

พอลิเมอร์ไรเซชันของเอทิลีนกับหนึ่งโอเลฟินด้วยตัวเร่งปฏิกิริยาเมทัลโลซีน  
บนตัวรองรับมีโซพอร์สไทเทเนีย



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COPOLYMERIZATION OF ETHYLENE/1-OLEFIN WITH  
MESOPOROUS TITANIA-SUPPORTED METALLOCENE CATALYST



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สมชาติ อมรเลิศปรีชา: โคพอลิเมอร์โรเซชันของเอทิลีนกับหนึ่ง โอลิฟินบนตัวเร่งปฏิกิริยาเมทัลโลซีนบนตัวรองรับมีไซพอร์สไทเทเนียม.(COPOLYMERIZATION OF ETHYLENE/1-OLEFIN ON MESOPOROUS TITANIA-SUPPORTED METALLOCENE CATALYST) อ. ที่ปริกษาวิทยานิพนธ์หลัก :รศ. ดร.บรรเจิด จงสมจิตร, 65 หน้า.

ทุกวันนี้ ตัวเร่งปฏิกิริยาเมทัลโลซีนได้รับความสนใจทั้งทางด้านงานวิจัย และ ด้านอุตสาหกรรม เห็นได้จากการมีการตีพิมพ์วารสารทางวิชาการออกมาจำนวนมากในระยะหลัง อย่างไรก็ตาม ตัวเร่งปฏิกิริยาเมทัลโลซีนในปฏิกิริยาทั่วไปมีข้อเสียหลักอยู่ 2 ประการ คือ ไม่สามารถควบคุมโครงสร้างพื้นฐานของพอลิเมอร์ที่ผลิตได้ และเกิดสิ่งตกปรกเกาะติดอยู่ภายในเครื่องปฏิกรณ์ เพื่อแก้ปัญหาที่กล่าวไปนี้ ตัวเร่งปฏิกิริยาเมทัลโลซีนชนิดมีตัวรองรับจึงถูกศึกษาและพัฒนาอย่างต่อเนื่อง นอกจากนี้ การนำระบบตัวรองรับมาใช้ ยังช่วยให้ปฏิกิริยาใช้ตัวร่วมปฏิกิริยาที่มีราคาสูงในปริมาณลดลง และยังสามารถนำตัวเร่งปฏิกิริยาเมทัลโลซีนไปใช้ในอุตสาหกรรมได้อีกด้วย ในงานวิจัยนี้ได้นำตัวเร่งปฏิกิริยาเมทัลโลซีนมาใช้ในการสังเคราะห์พอลิเอทิลีนความหนาแน่นต่ำชนิดโซ่ตรง ด้วยปฏิกิริยาโคพอลิเมอร์โรเซชันของเอทิลีนกับ 1-โอลิฟิน โดยใช้มีไซพอร์สไทเทเนียมที่มีพื้นที่ผิวต่างๆ เป็นตัวรองรับ โดยการทดลองเริ่มจากการสังเคราะห์มีไซพอร์สไทเทเนียมในหลายๆ อัตราส่วน (ไทเทเนียมต่อน้ำ) แล้วนำไปวิเคราะห์ด้วย BET, XRD และ SEM ไทเทเนียมที่ได้จะทราบว่า มีรูพรุนชนิด มีไซพอร์สถูกแสดงให้เห็นด้วย isotherms ชนิดที่ 4 ด้วยเทคนิค BET ทราบว่าเป็นเฟสอนาเทสได้จากการตรวจสอบด้วยเครื่องมือ XRD และ เห็นโครงสร้างของไทเทเนียมด้วยเครื่อง SEM ไทเทเนียมที่ได้จะถูกบดเกาะด้วยตัวเร่งปฏิกิริยาร่วมเมทิลอะลูมิเนียมออกเซนและวิเคราะห์ด้วย SEM/EDX, XPS, TGA และ พบว่าปริมาณอะลูมินาในเมทิลอะลูมิเนียมออกเซนมีการกระจายตัวได้ดีเมื่อดูด้วย SEM/EDX และ XPS โคพอลิเมอร์ที่ได้จะถูกนำไปวิเคราะห์ด้วย  $^{13}\text{C}$  NMR ความว่องไวในการเกิดปฏิกิริยาจะสูงสุดเมื่อใช้มีไซพอร์สไทเทเนียมที่มีพื้นที่ผิวสูงสุดเนื่องจากอันตรกิริยาที่เหมาะสมระหว่างตัวรองรับและตัวเร่งปฏิกิริยาร่วมดังที่เห็นได้จาก TGA โคพอลิเมอร์ที่ได้เป็นโคพอลิเมอร์แบบสุ่มที่มีทรานส์-1,2-พิกเชอร์ที่ต่างกันดังที่พิสูจน์ได้จาก  $^{13}\text{C}$  NMR

ภาควิชา.....วิศวกรรมเคมี..... ลายมือชื่อนิสิต..... *สมชาติ อมรเลิศปรีชา*.....  
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SOMCHAT AMORNLERTPREECHA : COPOLYMERIZATION OF  
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Nowadays metallocene catalysts have been interesting both research and commercial. However general metallocene catalysts have had two major disadvantages of homogeneous system that are the lack of controllable morphology and occur fouling in the reactor. To overcome these problems the supported metallocene catalyst system has been investigated and developed continually. Besides this strategy may be less amount of MAO usage and utilized in gas-phase processes. In this study, metallocene catalyst was used for linear low density polyethylene syntheses by ethylene and 1-olefin copolymerization with various surface area mesoporous titania as support. First, mesoporous titanias were synthesized in various hydrolysis ratios (Ti/H<sub>2</sub>O), and characterized by BET, XRD, SEM. The obtained titania was found that the mesoporous form of titania was obtained in isotherms type IV by BET technique. Anatase phase was detected by XRD and structure of mesoporous titania was seen by SEM. The various surface area mesoporous titanias were impregnated with methylaluminumoxane, and then characterized by SEM/EDX, XPS and TGA. It was found that the [Al]<sub>MAO</sub> distribution on the TiO<sub>2</sub> supports was good as seen by SEM/EDX and XPS. The copolymer obtained was further characterized by <sup>13</sup>C NMR. The highest activity occurred when the highest surface area of mesoporous TiO<sub>2</sub> was employed due to the optimal interaction between the support and cocatalyst as seen by TGA. The copolymer obtained were random copolymer having different triad distribution as proven by <sup>13</sup>C NMR.

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ศูนย์วิจัยทรัพยากร  
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# CHAPTER I

## INTRODUCTION

In the 21<sup>st</sup> century, everyone could not think of life without polymers. Almost everything can be and is, made from polymer. The most common polymers are polyolefin, especially polyethylene (PE) and polypropylene (PP). Polyolefin shows approximately 50% by weight of all goods from polymers. It is estimated amount to about 90% by weight of the global polymer production [Severn et al., 2008]. A polyolefin is a polymer produced from a simple olefin (also called an “alkene”) as a monomer, sometime known polyalkene. For example, polyethylene is a polymer consisting of ethylene monomer.

For last years, polyethylene is the most commodity plastics frequently seen in daily life due to their various applications. It is the polymer that makes plastic shopping bags, bottles, toys, to even bullet proof cloth [Hu and Rohr, 1999; Meng et al., 2005]. Many methods to improve the properties of polymer such as grafting, crosslink and sometimes some of the  $\alpha$ -olefin including 1-hexene, 1-heptene and 1-octene [Gao et al., 2008; Svoboda et al., 2008], instead of having hydrogen attached to main chain, will provide long chains of polyethylene. This is called branched or low-density polyethylene (LDPE).

Nowadays, LDPE is an important type of polymer because of its high flexibility and low cost [Knuuttila et al., 2004; Zavala et al., 2008]. LDPE is analyzed the worldwide markets in thousands of metric tons. This quantity of LDPE concludes for films & sheet, injection molding, extrusion coating, blow molding, and others. Many famous companies interest to apply LDPE to their product such as Chevron Phillips Chemical Company, Dow Chemical Company [Chum and Swogger, 2008], DuPont and Exxon. LDPE production first started in 1950s with high pressure process. However, the development of metallocene catalysts could further help with processing quality to LDPE.

The discovery of metallocene catalyst began era of modern olefins technology [Kaminsky and Laban, 2001]. Metallocene polyethylene grades promise a broader processing procedures and shorter cycle times, improved flow properties and potentially better microstructure control. To develop a sound market, it is important for users to understand what advantages of metallocene products will bring about as well as any technological difficulties still to be overcome. However, it was found that the homogeneous metallocene catalytic systems still have some drawbacks; for example, (1) the lack of morphology control of polymer causing the reactor fouling; (2) the limitation of being able to use only in the solution process, whereas the existing technologies are mainly based on the gas phase and slurry processes; and (3) they require a lot of cocatalysts, which cost highly. Hence, binding these metallocene catalysts onto suitable inorganic supports can provide a promising way to overcome these drawbacks [Jiamwijitkul et al., 2007; Bunchongturakarn et al., 2007]

One of methods to apply metallocenes for the polymerization of olefin in slurry or gas phase is supported them on suitable support. Typical supports are inorganic oxide such as silicon, aluminium, titania and zeolite [Ciardelli et al., 1998]. Silica has been the most interest support to study because of high surface area, good stability and low cost. Other supports that have high surface area like silica are mesoporous material such as MCM (mobil composition of matter), SBA (Santa Barbara amorphous) and mesoporous titania but they have been less investigated. This study focused on synthesis of LLDPE via the *in situ* polymerization of ethylene/ $\alpha$ -olefin (1-hexene and 1-octene) with titania-supported zirconocene/MAO catalyst. The effect of mesoporous titania-supported catalyst on the polymer properties was investigated.

The main objective of this work was to investigate the influence of surface area of mesoporous titania supports on the catalytic activity and polymer properties. The mesoporous titania supports have pore size ranging between 2-50 nanometer that different surface areas employed as supports for zirconocene/MAO catalyst system. The properties of the supports were characterized using N<sub>2</sub> physisorption, X-ray diffraction (XRD) and scanning electron microscope (SEM). The impregnated

supports were characterized using scanning electron microscope/energy dispersive X-ray spectroscopy (SEM/EDX) and thermal gravimetric analysis (TGA). The obtained copolymer was characterized by  $^{13}\text{C}$ -nuclear magnetic resonance ( $^{13}\text{C}$ -NMR), and differential scanning calorimeter (DSC).

This thesis was separated into five chapters. Chapter I involved an introduction of the metallocene catalyst. In Chapter II overviewed literatures using metallocene catalysis for olefin polymerization were presented. The literature review was emphasized on metallocene catalyst system used for copolymerization of ethylene with  $\alpha$ -olefins. In chapter III presented the experimental procedure as well as the instrument and techniques used for characterizing the obtained polymers. In Chapter IV presented the results of properties of synthesized mesoporous titania supports and catalytic activity of  $\alpha$ -olefins copolymerization using various titania supported zirconocene/MAO catalysts included discussion about the influences of various surface area of mesoporous titania supports on the catalytic activity and polymer properties in  $\alpha$ -olefins copolymerization. The characteristics support and catalyst precursors using  $\text{N}_2$  physisorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometer (EDX) and X-ray photoelectron spectroscopy (XPS) and obtained copolymer using differential scanning calorimetry (DSC) and  $^{13}\text{C}$ -nuclear magnetic resonance ( $^{13}\text{C}$ -NMR).

Finally, conclusions of this thesis and more recommendations for future research work were indicated in Chapter V.

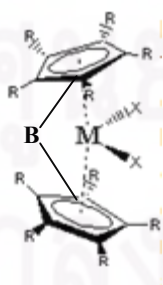
## CHAPTER II

### LITERATURE REVIEWS

#### 2.1 Metallocene catalysts

The mid 1970, Walter Kaminsky succeeded in polymerizing ethylene with the metallocene catalyst system and discovered the utility of MAO for catalysis accidentally. The experiment used the bis(cyclopentadienyl) zirconium dichloride ( $\text{Cp}_2\text{ZrCl}_2$ ) as metallocene catalyst and methylaluminoxane ( $\text{Al}(\text{CH}_3)_3$  or called MAO for short) as a cocatalyst, the system had water that react with trimethylaluminum (TMA) to give methylaluminoxane (MAO). This accident made the good result for activity of polymerization.

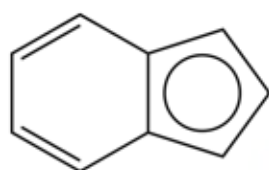
Metallocene compounds as show in **Figure 2.1** are discrete molecules that have two cyclic ligands [Nomura et al., 2002] bonded to a metal center [Guizado-Rodriguez et al., 2007]. These compounds have been named "sandwich complexes". In the other hand, organometallic compounds bearing only one cp-ligand are known as "half sandwich complexes". The metallocene is often used for all single-site catalysts. The single-site catalysts mean catalysts produce polymers with narrow molar mass distribution. The catalytic behavior of single-site catalysts can be controlled by modification of the structure of the catalyst [Cruz et al., 2007].



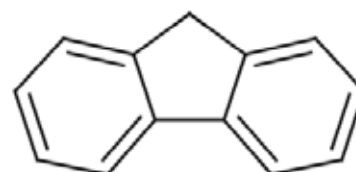
- When M = group 4 transition metal (e.g. Zr, Ti or Hf)  
B = an optional bridging unit (e.g. ethylene)  
R = hydrocarbyl substituents or fused ring systems  
(indenyl, fluorenyl and substituted derivatives)  
X = chlorine or other halogens or an alkyl group

**Figure 2.1** Matallocene structure





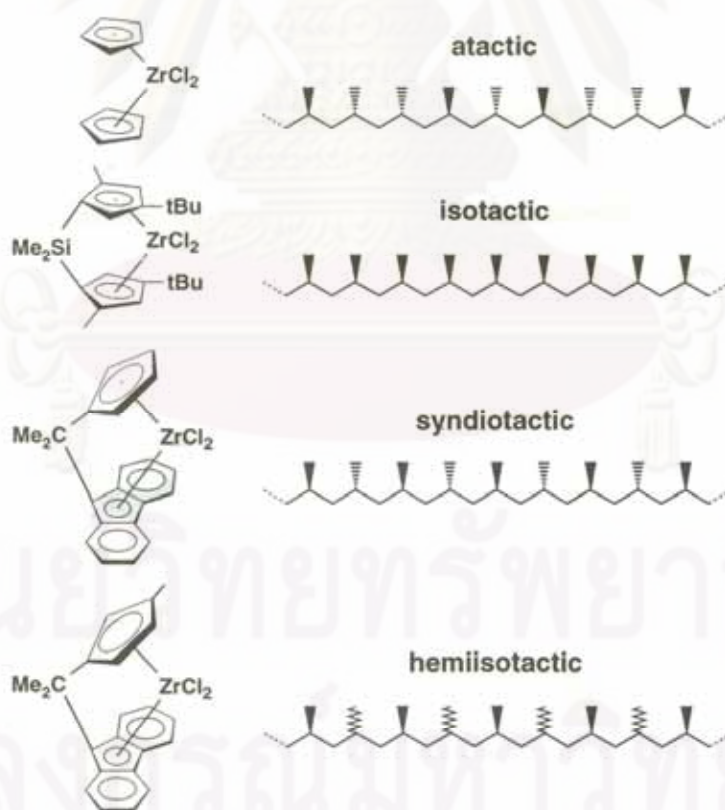
2.2a indenyl



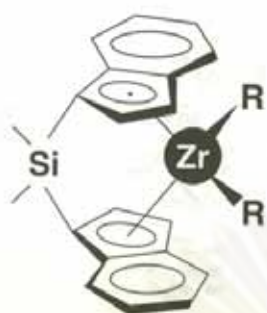
2.2b fluorenyl

**Figure 2.2** Hydrocarbonyl substituents of metallocene [<http://academic.sun.ac.za>]

Stereoselectivity can be controlled with many causes such as type of substituents as **Figure 2.3** and chiral effect following **Figure 2.4** shows racemic (rac) and meso form. The mixture of the rac form and the meso form will not produce the desired isotactic polymer. Therefore, the meso form has to be separated from the rac form in order to obtain a highly isotactic polymer.



**Figure 2.3** The control of stereoselectivity by substituents [<http://academic.sun.ac.za>]



2.4a rac form



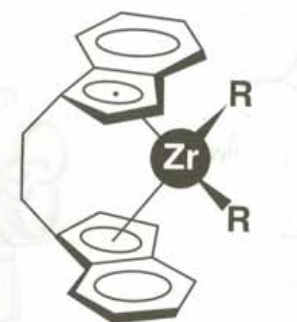
2.4b meso form

**Figure 2.4** Rac/meso form of metallocene [<http://academic.sun.ac.za>]

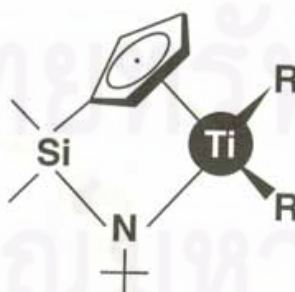
In addition to an important feature of polyethylenes is the amount of comonomer that is incorporated in the polymer. It is important to have metallocene catalysts as **Figure 2.5** that incorporate comonomers such as butene, hexene or octene very well.



2.5a fair



2.5b good

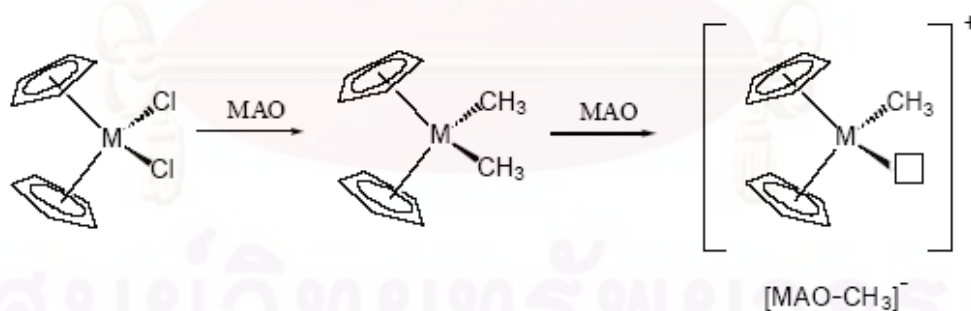


2.5c excellent

**Figure 2.5** Control of comonomer incorporation [<http://academic.sun.ac.za>]

The structure of catalyst determines whether an ethylene/ $\alpha$ -olefin copolymer contains a lot or just a little of comonomer at a given comonomer concentration in the polymerisation reactor. Here, the crucial point is the angle between the two ligands. If the angle is small the "metallocene mouth" is rather closed while a large opening angle means a wide open "mouth" that is ready to consume larger olefins (such as hexene and octene) much more easily. Single ligand complexes where one ligand has been replaced by another group (e.g. amido group) can be seen as metallocenes with only an "upper jaw". They have a very wide opening angle and are therefore very well suited to incorporate large amounts of comonomers.

Metallocenes are not active for polymerization by themselves. Cocatalyst usually used methylaluminoxane (MAO) is used to activate the metallocene system. Methylaluminoxane will alkylate metallocene as show in **Figure 2.6**. Methylaluminoxane is a poorly-structure defined material. Methylaluminoxane is assumed to chemically bond to the supports, and that the activated metallocene cation is fixed to the supported MAO by electrostatic interactions. The interaction between the catalytic complex and the support is essential since this will strongly influence the possibility of leaching. [R. Duchateau, 2002]



**Figure 2.6** Activation of metallocene with MAO [<http://academic.sun.ac.za>]

Generally, methylaluminoxane is prepared by a controlled hydrolysis of trimethylaluminium (TMA). Metallocene was very active when contacted with trimethylaluminium that had initially been precontacted with water. This relatively high activity was attributed to the reaction of water and alkyl aluminium to form

aluminumoxane, in this case methylaluminumoxane. Besides methylaluminumoxane presents the cocatalyst for effective metallocene activation, many investigate using other cocatalyst to activate system for example borane and borate that called methylaluminumoxane-free cocatalyst system.

There are three different industrial olefin polymerization processes. They are the solution, gas phase and slurry process. Homogeneous or heterogeneous catalysts can be used in the solution process. Metallocene catalysts are homogeneous catalyst (soluble catalyst). Therefore, the solution process was the first commercial process to use metallocene catalyst to produce polyethylenes. Gas phase and slurry process require heterogeneous catalyst. Metallocene catalysts need to be supported so that they can be applied in gas phase or slurry phase olefin polymerization processes.

## 2.2 Supported metallocene

Due to the fact, metallocene catalysts are not suitable for industrial olefin polymerization system (e.g. gas phase and slurry process). Supported metallocene catalysts are developed to overcome this disadvantage. Researcher use inorganic compounds such as oxide of silicon [Belelli et al., 2001; Galland et al., 2002], aluminium [Desharun et al., 2007], titanium [Ikenaga et al., 2007] and zeolite [Damiani et al., 2001]. Most of the supported metallocenes have exhibited lower catalytic activities in comparison to the homogenous system [Wang et al., 2005]. The reduction of catalytic activity has been attributed to three reasons:

1. The metallocene complexes are deactivated during the impregnating process.
2. The metallocene complexes inadequate react to the cocatalyst (methylaluminumoxane, MAO) and therefore hindering its activation.
3. The monomers are restricted approach to the active sites, thereby disappearing the chain propagation

Generally, supported metallocenes produced the polymers that had high average molecular weights because of a decrease rate of the termination reactions [W.

Kaminsky, F. Renner, *Makromol. Chem. Rapid. Commun.* 14 (1993) 239–248.]. Hence, the nature of the support seems to influence in the performance of the supported metallocene [Silveira et al., 2010]. Therefore the desired supports should enhance the activity close to the homogeneous system [Grieken et al., 2007]. The supports with high surface area, pore volume and controllable pore size are interesting. In addition, surface interaction between catalyst and support is another factor that affects on catalytic behavior. The more interaction causes the less activity because more interaction strongly bound MAO to support and hence MAO can not activate the metallocene. In the other hand, less interaction cause leaching of MAO from support. Consequently, the optimum interaction will be achieved for high activity [Ketloy et al., 2007]. Three main processes for the immobilization of the catalytic system on the silica support are described in the literature [Duchateau R., 2002].

1. Supports are impregnated by cocatalyst solution, followed by impregnation with metallocene.
2. Supports are anchored by metallocene and then reacting with cocatalyst solution.
3. Metallocene and cocatalyst are mixed then impregnating them on supports.

The impregnation of MAO on support before reacting with metallocene seems to be an effective technique.

### 2.3 Titania

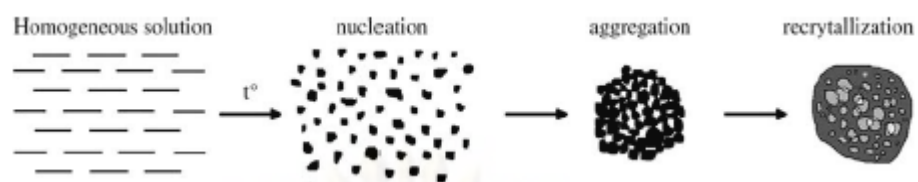
Titanium dioxide, also known as Titania, is oxide of titanium ( $\text{TiO}_2$ ). Titania has been interesting in recent years for its specific properties such as photocatalyst [Litter, 1999], semiconductor materials, water-gas shift reaction [Laniecki et al., 1999; Panagiotopoulou et al., 2006], polymer nano-composite and catalyst support. In natural, titania exists in three well-known phases, i.e. anatase, rutile and brookite.

## 2.4 Mesoporous titania

Porous materials are classified into several kinds by their size. According to IUPAC notation, microporous materials have pore diameters of less than 2 nm and macroporous materials have pore diameters of greater than 50 nm. The mesoporous category thus lies in the middle. A mesoporous material contains pores with diameters between 2 and 50 nm. The first mesoporous material was reported in the open literature in 1990, by Japanese researchers [Yanagisawa et al., 1990]. Mesoporous materials have attracted much attention in the field of catalysis because of their high surface area, pore volume and controllable pore size resulting in narrow pore size distributions. The recent application of mesoporous material is catalyst support [Silveira et al., 2007; Marques et al., 2008]. Many investigations focus their work on mesoporous metal oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}$  and  $\text{TiO}_2$ . The first synthesis of mesoporous titanium dioxide was achieved by Antonelli et al. in 1995. And synthesis methods have been developed gradually.

Mesoporous titania materials have been prepared using structure-directing agents as template [Zheng et al., 2001; Benkacerm and Agoudjil, 2008]. However, this technique has some disadvantages: for instance, the template may contaminate the final product because it can not be got rid of completely. Some literature revealed that treating at high temperature is an attractive way to eliminate template. Nevertheless this method causes a decrease in support surface area. Template-free way [Zheng et al., 2001; Liu et al., 2004; Huang et al., 2006; Shieh et al., 2006] has been developed continuously.

**Figure 2.7** demonstrated a formation model of mesoporous titania (anatase phase) can be described. According to this model [Kolen'ko et al.], primary  $\text{TiO}_2$  particles nucleation occurs from initially homogeneous aqueous solution due to hydrolysis at room temperatures. While the solution is evaporated, the aggregation of primary particles leads to their spheres. Then, as a result of recrystallization, mesoporous titania particles are formed.



**Figure 2.7** Scheme of mesoporous titania formation [Kolen'ko et al.]



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## CHAPTER III

### EXPERIMENT

#### 3.1 Objectives of the Thesis

The objective of this research was to investigate the effect of mesoporous anatase phase titanium dioxide supported zirconocene catalyst in ethylene/1-olefin copolymerization on the polymerization activities and polymer characteristics.

#### 3.2 Scopes of the Thesis

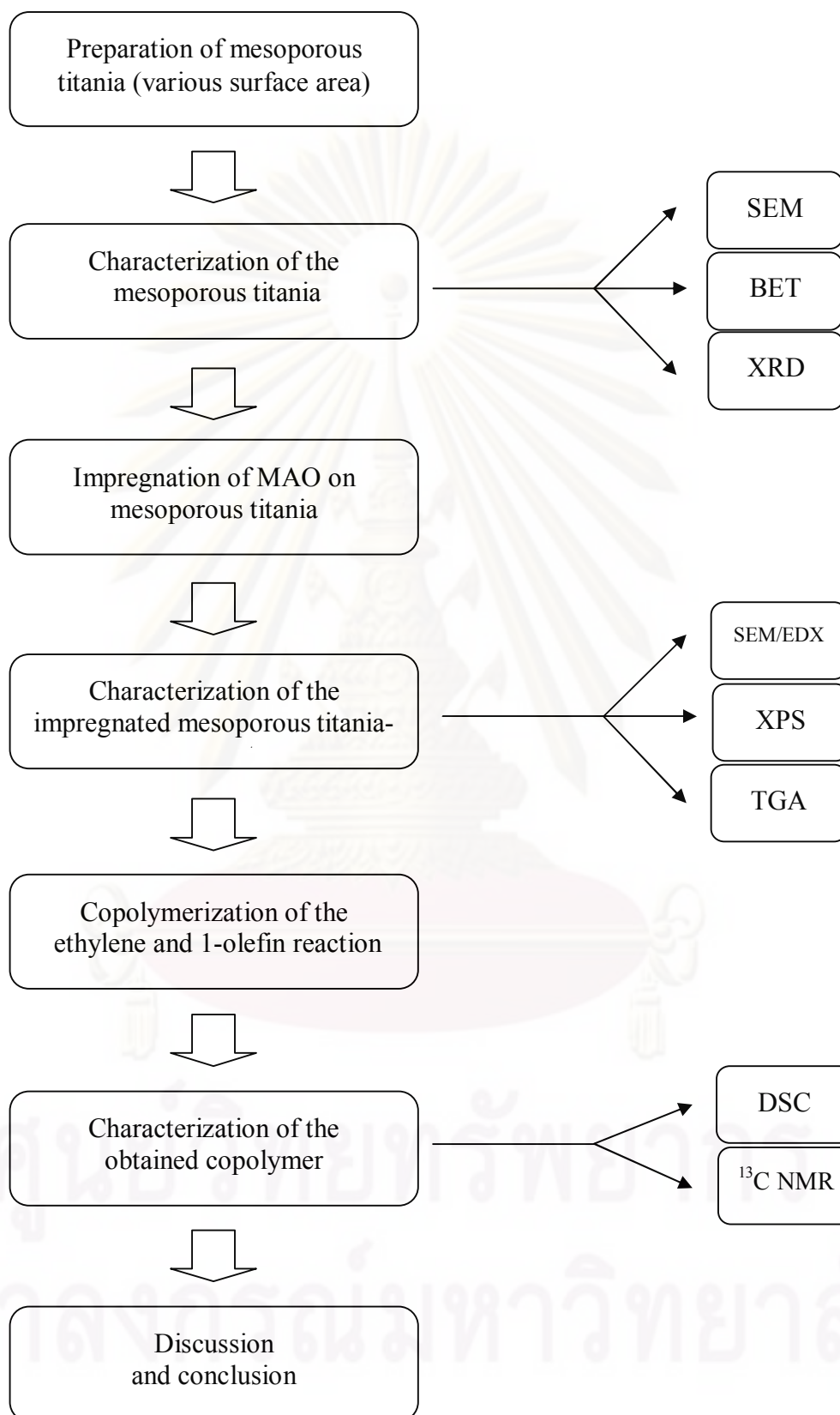
1. Preparation of mesoporous titania by hydrolysis and polycondensation reactions of tetrabutyl titanate with phosphoric acid as a catalyst
2. Variation of titania surface area by hydrolysis ratio
3. Characterization of the obtained titania supports using BET surface area, X-ray diffraction (XRD), scanning electron microscopy (SEM)
4. Preparation of supports by impregnation with methylaluminoxane (MAO)
5. Characterization of catalyst precursors using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometer (EDX), X-ray photoelectron spectroscopy (XPS) and Thermogravimetric analysis (TGA)
6. Copolymerization of ethylene/ $\alpha$ -olefin
7. Characterization of the obtained copolymer using differential scanning calorimeter (DSC) and  $^{13}\text{C}$ -nuclear magnetic resonance ( $^{13}\text{C}$ -NMR)

#### 3.3 Research Methodology

Research Methodology of flow diagram is show in **Figure 3.1**.

All reactions were conducted under argon atmosphere using Schlenk techniques and glove box.





**Figure 3.1** Flow diagram of research methodology

### 3.4 Experimental

#### 3.4.1 Chemicals

The chemicals were used in these experiments are analytical grade, but only major materials are specified as follows:

1. Ethylene gas (99.96%) was devolved from PTTChem Co., Ltd., Thailand and used as received.
2. 1-Hexene (97%) was purchased from Aldrich Chemical Company, Inc. and purified by distilling over sodium under argon atmosphere before use.
3. 1-Octene (97%) was purchased from Aldrich Chemical Company, Inc. and purified by distilling over sodium under argon atmosphere before use.
4. Hexane (95%) was donated from Shell (Public) Company, Inc. and purified by distilling over sodium under argon atmosphere before use.
5. Heptane ( $\geq 97\%$ ) was purchased from Fluka Chemie A.G. Switzerland and purified by distilling over sodium under argon atmosphere before used.
6. Toluene was devolved from EXXON Chemical Ltd., Thailand. This solvent was dried over dehydrated  $\text{CaCl}_2$  and distilled over sodium/benzophenone under argon atmosphere before use.
7. Methylaluminoxane (MAO) 20% M in toluene was devolved from PTTChem Co., Ltd., Thailand and used as received.
8. Trimethylaluminum (TMA) 2.0 M in toluene was supplied from Nippon aluminum Alkyls Ltd., Japan and used without further purification
9. Titanium (IV) butoxide was purchased from Aldrich Chemical Company, Inc. and used as received
10. Hydrofluoric acid (48%) was supplied from Carlo Erba and used as received.
11. Methanol (Commercial grade) was purchased from SR lab and used as received.
12. Sodium (99%) was purchased from Aldrich Chemical Company, Inc. and used as received.
13. Benzophenone (99%) was purchased from Fluka Chemie A.G. Switzerland and used as received.

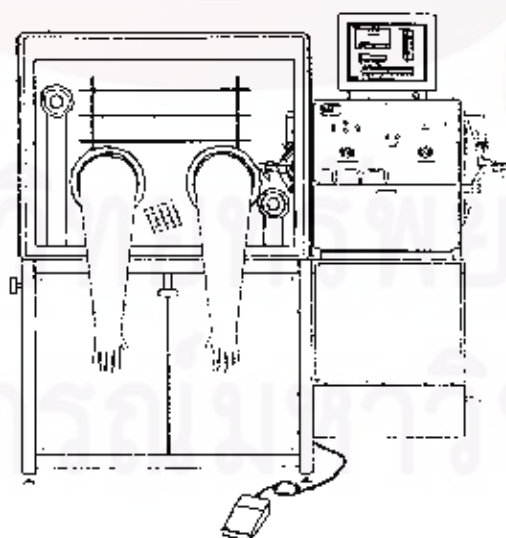
14. Calciumhydride (99%) was purchased from Fluka Chemie A.G. Switzerland and used as received.
15. Ultra high purity argon gas (99.999%) was purchased from Thai Industrial Gas Co., Ltd., and further purified by passing through columns packed with molecular sieve 3A, BASF Catalyst R3-11G, sodium hydroxide (NaOH) and phosphorus pentoxide ( $P_2O_5$ ) to remove traces of oxygen and moisture.

### 3.4.2 Equipments

Due to the metallocene system is extremely sensitive to the oxygen and moisture. Thus, the special equipments were required to handle while the preparation and polymerization process. For example, glove box: equipped with the oxygen and moisture protection system was used to produce the inert atmosphere. Schlenk techniques (Vacuum and Purge with inert gas) are the others set of the equipment used to handle air-sensitive product.

#### 3.4.2.1 Glove box

Vacuum Atmospheres operate with oxygen and moisture analyzer for handling solid reagents under inert atmosphere and for storing air-sensitive reagents. Inside the glove box, oxygen and moisture levels are normally controlled to below 0.1 ppm. The glove box is shown in **Figure 3.2**.



**Figure 3.2** Glove box

### 3.4.2.2 Schlenk tube

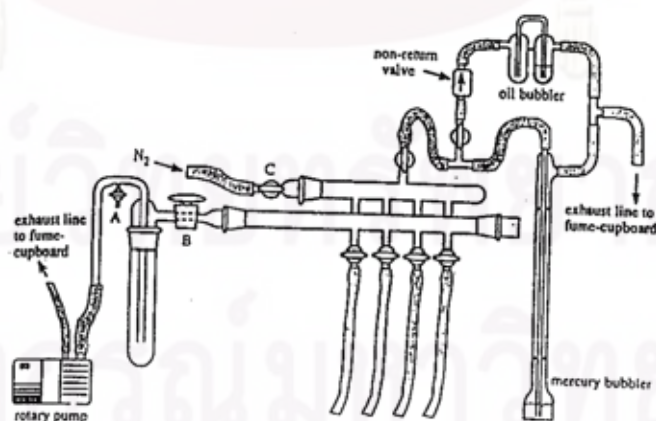
A tube with a ground glass joint and side arm was three-way glass valve. Sizes of Schlenk tubes were 50, 100 and 200 ml used to prepare catalyst and store materials which were sensitive to oxygen and moisture. The Schlenk tube is shown in Figure 3.3.



**Figure 3.3** Schlenk tube

### 3.4.2.3 Schlenk line

Schlenk line consists of vacuum and argon lines. The vacuum line was equipped with the solvent trap and vacuum pump, respectively. The argon line was connected with the trap and the mercury bubbler that was a manometer tube and contains enough mercury to provide a seal from the atmosphere when argon line was evacuated. The Schlenk line is shown in **Figure 3.4**.



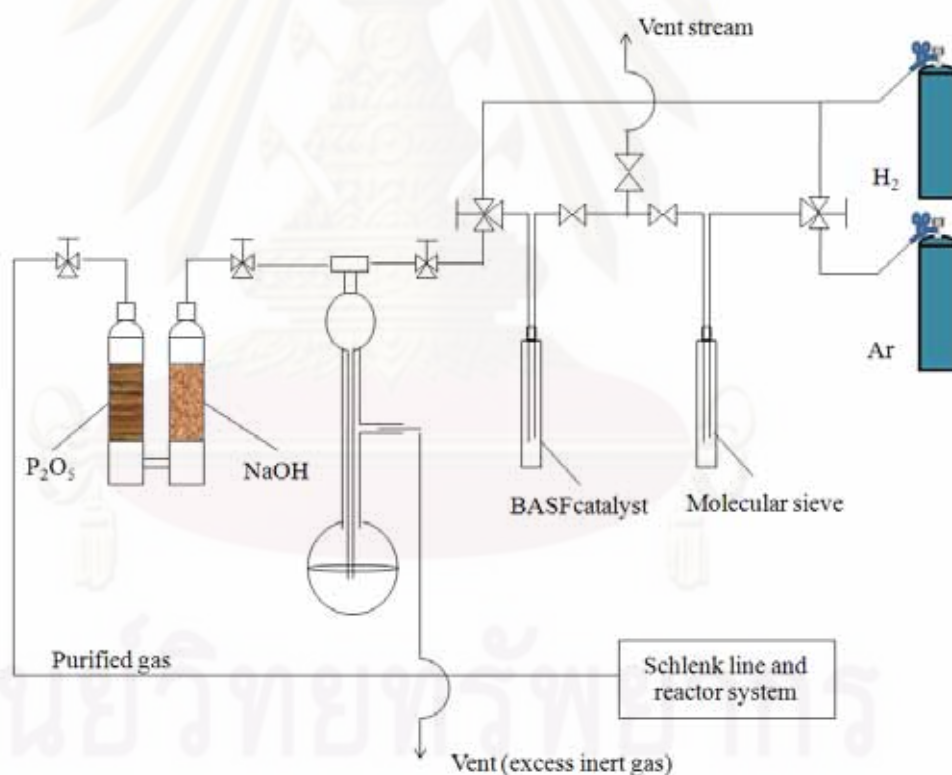
**Figure 3.4** Schlenk line

### 3.4.2.4 Cooling system

The cooling system was in the solvent distillation in order to condense the freshly evaporated solvent.

### 3.4.2.5 Inert gas supply

The inert gas (argon) was passed through columns of BASF catalyst R3-11G as oxygen scavenger, molecular sieve  $3 \times 10^{-10}$  m to remove moisture. The BASF catalyst was regenerated by treatment with hydrogen at  $300^\circ\text{C}$  overnight before flowing the argon gas through all the above columns. The inert gas supply system is shown in **Figure 3.5**.



**Figure 3.5** Inert gas supply system

### 3.4.2.6 Reactor

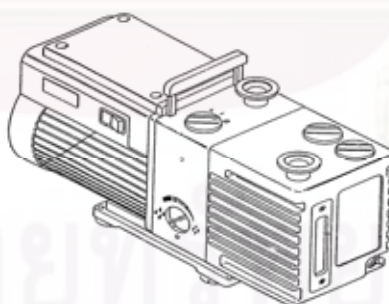
A 100 ml glass flask connected with 3-ways valve was used as the copolymerization reactor for atmospheric pressure system and a 100 ml stainless steel autoclave was used as the copolymerization reactor for high pressure systems. The reactor is shown in **Figure 3.6**.



**Figure 3.6** Reactor

### 3.4.2.7 Vacuum pump

The vacuum pump model 195 from Labconco Corporation was used. A pressure of  $10^{-1}$  to  $10^{-3}$  mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line. The vacuum pump is shown in **Figure 3.7**.



**Figure 3.7** Vacuum pump

### 3.4.2.8 Magnetic stirrer and heater

The magnetic stirrer and heater model RTC basis from IKA Labor Technik were used.

### 3.4.3 Supporting procedure: Preparation of supported MAO (catalyst precursor)

The TiO<sub>2</sub> support was reacted with the desired amount of MAO in 20 ml of toluene at room temperature for 30 min. The solvent was then removed from the mixture by evacuated and heated up at 50 °C. This procedure was done three times with toluene (20 ml x 3). Then, the solid part was dried under vacuum at 50 °C. The white powder of supported cocatalyst (support/MAO) was then obtained.

### 3.4.4 Ethylene/1-olefin Polymerization procedures

The ethylene/ $\alpha$ -olefin copolymerization reaction was carried out in a 100 ml semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. In the glove box, the desired amounts of *rac*-Et[Ind]<sub>2</sub>ZrCl<sub>2</sub> and TMA were mixed and stirred for 5 min for aging. Then, toluene (to make a total volume of 30 ml) and 100 mg of MAO/support were introduced into the reactor. After that, the mixture of *rac*-Et[Ind]<sub>2</sub>ZrCl<sub>2</sub> and TMA were injected into the reactor. The reactor was frozen in liquid nitrogen to stop reaction and then 0.018 mol of  $\alpha$ -olefin was injected into the reactor. The reactor was evacuated to remove argon. Then, it was heated up to polymerization temperature (70 °C) and the polymerization was started by feeding ethylene gas (total pressure 50 psi in the reactor). The reaction of polymerization was completely terminated by addition of acidic methanol. The time of reaction was recorded for purpose of calculating the activity. The precipitated polymer was washed with methanol and dried at room temperature.

### 3.4.5 Catalyst characterization

#### 3.4.5.1 N<sub>2</sub> physisorption

The BET surface areas pore volumes, average pore diameters, and pore size distributions of catalysts were determined by N<sub>2</sub> physisorption using a Micromeritic ASAP 2000 automated system. Each sample was degassed in the Micromeritics ASAP 2000 at 200°C for 4 hours prior to N<sub>2</sub> physisorption. The N<sub>2</sub> physisorption equipment is shown in **Figure 3.8**.



**Figure 3.8** N<sub>2</sub> physisorption equipment

#### 3.4.5.2 X-ray diffraction (XRD)

XRD was performed to determine the bulk crystalline phases of sample. It was conducted using a SIEMENS D-5000 X-ray diffractometer with CuK<sub>α</sub> ( $\alpha = 1.54439 \times 10^{-10}$  m). The spectra was scanned at a rate 2.4 degree/min in the range  $2\theta = 20$ -80 degrees. The X-ray diffraction equipment is shown in **Figure 3.9**.



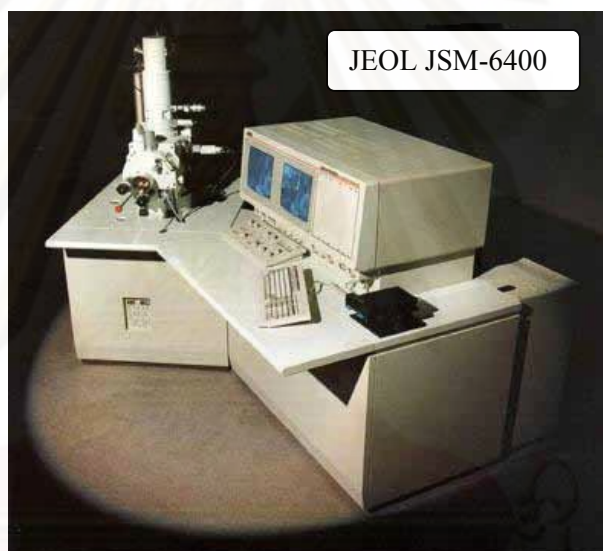
**Figure 3.9** X-ray diffraction (XRD) equipment

[[http://depts.washington.edu/mseuser/Equipment/XRD\\_D5000.shtml](http://depts.washington.edu/mseuser/Equipment/XRD_D5000.shtml)]



### 3.4.5.3 Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

SEM observation with a scanning electron microscope JEOL JSM-6400 and energy dispersion Microspec WDX at Scientific Technological Research Equipment Center, Chulalongkorn University was employed to investigate the morphology of catalyst precursor and polymer. The polymer samples for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimen. EDX was performed using Link Isis series 300 program. The scanning electron microscope and energy dispersive X-ray spectroscopy is shown in **Figure 3.10**.



**Figure 3.10** Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

[<http://www.lko.uni-erlangen.de/Media/Web-Bilder/bild-equipment/Jeol.jpg>]

### 3.4.5.4 X-ray photoelectron spectroscopy (XPS)

The XPS analysis was performed using an AMICUS photoelectron spectrometer ESCA-3400 equip with an Mg  $K\alpha$  X-ray as primary excitation and KRATOS VISION2 software. XPS elemental spectra were acquired with 0.1 eV energy step as a pass energy of 75 kV. The C 1s line was taken as an internal standard at 285.0 eV. The X-ray photoelectron spectroscopy is shown in **Figure 3.11**.



**Figure 3.11** X-ray photoelectron spectroscopy (XPS)

#### **3.4.5.5 Thermogravimetric analysis (TGA)**

TGA was used to determine interaction between cocatalyst and support in term of weight loss of catalyst precursors after impregnation. About 2 – 3 mg of each sample was analyzed by thermogravimetric and differential thermal analysis, PerkinElmer Thermal Analysis Diamond TG/DTA at Center of Excellences on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. The furnace was heated from 50 °C to 800 °C at a constant rate of 10 °C min<sup>-1</sup> and then cooled naturally. The whole TG/DTA measurement was made under nitrogen gas at gas flow rate of 100 mL min<sup>-1</sup>. The Thermogravimetric analysis equipment is shown in **Figure 3.12**.



**Figure 3.12** Thermogravimetric analysis (TGA) equipment

### 3.4.6 Polymer characterization

#### 3.4.6.1 Differential Scanning Calorimetry (DSC)

The melting temperature of ethylene/ $\alpha$ -olefin copolymer products was determined with a Perkin-Elmer diamond DSC from MEKTEC, at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University. The analyses were performed at the heating rate of 20 °C/ min in the temperature range of 50-150 °C. The heating cycle was run twice. In the first scan, samples were heated and the cooled to room temperature. In the second, samples were reheated at the same rate, but only the results of the second scan will be reported because the first scan was influenced by the mechanical and thermal history of samples. The Differential Scanning Calorimetry is shown in **Figure 3.13**.



Figure 3.13 Differential scanning calorimetry (DSC)

[<http://www.thermal-instruments.co.uk/diamonddsc.htm>]

#### 3.4.6.2. Nuclear magnetic resonance (NMR)

The  $^{13}\text{C}$ -NMR spectra were recorded at 100 °C using JEOL JNM-A500 operating at 125 MHz. Copolymer solutions were prepared using 1,2-dichlorobenzene as solvent and benzene- $\text{d}_6$  for internal lock. The Nuclear magnetic resonance equipment is shown in **Figure 3.13**.



**Figure 3.14** Nuclear Magnetic Resonance (NMR)

### **3.5 Preparation of mesoporous titania support followed Huang et al., 2005:**

1. 3.6 g of tetrabutyl titanate was dissolved in absolute ethanol 25.2 g under stirring at room temperature.
2. After 15 min, 0.48 ml of 0.28 M  $H_3PO_4$  was added.
3. After 30 min, deionized water was added in various quantitative under vigorous stirring.
4. After 2 h, solution was vaporized water and ethanol.
5. The obtaining solid was washed with deionized water and ethanol
6. Sample was dried in vacuum dry box at  $80^\circ C$  overnight. Then, calcine a sample at  $500^\circ C$  for 3 h

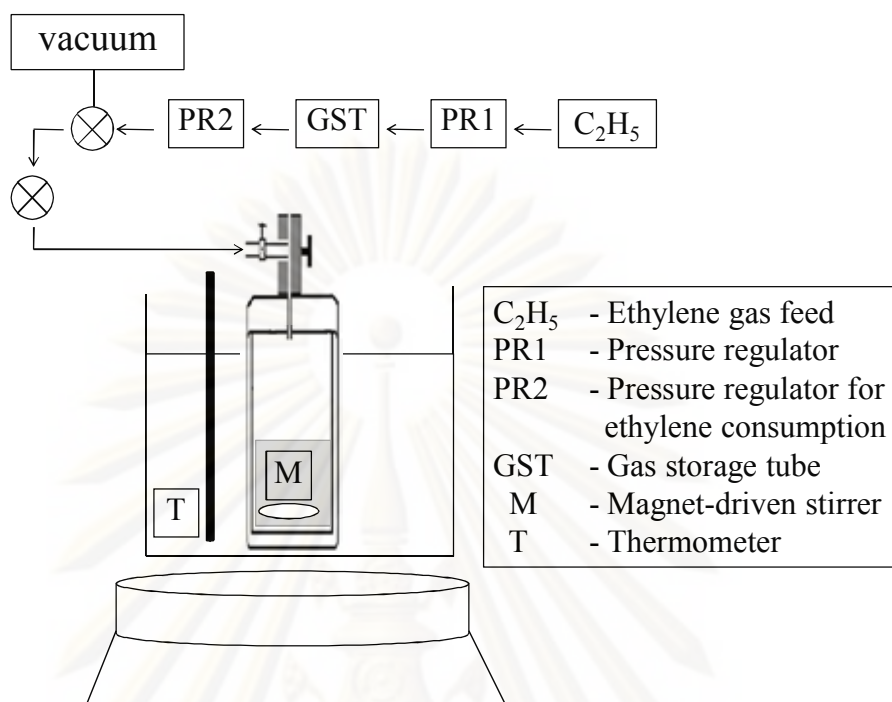
### **3.6 Preparation catalyst precursor:**

1. The support was heated under vacuum at  $400^\circ C$  for 6 h.
2. At room temperature, the support was reacted with the MAO in schlenk tube by inject 20 ml of toluene, stirred for 0.5 h and evacuated toluene. The mole ratio of support from MAO = 1:1.
3. The sample was washed with 20 ml of hexane, stir 0.5 h after evacuate hexane to ensure the removal of impurities for 3 times.

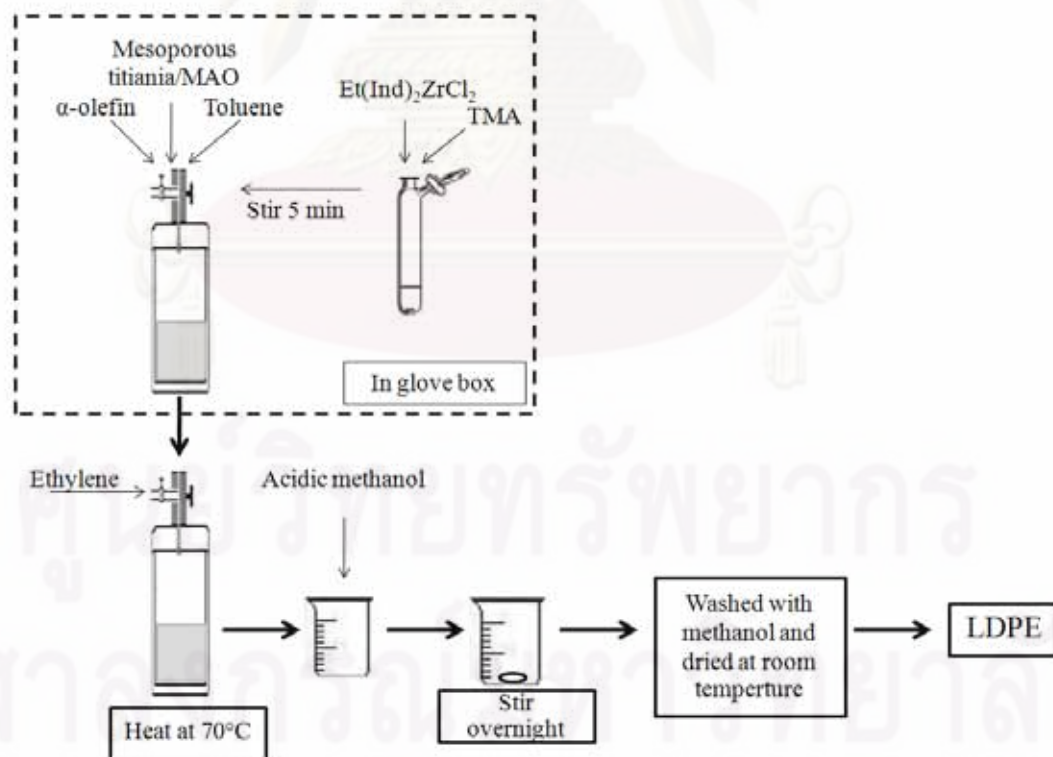
### 3.7 Ethylene and $\alpha$ -olefins copolymerization procedure

The ethylene and  $\alpha$ -olefins (1-hexene and 1-octene) copolymerization reaction were carried out in a 100 ml semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. The autoclave and magnetic bar were dried in oven at 110 °C for 30 min and were purged with argon 5 times in glove box before use in copolymerization of ethylene and  $\alpha$ -olefins. Toluene (to make a total volume of 30 ml), 100 mg of catalyst precursor, 0.018 mol of  $\alpha$ -olefins were introduced into the autoclave in the glove box. The amount of  $\text{Et(Ind)}_2\text{ZrCl}_2$  and TMA were mixed and stirred for 5 min at room temperature. After that, the mixture of metallocene and TMA were injected into the reactor. The reactor was frozen in liquid nitrogen to stop reaction and then the autoclave was evacuated to remove the argon. After that, the reactor was heated up to polymerization temperature and the polymerization was started by feeding ethylene gas (total pressure 50 psi). The small amount of ethylene was used to avoid the mass transfer effect and increase the homogeneity of polymer. If the amount of comonomer remained higher than 90% after the reaction, the obtained polymer was homogeneous. The reaction of polymerization was terminated by addition of acidic methanol. The time of reaction was recorded for purposes of calculating the activity. The precipitated polymer was washed with methanol and dried in room temperature.

The various effects on the ethylene/ $\alpha$ -olefins copolymerization with mixed supported metallocene catalyst and optimized condition were investigated. The effects of copolymerization on production of ethylene/ $\alpha$ -olefins copolymer systematically was investigated later.



**Figure 3.15** Diagram of system in slurry phase polymerization



**Figure 3.16** Flow diagram of ethylene and 1-olefin copolymerization

## CHAPTER IV

### RESULTS AND DISCUSSIONS

The purpose of this study is to investigate effects of different surface area of mesoporous titania supports on the catalyst activity and properties of copolymers during ethylene/ $\alpha$ -olefin polymerization with the zirconocene catalyst. The supports and supported/MAO (catalyst precursors) were also investigated to make better understanding about polymerization results.

#### 4.1 Characterization of supports and impregnated MAO supports

##### 4.1.1 Characterization of mesoporous titania supports with N<sub>2</sub> physisorption

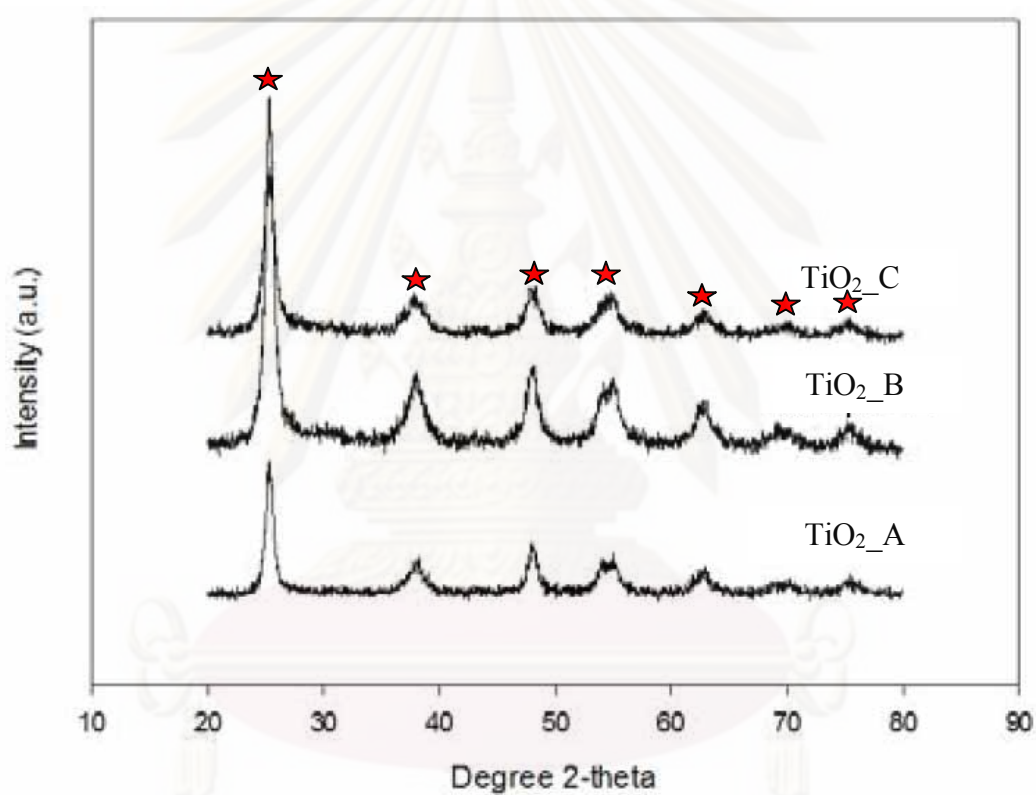
The surface areas, average pore diameter and pore volume for all mesoporous titania supports that synthesized by various hydrolysis ratios, such as TiO<sub>2</sub>\_A, TiO<sub>2</sub>\_B and TiO<sub>2</sub>\_C are listed in **Table 4.1**. It can be observed that titania synthesized using hydrolysis ratio of 26 (represented by TiO<sub>2</sub>\_B) exhibited the highest surface area and the smallest pore size, i.e. 145 m<sup>2</sup>/g and 3.1 nm, respectively. From N<sub>2</sub> physisorption technique, all samples exhibited type IV nitrogen adsorption/desorption isotherms and narrow unimodal pore size distribution.

**Table 4.1** Properties of different TiO<sub>2</sub> supports characterized by N<sub>2</sub> physisorption

Types of support	Hydrolysis ratio (H <sub>2</sub> O/Ti)	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
TiO <sub>2</sub> _A	10.5	70	0.067	33
TiO <sub>2</sub> _B	26	145	0.148	31
TiO <sub>2</sub> _C	42	100	0.111	32

#### 4.1.2 Characterization of mesoporous titania supports with X-ray diffraction (XRD)

The various mesoporous titania supports with different surface area were characterized after calcination at 500 °C. The XRD patterns of supports are shown in **Figure 4.1**. The characteristic seven peaks at  $2\theta$  for the anatase form of all sample at 25°, 38°, 48°, 54.7°, 62.7°, 70° and 76° were observed.

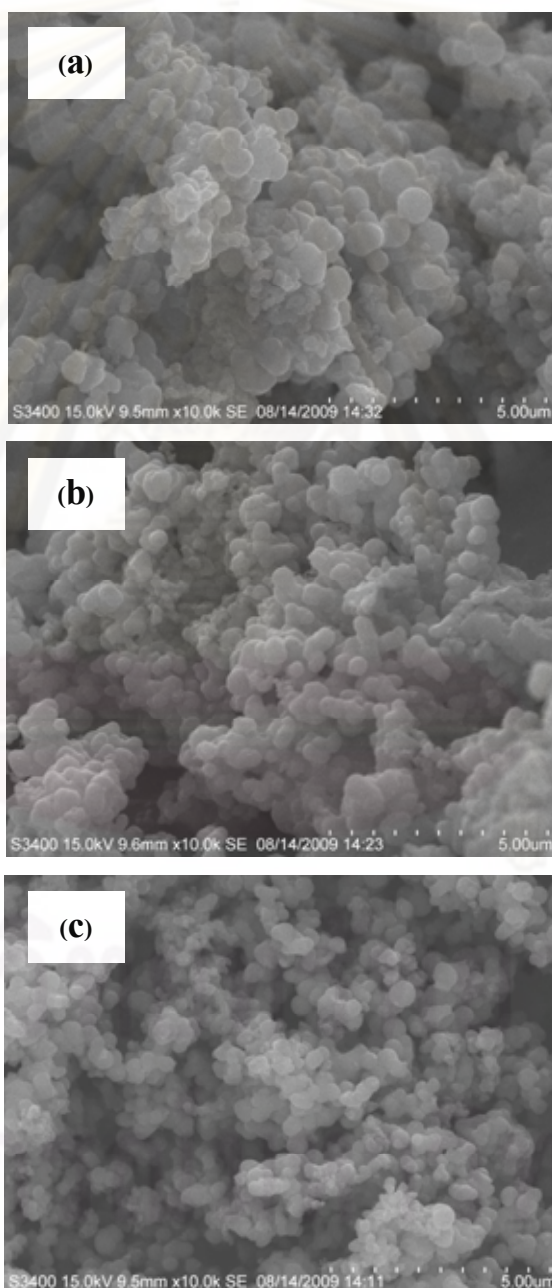


**Figure 4.1** XRD patterns of different TiO<sub>2</sub> supports after calcination at 500 °C



#### 4.1.3 Characterization of supports and supported MAO with scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

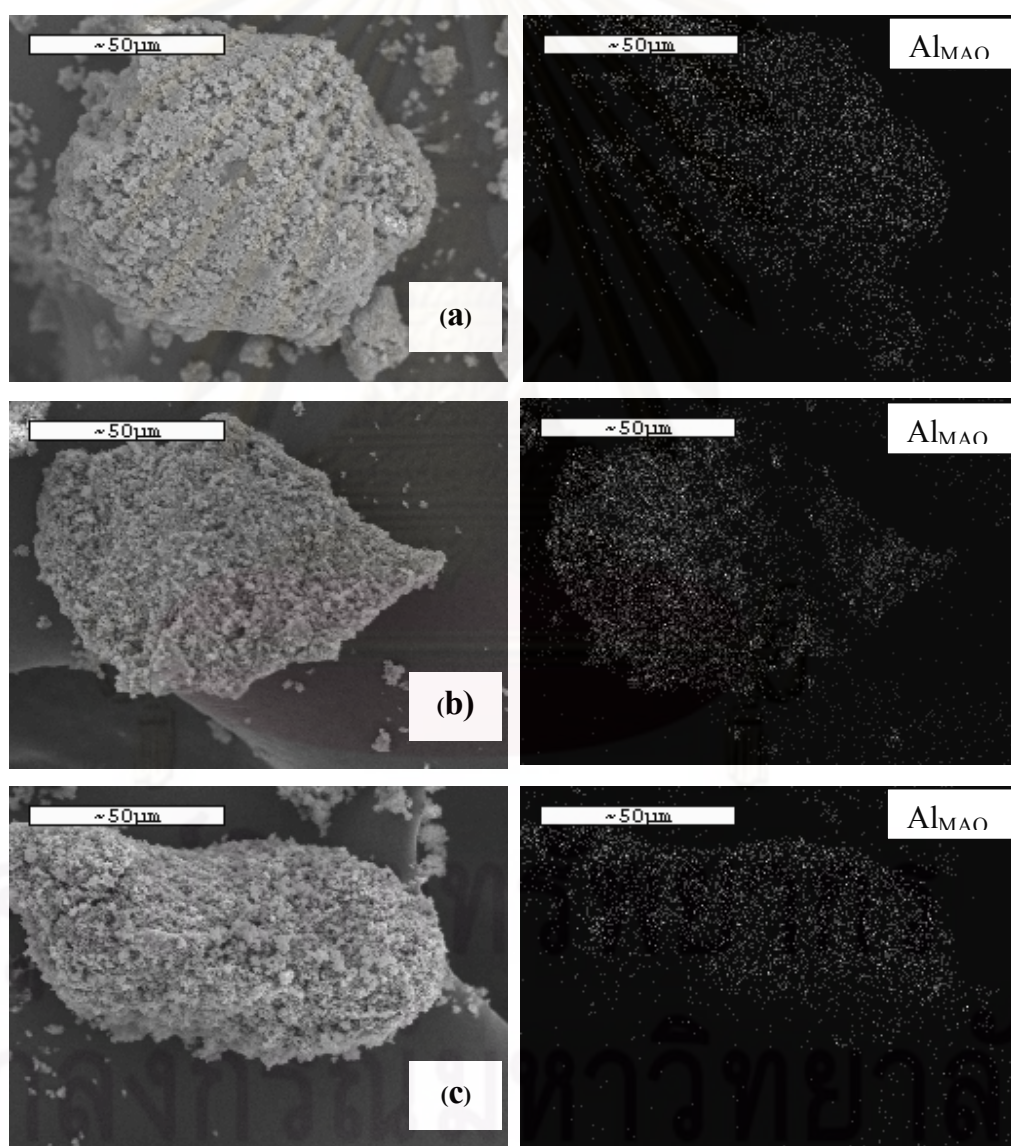
Scanning electron microscope (SEM) image shows morphology of different mesoporous titania supports. This SEM image magnified mesoporous titania by 10,000 times indicating that titania particles aggregate to crystal. It can be observed that each titania particle was measured have the particle size of 0.5  $\mu\text{m}$  as seen in **Figure 4.2**



**Figure 4.2** SEM image of mesoporous titania magnified by  $10^4$  times

(a)  $\text{TiO}_2\text{-A}$     (b)  $\text{TiO}_2\text{-B}$     (c)  $\text{TiO}_2\text{-C}$

After impregnated mesoporous titania with MAO, scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) were applied to determine the  $[Al]_{MAO}$  content and distributions on supports. The SEM micrographs and EDX mapping for the  $TiO_2/MAO$  samples are shown in **Figure 4.3**. All samples apparently exhibited the similar morphologies. It can be observed that the MAO was well distributed all over the  $TiO_2$  particles as seen by the EDX mapping. The  $[Al]_{MAO}$  content was measured using EDX. The amounts of  $[Al]_{MAO}$  in various  $TiO_2$  supports are listed in **Table 4.3**.



**Figure 4.3** SEM micrographs and EDX mapping for different  $TiO_2/MAO$  supports  
(a)  $TiO_2\_A$  (b)  $TiO_2\_B$  (c)  $TiO_2\_C$

**Table 4.2** Elemental analysis of Al and Ti obtained from EDX

Types of support	[Al] <sub>MAO</sub> content (% atomic)	[Ti] <sub>support</sub> content (% atomic)	[Al] <sub>MAO</sub> /[Ti] <sub>support</sub>
TiO <sub>2</sub> _A	7.18 ± 1.48 <sup>a</sup>	10.25 ± 2.61 <sup>a</sup>	0.70
TiO <sub>2</sub> _B	8.55 ± 0.97 <sup>a</sup>	8.92 ± 0.61 <sup>a</sup>	0.96
TiO <sub>2</sub> _C	5.95 ± 0.76 <sup>a</sup>	12.08 ± 1.88 <sup>a</sup>	0.49

<sup>a</sup> standard deviation calculated from three point on sample.

Because values obtained from EDX technique may not be an accurate compared to bulk technique, i.e. ICP. The average values and standard deviation must be used for identify content of Al on support. Results showed that the amounts of [Al]<sub>MAO</sub> on mesoporous titania supports from EDX technique ranged from 6 - 8.5 %, and TiO<sub>2</sub>\_B exhibited the highest ratio of Al content and Ti content in **Table 4.2**.

#### 4.1.4 Characterization of supported/MAO with X-ray photoelectron spectroscopy (XPS)

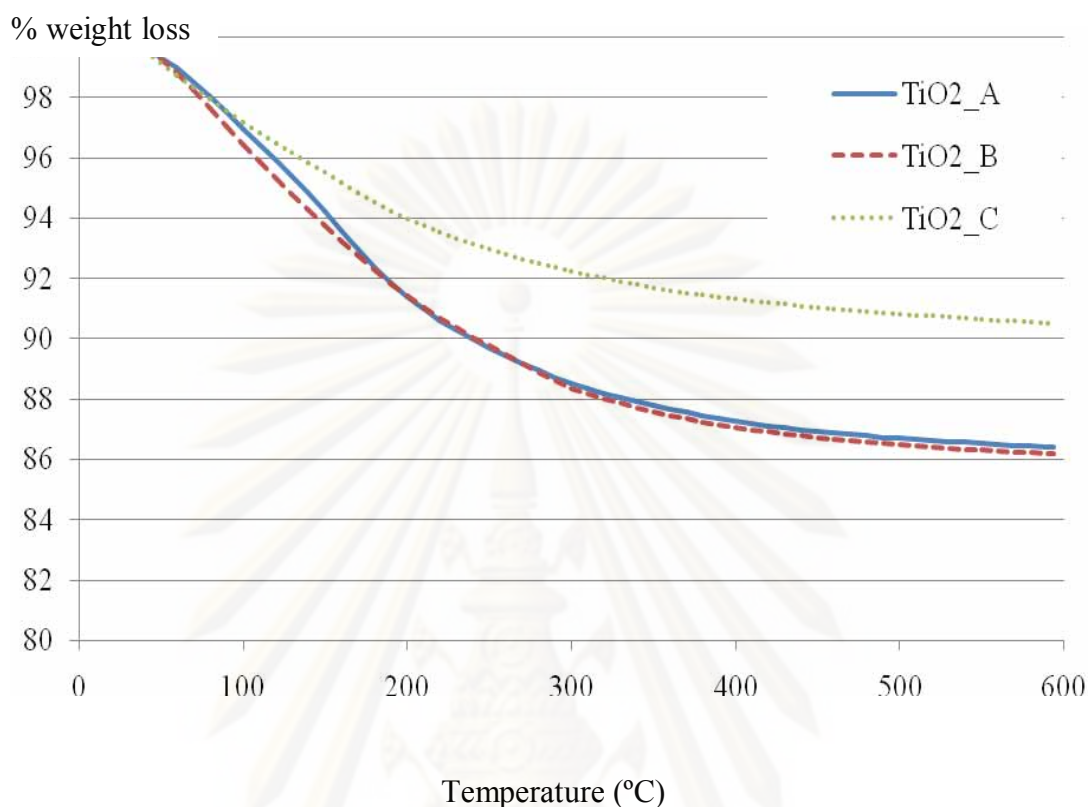
The surface property of impregnated supports was proven by X-ray photoelectron spectroscopy (XPS). The results shown in **Table 4.3** detected only 1-3 nm depth surface of supports while EDX method were detected about 1 μm. Therefore, the results of XPS technique represented the surface profile of supports. [Al]<sub>MAO</sub> found on surface more than [Ti]<sub>support</sub>. TiO<sub>2</sub>\_B contained the largest amount of [Al]<sub>MAO</sub> on surface and TiO<sub>2</sub>\_C had the lowest. The [Al]/[Ti] ratios that observed by XPS were presented more than [Al]/[Ti] ratios from EDX indicating that the [Al]<sub>MAO</sub> was abundant on the support surface.

**Table 4.3** Elemental analysis of Al and Ti obtained from XPS

Types of support	[Al] <sub>MAO</sub> content (% atomic)	[Ti] <sub>support</sub> content (% atomic)	[Al] <sub>MAO</sub> /[Ti] <sub>support</sub>
TiO <sub>2</sub> _A	19.14	0.34	56.29
TiO <sub>2</sub> _B	20.67	0.35	59.06
TiO <sub>2</sub> _C	17.18	2.54	6.76

#### 4.1.5 Characterization of supported/MAO with thermo gravimetric analysis (TGA)

In this study, MAO was dispersed onto the various supports by impregnation. The value of interaction between the support and the cocatalyst ( $Al_{MAO}$ ) can be characterized by the TGA measurement. The TGA provide information on the degree of interaction for the MAO bound to the support in terms of weight loss and removal temperature. The TGA profiles of  $[Al]_{MAO}$  on various supports are shown in **Figure 4.4** indicating the similar pattern for various supports. The species having strong interaction with the support was removed at 600 °C. It was observed that the weight loss of  $[Al]_{MAO}$  present on TiO<sub>2</sub>\_C, TiO<sub>2</sub>\_A and TiO<sub>2</sub>\_B supports were in the order of 9.48% < 13.59% < 13.82%, respectively. This indicated that  $[Al]_{MAO}$  present on TiO<sub>2</sub>\_C support had the strongest interaction. Moreover, distinguished low amount of  $[Al]_{MAO}$  on support TiO<sub>2</sub>\_C that observed by EDX and XPS techniques may make outstanding result of weight loss of TiO<sub>2</sub>\_C/MAO.



**Figure 4.4** TGA profile of  $[Al]_{MAO}$  on different  $TiO_2$  supports

#### 4.2 Characteristic and catalytic properties of ethylene/ $\alpha$ -olefin copolymerization

The various synthesized supports ( $TiO_2\_A$ ,  $TiO_2\_B$  and  $TiO_2\_C$ ) that impregnated by MAO ( $TiO_2\_A/MAO$ ,  $TiO_2\_B/MAO$  and  $TiO_2\_C/MAO$ ) were used and investigated for catalytic activities. The ethylene/ $\alpha$ -olefin copolymerization via various supported/MAO with (*rac*-Et[Ind]<sub>2</sub>ZrCl<sub>2</sub>) was performed in order to determine the characteristic and catalytic properties of copolymer influenced by the various supports. Methylaluminoxane (MAO) was used as cocatalyst which all supports were fixed at the  $[Al]_{MAO}/[Zr]_{cat}$  ratios of 1135. The copolymerization were performed in toluene at 70 °C feeding ethylene gas, pressure in reactor = 50 psi, 0.018 ml of 1-hexene and 1-octene and zirconium concentration  $10 \times 10^{-5}$  M with total solution volume of 30 ml.

### 4.2.1 The effect of various supports on the catalytic activity

The catalytic activities via various supports and the homogeneous system are listed in **Table 4.4**.

**Table 4.4** Polymerization activities for different TiO<sub>2</sub> supports

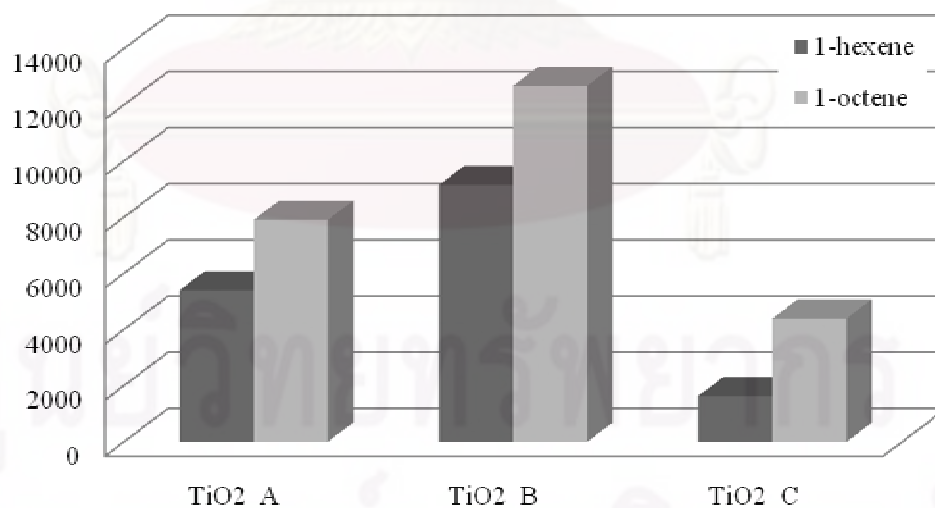
Types of support	1-hexene			1-octene		
	Time (s)	Polymer yield (g)	Catalytic activity <sup>a</sup> [kg polymer (mol Zr h) <sup>-1</sup> ]	Time (s)	Polymer yield (g)	Catalytic activity <sup>a</sup> [kg polymer (mol Zr h) <sup>-1</sup> ]
Homo- <sup>b</sup>	43	0.815	45,505	101	1.95	46,344
TiO <sub>2</sub> _A	101	0.227	5,398	78	0.257	7,907
TiO <sub>2</sub> _B	81	0.309	9,143	68	0.360	12,683
TiO <sub>2</sub> _C	159	0.108	1,636	90	0.165	4,394

<sup>a</sup> Activities were measured at polymerization temperature of 70 °C,  $[Al]_{dMMAO} / [Zr]_{cat} = 1135$ ,  $[Al]_{TMA} / [Zr]_{cat} = 2500$ , in toluene with total volume = 30 ml and  $[Zr]_{cat} = 5 \times 10^{-5}$  M.

<sup>b</sup> Homogeneous system or non-supported system

In this study, the polymerization activities of copolymerization of ethylene/ $\alpha$ -olefin such as 1-hexene and 1-octene upon the presence of various surface area mesoporous titania were measured. In each experiment, the  $[Al]_{MAO} / [Zr]_{catalyst}$  ratios were kept constant at 1135 by fixing the amount of catalyst and varying the amount of TiO<sub>2</sub>/MAO. The  $[Al]_{MAO}$  used for calculation based on the amount of present that measured by EDX. The polymerization activities of the homogeneous and the heterogeneous systems are listed in **Table 4.4**. The results that obtained from both 1-hexene and 1-octene for used co-monomer were similar. The homogeneous system showed the highest polymerization activity. As known, the activities of the supported system were apparently lower than homogeneous one due to supporting effect. The polymerization activities of heterogeneous system were in the order of TiO<sub>2</sub>\_B > TiO<sub>2</sub>\_A > TiO<sub>2</sub>\_C. Among the supported system, the polymerization activity of

TiO<sub>2</sub>\_B was the highest that may presume more high activity owing to more dispersion of the catalyst precursor. Because of the constant ratio of  $[Al]_{MAO}/[Zr]_{catalyst}$ , the interaction between the  $[Al]_{MAO}$  and TiO<sub>2</sub> supports was also important to consider. The TGA profile can only provide useful information on the degree of interactions for the MAO bound to the TiO<sub>2</sub> supports in terms of the removal temperature and weight loss. The stronger interaction between  $[Al]$  and TiO<sub>2</sub> can result in low weight loss leading to lower catalytic activity for polymerization, as seen from TiO<sub>2</sub>\_A and TiO<sub>2</sub>\_B support compared with TiO<sub>2</sub>\_C. The suitable interaction was attributed to appropriate for the MAO bound to the TiO<sub>2</sub> supports to react with Zr-complex during activation process, leading to higher catalytic activity for polymerization. In addition, the effect of  $\alpha$ -olefin indicated that the activity of ethylene/1-octene was higher than activity of ethylene/1-hexene copolymerization. This result is consistent with the result of Nomura et. al., 1999, Nomura et. al., 2001 and Pothirat et. al., 2007. The result also explained that the chain length of the  $\alpha$ -olefin has a little influence on the comonomer incorporation and catalyst activity [Gao et. al., 2008].



**Figure 4.5** The effect of various  $\alpha$ -olefins on the catalytic activity

It discovered that the catalyst activity of 1-octene system was higher than 1-hexene system due to the higher boiling point of 1-octene (b.p. of 1-octene = 122 °C, b.p. of 1-hexene = 63°C), which kept higher concentration of 1-octene in the reaction solution. 1-octene concentration in the liquid phase was higher than 1-hexene, which resulted in the higher polymerization activity [Li et. al., 2008].

#### 4.2.2 The effect of various supports on the incorporation of copolymers

The quantitative analysis of triad distribution for all copolymers was conducted on the basis assignment of the  $^{13}\text{C}$  NMR spectra of ethylene/ $\alpha$ -olefin copolymer and calculated according to the method of Randall et al. [1989]. The characteristics of  $^{13}\text{C}$  NMR spectra (as shown in appendix C) for all copolymers were similar indicating the copolymer of ethylene/  $\alpha$ -olefin. The triad distribution of all polymers is shown in **Table 4.4**.

**Table 4.5** Triad distribution of LLDPE/TiO<sub>2</sub> copolymer obtained from  $^{13}\text{C}$  NMR analysis and thermal property from DSC measurement

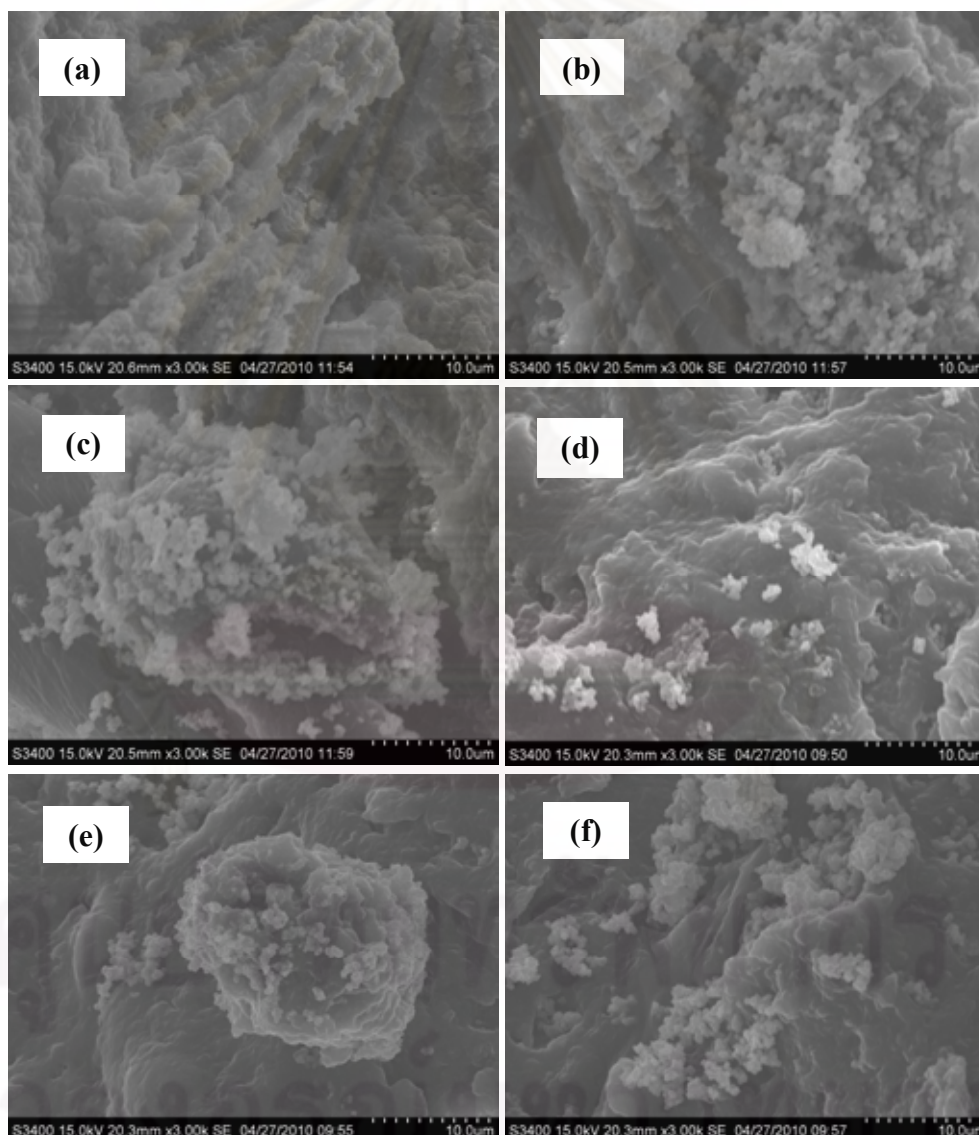
<i>1-hexene as comonomer</i>							
Type of supports	EEE	HEE + EEH	HEH	EHE	EHH + HHE	HHH	1-Hexene incorporation (%)
	TiO <sub>2</sub> _A	1.0	0	0	0	0	0
TiO <sub>2</sub> _B	1.0	0	0	0	0	0	nd
TiO <sub>2</sub> _C	1.0	0	0	0	0	0	nd
<i>1-octene as comonomer</i>							
Type of supports	EEE	OEE + EEO	OEO	EOE	EOO + OOE	OOO	1-Octene incorporation (%)
	TiO <sub>2</sub> _A	1.0	0	0	0	0	nd
TiO <sub>2</sub> _B	0.535	0.44	0	0	0.04	0	4
TiO <sub>2</sub> _C	1.0	0	0	0	0	0	nd

E refers to ethylene monomer  
O refers to 1-Octene comonomer  
H refers to 1-Hexene comonomer  
nd refers to not detect by NMR



### 4.2.3 The effect of various supports on the morphology and structure of copolymers

Scanning electron microscope was utilized in order to study the morphologies and  $\text{TiO}_2$  distribution on the LLDPE/ $\text{TiO}_2$  copolymer was shown in **Figure 4.6**. All samples apparently revealed the similar morphologies. Titania particle was well dispensed on copolymer surface. Copolymer and support was found that there was no significant difference in copolymer morphologies in both comonomer systems.



**Figure 4.6** SEM micrographs of LLDPE/ $\text{TiO}_2$

Ethylene/1-hexene; (a)  $\text{TiO}_2\_A$  (b)  $\text{TiO}_2\_B$  (c)  $\text{TiO}_2\_C$   
 Ethylene/1-octene; (d)  $\text{TiO}_2\_A$  (e)  $\text{TiO}_2\_B$  (f)  $\text{TiO}_2\_C$

X-ray diffraction was performed to verify pattern of polyethylene form. The XRD patterns for all polymer and copolymer was observed at  $2\theta = 21.8^\circ$  and  $24.3^\circ$  that shown the orthorhombic crystalline form of polyethylene [Kuo et. al., 2003 and Li et. al., 2007].

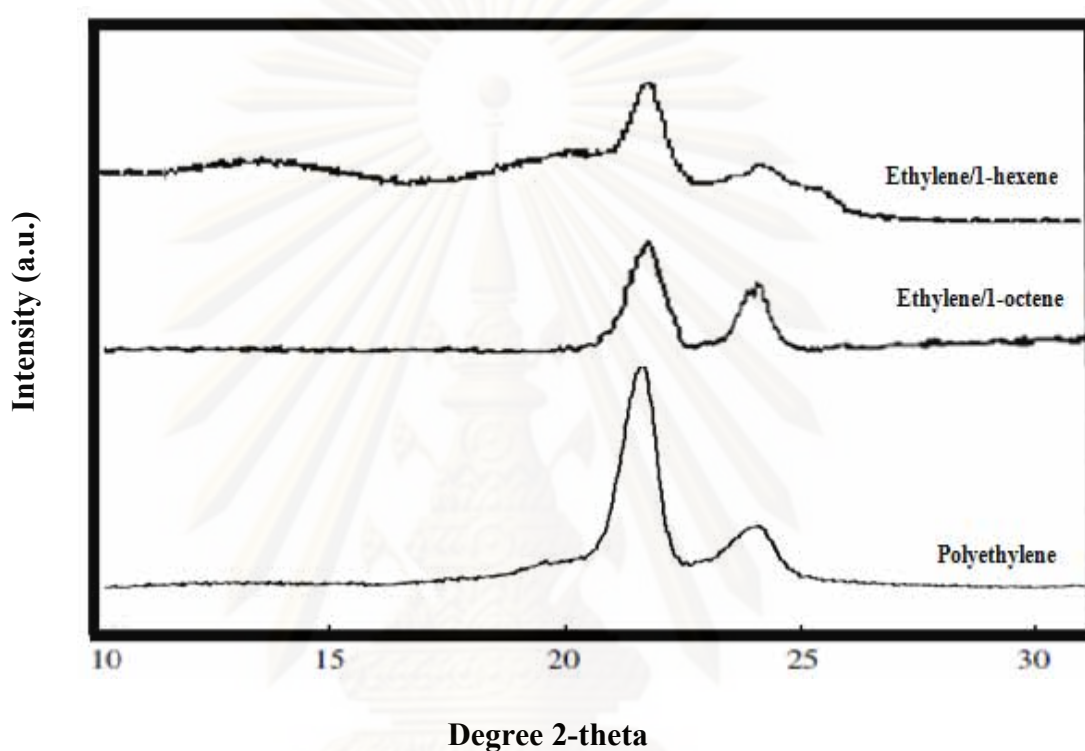


Figure 4.7 XRD patterns of polymer between  $2\theta = 10^\circ - 30^\circ$

## CHAPTER V

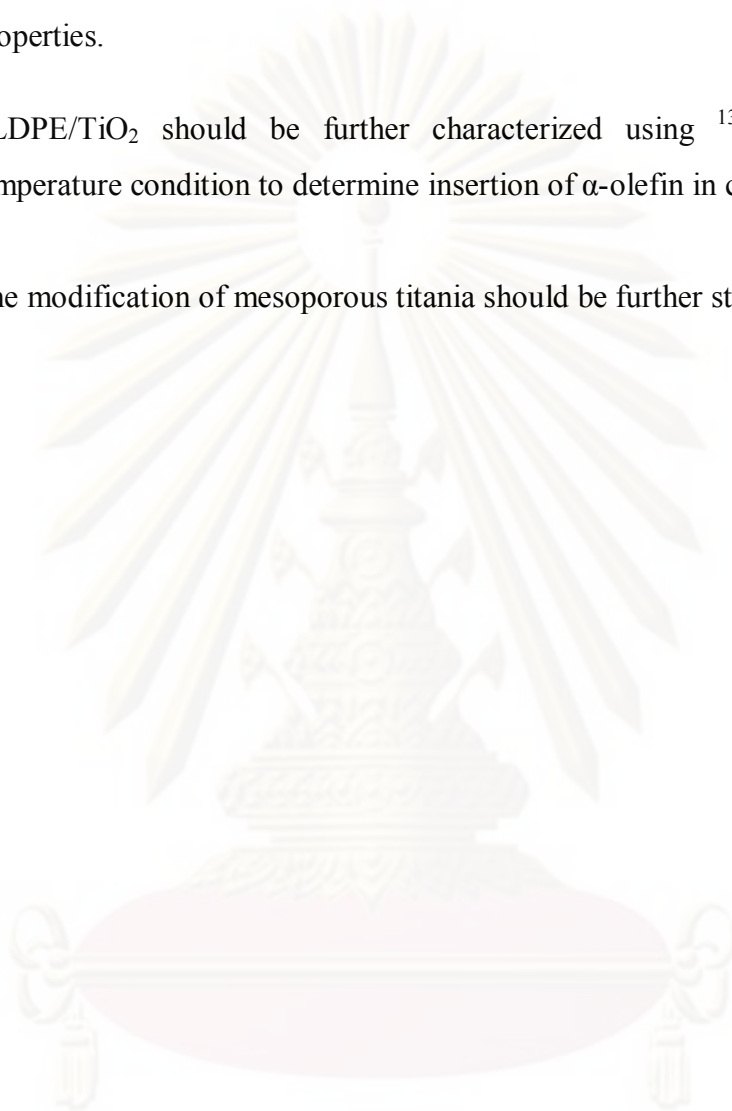
### CONCLUSIONS & RECOMMENDATIONS

#### 5.1 CONCLUSIONS

The mesoporous titania having different of surface areas was produced by a catalyzed hydrolysis and polycondensation reactions of tetrabutyl titanate with phosphoric acid as a catalyst method with various hydrolysis ratio ( $H_2O/Ti$ ). These titanias were used as support for impregnated with MAO and characterized by  $N_2$  physisorption, XRD and SEM to distinguish properties of synthesized titania. The results of  $N_2$  physisorption showed hydrolysis ratio equal 26 provide the largest surface area titania, and the results of XRD revealed the anatase phase present. After supports were impregnated with MAO, content of  $[Al]_{MAO}$  was detected by SEM/EDX and XPS equipment. It revealed the appearance of larger  $[Al]_{MAO}$  dispersed depending on high surface area of titania. The copolymer of ethylene and  $\alpha$ -olefin were synthesized using different  $TiO_2$  supports via in situ polymerization with zirconocene/MAO catalyst. The polymerization activities were in the order of  $TiO_2\_B > TiO_2\_A > TiO_2\_C$  due to the more highly dispersion of the catalyst precursor and exhibits optimal interaction between  $[Al]_{MAO}$  and  $TiO_2\_B$ . The strong interaction is caused by the active sites that were located on the pore more than outer surface resulting in hindering of active sites access leading to low activity. Moreover, the effect of  $\alpha$ -olefin indicated that the activity of ethylene/1-octene was higher than activity of ethylene/1-hexene copolymerization due to effects of the longer chain insertion. In addition the low insertion of  $\alpha$ -olefin was observed and undetectable using  $^{13}NMR$ , which is unusual. Thus, a more powerful technique is needed.

## 5.2 RECOMMENDATIONS

- LLDPE/TiO<sub>2</sub> should be further characterized using DSC to determine thermal properties.
- LLDPE/TiO<sub>2</sub> should be further characterized using <sup>13</sup>C NMR at high temperature condition to determine insertion of  $\alpha$ -olefin in copolymer.
- The modification of mesoporous titania should be further study.



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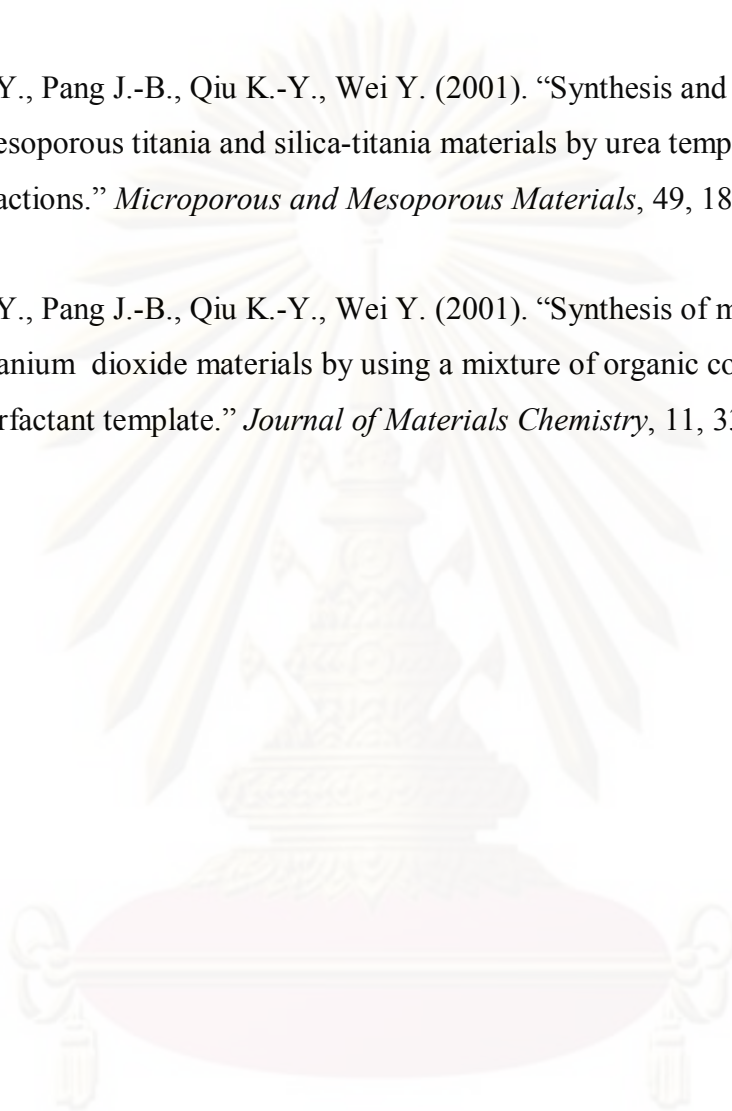
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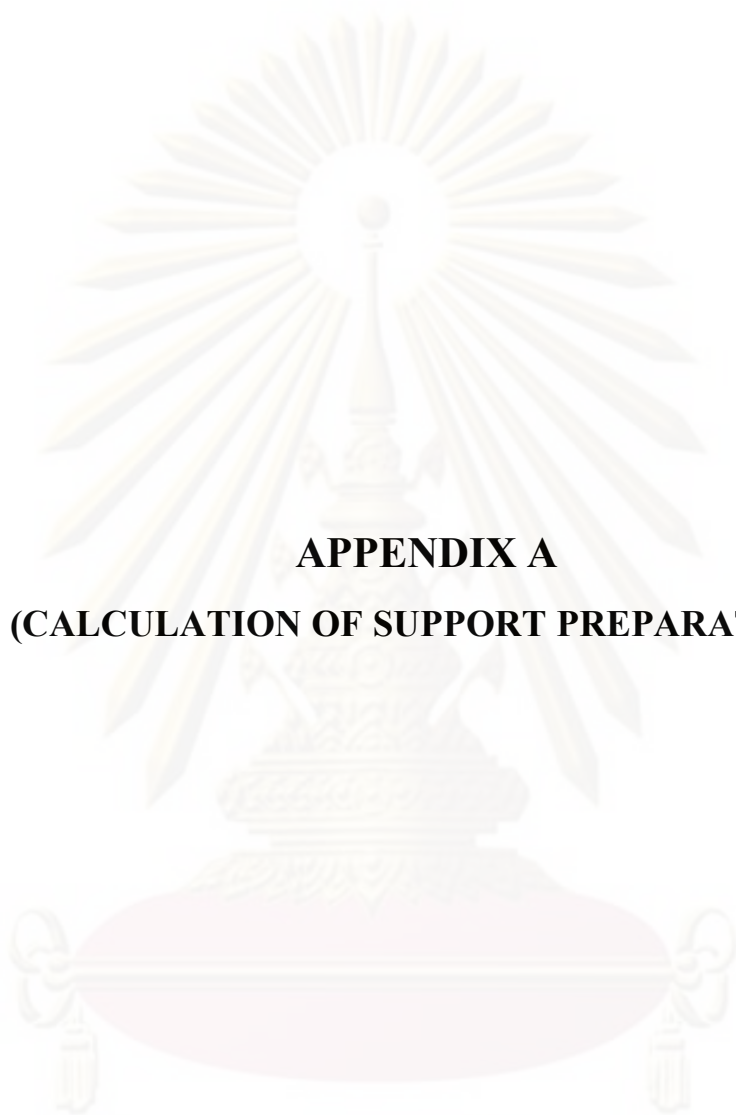


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APPENDICES

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**APPENDIX A**  
**(CALCULATION OF SUPPORT PREPARATION)**

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### A-1 Calculation of amount of reactant to synthesis support (mesoporous titania)

Preparation of mesoporous titania with hydrolysis ratio = 10.5, 26 and 42

Reagent:      Tetrabutyl titanate  
                  Absolute ethanol  
                  Phosphoric acid  
                  Deionized water

Start with 3.6 gram of tetrabutyl titanate (molecular weight = 340.36)

Uses 1/7 weight ratio of tetrabutyl titanate per absolute ethanol that equals 25.2 gram

Added 0.48 ml of 0.28 M phosphoric acid

Addition of quatitative deionized water followed hydrolysis ratio = 10.5, 26 and 42

Hydrolysis ratio is moles of deionized water per mole of titanium (Ti)

$$\text{Hydrolysis ratio} = \frac{\text{Mole of deionized water}}{\text{Mole of titanium}}$$

$$\text{Mole of deionized water} = \text{Hydrolysis ratio} \times \text{Mole of titanium}$$

**Table A-1** Amount of deionized water that used for synthesis mesoporous titania.

Hydrolysis ratio	Mole of titanium	Mole of deionized water	Amount of deionized water (ml)
10.5	0.0106	0.1113	<b>2</b>
26	0.0106	0.2756	<b>5</b>
42	0.0106	0.4452	<b>8</b>

**A-2 Calculation of amount of reactant to impregnated support (TiO<sub>2</sub>/MAO)**

Preparation of impregnated mesoporous titania with methylaluminoxane.

The mole ratio of support by MAO = 1:1.

Based on 1 gram of TiO<sub>2</sub> (MW = 79.866 g/mol)

So, TiO<sub>2</sub> 1 gram = 0.0125 mol

Fix 0.0125 mol of MAO (MW<sub>MAO</sub> = 58.02 g/mol),

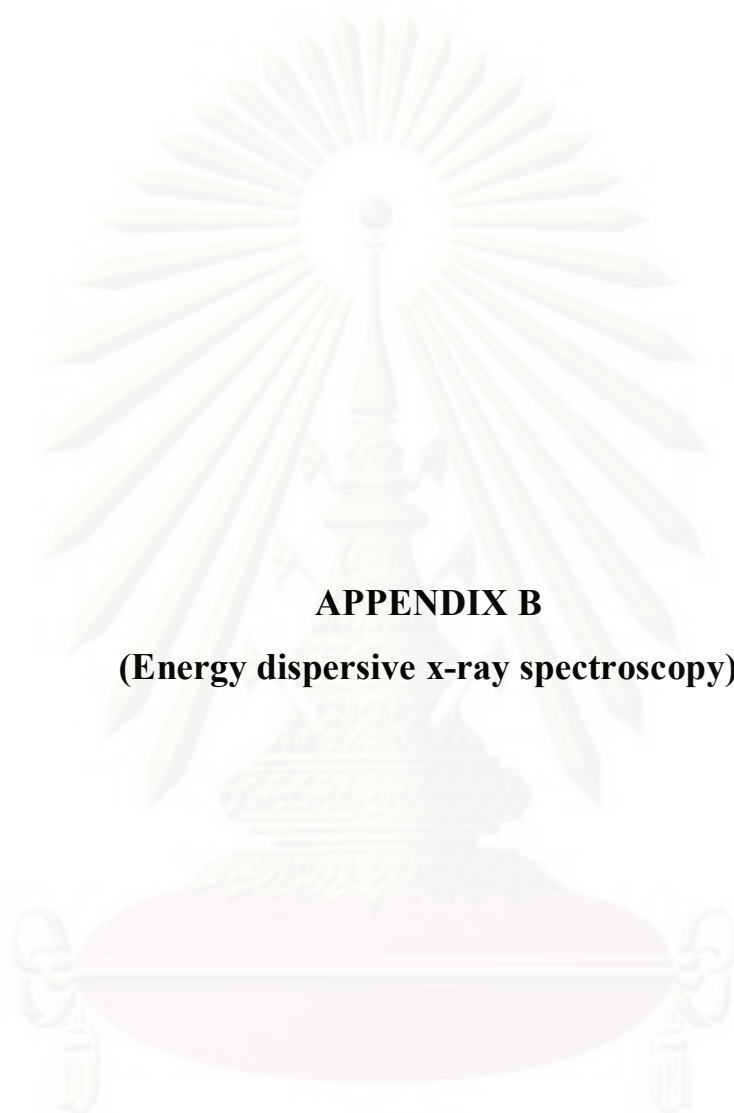
MAO is used for impregnation = 0.0125 x 58.02 = 0.726 g

(Density of 20% MAO = 0.91 g/ml)

MAO must be used for impregnation =  $\frac{0.726 \text{ g}}{0.91 \text{ g/ml}} = 0.798 \text{ ml}$

Then, inject 20 ml toluene as solvent stir 15 minute and evacuated solvent.

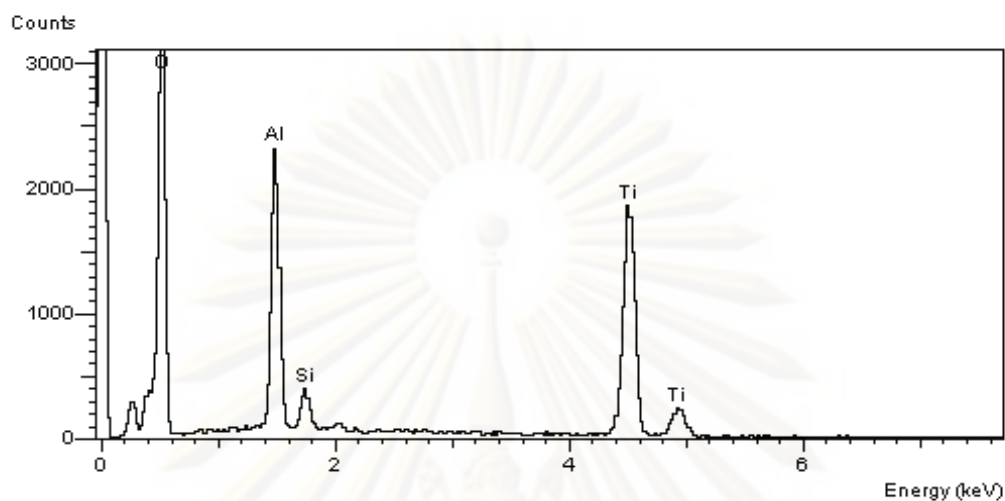
Repeat solvent injection and evacuation for more 2 times.



**APPENDIX B**  
**(Energy dispersive x-ray spectroscopy)**

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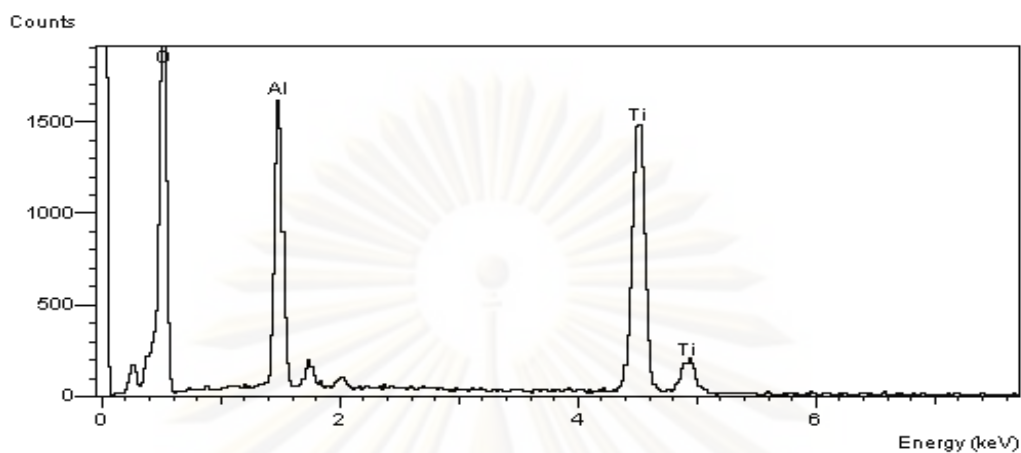


**Figure B-1** EDX profiles of [Al]<sub>MAO</sub> on TiO<sub>2</sub>\_A supports

**Table B-1** Content of element<sup>a</sup> on TiO<sub>2</sub>\_A supports

Element	Point 1		Point 2		Point 3		Average of % atomic	Derivation of % atomic
	% element	% atomic	% element	% atomic	% element	% atomic		
<b>O</b>	69.20	83.77	66.86	82.90	61.85	81.05	82.57	1.134
<b>Al</b>	12.05	8.65	10.52	7.73	6.63	5.15	7.17	1.48
<b>Ti</b>	18.74	7.58	22.64	9.37	31.53	13.80	10.25	2.61

<sup>a</sup>Amount of Al<sub>MAO</sub> on Ti<sub>support</sub> was calculated from average 3 point on sample.



**Figure B-2** EDX profiles of [Al]<sub>MAO</sub> on TiO<sub>2</sub>\_B supports

**Table B-2** Content of element<sup>a</sup> on TiO<sub>2</sub>\_B supports

Element	Point 1		Point 2		Point 3		Average of % atomic	Derivation of % atomic
	% element	% atomic	% element	% atomic	% element	% atomic		
<b>O</b>	65.64	81.42	66.06	82.45	68.56	83.70	82.52	0.93
<b>Al</b>	13.50	9.93	10.51	7.78	10.98	7.95	8.55	0.98
<b>Ti</b>	20.86	8.64	23.44	9.77	20.46	8.34	8.92	0.62

<sup>a</sup>Amount of Al<sub>MAO</sub> on Ti<sub>support</sub> was calculated from average 3 point on sample.

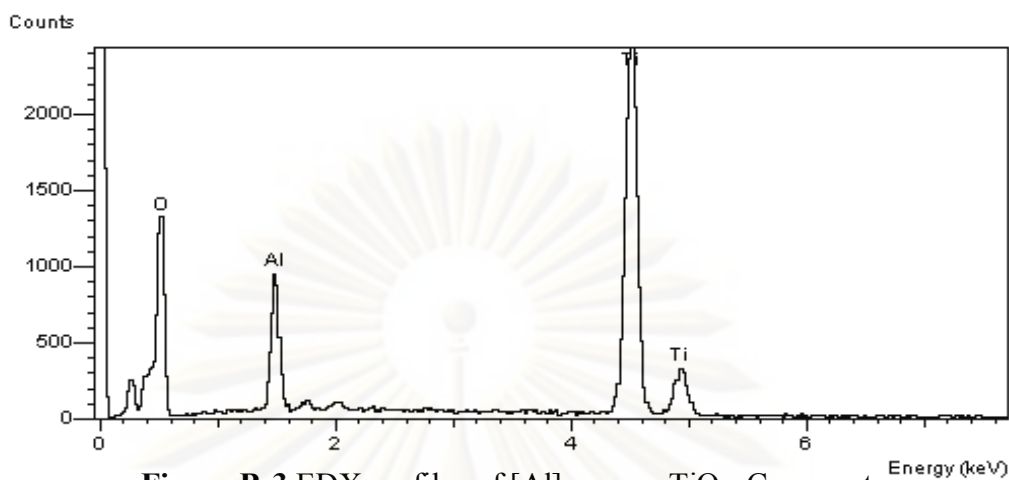


Figure B-3 EDX profiles of [Al]<sub>MAO</sub> on TiO<sub>2</sub>\_C supports

Table B-3 Content of element<sup>a</sup> on TiO<sub>2</sub>\_C supports

Element	Point 1		Point 2		Point 3		Average of % atomic	Derivation of % atomic
	% element	% atomic	% element	% atomic	% element	% atomic		
<b>O</b>	65.89	82.95	60.54	80.36	65.63	82.61	81.97	1.15
<b>Al</b>	8.30	6.20	6.25	4.92	9.03	6.74	5.95	0.76
<b>Ti</b>	25.81	10.85	33.22	14.73	25.34	10.65	12.08	1.88

<sup>a</sup>Amount of Al<sub>MAO</sub> on Ti<sub>support</sub> was calculated from average 3 point on sample.

**B-1 Calculation of amount of support used for polymerization**

$$\text{Fix } [\text{Al}]_{\text{MAO}}/[\text{Zr}]_{\text{catalyst}} = 1135$$

$$\text{Hereby } [\text{Zr}]_{\text{catalyst}} = 0.0000015 \text{ mol}$$

$$\begin{aligned} \text{And } [\text{Al}]_{\text{MAO}} &= 1135 \times 0.0000015 \\ &= 0.0017025 \text{ mol} \end{aligned}$$

$$\text{Assume find } [\text{Ti}]_{\text{support}}/[\text{Al}]_{\text{MAO}} = \mathbf{X}$$

$$\text{Then, multiply } \mathbf{X} \text{ by } 0.0017025 = \text{mol of used titania}$$

Then, multiply mol of used titania by molecularweight of titania (79.866 g/mol), so gram of used titania for polymerization will be provided.

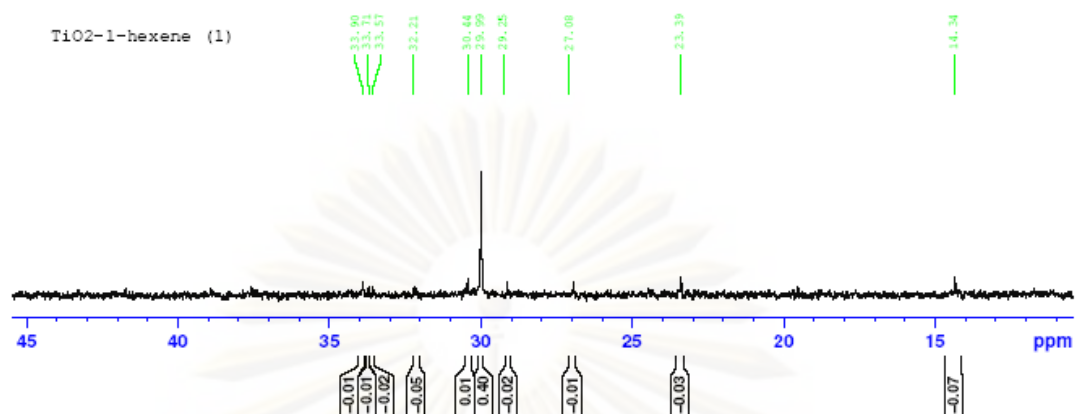
**Table B-4** Amount of used tiania for polymerization

Support	$[\text{Ti}]_{\text{support}}/[\text{Al}]_{\text{MAO}}$	Amount of used support for polymerization (g)
TiO <sub>2</sub> _A	1.43	0.19
TiO <sub>2</sub> _B	1.04	0.14
TiO <sub>2</sub> _C	2.03	0.28

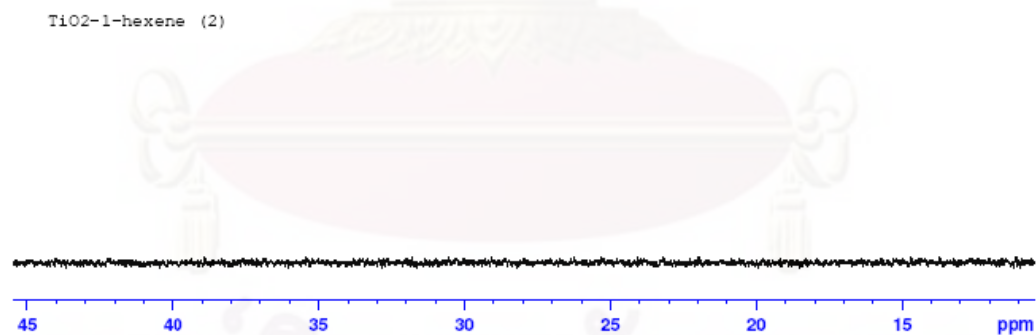


**APPENDIX C**  
**(NUCLEAR MAGNETIC RESONANCE)**

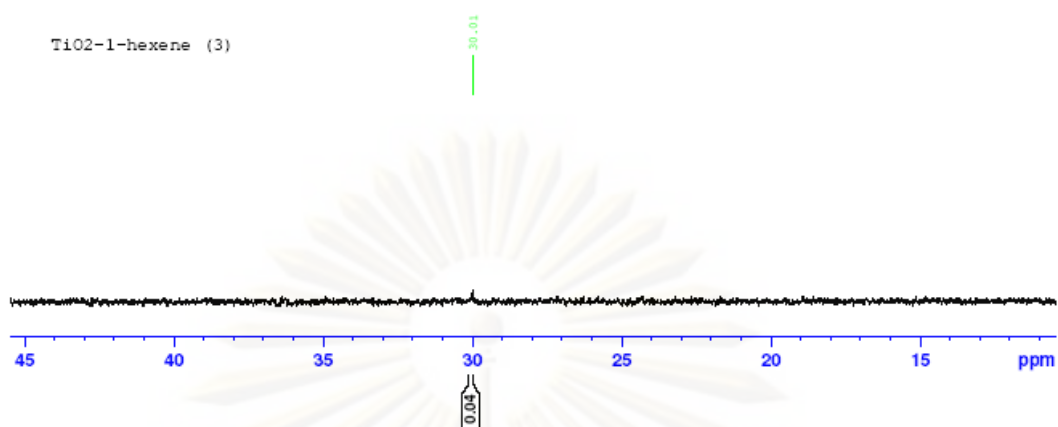
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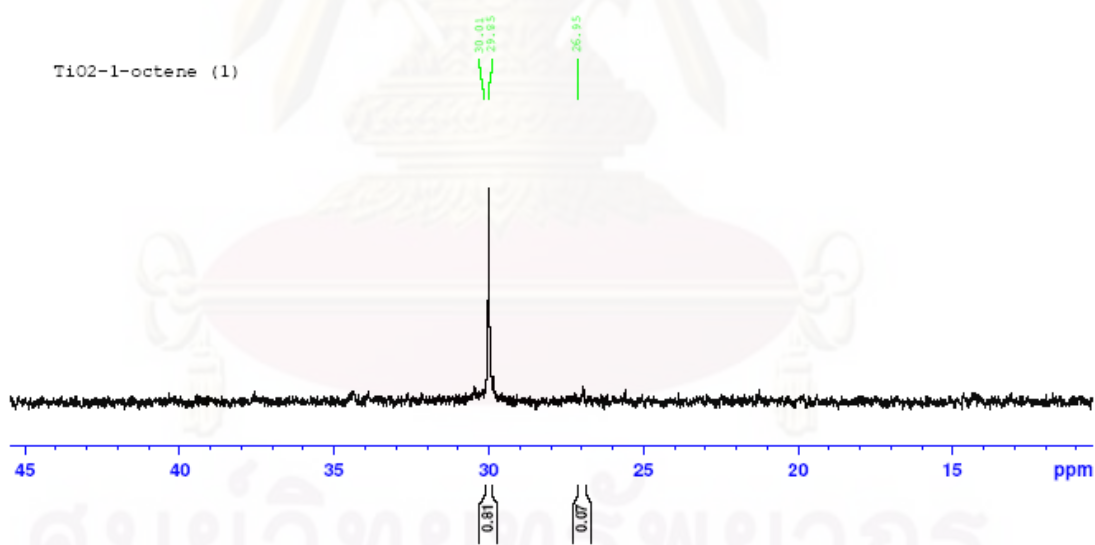
**Figure C-1**  $^{13}\text{C}$  NMR spectrum of ethylene/1-hexene copolymer produces with TiO<sub>2</sub>\_A support.



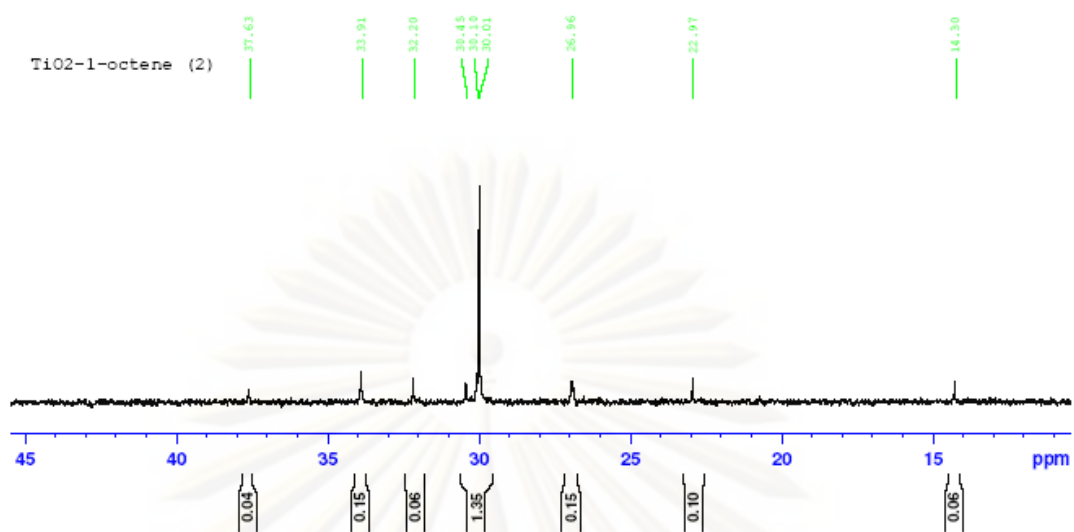
**Figure C-2**  $^{13}\text{C}$  NMR spectrum of ethylene/1-hexene copolymer produces with TiO<sub>2</sub>\_B support.



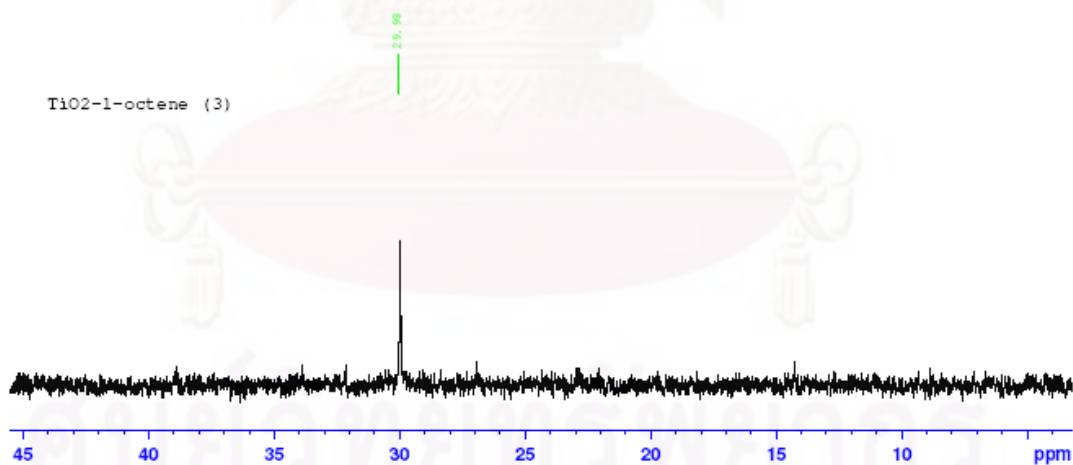
**Figure C-3**  $^{13}\text{C}$  NMR spectrum of ethylene/1-hexene copolymer produces with  $\text{TiO}_2\text{-C}$  support.



**Figure C-4**  $^{13}\text{C}$  NMR spectrum of ethylene/1-octene copolymer produces with  $\text{TiO}_2\text{-A}$  support.



**Figure C-5** <sup>13</sup>C NMR spectrum of ethylene/1-octene copolymer produces with TiO<sub>2</sub>\_B support.



**Figure C-6** <sup>13</sup>C NMR spectrum of ethylene/1-octene copolymer produces with TiO<sub>2</sub>\_C support.





**APPENDIX D**  
**(CALCULATION OF POLYMER PROPERTIES)**

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### D-1 Calculation of polymer microstructure

Polymer microstructure and also triad distribution of monomer can be calculated according to the Galland et al. [1996] and the Galland et al. [1999] in the list of reference for 1-hexene and 1-octene, respectively. The detail of calculation for ethylene/ $\alpha$ -olefin copolymer was interpreted as follow.

#### For 1-Hexene used as comonomer

The integral area of  $^{13}\text{C}$ -NMR spectrum in the specify range are listed.

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

Triad distribution was calculated as the followed formula.

$k[\text{HHH}]$	=	$2T_A - T_C + T_G + 2T_F + T_E$
$k[\text{EHH}]$	=	$2T_C - 2T_G - 4T_F - 2T_E - 2T_A$
$k[\text{EHE}]$	=	$T_B$
$k[\text{EEE}]$	=	$0.5T_D - 0.5T_G - 0.25T_E$
$k[\text{HEH}]$	=	$T_F$
$k[\text{HEE}]$	=	$T_E$

### For 1-Octene used as comonomer

The integral area of  $^{13}\text{C}$ -NMR spectrum in the specify range are listed.

$T_A$	=	39.5 - 42	ppm
$T_B$	=	38.1	ppm
$T_C$	=	36.4	ppm
$T_D$	=	33 - 36	ppm
$T_E$	=	32.2	ppm
$T_F$	=	28.5 - 31	ppm
$T_G$	=	25.5 - 27.5	ppm
$T_H$	=	24 - 25	ppm
$T_I$	=	22 - 23	ppm
$T_J$	=	14 - 15	ppm

Triad distribution was calculated as the followed formula.

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

All copolymer was calculated for the relative comonomer reactivity ( $r_E$  for ethylene and  $r_C$  for comonomer) and monomer insertion by using the general formula below.

$$r_E = \frac{2[EE]}{([EC]X)} \quad r_C = \frac{2([CC]X)}{[EC]}$$

Where

$$r_E = \text{ethylene reactivity ratio}$$

$$r_C = \text{comonomer } (\alpha\text{-olefin}) \text{ reactivity ratio}$$

$$[EE] = [EEE] + 0.5[CEE]$$

$$[EC] = [CEC] + 0.5[CEE] + [ECE] + 0.5[ECC]$$

$$[CC] = [CCC] + 0.5[ECC]$$

$$X = [E]/[C] \text{ in the feed}$$

$$= \frac{\text{Concentration of ethylene (mol/L) in the feed}}{\text{Concentration of comonomer (mol/L)}}$$

$$\%E = [EEE] + [EEC] + [CEC]$$

$$\%C = [CCC] + [CCE] + [ECE]$$

## D-2 Calculation of crystallinity for ethylene/ $\alpha$ -olefin copolymer

The crystallinities of copolymers were determined by differential scanning calorimeter. % crystallinity of copolymers is calculated from equation.

$$\% \text{ Crystallinity} = \frac{\Delta H_m}{\Delta H_m^0} \times 100$$

Where

$$\Delta H_m = \text{the heat of fusion of sample (J/g)}$$

$$\Delta H_m^0 = \text{the heat of fusion of perfectly crystalline polyethylene (286 J/g)}$$

## VITA

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Amornlertpreecha, S. and Jongsomjit, B. "Effect of mesoporous-titania surface area as zirconocene/MAO support for ethylene/1-octene copolymerization" (The Proceeding of 19<sup>th</sup> Thailand Chemical Engineering and Applied Chemistry Conference, TIChe 2009, Kanjanaburi)



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