ti-based ZN catalyst.

3) To investigate the effects of magnesium sources along with different cocatalyst types on catalytic activity and improving morphology in gas-phase ethylene polymerization.

1.3 Research scopes

All parts of this research on difference of cocatalyst types on the Ti oxidation state and catalytic activity with titanium-based Ziegler Natta catalyst in ethylene polymerization, ethylene/1-hexene copolymerization in both slurry phase and gas-phase, and propylene polymerization.

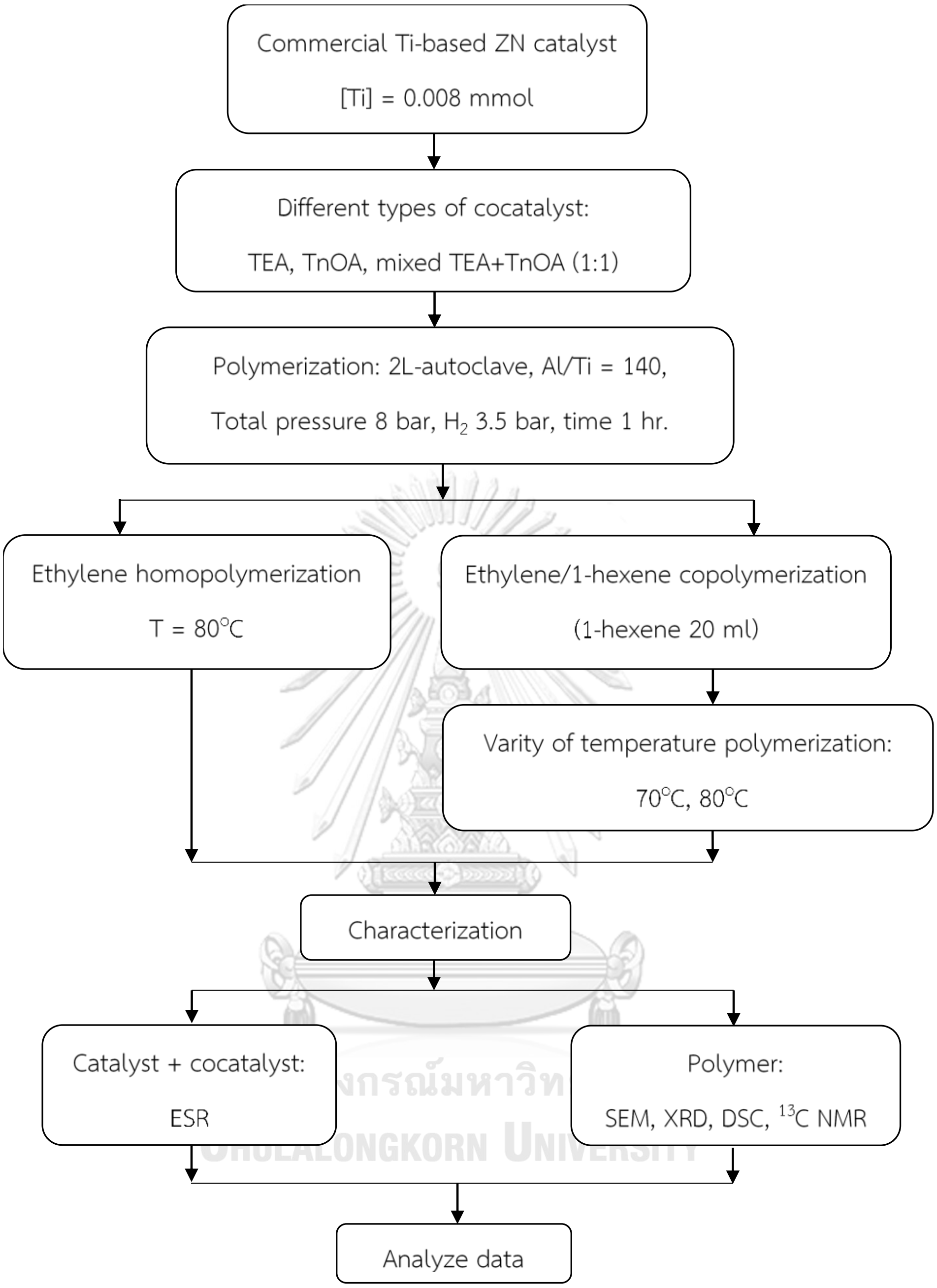
1) The commercial titanium-based Ziegler Natta catalyst was studied in ethylene polymerization, copolymerization of ethylene with 1-hexene, and propylene polymerization.
2) Difference of cocatalyst types in both single cocatalyst (TEA and TnOA) and mixed cocatalyst (TEA + TnOA) was mainly studied in this research.
3) Slurry ethylene polymerization and ethylene/1-hexene copolymerization in 2L-autoclave, Al/Ti molar ratio =140, total pressure 8 bar, partial pressure of hydrogen gas 3.5 bar, time 1 hour, 80°C for homopolymerization, and 70°C and 80°C for copolymerization were performed.
4) Propylene polymerization in 100 ml-stainless steel, total pressure 5 bar, time 15 minutes, Al/Ti molar ratio = 140 was fixed and varied polymerization temperature at 50°C, 60°C, and 70°C.
5) The synthesis of supported-catalyst as different magnesium sources was prepared in gas-phase ethylene polymerization and copolymerization of ethylene with 1-hexene system.

6) Gas-phase ethylene polymerization and ethylene/1-hexene copolymerization in 1L-cylindrical reactor, partial pressure of hydrogen gas 0.5 bar, total pressure 13.5 bar, time 1 hour at 75°C was operated.
7) Characterization of the catalyst by the following method;
    - Inductively Coupled Plasma (ICP)
    - Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)
    - Fourier Transform Infrared Spectroscopy (FTIR)
    - X-ray Diffraction (XRD)
    - Electron Spin Resonance (ESR)
8) Characterization of polymer by the following method;
    - Scanning Electron Microscopy (SEM)
    - Differential Scanning Calorimeter (DSC)
    - X-ray Diffraction (XRD)
    - Carbon-13 Nuclear Magnetic Resonance Spectroscopy (^{13}C NMR)
    - Soxhlet extractor for analyzing isotacticity index (I.I.) and insertion

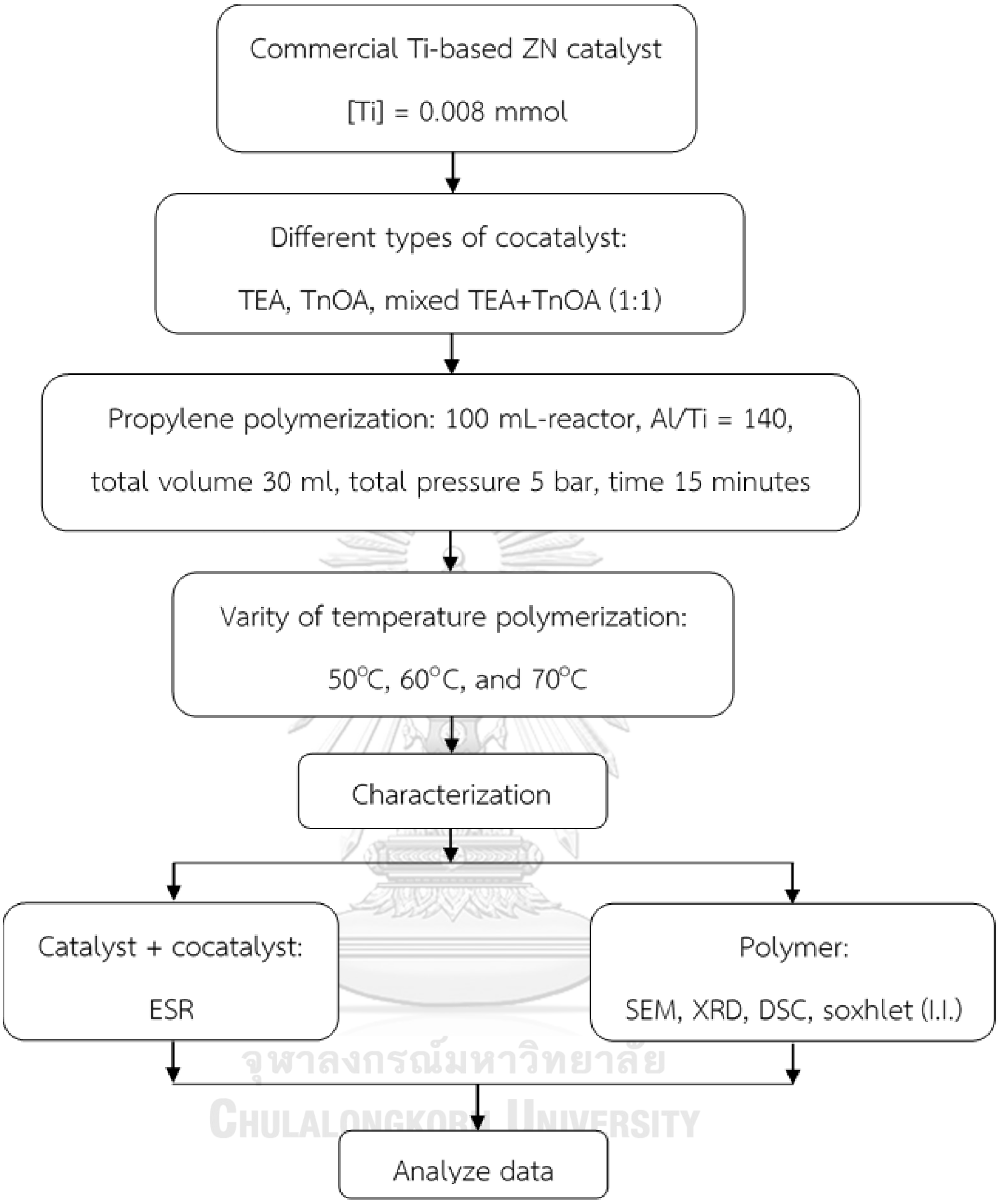
1.4 Research methodology

Research methodology is as shown;

Part I: Facile investigation of Ti^{3+} state in Ti-based Ziegler-Natta catalyst with a combination of cocatalysts using electron spin resonance (ESR)

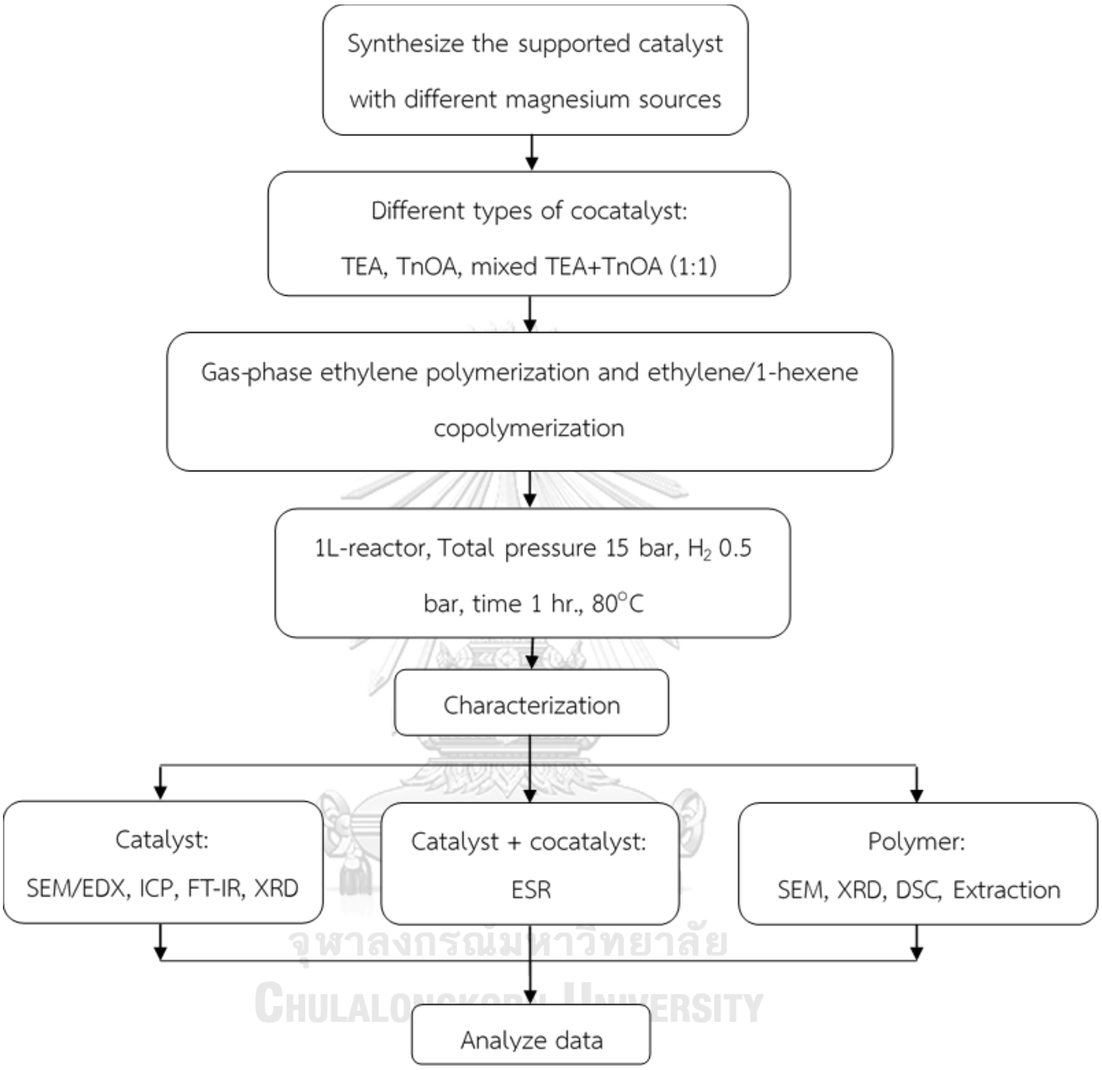


Part II: Temperature effect on propylene polymerization behavior over Ziegler-Natta catalyst with different cocatalyst systems



Part III: Gas-phase polymerization of ethylene over Ti-based Ziegler-Natta catalysts prepared from different magnesium sources and

Part IV: Different magnesium source supported titanium-based Ziegler-Natta catalyst in gas-phase ethylene/1-hexene copolymerization



1.5 Research plan

Table 1. 1 The research plan

Research plan	2017 (Semester)		2018 (Semester)		2019 (Semester)		2020 (Semester)
	1	2	1	2	1	2	1
1. Literature reviews	←	─	─	─	─	─	→
2. Slurry ethylene polymerization and copolymerization of ethylene with 1-hexene			←	→			
3. Characterization of catalyst and polymer	←	─	─	─	─	─	→
4. Propylene polymerization				←	→		
5. Preparation of different magnesium sources				←	─	→	
6. Gas phase ethylene polymerization and copolymerization of ethylene with 1-hexene					←	─	→
7. Results and discussion			←	─	─	─	→

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Polyolefins in industrial

Polyolefins are formed macromolecules by olefin monomer polymerization. The most polyolefins produced are polyethylene (PE) and polypropylene (PP). These polymers are preferable in applications depending on the characteristics of polymer. Molecular properties related to many parameters, such as material fatigue, impact strength, and resistance to degradation. These properties are routinely evaluated as part of research and development (R&D) as well as for quality control and assurance.

Polyolefin polymers have been commonly used as shown in various types;

- Polyethylene (PE) with high density polyethylene (HDPE), low density polyethylene (LDPE), and linear low-density polyethylene (LLDPE)
- Polypropylene (PP)
- Ethylene-propylene rubber (EPR)

The requirements of catalyst for olefins polymerization both slurry and gas-phase polymerization [16] are summarized in **Table 2. 1**.

Table 2. 1 The requirements of commercial catalysts for olefins polymerization

Requirements of process	**Improving polymer properties**
Control morphology of polymer	Chain-transfer and distribution
High productivity	Molecular weight of polymer
Incorporation of comonomer	Bulk density and particle size
Morphology of catalyst	Density and insertion of monomer
Low cost, save environment and reproducible catalyst	

2.1.1 Polyethylene

Polyethylene is probably produced in plastic product and has different molecular weight and structure forms. The operation of polyethylene at low pressure and low temperature produces linear polyethylene with high molecular weight or high-density polyethylene. However, low density polyethylene is produced at high temperature and high pressure. Its polymer occurred from ethylene monomer ($(-CH_2-CH_2-)_n$; n = amount of monomer as shown in **Figure 2. 1**.

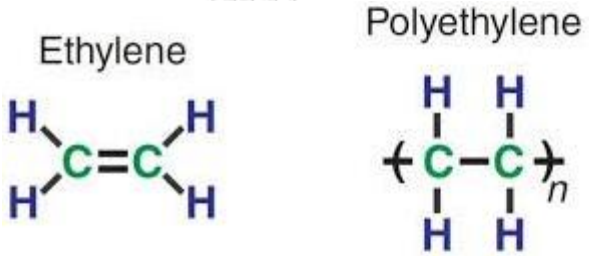


Figure 2. 1 Repeating units of polyethylene

In case of copolymer, 1-olefins have been used in industry process, such as 1-butene, 1-hexene, and 1-octene etc. Comonomer inserted in main chain have effect on degree of crystallinity from c.a.60% as polyethylene to 30-40% as shown semi-crystalline or amorphous *[17]*. The polyethylene has been classified in several types on mechanical properties as presented in **Table 2. 2** [18].

Table 2. 2 Polyethylene classification types

Polyethylene types	Crystallinity (%)	Density (g/cm^3)
Ultra-high molecular weight (UHMWPE)	>65	>0.960
High density polyethylene (HDPE)	60-65	0.941-0.960
Linear low-density polyethylene (LLDPE)	30-45	0.915-0.925
Low density polyethylene (LDPE)	<25	<0.915

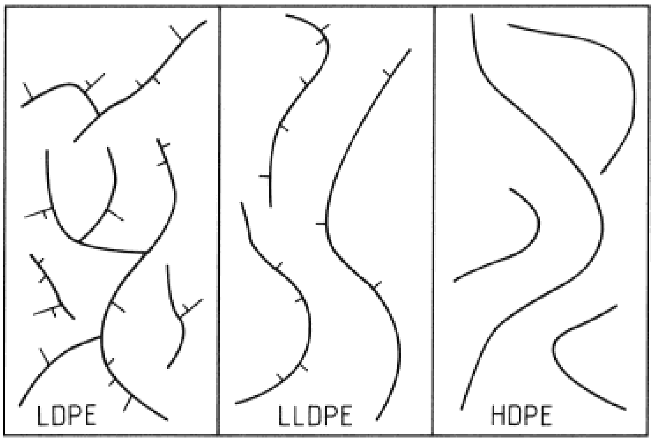


Figure 2. 2 Effect of branching on density

The difference of various polyethylene sheeting liners on density. Each polyethylene types have different its thickness and its flexibility due to molecules bond, structure forms.

High density polyethylene (HDPE) is the toughest, strongest, most chemical resistant of all polyethylene, but has the distinction least flexible plastic sheeting. It is also the most UV resistant packages. Strength of HDPE forms tight structure make it very difficult for other molecules to pass through its structure on a microscopic level. In industrial, the range of thickness is from 12 mils to 100 mils thick. HDPE is used as secondary containment liners for oil tanks, and most industrial ponds and canal liners where chemical resistance is needed. Applications of this are bottle caps, plastic bottles, fuel tanks, gas pipe, and fertilizer bag, etc. [19]

Low Density Polyethylene (LDPE) is the most common plastic sheeting types. It is not as strong or dense as some other types of plastic sheeting. LDPE is formed much flexible from 0.5 mils thick to 40 mils because its flexibility adapts variety of surfaces. LDPE is widely used in agriculture, construction, surface protection applications, and covers of all sorts; tarps, a tubing, plastic wrap, liquid containers, and waterproof membrane.

Linear low-density polyethylene (LLDPE) is the most flexible of polyethylene or the plastic sheeting films. LLDPE is combined form of LDPE that film has much more flexibility, tensile strength, softer and more conformability. Its polymer is used for blended into other films to make more flexibility and extra strength. The most range of common thickness is from 0.5 mils to 40 mils. Examples of this is film products, shopping bags, stretch wrap, toys, etc. It is strong enough to withstand foot traffic, the molecules all line up and strongly hold together as the film is stretched.

The applications of polyethylene depend on types of plastic sheeting to do all sort of thing to protect the surface.

Polyethylene branches is made by free radical polymerization. The metallocene catalyst produces ultra-high molecular weight polyethylene (UHMWPE). In part of Ziegler Natta catalyst, its produces linear polyethylene to more complicated procedure and makes linear density polyethylene (LDPE). For copolymerization of ethylene monomer with alkyl-branched comonomer (short hydrocarbon branches), this are called linear low-density polyethylene (LLDPE). LLDPE is formed ethylene with a comonomer as catchy 4-methyl-1-pentene and it is produced plastic films as shown it below (**Figure 2. 3**).

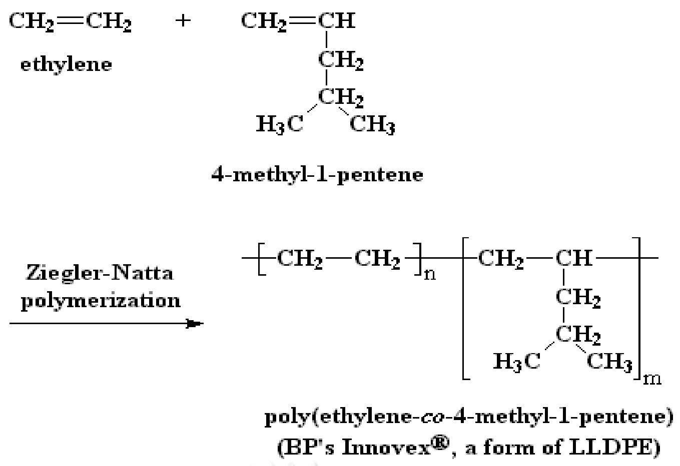


Figure 2. 3 Process of LLDPE from ethylene with 4-methyl-1-pentene

2.1.2 Polypropylene

In 1954, Giulio Natta found that first polymerized propylene to isotactic polymer as crystalline as well as by the German chemist Karl Rehn [20]. However, syndiotactic polypropylene was still synthesized by Natta and group. In 1957, the Italian firm Montecatini discovery led to large-scale commercial production of isotactic polypropylene. Polypropene or polypropylene is introduced chain transfer of polymerization from propene (propylene) of monomer as shown in **Figure 2. 4**. Polypropylene is non-polarity and semi-crystalline. Its features like polyethylene, but it is more heat resistant, higher chemical resistance, tough, flexible, and harder [21]. Polypropylene is the second-most commonly produced plastic.

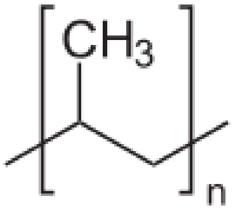


Figure 2. 4 Repeating units of propylene

The properties of polypropylene depend on molecular weight (MW), molecular weight distributions (MWD), stereotactic polypropylene (I.I.), and crystallinity. This arrangement created a greater degree of crystallinity and resulted in **Table 2. 3**. A stiffer material that is more resistant to creep than both atactic polypropylene and polyethylene. It is used in many applications. The production of polypropylene is packaging and labeling, piping, roofing, hinges, carpet, and auto parts.

Table 2. 3 Density of polypropylene

Polymer types	Density (g/cm^3)
Amorphous polypropylene	0.855
Crystalline polypropylene	0.946

Thermal properties, the melting temperature (T_m) of polypropylene showed different values from difference of structure polymer. Isotactic polypropylene has melting temperature around 160-170^{o}C in perfect structure. However, Syndiotactic polypropylene has crystallinity 30% and melting point of 130^{o}C. The thermal of polypropylene is very larger than polyethylene [22, 23]. Atactic polypropylene lacked any regularity which makes it unable to crystallize and amorphous (not crystalline).

The properties of polymer are summarized in **Table 2. 4**.

Table 2. 4 Summary of polymer properties

Polymer	Flexibility	Chemical resistance	Stress Crack	Impact Resistance
HDPE	Flexible (more rigid than LDPE)	Good	Good	
LDPE	Very Flexible	Good	Good	Good
LLDPE	Very Flexible	Good	Good	Good
PP	Rigid for containers	Good	Excellent	Excellent

2.2 Ziegler-Natta catalyst

In the past (1950s -1980), original Ziegler Natta catalyst used active component was titanium trichloride ($TiCl_3$) with usual cocatalyst as triethylaluminum (TEA). Then, to increase catalytic activity for producing linear polyethylene and stereoregular polypropylene was improved from Lewis base (electron donor). In addition, the improvement of Ziegler Natta catalyst was used by support as magnesium chloride ($MgCl_2$) or magnesium alkoxide ($Mg(OR)_2$) and silica (SiO_2) [24-29]. In the 1980s, morphology of Ziegler Natta catalyst was controlled for developed polyolefins and functional process. This process was commanded growing of porous particle with spherical shape. Since 1990s, $MgCl_2$ supported titanium catalyst produced polymer blends with polyolefins for improving mechanical and physical properties [30].

Transition metal catalysts in polyolefins industry was vital. The commercial catalyst in polymerization of olefins has been divided into three types; titanium halide, vanadium /aluminum alkyl or Ziegler Natta catalyst, organometallic (metallocene); titanium, hafnium, and zirconium-based catalyst, and Phillips (chrome-on-silica) catalysts. The Ziegler Natta catalysts were originally based on magnesium supports as $MgCl_2$, but silica was used to be supported its catalyst for produced polyethylene and polypropylene. Hence, ZN catalyst is mainly performed $TiCl_4$ [31].

Active centers of titanium-based catalyst occur around surface of grain particles. The reaction between active titanium species of catalyst and organoaluminium as cocatalyst is catch [32]. Ethylene molecules is inserted into active titanium (Ti-C bond) and growth chain of polyethylene [33]. Mechanism of ethylene polymerization depend on active center structural features and influence on formation of polymer. In addition, ethylene monomer pushed through between titanium active and cocatalyst. All polyethylene formation counts on several factors; ethylene concentration, addition of hydrogen, and temperature.

From more researches [33], summary about active center (C*) in ethylene polymerization introduced it below:

- The C* formation rate extremely depends on temperature.
- The C* formation rate does not rely on the free ethylene concentration. A small ethylene amount is enough to change titanium species on the catalyst surface into C*.
- The C* formation rate does not depend on concentration of TEA or $Al(C_2H_5)_3$ cocatalyst.
- Addition of hydrogen into ethylene polymerization essentially speed up the C* formation stage independently of the catalyst type.
- Incorporation of 1-olefins into ethylene polymerization essentially accelerates the C* formation rate.
- The C* formation rates in ethylene polymerization with various solid and supported catalysts based on different Ti (IV) and Ti (III) species are similar suggested that the nature of immediate precursors to the active centers is similar. Nevertheless, the C* formation rates are noticeably higher when the catalysts are derived from Ti (II) species as shown in **Figure 2. 5**.

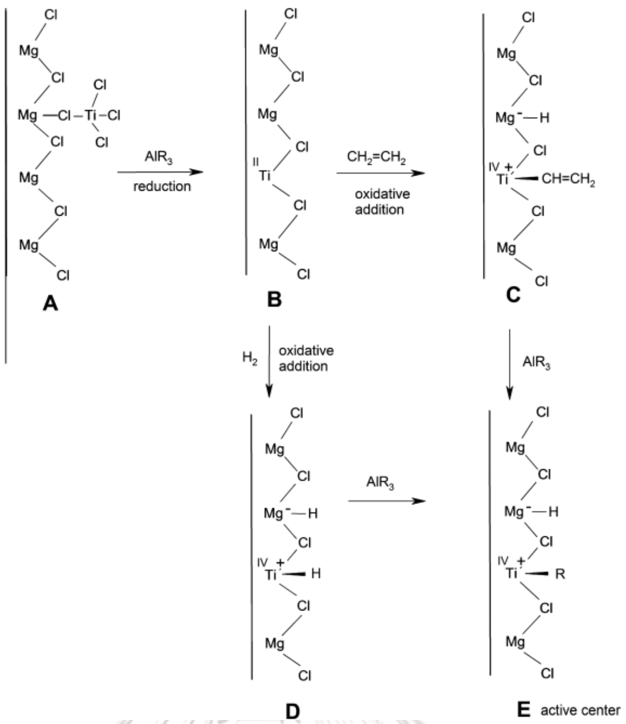


Figure 2. 5 Chemistry formation of active center

Reduction of titanium-based catalyst occurs from reaction of catalyst and cocatalyst from Ti^{4+} to Ti^{3+} and then Ti^{2+} species. Titanium isolated species form the surface of $MgCl_2$ easier than islands species. Due to $MgCl_2$ as Lewis acid withdraws alkyl anions from organometallic compounds [12, 34, 35].

2.2.1 Synthesis Ziegler-Natta catalyst

The supported catalyst was prepared with some Lewis base method, such as alcohol (adduct), tetrahydrofuran (THF), etc. In slurry ethylene polymerization, $MgCl_2$ adducts was commonly arranged by alcohol and this way is the most popular method due to get high activity and yield of polymer. The procedure has two steps; (1) synthesis of $MgCl_2$ support and (2) impregnation of supported with $TiCl_4$. $MgCl_2$ is formed with alcohol in different amounts. Alcohol dispersed into the supported for recrystallized. Other paths were THF. Its material is weak Lewis base that molecular complex formed with transition metal halides [36]. Metal complex are $MCl_3(THF)_3$ (M: metals) and widely used reagents. In the presence of a solid acid catalyst, THF was reacted with hydrogen sulfide to give tetrahydrothiophene [37].

Ziegler Natta catalyst on magnesium supported with tetrahydrofuran (THF) was synthesized to obtain any $TiCl_4(MgCl_2)_x(THF)_y$ complex. Then, the solvent was removed and evacuated [38-40].

$$MgCl_2 + TiCl_4 + THF \longrightarrow (TiCl_4)(MgCl_2)_{3.14}(THF)_x$$

$$MgCl_2 + TiCl_3{\bullet}1/3AlCl_3 + THF \longrightarrow (TiCl_3)(AlCl_3)_{1/3}(MgCl_2)_{3.14}(THF)_y$$

$$MgCl_2 + TiCl_3 + THF \longrightarrow (TiCl_3)(MgCl_2)_{3.14}(THF)_z$$

After that, the complex of support catalyst was impregnated by cocatalyst as TEA being very active in ethylene polymerization. The supported catalyst was performed by THF [15]. Moreover, THF still removed complex form.

Ziegler Natta catalyst synthesis from many titanium sources. The effect of titanium chloride with different oxidation state of titanium, such as titanium tetrachloride ($TiCl_4$), titanium trichloride ($TiCl_3$), and titanium dichloride ($TiCl_2$) was investigated about ethylene/1-hexene copolymerization [41]. This study showed that divalent and trivalent titanium exhibited stable polymerization profile with concentration of cocatalyst increased whereas tetravalent titanium firstly increased and dropped down when increased concentration of activators.

2.3 Preparation method for magnesium Sources ($MgCl_2$)

$MgCl_2$ support was attached by titanium-based Ziegler Natta catalyst in olefin polymerization. $MgCl_2$ support has been prepared in several methods. Ziegler Natta catalyst presented three components on scheme: active titanium/support/carrier.

The first component is active titanium consisting to titanium tetrachloride ($TiCl_4$), titanium trichloride ($TiCl_3$) or titanium alkoxide ($Ti(OR)_4$). The physical catalyst was mainly used a spherical shape of particles. However, fine particles of catalyst were not used. The support performed moderate activity, control morphology of polymer, and high reactive toward olefins. The second component in the major catalyst is support as microcrystalline $MgCl_2$. It associated to enhance activity of the catalyst. There are three preparation methods for formed to $MgCl_2$ support, such as soluble complexes of $MgCl_2$ method, chemical method as Grignard, and grinding method.

2.3.1 Solution method by Magnesium chloride ($MgCl_2$)

Many ways of magnesium chloride support were organized by anhydrous, hydrated, alcohol adducts [38]. After magnesium compound reacted with electron donor (i.e., ester or ether), titanium-based catalyst was added in during the preparation.

N Kashiwa (1980) studied to get a high activity for olefin polymerization by a supporting Ziegler-type catalyst on $MgCl_2$ was carried out. Only heating anhydrous $MgCl_2$ with $TiCl_4$ very little amount of TiCl4 was fixed because of high crystallinity and small surface of anhydrous $MgCl_2$. A pretreatment by some organic electron donner such as butanol or methyl acetate before the reaction with $TiCl_4$, resulted a considerable fixation of $TiCl_4$ onto $MgCl_2$ and gave high activity for ethylene polymerization by 70—90 times of conventional $TiCl_3$ catalyst [42].

2.3.2 Chemical method

Normally, magnesium alkyls and magnesium alkoxides reacts with titanium chloride compound while preparation of catalyst was activated with magnesium chloride support [19, 43].

2.3.2.1 Magnesium alkyls (MgR_2) and Grignard reagents (RMgX)

There is preparation of magnesium source using magnesium alkyls in Ziegler Natta catalyst was synthesized. Using magnesium alkyls (MgR_2) in Ziegler Natta catalyst was furnished by the discovery that magnesium salts [44]. Magnesium alkyls was encompassed both dialkylmagnesium compound (R_2Mg) and Grignard reagents or organomagnesium halides (RMgX) as following below;

$$2RMgX \rightleftharpoons R_2Mg + MgX_2$$

An alkyl halide reacted with magnesium metal in an ether; usually tetrahydrofuran (THF) or diethyl ether produced Grignard reagents. Temperature, rate of addition, rate of stirring, holding times affected on particle size distribution of catalyst. The *tert*-butyl chloride (t-BuCl) was slowly dropped into MgR_2 or dialkylmagnesium compound in the molar ratio of BuCl to MgR_2 and conversed to $MgCl_2$;

$$MgR_2 + 2\ t\text{-}BuCl \longrightarrow MgCl_2 + 2\ t\text{-}BuCl\text{-}R$$

From above reaction, the spherical porous had diameter of 25 – 50 mm. and $MgCl_2$ support was interacted $TiCl_4$ as Ti precursor and then reacted with AlR_2Cl for reducing titanium oxidation states.

$$TiCl_4 + AlR_2Cl \longrightarrow TiCl_3 + AlRCl_2 + R\text{-}R$$

Changing the nature of modified organic compound and varied amount produced active titanium catalyst in olefins [19].

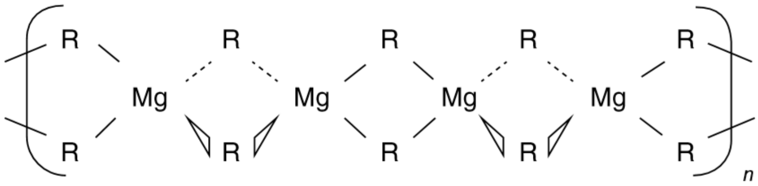


Figure 2. 6 Dialkylmagnesium oligomer structures

Dialkylmagnesium compounds are highly associated structure of linear as shown in **Figure 2. 6**. their magnesium atoms are tetracoordinate. However, excess amounts of ethers exhibited low activity of polymerization because of R_2Mg having poor hydrocarbon solubility in case of high molecular weight of R. Among Grignard reagents were not used in industrial Ziegler Natta catalyst [45].

In many research, magnesium chloride does not directly prepare. However, Grignard reaction between alkylmagnesiumalide (RMgX) and chlorinating agent as $TiCl_4$ was used in this research [46]. It was found that one of the highly effective ways to improve performance catalyst. Propylene polymerization activity increased although it was absence of electron donor. Moreover, chlorination agents have many types, such as alkylhalide (RX), aluminumhalide and thionylhalide ($SOCl_2$) and so on [47, 48].

2.3.2.2 Magnesium alkoxide ($Mg(OR)_2$)

Preparation of magnesium source, alcohol was dispersed into MgRR'. Then, $MgCl_2$ was fell and this form of $MgCl_2$ get high catalytic activity in olefin polymerization [49]. After that, chlorination agent was filled in suitable amount of its material. One of the chlorination agents is titanium chloride ($TiCl_x$). The addition of electron donor was to control particle size distribution of catalyst. Above preparation was mentioned by Shijing *et al* [50]. The interaction between $Mg(OEt)_2$ and $TiCl_4$ as precursor was converted to $MgCl_2$ and complex of magnesium and titanium being $Mg(OEt)_xCl_{2-x}$ and $Ti(OEt)_yCl_{4-y}$; which x = 0-2 and y = 0-4), respectively.

$$TiCl_4 + Mg(OEt)_2 \longrightarrow Mg(OEt)_xCl_{2-x} + Ti(OEt)_yCl_{4-y}$$

$Mg(OEt)_2$ is transformed to $MgCl_2$ in the theory as shown it below.

$$2TiCl_4 + Mg(OEt)_2 \longrightarrow MgCl_2 + 2Ti(OEt)Cl_3 \ / \ MgCl_2 + Ti(OEt)_2Cl_2$$

However, an ethoxyl titanium chloride is really formed;

$$TiCl_4 + Mg(OEt)_2 \longrightarrow Mg(OEt)Cl + Ti(OEt)Cl_3$$

The ethoxyl titanium chloride obtained was removed by dissolved with solvent. Reaction of dibutylmagnesium by *tert*-butyl chloride in a diisoamyl ether-hexane mixture produces $MgCl_2$ with very narrow particle size distribution. Highly porous $MgCl_2$ supports are prepared by the dealcoholysis of a $MgCl_2 \cdot 3EtOH$ adduct. These can react with zirconocene-MAO mixtures to form active supported catalysts for ethylene homo- and copolymerizations. The Cp_2TiCl_2-MAO- $MgCl_2$ catalysts exhibits higher activity in the xylene slurry polymerization of ethylene than does the homogeneous catalyst. Unlike the homogeneous catalyst, the catalyst activity increases with increasing temperature, but when hexane is the diluent, the activity declines above 50°C. A Cp_2ZrCl_2-$MgCl_2$ adduct is more active in ethylene polymerization (heptane slurry) if treated with a trialkylaluminum before contacting with MAO. The number of active sites is only about 20% of those in the homogeneous catalyst. [51]

The using $MgCl_2$ alcohol adduct are interesting for the support catalysts. Over years, many researchers have studied to effective immobilization, activation of catalyst and develop the catalyst. These researchers are shown as follows;

Han Seock C. and Wha Young L., (2003) [52] studied the preparation of $MgCl_2$-alcohol adduct for the impregnation of metallocene catalysts. The supported metallocene catalysts were characterized by XRD, ICP, TGA. This result to be concluded that anhydrous $MgCl_2$ showed a strong XRD pattern at 2 theta = 15, 35 and 50°. However, $MgCl_2$ adduct was found that peak intensities were weaker than anhydrous $MgCl_2$. Then, using TGA shows that $MgCl_2$ adduct desorbed at around 110, 140 and 250°C.

M. Smit et al., (2006) [53] showed that the reaction of AlR_3 with $MgCl_2$-ethanol adduct obtained $MgCl_2/AlEt_n(OEt)_{3-n}$, which gives higher activity than using SiO_2. The develop the support catalyst by using borate immobilization immobilized on $MgCl_2$. This research studied the compare between $MgCl_2$ and SiO_2 in ethylene and propylene polymerization. The results are $MgCl_2$-based support had higher activities than SiO_2-based support. The polymer molecular weight distributions were also somewhat narrower using $MgCl_2$-based support, the results indicating effective retention of the single-site characteristics of the catalyst. The morphology of polymer particle showed $MgCl_2$-derived polymer has spherical polymer having the more porous particle surface.

S. Damavandi et al., (2012) [54] investigated $MgCl_2$ may work as an activator for the bis(phenoxy-imine)Ti complexes since these complexes possess O and N heteroatoms in the ligands, which are capable of electronically interacting with $MgCl_2$. Thus, researcher decided to investigate $MgCl_2$ as an activator for the bis(phenoxy-imine)Ti complexes in the hope of developing high performance catalysts based on these complexes.

The use of a carrier in organometallic catalysts makes it possible to modify their catalyst performance in polymerization processes. Both SiO_2 and $MgCl_2$ may be employed as carriers for post-metallocene catalysts, with the latter obtained predominantly by thermal dealcoholizing of the adduct of $MgCl_2$ and alcohol, or its reaction with an alkylaluminium compound.

2.3.3 Grinding method

This procedure is to change physical properties of magnesium chloride ($MgCl_2$) for requested. This system is suitable with stopped-flow due to get high activity in the first period and reaction was stopped before catalyst was deactivated.

2.3.3.1 Ball Milling technique

Ball-milled solid or synthesis of solid-state was one of the most important industrial processes used in nanomaterials. Ball milling is a grinding method that grinds nanotubes into extremely fine powders. This process usually used spherical stainless steel balls, ceramic, flint pebbles, and alloying mechanical [19]. The quality of dispersion was improved, and functional groups was introduced onto nanotube surface. The milling time, speed of rotation, size of balls was the factor to affect to quality of dispersion [55].

2.3.3.2 Spray Drying technique

Spray drying is a technique of producing a dry power from slurry of liquid by using hot gas for elimination of moisture. This method is thermally-sensitive drying such as pharmaceuticals and foods [56]. A particle size distribution was controlled from spray drying some industrial products (i.e., catalysts). The spray nozzle to disperse, variety of factors, namely the spray dryer design, the feed characteristics and the processing parameters influenced on spray dryers. Fine particle powder is produced to occur in both poorly flow and dust, and then new generation of spray dryers called multiple effect spray dryers have been produced.

2.4 Cocatalysts or Aluminum Alkyls

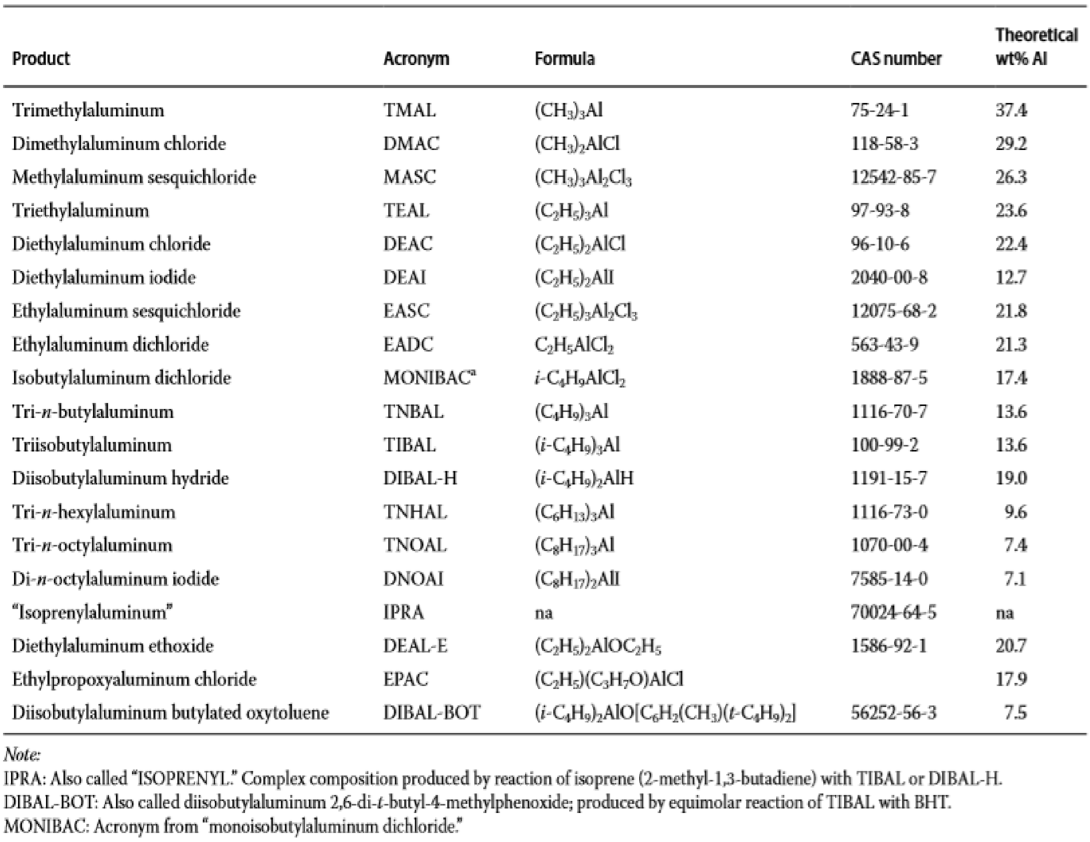
The alkyl aluminum included a direct carbon-aluminum σ-bond and encircled sesquichlorides (R_3Al, R_2AlCl, and $R_3Al_2Cl_3$) as shown in **Table 2. 5**. Ziegler Natta catalyst were worked with cocatalyst or alkylaluminum compound (sometimes called “activators”) to improve catalyst for activated form. The cocatalysts were the key role of activated catalyst in olefin polymerization. Moreover, important ways to produce stereoregular polymer, especially ethylene and propylene. The stereospecific polymer or structure of polymer lead to polymer chain closed packing and high crystallinity [40]. Trialkyl aluminum compounds are promoted over the halogen of catalyst. There are some alkylaluminums, such as triethylaluminum (TEA), trimethylaluminum (TMA), tri-n-octyl aluminum (TnOA), tri-n-hexyl aluminum (TnHA), triisobutylaluminum (TiBA), and diethyl aluminum chloride (DEAC) have been studied in olefin polymerization [42, 49, 57-61]. Moreover, they still assist to insert of monomer to provide active form. Cocatalyst changed oxidation state of titanium-based catalyst from tetravalent (Ti^{4+}) to trivalent (Ti^{3+}) and divalent (Ti^{2+}) state [62]. Based on olefin polymerization, ethylene polymerization has active all titanium oxidation state (i.e., tetravalent (Ti^{4+}), trivalent (Ti^{3+}), and divalent (Ti^{2+})). For ethylene/1-olefins copolymerization was active both Ti^{4+} and Ti^{3+}, titanium (IV) produces low molecular weights and high comonomer contents. On the contrary, titanium (III) produces high molecular weights. Either way, the same titanium state in ethylene/1-olefin copolymerization (tetravalent and trivalent) is active for propylene polymerization [41, 63]. However, stereospecificity and catalytic activity still depended on the structure of cocatalyst. In addition, aluminum alkyls also scavenged poison in catalyst, such as oxygen, moisture, others impurity. Contaminants were eliminated by poison in polyolefin process [64]. Each cocatalyst types showed different activity and yields.

- **Synthesis of catalyst with metal alkyls**

"Pre-catalyst” occurs the reduction of metal catalyst ($TiCl_4$) with ethyl aluminum sesquichloride ($(C_2H_5)_3Al_2Cl_3$);

$$2\mathrm{TiCl_4} + 2(\mathrm{C_2H_5})_3\mathrm{Al_2Cl_3} \rightarrow 2\mathrm{TiCl_3} + 4\mathrm{C_2H_2Al_2Cl_2} + \mathrm{C_2H_4} + \mathrm{C_2H_6}$$

Table 2. 5 Commercially available alkyl aluminum



Product	Acronym	Formula	CAS number	Theoretical wt% Al
Trimethylaluminum	TMAL	$(CH_3)_3Al$	75-24-1	37.4
Dimethylaluminum chloride	DMAC	$(CH_3)_2AlCl$	118-58-3	29.2
Methylaluminum sesquichloride	MASC	$(CH_3)_3Al_2Cl_3$	12542-85-7	26.3
Triethylaluminum	TEAL	$(C_2H_5)_3Al$	97-93-8	23.6
Diethylaluminum chloride	DEAC	$(C_2H_5)_2AlCl$	96-10-6	22.4
Diethylaluminum iodide	DEAI	$(C_2H_5)_2AlI$	2040-00-8	12.7
Ethylaluminum sesquichloride	EASC	$(C_2H_5)_3Al_2Cl_3$	12075-68-2	21.8
Ethylaluminum dichloride	EADC	$C_2H_5AlCl_2$	563-43-9	21.3
Isobutylaluminum dichloride	MONIBAC[a]	i-$C_4H_9AlCl_2$	1888-87-5	17.4
Tri-*n*-butylaluminum	TNBAL	$(C_4H_9)_3Al$	1116-70-7	13.6
Triisobutylaluminum	TIBAL	$(i\text{-}C_4H_9)_3Al$	100-99-2	13.6
Diisobutylaluminum hydride	DIBAL-H	$(i\text{-}C_4H_9)_2AlH$	1191-15-7	19.0
Tri-*n*-hexylaluminum	TNHAL	$(C_6H_{13})_3Al$	1116-73-0	9.6
Tri-*n*-octylaluminum	TNOAL	$(C_8H_{17})_3Al$	1070-00-4	7.4
Di-*n*-octylaluminum iodide	DNOAI	$(C_8H_{17})_2AlI$	7585-14-0	7.1
"Isoprenylaluminum"	IPRA	na	70024-64-5	na
Diethylaluminum ethoxide	DEAL-E	$(C_2H_5)_2AlOC_2H_5$	1586-92-1	20.7
Ethylpropoxyaluminum chloride	EPAC	$(C_2H_5)(C_3H_7O)AlCl$		17.9
Diisobutylaluminum butylated oxytoluene	DIBAL-BOT	$(i\text{-}C_4H_9)_2AlO[C_6H_2(CH_3)(t\text{-}C_4H_9)_2]$	56252-56-3	7.5

Note:
IPRA: Also called "ISOPRENYL." Complex composition produced by reaction of isoprene (2-methyl-1,3-butadiene) with TIBAL or DIBAL-H.
DIBAL-BOT: Also called diisobutylaluminum 2,6-di-*t*-butyl-4-methylphenoxide; produced by equimolar reaction of TIBAL with BHT.
MONIBAC: Acronym from "monoisobutylaluminum dichloride."

2.4.1 Triethylaluminum (TEA)

Triethylaluminum (TEA) as commonly used cocatalyst is reported being effective cocatalyst and the highest catalytic activity and important in Ziegler Natta catalyst [65].

Key reactions in Ziegler Natta catalyst process reacted with TEA as shown in hydrogenation and addition as presented in **Figure 2. 7**:

$$\text{Hydrogenation}: \ 2(C_2H_5)_3Al + Al + 3/2H_2 \rightarrow 3(C_2H_5)_2AlH$$

$$\text{Addition}: \ 3C_2H_4 + 3(C_2H_5)_2AlH \rightarrow 3(C_2H_5)_3Al$$

$$\text{Overall reaction}: \ 3C_2H_4 + Al + 3/2H_2 \rightarrow (C_2H_5)_3Al$$

Figure 2. 7 The reactions of cocatalyst

- **Metal alkyls as cocatalysts in synthesis of catalyst:**

Titanium trichloride ($TiCl_3$) was reacted with triethylaluminum (TEA) in the alkylation of the transition metal compound reaction and reduced to produce active sites in polymerization as shown in **Figure 2. 8**. The interaction of catalyst with cocatalyst leads to transition oxidation state [63, 66, 67]. One of alkyl group in cocatalyst incorporates with transition metal; ethyl group of TEA as cocatalyst displaces in chlorine ion of $TiCl_4$ as catalyst

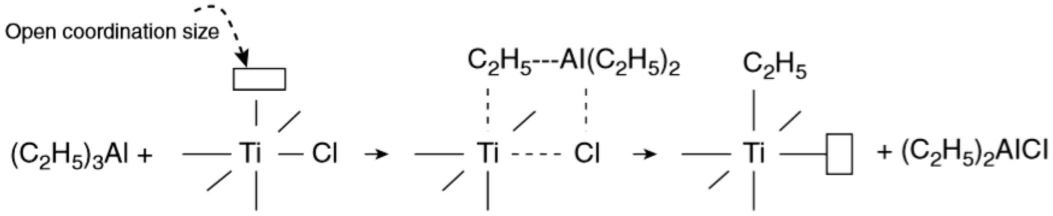


Figure 2. 8 Alkylation of the transition metal compound

Titanium tetrachloride ($TiCl_4$) with cocatalyst mechanism process showed alkylation reactions as predication of basic steps;

$$TiCl_4 + AlEt_3 \rightarrow EtTiCl_3 + AlEt_2Cl$$

$$TiCl_4 + AlEt_2Cl \rightarrow EtTiCl_3 + AlEtCl_2$$

$$TiCl_4 + AlEtCl_2 \rightarrow EtTiCl_3 + AlCl_3$$

Titanium has been formed in active forms, which are Ti-C_2H_5 bond [17]. The chain propagation of ethylene occurs at Ti-C bond as vacant site of active centers at

π-complex, and then vacant site is free again and correlated with next ethylene molecule. Ethylene grows on the catalyst surface as shown in **Figure 2. 9**.

Because of Ti-C (alkyl) is unsteady, the monomer inserts into Ti-C (alkyl) bond, while difference on the contributor of Al-alkyl to Ti-alkyl. The coordination of Al-alkyl is stabilized Ti-C_2H_5 active sites.

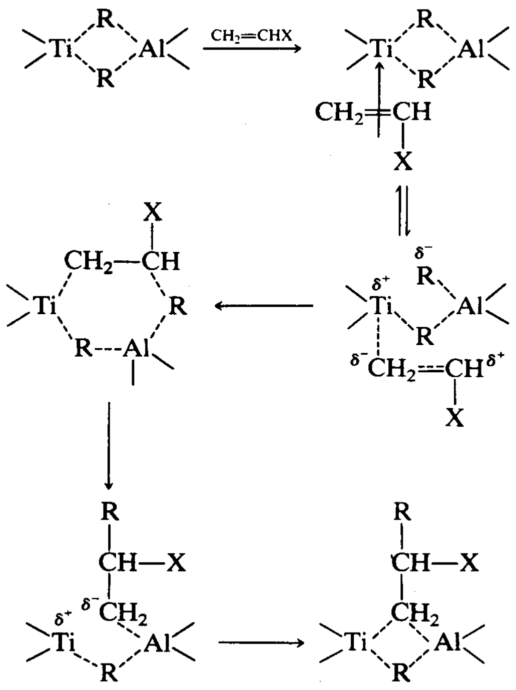


Figure 2. 9 The propagation step of ethylene on active catalyst

The termination step, polymer chain removes from active centers reaching to lower propagation rate [68]. Nevertheless, termination of polymer occurs from transfer of monomer to titanium. Monomer or hydrogen is used to done reaction of chain transfer.

Alkyls aluminum still assist to scavenge impurities or contaminants and poisons, such as oxygen, moisture, etc. Normally, alkylaluminum reacts with the catalyst, and then alkyls aluminum is used in more amounts than catalyst for scavenge.

Polymerization time influences on the nature of catalyst. Cocatalyst types have affected on productivity of polymer. Moreover, molar ratio of Al/Ti, contacting time of catalyst with cocatalyst, polymerization condition, etc. were studied in many researchers [65]. Among modify of the catalyst has been achieved performance and product.

The other resulted [69] about titanium complexes on $MgCl_2$ support were higher activity than the absence of support, and then the activators change in efficiency as following by; MAO > Me_3Al > Et_3Al > Et_2AlCl > $EtAlCl_2$, while the last two of all offer negligible yields of polymer only.

2.4.2 Combination of cocatalysts

Mixed cocatalyst has also been found to generate new alkyl group around aluminium. Mixture of TEA+TIBA in propylene polymerization. The study by Zhang B. *et al.* [70] revealed that the catalyst activated with TEA/TiBA mixture had the highest catalytic activity in propylene polymerization and highly isotactic polypropylene chains. Mixed cocatalyst showed the fast alkyl exchanges in mixture between different cocatalyst types. Effect of TEA and TiBA mixture in propylene polymerization exhibited less power of alkylation and lower Lewis acidity than pure TEA.

From research of D. Liu et al., (2006) [71] studied compared with different cocatalyst types (Et_3Al, He_3Al, Me_3Al with MAO) over bis(phenoxy-imine)zirconium complexes. The activity of complexes 1 with Et_3Al is as well as with MAO at the same Al/Zr molar ratio, while the activity of others cocatalyst is lower than with

MAO. It resulted that the activity of cocatalyst had efficiency as follow in the order Et_3Al > Me_3Al > He_3Al.

Not only oxidation state of titanium as active center, but also molecular weight distribution of polymer is influenced by cocatalysts types. Fukuda *et al*. studied molecular weight distribution of polyethylene variety induced by different cocatalyst types (triethylaluminum; TEA and diethylaluminumchloride; DEAC) using silica supported Ziegler Natta catalyst [72]. This resulted that cocatalyst types affect on active site multiplicity and effect on polymer properties. This purposed that increase of molecular weight maybe due to occur cocatalyst chain transfer [73]. The diffusion of cocatalyst on catalyst to active site depends on bulky group size. Hence, chain of polymer from bulky cocatalysts became long, concluding in high molecular weight of polymers [74].

2.5 Olefins Polymerization

2.5.1 Slurry polymerization processes

This process is one of the most process in olefins production. The advantages of this process are mainly simple process, high yields, high conversions, high purity product, and easy to remove heat [75]. Normally, slurry polymerization was operated around 80 to 110°C. Diluents with inert gas are usually fulfilled hydrocarbons, such as hexane, heptane, propane. Polyolefins was suspended in diluent. Generally, the conversion of ethylene to polyethylene is around 98% and in case of propylene conversed to polypropylene is lower (c.a. 90%) than polyethylene. Ethylene polymerization is also enabled direct recycle of diluent back to reactor, which is without purified, drying, and classified oligomer system.

2.5.2 Gas-phase ethylene polymerization

Slurry reactors are commonly used in laboratory studies of olefins polymerization and more than preferable gas-phase reactors. Including semi-batch slurry process is still easier to operate than semi-batch gas-phase process. Gas-phase system has substantially produced for polyolefins in commercial production [76]. The problem in its process has two main operation. For example, temperature control and typical suspension of particles or stirring [77, 78]. Heat exchange of active sites in core catalyst influenced on effective surrounding for gas-phase being poor heat transfer and removal heat to the surface reactor [79]. Hence, the chain transfer of polymer had higher temperature than measured in the autoclave. Too high temperature affects on deactivation of catalyst and maybe melted polymer to cover catalyst. Nevertheless, design of gas-phase and operating methods and conditions relieved these problems.

From comparing of slurry and gas-phase polymerization, slurry process requires solvent for improving dispersion of catalyst. The advantages of slurry process are to control temperature in system but purification of solvent, removal of solvent, recycle of solvent, and drying production necessarily have this section. The other process is lower cost in plant [80] and save environment [81].

CHAPTER 3

EXPERIMENTAL

This chapter describes about all chemical materials, the preparation of supported catalyst, olefins polymerization procedure consisting of slurry polymerization of ethylene, propylene, and ethylene/1-hexene copolymerization and gas-phase reaction for both ethylene polymerization and copolymerization of ethylene/1-hexene. Moreover, characterization techniques of the catalyst and polymer are also explained.

3.1 Chemicals

The chemical materials used in this research were specified with details as following below;

Chemicals	Donation/Supplier
Anhydrous magnesium chloride ($MgCl_2$)	Thai Polyethylene Co., Ltd.
Magnesium oxide (MgO)	Thai Polyethylene Co., Ltd.
Magnesium ethoxide ($Mg(OEt)_2$)	Thai Polyethylene Co., Ltd.
Commercial titanium-based catalyst	Thai Polyethylene Co., Ltd.
Triethylaluminum (TEA)	Thai Polyethylene Co., Ltd.
Tri-n-octyl aluminum (TnOA)	Thai Polyethylene Co., Ltd.
n-hexane for polymerization grade	Thai Polyethylene Co., Ltd.
Titanium tetrachloride ($TiCl_4$)	Merck Ltd.
Tetrahydrofuran (THF)	Sigma-Aldrich Inc.
Ethanol	Sigma-Aldrich Inc.
Heptane (C_7H_{16})	Sigma-Aldrich Inc.

Chemicals	Donation/Supplier
Ethylene gas (C_2H_4)	Linde (Thailand) PLC.
Propylene gas (C_3H_6)	Linde (Thailand) PLC.
1-hexene (1-C_6H_{12})	Thai Polyethylene Co., Ltd.
Hydrogen gas (H_2)	Linde (Thailand) PLC.
Argon gas (Ar)	Linde (Thailand) PLC.
Nitrogen gas (N_2)	Linde (Thailand) PLC.
Sodium chloride (NaCl 0.5 mm.)	Fisher Co., Ltd.

3.2 Titanium-based ZN catalyst preparation method

3.2.1 Commercial titanium-magnesium supported Ziegler-Natta catalyst (TMC)

The industrial titanium-based Ziegler-Natta catalyst (M-cat) for polyethylene production was supplied from Thai Polyethylene Co., Ltd. M-catalyst was prepared from magnesium powder source by Grignard method. This catalyst was used for catalyzing ethylene polymerization and reacting with cocatalyst.

3.2.2 Preparation of $TiCl_4/MgCl_2/THF$ supported catalyst

The $MgCl_2$-supported Ziegler-Natta catalyst was synthesized under nitrogen atmosphere. First, anhydrous $MgCl_2$ supports (2 g) was added into 500 ml three-neck flask with magnetic stirrer and followed by 150 ml tetrahydrofuran (THF) at room temperature. After 1-hour of the mixture, 2 ml titanium tetrachloride ($TiCl_4$) was slowly dropped. The flask was heated to reflux at 70°C and kept it constant for 2 hours. The supported catalyst was washed out more than five times with n-hexane, dried under vacuum, and stored in glove box.

3.2.3 Preparation of magnesium powder supported catalyst

First, 2 g of magnesium powder, 250 ml of n-hexane, and iodine were consequently added into 500 ml glass flask with magnetic stirrer at room temperature. Then, the desired amount of ethanol and titanium precursor (titanium alkoxide) were introduced, respectively. The flask was suddenly heated up to 80°C and maintained at this temperature for 2 h. After that, 10 ml of titanium tetrachloride and n-butyl chloride (BuCl) having molar ratio of BuCl:Mg = 0.75:1 was slowly dropped around 10 min. The brown slurry mixture was observed. The catalyst slurry was purified by washing with n-hexane for seven times and dried under vacuum [82].

3.2.4 Preparation of magnesium ethoxide supported catalyst

A mixture of 2 g of $Mg(OEt)_2$ and n-hexane was added into the 500 mL four-necked round bottom flask with magnetic stirrer. Under controlled low temperature, 10 ml of $TiCl_4$ was slowly dropped and heated up to 70°C within 1 h and kept at this temperature for 2 h. Then, the mixture was cooled down and washed with n-hexane for seven times to obtain the final catalyst.

3.3 Slurry ethylene polymerization and ethylene/1-hexene copolymerization

Ethylene polymerization and ethylene/1-hexene copolymerization were executed in 2L-autoclave equipped with monitoring stirrer. The reactor directly linked with nitrogen, hydrogen and ethylene gases line. Before polymerization, the autoclave was dried by heating at 70°C under vacuum and purged with nitrogen gas more than three times for purify system. After that, dry nitrogen gas was accumulated in the system for 50 minutes. Designed volume of n-hexane was injected into the reactor under nitrogen gas. Cocatalyst types (TEA, TnOA, and combination of TEA and TnOA) and slurry commercial catalyst were introduced in

Al/Ti molar ratio at 140. Then, atmosphere nitrogen gas and hydrogen 3.5 bars were filled into the reactor, respectively. At 80°C, ethylene gas was kept continuously within the autoclave at total pressure of 8 bars during polymerized for 1 hour. Finally, the obtained polymer was dried and filtered at room temperature. Ethylene/1-hexene copolymerization was conducted under the similar procedure. The addition of 20 ml of 1-hexene as comonomer was performed after feeding solvent. Moreover, copolymerization of ethylene with 1-hexene was varied by comparing the polymerization temperature at 70 and 80°C.

3.4 Propylene polymerization

The propylene polymerization was carried out in 100 ml semi-batch stainless steel reactor with a magnetic stirring bar. Preparation of all chemicals including to solid titanium-based catalyst powder, n-hexane as solvent, and cocatalyst (TEA, TnOA, and mixtures of TEA and TnOA) was conducted under argon atmosphere in glove box. The desired amount of Al/Ti molar ratio was at 140 and cocatalyst with solvent (total volume 30 ml) was successively added into the reactor and followed by catalyst. The reactor was evacuated and filled propylene gas for many times to purify system at different polymerization temperature (50, 60, and 70°C). Gaseous propylene at 5 bars was supplied to the reactor and kept constant during the reaction for 15 minutes. The termination of polymerization was stopped by adding acidic solution with excess methanol. The polymer was precipitated and vacuum dried.

3.5 Gas phase ethylene polymerization and ethylene/1-hexene copolymerization

The gas phase ethylene polymerization and copolymerization of ethylene with 1-hexene were performed in 1L-semi-batch cylindrical reactor. The reactor was related to all purified gas line. First, 80 g of NaCl was added into the reactor, and then the autoclave was dried by heating it with evacuation at 90°C overnight for removal of moisture. After the system was evacuated and flushed with dry nitrogen for five times, nitrogen gas was introduced at 0.5 bar. In case of copolymerization at 70°C, 10 %vol of 1-hexene was added and stirred. After 25 minutes, cocatalyst was injected into the reactor for scavenging of impurity. Then, feeding catalyst by purged nitrogen gas of 1.5 bar and stirring for 30 minutes was elucidated. After that, pressurized 0.5 bar of hydrogen gas was filled. The ethylene gas was immediately filled to autoclave to control a total pressure 15 bar and continuously fed during polymerization. After 1-hour polymerization, the ethylene gas was stopped by released pressure and cooled down the reactor. The solid polymer was washed by DI water to remove salt, and then dried at 60°C.

3.6 Characterization of catalyst and polymer

3.6.1 Inductively Coupled Plasma (ICP)

The titanium (Ti) and aluminium (Al) element contents in bulk of solid supported catalyst were determined by inductively couple plasma optical emission spectrometer (ICP-OES) on a 2100 DV from Perkin Elmer. The sample was seriously weighted of 0.01 g and dissolved with hydrochloric acid (5 ml), and then DI water diluted the solution. The energy from coupled plasma was used in this instrument.

3.6.2 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

The catalyst and polymer morphology were observed using SEM on JEOL model S-3400, while the element contents on surface of supported catalyst was performed by EDX using Link Isis series 300 program.

3.6.3 Fourier Transform Infrared Spectroscopy (FTIR)

Functional groups of supported catalyst were identified by Fourier transform infrared spectroscopy (FT-IR) using Nicolet 6700 FT-IR measurement. The sample was analyzed in the scanning range of 4000-500 cm^{-1}. The solid catalyst was covered on NaCl disk under argon atmosphere.

3.6.4 X-ray Diffraction (XRD)

Powder XRD measurement of the catalyst and polymer was carried out using Bruker of D8 Advance model. This analyzer was to investigate crystalline phases and crystallinity of catalyst and polymer. The time per step was 0.3 and the scan size was 0.02° and used in the diffraction 2Θ range = 10° to 70°.

3.6.5 Electron Spin Resonance (ESR)

The interaction between slurry catalyst and cocatalyst was determined by ESR using Bruker Elexys 500 model to study about intensity of titanium oxidation state (unpaired electron of titanium). The samples were prepared under argon atmosphere in glove box. This technique was operated as following polymerization temperature for 90 minutes and recorded for each 15 minutes until operation.

3.6.6 Differential Scanning Calorimeter (DSC)

Melting temperature (T_m) and crystallinity percentage ($\%X_c$) were determined by DSC analysis. The stepwise annealed fraction DSC analysis was performed with TA Instrument SDT Q600 V.81 Build 99. The heating rate of 10°C/minute in temperature from 20 to 300°C was studied. The crystallinity of polymer can calculate from equation below;

$$\%X_c = \frac{\Delta H}{\Delta H^0} \times 100$$

Where;

ΔH refers to heat of fusion of polyethylene and polypropylene sample

ΔH^0 refers to heat of fusion of polyethylene and polypropylene reference having 291.7 J/g and 207 J/g, respectively.

3.6.7 Carbon-13 Nuclear Magnetic Resonance (^{13}C NMR)

The insertion of comonomer in main chain polymer was also analyzed by ^{13}C NMR Bruker DRX 500 spectrometer. The polymer samples were dissolved in benzene-D6 and recorded at 125°C. The pulse angle 90° and a pulse interval of 12 sec were studied.

3.6.8 Kumagawa Soxhlet Extractor

A Soxhlet extractor based on Kumagawa extractor was used to study the isotactic index (I.I.) of polypropylene. Using 1 g sample in filtered paper was extracted with boiling n-heptane for 6 hours, and then the insoluble part was dried and taken the isotactic index. In addition, copolymer from gas-phase copolymerization of ethylene with 1-hexene was analyzed in this measurement for observed amorphous and crystallize of polymer.

CHAPTER 4

RESULTS AND DISCUSSION

This topic has been divided into 4 main parts. All this section, the effect of cocatalyst types in titanium-based Ziegler-Natta catalyst on olefin polymerization is studied. The commercial catalyst and different magnesium sources are used in first two parts and Part 3, 4, respectively. All parts studied about effect of cocatalyst types (TEA, TnOA, and TEA+TnOA).

Facile investigation of Ti^{3+} state in Ti-based Ziegler-Natta catalyst with a combination of cocatalysts using electron spin resonance (ESR)

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Part 1: Facile investigation of Ti^{3+} state in Ti-based Ziegler-Natta catalyst with a combination of cocatalysts using electron spin resonance (ESR)

Abstract

This study aims to investigate the influences of a combination of cocatalysts including triethylaluminum (TEA) and tri-n-octylaluminum (TnOA) for activation of a commercial Ti-based Ziegler-Natta catalyst during ethylene polymerization and ethylene/1-hexene copolymerization on the change in Ti^{3+} during polymerization. Thus, electron spin resonance (ESR) technique was performed to monitor the change in Ti^{3+} depending on the catalyst activation by a single and combination of cocatalyst. It revealed that the amount of Ti^{3+} played a crucial role on both ethylene polymerization and ethylene/1-hexene copolymerization. For ethylene polymerization, the activation with TEA apparently resulted in the highest catalytic activity. The activation with TEA+TnOA combination exhibited a moderate activity, whereas TnOA activation gave the lowest activity. In case of ethylene/1-hexene copolymerization, it revealed that the presence of 1-hexene decreased activity. The effect of different cocatalysts tended to be similar to the one in the absence of 1-hexene. The decrease of temperature from 80 to 70 °C in ethylene/1-hexene copolymerization tended to lower catalytic activity for TnOA and TEA+TnOA, whereas only slight effect was observed for TEA system. The effect of different cocatalyst activation on the change of Ti^{3+} state of catalyst was elucidated by ESR measurement. It appeared that the activation of catalyst with TEA+TnOA combination essentially inhibited the reduction of Ti^{3+} to Ti^{2+} leading to lower activity. Furthermore, the polymer properties such as morphology and crystallinity can be altered by different cocatalysts.

Keywords: Ethylene polymerization; Ziegler-Natta catalyst; Cocatalysts; Titanium oxidation state; Electron spin resonance

4.1 Introduction

Currently, the demand of plastics leads to high productivity of polyolefins, especially films for bags, sheets, and the packaging industry. Plastics are made from different structure of polyolefins such as polyethylene (PE) and polypropylene (PP), but somehow those popularly produced from polyethylene are widely used [83, 84]. Linear-low density polyethylene (LLDPE) as linear polymer with short branches is one of the most consumption of PE and importance in industries. LLDPE is produced by copolymerization of ethylene and higher olefins such as 1-butene, 1-hexene, 1-octene, etc. The insertion of olefins as comonomer can be obtained differently depending on various comonomer sizes, its content, its structure, catalysts and cocatalysts used, and condition of polymerization. It is well known that types of catalyst play important roles on improvement of polymerization process and activity. The productions of this copolymer normally undergo using supported metallocene catalyst or Ziegler-Natta catalysts (ZN) with proper cocatalysts [85-87]. In fact, the metallocene catalysts as single site catalyst produces polymers with narrow molecular weight distribution (MWD) and chemical composition distribution (CCD) including high insertion of comonomer. Conversely, the Ziegler-Natta catalysts generate polymers with broader MWD and CCD. Although metallocene catalyst is an effective catalyst, it only shows enhancement of 1-olefins insertion in polymer chain without increasing catalytic activity [88]. In industrial scale, the metallocene catalysts can be used in ethylene polymerization [89], but the polymerization system is more sensitive and it requires large amounts of cocatalyst such as methylalumoxane (MAO) [87, 90, 91]. It is necessary to rely on more suitable catalyst for improving properties of polymer and easy control of the catalytic system.

Ziegler-Natta catalyst is one of the most suitable choices of catalysts in the polyolefins industry used to control mechanical polymer properties having high catalytic activity. Furthermore, ZN catalysts still have low cost and less poison. This catalyst must have support for improving morphology, protecting fine particles, and fouling in reactor. Since these titanium catalysts cannot activate themselves, they are essential to use with cocatalyst in olefins polymerization. The cocatalysts or activators are mainly composed of alkyl aluminum compounds, which have been used in polymerization of olefin. Many industries use alkylaluminums such as triethylaluminum (TEA), trimethylaluminum (TMA), tri-iso-buthylaluminum (TiBA), tri-n-octylaluminum (TnOA), and diethyl aluminum chloride (DEAC) in polymerization processes [92-94]. The main function of these alkyl aluminum groups is to reduce the oxidation state of titanium (Ti) complex in catalyst into the suitable active forms for olefin polymerization. As known, ethylene polymerization can occur via both titanium (II) and titanium (III) species, whereas propylene polymerization needs only active titanium (III) ions [41]. Based on many researches, ZN catalyst is more popular for polymerization of ethylene due to its high activity. Thus, this research chose the commercial ZN catalyst for ethylene polymerization and ethylene/1-hexene copolymerization. As well known, LLDPE is produced using the commercial catalyst probably due to increased insertion of comonomer [95]. Hence, the suitable cocatalysts are preferred for reduction of Ti^{4+} to obtain high polymer yields. In addition, alkyl aluminums also scavenge impurities. In this reason, these activators are used in polymerization of ethylene and copolymerization of ethylene/1-olefins with Ziegler-Natta catalysts [95]. Previously, Hongmanee *et al*. revealed the effect of different reducing power of cocatalyst and Al/Ti molar ratios in synthesized ZN catalyst for ethylene polymerization. They showed that TEA exhibited the highest activity and the activity enhanced with increased Al/Ti molar ratios (from 2 to 5). They concluded that an increase in Al/Ti molar ratios can alter the catalytic activity [82]. Later, other researchers suggested that different activators likely increased the insertion of 1-hexene in polyethylene. Furthermore, using different types of single and combination of alkylaluminum compounds for suitable alkyl aluminum groups were investigated [13, 65, 96]. Commonly, TEA as activator having high reducing power is preferred. However, several cocatalysts have been also studied. For instance, TnOA was selected because it is also available and has octyl group, which can combine with other cocatalysts. This perhaps facilitate the insertion of 1-olefins and stability of Ti^{3+}. Since the catalyst and cocatalysts in this system are very sensitive to oxygen and moisture, it is a difficult task to characterize the change in catalyst properties under inert condition. Therefore, more powerful techniques are crucial to monitor the change in active sites during activation with cocatalyst and polymerization. One of the most powerful techniques is electron spin resonance (ESR) that can be used to observe the change in Ti^{3+} state in Ti-based ZN catalysts. Although the application of ESR is promising, only few studies [82, 97] were used this technique to determine the change in active species in polymerization catalysts.

In this present work, effects of different cocatalyst activation on a commercial Ti-based ZN catalyst on the change of Ti^{3+} state were elucidated by means of ESR. The change in Ti^{3+} state essentially plays an important role on the behaviors of ethylene polymerization and ethylene and 1-hexene copolymerization.

4.2 Materials and Methods

4.2.1 Materials

A commercial ZN catalyst (Cat-A) containing ca. 4 wt% of Ti was used. Triethylaluminum (TEA), trioctylaluminum (TnOA), and n-hexane for polymerization grade were donated from Thai Polyethylene Co. Ltd. Ethylene gas, hydrogen, and nitrogen were supplied from Linde (Thailand) Ltd. 1-hexene ($1\text{-}C_6H_{12}$) was purchased from Sigma Aldrich and dehydrated with the 3Å molecular sieve. All chemicals were prepared under argon atmosphere with glove box and 1-hexene was handled with Schlenk technique under nitrogen atmosphere.

4.2.2 Polymerization procedure

The slurry ethylene polymerization and ethylene/1-hexene copolymerization were operated in 2L-autoclave reactor linked with the purified nitrogen, hydrogen, and ethylene gases line and directly connected with purified n-hexane as solvent line. First, all equipment as the reactor and all feed lines were evacuated and purged with nitrogen gas to purify system many times at 70 °C. Then, purging nitrogen gas to fill in for 50 minutes. Next, the reactor was cooled down to 40 °C and 1 L of n-hexane as solvent was filled into the reactor. In case of ethylene/1-hexene copolymerization, 20 ml of 1-hexene as comonomer was injected into the reactor at constant stirring. Cocatalysts [TEA, TnOA and TEA+TnOA (1:1)] were added into the system, followed by injection of desired amount of slurry catalyst at Al/Ti molar ratio equal to 140 and heated up to 70 °C. Then, nitrogen gas was released until steady at 1 bar of nitrogen and pressurized with 3.5 bars of hydrogen gas followed by total pressure of ethylene gas at 8 bars. Polymerization was started at 75 °C and continued for 1 h at 80 °C. Finally, the polymerization was terminated by diluting hydrochloric and methanol. The obtained polymer was dried.

The polymer nomenclatures are given as listed in **Table 4. 1**.

Table 4. 1 Given polymer nomenclatures depending on different polymerization systems

Polymer Samples	**Nomenclatures**		
	Monomer	**Activator**	**Polymerization Temperature (°C)**
PE/TEA/80	Ethylene	TEA	80
PE/TnOA/80	Ethylene	TnOA	80
PE/TEA+TnOA/80	Ethylene	TEA+TnOA	80
CoPE/TEA/80	Ethylene/1-hexene	TEA	80
CoPE/TnOA/80	Ethylene/1-hexene	TnOA	80
CoPE/TEA+TnOA/80	Ethylene/1-hexene	TEA+TnOA	80
CoPE/TEA/70	Ethylene/1-hexene	TEA	70
CoPE/TnOA/70	Ethylene/1-hexene	TnOA	70
CoPE/TEA+TnOA/70	Ethylene/1-hexene	TEA+TnOA	70

4.2.3 Measurement of Ti^{3+} state by electron spin resonance (ESR)

Intensity of Ti^{3+} oxidation state was analyzed by electron spin resonance (ESR) technique. The slurry catalyst in n-hexane was prepared and activated by activators as TEA, TnOA, and mixed cocatalysts (TEA+TnOA, 1:1) in glove box. To collect the ESR spectra, the microwave frequency (9.419 GHz) was measured by Bruker Elexys 500 model under *in situ* condition. A typical microwave power 2.005 mW was chosen in ESR method. The ESR tubes were heated to 70 °C and held for 90 minutes. And then, the ESR spectra were captured for each 15 minutes until 90 minutes.

4.2.4 Characterization of polymer

The polymer morphology at x50 and x1k micrographs was observed by SEM. Melting temperature of polymer and %crystallinity was analyzed by differential scanning calorimetry (DSC). These measurements were operated in the temperature range from room temperature to 300 °C and heating rate of 10 °C/min. Moreover, calculation of %crystallinity of polymer was conducted based on this following equation as shown in Equation (1). The crystalline phase of obtained polymer was determined with XRD using Bruker of D8 advance model. Diffraction patterns were examined in diffraction angle range of 2θ = 10-80 degree with scan size of 0.02 and scan speed of 0.3 sec/step. ^{13}Carbon Nuclear Magnetic Resonance (^{13}C NMR) using a high solution ^{13}C NMR Bruker DRX 500 spectrometers was performed to determine the comonomer incorporation. The samples were measured in benzene-D6 at 125°C. The ^{13}C NMR was operated pulse angle 90° and pulse interval 12 sec.

% crystallinity $(\mathbf{X_c}) = \Delta\mathbf{H_f} \times \frac{\mathbf{100}}{\mathbf{291.7\ J/g}}$; ΔH_f is heat of fusion of polyethylene (1)

4.3 Results and Discussion

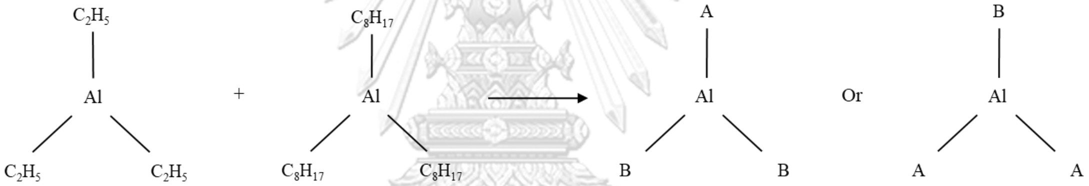
4.3.1 Catalytic activity

Table 4. 2 Catalytic activity of ethylene polymerization and ethylene/1-hexene copolymerization under different activator [a]

Run number	Polymer Samples	PE yield (g)	Catalytic Activity (kgPE/gTi.h)
1	PE/TEA/80	297	776
2	PE/TnOA/80	109	285
3	PE/TEA+TnOA/80	185	483
4	CoPE/TEA/80	185	484
5	CoPE/TnOA/80	96	250
6	CoPE/TEA+TnOA/80	167	437
7	CoPE/TEA/70	184	480
8	CoPE/TnOA/70	38	100
9	CoPE/TEA+TnOA/70	133	348

[a] Polymerization condition: 2-L autoclave reactor, catalyst 0.008 mmol Ti, solvent = n-hexane, total pressure = 8 bars, H_2 = 3.5 bars, Al/Ti molar ratio = 140, polymerization time = 1 h, ICP_Ti = 3.99%

Ethylene polymerization and ethylene/1-hexene copolymerization activity data are shown in **Table 4. 2**. There are four variables studied including bulkiness size of cocatalyst types (TEA and TnOA), a single (TEA or TnOA) and combination (TEA+TnOA) of cocatalysts, polymerization types (homo- or copolymerization) and polymerization temperatures (70 or 80 ^{o}C in copolymerization). First, when considered the ethylene polymerization (Runs 1-3), it appeared that TEA (Run 1, PE/TEA/80) exhibited the highest catalytic activity among other cocatalysts including TnOA and TEA+TnOA (Runs 2 and 3). It is known that the larger size of activator group diffuses slower than small one. Thus, the bulkiness of cocatalysts responds to the diffusion of activator through titanium active site, and then catalytic activity. On the other words, the less bulkiness of cocatalysts exhibit high reducing power (TEA > TnOA). Considering in the case of TEA+TnOA, the polymerization activity was in between both activators. It was not surprising since the combination of cocatalysts may result in the random insertion of different alkyl groups from each cocatalyst to form new cocatalyst having mixed alkyl groups as shown in **Scheme 4. 1**. It is presumable that the reducing power of the mixed cocatalyst should be in the average value, and then giving the average polymerization activity.



Scheme 4. 1 The possible new alkyl aluminum to produce suitable activators (A and B refer to randomly -C_2H_5 or – C_8H_{17})

In case of ethylene/1-hexene copolymerization (Runs 4-6), the catalytic activity tended to be similar as seen from the homopolymerization system (TEA > TEA+TnOA > TnOA). However, it seemed that the catalytic activities for the copolymerization system was lower than those obtained from the homogeneous system for all cocatalysts. It should be mentioned that with the use of TEA (Runs 1 and 4), the catalytic activity of copolymerization system (Run 4) remarkably decreased (from 776 to 484 kgPE/gTi.h) when compared to the homopolymerization system (Run 1), whereas only slight decrease in catalytic activities of copolymerization system using TnOA (Run 5) and TEA+TnOA (Run 6) was observed. It indicated that the change in active Ti species activated by TEA played a key role on different catalytic activity for both homo- and copolymerization in this specified condition. To study the temperature effect on copolymerization system, the polymerization temperature was lower from 80 to 70 °C (Runs 7 to 9). It revealed that activity decreased with decreasing polymerization temperature for TnOA and TEA+TnOA, whereas it did not affect in case of TEA. It suggested that the use of TnOA was more sensitive to polymerization temperature.

In order to elucidate the change of active Ti species depending on different cocatalysts, the electron spin resonance (ESR), which is one of the most powerful techniques, was performed. It is known that in ethylene polymerization or ethylene/1-hexene copolymerization, $TiCl_4$ (Ti^{4+}) as catalyst was reduced to bulk $TiCl_3$ (Ti^{3+}) by cocatalysts. In this investigation, the *in situ* ESR was conducted at 70 °C after activation of catalyst with different cocatalysts for 90 minutes. The ESR spectra of catalyst activated with various activators are shown in **Figure 4. 1(a) to (c).** In fact, the change in Ti^{3+} oxidation state, which was reduced from $TiCl_4$ [98] can be monitored. The major peaks of Ti^{3+} were observed at the g-factor value of 1.95, 1.96, 1.98, and 1.99 in **Figure 4. 1(a)** for TEA activation, 1.95, 1.97, 1.98, and 1.99 in **Figure 4. 1(b)** for TnOA activation, and 1.94, 1.95, 1.96, 1.97, 1.98, and 2.00 in **Figure 4. 1(c)** for TEA+TnOA activation. In the absence of interaction between the catalyst and cocatalyst, peaks at g-factor of 1.98, 1.95, and small peak at g = 1.96 were assigned to tetrahedral Ti^{3+} species, probably lowest Ti/Mg ratios, and interaction between Ti^{3+} and electron donor, respectively. [99] The peak at 1.95 tended to increase with time indicating the transformation of Ti^{4+} to Ti^{3+}. The generation of a new signal at g-value of 1.99 can be assigned to the lowest Ti/Mg stoichiometry. However, addition of TEA results in the disappearance of peaks at g-factor of 1.96 and 1.98 [100, 101]. In recent work, more complex EPR spectrum of titanium- magnesium catalysts are commonly observed for signals with wide ranges between 1.89 and 1.99. **Figure 4. 1(b)** shows a broad peak with g = 1.99 indicating the lowest Ti to Mg molar ratio and increased signal of g-factor at 1.97 in the ESR spectrum [101, 102]. Moreover, the g value at 1.94 refers to six-coordinated Ti^{3+} dissolved in $MgCl_2$ and isolated octahedral Ti^{3+} ions [102, 103]. From other researches, ESR spectra of $TiCl_3$ were observed with g = 1.94 along with a new g-factor of 1.97 corresponding to alkylated Ti^{3+} on surface [100, 104]. After activation of the catalyst with TEA+TnOA as shown in **Figure 4. 1(c)**, the appearance of peak at g = 1.98 also assigned to tetrahedral Ti^{3+} and a small signal g value of 1.97 was observed showing the alkylated Ti^{3+} on surface. In addition, the g-value of 1.95 appeared to increase with the activation time indicating the presence of Ti^{3+} ions.

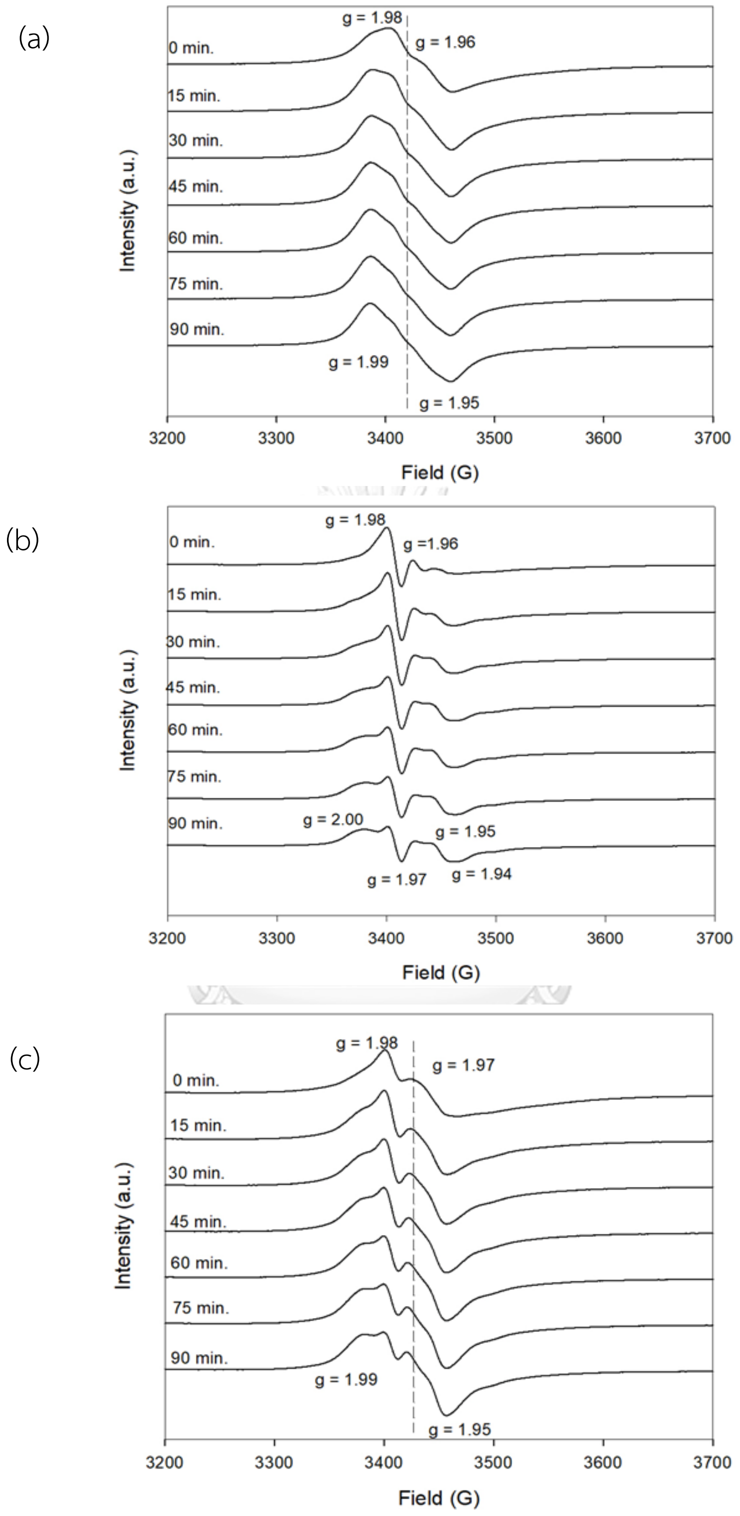


Figure 4. 1 The *in situ* ESR spectra of catalyst activated with different cocatalysts; (a) TEA, (b) TnOA, and (c) TEA+TnOA

For quantitative analysis of Ti^{3+} species, ESR peak area relating to the relative amounts with activation time of Ti^{3+} species was calculated by double integration [82]. In addition, the ESR results obtained from **Figure 4. 1** were further calculated by double integration technique and normalized peak areas of interval time to compare with the data at initial time (no activation) to obtain the plot of relative area (corresponding to the amount of changes in Ti^{3+}) with time in **Figure 4. 2**. In **Figure 4. 2**, it shows the Ti^{3+} intensity change (relative area) in catalyst and cocatalyst system with time at 70°C. The relative peak area corresponding to the amounts of Ti^{3+} species and activation time are plotted as shown in **Figure 4. 2**. It was found that the Ti^{3+} amounts of TEA activation tended to abruptly increase within 15 min, and then consistently decrease. Similarly, for TnOA activation, the relative area Ti^{3+} reached the maximum within the first 15 min, and then consistently declined with time. It is worth noting that the Ti^{3+} amounts for TEA+TnOA activation tended to slightly decrease within first 30 min, and then being quite constant with time. On the other words, the Ti^{3+} can be stabilized with the combination of TEA+TnOA. Moreover, all cocatalysts also reduced titanium state from Ti^{4+} to Ti^{3+} and then to Ti^{2+} differently. For TEA activation, it showed the highest catalytic activity in ethylene polymerization because ethylene polymerization is active both Ti^{3+} and Ti^{2+}, but Ti^{2+} is recognized to be more active than Ti^{3+} [105, 106]. In case of TnOA activation, the catalytic activity was found to be the lowest relating to the lowest relative area of Ti^{3+} because it is too bulky resulting in low reducing power.

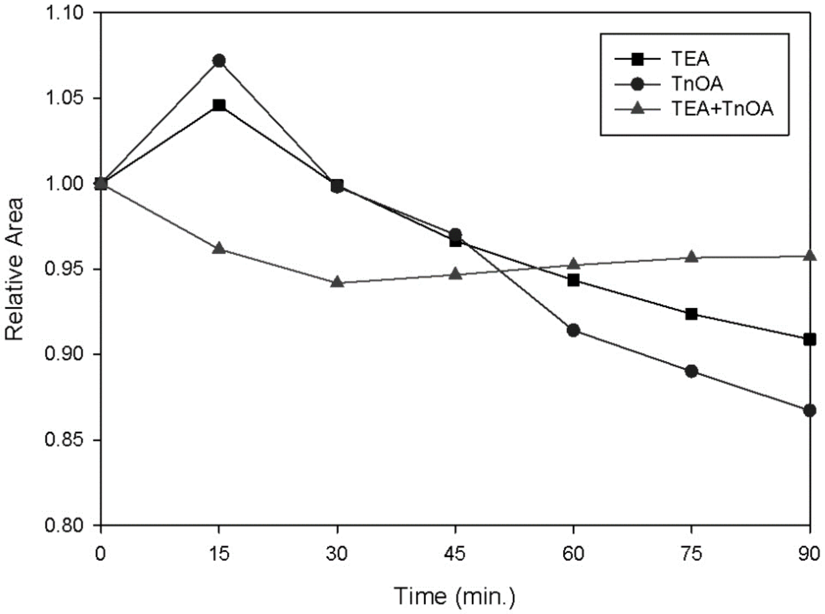


Figure 4. 2 Stability of Ti^{3+} in the catalyst activated with different cocatalysts at 70 °C for 90 min.

4.3.2 Polymer properties

Morphology of polymers was observed as seen in **Figure 4. 3** and **Figure 4. 4**. The shapes of polymer obtained with different cocatalysts were highly porous and had both small and large spheroidal lump. When compared the polymer samples in **Figure 4. 3** and **Figure 4. 4**, it revealed that no significant differences in morphology of polymers and copolymer obtained from different cocatalysts.

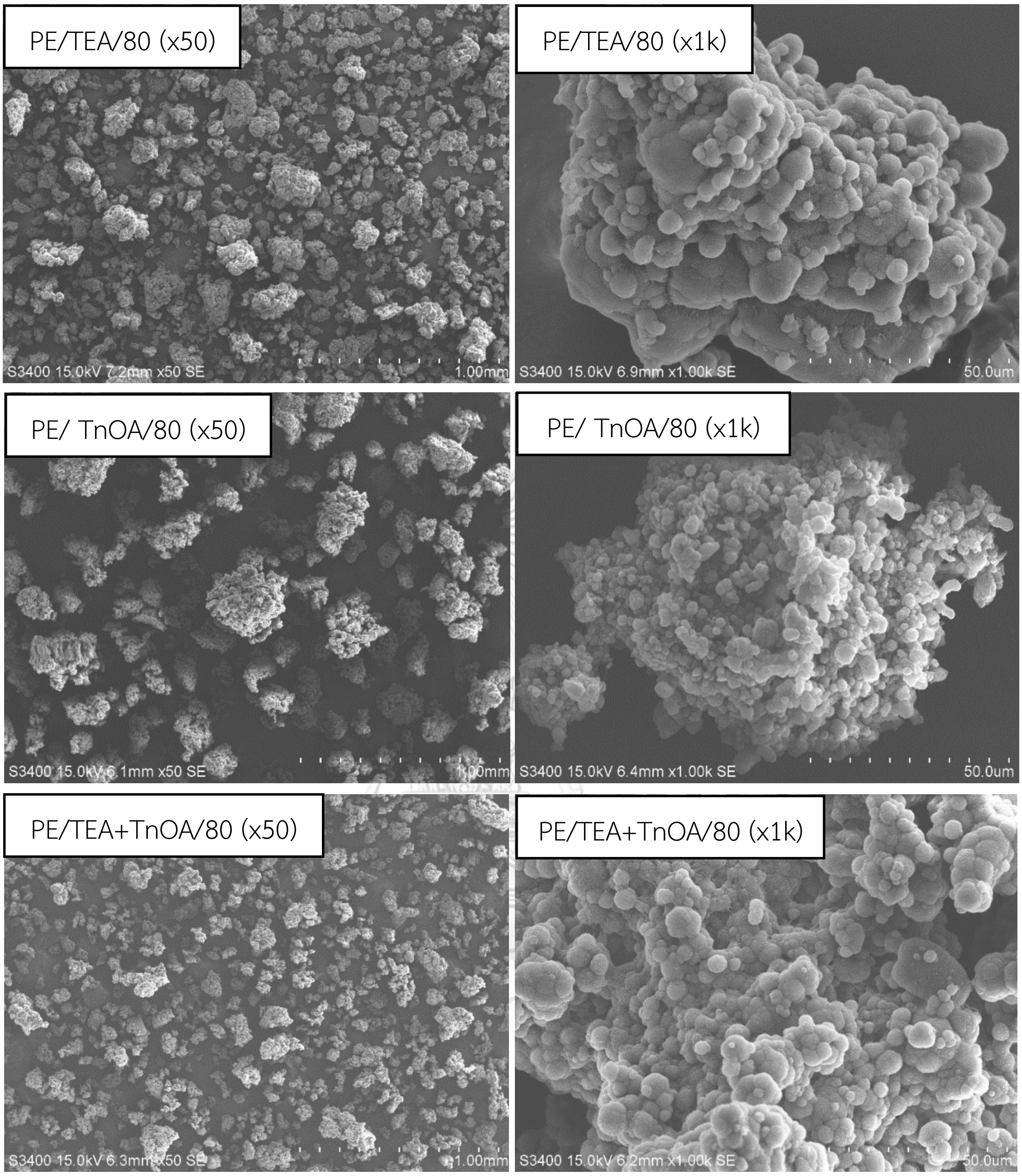


Figure 4. 3 SEM micrographs of the obtained polymer samples

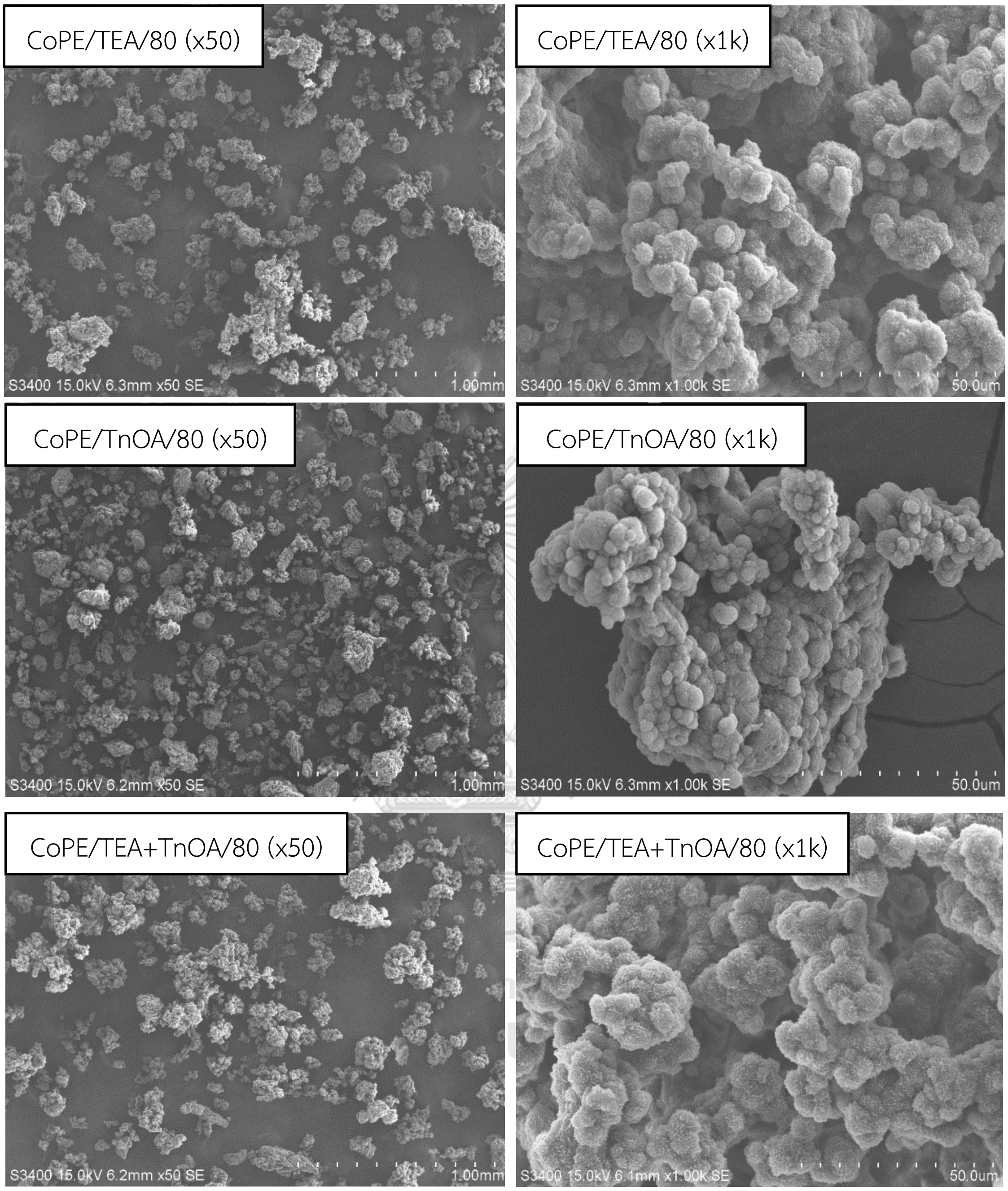


Figure 4. 4 SEM micrographs of the obtained copolymers

The XRD technique was used to ensure the characteristics of polyethylene obtained. The crystal structure of homopolymer and copolymer under ambient condition was confirmed using XRD measurement as shown in **Figure 4. 5**. All homopolymer and copolymer samples exhibited the two sharp peaks at 2θ degree of ca. 21.6° and 23.8° attributed (110) and (200) plane of polyethylene. Previously, Kageyama *et al*. [107] also confirmed the XRD peaks of polyethylene located at 21.6° and 23.8°.

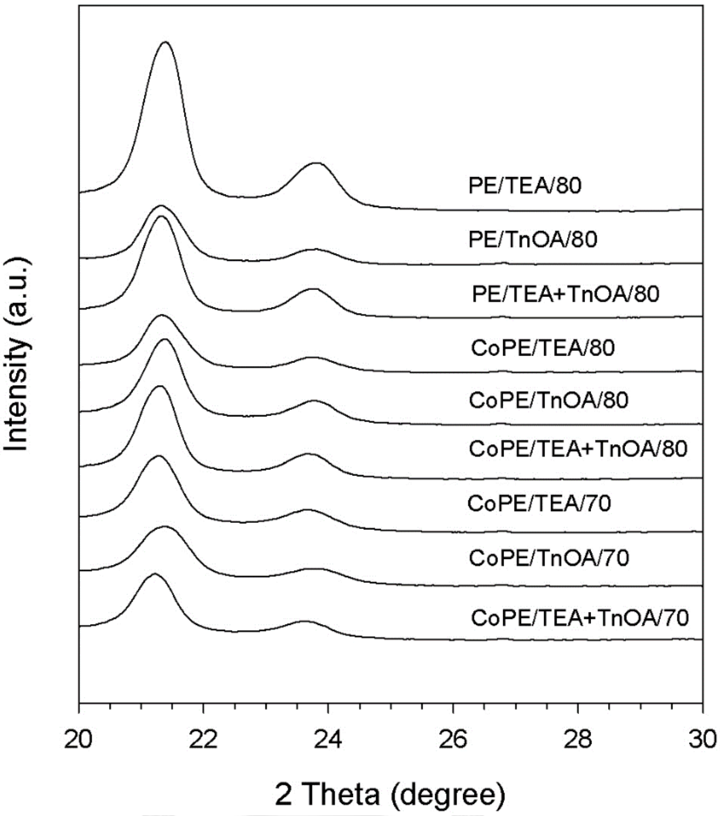


Figure 4. 5 XRD patterns of the obtained polymer samples

In addition, the intensity of XRD peaks may relate to the degree of crystallinity in polymer obtained from DSC technique under thermal condition.

Table 4. 3 Properties of homopolymer and copolymer with different cocatalysts types and polymerization temperature [a]

Run number	Polymer Samples	T_m [a] (°C)	Heat reaction (J/g)	%Crystallinity [b]	1-hexene insertion [c] (%mol)
1	PE/TEA/80	135.62	210.9	72.3	-
2	PE/TnOA/80	135.15	221.2	75.8	-
3	PE/TEA+TnOA/80	134.60	218.4	74.9	-
4	CoPE/TEA/80	128.63	164.8	56.5	0.67
5	CoPE/TnOA/80	130.61	183.3	62.8	0.38
6	CoPE/TEA+TnOA/80	128.27	172.8	59.2	0.59
7	CoPE/TEA/70	129.86	171.9	58.9	0.40
8	CoPE/TnOA/70	132.73	167.5	57.4	0.29
9	CoPE/TEA+TnOA/70	130.00	179.2	61.4	0.35

[a] Melting temperature (T_m) was analyzed by DSC.

[b] %crystallinity $(X_c) = \Delta H_f \times \frac{100}{291.7\ J/g}$

[c] analyzed by ^{13}C NMR

Thus, in this study, we used DSC technique to determine the meting temperature (T_m) and crystallinity of polymer as reported in **Table 4. 3**. Based on DSC results, %crystallinity of polymer was calculated from heat of fusion and the typical DSC spectra for polymer samples are also shown in **Figure 4. 6**.

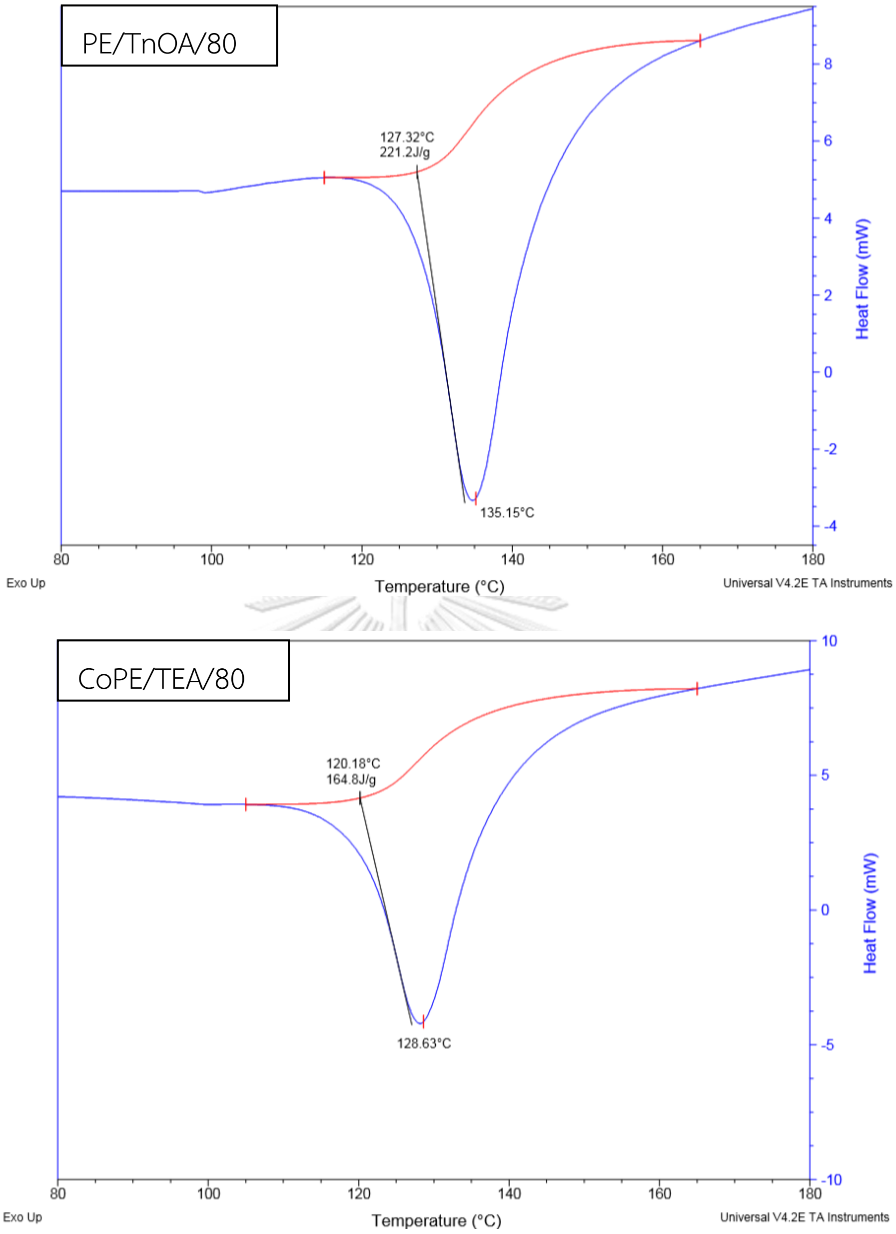


Figure 4. 6 Typical DSC spectra of polyethylene and ethylene/1-hexene copolymers

However, different types of cocatalysts and variety of polymerization temperature may not affect crystallinity of polyethylene. It is known that increased comonomer insertion would result in decreased crystallinity degree. The decrease in melting temperature perhaps suggests a higher degree of comonomer insertion. It is obvious that T_m of homopolymers (134-135 $^{\circ}$C) was higher than that of copolymers

(128 to 132 ^{o}C). The ^{13}C NMR analysis is one of the most powerful techniques used to determine the degree of comonomer insertion. The % insertion of 1-hexene is also listed in **Table 4. 3.** The incorporation of 1-hexene into polyethylene slightly improved in the order of TEA > TEA+TnOA > TnOA. However, changing the temperature of polymerization did not have significant effect on the polymer properties.

Temperature effect on propylene polymerization behavior over Ziegler-Natta catalyst with different cocatalyst systems

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Part 2: Temperature effect on propylene polymerization behavior over Ziegler-Natta catalyst with different cocatalyst systems

Abstract

This study focused on the effect of temperature in propylene polymerization behaviors up on different cocatalysts employed. It revealed that triethylaluminum (TEA) exhibited higher activity than tri-n-octylaluminum (TnOA) with the optimal temperature of 60°C, whereas the over reduction of catalyst occurred at 70°C. However, at low temperature (ca. 50°C), the mixed cocatalysts (TEA + TnOA) gave the highest activity among the sole cocatalyst. This can be attributed to the occurrence and stabilization of proper Ti oxidation state (Ti^{3+}) form as proven by the electron spin resonance (ESR) with the combination of cocatalysts. In addition, temperatures and types of cocatalyst did not have significant effects on morphology and crystallinity of polymer.

Keywords: Propylene polymerization; Temperature effect; Triethylaluminum; Trioctylaluminum; Electron spin resonance; Ziegler-Natta catalyst

4.1 Introduction

Titanium-based Ziegler-Natta (ZN) catalyst is widely used in industrial olefins polymerization. Majority of titanium-based catalyst is employed in ethylene polymerization and highly active [108-110]. For ethylene polymerization, this produces more active sites of titanium for both divalent (Ti^{2+}) and trivalent (Ti^{3+}). Hence, these valences are the key to improve catalytic activity in polymerization of ethylene. Besides, the synthesis of this catalyst is not complicated. Therefore, catalysts for ethylene polymerization are usually employed in propylene polymerization with a slight adjustment. For propylene polymerization, it can be catalyzed by only titanium state of oxidation at trivalent [41]. Therefore, the stabilization of Ti^{3+} is very crucial for this reaction and types of cocatalyst play important roles on this. In the activation process, the catalyst must react with cocatalyst or alkyl aluminum compounds to transform the inactive titanium (Ti^{4+}) into active form (Ti^{3+}). In general, cocatalysts such as triethylaluminum (TEA), tri-iso-butyl aluminum (TIBA), and tri-octyl aluminum (TnOA) are used widely [92-94]. Each cocatalyst or activator has different reducing power depending on the steric hindrance. Thus, the suitable cocatalyst must be chosen in order to stabilize the active form of Ti state [13, 111].

Besides types of cocatalyst, polymerization temperature strongly affects the polymerization behaviors. This is because a change in temperature can essentially alter the activation and stabilization of active form of Ti state. In previous study, effect of temperature in propylene polymerization with metallocene catalysts was investigated to produce isotactic polypropylene [112-114]. Based on researches, various temperatures were manipulated and found to differently produce isotactic and syndiotactic polypropylene [115]. These results reveal that both temperature effect and types of cocatalyst play a key role to alter the polymerization behaviors, especially for the stabilization of active Ti species.

Therefore, the present study aims to investigate the effects of polymerization temperature along with different types of cocatalyst on propylene polymerization behaviors using titanium-based ZN catalyst. The polymerization temperature was varied from 50 to 70°C, whereas TEA, TnOA and mixed TEA + TnOA as cocatalyst were used for each temperature. Moreover, the real time of Ti^{3+} present during activation of catalyst was monitored using electron spin resonance (ESR). The effects of polymerization temperature up on variation of cocatalyst types can be elucidated by the stabilization of Ti^{3+} in each catalytic system.

4.2 Experimental

4.2.1 Materials

All materials and steps in operation were conducted under oxygen and moisture free system in nitrogen and argon atmospheres using glove box. Polymerization grade of propylene gas (99.9%) and purified nitrogen gas were supplied from Linde Co., Ltd. The commercial titanium-magnesium catalyst (TMC) (ca. 4 wt% of titanium) for propylene polymerization, n-hexane, triethylaluminum (TEA), and tri-n-octylaluminum (TnOA) were donated from Thai polyethylene Co., Ltd.

4.2.2 Polymerization procedure

The polymerization of propylene was operated in 100 ml semi-batch stainless steel autoclave reactor with magnetic stirrer. All chemicals such as catalyst, cocatalysts (TEA, TnOA, and TEA + TnOA mixtures), and n-hexane as solvent were prepared in glove box. The purification of reactor was evacuated and purged with propylene gas for many times. First, the designed amount of cocatalyst and catalyst was injected into the reactor, consecutively. The Al/Ti molar ratio of 140 was used in this study. Then, 30 ml of n-hexane was introduced under argon atmosphere into the reactor. The polymerization was started by pressurizing with propylene gas to 5 bars. The polymerization time was kept for 15 min at each run and polymerization temperatures were varied at 50, 60, and 70°C. Then, polymerization was terminated by addition of acidic methanol (HCl in excess methanol). Finally, the precipitated polymer powder was filtered and vacuum dried. The nomenclature of polymers obtained was given as follows;

PP-X-Y

Where;

PP refers to polypropylene

X refers to polymerization temperature in °C (50, 60, and 70)

Y refers to cocatalyst types (**A** is TEA, **B** is TnOA, and **AB** is TEA + TnOA)

4.2.3 Characterization of catalyst

The commercial Ziegler-Natta catalyst (TMC) was chosen. The catalyst components mainly consist of titanium and magnesium-based compounds. The alkylaluminums such as TEA, TnOA, and mixed TEA + TnOA were used as cocatalyst or activator to obtain proper oxidation state of Ti^{3+} for propylene polymerization. Besides high catalytic activity, the stabilization of titanium states is crucial for this reaction. It is known that the polymerization temperature up on different cocatalysts play important roles in polymerization behavior due to the stabilization of titanium active species. Thus, it is captivating to determine the temperature effect with different cocatalysts in this present study. Moreover, the electron spin resonance (ESR) is one of the most powerful techniques used for studying unpaired electrons. In this study, ESR was used to observe the trivalent titanium state (Ti^{3+}) intensity during the activation of TMC with different cocatalyst system under specified temperature. The Bruker Elexys 500 model of ESR instrument with magnetic frequency of 9.419 GHz was used for this analysis. ESR was performed to elucidate the different activation behaviors regarding to different cocatalyst systems at 50°C. It was conducted under three different cocatalyst systems including TMC with TEA, TMC with TnOA, and TMC with TEA + TnOA using Al/Ti molar ratio of 140 as being used in polymerization. Besides, ESR was also used to track the change of Ti^{3+} with time. For each measurement, it was operated at 50°C for 90 minutes. The relative amount of Ti^{3+} as a function of time for each measurement was calculated and compared [116].

4.2.4 Characterization of polymer

Polymeric crystalline structure of polypropylene and the degree of crystallinity were determined by X-ray diffraction (XRD) analysis. The XRD measurement was performed using Bruker D8 advance model, operating Cu K_α radiation with step time of 0.3 sec and 0.02° of scan size in range of 2θ equals to between 10° and 60°. Differential scanning calorimeter (DSC) was carried out to determine melting temperature of polymer and percentage of polypropylene crystalline. The heat of fusion value obtained from DSC is used to calculate the crystallinity of polymer. This analysis was conducted using TA instruments SDT Q600 V8.1 Build 99 with a heating rate of 10°C/min. The range of temperature was scanned from room temperature to 200°C. % crystallinity (X_c) can be calculated from equation below; [117, 118]

$$X_c = heat\ of\ fusion\ of\ polypropylene\ (\Delta H_f) \times \frac{100}{207\ J/g}$$

Scanning electron microscope (SEM) with JEOL S-3400N of Hitachi mode was used to scan over polymer morphology to obtain SEM micrographs at 20x magnification. The isotactic index (I.I.) of polypropylene was measured using Soxhlet extraction (Kumagawa extractors). It was performed using 1 g of polymer in 250 ml of boiling n-heptane as extraction solvent for 6 h. The obtained heptane-insoluble residue (as isotactic PP portion) was dried at 70°C for 16 h, and then weighted.

4.3 Results and discussion

4.3.1 Catalytic activity

Table 4. 4 Catalytic activity and characterization of polypropylene obtained by Ti-based ZN catalyst

Run number	Polymer Samples	Activity (gPP/gTi.h)	T_m [a] (°C)	%Crystallinity[b]	Isotactic index[c] (%)
1	PP-70-A	836	154.2	36.6	71.2
2	PP-70-B	868	152.8	32.7	68.1
3	PP-70-AB	756	153.6	38.3	71.3
4	PP-60-A	1486	157.0	34.7	74.7
5	PP-60-B	1059	153.2	30.3	72.4
6	PP-60-AB	977	155.1	30.7	74.1
7	PP-50-A	1185	152.2	38.2	75.6
8	PP-50-B	624	153.0	33.5	69.4
9	PP-50-AB	1242	153.9	39.8	78.3

[a] Melting temperature (T_m) was analyzed by DSC.

[b] Calculated from DSC.

[c] Calculated from residual polymer after extracted with boiling n-heptane for 6 h.

Table 4. 4 shows the polymerization activity under different temperatures and cocatalysts. Considering polymerized at 70°C (high temperature) up on different cocatalyst types (Run 1-3), the TnOA (PP-70-B) exhibited the highest catalytic activity followed by TEA (PP-70-A) and mixed cocatalysts (PP-70-AB). It is well known that TEA has higher reducing power than TnOA due to its less steric hindrance. Thus, it would have higher activity than that obtained from TnOA. However, in propylene

polymerization, the active site is Ti^{3+}, while Ti^{2+} is inactive form [41]. Therefore, the over reduction of Ti^{3+} to Ti^{2+} was likely occurred with TEA activation at 70°C resulting in lower activity compared to the system with TnOA activation. The mixed cocatalysts rendered the lowest activity at 70°C. When the polymerization temperature was lower down to 60°C (Run 4-6), the polymerization behavior is quite different. As expected, the TEA activation system exhibited the highest activity (1486 gPP/gTi.h.) among other systems (PP-60-A > PP-60-B > PP-60-AB). This can be attributed to the optimal temperature to activate the catalyst for each cocatalyst system. Moreover, the polymerization temperature at 50°C (Run 7-9) was also studied. Surprisingly, at this low temperature, it can be observed that the mixed cocatalyst system (PP-50-AB) gave the highest activity (1242 gPP/gTi.h). It was suggested that the stabilization of Ti^{3+} at this temperature was suitable for the activation of this catalyst with mixed TEA+TnOA cocatalysts. In order to better understand the temperature effect up on different cocatalyst types, the summarized result is illustrated in **Figure 4. 7**. It can be concluded that for a single cocatalyst system including TEA and TnOA, the optimal temperature for polymerization is 60°C due to both cocatalysts exhibited high activity. Increased temperature to 70°C apparently led to over reduction of Ti^{3+} to Ti^{2+} resulting in low activity. However, when this polymerization was performed at 50°C, it is quite interesting that the mixed TEA + TnOA cocatalyst system render the highest activity. As we mentioned earlier, the high activity found it this low temperature should be related to the stabilization of Ti^{3+}.

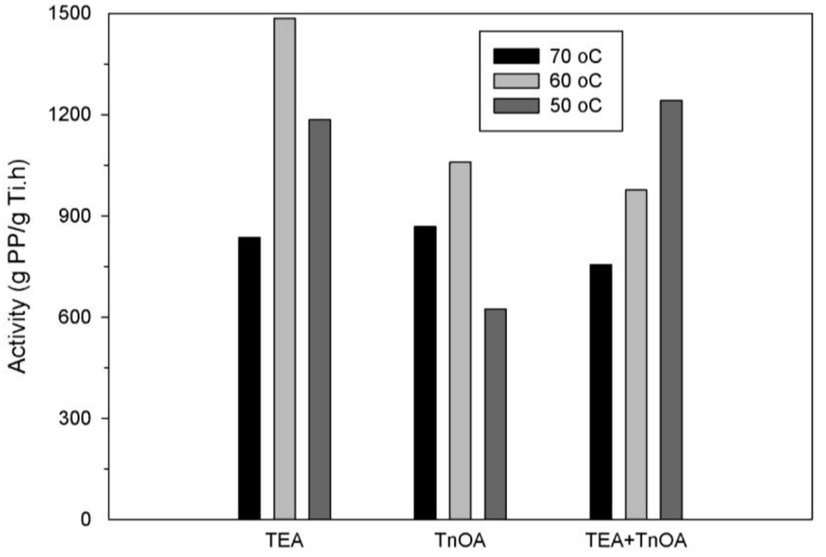


Figure 4. 7 Catalytic activity to effect of temperature of propylene polymerization compared with difference activators at Al/Ti =140

The ESR technique detects only unpaired spin of the radicals such as trivalent Ti (Ti^{3+}). In case of Ti-based Ziegler-Natta catalyst, Ti has oxidation state of 4+ at the beginning, and then it is reduced to Ti^{3+} by cocatalyst in the activation process. However, polymerization of propylene can be energetic with Ti^{4+} and Ti^{3+} species. It is attested that active species as Ti^{3+} of catalyst can be measured from this technique. The obtained ESR raw data between field wavelength (G) and intensity values were captured in every 15 minutes until 90 minutes and computed to double integration. Therefore, these data were resulted in normalized peak with no reaction time. Thus, a change of Ti^{3+} amount with time was plotted in relative area form as seen in **Figure 4. 8**.

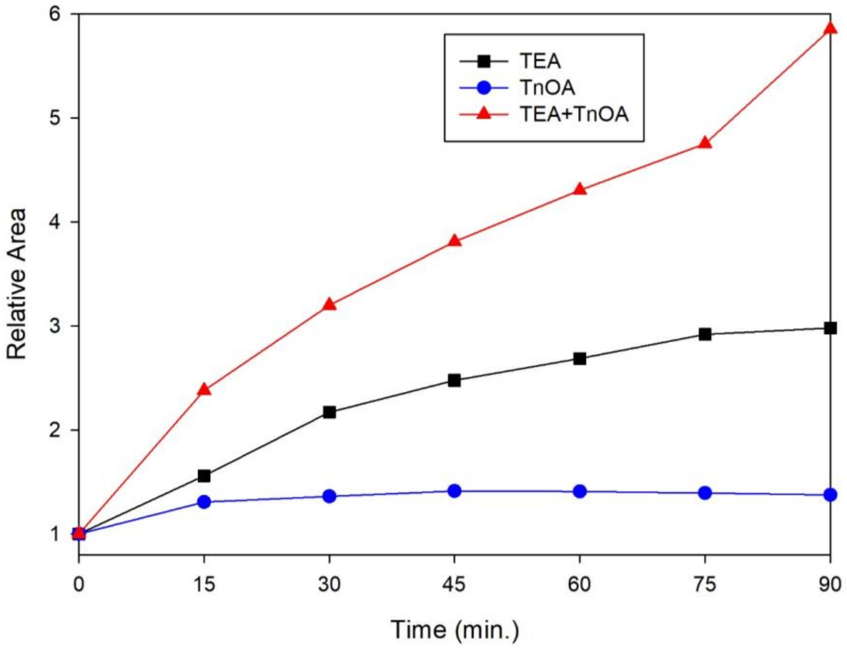
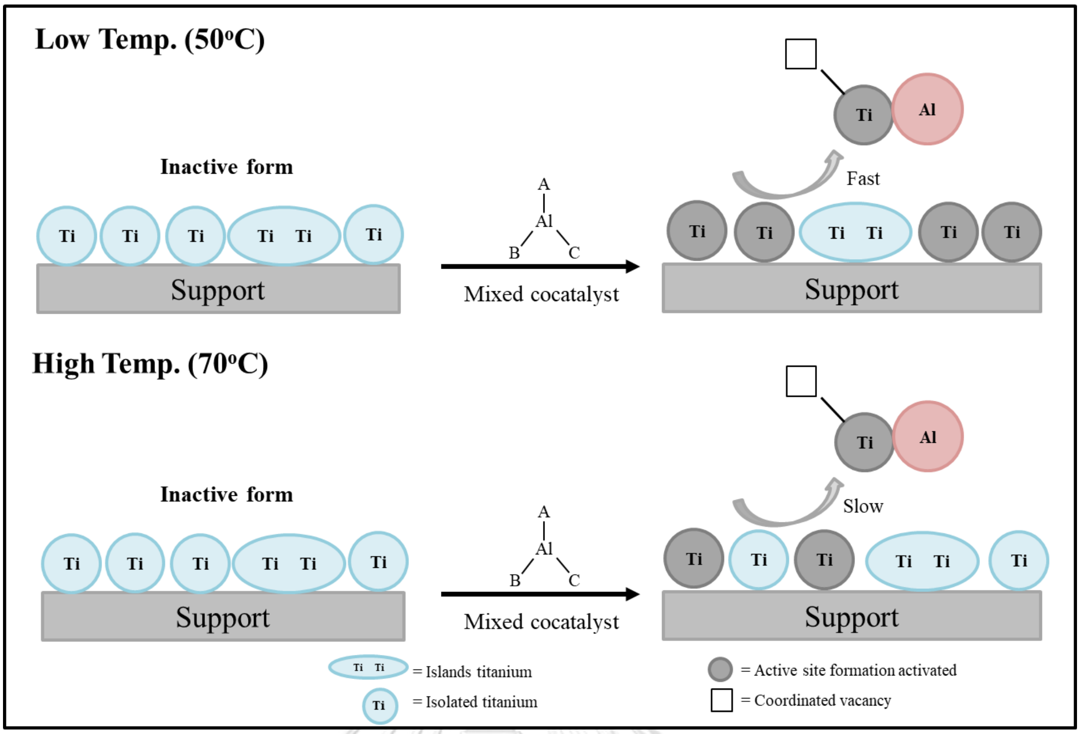


Figure 4. 8 Relative area correlated with reaction time in effect of cocatalyst types at Al/Ti =140 and T = 50°C

Figure 4. 8 shows ESR spectra at 50°C for the catalyst during activation with three different cocatalyst types over a period of 90 minutes. The relative area of all cocatalysts tended to significantly rise with increased time. For TnOA activation, the relative area of Ti^{3+} was the lowest and slightly increased at the beginning, and then it was rather constant throughout the measurement. When compared to TnOA, the TEA activation rendered higher relative area of Ti^{3+} indicating that TEA system exhibited higher activity due to higher amount of Ti^{3+}.

This result is in accordance with that as seen from **Table 4. 4**. Moreover, it was found that for the mixed cocatalyst system, the relative area of Ti^{3+} is the highest suggesting that this system exhibited the highest activity as also confirmed by the results from **Table 4. 4**. Thus, results from ESR measurement are in agreement with those seen from Run 7-9 in **Table 4. 4**.



Scheme 4. 2 Plausible mechanism of mixed cocatalyst (TEA+TnOA) at different temperature

It is likely that the mixed cocatalysts generate new active site formation as shown in **Scheme 4. 2**. From previous theories and literatures, propylene polymerization is active for both 4+ and 3+ of titanium site, but bivalence of the catalyst was not active in reaction. Thus, new active center formation was possibly produced, and then more active centers can stabilize the Ti oxidation state [119-122]. Moreover, it indicated that Ti-based Ziegler-Natta catalyst slowly decomposed or the active centers moderately deactivated. In agreement with at low reaction temperature directly replied on propylene chain-transfer because of new cocatalysts model and mainly saved thermal energy. It is surprising that combination of cocatalyst impacts on the increment in the catalytic activity with decreased temperature of reaction. In consequence of new formation model of cocatalysts, it may be due to more stabilization of trivalent titanium can facilitate the yield of polymer [106, 123-125]. Hence, it is interesting that stability of Ti^{3+} for combination of activators at 50°C can powerfully confirm from ESR technique.

4.3.2 Polymer characteristics

Morphologies of polymer obtained using different cocatalyst types at reaction temperature of 50°C were typically displayed as shown in **Figure 4. 9**. All polypropylenes obtained exhibited similar shape. The PP-50-A had characteristic of fluffy pellet, whereas PP-50-B exhibited mostly inflexible fiber. As expected, the PP-50-AB was present as the combination of both PP-50-A and PP-50-B morphologies.

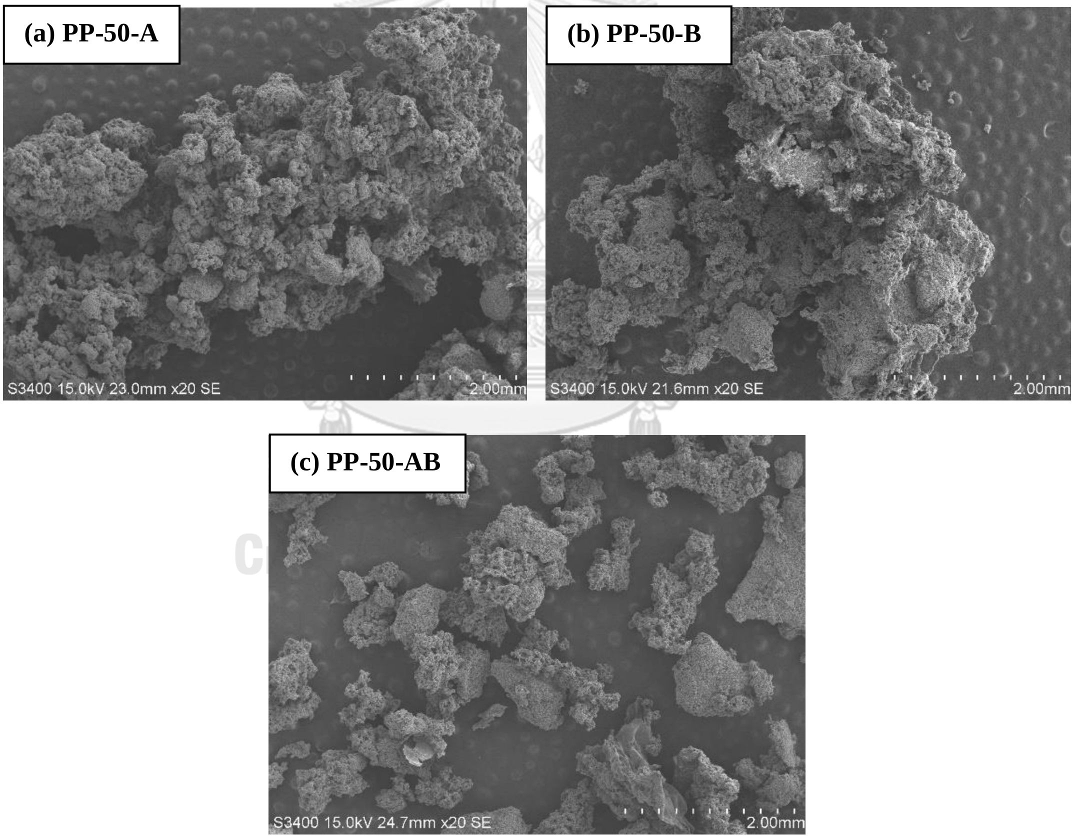


Figure 4. 9 Typical morphologies of polypropylene in variation of cocatalyst at 50°C

The crystalline structure under ambient condition of polymer is simply determined using X-Ray diffraction (XRD). The XRD patterns of polypropylene with different cocatalyst types, and polymerization temperature are displayed in **Figure 4. 10**. Typically, it showed two diffraction sharp peaks located at 2θ angles of 14.2° and 17.2° indicating isotactic PP in (110) and (040) planes, respectively. Moreover, there were also two peaks at 2θ degree of 18.6° and 21.6° for isotactic PP at planes (130) and (111) reflection [126, 127]. At 50°C, the XRD peaks were sharper than those obtained at 60 and 70°C. The crystallinity and melting temperature are shown in **Table 1**. It revealed that PP-50-AB exhibited high crystallinity at ca. 40 %. The other PPs gave almost similar crystalline value. Based on DSC measurement, polypropylenes have melting temperature about 152-156°C [128]. It can predict that high melting point is related to more isotactic since its better tendency to crystal formation.

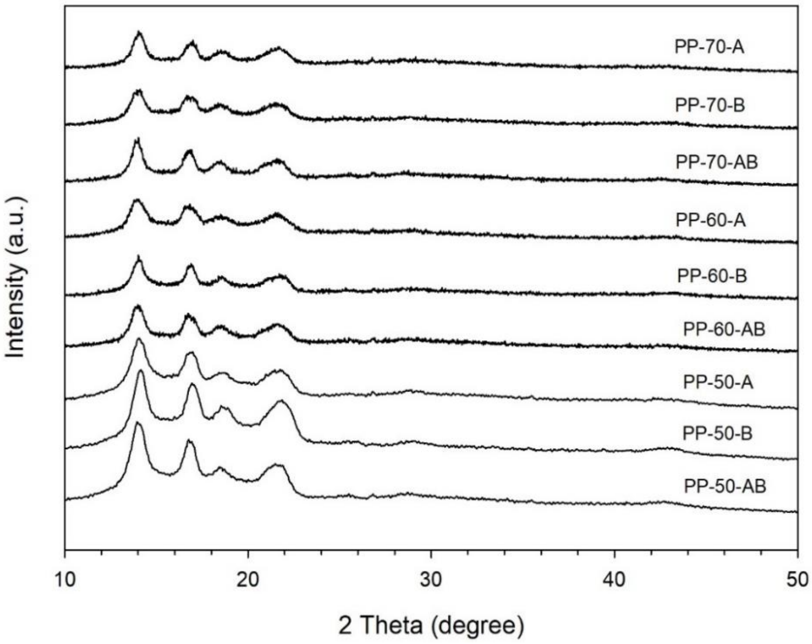


Figure 4. 10 XRD patterns of polypropylene obtained from different cocatalyst and temperature

In addition, isotacticity index (I.I.) indicated the formation of stereoregularities of polypropylene. Combination of cocatalyst also presented more isotacticity polymer than that obtained from a single activator. On the contrary, TnOA activators exhibited the lowest isotactic index because alkyl group of activators maybe blocked to chain-transfer and interaction of propylene. Furthermore, isotacticity also directly affected stereoregularity, and then a stereoregulated adsorption of catalyst active sites [129-131]. It is possible that different cocatalyst types attached dissimilar alkyl group around aluminum reported that selectively stereospecific sites to more isotactic. In case of polypropylene, it is possible that catalytic centers had α-$TiCl_3$ on surface (random), but β-$TiCl_3$ surface (linear) appeared to be covered with polymer. Thus, α and β having arrangements of Ti^{3+} state was different. It should be noted that the variation of Ti oxidation state can alter the polymer structure and can be confirmed as also seen from **Figure 4. 8**.

Gas-phase polymerization of ethylene over Ti-based Ziegler-Natta catalysts prepared from different magnesium sources

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Part 3: Gas-phase polymerization of ethylene over Ti-based Ziegler-Natta catalysts prepared from different magnesium sources

Abstract

This study focuses on gas-phase polymerization of ethylene using the titanium-based Ziegler-Natta catalysts prepared from different magnesium sources including $MgCl_2$ (Cat A), magnesium powder (Cat B) and $Mg(OEt)_2$ (Cat C). During polymerization, different cocatalysts were also employed. It was found that Cat C with TEA as cocatalyst exhibited the highest activity. This was likely attributed to optimal distribution of active site on catalyst surface. It can be observed by increased temperature in the reactor due to highly exothermic reaction during polymerization. By the way, the morphologies of polymer obtained from this catalyst were spherical, which is more preferable. Besides the catalytic activity, crystallinity and morphology were also affected by the different magnesium sources used to prepare the catalysts.

Keywords: Gas-phase ethylene polymerization; Magnesium sources; Ziegler-Natta catalyst; Triethylaluminum; Trioctylaluminum

4.1 Introduction

Ziegler-Natta (ZN) catalyst is popularly used in olefin polymerization industries, especially in the slurry polymerization system [132-134]. This catalyst mainly consists of transition metal compounds mostly including titanium and vanadium precursors [135, 136]. Commonly, Ziegler-Natta catalyst has been chosen as the first choice due to its high productivity in olefin polymerization industries and good morphology control [14, 137, 138]. Moreover, the catalyst is activated with activator or cocatalyst to change an inactive into active form as trivalent and divalent state of metal for ethylene polymerization [139]. Many kinds of alkylaluminum such as triethylaluminum (TEA), tri-iso-butyl aluminum (TIBA), and tri-octyl aluminum (TnOA) are normally used as cocatalyst. In fact, each cocatalyst has different alkyl groups bound to aluminum affecting the reducing power to activate the catalyst. So, the selection of suitable cocatalyst type is very crucial for polymerization process [82]. Furthermore, this catalyst can be immobilized on proper carriers for improving catalytic activity. One of the most important aspects in polymerization is good morphology of polymer. Among all supports or carriers, magnesium chloride ($MgCl_2$) is the most employed support in Ziegler-Natta catalyst [139-141]. However, the magnesium chloride support can be prepared using different magnesium sources. Different magnesium sources can be used to prepare the catalyst using different methods, especially the catalysts for ethylene polymerization. The mostly applied polymerization operation modes are usually slurry process and gas-phase process [142, 143]. At present, gas-phase ethylene polymerization becomes more captivating, especially for modern olefin polymerization industries [144, 145]. This is due to good properties of produced polyethylene, absence of solvent and low capital cost for none removal or recycle of solvent [146-148]. However, gas-phase olefin polymerization is also difficult to handle due to increased temperature during polymerization arising from exothermic reaction. This problem can result in melted polymer and agglomeration along with deactivation of the catalysts. Thus, the catalyst design and the proper cocatalyst chosen for gas-phase polymerization are the key to overcome these problems. The suitable catalyst and cocatalysts must be considered.

This research aims to investigate the effects of magnesium source along with different cocatalyst types on the catalytic behaviors of titanium-based Ziegler-Natta catalysts for gas-phase ethylene polymerization. In fact, TEA was employed because it has been the most used cocatalyst for Ziegler-Natta catalysts, whereas TnOA is also available and used in some industrial process. The mixture of TEA and TnOA can possibly compromise to obtain the proper catalytic system. The magnesium sources in this study included $MgCl_2$, magnesium powder and $Mg(OEt)_2$. The catalysts were prepared with different routes and used in gas-phase ethylene polymerization. The catalytic activity and polymer properties related to different catalytic system are elucidated.

4.2 Catalyst preparations and Methods

4.2.1 Materials

All reactions and material handling were performed in moisture and oxygen free system under nitrogen or vacuum atmospheres using glove box or Schlenk technique. Polymerization grade of ethylene gas (99.9%), hydrogen and nitrogen were supplied from Linde Co., Ltd. Titanium (IV) chloride ($TiCl_4$) and ethanol were purchased from Merck. Tetrahydrofuran (THF) was obtained from Sigma-Aldrich. Anhydrous $MgCl_2$, magnesium powder, magnesium alkoxide, butyl chloride, n-hexane, triethylaluminum (TEA), and trioctylaluminum (TnOA) were donated by Thai polyethylene Co., Ltd.

4.2.2 Synthesis of titanium-based ZN catalyst with different magnesium sources

The catalysts were synthesized up on different magnesium sources including $MgCl_2$, magnesium powder and $Mg(OEt)_2$. Details are shown as follows;

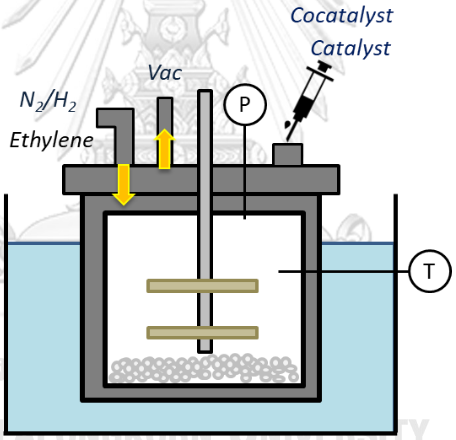
Cat A was synthesized according to the use of magnesium chloride ($MgCl_2$) source [140]. First, 2 g of anhydrous $MgCl_2$ and 150 mL tetrahydrofuran (THF) were mixed in the 500 mL four-necked round bottom flask and stirred with a magnetic stirrer at room temperature for 2 h. After that, 10 ml of $TiCl_4$ was introduced dropwise. Then, the solution was heated up to 70°C and held for 3 h. The mixture was filtered, and the precipitate was then washed with n-hexane for seven times and dried under vacuum to obtain the final catalyst.

Cat B was synthesized according to the use of magnesium powder source. First, 2 g of magnesium powder, 250 ml of n-hexane, and iodine were consequently added into 500 ml glass flask with magnetic stirrer at room temperature. Then, the desired amount of ethanol and titanium precursor (titanium alkoxide) were introduced, respectively. The flask was suddenly heated up to 80°C and maintained at this temperature for 2 h. After that, 10 ml of titanium tetrachloride and n-butyl chloride (BuCl) having molar ratio of BuCl:Mg = 0.75:1 was slowly dropped around 10 min. The brown slurry mixture was observed. The catalyst slurry was purified by washing with n-hexane for seven times and dried under vacuum [82].

Cat C was synthesized according to the use of $Mg(OEt)_2$ source. First, a mixture of 2 g of $Mg(OEt)_2$ and n-hexane was added into the 500 mL four-necked round bottom flask with magnetic stirrer. Under controlled low temperature, 10 ml of $TiCl_4$ was slowly dropped and heated up to 70°C within 1 h and kept at this temperature for 2 h. Then, the mixture was cooled down and washed with n-hexane for seven times to obtain the final catalyst.

4.2.3 Gas-phase ethylene polymerization procedure

All catalysts and activators (TEA, TnOA, and TEA + TnOA mixtures) were arranged under argon atmosphere in glove box or Schlenk techniques. The gas-phase ethylene polymerization was carried out in 1 L stirred-bed cylindrical reactor with monitoring stirrer under semi-batch mode. This stirred-bed reactor for gas-phase polymerization system is illustrated in **Scheme 4. 3** and was donated by Wanke et al. [147, 148] with some modification by our group. Prior to reaction, about 80 g of sodium chloride used as gas and catalyst distributor was added and dried at 90°C under nitrogen overnight for removal of moisture in the reactor. After that, the system was purified by vacuity and purged with nitrogen gas for several times. Then, cocatalyst was injected into the reactor at 70°C. The Al/Ti molar ratio of 20 was used in this study. The catalyst was fed with nitrogen gas at 3.5 bar and constant stirring for 30 minutes. After that, hydrogen gas at 0.5 bar was filled and followed by feeding ethylene gas to operate at total pressure of 15 bar. The polymerization of ethylene started after ethylene gas was added into the reactor at 80°C for 1 h. After 1 h, the polymerization was terminated by released pressure and cooled down. Finally, solid polymer was collected and cleaned by DI water to remove NaCl and dried at 60°C.



Scheme 4. 3 Model of gas-phase polymerization system

4.2.4 Morphology observation

The external morphologies of catalyst and polymer were overlooked by JEOL S-3400N of Hitachi model scanning electron microscope (SEM). Preparation of all catalysts was eliminated under nitrogen atmosphere. SEM micrographs were obtained to reveal the morphology of samples after the particles were sputtered with gold.

Moreover, distribution of elements on surface particles was examined using Link Isis series 300 program energy dispersive X-ray spectroscopy (EDX). This analysis can determine the distribution of elements such as titanium (Ti) and magnesium (Mg) located on the external surface of catalyst.

4.2.5 Characterization of catalyst

All catalysts are prepared under argon and nitrogen atmosphere to prevent the deactivation of catalyst. The elemental composition in bulk catalyst was analyzed by inductively couple plasma techniques (ICP) using ICP-OES optima 2100 DV from Perkin Elmer. N_2 physisorption was performed to obtain a single point on specific surface area of catalysts from the Micromeritics Chemisorb 2750 Pulse Chemisorption by N_2 physisorption isotherm method. The X-ray diffraction (XRD) as SIEMENS D-5000 X-ray diffractometer was used to observe the crystal forms and identify the crystal phases of catalyst. The samples were put into the center holder with the scanning range of 2θ = 10 to 70 degrees with scan speed of 0.3 sec/step and step size of 0.02. Moreover, the catalysts can recognize the functional groups of chemical bonds from Fourier transform infrared spectroscopy (FT-IR) using the Nicolet 6700 FTIR spectrometer in transmittance mode. Scanning is recorded from 400 to 4000 per cm.

4.2.6 Characterization of polymer

Crystalline structure and crystallinity degree of polyethylene were confirmed by X-ray diffraction (XRD) analysis. The XRD patterns were examined using Bruker D8 advance model from performing with Cu K_α radiation with scan size of 0.02° and step time of 0.3 sec per step in range of 2θ equals to 10°-70°. In addition, properties of polymer as melting temperature and % crystallinity of polymer were also measured by differential scanning calorimetry (DSC). Operation condition in this measurement was as following; heating rate of 10°C/min and final temperature was 300°C. Besides, % crystallinity (X_c) was calculated from heat of fusion of polymer in equation:

$$X_c = \Delta H_f \times \frac{100}{291.7\, J/g}$$

4.3 Results and discussion

4.3.1 Characteristics of different catalysts

Morphology of different catalysts identified by SEM images is shown in **Figure 4. 11**. All catalyst particles were scanned in several magnifications (x200, x600, and x2.5k micrographs) for better view through overall morphology of catalysts. Cat A shows the bar shape covering with particles as seen in irregular shape of catalyst particles attached on support surface. On the contrary, Cat B displays characteristic of fluffy pellet and more porous layers, while Cat C presents the spherical shape due to its replication from magnesium alkoxide having a global shape.

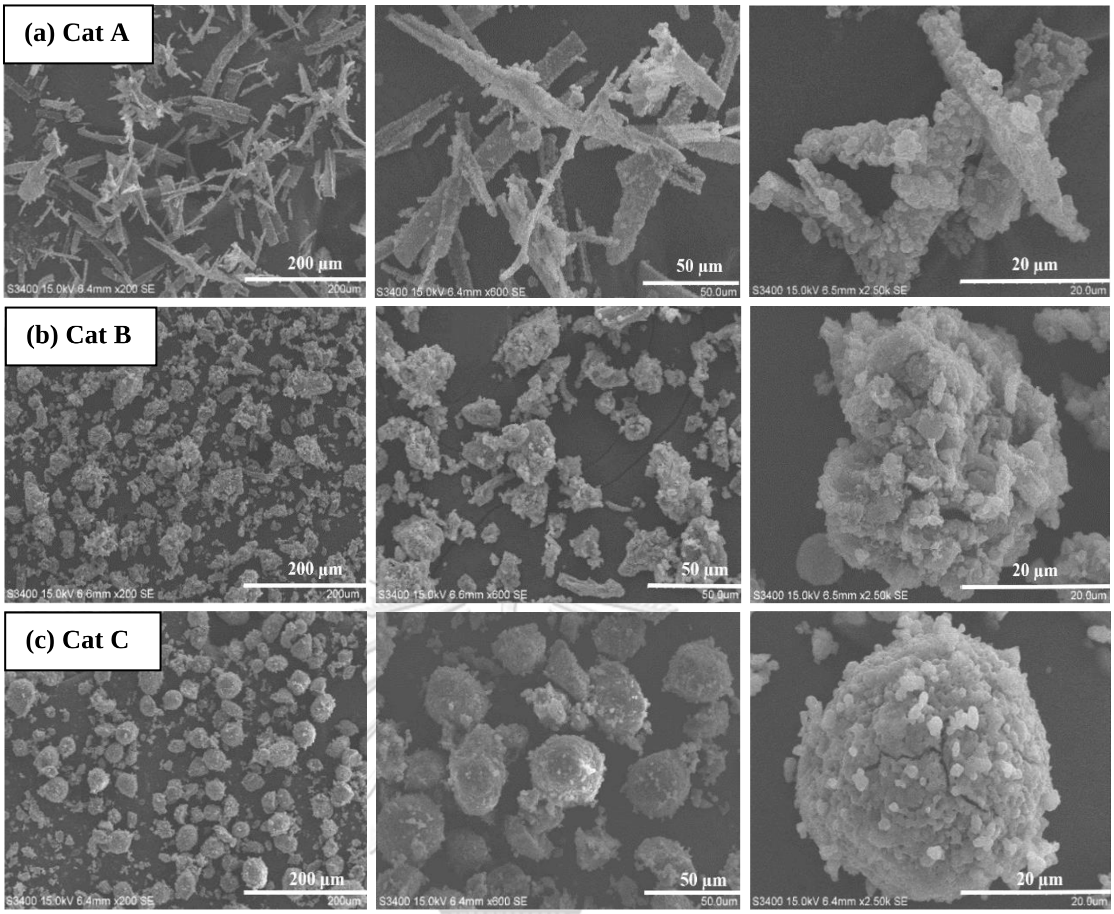


Figure 4. 11 Morphologies of catalyst particles from SEM images

Table 4. 5 Elemental composition in bulk catalysts obtained from ICP

Catalysts	Elemental contents (%wt)		Ti/Mg
	%Ti	%Mg	(mol/mol)
Cat A	3.21	5.95	0.27
Cat B	4.80	10.54	0.23
Cat C	5.12	8.98	0.29

To identify the elemental composition in bulk catalysts, ICP result is presented in **Table 4. 5**. The composition of elements on titanium-magnesium catalysts was measured from ICP techniques. The titanium content in all catalysts was around 3-5 wt%, while Cat C (magnesium alkoxide support) exhibited the highest titanium content (ca. 5.12 wt%). Moreover, elemental distribution on catalyst surface was also analyzed by EDX technique. All catalysts displayed higher titanium content at surface than that in the bulk catalysts.

Table 4. 6 Elemental distribution on catalyst surface (EDX), particle sizes (SEM), and specific surface area of each catalyst

Catalysts	Elemental contents (%wt)		Ti/Mg (mol/mol)	Particle size (μm)	Particle size distribution (μm)	Specific surface area (m^2/g)
	%Ti	%Mg				
Cat A	38.84	61.16	0.32	6.45:1*	n/a	119
Cat B	43.17	56.83	0.39	35.92	20.5-64.4	127
Cat C	44.28	55.72	0.40	36.14	24.8-48.5	143

* aspect ratio (wide: length) of particles

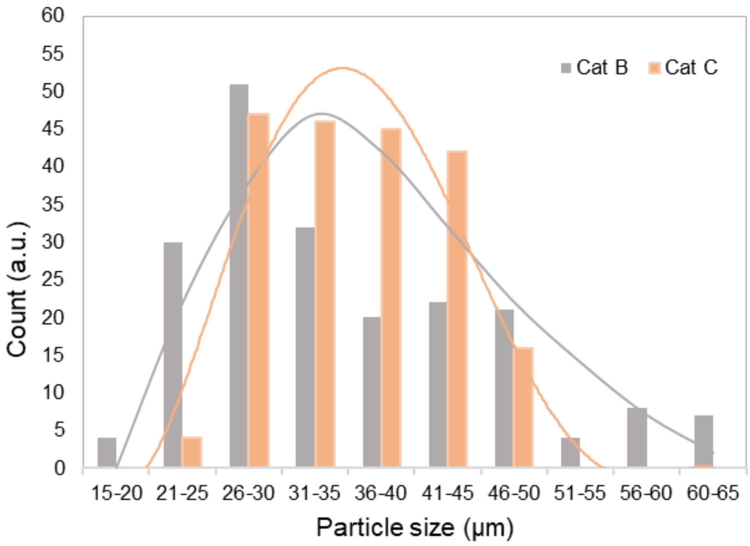


Figure 4. 12 Particle size distribution of Cat B and Cat C

Table 4. 6 shows that Cat C had the highest titanium dispersion on catalyst surface and Ti/Mg ratio. The amount of titanium on catalyst surface tends to be similar to the titanium content in bulk catalysts. It should be mentioned that the dispersion of active sites was mainly located on the external surface of catalyst rather than within pores of catalyst. It can be estimated that active site of titanium on surface of Ziegler-Natta catalyst is beneficial for catalytic activity during polymerization. Moreover, the particle size of catalysts is also listed in **Table 4. 6**. The average diameter size (**Figure 4. 12**) of catalyst granules (Cat B and Cat C) obtained from SEM measurement was approximately 36 μm, whereas Cat A showed the particle size in term of aspect ratio equaled to 6.45:1. Besides, their specific surface area is also the most important characteristic of these catalysts as shown in **Table 4. 6**. Cat C exhibited the largest specific surface area 143 m^2/g. and followed by Cat B and Cat A had the surface area as 127 m^2/g, and 119 m^2/g respectively. These catalysts have a few diversities of the specific surface area. Whatever, the physico-chemical properties of catalyst related to the polymerization behaviors were described with several techniques.

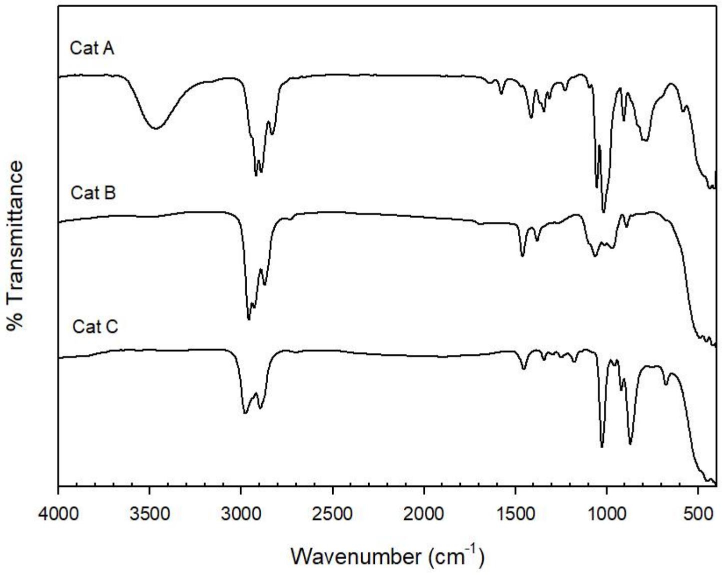


Figure 4. 13 FT-IR spectra of the catalysts

For instance, IR spectroscopy was used to specify the functional group of chemical linkage of these catalysts as shown in **Figure 4. 13**. The characteristic of Ziegler-Natta catalyst peak at 1380-1260 and 1080-910 cm^{-1} was observed indicating the C-O-C asymmetric and symmetric stretching of ester group indicating interaction of catalyst with alcohol group. Moreover, THF peak at 1080-910 cm^{-1} revealed C-O-C stretching for both asymmetric and symmetric stretching. The Ti (III)-Mg-THF complex exhibited the vibration of the C-O-C stretching bands of THF [102, 149]. The C-H stretching band from 2950 to 2850 cm^{-1} also appeared in these catalysts [150]. For Cat A, the IR band in the range of 3500 to 3350 cm^{-1} was attributed to the O-H stretching for alkoxide titanium species with THF opening ring. It suggests that the incorporation of $MgCl_2$ and THF likely changed the titanium species and generated alkoxide titanium species to open ring of THF [151].

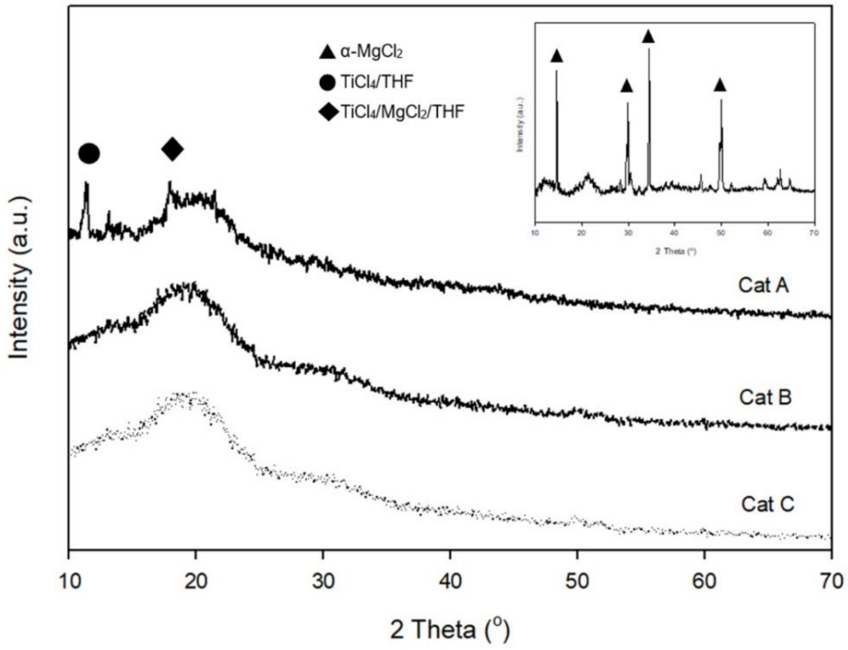


Figure 4. 14 XRD patterns of catalyst with different magnesium sources

The crystal structure of catalysts was analyzed from the obtained XRD patterns in the range of 10-70 degree as illustrated in **Figure 4. 14**. It showed $MgCl_2$ support as mentioned, in which the four diffraction sharp peaks located at 2θ of 14.7°, 29.9°, 34.5°, and 49.9° indicated the formation of α-$MgCl_2$ support (anhydrous $MgCl_2$). The stacking faults of Cl-Mg-Cl triple layers as the direction of crystallographic structure were also identified. The peaks at $2\theta = 34.5^{\circ}$ and 49.9° were defined as the (104) and (110) plane of $MgCl_2$ triple layers, respectively [53, 152, 153]. Cat A displayed the characteristic peaks of $TiCl_4$/THF and $TiCl_4/MgCl_2$/THF complex, which were observed around $2\theta = 11.8^{\circ}$ and 17.8°, respectively [154-156]. For Cat B and Cat C, they showed broad peak or amorphous (less crystallinity). This is likely due to the interaction of Mg^{2+} and alcoholic adduct. This is suggested that the addition of alcohol group can result in less crystallinity. Moreover, the increased distance of plane and decreased 2θ depends on insertion of alcohol group into between $MgCl_2$ triple layers [157]. It is suggested that the presence of alcohol group assisted good dispersion and decreased crystallize size, in which the smaller size than 3 nm cannot be detected by XRD resulting in broad peak observation.

4.3.2 Polymerization of different catalysts

As known, the titanium and magnesium-based Ziegler-Natta catalyst (TMC) is the most employed catalyst in slurry polymerization of polyolefin industries. In this study, TMCs prepared from different magnesium sources and used in gas-phase polymerization were investigated. In addition, different activators (TEA, TnOA, and mixed cocatalyst) affected the polymerization behavior were also studied as mentioned earlier. Catalytic activity of ethylene polymerization with various catalysts and cocatalysts is revealed in **Table 4. 7**.

Table 4. 7 Catalytic activity and particle size distribution of polymer samples

Run number	Polymer Samples	Activity (gPE/gTi.h)	Particle size (μm)	Particle size distribution (μm)
1	PE-Cat A-TEA	48	254.3	119-514
2	PE-Cat A-TnOA	44	289.2	126-539
3	PE-Cat A-TEA+TnOA	71	248.2	88-643
4	PE-Cat B-TEA	557	272.6	99-599
5	PE-Cat B-TnOA	158	274.8	104-469
6	PE-Cat B-TEA+TnOA	305	258.7	95-596
7	PE-Cat C-TEA	1317	431.9	159-754
8	PE-Cat C-TnOA	120	172.9	56-402
9	PE-Cat C-TEA+TnOA	1129	492.2	254-782

Considering Cat A up on different cocatalyst types (Run number 1-3), the mixed cocatalyst (Cat A-TEA+TnOA) has the highest catalytic activity in ethylene polymerization followed by TEA (Run 1) and TnOA (Run 2). It was suggested that $MgCl_2/TiCl_4$ catalyst has good response on coordination of TEA and TnOA. For Cat B, the magnesium powder was used in synthesis and the activity results (Runs 4-6) are also shown. The activity obtained from Cat B-TEA exhibited the highest activity among other cocatalyst systems in the order of Cat B-TEA > Cat B-TEA+TnOA > Cat B-TnOA. This is because TEA has high reducing power compared to other cocatalysts (TnOA and mixed TEA+TnOA) based on its less steric hindrance. Thus, TEA is more active during polymerization. Not only magnesium chloride ($MgCl_2$) and magnesium powder (MgO) were used as support, but the magnesium alkoxide [$Mg(OEt)_2$] (Runs 7-9) was also employed. From **Table 4. 7**, Cat C tended to exhibit the similar activity trend as observed in the Cat B system and it rendered the maximum catalytic activity in gas-phase ethylene polymerization among other catalysts. It was observed that TEA (Cat C-TEA) also exhibited the highest activity (1,317 gPE/gTi.h) followed by the mixed cocatalyst system (1,129 gPE/gTi.h). To compare the catalytic activity depending on types of catalyst and cocatalyst, results are illustrated in **Figure 4. 15**. It should be emphasized that Cat B and Cat C had a similar trend of catalytic activity, whereas Cat A was different. In addition, Cat C reacting with TEA and combination of TEA and TnOA, exhibited high activity. This is due to TEA has high reducing power for changing the titanium species to be high active form. One of important keys in gas-phase ethylene polymerization is temperature profile in reactor during polymerization, which is related to activity of catalyst. The temperature profiles of all catalyst systems are shown in **Figure 4. 16** indicating the fluctuation of temperature in the range of ca. 80 to 90 °C. It can be observed that Cat C-TEA showed the highest increased temperature due to its high activity resulting in highly exothermic released from the polymerization.

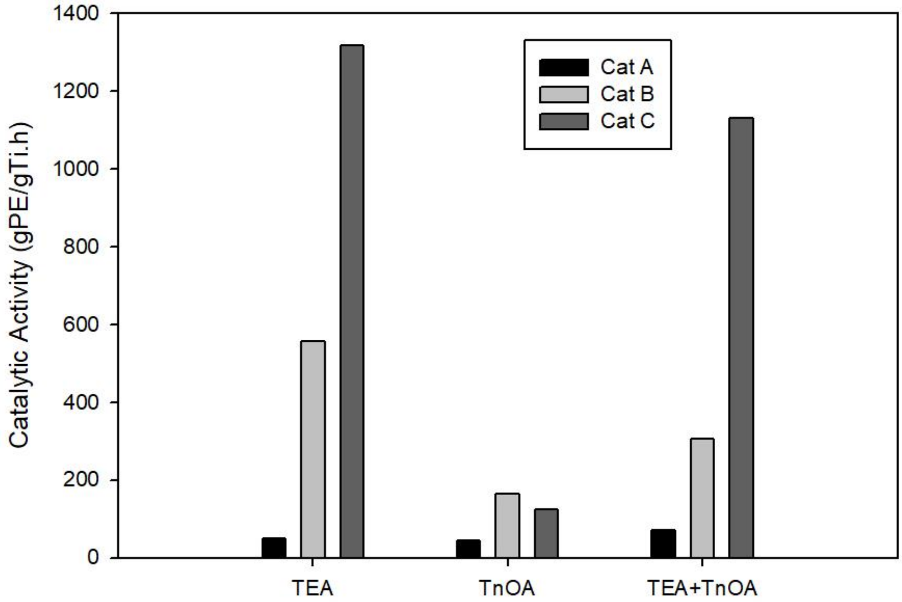


Figure 4. 15 Catalytic activity affected by magnesium sources compared with different activators

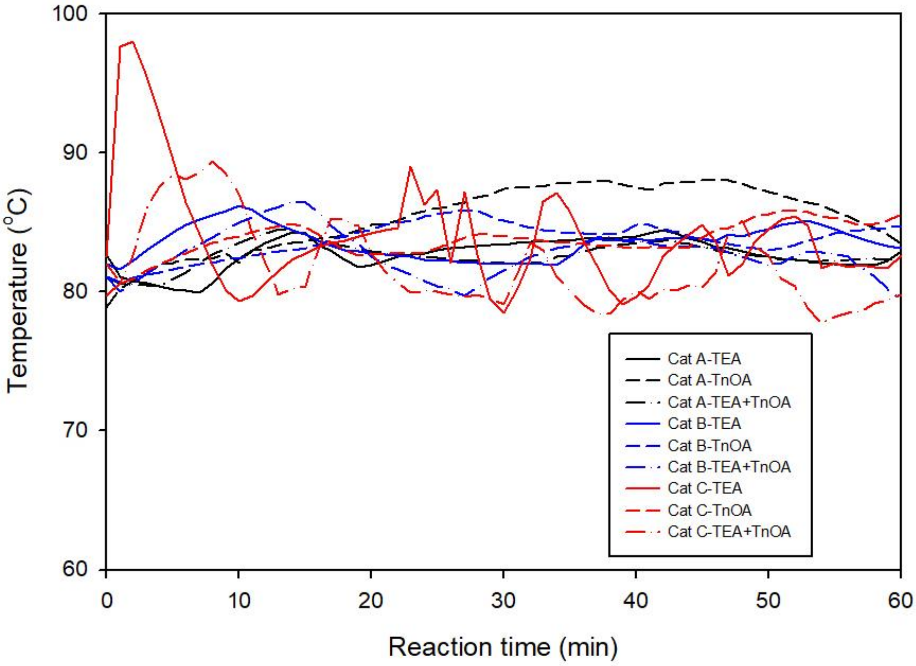


Figure 4. 16 Temperature profiles in reactor with reaction time affected by magnesium sources and cocatalyst types

In addition, the kinetic profiles up on ethylene consumption of each catalyst with combination of cocatalysts (TEA+TnOA) are quite similar as seen in **Figure 4. 17.** As known, the ethylene consumption profiles are distinct the quantities of ethylene consumption for each catalyst, which is related to the polymerization behaviors. As seen in **Figure 4. 17**, all catalysts exhibited the similar ethylene consumption pattern indicating similar polymerization behavior for all catalysts. However, the amounts of ethylene consumption were different, and it reflected the different activity among three catalysts. For instance, using the mixed cocatalyst system, Cat C exhibited the highest activity (highest ethylene consumption rate) followed by Cat B and Cat A as also mentioned in **Table 4. 7**.

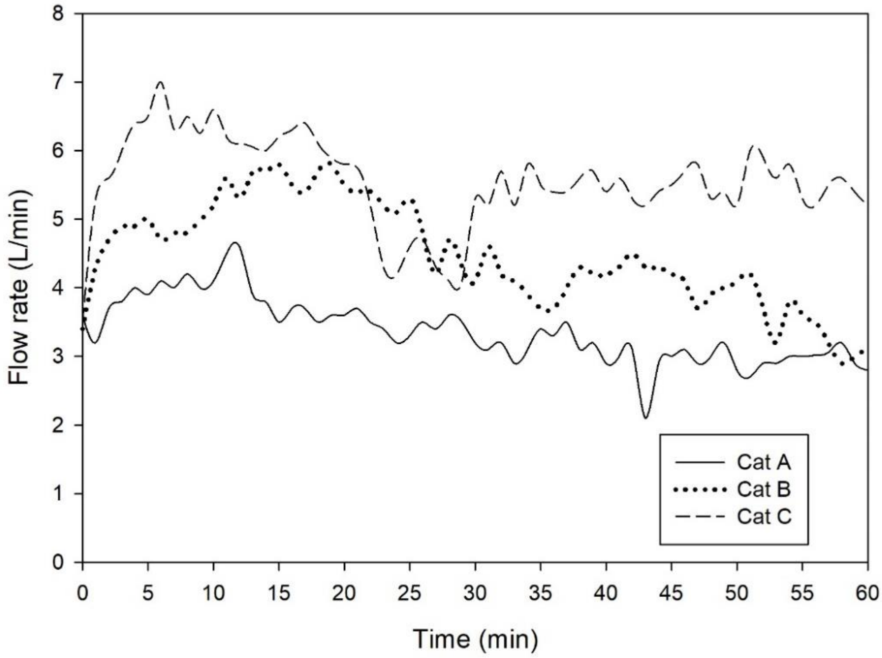


Figure 4. 17 Typical kinetic profiles of each catalyst based on ethylene consumption with mixed cocatalysts

4.3.3 Characteristics of polymer obtained from different catalysts

All polyethylenes obtained were observed from scanning overall morphology as seen from typical SEM images, which are illustrated in **Figure 4. 18**. As shown, the polymer obtained from PE-Cat A-TEA displays fluffy irregular shapes, whereas that derived from PE-Cat B-TEA mostly exhibits spheroidal lump and the one obtained from PE-Cat C-TEA shows spherical particles.

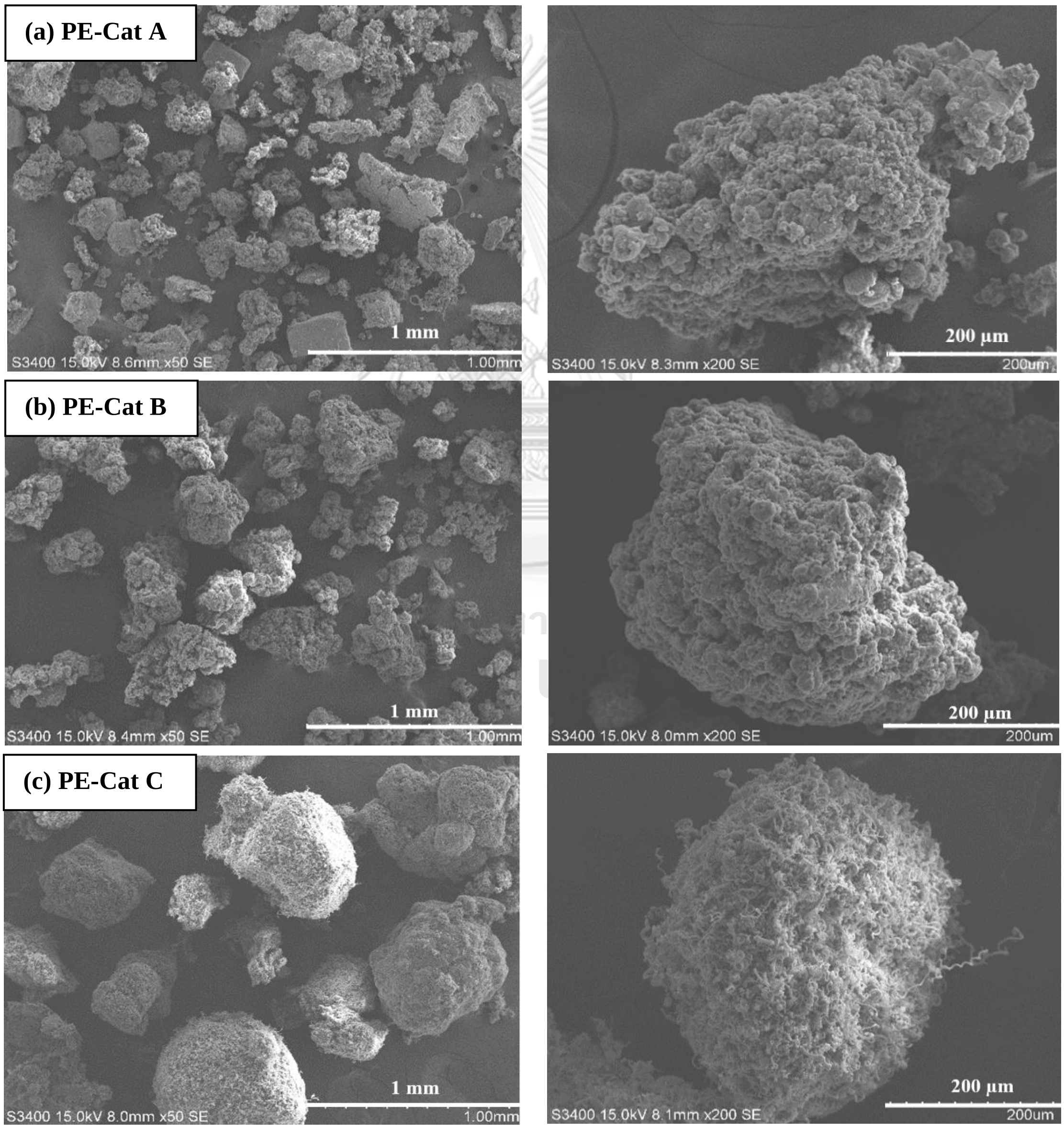


Figure 4. 18 Typical morphologies of polyethylene in variation of catalysts with TEA

When compared polymers obtained from these catalysts, they all replicated the morphology of catalysts with larger size as shown in **Table 4. 7**. In addition, polymer particle distribution of each catalyst with different cocatalyst types is displayed in **Figure 4. 19**. Differently, the particle size of PE-Cat C-TEA and PE-Cat C-TEA+TnOA was around 450-500 µm, which was larger than other polymers (ca. 250-280 µm). As expected, the polyethylenes had almost tenfold in size of support, whereas PE-Cat C-TEA and PE-Cat C-TEA+TnOA was over tenfold in size. The activity of Cat C increased along with the growth of polymer size indicating that polymerization gradually proceeded. Furthermore, active sites on surface were directly affected by titanium distribution on support. It can be attributed to different magnesium sources used to prepare the catalysts and cocatalysts leading to different formation of polymer seed, which was related to the growing of monomers into catalyst porous causing in differences on particle size of polymer.

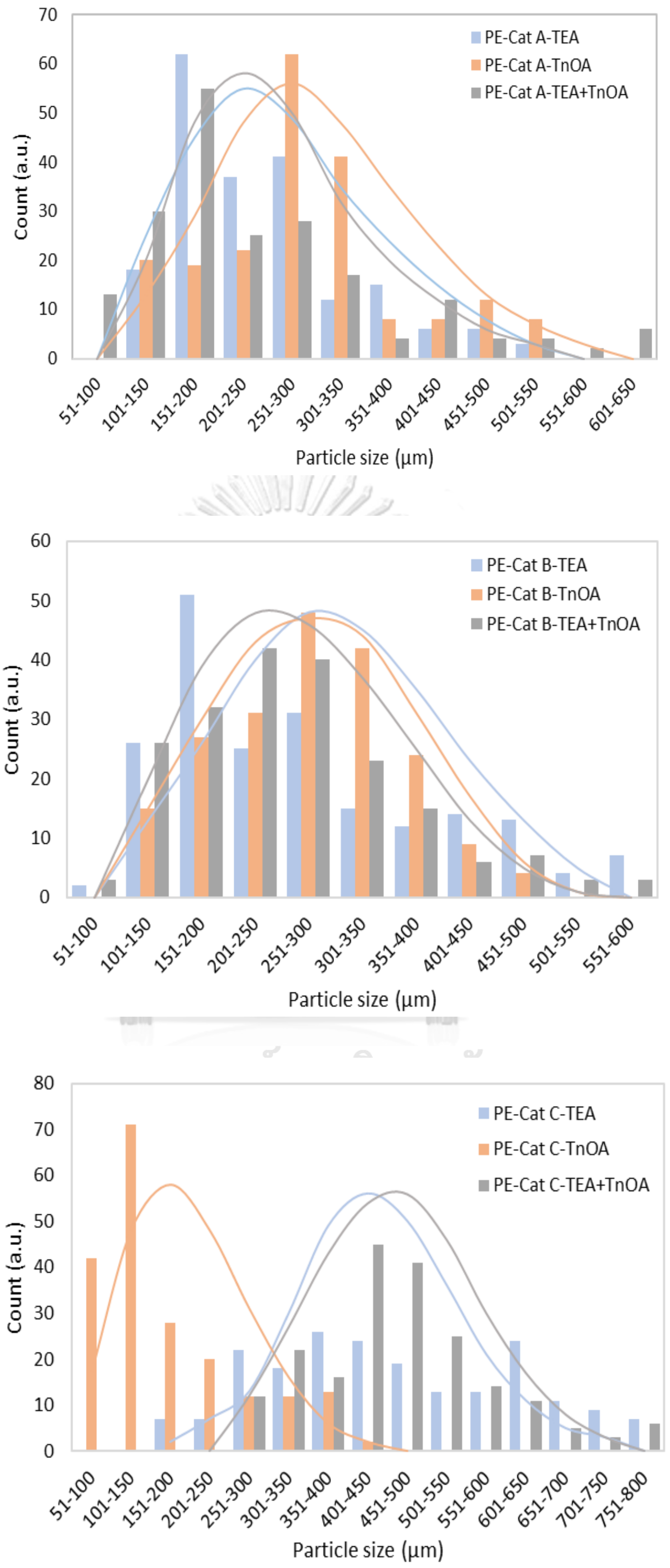


Figure 4. 19 Particle size distribution up on different catalyst types and cocatalysts

Besides, X-ray diffraction (XRD) measurement was used to analyze the crystalline structure of polymer under ambient condition. **Figure 4. 20** shows that the characteristics of polyethylene peaks, in which they all exhibited two diffraction sharp peaks at the 2θ position of 21.7° and 23.9°, indicating polyethylene in (110) and (200) plane, respectively [158-161]. Polymer obtained from Cat B and Cat C had higher intensities than that obtained from Cat A. It is suggested that the crystal structures of polymer also depend on the magnesium sources and cocatalyst types as seen from the XRD results. Another measurement used to obtain melting temperature and crystallinity of polymer is DSC measurement. Results are shown in **Table 4. 8**. Melting temperature of polyethylene was observed between 125^{o}C and 129^{o}C. From melting temperature data, catalyst types have only slight effect on melting temperature using different cocatalysts. Considering %crystallinity, it revealed that PE-Cat C-TEA+TnOA presented high crystallinity (79%).

Table 4. 8 Melting temperature and heat of fusion of polyethylene

Run number	Polymer Samples	T_m (°C)	Heat reaction (J/g)	%Crystallinity
1	PE-Cat A-TEA	125.58	160.9	55.1
2	PE-Cat A-TnOA	126.97	166.5	57.1
3	PE-Cat A-TEA+TnOA	127.08	182.9	62.7
4	PE-Cat B-TEA	127.08	201.8	69.2
5	PE-Cat B-TnOA	126.32	158.0	54.2
6	PE-Cat B-TEA+TnOA	128.81	218.3	74.8
7	PE-Cat C-TEA	127.88	225.4	77.3
8	PE-Cat C-TnOA	126.12	167.1	57.3
9	PE-Cat C-TEA+TnOA	128.68	230.4	79.0

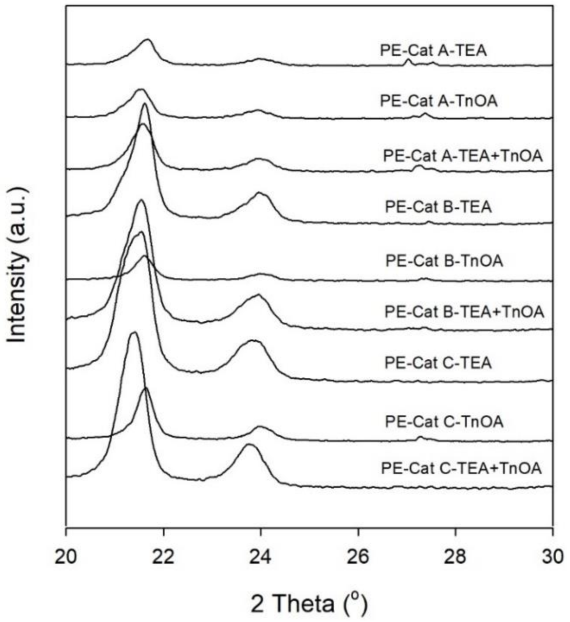


Figure 4. 20 XRD patterns of polyethylene obtained from different catalysts and cocatalysts

Part 4: Different magnesium source supported titanium-based Ziegler-Natta catalyst in gas-phase ethylene/1-hexene copolymerization

4.1 Results and discussion

4.1.1 Catalytic activity with different support sources and polymer properties

Various magnesium sources on titanium-based catalyst from part 3 was studied in gas-phase copolymerization of ethylene with 1-hexene. Moreover, effect of cocatalyst types was also investigated as well. Catalytic activity of copolymerization between ethylene and 1-hexene with different magnesium sources and cocatalysts is presented in **Table 4. 9**.

Table 4. 9 Activity and particle size distribution of copolymer from different magnesium sources

Run number	Polymer Samples	Activity (gCoPE/gTi.h)	Particle size distribution (µm)
1	CoPE-Cat A-TEA	992	159.4
2	CoPE-Cat A-TnOA	381	181.4
3	CoPE-Cat A-TEA+TnOA	502	207.1
4	CoPE-Cat B-TEA	612	420.6
5	CoPE-Cat B-TnOA	425	263.8
6	CoPE-Cat B-TEA+TnOA	703	224.6
7	CoPE-Cat C-TEA	1382	242.1
8	CoPE-Cat C-TnOA	1006	423.0
9	CoPE-Cat C-TEA+TnOA	1141	284.8

Considering $MgCl_2$/THF catalyst in Run number 1-3 with different cocatalyst types, Cat A-TEA (Run 1) exhibits the highest value of copolymerization activity of ethylene and 1-hexene due to THF as Lewis base improved insertion of 1-olefin in copolymerization. Even though THF provides low catalytic activity in polymerization, yield of polymer from copolymerization increases when compared with homo-polymerization of ethylene. Moreover, TEA is more highly active to activate the titanium-based catalyst in polymerization. It was concluded that $MgCl_2$/THF was appropriate to cooperate with TEA in enhancement of 1-hexene into main chain polymer. As mentioned, for magnesium powder (MgO) and activator types in Run number 4-6, the activity value shows that Cat B-TEA+TnOA had the highest activity followed by Cat B-TEA (Run 4) and Cat B-TnOA (Run 5). This indicated that the mixed cocatalyst was suitable depending on the combination of activators and properly satisfied. Besides, the magnesium ethoxide based titanium catalyst is also used in gas-phase ethylene/1-hexene copolymerization as shown in **Table 4. 9**. As described in Runs 7-9, Cat C-TEA also exhibited the maximum catalytic activity (1382 g of co-polyethylene/gTi.h) in the gas-phase system among other supported-catalysts.

The catalytic activity between homo- (**Table 4. 7**) and co-polymerization of ethylene/1-hexene (**Table 4. 9**) is correlated. It is observed that all copolymerization system had higher catalytic activity than all homo- system. The polymerization rate is counted on the addition of 1-olefin as comonomer. This is called “comonomer effect”. The numbers of active sites or titanium species are increased and activated by comonomer as Lewis base in polymerization.

Gas-phase polymerization system mainly concerns about good morphology of polymer or spherical shape. Surface and morphology of polymer is previewed in SEM micrographs (see **Figure 4. 21**). Perspective polymer shows almost spherical polymer.

Furthermore, surface of polymer is also more porous and smoother coated by 1-olefin. Moreover, the particle size of polymer obtained from Cat A has an average size between 150–200 μm, but CoPE-Cat B and CoPE-Cat C exhibits larger size than CoPE-Cat A. From **Table 4. 9**, the average polymer size was around 220-430 μm. As expected, particle sizes of polymer probably indicate insertion to attach 1-hexene on surface catalyst.

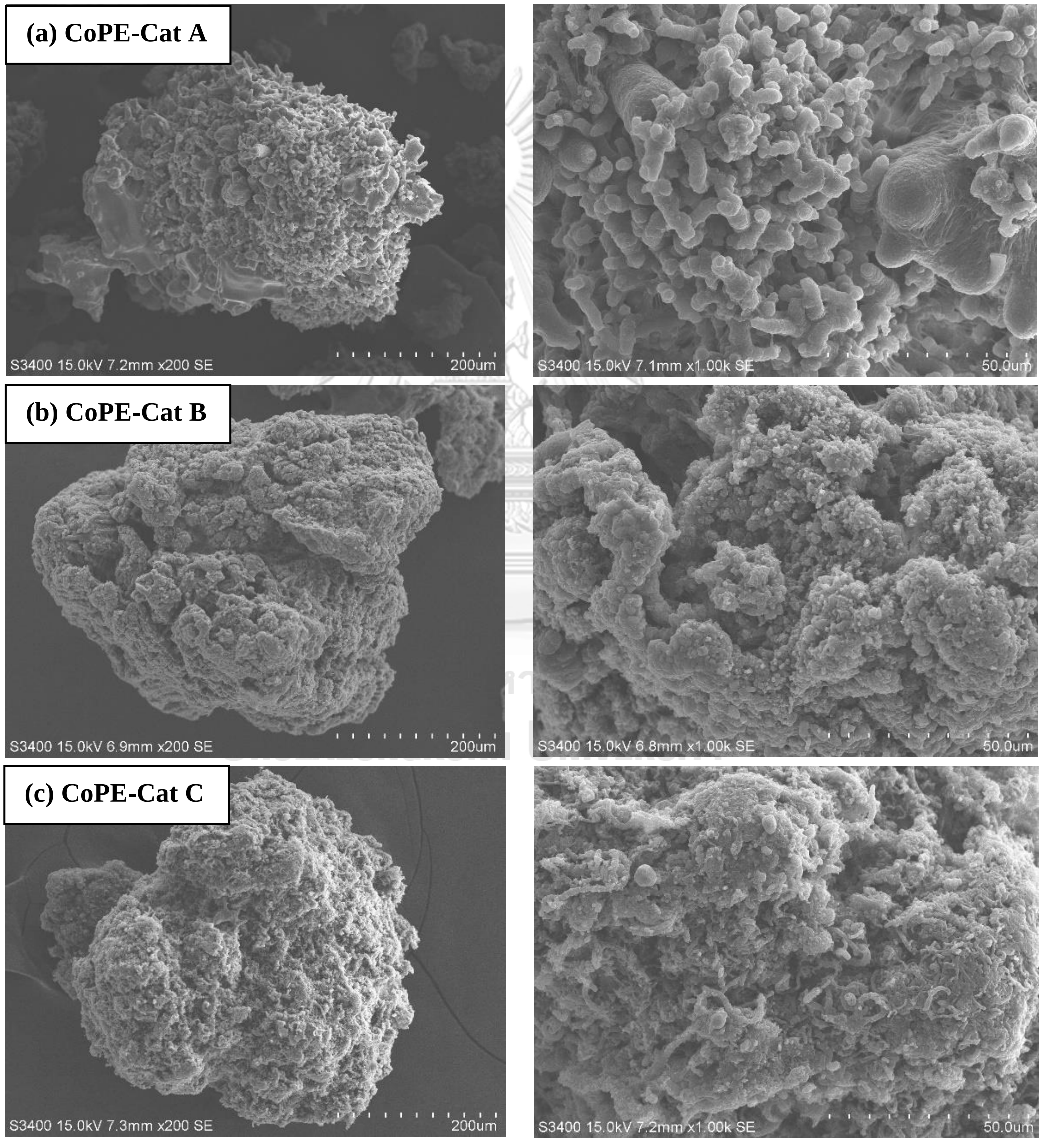


Figure 4. 21 Typical overall structure of polymer from 1-hexene and ethylene by mixed TEA and TnOA

Table 4. 10 Suggested insertion of 1-hexene on polyethylene from extraction method

Run number	Polymer Samples	Activity (gCoPE/gTi.h)	Boiling n-heptane solution (%wt)
1	CoPE-Cat A-TEA	992	10.4
2	CoPE-Cat A-TnOA	381	11.4
3	CoPE-Cat A-TEA+TnOA	502	13.0
4	CoPE-Cat B-TEA	612	16.3
5	CoPE-Cat B-TnOA	425	13.4
6	CoPE-Cat B-TEA+TnOA	703	15.3
7	CoPE-Cat C-TEA	1382	20.5
8	CoPE-Cat C-TnOA	1006	25.4
9	CoPE-Cat C-TEA+TnOA	1141	25.1

In addition, the polymers obtained from ethylene/1-hexene copolymerization were analyzed in Soxhlet extraction method. This method is estimated for implied incorporation of 1-hexene. Boiling n-heptane can dissolve some parts of polymer in amorphous section (1-hexene insertion), but insoluble part refers to crystallization of main chain polyethylene. These previous reason hints the amount of 1-olefin insertion. From **Table 4. 10**, Cat C ($Mg(OEt)_2$) introduces the highest solubility of polymer in boiling n-heptane. TnOA and mixed cocatalyst (TEA+TnOA) show the similar percentage of soluble weight. This is due to cocatalyst group had more steric hindrance and affected to rapid reaction. However, polymer obtained from Cat C is also more soluble than other catalysts. Cat A and Cat B has nearly soluble polymer between 10 to 16. CoPE-Cat C-TnOA and CoPE-Cat C-TEA+TnOA suggesting higher incorporation of 1-hexene. It means that polymer obtained are more insertion and influence on more amorphous polymer. Another analysis used to confirm insertion of 1-hexene in polymer is DSC analyzer measured melting temperature and crystallinity of polymer as seen in **Table 4. 11**. All copolymers reveal melting temperature around 112°C -115°C when compared homo-polyethylene (see **Table 4. 8**) showed these values between 125°C and 129°C. It indicated that 1-hexene is incorporated in polyethylene. Hence, crystallinity of polymer decreases when insertion of 1-hexene increases. In agreement with %copolymer crystallinity, the melting temperature of polymer relates to heat of reaction and %crystallinity. CoPE-Cat A exhibits more amorphous than other polymers. This is due to enhancement of 1-hexene insertion had an effect on crystal structure.

Table 4. 11 Copolymer properties from DSC measurement

Run number	Polymer Samples	T_m (°C)	Heat reaction (J/g)	%Crystallinity
1	CoPE-Cat A-TEA	113.7	31.27	10.72
2	CoPE-Cat A-TnOA	112.6	37.32	12.79
3	CoPE-Cat A-TEA+TnOA	114.5	38.24	13.11
4	CoPE-Cat B-TEA	114.0	50.51	17.32
5	CoPE-Cat B-TnOA	113.7	42.3	14.50
6	CoPE-Cat B-TEA+TnOA	114.5	70.34	24.11
7	CoPE-Cat C-TEA	115.3	52.74	18.08
8	CoPE-Cat C-TnOA	112.1	45.35	15.55
9	CoPE-Cat C-TEA+TnOA	113.9	47.84	16.40

CHAPTER 5

General conclusions

5.1 General summary

This dissertation focused on titanium-based Ziegler-Natta catalyst with different cocatalyst types (TEA, TnOA, and mixed TEA+TnOA) using in olefin polymerization system for both ethylene and propylene. Chapter 4 has been divided into 4 parts. In the first two parts, the commercial catalyst as titanium-based was used in slurry polymerization. In the first part, the commercial catalyst using TEA had the highest activity in both homo- and co-polymerization system and different reaction temperatures. Besides, this part chiefly emphasized the titanium (III) oxidation state to verify by ESR technique. The results showed that mixed cocatalyst (TEA+TnOA) can stabilize titanium (III) state. As expected, the stability of titanium state (Ti^{3+}) brought about more insertion of 1-olefin and more polypropylene yields. To confirm the oxidation state of titanium, effect of cocatalyst types and reaction temperature (50^oC-70^oC) using similar catalyst in propylene polymerization was also investigated in Part 2. At 60^oC, TEA provided the maximum catalytic activity, whereas combination of TEA and TnOA at 50^oC exhibited the second highest activity and the most isotactic index for PP. It was found that combination of cocatalyst at 50^oC resulted in more stabilized Ti^{3+}. Not only slurry polymerization was evaluated, but also gas-phase polymerization was studied in Parts 3 and 4. Different magnesium sources-based titanium Ziegler-Natta catalyst were considered. Cat C-TEA [$Mg(OEt)_2$ supported] was employed to obtain the maximum polymerization activity for both ethylene polymerization and ethylene/1-hexene copolymerization. However, the yield of copolymer was higher than homopolymer. It called “Comonomer effect” that surely occurred in gas-phase process. Moreover, the main point of gas-phase polymerization is good morphology of polymer. It obtained nearly spherical particles.

5.2 Conclusions

Part 1: Facile investigation of Ti^{3+} state in Ti-based Ziegler-Natta catalyst with a combination of cocatalysts using electron spin resonance (ESR)

In summary, the TEA activation exhibited the highest catalytic activity in both ethylene polymerization and ethylene/1-hexene copolymerization. From ESR measurement, it revealed that TEA has high reducing power having more Ti^{2+}, which is highly active for ethylene polymerization. The TnOA activation resulted in the lowest activity due to its lowest reducing power. It was surprising that the use of TEA+TnOA combination to activate ZN catalyst led to increase the stability of Ti^{3+} species, even though it exhibited lower activity in ethylene polymerization. In most case, different cocatalysts did not have significant effect on polymer properties.

Part 2: Temperature effect on propylene polymerization behavior over Ziegler-Natta catalyst with different cocatalyst systems

Among effects of polymerization temperature (ca. 50, 60 and 70°C) for three cocatalyst systems, TEA exhibited the highest activity at 60°C (PP-60-A) for propylene polymerization. At 70°C, the catalyst seemed to be over reduction to Ti^{2+} leading to decreased activity for each cocatalyst system. When the polymerization temperature was lower to 50°C, the mixed cocatalyst system rather gave the highest activity. This can be attributed to the stabilization of Ti^{3+} throughout polymerization as proven by ESR measurement. Moreover, isotactic polypropylene can confirm from melting temperature around 152-156°C and XRD patterns indicating at 14.2°, 17.2°, 18.6° and

21.6^{o}. It resulted that no significant effect found on the polymer properties regarding to changes of polymerization temperature and types of cocatalysts.

Part 3: Gas-phase polymerization of ethylene over Ti-based Ziegler-Natta catalysts prepared from different magnesium sources

Different magnesium sources used to prepare the catalysts with various cocatalyst types apparently affected the gas-phase ethylene polymerization behaviors. It revealed that Cat C [$Mg(OEt)_2$] exhibited the highest catalytic activity using TEA as cocatalyst (Cat C-TEA). This is likely due to optimal distribution of active sites in this catalyst. Based on activity results, Cat C was the most active catalyst probably due to good active site distribution under the specified condition. In addition, Cat B tended to similarly behave like Cat C when TEA was employed showing high activity. Nevertheless, Cat A with combination of cocatalysts (Cat A-TEA+TnOA) exhibited the highest activity among other cocatalyst systems. Morphology of catalyst and polymer was depicted. The polymer size appeared over tenfold of catalyst size using Cat C-TEA and Cat C-TEA+TnOA, whereas the other catalysts gave almost tenfold. It can be concluded that catalyst has more pronounced effect on polymer size than cocatalyst.

Part 4: Different magnesium sources supported titanium-based Ziegler-Natta catalyst in gas-phase ethylene/1-hexene copolymerization

The catalyst in part 3 (different magnesium sources) was used in gas-phase ethylene/1-hexene copolymerization. The Cat C-TEA exhibited the maximum activity. Comparison between homo- and co-polymerization using the similar catalyst was studied. The yield from copolymerization was higher than homo- system; called “comonomer effect”. The Soxhlet extraction was used to indirectly analyze 1-

hexene insertion into main polyethylene. Cat C-TnOA and Cat C-TEA+TnOA provided the most solubility polymer (comonomer insertion) in boiling n-heptane. It presumed that the polymer was more soluble, more amorphous (more insertion) was predicated. Moreover, incorporation of 1-hexene was also confirmed from DSC analyzer showing melting temperature and %crystallinity of polymer obtained. So, both results in copolymerization presented lower than homo- process.

5.3 Recommendations

- The X-ray photoelectron spectroscopy (XPS) measurement would be used to analyze all oxidation state of titanium (Ti^{2+}, Ti^{3+}, and Ti^{4+}).
- The morphology of polymer would be improved good spherical particles from the other methods.
- The addition of Lewis acid sites in $TiCl_4$/Lewis acid/$MgCl_2$/THF would be demonstrated in gas-phase copolymerization for study of insertion of 1-hexene.

APPENDIX A

FOURIER TRANSFORM INFRARED SPECTROSCOPY

Table A.1 Characteristic IR and Raman vibrations of the Ziegler-Natta catalyst

Vibration	Type of vibration	Region (cm^{-1})	
		IR	Raman
$C–H_{Ar}$	Stretching	3070	3080
CH_2/CH_3	Stretching	2800–3000	2800–3000
CO	Stretching	1684	1685
$C\text{-}C_{Ar}$	Stretching	–	1592
CH_2/CH_3	Deformation vibration	1454	1449
CH_3	Symmetric deformation vibration	1392	1395
C–O–C	Asymmetric stretching	1308	1302
C–O–C	Symmetric stretching	1156	1156
$C–H_{Ar}$	In plane deformation vibration	–	1140
O–C=O	Asymmetric stretching	1082	–
$C–H_{Ar}$	In plane deformation vibration	–	1052
O–C=O	Symmetric stretching	934	–
C–H	Out of plane deformation vibration	736	647
M–O (Mg–O or Ti-O)	Stretching	460	–
Titanium compound	Stretching	–	419
M–O (Mg–O or Ti-O)	Stretching	350	350
M–O (Mg–O or Ti-O)	Stretching	314	303
Ti–Cl	Stretching	375	–
Ti–Cl	Stretching	365	–
Ti–Cl	Stretching	382	–
Mg–Cl	Stretching	233	238
Mg–Cl	Stretching	242	–

APPENDIX B

LIST OF PUBLICATIONS

B-1 Publications

1. Thanyaporn Pongchan, Piyasan Praserthdam, and Bunjerd Jongsomjit, “Facile Investigation of Ti3+ State in Ti-based Ziegler-Natta Catalyst with A Combination of Cocatalysts Using Electron Spin Resonance (ESR)”, *Bulletin of Chemical Reaction Engineering & Catalysis*, 15 (1) 2020, 55-65.

2. Thanyaporn Pongchan, Piyasan Praserthdam, and Bunjerd Jongsomjit, “Temperature effect on propylene polymerization behavior over Ziegler-Natta catalyst with different cocatalyst systems”, *Materials Research Express*, 7 (2020) 025309.

3. Thanyaporn Pongchan, Piyasan Praserthdam, and Bunjerd Jongsomjit, “Gas-Phase Polymerization of Ethylene over Ti-based Ziegler-Natta Catalysts prepared from Different Magnesium Sources”, *Materials Today Chemistry,* 18 (2020) 100366.

B-2 Conference contributions

1. Oral presentation: Thanyaporn Pongchan, Piyasan Praserthdam, and Bunjerd Jongsomjit, Effect of Co-Catalyst Combination on Ti-Based Ziegler-Natta Catalyst in Gas-Phase Ethylene Polymerization, Fourth edition of International Conference on Catalysis and Chemical Engineering 2020 (CCE-2020), Los Angeles, California, United States, February 24-26, 2020.

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