

MODIFICATION OF $MgCl_2$ -SUPPORTED ZIEGLER-NATTA CATALYST
WITH LEWIS ACIDS FOR ETHYLENE COPOLYMERIZATION

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โคพอลิเมอร์ไรเซชัน

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วิทยานิพนธ์ฉบับนี้ได้ทำการศึกษาผลของกรดลิวอิสในการสังเคราะห์ตัวเร่งปฏิกิริยาซี
เกลอร์-นัตตาในระบบ แมกนีเซียมคลอไรด์-กรดลิวอิส/ไดเอทิลอะลูมิเนียมคลอไรด์/ไททานเนียมเตตระ
คลอไรด์ สำหรับปฏิกิริยาพอลิเอทิลีนโดยเปลี่ยนแปลงปริมาณของกรดลิวอิสที่อัตราส่วนต่างๆกัน
โดยกรดลิวอิสที่ใช้ประกอบไปด้วยอะลูมิเนียมคลอไรด์และซิงค์คลอไรด์ ตัวเร่งปฏิกิริยาถูกวิเคราะห์
ด้วย ESR, SEM-EDX, ICP และ XRD จากการวิเคราะห์ด้วยวิธี ICP พบว่าปริมาณไททานเนียมที่พบ
ในตัวเร่งปฏิกิริยาลดลงเมื่อมีการเติมกรดลิวอิสในตัวเร่งปฏิกิริยาเปรียบเทียบกับตัวเร่งปฏิกิริยาที่
ไม่มีกรดลิวอิส อย่างไรก็ตามจากการวิเคราะห์ด้วยวิธี SEM-EDX นั้นกลับพบว่าปริมาณไททานเนียม
ที่บริเวณผิวนั้นเพิ่มมากขึ้นเมื่อมีการเติมกรดลิวอิสในตัวเร่งปฏิกิริยา ทำให้ค่าความว่างไวในการ
เกิดปฏิกิริยานั้นมีแนวโน้มที่เพิ่มขึ้นเมื่อเติมกรดลิวอิสในตัวเร่งปฏิกิริยาเนื่องจากปฏิกิริยาส่วน
ใหญ่ที่บริเวณผิวของตัวเร่งปฏิกิริยา อีกทั้งน้ำหนักโมเลกุลของพอลิเมอร์ที่ได้จากตัวเร่ง
ปฏิกิริยาดังกล่าว แสดงผลโดยใช้วิธีการวิเคราะห์ GPC ผลการวิเคราะห์แสดงให้เห็นว่าค่า การ
กระจายตัวน้ำหนักโมเลกุลของพอลิเมอร์นั้นเพิ่มขึ้นเมื่อเติมกรดลิวอิสในตัวเร่งปฏิกิริยา เป็นผล
มาจากการมีกรดลิวอิสเป็นองค์ประกอบร่วมในตัวเร่งปฏิกิริยาทำให้มีจำนวนส่วนว่างไวเพิ่มมากขึ้น
จากตัวเร่งปฏิกิริยาที่ไม่มีกรดลิวอิส

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This research aims to investigate the effect of Lewis acids on the synthesized Ziegler-Natta (ZN) catalyst ($MgCl_2$ +Lewis acid/DEAC/ $TiCl_4$) for ethylene polymerization with various ratios of $AlCl_3$ and $ZnCl_2$ as the Lewis acids employed. The catalysts were characterized by ESR, SEM-EDX, ICP, and XRD. From the ICP analysis, it was found that the titanium content in catalyst decreased with increasing the amount of Lewis acid compared with in the absence of Lewis acid system. However, the result obtained from SEM-EDX showed that titanium content at surface of catalyst increased with increasing amounts of Lewis acid resulting in better catalytic activity due to most of reaction also occurred at the surface of catalyst. Moreover, the molecular weight distribution obtained from the GPC result apparently increased because the Lewis acid can be a part of catalyst leading to increased number of active centers.

Department: ...Chemical Engineering Student's Signature

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CHAPTER I

INTRODUCTION

A heterogeneous Ziegler-Natta catalyst was defined as the products from the reactions of transition metal catalysts within group IV-VII and alkyl or aryl aluminum compounds. Ziegler-Natta catalyst have been used in the commercial manufacture of various polymeric materials since 1953 [1, 2] and had continuous development in the polymer synthesis which is widespread application in worldwide. Nowadays, there are many kinds of synthetic polymers, but polyethylene (PE) has the highest productivity in plastic industry [3]. Because of the polyethylene has many benefits such as, excellent chemical resistance, high impact strength, and stiffness even at low temperature [5, 6], so polyethylene was chosen to study in this research.

The molecular weight (Mw) and the molecular weight distribution (MWD) play very important role in the properties and processability of polymer. When the Mw increases, polyethylene has better mechanical properties, but it is difficult for processing. When the MWD increases, polyethylene tends to have the good melt flow rate at high shear rate, which is important for blow molding and extrusion techniques. Therefore, the Mw and MWD of polyethylene should be controlled to obtain the desired properties and easier processability [5, 7].

The Ziegler-Natta heterogeneous catalyst has been well known that it can produce polymers with broad MWD, because of the presence of multiple active centers in catalysts. It is believed that the MWD are mainly determined by active center distribution. There are several ways to control Mw and MWD of polymer. Many literatures have been reported that it can be controlled by using new type of internal and external electron donors, using composite of different catalysts in a single reactor polymerization process or modifying support by doping [4]. Since, modifying supported method is one of the powerful way for control Mw and MWD by doping inorganic compounds on the $MgCl_2$ support, such as $MnCl_2$ [6], $ZnCl_2$ [7], $NaCl$ [8], $AlCl_3$ [4] and $LiCl$ [5]. These literatures were reported that when modifying support with above inorganic compounds, the catalytic activity was increased and MWD was broader at the optimal ratio of inorganic compound. Furthermore, the modification of

MgCl₂ support with inorganic salts can change the active center distribution of catalyst, and it has been proven through deconvolution of polymer MWD curves by using multiple Flory functions. The synthesis of catalysts can be performed using many methods, such as coprecipitation, co- ball milling, and chemical reaction method. However, the coprecipitation method is chosen because it can control the morphology of the catalyst and has been found that activation of MgCl₂ is more effective than mechanical activation by ball milling [13].

The effect of MgCl₂ modifying with other Lewis acids on ethylene polymerization and ethylene/ α -olefins copolymerization is still rare. Therefore, in the present work, we have investigated the preparation of MgCl₂/AlCl₃+ZnCl₂/DEAC/TiCl₄-type supported catalysts carried out via coprecipitation method and varying the amounts of Lewis acid. Then, the catalysts were used in slurry phase ethylene polymerization. The polyethylene properties were characterized through the catalytic activity, Mw and MWD. Moreover, in copolymerization we also investigated the effect on comonomer insertion.

1.1 Motivations

1. The modification of MgCl₂ support with addition of 2nd metal chloride can improve properties of catalyst and polymer
2. The modification of MgCl₂ support is less investigated in ethylene polymerization

1.2 Objective

The aim of this research is to investigate the effect of Lewis acid combining with MgCl₂ support in the synthesis of Ziegler-Natta catalysts using MgCl₂/AlCl₃+ZnCl₂/DEAC/TiCl₄ system for ethylene polymerization. AlCl₃ and ZnCl₂ are represent to the Lewis acids as mentioned above.

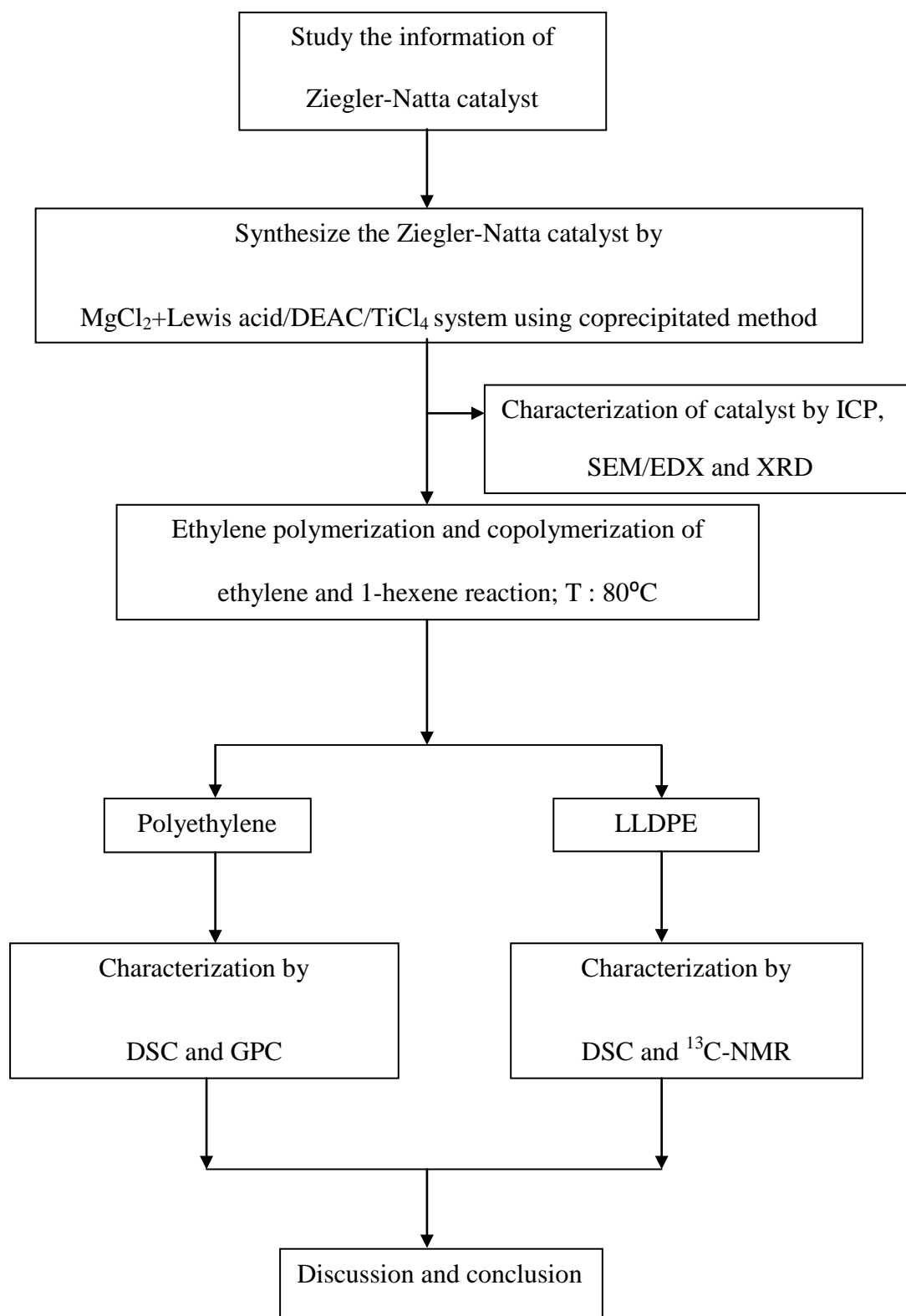
1.3 Research Scopes

1. Synthesize the Ziegler-Natta catalyst by system of MgCl_2 +Lewis acid/DEAC/ TiCl_4
2. Synthesize the polyethylene by slurry phase polymerization with synthesized catalyst upon the specified condition.
3. Determine the effect of Lewis acid amount such as AlCl_3 and ZnCl_2 .
4. Determine the effect of Lewis acid on the catalytic activity and polymer properties for the ethylene polymerization.
5. Characterize the polyethylene with differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and ^{13}C Nuclear magnetic resonance (NMR).
6. Characterize the synthesized catalyst with X-ray diffraction (XRD), scanning electron microscopy (SEM) and inductively coupled plasma (ICP)
7. Discussion and summarization of the results.

1.4 Benefits

1. Polyethylene synthesized by slurry phase polymerization with Ziegler-Natta catalyst having modified MgCl_2 support by Lewis acid changed the catalytic activity and polymer properties.
2. The properties of catalyst and polymer improved due to the modification of surface structure in support of the catalyst.
3. These information used as a reference for polymer industries.

1.5 Research methodology



CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Ziegler-Natta catalyst

2.1.1 Introduction

The most important discovery in polymer science and catalysis since 50 years ago is the polymerization of olefins using metal-based catalysts[1]. Karl Ziegler was the first one who discovers that transition metal halides such as $TiCl_4$, $TiCl_3$, $ZrCl_4$ and other, in combination with alkylaluminum compounds convert ethylene to high molecular weight linear polyethylene and next time, Giulio Natta discovered stereoregular polymers of α -olefins such as propylene, 1-butene and other. Ziegler and Natta shared the 1963 Nobel Prize for this contribution to chemistry [2].

2.1.2 Basic concepts of Ziegler-Natta catalyst

Ziegler-Natta catalyst systems was defined as products formed from involving transition metal compound of group IV-VII, such as Ti, V or Cr compounds called “active catalyst” reactions with alkyl or aryl halides of group I-III metals called “cocatalyst” under inert atmosphere.

The Ziegler-Natta heterogeneous catalysts can be divided into unsupported and supported. First, $TiCl_3$ is a successful unsupported heterogeneous Ziegler-Natta catalyst and it can commonly prepared by the reduction of $TiCl_4$ with an alkyl. Natta discovered on this catalyst system that only a very small percentage of Ti in $TiCl_3$ participates during polymerization. This recognition led to the development of supported catalysts [13, 14].

2.1.2.1 $MgCl_2$ -supported Ziegler-Natta catalyst

The large efforts to characterize the structure, morphology, and other properties of the supports that have important role with how catalyst activity changes. Through a development of $MgCl_2$ supported to make Ziegler-Natta has higher catalytic activity among various solid carriers [11]. $MgCl_2$ has been found to

be the best support material among several solid carriers due to atomic size, shape and coordination number are similar between Mg and Ti [17, 18]. Moreover, MgCl_2 is not only act as a support material, but also as a part of the active complex and dispersion of the titanium atoms over a high surface area [1, 16]. It is believed that the support plays an inert role in the polymerization mechanisms. The most commonly used support is based on anhydrous MgCl_2 . The crystal form of catalyst is also important because the crystal form can show that MgCl_2 was activated to δ - MgCl_2 form. Previous development of the support, MgCl_2 were prepared via ball milling, which is physical reaction method, convert α - MgCl_2 into δ - MgCl_2 by it is only disordered from rotation and translation of the layer. The important and clearly observable X-ray diffraction spectrum in δ - MgCl_2 form was characterized by a peak at $2\theta \approx 15^\circ$ representing the separation of successive Cl-Mg-Cl triple layers and the reflection at $2\theta \approx 30^\circ$ and $2\theta \approx 50.5^\circ$ representing the (104) and (110) peak, respectively [13]. If compare between the α forms and δ form of MgCl_2 are characterized by the substitute of the peak $2\theta \approx 30^\circ$ by a broad halo. In highly activated MgCl_2 , the diffraction peak at $2\theta \approx 15^\circ$ may be completely disappeared, indicating that the support comprises single Cl-Mg-Cl structural layers (monolayers). The important factor of the catalysts is δ - MgCl_2 , which show a disordered structure arising from the translation and rotation of structural Cl-Mg-Cl layers with respect to one another that destroy the crystal order in the stacking direction and δ - MgCl_2 can called that "Activated MgCl_2 ". Consequently, the X-ray spectrum displays in the figure 2.1

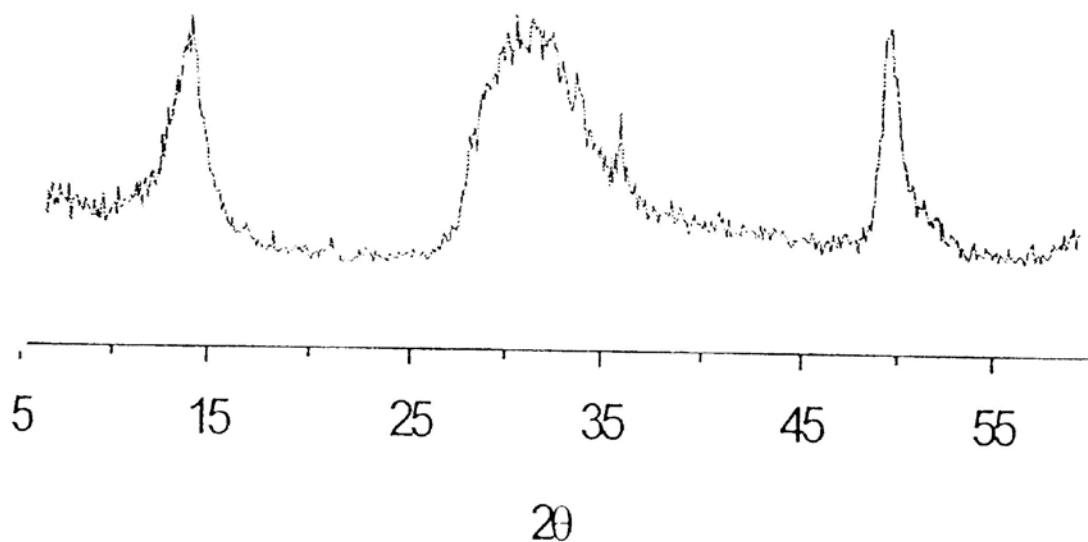


Figure 2.1 X-ray diffraction pattern of δ -MgCl₂[7].

The disordered δ -MgCl₂ structure showed broad band centered at $2\theta \approx 30^\circ$. Furthermore, δ -MgCl₂ and δ -TiCl₃ have the same crystal structure and the almost equal in ionic radius and lattice distance as shown in Table 2.1

Table 2.1 Crystalline data of δ -MgCl₂ and δ -TiCl₃ [17]

δ -MgCl ₂	δ -TiCl ₃
Ionic radii of hexagonal close packing of the Cl ions	
a = 3.63 °A	a = 3.54 °A
b = 3.63 °A	b = 3.54 °A
c = 5.93 °A	c = 5.86 °A
Lattice distance of cation coordination : octahedral	
Mg-Cl = 1.23 °A	Ti-Cl = 1.25 °A
Mg ²⁺ = 0.65 °A	Ti ⁴⁺ = 0.68 °A
	Ti ³⁺ = 0.76 °A

2.1.3 The preparation of Ziegler-Natta catalysts

The catalyst design is very important and necessary for final polymer properties. The efficiency of catalyst preparation must be improved for controlling catalyst morphology, particle size, particle size distribution and other properties of catalyst. The catalyst properties can be predicting the efficiency of olefin polymerization such as morphology of polymer. There are several methods to prepare the catalyst. In this work, we will describe only main methods which commonly use in the industrial [1].

2.1.3.3 Precipitated and support MgCl₂-based catalysts

Precipitation of Ziegler-Natta catalysts is the process in which a phase-separated solid is formed from homogeneous solution. First, bringing support and catalyst components dissolved in the solutions and then these catalyst components and support are precipitated as an amorphous material to achieving high catalytic activity to the catalyst. There are several methods to make the precipitated solid from the solution such as decreasing the temperature to under melting temperature of these components in solution, changing pH has directly affect to control the degree of super saturation, addition of a suitable chlorination agent which titanium can be added either as soluble complex or used as one of the chlorination agents. The properties of catalyst can be controlled via precipitation step. For example, particle size and its distribution can be controlled by quenching precipitated method that can be control the catalyst morphology to sphere shape like using silica as the based-support, and its chemical dispersion as well because having a short precipitated time therefore all catalyst components are simultaneously precipitated.

A large number of the investigations have been carried out to measure the number of active sites on these catalysts and catalytic activities [5, 7, 9, 22], these works reported that modify MgCl₂ supported by inorganic compound can be influential with number of active site distribution which can be prove through deconvolution of polymer MWD curves by using multiple Flory functions.

The precipitated and support MgCl_2 -based catalysts method is interested method because it can control the catalyst morphology and easy to synthesize catalyst because it is not required complicated instruments.

2.1.4 Olefin polymerization

2.1.4.1 Nature of the catalyst

The crystal form of the catalyst is also important, and the violet α , γ , and δ form of TiCl_3 produce a greater quantity of polyethylene when combined with an aluminum alkyl (cocatalyst) than the brown β -structure. As the active sites for heterogeneous polymerizations are believed to be situated on the crystal surfaces, the structure is all-important. In the layered structure of α - TiCl_3 , where every third Ti^{3+} ion in the lattice is missing, a number of Cl vacancies occur on the surface to maintain electrical neutrality in the crystal.

In β - TiCl_3 , the linear chains form bundles in which some Ti ions are surrounded by five Cl^- ions and some by only four Cl^- . This means that the steric control at the sites with two vacancies is now less rigid and stereoregulation is much poorer.

2.1.4.2 Nature of active centers

Most of the experimental evidence points to propagation taking place at a carbon-to-transition metal bond with the active center being anionic in character. Free-radical reactions are considered to be nonexistent in the Ziegler-Natta systems because neither chain transfer nor catalyst consumption occurs. The active centers also live longer than radicals and resemble "living" polymer systems in many ways, one being that block copolymers can be produced by feeding two monomers alternatively into the system.

Majority opinion now favors the concept that the d-orbitals in the transition element are the main source of catalytic activity and that chain growth occurs at the titanium-alkyl bond. The ideas now presented are predominantly those of Cossee and Arlman, and will be developed using propylene as the monomer.

The first stage of monometallic is the formation of the active center, illustrated here using α -TiCl₃ as the catalyst. The suggestion is that alkylation of the 5-coordinated Ti³⁺ ion takes place by an exchange mechanism after chemisorptions of the aluminum alkyl on the surface of the TiCl₃ crystal. The four chloride ions remaining are the ones firmly embedded on the lattice, and the vacant site is now ready to accommodate the incoming monomer unit. The reaction is confined to the crystal surface, and the active complex is purely a surface phenomenon in a heterogeneous system as shown in Figure. 2.2

The attacking monomer is essentially nonpolar but forms a π -complex with the titanium at the vacant d-orbital. A diagram of a section shows that the propylene molecule is not much bigger than a chloride ion and, consequently, the double bond can be placed adjacent to the Ti ion and practically as close as the halide. After insertion of the monomer between the Ti-C bonds, the polymer chain then migrates back into its original position ready for a further complexing reaction.

The main features of the monometallic mechanism are as follows: 1. an octahedral vacancy on the Ti³⁺ is available to complex the olefin, 2. the presence of an alkyl to transition metal bond at this site is required, and 3. the growing polymer chain is always attached to the transition metal.

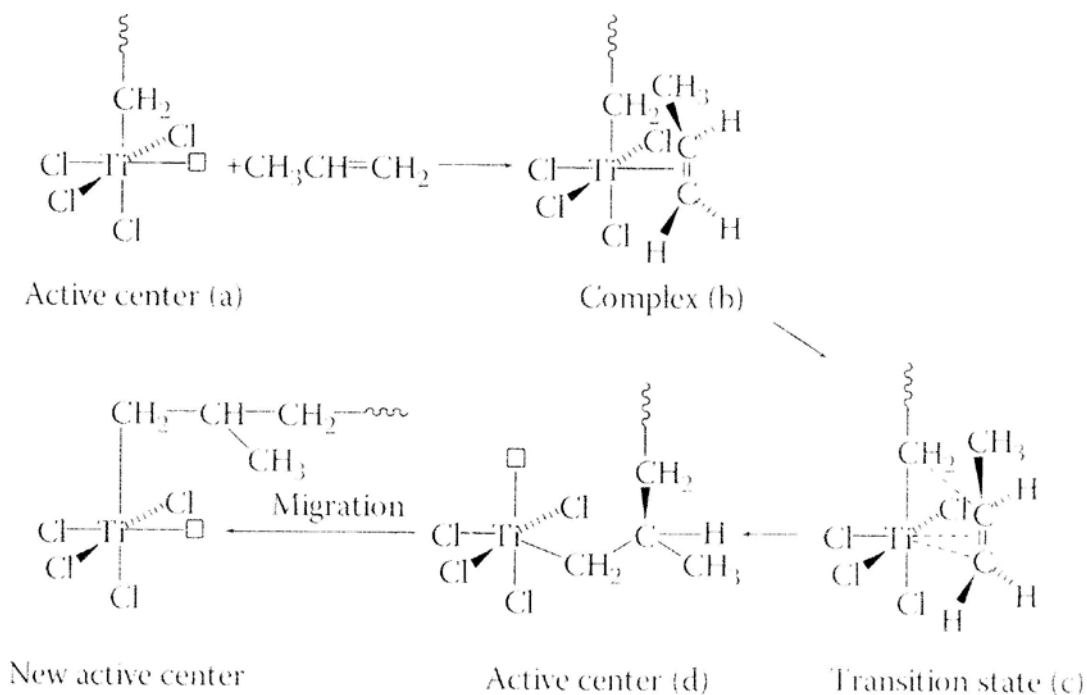


Figure 2.2 monometallic mechanisms [10]

Catalyst composition affects both stereoregulation and polymer yield. Thus, Ti^{3+} is more active producer of isotactic polypropylene than Ti^{4+} or Ti^{2+} . Although, increasing the length of the associating alkyl group is decrease the efficiency of stereo regular placements. Varying the transition metal and the associated aluminum compounds in the catalysts also influences the nature of the product [10].

2.2 Polyethylene

Well known that one of all polymers which has the highest productivity and widely used everywhere in the world is the Polyethylene [4, 24]. The first major polymer types (Polyethylene and polypropylene) are often given a special name, polyolefins, because of their similar chemical properties. The term means “oil-like” and refers to the oily or waxy feel that these materials have. Polyolefins consist of only carbons and hydrogens, without other atoms in polymer. Polyethylene is the simplest of all polymers, with just two carbons and four hydrogens in the basic polymer repeating unit. Figure 6 shown the polymer unit for polyethylene(PE)[12, 25].

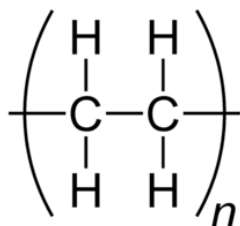


Figure 2.3 polymeric representation of polyethylene(PE)

Perhaps the most important applications for PE are based upon its low cost and ease of manufacture. Polyethylene is easily polymerized from ethylene gas and cheap obtained from either natural gas (methane) or from crude oil. Moreover, the processes used to make PE are easily scaled to produce the polymer in very large quantities. PE applications has many benefits from the low cost of production and ease of processing for instance, trash bags, packaging and other films, containers (such as milk bottles), many children's toys, and various house wares.

The major difference of PE is the shape; molecules originate from changing the polymerization conditions in the reactor during the polymerization reaction. The major factors in conditions such as pressure, temperature, and catalyst type have a main effect on the shape by both of the creating and suppressing the formation of molecular branching. Branching is the formation of side chains off the basic polymer backbone. These side chains can occur when a hydrogen-carbon bond is broken during the polymerization reaction. Although, polymerization is operating at high temperature, there is often enough energy in the molecules that some carbon-hydrogen bonds break, thus creating a free radical on the carbon. (The hydrogen takes with it one electron from the bond and leaves the other electron localized on the carbon, thus forming a carbon free radical.) This free radical of carbon can then act as a site for chain growth to begin. When this happens, the chain can grow at two locations simultaneously. The normal end of the chain and the newly created free radical location. The net result is a branch off the main carbon backbone. The mechanism for the breaking of carbon-hydrogen bonds and formation of side chains (branches) is illustrated in Figure 2.4.

2.2.1 Types of polyethylene

2.2.1.1 Low-density polyethylene (LDPE)

The type of PE formed under high-temperature and high-pressure polymerization conditions are called low-density polyethylene (LDPE). The density is low because these polymerization conditions give increase to the formation of several branches, which are often quite long and prevent the molecules from packing close together to form crystal structures. Therefore, LDPE has low crystallinity (generally below 40%) and the structure is mostly amorphous.

The low density and highly amorphous nature of the structure affects the physical properties of LDPE. LDPE is therefore used in applications that required its flexibility, impact toughness, and stress crack resistance. Furthermore, LDPE is the lowest melting and easiest to process of the PE types so it is used extensively in high-volume applications. Especially, when strength and other mechanical properties are not critical.

2.2.1.2 High-density polyethylene (HDPE)

At low temperature and pressure in polymerization conditions result in limited branching. A PE that is more linear, with only a bit, short branches, is created. This type of PE is called high-density polyethylene (HDPE). As the name implies, the polymer chains in HDPE can easily pack tightly and form crystalline structures, thus enlarge the density. In general, HDPE is stiffer, stronger, and more abrasion resistant than LDPE. HDPE has disadvantage of increased brittleness compared to LDPE. For applications where the high strength of HDPE and high impact toughness are required, a very high molecular weight grade of HDPE has been produced. This material, called ultra high molecular weight polyethylene (UHMWPE), is really a sub group of HDPE, since it is made by a similar process. UHMWPE will typically have molecular weights in the range of 3 million to 6 million versus typical HDPE molecular weights of 50,000 to 300,000.

In order to get long polymer chains under the HDPE conditions, a process that requires much lower temperatures and lower pressures than the process used to

make LDPE, a catalyst is required. The first catalyst was developed by Karl Ziegler in 1952 and was then applied to polymerizations of other monomers by Giulio Natta. The catalyst is called a Ziegler-Natta catalyst, which is a general name applied to all similar catalysts even though some more recent types were developed and patented by different inventor.

2.2.1.3 Linear low-density polyethylene (LLDPE)

A third type of PE is operate at at low pressure in polymerization like the HDPE process can produce the linear low-density polyethylene (LLDPE), but which produces longer and more branches. LLDPE generally has 26 to 35 branches per 1000 backbone carbons, whereas HDPE generally has 1 to 2 branches per 1000 backbone carbons. This branching in LLDPE is adequate to prevent close packing of the molecules. Hence, LLDPE has a low density like LDPE but a linear structure much like HDPE.

The side chains are actually made by adding another monomer (called a comonomer) to the ethylene monomer during the polymerization process, along with an appropriate catalyst. The comonomer must contain a carbon-carbon double bond and then few (two, four, or six) additional carbons. (Organic molecules of this type are called α -olefins, where the α indicates that the double bond is between the first and second carbons.) The additional carbons become the side chains and are two, four, or six carbons long, depending on the comonomer used (butane, hexane, or octene). Longer side chains generally give improved physical properties because of increased chain entanglement and stronger secondary bonding. The number of side chains is determined by the concentration of the comonomer relative to the amount of ethylene and is typically 8% to 10% in most commercial grades.

2.3 Polymerization processes and reactors for polymerization with heterogeneous catalysts.

2.3.1 Slurry/Bulk Processes

In slurry polymerization the catalysts are suspended in an inert suspension medium, typically alkanes such as hexane, isobutene, or propane. The monomer, comonomer and chain-transfer agent must be dissolved in the suspension medium. The slurry process is used for the polymerization of polyethylene, predominantly to produce high-density polyethylene (HDPE). The slurry polymerization of ethylene is limited to higher densities, since linear low-density polyethylene (LLDPE) fractions with a high comonomer content and/or a low molecular weight would partially dissolve in the suspension medium and this would lead to reactor fouling [1].

In bulk- or liquid pool polymerization, the monomer is used as a suspension medium. In bulk polymerization, which is widely used for the production of PP, heat removal from the polymer particle to the liquid bulk-phase is superior to that seen with gas-phase polymerization.

When designing a catalyst for use in slurry- or bulk polymerization, the avoidance of leaching (i.e., the extraction of active components into the liquid phase) is essential. Leaching can lead to uncontrolled homogeneous polymerization in the liquid phase and the formation of deposits on the reactor walls. This so-called “reactor fouling” significantly reduces the operability and hence the economy of a process.

2.4 Molecular weight and Molecular weight distribution

2.4.1 Molecular weight

The molecular weight of polymer is defined as the sum of the atomic weights of each of the atoms in the molecule. A much simpler experimental measurement of the size of the polymer is to determine the molecular weight. The atomic weights can be found by referring to the periodic table. For instance, the atomic weight of carbon is 12 g/mol, so each carbon in the molecule would be counted as 12. The atomic

weight of hydrogen is 1 g/mol; of oxygen, 16 g/mol; and so on. When the exact molecular formula is known, the molecular weight is easy to calculate. For example, water (H₂O) would have a molecular weight of 18 g/mol (16+1(2)) and benzene (C₆H₆) would have a molecular weight of 78 g/mol [(6x12)+(6x1)]. The molecular weight of a polymer could be likewise calculated if the exact formula is known [2]. For instance, if the polymer is polyethylene with n equal to 1000, the molecular (repeat unit) formula would be as follows: **(C₂H₄)₁₀₀₀** The molecular weight would be 28,000 g/mol {[(2x12) + 4] x 1000} since each C₂H₄ would have a weight of 28 g/mol and there would be 1,000 of these units.

2.4.1.2 Average molecular weight

In a real polymer systems the nature of the polymerization process results in chains with many different lengths. There are four molecular weight averages in common use; the number-average molecular weight, M_n ; the weight-average molecular weight, M_w ; the z-average molecular weight, M_z ; and the viscosity-average molecular weight, M_v . These are defined below in terms of the numbers of molecules N_i having molecular weights M_i , or in term of w_i , the weight of species with molecular weights M_i [14],

$$M_n = \frac{\sum_i M_i N_i}{\sum_i N_i} = \frac{\sum_i w_i}{\sum_i (w_i/M_i)}$$

$$M_w = \frac{\sum_i M_i^3 N_i}{\sum_i N_i M_i^2} = \frac{\sum_i w_i M_i}{\sum_i w_i}$$

$$M_z = \frac{\sum_i M_i^2 N_i}{\sum_i N_i M_i} = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i}$$

$$M_v = \left[\frac{\sum_i N_i M_i^{1+\alpha}}{\sum_i N_i M_i} \right]^{\frac{1}{\alpha}}$$

Where M_i is the molecular weight of species I (that is, the weight of molecules in counting cell i) and N_i is the number of molecules of a particular molecular species I (comprising molecules in the same counting cell).

For polymers, an important value to be examined is the molecular weight. Therefore the molecular weight distribution (MWD) is simply a count of the number of molecules of each molecular weight. The molecular weight distribution can be envisioned by plotting the number of molecules of each molecular weight against the molecular weights, as shown in Figure 2.5. Rather than plot every single molecular weight along the x axis, the molecular weights are often grouped so that similar weights can be counted together. These groups are called counting cells. The counting cells would, therefore, be plotted along the x axis with the width of the cell corresponding to the range of values to be put into the cell. The number of molecules in each counting cell would be plotted on the y axis and would determine the height of the cell. The counting cells are, therefore, rectangles with a width the same as the spread in values and the height the number of values within that spread. The counting cells are given a subscript (i) so that each can be identified in a general representation, as shown in Figure 2.5. When this is done, the histogram is completed.

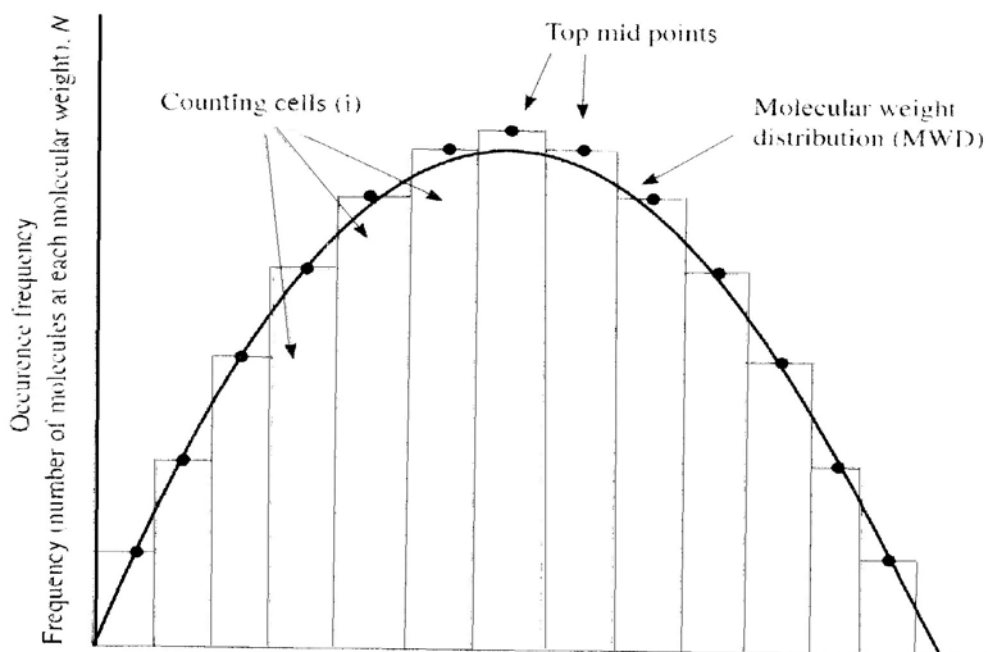


Figure 2.5 Plot of number of molecules at each molecular weight versus molecular weight, thereby defining a molecular weight distribution. [12]

A curve can be drawn representing the overall shape of the plot by connecting the tops of each of the cells as their midpoints. This curve between top mid points can then be modified slightly to be continuous and smooth, as is represented by line labeled molecular weight distribution (MWD) in Figure 2.5.

2.4.2 Molecular weight distribution

As already indicated, the nature of the polymerization process results in chains of varying size (molecular weight) and a distribution of the size and weight of the polymers. In some polymerization processes, growing chains would successfully react with many monomers to form very long chains, and in other processes, the chains would be considerably shorter. This variance in chain size or molecular weight is called the molecular weight distribution (MWD), which is another important method of characterizing polymers.

In some cases, the molecular weight distribution would be very narrow indicating that most of the polymers were nearly the same length. Other molecular weight distributions would be quite broad indicating that the polymer batch has some short and some long polymer chains. Examples of narrow and broad molecular weight distributions are given in Figure 2.6.

The molecular weight distribution (MWD), sometimes called a molar mass distribution, or polydispersity index (PDI), equal to M_w/M_n , which is a convenient measure of the width of the molecular weight distribution.

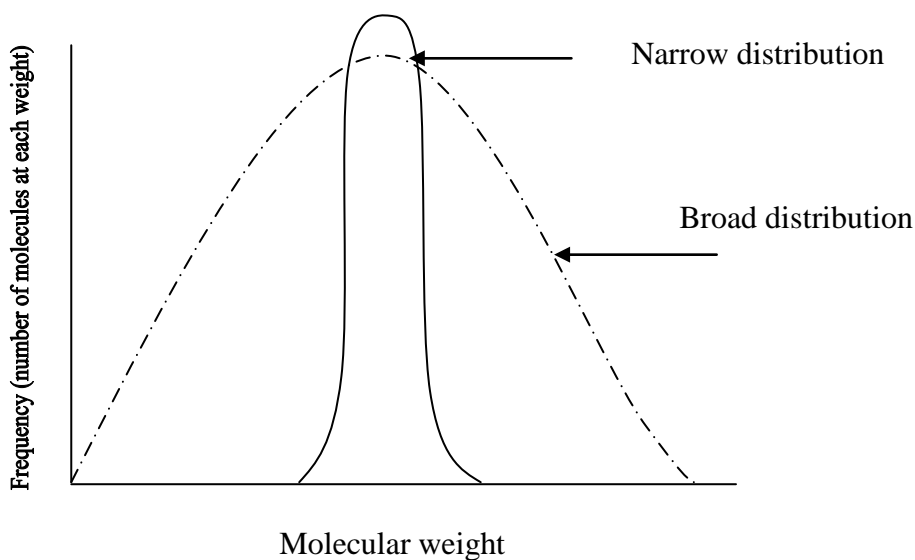


Figure 2.6 Broad and narrow molecular weight distributions.

2.5 Characterization

2.5.1 Scanning electron microscope (SEM)

The main advantage of electron microscopy is its much-improved resolution compared to that of light microscopy. In the SEM, a finely focused electron beam is scanned across the specimen, and scattered electrons emitted at each point are collected by appropriate detectors and forming an image. SEM instruments have resolutions better than 5nm and are useful for the characterization of surfaces and the determination of surface topography [10]. Figure 2.7 shows the range of events that take place when the incident electron beam strikes the specimen. Backscattered electrons are high-energy electrons that have been elastically scattered by interaction of the incident beam with the nucleus. The energy of these electrons is comparable to that of the incident beam.

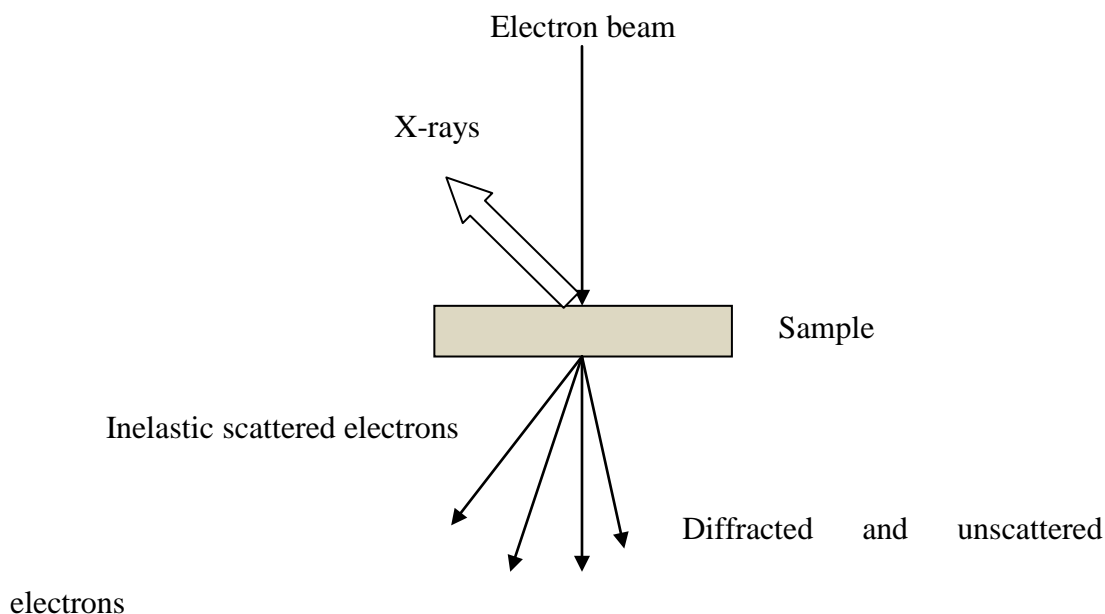


Figure 2.7 Illustration of the types of radiation produced following interaction of an electron beam with a specimen.

2.5.2 Differential Scanning Calorimetry (DSC)

The most important method for determining glass transition temperature (T_g) is the differential scanning calorimetry (DSC) test. This test involves measuring the heat absorbed by a sample when that sample goes through thermal transitions. The DSC test allows these transitions to be identified by noting the absorption of heat from a plot of heat versus time as the sample is gradually heated. The result identifies the temperatures of the transitions. Moreover, the DSC can measure melting temperature (T_m) and from its data can be calculate percent crystallinity, also.

2.5.3 Nuclear magnetic resonance (NMR)

High-resolution NMR has proved to be a useful tool in the study of the microstructure of polymer in solution, where the extensive molecular motion reduces the effect of long-range interactions and allows the short-range effects to dominate. For the purposes of NMR measurements, three or more consecutive monomer units in a chain are considered to define a configuration and are called a triad. The term heterotactic is used now to define a triad that is neither isotactic nor syndiotactic. In

the structure shown, the three equivalent protons of the α -methyl group absorb kinds of triad because the environment of the α -methyl group in each is different [10].

2.5.4 Gel Permeation Chromatography (GPC)

The molar weight distribution (MWD) of the polymer sample has a significant influence on its properties. The determination of the MWD by conventional fractionation techniques is time consuming, and a rapid, efficient, and reliable method that can provide a measure of the MWD in a matter of hours has been developed. This is Gel Permeation Chromatography (GPC). Known alternatively by its more descriptive name size exclusion chromatography (SEC), the method depends on the use of mechanically stable, highly cross-linked gels, which have a distribution of different pore sizes and can, by means of a sieving action, effect separation of a polymer sample into fractions dictated by their molecular volume[10]. The size of the molecule, defined by its hydrodynamic radius, can or cannot enter small pores in a bed of cross-linked polymer particles [9], the most common form of the stationary phase. The smaller molecules diffuse in and out of the pores via Brownian motion and are delayed. The larger molecules pass by and continue in the mobile phase.

The instrumentation most commonly used in GPC work is illustrated in Figure 2.8. The stationary phase consists of small and porous particles. While the mobile phase flows at a specified rate controlled by the solvent delivery system, the sample is injected into the mobile phase and enters the columns. The length of time that particular fraction remains in the column is called the retention time[15]. As the mobile phase passes the porous particles, the separation between the smaller and the larger molecules becomes greater. While separation of polymer chains according to size remains the most important experiment. [14]

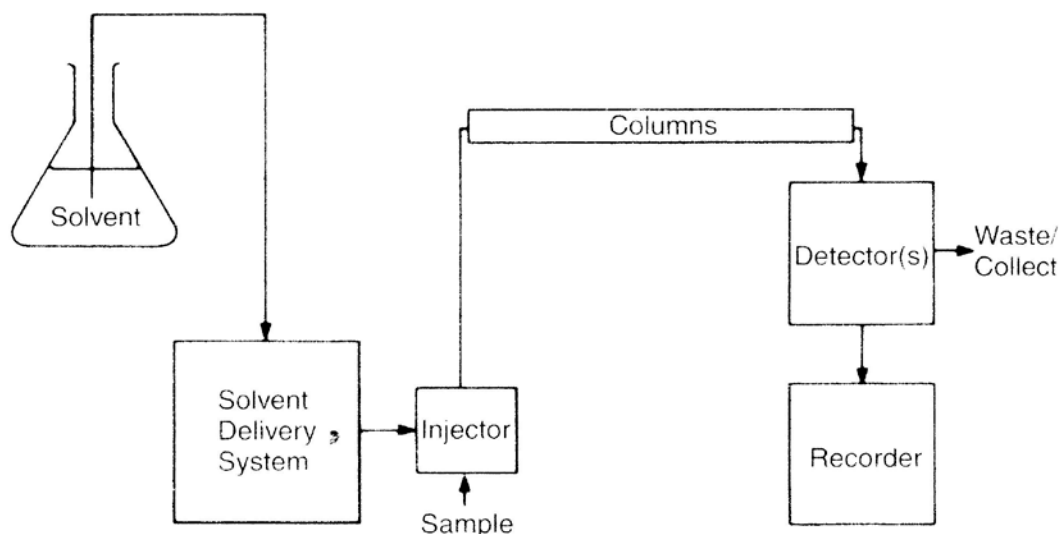


Figure 2.8 An illustration of the modules that make up GPC instrumentation [16]

2.5.5 X-ray diffraction (XRD)

Scattering techniques, such as x-ray, neutron, and light are extensively used to investigate various structural features of polymeric system or catalytic system, including crystalline order and crystallinity, conformation, local structure, domain size, etc.

The basic features of scattering experiment are schematically represented in figure 2.9. They consist of (1) a radiation source, (2) a system of collimation and/or monochromation, (3) the sample, and (4) a detection system. The incident radiation is characterized in terms of its wavelength, λ_0 , wave vector k_0 with magnitude $2\pi/\lambda_0$, and energy E_0 . In the case of the elastic scattering, no energy change occurs during the process, but only a change in the direction of travelling of the wave, defined by the scattering angle, Θ . Thus, for elastic scattering, the magnitude of the initial wave vector k_0 coincides with that of the final wave vector k . The wave vector change, $Q = k - k_0$, defines this change, and it is referred to as the scattering vector or the momentum transfer. For an elastic process, $Q = (4\pi/\lambda_0)\sin(\Theta/2)$

Structural investigations are based on measurements of elastic scattering, and so the scattered intensity needs only be monitored as a function of the scattering angle the scattering vector Q makes it possible to distinguish between wide- and small- angle regimes, though Bragg's law:

$$n\lambda = 2d\sin(\Theta/2)$$

Where d is distance between two crystallographic planes and n is the order of reflection. By combining Bragg's law with the definition of Q , a relationship between structure in real space and scattering in Q -space is derived:

$$D = 2\pi / Q$$

This equation indicated that an inverse relationship exist between d and Q and so low Q values probe large distances characteristic of chain dimensions, lamellar spacing, and domain structures, whereas large Q value give information on the local polymer structure.

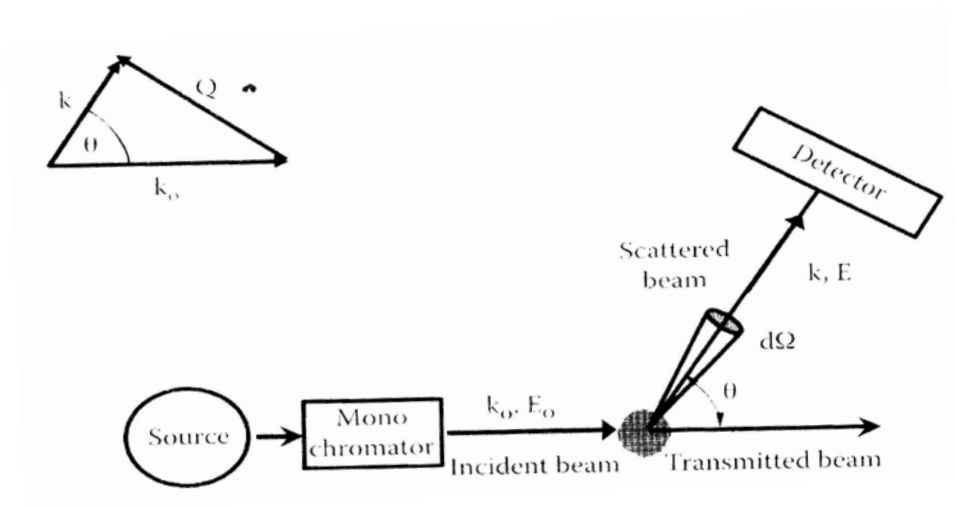


Figure 2.9 Schematic diagram of a scattering experiment [10]

2.5.6 Inductively Coupled Plasma (ICP)

Inductively Coupled Plasma (ICP) is an analytical technique used for the detection of trace metals in environmental samples. The primary goal of ICP is to get elements to emit characteristic wavelength specific light which can then be measured.

ICP hardware is designed to generate plasma, which is a gas in which atoms are present in an ionized state. The basic set up of an ICP consists of three concentric tubes, most often made of silica. These tubes, termed outer loop, intermediate loop, and inner loop, collectively make up the torch of the ICP. The torch is situated within a water-cooled coil of a radio frequency (r.f.) generator. As flowing gases are introduced into the torch, the r.f field is activated and the gas in the coil region is made electrically conductive. This sequence of events forms the plasma. The formation of the plasma is dependent upon an adequate magnetic field strength and the pattern of the gas streams follows a particular rotationally symmetrically pattern. The plasma is maintained by inductive heating of the flowing gases. The induction of a magnetic field generates a high frequency annular electric current within the conductor. The conductor, in turn, is heated as the result of its ohmic resistance.

2.6 Literature reviews

Zhi-Quang Fan et al., 2006 [4] have studied on effect of doping several amount of AlCl_3 on MgCl_2 supported Ti-based Ziegler-Natta catalyst via recrystallize support method or coprecipitated support method by dissolved in EtOH and reaction the support with TiCl_4 . From WAXD analysis found that in AlCl_3 -doped catalyst were not detected AlCl_3 crystallites. The catalyst performance in ethylene polymerization was investigated. The results showed that the doping of AlCl_3 in catalyst can slightly improved activity than undoping with AlCl_3 and the molecular weight distribution are higher from 10.8 to 47.9 when increasing amount of AlCl_3 in catalysts. The GPC curve was deconvoluted by multiple flory functions for investigation of active center distribution changing. It was found that when adding AlCl_3 in catalyst it can increase types of active centers.

Fregonese, D., and Bresadola, S., 1999 [7] have prepared MgCl_2 doped with ZnCl_2 Ziegler-Natta catalyst for propylene polymerization to investigate the effect from amount of ZnCl_2 doped such as 0, 2, 5, 10 wt% on catalytic activity and its properties. The result displayed that catalytic activity are increased when adding the ZnCl_2 in catalyst. There is the highest activity at ZnCl_2 added 5 wt% and if going higher wt%, it was found that the activity decreases. The isotactic index also tend to the activity trend. The polydispersity was found to be only little affected. The XRD analysis was discovered that all of the ZnCl_2 doped supports reveal broader band at $2\theta=15, 32, \text{ and } 50.5^\circ$, which resemble with $\delta\text{-MgCl}_2$. Surprisingly, the Zn doped MgCl_2 show the broader band at $2\theta\approx 32^\circ$. May be ascribe this situation that both to the presence of alkyl metal derivatives and to structures in which magnesium is partially substituted by zinc base on consider if ionic radii are very closely ($\text{Zn}^{2+} = 0.88^\circ\text{A}$, $\text{Mg}^{2+} = 0.86^\circ\text{A}$).

Garoff, T. and Leinonen, T., 1996 [6] have investigated the properties of Ziegler-Natta catalyst that were doped by MnCl_2 and polypropylene were produced from these catalysts. MnCl_2 was chosen as a doping salt because it has a XRD pattern that corresponds with MgCl_2 . The five catalysts with five mole ratio of MnCl_2 in the support were prepared, such as 0, 3, 10, 30, and 60 mol%. The result showed that, the catalyst is achieved in a good morphology when adding MnCl_2 below 30 mol% and the optimum ratio of Mn doping was 10 mol% which give the activity increased 25% and lossless in isotacticity. After 30 mol% of doped MnCl_2 , activity linearly decreased. The markedly change in molecular weight distribution when increase MnCl_2 which increase from 3 to 7.

Zhi-Quang Fan et al., 2011 [5] were interesting in effect of doping LiCl into MgCl_2 -supported Ziegler-Natta catalyst on the molecular weight distribution and isotacticity of propylene polymerization. The supports were coprecipitated from ethanol and then the supports were dipped by TiCl_4 solution. The crystalline and morphology structures of adduct supports and catalysts were characterized by WAXD and TEM, these characterization found that the mixed crystals Li_2MgCl_4 and LiMgCl_3 were discovered in catalysts. The MWD and isotacticity of polypropylene changed with amount of LiCl doped in catalyst. The broader MWD PP

was found in catalyst using LiCl-doped contain 11-18 mol% LiCl. Deconvolution of the MWD profiles with multiple Flory functions were used to consider the distribution of active centers. The LiCl 18% doped catalyst has six types of active centers that much larger than other catalysts.

Zhi-Quang Fan et al., 2006 [19] have studied a $\text{TiCl}_4/\text{AlCl}_3/\text{MgCl}_2$ catalyst containing 5.2 wt% Al (Cat-B). The catalyst prepared by the reaction of TiCl_4 solution with ethanol adduct of $\text{AlCl}_3/\text{MgCl}_2$ mixture. Cat-A without doped AlCl_3 was also prepared. The synthesis of LLDPE were studied and catalyzed by Cat-B in the presence of hydrogen displayed a bit higher efficiency and higher 1-hexene incorporation than Cat-A. There are two possible points to explain the effect of doped AlCl_3 . First, AlCl_3 has higher Lewis acidity than MgCl_2 , its presence in the catalyst might reduce electron density on some types of active center, which is beneficial to the coordination of more electron-donating α -olefin on active center than ethylene. Second, doping AlCl_3 in the catalyst may change the active center distribution, resulting in formation of more active centers with high copolymerization ability. The appropriated cocatalyst in this catalyst system is $\text{Al}(\text{i-Bu})_3$ compared with TEA. The addition of external electron donor ($\text{Ph}_2\text{Si}(\text{OMe})_2$) caused decreasing in activity and 1-hexene insertion.

CHAPTER III

EXPERIMENTAL

3.1 Preparation of the catalysts

The catalyst was prepared according to a reported procedure by Mitsui Petrochemical Industries Ltd [18]. The catalyst was synthesized by coprecipitation method. First, 2 g of anhydrous magnesium dichloride (MgCl_2) and (AlCl_3 and/or ZnCl_2) was added in to a 4-necked 500-ml Schlenk flask which all of support components are basis total 2 g under an argon atmosphere glove box. There are five ratios of catalysts modifying with Lewis acid consisting of $\text{MgCl}_2:\text{AlCl}_3:\text{ZnCl}_2 = 100:0:0, 85:15:0, 85:0:15, 70:30:0, 70:0:30,$ and $70:15:15$ which are called Cat-A, Cat-B, Cat-C, Cat-D, Cat-E and Cat-F, respectively. Then, in the 4-necked 500-ml Schlenk flask equipped with a condenser and overhead stirrer, 100 ml of n-heptane was added under protection of argon, and then absolute ethanol was added into the flask with ethanol molar ratio $[(\text{MgCl}_2 + \text{Lewis acid}) : \text{EtOH}]$ equal 1:12. The flask was heated and hold until solid was completely dissolved. Then, the system was cooled with ice bath and the solid was precipitated from the liquid phase during cooling. The remaining ethanol and solvent were removed by siphoned off. The solid adduct was washed two times with 100 ml of n-heptane, and then diethyl aluminum chloride (DEAC) was added drop wise into the cooled flask under stirring. The flask was then heated and held with stirring continued for 2 h. After that the system was cooled down to room temperature. The unreacted DEAC and solvent were removed by siphoned off. The solid was washed five times with 100 ml of n-heptane. Finally, TiCl_4 was injected drop wise into the flask at 70°C and held for 2 h under stirring. Finally, after the same operation as mentioned above, such as cooling, separation, and washing at 70°C six times, thereafter the catalyst powder was vacuum dried and stored in a glass bottle under argon atmosphere.

3.2 Polymerization

3.2.1 Ethylene polymerization

The ethylene polymerization was carried out at a 2 L autoclave reactor Buchi polyclave, equipped with a thermostatic system and a turbine stirrer. The reactor was connected with the lines available with argon, hydrogen and ethylene gases and also the hexane feed line. The reactor and all the connected feed lines were cleared humid and oxygen first by evacuation with the vacuum pump for 20 minutes, and then followed by purging with the argon gas and evacuation for 10 times for ensuring. The hexane was filled with 1 liter and heated to 80°C. The TEA (Al/Ti molar ratio = 164) was injected into the reactor subsequence by the stirred catalyst at 60°C. In this condition of presence of hydrogen, the reactor was pressurized with 1 bar of argon followed by pressurizing with hydrogen gas to 4 bars and finally pressurizing with ethylene gas to 8 bars and feed the ethylene gas continuously until 2 h polymerization was stopped. Then, polymer was dried at room temperature overnight and measured the polymer weight.

3.2.2 Ethylene/1-Hexene copolymerization

The ethylene/1-hexene copolymerization was carried out in a 100 ml stainless steel autoclave reactor equipped with magnetic stirrer. In the glove box, the desired amounts catalyst and cocatalyst were filled in reactor (Al:Ti=140), after that hexane to make a total volume of 30 ml was added. The reactor was frozen in liquid nitrogen to stop reaction and the reactor was evacuated to remove argon, and then followed by adding 1-hexene (0.3 mol/L) into the reactor. After that, the reactor was heated up to the polymerization temperature (80 °C) and start polymerization by feeding ethylene gas until the ethylene consumption is 6 psi from pressure gauge (0.018 mol) was reached. The reaction was terminated by adding acidic methanol. The obtained copolymer was washed by methanol and dried at room temperature.

3.3 Characterizations

3.3.1 Scanning Electron Microscope and Energy-Dispersive X-ray Spectroscopy (SEM/EDX)

SEM observation with a JEOL mode JSM-6400. SEM was analyzed to investigate the morphology of catalyst and polymer. The polymer samples for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimen. The catalyst samples were prepared in an argon atmosphere glove box and place in closed bottle. Before the catalyst samples were coated with gold particles, during the catalyst was moved to ion sputtering device, argon gas was injected around the catalyst samples for protect the catalyst samples from oxygen.

3.3.2 Differential Scanning Calorimetry (DSC)

The melting temperature (T_m) and crystallinity (X_c) of the polymer samples were observed by using Perkin-Elmer diamond DSC from MEKTEC. The analysis of polymer samples was performed at the heating rate of $10^\circ\text{C min}^{-1}$ in the temperature range of 50-200 °C. The heating cycle was run twice. In the first scan, samples were heated and the cooled to room temperature. In the second, samples were reheated at the same rate, but only the results of the second scan were 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 values using the formula.

$$X_c = H_m/H_p$$

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

3.3.3 Nuclear Magnetic Resonance (NMR)

^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer at 120°C using 20% (w/v) solutions in 1,2,4-trichlorobenzene. 10% (v/v) benzene- d_6 was added for the internal lock, and hexamethyldisiloxane was used as the reference (internal chemical shift).

3.3.4 Gel Permeation Chromatography (GPC)

Molecular weight (Mw) and molecular weight distribution (MWD) of the polymer samples were determined by using Gel Permeation Chromatography (GPC) at 150 °C with 1,2,4-trichlorobenzene as the solvent.

3.3.5 X-ray Diffraction (XRD)

XRD was performed to determine the bulk crystalline phases of the catalyst and polymer samples. It was determined by 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 $2\theta = 10$ -50 degrees for polymer samples and $2\theta = 10$ -80 degrees for catalyst samples. For the catalyst samples was prepared in an argon atmosphere glove box by add catalyst on the sample holder and cover the sample holder by mylar film. For polymer, sample was prepared without an argon atmosphere and mylar film.

3.3.6 Inductively Coupled Plasma (ICP)

Titanium content is measured using Perkin Elmer Optical. To digest the catalyst samples, the samples were dissolved with 5 ml of hydrofluoric acid and stirred over night. After the catalyst sample was completely dissolved, the solution was diluted to a volume of 100 ml in a plastic volumetric flask. Then, the sample was measured the quantity of trace metal in diluted sample.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preliminary study in catalytic activity

In the first part, we prepared catalysts consisting of MgCl_2 and mixed with only AlCl_3 for the comparison of catalytic activity among these catalysts at different amount of AlCl_3 and tested catalysts upon this synthesized system. Table 4.1 shows the catalytic activity, Ti content, percent crystallinity, and melting temperature. From the results, it was found that the catalytic activity tends to increase with increasing the amount of AlCl_3 in catalyst. Upon the $\text{MgCl}_2:\text{AlCl}_3$ weight ratio of 70:30, it exhibited the highest PE yield. However, Ti content and PE yield had different trends compared to activity, leading to modification of the catalyst preparation for more reliable data. By improving the washing after Ti impregnation step, which is the last step in catalyst preparation, such as to increase washing round from 4 to 6 times, increase washing temperature from 30° C to 70° C, it confirmed that the catalyst was completely washed out the unreacted and unimpregnated Ti with support.

4.2 Amount of element in catalyst

In second part, the four catalysts were prepared by solving the washing problem which consists of four weight ratios of supports ($\text{MgCl}_2:\text{AlCl}_3:\text{ZnCl}_2 = 100:0:0, 85:15:0, 85:0:15, 70:30:0, 70:0:30,$ and $70:15:15$) called Cat-A, Cat-B, Cat-C, Cat-D, Cat-E and Cat-F, respectively. The catalyst components were characterized by ICP as shown in Table 4.2. It was found that Mg, Al, and Zn are varied upon to changing the amount of support ratio. Ti contents slightly decreased when adding AlCl_3 and ZnCl_2 . It is possible that high amount of Al and Zn may incorporate in the catalyst crystal lattice and abundant for substitution of Ti atom in the catalyst [20].

Table 4.1 Catalytic activities and other properties

Sample	^a MgCl ₂ :AlCl ₃ weight ratio	^b Ti content(wt%)	PE yield (g)	^c Activity	^d % χ_c	T _m (°C)
1	100:0	2.480	145.90	14027	40.8	134.4
2	95:5	0.998	66.69	15933	58.9	134.6
3	85:15	1.523	106.25	16634	55.8	134.5
4	70:30	3.650	258.80	16906	59.8	135.6
5	50:50	1.230	87.40	16942	58.6	136.6

^aMgCl₂:AlCl₃ ratio by wt%, ^bCharacterized by ICP technique, ^cActivity unit kgPE/molTi•h

^d% χ_c , T_m Characterized by DSC of polyethylene

Polymerization condition: Autoclave 2 L, T = 80 °C, t = 2 h, P_{H₂} = 2.5 bar, P_{total} = 8 bar cocat = TEA, Al/Ti = 164, solvent = hexane 1 L

Table 4.2 catalyst component characterized by ICP technique

Catalyst	Mg(wt%)	Al(wt%)	Zn(wt%)	Ti(wt%)
Cat-A	10.49	0.289	-	1.45
Cat-B	8.841	0.816	-	0.812
Cat-C	9.162	0.303	34.19	0.708
Cat-D	7.975	1.413	-	0.599
Cat-E	8.175	0.624	48.22	0.656
Cat-F	8.203	0.924	36.86	1.326

4.3 Amount of element at catalyst surface

From Table 4.3, it can be observed that the titanium content on surface is higher with increasing the amount of Lewis acids. As seen, Cat-A that was the catalyst that not modified by Lewis acid exhibited the lowest amount of titanium on the surface. When consideration of only one Lewis acid, such as Cat-B to Cat-E, it exhibited higher amount of Ti content on the surface when compared with Cat-A. It reveals that amount of Ti on the surface is the highest can found in the catalyst modified with 15 wt% of Lewis acid, such as Cat-B and Cat-C. However, it decreased when modify with over 15 wt% of Lewis acid, such as Cat-D and Cat-E. However, Cat-F showed the highest titanium content at the surface which is corresponding to the highest catalytic activity as well. It is well known that the reaction frequently occurs on the surface of catalyst, so the high amount of titanium on surface might be the major cause for the higher catalytic activity [21]. Hence, the high catalytic activity can be attributed to the amount of Ti content on the surface, not in the catalyst bulk.

Table 4.3 EDX analysis of catalyst surface

catalyst	Mg(wt%)	Al(wt%)	Zn(wt%)	Cl(wt%)	Ti(wt%)
Cat-A	24.14	1.91	-	71.91	2.04
Cat-B	24.13	1.55	-	71.79	2.53
Cat-C	22.09	1.41	3.56	70.53	2.41
Cat-D	24.25	2.14	-	71.47	2.14
Cat-E	20.92	1.76	9.55	65.50	2.27
Cat-F	22.59	1.89	7.88	64.13	3.51

Analysis on K subshell.

4.4 XRD patterns of the catalysts

Figure 4.1 shows the X-ray diffraction of catalyst A to F, in chapter 2 we explain about activation of MgCl_2 that consists of X-ray diffraction at $2\theta = 15, 30,$ and 50.5° . These peaks were found in Cat-A, but it was slightly shifted from $2\theta \approx 15^\circ$ to 13.5° . The analysis of these Lewis acids on defect of $\delta\text{-MgCl}_2$ was focused on $2\theta \approx 15, 30,$ and 50.5 . We observed that there was no different peak on $2\theta \approx 50.5$, but it slightly changed on $2\theta \approx 30^\circ$. When compared the peak of Cat-A to Cat-F, it can be observed that there was an absence of $2\theta \approx 15^\circ$. Therefore, it can be described that the Lewis acids can alter the Cl-Mg-Cl triple layers to single Cl-Mg-Cl structural layers (monolayers) [13]. Furthermore, Cat-B and Cat-D also exhibit the lower peak at around 30° compared with Cat-A. It can be explained that Cat-B and Cat-D has more amorphous than Cat-A indicating that MgCl_2 was disordered by AlCl_3 . Cat-B has more amorphous than Cat-C, which has more activity than Cat-C.

Therefore, it is possible that only the optimum of amorphous peak around 30° causes the higher catalytic activity. If it has more crystallinity (Cat-E) or more amorphous (Cat-D) than optimum, it will be disadvantage to activity. Cat-F still has a slight peak, but almost peak around $2\theta \approx 30^\circ$ is amorphous, which it produces an effect to higher activity. For a comparison of two Lewis acids such as AlCl_3 and ZnCl_2 , it can be seen that AlCl_3 changed XRD pattern around 30° to more amorphous, but ZnCl_2 exhibited more crystallize peak around 30° .

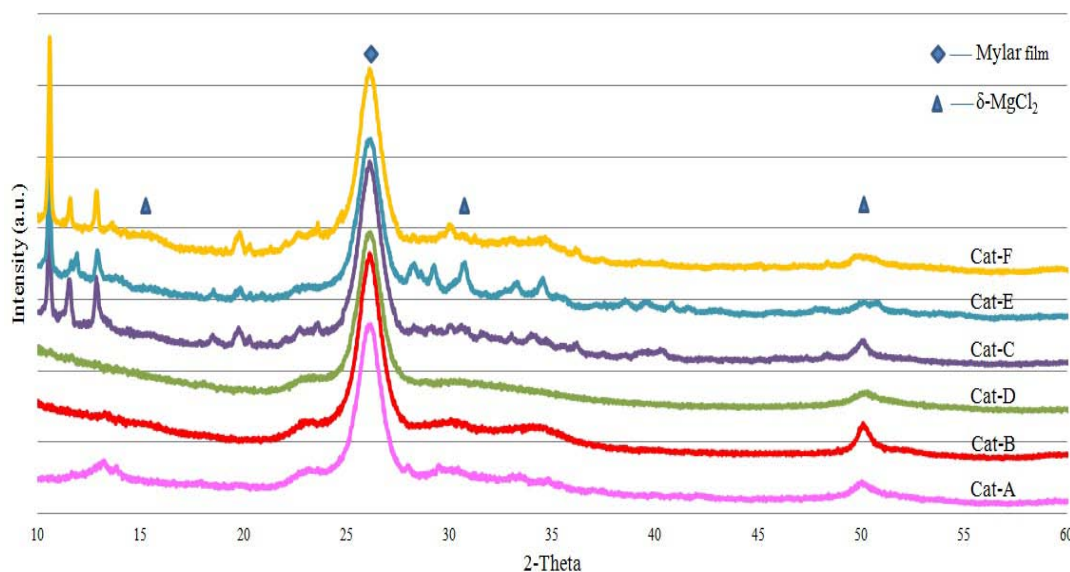


Figure 4.1 XRD patterns of the catalysts

4.5 Catalytic activities for ethylene polymerization

Table 4.4 shows the catalytic activity for ethylene polymerization on these catalysts. From the result, it was found that even though the catalyst has decreased Ti content in bulk of catalyst, the activities increased when the catalyst had higher Lewis acid amount. The highest activity can be found in Cat-F modified with two Lewis acids. Therefore, Lewis acid may help the distribution of Ti atoms on the catalyst surface which corresponds to Ti content on surface that characterized by EDX. It is generally agreed that a large percentage of active sites are formed at edges, cuts, and surface defect of MgCl_2 crystallites. The modification of catalyst by modifying with Lewis acid can change the distribution of these defects and it helps distribution of Ti atom, too [4]. Therefore, the catalytic activities increase due to increased Ti on the surface. The comparison of catalyst modified by Lewis acid at 15 wt% showed that Cat-B has higher activity than Cat-C, whereas at 30 wt% modification, it revealed that activity of Cat-E increased from Cat-D. However, the appropriate amount of support modification is to modify with 15 wt% of Lewis acids after this amount the catalytic activity apparently decreased.

Table 4.4 Catalytic activity of the present hydrogen for ethylene polymerization

Catalyst	PE yield(g)	^a Activity	^b Activity ratio
Cat-A	38.56	6340	1
Cat-B	36.95	10849	1.71
Cat-C	21.57	7464	1.15
Cat-D	14.56	5795	0.91
Cat-E	18.56	6745	1.06
Cat-F	71.87	12923	2.04

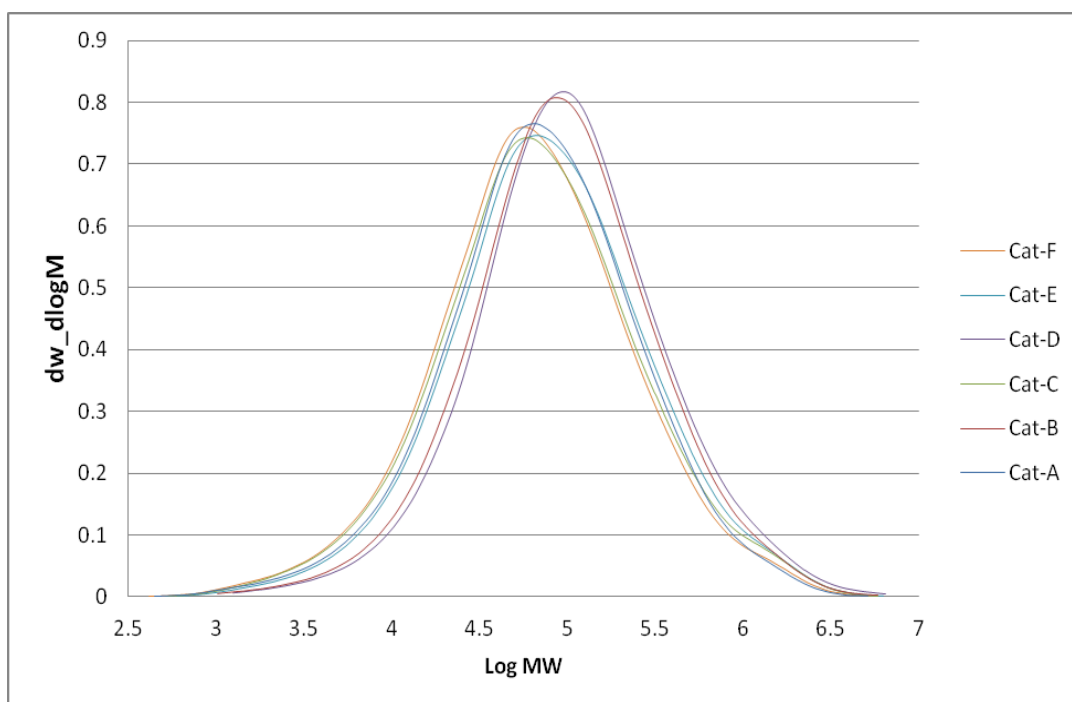
^aActivity unit kgPE/molTi•h ^bActivity of any catalyst divide by Cat-A
 Polymerization condition: Autoclave 2 L, T = 80 °C, t = 2 h, P_{H₂} = 3 bar, P_{total} = 8 bar cocat = TEA, Al/Ti = 164, solvent = hexane 1 L

4.6 Molecular weight and Molecular weight distribution

Considering, the molecular weight and molecular weight distribution as seen in Table 4.5 and Figure 4.2, it shows that Cat-B and Cat-D modified with AlCl₃, have the narrower of MWD than Cat-A and molecular weight distribution curve tends to shift to high molecular weight. Cat-C and Cat-E modified with ZnCl₂ have the broader MWD than Cat-A and molecular weight distribution curve tends to shift to low molecular weight. Although, Cat-F exhibits broader MWD than Cat-C, it has broader MWD and higher catalytic activity than Cat-A.

Table 4.5 Molecular Weight and Molecular Weight Distribution

Catalyst	Mv	Mn	Mw	MWD
Cat-A	123156	28446	157802	5.55
Cat-B	154833	40901	199270	4.87
Cat-C	127686	26860	170878	6.36
Cat-D	169576	46038	221123	4.80
Cat-E	139642	31212	184698	5.92
Cat-F	116443	25443	153321	6.03

**Figure 4.2 Molecular weight distribution curve**

4.7 Crystallinity, melting temperature and catalytic activities for ethylene/1-hexene copolymerization

This part, we investigated the effect of Lewis acid on ethylene/1-hexene copolymerization. From the above part, the catalysts were selected only 15 wt% modified by Lewis acids such as Cat-B and Cat-C due to their high activity. Table 4.6 shows the catalytic activity for ethylene/1-hexene copolymerization. From the results, it shows that the catalytic activity of catalyst modified with Lewis acid exhibited higher activity for ethylene/1-hexene copolymerization than ethylene homopolymerization. There is possible reason to describe the effect of modified Lewis acids, such as $ZnCl_2$ and $AlCl_3$ that has more Lewis acidity than $MgCl_2$. Thus, they decrease the electron density on some types of active center, which is useful for the coordination of more electron-donating α -olefin on active center than ethylene. Alternatively, the Lewis acids in catalyst may change the active center distribution affecting on formation of more active centers with high copolymerization ability [19]. The decrease of crystallinity(χ_c) and melting temperature(T_m) was observed with higher 1-hexene concentration (0.3 mol/L) because the polymer chain has more 1-hexene insertion causing the decreasing of crystallinity of polymer chain.

4.8 Triad distribution for ethylene/1-hexene copolymerization

Table 4.7 lists detailed data of triad distribution and insertion of 1-hexene in copolymer based on ^{13}C NMR analysis. It can be seen that Cat-D had higher 1-hexene insertion than Cat-A and the highest 1-hexene insertion was found in Cat-F. These results are corresponding to decreasing of χ_c , it can be explained that 1-hexene incorporates more in polyethylene chain causing of lower crystallinity.

Table 4.6 Ethylene/1-hexene copolymerization of the absent hydrogen

Catalyst	1-hexene (M)	^b Activity	^a % χ c	^a Tm	^b 1-hexene insertion (mol %)
Cat-A	0	942	49.88	131.9	-
Cat-B	0	1104	58.92	134.86	-
Cat-C	0	1008	51.69	130.8	-
Cat-F	0	1272	46.8	128.6	-
Cat-A	0.3	1405	19.58	125.6	7.64
Cat-B	0.3	1717	14.15	125.07	11.94
Cat-C	0.3	1566	15.53	124.76	8.67
Cat-F	0.3	2060	13.65	123.8	14.95

^acalculated from the DSC of polymer ^bActivity unit kgPE/molTi•h
 Polymerization condition: Autoclave 100 mL, T = 80 °C, P_{total} = 6 psi, cocat = TEA, Al/Ti = 140, solvent = hexane 25 mL, No H₂ gas

Table 4.7 Triad distribution

Catalyst	1-hexene (M)	Triad distribution						^b 1-hexene insertion (mol %)
		EEE	EEH	EHE	EHH	HEH	HHH	
Cat-A	0.3	0.815	0.089	0.053	0.024	0.019	0	7.64
Cat-B	0.3	0.731	0.119	0.061	0.058	0.031	0	11.94
Cat-C	0.3	0.788	0.107	0.059	0.027	0.019	0	8.67
Cat-F	0.3	0.668	0.143	0.076	0.073	0.040	0	14.95

^b1-hexene in copolymer calculated from the ¹³C NMR spectrum of copolymer.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The effect of ZnCl_2 and AlCl_3 in synthesis of MgCl_2 +Lewis acid/DEAC/ TiCl_4 catalyst system was investigated. It had effect mainly on the titanium content of catalysts that decreasing with the presence of Lewis acid components. However, these Lewis acids can improve catalyst surface to higher amount of titanium, which is the important point to increase the activity during ethylene polymerization. The XRD analysis confirms that the Lewis acids make the defect on MgCl_2 support which AlCl_3 making more amorphous on XRD pattern around 30° , but ZnCl_2 exhibits more crystallinity. Due to these defects occurred in catalyst, it causes increased Ti content on the surface of catalyst. The optimum amount of modified Lewis acids should be about 15 wt%. The highest catalytic activity was found in Cat-F. The MWD of catalyst was modified by only AlCl_3 (Cat-B and Cat-D), they have lower MWD than unmodified catalyst (Cat-A). However, the catalyst was modified by ZnCl_2 (Cat-C and Cat-E), they have a slightly high MWD than Cat-A. Moreover, Cat-F has more activity and MWD than Cat-A. In ethylene/1-hexene copolymerization with absent hydrogen, it was found that catalyst modified by Lewis acid has increasing of 1-hexene insertion and Cat-F has the highest 1-hexene insertion. Therefore, it can be summarized the role of Lewis acid in this catalyst system is as follows. The AlCl_3 has more activity than ZnCl_2 , but when considering on the broader MWD, the ZnCl_2 is better than AlCl_3 .

5.2 Recommendations

1. Tuning the optimum ratio of Lewis acids to give the desired activity and polymer properties.

2. If the catalyst is used in commercial, it should improve the catalyst preparation in the prepared support step for the better catalyst morphology which directly affects on polymer morphology such as, quenching method, spray dried method etc.

3. Proving the mechanism of these catalyst component reactions and proving the effect from each Lewis acid to catalyst and polymer properties.

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Appendices

Appendix A

(NUCLEAR MAGNETIC RESONANCE)

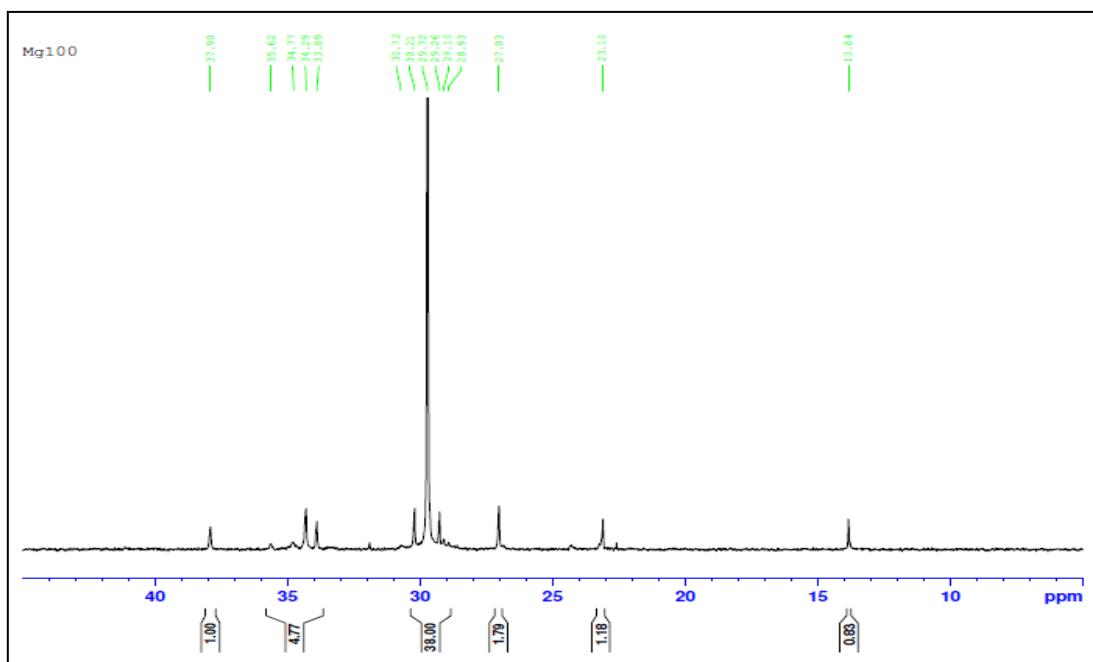


Figure A-1 ^{13}C NMR spectrum of ethylene/1-hexene copolymer with 1-hexene 0.3 mol/L obtained from the Cat-A.

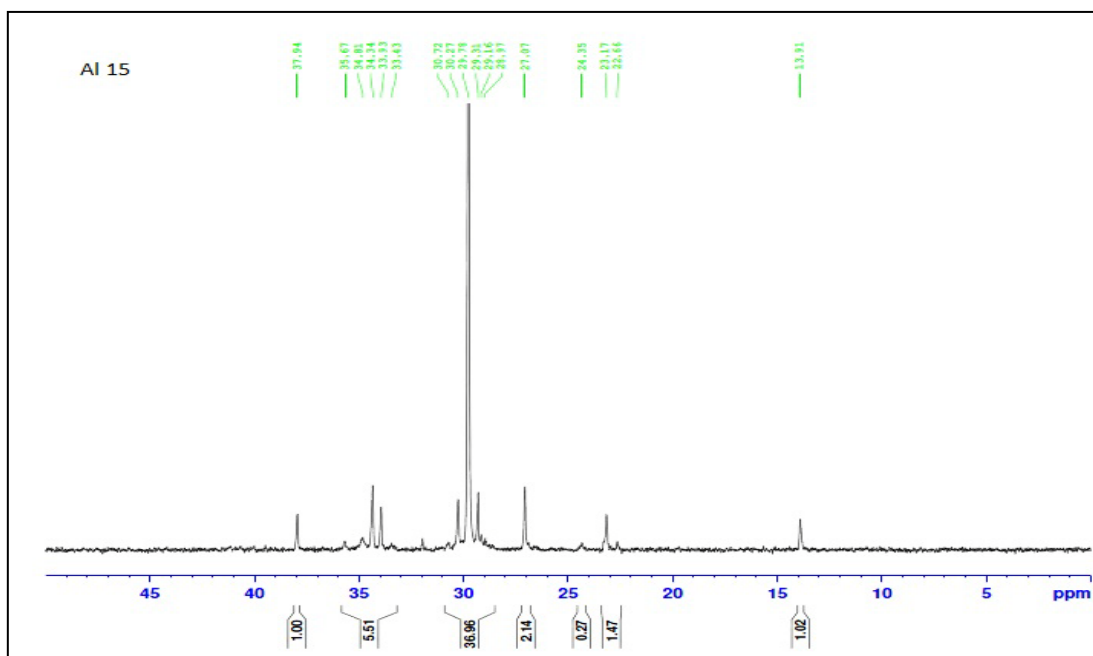


Figure A-2 ^{13}C NMR spectrum of ethylene/1-hexene copolymer with 1-hexene 0.3 mol/L obtained from the Cat-B

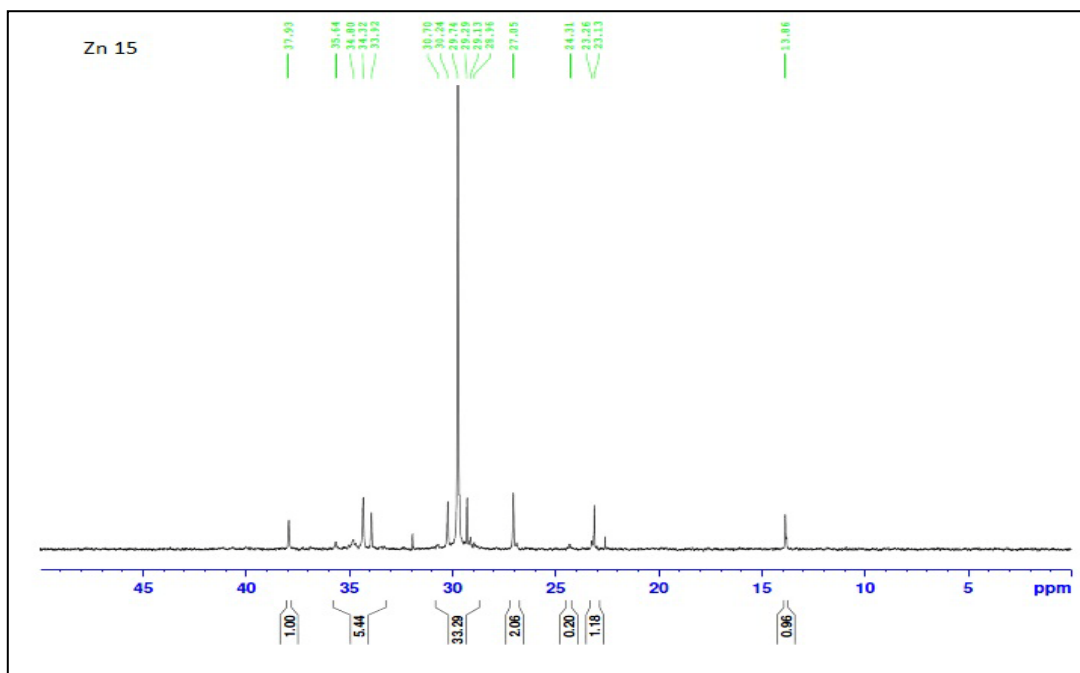


Figure A-3 ^{13}C NMR spectrum of ethylene/1-hexene copolymer with 1-hexene 0.3 mol/L obtained from the Cat-C

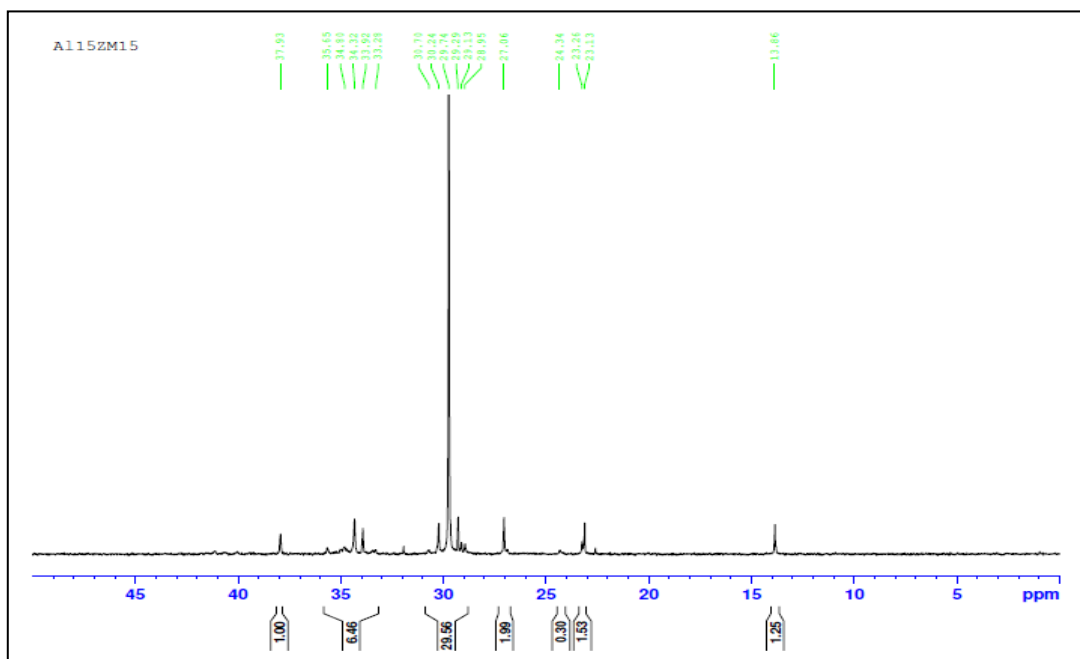


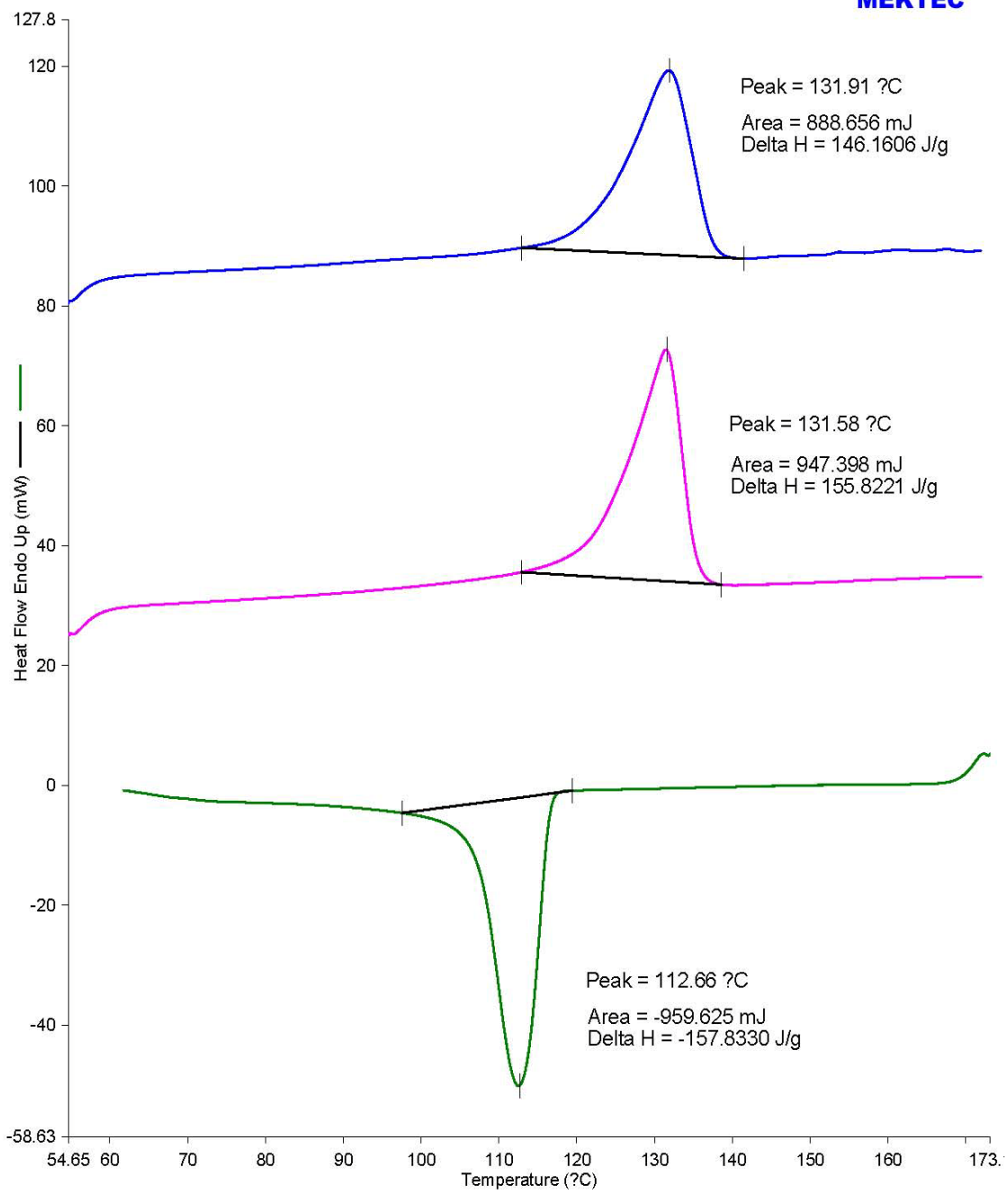
Figure A-4 ^{13}C NMR spectrum of ethylene/1-hexene copolymer with 1-hexene 0.3 mol/L obtained from the Cat-F

Appendix B

(DIFFERENTIAL SCANNING
CALORIMETRY)

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Operator ID:
Sample ID: Mg100 Homo
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MEKTEC

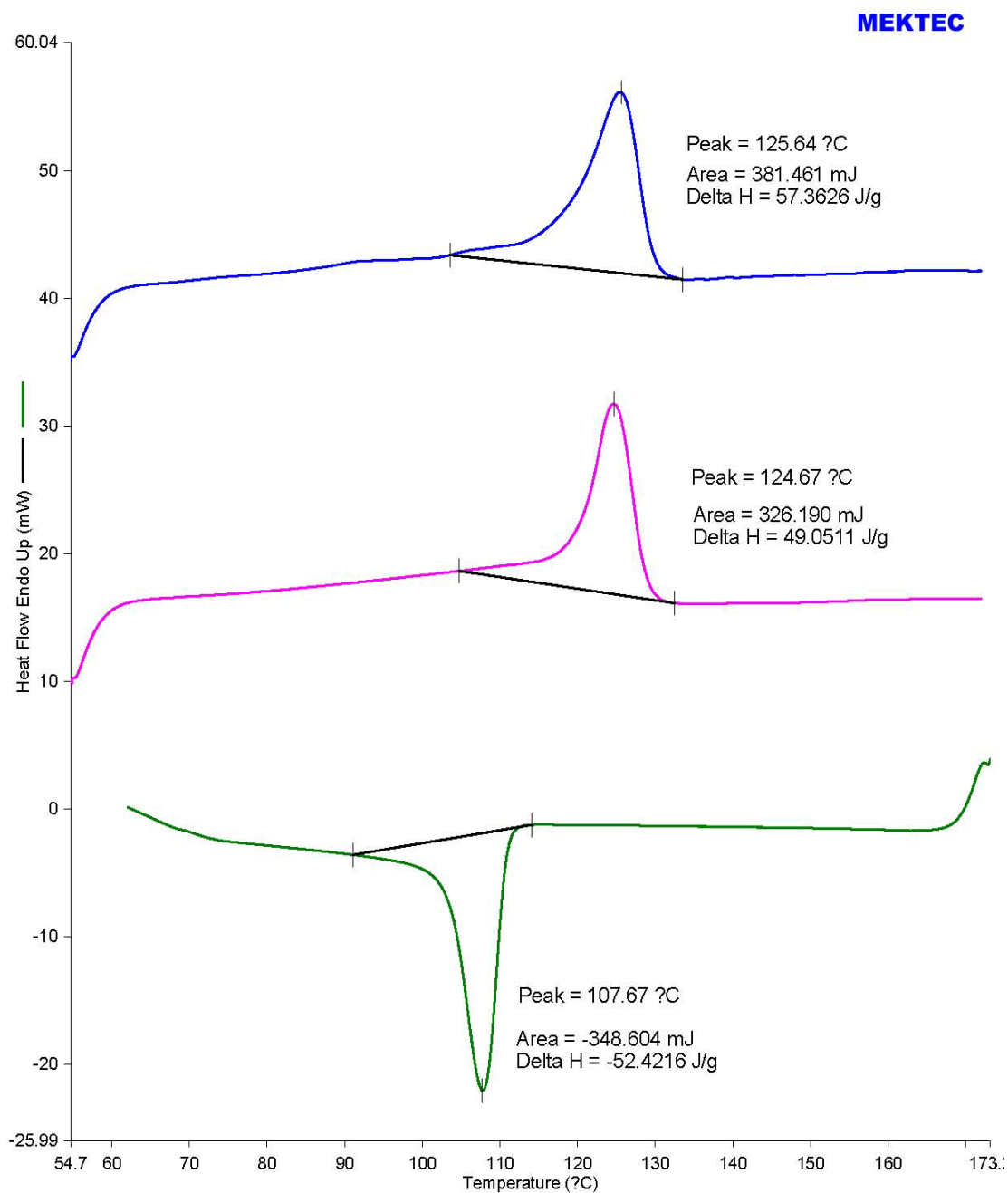


30/3/2555 13:43:56

- | | |
|---|---|
| 1) Hold for 1.0 min at 50.00°C | 5) Hold for 1.0 min at 50.00°C |
| 2) Heat from 50.00°C to 170.00°C at 20.00°C/min | 6) Heat from 50.00°C to 170.00°C at 20.00°C/min |
| 3) Hold for 1.0 min at 170.00°C | 7) Hold for 1.0 min at 170.00°C |
| 4) Cool from 170.00°C to 50.00°C at 20.00°C/min | |

Figure B-1 DSC of ethylene polymer obtained from the Cat-A

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 Comment:

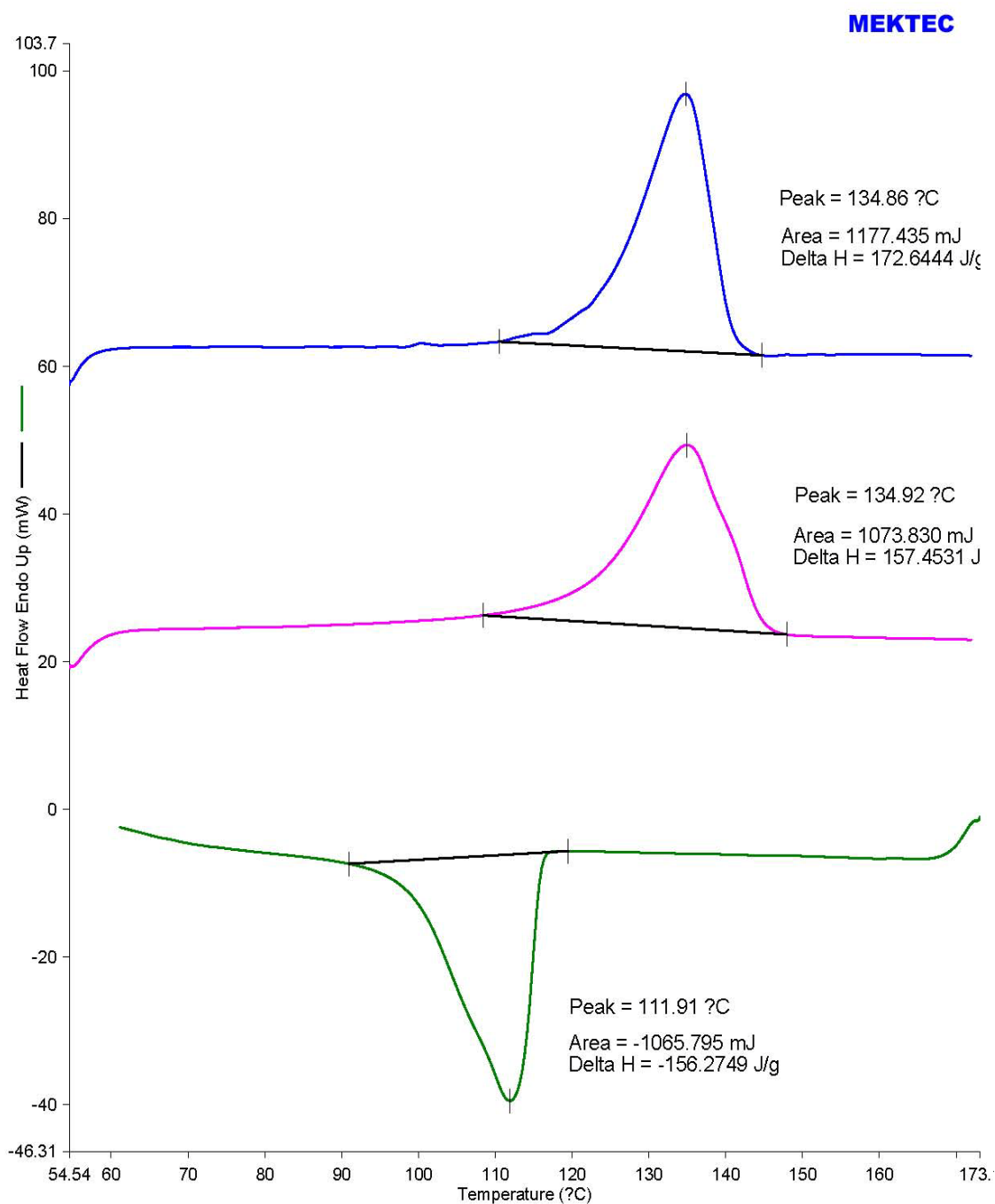


30/3/2555 14:07:12

- | | |
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| 2) Heat from 50.00°C to 170.00°C at 20.00°C/min | 6) Heat from 50.00°C to 170.00°C at 20.00°C/min |
| 3) Hold for 1.0 min at 170.00°C | 7) Hold for 1.0 min at 170.00°C |
| 4) Cool from 170.00°C to 50.00°C at 20.00°C/min | |

Figure B-2 DSC of ethylene/1-hexene copolymer with 1-hexene 0.3 mol/L obtained from the Cat-A

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 Sample Weight: 6.820 mg
 Comment:



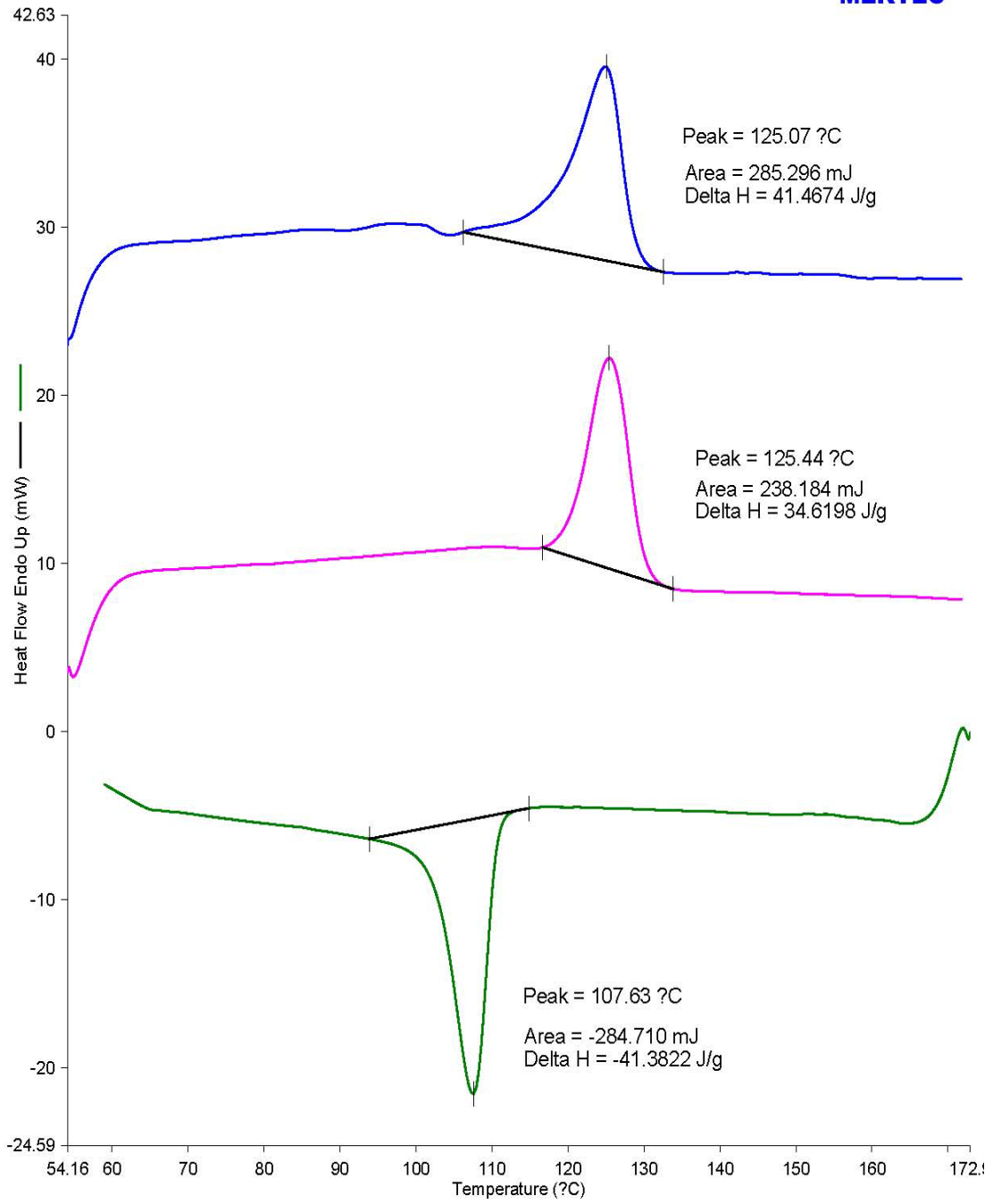
16/5/2555 14:35:39

- | | |
|---|---|
| 1) Hold for 1.0 min at 50.00°C | 5) Hold for 1.0 min at 50.00°C |
| 2) Heat from 50.00°C to 170.00°C at 20.00°C/min | 6) Heat from 50.00°C to 170.00°C at 20.00°C/min |
| 3) Hold for 1.0 min at 170.00°C | 7) Hold for 1.0 min at 170.00°C |
| 4) Cool from 170.00°C to 50.00°C at 20.00°C/min | |

Figure B-3 DSC of ethylene polymer obtained from the Cat-B

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Sample ID: AI 15 Copo
Sample Weight: 6.880 mg
Comment:

MEKTEC

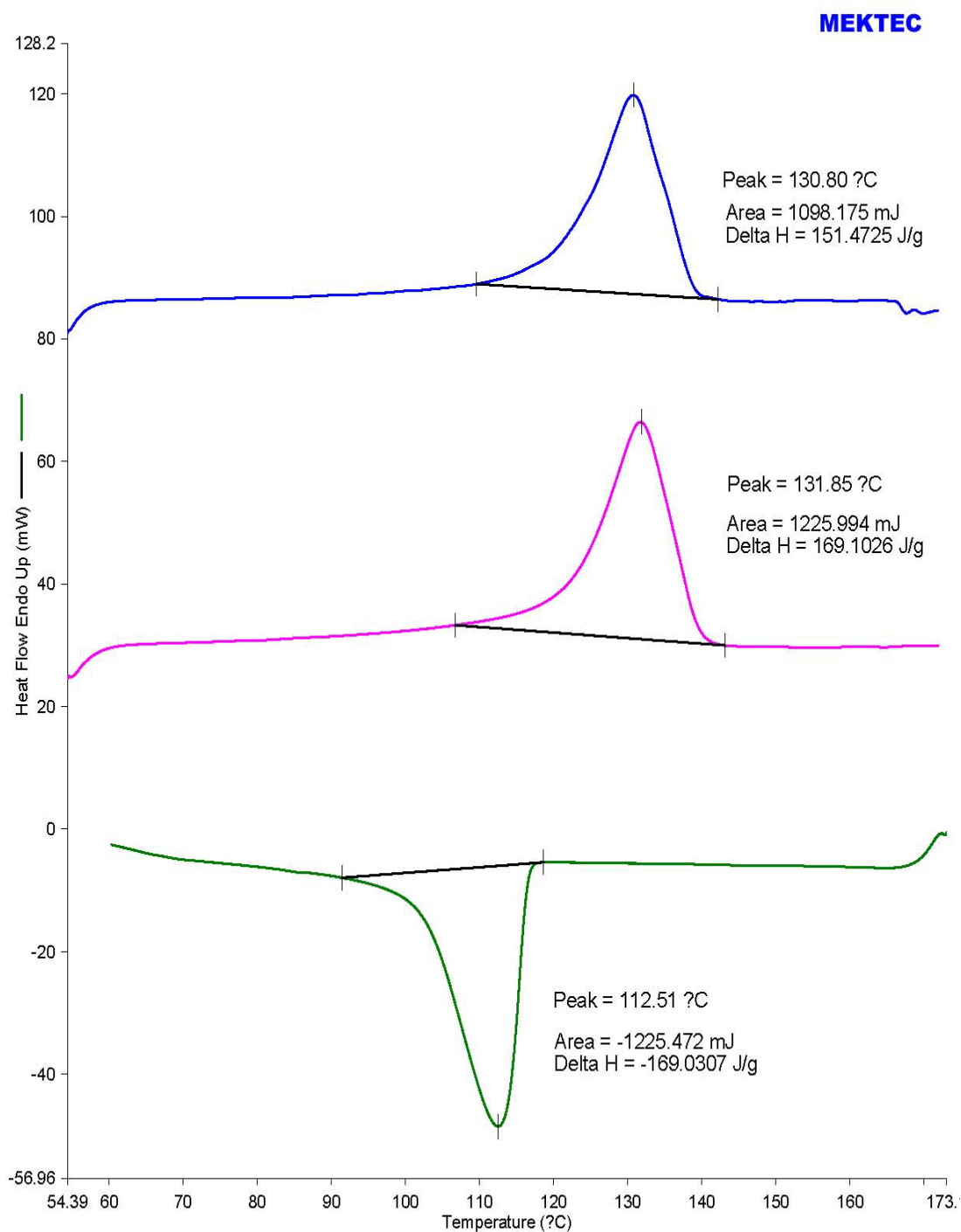


16/5/2555 13:00:07

- | | |
|---|---|
| 1) Hold for 1.0 min at 50.00°C | 5) Hold for 1.0 min at 50.00°C |
| 2) Heat from 50.00°C to 170.00°C at 20.00°C/min | 6) Heat from 50.00°C to 170.00°C at 20.00°C/min |
| 3) Hold for 1.0 min at 170.00°C | 7) Hold for 1.0 min at 170.00°C |
| 4) Cool from 170.00°C to 50.00°C at 20.00°C/min | |

Figure B-4 DSC of ethylene/1-hexene copolymer with 1-hexene 0.3 mol/L obtained from the Cat-B

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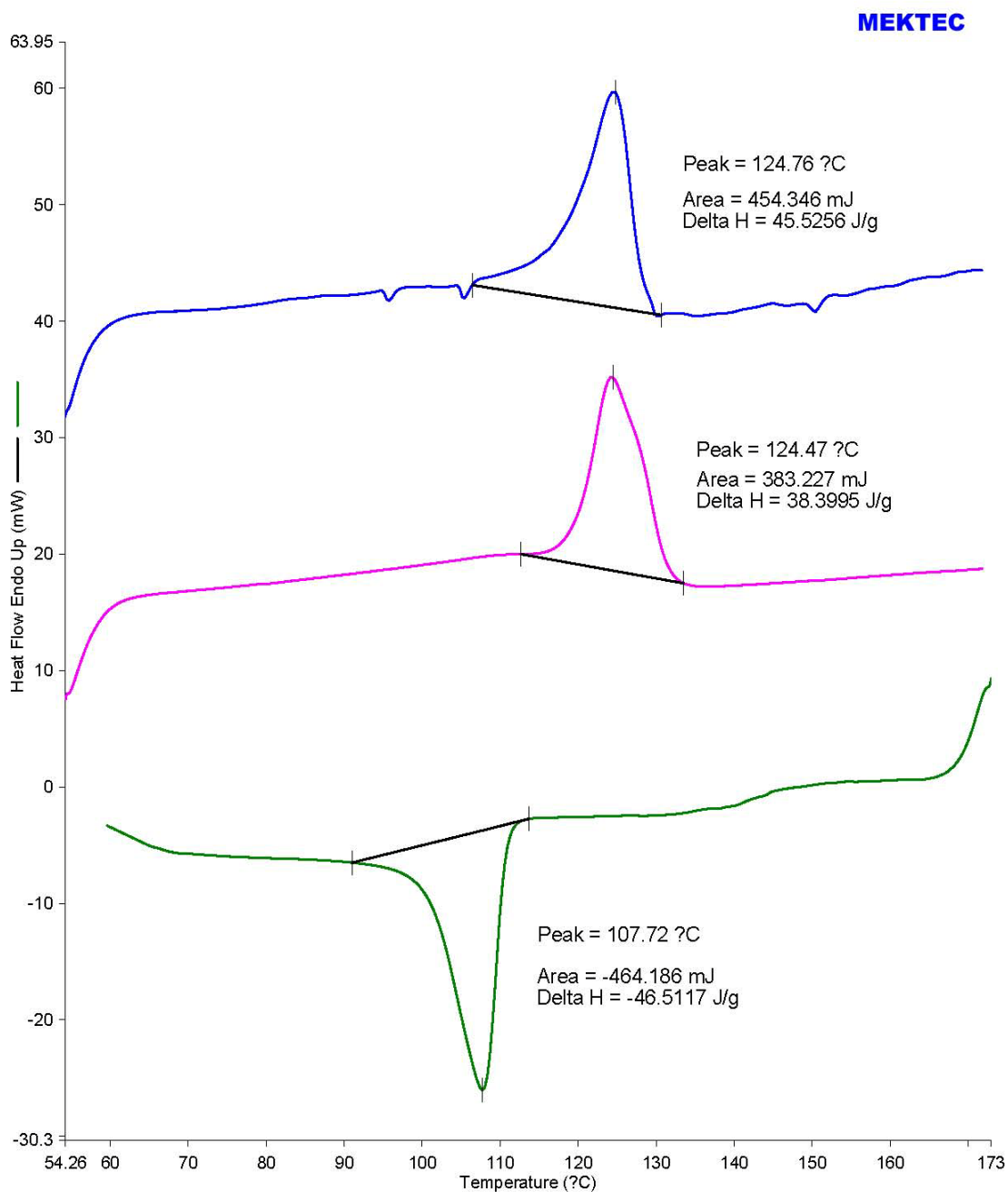


16/5/2555 14:30:38

1) Hold for 1.0 min at 50.00°C	5) Hold for 1.0 min at 50.00°C
2) Heat from 50.00°C to 170.00°C at 20.00°C/min	6) Heat from 50.00°C to 170.00°C at 20.00°C/min
3) Hold for 1.0 min at 170.00°C	7) Hold for 1.0 min at 170.00°C
4) Cool from 170.00°C to 50.00°C at 20.00°C/min	

Figure B-5 DSC of ethylene polymer obtained from the Cat-C

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 Sample ID: Zn 15 Copo
 Sample Weight: 9.980 mg
 Comment:

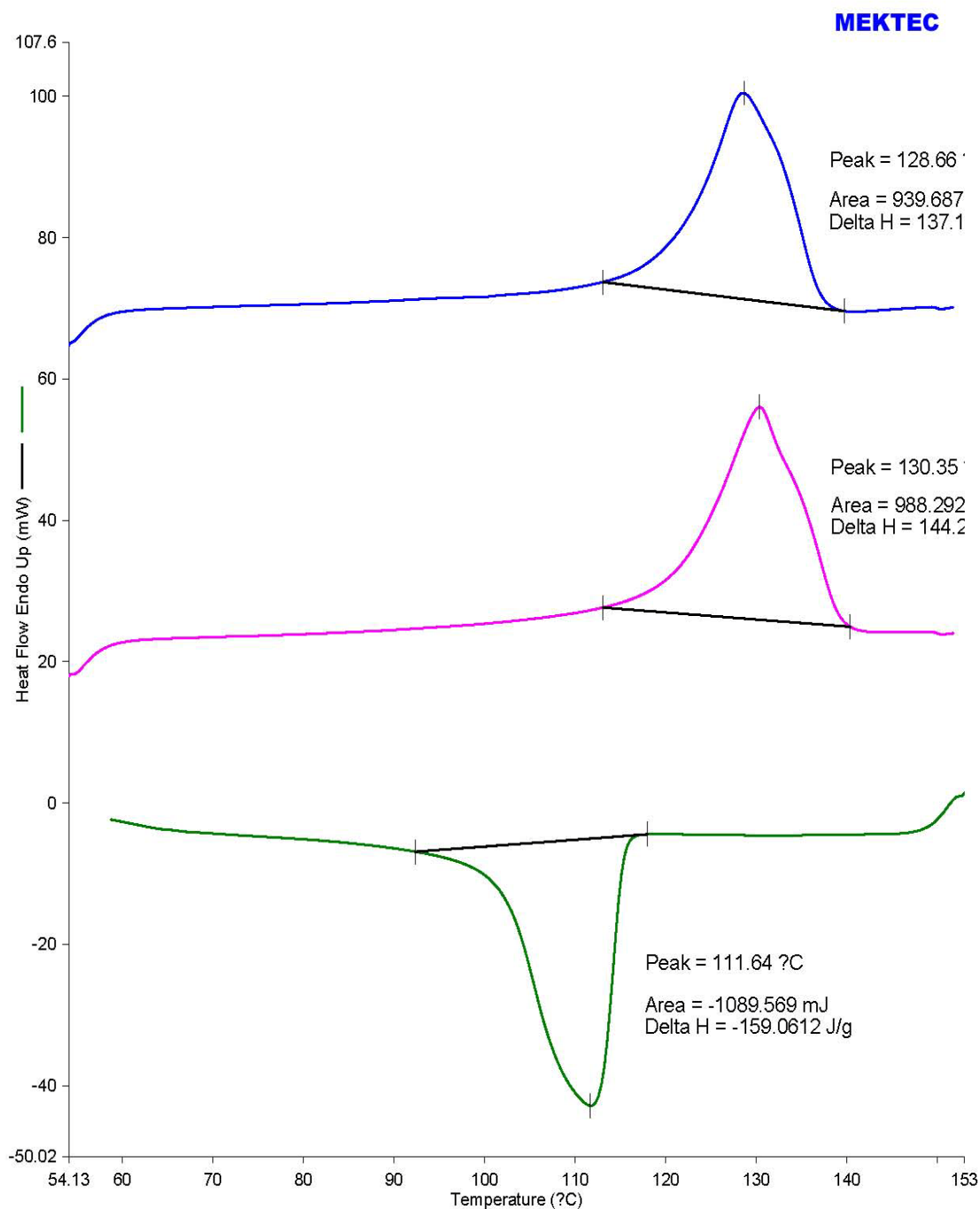


16/5/2555 13:06:52

- | | |
|---|---|
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| 2) Heat from 50.00°C to 170.00°C at 20.00°C/min | 6) Heat from 50.00°C to 170.00°C at 20.00°C/min |
| 3) Hold for 1.0 min at 170.00°C | 7) Hold for 1.0 min at 170.00°C |
| 4) Cool from 170.00°C to 50.00°C at 20.00°C/min | |

Figure B-6 DSC of ethylene/1-hexene copolymer with 1-hexene 0.3 mol/L obtained from the Cat-C

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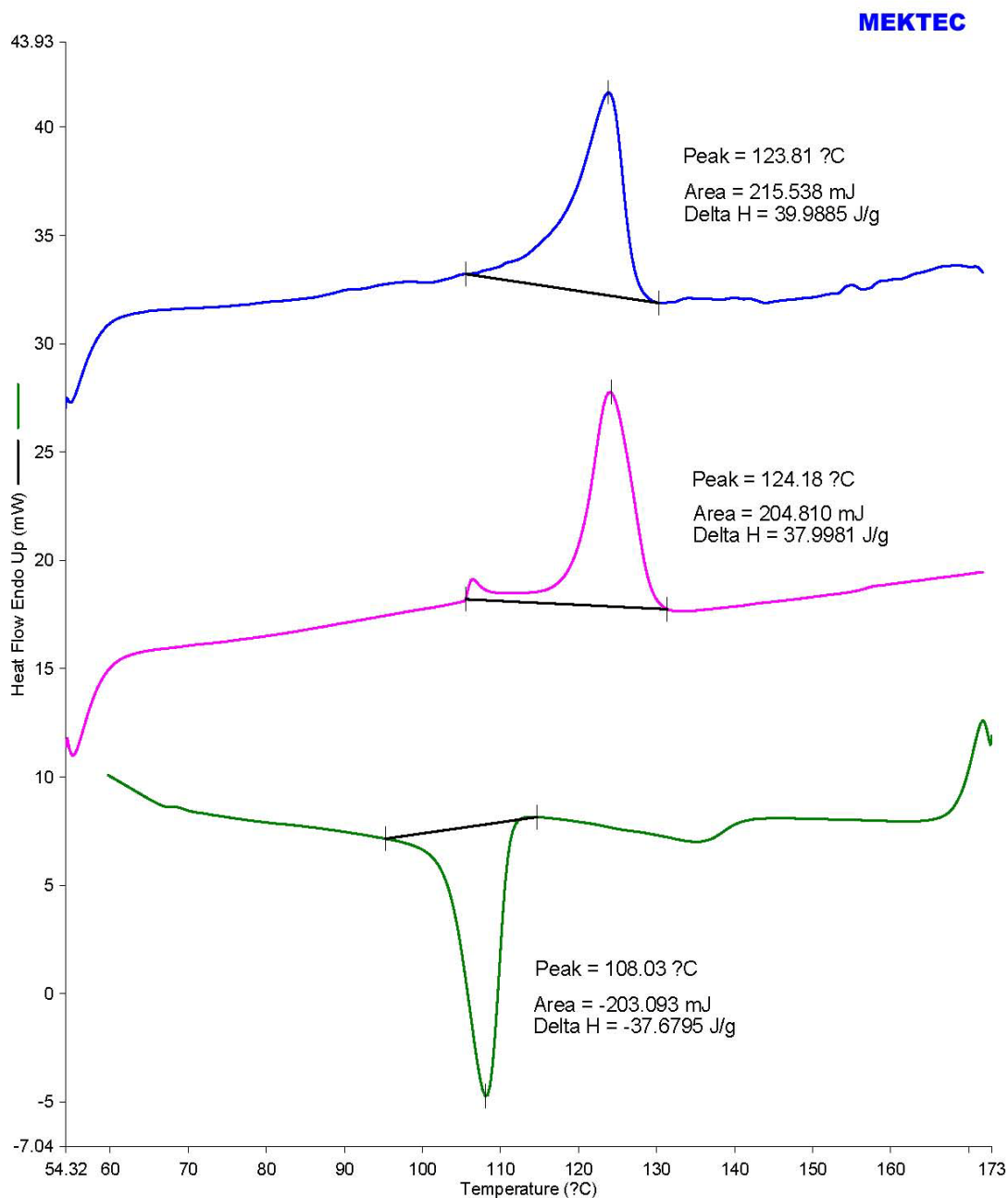


30/3/2555 11:26:54

- | | |
|---|---|
| 1) Hold for 1.0 min at 50.00°C | 5) Hold for 1.0 min at 50.00°C |
| 2) Heat from 50.00°C to 150.00°C at 20.00°C/min | 6) Heat from 50.00°C to 150.00°C at 20.00°C/min |
| 3) Hold for 1.0 min at 150.00°C | 7) Hold for 1.0 min at 150.00°C |
| 4) Cool from 150.00°C to 50.00°C at 20.00°C/min | |

Figure B-7 DSC of ethylene polymer obtained from the Cat-F

Filename: D:\Student\2555\Art\Al15Zn15 Copo.pdid
 Operator ID:
 Sample ID: Al15Zn15 Copo
 Sample Weight: 5.390 mg
 Comment:



30/3/2555 13:03:24

1) Hold for 1.0 min at 50.00°C	5) Hold for 1.0 min at 50.00°C
2) Heat from 50.00°C to 170.00°C at 20.00°C/min	6) Heat from 50.00°C to 170.00°C at 20.00°C/min
3) Hold for 1.0 min at 170.00°C	7) Hold for 1.0 min at 170.00°C
4) Cool from 170.00°C to 50.00°C at 20.00°C/min	

Figure B-8 DSC of ethylene/1-hexene copolymer with 1-hexene 0.3 mol/L obtained from the Cat-F

Appendix C

(POLYMER PROPERTIES
CALCULATION)

Calculation of Ethylene/1-Hexene copolymer insertion

Polymer triad distribution of monomer can be calculated according to Randell's method [41] and further developed by Galland [42]. The calculation for ethylene/1-hexene incorporation was solved as follow.

The integration areas of ^{13}C -NMR spectrum in the specific ranges are listed.

$$\begin{aligned} T_A &= 39.5 - 42 \text{ ppm} \\ T_B &= 38.1 \text{ ppm} \\ T_C &= 33 - 36 \text{ ppm} \\ T_D &= 28.5 - 31 \text{ ppm} \\ T_E &= 26.5 - 27.5 \text{ ppm} \\ T_F &= 24 - 25 \text{ ppm} \\ T_G &= 23.4 \text{ ppm} \\ T_H &= 14.1 \text{ ppm} \end{aligned}$$

Triad distribution was calculated as the followed;

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

Then the fractions of ethylene and 1-hexene insertions were calculated;

$$\begin{aligned} \%E &= [\text{EEE}] + [\text{EEH}] + [\text{HEH}] \\ \%C &= [\text{HHH}] + [\text{HHE}] + [\text{EHE}] \end{aligned}$$

Appendix D

(SCANNING ELECTRON MICROSCOPE
AND ENERGY-DISPERSIVE X-RAY
SPECTROSCOPY)

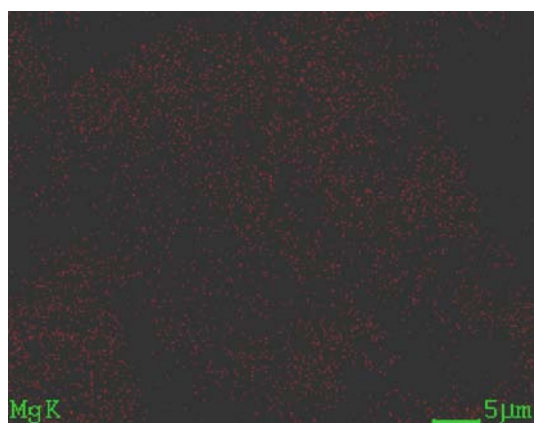
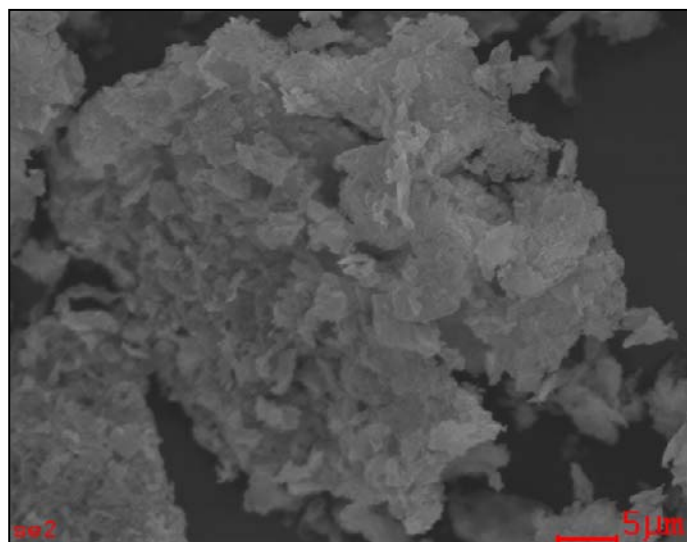


Figure D-1 SEM/EDX of Cat-A under 2000x microscopy

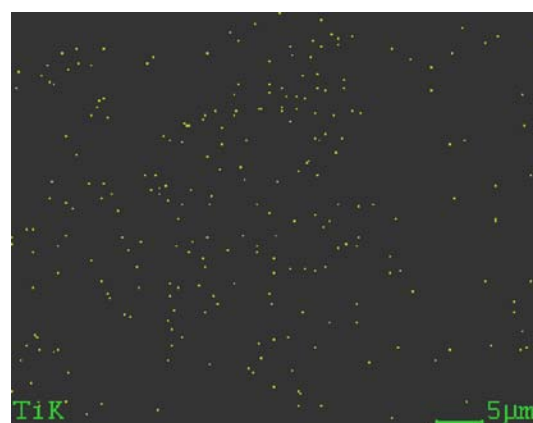
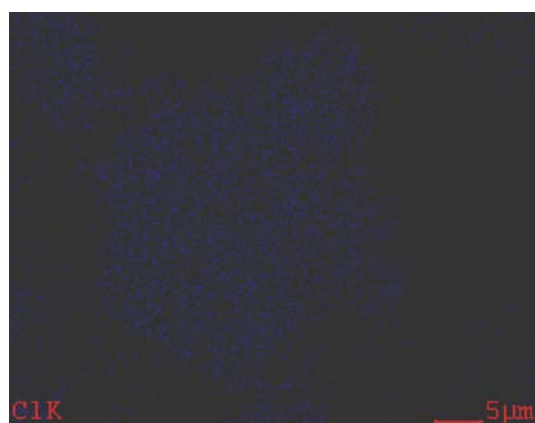
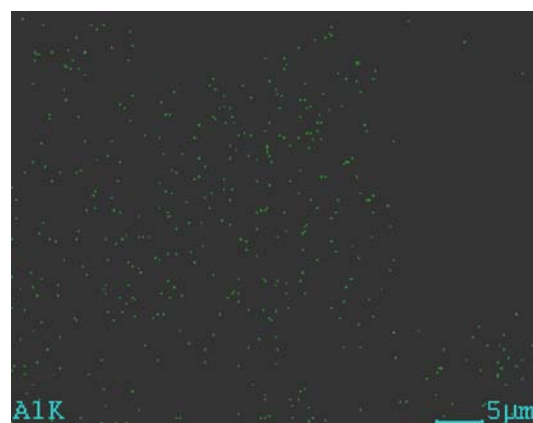
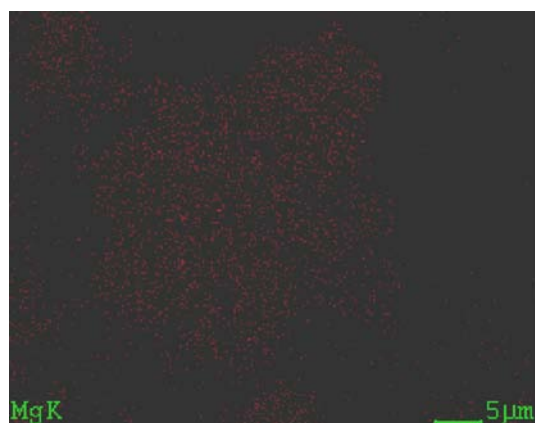
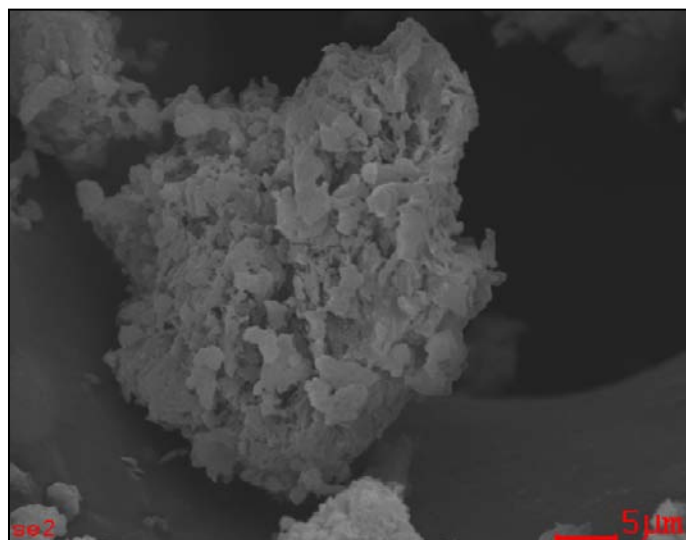


Figure D-2 SEM/EDX of Cat-B under 2000x microscopy

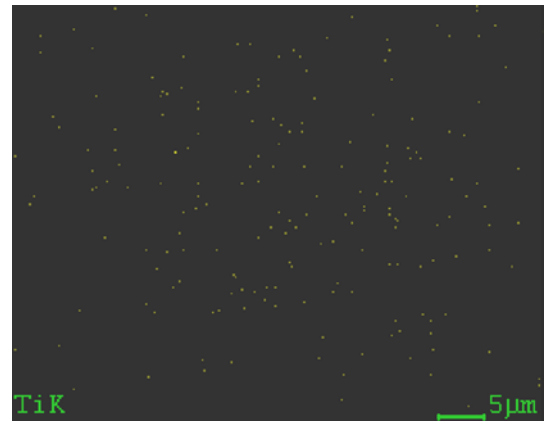
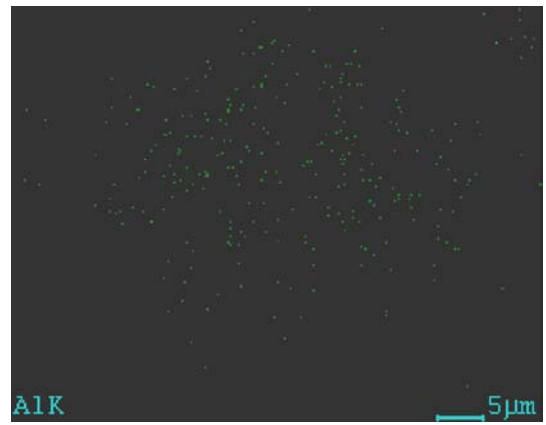
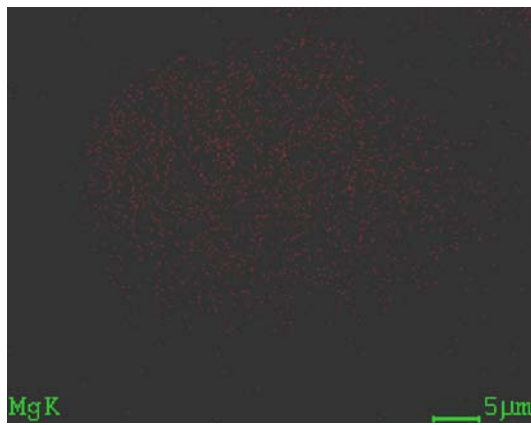
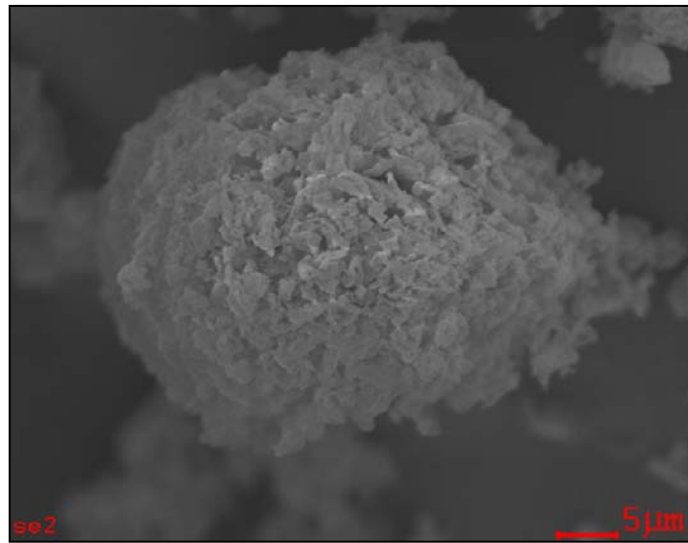
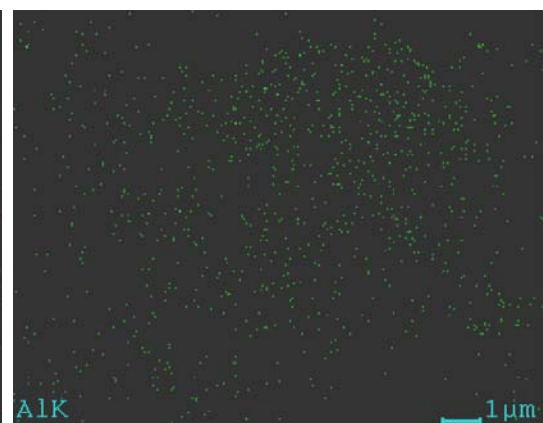
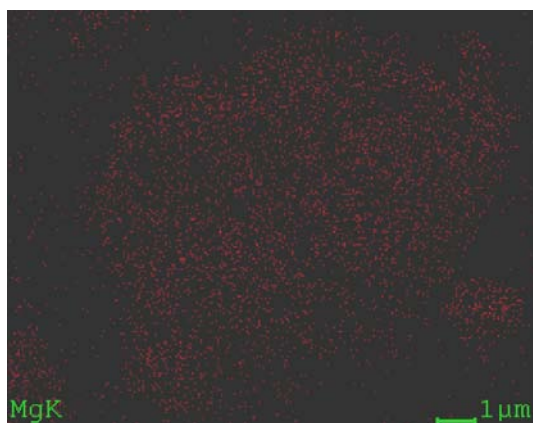
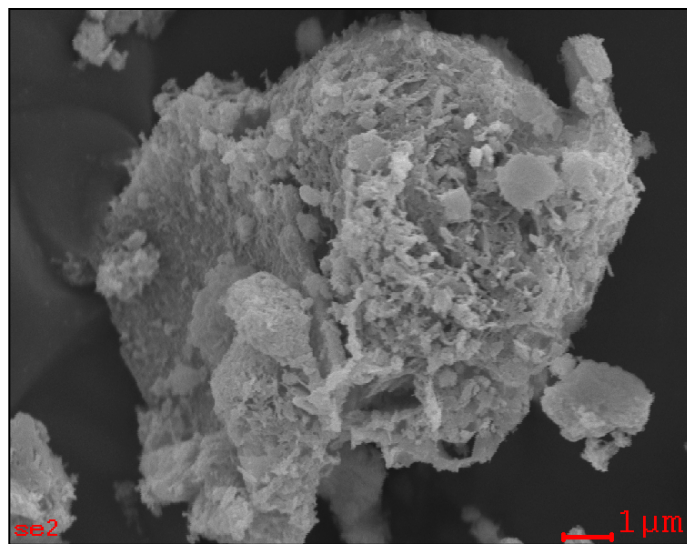




Figure D-3 SEM/EDX of Cat-C under 2000x microscopy



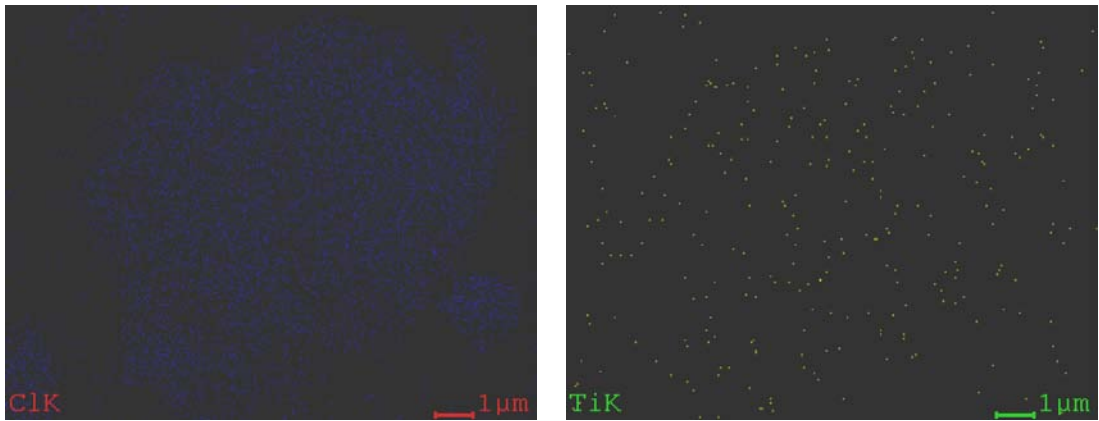
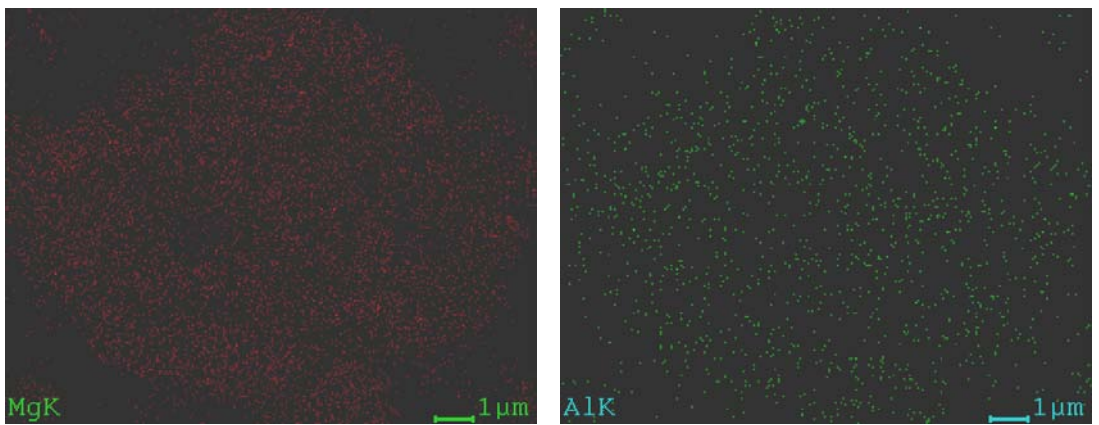
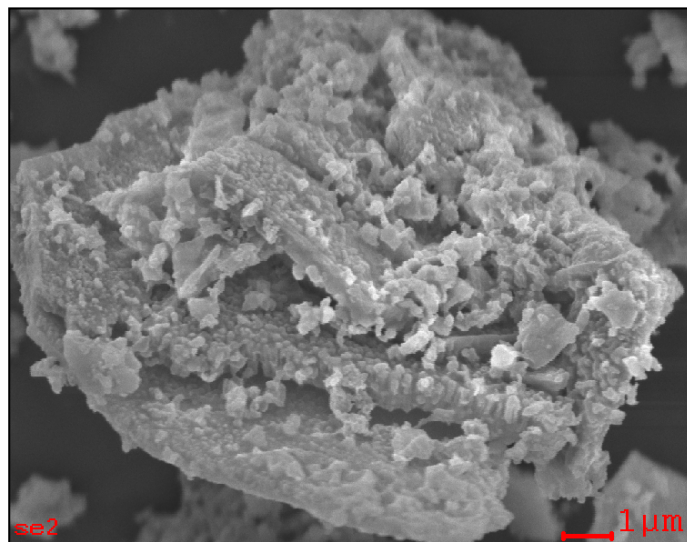


Figure D-4 SEM/EDX of Cat-D under 2000x microscopy



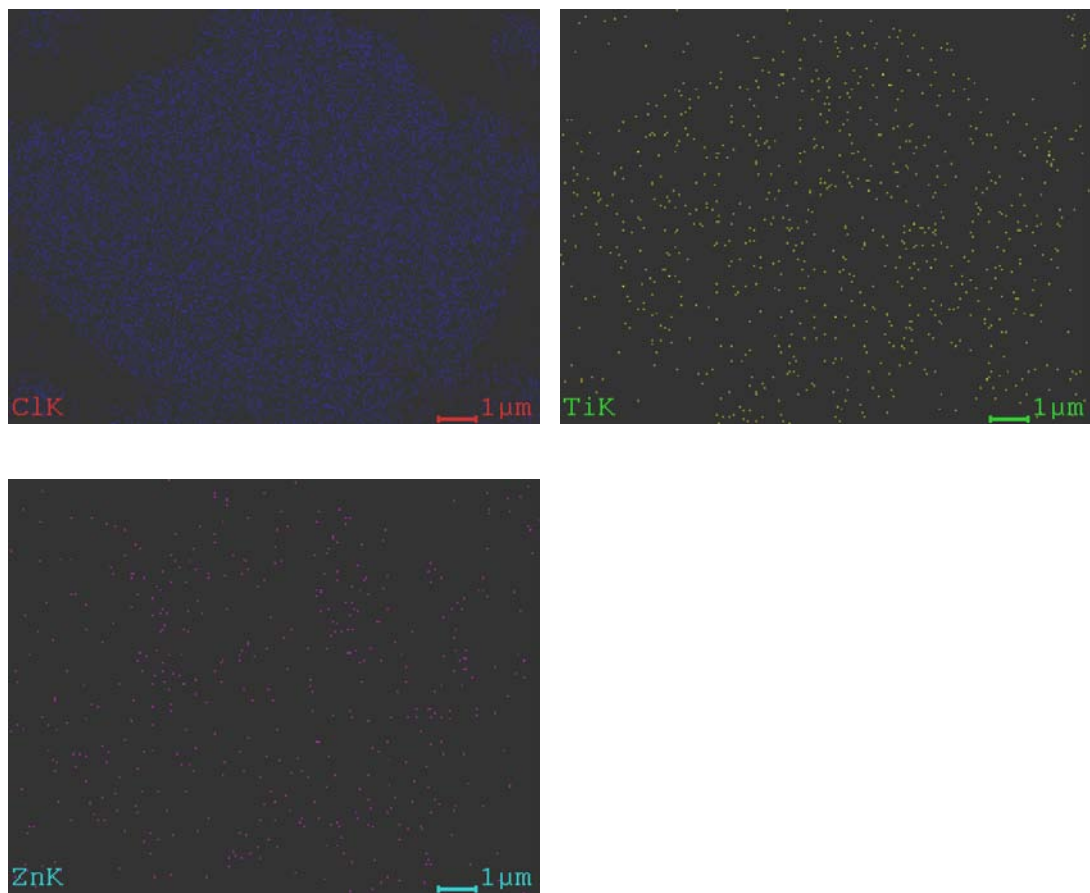
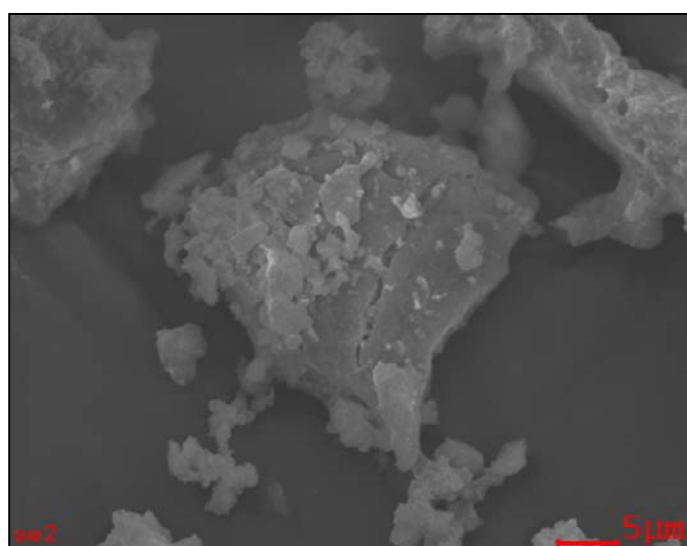


Figure D-5 SEM/EDX of Cat-E under 2000x microscopy



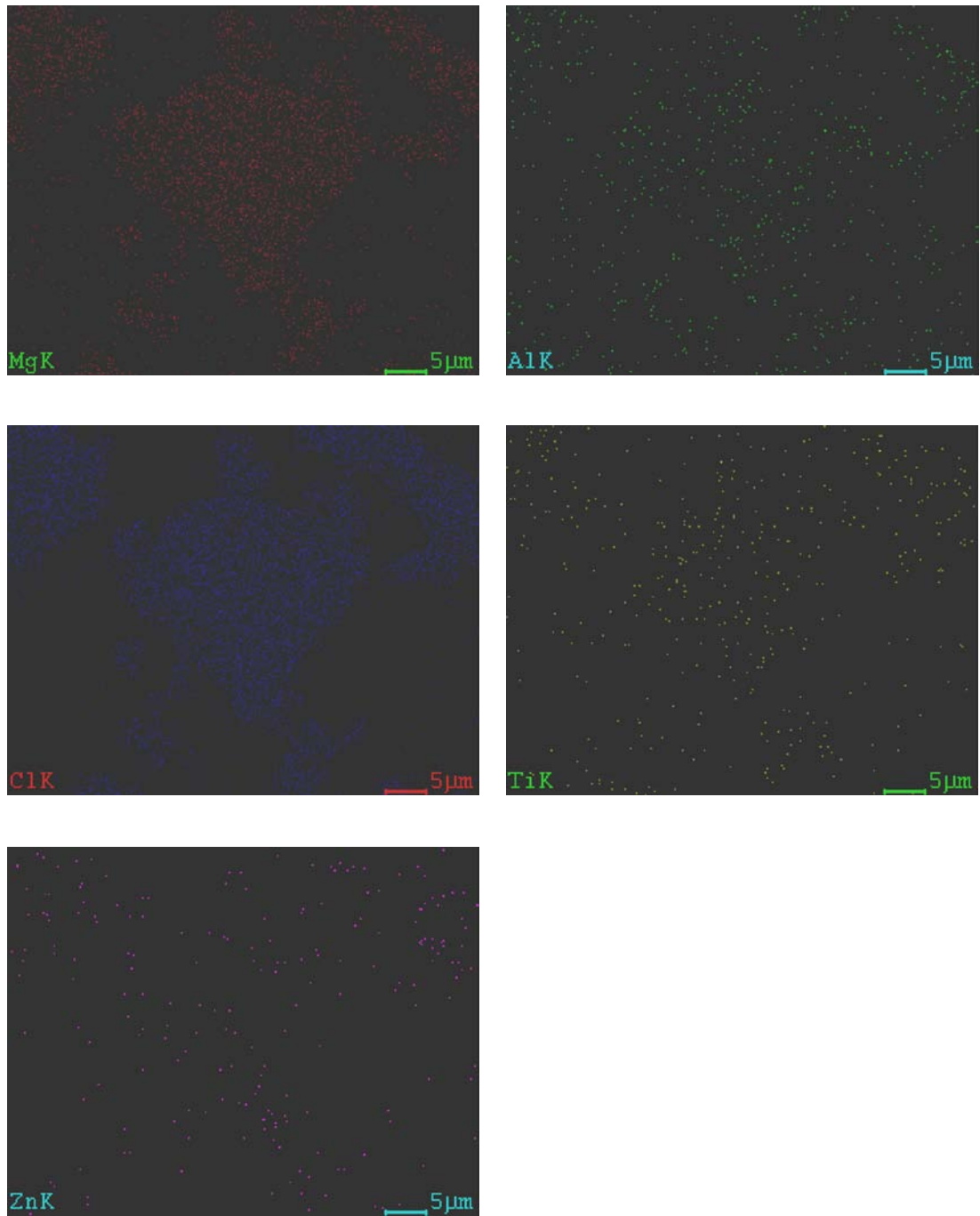


Figure D-6 SEM/EDX of Cat-F under 2000x microscopy

Table D-1 EDX analysis of catalyst surface

catalyst	Mg(wt%)	Al(wt%)	Zn(wt%)	Cl(wt%)	Ti(wt%)
Cat-A	24.14	1.91	-	71.91	2.04
Cat-B	24.13	1.55	-	71.79	2.53
Cat-C	22.09	1.41	3.56	70.53	2.41
Cat-D	24.25	2.14	-	71.47	2.14
Cat-E	20.92	1.76	9.55	65.5	2.27
Cat-F	22.59	1.89	7.88	64.13	3.51

Analysis on K subshell.

Appendix E

(LIST OF PUBLICATION)

1. Tharawadee, C. and Jongsomjit, B. “ Modification of MgCl₂-supported Ziegler-Natta catalyst with Lewis acids for ethylene polymerization” (The Proceeding of 21th International Chemical Engineering and Applied Chemistry Conference, TIChe 2011, Hatyai, Songkhla)

VITA

Chatchai Tharawadee was born on February 15, 1988 in Mahasarakham, Thailand. He graduated in a chemical engineering major with GPA 2.80 from King Mongkut's University of Technology Thonburi in June 2010 and he continued his Master's degree in Chemical Engineering, Chulalongkorn University under the Catalysis and Catalytic Reaction Engineering group in June 2010.