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THE CHEMISTRY OF TITANIUM PRECURSORS, BUTYLCHLORIDE AND COCATALYST FOR IMPROVEMENT OF CATALYST ACTIVITY IN ETHYLENE POLYMERIZATION

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การปรับปรุงความว่องไวของตัวเร่งปฏิกิริยาซีเกลอร์ -นัตตาสามารถทำได้โดยการปรับเปลี่ยนปัจจัยต่างๆ ในงานวิจัยนี้มุ่งเน้นการศึกษาผลของสารตั้งต้นไทเทเนียม 2 ชนิด, บิวทิลคลอไรด์ และ ตัวเร่งปฏิกิริยาร่วมต่อความว่องไวของตัวเร่งปฏิกิริยาสำหรับปฏิกิริยาพอลิเมอร์ไรเซชันของเอทิลีน โดยการปรับเปลี่ยนอัตราส่วนของสารเคมีที่ใช้ในการสังเคราะห์ตัวเร่งปฏิกิริยาและนำไปทำปฏิกิริยาที่อุณหภูมิ 80 องศาเซลเซียส เป็นเวลา 2 ชั่วโมง จากการศึกษาพบว่าเมื่อเพิ่มปริมาณไทเทเนียมแอลคอกไซด์ ทำให้ความว่องไวของตัวเร่งปฏิกิริยาลดลงตรงข้ามกับการเพิ่มปริมาณบิวทิลคลอไรด์ซึ่งส่งผลให้ความว่องไวของตัวเร่งปฏิกิริยามีค่าเพิ่มขึ้น

ส่วนการทดลองเปลี่ยนชนิดและปรับปริมาณของตัวเร่งปฏิกิริยาร่วมสามชนิด ได้แก่ TEA, TiBA และ TnOA พบว่า ค่าความว่องไวของตัวเร่งปฏิกิริยาจะเพิ่มขึ้นอย่างเห็นได้ชัดเมื่อเพิ่มปริมาณตัวเร่งปฏิกิริยาร่วม โดยใช้ตัวเร่งปฏิกิริยาร่วมเป็น TEA เมื่อเทียบคุณสมบัติของพอลิเอทิลีนที่ได้เมื่อใช้ตัวเร่งปฏิกิริยาร่วมเป็น TEA ที่อัตราส่วนต่อตัวเร่งปฏิกิริยาเท่ากับ 5 กับเมื่อใช้ตัวเร่งปฏิกิริยาโดยมีอัตราส่วนระหว่างบิวทิลคลอไรด์ต่อแมกนีเซียมเท่ากับ 2.5 ซึ่งได้ค่าความว่องไวของตัวเร่งปฏิกิริยาใกล้เคียงกัน พบว่า ลักษณะภายนอกของพอลิเมอร์ที่ได้มีความคล้ายคลึงกันคือ มีลักษณะเป็นอสัณฐาน เช่นเดียวกับลักษณะของตัวเร่งปฏิกิริยา แต่ค่าน้ำหนักโมเลกุลและค่าการกระจายตัวของน้ำหนักโมเลกุลที่ได้ แคบกว่า เมื่อใช้ตัวเร่งปฏิกิริยาร่วมเป็น TEA ที่อัตราส่วนต่อตัวเร่งปฏิกิริยาเท่ากับ 5

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต

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GOOND HONGMANEE : THE CHEMISTRY OF TITANIUM PRECURSORS, BUTYLCHLORIDE AND COCATALYST FOR IMPROVEMENT OF CATALYST ACTIVITY IN ETHYLENE POLYMERIZATION. ADVISOR : ASSOC. PROF. BUNJERD JONGSOMJIT, Ph.D., 147 pp.

The improvement of Ziegler-Natta catalyst activity can be achieve by adjusting the related factors. This research was aimed to investigate the effects of titanium precursors, butylchloride and cocatalyst on the ethylene polymerization activity. The amount of precursors was varied, and then polymerized at 80 ^{0}C for 2 h. The results showed that the decrease of catalytic activity was observed when the amount of titanium (IV) alkoxide was increased. Inversely, an increase of butylchloride amount resulted in an increase of catalytic activity

Moreover, the effects of types and amount of cocatalyst were also investigated. The obvious increase of catalytic activity was obtained when the amount of cocatalyst was increased and the cocatalyst type was TEA. In addition, the obtained activity from butylchloride per magnesium ratio of 2.5 was similar to the usage of TEA as cocatalyst and a mole ratio per titanium of 5. The external morphology of the obtained polymers was amorphous as the catalyst morphology. However, the molecular weight and molecular weight distribution were narrower when the TEA having molar ratio per titanium of 5 was used

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CHAPTER I

INTRODUCTION

Since the Ziegler-Natta catalyst was discovered, the progress of polymer technologies has been rapidly developed. Although there are many other types of polymerization catalysts such as single-site catalyst (metallocene) and chromium-based catalyst (Phillips catalyst), Ziegler-Natta has still taken the largest part for polymer production in industrial sector, especially for polyethylene (PE), because of its low cost and less poison. The challenges in catalyst modification have begun as the demand of polymers and their special properties drastically increases. The catalyst can be generally developed to achieve the required properties by several factors such as synthesis methods, catalyst precursors, cocatalysts, electron donor, and reactor design.

For Ziegler-Natta catalyst, titanium and vanadium are the main component in its structure. However, titanium is more popular than vanadium because of its higher stability [1]. Nowadays, titanium (IV) chloride ($TiCl_4$) is used as the main precursor because it shows good potential in productivity. In addition, other sources of titanium, titanium (IV) alkoxide, is also found to have ability to increase the melt flow rate and impact resistance of polymer [2].

The heterogeneous system for polymer production is one of the strong points of Ziegler-Natta catalyst. In addition to advantages of the catalyst such as good morphology controlling and reduction of production complexity [3], the development of support for this catalyst is also the purpose of many researchers to achieve good catalyst properties. Magnesium chloride ($MgCl_2$) is the most popular support for Z-N catalyst because its structure is well compatible to $TiCl_4$. However, there are many attempts to invent novel catalyst supports to replace it such as mixed support between silica and $MgCl_2$ (SiO_2-$MgCl_2$) [4], single SiO_2 support [5], and polyolefin support [6]. Grignard route which could provide high catalytic activity [7] with butylchloride (BuCl) as a precursor is an effective method to design catalyst supports. The amount of BuCl is found to affect on the activity and morphology. Unfortunately, the exact mechanism and role of this precursor are still unclear.

The other interesting factor for development of the catalyst performance is a cocatalyst. Normally, alkylaluminum compounds are used as a cocatalyst or an activator in polymerization process. It has two main roles; (i) elimination of moisture and oxygen, (ii) formation the active centers. The selection of cocatalyst type is one of the principal factors needing to be considered for high catalytic activity achievement because the oxidation state of titanium is crucial for olefin polymerization. The Ti^{2+} species can polymerize both of ethylene and propylene, whereas the Ti^{3+} species can polymerize only propylene [8]. Typically, the catalytic activity increases with an increase of cocatalyst concentration, and then decreases because of over reduction or adsorption competition between ethylene and cocatalyst [9]. Thus, the selection and amount of cocatalyst have to be seriously concerned.

In this study, the research is divided into three parts. In the first part, two titanium precursors [$Ti(OPr)_4$:$TiCl_4$] were mixed, and then investigated their effects on catalytic activity and polymer properties. In the second part, the amount of BuCl was varied. From these two parts, we expected to obtain a suitable amount of catalyst precursors for synthesis of a high performance catalyst. In last part, three types of cocatalyst types and their concentration were varied, and then used them together with the catalyst obtained from the first and second part in order to acheive high catalytic activity and desirable polymer properties.

1.1 Objectives

1. To investigate the effect of variation of titanium precursors, butylchloride and cocatalyst on catalyst activity and polymer properties.
2. To obtain a high performance catalyst for polyethylene polymerization.

1.2 Research Scopes

1. Synthesize the polyethylene catalyst by varying the ratio of titanium precursor.
2. Synthesize the polyethylene catalyst by vary the ratio of BuCl:Mg.

3. Polymerize the polyethylene by various ratios of Al:Ti.
4. Determine the effect of titanium precursor, butylchloride and cocatalyst ratio on polymerization activity and properties of polymer
5. Cocatalysts used in this work are TnOA, TEA and TiBA.
6. Polyethylene polymerization step is conducted by the 2L reactor under a slurry process
7. Characterize the catalyst and polyethylene with scanning electron microscope (SEM), energy dispersive spectrometer (EDX), Fourier transforms infrared spectroscopy (FT-IR), gel permeation chromatography (GPC), electron spin resonance (ESR), inductively coupled plasma - mass spectrometry (ICP-MS), and melt index.

1.3 Benefits

1. Obtain an appropriate synthesis method and precursor ratio for high performance catalyst.
2. Understand the chemistry of precursors for improvement of catalytic activity.
3. Achieve the required polymer properties.
4. Use this information as a basic knowledge for polymer industry.

CHAPTER II

THEORY

2.1 Ziegler-Natta Catalyst

2.1.1 Introduction

In fact, Ellis investigated catalyst as complex substance since 1941. He used the heterogeneous catalysts which consist of lithium alkyl and nickel oxide on silica. This catalyst system was tested in Alfa-olefin polymerization under hydrogen atmosphere. However, stereo-polymerization was seriously started by Ziegler in 1953. He revealed that high density polyethylene was easily made at low pressure with binary mixture of metal alkyls and transition metal salts, and in the next year Natta demonstrated the ability of the same type of catalysts to form isotactic polymers from α-olefins then in 1963 Karl Ziegler and Giulio Natta were awarded the Nobel Prize for Chemistry for their landmark discoveries of the polymerization catalysts named after them. The discoveries changed polymer chemistry forever, and provoked a worldwide research and development effort that culminated in many new commercial plastics and elastomers. The Ziegler-Natta catalyst has now joined the ranks of conventional cationic, anionic and radical initiators as one of the major methods available to initiate polymerizations, and it is doubtful that it can be challenged by any other catalyst for its versatility. Ziegler-Natta catalysts became prominent in a special period in the history of polymer science, a period that not only produced many new commercial polymers but also enhanced our basic knowledge of polymer properties and structure as well as polymerization processes [10].

2.2.2 General concepts of Ziegler-Natta Catalyst

Ziegler-Natta catalysts are formed by reacting a metal alkyl (or hydride) and a transition metal salt, such as $AlEt_3$+$TiCl_3$, under an inert atmosphere. Binary mixtures have usually been used; however more than one metal alkyl or transition metal salt can be present. It has been manifested that there is a definite advantage to have a ternary or quaternary system in only a few cases. Organic and inorganic molecules are added to modify some aspects of the polymerization; hydrogen, for example, is added to terminate chain growth process.

The literature report that the Ziegler-Natta catalysts are complexes formed by reaction of a transition metal compound (halide, alkoxide alkyl or aryl derivative) of group IV-VIII transition metals with a metal alkyl or alkyl halide of group I-III base metal [11]. The former component is usually called the catalyst and the latter called the cocatalyst. There are a very large number of patents involving every combination of pure or mixed metal alkyls with transition metal compounds, each claiming particular advantages. In practice, only a few group I-III metal alkyls are effective. Aluminum alkyls (such as $AlEt_3$, $Al\text{-}i\text{-}Bu_3$, $AlEt_2Cl$, $AlEtCl_2$ and $AlEt_2OR$) have been overwhelmingly preferred [12]. Also, transition metals compounds containing titanium (Ti), vanadium (V), and chromium (Cr) and, in special cases, molybdenum (Mo), cobalt (Co), rhodium (Rh) and nickel (Ni) are primarily used.

A metal alkyl or a transition metal salts forms an active catalyst for a particular monomer. In practice, the choice of a particular combination of a metal alkyl and a transition metal salt is largely governed by the monomer structure. For example, Ziegler-Natta catalysts based on group VIII transition metal salts, such as $AlEt_2$ + $CoCl_2$, readily polymerize dienes but not ethylene or α-olefins. On the other hand, the catalysts based on group IV, V, and VI transition metal are active for both dienes and α-olefins, such as Ti-, V-, and Cr- based catalysts. A particular catalyst: $(C_5H_5)_2TiCl_2$, in combination with an aluminum alkyl, polymerizes ethylene but not propylene.

Ethylene is polymerized by a substantially larger number of catalysts than are propylene and higher α-olefins. While all catalysts which are active for polymerization of alpha olefins are also active for polymerization of ethylene, but the reverse is not true.

Sometimes an exchange reaction occurs between the transition metal and the metal alkyl to generate a new transition metal salt. When $Ti(OR)_4$ and $AlEt_2Cl$ are reacted, for example, the exchange shown in **Equation 2.1** takes place.

$$\text{Al-Cl} + \text{Ti-OR} \longrightarrow \text{Al-OR} + \text{TiCl} \qquad (2.1)$$

The real catalyst maybe the end product of this exchange rather than the starting mixture; at an AI/Ti ratio of 4, β-$TiCl_3$ is formed.

The notation "Ziegler-Natta Catalyst" has been adopted in this thesis. The reader may have noted that the literature contains a variety of other designations for this catalyst, including Ziegler catalyst, Ziegler-type catalyst, Natta catalyst, coordinated-anionic catalyst, mixed metal complex catalysts, etc. In the initial period after Ziegler's discovery, the catalysts were reported by his school to polymerize ethylene (and copolymerize ethylene and propylene) contained the transition metal in the highest oxidation state, e.g., $TiCl_4$ and VCl_4. These were named as Ziegler catalysts. Later, Natta discovered that polypropylene of greater isotacticity was produced if preformed lower oxidation state transition metal salts were used, such as $TiCl_3$ and VCl_3. While he referred to these as modified Ziegler catalysts or Ziegler-type catalysts, others, in order to separate them from Ziegler catalysts, designated as Natta catalysts. Particular catalysts developed by other laboratories sometimes assumed the names of that company to denote a special modification of the catalyst.

Some researchers chose to refer to all of the above as Ziegler-type catalysts, others used the name Ziegler-Natta catalysts so as to include the large number of catalyst discovered and elucidated later, not only by the Natta school, but also by other researchers worldwide. The latter nomenclature has been favored in more recent years. It means that the active catalyst contains a metal alkyl (or hydride) and a transition metal salt regardless of additional modifications, such as the presence of third component, support of the catalyst, and in situ synthesis of catalyst component.

Not long after Ziegler-Natta catalysts were discovered, it was found that electron donors could greatly affect the catalyst's kinetic and stereochemical behavior. Electron donor compounds, such as amines, ethers and esters, have the potential of complexing and reacting with the components of the catalyst or the active centers. They have been used in controlled amounts in many Ziegler-Natta catalytic systems as a third component to increase catalyst activity and/or stereoselectivity [10]. Heterogeneous Ziegler-Natta catalyst systems have been a great success in commercial production of linear polyethylene and isotactic polypropylene and higher α-olefin polymers. In Ziegler-Natta catalyst, they divided into Homogeneous catalyst and Heterogeneous catalyst.

2.2.2.1 Homogeneous Catalysts

The discoveries by Ziegler were concerned with ethylene polymerization in the presence of an in situ prepared catalyst. They were obtained as a precipitate from the reaction of a soluble transition metal halide, especially $TiCl_4$, with a metal alkyl or alkyl metal halide, primarily $Al(C_2H_5)_3$ or $A1(C_2H_5)_2Cl$. The reaction was carried out at the activator to a procatalyst molar ratio not much greater than unity and in an inert hydrocarbon medium. Most non-supported catalysts used for alkene slurry polymerization process are obtained using the σ-$TiCl_3.l/3AlCl_3$ solid solution. Titanium was found that ball milling of the product obtained from the reduction of $TiCl_4$ by aluminum metal or aluminum alkyls led to a more active catalyst than pure α-$TiCl_3$. Furthermore, it was revealed that during the milling process both the α- and the γ-forms of $TiCl_3$ was converted to the δ-form, which displayed double-layer stacking. Catalysts of the above type are referred to as 1st-generation Ziegler-Natta catalysts. Most 1st-generation commercial catalysts are based on a precursor of the δ-$TiCl_3.xAlCl_3$ solid solution type and have been dry milled and heat-treated. These catalysts have specific surface areas in the range 10-40 m^2/g. Their productivity is a few kilograms of polyethylene or polypropylene (with an isotactic index of 88-93 %) per gram Ti per hour. The production processes, involving slurry-type polymerization were complicated and expensive and, because of their complexity, not very versatile. Although the catalyst productivity could be much higher for ethylene than for propylene, it was necessary to extract the catalyst residues in order to reduce the quantities of Ti and Cl in the product to acceptable levels.

2.2.2.2 Heterogeneous Catalysts

The large-scale production of polyolefins has been enhanced by the development of very high-activity supported Ziegler-Natta catalysts. Higher catalyst activities can lower production cost owing to possibilities of eliminating some operations from the production technology. Since Natta *et al*. demonstrated that only a small percentage of the Ti atoms in the non-supported catalysts (typically less than 1% in the first-generation catalysts) were active for alkene polymerization. It was realized that much of the procatalyst mass acted simply as a support for the active sites fromed by activation. **Equation 2.2** shows this relation

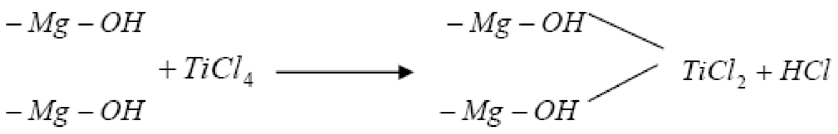
$$(TiCl_3)_{x+y} + zAlR_3 \longrightarrow (TiCl_3)_y.(TiRCl_2)_z + zAlR_2Cl \qquad (2.2)$$

Depositing the active Ti species on a support could make significant improvement whose residues, unlike those to $TiCl_3$, would be inert and not detrimental to the properties of the polymer. Thus, it was evident that higher catalyst activities were likely to be achieved through the use of transition metal compounds supported on appropriate matrices. Early attempts to support $TiCl_4$ directly on silica, alumina or magnesia did not lead to a sufficient increase in catalyst productivity. The first useful high-yield catalyst involved Mg(OH)Cl as a support. Over the years, a wide range of support catalyst have been successfully developed and used for the industrial polymerization of ethylene, and more recently propylene. In the case of ethylene polymerization, supported catalysts have been implemented in to practice relatively easily. Various metal oxides, chloride, oxychlorides and alkoxides such as $A1_2O_3$, SiO_2, $Al_2O_3.SiO_2$, MgO, ZnO, TiO_3, ThO, Mg(OH)Cl, $Mg(OC_2H_5)_2$ and $MgCl_2$ have been applied as catalyst supports. Organic polymers may also play the function of the catalyst support. However, a variety of magnesium compounds have been used most successfully as supports; pre-eminent among these is $MgCl_2$ or reaction mixtures that can produce this compound, at least on the support surface. The massive increase in activity of $MgCl_2$-supported catalysts has been claimed to be due to an increase in the percentage of Ti atoms forming active sites (approaching nearly 100%) and not to a significant increase in reaction rate at the active site (intrinsic catalyst activity). This was the 3rd-generation catalyst system, and the discovery of magnesium chloride in the active from, as an ideal support for the fixation of $TiCl_4$ and its derivatives, opened a new era in the field of Ziegler-Natta catalyzed polymerization, from both industrial and scientific points of view. During the 1980s, active $MgCl_2$-supported catalysts brought about revolutionary developments in the production of polyolefin compared with the first-and second-generation Ziegler-Natta catalysts. The introduction of the catalyst support concept significantly increased the complexity of the catalyst construction but also reduced the complexity of industrial olefin polymerization processes. The active polymerization centre could now be dispersed throughout the support surface, making them all essentially accessible to the polymerized monomer. Since all the titanium chloride molecules were now available to take part in the polymerization, fewer were needed. Consequently, the yield of polymer per gram of titanium was so high that no extraction procedures were necessary in order to produce a viable commercial resin. Elimination of the de-ashing part of the industrial process had obvious economic and environmental advantages and resulted in the explosive growth of polyolefin in the global plastic marketplace.

Supports used for obtaining Ziegler-Natta catalysts can differ essentially from one another. Some of the supports may contain reactive surface groups (such as hydroxyl groups present in specially prepared metal oxides) while others do not contain such reactive functional groups (such as pure anhydrous metal chlorides). Therefore, the term “supported catalyst” is used in a very wide sense. Supported catalysts comprise not only systems in which the transition metals compound is linked to the support by means of a chemical covalent bond. But also systems in which the transition metal atom may occupy a position in a lattice structure, or where complexation, absorption or even occlusion may take place. The transition metal may also be anchored to the support via a Lewis base; in such a case the metal complexes the base, which is coordinatively fixed on the support surface. Supported precursors for Ziegler-Natta catalysts may be obtained in two ways depending on the kind of support. By treatment of the support containing surface hydroxyl groups with a transition metal compound with chemical covalent bond formation. And by the treatment of a magnesium alkoxides or magnesium chloride support with a Lewis base and transition metal compound with coordination bond formation.

The use of supports containing hydroxyl groups such as alumina, silica, Mg (OH)C1, etc., for chemical fixing of the transition metal compound has been widespread since the early 1960s. Heat treatment of such supports can control the number and type of surface hydroxyl groups and indirectly the amount and distribution of transition metal atoms anchored to the surface. The most commonly used Ziegler-Natta catalyst of this type is obtained by application of the precursor yield from the reaction of Mg(OH)Cl support and $TiCl_4$:

$$\mathrm{Mg - OH + TiCl_4 \rightarrow -Mg - OTiCl_3 + HCl} \tag{2.3}$$



$$\left.\begin{matrix} -Mg-OH \\ -Mg-OH \end{matrix}\right. + TiCl_4 \longrightarrow \left.\begin{matrix} -Mg-OH \\ -Mg-OH \end{matrix}\right\rangle TiCl_2 + HCl \tag{2.4}$$

The obtained supported precursors are then subjected to activate by trialkylaluminium, which can be show schematically for the $MgOTiCl_3$ species as follows:

$$\mathrm{-Mg\text{-}OTiCl_3 \xrightarrow[+AlR_2Cl]{+AlR_3} -Mg\text{-}OTiRCl_2 \longrightarrow} \\ \mathrm{\xrightarrow[-R]{} -Mg\text{-}OTiCl_2 \xrightarrow[+AlR_2Cl]{+AlR_3} -Mg\text{-}OTiRCl} \tag{2.5}$$

Supporting the titanium catalyst component has been claimed to lessen the tendency of titanium active site to be reduced by the activator. Many of the catalysts obtained from such precursors and trialkylaluminium as the activator exhibit high activity in the polymerization of ethylene, but are not, however, useful for the polymerization of propylene and higher α-olefins [13].

2.2 Preparation of Ziegler-Natta catalyst support [14]

The $MgCl_2$-supported catalysts have been more using trendy due to the encouraging huge qualitative activity. In addition, the $MgCl_2$-supported catalysts are generally used in a few forms come through as following preparations here.

2.2.1 Ball-milled $MgCl_2$-based Ziegler Catalysts

Magnesium chloride usually cannot use directly for the preparation of a Ziegler catalyst without some transformation that makes stacking defects on the $MgCl_2$ crystal structure. The $MgCl_2$ crystal has to be transformed from the α-form to the δ-form which can provide enormously active catalysts. To make defections, $TiCl_4$ or $TiCl_3$ are occasionally co-milled with $MgCl_2$. The high polyethylene yields have succeeded directly with high titanium loading on the catalysts, but the more high titanium loading, often the less specific activity in unit of per grams-titanium. The productivities have been around 10 kg PE per g catalyst per hour with generally Ti content approximately 3 wt%. However, this preparation method is not recently common.

2.2.2 $MgCl_2$-Titanium Catalysts on Silica

Silica-based catalysts have used commonly in gas-phase processes due to the controllable particle size and particle size distribution of supports to keep the bed positioning. The silica support acts as a carrier inert material contribute to duplication of a catalyst shape. It is considered not a part of active complex as such as $MgCl_2$ be but it commonly provides a large pore volume and surface area in order to directly impregnate titanium active site element or to keep a recrystallized precursor of titanium and magnesium chloride on its surface. A wide variety of catalysts can be achieved by varying the physical properties of the silica support such as particle size, particle size distribution, porosity, surface area, etc. In addition, the pore walls and outer surfaces of silicas prepared in aqueous solutions are normally occupied by the hydroxyl droups of two or three types of silanols. The heat treatment of the silica support can be considered in order to transform the isolated and hydrogen-boned hydroxyl groups into siloxane bridge groups. The silica-based catalysts typically improve chemical composition distributions (CCD) in ethylene copolymerization.

2.2.3 Precipitated and Supported $MgCl_2$-based catalysts

Precipitated Ziegler catalysts are mostly prepared along with silica-based system. The precipitation are in following steps by, first, bringing the $MgCl_2$ into a dissolved state with the catalyst components, then, $MgCl_2$ is precipitated by a suitable chlorination agent. Titanium chloride can be added either as a soluble complex or as a chlorination agent. In the precipitation, the procedures may use different tricks and/or adding suitable donor compounds. The commonly method is to prepare via the titanation of a support of magnesium chloride and ethanol. Many investigations have reported results that the titanium amounts typically vary between 1% and 4% and possibly vary in wide a range of 0.1 to 100%.

2.3 Ti oxidation state

$MgCl_2$-supported catalyst are much more complex systems than the $TiCl_3$-based ones, not only because of the presence of Lewis base, which can interact with both the catalyst and the cocatalyst, but also owing to the different type of Ti compound used, which is normally in a tetravalent state and prone to undergo reduction upon interaction with the Al-alkyl. On the other hand, the latter is normally a trialkyl and thus possesses a higher reducing power than DEAC used along with the earlier generation catalysts.

Because the oxidation state of the transition metal of the active center significantly affects the structure of that center, much work has been done to establish its value for different Ziegler-Natta catalysts. It is, however, important to distinguish between the measured average oxidation state of the whole catalyst and the oxidation state or states of the individual centers. The first can usually be determined easily, but a direct assignment of oxidation state of the active centers is more difficult. First of all, the fraction of the total transition metal atoms that are active centers is small, about 1% or less. Suggestions that traces of the transition metal in an unmeasured oxidation state actually form the active centers in some catalysts cannot be lightly dismissed.

The role in the transition metal oxidation state reduction has been widely demonstrated through both physical analysis and chemical measurements. Using techniques such as electron spin resonance spectrometry (ESR), photometry, chemical ionization-mass spectrometry (CI-MS), X-ray absorption spectroscopy, and chemical titration methods, the occurrence of oxidation state reduction upon the mixing of catalyst and cocatalyst has been confirmed.

The literature shows different procedures and methods to determine the concentrations of Ti^{2+}, Ti^{3+}, and Ti^{4+}. Redox titration was used by Goto and Takeyama to determine $[Ti^{2+}]$, $[Ti^{3+}]$ and $[Ti^{4+}]$. Kashiwa *et al.* used H_2 evolution for $[Ti^{2+}]$ determination and polarography for determination of $[Ti^{3+}]$ and $[Ti^{4+}]$. Baulin *et al.* used potentiometric titrations for $[Ti^{n+}]$ determination. Chien *et al.* used two redox titrations for $([Ti^{3+}] + [Ti^{2+}])$ and $([Ti^{3+}] + 2[Ti^{2+}])$ determination and atomic adsorption for $[Ti^{n+}]$, whereas $[Ti^{4+}]$ was obtained by working out the difference.

While it is generally accepted that in the $TiCl_3$/DEAC system Ti^{3+} species are almost exclusively present [15], a more extensive reduction of Ti from the initial tetravalent oxidation state is likely to occur in supported catalysts. Keii *et al.* [16] reported that premixing of catalyst and cocatalyst reduced the activity of $MgCl_2$-supported type catalyst, which means that the cocatalyst has some role in catalyst deactivation. On the other hand, they suggested that the rapid decay of the polymerization rate may be attributed to the deactivation of the surface active sites by a strongly adsorbed cocatalyst species, which may lead to the reduction of Ti^{3+} to Ti^{2+}. Tait *et al.* [17] suggested that an increase in cocatalyst concentration causes an overreduction of the oxidation states of titanium ions. Kashiwa *et al.* [18] showed that the Ti^{2+} species polymerizes ethylene only, whereas the Ti^{3+} species polymerizes α-olefin. They reported that pretreatments of catalyst with TEA result in a catalyst that is active only for ethylene polymerization. However, reoxidation of the catalyst with Cl_2 results in reactivating the catalyst for propylene polymerization. In the same way, Soga *et al* established that Ti^{3+} species are active for the polymerization of both ethylene and propylene during copolymerization. However, further reduction of Ti^{3+} to Ti^{2+} results in polymerization of ethylene only.

From the above results, despite the different catalysts and conditions investigated, it seems reasonable to conclude that under polymerization conditions a considerable reduction of Ti takes place; Ti^{3+} is believed to be the active site for propylene polymerization while Ti^{2+} is supposed to be active for ethylene polymerization only.

2.4 Cocatalyst Chemistry

The cocatalysts used with $MgCl_2$-supported catalysts are invariably Al-trialkyls, triethyl aluminum (TEA) and triisobutylaluminum (TiBA) being by far the most preferred ones. Al-alkyl-chlorides, in fact, afford a much poorer performance and can be used only in combination with trialkyls.

On the other hand, the external donor which can be used appears to be dependent on the type of internal donor (ID). If ID is an aromatic monoester (ethylbenzene is the most usual), esters of the same type are normally required, such as methyl-*p*-tolulate (MPT), ethylanisate (EA), *p*-ethoxy-ethylbenzoate (PEEB) and the like, whereas alkoxysilanes are required with phthalates (or diethers). Hindered piperidines, such as 2,2,6,6-tetramethylpiperidine (TMP), on the other hand, seem to work well with diethers, but not as well with monoesters. Whichever is the external donor, however, owing to its basic nature and the acidic nature of the AlR_3, a more or less complex interaction between the two components takes place.

Most of the literature deals with the interaction between TEA or TIBA and aromatic monoesters, whose chemistry has recently been reviewed by several authors. According to most of the findings, the interaction involves first the formation of an acid-base complex through the carbonyl oxygen, as demonstrated by the shift of the infrared C═O stretching frequency from ~1725 cm^{-1} in the free ester to 1655 cm^{-1} to 1670 cm^{-1} in the AlR_3/ED mixture. The complex is most often assumed to exist in a 1:1 ratio, but on the basis of spectroscopic evidence and calorimetric studies, complexes involving two moles of AlR_3 per mole of ED also have been hypothesized. Structures such as those represented in **Figure 2.1** have been proposed by Spitz *et al.*, while not very different structures were assumed by Chien *et al.* and Tashiro *et al.* The complex formation is very fast even at low temperature and in dilute solutions.

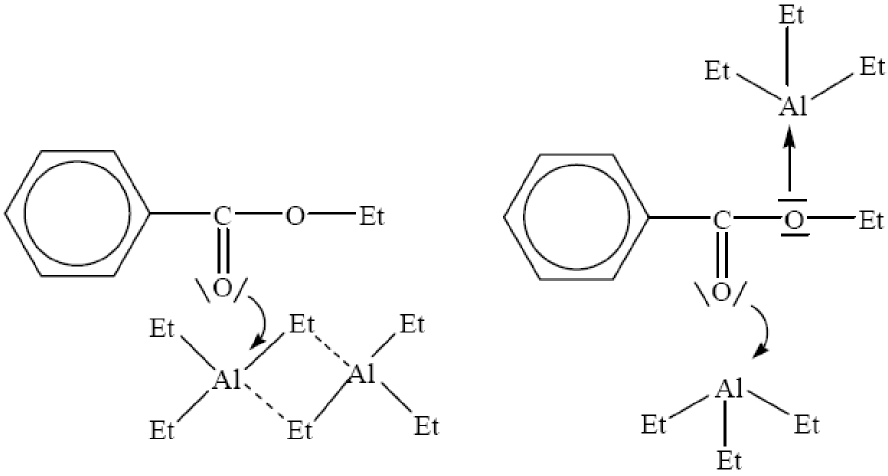


Figure 2.1 Possible structures of 1:2 EB/TEA complexes.

As regards alkoxysilanes, the formation of a 1:1 complex between TEA and phenyltriethyoxysilane (PES) has been indicated by means of ^{13}C NMR spectroscopy, at least at relatively high TEA concentrations (0.5 mol/L). The complex seems to involve the O atom from only one OR group, irrespective of the number of OR groups attached to Si.

The above complexes can undergo a further reaction, especially in the presence of excess AlR_3 as is usual for polymerization. In the case of aromatic monoesters, such as EB, a nucleophilic attack of free AlR_3 on the carbonyl group complexed with AlR_3 has been postulated. The reaction leads finally to the formation of two moles of dialkylaluminium alkoxide per one mole of ester, according to the **figure 2.2**.

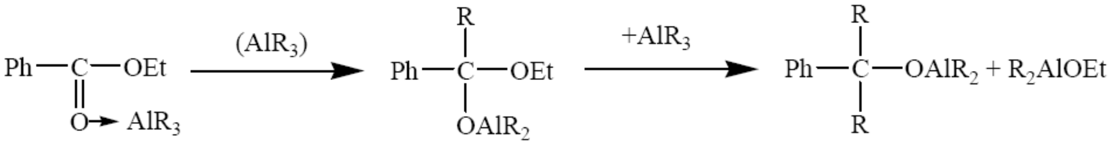


Figure 2.2 The formation of EB and AlR_3 complexation.

Reduction of the C═O group, rather than alkylation, prevails with TIBA with the concomitant elimination of isobutene. The reaction rate is higher for TEA than TIBA and is greatly enhanced in concentrated solutions. Even at the mild conditions used in the polymerization and in the presence of the monomer, however, the reaction proceeds to a considerable extent. Silyl ethers, in turn, can undergo an exchange reaction with the Al-alkyl, with the formation of alkylated silylethers and dialkyl-Al-alkoxides. The reaction rate is appreciable for silanes containing three or four OR groups and at high concentrations of the Al-alkyl. Starting from $PhSi(OMe)_3$ and TEA, for instance, the reaction at 75^{o}C can proceed up to the formation of $PhEt_2SiOMe$, according to the scheme of **Figure 2.3**.

Under the much more diluted polymerization conditions, however, the reaction is much slower and only 20% of PES, for example, is converted in 1 hour at 70^{o}C, with TEA = 5 mmol/L and PES = 0.5 mmol/L. The reaction is even slower, and sometimes absent for dialkoxysilanes and practically absent at all for monoalkoxysilanes. On the other hand, in the case of trialkoxysilanes the main reaction product besides the Al-alkoxide is a dialkoxy-Si derivative which, differently from the aromatic ester derivatives, still behaves as a good stereoregulating agent.

In conclusion, it can be stated that all types of external donor easily form complexes with the AlR_3 cocatalyst. These complexes are rather stable for silanes, whereas in the case of aromatic esters, they further react, leading to the partial destruction of the ester and its replacement with significantly less stereoregulating products. The true cocatalyst is, in this case, a mixture including free AlR_3, unconverted AlR_3/ester complex, and a mixture of Al-alkoxides of different bulkiness. Some free ED also can be present if the Al/ED ratio is very low.

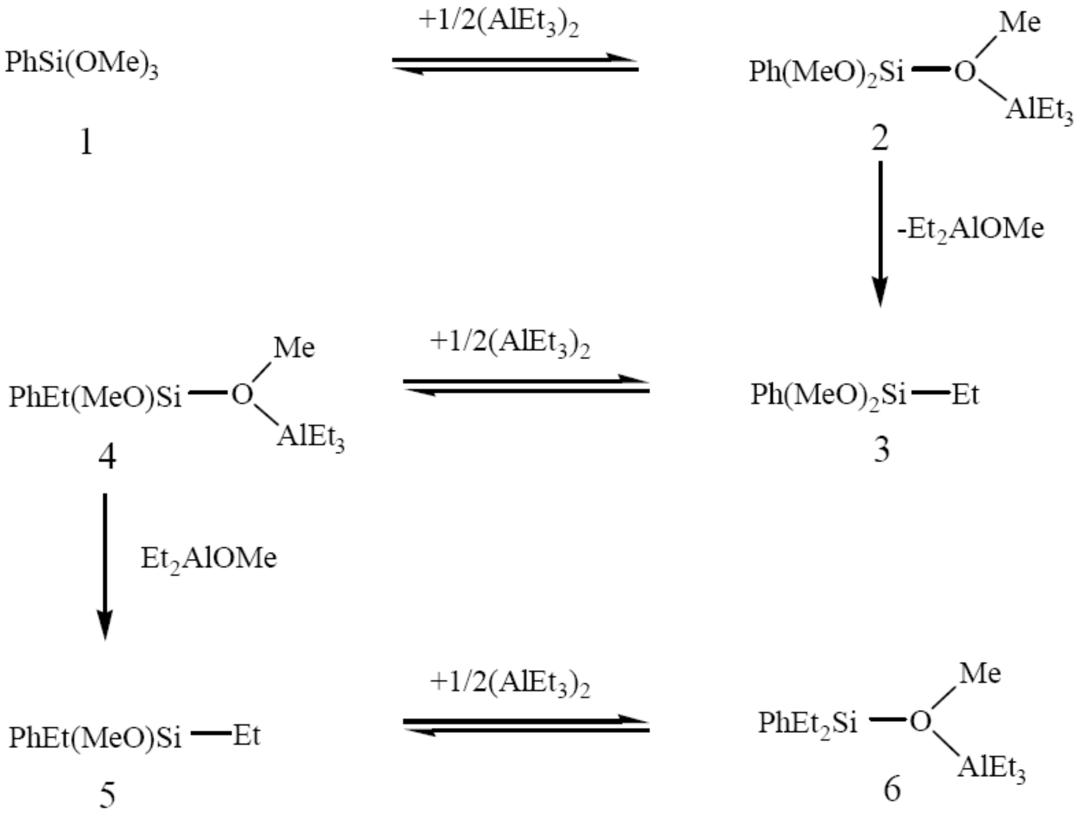


Figure 2.3 Pathway of the reaction between TEA and PhSi(OMe)$_3$.

CHAPTER III

LITERATURE REVIEW

3.1 Titanium precursor

For synthesis the Ziegler-Natta catalyst, many titanium sources can be used depending on the objectives of the researches. Titanium chloride compounds with different titanium oxidation states such as titanium(II) chloride ($TiCl_2$), titanium(III) chloride ($TiCl_3$) and titanium(IV) chloride ($TiCl_4$) were used to investigate the effect of the oxidation state on ethylene/1-hexene copolymerization activity [19]. It was found that $TiCl_2$ and $TiCl_3$ gave a quite stable polymerization profile with increasing the concentration of cocatalyst while the activity obtained from $TiCl_4$ firstly increased, and then dropped as seen in **Figure 3.1**.

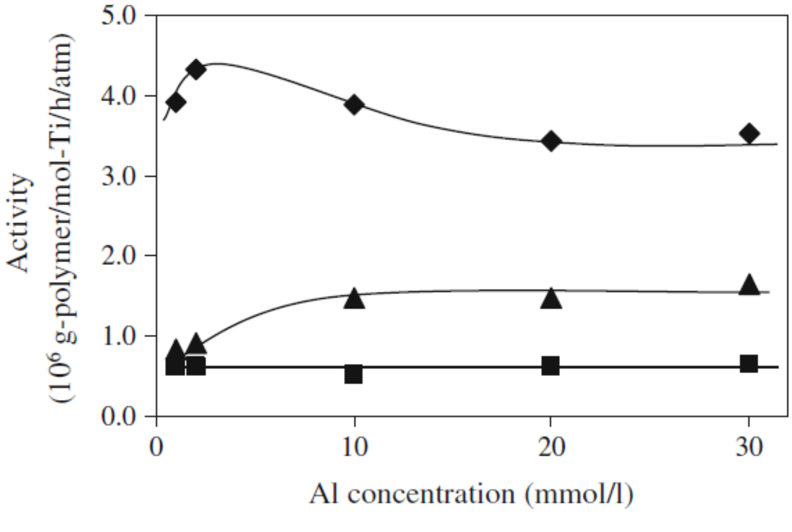


Figure 3.1 Influence of the Al concentration on the ethylene polymerization activities. (filled diamond Ti^{4+}, filled triangle Ti^{3+}, and filled square Ti^{2+})

Another titanium precursor source was titaniumtetraalokoxide species [$Ti(OR)_4$]. The addition of $Ti(OR)_4$ species could improve the impact resistance of polymers and also reduce the catalyst synthesis time. From previous work [2], alkyl groups, sequence of precursors addition and precursor ratios were varied. It was found that the bulkiness of alkyl groups and the addition sequence affected on the impregnation of $TiCl_4$ and also on the nature of active sites. This was obviously seen in **Figure 3.2** and **Table 3.1**.

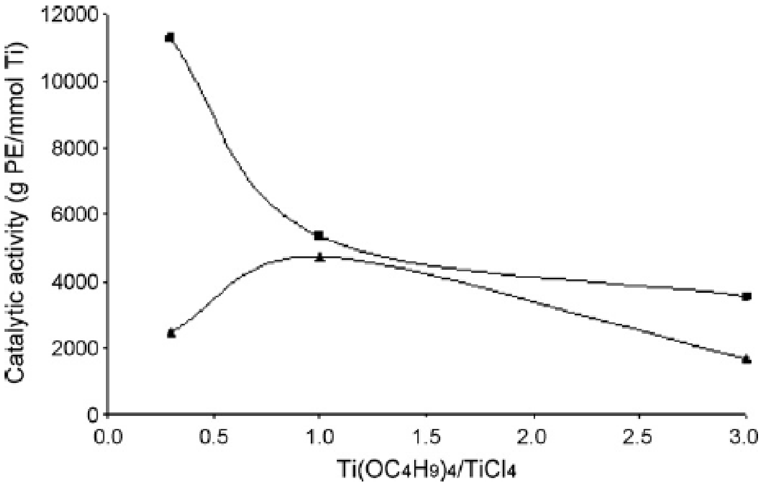


Figure 3.2 The effect of the $Ti(OC_4H_9)_4/TiCl_4$ ratio on the catalytic activity of the ZNBUa- TEA (■) and ZNBUd-TEA (▲) systems

Table 3.1 Influence of the type and addition order of $Ti(OR)_4$ on the performance of the catalytic system

Catalytic system	$Ti(OR)_4:TiCl_4$	R	Catalytic activity (g PE/mmol.Ti)	MFR (190/5.0) (g/10 min)
ZNETa-TEA	0.3	Ethyl	4929 ± 455	13.7 ± 2.5
ZNBUa-TEA		Butyl	15667 ± 7708	25.7 ± 15.0
ZNETd-TEA		Ethyl	8362 ± 3714	22.0 ± 4.0
ZNBUd-TEA		Butyl	8822 ± 788	21.5 ± 0.7
ZNC-TEA	-	-	5451 ± 1141	13.0 ± 3.0
ZNT-TEA			4789 ± 654	5.1 ± 0.6

3.2 Grignard reaction and chlorinating agent

At present, many routes have been studied for synthesis the Ziegler-Natta catalyst. Although the original goal of Grignard reaction was not used for synthesis the catalyst when it was discovered, it was found to be one of the highly effective ways to obtain a good performance catalyst. The reactants of this reaction are alkylmagnesiumalide (RMgX) and chlorinating agent. From the previous work [7], phenylmagnesiumchloride (PhMgCl) and $TiCl_4$ were used as reactants. They could enhance the propylene polymerization activity whether the electron donor was not added as seen in **Figure 3.3**.

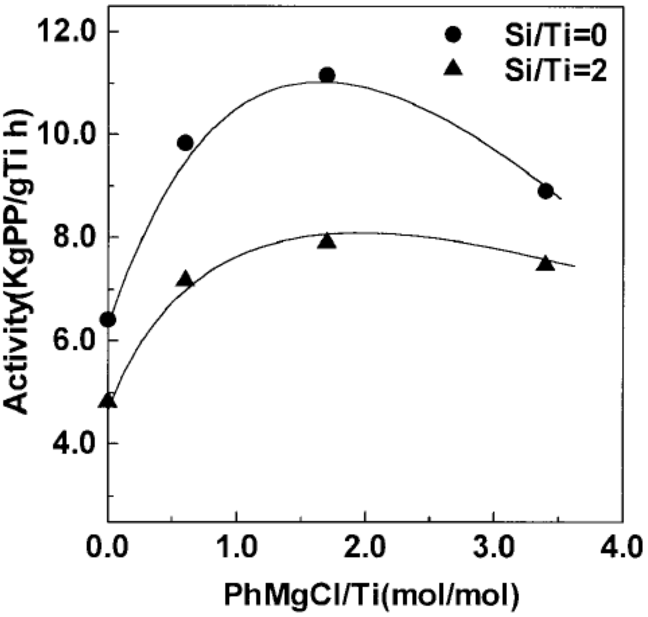


Figure 3.3 The dependence of catalytic activity on PhMgCl/Ti ratios.

As mentioned, $TiCl_4$ acted as a chlorinating agent; however, other works showed that there were many types of chlorination agent such as alkylhahide (RX), aluminumhalide (AlR_3) and thionylhalide ($SOCl_2$) could be used as well [20, 21].

3.3 Cocatalysts

Cocatalyst is an unforgettable part for polymerization. It is involved in catalytic activity and polymer properties. The real mechanism of active centers activation is still unclear; however, there is a proposal about it. From the previous work, the diffusion of cocatalyst to titanium center was purposed as an activation mechanism [22]. It depends on the size of cocatalysts. The large cocatalyst size makes a difficult diffusion to titanium centers. Thus, a small size cocatalyst can form more active sites resulting in higher catalytic activity. By the way, the selection of cocatalysts for each polymerization systems cannot consider only one factor. First, types of polymerization such as homo- or co-polymerization, ethylene, propylene or α-olefins polymerization have to be already selected because the reducing power of cocatalyst had to be considers. As seen in many works, types of cocatalysts were varied to investigate the catalytic activity and polymer properties. Generally, Ti^{2+} and Ti^{3+} are found to active for ethylene polymerization while Ti^{3+} is active only for propylene polymerization [8]. Although both Ti^{2+} and Ti^{3+} can polymerize ethylene, the obtained polymer characteristics are different. Ti^{2+} tends to produce longer chain of polymer than Ti^{3+} because lower valence state can reduce chain transfer to hydrogen rate in comparison to olefins insertion [23]. Thus, the polymers obtained from Ti^{2+} catalyst have higher molecular weight than Ti^{3+} catalyst. From the first step, it can be seen that the oxidation states of active center affect on polymer properties. Thus, the next step of consideration is polymer properties. The molecular weight distribution of polymers is affected by both cocatalyst concentrations and cocatalyst types. Fukuda *et al*. [24] investigated the variation of molecular weight distribution of polyethylene induced by different alkyl-Al co-catalysts using a novel surface functionalized SiO2-supported Ziegler-Natta catalyst. They used triethylaluminum (TEA) and diethylaluminumchloride (DEAC) as cocatalysts and found the difference of MWD curves as seen in **Figure 3.4**. From the result, it can be purposed that cocatalyst types affect on the multiplicity of active sites which also affect on polymer properties.

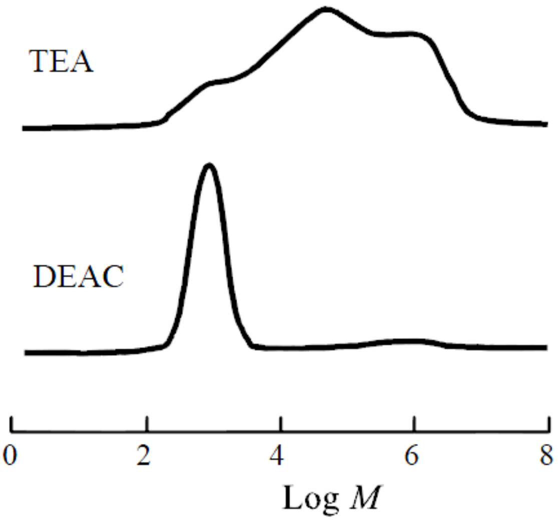


Figure 3.4 GPC curves for polyethylenes produced by the novel surface functionalized SiO_2-supported Ziegler-Natta catalyst using TEA or DEAC as cocatalyst with MW and MWD for TEA: Mw = 900,000, Mw = Mn = 30; DEAC: Mw = 1400, Mw = Mn = 1.6

In addition, not only the oxidation state of titanium that can affect on the molecular weight of polymer but also cocatalyst type [8]. It was found that cocatalysts can also terminate the polymer chain via termination route named “chain transfer to cocatalyst” [25]. The results of cocatalyst types variation and obtained the propylene properties were revealed by Zhang *et al.* as seen **Table 3.2**.

They purposed that the increase of molecular weight was probably due to the chain transfer ability of cocatalysts. The bulky cocatalyst diffuses to active site more difficult than the small size. Thus, the polymer chain from bulky cocatalyst system became long, resulting in high molecular weight of polymers.

Table 3.2 Effect of the Cocatalyst and H_2 on Propylene Polymerization

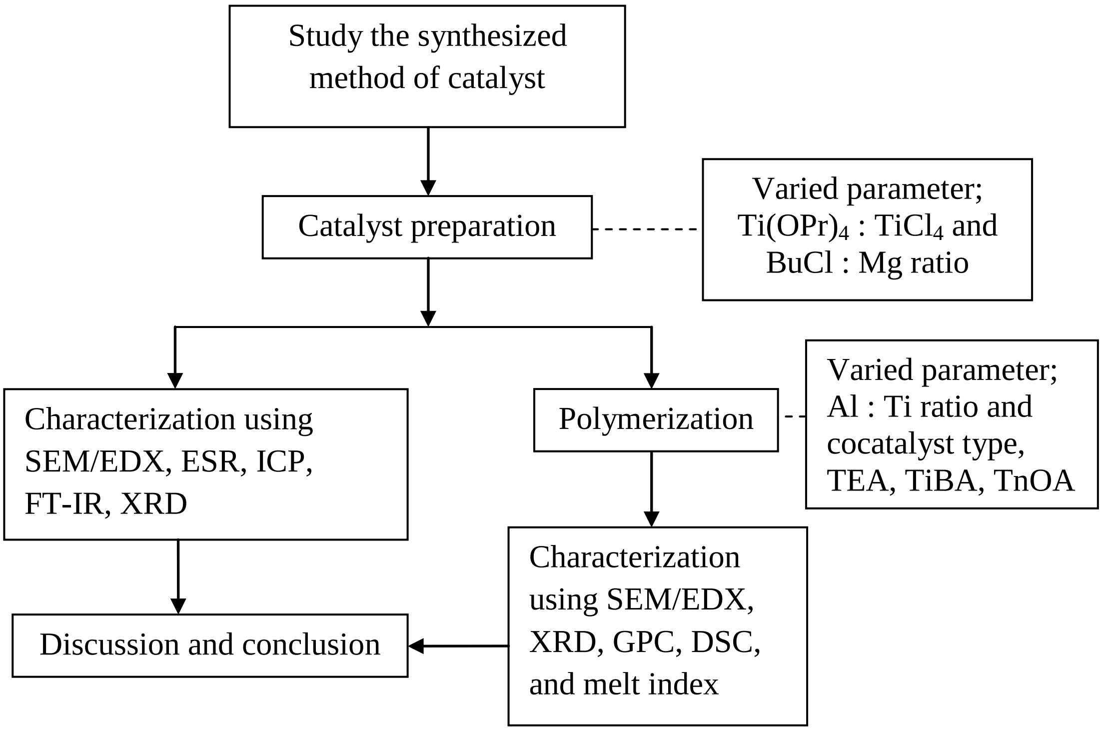
Cocatalyst	Feed ratio (H_2/C_3H_6)	Activity	Isotactic index (wt %)	Tm	Xc	Mw	PDI
TEA	—	4.3	98.8	159.1	41.3	61	6.5
	0.25	6.8	97.9	165.7	43.2	11.5	5.7
TiBA	—	1	97.8	160.8	40.6	76.1	7
	0.25	2.9	96.8	166.7	43.1	20.7	6
THA	—	0.6	97.1	161.4	35.7	77.8	7.8
	0.25	0.9	97.2	167.1	37.7	19.5	7
TnOA	—	0.7	97.2	161.1	38.2	96.8	9.4
	0.25	0.9	96.8	167.7	40.8	23.8	6.8
DEAC	—	0.4	96.8	159.5	36.8	45.5	7.6
	0.25	0.9	95.6	165.1	37.3	12.8	5.9
TEA + TiBA	—	1.6	96.2	161.2	37.9	62.8	6.9
	0.25	2.9	97.2	164	40.7	17.7	6.4
TEA + THA	—	2.2	96.6	160.4	39.6	66.7	7.6
	0.25	3.7	96.4	166.7	42.9	15.6	5.6
TEA + TnOA	—	3.1	96.8	159.8	39.8	69.9	8.1
	0.25	4.9	95.8	166.1	42.8	16.1	5.8
TEA + DEAC	—	2.8	98.3	161.3	40.6	54	6.9
	0.25	3.1	96.4	163.9	44.6	7.1	6.2
TiBA+ THA	—	0.8	96.6	159.9	39.2	76.8	7.9
	0.25	1.2	98.2	167.3	40.5	22.7	6.5
TiBA + TnOA	—	0.9	98.2	158.7	40.6	80.5	8.4
	0.25	1.4	97.6	166.5	42.2	23	6.6
TiBA + DEAC	—	1.9	96.4	160.4	39.5	64	8
	0.25	2.7	95.7	164.5	44.1	10.6	6.9

THA + TnOA	—	0.6	95.8	162.4	40.6	87.3	8.9
	0.25	0.9	96.7	167.9	42.7	24.4	6.8
THA + DEAC	—	0.9	97.6	159.1	38.7	55.1	8.5
	0.25	1.4	97.3	164.7	40.9	13.8	6.6
TnOA + DEAC	—	1.3	96.8	160.7	41.6	72.4	9.5
	0.25	2.7	95.4	166.3	45	11.5	6.7

CHAPTER IV

EXPERIMENTAL

4.1 Research methodology



4.2 Chemicals

No	Chemicals	Supplier	Details
1	Magnesium powder	Sigma-Aldrich Co. LLC.	≥99%
3	Hexane	Sigma-Aldrich Co. LLC.	Anhydrous, 95%
5	Butylchloride	Sigma-Aldrich Co. LLC.	Anhydrous, 99.5%
6	Titaniumtetraproproxide	Sigma-Aldrich Co. LLC.	99.999%
7	Titaniumtetrachloride	Sigma-Aldrich Co. LLC.	≥99.0%
8	Ethylene	Linde Co., Ltd.	-
9	Argon	Linde Co., Ltd.	-

4.3 Catalyst preparation

The catalyst was synthesized according to the company's procedure using $[Ti(OPr)_4]$ and $TiCl_4$ as Ti precursor.

4.4 Polymerization

The ethylene polymerization was carried out in 2 L autoclave reactor connected with the lines available for argon, hydrogen and ethylene gases and also the hexane feed line. The reactor and all connected feed lines were cleared humid and oxygen by evacuation, and then followed by purging with the argon many times. First, 1 L of hexane was filled and heated to 80 ^{0}C. The desired amount of TEA, TiBA, and TnOA was injected into the reactor subsequence by the injection of desired amount of titanium. In the condition with the presence of hydrogen, the reactor was pressurized with 1 bar of argon followed by pressurizing with hydrogen and finally pressurizing with ethylene gas.

4.5 Characterization

4.5.1 Gel permeation chromatography (GPC)

The molecular weight and molecular weight distribution of obtained polymer in this study was determined by gel permeation chromatography (GPC) with a Waters 150CV at 135^{o}C using *o*-dichlorobenzene as the solvent. The parameters for universal calibration are $K = 7.36\times10^{-5}$, $\alpha = 0.75$ for polystyrene standard.

4.5.2 Differential scanning calorimetry (DSC)

The melting temperature (T_m) and crystallinity (χ_c) of polyethylene was determined with a Perkin-Elmer diamond DSC from MEKTEC, at Chulalongkorn University. The analyses were performed at the heating rate of 10 ^{0}C min^{-1} in the temperature range of 50-200 ^{0}C. Two heating cycles were employed. In the first scan, samples were heated to 200 ^{0}C, and then cooled to room temperature. In the second scan, samples were reheated at the same rate. The results of the second scan were only reported because the first scan was influenced by impurities of samples. The overall crystallinity (χ_c) is calculated from the heat of fusion using the formula.

$$\chi_c = H_m/H_p$$

where H_m is the enthalpy of the tested samples and H_p is the enthalpy of a totally crystalline PE which was assumed to be 293 J/g.

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

SEM and EDX observation are used to investigate the morphology of catalyst precursor and polymer and elemental distribution, respectively. For catalyst, the samples are stuck on carbon tape under argon atmosphere. The polymers are also stuck on carbon tape. The samples for SEM (JEOL mode JSM-6400) analysis are coated with gold particles by ion sputtering device to provide electrical contact to the specimen. The EDX is performed using Link Isis series 300 program.

4.5.4 Melt index (MI)

The polyethylenes are characterized the melt flow rate with a DYNISCO polymer test with 2.16 and 10 kg loading.

4.5.5 X-ray diffraction (XRD)

XRD is performed to identify phases and crystallinity of the samples. For catalyst, the samples are placed on holder and sealed with mylar film by grease under argon atmosphere. For polymer, the samples are placed on holder. It is conducted using a SIEMENS D-5000 X-ray diffractometer with CuK_α ($\lambda = 1.54439\times10^{-10}$ m). The spectra are scanned at a rate of 2.4 degree/min in the range 2θ = 20-80 degrees. The mylar film is used to protect of samples from air and moisture.

4.5.6 Inductively coupled plasma (ICP)

Titanium and Magnesium contents are measured using Perkin Elmer Optical. To digest the sample, 0.01 g of catalyst was dissolved in concentrated sulfuric acid solution. The mixture was stirred 2 h, at 80 ^{0}C. After the catalyst was completely digested, the solution was diluted with distilled water to a certain volume of 100 ml and then kept in refrigerator.

4.5.7 Fourier transforms infrared spectroscopy (FT-IR)

The bonding of magnesium and titanium were observed by a THERMO model Nicolet 6700 with an ATR mode. The catalyst samples are prepared under argon atmosphere in glovebox by coating the samples on the sodiumchloride disks, and then sealed with carbon tape around sodiumchloride disks.

4.5.8 Electron spin resonance (ESR)

The Ti^{3+} content of the catalysts stirred with various ratios of precursors was observed by electron spin resonance technique. The catalyst samples were prepared in glove box and activated by TnOA. The ESR equipment is JEOL model JES-RE2X and used under argon atmosphere begin at room temperature 25°C and held at 80°C for 90 minutes. DPPH standard was used for g-factor calibration.

CHAPTER V

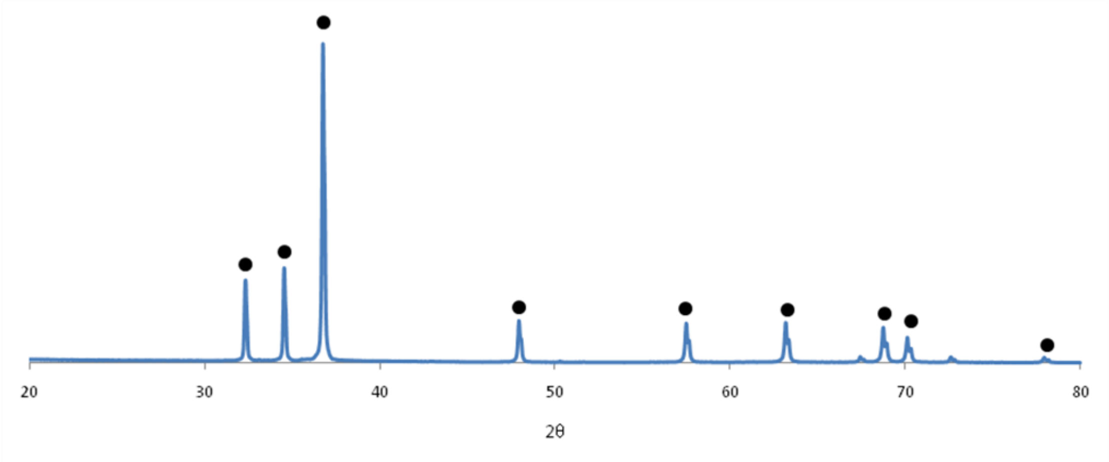
RESULTS AND DISCUSSION

In this chapter, we are going to discuss all of the experimental results. Titanium precursors, butylchloride:magnesium ratios, cocatalyst types, and Al/Ti ratios, which affect on catalytic activity and polymer properties were investigated. Many characterization techniques such as FT-IR, ICP, XRD, DSC, and SEM-EDX, were used for revealing both of the catalyst characteristics and polymer properties.

5.1 Effect of titanium precursor ratios

5.1.1 Catalyst characterization

The synthesized catalysts were characterized by several techniques under argon atmosphere. X-ray diffraction (XRD) provides the crystallinity and chemical species of raw material, magnesium powder and catalysts, as shown in **Figures 5.1**. The peaks at 2θ of 32, 34, 36, 48, 58, 63, 68, and 70 were verified as magnesium carbonate on the surface of magnesium powder [26]. The peaks at 2θ≈27 and 2θ≈50 were referred to a mylar film and δ-$MgCl_2$, respectively. The height of XRD peaks indicated the disorder of catalyst structure. The peaks of magnesium powder slightly decreased with increasing of the titanium precursor ratios. Inversely, the peak of δ-$MgCl_2$ slightly increased. These were probably due to titanium(IV) chloride acted as a chlorinating agent, which was related to the δ-$MgCl_2$ formation. Scanning electron microscopy (SEM) could provide the morphology and also evaluate the size of catalysts. As can be seen in **Figure 5.2**, the morphology of catalysts was not noticeably different. The average size of catalysts tended to increase with an increase of titanium precursor ratios as shown in **Table 5.1**. From **Figure 5.2a**, the magnesium powder has an average size of 50 μm and its surface was smooth and partially cracked; meanwhile. Those of the catalysts were rough and their sizes were not uniform, as shown in **Figure 5.2(b-e)**. This might be due to fragmentation phenomena in magnesium particles during the catalyst synthesis reaction was carrying out.



(a)

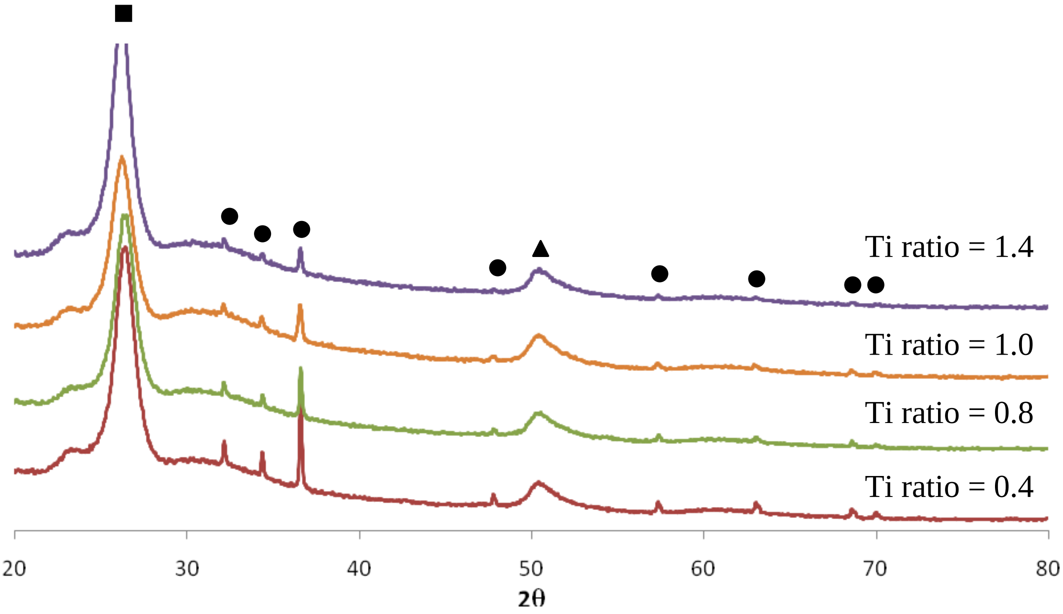


Figure 5.1 XRD patterns of (a) magnesium powder (●), (b) catalysts with different [$Ti(OPr)_4$:$TiCl_4$], δ-$MgCl_2$(▲), Mylar film (■)

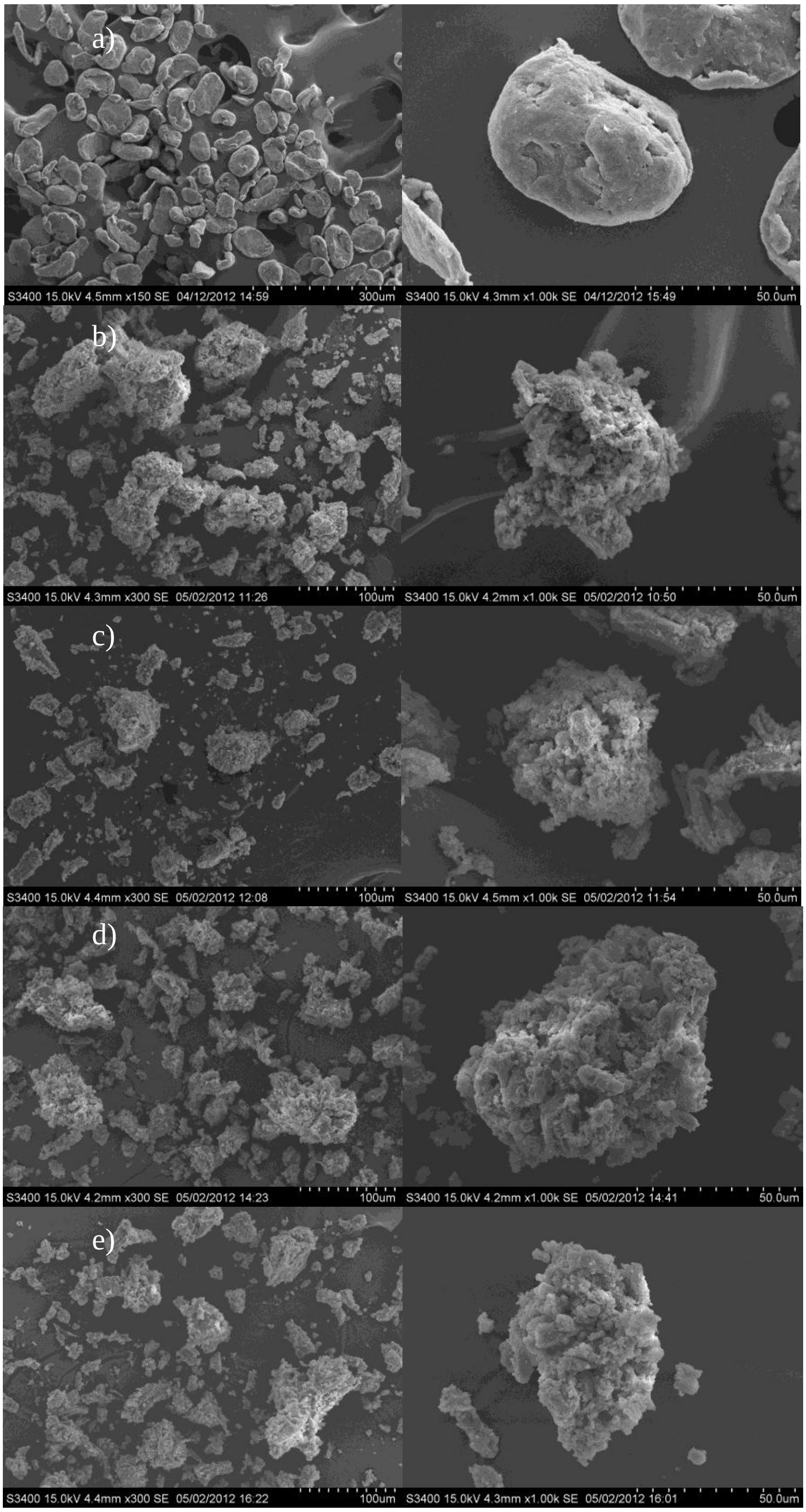


Figure 5.2 Morphology of (a) magnesium powder and catalysts with different titanium precursor ratios of (b) 0.4, (c) 0.8, (d) 1.0, and (e) 1.4.

Table 5.1 Average particle sizes of catalysts with different titanium precursor ratios

$Ti(OPr)_4$: $TiCl_4$	**Average particle size[a] (μm)**
0.4	88
0.8	89
1.0	133
1.4	135

[a] Measured by SEM

5.1.2 Catalytic activity

The precursors used in this experiment were titanium (IV) isopropoxide [$Ti(OPr^i)_4$] and titanium (IV) chloride ($TiCl_4$). They were mixed cooperatively in order to investigate the effects of precursors on catalytic activity and polymer properties. The main advantages of the combination of dual titanium precursors are to reduce the period of time upon the catalyst synthesis step and to improve the impact resistance of polymers [2]. The amount of $TiCl_4$ was fixed at 14.8 mmol and the amount of [$Ti(OPr^i)_4$] was varied. The polymerization results were collected and represented in **Table 5.2**.

Table 5.2 Amounts of titanium and magnesium in catalysts and catalytic activity

$Ti(OPr)_4$:$TiCl_4$ ratio	**Ti[a] (wt%)**	**Mg[a] (wt%)**	**Yield (kg)**	**Activity[b] (kgPE/molTi.h)**	**Activity[b] (kgPE/gcat.h)**
0.4	4.55	13.14	0.34	2855	2.71
0.8	5.05	13.15	0.31	2546	3.30
1.0	6.20	15.51	0.19	1621	2.15
1.4	6.36	12.56	0.06	483	0.63

[a] Characterized by ICP

[b] Polymerization conditions: [Al]:[Ti] = 2, total pressure = 8 bar, Temperature = 80 ^{0}C, polymerization time = 4 h.

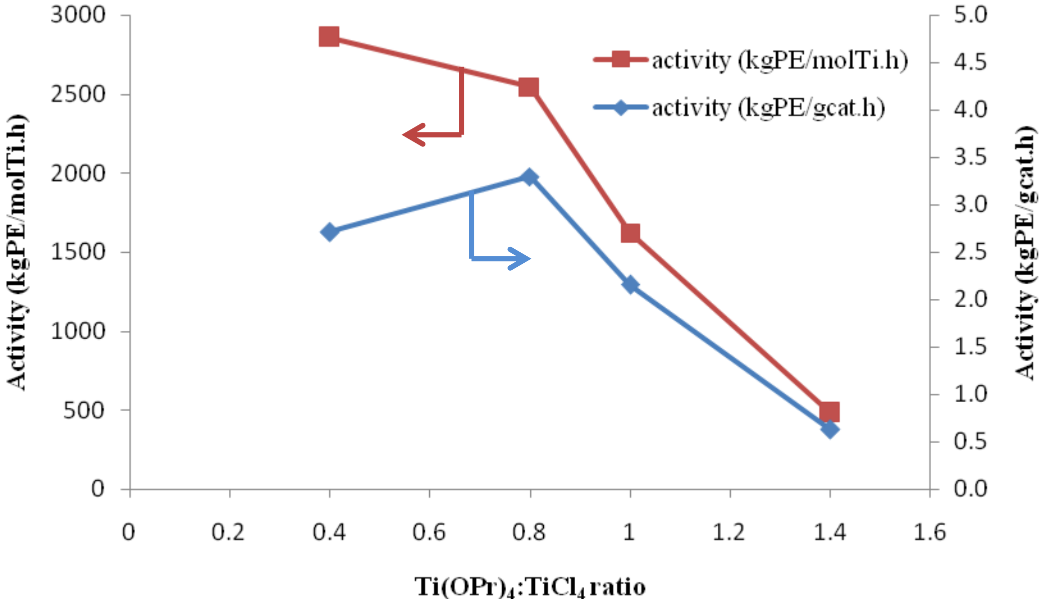


Figure 5.3 Catalytic activities with different unit

Figure 5.3 shows the trends of catalytic activities with different units. The differences in two catalytic activity units implied the 2 different assessments, qualitative and quantitative aspects. Qualitatively, at high ratios of titanium precursors, a large portion of titanium in catalyst is generated from an incomplete chlorination reaction. The unit of kgPE/molTi.h was calculated by basing on the ignorance of titanium species containing in the catalyst. Thus, the addition of alkoxide species led to a decrease in catalytic activity because titanium alkoxide was an inactive species for ethylene polymerization [27]. However, the mechanism of chlorination on the catalyst surface has been still unclear. The possible mechanism was suggested as seen in **Equation 5.1**.

$$\mathrm{Ti(OR)_xCl_{4-x}} + \mathrm{Cl^-} \longrightarrow \mathrm{Ti(OR)_{x-1}Cl_{5-x}} + \mathrm{OR^-} \qquad (5.1)$$

The titaniumalkoxide was impregnated on the support in the titanium chloroalkoxide form. Then, the alkoxide group was eliminated by chloride ion from titanium tetrachloride. This could reduce an alkoxide group from the catalyst and also enhance the catalytic activity. Quantitatively, kgPE/gcat.h, the catalytic activity was calculated by basing on the amount of catalyst. We focused on the amount of polymer, so the titanium species containing in the catalyst cannot be ignored. The highest catalytic activity indicated to the maximum of titanium active species or the completion of chlorination reaction. The evidence can be seen in **Figure 5.3**. Although the titanium content in a catalyst of titanium ratio of 1.4 was higher than the ratio of 0.8, the activity was lower. This means most of the titanium species containing in the catalyst titanium ratio of 1.4 were an inactive form.

5.1.3 Polymer properties

The obtained polymers were characterized by different techniques and the resulted specific gravity within 0.9410 – 0.9584, shows that all synthesized polyethylenes were the high density polyethylene (HDPE) [28].

Table 5.3 Polymer properties obtained from catalysts upon various titanium precursor ratios.

$Ti(OPr)_4:TiCl_4$ ratio	Density (g/ml)	MI (g/10min)	Bulk density (g/ml)	Average particle size (µm)	χ_c (%)	MWD[a]
0.4	0.9584	1.902	0.240	87.8	60.1	6.76
0.8	0.9493	0.516	0.235	92.7	54.3	6.66
1.0	0.9462	0.480	0.215	137.6	53.1	5.27
1.4	0.9410	0.476	0.190	140.1	46.2	4.64

[a] Characterized by GPC

As shown in **Table 5.3**, the decrease of melt index indicated that the molecular weight of polymers was increased. This was due to the increase of titanium alkoxide group, which was an inactive titanium species in catalysts [29]. The existence of titanium alkoxide species in catalysts resulted in an increase of bulkiness on catalyst surface. Furthermore, hydrogen hardly diffuses to titanium centers, and then terminates the polymer chains leading to an increase of molecular weight. Moreover, the addition of alkoxide species could reduce the heterogeneity of active site as well as decrease the catalytic activity, so the molecular weight distribution of polymers decreased. Furthermore, the external characteristic of a polymer such as bulk density and particle size was investigated. The bulk density tended to decrease with an increase of titanium precursors as well as particle size, evaluated by SEM (**Figure 5.4**). At the titanium precursor ratio of 0.4, the polymer particle was fine because of high catalytic activity which caused the fragmentation phenomena during the polymerization. This phenomenon generates from the formation of polymers which grows inside the catalyst pores. The polymer chain which keeps growing longer in the pore could pressurize and break the catalyst particle, finally resulting in small polymer size.

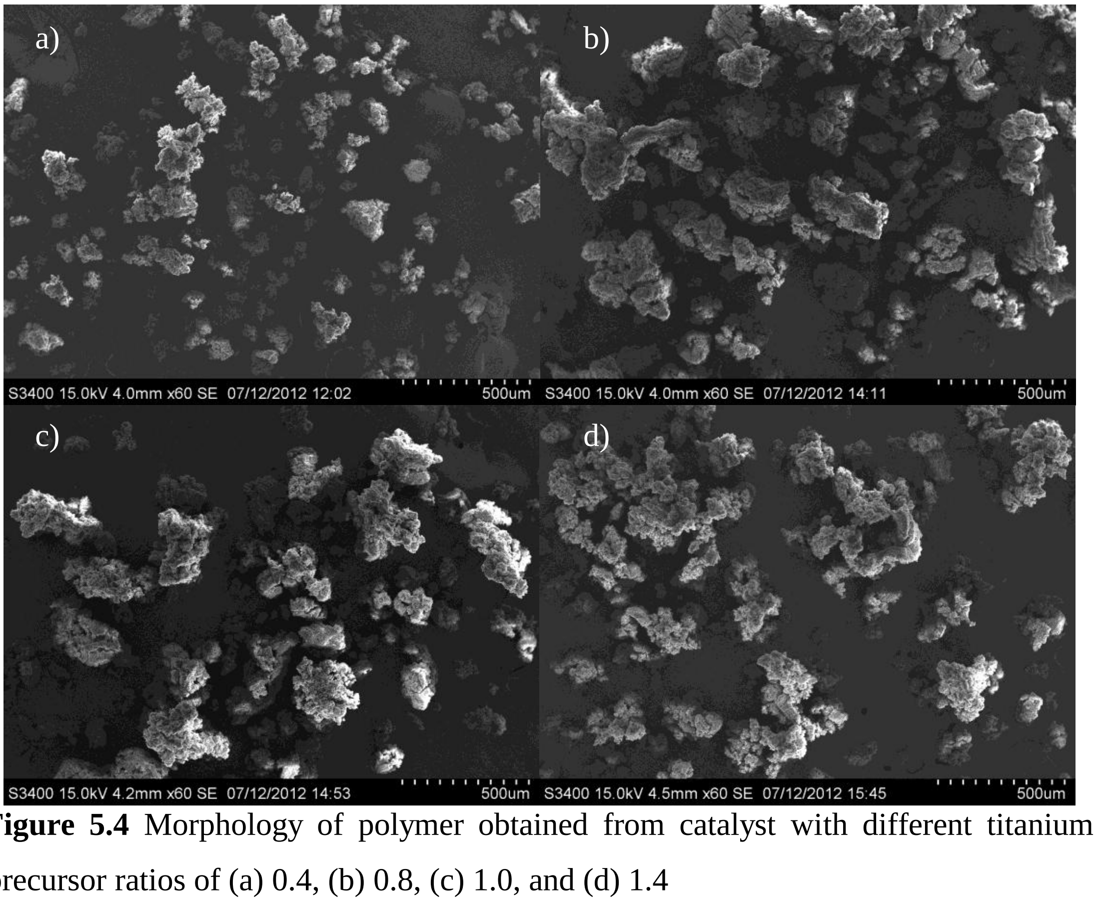


Figure 5.4 Morphology of polymer obtained from catalyst with different titanium precursor ratios of (a) 0.4, (b) 0.8, (c) 1.0, and (d) 1.4

5.2 Effect of butylchloride and magnesium ratios

5.2.1 Catalyst characterization

As seen in **Figure 5.5**, the XRD patterns of catalyst were noticeably changed. The peaks at $2\theta \approx 32$, 34, 36, 48, 58, 63, 68 and 70, assigned to the magnesium carbonate on magnesium powder surface, were decreased with an increasing of BuCl:Mg ratio. Inversely, the peak at $2\theta \approx 51$ referred to δ-$MgCl_2$ was obviously increased. These indicated that more amounts of BuCl can result in more formation of δ-$MgCl_2$. The formular equation was purposed in **Equation 5.2**. The reactants are alkylmagnesiumhalide (R'MgX) and alkylhalide (R"X), and the products are magnesiumhalide (MgX_2) and hydrocarbon (R'R"). This reaction is known as the Grignard reaction. The evidence of reaction can be proven by SEM (**Figure 5.6** and **Table 5.4**). The particle size of catalyst decreased with increasing of BuCl amount, which is the result of the reaction. While the reaction was carrying out, the hydrocarbon was simultaneously forming. The large size of hydrocarbon could pressurize the particle inside particle pores, and then cracked the particles into many small fragments.

$$\text{RMgX} + \text{BuCl} \longrightarrow \text{MgClX} + \text{R-Bu} \qquad (5.2)$$

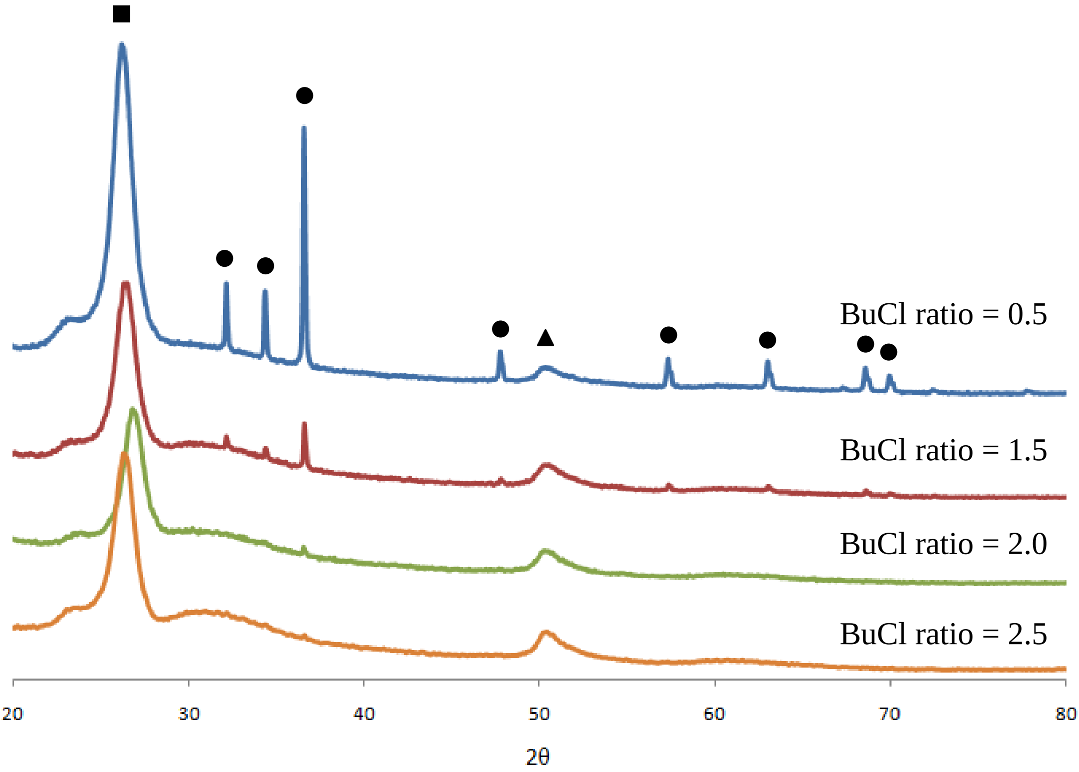


Figure 5.5 XRD patterns of catalyst with different BuCl amounts, magnesium powder (●), δ-$MgCl_2$ (▲), Mylar film (■)

Table 5.4 Average particle sizes of catalysts with different BuCl:Mg ratios

BuCl:Mg	**Average particle size**[a] **(μm)**
0.5	59
1.5	52
2.0	30
2.5	< 20

[a] Measured by SEM

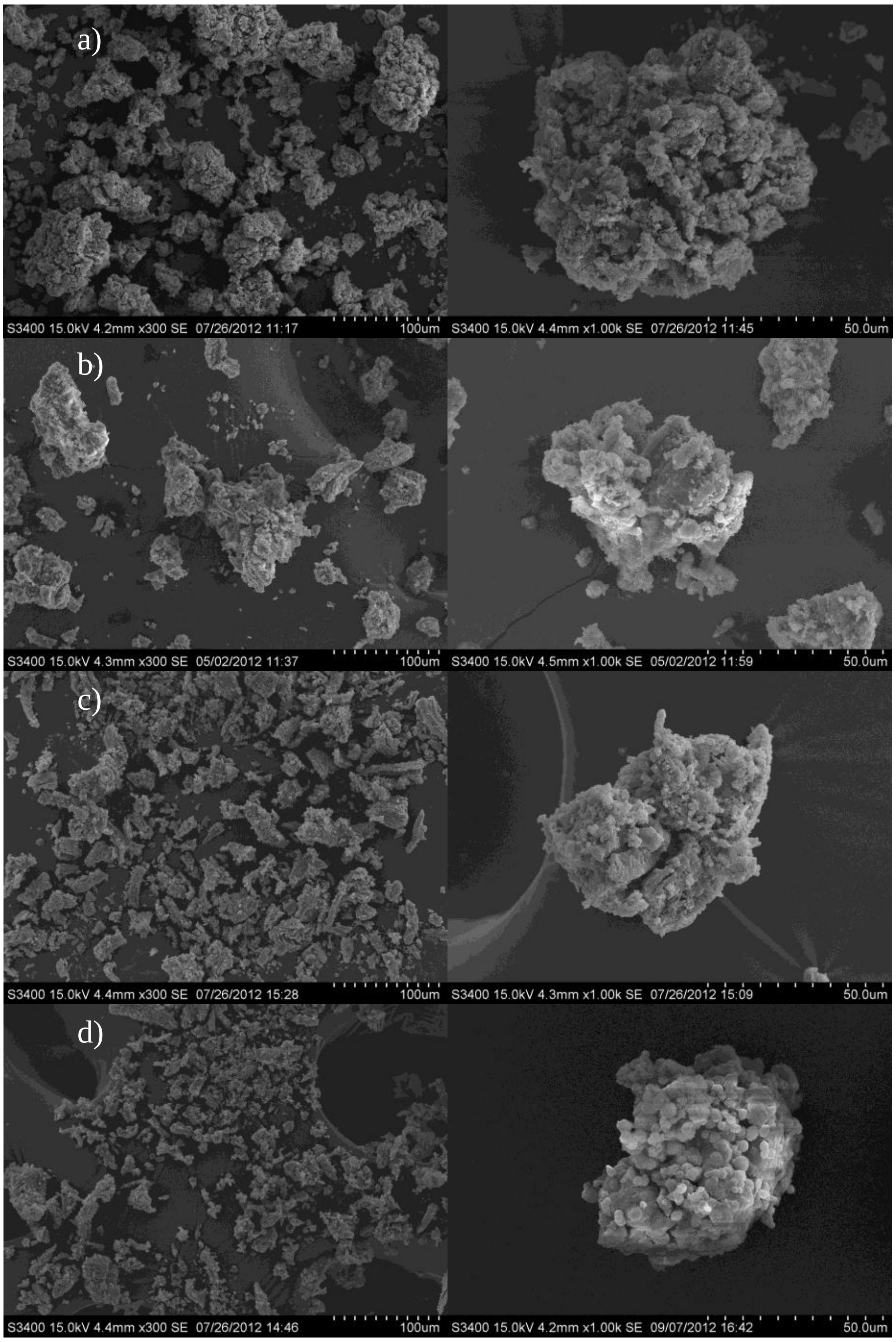


Figure 5.6 Morphology of catalysts with different BuCl ratios of (a) 0.5, (b) 1.5, (c) 2.0, and (d) 2.5.

5.2.2 Catalytic activity

Table 5.5 Amounts of titanium and magnesium in catalysts and catalytic activity

BuCl:Mg ratio	**Ti[a] (wt%)**	**Mg[a] (wt%)**	**Yield (kg)**	**Activity[b] (kgPE/molTi.h)**	**Activity[b] (kgPE/gcat.h)**
0.5	7.65	18.35	0.21	1712	2.74
1.5	6.20	15.51	0.31	2546	3.30
2.0	5.39	11.94	0.37	3103	3.49
2.5	5.23	11.335	0.46	3792	4.14

[a] Characterized by ICP

[b] Polymerization conditions: [Al]:[Ti] = 2, total pressure = 8 bar, Temperature = 80 ^{0}C, polymerization time = 4 h

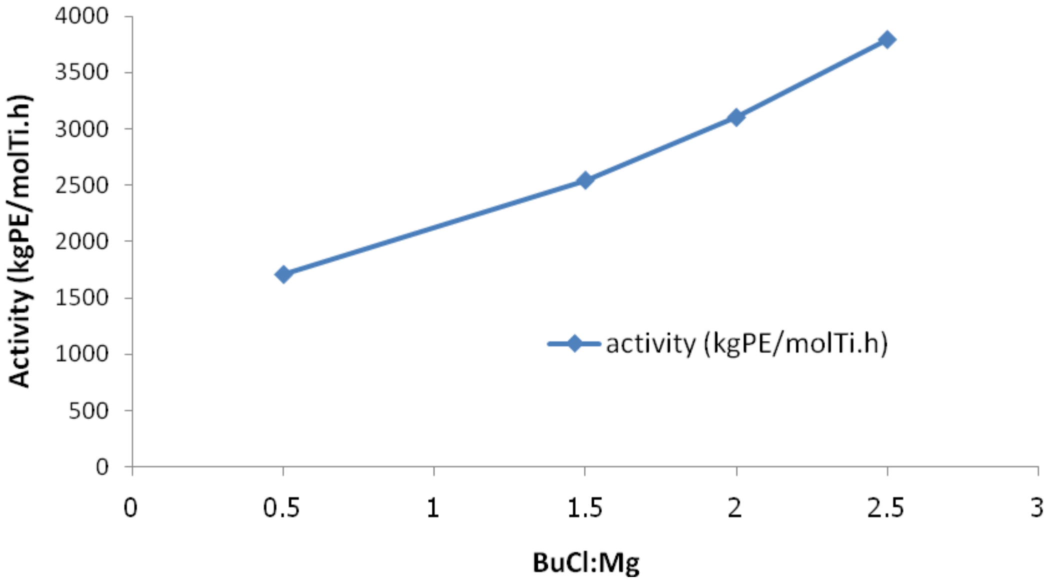


Figure 5.7 Catalytic activity with different BuCl:Mg ratios

As seen in **Table 5.5** and **Figure 5.7**, the catalytic activity increased almost linearly. From the previous work [21], Vives *et al.* were found that BuCl can act as chlorinating agent, which has potential to replace alkoxide by chloride ion finally resulting in an increase of catalytic activity (**5.1**). The evidence of existence of titanium alkoxide groups containing in catalysts was the peak at 1065 [30] cm^{-1} as shown in FT-IR spectra (**Figure 5.8**).

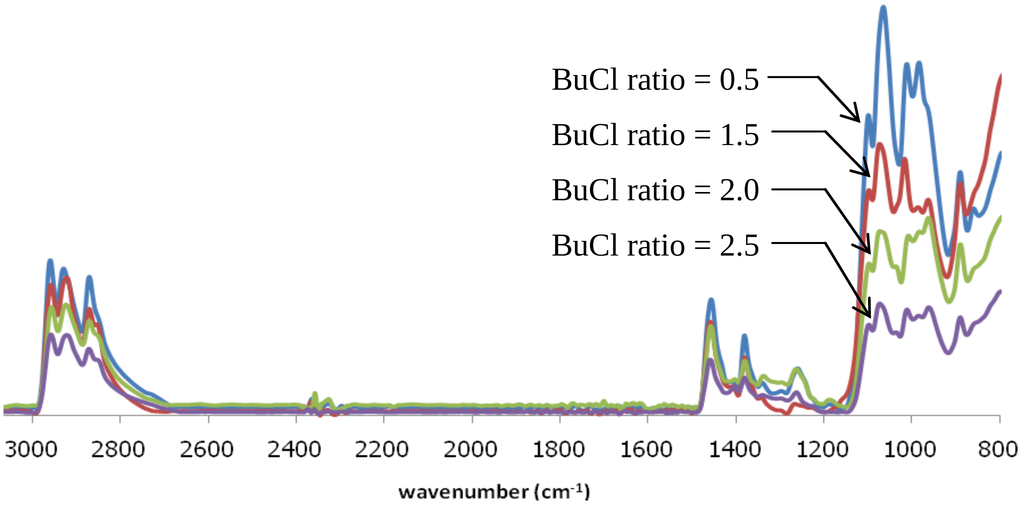


Figure 5.8 FT-IR spectra of catalyst which vary BuCl:Mg ratios.

5.2.3 Polymer properties

The properties of polymers can be summarized as seen in **Table 5.6**.

Table 5.6 Polymer properties

BuCl:Mg	Density (g/ml)	MI (g/10min)	Bulk density (g/ml)	Average size (μm)	χ_c (%)	MWD[a]
0.5	0.9350	0.258	0.20	294.6	49.0	4.89
1.5	0.9470	0.483	0.23	259.7	52.4	5.13
2.0	0.9526	1.438	0.24	226.3	53.0	5.89
2.5	0.9566	1.092	0.28	151.5	55.2	6.96

[a] Characterized by GPC

The increase of melt index indicated to the decrease of molecular weight of polymers. We purposed that less amounts of alkoxide with increased BuCl resulted in less steric hindrance, so the hydrogen can easily diffuse to titanium center and finally terminate the polymer chain. Thus, the molecular weight of polymer decreases with an increase of butylchloride. This result also conformed to the crystallinity result obtained by the DSC analysis. The crystallinity of polymers which molecular weight greater than 20,000 depended on the molecular weight [31]. As seen in **Equation 5.2**, BuCl has an important role to form the support, so more amount of BuCl resulted in more support formed. Because of the replication phenomena, the particle size of polymer decreased because the polymer chains pressurize the catalyst particle inside the pores, and then cracked the particles as well as the catalytic activity was increased due to the formation of fresh active sites.

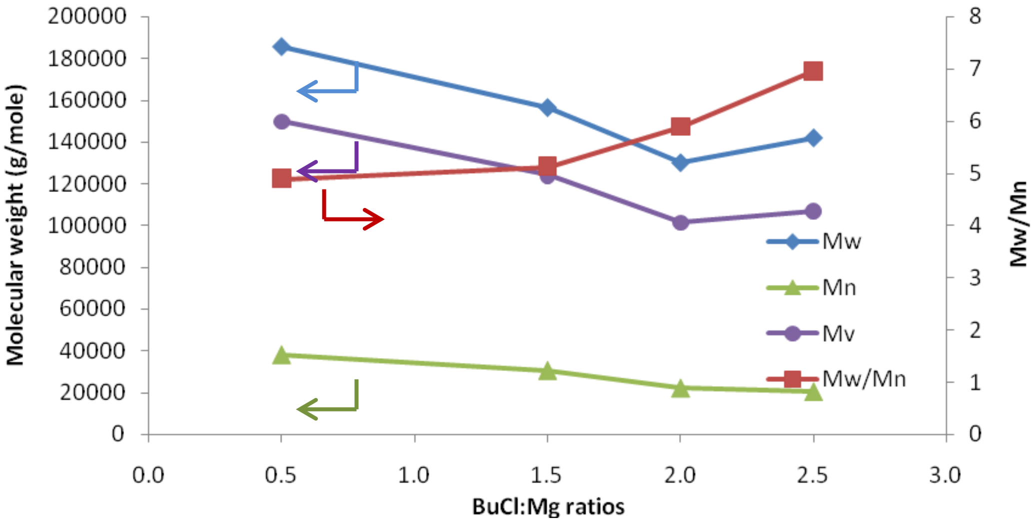


Figure 5.9 Molecular weight and molecular weight distribution from GPC

5.3 Effect of cocatalyst types and Al/Ti ratios

From previous factors, it was found that the proper ratios of titanium precursor and BuCl ratio for synthesis of the highest catalytic activity were 0.8 and 1.5, respectively. The criterion for making a decision to select the proper amount of precursors was polymer properties and catalytic activity. For polymer properties, the polymer size should not be fine because it may cause a fouling in transportation step in production process. For catalyst performance, the activity should be high to achieve great productivity. By the way, to improve the catalyst performance, cocatalyst types and Al/Ti ratios have to be also considered. Cocatalysts or activators for Ziegler-Natta catalyst are usually alkylaluminum compound (AlR_3). They have two main functions; (i) to scavenge the impurities such as moisture and oxygen, and (ii) to form an active site. Nowadays, although the functions of cocatalyst are clearly known; however, the active center formation mechanism has been still unclear.

5.3.1 Catalytic activity

Normally, the catalytic activity increases with an increase of cocatalyst concentration till it meets the maximum point after that it will gradually decrease due to the over reduction or adsorption competition between ethylene and cocatalyst [9]. Moreover, the increase of activity also depends on the reducing power of cocatalyst, which is related to the bulkiness of cocatalyst molecules [8]. The bulkiness of cocatalyst depends on the size of alkyl group contained in cocatalyst. That is, more bulky of cocatalyst hinders the diffusion of aluminum into the titanium for the active species formation [8]. Thus, from the bulky dimension of each cocatalyst we expect that the activity obtained from TEA would be the highest, whereas the lowest one would be TnOA. The actual experimental results were shown in **Table 5.7**.

Table 5.7 Catalytic activity with different cocatalyst types and Al/Ti molar ratios

Cocatalyst	Al/Ti molar ratio	Catalytic activity (kgPE/molTi.h)
TEA	2	543
	3	623
	5	780
TiBA	2	504
	3	498
	5	535
TnOA	2	506
	3	547
	5	552

The activity obtained from TEA was the highest, while the TiBA and TnOA were almost equal. The similar result was also achieved when the Al/Ti ratio was changed as seen in **Figure 5.10**. This phenomenon is probably due to the existence of alkoxide species contained in the catalyst as proven by FT-IR (**Figure 5.8**).

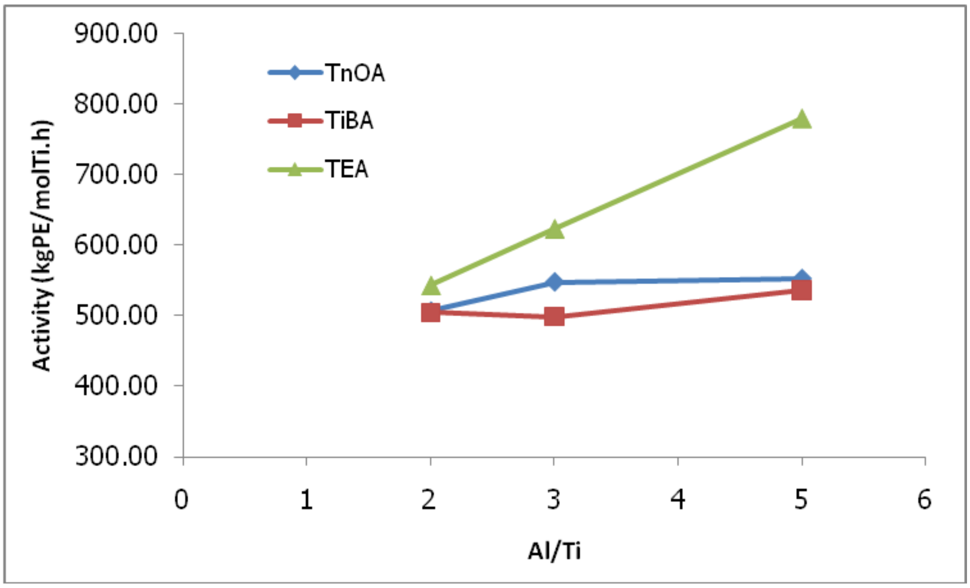


Figure 5.10 Activities upon different cocatalyst types and Al/Ti molar ratios

We believed that the bulkiness of alkoxide group on the surface of catalyst is also the significant factor affecting on the catalytic activity. The branches of alkyl group, isopropyl, can obstruct the diffusion of cocatalyst to titanium in order to form active sites. Therefore, higher bulky cocatalyst cannot allow the formation of active sites as much as lower bulky cocatalyst.. As this reason, inactive species (Ti 3+) should be more residual in the catalyst activated by higher bulky cocatalyst. The ESR technique was used for support this assumption. The ESR spectrum (**Figure 5.11**) shows the g-value of 1.94 which refers to the six-coordinated Ti^{3+} dissolved in $MgCl_2$ [14] or the isolated octahedral coordinated Ti^{3+} [15].

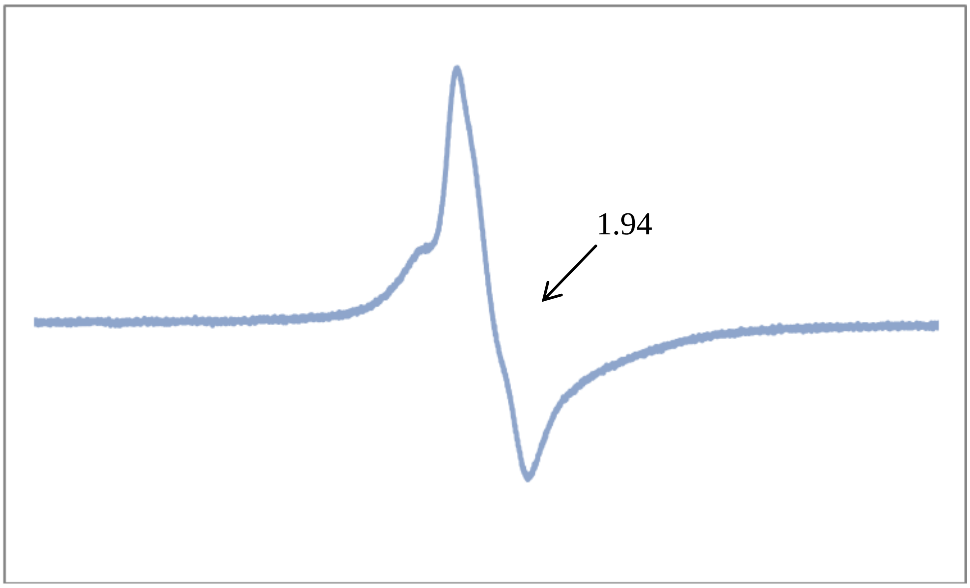


Figure 5.11 The typical of ESR spectrum of the catalyst

After double integration of all spectra, the obtained area, which referred to Ti^{3+} amount, were plotted in the term of relative area as seen in **Figure 5.12**. The Ti^{3+} amount of TnOA tended to increase with time while TiBA only increased within 45 minutes and then still remained constantly. This implied that TnOA did not finish forming the active sites due to its difficulty of diffusion to active centers, which is more difficult than TiBA because of its higher bulky structure. For TEA, the Ti^{3+} was maximized in the first 45 minutes, and then continuously decreased. This is probably due to low bulkiness TEA can more activate the titanium to be active centers than the others. The decline of Ti^{3+} is the effect of over reduction. It was believed that TEA has high reducing power because of its small size [22], so it has ability to generate Ti^{2+} which is more active than Ti^{3+} for ethylene polymerization [16] resulting in the highest catalytic activity among these three cocatalysts. In addition, high concentrations of cocatalyst increased the reducibility of cocatalysts. Thus, in case of TEA, higher concentration leads to more active sites formed, resulting in the obvious increase of catalytic activity when compare to TnOA and TiBA

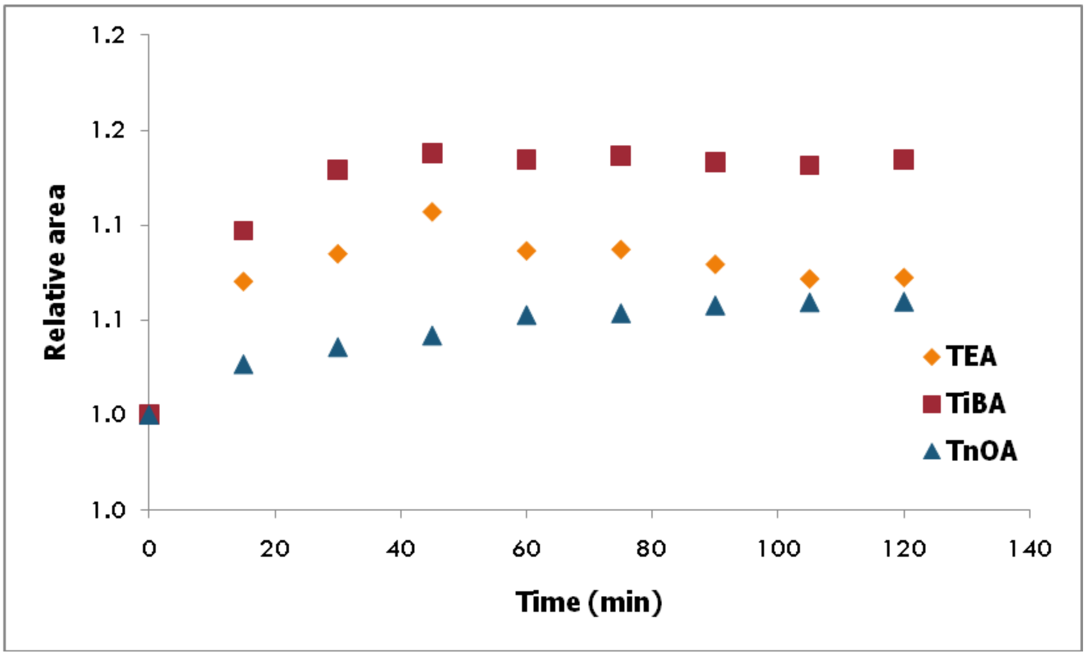


Figure 5.12 The relative amount of Ti^{3+} with the Al/Ti molar ratio of 2

5.3.2 Polymer properties

All of polymer characterization results were represented in **Table 5.8**. The particle size tended to decrease with increase of Al/Ti ratio because of fragmentation phenomena [32]. The morphology of polymer was illustrated in **Figure 5.13**. The polymer size obtained only from TEA noticeably decreased when Al/Ti increased. This conformed to the catalytic activity results. The increase of TEA molecules results in more fresh active sites formation, so the polymerization rate increases. In case of TiBA and TnOA, the bulkiness of their molecules results in difficulty of diffusion to titanium centers, so the amount of active sites and activity became lower compare with TEA.

Table 5.8 Polymer properties with different cocatalyst types and Al/Ti ratios

Cocatalyst	Al/Ti	Density (g/ml)	Bulk density (g/ml)	Average particle size (μm)	MWD	MI (g/10min)
TEA	2	0.9462	0.25	111.5	5.14	0.833
	3	0.9546	0.28	97.4	5.46	1.606
	5	0.9557	0.30	82.5	5.65	1.406
TiBA	2	0.9498	0.27	161.8	5.47	2.852
	3	0.9499	0.23	150.4	5.23	3.346
	5	0.9512	0.23	137.7	5.21	2.793
TnOA	2	0.9398	0.25	165.6	5.34	0.250
	3	0.9489	0.23	149.2	5.30	0.608
	5	0.9564	0.24	157.5	5.88	3.289

All of polymer characterization results were represented in **Table 5.8**. The particle size tended to decrease with increase of Al/Ti ratio because of fragmentation phenomena [32]. The morphology of polymer was illustrated in **Figure 5.13**. The polymer size obtained only from TEA noticeably decreased when Al/Ti increased. This conformed to the catalytic activity results. The increase of TEA molecules results in more fresh active sites formation, so the polymerization rate increases. In case of TiBA and TnOA, the bulkiness of their molecules results in difficulty of diffusion to titanium centers, so the amount of active sites and activity became lower compare with TEA.

In addition, the increase of cocatalyst resulted in decrease of molecular weight because cocatalyst can act as chain transfer agent as seen in previous work [33]. However, the chain transfer ability of cocatalyst is different. It depends on the bulkiness of alkyl in the molecule. If a cocatalyst has large size of alkyl group, it will obstruct the diffusion to titanium center. Thus, it can be summarized that the chain transfer ability of cocatalyst will decrease, if the bulkiness of cocatalyst molecule increases. For TEA, we believe that almost of molecules can pass the barrier and activate the titanium to be active sites. Thus, the effect of chain transfer to cocatalyst for TEA is lower when compare to chain transfer to hydrogen. For TiBA and TnOA, we believe that there are a few of their molecules can pass the alkoxide barrier because of their bulkiness. Thus, the increase of their concentration was the same as the increase amount of chain transfer to cocatalyst agent. The chain transfer ability of cocatalyst depends on the bulkiness of alkyl group in cocatalyst [7]. The n-octyl of TnOA is more bulky than the i-butyl in TiBA; therefore, the chain transfer to TnOA is slower than to TiBA. This resulted in the evidence that the molecular weight of polymer from TnOA is higher than that obtained from TiBA. Moreover, the concentration of cocatalyst also confirmed the chain transfer ability. The molecular weight of polymer showed that the chain transfer ability of TnOA was equal to the TiBA at the Al/Ti ratio of 5. However, the amount of cocatalyst did not affect on the molecular weight distribution. This revealed that the active site species of catalyst were not affected by the cocatalyst amount.

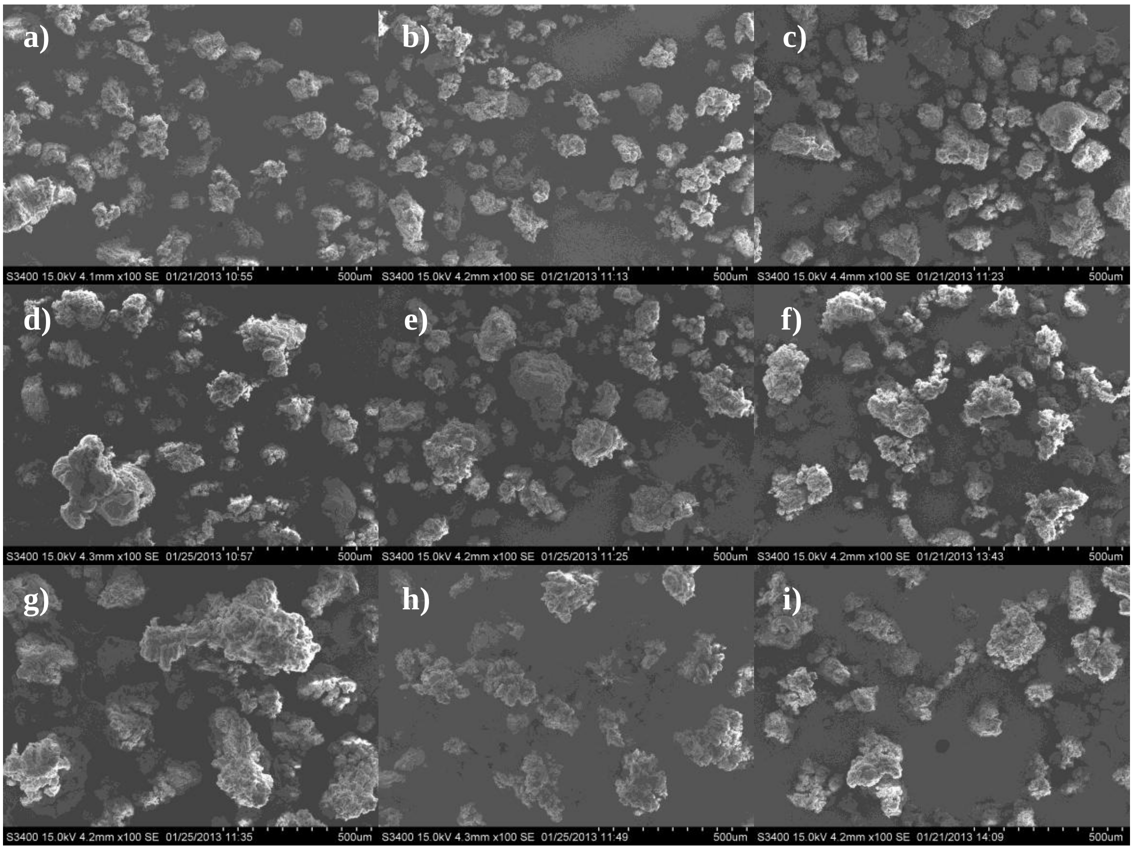


Figure 5.13 Morphology of polymers with different cocatalyst type and Al/Ti ratio

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

6.1.1 The effect of titanium precursor combination on catalytic activity and polymer properties

- The combination of titanium source, $TiCl_4$ and $Ti(OPr^i)_4$, can be employed as effective titanium precursor for Ziegler-Natta catalyst synthesis.
- The increase of titanium (IV) alkoxide amount resulting in decrease of catalytic activity.
- The difference of catalytic activity unit affects on the catalytic activity trends due to the different aspects.
- The increase of titanium (IV) alkoxide resulting in decreasing in MI, bulk density, MWD, and crystallinity of polymer, while the Ti residue and particle size of polymer increased.

6.1.2 The effect of butylchloride on catalytic activity and polymer properties

- The addition of BuCl resulting in increasing of catalytic activity.
- The increase of titanium (IV) alkoxide resulting in increasing of MI, bulk density, MWD, and crystallinity of polymer, while the Ti residue and particle size of polymer decreased.

6.1.3 The effect of cocatalyst on catalytic activity and polymer properties

- TEA was found to be the best cocatalyst for enhancement of catalytic activity.
- The increase of TEA concentration can gradually enhance the catalytic activity while TiBA and TnOA can slightly enhance the catalytic activity.
- The bulkiness of cocatalysts affects on the molecular weight of polymer since they can act as chain transfer agent.
- The bulkiest cocatalyst, TnOA, was the worst chain transfer agent so the molecular weight of polymer became relatively high.

6.2 Recommendations

- The quantitative technique for evaluation of alkoxide species have to be improve. Other spectroscopy techniques such as fourier transform far infrared spectroscopy might be integrated.
- The other chlorinating agents such as silicon compound are interesting because we expected to obtain a bi-supported, SiO_2-$MgCl_2$/$TiCl_4$ catalyst which has better morphology than $MgCl_2$ support.

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Appendices

Appendix A

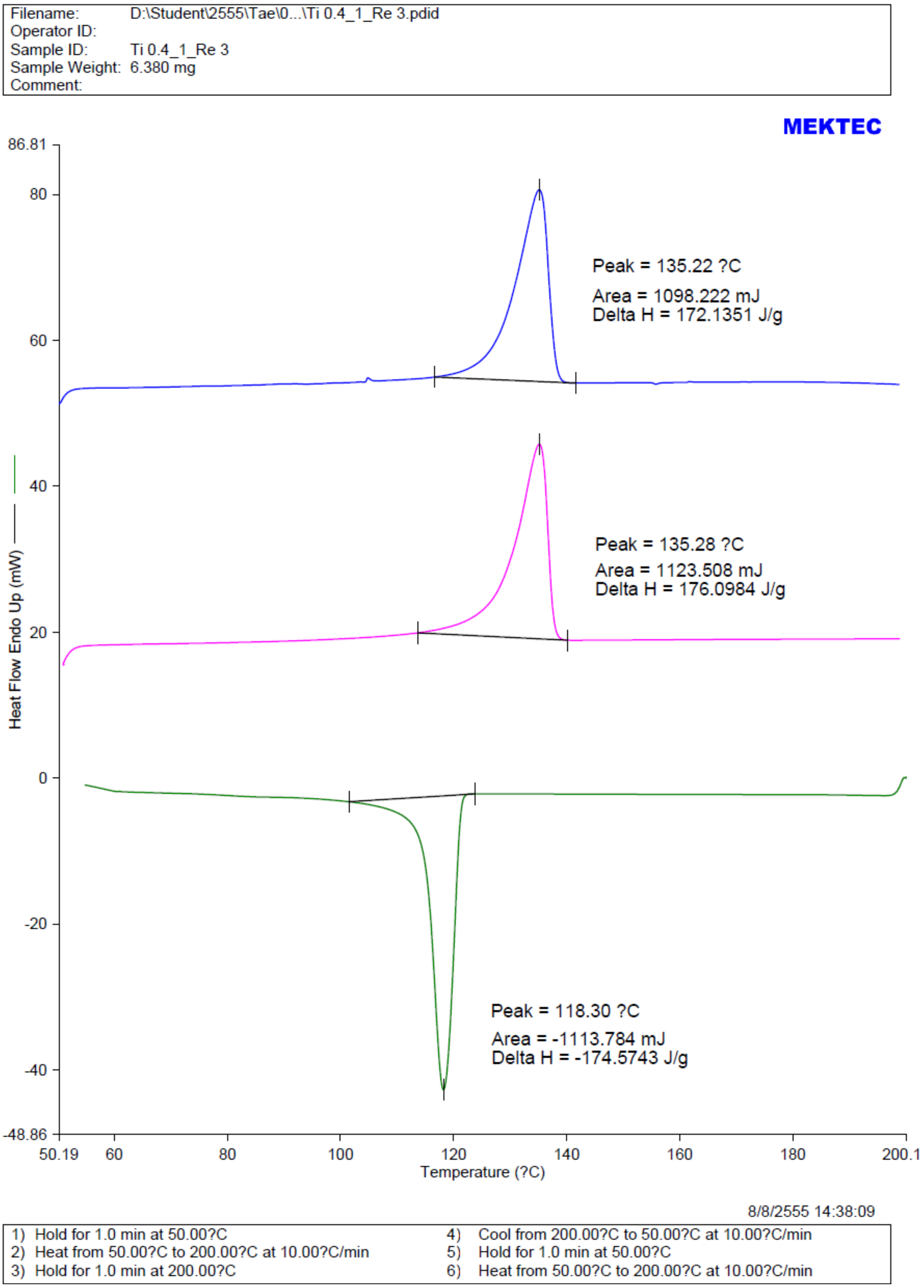
(FOURIER TRANSFORM INFRARED SPECTROSCOPY)

Table A.1 Characteristic IR and Raman vibrations of the Ziegler-Natta catalyst sample [34]

Vibration	Type of vibration	Region (cm^{-1})	
		IR	Raman
C–HAr	Stretching	3070	3080
CH_2/CH_3	Stretching	2800–3000	2800–3000
CO	Stretching	1684	1685
C Car	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–HAr	In plane deformation vibration	–	1140
O–C=O	Asymmetric stretching	1082	–
C–HAr	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

(DIFFERENTIAL SCANNING CALORIMETRY)



Filename: D:\Student\2555\Tae\0...\Ti 0.4_1_Re 3.pdid
Operator ID:
Sample ID: Ti 0.4_1_Re 3
Sample Weight: 6.380 mg
Comment:

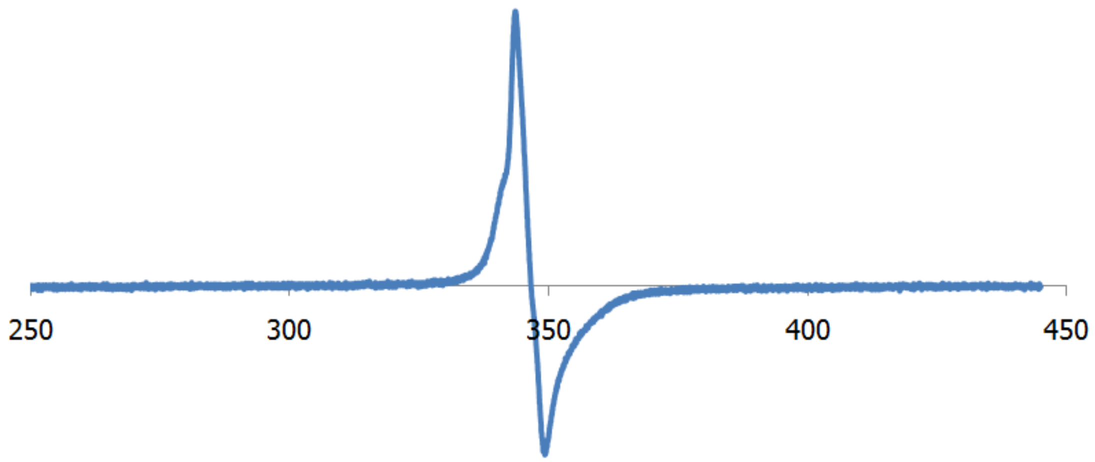
8/8/2555 14:38:09

1) Hold for 1.0 min at 50.00?C
2) Heat from 50.00?C to 200.00?C at 10.00?C/min
3) Hold for 1.0 min at 200.00?C
4) Cool from 200.00?C to 50.00?C at 10.00?C/min
5) Hold for 1.0 min at 50.00?C
6) Heat from 50.00?C to 200.00?C at 10.00?C/min

Appendix B.1 Typical DSC curve of polyethylene.

Appendix C

(ELECTRON SPIN RESONANCE)



Appendix C.1 Typical ESR spectra

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