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COMPARATIVE STUDY OF ZIEGLER-NATTA CATALYST SYNTHESIS FOR
ETHYLENE POLYMERIZATION



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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

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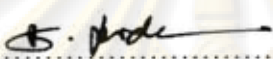
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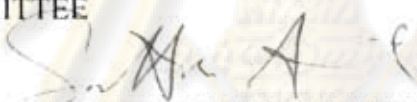
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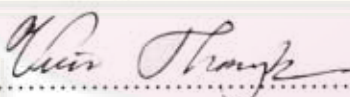
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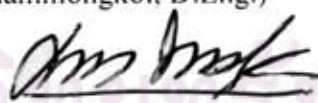

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 อ.ที่ปรึกษาวิทยานิพนธ์: ศ. ดร. ปิยะสาร ประเสริฐธรรม, 116 หน้า

ในปัจจุบันพอลิเอทิลีนเป็นพอลิเมอร์ที่มีปริมาณการใช้งานในอุตสาหกรรมอย่างมาก โดย
 ใช้ตัวเร่งปฏิกิริยาซีเกลอร์-แนนดคาในการสังเคราะห์ แนวทางหนึ่งที่สำคัญในการพัฒนาตัวเร่ง
 ปฏิกิริยาชนิดนี้คือการสังเคราะห์ตัวเร่งปฏิกิริยาให้มีความว่องไวสูงและสามารถสังเคราะห์พอลิ
 เมอร์ที่มีคุณสมบัติที่ดีได้ ในงานวิจัยนี้ตัวรองรับแมกนีเซียมคลอไรด์โดยวิธีการตกผลึกซ้ำ
 (recrystallization) และแมกนีเซียมเอทอกไซด์โดยวิธีเคมีคอลรีแอกชัน (chemical reaction) ถูกใช้
 เพื่อศึกษาผลของตัวแปรในการสังเคราะห์ตัวเร่งปฏิกิริยาคือความว่องไวในการเกิดปฏิกิริยาและ
 คุณสมบัติของพอลิเมอร์ โดยตัวแปรที่ศึกษาคือ ความเร็วใบพัด อุณหภูมิ และอัตราการหยดสาร
 พบว่า ความเร็วใบพัดที่ 100 และ 200 รอบต่อนาที ให้ค่าความว่องไวสูงสุดสำหรับวิธีการตกผลึกซ้ำ
 และวิธีเคมีคอลรีแอกชัน ตามลำดับ วิธีการตกผลึกซ้ำ อุณหภูมิมีผลกระทบเล็กน้อยต่อความว่องไว
 ของตัวเร่งปฏิกิริยา ส่วนวิธีเคมีคอลรีแอกชัน อุณหภูมิที่ 90 องศาเซลเซียสให้ค่าความว่องไวที่สูง
 ที่สุด และทั้งสองวิธี อัตราการหยดสารมีผลกระทบเล็กน้อยต่อค่าความว่องไวของตัวเร่งปฏิกิริยา
 นอกจากนี้ยังได้ศึกษาความไวต่อการเปลี่ยนแปลงตัวแปร ผลปรากฏว่า วิธีการตกผลึกซ้ำ จะไวต่อ
 การเปลี่ยนแปลงความเร็วใบพัดมากกว่าวิธีเคมีคอลรีแอกชัน เนื่องจากความหนืดที่มากกว่า วิธีเคมี
 คอลรีแอกชัน ไวต่อการเปลี่ยนแปลงอุณหภูมิมากกว่าวิธีการตกผลึกซ้ำ เพราะสารที่ไม่ว่องไวใน
 วิธีเคมีคอลรีแอกชันสามารถละลายกลับเข้ามาที่อุณหภูมิสูงได้ และทั้งสองวิธีไม่มีความไวต่อการ
 เปลี่ยนแปลงอัตราการหยดสารเหมือนกัน จากการสังเคราะห์ตัวเร่งปฏิกิริยาที่สภาวะของตัวแปรที่ดี
 ที่สุดในแต่ละวิธีพบว่า ผลของวิธีตกผลึกซ้ำให้ค่าความว่องไวที่ดีกว่าวิธีเคมีคอลรีแอกชันเนื่องจาก
 มีปริมาณไททานเนียม (Ti^{IV}) มากกว่า

ศูนย์วิจัยทรัพยากร

จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา...วิศวกรรมเคมี..... ลายมือชื่อนิสิต..... ปิยะวิทย์ โภคาเสริมส่ง.....
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KEY WORD: ZIEGLER-NATTA CATALYST/SUPPORT CATALYST/
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PIYAVIT POKASERMSONG: COMPARATIVE STUDY OF ZIEGLER-
NATTA CATALYST SYNTHESIS FOR ETHYLENE POLYMERIZATION.
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Dr.Ing., 116 pp.

Nowadays, polyethylene becomes more usage in olefin industries. Ziegler-Natta catalyst was used to synthesize polyethylene. Therefore, it is important to develop this catalyst efficiently to obtain the high activity and can be used to synthesize polymer that we desire. For this research, $MgCl_2$ synthesized by the recrystallization method and $Mg(OEt)_2$ synthesized by the chemical reaction method were chosen to investigate synthesis parameters which affect on the catalytic activity. Synthesis parameters include that paddle speed, holding temperature and dropping rate. The results showed that the paddle speed at 100 and 200 rpm gave the highest catalytic activity for recrystallization and chemical reaction method, respectively. For the recrystallization method, the holding temperature had little effect on activity and holding temperature at 90 °C exhibited the highest activity for the chemical reaction method. Dropping rate had only little effect on activity. Sensitivity of parameters on catalytic activity were compared both recrystallization and chemical reaction method. It was found that recrystallization method was more sensitive than chemical reaction method for paddle speed effect due to more viscosity. For holding temperature effect, chemical reaction method was more sensitive than recrystallization method because inactive species from conversion $Mg(OEt)_2$ to $MgCl_2$ can be dissolved back into the solvent at high temperature by chemical reaction method. Both recrystallization and chemical reaction methods were not sensitive to the dropping rate effect. The best synthesis catalyst condition of each method was used to compare activity. Activity from recrystallization method was higher than that from chemical reaction due to more amount of Ti^{3+} present.

Department :Chemical Engineering.. Student's signature : ..Piyavit Pokasermsong

Field of study : ..Chemical Engineering.. Principal Advisor's signature : ..P. Praserttham

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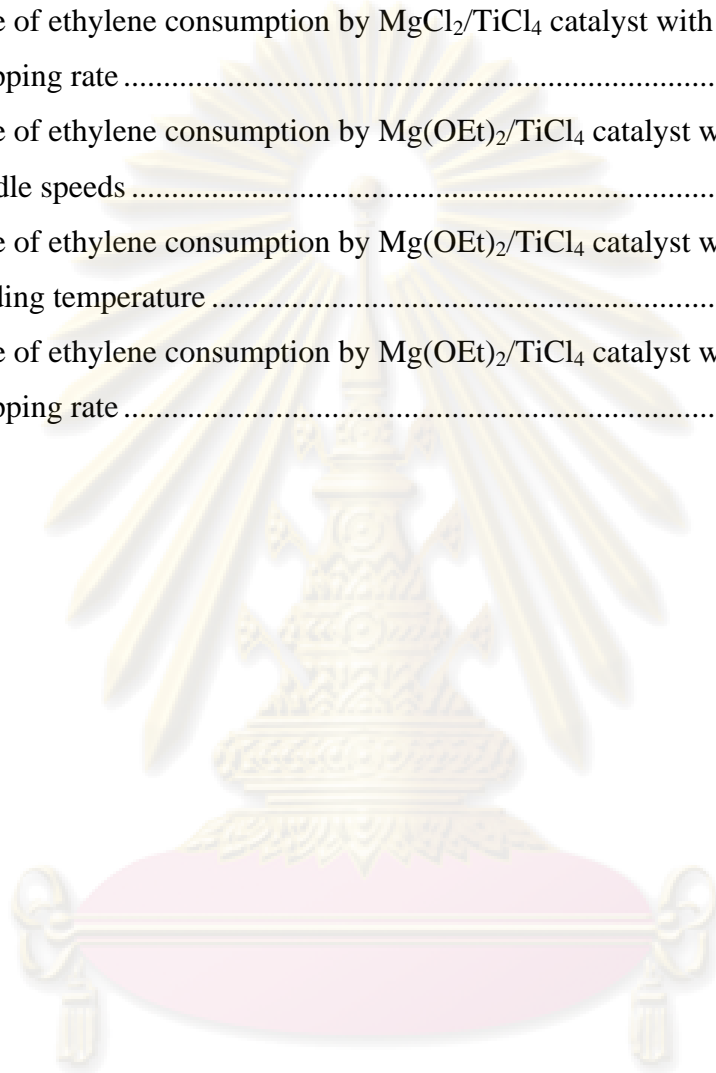
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CHAPTER I

INTRODUCTION

Polyolefin such as polyethylene (PE) and polypropylene (PP) are major plastics in the world-wide polymer industry [1]. Since 1950 polymer materials have experienced a rapid development from cheap, low-quality surrogates to materials that allow for new applications or replace established materials such as metal, wood or glass due to their better properties. Therefore, the worldwide production volume of polyolefin has grown to more than 80 million tons per year until now and is predicted to rise continuously to exceed 140 million tons in 2010 [2].

Polyethylene (PE) has the highest production volumes of all synthetic polymers, because of its many advantages, e.g., excellent chemical resistance, high impact strength, and stiffness even at low temperatures. These commodity polymers have been produced with the Ziegler-Natta type or metallocene type organometallic coordination catalysts [1, 3]. Since then numerous generations of catalysts and processes have been introduced on the commercial scale to produce a large variety of materials ranging from commodity thermoplastics to rubbers, e.g., high density polyethylene (HDPE), linear low-density polyethylene (LLDPE), isotactic polypropylene, ethylene-propylene rubber (EPR), ethylene-propylene-diene monomer rubber (EPDM), polybutadiene and polyisoprene. Nowadays, tens of millions tons of polyethylene (PE) are being produced by Ziegler-Natta catalysts each year [4].

The Ziegler-Natta catalysts have been used for ethylene polymerization since 1950. Ziegler-Natta catalysts have advantages of producing product with high molecular weight, high melting point and controllable morphology. However the disadvantages of Ziegler-Natta catalysts are: (i) less control of growing polymer branching due to multiple metal sites of transition metal, (ii) encapsulation effect of polymer chains and (iii) difficulty of catalyst removal from the final product [5].

Many modern Ziegler-Natta catalysts for stereospecific olefin polymerization employ the high surface area support matrices for active transition metal catalyst sites. The first significant results were obtained in the early 1960s by using the reactive Mg compounds such as $\text{Mg}(\text{OH})\text{Cl}$, hydroxylated MgO or MgSO_4 . In the past 20 years,

there have been many reports about the various supports for TiCl_4 catalysts including such magnesium compounds as MgO , $\text{Mg}(\text{OH})_2$, MgCl_2 , Grignard compounds, and Mg alkyl [6].

The manufacture of high-activity Ziegler-Natta catalysts for polymerizing ethylene requires a support that stabilizes the active centers of the catalysts. A variety of metal halides and oxides have been reported as suitable supports for the catalysts. Magnesium alkoxides were reported as efficient supports in some patients [6] and anhydrous MgCl_2 has been known as a preferred support for highly efficient Ziegler-Natta catalysts for the polymerization of olefins [7]. Inorganic oxides such as Mg compound, SiO_2 , Al_2O_3 , and etc., have been used as catalyst supports due to their high surface area and good morphology [8]. The best support is MgCl_2 due to the fact that Mg and Ti have similar atomic size and shape. Moreover, MgCl_2 has a similar crystalline structure to that of TiCl_3 [9].

Since the excellent properties of MgCl_2 supported Ziegler-Natta catalysts for production of polyolefins were discovered, many studies on treating methods of MgCl_2 have been carried out in order to improve the yield of catalysts through the increase of the surface area and through a better interaction between MgCl_2 and TiCl_4 . These treatments are the ball-milling, the recrystallization methods and the chemical reaction [10]. The recrystallization method consists of a chemical activation by reaction of crystalline MgCl_2 with alcohol to form $\text{MgCl}_2 \cdot n\text{ROH}$ adducts, followed by a controlled regeneration of the active support through recrystallization by removing the added compound (quick cooling, solvent evaporation or titration). In consequence, the assemblies of spherically fined MgCl_2 crystallites with highly distort and high number of uncoordinated magnesium sites is produced. For chemical reaction method procedure, the reaction between TiCl_4 and magnesium alkoxides such as $\text{Mg}(\text{OEt})_2$ shows a very high activity for the polymerization of ethylene. During the reaction with TiCl_4 , hydrocarbon solvents are incorporated and a reaction with TiCl_4 takes place in this layer to form MgCl_2 and $\text{TiCl}_{4-n}(\text{OEt})_n$ compounds. The suspended magnesium ethoxide is transformed into the MgCl_2 support and at the same time, TiCl_4 is absorbed. The soluble $\text{TiCl}_{4-n}(\text{OEt})_n$ compounds are removed by washing with petrol. A catalyst particle with spherical shape, high porosity and high specific surface area is achieved [11]. Moreover, the catalyst synthesis procedure

seems to be the most important factor for determining the catalyst performance since they give the final polymer with different properties.

In the present work, we have prepared two types of catalysts with different preparation procedures. For example, the first catalyst was synthesized by forming the adduct of $\text{MgCl}_2 \cdot \text{EtOH}$ and the second catalyst was prepared by using $\text{Mg}(\text{OEt})_2$ as the starting material for support. The investigation was aimed at differentiating the nature of the catalyst obtained as well as their polymerization behaviors.

This thesis is divided into five chapters. Chapter I is the general introduction to lead the objective of this research. Chapter II is an introduction to Ziegler-Natta catalyst with a brief review on catalyst history and development. We also address the basic chemical principles on both catalysis and polymerization. The experimental procedure as well as the instrument and techniques used for characterizing the resulting polymers are also described in Chapter III.

In Chapter IV, the results on ethylene polymerization using different preparation procedures of Ziegler-Natta catalyst are presented. The influences of the MgCl_2 and $\text{Mg}(\text{OEt})_2$ supports were also investigated regarding different parameters on the catalytic activity and polymer properties. The characteristics of supports and catalyst precursors using N_2 physisorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) and obtained polymer using differential scanning calorimetry (DSC)

Finally, conclusions of this work and some recommendations for future research work are provided in Chapter V.

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CHAPTER II

THEORY AND LITERATURE REVIEWS

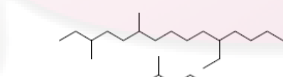
The early history of polyolefin started with the discovery of low density polyethylene (LDPE) by ICI. The obtained polymer has a highly branched structure and is produced radically at ethylene pressures of 1000-3000 bars. In contrast to the free radical ethylene polymerization, the discovery of the catalyst based on the activation of transition metal compounds with aluminum alkyls in 1953 by Karl Ziegler led to the formation of high density polyethylene (HDPE) [12]. A year later, Gullio Natta was able to demonstrate that an appropriate catalyst system was capable of polymerizing propylene into semi-crystalline polypropylene [13].

2.1 Polyethylene

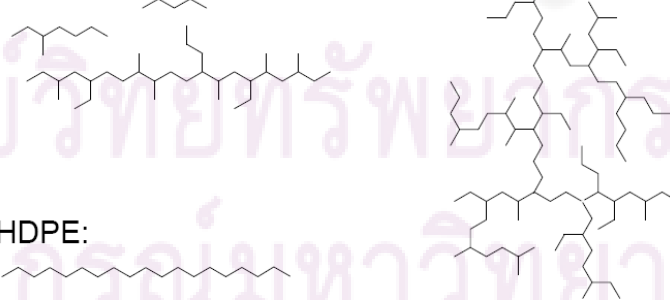
Polymers are widely used everywhere in the world. Polyethylene composes of one-third of the world's total production of polymeric thermoplastics [14]. This section describes the most common types of polyethylene and compares their most important physical properties

Classification of Polyethylenes and Their Applications

LLDPE:



LDPE:



HDPE:



Figure 2.1 Chain Structures of LDPE, HDPE and LLDPE

Generally speaking, polyethylene can be divided into two categories, i.e., low-density polyethylene (LDPE) and high-density polyethylene (HDPE). LDPE refers to the polyethylene of density between 0.910 g/cm³ and 0.940 g/cm³, and HDPE is polyethylene of density higher than 0.940 g/cm³ [15]. LDPE can be further divided into normal LDPE and linear low-density polyethylene (LLDPE) based on the microstructures of the polyethylene chains. In most cases, normal LDPE is made by a free-radical polymerization process. As a result, LDPE contains short-chain branches, as well as long-chain branches in the polymer chains (**Figure 2.1**), which lower the crystallinity, the melting point, and the density of LDPE compared to HDPE. As a result, LDPE is flexible and has high impact strength [9]. Linear low density polyethylene (LLDPE) seems to fit these requirements as a polymer suitable for several fields. In addition, the production technology and processing machines currently used for traditional polyethylene may be used. The characteristics determining the advantages of LDPE for some particular use are excellent processability at relatively low temperatures, excellent optical characteristics, impact and tearing resistance, and flexibility. These are the properties which lead to the utilization of LDPE in industrial packaging films. The considerable industrial interest in HDPE is due to the economics allowed by the low pressure production processes (the same used for HDPE) as to its suitability in field where it can be replaced conventional LDPE.

HDPE is an extremely versatile polymer which is employed in nearly all application fields. Each practical use depends on the specific properties arising from an optimal balance among the following parameters: density, molecular weight distribution (MWD), and branching content. A proper balance determines both good processability performance and high quality of the manufactured item.

The purpose of processing technology is to transform a polymer (generally powder or pellets) into shaped manufactured items. This transformation of the material is related to its chemical-physical properties which affect the useability of the end products. Transformation processes may be subdivided as follows.

Simple extrusion: monofilaments, sheets, pipes, and other special profiles may be obtained by the use of extruders with different geometries

Extrusion followed by a second processing phase: blow molding, coating, spinning, etc.

Injection and compression molding: these are the most employed technology.

Various technologies: calendering, vacuum forming, foaming, rotational molding, etc.

In the case of HDPE, the most interesting application field is blown field with high mechanical resistance at thickness lower than 10 μm . These results can be obtained by using products with molecular weights high enough to give good mechanical properties, wide MWD for good processability, and linear macromolecules for maximum orientation and thus thin films.

Other typical HDPE application fields involve extrusion of pipes and large sized containers. Requirements are high melt strength at low shear rates to give consistency to the pipe or parison, and this involves high molecular weight together with the good processing achievable with wide MWD polymers.

In the injection molding field it is important to use HDPE with narrow MWD in order to minimize distortion and shrinkage of manufactured items, and with low molecular weight in order to reach the highest injection rates and shorten molding cycles. It is always necessary to achieve the best balance among processing characteristics, mechanical resistance, and dimensional stability [16].

HDPE comprises linear polyethylene chains with few branches (**Figure 2.1**). This microstructure results in better packing of polymer chains in solid state, so HDPE has higher density and crystallinity than LDPE. As a result, HDPE is a rigid thermoplastic. HDPE is more useful as a structural material due to its rigidity. Applications of HDPE include formed packaging (such as milk bottles), pipe, and molded pieces such as kitchenware and toys [9].

As is known, HDPE and LLDPE are polymerized in the low pressure process in the present of catalyst. A key to the successive process is the large family of transition metal catalysts that trigger the polymerization reaction at very low pressure and temperature. It is convenient to categorize the catalyst system into the following four classes according to the base transition metal compounds constituting the catalyst complexes [17]:

- (1) Unsupported high activity Ziegler-Natta type catalyst
- (2) Supported Ziegler-Natta type catalyst
- (3) Supported metal oxide catalyst

(4) Supported organotransition metal catalyst

Transition metal oxide supported on refractory metal oxide was among the earliest low-pressure catalyst for olefin polymerization [18-21]. These catalysts consist generally of oxides of transition metal elements from group V, VI, and VII of the Periodic Table. For catalytic activity, the transition metal oxides are supported on high surface area solids such as silica, alumina, silica-alumina, and clay. In many cases, polymerization activity of supported transition metal oxide catalysts can be enhanced by use of promoters chosen from the metals, or their hydrides and alkyls, of elements of group I, II, III of the Periodic Table. Chromium oxide catalysts, supported on silica ($\text{CrO}_3/\text{SiO}_2$) or silica - alumina ($\text{CrO}_3/\text{SiO}_2.\text{Al}_2\text{O}_3$) were developed at Phillips Petroleum Company. These supported catalysts represent the most important metal oxides for ethylene polymerization. Ethylene polymer made with these catalysts is predominately linear, high density products. With propylene and higher α -olefins, polymerization rates, polymer yields, and degrees of crystallinity are significantly lower than for the polymerization of ethylene.

Deposition of certain organotransition metal compounds on dehydrated supports, such as silica or silica-alumina, leads to catalysts representing the fourth category of catalysts. However, reducing agents or modifiers can be optionally used. Some attention has been devoted to supported chromocene, $(\text{C}_5\text{H}_5)_2\text{Cr}/\text{SiO}_2$ [22-23] and supported bis(triphenylsilyl) chromate, $[(\text{C}_6\text{H}_5)_3\text{SiO}]_2\text{CrO}_2/\text{SiO}_2.\text{AlO}_3$ [24]. These catalysts can be used for homopolymerization of ethylene and copolymerization of ethylene with α -olefins. The absence of a support for these chromium compounds results in tremendously reduced activity and, in the case of chromocene, to no activity at all

HDPE is made by homopolymerization of ethylene using Ziegler-Natta catalysts [18]. Since the Ziegler-Natta catalysts are the most frequently used in α -olefins polymerization. Catalysts of this type can also polymerize dienes and some other vinyl monomers with very high activity and selectivity under a wide range of conditions. Their existence has had a dramatic effect on the shape of the present petrochemical industries. So the details of this are further breakthrough

2.2 Ziegler-Natta Catalyst

2.2.1 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 [25].

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 AEt_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 [20]. 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 AlEt₃, Al-i-Bu₃, AlEt₂Cl, AlEtCl₂ and AlEt₂OR) have been overwhelmingly preferred [26]. 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 AlEt₂ + CoCl₂, 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: (C₅H₅)₂TiCl₂, 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 AlEt₂Cl are reacted, for example, the exchange shown in **Eq 2.1** takes place.



The real catalyst maybe the end product of this exchange rather than the starting mixture; at an Al/Ti ratio of 4, β -TiCl₃ 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 [25]. 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 $\text{Al}(\text{C}_2\text{H}_5)_3$ or $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. 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 $\sigma\text{-TiCl}_3 \cdot 1/3\text{AlCl}_3$ 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 $\alpha\text{-TiCl}_3$. 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 first-generation Ziegler-Natta catalysts. Most first-generation commercial catalysts are based on a precursor of the $\delta\text{-TiCl}_3 \cdot x\text{AlCl}_3$ solid solution type and have been dry milled and heat-treated. These catalysts have specific surface areas in the range $10\text{-}40 \text{ m}^2/\text{g}$. 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 formed by activation. **Eq 2.2** shows this relation

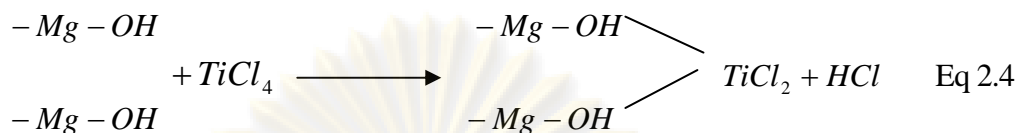
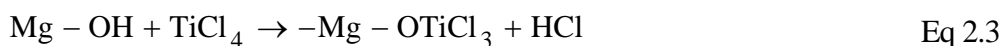


Depositing the active Ti species on a support could make significant improvement whose residues, unlike those to $TiCl_3$, would be inert and not detrimental to the properties of the polymer. Thus, it was evident that higher catalyst activities were likely to be achieved through the use of transition 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 Al_2O_3 , SiO_2 , $Al_2O_3 \cdot SiO_2$, 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 third-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

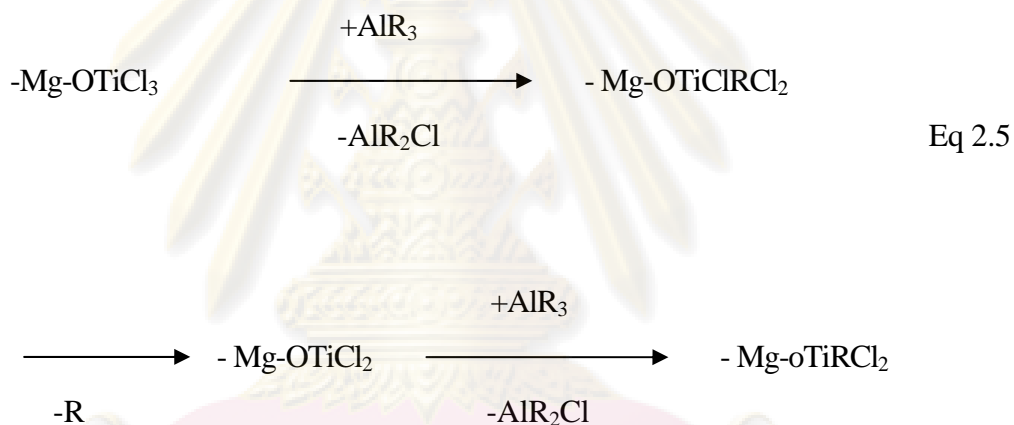
olefin polymerization processes. The active polymerization centre could now be dispersed throughout the support surface, making them all essentially accessible to the polymerized monomer. Since all the titanium chloride molecules were now available to take part in the polymerization, fewer were needed. 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)Cl, 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 TiCl₄:



The obtained supported precursors are then subjected to activate by trialkylaluminium, which can be show schematically for the MgOTiCl₃ species as follows:



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 [27].

2.3 Factor to Determined Behavior of Polyolefin Catalysts

Behavior of catalyst is meaning the catalyst activity, molecular weight of resulted polymer and others. The factors described are related to the chemical structure of the metal alkyl and the transition metal salt.

2.4 The Metal Alkyl

2.4.1 Group of Metal

Not every metal in group I to III form an active metal alkyl as in claimed in many of the patent relating to Ziegler-Natta catalysts. Active catalysts from the following metals have been established for ethylene and/or propylene.

Table 2.1 Metal group I to III for Ziegler-Natta catalyst preparation

Group I	Group n	Group III
Li	Be	Al
Na	Mg	Ga
K	Zn	
	Cd	

Aluminum alkyls have been the most extensively used, and the reason for this is partly scientific and partly economic. They were much safer to use in solution because, once properly diluted, they were less pyrophoric and not flammable unless contacted with a combustible material. Simple syringing techniques, using N₂ or Ar as an inert atmosphere

2.4.2 Ligands of Metal

Two types of ligands are compared: (1) an all-hydrocarbon alkyl or an aryl, such as ethyl or phenyl; and (2) a heteroatom or a radical containing a heteroatom, such as Cl or -OC₆H₅. Both of these types of ligands have the potential of undergoing exchange reactions with the ligands of the transition metal. When the alkyl or aryl group is exchanged, a transition metal-carbon bond is formed as the active center. The heteroatom should be exchanged for a ligand of the transition metal, an active center is not formed because the transition metal-heteroatom bond is not active. However, the electronic and steric environment of the metal atom is altered. The chemical

behavior of a metal alkyl is strongly influenced by the nature and number of these two types of ligands.

2.5 Transition Metal Salts

2.5.1 Choice of Transition Metal

The availability of TiCl_4 as an inexpensive material in the 1950's undoubtedly promoted considerable research aimed at industrial applications. It is not surprising that many papers and patents have appeared that use TiCl_4 or a derivative, especially TiCl_4 and TiCl_2 of varying compositions and crystal structures. As a result, many interaction and important findings developed with these TiCl_3 's, and this led to more research on elucidation of mechanism, etc. The same was true for aluminum alkyls.

2.5.2 Ligand of Transition Metal

Active catalysts for ethylene polymerization have been made from transition metal salts bearing ligands of varied structures. These ligands include the groupings as shown in **table 2.2**.

Table 2.2 Ligand of transition metal

Ligands	
-Cl, Br, I or F	indenyl
-OR(R = alkyl such as Bu, Me)	arenes
-SR(R = alkyl such as Bu, Me)	O-CO-R(R = CH_3)
-NR ₂ (R = alkyl such as Bu, Me)	oxide
Acetylacetonate	sulfide (disulfide)
Nitroso	sulfate
Phosphate	carbon monoxide
$\pi\text{-C}_5\text{H}_5$, Cp	

Ethylene can be polymerized to highly linear products with catalysts containing array of transition metal salts, that is, those having different ligand structures. Economics and the balance of properties shown by the polyethylene probably dictate the choice of the salt. The variation in ligand structure is great, including sulfides, oxides, oxychlorides dialkylamine, alkoxy, acetylacetonate, arene, cyclopentadienyl, halide (= Cl, Br, F, or I), phosphate, sulfate, and so on. Because in many of these catalysts the transition metal salt and the metal alkyl undergo exchange of ligands in varying degrees, the activity of the catalyst is sensitive to the molecular ratio of the two components. In addition, the ligand structure of the active center may be significantly different from that of the starting salt, and only little insight is gained by consideration of the structure of the parent salt. One should be wary about comparisons of activities of the transition metal salts bearing different ligands if the polymerizations are not done under similar conditions [27].

2.6 The role of MgCl₂ as Support for Ethylene Polymerization Catalyst

After Ziegler-Natta catalysts were discovered, much research to gain higher efficiency of the catalysts has been done. The catalysts have evolved into a supported form by dispersing the transition metal onto solid supports which provide the efficient use of the transition metal as an active center. Many types of supports such as magnesium compounds, silica and alumina been employed. But the most widely used supports are magnesium compounds, such as MgCl₂ and Mg(OEt)₂. But the MgCl₂ is the most popular due to the fierce competition in the polyolefin industry, much of the research in recent years has focused on a highly active MgCl₂ supported catalyst which is the most common commercial catalyst [28].

MgCl₂ has a layer structure. Using the Arlman-Cossee technique it was found that three different types-one single and two double vacancies of MgCl₂ can be distinguished on the surface of a magnesium dichloride crystal. The free vacancy places are responsible for the interaction with TiCl₄ and Lewis base

MgCl₂ has been found to be the ideal support, its host lattice can support chiral titanium-active sites. This has been widely attributed to near isomorphism of MgCl₂ and TiCl₃ crystals. Two crystalline modifications are known for MgCl₂, the commercial α form and the less stable β form. Similar to the γ -TiCl₃, the α -form has a

layer structure of the CdCl_2 type and shows a cubic close-packed stacking (ABC...ABC...) of double chlorine layers with interstitial Mg^{2+} ions in sixfold coordination [29]. The β -form, on the contrary, shows a hexagonal close packing like that of $\alpha\text{-TiCl}_3$ [30]. The layer structure of $\alpha\text{-MgCl}_2$ displays an X-ray diffraction spectrum with a strong (104) reflection at $d = 2.56 \text{ \AA}$ as a result of the cubic close-packed arrangement of the Cl ions. The internal structures of hexagonal layers in both cases are almost equivalent since vanderwaals interaction between layers is weak.

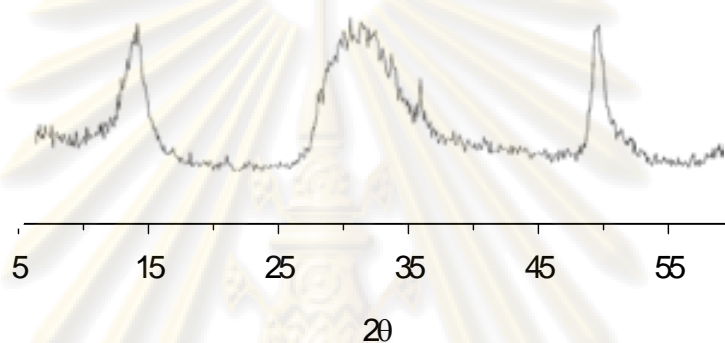


Figure 2.2 Powder X-ray diffraction pattern of $\delta\text{-MgCl}_2$

The key ingredient of the catalysts is the “activated” or $\delta\text{-MgCl}_2$, which exhibits a disordered structure arising from the translation and rotation of the structural Cl-Mg-Cl layers with respect to one another that destroy the crystal order in the stacking direction [31]. In consequence, the X-ray spectrum shows a gradual disappearance of the (104) reflection and its replacement by a broad “halo” centered at $d = 2.65 \text{ \AA}$. As shown in the **Figure 2.2**, the structurally disordered $\delta\text{-MgCl}_2$ exhibited broad bands centered at $2\theta = 15, 32$ and 50.5° . There are four crystalline forms of TiCl_3 known as α, β, γ and δ , of which the α, γ and δ are violet forms with respectively cubic and hexagonal close packing of the chloride ions. The β -form of TiCl_3 has a fiber structure and is brown or dark brown, depending on the method of preparation. Particular attention has been paid to a disordered $\delta\text{-TiCl}_3$ which shows the best catalytic properties [32]. Moreover, it is believed that the outstanding success of MgCl_2 is because $\delta\text{-MgCl}_2$ and $\delta\text{-TiCl}_3$ have the same crystal structure and the nearly identical ionic radii and lattice distances (**Table 2.3**). Such a dramatic increase in activity was revealed to be caused by marked increases in the propagation rate constant (k_p) as well as the number of active species [C^*] [31]. The latter effect is

easily understood in terms of a high dispersion of the active titanium species on the large surface of MgCl_2 .

Table 2.3 Crystallographic data for $\delta\text{-MgCl}_2$ and $\delta\text{-TiCl}_3$

$\delta\text{-MgCl}_2$	$\delta\text{-TiCl}_3$
<u>hexagonal close packing of the Cl ions</u>	
$a = b = 3.63\text{\AA}$	$a = b = 3.54\text{\AA}$
$c = 5.93\text{\AA}$	$c = 5.86\text{\AA}$
<u>Cation coordination: octahedral</u>	
$\text{Mg-Cl} = 1.23\text{\AA}$	$\text{Ti-Cl} = 1.25\text{\AA}$
$\text{Mg}^{2+} = 0.65\text{\AA}$	$\text{Ti}^{4+} = 0.68\text{\AA}$
	$\text{Ti}^{3+} = 0.76\text{\AA}$

Experimental data suggest that preferential lateral cuts correspond to the (100) and (110) planes [31] and theoretical calculations of the lattice electrostatic energies give a lower energy for the (110). The activation processes (mechanical or chemical) of the MgCl_2 increase the portion of (100) and (110) surfaces on the MgCl_2 surface [33]. These two lateral cuts contain coordinatively unsaturated Mg^{2+} ions, with coordination number 4 on the (110) cut and 5 on the (100) cut, as shown in **Figure 2.3** [34]. That is to say, the magnesium atoms are coordinated with 4 or 5 chlorine atoms, as opposed to 6 chlorine atoms in the bulk of the crystal.

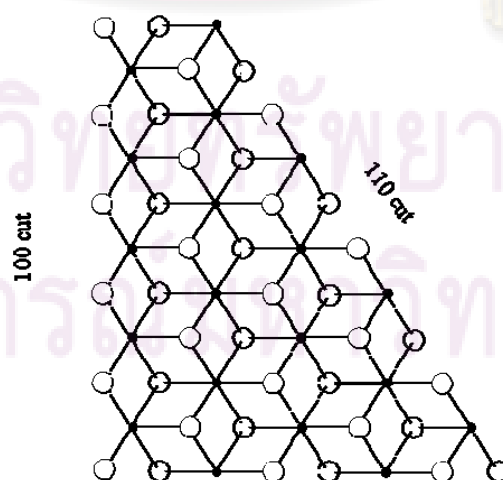


Figure 2.3 Model of MgCl_2 layer showing the (100) and (110) cuts.

MgCl₂ also has desirable morphology as a support for the new generation of olefin polymerization catalyst. It is a highly porous polycrystalline material probably due to a large number of uniformly distributed microcracks. It is sufficiently resistant to rupture by mechanical manipulation and used in gas phase polymerization, but it is weak enough so that it is broken down during polymerization. The porous morphology permits the diffusion of monomer into the interior of the catalyst particles and replicates it to the polymer.

In conclusion, MgCl₂ is a rather inert chemical so it can be left in the polymer without a deashing process.

The situation on crystal edges and corners could present additional differences, so that the presence on the MgCl₂ surface of Lewis acidic sites with different acid strength and steric requirements is likely to occur and actually has been verified through interaction with Lewis bases of different strength and steric hindrance. The “activated” MgCl₂ support, as it exists in the catalyst, can thus be envisaged as an agglomerate of very small crystallites (primary units) bearing on their side surfaces a variety of exposed Mg²⁺ ions with different degrees of unsaturation, Lewis acidic strength and steric hindrance, and thus potentially able to coordinate with the other catalytic components.

2.7 Catalyst Chemistry

It is well known that neither TiCl₄ nor the internal donor can be easily removed from the catalyst unless severe thermal treatments or strongly coordinating solvents are used. Thus, it seems that the catalyst components lose their identity and become strongly linked together, forming new complexes. A considerably amount of work has been aimed at elucidating the nature of this bonding mainly by means of spectroscopic observations (IR, NMR) and thermogravimetric (TG) analyses carried out on both the true catalyst and model combinations of its components (i.e., MgCl₂/ID, TiCl₄/ID, TiCl₄/MgCl₂, TiCl₄/ID/MgCl₂ complexes or comilled mixtures).

A great deal of IR data is available for catalysts containing ethylbenzoate (EB) as internal donor [35-37] for which a shift of the C=O stretching frequency from 1725 cm⁻¹ in the free ester to 1680 cm⁻¹ to 1700 cm⁻¹ is most commonly observed in both the catalyst and the comilled EB/MgCl₂ mixtures. This result has been interpreted as

an indication that a complexation of EB through the carbonyl oxygen takes place to Mg and not to Ti. The concomitant broadening of the C=O absorption band has been attributed to the presence of a variety of coordination complexes with different bond strengths [38].

Solid state CP MAS (cross polarization with magic angle spinning) ^{13}C NMR investigations on both the catalyst [39,40] and model $\text{TiCl}_4\cdot\text{EB}$ complexes or EB/MgCl_2 comilled mixtures also led to the conclusion that EB is prevalingly complexed to MgCl_2 . Possible structures for EB complexed to the (100) and (110) faces of MgCl_2 have been proposed by Chien *et al.* [39] and are shown in **Figure 2.4**.

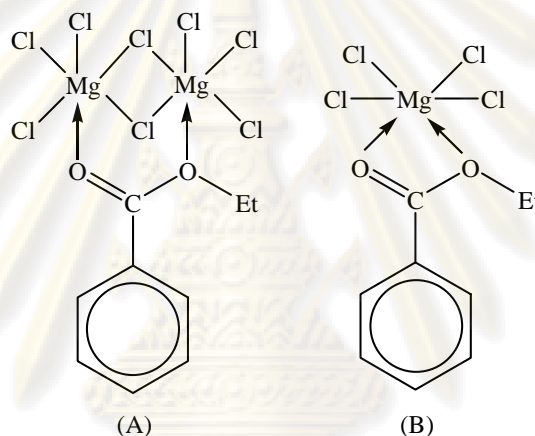


Figure 2.4 Possible models for EB coordination on the (100) (A) and (110) (B) faces of MgCl_2 .

According to some authors [41,42], however, a slight difference can be noticed in the infrared C=O absorption frequency of the catalyst ($\sim 1680\text{ cm}^{-1}$) and that of the EB/MgCl_2 mixture ($\sim 1690\text{ cm}^{-1}$) and this would suggest that in the former, EB is in some way complexed to both Mg and Ti. On the other hand, from electron spin resonance (ESR) analysis of the catalyst after interaction with TEA, some evidence for the presence of small amounts of EB or phthalates complexed to Ti^{3+} has been reported as well [43,44].

The information concerning bifunctional donors (phthalates, diethers) is not as abundant. For phthalic acid esters, however, IR observations show a shift of the C=O stretching frequency from $\sim 1730\text{ cm}^{-1}$ in the free ester to 1685 cm^{-1} to 1700 cm^{-1} in

both the catalyst and the $\text{MgCl}_2/\text{ester}$ complex. Similarly, the C–O stretching frequency of diethers (1113 cm^{-1}) is shifted to a doublet at 1059 cm^{-1} and 1024 cm^{-1} in both the catalyst and the $\text{MgCl}_2/\text{diether}$ mixture, with no bands from the TiCl_4 -diether complex being detectable in the former [45]. The same indication is provided by ^{13}C NMR observations on catalyst containing either diethers [45] or phthalates [46], though in the latter case a considerable line narrowing observed in binary ester/ MgCl_2 mixture after treatment with TiCl_4 would suggest, according to the authors [46], that a separate crystalline phase is formed on the support surface.

From all the above, it seems possible to conclude that both monofunctional and bifunctional donors are essentially complexed to Mg rather than to Ti. The structure of the complexes could, however, be different for the different donor types. As a matter of fact, bifunctional Lewis bases could form either 1:1 chelate complexes with tetracoordinated Mg ions on the (100) face [45].

As far as the TiCl_4 bonding is concerned, the most widely accepted models, supported by energy calculations, are those based on epitaxial adsorption on the different MgCl_2 faces. According to Corradini and his group [47,48], for instance, the (100) cut is more basic than the (110) one as far as TiCl_4 coordination is concerned. Also, calculations suggest that TiCl_4 coordination as a Ti_2Cl_8 dimer on the former face and as a monomer on the latter are energetically favored. Similar models were proposed by Chien [49] who, however, assumed the presence of tetracoordinated rather than hexacoordinated monomeric species on the (110) face, both in clusters and in isolated form. As a consequence of the presence of TiCl_4 to coordinate on the (100) face, the situation in the catalyst, before and after reduction with the Al-alkyl, can be roughly represented as in **Figure 2.5**, with the (100) face being prevalingly occupied by Ti_2Cl_8 dimers and the (110) face by the Lewis base.

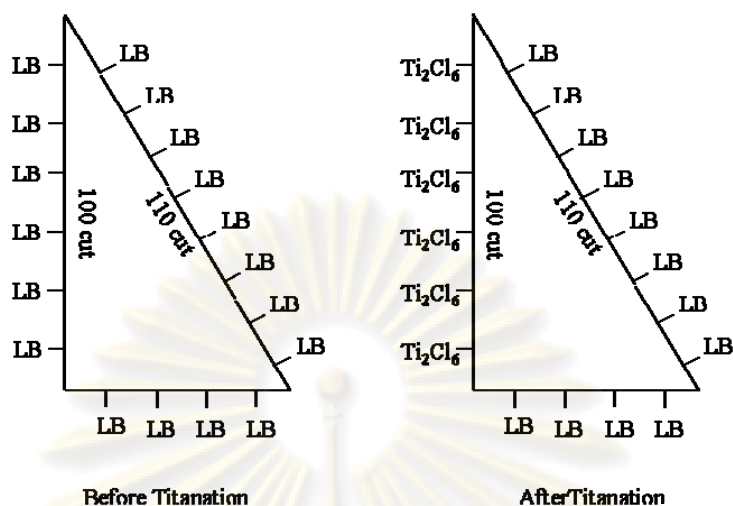


Figure 2.5 Schematic drawing of the Lewis base and Ti halide distribution on the (110) and (100) cuts MgCl_2 : (left) = support, (right) = catalyst activated with the Al-alkyl.

However, recent spectroscopic studies using FT-Raman have provided evidence for strong adsorption of TiCl_4 on the (110) lateral cut of MgCl_2 , giving a monomeric species with octahedrally coordinated titanium, which can be the precursor for active and stereospecific sites [50,51] as shown in **Figure 2.6**.

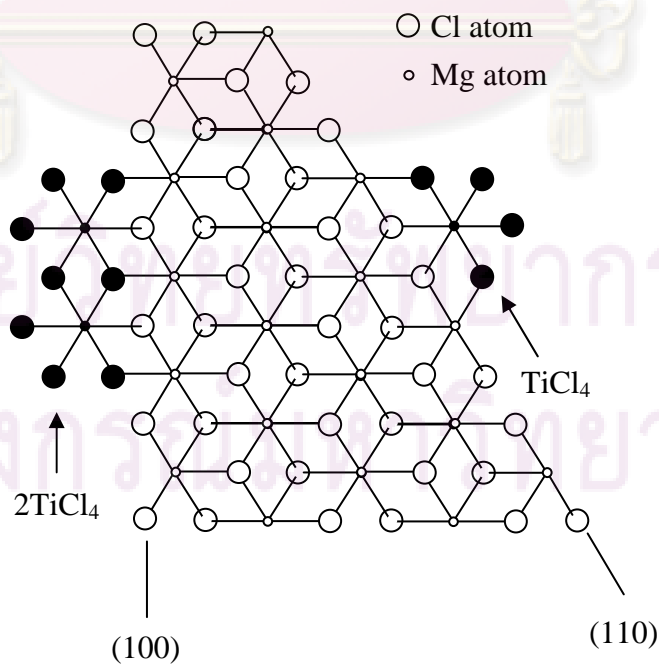


Figure 2.6 Epitaxial binding of TiCl_4 on to the surface of $\delta\text{-MgCl}_2$.

2.8 Cocatalyst Chemistry

The cocatalysts used with MgCl_2 -supported catalysts are invariably Al-trialkyls, triethyl aluminium (TEA) and triisobutyl aluminium (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 [52].

On the other hand, the external donor which can be used appears to be dependent on the type of internal donor. If ID is an aromatic monoester (EB is the most usual), esters of the same type are normally required, such as methyl-*p*-toluate (MPT), ethylacetate (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 $\text{C}=\text{O}$ stretching frequency from $\sim 1725\text{ cm}^{-1}$ 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 [53] and calorimetric studies [38], complexes involving two moles of AlR_3 per mole of ED also have been hypothesized. Structures such as those represented in **Figure 2.7** have been proposed by Spitz *et al.* [53], while not very different structures were assumed by Chien *et al.* [54] and Tashiro *et al.* [55]. The complex formation is very fast even at low temperature and in dilute solutions.

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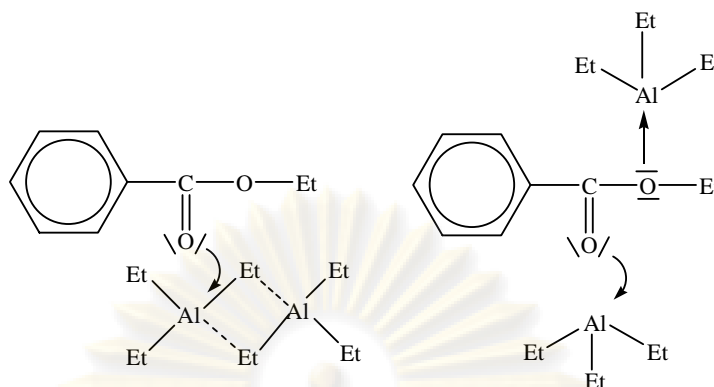


Figure 2.7 possible structures of 1:2 EB/TEA complexes.

As regards alkoxy silanes, the formation of a 1:1 complex between TEA and phenyltriethoxysilane (PES) has been indicated by means of ^{13}C NMR spectroscopy, at least at relatively high TEA concentrations (0.5 mol/L) [56]. 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 2.8** [52,57,58].

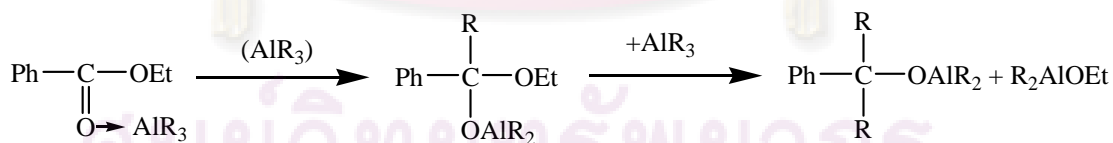


Figure 2.8 The formation of EB and AlR_3 complexation.

Reduction of the $\text{C}=\text{O}$ 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 $\text{PhSi}(\text{OMe})_3$ and TEA, for instance, the reaction at 75°C can proceed up to the formation of $\text{PhEt}_2\text{SiOMe}$, according to the scheme of **Figure 2.9** [56].

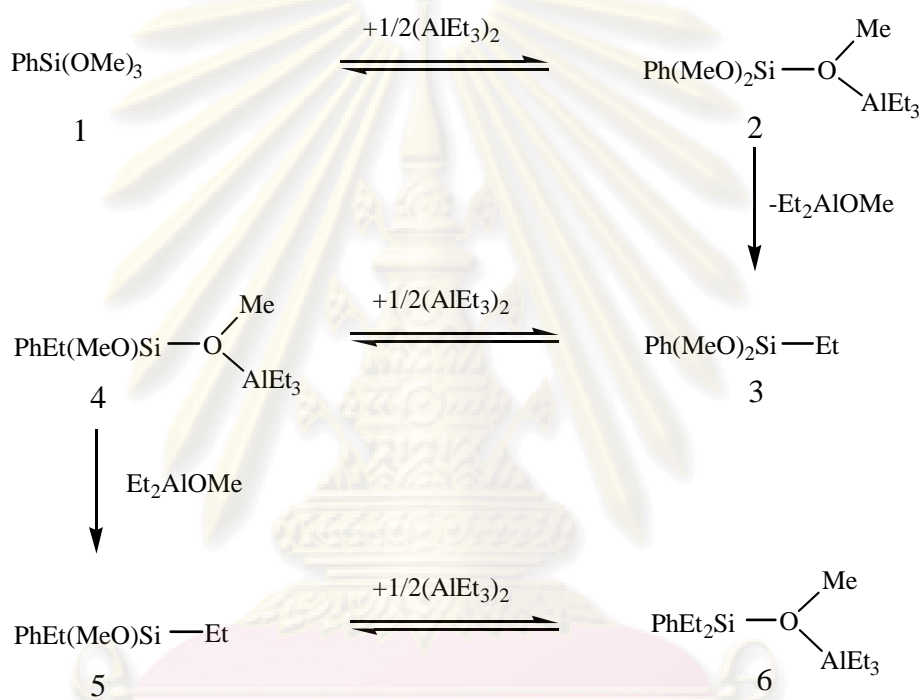


Figure 2.9 Pathway of the reaction between TEA and $\text{PhSi}(\text{OMe})_3$.

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°C , with $\text{TEA} = 5 \text{ mmol/L}$ and $\text{PES} = 0.5 \text{ mmol/L}$ [59].

The reaction is even slower, and sometimes absent for dialkoxysilanes and practically absent at all for monoalkoxysilanes [66]. 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.

2.9 The preparation of high activity catalysts

The efficiency of olefin polymerization catalysts can be improved by several methods. Since the excellent properties of $MgCl_2$ supported Ziegler-Natta catalysts for production of polyolefins were discovered, many studies on treating methods of $MgCl_2$ have been carried out in order to improve the yield of catalysts through the increase of the surface area and through a better interaction between $MgCl_2$ and $TiCl_4$. These treatments have been the ball-milling, the chemical reaction and the recrystallization methods [10].

Three main industrially viable synthetic routes have been followed to fulfill the requirements. A short description is given below.

2.9.1 Ball milling

The ball-milling method allows to reduce the size of $MgCl_2$ crystallites increasing, as a consequence, the surface area of the catalyst and its activity. Nevertheless, its major disadvantage is a prevalent difficulty in controlling the polymer morphology [10].

2.9.2 Recrystallization

A further development has been the use of an alcoholate of $MgCl_2$, allowing the preparation of spherically shaped support and hence catalyst particles [60]. This important advance resulted from the establishment of catalyst particle replication during polymerization [61,62] which is an important consideration both for slurry and

gas phase commercial polymerization. The method consists of a chemical activation by reaction of crystalline MgCl_2 with alcohol to form $\text{MgCl}_2 \cdot n\text{ROH}$ adducts, followed by a controlled regeneration of the active support through recrystallization by removing the added compound (quick cooling, solvent evaporation or titration). In consequence, the assemblies of spherically fined MgCl_2 crystallites with highly distort and high number of uncoordinated magnesium sites is produced.

2.9.3 Chemical reaction

Catalysts prepared from the reaction between TiCl_4 and magnesium alkoxides such as $\text{Mg}(\text{OEt})_2$ show a very high activity for the polymerization of ethylene and propylene. Such catalysts were successfully developed for ethylene polymerization by Hoechst AG [63] and Solvay & Cie [64] during the late 1960s and early 1970s. Further advances have been achieved by the Toho Titanium Company [65] in the preparation of a high activity catalyst for the polymerization of propylene. Magnesium alkoxide compounds consist of crystals with layers of magnesium cations and alkoxy anions with loose layers of alkyl chains of the alkoxy groups in between [66]. Solvent can penetrate into these loose layers. These layers swell and the bonds are weakened. During the reaction with TiCl_4 , hydrocarbon solvents are incorporated and a reaction with TiCl_4 takes place in this layer to form MgCl_2 and $\text{TiCl}_{4-n}(\text{OEt})_n$ compounds. The in petrol suspended magnesium ethoxide is transformed into the MgCl_2 support and at the same time, TiCl_4 is absorbed. The soluble $\text{TiCl}_{4-n}(\text{OEt})_n$ compounds are removed by washing with petrol. A catalyst particle with spherical shape, high porosity and high specific surface area is achieved.

2.10 Ethylene Polymerization Catalyst

Catalysts derived from the reduction of TiCl_4 by an aluminium alkyl, or using TiCl_3 prepared by hydrogen or aluminium reduction of TiCl_4 , have been used to polymerize ethylene. The relative ease of ethylene polymerization has meant that simpler catalysts can be used, but also that a wider range of catalyst types is possible. However, there are other desirable catalysts attribute to high activity; for examples,

high bulk density polymer, controlled shape and particle size range also controlled molecular weight distribution.

2.10.1 Magnesium halide supported catalysts

Catalysts based on magnesium chloride are important in the field of polyethylene. Extremely active catalysts can be prepared by milling MgCl_2 and TiCl_4 together. Polymerization is carried out by trialkylaluminum as an activator. In commercial process, these catalysts can produce polymer containing a very low ash.

Analogous catalysts developed for polypropylene can be made by milling MgCl_2 with a Lewis base and then treating with liquid TiCl_4 . The bases are alcohols rather than esters. These catalysts have even higher activities based on transition metal component. Other advantages related to the polymer's performance in a given application; for example, the ease of blow moulding. Examples are given in the table of methods other than ball-milling for producing an active MgCl_2 . These include chlorination of a magnesium alkyl, oxide, hydroxide or alkoxide and dehydration of $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ using SOCl_2 . The necessity for the elimination of oxygen containing species is critical with polyethylene catalysts; MgO is a very effective support.

2.10.2 Other magnesium supports

An early Solvay patent describes a catalyst produced from the reaction between MgO and TiCl_4 . $\text{Al}(\text{iBu})_3$ was an activator to produce a high activity catalyst. Methods of producing magnesium oxide include dehydration of $\text{Mg}(\text{OH})_2$ and decomposition of the metal acetate. Alcohols can be added to the support; magnesium alkoxides are effective support materials.

2.11 Mechanisms of Olefin Polymerization

Usually, Ziegler-Natta catalyst consists of two components (i.e., a transition metal salt such as a TiCl_3 or TiCl_4 (catalyst) and main-group metal compounds involving alkyl-Al (cocatalyst). It is generally accepted that the formation of active sites on Ziegler-Natta catalysts for olefin polymerization is accomplished through

reduction and alkylation of surface Ti species by interaction of the catalyst with Al-alkyl cocatalyst [67].

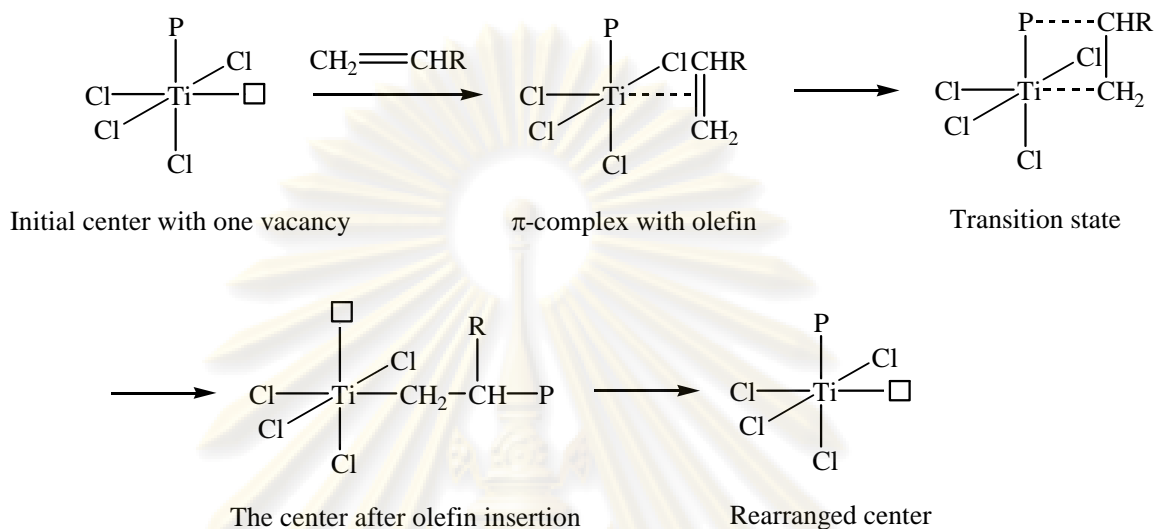


Figure 2.10 Monometallic polymerization mechanism.

The mechanisms of chain propagation can be divided into two groups (i.e., monometallic and bimetallic mechanism) according to the role of the cocatalyst. In monometallic mechanism proposed by Cossee and Arlman [68, 69], the cocatalyst generates the active species from the transition metal but is not involved in the chain growth reaction itself (**Figure 2.10**). The Ti atom is in an octahedral coordination environment with one vacant site and an adjacent coordination site bonded to an alkyl group of polymer chain. For MgCl_2 -supported catalysts this structure is created when bound TiCl_4 reacts with alkyl-Al. The two-step mechanism for propagation involves π -coordination of an incoming monomer by the Ti atom at its vacant coordination site, followed by insertion, via a four-center transition state, into the Ti-polymer bond. An insertion reaction takes place, shifting the vacant octahedral position. Then migration of the polymer chain occurs to reestablish the vacant site on the original position. The weakness of this mechanism is that active Ti^{3+} has only one outer shell electron available for the formation of π back-bonding, which is a requirement for metal-olefin π -bond formation [70, 71].

Bimetallic mechanism proposed by Rodrigues and van Looy [72] involves initial π complexation of monomer to Ti atom that is bridged through alkyl groups to an Al atom (**Figure 2.11**). This is followed by ionization of the transition metal-alkyl bond, formation of a six-membered cyclic transition state, then insertion. In both mechanisms, the polymer chain grows from the catalyst surface by successive insertion reactions of complexed monomer, and the alkyl group originally present in the cocatalyst ends up as one of the terminal group of the polymer chain.

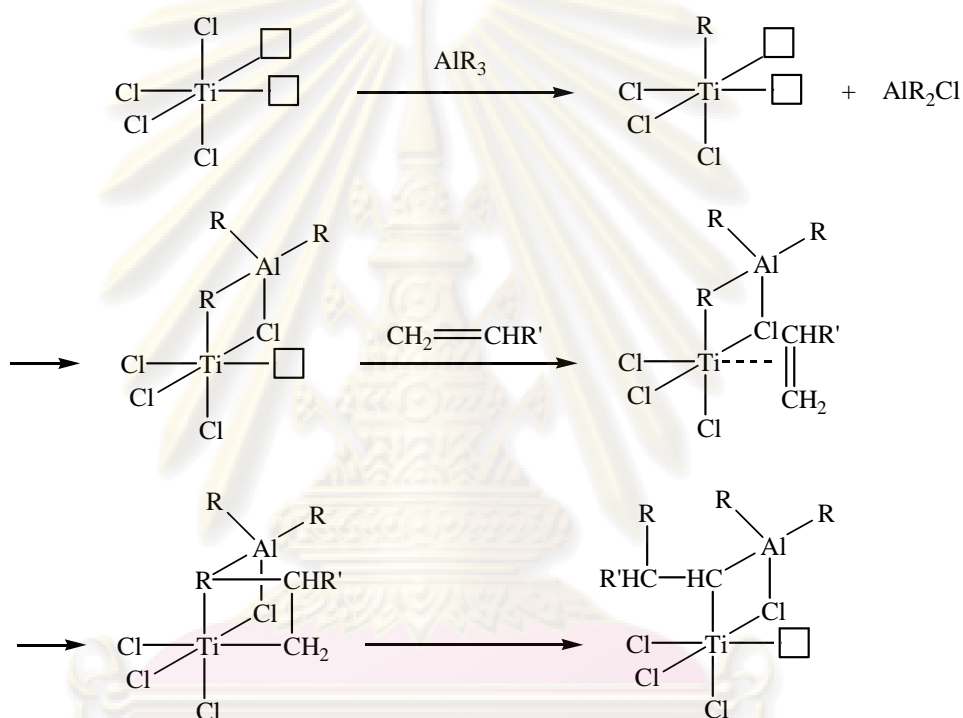


Figure 2.11 Bimetallic polymerization mechanism.

2.12 Traditional Active Sites Models

A great number of models for active sites have been proposed to interpret the stereospecific polymerization of olefins with Ziegler-Natta catalyst. The model proposed in early stages was arguing about monometallic or bimetallic active center.

In monometallic active sites proposed by Cossee and Arlman [70,72,73], the cocatalyst generates the active species from the transition metal but is not involved in the chain growth reaction itself (**Figure 2.12 (a)**). The Ti atom is in an octahedral coordination environment with one vacant site and an adjacent coordination site

bonded to an alkyl group of polymer chain. For MgCl_2 -supported catalysts this structure is created when bound TiCl_4 reacts with Al-alkyls. In this model, the two-step mechanism for propagation involves π -coordination of an incoming monomer by the Ti atom at its vacant coordination site, followed by insertion, via a four-center transition state, into the Ti-polymer bond. Stereoselectivity is assumed only if, before a further insertion, the chain skips back to the position occupied before the insertion.

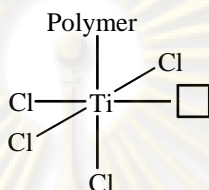


Figure 2.12 (a) Monometallic active sites proposed by Cossee.

The surface model proposed by Allegra [74] obviates the necessity of the back skip step to assure the stereoselectivity because a C_2 symmetry axis locally relates the atoms relevant to the non-bonded interactions with the monomer and the growing chain (**Figure 2.12 (b)**). Therefore, the two situations resulting by exchanging, in the coordination step, the relative positions of the growing chain and of the incoming monomer are identical.

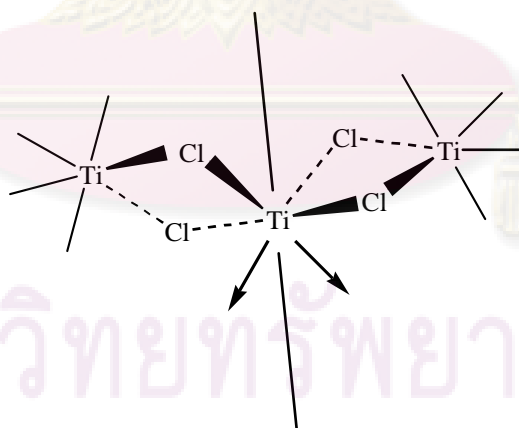


Figure 2.12 (b) Monometallic active sites proposed by Allegra.

Corradini et al. [75], on the basis of some evaluations of the non-bonded interactions for the Cossee and Allegra models, suggest that the chiral environment of the metal atom imposes a chiral orientation of the first C–C bond of the chain, and this orientation has been identified as a crucial factor in determining the

stereospecificity (**Figure 2.12 (c)**). As a matter of fact, the non-bonded interactions between the methyl group of the propylene molecule and the C-atom of the growing chain in β -position to the metal induce a preferential coordination of the enantioface of the monomer which allows the methyl group and the β -carbon atom to be located on opposite sites with respect to the plane defined by the Ti-C and the double bond.

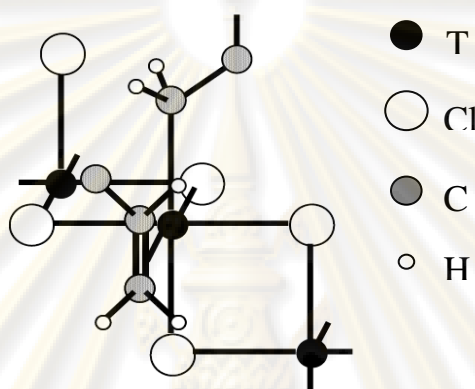


Figure 2.12 (c) Monometallic active sites proposed by Corradini.

This model is in good agreement with the experimental finding about the stereochemical structure of the end groups of PP obtained with -TiCl_3 and ^{13}C -enriched different Al-alkyls [76,77]. Insertion of propylene into a Ti- CH_3 bond is not stereospecific, while insertion on Ti- $^{13}\text{CH}_2\text{-CH}_3$ is partially stereospecific; when the alkyl group is isobutyl, the first insertion is stereospecific as are the successive insertions. This model justifies also the retention of configuration, in the growing chain, after the insertion of an ethylene unit because the model maintains its behavior also when a secondary carbon atom is in β -position relative to the metal. According to the mechanism proposed by Brookhart and Green [78], the monomer insertion is assisted by strong α -agostic interactions between titanium and the C-H bond of the growing chain. Bimetallic catalytic centers have been proposed by Patat and Sinn [79], Natta [80], and Rodrigues and van Looy [72]. In these models, a ligand (Cl or alkyl group) and the last carbon atom of the growing chain link Ti and Al through a double bridge. Polymerization mechanism proposed by Rodrigues and van Looy involves initial π complexation of monomer to Ti atom that is bridged through alkyl

groups to an Al atom (**Figure 2.13**). This is followed by ionization of the transition metal-alkyl bond, formation of a six-membered cyclic transition state, then insertion.

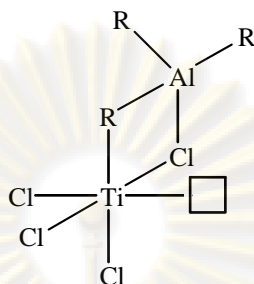


Figure 2.13 Bimetallic active sites proposed by Rodrigues and van Looy;

□: vacant site, R: alkyl group.

In these traditional models, center metal of active sites is being fixed to one (Ti) or two (Ti and Al), however, there is no explanation of transformation of these active sites occurring during the polymerization.

2.13 Recent Active Sites Models

During the last several decades, various stereospecific active sites models regarding the interconversion of active sites on heterogeneous Ziegler-Natta catalysts have been reported. Based on the microstructural and stereochemical analyses of atactic PPs produced from various types of heterogeneous Ti-based catalysts, Doi [81] proposed a reversible interconversion between isospecific sites and syndiospecific sites to explain the coexistence of isotactic and syndiotactic stereoblocks (**Figure 2.14**). The stereoblock characteristic was also found in PP prepared from donor-free $\text{TiCl}_4/\text{MgCl}_2\text{-TEA}$ catalyst system by Xu et al. [82]. To account for this, they suggested the existence of equilibrium between monometallic sites and bimetallic sites in terms of reversible complexation with TEA.

In these models, both monometallic and bimetallic active sites exist together. However, it is considered that center metal which can proceed polymerization is a Ti atom.

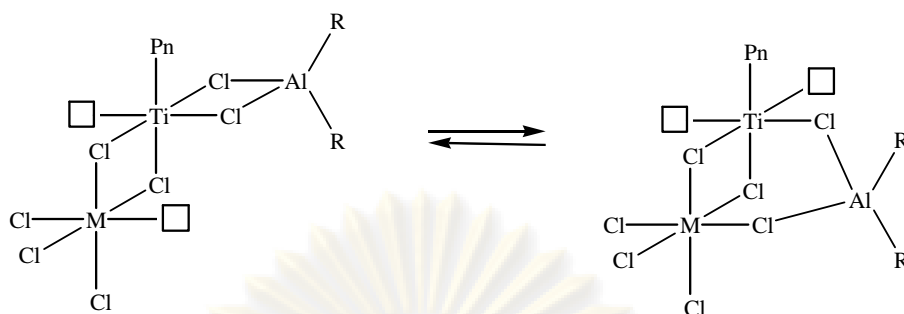


Figure 2.14 Bimetallic active sites proposed by Doi [81]; □: vacant site, R: alkyl group, Pn: growing polymer chain.

More recently, Corradini and Busico et al. [83-89] established a three-site model in terms of equilibrium interconversion between three kinds of stereospecific active sites namely highly isospecific, poorly isospecific and syndiospecific sites to explain the stereoblock characteristics of the synthesized PPs with MgCl_2 -supported Ziegler-Natta catalysts within the last decade (**Figure. 2.15**) the stereospecificity of the active sites providing reasonable explanation not only for Ziegler-Natta catalysts, but also for metallocene catalysts with well-defined steric structure [90]. Whereas, the influence of the difference in various groups (Cl atom, Alkyl group, and electron donor) which exists in the positions of L_1 and L_2 affects stereospecificity is not explained.

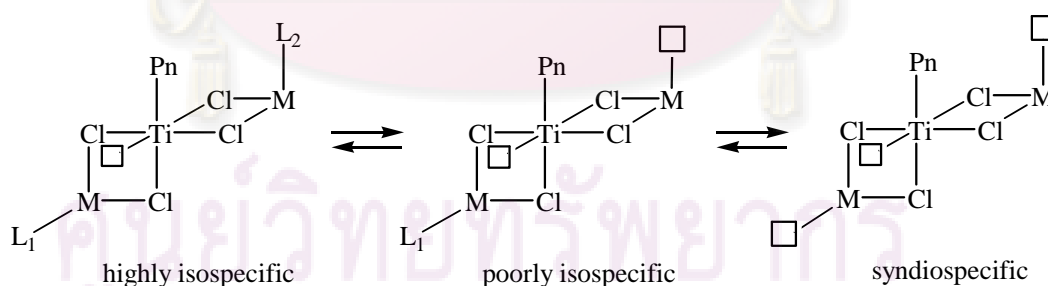


Figure 2.15 Three-sites model proposed by Busico et al. [79]; □: vacant site, Pn: growing polymer chain, L_1 and L_2 : Cl atom, Al-alkyl or electron donor molecules.

Terano et al. [91,92]. Thereafter proposed a modified three-sites model with precise description of the stereospecific nature of various types of active sites stemmed from surface titanium species, Al-alkyl compounds, Mg-compounds and

electron donors. They also suggested that isospecificity of active sites greatly depends upon the bulkiness of the ligands situated at the two most important ligand positions for construction of the asymmetry and chirality of the active sites with steric hindrance.

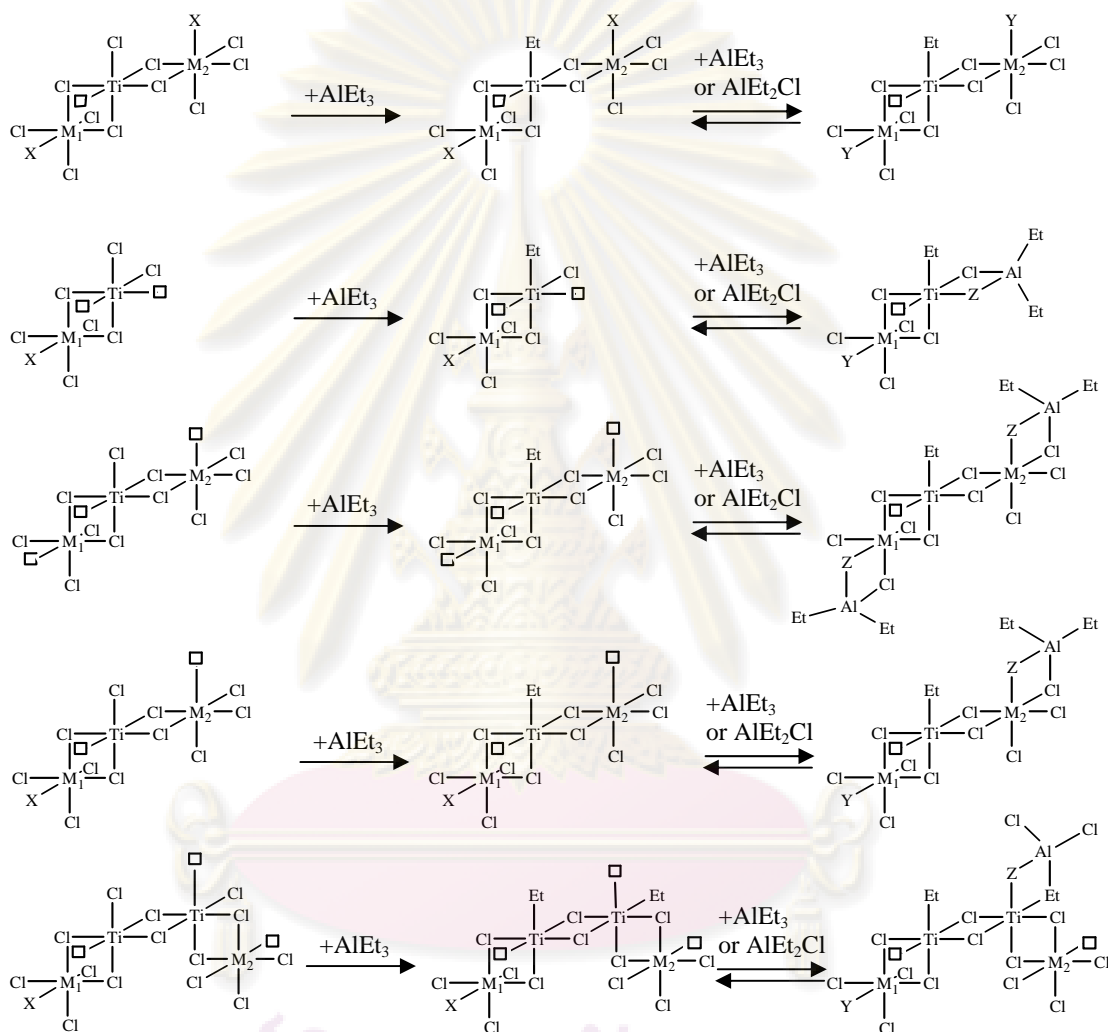


Figure 2.16 Modified three-sites model in terms of formation and transformation of stereospecific active sites on Ziegler-Natta catalyst, M_1 and M_2 : Ti or Mg, and M_1 and M_2 are bound to the catalyst substrate through chlorine bridges; X: Cl, or ED; Y: Cl, Et or ED; Z: Cl or Et; \square : coordination vacancy, for donor-free $TiCl_4/MgCl_2$ catalyst: X=Cl, Y=Cl or Et; for $TiCl_4/EB/MgCl_2$ and $TiCl_4/DBP/Mg(OEt)_2$ catalyst: X=Cl or ED, Y=Cl or ED or Et

2.14 Replication and Polymer Morphology

The reasons why a full control of the polymer morphology is highly desirable in PP manufacturing can be easily understood in terms of process economics and viability. A regular polymer morphology (i.e., particles with high density, regular shape, and narrow particle size distribution (PSD) means both a high reactor throughput, good flowability and packing, and even, as a limiting case, no need of further pelletization. In addition, a proper porosity, though lowering bulk density, helps the retention of the rubbery phase in heterophasic copolymers. Finally, the absence of fines prevents reactor fouling and explosion hazards during handling, and the absence of coarse eliminates undesirable fluidization effects.

In general, the MgCl_2 -supported titanium catalysts consist of particles which average between 10 and 100 μm in diameter. The average particle size can be adjusted during the catalyst synthesis. The catalyst particle is composed of much smaller particles with a size in the nm range. These particles are called primary particles. By agglomeration of many primary particles, a catalyst particle with high porosity and high specific surface area is formed. The pore volume is in the range of 0.3 to more than 1 cm^3g^{-1} . The specific surface area reaches values between 50-300 m^2g^{-1} [93].

The catalyst particles are transformed into polymer particles during polymerization. When polymerization starts at the surface of the primary particles, the primary particle agglomerate is disrupted. The polymeric phase is formed around each catalyst fragment, growing larger and larger by polymer formation. In this way these catalyst fragments are distributed more homogeneously in the growing particle. The catalyst particle shape is replicated in the polymer particle shape. This means that particle shapes and particle size distributions are the same for the catalyst and the polymer. The particle grows in diameter by a factor of 10 to 25 corresponding to a volume increase by a factor of 10^3 to 10^4 .

A fast and extensive catalyst “fragmentation” and a uniform polymer growth rate across the particle seem, thus, to be the key features for a faithful replication [94]. However, several requirements concerning both the catalyst structure and the reaction conditions must be fulfilled for a uniform catalyst fragmentation and polymer growth rate to occur.

2.15 Literature Reviews

B.V. Kokta and R.G. Raj [95] had investigated the interaction between the catalytic components of a Ziegler-Natta stereospecific system formed by TiCl_4 and AlEt_3 in heptane by IR spectroscopy. The first step of reaction between $\alpha\text{-TiCl}_3$ with AlEt_3 was an alkylation or exchange of Cl for ethyl. They prepared TiCl_3 from the reduction of TiCl_4 with hydrogen on Tungsten spiral. It was ground under inert atmosphere. The extent of interaction was determined quantitatively by the analysis of chlorine exchange in liquid phase. The IR spectroscopy was carried out to follow the AlEt_2Cl formation during the interaction of catalyst components in Ziegler-Natta catalytic system.

D.N.Taveira Magalhaes [96] had prepared a number of catalysts from $\text{MgCl}_2\cdot(\text{ROH})_n$ and evaluated them in ethylene and propylene polymerization. Highly active MgCl_2 was prepared by precipitate it from solution. MgCl_2 had some solubility in electron donor solvents such as alcohols and ethers and their dissolution products used as supports for Ziegler-Natta catalysts. It was found that the alcohol-adduct from both methanol and ethanol had porous and irregular surfaces. The catalysts obtained through single and double treatments with TiCl_4 . The titanium content from double treatment method has lower content than that from single treatment. These results indicated that, in the second treatment with TiCl_4 , the catalyst surface was “cleaned” by removing some titanium derivatives soluble in TiCl_4 . These titanium derivatives were inactive sites for ethylene and propylene polymerization.

D.N.Taveira Magalhaes and his coworkers [97] had also studied more active support for the catalysts prepared through the elimination of alcohol molecules by thermal desorption. The ethylene polymerization was carried out at Al/Ti ratio of 100. The titanium content of the catalysts depended on type of support and on the number of treatments with TiCl_4 . It indicated that the double treatment of TiCl_4 facilitated the deposition of TiCl_4 on the supports. The catalysts from the single treatment with internal base, ethyl benzoate, had high Ti content than that without internal base. This difference can be explained by the possible complexation of TiCl_4 with ethyl benzoate, facilitating the deposition of TiCl_4 on the surface of support.

Hong Man Park and Wha Young Lee [98] investigated the reaction of the ethanol of $\text{MgCl}_2\cdot 6\text{EtOH}$ completely forming a complex with TiCl_4 . The $\text{EtOH}\cdot\text{TiCl}_4$

complexes couldn't remove during the washing of catalyst and it contributed to the enhancement of Ti contents. TEA in the preparation catalyst step removed ethanol in MgCl_2 before the impregnation of TiCl_4 . Organoaluminium compounds could react with an internal alcohol in a crystal very well. From the SEM photographs, it found that the particles of MgCl_2 before the impregnation of TiCl_4 fragmented into small particles in this step. It supposed that the activity enhances because of the removal of ethanol through TEA treatment.

Gregory M. Smith et.al. [99] investigated Solid ClMg(OEt) (1) has been prepared and characterized for the first time as a pure, spectroscopically homogeneous material. The novel material, $\text{Cl}_3\text{Mg}_2\text{OEt}$ (2), has also been prepared and characterized as a pure, spectroscopically homogeneous solid. These materials are made by stepwise alcoholysis and chlorination of butylethylmagnesium. The systematic solid-state chemistry emerges for alkoxy magnesium halides. At least 2 well defined compositions of ethoxymagnesium chloride exist, with distinctive spectroscopic and physical properties. In the case of ClMg(OEt) it can be demonstrated that the physical form of the material is highly dependent on synthetic reaction conditions. These novel alkoxy magnesium halides can be converted with the usual techniques to active olefin polymerization catalysts.

A. Parada et.al. [10] investigated magnesium dichloride supported titanium catalysts which were prepared by dissolving anhydrous MgCl_2 in 1-hexanol/isooctane. MgCl_2 support was recrystallized by evaporation of the solvents, by cooling, by precipitation with SiCl_4 and by precipitation with TiCl_4 . The catalysts, in turn, were tested in the polymerization of ethylene. It was found that the most active catalysts in the polymerization of ethylene were those obtained recrystallizing MgCl_2 by precipitation with SiCl_4 . On the other hand, those directly recrystallized with TiCl_4 were the least reactive and the ones that produced polyethylenes with the highest molecular weights and the lowest degrees of crystallinity.

A. Parada et.al. [100] investigated comparative study of the performance of TiCl_4 catalysts supported on recrystallized MgCl_2 through different techniques for the polymerization of ethylene, propylene and ethylene-propylene copolymers. MgCl_2 was dissolved in 1-hexanol and recrystallized through solvent evaporation, quick cooling and precipitation with SiCl_4 . The catalysts presented an order of activities in the polymerization of ethylene, propylene and copolymers of ethylene-propylene:

RPSi > RPT > RET, corresponding respectively to recrystallization by SiCl₄ precipitation, quick cooling and solvent evaporation. The catalyst obtained through SiCl₄ recrystallization was not only the most active, but it also showed the highest isotacticity indexes for propylene polymerization.

Gholamhossein Zohuri et.al. [101] investigated Bisupported Ziegler-Natta catalyst of SiO₂/MgCl₂ (ethoxide type) /TiCl₄ which was prepared for polymerization of ethylene. SiO₂ and Mg(OEt)₂ were used as supports in slurry polymerization of ethylene. The prepared catalyst system of SiO₂/Mg (OEt)₂/TiCl₄ with Mg/Ti = 1.5:1 molar ratio, the SMT-3 catalyst, has relatively high activity for polymerization of ethylene and optimum productivity was obtained at 60°C and increasing the pressure of monomer, the productivity of the SMT-3 increased almost exponentially. Viscosity average molecular weight (M_v) for some polymers obtained were determined. Increasing Al concentration and H₂ decreased M_v of polymer obtained.

R. Jamjah et.al. [102] had prepared of spherical particles of MgCl₂.nEtOH by adducting ethanol to MgCl₂ using melt quenching method. Effect of molar ratio of [EtOH]/[MgCl₂] = 2.8 –3.05 on the morphology and particle size of the MgCl₂.nEtOH were studied. The best adduct of spherical morphology was obtained when 2.9 mol ethanol to 1 mol MgCl₂ was used. Stirrer speed of emulsion section in the melt quenching method for the preparation of spherical support of MgCl₂ is influenced by PSD and the morphology of the particles obtained. Heat removal of ethanol from the MgCl₂.nEtOH increases its surface area. Treatment of the support with TiCl₄ also significantly increases its surface area. SEM study of the polyethylene obtained using the MgCl₂(spherical)/TiCl₄/TEA catalyst system of spherical morphology obtained from spherical support shows particles with no regular shape.

Saeid Ahmadjo et.al. [103] investigated highly active supported catalyst of Ziegler-Natta type which was prepared by reaction of a Grignard reagent. The active MgCl₂ was prepared using C₄H₉MgCl with CH₃Si(OC₂H₅)₃ and AlCl₃.MgCl₂ was reacted with TiCl₄ to prepare the catalyst which was studied for polymerization of ethylene. New method was used for the catalyst preparation which led to a higher range of density in HDPE and almost stable rate/time profile comparing with TiCl₄ supported MgCl₂ catalyst, characteristics of the catalyst. There was an optimum [Al]/[Ti] molar ratio and temperature to obtain the highest activity of the catalyst. The maximum activity was obtained at 60°C, and [Al]/[Ti]=714:1. Productivity of 14700 g

PE/mmol Ti.h was obtained at monomer pressure of 8 bars. Addition of hydrogen decreased the activity of catalyst and the viscosity average molecular weight (M_v) of the polymer obtained, while; increasing monomer pressure increased its activity. Density of the polymer obtained was 0.93- 0.95 g/cm³ which is in the range of high density polyethylene. Melting point of the polymer was in the range of 140-144°C.



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CHAPTER III

EXPERIMENTAL

3.1 Objectives of the Thesis

Study the effects of preparation procedures of Ziegler-Natta catalyst for ethylene polymerization on the catalytic activity and polymer properties.

3.2 Scopes of the Thesis

1. Preparation of $MgCl_2$ from recrystallization method and $Mg(OEt)_2$ from chemical reaction method.
2. Investigation the effects of the catalyst synthesis parameter, i.e. paddle speed, temperature and dropping rate, on the catalytic activity and polymer properties.
3. Comparison the performance of the catalyst synthesis from both recrystallization and chemical reaction method at different preparation conditions.

3.3 Research Methodology

The flow diagram research methodology is shown in **Figure 3.1**.

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

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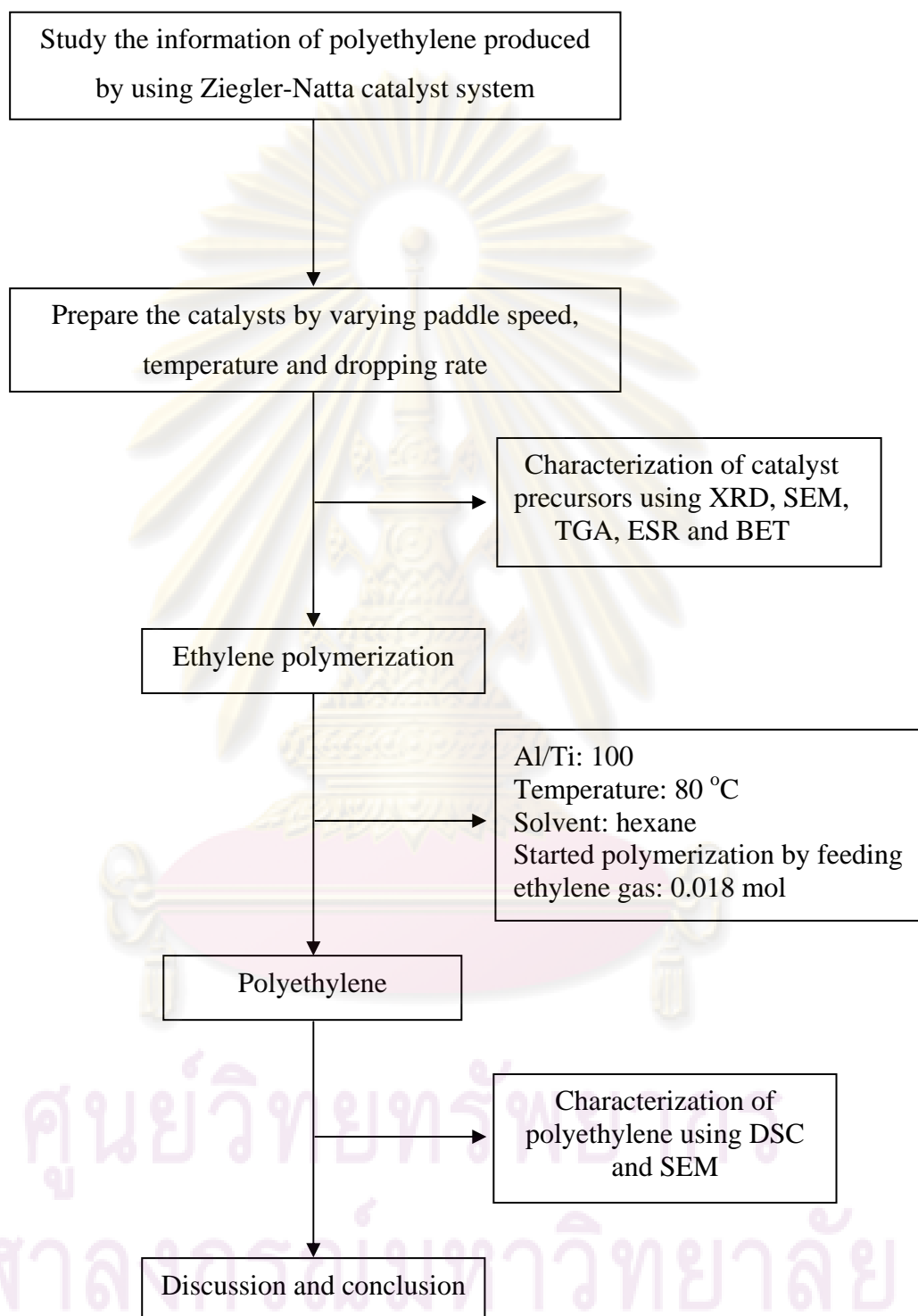


Figure 3.1 Flow diagram of research methodology

3.4 Experimental

3.4.1 Chemicals

The chemicals used in these experiments, carried out at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, were specified as follows:

1. Polymerization-grade ethylene (C_2H_4) was used as received from PTT Chemical Plc. (Thailand)
2. Ultra high purity argon (99.999%) was purchased from Thai Industrial Gas Co., Ltd. (TIG) and was further purified by passing through the column packed with molecular sieve 3Å, BASF Catalyst R3-11G (copper catalyst), sodium hydroxide (NaOH) and phosphorus pentoxide (P_2O_5) in order to remove traces of oxygen and moisture.
3. Anhydrous magnesium chloride ($MgCl_2$, >98%) was purchased from Sigma-Aldrich Inc.
4. Anhydrous magnesium ethoxide ($Mg(OEt)_2$, >98%) was purchased from Sigma-Aldrich Inc.
5. Anhydrous magnesium chloride ($MgCl_2$, >98%) was donated from Tosoh Finechem, Japan.
6. Anhydrous magnesium ethoxide ($Mg(OEt)_2$, >98%) was donated from Tosoh Finechem, Japan.
7. Ethanol (C_2H_5OH >99%) was purchased from MERK.
8. Titanium tetrachloride ($TiCl_4$, > 99%) was purchased from MERK.
9. Diethyl aluminum chloride (DEAC) was donated from Tosoh Finechem, Japan
10. Triethylaluminum ($Al(C_2H_5)_3$) in hexane solution, was donated from PTT Chemical Plc., (Thailand)
11. Polymerization-grade *n*-hexane (C_6H_{14}) was donated from Exxon Chemical Thailand Ltd. It was dried over dehydrated $CaCl_2$ and was purified by refluxing over sodium/benzophenone under argon atmosphere prior to use.

12. *n*-Heptane (C₇H₁₄, 99.84%) was supplied from Carlo Erba. It was dried over dehydrated CaCl₂ and was purified by refluxing over sodium/benzophenone under argon atmosphere prior to use.
13. Toluene was deviated from EXXON Chemical Ltd., Thailand. This solvent was dried over dehydrated CaCl₂ and distilled over sodium/benzophenone under argon atmosphere before use.
14. Benzophenone (purum 99.0%) was obtained from Fluka Chemie A.G. Switzerland.
15. Sodium (lump in kerosene, 99.0%) was supplied from Aldrich chemical Company, Inc.
16. Calcium chloride (Dehydrated) was manufactured from Fluka Chemie A.G. Switzerland.
17. Commercial-grade methanol was purchased from SR lab.
18. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma-Aldrich Inc.

3.4.2 Equipments

Ziegler-natta system is extremely sensitive to oxygen and moisture. Thus, special equipments are required during the catalyst preparation and ethylene polymerization processes. These equipments include glove box and schlenk line. Glove box equipped with the oxygen and moisture protection system was used to provide inert atmosphere. Schlenk line (Vacuum and Purge with inert gas) is the other equipment used to handle air-sensitive product.

3.4.2.1 Cooling system

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

3.4.2.2 Inert gas supply

The inert gas (argon) was passed through columns of BASF catalyst R3-11G as oxygen scavenger, molecular sieve 3×10^{-10} m to remove moisture. The BASF catalyst was regenerated by treatment with hydrogen at 300 °C overnight before

flowing the argon gas through all the above columns. The inert gas supply system is shown in **Figure 3.2**.

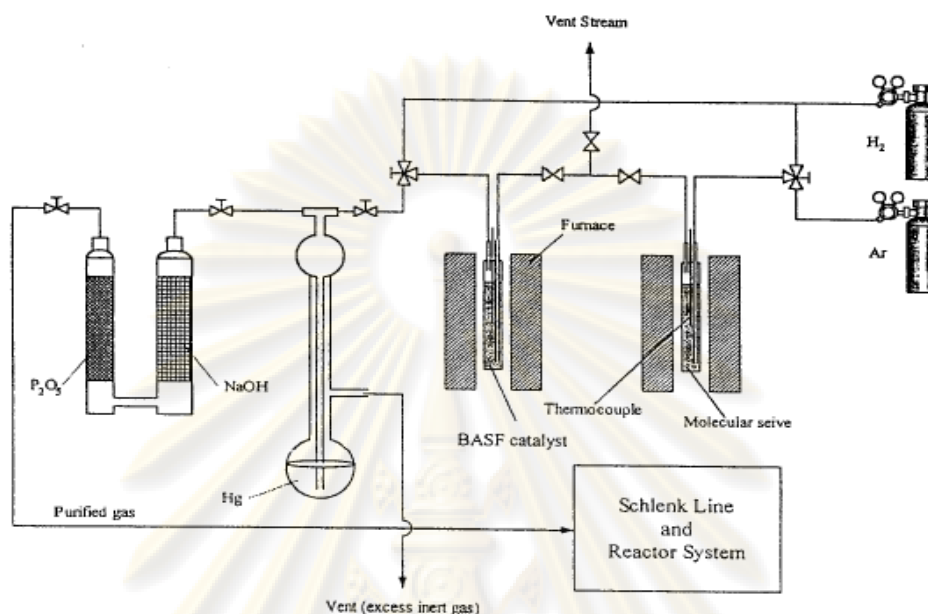


Figure 3.2 Inert gas supply system

3.4.2.3 Magnetic stirrer and heater

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

3.4.2.4 Reactor

A 100 ml glass flask connected with 3-ways valve was used as the polymerization reactor for atmospheric pressure system and a 100 ml stainless steel autoclave was used as the polymerization reactor for high pressure systems.

3.4.2.5 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 was shown in **Figure 3.3**.

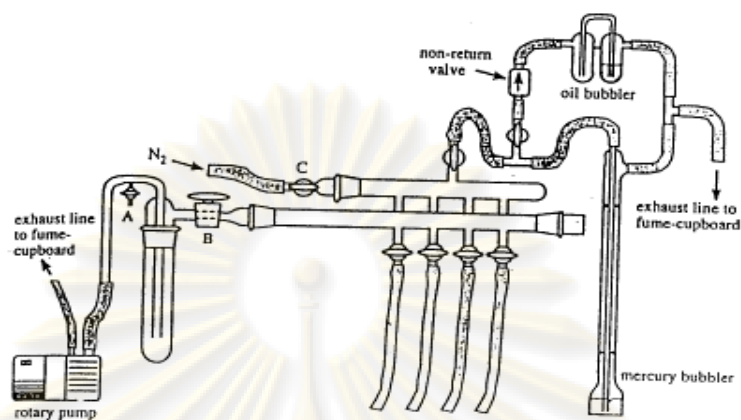


Figure 3.3 Schlenk line

3.4.2.6 Schlenk tube

Schlenk tube with a ground glass joint and side arm which is three-way glass valve is illustrated in **Figure 3.4**. Schlenk tubes with the volume of 50, 100 and 200 ml are used to prepare catalyst and store materials which were sensitive to oxygen and moisture.



Figure 3.4 Schlenk tube

3.4.2.7 Vacuum pump

The vacuum pump model 195 from Labconco Corporation was used. Pressure in the range of 10^{-1} to 10^{-3} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

3.4.2.8 Polymerization line

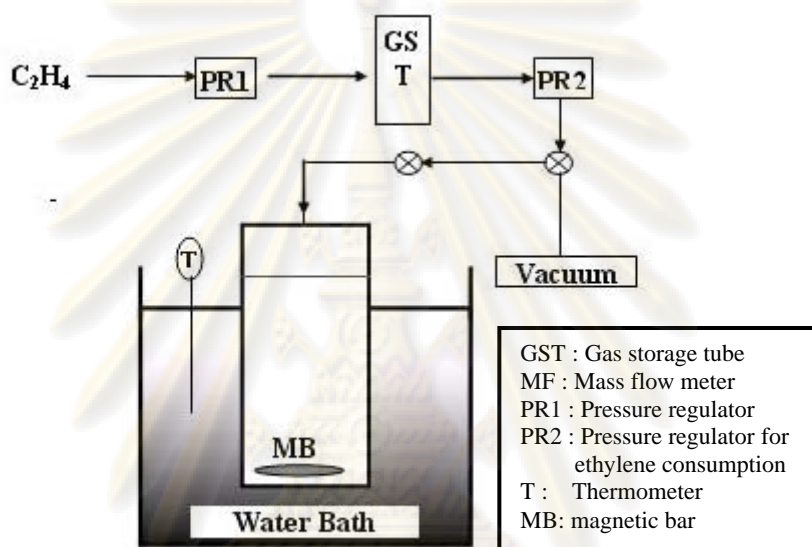


Figure 3.5 diagram of slurry phase polymerization system

3.5 Preparation of Catalyst Precursors

3.5.1 Recrystallization method: Catalyst A

$\text{TiCl}_4/\text{MgCl}_2$ catalyst was prepared by recrystallization method reacting MgCl_2 -ethanol adduct with TiCl_4 in the following procedure: 2 g (0.0210 mol) of anhydrous magnesium dichloride was suspended in 100 ml of heptanes and 0.1259 mol of ethanol was added dropwise at room temperature. After the end of addition, the solution was stirred for 2 hours. Then 28 mol of diethyl aluminum chloride (DEAC) was introduced dropwise and heated up to desired temperature and hold for 2 hours. Thereafter, 0.0255 mol of titanium tetrachloride was added and the mixture was

stirred for 2 hours. Finally, the catalyst obtained was washed with heptane for several times.

3.5.2 Chemical reaction method: Catalyst B

In the current study, a monoester-type catalyst $\text{TiCl}_4/\text{Mg}(\text{OEt})_2$ was prepared by a chemical reaction method without mechanical treatment (e.g. ball milling). TiCl_4 was reacted with a mixture of $\text{Mg}(\text{OEt})_2$ in the following procedure: $\text{Mg}(\text{OEt})_2$ 2.3 g (0.02 mol) and TiCl_4 4 ml (0.036 mol) in toluene (96 ml) were heated up to desired temperature and hold for 2 hours. The mixture was washed with toluene and reacted again with TiCl_4 (4ml) in toluene (96 ml) and then heated up to desired temperature and hold for 2 hours. Finally, the catalyst obtained was washed with hexane for several times.

3.6 Ethylene Polymerizations

Ethylene polymerization was carried out in a 100-ml semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. The required amounts of hexane (30 ml), TEA, catalyst (Al/Ti molar ratio = 100) were added into the reactor. The reactor was then immersed in liquid nitrogen to freeze the solution and evacuated to remove argon. The reactor was heated to polymerization temperature (80°C). Polymerization was started by continuous feeding of ethylene. The pressure in the reactor was kept at 50 psi. Ethylene consumption was fixed at 18 mmole. The reaction time was recorded for the activity calculation. After polymerization, the reaction was terminated by the addition of acidic methanol. The resulting polymer was then filtered and dried in an oven at 60°C for 6 h. The ethylene polymerization was prepared by $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst and $\text{MgCl}_2/\text{TiCl}_4$ catalyst using the same condition.

3.7 Characterization

3.7.1 N_2 physisorption

BET surface area of the samples after various pretreatments was performed to determine whether the total surface area changes upon the various

pretreatment conditions. It was determined using N₂ adsorption at 77 K in a Micromeritics ASAP 2000.

3.7.2 X-ray diffraction (XRD)

XRD was performed to determine the bulk crystalline phases of the samples. It was conducted using a SIEMENS D-5000 X-ray diffractometer with CuK_α ($\lambda = 1.54439 \times 10^{-10}$ m). The spectra were scanned at a rate of 2.4 degree/min in the range $2\theta = 20-80$ degrees.

3.7.3 Scanning electron microscopy (SEM)

SEM observation with a JEOL mode JSM-6400 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.

3.7.4 Thermogravimetric Analysis (TGA)

TGA was performed using TA Instruments SDT Q 600 analyzer. The samples of 10-20 mg and a temperature ramping from 40 to 600°C at 10°C/min were used in the operation. The carrier gas was N₂ UHP grade.

3.7.5 Electron Spin Resonance (ESR)

The electron spin resonance (ESR) spectra of catalyst samples were recorded at ambient temperature, with the use of JEOL JES-FE1XG spectrometer under N₂ atmosphere. The values of the g factor were determined against the Mn²⁺ standard.

3.7.6 Inductively Coupled Plasma (ICP)

Titanium content is measured using Perkin Elmer Optical. To digest the sample, the catalyst was with sulfuric acid. The mixture was stirred over night. After the catalyst was completely digested, the solution was diluted to a volume of 100 ml.

3.7.7 Differential Scanning Calorimetry (DSC)

The melting temperature (T_m) and crystallinity (X_c) of ethylene polymer products were 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 $10^\circ\text{C min}^{-1}$ in the temperature range of 50-200 $^\circ\text{C}$. Two heating cycles were employed. In the first scan, samples were heated to 200 $^\circ\text{C}$ 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 the mechanical and thermal history of samples. The overall crystallinity was calculated from the heat of fusion using the formula

$$X_C = H_m/H_p$$

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 [104,105].



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CHAPTER IV

RESULTS AND DISCUSSION

The purpose of this study is to investigate effects of different preparation procedures and characterize of the Ziegler-Natta catalyst for ethylene polymerization on the catalytic activity and polymer properties. The MgCl_2 and $\text{Mg}(\text{OEt})_2$ supports were also investigated regarding different parameters such as paddle speed, holding temperature and dropping rate, on the catalytic activity and polymer properties to make better understanding about polymerization nature.

4.1 Characterization of supports and catalysts

4.1.1 Titanium content with Inductively Coupled Plasma (ICP)

The MgCl_2 support was prepared by the recrystallization method in the same manner reported by of Norio Kashiwa et al. [106] and the $\text{Mg}(\text{OEt})_2$ support was prepared by the chemical reaction method in the same manner as that of Minoru Terano et al. [65]. During preparation of catalyst, the synthesis parameters such as paddle speed, holding temperature and dropping rate were varied. **Table 4.1** and **Table 4.2** show titanium content of two catalyst systems under different synthesis conditions. The titanium content of recrystallization method was in range of 2.0-6.0 %wt and that of chemical reaction method was in range of 8.0-10.0 %wt.

4.1.2 BET specific surface area with N_2 physisorption

The various catalysts with different the specific surface area were characterized by BET method. **Table 4.3** and **Table 4.4** show BET specific surface area of two catalyst systems under different synthesis conditions. The surface areas of recrystallization method were in range of 55.7 – 138.5 m^2/g and that of chemical reaction method were in range of 99.2 – 142.2 m^2/g .

Table 4.1 Ti content obtained by ICP of MgCl₂/TiCl₄ catalyst by recrystallization

Sample	Condition	% wt Ti
A 001	Paddle speed 100rpm	3.09
A 002	Paddle speed 200rpm	2.86
A 003	Paddle speed 300rpm	4.91
A 004	Paddle speed 400rpm	5.94
A 005	Holding temperature 50 °C	3.18
A 006	Holding temperature 60 °C	2.96
A 007	Holding temperature 70 °C	3.09
A 008	Holding temperature 80 °C	2.75
A 009	Holding temperature 90 °C	3.12
A 010	Dropping rate 5 cc/hr	3.16
A 011	Dropping rate 10 cc/hr	3.08
A 012	Dropping rate 20 cc/hr	3.12
A 013	Dropping rate 40 cc/hr	3.04

A001-A004: Holding temperature = 70 °C, dropping rate = 20 cc/hr

A005-A009: Paddle speed = 100 rpm, dropping rate = 20 cc/hr

A010-A013: Paddle speed = 100 rpm, Holding temperature = 90 °C

Table 4.2 Ti content obtained by ICP of Mg(OEt)₂/TiCl₄ catalyst by chemical reaction

Sample	Condition	% wt Ti
B 001	Paddle speed 100rpm	10.60
B 002	Paddle speed 200rpm	9.94
B 003	Paddle speed 300rpm	9.50
B 004	Paddle speed 400rpm	8.85
B 005	Holding temperature 50 °C	8.50
B 006	Holding temperature 60 °C	9.92
B 007	Holding temperature 70 °C	8.64
B 008	Holding temperature 80 °C	9.93
B 009	Holding temperature 90 °C	9.94
B 010	Dropping rate 5 cc/hr	10.93
B 011	Dropping rate 10 cc/hr	10.36
B 012	Dropping rate 20 cc/hr	9.94
B 013	Dropping rate 40 cc/hr	9.67

B001-B004: Holding temperature = 90 °C, dropping rate = 20 cc/hr

B005-B009: Paddle speed = 200 rpm, dropping rate = 20 cc/hr

B010-B013: Paddle speed = 200 rpm, Holding temperature = 90 °C

Table 4.3 BET specific surface area of MgCl₂/TiCl₄ catalyst by recrystallization

Sample	Condition	specific surface area (m ² /g)
A 001	Paddle speed 100rpm	123.1
A 002	Paddle speed 200rpm	89.0
A 003	Paddle speed 300rpm	80.5
A 004	Paddle speed 400rpm	55.7
A 005	Holding temperature 50 °C	114.1
A 006	Holding temperature 60 °C	111.5
A 007	Holding temperature 70 °C	123.1
A 008	Holding temperature 80 °C	125.3
A 009	Holding temperature 90 °C	138.5
A 010	Dropping rate 5 cc/hr	124.1
A 011	Dropping rate 10 cc/hr	121.0
A 012	Dropping rate 20 cc/hr	138.5
A 013	Dropping rate 40 cc/hr	120.6

A001-A004: Holding temperature = 70 °C, dropping rate = 20 cc/hr

A005-A009: Paddle speed = 100 rpm, dropping rate = 20 cc/hr

A010-A013: Paddle speed = 100 rpm, Holding temperature =90 °C

Table 4.4 BET specific surface area of Mg(OEt)₂/TiCl₄ catalyst by chemical reaction

Sample	Condition	specific surface area (m ² /g)
B 001	Paddle speed 100rpm	110.1
B 002	Paddle speed 200rpm	142.2
B 003	Paddle speed 300rpm	119.8
B 004	Paddle speed 400rpm	115.2
B 005	Holding temperature 50 °C	99.2
B 006	Holding temperature 60 °C	108.9
B 007	Holding temperature 70 °C	117.2
B 008	Holding temperature 80 °C	124.5
B 009	Holding temperature 90 °C	142.2
B 010	Dropping rate 5 cc/hr	126.9
B 011	Dropping rate 10 cc/hr	121.2
B 012	Dropping rate 20 cc/hr	142.2
B 013	Dropping rate 40 cc/hr	120.3

B001-B004: Holding temperature =90 °C, dropping rate = 20 cc/hr

B005-B009: Paddle speed = 200 rpm, dropping rate = 20 cc/hr

B010-B013: Paddle speed = 200 rpm, Holding temperature = 90 °C

4.1.3 Crystalline phases with X-ray diffraction (XRD)

XRD patterns represent the crystal structure of the MgCl₂ support and Mg(OEt)₂ supports as demonstrated in **Figure 4.1**. Anhydrous MgCl₂ has a cubic close packing (ccp) structure, which gives strong XRD patterns at $2\theta = 15^\circ$ (0 0 3 plane), 30° (0 0 6 plane), 35° (0 0 4 plane) and 50° (1 1 0 plane) [107-109] and the

paraffin film, which gives XRD peaks at $2\theta = 14^\circ$, 21° and 24° , was used to protect all samples from air. The literature from Giannini has reported that δ - MgCl_2 , which provided disorder structure was the key factor for the active MgCl_2 [111]. For the magnesium ethoxide support, XRD patterns cannot be observed due to its highly dispersed form.

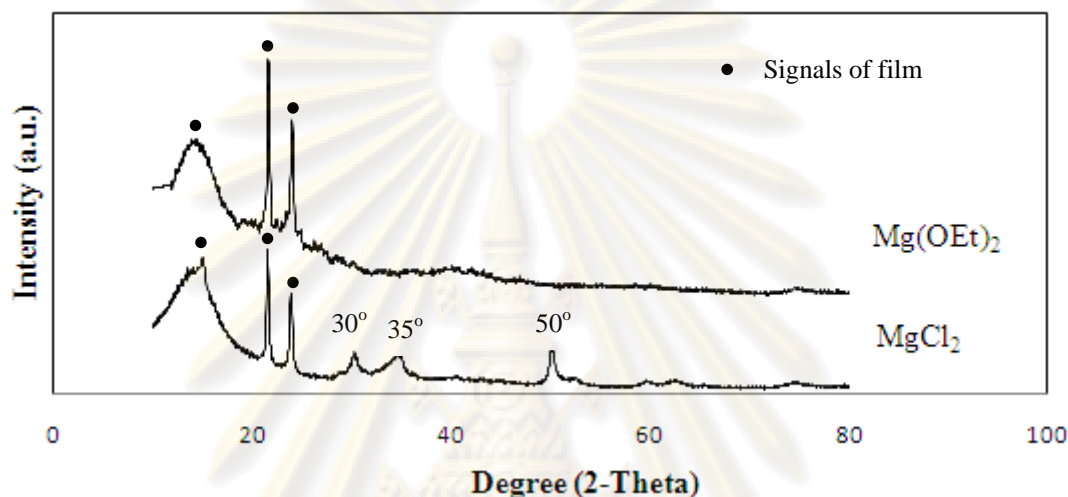
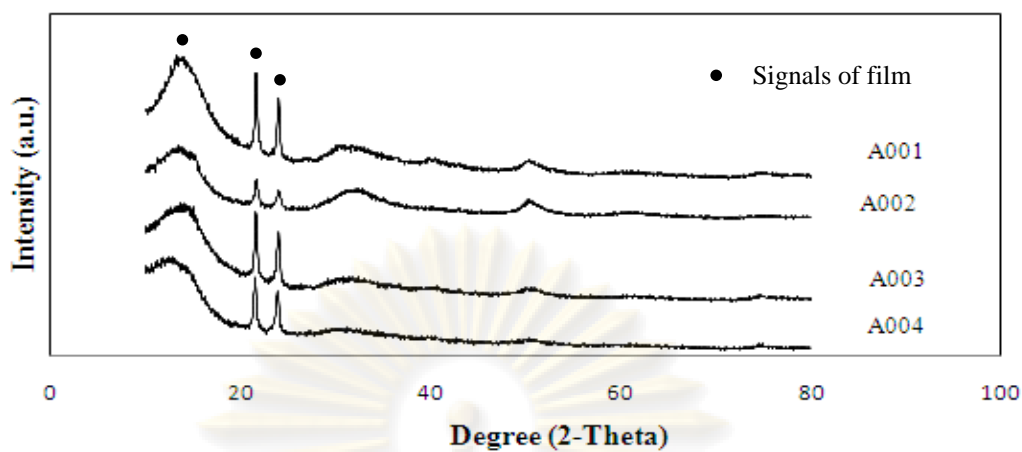
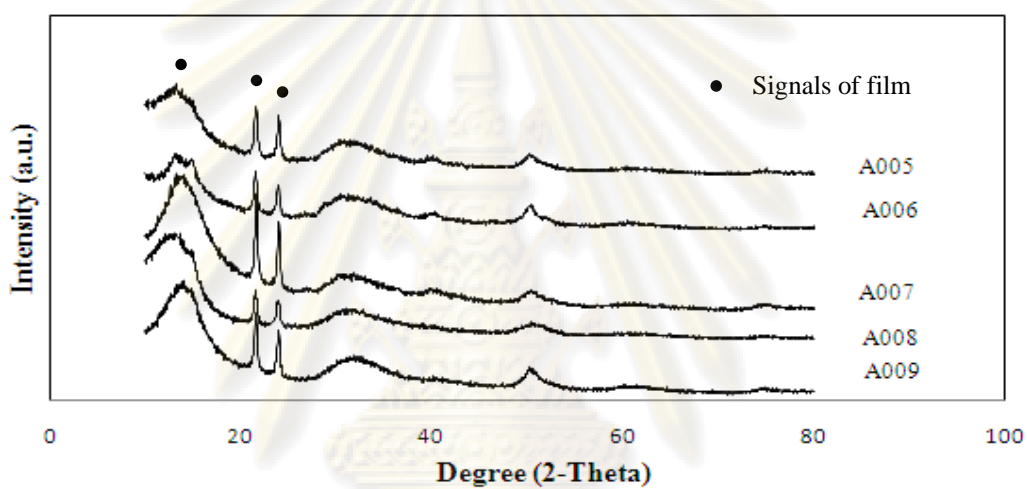


Figure 4.1 XRD patterns of different supports

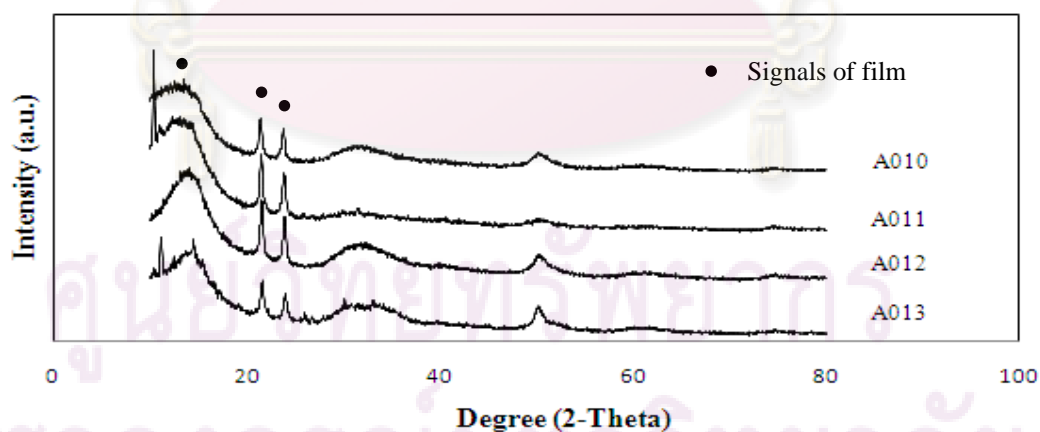
Figure 4.2 shows XRD patterns of $\text{MgCl}_2/\text{TiCl}_4$ with different synthesis condition. After treatment of MgCl_2 with TiCl_4 , the peak intensity of XRD pattern of the recrystallized MgCl_2 decreased, while still gives similar pattern with those of anhydrous MgCl_2 [107]. **Figure 4.3** shows XRD patterns of $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ with different synthesis conditions. For the $\text{Mg}(\text{OEt})_2$ was prepared by the chemical reaction method, it has been already known that $\text{Mg}(\text{OEt})_2$ is converted to MgCl_2 by reaction with TiCl_4 . It was noticed that no characteristic peaks of $\text{Mg}(\text{OEt})_2$ were present in the XRD patterns of $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst, namely, the original structure of $\text{Mg}(\text{OEt})_2$ was destroyed by reaction with TiCl_4 . $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst shows a similar diffractogram to the activated MgCl_2 . These results confirmed again that $\text{Mg}(\text{OEt})_2$ is converted to MgCl_2 by reaction with TiCl_4 [6]. The XRD patterns did not change with effect of synthesis parameters.



(a)



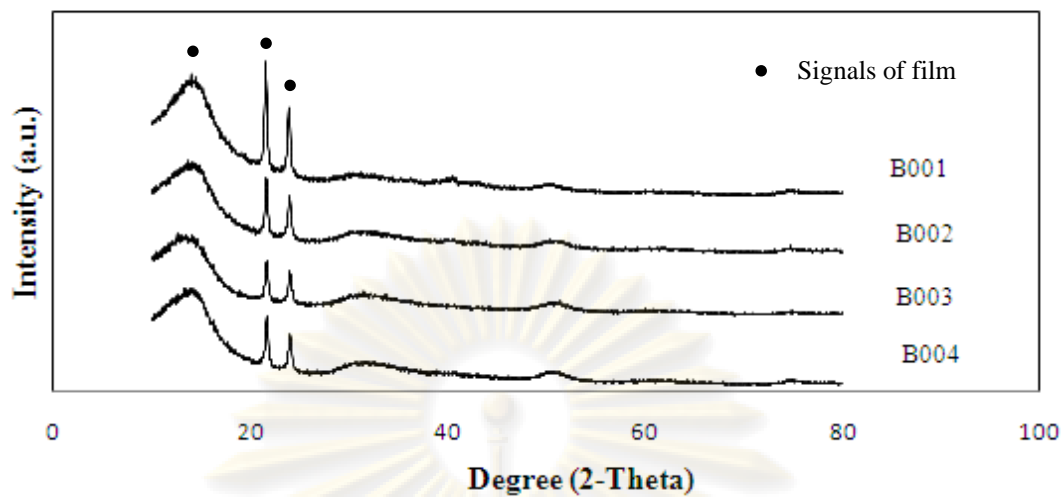
(b)



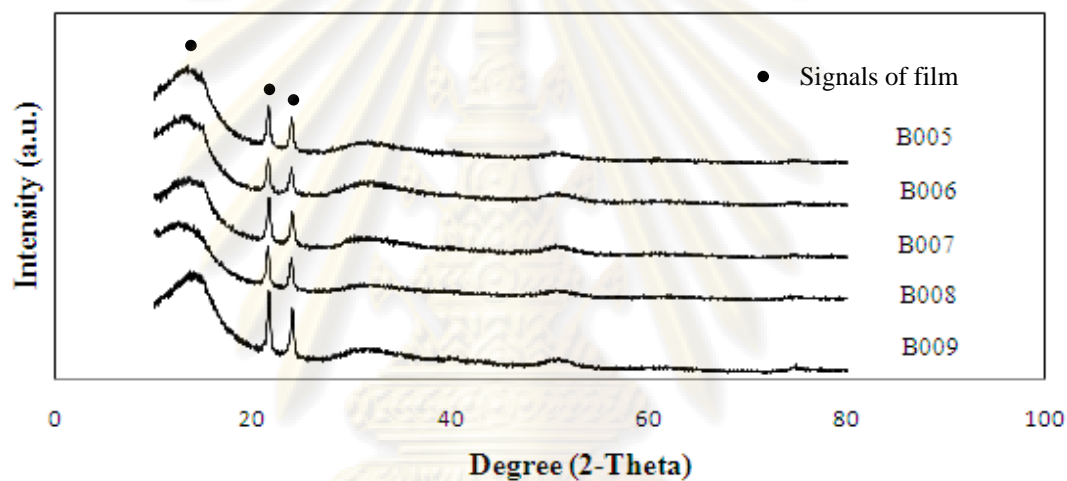
(c)

Figure 4.2 XRD pattern of $\text{MgCl}_2/\text{TiCl}_4$ with different synthesis conditions

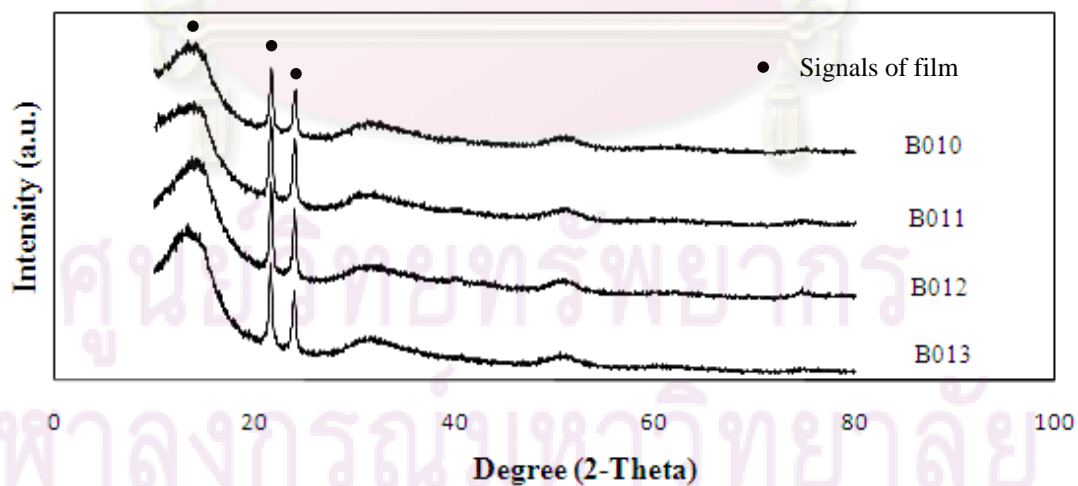
(a) Paddle speed (b) Holding temperature (c) Dropping rate



(a)



(b)



(c)

Figure 4.3 XRD pattern of $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ with different synthesis conditions

(a) Paddle speed (b) Holding temperature (c) Dropping rate

4.1.4 Weight loss with Thermogravimetric analysis (TGA)

In this study, TiCl_4 was dispersed by treatment onto the various supports, such as MgCl_2 and $\text{Mg}(\text{OEt})_2$. The degree of interaction between the support and the TiCl_4 can be determined by the TGA measurement. The TGA provide information on the degree of interaction for the TiCl_4 bound to the support in terms of weight loss and removal temperature. The TGA profiles of $\text{MgCl}_2/\text{TiCl}_4$ and $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ with different synthesis conditions was shown in **Figure 4.4 - Figure 4.6**. All of profiles are similar upon various synthesis parameters. Because of the same XRD patterns, all components in $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ system were similar to all components in $\text{MgCl}_2/\text{TiCl}_4$ system after treated with TiCl_4 . As a result, TGA patterns were the similar. A weight loss around 213°C can be attributed to the removal of TiCl_4 from the crystalline MgCl_2 matrix and around 515°C was due to the removal of electron donor as reported by Forte et al. [113]. For our result, a weight loss for the removal TiCl_4 occurred around 200°C and no weight loss around 515°C was observed because electron donor was absent in our system.

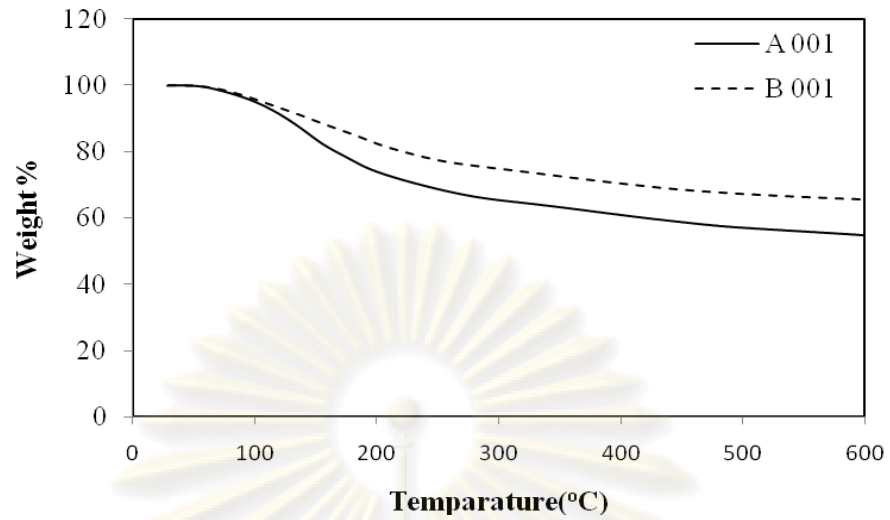


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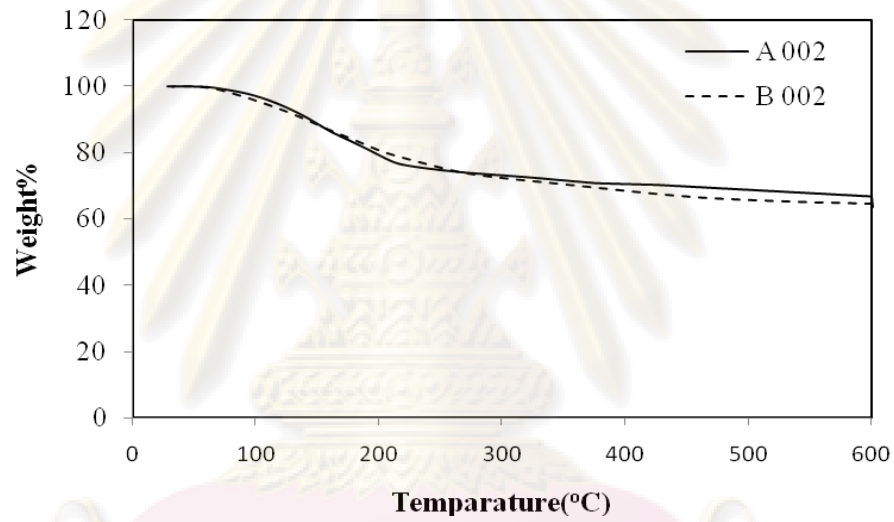
Table 4.5 Weight loss onset temperature of $\text{MgCl}_2/\text{TiCl}_4$ by recrystallization and $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst by chemical reaction

System	catalyst	weight loss onset temperature ($^{\circ}\text{C}$)	weight loss (%)
$\text{MgCl}_2/\text{TiCl}_4$	A 001	138	25
	A 002	185	21
	A 003	257	29
	A 004	257	40
	A 005	155	30
	A 006	150	28
	A 007	138	25
	A 008	134	36
	A 009	140	24
	A 010	228	26
	A 011	262	40
	A 012	250	32
	A 013	289	35
$\text{Mg}(\text{OEt})_2/\text{TiCl}_4$	B 001	190	20
	B 002	194	30
	B 003	210	35
	B 004	231	29
	B 005	207	33
	B 006	225	32
	B 007	162	32
	B 008	211	30
	B 009	194	30
	B 010	226	23
	B 011	222	32
	B 012	194	30
	B 013	209	25

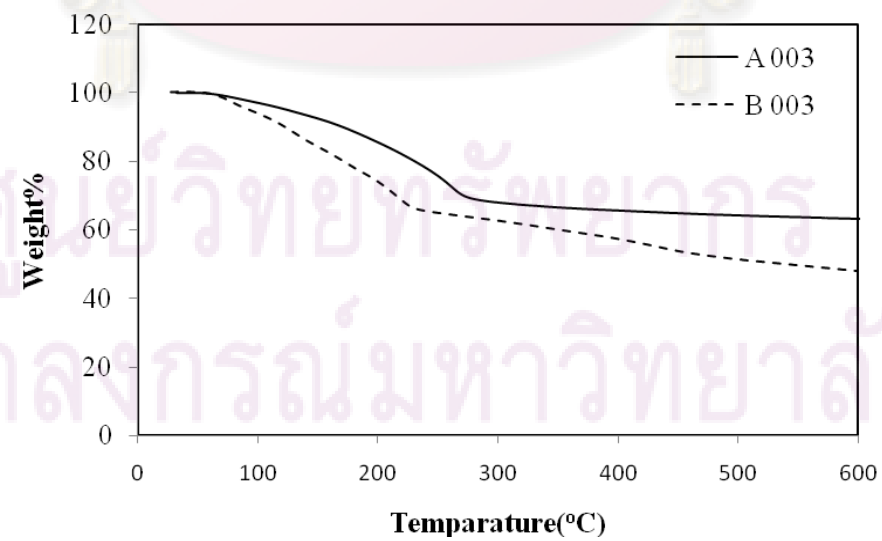
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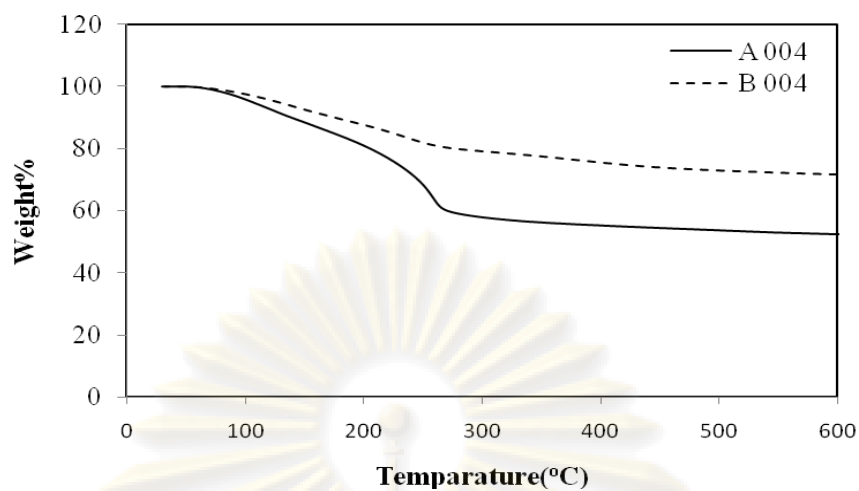
(a)



(b)

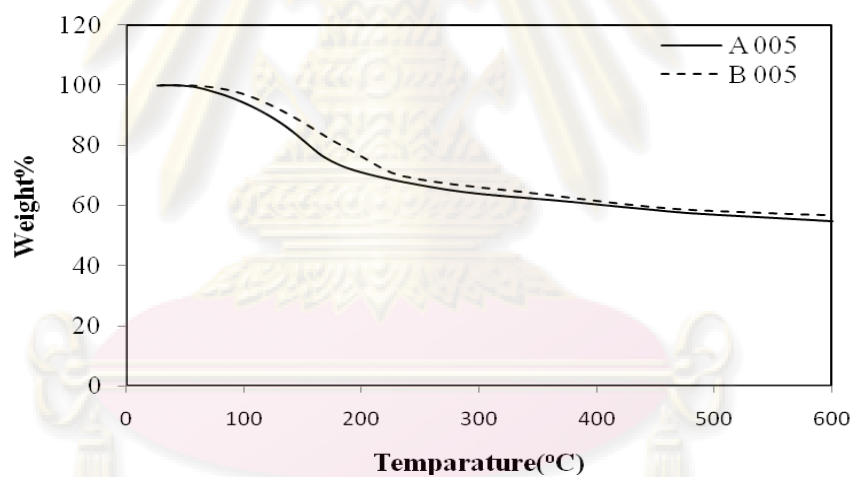


(c)

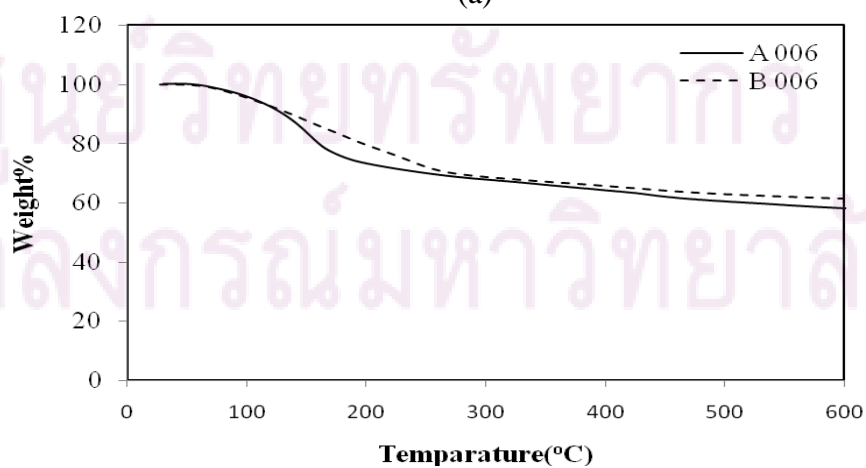


(d)

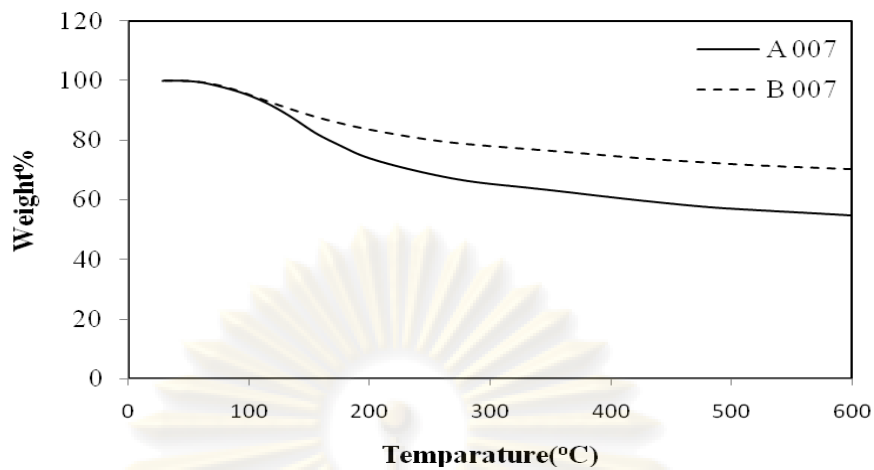
Figure 4.4 TGA profile of $\text{MgCl}_2/\text{TiCl}_4$ and $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ with various paddle speed (a) 100 rpm (b) 200 rpm (c) 300 rpm (d) 400 rpm



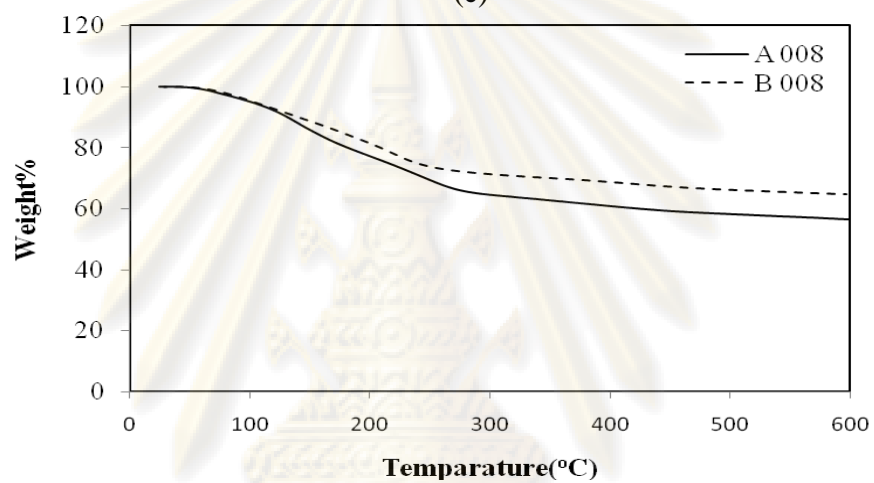
(a)



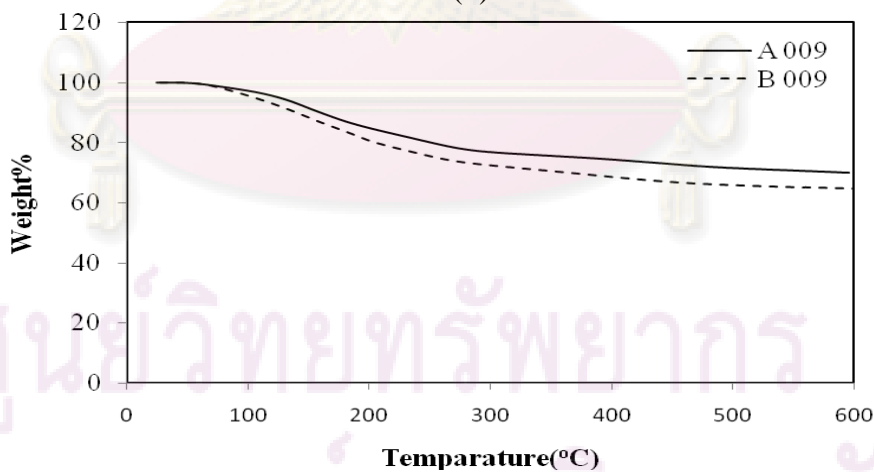
(b)



(c)

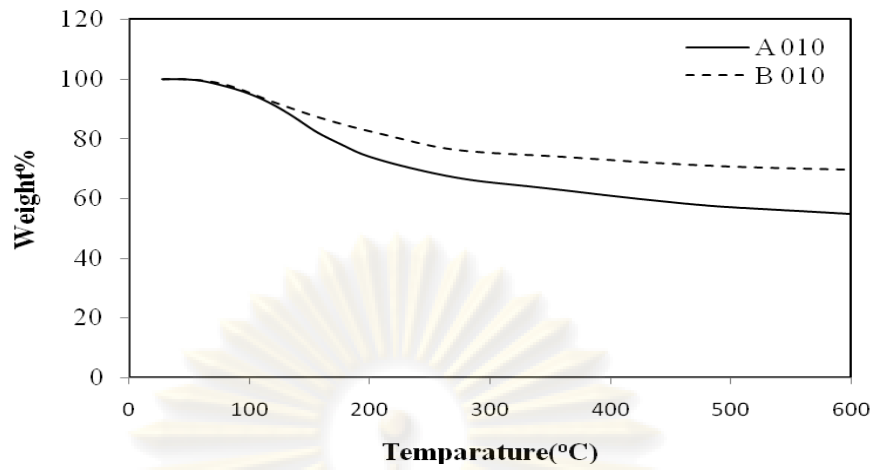


(d)

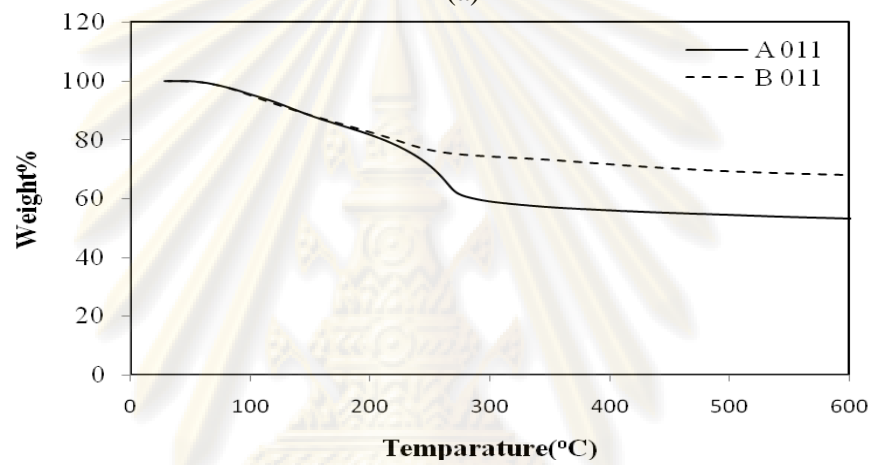


(e)

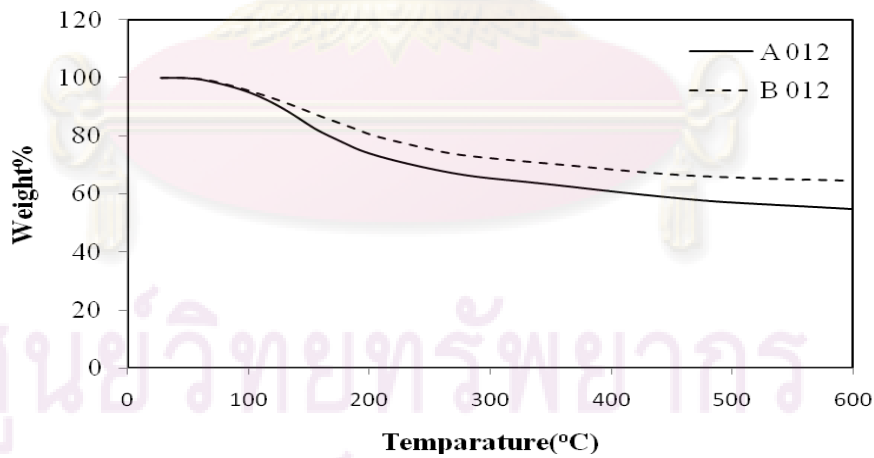
Figure 4.5 TGA profile of $\text{MgCl}_2/\text{TiCl}_4$ and $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ with various holding temperature (a) 50°C (b) 60°C (c) 70°C (d) 80°C (e) 90°C



(a)

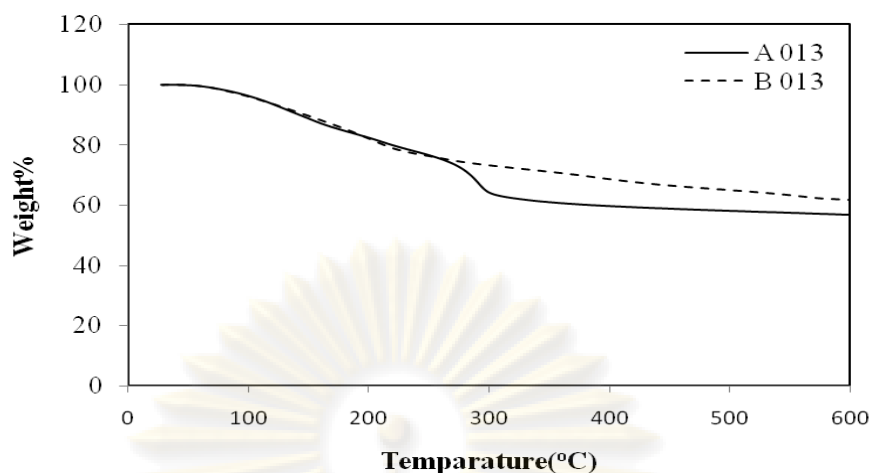


(b)



(c)

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(d)

Figure 4.6 TGA profile of $\text{MgCl}_2/\text{TiCl}_4$ and $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ with various dropping rate (a) 5 cc/hr (b) 10 cc/hr (c) 20 cc/hr (d) 40 cc/hr

4.1.5 Electron Spin Resonance (ESR) spectroscopy

It is well known that three various titanium valences; Ti^{4+} , Ti^{3+} and Ti^{2+} are formed by reacting TiCl_4 with an alkylaluminium such as AlR_3 (R = alkyl group). Ti^{3+} species is considerably active for the polymerization of both ethylene and propylene while over-reduction of Ti^{3+} to Ti^{2+} leads to ethylene polymerization only [113, 114]. These transition metal oxidation states have been widely investigated through electron spin resonance (ESR) spectroscopy which is useful in detecting free radicals from paramagnetic solid materials. The ESR spectra of the catalyst solution from recrystallization and chemical reaction method are shown in **Figure 4.7** It was noted that the amount of Ti^{3+} species could be obtained from relative intensity of a signal with a g-factor of 1.97 for recrystallization method and 1.97 for chemical reaction method, which was presented in two catalyst systems [115]. The recrystallization method can result in higher amount of Ti^{3+} more than the chemical reaction method.

The titanium content from chemical reaction was higher than recrystallization method as shown in **Table 4.2**. The organoaluminum cocatalyst plays an important role in active site formation by alkylation and reduction of the titanium species. Then, the various Al/Ti ratios at 50, 100, 150, 200 and 250 were investigated to effect on the amount of Ti^{3+} for chemical reaction method as shown in **Figure 4.8**. The various Al/Ti ratios have slightly effect on the amount of Ti^{3+} from ESR spectra.

The formation to active site (amount of Ti^{3+}) between catalyst and cocatalyst was not high with Al/Ti ratio increase, then recrystallization method has the amount of Ti^{3+} higher than chemical reaction method.

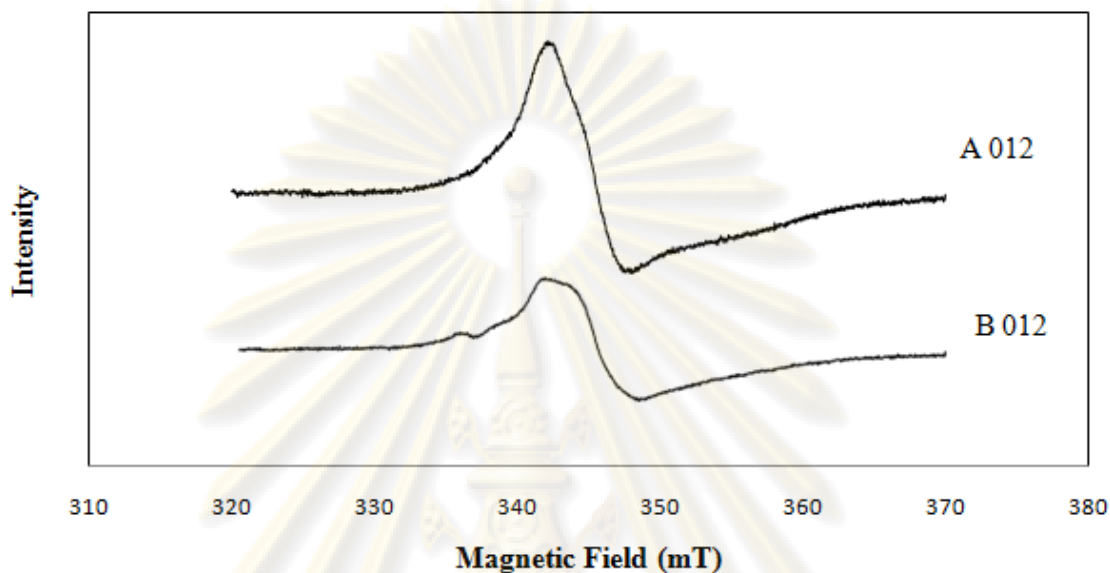


Figure 4.7 ESR spectra of the catalyst $TiCl_4/MgCl_2$ and $TiCl_4/ Mg(OEt)_2-TEA$ treated

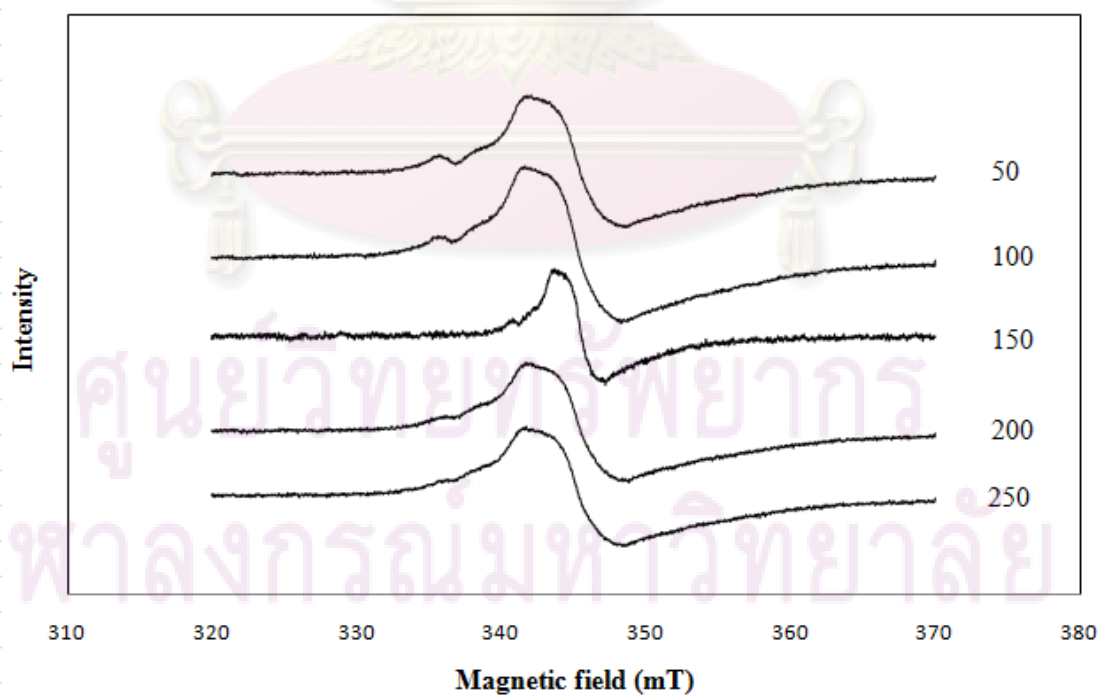
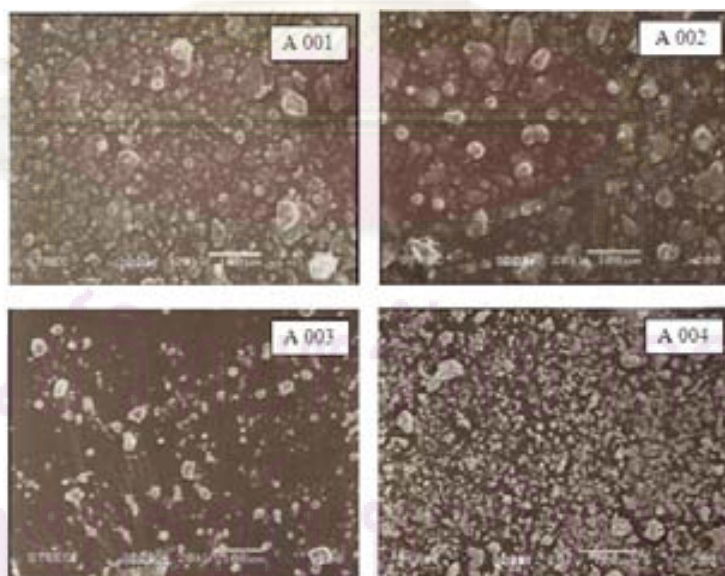


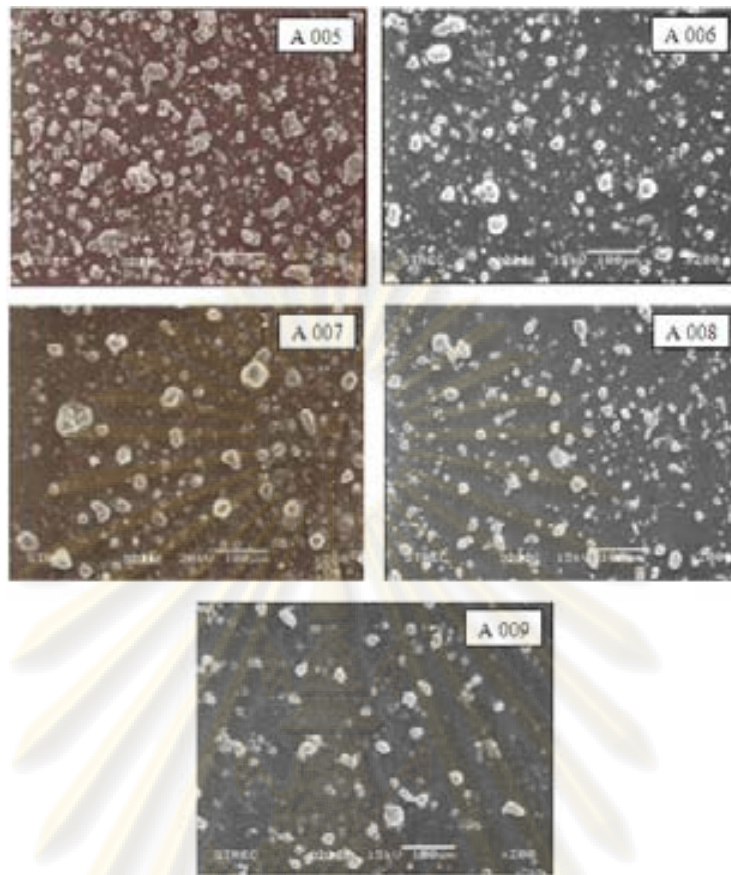
Figure 4.8 ESR spectra of catalyst by chemical reaction at different Al/Ti ratios

4.1.6 Morphology with Scanning Electron Microscopy (SEM)

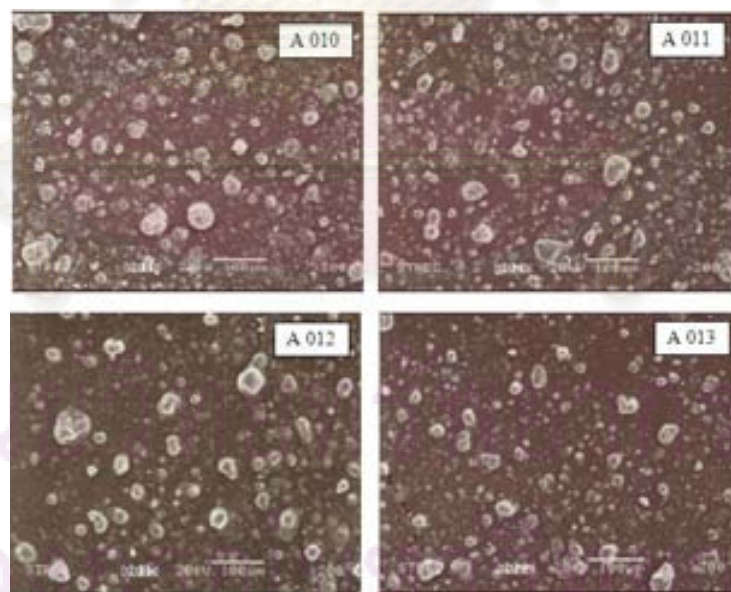
SEM was performed to determine morphologies of two catalyst systems with various synthesis conditions. **Figure 4.9** reveals SEM micrographs of catalyst by recrystallization method with various paddle speeds, holding temperatures and dropping rates. SEM micrograph of paddle speeds was shown in **figure 4.9 (a)**. It shows that crystal size slightly decreased with faster speed of paddle. **Figure 4.9 (b)** shows that crystal size did not change with holding temperatures. **Figure 4.9 (c)** shows that the crystal shape varied with dropping rate. Crystal shape was almost sphere from dropping rate at 40 cc/hr to 5 cc/hr. As exothermic reaction, the fast dropping rate contributes to increase the temperature of system. Heat of reaction could not release from system leading to very difficult to control of temperature and then the supports might rapidly break [116]. As a result, the catalyst shape was not sphere. For slow dropping rate, heat can be well removed from the system and, then it can control morphology better than the fast dropping rate. **Figure 4.10** (a), (b) and (c) is SEM micrograph of catalyst by chemical reaction method with various paddle speeds, holding temperatures and dropping rates. The various synthesis conditions results were similar to that of recrystallization method.



(a)

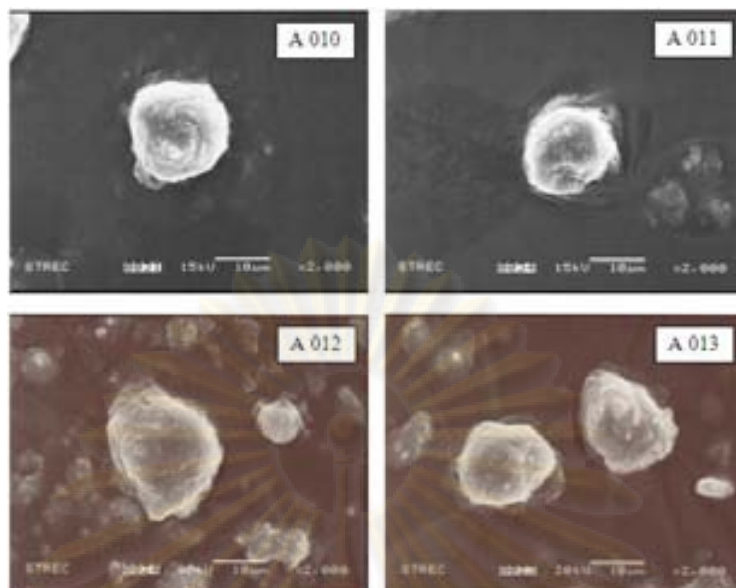


(b)



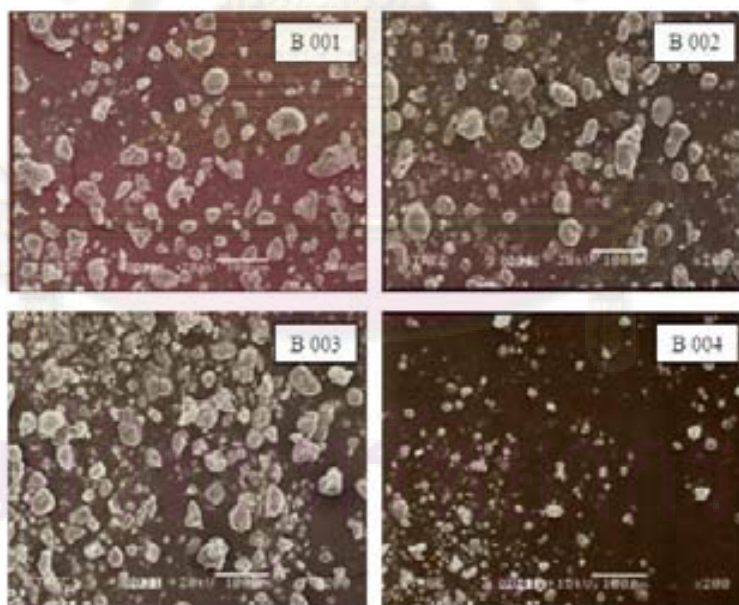
(c) 200X

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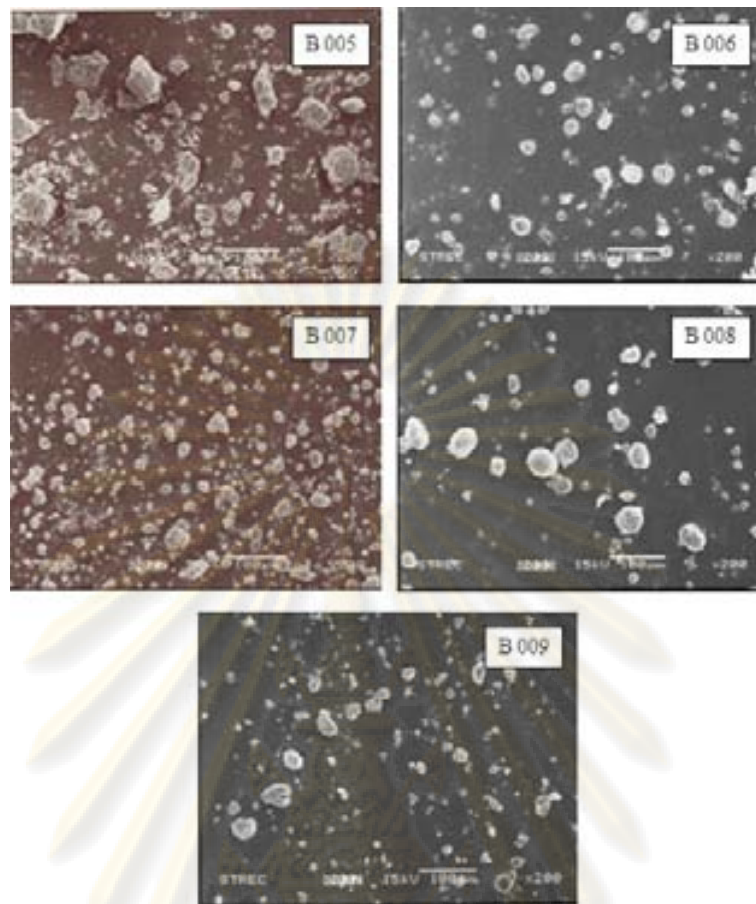


(c) 2000X

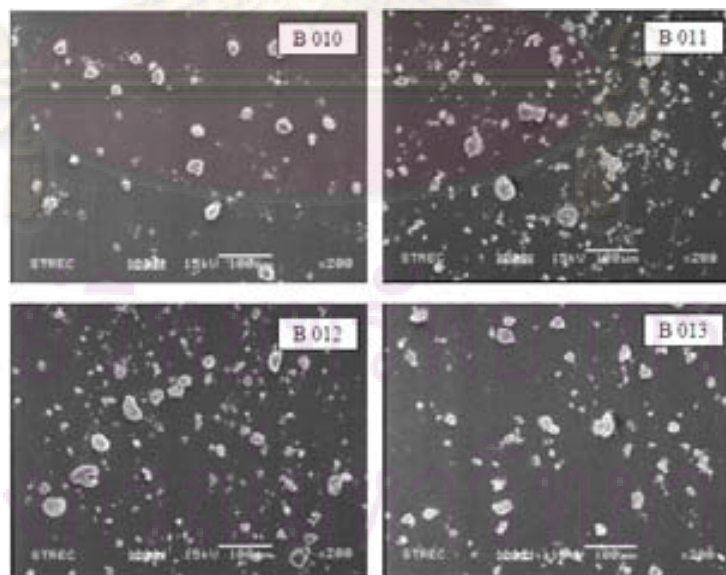
Figure 4.9 SEM micrographs of catalyst with recrystallization method (a) Paddle speed (b) Holding temperature and (c) Dropping rate



(a)

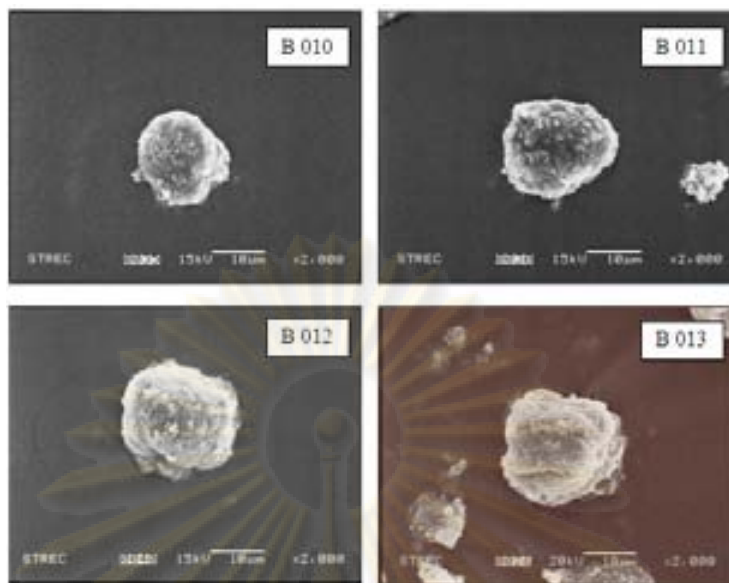


(b)



(c) 200X

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(c) 2000X

Figure 4.10 SEM micrographs of catalyst with chemical reaction method (a) Paddle speed (b) Holding temperature and (c) Dropping rate

4.2 Characteristics and catalytic properties ethylene polymerization

The different preparation methods (recrystallization and chemical reaction) were used to investigate the catalytic activities. The ethylene polymerization via different supports of MgCl_2 and $\text{Mg}(\text{OEt})_2$ was performed in order to determine the characteristics and catalytic properties of polymer influenced by the various synthesis parameters such as paddle speeds, holding temperatures and dropping rates. Triethylalumina (TEA) was used as cocatalyst having the molar ratios of $\text{Al/Ti} = 100$. The ethylene polymerization were performed in hexane at 80°C feeding 0.018 mol of ethylene gas (6 psi was observed from the pressure gauge), pressure in reactor = 50 psi, catalyst 0.01 g with total solution volume of 30 ml.

4.2.1 $\text{MgCl}_2/\text{TiCl}_4$ catalyst by recrystallization method

4.2.1.1 The effect of paddle speed on the catalytic activity

The catalytic activities via various paddle speed are listed in **Table 4.6**.

Table 4.6 Activity for paddle speed effect by recrystallization method

Entry	Holding Temperature (°C)	Paddle Speed	Time(s)	Yield(g)	Activity (KgPE/molTi.h)
1	70	100	150	0.4578	1702
2	70	200	280	0.4513	971
3	70	300	270	0.4756	618
4	70	400	280	0.4411	457

Polymerization condition: catalyst: 10 mg , cocatalyst: TEA, Al/Ti (mol/mol) = 100 , solvent: n-hexane(30 ml), Pressure 6 psi , Temperature = 80 °C

Effect of paddle speed on catalytic activity was investigated by using $MgCl_2/TiCl_4$ catalyst, prepared by recrystallization method, was shown in **Table 4.6** Paddle speed has significant effect on catalytic activity; catalytic activity results with various paddle speeds from 100, 200, 300 and 400 rpm showed the maximum catalytic activity at 100 rpm. It was suitable stirring-speed, which results in uniform and smooth emulsion [102]. Considering the paddle speed at 200, 300 and 400 rpm, the emulsion was more turbulent leading to increasing $MgCl_2$ attachment at the wall of reactor. Therefore, ratio of substance during reactions was error, hence catalytic activity then decreases at that paddle speed. The BET surface area showed the value with in agreement with the catalytic activity. On the other words, the high surface area was high catalytic activity obtained.

4.2.1.2 The effect of holding temperature on the catalytic activity

The catalytic activities via different holding temperature are listed in

Table 4.7.**Table 4.7** Activity for holding temperature effect by recrystallization method

Entry	Optimum Paddle Speed	Holding Temperature (°C)	Time (sec)	Yield (g)	Activity (KgPE/molTi.h)
1	100	50	168	0.4671	1507
2	100	60	180	0.4787	1548
3	100	70	150	0.4578	1702
4	100	80	175	0.4762	1705
5	100	90	150	0.4669	1719

Polymerization condition: catalyst: 10 mg , cocatalyst: TEA, Al/Ti (mol/mol) = 100 , solvent: n-hexane(30 ml), Pressure 6 psi , Temperature = 80 °C

Table 4.7 shows effect of holding temperature on catalytic activity was studied using $\text{MgCl}_2/\text{TiCl}_4$ catalyst prepared by recrystallization method. The paddle speed at 100 rpm was chosen to examine holding temperature effect because it obtained the maximum catalytic activity. The BET surface area showed the value that matched with the catalytic activity value. Considering various holding temperatures at 50, 60, 70, 80 and 90°C, it showed that at holding temperature lower than 70°C had slightly effect on catalytic activity, meanwhile holding temperature at higher than 70°C had no effect on the catalytic activity. Holding temperature had slightly effect on catalytic activity because heat of reaction had no effect on active site of catalyst. High temperature caused only fast reaction. Moreover ethanol was used to adduct MgCl_2 during reaction. Due to boiling point of ethanol, it might remain in the system at low temperature, that activity slightly decreased. When temperature was heated up to high temperature, ethanol did not remain in the system, it will not affect to the reaction.

4.2.1.3 The effect of dropping rate on the catalytic activity

The catalytic activities via different dropping rate are listed in **Table 4.8**.

Table 4.8 Activity for dropping rate effect by recrystallization method

Entry	Optimum Paddle Speed	Optimum Holding Temperature (°C)	Dropping rate (cc/hr)	Time (sec)	Yield (g)	Activity (KgPE/molTi.h)
1	100	90	5	150	0.4457	1620
2	100	90	10	164	0.4492	1532
3	100	90	20	150	0.4669	1719
4	100	90	40	167	0.4586	1557

Polymerization condition: catalyst: 10 mg, cocatalyst: TEA, Al/Ti (mol/mol) = 100, solvent: n-hexane (30 ml), Pressure 6 psi, Temperature = 80 °C

$\text{MgCl}_2/\text{TiCl}_4$ catalyst from recrystallization method was prepared with various dropping rates of TiCl_4 . Effect of various dropping rates of TiCl_4 on catalytic activity was shown in **Table 4.8**. Paddle speed at 100 rpm and holding temperature at 90°C obtained the maximum activity were chosen to prepare catalyst. Dropping rate was varied from 5, 10, 20 and 40 cc/hr. The polymer grain was similar to the crystal shape of catalyst. The result showed that catalytic activity did not significantly change with dropping rate. Dropping rate had little effect on crystal shape of catalyst and polymer grain of polyethylene. For slow dropping rate, heat could be removed from system,

and then it prefers to control morphology than fast dropping rate. The BET surface area with showed the value that matched with the catalytic activity value.

4.2.2 Mg(OEt)₂/TiCl₄ catalyst by chemical reaction method

4.2.2.1 The effect of paddle speed on the catalytic activity

The catalytic activities via various paddle speeds are listed in **Table**

4.9.

Table 4.9 Activity for paddle speed effect by chemical reaction method

Entry	Holding Temperature (°C)	Paddle Speed	Time(s)	Yield(g)	Activity (KgPE/molTi.h)
1	90	100	235	0.4445	307
2	90	200	140	0.4455	551
3	90	300	166	0.4231	462
4	90	400	216	0.4867	438

Polymerization condition: catalyst: 10 mg, cocatalyst: TEA, Al/Ti (mol/mol) = 100 , solvent: n-hexane(30 ml), Pressure 6 psi , Temperature = 80 °C

Effect of paddle speed on catalytic activity was investigated by using Mg(OEt)₂/TiCl₄ catalyst, which was prepared by chemical reaction method, as shown in **Table 4.9**. Catalytic activity results with various paddle speed from 100, 200, 300 and 400 rpm showed the maximum catalytic activity at 200 rpm. It was suitable stirring-speed which results in uniform and smooth emulsion [102]. Emulsion was not homogenous at paddle speed 100 rpm due to too slow speed. Emulsion was more turbulent at paddle speed 300 and 400 rpm due to too high speed. Those results led to decreased catalytic activity.

4.2.2.2 The effect of holding temperature on the catalytic activity

The catalytic activities via various holding temperatures are listed in

Table 4.10.

Table 4.10 Activity for holding temperature effect by chemical reaction method

Entry	Optimum Paddle Speed	Holding Temperature (°C)	Time (sec)	Yield (g)	Activity (KgPE/molTi.h)
1	100	50	306	0.3584	237
2	100	60	244	0.4738	337
3	100	70	220	0.4667	423
4	100	80	157	0.4367	482
5	100	90	140	0.4455	551

Polymerization condition: catalyst: 10 mg, cocatalyst: TEA, Al/Ti (mol/mol) = 100 , solvent: n-hexane(30 ml), Pressure 6 psi , Temperature = 80 °C

Table 4.10 shows the effect of holding temperature on catalytic activity using $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst, which was prepared by chemical reaction method. Paddle speed at 200 rpm was chosen to examine holding temperature effect because it obtained the maximum catalytic activity. Considering various holding temperatures at 50, 60, 70, 80 and 90°C, it showed that the holding temperature at 50°C gave minimum activity, while the holding temperature at 90°C gave maximum activity. Holding temperature had effect on reaction of catalyst for chemical reaction method because alkyl group was changed to Cl group. During the reaction with TiCl_4 , hydrocarbon solvent are incorporated and a reaction with TiCl_4 takes place in this layer to form MgCl_2 and $\text{TiCl}_{4-n}(\text{OEt})_n$ compounds. $\text{TiCl}_{4-n}(\text{OEt})_n$ compounds are inactive in system. The suspended magnesium ethoxide is transformed into the MgCl_2 support and at the same time, TiCl_4 is absorbed. For high temperature, $\text{TiCl}_{4-n}(\text{OEt})_n$ compounds can be dissolved in the system again and the soluble $\text{TiCl}_{4-n}(\text{OEt})_n$ compounds are removed by washing with petrol[117]. Therefore, holding temperature at 90°C gave the maximum activity.

4.2.2.3 The effect of dropping rate on the catalytic activity

The catalytic activities via various dropping rates are listed in **Table**

4.11.

Table 4.11 Activity for dropping rate effect by chemical reaction method

Entry	Optimum Paddle Speed	Optimum Holding Temperature (°C)	Dropping rate (cc/hr)	Time (sec)	Yield (g)	Activity (KgPE/molTi.h)
1	100	90	5	140	0.4286	482
2	100	90	10	160	0.4412	458
3	100	90	20	140	0.4455	551
4	100	90	40	175	0.4511	459

Polymerization condition: catalyst: 10 mg , cocatalyst: TEA, Al/Ti (mol/mol) = 100 , solvent: n-hexane(30 ml), Pressure 6 psi , Temperature = 80 °C

Mg(OEt)₂/TiCl₄ catalyst from recrystallization method was prepared with various dropping rate of TiCl₄. Effect of various dropping rate of TiCl₄ on catalytic activity is shown in **Table 4.11**. Paddle speed at 200 rpm and holding temperature at 90°C obtained the maximum activity were chosen to prepare catalyst. Dropping rate was varied from 5, 10, 20 and 40 cc/hr. The result showed that catalytic activity slightly changed, indicating that dropping rate had no effect on catalytic activity, but dropping rate had effect on crystal shape of catalyst. The polymer gain was similar to the crystal shape of catalyst. The reason could be explained the same as dropping rate effect on SEM micrograph.

For comparative studies, the different preparation methods (recrystallization and chemical reaction) were used and investigated for catalytic activities. The ethylene polymerization via different supports with MgCl₂ and Mg(OEt)₂ was performed in order to determine the characteristics and catalytic properties of polymer influenced by the various synthesis parameters such as paddle speed, holding temperature and dropping rate. Effect of paddle speed from recrystallization method was more sensitive to reaction than that from chemical reaction. **Figure 4.11** shows comparison of paddle speed sensibility to catalytic activity between two methods. It revealed that the activity for recrystallization method has more effects upon changing of paddle speed than that of chemical reaction method. Emulsion from recrystallization method was more viscous than that from the chemical reaction. Therefore, it was very difficult to control paddle speed which obtained emulsion was smooth and uniform during reaction. For chemical reaction method, paddle speed only obtained the homogeneous emulsion. Moreover, substance was easy attached to the wall of reactor; ratio of substance directly affected to product formation.

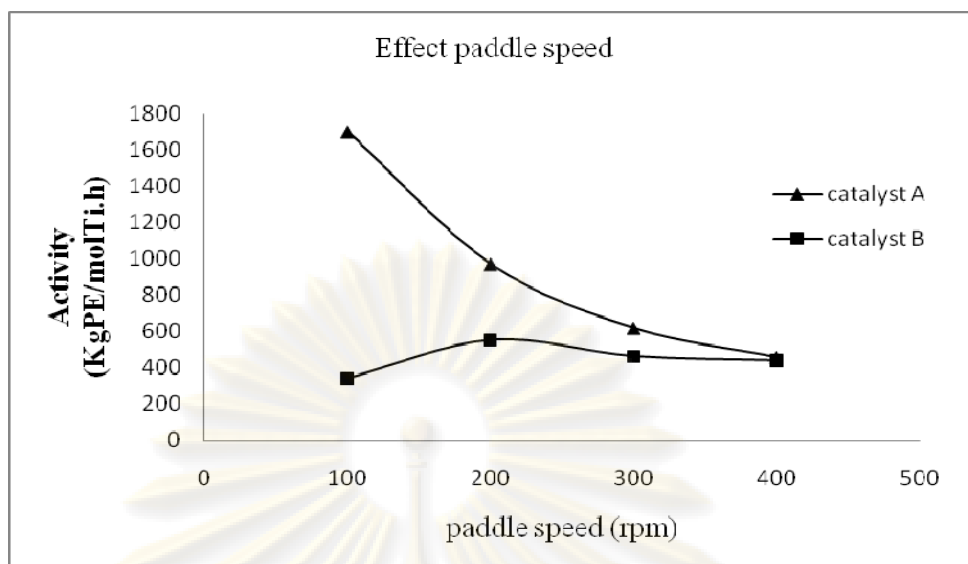


Figure 4.11 Sensibility of paddle speed on activity

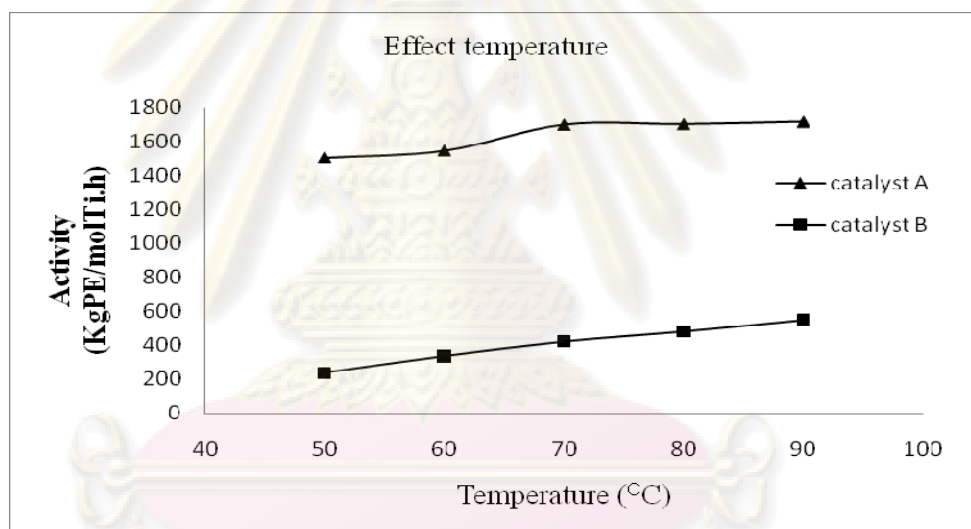


Figure 4.12 Sensibility of holding temperature on activity

For holding temperature effect as shown in **Figure 4.12**, it reveals that the activity for chemical reaction method has more effect upon changing of holding temperature than that of recrystallization method. Therefore holding temperature effect from the chemical reaction method was more sensitive than that from recrystallization method. Chemical change occurred during reaction, alkyl group was changed to Chloride group for chemical reaction method. As a result, inactive species such as $TiCl_{4-n}(OEt)_n$ remained in the system. It could be dissolved in solvent and returned to system again when the holding temperature increased. For recrystallization method, catalyst only physically changed the structure, but no change

of element, no inactive species occurred in system. Holding temperature effect was a little sensitive to the reaction.

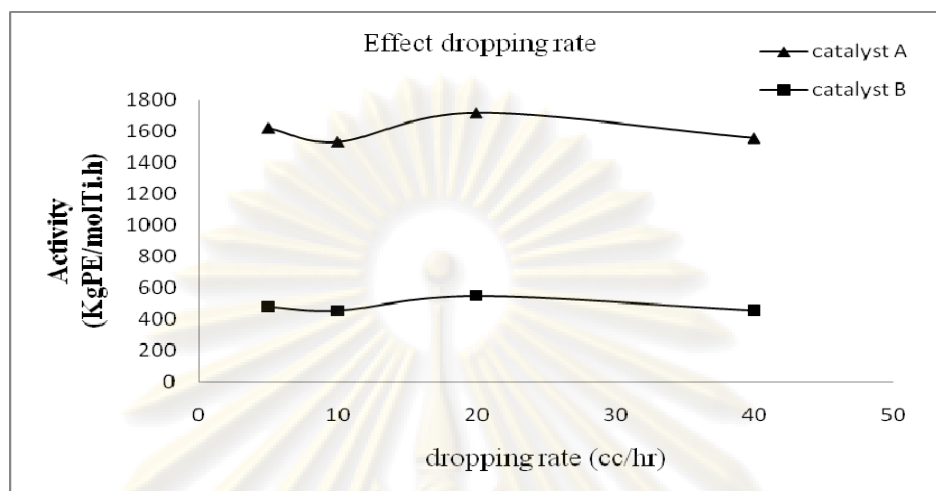


Figure 4.13 Sensibility of dropping rate on activity

For dropping rate effect, as shown in **Figure 4.13**, it shows that the activity has little effect upon changing of dropping rate both recrystallization and chemical reaction method dropping rate effect from chemical reaction method was not sensitive as seen from recrystallization method.

Normally, if the titanium content was high catalytic activity should be also high. However, for chemical reaction method, although, titanium content was high, the catalytic activity was low as shown in **Table 4.2**. The catalytic activity from chemical reaction was lower than recrystallization method because $\text{Mg}(\text{OEt})_2$ was converted to MgCl_2 , which transformed from alkyl group to Cl group. According to results of XRD and TGA confirmed again that $\text{Mg}(\text{OEt})_2$ transformed to MgCl_2 , thus probability of titanium was attached to support. The catalytic activity depended on active site of reaction. Catalyst reacted with cocatalyst to form active site, which was high contributed to highly activity. Chemical reaction method had more titanium attachment. Titanium might contribute to the attachment on inner and outer support as shown in **Figure 4.14** [11]. When various Al/Ti ratios, spectra signals from ESR were not different led to no effect on Ti^{3+} as shown in **Figure 4.8**. Because catalyst reacted with cocatalyst to form active site, which formed at the outer support (surface), **Figure 4.14**, titanium attached inner support was more than outer support, thus

probability of formation to active site in chemical reaction was low led to lower activity than recrystallization method. The result of ESR confirmed that titanium attached inner support was more than outer support. The catalytic activity from chemical reaction was less than recrystallization method because overall titanium attached at surface led to more probability of formation to active site, which accorded with results of ESR. **Figure 4.7** shows the ESR result of catalyst from two methods.

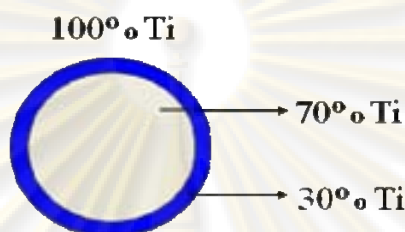


Figure 4.14 Titanium content of catalyst

4.3 Properties of polymer

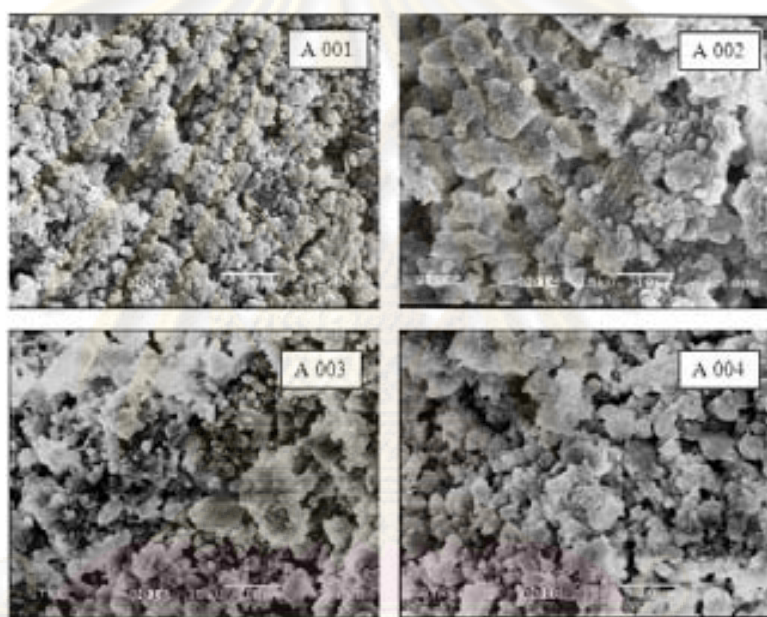
4.3.1 Morphologies of the polymers

Figure 4.15 a) and **b)** show SEM micrographs of polyethylene by recrystallization method with various paddle speeds, holding temperatures and dropping rates. **Figure 4.9 a)** and **b)** show crystal structure of catalyst with paddle speed and holding temperature effect, respectively. The SEM micrograph show that the crystal shapes of catalyst were nearly similar to every condition both paddle speed and holding temperature. As a result, paddle speed and holding temperature have no effect to the polymer grain shape of ethylene with chemical reaction method. For dropping rate of TiCl_4 effect, SEM micrograph of polyethylene is shown in **Figure 4.15 c)**. **Figure 4.9 c)** shows crystal structure of catalyst with dropping rate effect. Shape of polyethylene grain was fine when dropping rate was slow, this result was similar to crystal structure of catalyst.

Figure 4.16 a) and **b)** show SEM micrographs of polyethylene by chemical reaction method with various paddle speeds, holding temperatures and dropping rates. **Figure 4.9 a)** and **b)** show crystal structure of catalyst with paddle speed and holding temperature effect respectively. The SEM micrograph shows that the crystal shapes of catalyst were nearly similar to every condition both paddle speed and holding

temperature. SEM micrograph of polyethylene is shown in **Figure 4.16 c)**. **Figure 4.10 c)** shows crystal structure of catalyst with dropping rate effect. The result was similar to that of recrystallization method.

Morphologies of polyethylene using $\text{MgCl}_2/\text{TiCl}_4$ by recrystallization were similar to that of polyethylene using $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ by chemical reaction. Because of the same morphologies of polyethylene and catalyst, it can be described in catalyst principle. Because the original structure of $\text{Mg}(\text{OEt})_2$ is destroyed by the reaction of $\text{Mg}(\text{OEt})_2$ with TiCl_4 and, then highly disordered MgCl_2 is obtained [6] ,which was described in the X-ray diffraction pattern of the catalyst.



(a)

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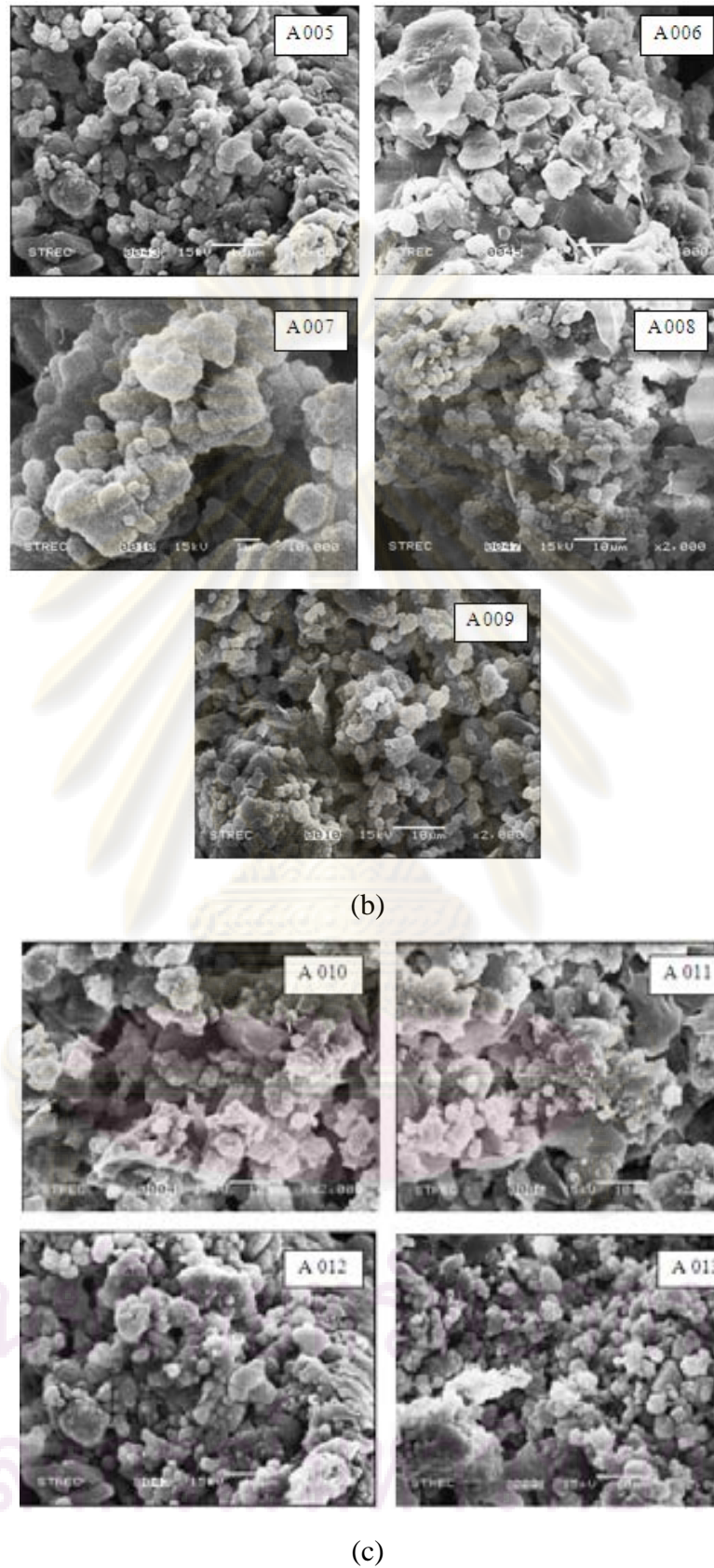
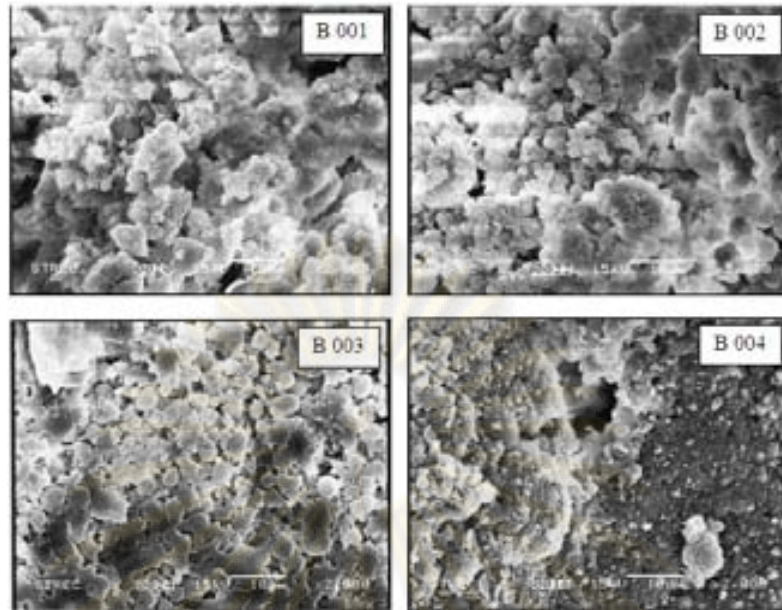
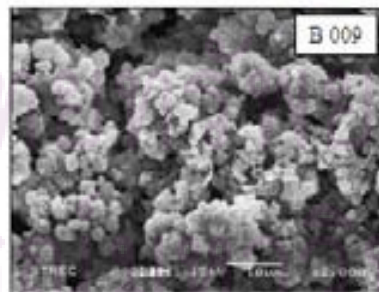
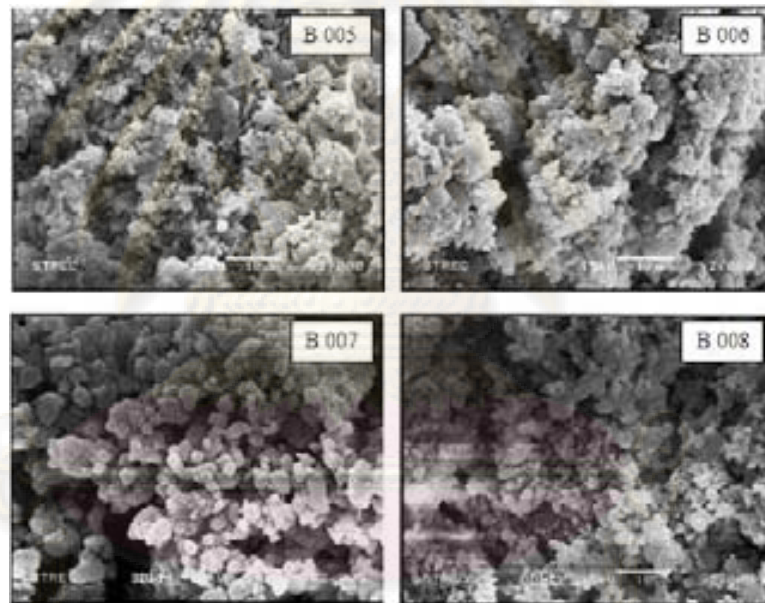


Figure 4.15 SEM micrographs of polyethylene with recrystallization method (a) paddle speed (b) temperature (c) dropping rate

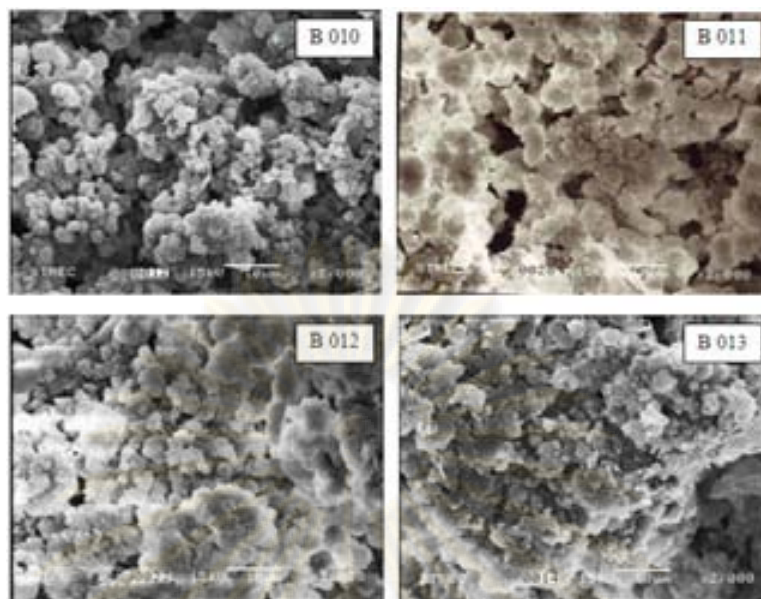


(a)



(b)

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(c)

Figure 4.16 SEM micrographs of polyethylene with chemical reaction method (a) paddle speed (b) temperature and (c) dropping rate

4.3.2 Thermal properties

Results of thermal behavior of polyethylene (PE) obtained from the differential scanning calorimetry (DSC) are shown in **Table 4.12**

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Table 4.12 Melting temperature and percent crystallinity of polymer produced

System	catalyst	$T_m(^{\circ}\text{C})$	X_c^a
MgCl ₂ /TiCl ₄	A 001	130	55.50
	A 002	132	55.95
	A 003	131	55.72
	A 004	130	56.20
	A 005	130	55.82
	A 006	130	55.74
	A 007	128	51.53
	A 008	129	54.78
	A 009	129	55.14
	A 010	129	54.30
	A 011	132	55.42
	A 012	130	55.50
	A 013	130	51.14
Mg(OEt) ₂ /TiCl ₄	B 001	130	53.33
	B 002	129	54.78
	B 003	129	55.86
	B 004	130	54.64
	B 005	132	55.83
	B 006	131	55.81
	B 007	131	55.10
	B 008	132	55.88
	B 009	130	55.96
	B 010	130	55.73
	B 011	132	55.15
	B 012	129	54.78
	B 013	131	55.01

^a Obtained from DSC

The degree of crystallinity was calculated by comparison with heat of fusion (ΔH_f) of a perfectly crystalline polyethylene, i.e., 293 J/g and the melting temperatures (T_m) of the polymer are in the range 129 – 132 °C. It indicated that there were no significant different for their melting temperature and degree of crystallinity as can be seen in Table 4.11 upon different catalysts used.

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CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

In summary, the impact of various parameters on the catalytic activities during synthesis catalyst was investigated. It was found that paddle speed use to obtain the highest activity for the recrystallization method was 100 rpm. Holding temperature lower than 70 °C had little effect on activity and no effect of temperature higher than 70 °C was observed. The dropping rate had little effect on activity. For chemical reaction method, paddle speed and holding temperature use to obtain the highest activity were 200 rpm and 90 °C, respectively and the dropping rate had only little effect on activity. Sensitivity of parameters on catalytic activity was compared for both recrystallization and chemical reaction methods. It was found that the recrystallization method was more sensitive than the chemical reaction method for paddle speed effect due to more viscosity. For holding temperature effect, chemical reaction method was more sensitive than recrystallization method. Inactive species from conversion $\text{Mg}(\text{OEt})_2$ to MgCl_2 can be dissolved back into the solvent at high temperature by chemical reaction method. Recrystallization and chemical reaction method were not sensitive to the dropping rate. The best condition of each method was used to synthesize catalyst to compare activity. Activity from the recrystallization method was higher than that from the chemical reaction due to more amount of Ti^{3+} . Dropping rate had effect on morphology of catalyst; slow dropping rate was more round than fast dropping rate. Moreover, morphology of polymer was similar to that of catalyst. Properties of polymer such melting temperature (T_m) was similar to not only the recrystallization method, but also to the chemical reaction method due to the same catalyst system.

5.2 RECOMMENDATIONS

- Different ratios of Mg/ethanol should be further investigated.
- The other types of alcohol adduct should be studied.
- Amount of TiCl_4 should be excessively added for recrystallization method.
- Hexane should be changed to heptanes to wash catalyst in final stage for chemical reaction method.



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APPENDICES

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APPENDIX A
(Differential scanning calorimeter)

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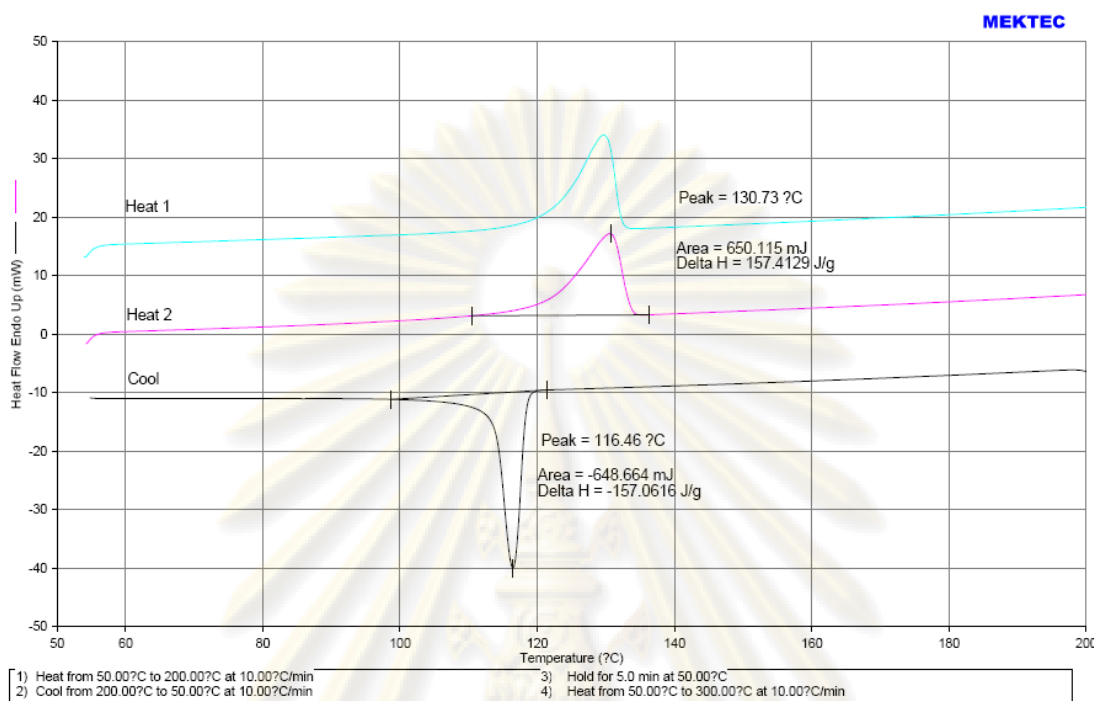


Figure A-1 DSC curve of polyethylene produce by $MgCl_2/TiCl_4$ catalyst with paddle speed 100 rpm

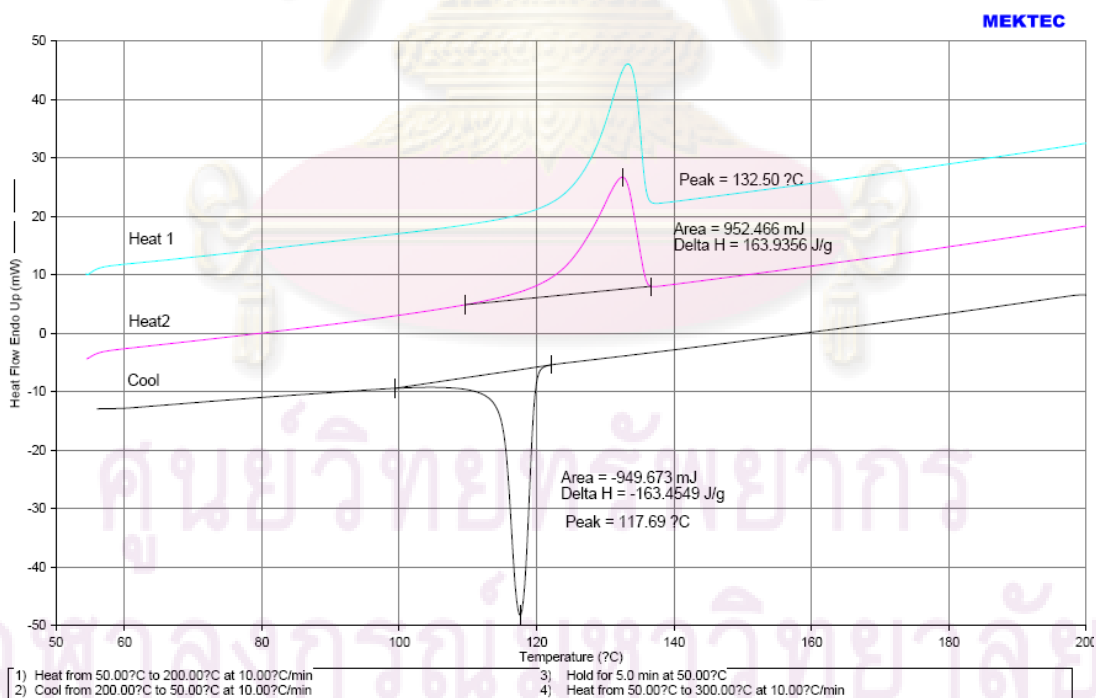


Figure A-2 DSC curve of polyethylene produce by $MgCl_2/TiCl_4$ catalyst with paddle speed 200 rpm

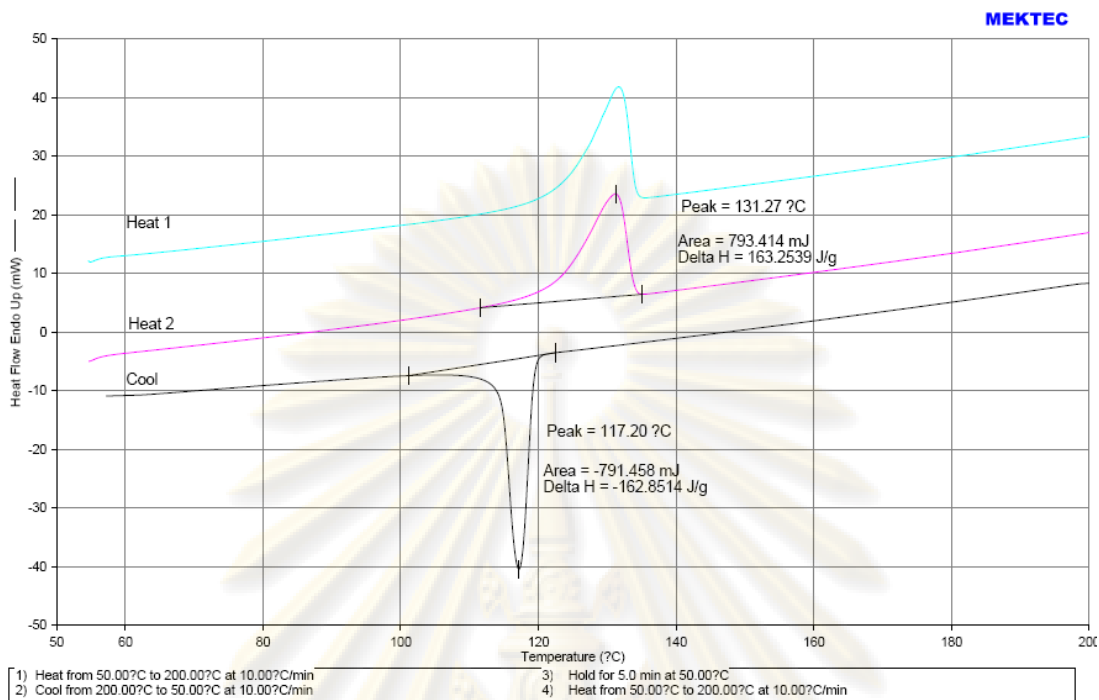


Figure A-3 DSC curve of polyethylene produce by $MgCl_2/TiCl_4$ catalyst with paddle speed 300 rpm

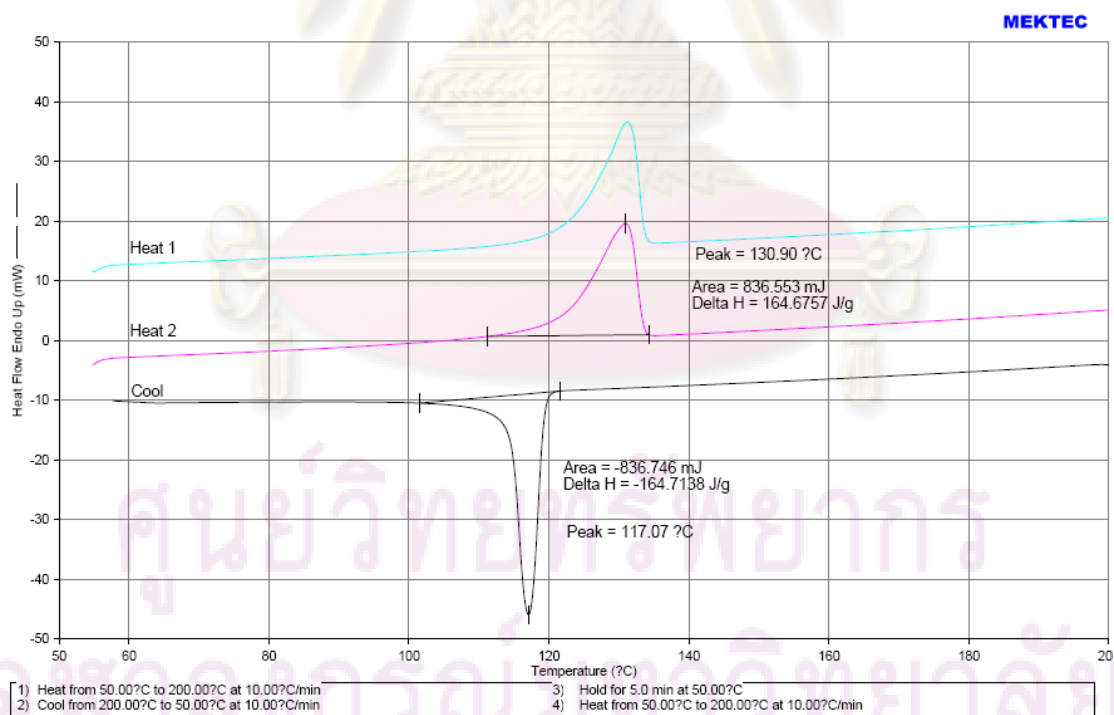


Figure A-4 DSC curve of polyethylene produce by $MgCl_2/TiCl_4$ catalyst with paddle speed 400 rpm

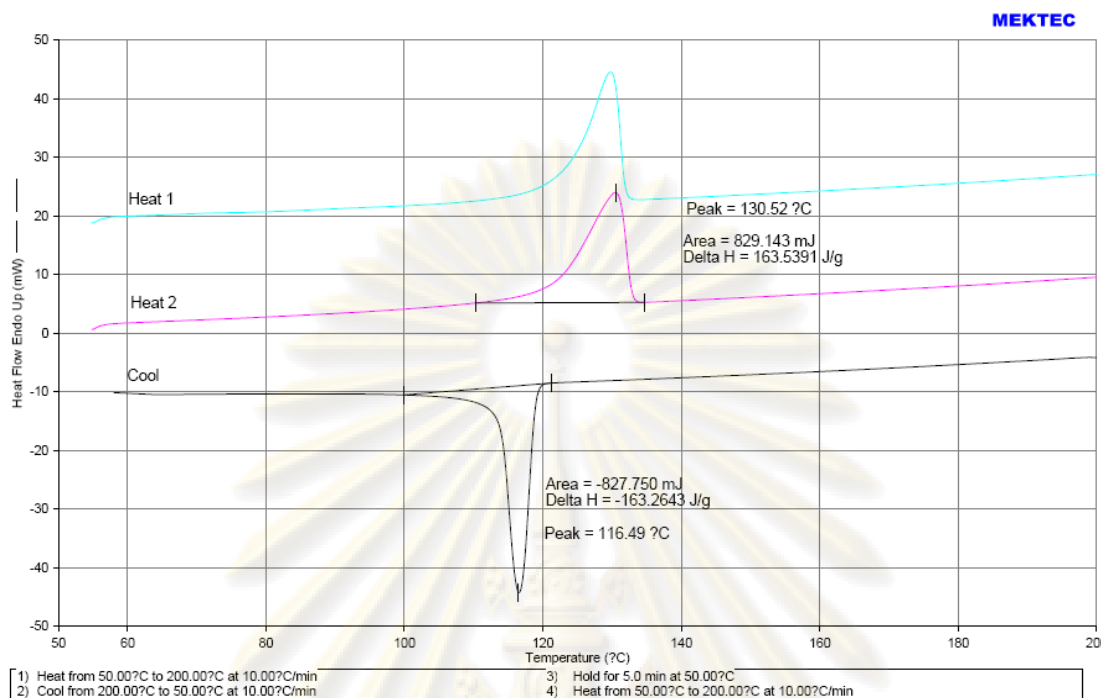


Figure A-5 DSC curve of polyethylene produce by $MgCl_2/TiCl_4$ catalyst with holding temperature 50 °C

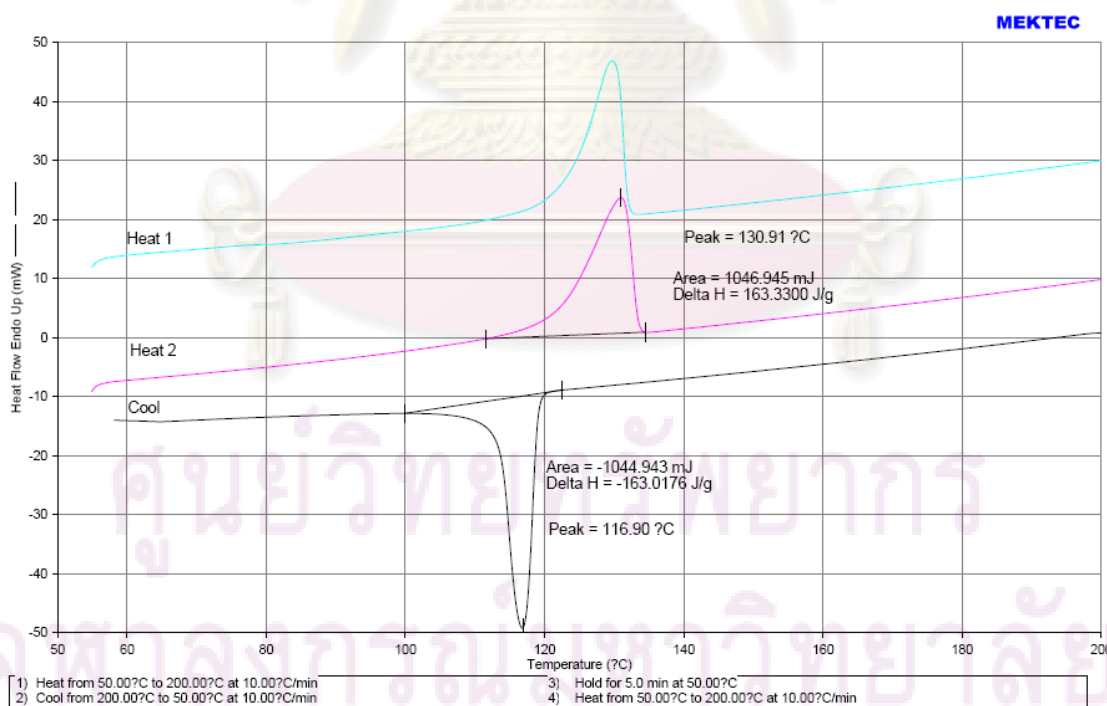


Figure A-6 DSC curve of polyethylene produce by $MgCl_2/TiCl_4$ catalyst with holding temperature 60 °C

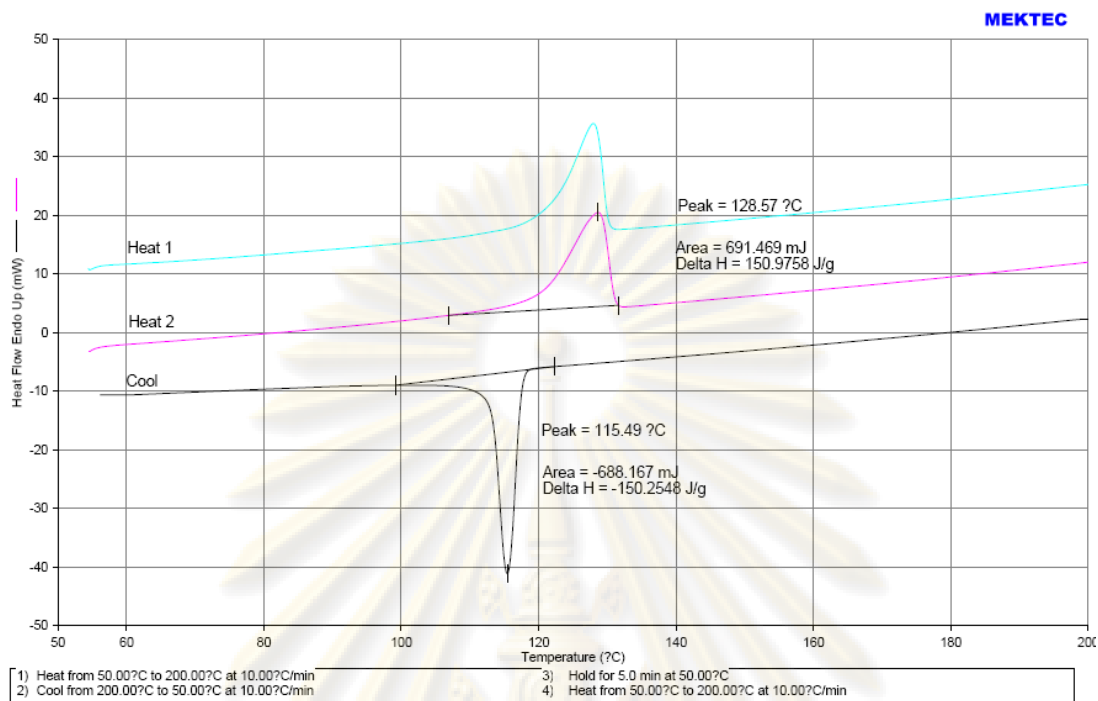


Figure A-7 DSC curve of polyethylene produce by $MgCl_2/TiCl_4$ catalyst with holding temperature 70 °C

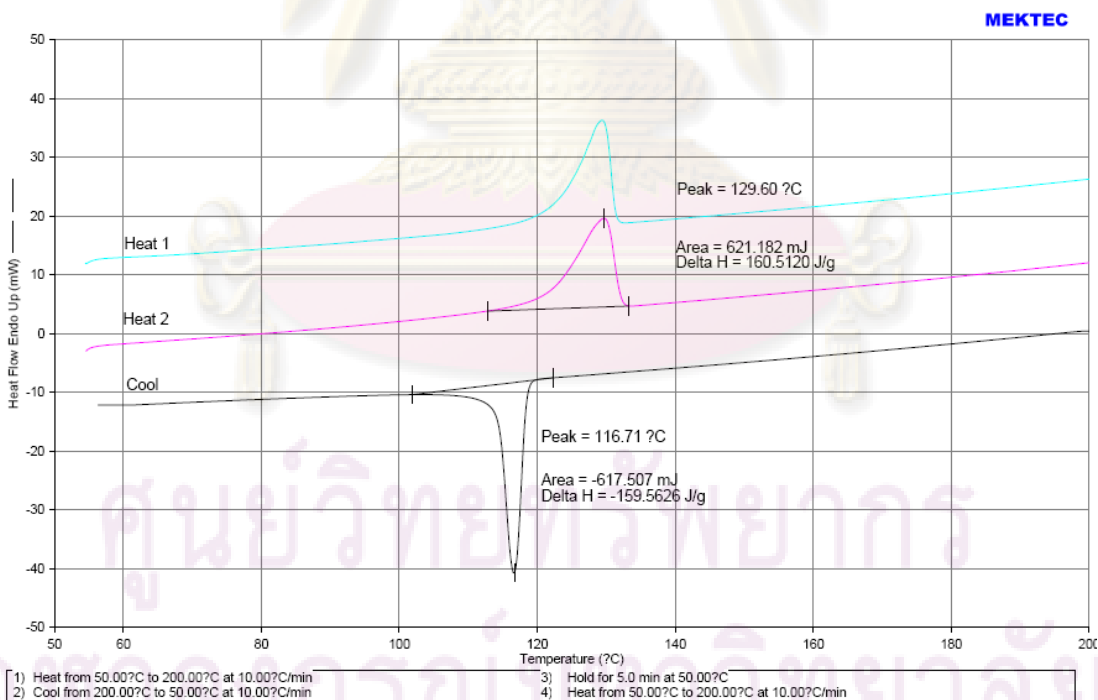


Figure A-8 DSC curve of polyethylene produce by $MgCl_2/TiCl_4$ catalyst with holding temperature 80 °C

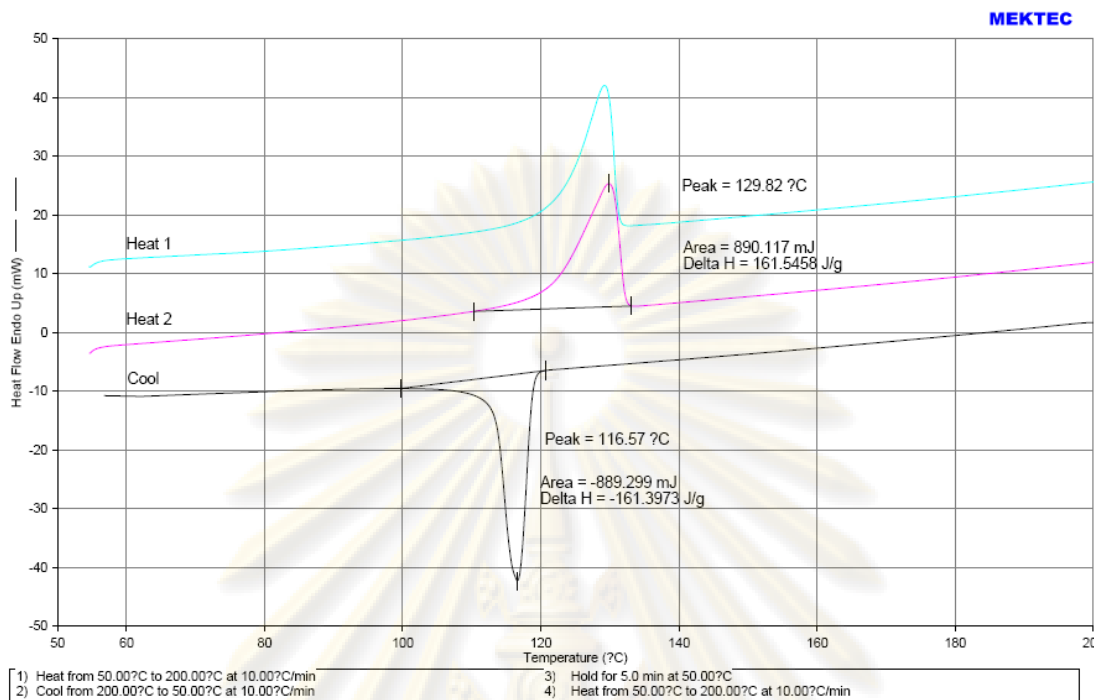


Figure A-9 DSC curve of polyethylene produce by $MgCl_2/TiCl_4$ catalyst with holding temperature 90 °C

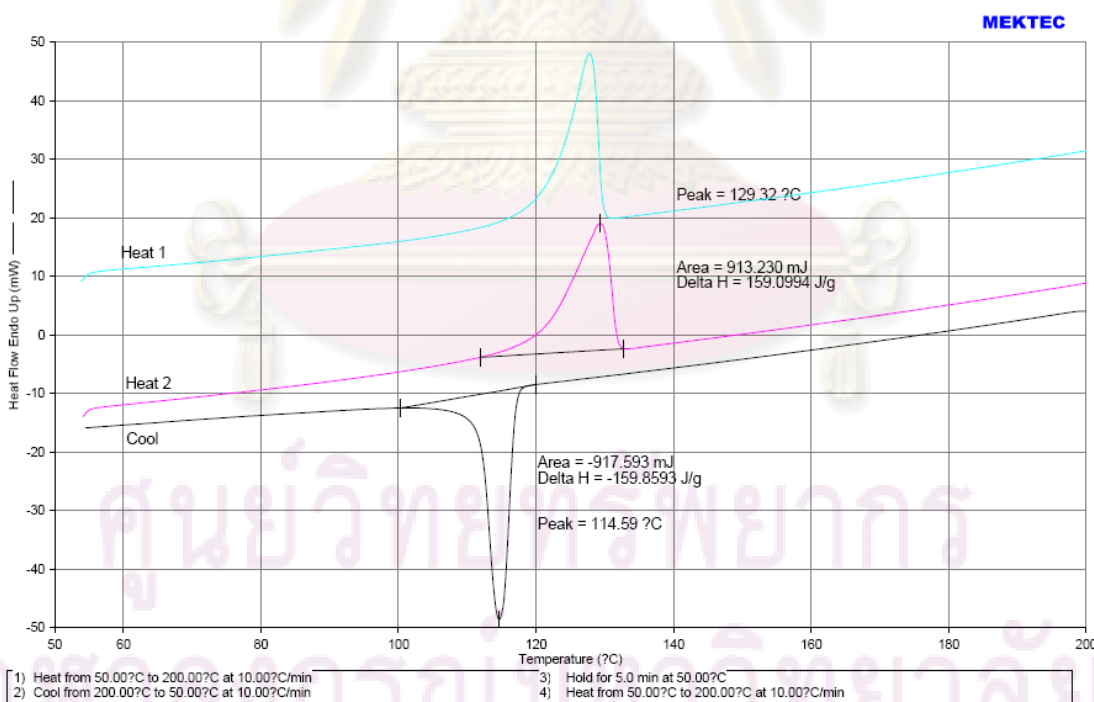


Figure A-10 DSC curve of polyethylene produce by $MgCl_2/TiCl_4$ catalyst with dropping rate 5 cc/hr

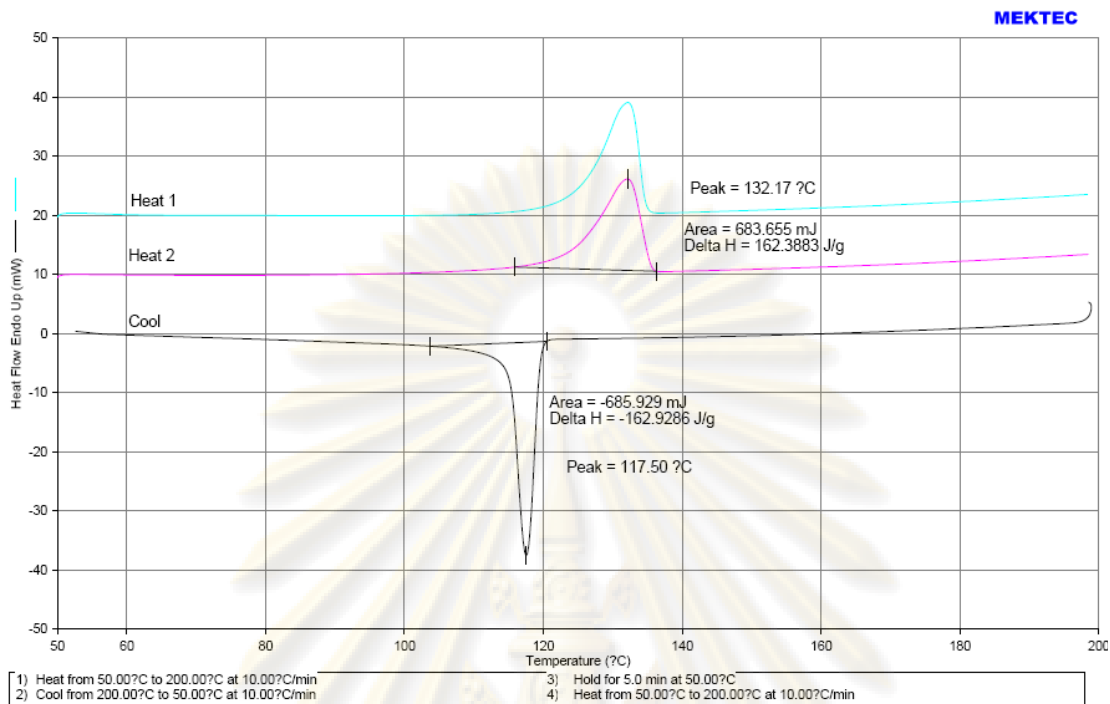


Figure A-11 DSC curve of polyethylene produce by $MgCl_2/TiCl_4$ catalyst with dropping rate 10 cc/hr

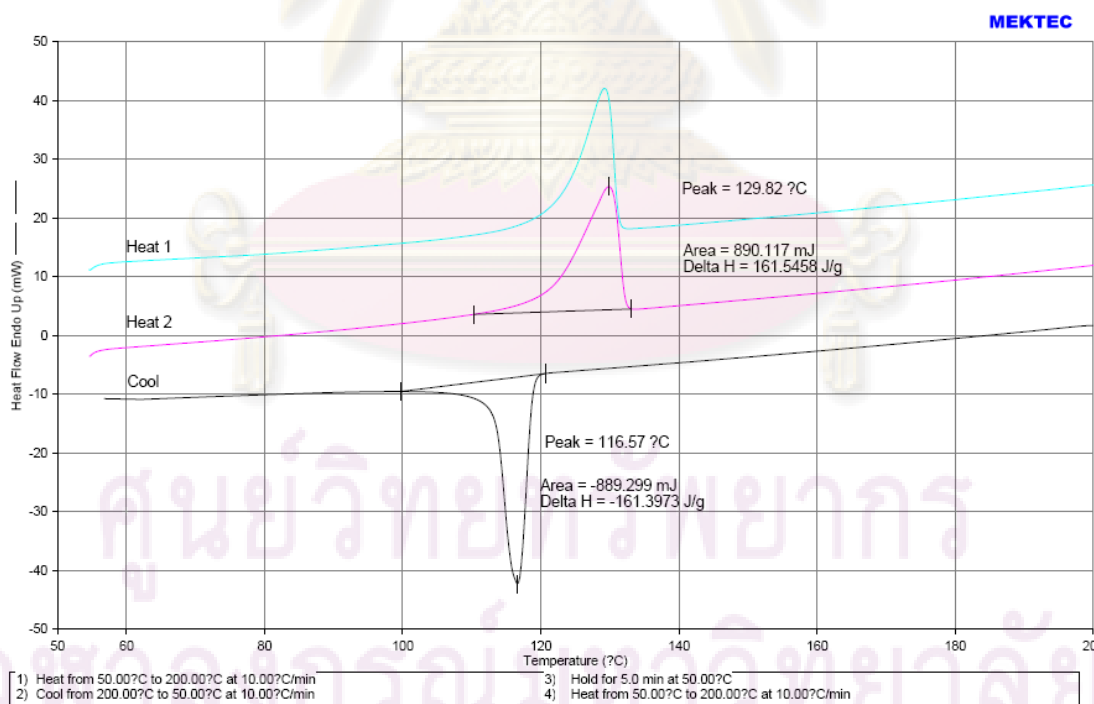


Figure A-12 DSC curve of polyethylene produce by $MgCl_2/TiCl_4$ catalyst with dropping rate 20 cc/hr

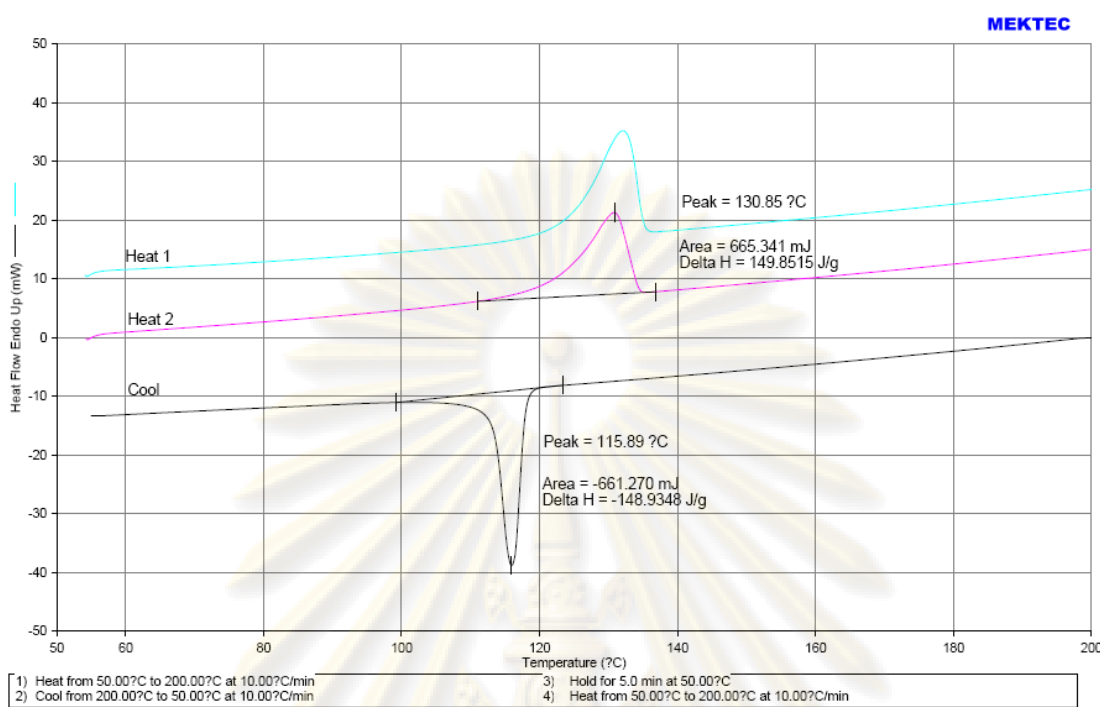


Figure A-13 DSC curve of polyethylene produce by $\text{MgCl}_2/\text{TiCl}_4$ catalyst with dropping rate 40 cc/hr

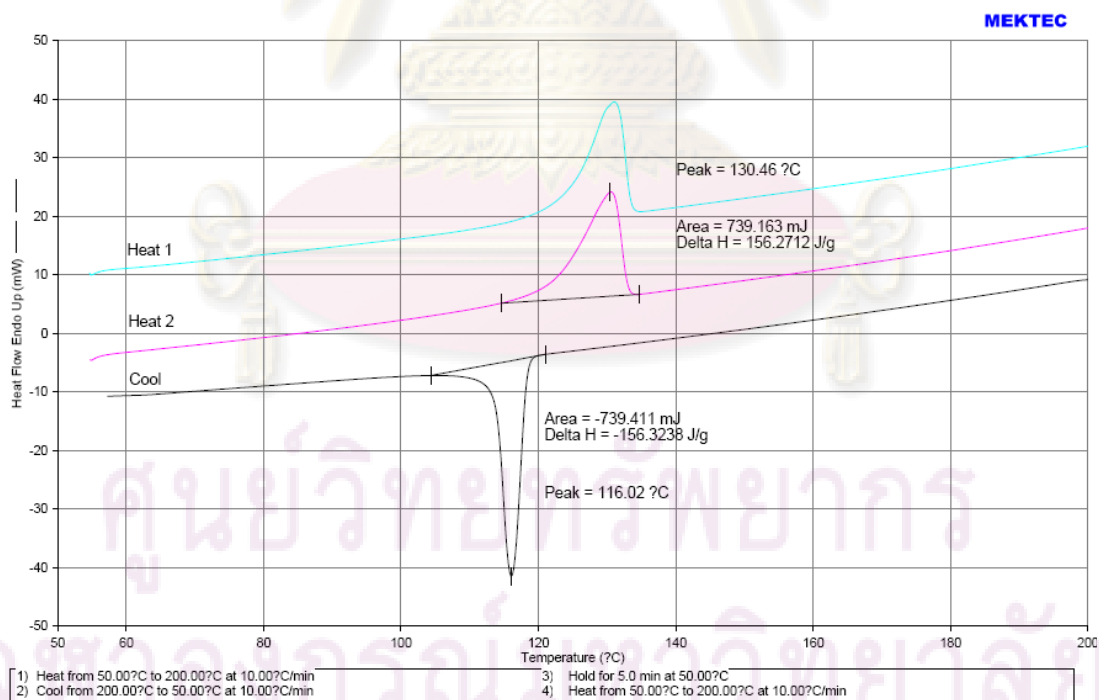


Figure A-14 DSC curve of polyethylene produce by $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst with paddle speed 100 rpm

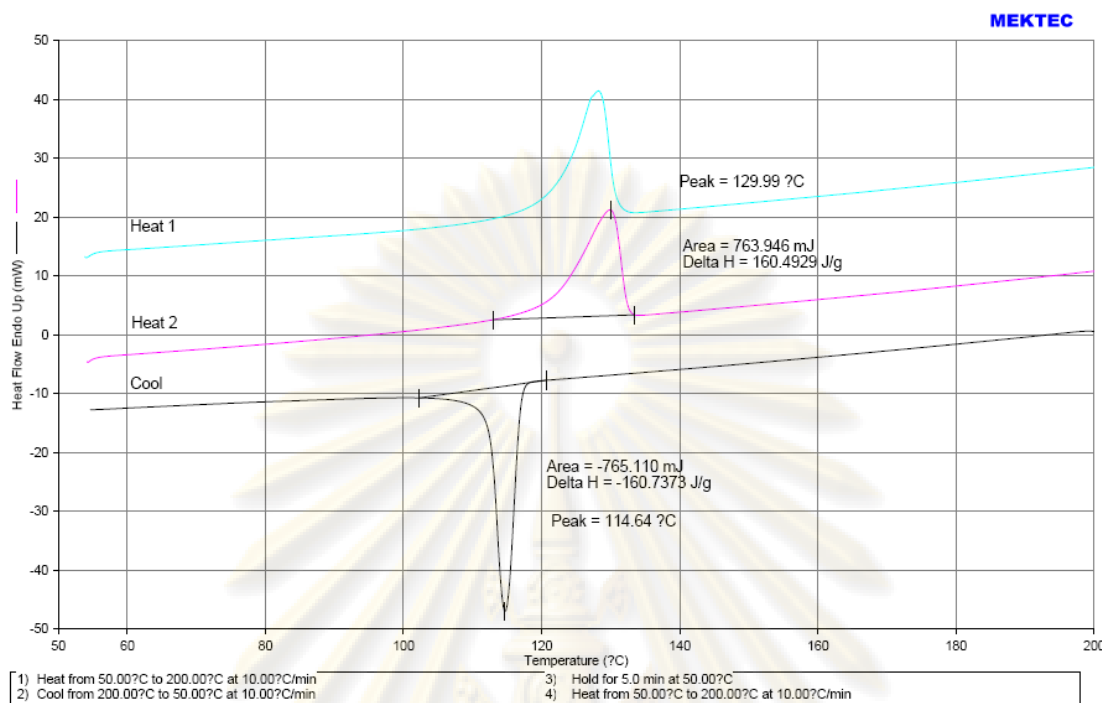


Figure A-15 DSC curve of polyethylene produce by $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst with paddle speed 200 rpm

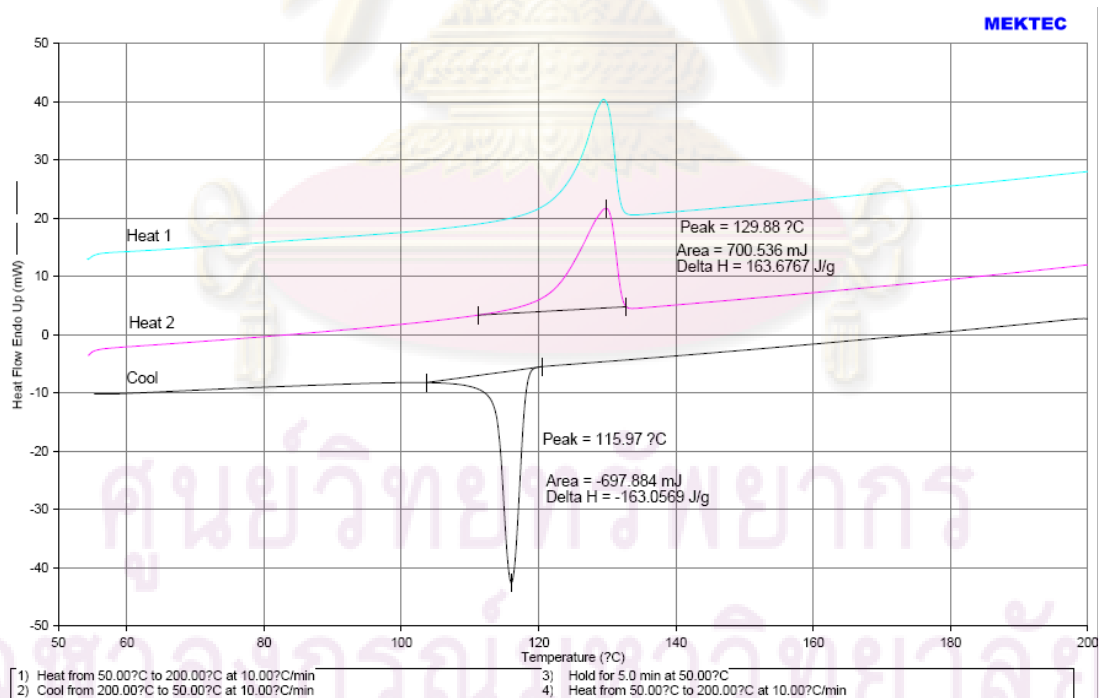


Figure A-16 DSC curve of polyethylene produce by $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst with paddle speed 300 rpm

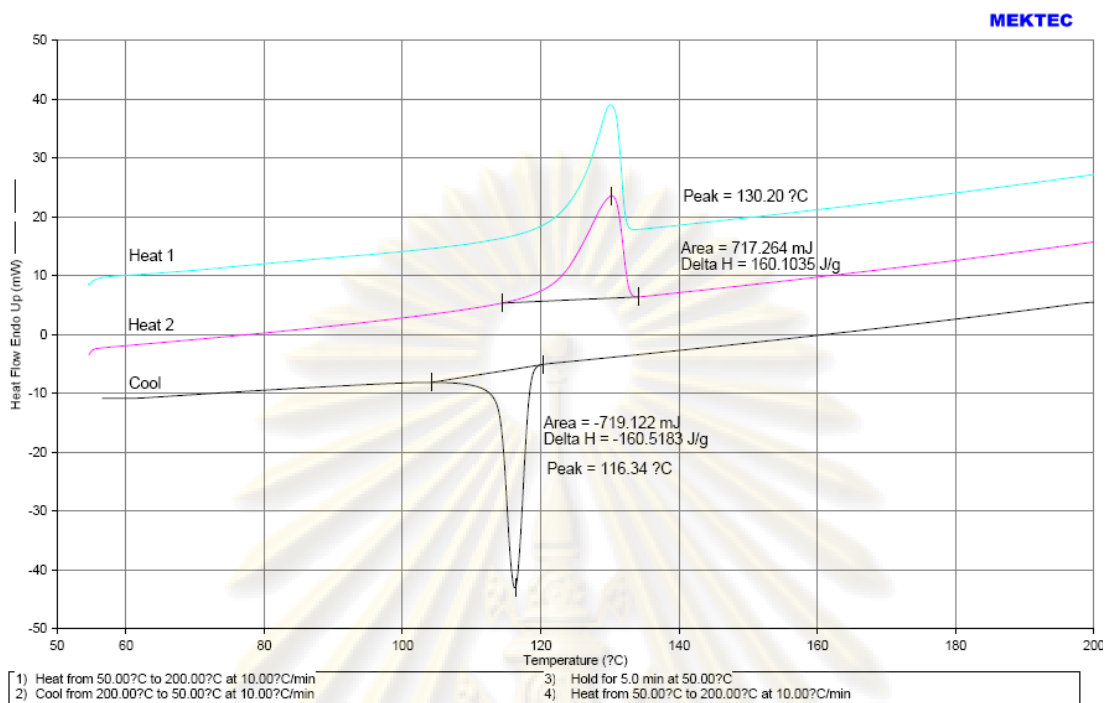


Figure A-17 DSC curve of polyethylene produce by $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst with paddle speed 400 rpm

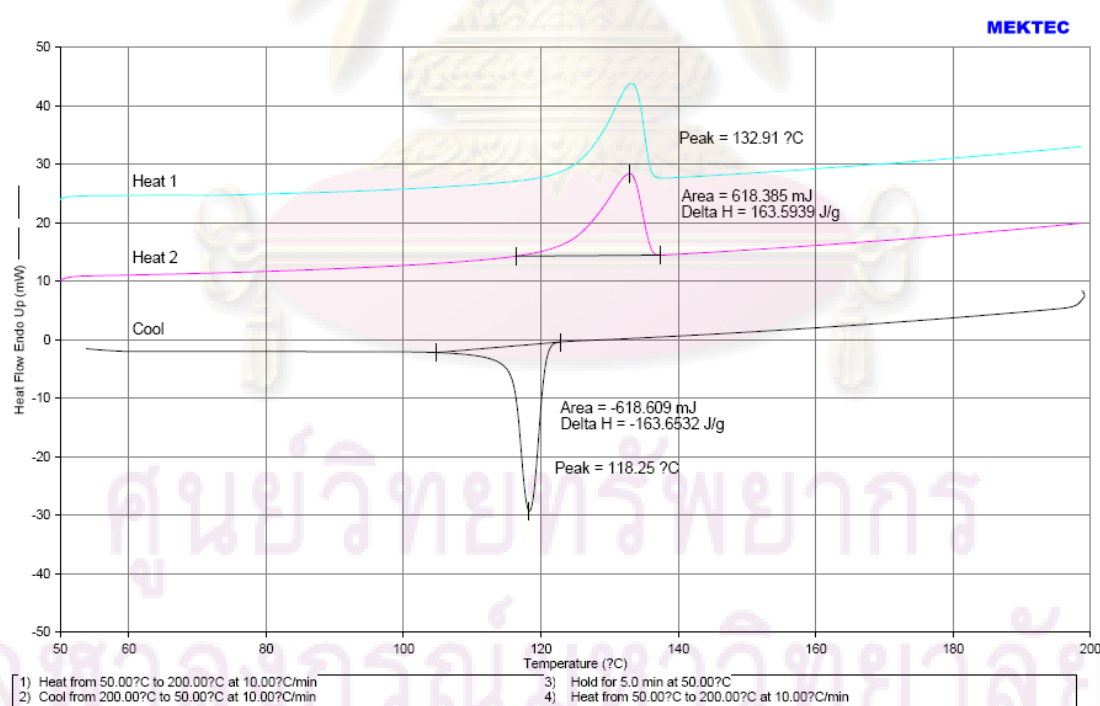


Figure A-18 DSC curve of polyethylene produce by $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst with holding temperature 50 °C

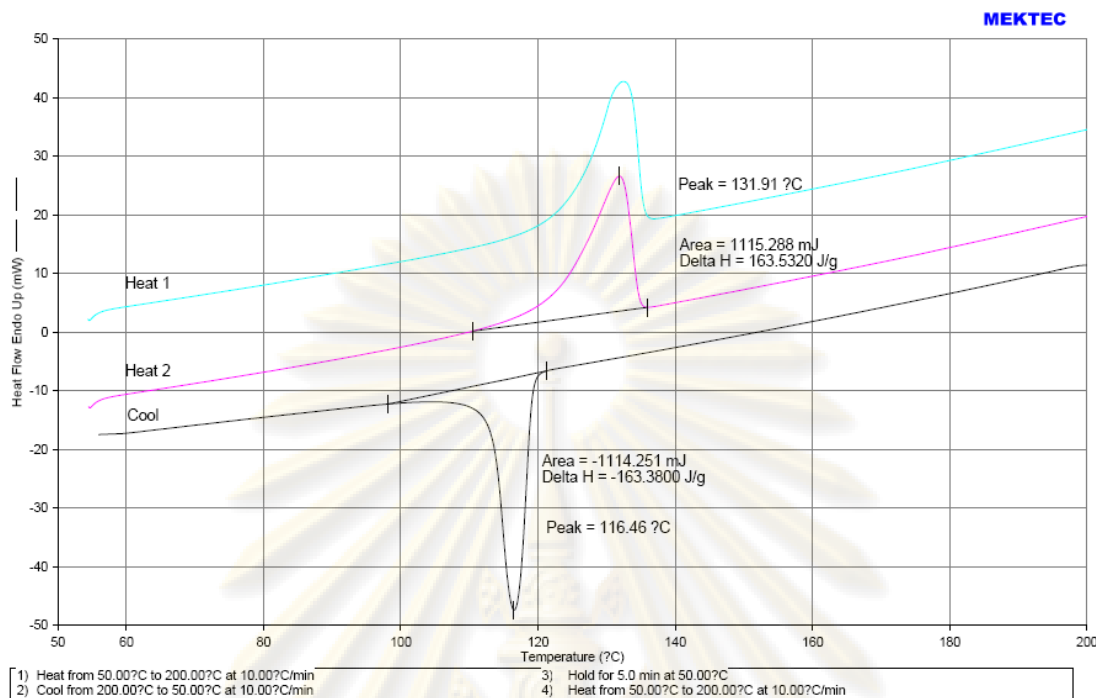


Figure A-19 DSC curve of polyethylene produce by $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst with holding temperature $60\text{ }^\circ\text{C}$

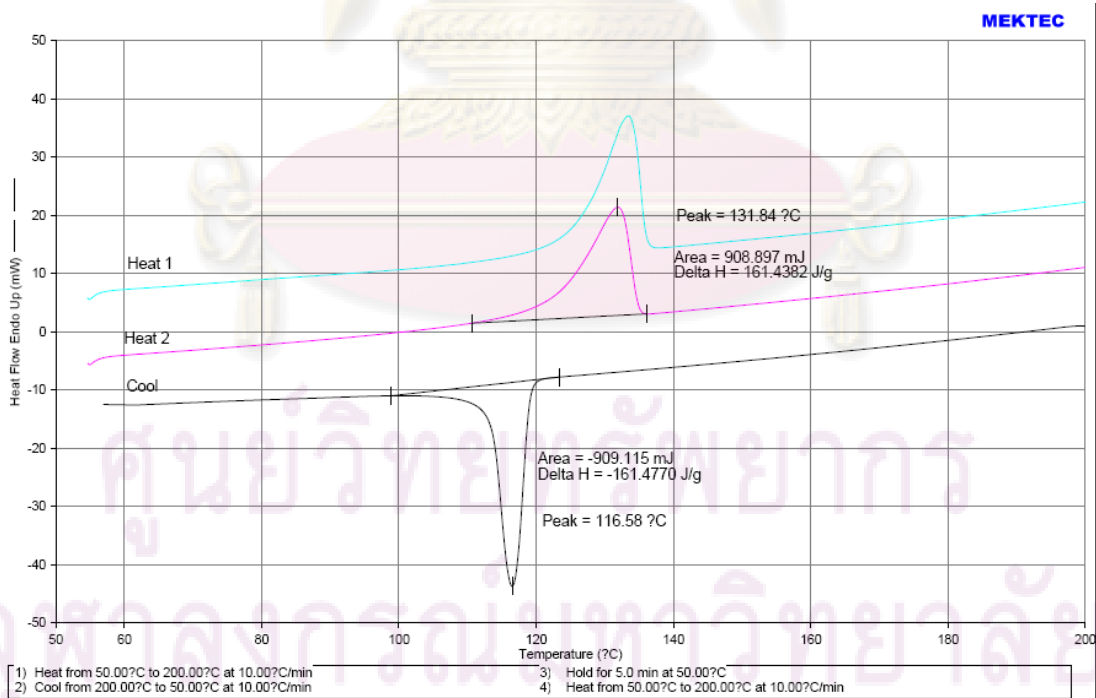


Figure A-20 DSC curve of polyethylene produce by $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst with holding temperature $70\text{ }^\circ\text{C}$

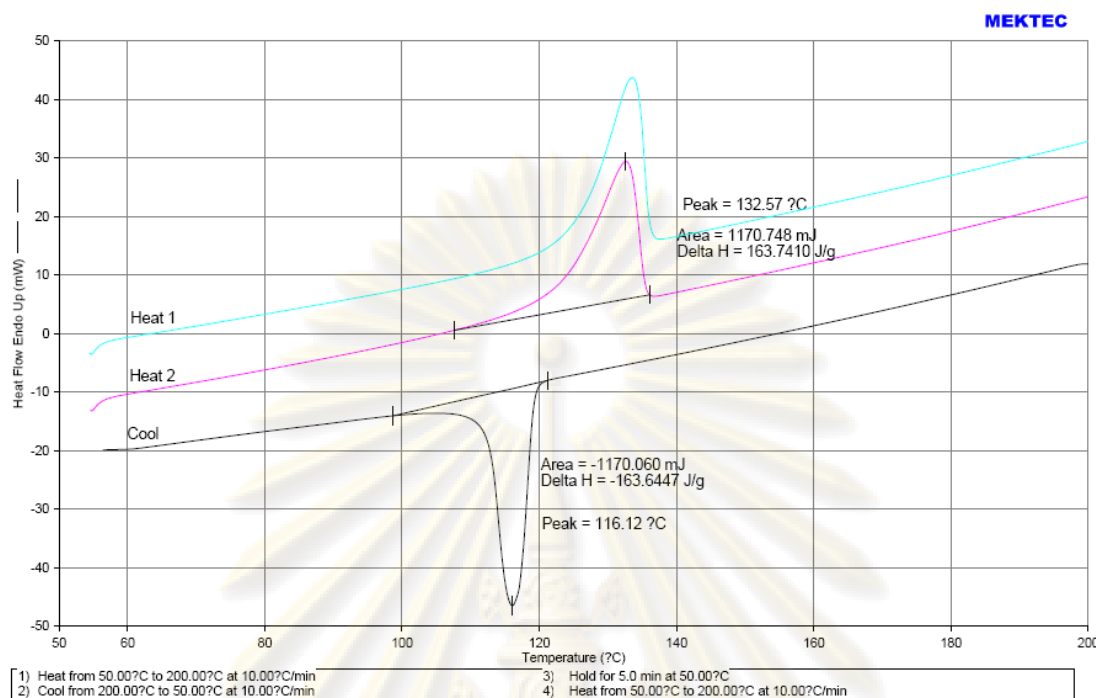


Figure A-21 DSC curve of polyethylene produce by $\text{Mg}(\text{OET})_2/\text{TiCl}_4$ catalyst with holding temperature $80\text{ }^\circ\text{C}$

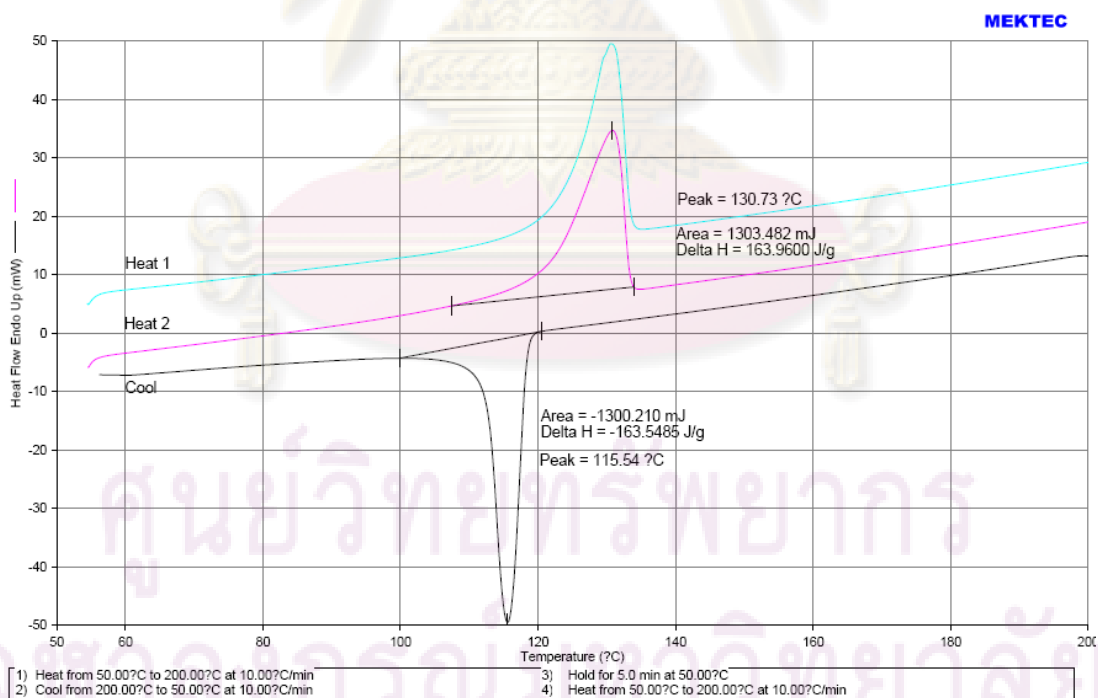


Figure A-22 DSC curve of polyethylene produce by $\text{Mg}(\text{OET})_2/\text{TiCl}_4$ catalyst with holding temperature $90\text{ }^\circ\text{C}$

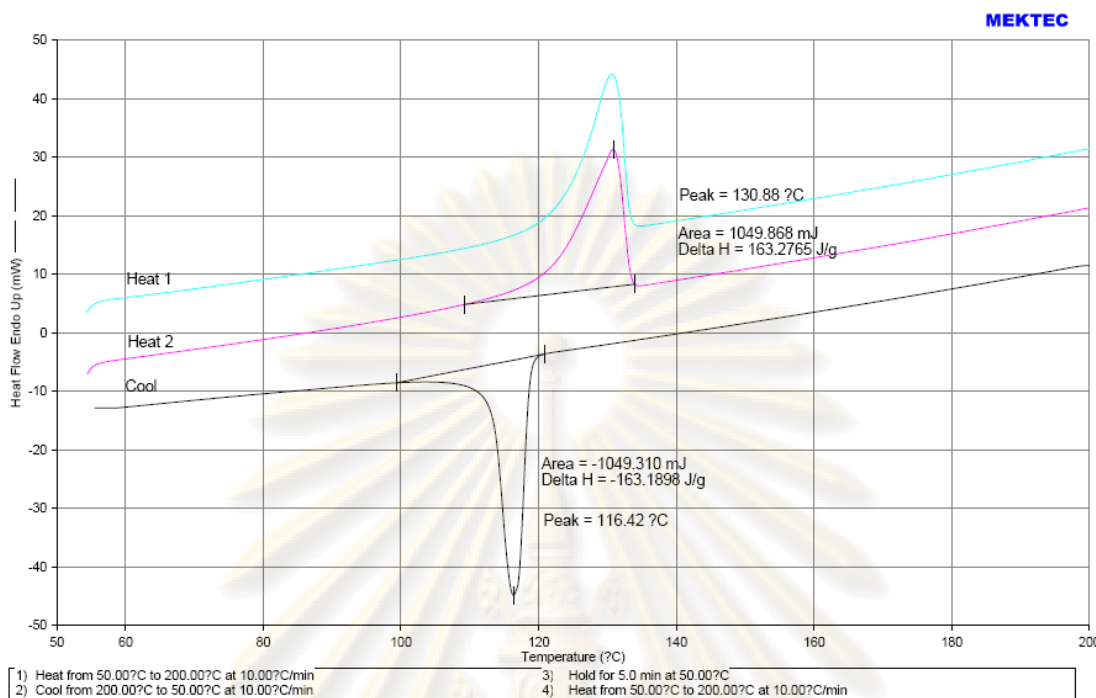


Figure A-23 DSC curve of polyethylene produce by $\text{Mg}(\text{OET})_2/\text{TiCl}_4$ catalyst with dropping rate 5 cc/hr

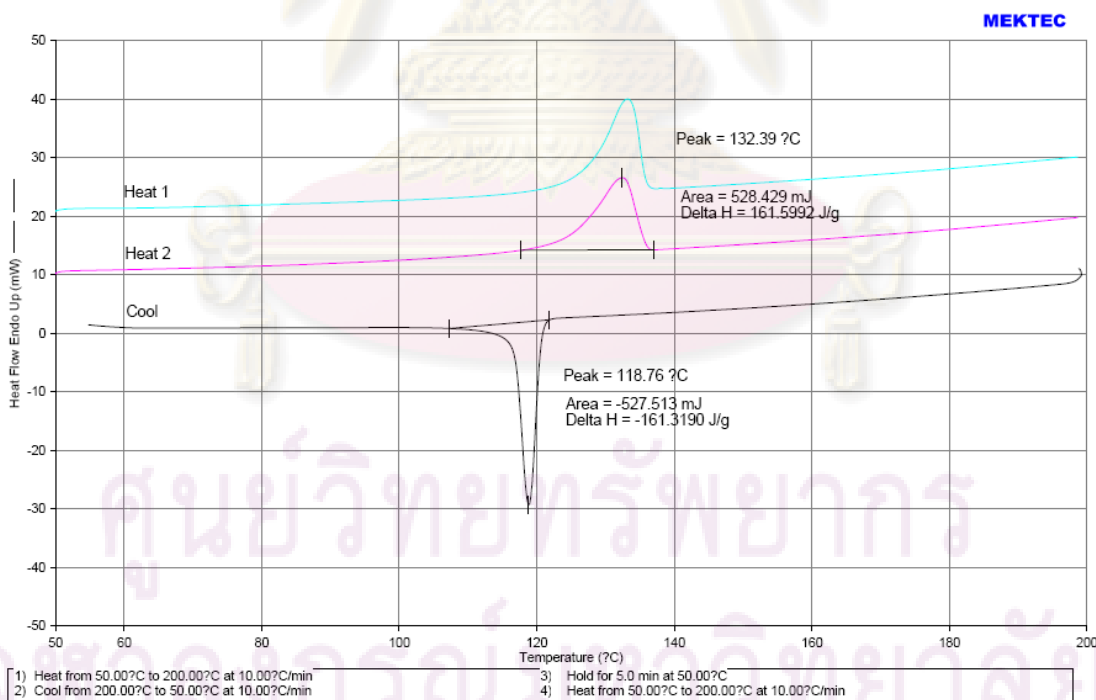


Figure A-24 DSC curve of polyethylene produce by $\text{Mg}(\text{OET})_2/\text{TiCl}_4$ catalyst with dropping rate 10 cc/hr

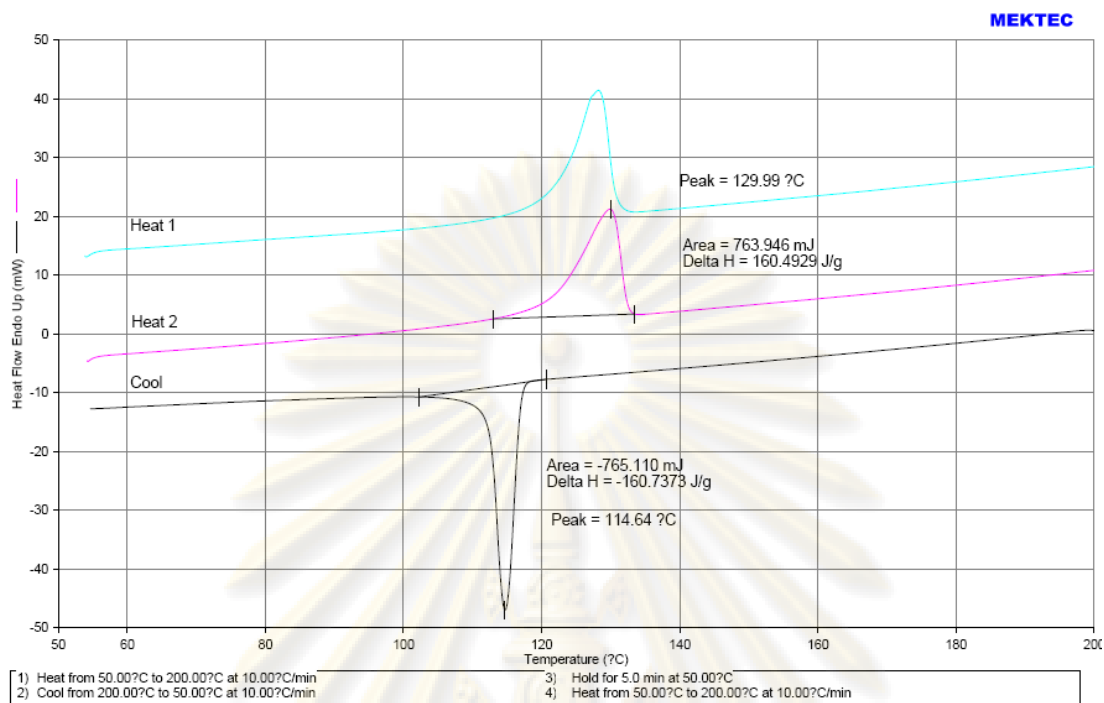


Figure A-25 DSC curve of polyethylene produce by $\text{Mg}(\text{OET})_2/\text{TiCl}_4$ catalyst with dropping rate 20 cc/hr

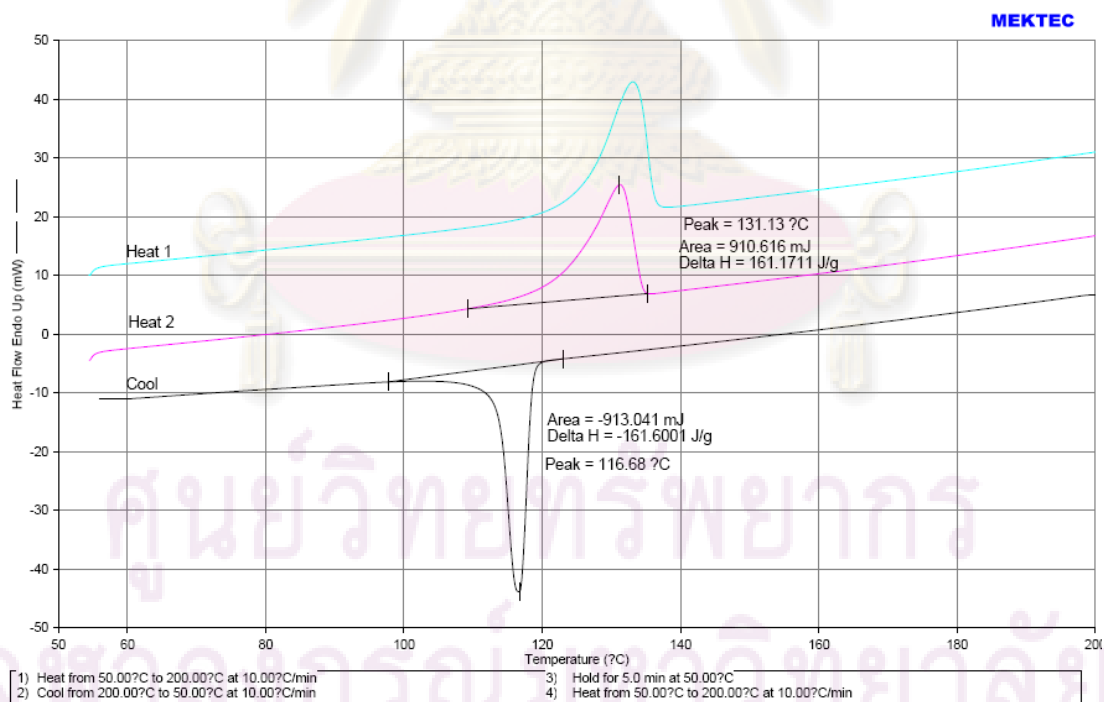
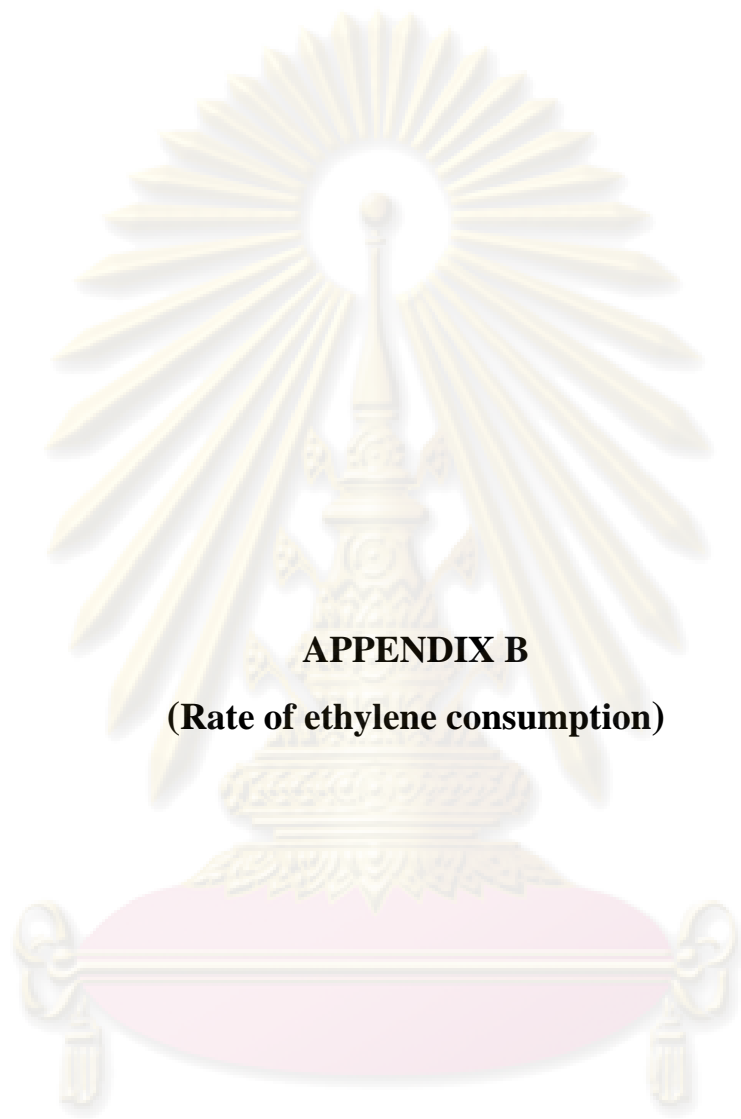


Figure A-26 DSC curve of polyethylene produce by $\text{Mg}(\text{OET})_2/\text{TiCl}_4$ catalyst with dropping rate 40 cc/hr



APPENDIX B

(Rate of ethylene consumption)

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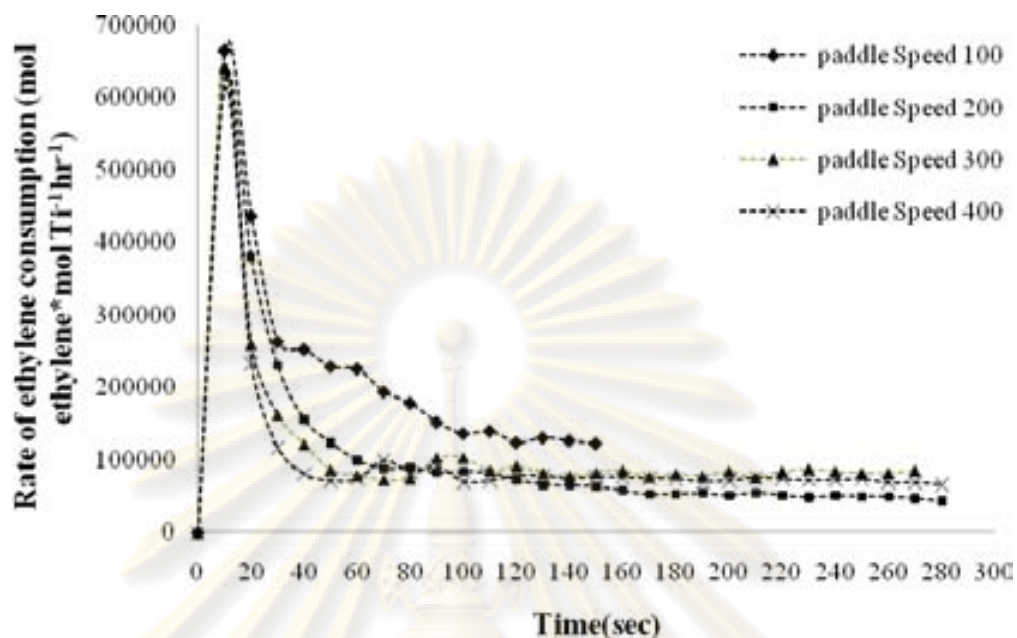


Figure B-1 Rate of ethylene consumption by $MgCl_2/TiCl_4$ catalyst with different paddle speeds

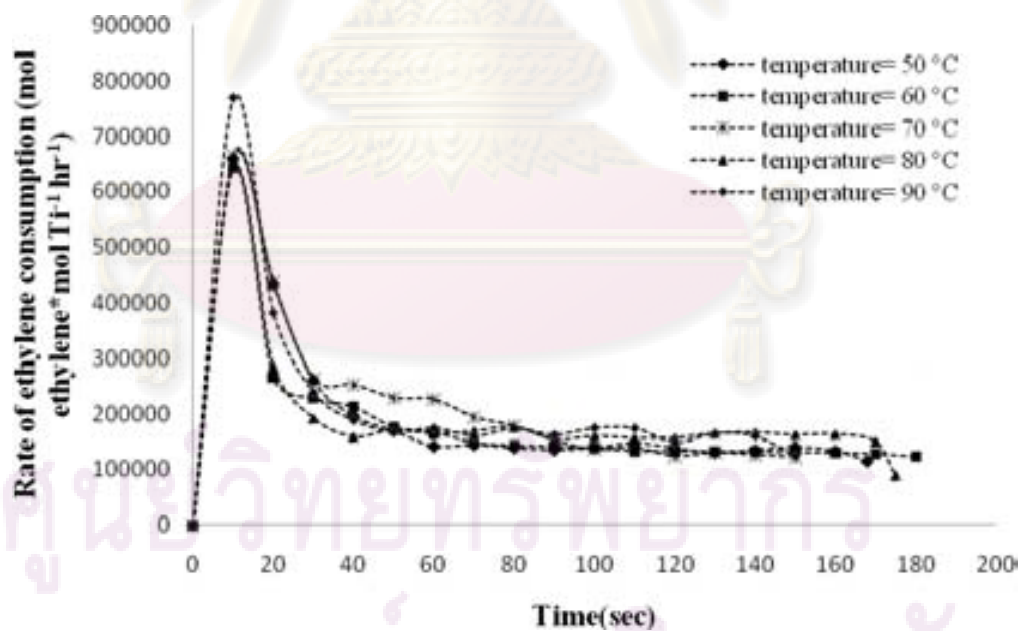


Figure B-2 Rate of ethylene consumption by $MgCl_2/TiCl_4$ catalyst with different holding temperature

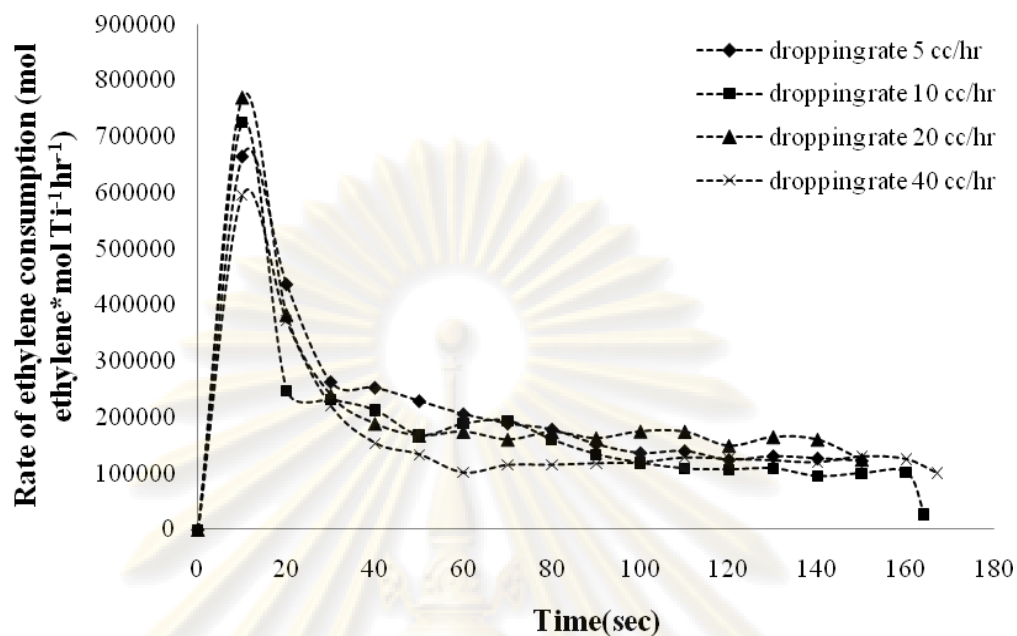


Figure B-3 Rate of ethylene consumption by MgCl₂/TiCl₄ catalyst with different dropping rate

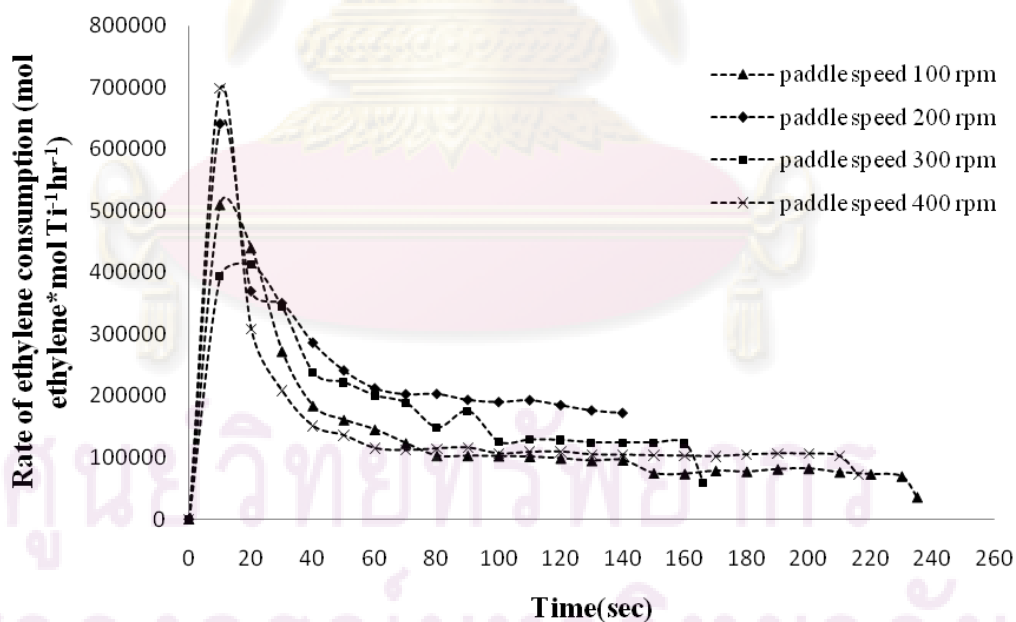


Figure B-4 Rate of ethylene consumption by Mg(OEt)₂/TiCl₄ catalyst with different paddle speed

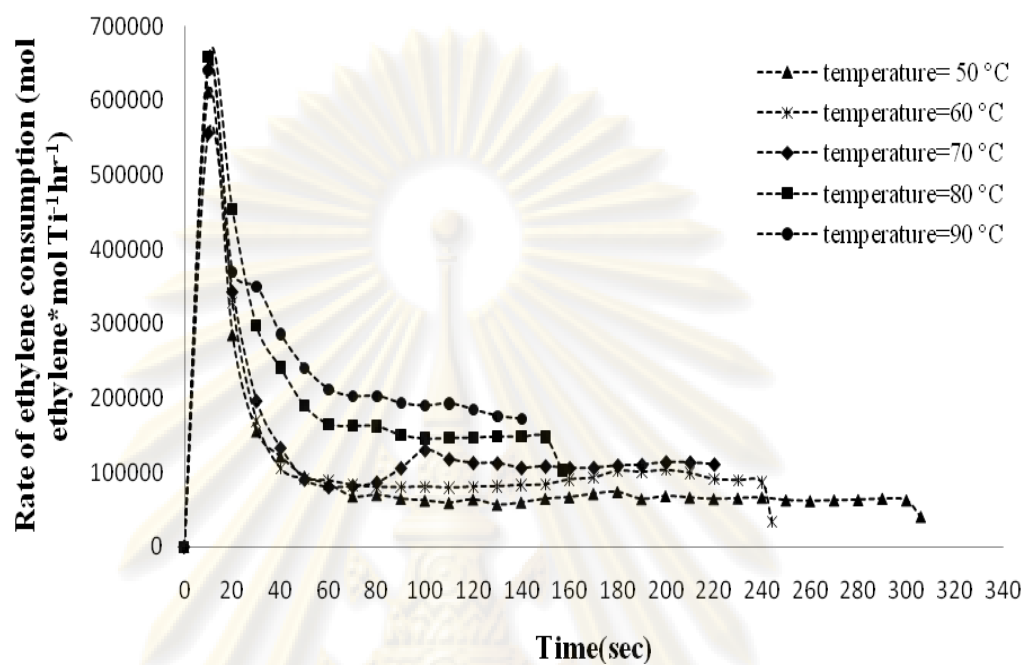


Figure B-5 Rate of ethylene consumption by $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst with different holding temperature

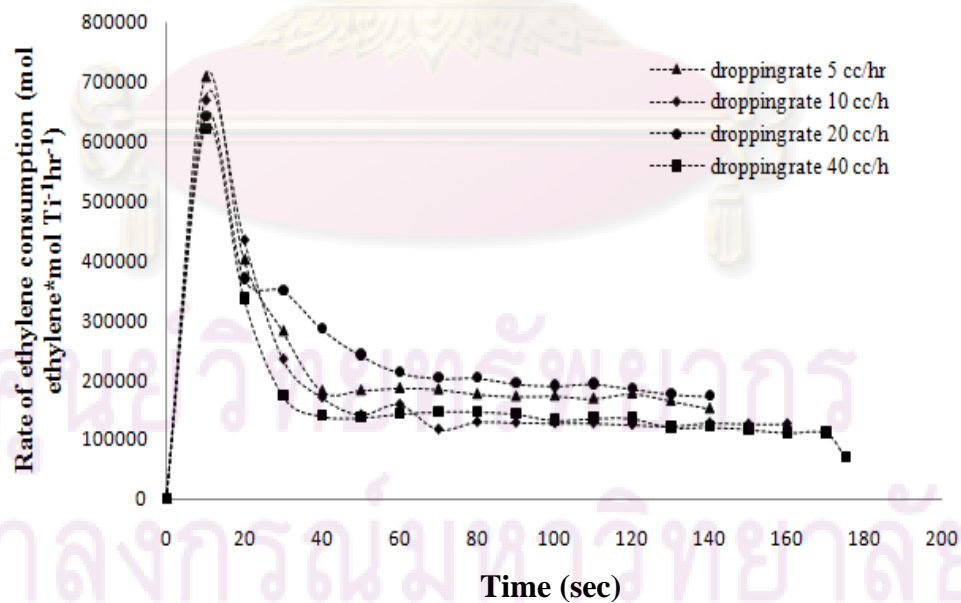
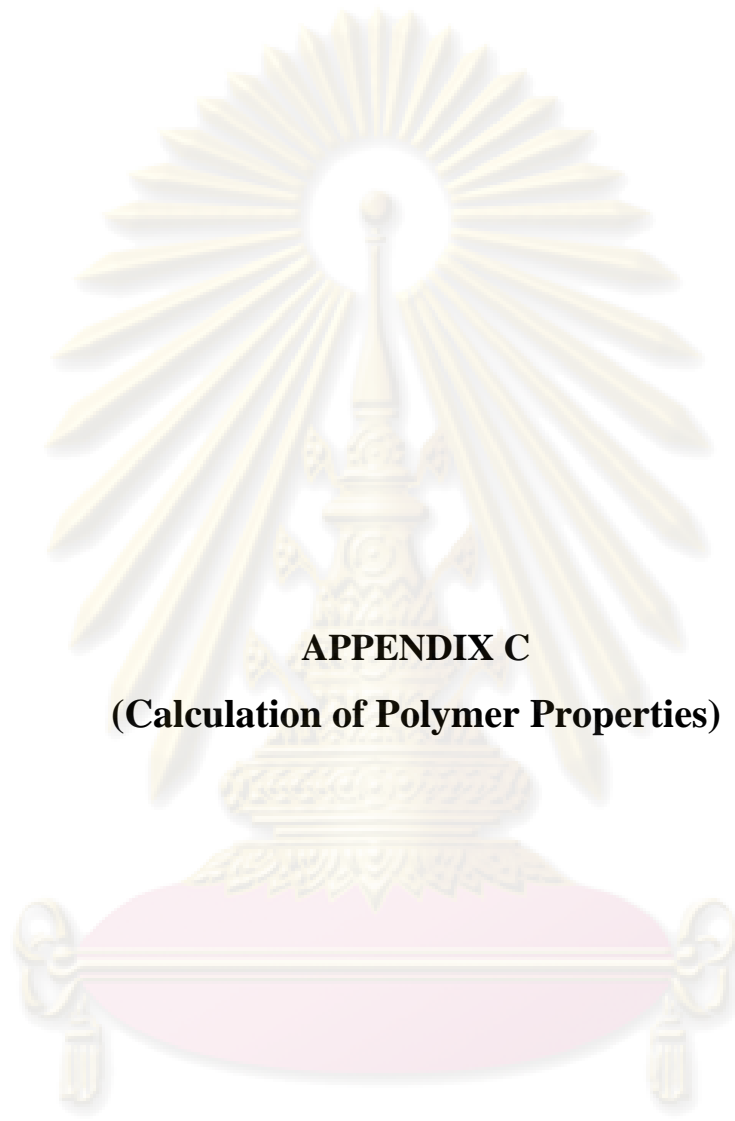


Figure A-6 Rate of ethylene consumption by $\text{Mg}(\text{OEt})_2/\text{TiCl}_4$ catalyst with different dropping rate



APPENDIX C
(Calculation of Polymer Properties)

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C.1 Calculation of crystallinity for polymer

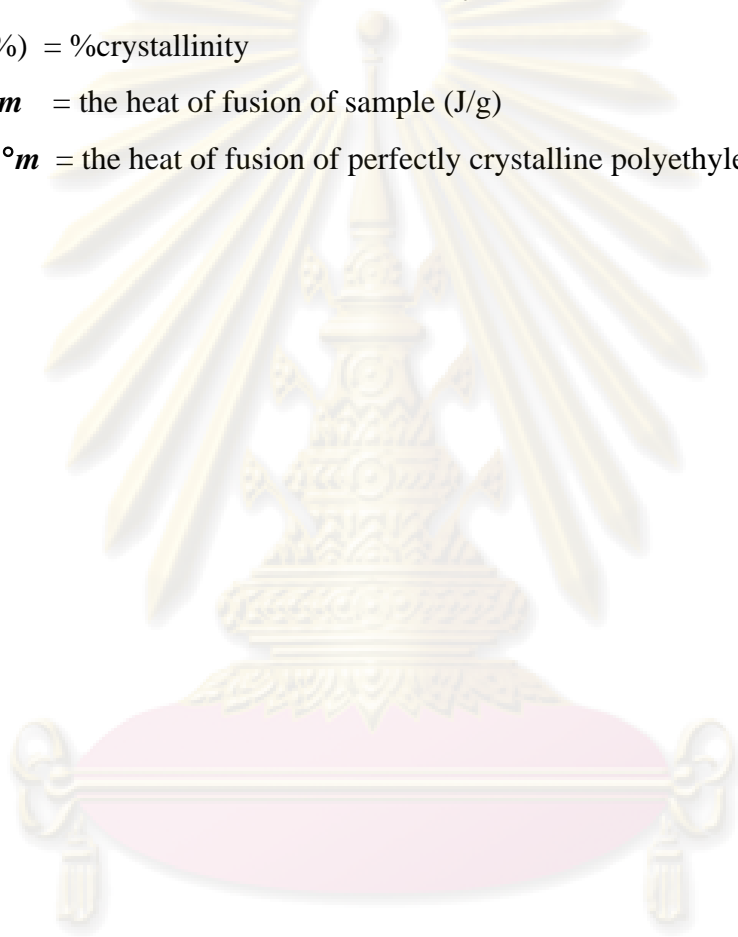
The crystallinities of polymers were determined by differential scanning calorimeter. % Crystallinity of polymer is calculated from equation

$$\chi (\%) = \frac{\Delta H_m}{\Delta H^{\circ}m} \times 100$$

Where $\chi (\%) = \%$ crystallinity

ΔH_m = the heat of fusion of sample (J/g)

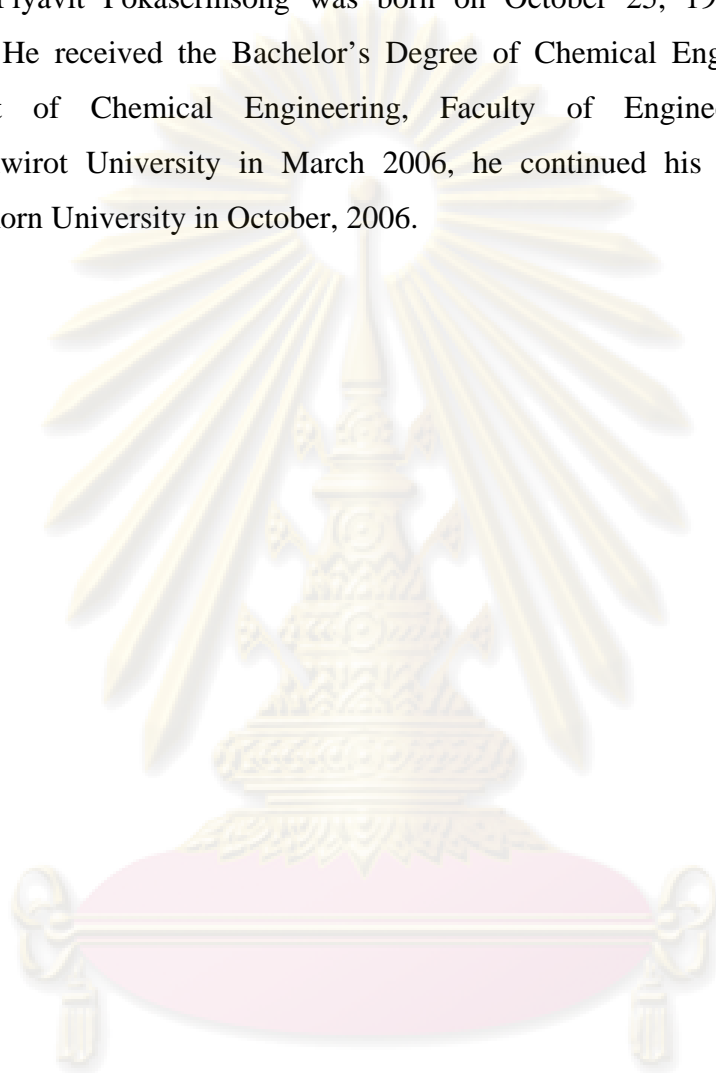
$\Delta H^{\circ}m$ = the heat of fusion of perfectly crystalline polyethylene 293 J/g [56]



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