ผลของ AlCl$_3$ และโคมอนอเมอร์ต่อเอทิลีนพอลิเมอไรเซชันด้วยตัวเร่งปฏิกิริยาซีเกลอร์-นัตตา

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EFFECT OF AlCl$_3$ AND COMONOMERS ON ETHYLENE POLYMERIZATION USING ZIEGLER-NATTA CATALYST

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จุดมุ่งหมายของงานวิจัยนี้ คือการศึกษาผลของวิธีการเตรียมตัวเร่งปฏิกิริยาซีเกลอร์-นัตตาแตกต่างกันต่อเอทิลีนพอลิเมอไรเซชันที่มีโคมอนอเมอร์ ใช้วิธีการเตรียมตัวเร่งปฏิกิริยาซีเกลอร์-นัตตาสองแบบ ได้แก่ การเติมอะลูมิเนียมไทรคลอไรด์โดยการทำปฏิกิริยาเคมี (ตัวเร่งปฏิกิริยา A) และโดยการผสมแบบกายภาพ (ตัวเร่งปฏิกิริยา B) และเปรียบเทียบกับตัวเร่งปฏิกิริยาที่ไม่เติมอะลูมิเนียมไทรคลอไรด์ (ตัวเร่งปฏิกิริยา C) วิเคราะห์ตัวเร่งปฏิกิริยาที่เตรียมได้ด้วยเทคนิค SEM, XRD, PSD และการวิเคราะห์ธาตุ พบว่าตัวเร่งปฏิกิริยา A มีรูปร่างคล้ายทรงกลมและมีขนาดสม่ำเสมอ ในขณะที่ตัวเร่งปฏิกิริยา B และ C มีรูปร่างที่ไม่สม่ำเสมอ PSD ของตัวเร่งปฏิกิริยา A แคบกว่าของตัวเร่งปฏิกิริยา B และ C ที่ปริมาณอะลูมิเนียมที่กำหนด ได้พิจารณาความสามารถในการเร่งปฏิกิริยาของกระบวนการพอลิเมอไรเซชัน และการเข้ารวมของโคมอนอเมอร์ ได้เลือกโคมอนอเมอร์ 5 ชนิดสำหรับการศึกษานี้ ได้แก่ 1-บิวทีน, 1-เฮกซีน, 1-ออกทีน, 1-เดคซีน และ 1-โดเดซีน ได้วิเคราะห์พอลิเมอร์ที่ได้ด้วย MFI tester, density gradient tube, DSC และ GPC-IR ผลการทดลองแสดงว่า เมื่อความเข้มข้นของโคมอนอเมอร์เพิ่มขึ้น ความหนาแน่นของพอลิเมอร์ที่สังเคราะห์ด้วยตัวเร่งปฏิกิริยา A มีค่าต่ำกว่าตัวเร่งปฏิกิริยา B และ C โดยทั้งชนิดและปริมาณของโคมอนอเมอร์ bulk CH_3/1000C ของพอลิเมอร์มีค่าสูงขึ้นเมื่อปริมาณของโคมอนอเมอร์เพิ่มขึ้น นอกจากนี้ bulk CH_3/1000C ของพอลิเมอร์ที่ใช้ตัวเร่งปฏิกิริยา A มีค่ามากกว่าตัวเร่งปฏิกิริยา B และ C ทั้งชนิดและปริมาณของโคมอนอเมอร์ จึงสรุปได้ว่า ตัวเร่งปฏิกิริยาซีเกลอร์-นัตตา ที่เตรียมด้วยวิธีการเติมอะลูมิเนียมไทรคลอไรด์โดยการทำปฏิกิริยาเคมี ทำให้ได้พอลิเมอร์ที่มีการเข้ารวมของโคมอนอเมอร์สูงกว่าวิธีการผสมแบบกายภาพ

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KEYWORDS: ZIEGLER-NATTA, POLYETHYLENE, ALCL3, COMONOMER INCORPORATION

NATTAPOL SAMANUKUL: EFFECT OF $AlCl_3$ AND COMONOMERS ON ETHYLENE POLYMERIZATION USING ZIEGLER-NATTA CATALYST. ADVISOR: PROF. DR. SUPAWAN TANTAYANON, CO-ADVISOR: DR. SUTHEERAWAT SAMINGPRAI, 89 pp.

The aim of this research is to study the effect of different Ziegler-Natta catalyst preparation methods on ethylene polymerization in the presence of comonomers. Two different preparation methods of Ziegler-Natta catalysts, addition of $AlCl_3$ via chemical treatment (Cat.A), and by physical blending (Cat.B) were used, and compared with one without $AlCl_3$ (Cat.C). The prepared catalysts were characterized by SEM, XRD, PSD, and elemental analysis. It was found that Cat.A was uniformly spherical-like particles while Cat.B and Cat.C had irregular shape. PSD of Cat.A was narrower than Cat.B and Cat.C. At the given Al content of catalyst, catalytic activity of individual polymerization process and comonomer incorporation was determined. Five comonomers, i.e., 1-butene, 1-hexene, 1-octene, 1-decene, and 1-dodecene were selected for this study. The obtained polymers were characterized by MFI tester, density gradient tube, DSC, and GPC-IR. The results showed that when the concentration of comonomer increased, the density of the polymers using Cat.A was lower than Cat.B and Cat.C for both type and quantity of comonomers. The bulk CH_3/1000C of the polymers was higher when the amount of comonomer increased. In addition, the bulk CH_3/1000C of the polymers using Cat.A was higher than Cat.B for both type and quantity of comonomers. It can be concluded that Ziegler-Natta catalyst prepared via chemical treatment provided the polymers with higher comonomer incorporation than by physical blending.

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CHAPTER I

INTRODUCTION

1.1 Ziegler-Natta catalysts in polymerization of ethylene and propylene

Polyethylene plays an important role for the plastic industry for both homopolymer and copolymer. The copolymers refer to ethylene in combination with α-olefins such as 1-butene, 1-hexene, 1-octene etc. These copolymers are important because they have better properties in comparison to homopolymer of ethylene [1]. Many studies showed that the introduction of α-olefins comonomers can change the properties and microstructures of the copolymers [2, 3]. Furthermore, W. Meng *et al.* found that the introduction of longer chain α-olefins, 1-hexene compared with 1-butene, can increase the mechanical properties such as tensile strength and elongation at break [3] which is good for the industry. However, M. Bialek *et al.* found that the comonomer reactivity decreases with the increase of the size of the α-olefins chain, especially in the case of comonomers longer than octene [2]. This information shows that it is hard to synthesize polyethylene with special property due to the difficulty in the incorporation the longer chain α-olefins into the polymer chains.

One important factor that affects the property and microstructure of the polymer is the catalytic system. Generally, for HDPE, Ziegler-Natta catalyst has been used in polymerization. There are many types of Ziegler-Natta catalyst employed in the industrial polymerization which are based on titanium or vanadium compounds [2, 4]. Each type also can make the polymer to be different in many ways. For example, even though the same condition is applied to the polymerization, if the catalyst is different, the properties of the polymers such as MFI, density are also different. Previous studies showed that the addition of some modifiers called Lewis acid can increase the catalyst activity and comonomer incorporation. There are a few literatures reporting the compounds used for the modification of Ziegler-Natta catalysts, such as $ZnCl_2$ [5], $AlCl_3$ [3, 6], LiCl [7], $MnCl_2$ [8], and NaCl [9]. In case of polypropylene, most researches focus mainly on the isotacticity and molecular weight distribution of the polymer. X. Jiang *et al.* found that doping LiCl around 11-18 mol% into $MgCl_2$-supported Ziegler-Natta catalyst increased the molecular weight distribution and isotacticity of polypropylene while slightly decreased the catalytic activity [7]. X. Jiang *et al.* also reported that doping NaCl could lead to lower catalytic activity, higher molecular weight distribution and isotacticity [9]. T. Garoff *et al.* found that doping $MnCl_2$ with the concentration below 30 mol% into $MgCl_2$ support material led to large catalyst particle and good morphology. Also, the catalytic activity of producing polypropylene increased 25% when doping concentration was 10 mol% [8]. However, the polyethylene research focuses mainly on the catalytic activity and comonomer incorporation. D. Fregonese. *et al.* found that a small amount of $ZnCl_2$ (0.73 wt%) doping on the catalyst increased the catalytic activity compared to the reference catalyst ($TiCl_4/MgCl_2$ without $ZnCl_2$) but decreased when higher amount was used [5]. Y. P. Chen *et al.* reported that doping $AlCl_3$ (5.2 wt%) into $MgCl_2$-Supported Ziegler-Natta catalyst slightly increased the catalytic activity and 1-hexene comonomer incorporation and also increased molecular weight distribution of the polymer [6, 10]. Since increasing in catalytic activity and comonomer incorporation is what the polyethylene industry wants and Ziegler-Natta catalyst with $AlCl_3$ is quite famous in the present industry, $AlCl_3$ is chosen to be the modifier in our study.

However, we believed that not only the types of catalyst affect the property of the polymers but also the methodology to prepare a good quality catalyst. Therefore, in this study, 2 types of Ziegler-Natta catalyst which are $TiCl_4/MgCl_2{\cdot}AlCl_3$ by physical blending, and $TiCl_4/AlCl_3/MgCl_2$ by chemical treatment will be synthesized with various $AlCl_3$ content (Lewis acid) in the catalyst in order to evaluate the effect of $AlCl_3$ on amounts of comonomers incorporation for each type of comonomer and how the preparation techniques of catalyst affect the catalytic activity. $TiCl_4/MgCl_2$ without $AlCl_3$ will be used as a reference catalyst in order to evaluate the improvement. The catalysts will be characterized by SEM, XRD, PSD, and elemental analysis to evaluate their morphologies and components. Ethylene polymerization with various types of comonomers such as 1-butene, 1-hexene, 1-octene, 1-decene, and 1-dodecene will be investigated in 3 types of catalyst system (vide supra). After that, the polymers will be characterized to evaluate the melt flow index, density, thermal properties, molecular weight, molecular weight distribution, and comonomer incorporation of the polymer.

1.2 Motivations

The modification of $TiCl_4/MgCl_2$ Ziegler-Natta catalyst with $AlCl_3$ by chemical treatment should improve the catalyst activity and comonomer incorporation in ethylene polymerization.

1.3 Objective

The aim of this research is to study the effect of $AlCl_3$ content on the preparation of Ziegler-Natta catalyst and to use these catalysts in ethylene polymerization with comonomers.

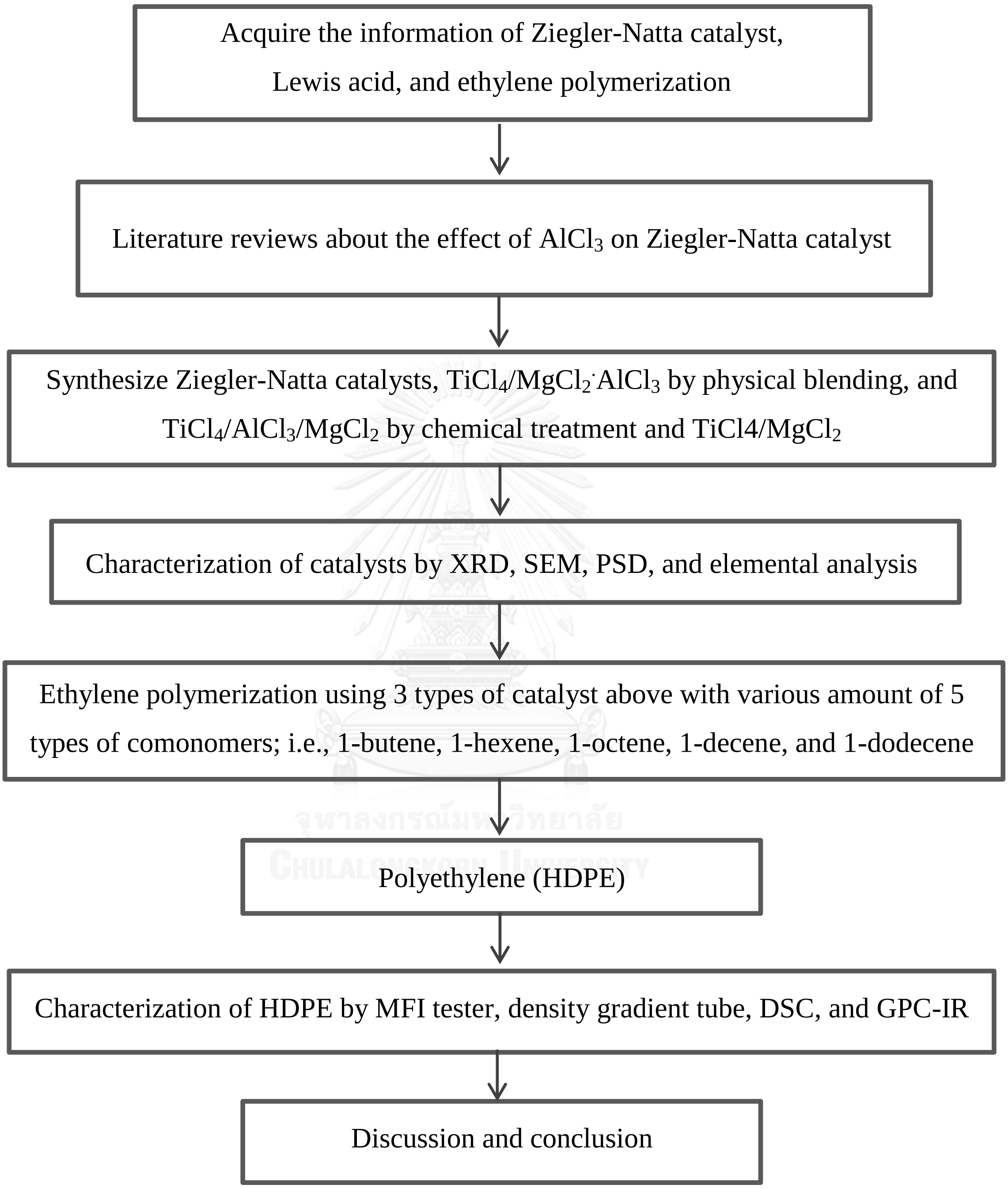
1.4 Research scopes

1. Prepare and characterize Ziegler-Natta catalysts using two different ways in addition of $AlCl_3$.
2. Synthesize and characterize the polyethylene by slurry phase polymerization with various types of comonomers using two types of Ziegler-Natta catalysts.
3. Investigate the catalytic activity and comonomer incorporation in all ethylene polymerizations using both types of Ziegler-Natta catalysts comparing to the catalyst without $AlCl_3$.

1.5 Benefits

Ziegler-Natta catalyst prepared by this new method can improve the catalytic activity and comonomer incorporation of long-chain α-olefins.

1.6 Research methodology



Acquire the information of Ziegler-Natta catalyst, Lewis acid, and ethylene polymerization

Literature reviews about the effect of $AlCl_3$ on Ziegler-Natta catalyst

Synthesize Ziegler-Natta catalysts, $TiCl_4/MgCl_2{\cdot}AlCl_3$ by physical blending, and $TiCl_4/AlCl_3/MgCl_2$ by chemical treatment and TiCl4/$MgCl_2$

Characterization of catalysts by XRD, SEM, PSD, and elemental analysis

Ethylene polymerization using 3 types of catalyst above with various amount of 5 types of comonomers; i.e., 1-butene, 1-hexene, 1-octene, 1-decene, and 1-dodecene

Polyethylene (HDPE)

Characterization of HDPE by MFI tester, density gradient tube, DSC, and GPC-IR

Discussion and conclusion

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Polyethylene

2.1.1 Introduction

Polyethylene (PE) is the most common plastic polymer used nowadays. It has the highest productivity among other polymers. Figure 1shows that the market share of the polyethylene takes more than 30% of the entire polymer's market sharing. Its primary use is in packaging such as plastic bag, plastic films, geomembranes, and containers including bottles. Polyethylene is important in the polymer industries because its demand increases every year like shown in Figure 2. The monomer is ethylene, a gaseous hydrocarbon with the formula of C_2H_4. Ethylene is normally produced from petrochemical sources. The polymerization occurs when there are catalysts in the system. The polymerization is highly exothermic. The structure of ethylene monomer and polyethylene are shown in the Figure 3 below [4].

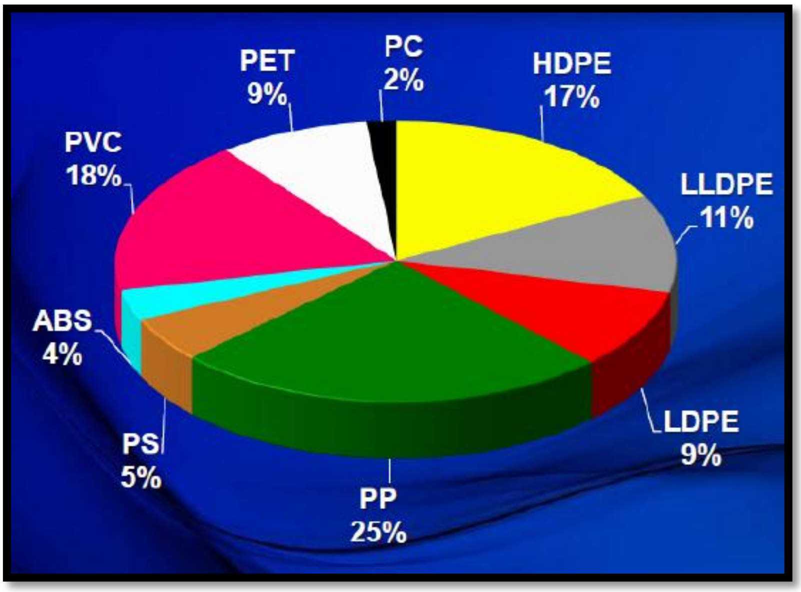


Figure 1 The pie chart showing the global percentage of each polymer's market sharing (2012). [4]

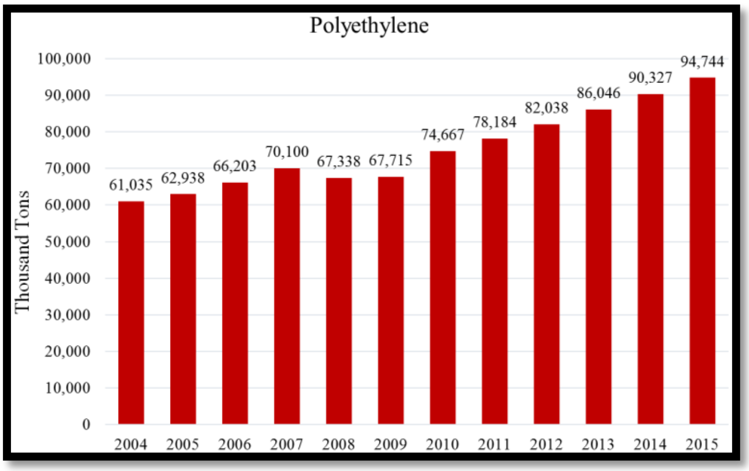


Figure 2 The world's demand for PE from 2004 to 2015. [4]

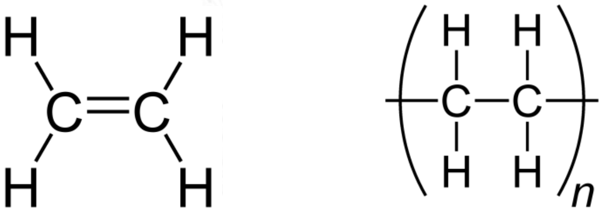


Figure 3 Structure of ethylene monomer (left) and polyethylene (right).

Polyethylene can be classified into several different categories based mostly on its density and branching. Its mechanical properties depend significantly on variables such as the extent and type of branching, the crystal structure and the molecular weight. The most important polyethylene grades in the present are HDPE, LLDPE and LDPE.

2.1.2 Types of polyethylene

2.1.2.1 High-density polyethylene (HDPE)

HDPE, defined by a density of greater or equal to 0.940 g/cm^3, it has a low degree of branching and thus low intermolecular forces and tensile strength. It can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or mettallocene catalysts. The major use is in products and packaging such as milk jugs, detergent bottles, butter tubs, garbage containers and water pipes. HDPE can be synthesized by polymerization of ethylene with or without the comonomers. Nowadays, the copolymerization of ethylene with α-olefins such as 1-butene, 1-hexene, 1-octene become the important product for the plastic industry.

2.1.2.2 Low-density polyethylene (LDPE)

LDPE is defined by a density range of 0.910–0.940 g/cm^3. LDPE has a high degree of short and long chain branching. It has low tensile strength and high ductility. It is created by free radical polymerization. The high degree of branching with long chains gives molten LDPE unique and desirable flow properties. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap.

2.1.2.3 Linear low-density polyethylene (LLDPE)

LLDPE is defined by a density range of 0.915–0.925 g/cm^3. LLDPE is a linear polymer with significant numbers of short branches, commonly made by copolymerization of ethylene with short-chain alpha-olefins (for example, 1-butene, 1-hexene and 1-octene). LLDPE has higher tensile strength than LDPE, it exhibits higher impact and puncture resistance than LDPE. Their use is in packaging, particularly film for bags and sheets. Cable covering, toys, lids, buckets, containers and pipes are also available. LLDPE is used predominantly in film applications due to its toughness, flexibility and relative transparency.

2.2 Ziegler-Natta catalyst

Ziegler–Natta catalyst is a catalyst used in the synthesis of polymers of 1-alkenes (α-olefins) such as polyethylene. It was named after Karl Ziegler and Giulio Natta. There are two classes of Ziegler–Natta catalysts distinguished by their solubility which are heterogeneous and homogeneous catalyst. The heterogeneous catalyst is based on titanium compounds and has a support which is usually $MgCl_2$. This catalyst has to use in combination with cocatalysts, organoaluminum compounds such as triethylaluminium, $Al(C_2H_5)_3$. This class of catalyst is well known in the industry. Another one is homogeneous catalyst which usually based on complexes of Ti, Zr or Hf. It is usually used in combination with a different organoaluminum cocatalyst such as methylaluminoxane, MAO. Metallocenes are well known in this class of catalyst [11].

Ziegler–Natta catalysts are used to polymerize terminal 1-alkenes (ethylene and alkenes with the vinyl double bond). For the heterogeneous catalyst, the reaction occurs at special Ti centers located on the exterior of the catalyst crystallites. Some titanium atoms in these crystallites react with organoaluminum cocatalysts with the formation of Ti–C bonds. The reaction occurs as followed:

$$L_nTi–CH_2–CHR–Polymer + CH_2=CHR \rightarrow L_nTi–CH_2\text{-}CHR–CH_2–CHR–Polymer$$

The two chain termination reactions occur quite rarely in Ziegler–Natta catalysis and the formed polymers have a too high molecular weight to be of commercial use. To reduce the molecular weight, hydrogen is added to the polymerization reaction:

$$L_nTi–CH_2\text{-}CHR–Polymer + H_2 \rightarrow L_nTi\text{-}H + CH_3\text{-}CHR–Polymer$$

2.3 Lewis acid in catalyst

The definition of Lewis acid is any substance, such as the H^+ ion, that can accept a pair of nonbonding electrons. In other words, a Lewis acid is an electron-pair acceptor.

2.3.1 Role of Lewis acid and $AlCl_3$ in Ziegler-Natta catalyst

In Ziegler-Natta catalyst, a metal-based Lewis acid acts as an electron pair acceptor to increase the reactivity of a substrate. Common Lewis acid catalysts are based on main group metals such as aluminum, boron, silicon, and tin, as well as many early (titanium, zirconium) and late (iron, copper, zinc) d-block metals. The examples of Lewis acid in Ziegler-Natta catalyst application are $ZnCl_2$ [5], $AlCl_3$ [6], LiCl [7], $MnCl_2$ [8], and NaCl [9]. However, $AlCl_3$ is a famous one in the industry due to its availability and price. To explain the role of Lewis acid, in the polymerization process, the monomer has negative charge and the catalyst has positive charge, when the Lewis acid is added in to the system, it can increase the positive charge of the catalyst resulting in increasing the capability of binding between monomer and catalyst [10, 11].

2.4 Ethylene polymerization

2.4.1 Slurry process

Slurry polymerization process is well known for the polymerization of ethylene, usually to produce HDPE. In this process, the catalyst will be suspended in an inert medium, i.e., hexane, heptane and the monomer, comonomer, hydrogen and other substance must be dissolved in the medium. When designing a catalyst for use in slurry polymerization, the avoidance of leaching, i.e., the extraction of active components into the liquid phase, must be considered because leaching can lead to reactor fouling, formation of polymer powder on the wall of the reactor, and hence reduce the operability and economy of the process.

2.4.2 Catalytic activity/ Productivity

Catalytic activity, or productivity, is the parameter used to evaluate the catalyst performance of converting ethylene to polyethylene in the unit of g polymer/mmol Ti (active site). Generally, when talking about the activity, the conditions of polymerization must be specified for easy comparison among each catalyst. This parameter is one important in the ethylene polymerization industry.

2.5 Properties of polymer

2.5.1 Melt flow index (MFI)

Melt flow index (MFI) or melt flow rate (MFR) of a polyethylene resin is the weight in grams of polymer that extrudes from a standard capillary die under a fixed load, measured according to ASTM D 1238. The purpose of this measurement is to provide a value that reflects the ease of flow of a molten polymer. The MFI of a sample is primarily dependent upon its average molecular weight, but this relationship is strongly influenced by such factors as the molecular weight distribution and degree of long-chain branching.

To determine the MFI of a polyethylene resin, a suitable mass of it (about 5 grams) is charged into the barrel of a melt indexer (also known as an extrusion plastometer) preheated to 190 °C. A weighted piston with a total mass of 2.16 kg is then placed atop the sample. The sample is allowed to preheat and melt for 6–8 min. During the time allowed for melting, a small quantity of polymer extrudes from the capillary die, of length 8.0 mm and diameter 2.0955 mm. At the conclusion of the melting period, the extrudate is sliced off flush with the bottom of the die and a timer is started. The polymer is allowed to extrude for a preset period of time, after which it is severed and weighed. The melt index is the weight, in grams, of the extrudate multiplied by 10 divided by the extrusion time in minutes:

$$\mathrm{MFI} = \frac{\mathrm{mass\ (g)\ x\ 10}}{\mathrm{time\ (min)}}$$

This corresponds to the weight of the polymer that would have extruded in a ten minute period. The precise methodology for determining the melt index is described in ASTM method [12].

2.5.2 Density

Density is one of the descriptors most commonly used when discussing polyethylene resins. This is primarily because many of the physical properties of a polyethylene sample can be predicted to a fair approximation based solely upon its density. The relationship between certain mechanical properties and the density of a sample arises from the semi-crystalline nature of polyethylene. The higher the proportion of crystalline phases, the higher the density. Density is a function of molecular weight characteristics, branch content, and preparation conditions. When all other factors remain constant, the density of a specimen will increase as the branch content, molecular weight, or rate of crystallization decrease or the degree of orientation increases [12].

2.5.3 Molecular weight & molecular weight distribution

The molecular weight of polymer is defined as the sum of the atomic weights of each of atoms in the molecule. A much simpler experimental measurement of the size of the polymer is to determine the molecular weight. The atomic weight can be found by referring to the periodic table. For example, the atomic weight of carbon is 12 g/mol, the atomic weight of hydrogen is 1g/mol and so on. When the exact molecular formula is known, the molecular weight is easy to be calculated. For example, benzene (C_6H_6) would have a molecular weight of 78 g/mol [(6*12)+(6*1)].

The molecular weight of the polymer could also be calculated too if the exact formula is known. For instance, if the polymer is polyethylene with n equal to 1000, the molecular (repeat unit) formula would be as follows: $(C_2H_4)_{1000}$ The molecular weight would be 28,000 g/mol ((2*12) + 4) x 1000 since each C_2H_4 would have a weight of 28 g/mol and there would be 1,000 of these units. However, in the real polymer systems, the polymerization process results in chains with many different lengths. There are many types of molecular weight but in common use, there are three types which are number-average molecular weight (Mn), weight-average molecular weight (Mw), and z-average molecular weight (Mz). Each molecular weight is calculated as followed.

$$\overline{M}_n = \frac{\sum M_i N_i}{\sum N_i} = \frac{\sum W_i}{\sum N_i}$$

$$\overline{M}_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i} = \frac{\sum M_i W_i}{\sum W_i}$$

$$\overline{M}_z = \frac{\sum M_i^3 N_i}{\sum M_i^2 N_i} = \frac{\sum M_i^2 W_i}{\sum W_i}$$

where: Mi = molecular weight of chains in fraction i
Ni = number of chains in fraction i
Wi = weight of chains in fraction i

2.5.4 Thermal properties

Semicrystalline polymers in general differ from most crystalline solids in that they display a melting range rather than a discrete melting point. Polyethylene exhibits a range of melting phenomena that can occur at temperatures from as low as room temperature up to 140 °C. The melting range is a consequence of the inevitable distribution of lamellar thicknesses in the solid state. Thermal properties for polyethylene refer to many parameters, for example, melting temperature (Tm), glass transition temperature (Tg), heat distortion temperaturte (HDT), heat of fusion (ΔH_f), heat conduction, and heat capacity etc. In the industry, the thermal characteristics of polyethylene, especially its relatively low melting and softening temperatures, are some of the primary elements that define its realm of applications. There are some parameters and conditions that can affect the melting temperature of the polyethylene. Some of them are summarized in Table 1 [12].

Table 1 Effect of molecular, processing, and morphological characteristics on melting temperature of polyethylene. [12]

Variable	Effect on Tm	Notes
Increased branch content	Decrease	Very high branch contents reduce melting temperature to just above room
Increased molecular weight	Decrease	Drop of 5°C for linear polyethylene increasing from 50,000 to 10000000
Decreased density/crystallinity	Decrease	Branch content has greater effect than molecular weight
Increased cooling rate	Decrease	Greatest effect on linear polyethylene
Increased orientation	Increase	Greatest effect on high molecular weight linear polyethylene

2.6 Characterization

2.6.1 Scanning electron microscopy (SEM)

SEM is used to examine polymer surfaces. It yields images with a very large depth of field compared to that of optical microscopy at equivalent magnifications. Most scanning electron microscopes use relatively high voltages to accelerate the electrons that strike the sample. The net result is that the electrons hitting the surface are highly energetic and impart much of their energy to the sample in the form of heat. Due to the non-conducting nature of polyethylene, unprotected surfaces rapidly heat up, causing thermal degradation of features by melting and cracking (due to localized expansion). Samples may also undergo reactions with the incoming electrons that directly change the sample morphology. Such effects are generically known as beam damage. Additionally, the high flux of electrons striking non-conducting surfaces builds up static charge on the sample, which deflects incoming electrons from their path, thus reducing the quality of the image. The higher the magnification, the worse these problems become. These troubles may be reduced by coating the surface of the sample with a conductive layer such as a layer of gold or carbon. The conducting layer has the disadvantage that it tends to obscure fine details on the sample. There is inevitably a trade-off between loss of detail and protection of the sample. The thicker the layer, the greater the obscuration of fine details; typical conductive coatings are 50–200 A° thick [12].

2.6.2 Differential scanning calorimetry (DSC)

DSC is a technique used to determine thermal characteristics of polyethylene samples relevant to both real-life applications and fundamental morphological investigations. As its name implies, differential scanning calorimetry involves dynamic calorimetric analysis of a sample whose temperature is being risen at a controlled rate. This is achieved by measuring the instantaneous heat capacity of a sample as a function of its function of temperature in a plot known as a thermogram. Endothermic and exothermic peaks respectively correspond to melting and crystallization processes, while step changes reflect material transitions, such as the glass–rubber transition. Quantitative information can be obtained with respect to both the temperature at which events occur and the heat flow associated with them. DSC can also be used to measure transitions involving heat transfer that occur at fixed temperatures, such as isothermal crystallization [12].

2.6.3 Size exclusion chromatography (SEC) or gel permeation chromatography (GPC)

SEC or GPC is based on the premise that molecules in solution adopt random coil configurations with hydrodynamic volumes that increase as a predictable function of their molecular weight. By separating the molecules according to their random coil dimensions, a molecular weight distribution plot can be generated. A dilute solution of polymer is pumped through a column packed with microscopic beads, the surfaces of which are riddled with pores whose range of sizes encompasses that of the polymer random coils. The largest molecules can only diffuse into a small fraction of the pores and are quickly eluted from the column. Progressively smaller molecules find a larger fraction of pores accessible and are thus impeded in their passage through the column in proportion to the numbers of pores available for them to enter. Thus the smaller the molecule, the longer it will take to pass through the column. The concentration of the solution eluting from the column is recorded as a function of time. With suitable calibration, a plot of the molecular weight distribution can be generated. From the distribution plot the various parameters of the molecular weight (Mn, Mw etc.) can be calculated [12].

2.6.4 UV-Visible spectroscopy

UV-Visible spectroscopy is a technique used in analytical chemistry for the quantitative determination of different components such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Ultraviolet (UV) light is an electromagnetic radiation with a wavelength shorter than that of visible light, but longer than X-rays, in the range 10 nm to 400 nm. The visible spectrum is the portion of the electromagnetic spectrum that is visible to the human eye, in the range of 390 to 750 nm. The instrument used in UV-visible spectroscopy is called a UV/Vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (Io). The ratio I/Io is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance:

$$A = -\log (T\% / 100\%)$$

The principle of this technique is when light is absorbed by matter the result is an increase in the energy content of molecules (or atoms). The absorption of ultra violet or visible light by a chemical species produces a characteristic spectrum. The intensity of the spectrum is proportional to the amount of component in the sample. So, this technique can be used to identify the species and contents of the component. The analysis is commonly carried out in solutions but solids and gases may also be studied [13].

In this research, the concept was that the titanium tetrachloride in the catalyst was decomposed by sulfuric acid and colorized by hydrogen peroxide. The intensity of color will be proportional to the amount of Ti content in the catalyst which can be evaluated by measuring the absorbance by the UV-Vis spectrophotometer and comparing the result with the standard curve.

2.6.5 Auto-titration

Auto-titration is a technique to determine the amount of substance or component using a machine called auto-titrator. This machine has some significant benefits such as it can give more accurate reading than human could, it can perform the test faster than human could, and the endpoint detection does not rely on human color perception and thus give less the percentage error. In this research, this technique can be used to determine the Mg and Cl content in the catalyst.

2.6.6 Inductively coupled plasma (ICP)

Inductively Coupled Plasma (ICP) is an analytical techniques used for the detection of metal and non-metal in the samples. The principle of this technique is to get the elements to emit characteristic wavelength specific light which can be measured by mass spectrometer to separate and quantify them. ICP can detect the concentration as low as one part in 10^{15} (ppq)

2.6.7 X-ray diffraction (XRD)

X-ray diffraction (XRD) is one of light scattering techniques used to investigate the morphological character of polymeric system or catalytic system. It is a powerful technique that provides both qualitative and quantitative information including unit cell parameters, degrees of crystallinity, lamellar periodicity, and degrees of orientation. The distribution of scattering angles obtained by each technique is characteristic of the distribution of the periodicities of the features being probed, according to Bragg’s law,

$$n\lambda = 2d \sin \theta$$

where n = an integer
λ = wavelength of incident radiation
d = periodicity of scattering features
θ = scattering angle

There are two types of XRD which are wide angle X-ray diffraction (WAXRD) and small angle X-ray diffraction (SAXRD). WAXRD refers to the scattering of X-rays over a range of angles from about 2° to 180° and SAXRD refers to a range of angles from about 0.2° to 2° [12].

2.6.8 Particle size distribution (PSD)

Particle size distribution of a material can be important in understanding its physical and chemical properties. It affects the strength and load-bearing properties of rocks and soils. It affects the reactivity of solids participating in chemical reactions, and needs to be tightly controlled in many industrial products such as the manufacture of catalyst and polymer. There are many ways of determining the particle size but in this research, we used the technique called Focused Beam Reflectance Measurement (FBRM) technology.

Focused Beam Reflectance Measurement (FBRM) provides the unique ability to measure particles and droplets in concentrated suspensions and emulsions at full process concentration without the need for sample extraction and sample preparation. The basic principle of the FBRM technique is very simple. The machine uses the probe that has a laser light source to scan the particles in the sample and translated into Chord Lengths which is simply defined as the straight-line distance from one edge of a particle or particle structure to another edge. Thousands of individual chord lengths are typically measured each second to produce the particle size distribution [14]

2.7 Literature reviews

F. Hindryckx et al., (1998) studied the ethylene polymerization by a high activity $MgCI_2$ supported Ti catalyst in the presence of hydrogen and/or 1-octene. Al/Ti/Mg catalyst (DOW) was used. The result showed that the presence of hydrogen was efficient in decreasing the PE molecular weight, activity, and polymer melting temperature and increasing the crystallinity, melt index, and elongation at break of PE. Also, the addition of 1-octene decreased the polymerization rate [15].

D. Fregonese et al., (1999) studied the catalytic systems supported on $MgCl_2$ doped with $ZnCl_2$ for olefin polymerization. The $MgCl_2$ doped with $ZnCl_2$ Ziegler-Natta catalyst was prepared for propylene polymerization. The effect from amount of $ZnCl_2$ doped was investigated on catalytic activity and its properties. The result showed that the catalytic activity increased when adding $ZnCl_2$ in catalyst. The highest activity was at 5 wt% added $ZnCl_2$ and the activity decreaed when the amount of $ZnCl_2$ increased. The isotactic index was in the same trend as the activity [5].

M. Bialek et al., (2000) studied the effect of comonomer on the copolymerization of ethylene with long chain α-olefins using Ziegler-Natta catalysts. 3 types of ZN catalysts which were $VOCl_3$, VCl_4, and $TiCl_4$ supported on $MgCl_2(THF)_2$ and used 1-pentene, 1-hexene, 1-octene, 1-decene and 1-dodecene as the long chain α-olefins. The results showed that the introduction of the long chain α-olefins decreased the catalyst activity. The catalyst activity did not depend on the type of comonomer but changed with the concentration of loaded comonomer. The %

incorporation increased with the increase of the comonomer concentration in the polymerization feed and the comonomer reactivity decreased with the increase of the size of the α-olefin chain, especially in the case of comonomers longer than octene. IR technique, DSC, Polish Standard PN-92/C-89035 were used to determine the copolymer compositions, % crystallinity, melting temperature (Tm), and density of polymer [2].

Y. Chen et al., (2006) studied the molecular weight distribution of polyethylene catalyzed by Ziegler-Natta catalyst supported on $MgCl_2$ doped with $AlCl_3$. $TiCl_4/MgCl_2/AlCl_3$ supported catalyst was used in ethylene polymerization by varying $AlCl_3$ content in the catalyst. The results showed that the activity increased when the amount of $AlCl_3$ doped increased but the activity dropped dramatically at high $AlCl_3$ content. Furthermore, the molecular weight distribution increased when the amount of $AlCl_3$ doped increased [6].

Y. Chen et al., (2006) also studied the ethylene/1-hexene copolymerization with $TiCl_4/MgCl_2/AlCl_3$ catalyst in the presence of hydrogen. $TiCl_4/MgCl_2$ with and without $AlCl_3$ were used in the polymerization of ethylene with hexane as comonomer. The results showed that the activity and the % comonomer incorporation increased when using $TiCl_4/MgCl_2$ doped with $AlCl_3$ catalyst [10].

Y. Kong et al. (2010) studied the different structure ligands in heterogeneous Ziegler-Natta catalysts for the preparation of copolymer of ethylene and 1-octene with high comonomer incorporation. Three catalyst systems, the conventional Ziegler-Natta catalyst $TiCl_4/MgCl_2$, the modified supported Ziegler-Natta catalysts (iso-pentylO)$TiCl_3/MgCl_2$, and (BzO)$TiCl_3/MgCl_2$, were used. The result showed that the modified support catalysts gave higher molecular weight, higher comonomer incorporation and good yield even at high temperature (80 °C) and low Al/Ti molar ratio (100) in the production of random ethylene/1-octene copolymers [16].

W. Meng et al., (2011) studied the effect of comonomer type and content on the properties of Ziegler-Natta bimodal high-density polyethylene. Two types of comonomers, 1-hexene and 1-butene, were used and varied the amount of comomer content in the polymer. The results showed that the longer chain (1-hexene) and the higher comonomer content gave higher tensile strength at break and elongation at break but lower tensile strength at yield compared to the shorter chain (1-butene) [3].

X. Jiang et al., (2011) studied the effects of doping LiCl into $MgCl_2$-supported Ziegler-Natta catalyst on the molecular weight distribution and isotacticity of polypropylene. LiCl dosage was varied from 0-62 %. The result showed that the molecular weight distribution and isotacticity of polypropylene changed with amount of LiCl doped in catalyst. The broader molecular weight distribution was found in catalyst using LiCl-doped contain 11-18 mol% [7].

CHAPTER III

EXPERIMENTAL

3.1 Preparation of the catalysts

For $TiCl_4/MgCl_2$, $MgCl_2$ and ethanol in mole ratio of 1:3 were added into a flask and equal volume of dry n-heptane was also added. The flask was then heated to about 120 °C with stirring under protection of argon, until $MgCl_2$ was completely dissolved. After the system was cooled to room temperature, solvent and the remained ethanol were removed by evacuation. The dried adduct powder was sealed in a glass bottle and stored under argon. About 4–6 g $MgCl_2 \cdot nEtOH$ adduct was added into a three-neck flask, and 50 ml $TiCl_4$ was injected into the flask at temperature lower than 10 °C under stirring. The temperature was then raised to 90°C and maintained for 1h. Then the flask was maintained at 90 °C, and the upper liquid phase was siphoned off. The crude catalyst was washed five times with heptane at 90 °C, and then vacuum dried and stored in a sealed glass bottle under argon.

For $TiCl_4/MgCl_2 \cdot AlCl_3$ by physical blending, the same procedure was adopted as the preparation of $TiCl_4/MgCl_2$, except for adding $AlCl_3$ along with $MgCl_2$. The ratio of $AlCl_3/MgCl_2$ was 3:1 by mol

For $TiCl_4/AlCl_3/MgCl_2$ by chemical treatment, the same procedure was adopted as the preparation of $TiCl_4/MgCl_2$, except adding diethyl aluminium chloride (DEAC) after $MgCl_2 \cdot nEtOH$ adduct was formed.

3.2 Characterization of catalysts

The 0.25 g of dried catalyst sample was mixed in 60 ml of 6 M aqueous solution of H_2SO_4 and stirred for 1 h. The volume was made up to 250 ml and the acid solution was employed for Ti, Mg and Cl determination.

3.2.1 Elemental analysis

The total Ti content in the catalyst was evaluated by UV-Visible spectrophotometer. Ti determination was performed by diluting 10 ml of acid solution in a 100 ml volumetric flask, containing 7.6 ml of 10 % v/v solution of H_2SO_4 and 10 ml of H_2O_2 (3% v/v) reagent. The yellow complex of $[Ti(H_2O_2)]^{4+}$ was measured at 400 nm.

The content of Mg in the catalyst was determined by auto-titrator with DP5 phototrode. Mg was determined by titration with EDTA in the presence of Eriochrome black T. The 60 ml of the buffer NH_3 solution was added to the 10 ml of acid solution and the pH of the solution was raised to 10. Then, the resulting solution was titrated with 0.1 M of EDTA.

The Cl content was also determined by auto-titrator with Ag/AgCl Ionic Selective Electrode. The 40 ml of deionized water was added to 10 ml of the acid solution, and then titrated with 0.1 M of $AgNO_3$.

The Al content was determined by ICP-MS. The used model was Perkin Elmer Optical. The catalyst samples was dissolved with 5 ml of hydrofluoric acid and stirred overnight. After that the solution was diluted to a volume of 100 ml in a plastic volumetric flask. Then, the Al content was measured.

3.2.2 X-ray diffraction (XRD)

XRD was performed to determine the bulk crystalline phases of the catalyst samples. It was determined by using Bruker D8 ADVANCE X-ray diffractometer with CuK (1.542 A°). The spectra were scanned at a rate of 0.02 (Increment) in the range 2ϴ = 5-80 degrees. The catalyst samples were prepared in an argon atmosphere glove box by adding catalyst on the sample holder and covering the sample by mylar film.

3.2.3 Scanning electron microscope (SEM)

The morphology of the catalyst was observed by SEM. The model used to observed was JEOL JSM-6510LV. The catalyst samples were prepared in an argon atmosphere glove box and placed in closed vial bottle.

3.2.4 Particle size distribution (PSD)

The particle size and the particle size distribution of the catalysts were determined by Particle Track G400 with FBRM Technology (METTLER TOLEDO) The catalyst samples were prepared in slurry phase using hexane as a solvent.

3.3 Polymerization

3.3.1 Ethylene polymerization using $TiCl_4/AlCl_3/MgCl_2$ by chemical treatment catalyst with varied amount of $AlCl_3$

The 5-liter batch reactor was heated to 70 °C and purged by the nitrogen gas for 1 hour. After that the reactor was purged by ethylene and hydrogen gas, respectively. At first, 2.5 liters of hexane were introduced into the reactor. Then, the co-catalyst, triethyl aluminium 1 mmol/L, and the catalyst which is $TiCl_4/AlCl_3/MgCl_2$ by chemical treatment, 0.01 mmol/L, were put into the reactor. After that, H_2 pressure 3.5 bar was filled into the reactor, followed by ethylene and then the pressure was kept at 8 bar. The agitator was at 400 rpm. The reaction temperature was kept at 80 °C and the polymerization process was stopped when the time of polymerization was 120 minutes. The obtained slurry polymer was dried by the oven to get the dry polymer powder. The process was repeated with different amount of $AlCl_3$ in the catalyst. This process is to determine the appropriate amount of $AlCl_3$ used in the catalyst in order to produce the highest catalytic activity.

3.3.2 Ethylene/1-hexene copolymerization with $TiCl_4/AlCl_3/MgCl_2$ by chemical treatment catalyst

The 5-liter batch reactor was heated to 70 °C and purged by the nitrogen gas for 1 hour. After that the reactor was purged by ethylene and hydrogen gas, respectively. At first, 2.5 liters of hexane were introduced into the reactor. Then, the co-catalyst, triethyl aluminium 1 mmol/L, and the catalyst which is $TiCl_4/AlCl_3/MgCl_2$ by chemical treatment, 0.01 mmol/L, were put into the reactor followed by comonomers (1-hexene) with the amount of 0.1, 0.2, 0.3, 0.4, and 0.5 mol. After that, H_2 pressure 3.5 bar was filled into the reactor, followed by ethylene and then the pressure was kept at 8 bar. The agitator was at 400 rpm. The reaction temperature was kept at 80 °C and the polymerization process was stopped when the time of polymerization was 70 minutes. The obtained slurry polymer was dried by the oven to get the dry polymer powder. This process is to confirm how much the comonmers can insert into the polyethylene by using 1-hexene as a standard.

3.3.3 Ethylene/1-butene copolymerization with 3 types of catalyst

The process was similar to 3.3.2 except for changing the comonomers to be the mixed gas of ethylene/1-butene. The amount of 1-butene was 0.9, 1.8, 3.0 and 4.2 mol%. The process was repeated with 3 different types of catalyst.

3.3.4 Ethylene/1-hexene, 1-octene, 1-decene, 1-dodecene copolymerization with 3 types of catalyst

The process was similar to 3.3.2 except for changing the comonomers to be 1-hexene, 1-octene, 1-decene, or 1-dodecene with the amount of 0.25 and 0.5 mol. The process was repeated with 3 different types of catalyst.

3.3.5 Ethylene polymerization with 3 types of catalyst and various amount of hydrogen in feed

The process was similar to 3.3.1 except for using 3 types of the catalyst and varying the hydrogen pressure in the feed to be 2.0, 3.5, 4.4, 5.0, 5.4, and 5.8 bar for each type of catalyst.

3.4 Polymer characterizations

3.4.1 Melt flow index (MFI)

Melt flow index was analyzed by melt flow index tester with ASTM D1238 method. A die with an opening of typically 2.0955 mm diameter and 8.0 mm length is inserted into the tester and then a small amount of the polymer samples (4-5 grams) were put in too. The samples were packed properly inside the barrel to avoid the formation of air in the barrel. A piston was introduced which acted as the medium for causing the extrusion of molten polymer. The samples were pre-heat for 5 minutes with the temperature of 190 °C in order to melt the samples. After that the weight of 2.16 kg was introduced on the piston in order to exert the molten samples through the die. The weight of the samples and the time for extrusion were measured accurately. MFI is expressed in grams of polymer per 10 minutes of duration of the test.

3.4.2 Density

Density was analyzed by density gradient technique with ASTM D-1505 method. A sample from the melt flow index testing in the form of rod was taken into the annealing bath which can heat the sample to adjust the process condition of the sample to be the same before testing. After that, the sample was prepared in the rod shape with length 3-7 mm. and placed into the density gradient tube that has the standard glass float inside. The solvent used in the density gradient tube was the mixture of isopropyl alcohol and water. The density of the sample was determined by interpolation between the two standard glass floats around the sample.

3.4.3 Differential scanning calorimetry (DSC)

The melting temperature (Tm) and the crystallinity of polymers were determined by differential scanning calorimetry (DSC) using a model: DSC 204 F1 Phoenix (NETZSCH). The analysis was performed at a heating rate of 10 °C/min from the temperature 30 to 200 °C. The heating cycle was run twice. In the first scan, samples were heated and cooled to 30 °C. In the second scan, samples were reheated at the same rate. Only the results of the second scan were reported because the first scan was influenced by the thermal and mechanical history of samples. From the resultant curve, the heat of fusion was obtained, and the %crystallinity of the polymer was calculated with the following equation:

$$\text{Crystallinity} = (\Delta Hf / \Delta H^*f) \times 100\%$$

where ΔH^*f is the heat of fusion of completely crystalline polyethylene samples which is equal to 293 J/g.

3.4.4 Gel permeation chromatography with IR detector (GPC-IR)

Molecular weight (MW), molecular weight distribution (MWD), and bulk CH_3/1000C of the polymer samples were determined by using Gel Permeation Chromatography (GPC) with Infrared (IR) detector model from Polymer Char with ASTM D6474 method. The samples used 1,2,4-trichlorobenzene as a solvent and the temperature was at 140 °C.

CHAPTER IV

RESULTS AND DISCUSSION

It has been known that the discovered Ziegler-Natta catalyst would be in the form of $TiCl_4/MgCl_2$ that was low in catalytic activity. Later on, it was found that adding of $AlCl_3$, called physical blending, could improve both the catalytic activity and comonomers incorporation [6, 10].

In this research, a new catalyst preparation approach which could be referred as chemical treatment was studied. Two catalysts: $TiCl_4/AlCl_3/MgCl_2$ by chemical treatment (Cat.A) and $TiCl_4/MgCl_2{\cdot}AlCl_3$ by physical blending (Cat.B) were synthesized and used for evaluate polymerization comparing with $TiCl_4/MgCl_2$ (Cat.C) as a reference. The catalytic activity and comonmer incorporation of polymers were evaluated.

4.1 Investigation of appropriate Al content in Cat.A

It is important to know the appropriate Al content in Cat.A because Al content is directly influential in catalytic activity [6]. In the preparation of Cat.A, $AlCl_3$ will be in-situ generated along the addition of diethyl aluminium chloride (DEAC) into $MgCl_2$ in ethanol, then reacted with $TiCl_4$ as shown below.

$$\underset{\text{“}MgCl_2\text{ complex”}}{MgCl_2\cdot nEtOH\ (l)} \xrightarrow{AlEt_2Cl} \underset{\text{“}MgCl_2\text{ adduct”}}{MgCl_2\cdot Al(OEt)_3\ (s)} \xrightarrow{TiCl_4} TiCl_4/AlCl_3/MgCl_2\ (s)$$

Cat.A was prepared at various $DEAC/MgCl_2$ ratios which were in the range from 1 to 4 by mol. Then, the prepared catalysts were used in ethylene polymerization in order to evaluate the catalytic activity. In Figure 4, the plot between the catalytic activity and $DEAC/MgCl_2$ ratio clearly displayed that the highest catalytic activity was obtained when the ratio of $DEAC/MgCl_2$ was around 3.0. This ratio would be used for further study.

In the preparation of Cat.B, the ratio used was $AlCl_3/MgCl_2$ instead of $DEAC/MgCl_2$ because Al content in DEAC and $AlCl_3$ was the same and the value is around 3.0, same as Cat.A.

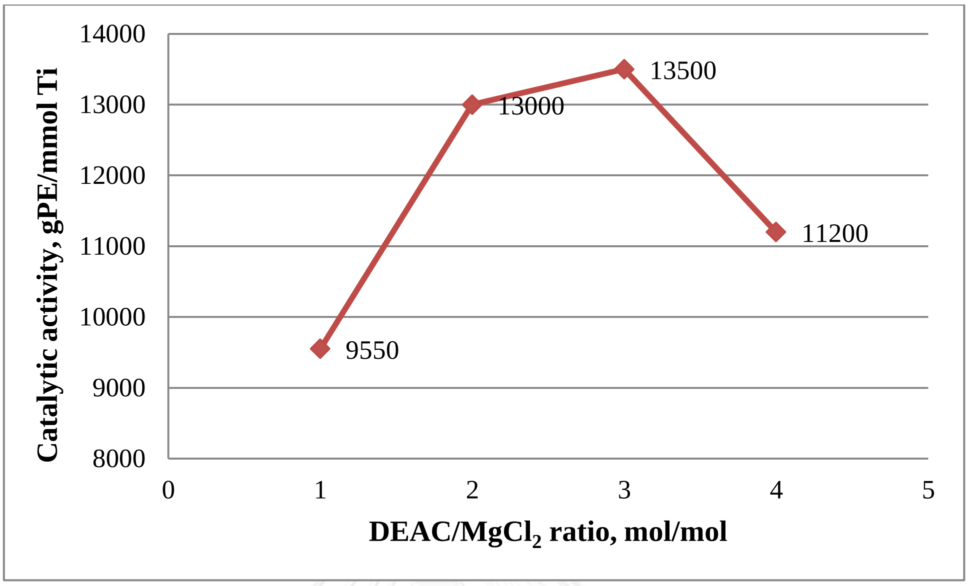


Figure 4 Plot between $DEAC/MgCl_2$ ratio and the catalytic activity of Cat.A.

4.2 Catalyst characterization

Three catalysts were characterized for catalyst composition by elemental analysis, phase formation by X-ray diffraction (XRD), catalyst morphology by scanning electron microscope (SEM), and catalyst particle size distribution by laser particle sizer.

4.2.1 Elemental analysis

From the fact that the differences in catalyst preparation could effect on the catalyst composition, for this research, the objective is to investigate the catalyst performance especially catalytic activity and comonomer incorporation without the influence of catalyst modifier concentration via the different catalyst preparation. Therefore, the Al content containing in synthesized catalysts had to be fixed. The obtained catalyst was analyzed namely Ti as an active site, Mg as a support, Al as a catalyst modifier, and Cl as a major part of Ziegler-Natta catalyst. Ti content analyzed by UV-vis spectroscopy, Mg and Cl content analyzed by auto-titration, and Al content analyzed by ICP-MS were exhibited in Table 2.

Table 2 Catalyst component.

Catalyst	Al (wt%)	Ti (wt%)	Mg (wt%)	Cl (wt%)
Cat.A	**2.3**	**6.7**	**16.1**	**60.3**
Cat.B	**2.5**	**6.6**	**16.5**	**60.1**
Cat.C	**-**	**6.8**	**17.0**	**63.0**

Remark: The catalyst composition did not combine to be 100% because there might be some components such as C and H remaining in the catalysts.

It was found that the catalyst components were in the same range so it could be implied that there was no effect from catalyst preparation technique. So, the differences in these catalysts would be only from the morphology and microstructure of the catalyst.

4.2.2 Phase formation

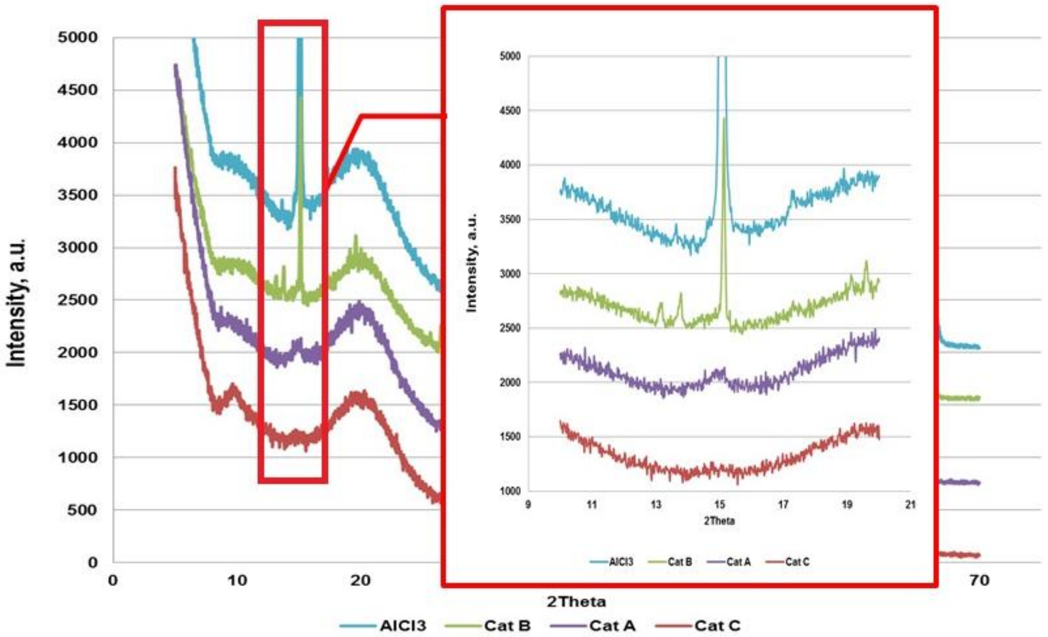


Figure 5 XRD patterns of the three catalysts.

In order to evaluate the compatibility of phase formation among $MgCl_2$ as a support, $TiCl_4$ as an active site, and $AlCl_3$ as a catalyst modifier, the catalysts were analyzed by X-ray diffraction. Figure 5 displayed the X-ray diffraction patterns of three catalysts. The sharp peak of $AlCl_3$ at $2\theta = 15°$ was clearly observed in Cat.B. It implied that $AlCl_3$ was mainly in the crystalline form while the other parts of such catalyst were in amorphous one. This might be because $AlCl_3$ did not dissolve in $MgCl_2$ when preparing Cat B and thus $AlCl_3$ could not be well compatible with

$TiCl_4/MgCl_2$. For Cat.A, no sharp peak at $2\theta = 15°$ was observed. However, the existence of $AlCl_3$ in Cat.A was indicated by the elemental analysis in section 4.2.1 which indicated that $AlCl_3$ was in the amorphous form like any other parts of the catalyst. This might be because DEAC dissolved completely when preparing Cat A.

4.2.3 Morphology and particle size distribution

The morphology uniformity of Cat.A, Cat.B, and Cat.C was displayed in Figure 6, Figure 7, and Figure 8, respectively. It was found that the SEM images of Cat.A at 65x showed more uniformly distribution of catalyst's particle size compared to the others. At 250x and 2000x, the SEM images of Cat.A also showed the spherical-like shape of catalyst's particle while Cat.B and Cat.C showed irregular shape. It indicated obviously that the catalyst preparation via chemical treatment method could provide Ziegler-Natta catalyst that has uniform morphology.

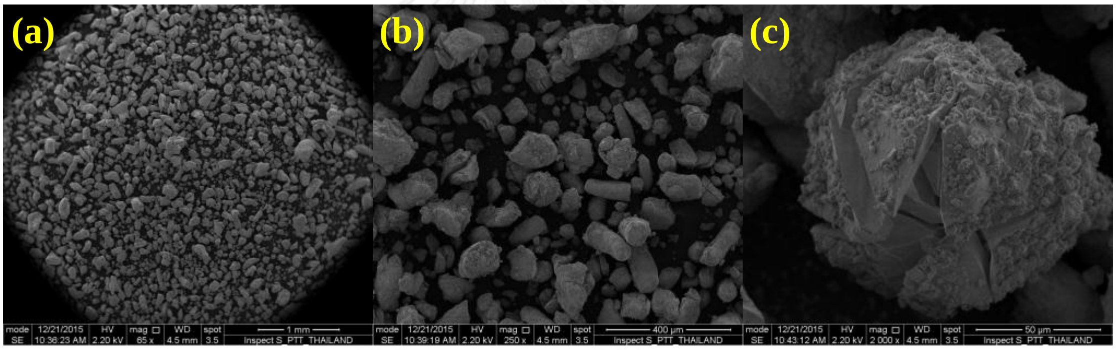


Figure 6 SEM images of Cat.A with magnification of 65x (a), 250x (b), and 2000x (c) respectively.

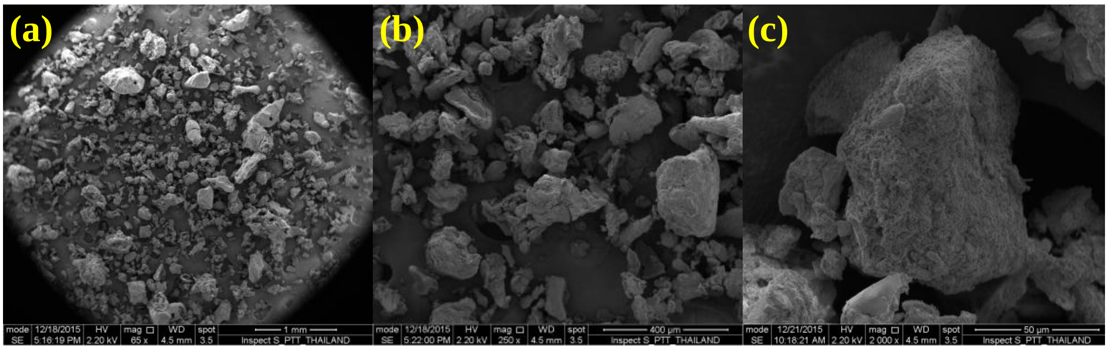


Figure 7 SEM images of Cat.B with magnification of 65x (a), 250x (b), and 2000x (c) respectively.

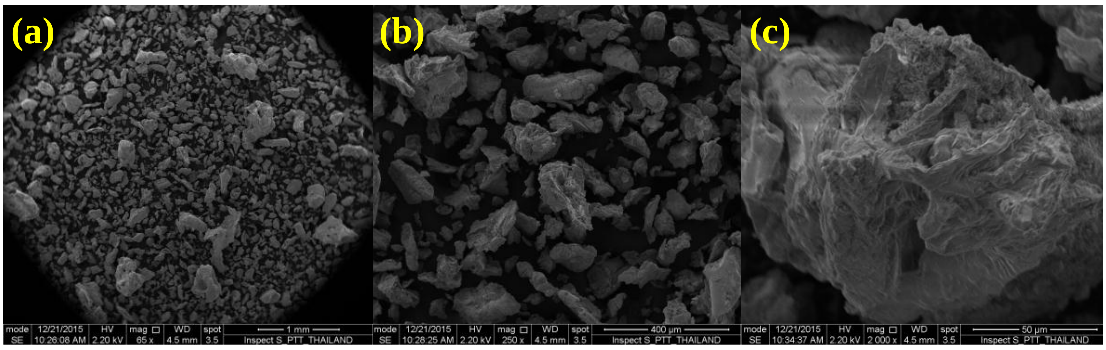


Figure 8 SEM images of Cat.C with magnification of 65x (a), 250x (b), and 2000x (c) respectively.

The measurement of particle size of the catalysts was performed by using the laser particle sizer. In Figure 9, Figure 10, Figure 11, and Table 3, it was found that the PSD of Cat.A (span = 3.12) was clearly narrower than Cat.B (span = 3.70) and Cat.C (span = 5.04) and the average particle size was smaller than the others too. From Figure 12, PSD of Cat.B and Cat.C were mainly from $MgCl_2$ because they showed similar pattern as pure $MgCl_2$. However, PSD from Cat.A was different. This could be explained that $AlCl_3$ in chemical treatment catalyst had some interaction which helped prevent the agglomeration of $MgCl_2 \cdot nEtOH$ resulting in the reduction of average particle size while $AlCl_3$ in physical blending catalyst did not have the effect because $AlCl_3$ was not compatible with the other part of catalyst. These results conformed to the morphology study, discussed in the previous part.

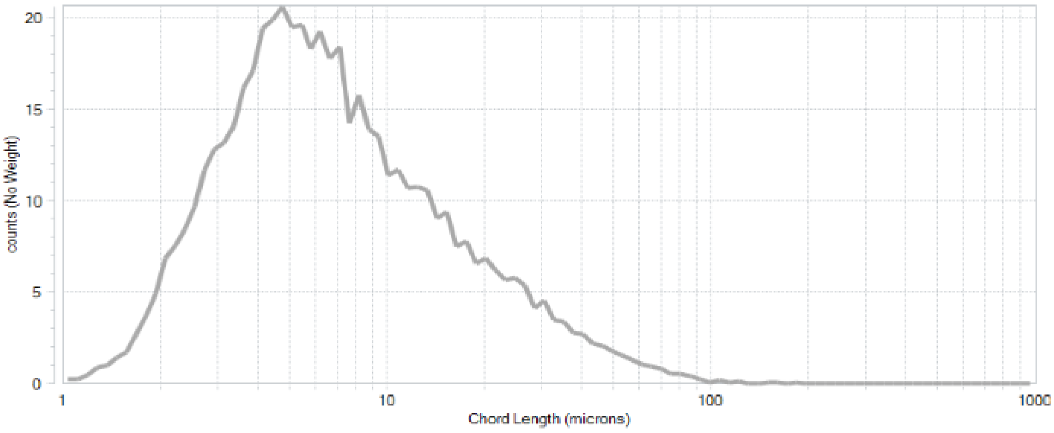


Figure 9 PSD of Cat.A.

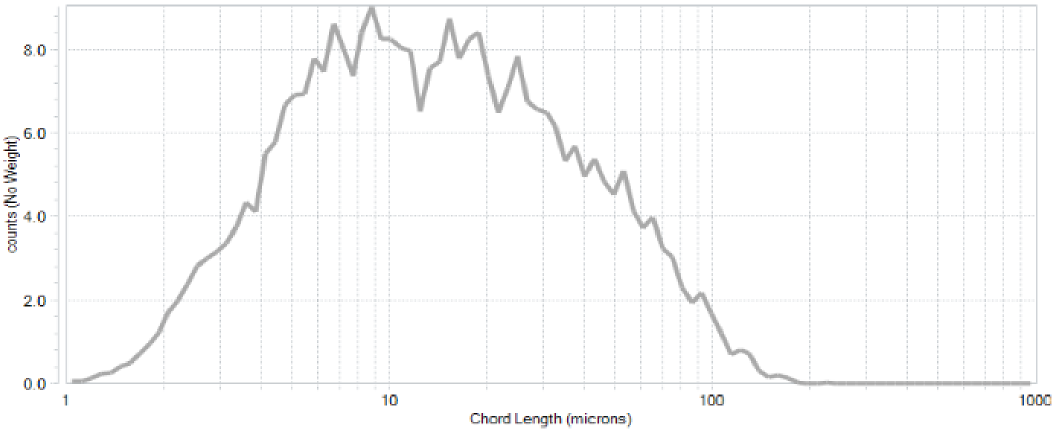


Figure 10 PSD of Cat.B.

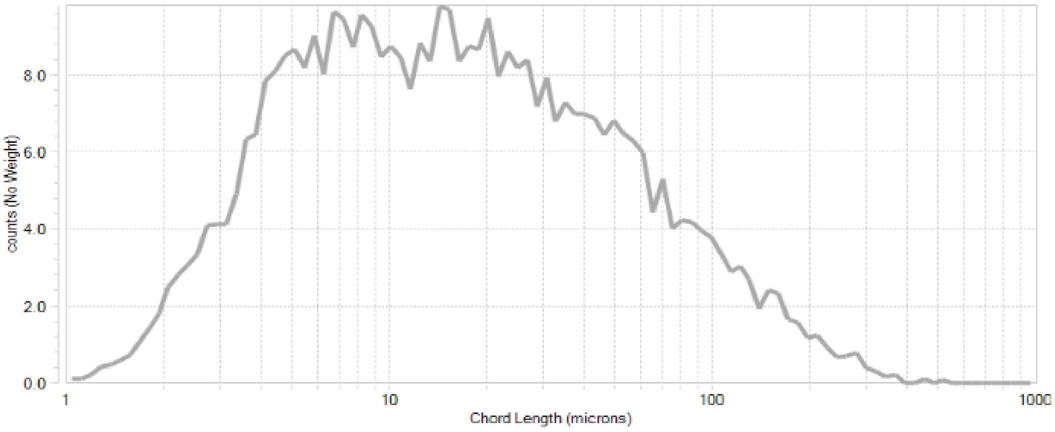


Figure 11 PSD of Cat.C.

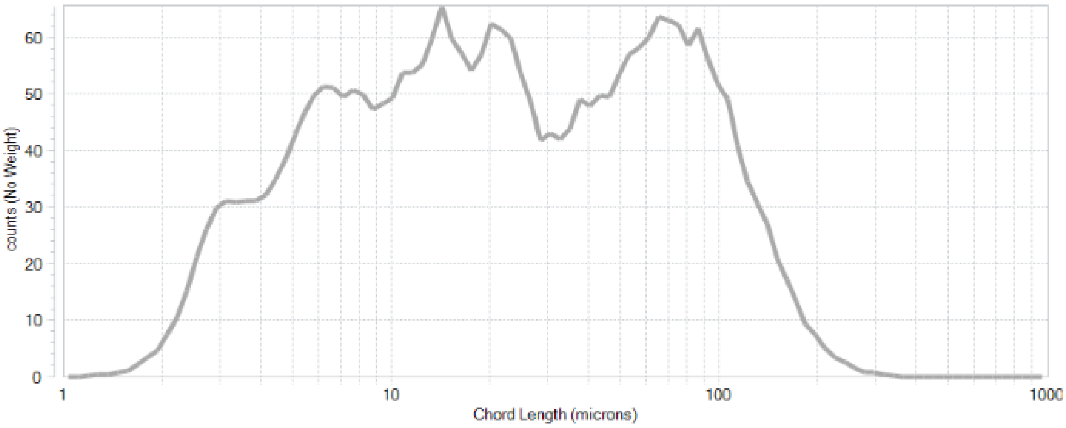


Figure 12 PSD of Pure $MgCl_2$.

Table 3 Average particle size and distribution of three catalysts (microns).

	Particle size (microns)		
Value	**Cat.A**	**Cat.B**	**Cat.C**
d10	2.67	3.86	3.76
d50	6.26	13.3	15.04
d90	22.2	53.01	79.63
Span	3.12	3.70	5.04
Mean	10.15	21.86	31.58

Remark: d10, d50, d90 = Particle size which is smaller than 10, 50, 90 % respectively
Span = $\frac{d90-d10}{d50}$, Mean = Average particle size

4.3 The evaluation of the catalyst performance

Generally, several parameters such as catalytic activity, ethylene profile, hydrogen response, and comonomer response are necessary to be monitored in order to indicate not only the catalyst behavior during polymerization but also the physical properties and microstructures of obtained polymers. The evaluation results were reported as following:

4.3.1 Catalytic activity for ethylene polymerization

The catalytic activity for ethylene polymerization shown in Table 4 exhibited clearly that Cat.A provided higher catalytic activity than Cat.B and Cat.C, respectively. It implied that the existence of $AlCl_3$ as a catalyst modifier increased the catalytic activity, about 3.8 times for Cat.A (chemical treatment) and 2.3 times for Cat.B (physical blending) higher than Cat.C (no $AlCl_3$). Furthermore, Cat.A had the catalytic activity 1.6 times higher than Cat.B. These results indicated that doing chemical treatment could improve the catalytic activity more than physical blending method.

Table 4 Catalytic activity of Cat.A, Cat.B, and Cat.C.

	Activity (g polymer/mmol Ti)	
Catalyst	**1st run**	**2nd run**
Cat.A	22900	21800
Cat.B	14000	14500
Cat.C	6000	5700

Remark: Polymerization condition: Reactor 5 L, solvent = hexane 2.5 L, T = 80°C, time = 2 h, P_{H2} = 3.5 bar, P_{total} = 8 bar, Cocat = TEA 1mmol/L, Cat = 0.01 mmol/L

Ethylene profile is the graph that shows the consumption rate of ethylene vs polymerization time. From the ethylene consumption plot, it displays the ethylene consumption behavior of catalyst which, in this study, depends mainly on the catalyst preparation methods. Referring to Figure 13, at around 300 seconds after the reaction started, the ethylene consumption rates were recorded to be about 10, 5 and 3 g/min, when Cat.A, Cat.B and Cat.C were employed, respectively. Then all the ethylene consumption rates gradually dropped and remained constant after 3,000 seconds to be 4, 3 and 2 g/min, respectively. The results indicated that Cat.A was more active than Cat.B and Cat.C, in a sequence. This observation in both catalytic activity and ethylene profile can be elaborated that the phase transformation of $AlCl_3$ in Cat.A might occur and became more compatible with $TiCl_4$/$MgCl_2$ phase than Cat.B. Since $AlCl_3$ has higher Lewis acidity than $MgCl_2$, its presence in the catalyst may reduce electron density on some sites of active center, which is beneficial to the catalytic activity. These results were perfectly aligned with the research work of Y. P. Chen. *et al* [10]. They discovered that the addition of $AlCl_3$ showed slightly higher efficiency than one without $AlCl_3$.

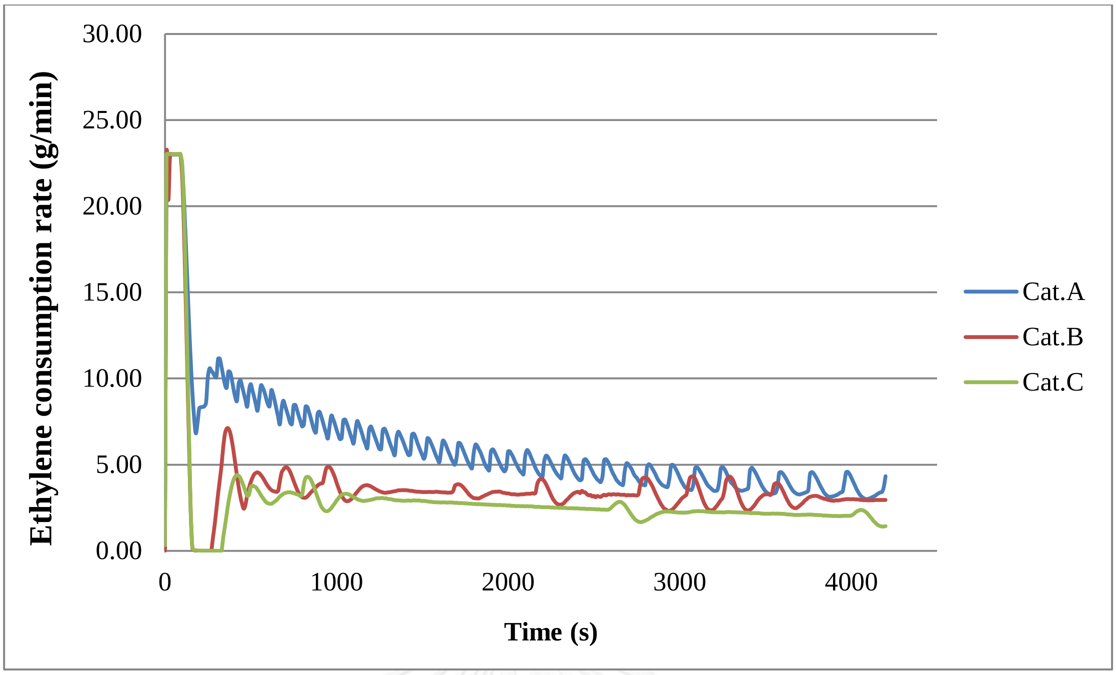


Figure 13 Ethylene consumption profiles of Cat.A, Cat.B, and Cat.C.

4.3.2 Hydrogen response

Hydrogen response, one of several parameters to evaluate the catalyst performance, represents the concentration in term of hydrogen per ethylene (H_2/C_2H_4) ratio which affects not only catalytic activity but also Melt Flow Index (MFI). From this study, it was expected that the catalyst preparation with different methods could also affect the hydrogen response. If the hydrogen response of the catalyst is high, it means that the MFI of the polymer synthesized by a given catalyst can be dramatically changed with little change in the hydrogen concentration in the process. Hydrogen response is one of the important parameters that used to determine which application is suitable for the catalyst because some applications require the catalyst with low hydrogen response, while some require high hydrogen response. The hydrogen responses shown in the Figure 14 exhibited that the MFI increased when H_2/C_2H_4 ratio increased. However, the change of MFI in Cat.A was lower than Cat.B and Cat.C which could be implied that the hydrogen response of Cat.A was lower than Cat.B and Cat.C. Furthermore, the catalytic activity decreased when H_2/C_2H_4 ratio increased which could be explained that the increase in hydrogen used in the process caused the deactivation of the catalyst due to the formation of β-agostic coordination from the ethyl groups formed after hydrogen termination and then caused a decrease in activity. Such phenomena could be explained by Kissin‘s β-agostic deactivation theory [17] shown in Figure 15. This theory concludes that the more H_2 that is present in the polymerization, the more H_2 terminations take place and the more Ti-H groups are formed.

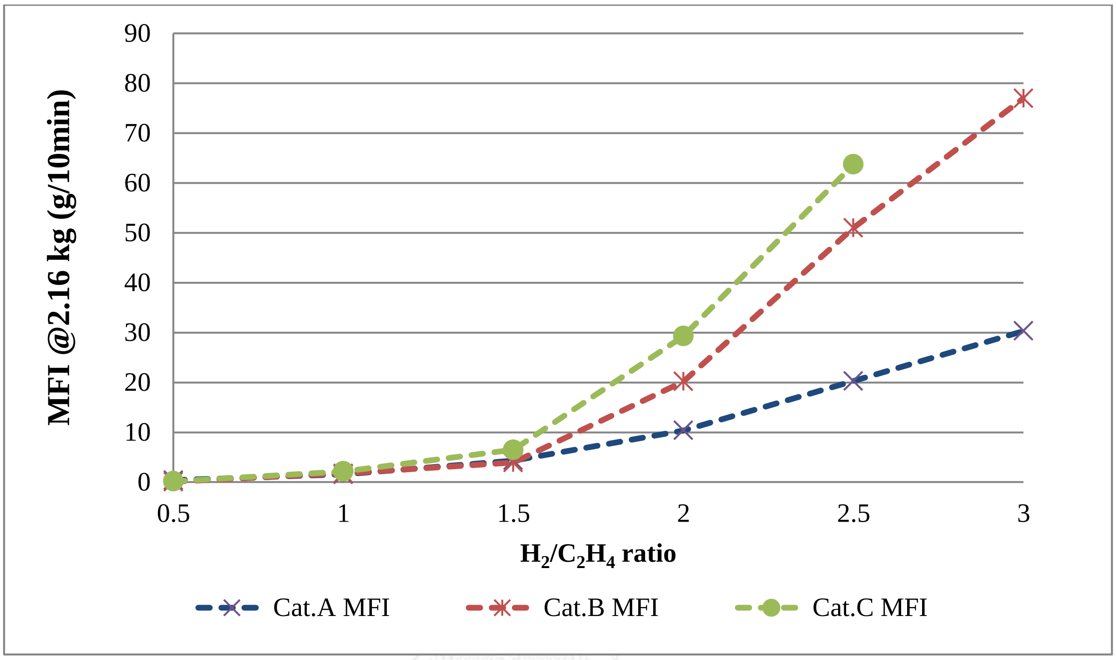


Figure 14 Hydrogen responses of Cat.A, Cat.B, and Cat.C.

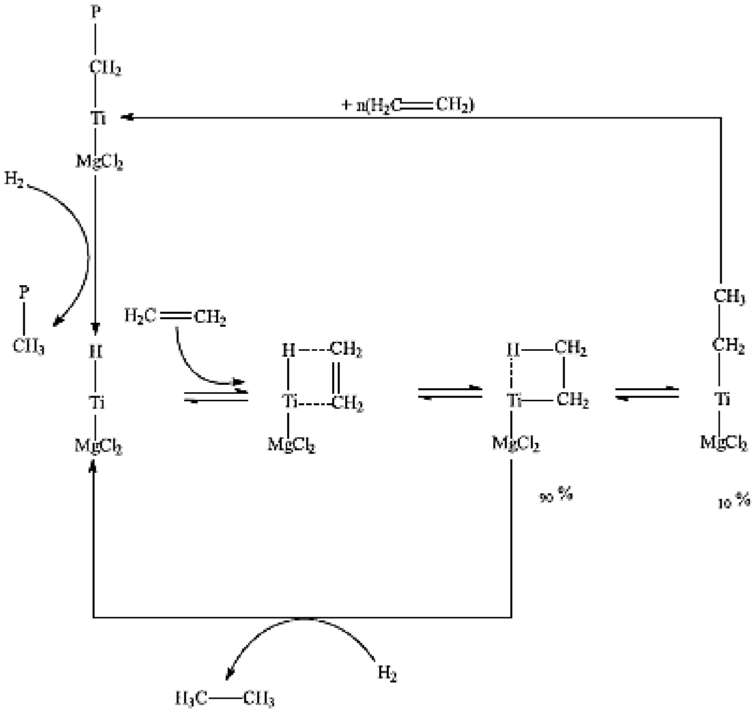


Figure 15 The deactivation effect of hydrogen in Kissin model. [17]

4.3.3 Ethylene/1-hexene polymerization using Cat.A

From section 4.3.1, it was found that the highest catalytic activity in ethylene polymerization was achieved when using Cat.A. In this section, Cat.A was employed as a representative catalyst for evaluation of comonomer response in ethylene/1-hexene polymerization. At various concentrations of 1-hexene from 0 to 0.5 mol, the copolymerization of ethylene with 1-hexene was carried out at the same condition as described in section 3.3.2. The obtained polymers were dried and their MFI and density were measured. As 1-hexene is the smallest liquid comonomer, it is more convenient to deal with during the polymerization process. In order to evaluate how much comonomer incorporated into the polymer chain, the density is measured. The catalytic activity, MFI, and density results were shown in Table 5 as followed.

Table 5 Catalytic activity, MFI, and density of polyethylene/1-hexene with various amount of 1-hexene synthesized by Cat.A.

	Amount of 1-hexene used					
	0 mol	**0.1 mol**	**0.2 mol**	**0.3 mol**	**0.4 mol**	**0.5 mol**
Catalytic activity (gPE/mmol Ti)	22900	25200	28200	26800	26000	23600
MFI (g/10min)	2.29	2.95	3.44	3.52	4.81	4.09
Density (g/cm^3)	0.9620	0.9600	0.9577	0.9566	0.9562	0.9559

From Table 5, MFI of the obtained polymers increased when the amount of 1-hexene increased whereas the density slightly decreased. The density was obviously decreased when the amount of 1-hexene used was in the range 0-0.3 mol then almost constant at around 0.4-0.5 mol. These implied that at higher amount of 1-hexene, more 1-hexene incorporated into the polymer and so lower density of polymer was resulted. However at the concentration of 0.4-0.5 mol, no more incorporation of 1-hexene was observed. The possible reason is because of the hindrance effect caused by the side chains of the polymer, from the optimum 1-hexene moieties in the polymer. Moreover, the catalytic activity of the obtained polymer was slightly increased when a little amount of comonomer was present but decreased when higher amount was present. This might be because comonomer acted as a chain transfer agent when it was added too much. These results were perfectly aligned with M.

Bialek. *et al* [2]. They found that the comonomer incorporation was not increased when the comonomer feed was higher than some certain value.

Furthermore, both Tm and %Crystallinity analyzed by means of DSC could be used for investigating the performance of comonomer incorporation. According to Table 6, it showed that Tm and %Crystallinity decreased when the amount of 1-hexene was increased and the value of Tm and %Crystallinity was almost constant at the amount of 1-hexene around 0.4-0.5 mol. This could be implied that the amount of 1-hexene higher than 0.5 mol had no significant effect on the comonomer incorporation and the appropriate amount of incorporated comonomer should be less than 0.5 mol. Similar observation was reported by W. Meng *et al* [3]. They found that the insertion of the comonomer reduced the degree of crystallization of the polymer and the more comonomer incorporated, the more degree of crystallization decreased.

Table 6 DSC data of polyethylene/1-hexene at various amount of 1-hexene synthesized by Cat.A.

Sample	Tm (°C)	Tc (°C)	%Crystallinity
No comonomer	134.7	112.6	68.3
1-hexene 0.1 mol	133.5	111.3	65.0
1-hexene 0.2 mol	132.8	113.3	62.2
1-hexene 0.3 mol	132.2	110.9	62.4
1-hexene 0.4 mol	131.7	110.3	61.4
1-hexene 0.5 mol	131.9	110.8	61.8

4.3.4 Comonomer incorporation

As 1-butene is in the gas phase, the mixed gas of ethylene and 1-butene at various concentrations was used. However, in the industry for HDPE production, 1-butene concentration used is not more than 4.2 mol%, therefore the concentration of 1-butene was varied upto 4.2 mol% in this research. For the copolymerization of ethylene with 1-butene, 1-hexene, 1-octene, 1-decene, and 1-dodecene, it was performed by using Cat.A, Cat.B, and Cat.C, respectively. For 1-butene comonomer, the mixed gas of ethylene and 1-butene, 0.9, 1.8, 3.0, and 4.2 mol%, was used. For 1-hexene, 1-octene, 1-decene, and 1-dodecene comonomer, their concentration was fixed at 0.25 and 0.5 mol. The obtained polymers were characterized their Melt Flow

Index (MFI), density, Tm and %crystallinity, and microstructure (Number average molecular weight (Mn), Weight average molecular weight (Mw), Higher average molecular weight (Mz), Molecular weight distribution (MWD), and Short Chain Branching Index called Bulk CH_3/1000C) by MFI tester, density gradient tube, DSC and GPC-IR, respectively.

To evaluate the comonomer incorporation for each type of catalyst and comonomer, the plots between the density, %crystallinity and amount of comonomer added were shown below in Figures 16 to 20.

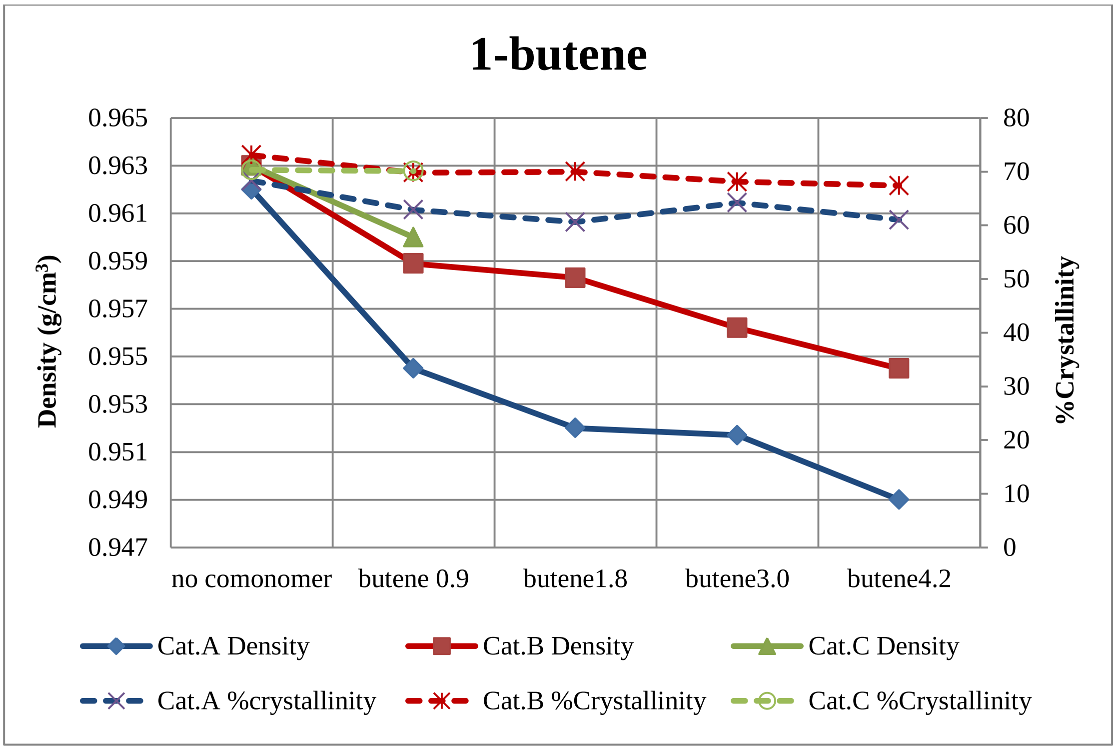


Figure 16 Effect of 1-butene content on density and %crystallinity of polyethylene synthesized by three types of catalyst.

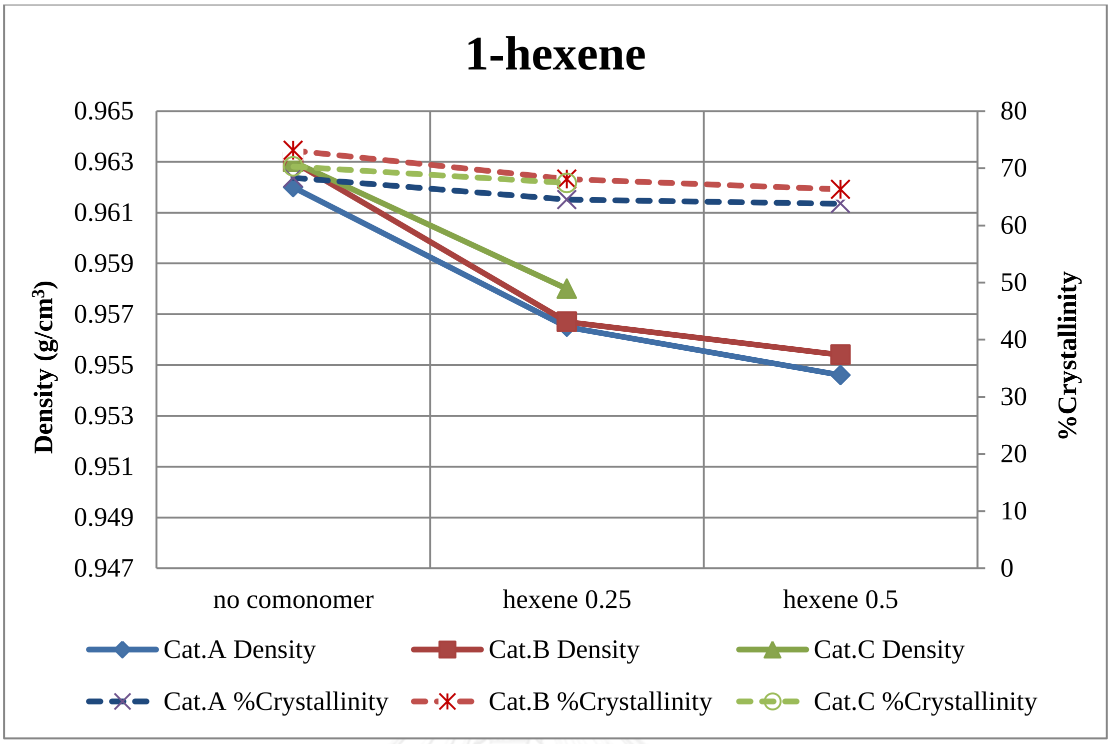


Figure 17 Effect of 1-hexene content on density and %crystallinity of polyethylene synthesized by three types of catalyst.

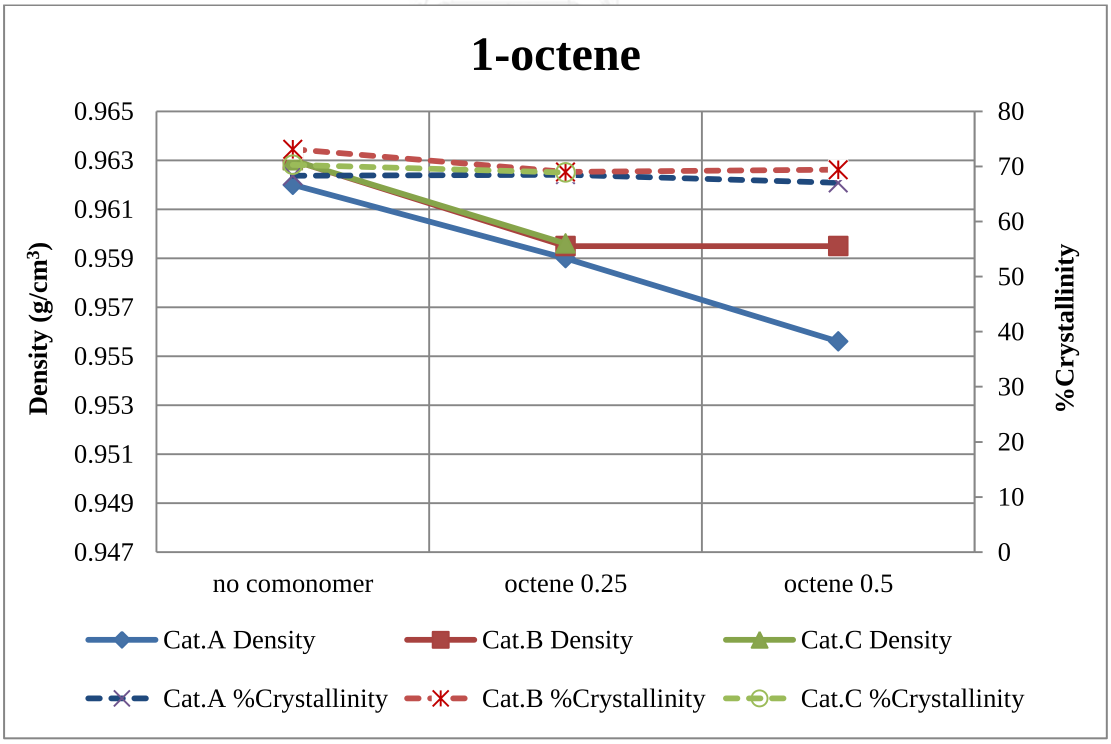


Figure 18 Effect of 1-octene content on density and %crystallinity of polyethylene synthesized by three types of catalyst.

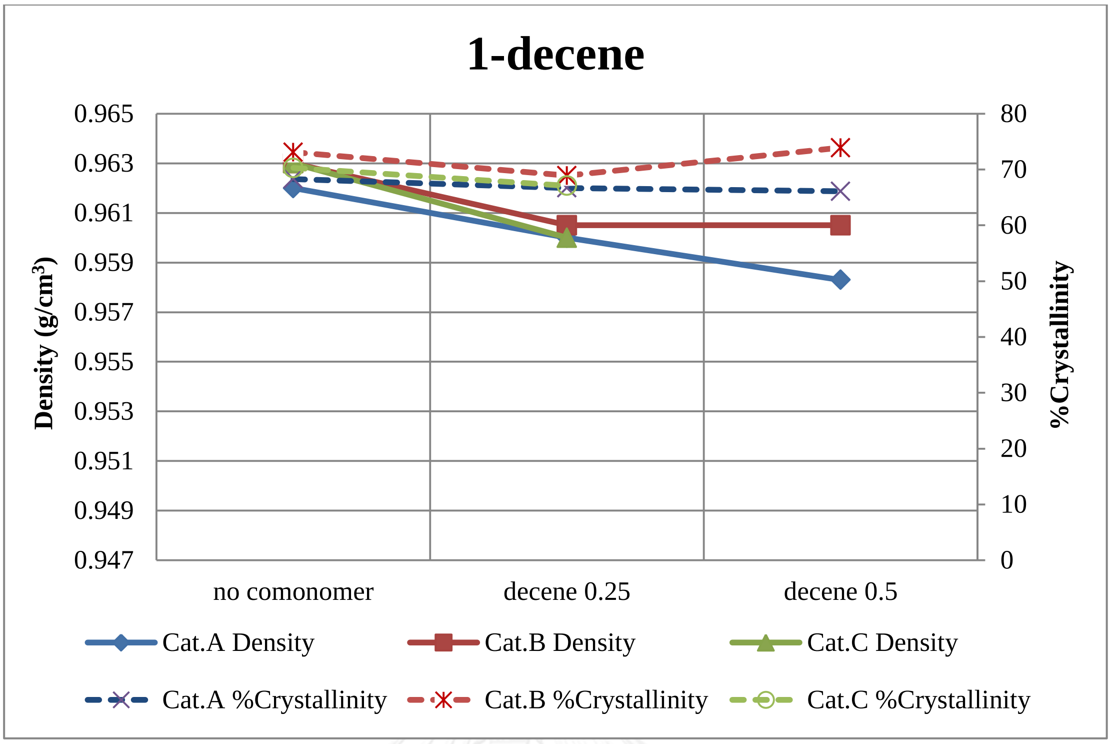


Figure 19 Effect of 1-decene content on density and %crystallinity of polyethylene synthesized by three types of catalyst.

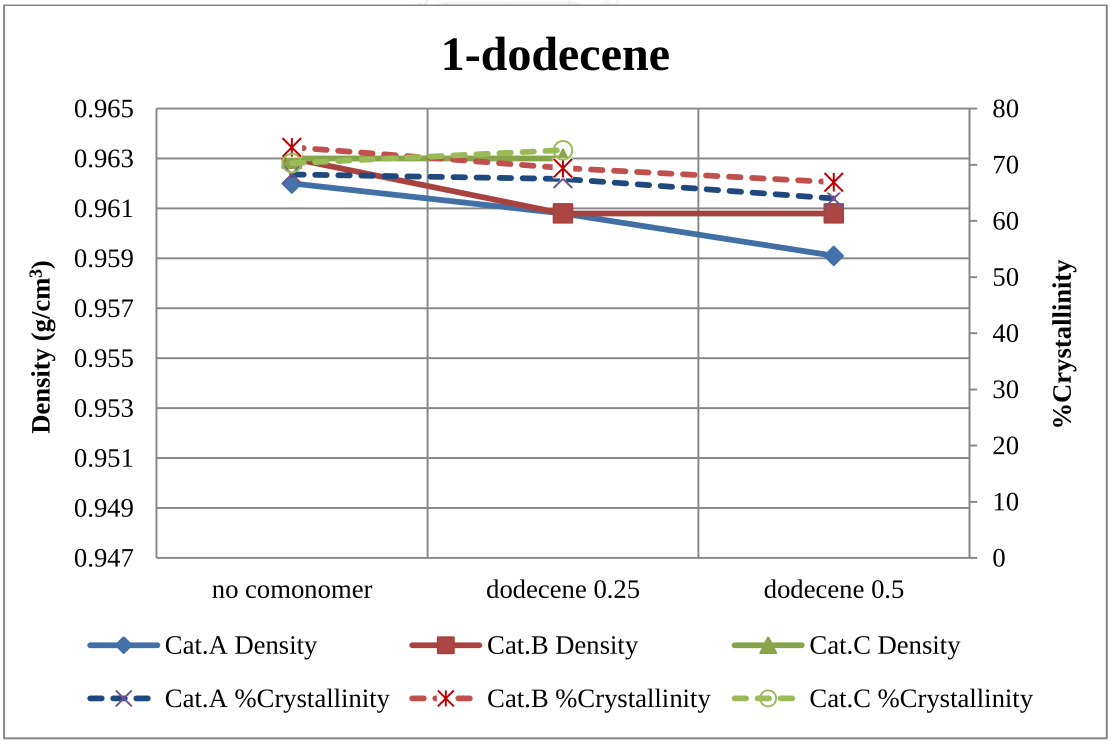


Figure 20 Effect of 1-dodecene content on density and %crystallinity of polyethylene synthesized by three types of catalyst.

The result exhibited obviously that the density decreased when the amount of comonomer was increased. Especially, the density of synthesized polymer using Cat.A was lower than Cat.B and Cat.C for every comonomer. For 1-butene, the difference in density and %crystallinity was quite high. For 1-hexene, the difference in density and %crystallinity was slightly lower than 1-butene. For the larger comonomers, 1-octene, 1-decene, and 1-dodecene, there were two notices. First, at the comonomer's concentration 0.25 mol, there was almost no difference in density and %crystallinity between Cat.A and Cat.B. Second, at the comonomer's concentration 0.5 mol, the density and %crystallinity of Cat.B were still the same while the density and %crystallinity of Cat.A could go lower. These results will be discussed further in the next part.

In addition, the microstructure information such as molecular weight, molecular weight distribution, and bulk CH_3/1000C was also investigated by using GPC-IR. From Figure 21 and Table 7, it indicated that the average molecular weight of polymers synthesized by using Cat.A, Cat.B, and Cat.C without comonomers were almost the same but the molecular weight distribution curve of Cat.A was slightly broader than Cat.B and Cat.C. This result was perfectly aligned with Y. P. Chen. *et al* [6]. They explained that addition of $AlCl_3$ could increase the types of active centers in the catalyst. However, for ethylene/comonomers polymerization, the molecular weight and molecular weight distribution were hard to explain due to many parameters that affected them. For example, if the comonomer incorporated into the polymer chain much, Mn, Mw, and Mz could reduce and caused the change in molecular weight distribution. From Table 7, for the gas comonomer, 1-butene, the molecular weight distribution of Cat.A was slightly narrower than Cat.B but for the liquid comonomers, 1-hexene to 1-dodecene, the molecular weight distribution of Cat.A was slightly broader than Cat.B. From Figures 22 to 26, it exhibited that the molecular weight distribution curve of Cat.C was shifted to the right meaning that the average molecular weight of synthesized polymer using Cat.C was higher than Cat.A and Cat.B. This was because comonomer, one of the chain transfer agent, incorporated into polymer synthesized by Cat.C lower than Cat.A and Cat.B and thus resulted in higher average molecular weight.

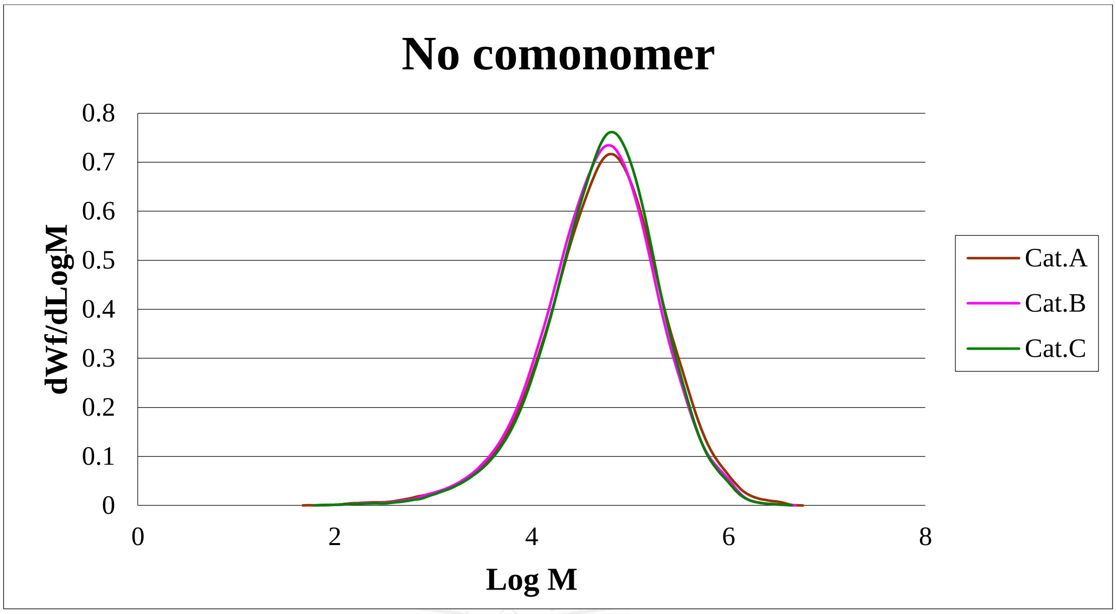


Figure 21 Molecular weight distribution curve of synthesized polymer using all types of catalysts with no added comonomer.

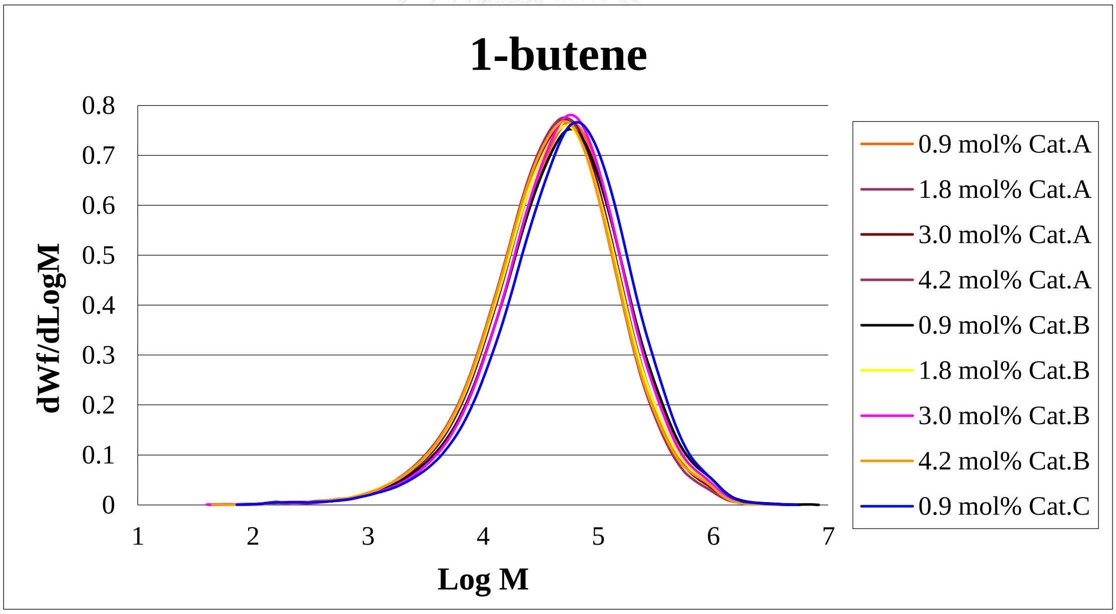


Figure 22 Molecular weight distribution curve of synthesized polymer using all types of catalysts with 1-butene as a comonomer.

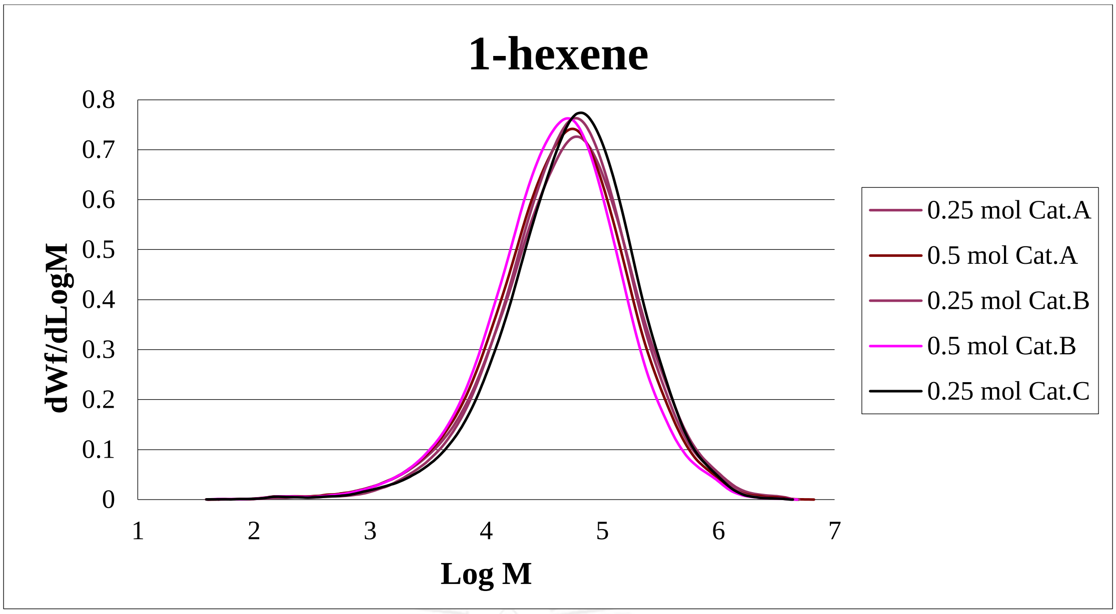


Figure 23 Molecular weight distribution curve of synthesized polymer using all types of catalysts with 1-hexene as a comonomer.

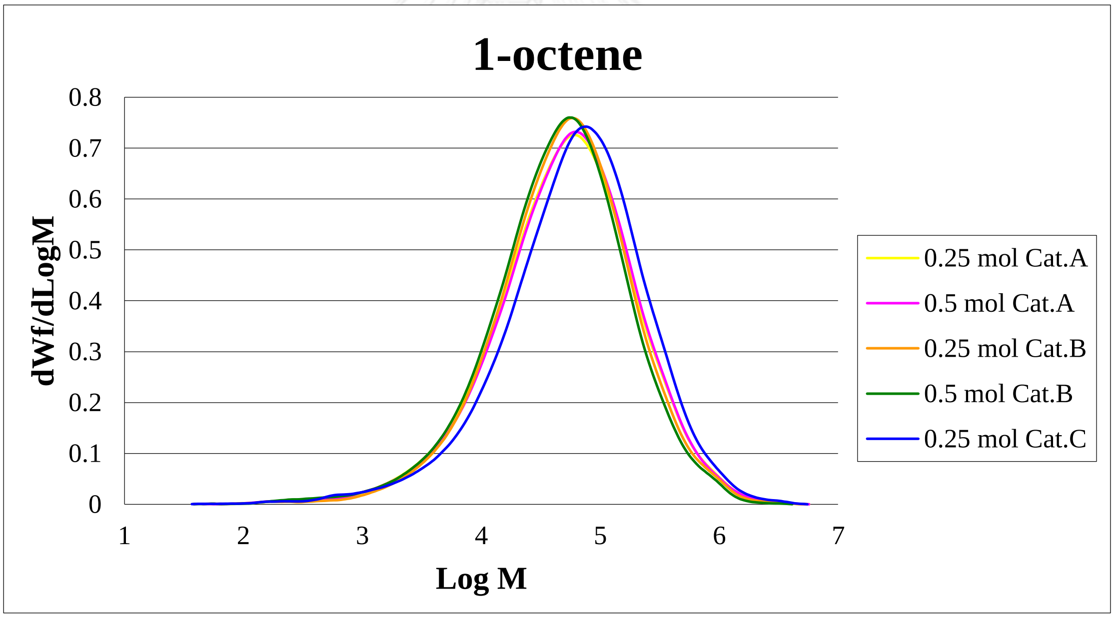


Figure 24 Molecular weight distribution curve of synthesized polymer using all types of catalysts with 1-octene as a comonomer.

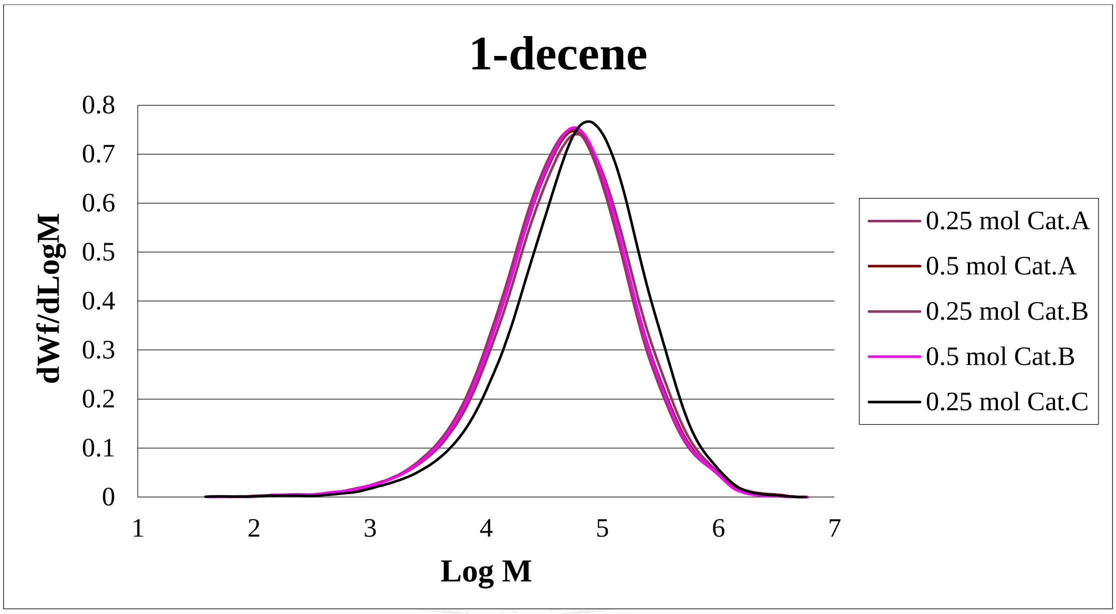


Figure 25 Molecular weight distribution curve of synthesized polymer using all types of catalysts with 1-decene as a comonomer.

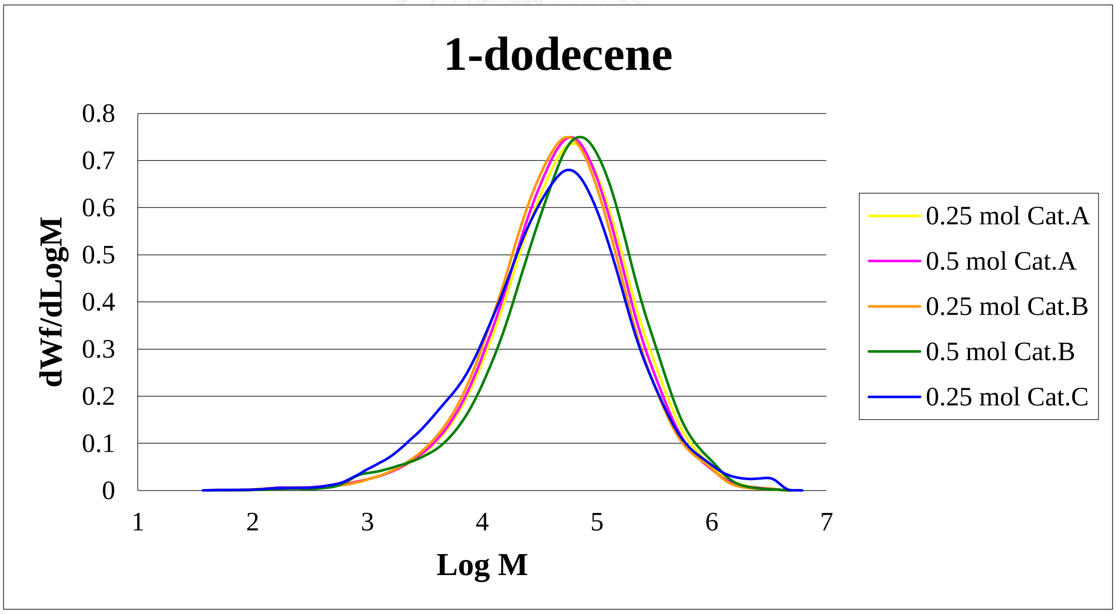


Figure 26 Molecular weight distribution curve of synthesized polymer using all types of catalysts with 1-dodecene as a comonomer.

Table 7 Molecular information of synthesized polymers using different catalysts and various comonomers.

		Mn	Mw	Mz	MWD	Bulk CH_3/1000C
No comonomer	Cat.A	13737	128216	569494	9.33	3.7
	Cat.B	14351	111059	419833	7.74	3.7
	Cat.C	15744	113016	406992	7.18	3.7
1-butene 0.9 mol%	Cat.A	13342	100618	387680	7.54	5.6
	Cat.B	13766	107347	477983	7.80	4.5
	Cat.C	15946	113667	397161	7.13	4.3
1-butene 1.8 mol%	Cat.A	14279	91275	361432	6.39	6.1
	Cat.B	13441	91397	337329	6.80	4.7
1-butene 3.0 mol%	Cat.A	13092	91161	367171	6.96	6.5
	Cat.B	14203	98739	345847	6.95	5.2
1-butene 4.2 mol%	Cat.A	13145	83565	319084	6.36	7.1
	Cat.B	12631	87067	323381	6.89	5.7
1-hexene 0.25 mol	Cat.A	13332	117651	539462	8.82	4.8
	Cat.B	15367	108396	419430	7.05	4.7
	Cat.C	14934	112760	394719	7.55	4.2
1-hexene 0.5 mol	Cat.A	12392	103667	487417	8.37	6
	Cat.B	12142	90918	394475	7.49	5.3
1-octene 0.25 mol	Cat.A	14057	116799	506712	8.31	4.2
	Cat.B	13978	108999	452753	7.80	4.2
	Cat.C	13730	137272	552185	10.00	4.2
1-octene 0.5 mol	Cat.A	13440	118039	511903	8.78	4.5
	Cat.B	12218	98310	370193	8.05	4.2
1-decene 0.25 mol	Cat.A	12999	114709	493267	8.82	3.8
	Cat.B	13531	101567	416633	7.51	3.8
	Cat.C	16863	130294	455088	7.73	3.8
1-decene 0.5 mol	Cat.A	14068	108132	478930	7.69	4.3
	Cat.B	13747	103148	400178	7.50	3.8
1-dodecene 0.25 mol	Cat.A	13201	117226	487765	8.88	4.1
	Cat.B	12413	102119	416795	8.23	4.1
	Cat.C	10270	127268	914645	12.39	4.1
1-dodecene 0.5 mol	Cat.A	13031	109092	458971	8.37	4.3
	Cat.B	14660	127008	460980	8.66	4.1

The plots between the values of bulk CH_3/1000C and the amount of comonomer added were shown below in Figures 27 to 31. As could be seen, the result showed that the bulk CH_3/1000C increased when the amount of comonomer was increased. Comparing the three catalysts, the bulk CH_3/1000C of polymer synthesized by Cat.A was higher than Cat.B and Cat.C for every type of the comonomer but there were differences of the bulk CH_3/1000C for each type of comonomer. For 1-butene, the difference in bulk CH_3/1000C was high. For 1-hexene, the difference in bulk CH_3/1000C was slightly lower than 1-butene. For the big comonomers, 1-octene, 1-decene, and 1-dodecene, there were two notices. First, at the comonomer's concentration of 0.25 mol, there was no difference in bulk CH_3/1000C between Cat.A and Cat.B. Second, at the comonomer's concentration of 0.5 mol, the bulk CH_3/1000C of Cat.B was remained constant while that of Cat.A could go higher.

These results were related to each other. For 1-butene, the bulk CH_3/1000C of Cat.A was higher than Cat.B and Cat.C meaning that the synthesized polymer using Cat.A had more comonomer incorporation than Cat.B and Cat.C which led to lower density and smaller average molecular weight. The more comonomer incorporated into the polymer chain, the more branching was observed which explained the lowering in density. As for average molecular weight, it could be explained that it was because the comonomer, one of the chain transfer agent which could lead to a decrease in molecular weight of synthesized polymer, incorporated into the synthesized polymer using Cat.C lower than Cat.A and Cat.B. For 1-hexene, the bulk CH_3/1000C of Cat.A was also higher than Cat.B and Cat.C but the difference in value of bulk CH_3/1000C was smaller compared to 1-butene. This implied that the comonomer incorporation in synthesized polymer using Cat.A was still higher than Cat.B and Cat.C but the effect was not obviously significant in bigger comonomers. For 1-octene, 1-decene, and 1-dodecene, the bulk CH_3/1000C of Cat.A at 0.25 mol comonomer concentration was the same as Cat.B and Cat.C which indicated that the comonomer incorporation in synthesized polymer using Cat.A, Cat.B, and Cat.C was the same. However, at 0.5 mol comonomer concentration, it was found that the bulk CH_3/1000C of Cat.A was higher than Cat.B and Cat.C. This implied that Cat.A could extend the limit of comonomer incorporation for bigger comonomers.

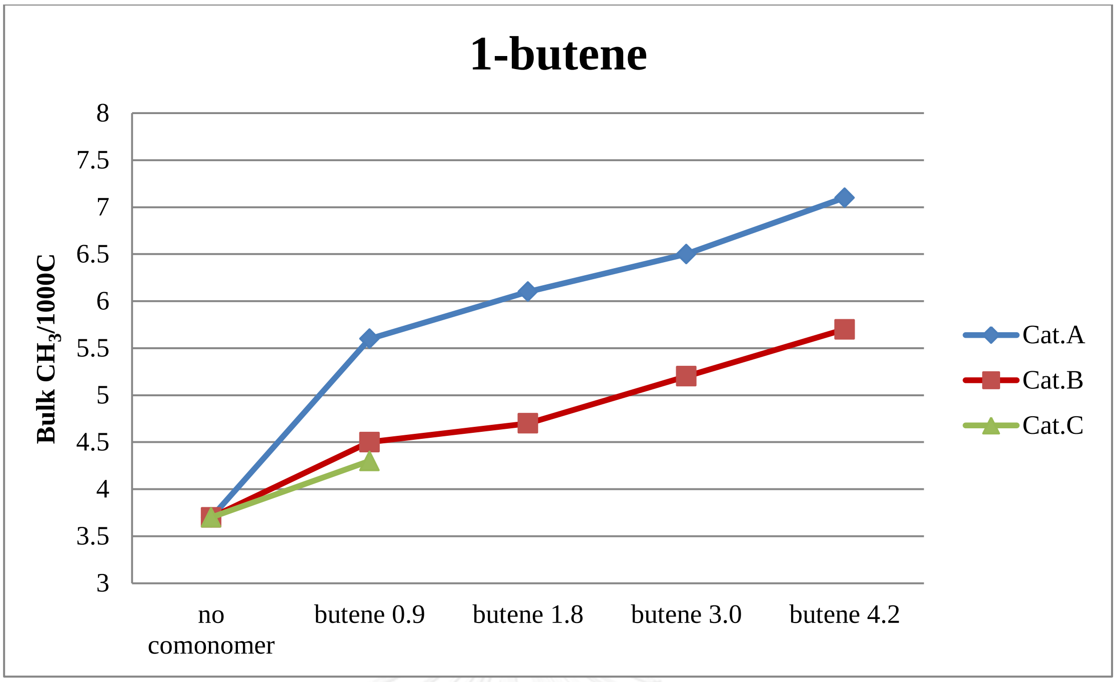


Figure 27 Effect of 1-butene content on bulk CH_3/1000C of polyethylene synthesized by three types of catalyst.

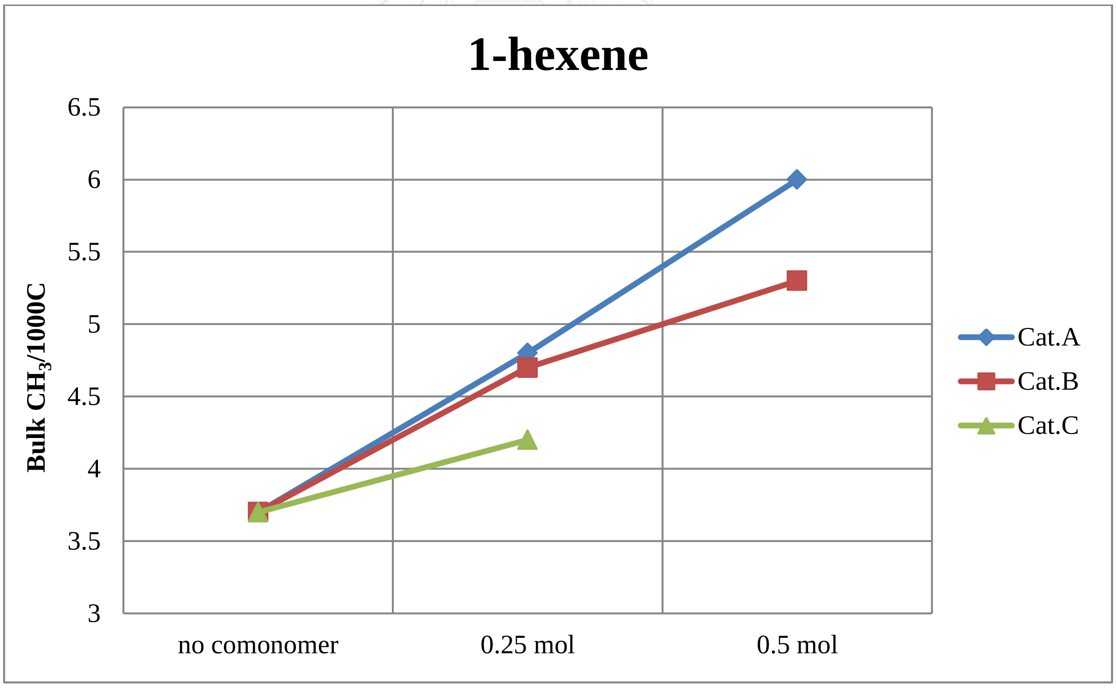


Figure 28 Effect of 1-hexene content on bulk CH_3/1000C of polyethylene synthesized by three types of catalyst.

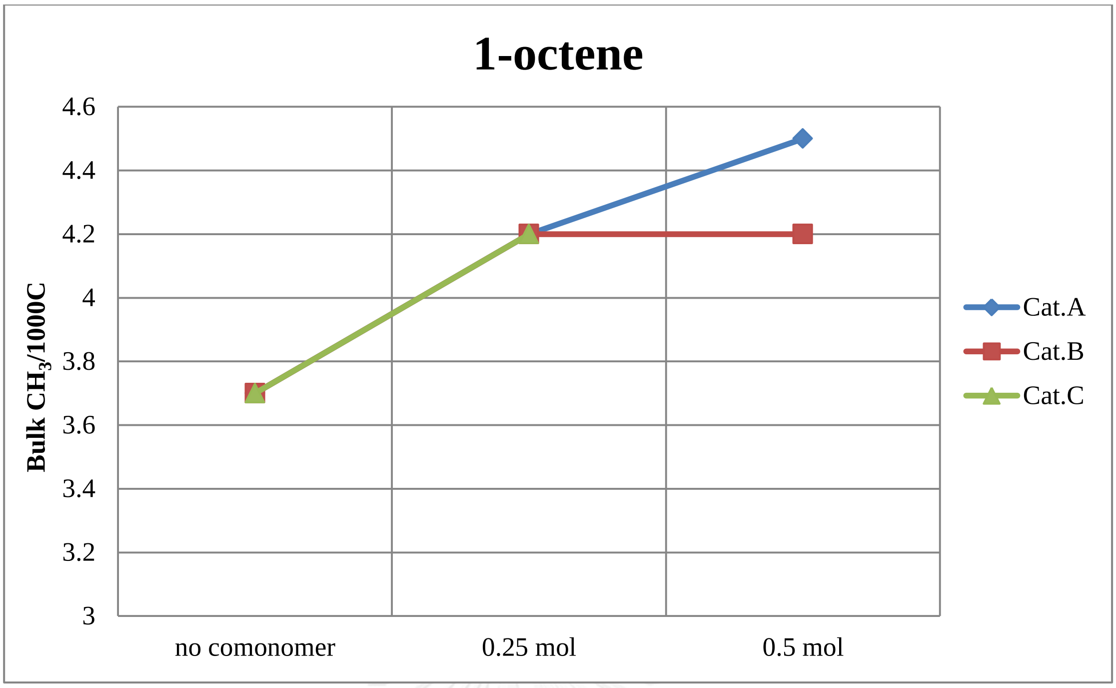


Figure 29 Effect of 1-octene content on bulk CH_3/1000C of polyethylene synthesized by three types of catalyst.

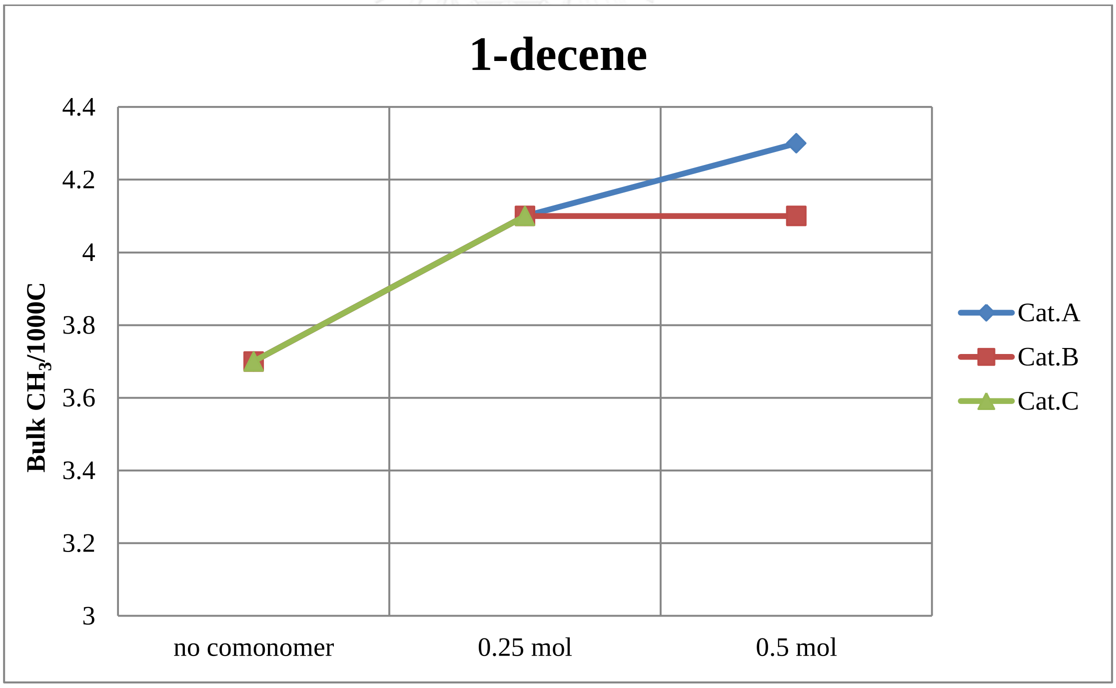


Figure 30 Effect of 1-decene content on bulk CH_3/1000C of polyethylene synthesized by three types of catalyst.

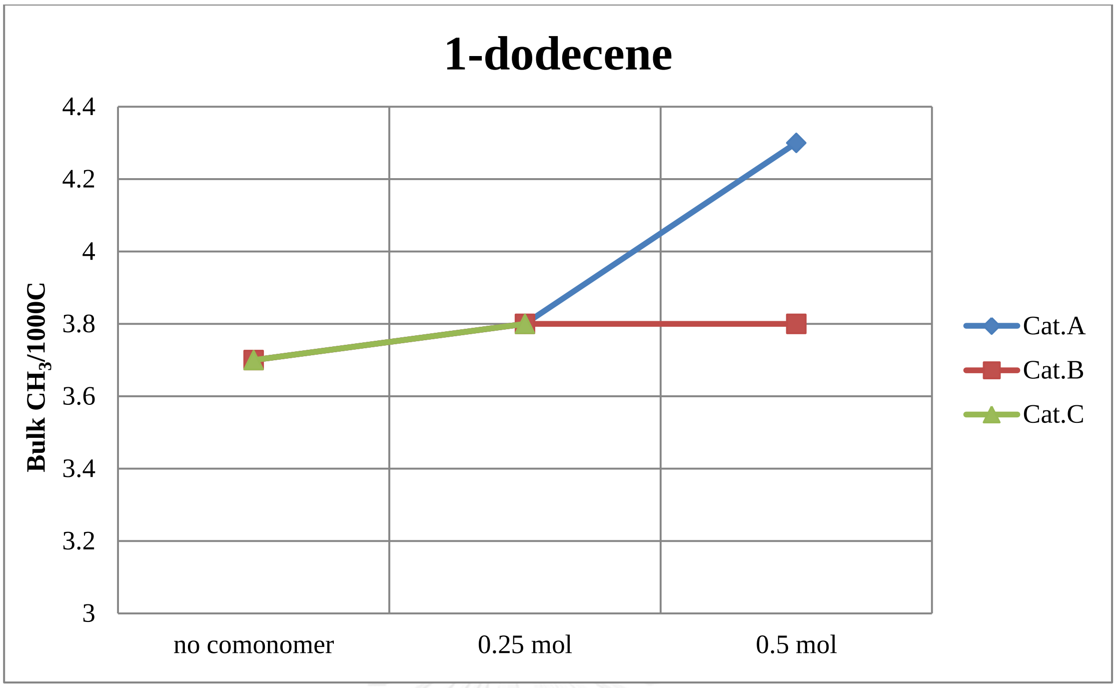


Figure 31 Effect of 1-dodecene content on bulk CH_3/1000C of polyethylene synthesized by three types of catalyst.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The conclusion of this research could be divided into 2 parts: which were (1) the catalyst preparation and (2) the characterization and the evaluation of catalyst performance by polymerization of ethylene

For the catalyst preparation, $TiCl_4/AlCl_3/MgCl_2$ by chemical treatment (Cat.A), $TiCl_4/MgCl_2{\cdot}AlCl_3$ by physical blending (Cat.B), and $TiCl_4/MgCl_2$ (Cat.C) were successfully synthesized with the similarity in catalyst component. XRD patterns showed the short and broad peak of $AlCl_3$ in Cat.A but sharp peak in Cat.B which indicated that $AlCl_3$ was compatible in Cat.A but was not in Cat.B. SEM image of Cat.A showed uniformly spherical-like shape particle size while Cat.B and Cat.C showed none uniformly irregular shape particle size. Also, PSD of Cat.A showed narrower particle size distribution and smaller average particle size than any others.

For the evaluation of catalyst performance by ethylene polymerization, the catalytic activity of Cat.A and Cat.B was around 4 times and 2 times of Cat.C, respectively. The ethylene consumption rate of Cat.A was higher than Cat.B and Cat.C which indicated that the deactivation of Cat.A was slower than the others. Besides, hydrogen sensitivity of Cat.A was lower than the others. For comonomer response, small comonomer molecule such as 1-butene and 1-hexene, Cat.A had more comonomer incorporation than Cat.B and Cat.C which indicated by higher bulk CH_3/1000C, lower density and %crystallinity, and large comonomers such as 1-octene, 1-decene, and 1-dodecene, Cat.A could increase the maximum limit of comonomer incorporation.

In addition, the important parameters of these three catalysts can be summarized in Figure 32. As could be seen, Cat.A has higher score than Cat.B and Cat.C in terms of catalytic activity, catalyst particle size, catalyst particle uniformity, hydrogen sensitivity, molecular weight distribution, and comonomer incorporation.

Therefore, from these results, it can be summarized that Cat.A is better than Cat.B and Cat.C. Finally, this research proved that:

1. The introduction of Lewis acid ($AlCl_3$) into the catalyst can both improve the catalytic activity and comonomer incorporation.

2. The catalyst preparation methodology affects the characteristics such as particle size and uniformity of the catalysts and thus resulting in different properties of polymer. In this research, chemical treatment (Cat.A) provides better catalytic activity and comonomer incorporation than physical blending (Cat.B).

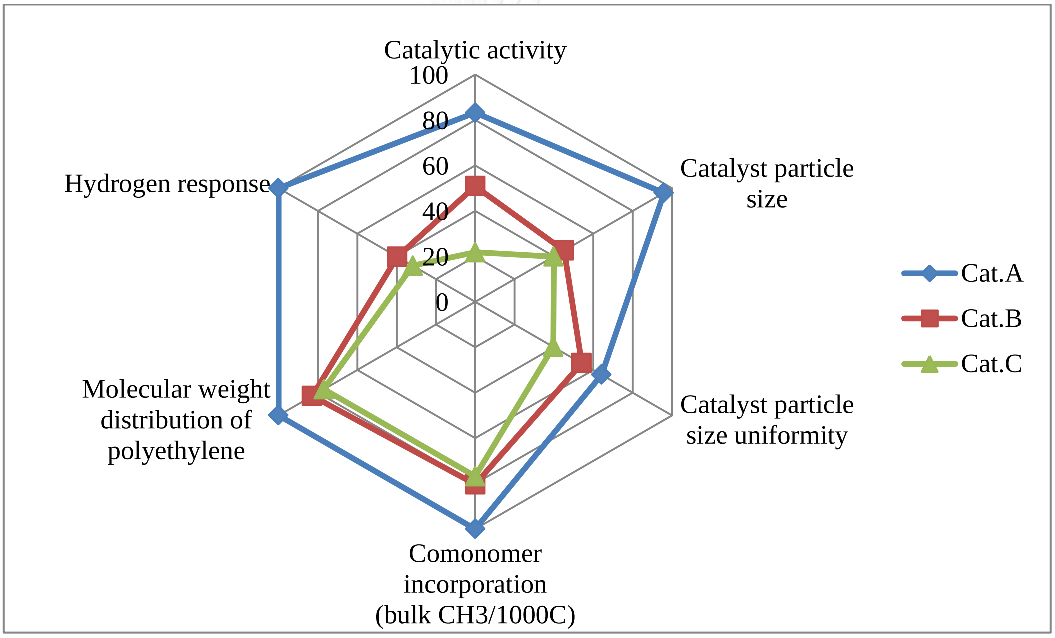


Figure 32 The catalytic performance of Cat.A, Cat.B, and Cat.C.

5.2 Recommendations

The distribution of Ti species, Ti^{2+}, Ti^{3+}, and Ti^{4+}, in each catalyst should be studied further in order to evaluate how Lewis acid and preparation technique affect their performance. Also, the chemical structure model of Cat.A and Cat.B should be investigated in order to understand the mechanism of Lewis acid in ethylene polymerization further.

REFERENCES

1. Swogger, P.S.C.a.K.W., *Olefin polymer technologies—history and recent progress at the Dow Chemical Company*. Progress in Polymer Science 2008. **33**: p. 797-819.
2. Czaja, M.B.a.K., *The effect of the comonomer on the copolymerization of ethylene with long chain α-olefins using Ziegler-Natta catalysts supported on MgCl2(THF)2*. Polymer, 2000. **41**: p. 7899-7904.
3. W. Meng, H.L., J. Li, and B. Chen, *The effect of comonomer type and content on the properties of Ziegler-Natta bimodal high-density polyethylene*. Journal of the Korean Chemical Society 2011. **55**: p. 673-679.
4. A. Shamiri, M.H.C., S. Jahan, M. A. Hussain, W. Kaminsky, P. V. Aravind, and W. A. Yehye, *The influence of Ziegler-Natta and Metallocene catalysts on polyolefin structure, properties, and processing ability*. Materials, 2014. **7**: p. 5069-5108.
5. Bresadola, D.F.a.S., *Catalytic systems supported on MgCl2 doped with ZnCl2 for olefin polymerization*. Journal of Molecular Catalysis A: Chemical 1999. **145**: p. 265-271.
6. Y. Chen, Z.F., J. Liao, and S. Liao, *Molecular weight distribution of poly ethylene catalyzed by Ziegler-Natta catalyst supported on MgCl2 Doped with AlCl3*. Journal of Applied Polymer Science 2006. **102**: p. 1768-1772.
7. X. Jiang, H.W., X. Tian, Y. Yang, and Z. Fan, *Effects of doping LiCl into MgCl2-supported Ziegler-Natta catalyst on the molecular weight distribution and isotacticity of polypropylene*. Industrial & Engineering Chemistry Reseach 2011. **50**: p. 259-266.
8. Leinonen, T.G.a.T., *Mn doping of the Ziegler-Natta PP catalyst support material*. Journal of Molecular Catalysis A: Chemical 1996. **104**: p. 205-212.
9. X. Jiang, Y.C., Z. Fan, Q. Wang, Z. Fua, and J. Xua, *Propylene polymerization catalyzed by novel supported titanium catalysts MgCl2/NaCl/DNBP/TiCl4 with different NaCl content*. Journal of Molecular Catalysis A: Chemical 2005. **235**: p. 209-219.
10. Fan, Y.C.a.Z., *Ethylene/1-hexene copolymerization with TiCl4/MgCl2/AlCl3 catalyst in the presence of hydrogen*. European Polymer Journal 2006. **42**: p. 2441–2449.
11. Jr., J.B., *Ziegler-Natta catalysts and polymerizations*. 1979, London: Academic Press Inc.
12. Peacock, A.J., *Handbook of polyethylene structures, properties, and applications*. 2000: Exxon chemical company
13. Innovateus, *What is UV spectrophotometer*.
14. Inc, M.-T.I., *FBRM® (focused beam reflectance measurement) technology*.
15. F. Hindryckx, P.D., R. Jerome, and M. Garcia Marti, *Ethylene polymerization by a high activity MgCI2 supported Ti catalyst in the presence of hydrogen and/or 1-octene*. Polymer, 1998. **39**: p. 621-629.
16. Y. Kong, J.Y., X. Dou, W. Liu, Q. Huang, K. Gao, and W. Yang, *With different structure ligands heterogeneous Ziegler-Natta catalysts for the preparation of copolymer of ethylene and 1-octene with high comonomer incorporation*. Polymer, 2010. **51**: p. 3859-3866.

17. T. Garoff, S.J., K. Pesonen, P. Waldvogel, and D. Lindgren, *Decrease in activity caused by hydrogen in Ziegler-Natta ethane polymerization.* European Polymer Journal, 2002. **38**: p. 121-132.

APPENDIX

Appendix A

Scanning electron microscope

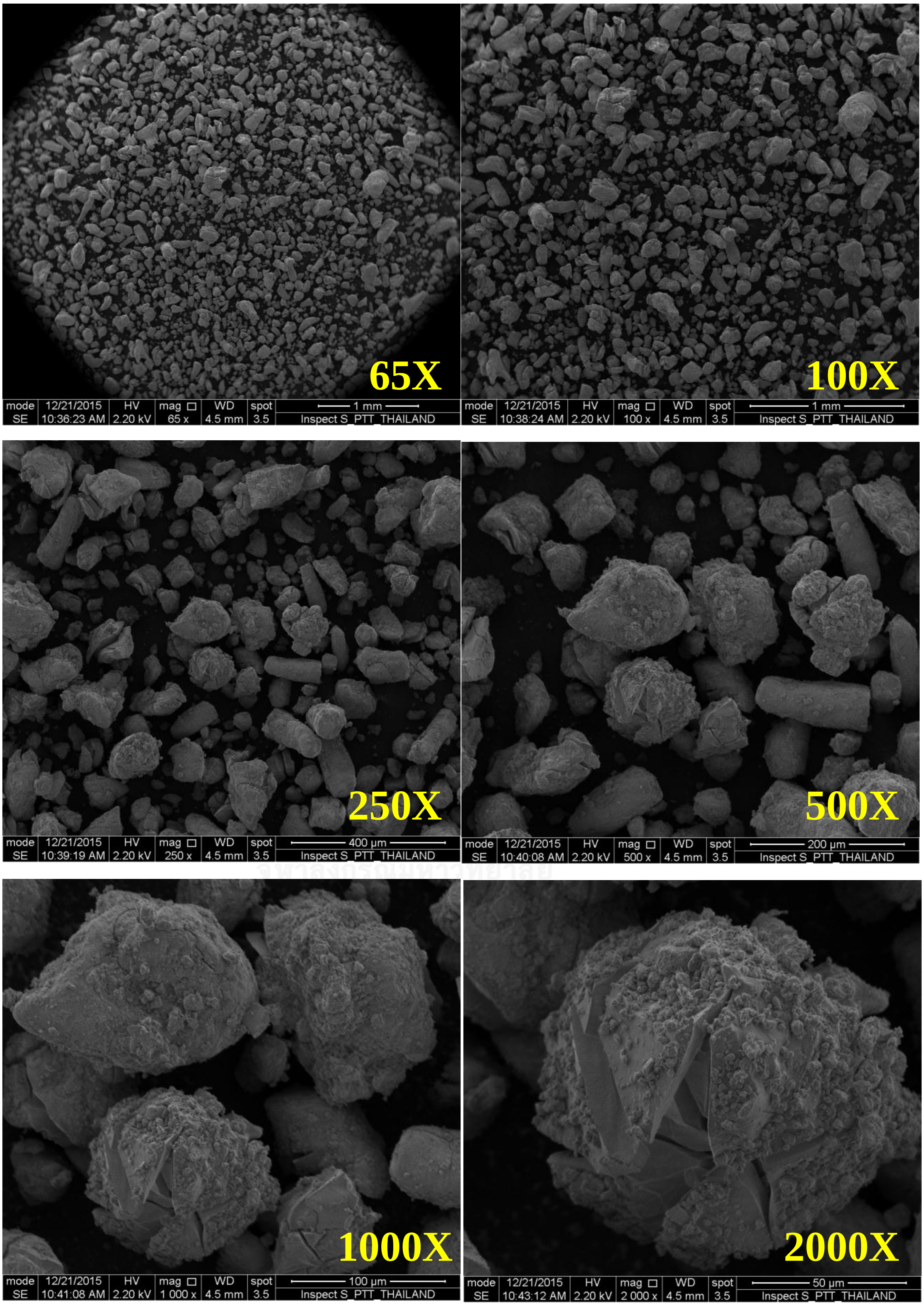


Figure 33 SEM images of Cat.A with various magnifications**.**

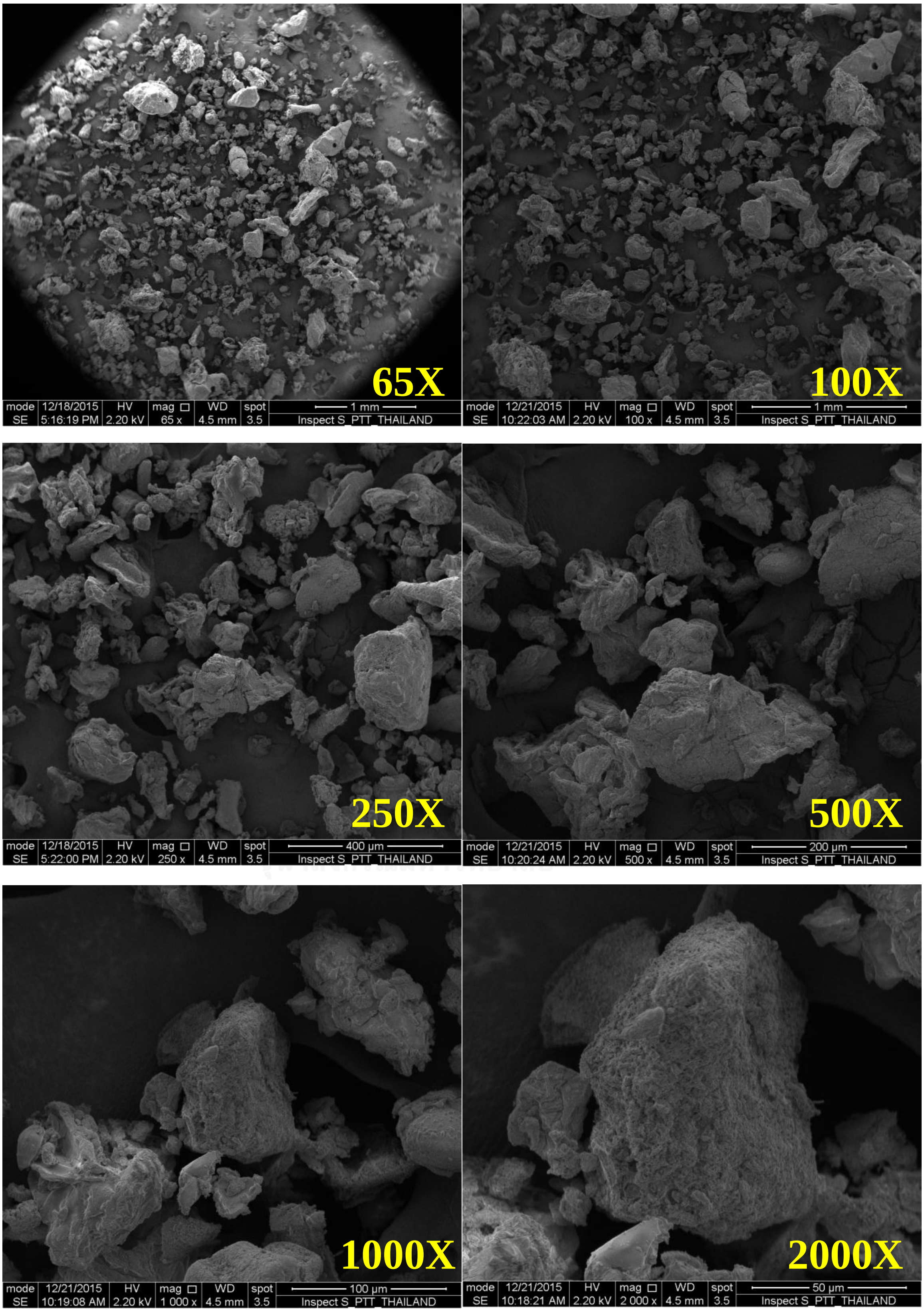


Figure 34 SEM images of Cat.B with various magnifications**.**

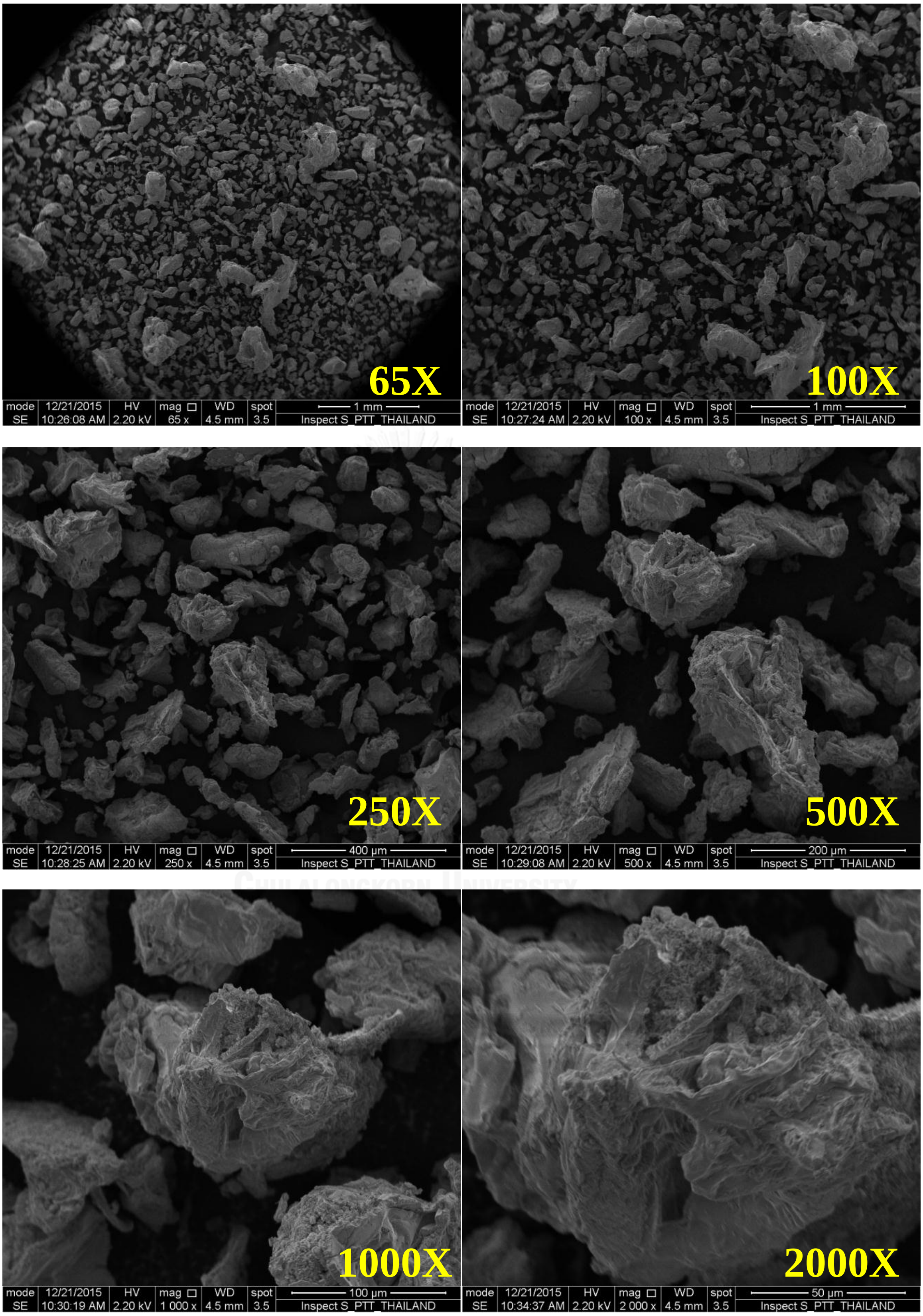
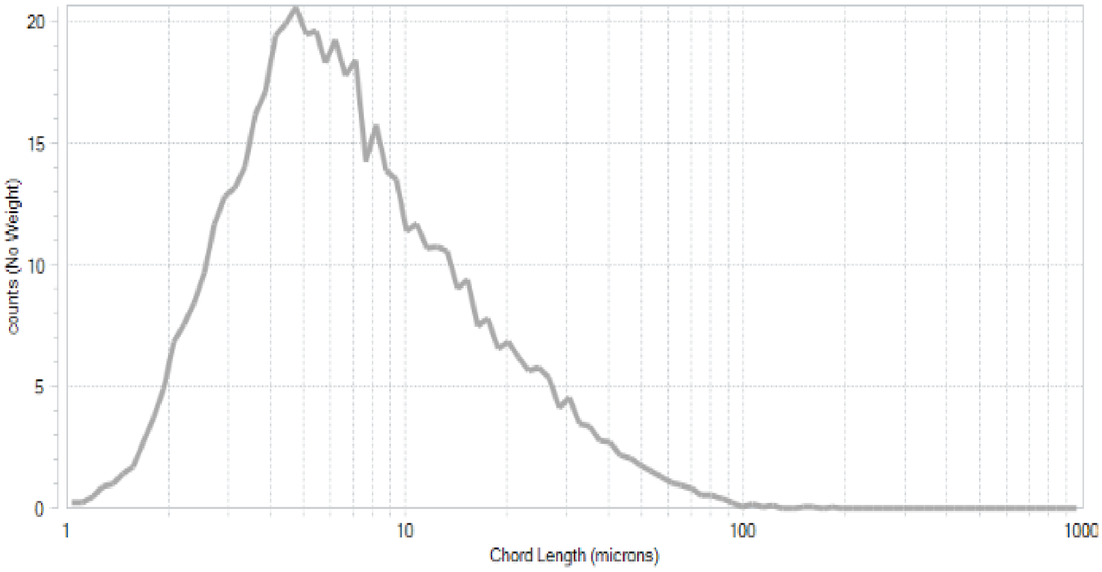


Figure 35 SEM images of Cat.C with various magnifications.

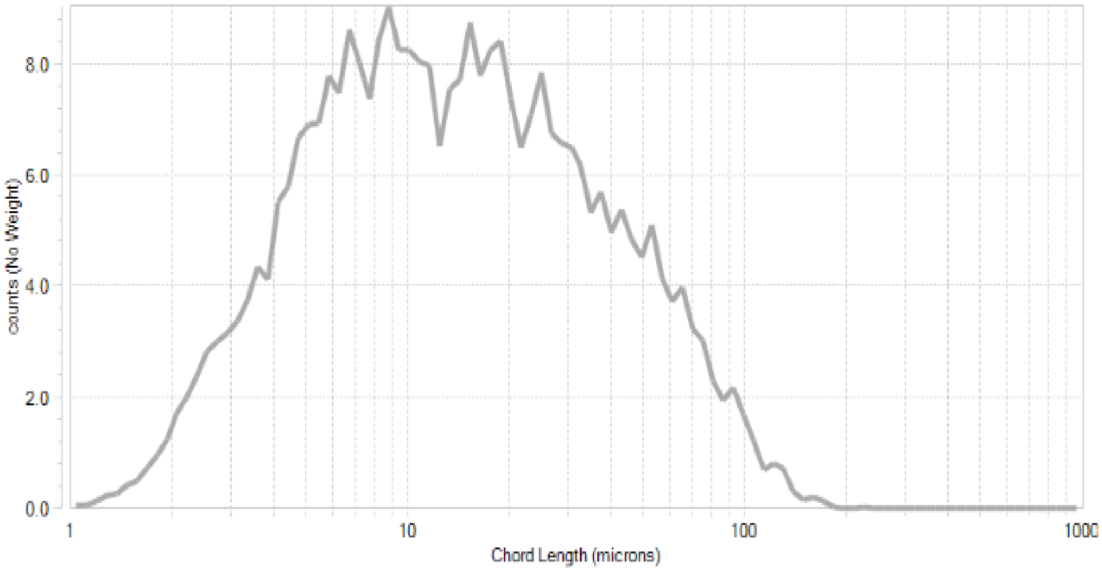
Appendix B

Particle size distribution



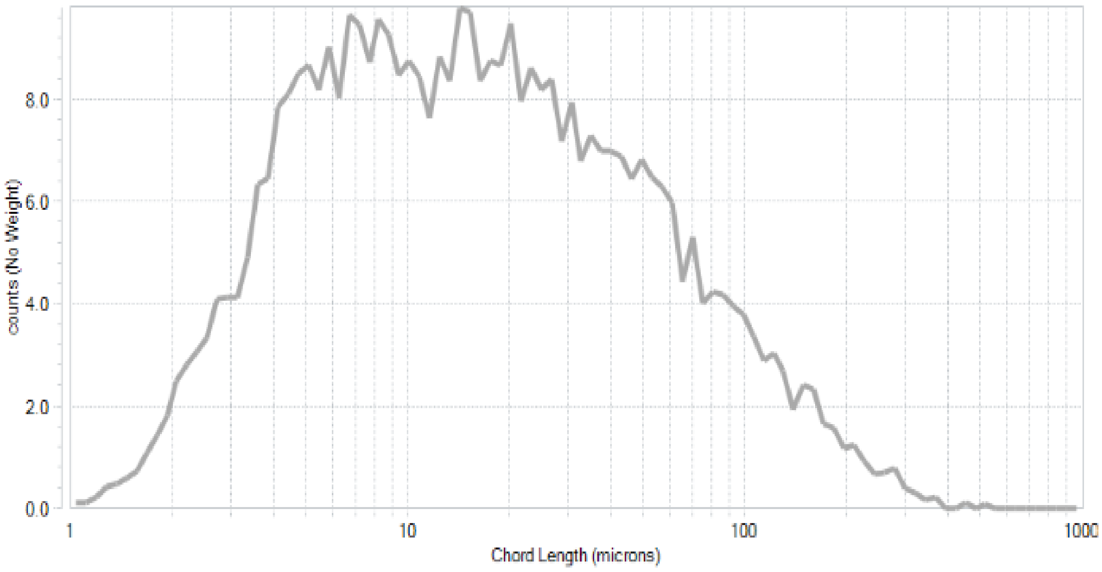
Particle size (microns)	
Value	Size (microns)
d10	2.67
d50	6.26
d90	22.2
Span	3.12
Mean	10.15

Figure 36 Particle size and particle size distribution of Cat.A**.**



Particle size (microns)	
Value	Size (microns)
d10	3.86
d50	13.3
d90	53.01
Span	3.70
Mean	21.86

Figure 37 Particle size and particle size distribution of Cat.B.



Particle size (microns)	
Value	Size (microns)
d10	3.76
d50	15.04
d90	79.63
Span	5.04
Mean	31.58

Figure 38 Particle size and particle size distribution of Cat.C.

Appendix C

Polymer properties

	Cat.A		Cat.B		Cat.C	
Sample	MFI (g/10min)	Density (g/cm^3)	MFI (g/10min)	Density (g/cm^3)	MFI (g/10min)	Density (g/cm^3)
No comonomer	2.29	0.962	2.12	0.963	1.83	0.963
1-butene 0.9 %mol	2.95	0.9545	2.69	0.9589	1.72	0.96
1-butene 1.8 %mol	4.07	0.952	4.41	0.9583		
1-butene 3.0 %mol	4.46	0.9517	3.4	0.9562		
1-butene 4.2 %mol	5.93	0.949	5.49	0.9545		
1-hexene 0.25 mol	1.68	0.9565	2.33	0.9567	1.8	0.958
1-hexene 0.5 mol	2.72	0.9546	4.88	0.9554		
1-octene 0.25 mol	1.66	0.959	2.36	0.9592	0.95	0.9596
1-octene 0.5 mol	1.74	0.9556	3.32	0.9595		
1-decene 0.25 mol	1.78	0.96	3.13	0.9605	1.04	0.96
1-decene 0.5 mol	2.5	0.9583	2.86	0.9607		
1-dodecene 0.25 mol	1.76	0.9608	3.12	0.9608	2.47	0.963
1-dodecene 0.5 mol	2.67	0.9591	1.31	0.961		

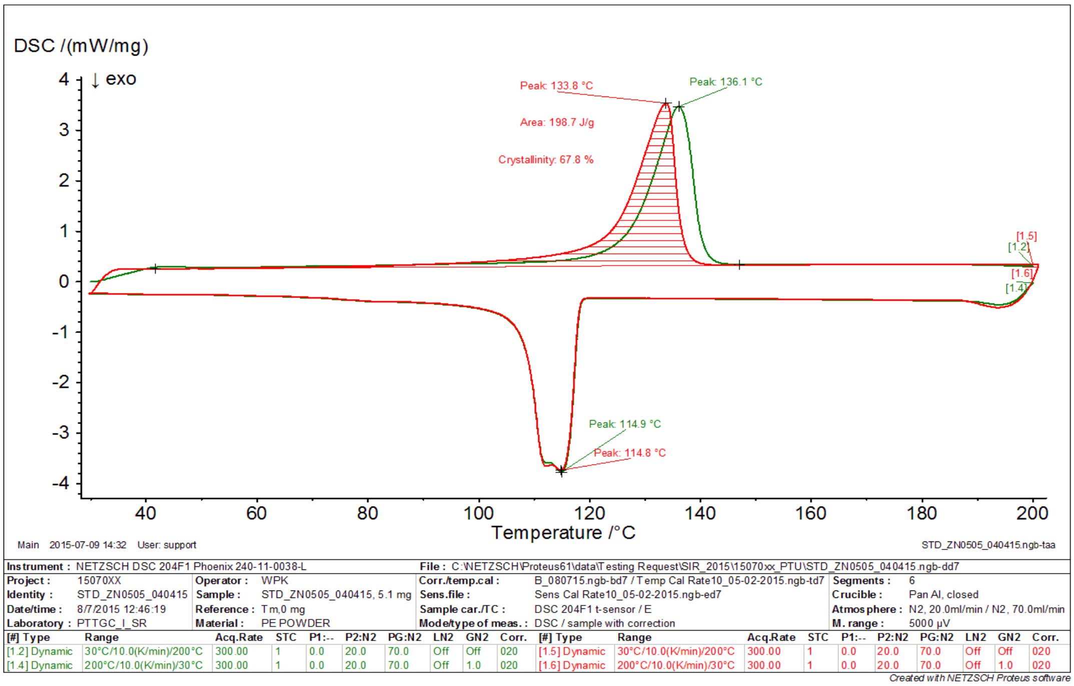
Table 8 MFI/Density of polyethylene with various comonomers and catalysts.

	Cat.A			Cat.B			Cat.C		
Sample	Tm (°C)	Tc (°C)	%Crystal linity	Tm (°C)	Tc (°C)	%Crystal linity	Tm (°C)	Tc (°C)	%Crystal linity
No comonomer	134.7	112.6	68.3	134.2	115.3	73.1	133.7	113.4	70.3
1-butene 0.9 %mol	131.2	112.3	62.9	132.3	112.2	69.8	133.1	112.8	70.1
1-butene 1.8 %mol	130	110.1	60.6	132	112.2	70			
1-butene 3.0 %mol	129.8	109.9	64.2	131.5	112.6	68.1			
1-butene 4.2 %mol	128.8	109.7	61	130	110.9	67.4			
1-hexene 0.25 mol	132.7	114.1	64.5	132.2	113.9	68.1	132.3	112.5	67.4
1-hexene 0.5 mol	131.6	113	63.8	130.2	112	66.3			
1-octene 0.25 mol	133.9	114.6	68.5	132.4	114.6	69	132.9	112.9	68.9
1-octene 0.5 mol	133.2	114.2	67	132.3	112.8	69.4			
1-decene 0.25 mol	133	114.6	66.7	132.2	112.3	68.9	132.9	113.1	67.1
1-decene 0.5 mol	132.5	114.4	66.1	133.2	114.5	73.9			
1-dodecene 0.25 mol	132.9	114.5	67.5	132.3	113.8	69.4	133.3	113.4	72.6
1-dodecene 0.50 mol	132	113.6	64	131	113.4	66.9			

Table 9 DSC data of polyethylene with various comonomers and catalysts.

Appendix D

Differential scanning calorimetry



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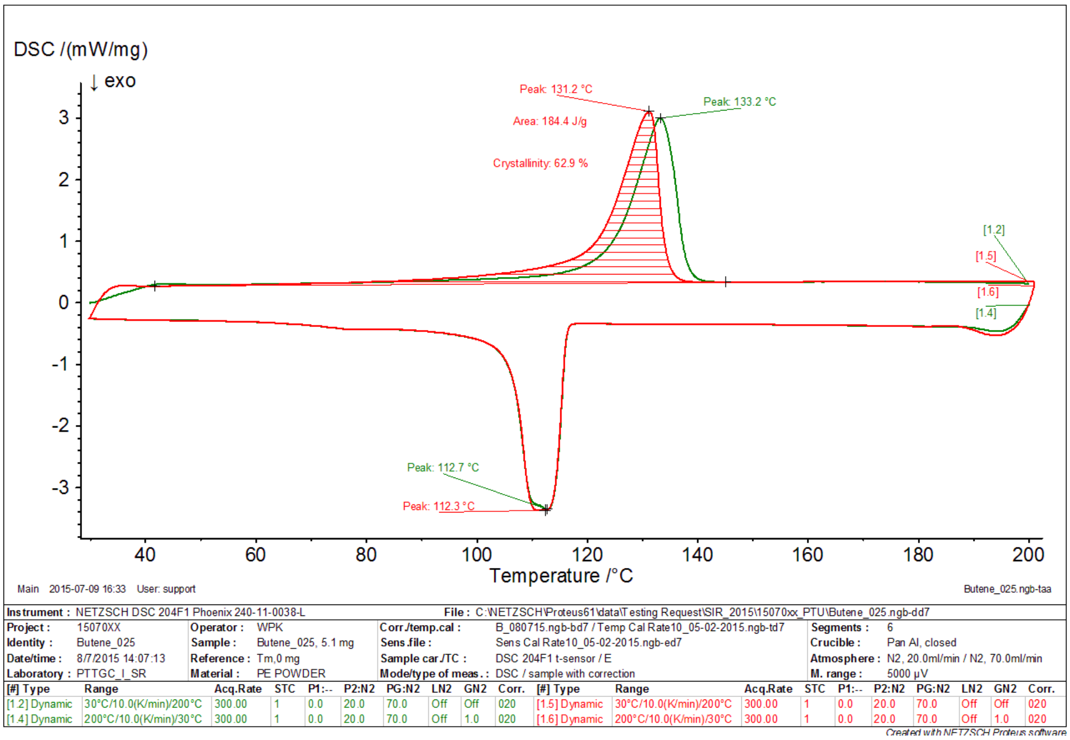
Date/time : 8/7/2015 12:46:19
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : STD_ZN0505_040415, 5.1 mg
Reference : Tm,0 mg
Material : PE POWDER
Corr./temp.cal : B_080715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction
Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Figure 39 DSC of ethylene polymer (Cat.A nocomonomer).



Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L
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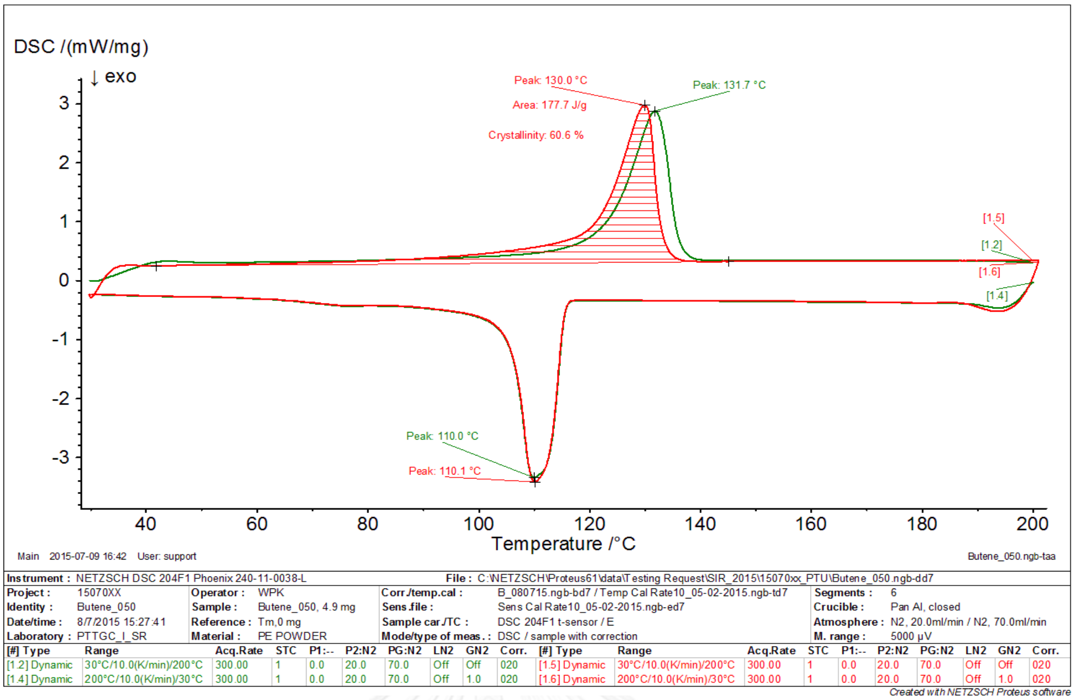
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Butene_025, 5.1 mg
Reference : Tm,0 mg
Material : PE POWDER
Corr./temp.cal : B_080715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction
Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Figure 40 DSC of ethylene polymer (Cat.A 1-butene 0.9 mol%).



Main 2015-07-09 16:42 User: support

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Date/time :	8/7/2015 15:27:41	**Reference :**	Tm,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Atmosphere :**	N2, 20.0ml/min / N2, 70.0ml/min
Laboratory :	PTTGC_I_SR	**Material :**	PE POWDER	**Mode/type of meas. :**	DSC / sample with correction	**M. range :**	5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

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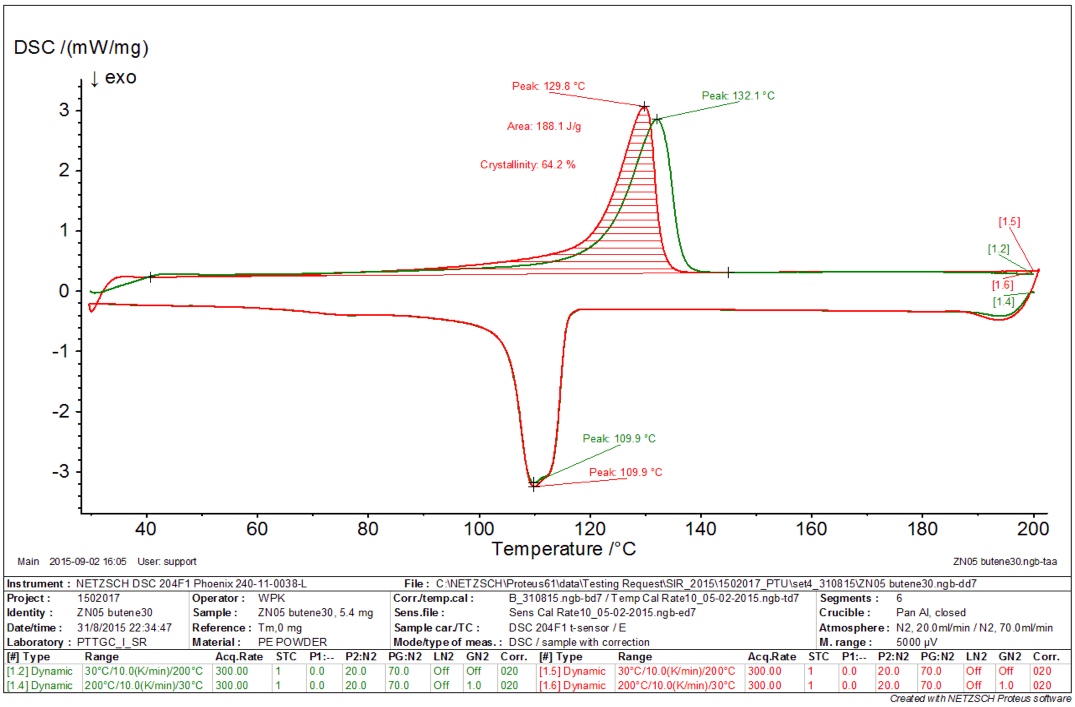
Figure 41 DSC of ethylene polymer (Cat.A 1-butene 1.8 mol%).



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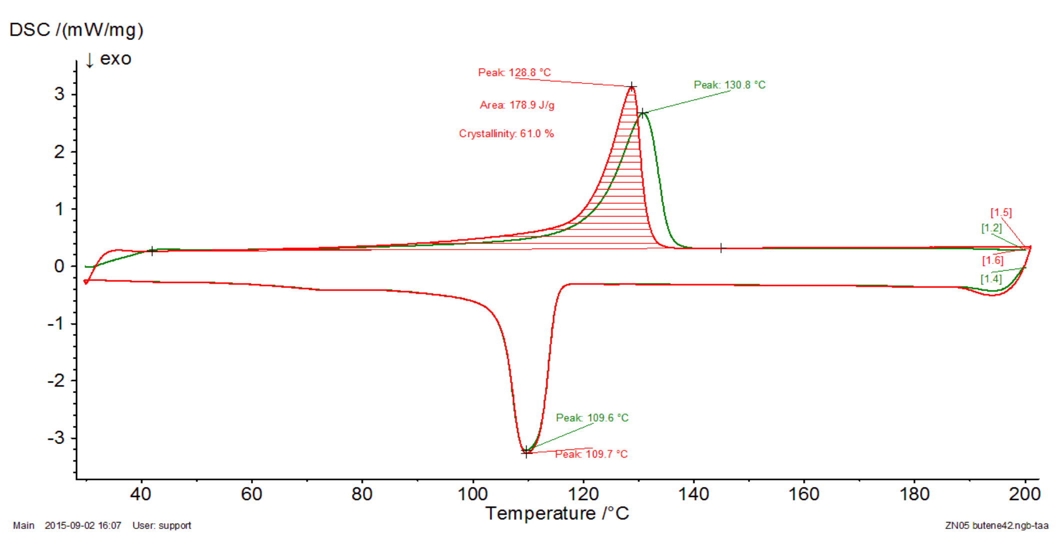
Identity :	ZN05 butene30	**Sample :**	ZN05 butene30, 5.4 mg	**Sens.file :**	Sens Cal Rate10_05-02-2015.ngb-ed7	**Crucible :**	Pan Al, closed
Date/time :	31/8/2015 22:34:47	**Reference :**	Tm,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Atmosphere :**	N2, 20.0ml/min / N2, 70.0ml/min
Laboratory :	PTTGC_I_SR	**Material :**	PE POWDER	**Mode/type of meas. :**	DSC / sample with correction	**M. range :**	5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 42 DSC of ethylene polymer (Cat.A 1-butene 3.0 mol%).



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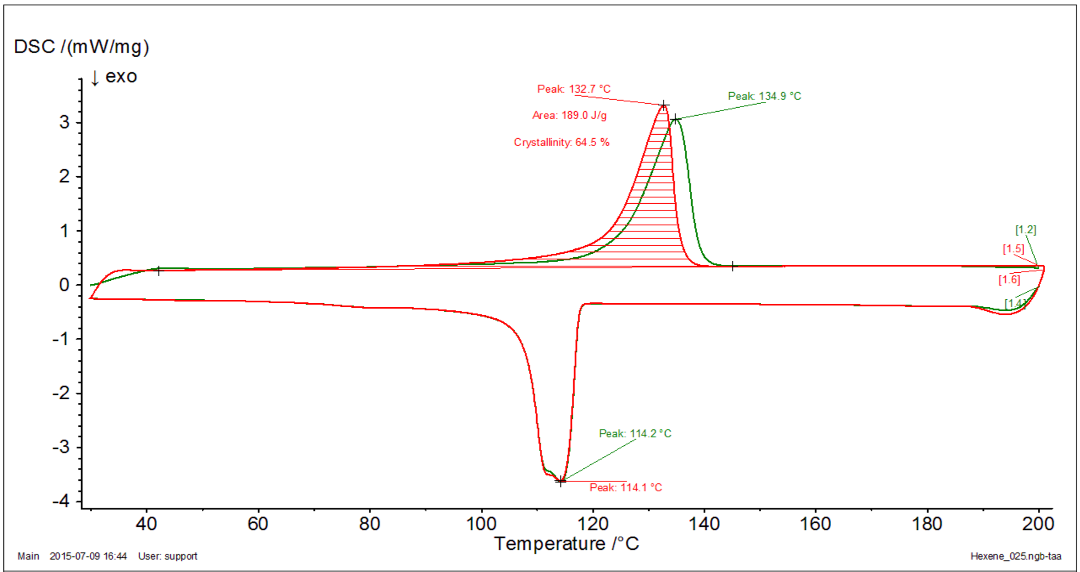
Identity :	ZN05 butene42	**Sample :**	ZN05 butene42, 5.5 mg	**Sens.file :**	Sens Cal Rate10_05-02-2015.ngb-ed7	**Crucible :**	Pan Al, closed
Date/time :	31/8/2015 23:55:49	**Reference :**	Tm,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Atmosphere :**	N2, 20.0ml/min / N2, 70.0ml/min
Laboratory :	PTTGC_I_SR	**Material :**	PE POWDER	**Mode/type of meas. :**	DSC / sample with correction	**M. range :**	5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 43 DSC of ethylene polymer (Cat.A 1-butene 4.2 mol%).



Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\15070xx_PTU\Hexene_025.ngb-dd7

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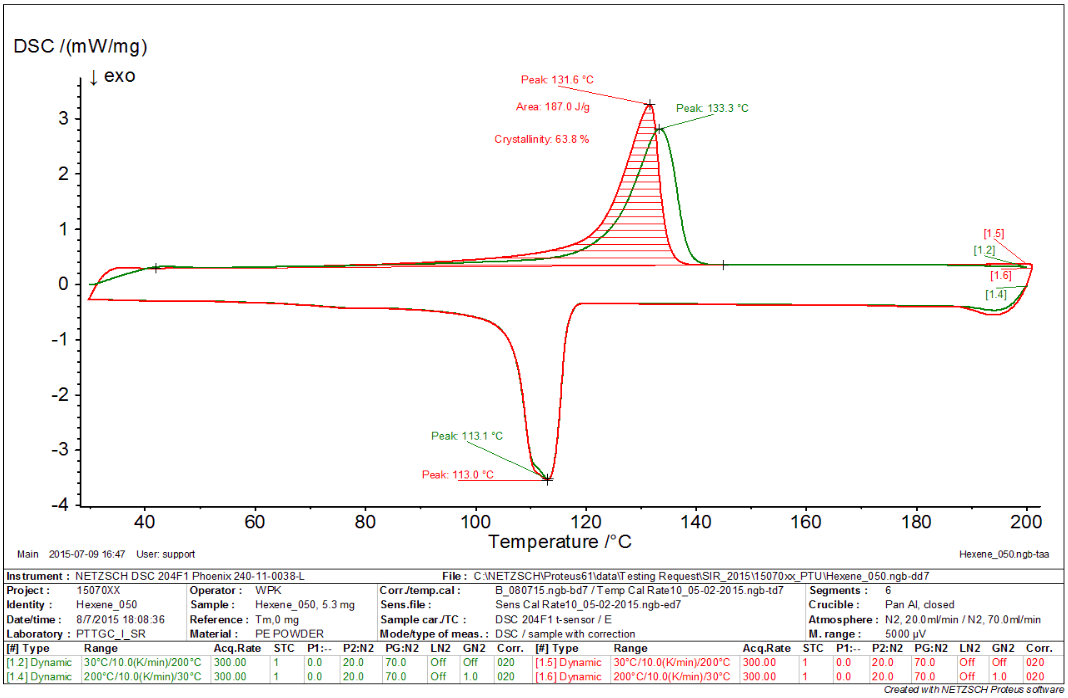
Identity :	Hexene_025	**Sample :**	Hexene_025, 5.4 mg	**Sens.file :**	Sens Cal Rate10_05-02-2015.ngb-ed7	**Crucible :**	Pan Al, closed
Date/time :	8/7/2015 16:48:09	**Reference :**	Tm,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Atmosphere :**	N2, 20.0ml/min / N2, 70.0ml/min
Laboratory :	PTTGC_I_SR	**Material :**	PE POWDER	**Mode/type of meas. :**	DSC / sample with correction	**M. range :**	5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 44 DSC of ethylene polymer (Cat.A 1-hexene 0.25 mol).



Main 2015-07-09 16:47 User: support
Hexene_050.ngb-taa

Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\15070xx_PTU\Hexene_050.ngb-dd7

Project :	15070XX	**Operator :**	WPK	**Corr./temp.cal :**	B_080715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7	**Segments :**	6
Identity :	Hexene_050	**Sample :**	Hexene_050, 5.3 mg	**Sens.file :**	Sens Cal Rate10_05-02-2015.ngb-ed7	**Crucible :**	Pan Al, closed
Date/time :	8/7/2015 18:08:36	**Reference :**	Tm,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Atmosphere :**	N2, 20.0ml/min / N2, 70.0ml/min
Laboratory :	PTTGC_I_SR	**Material :**	PE POWDER	**Mode/type of meas. :**	DSC / sample with correction	**M. range :**	5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

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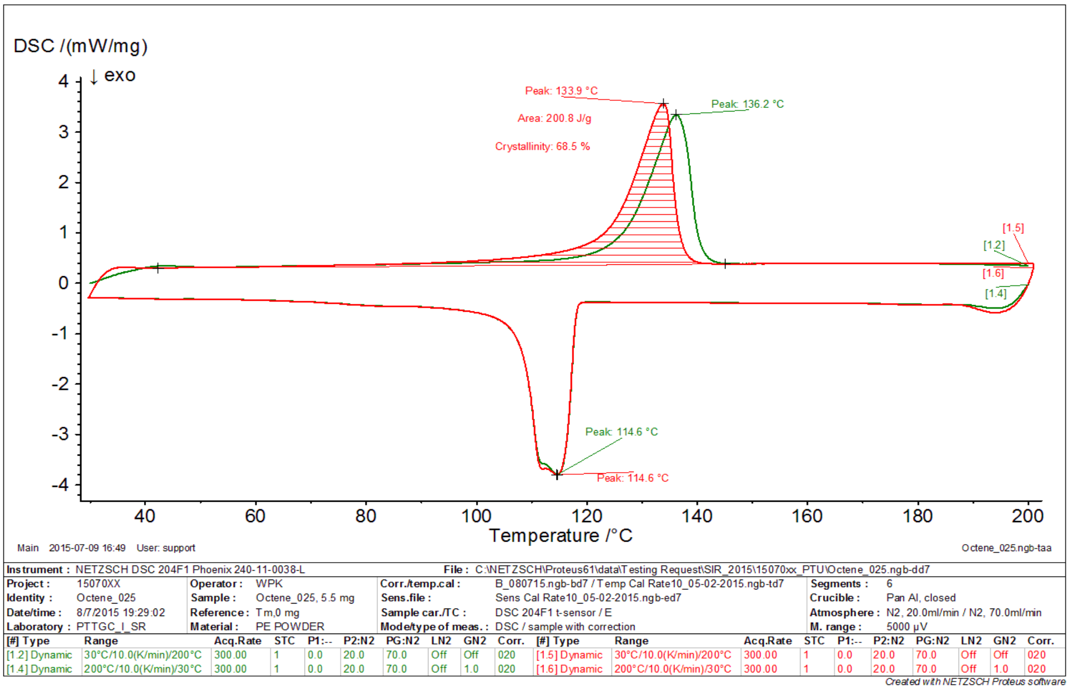
Figure 45 DSC of ethylene polymer (Cat.A 1-hexene 0.5 mol).



Main 2015-07-09 16:49 User: support
Octene_025.ngb-taa

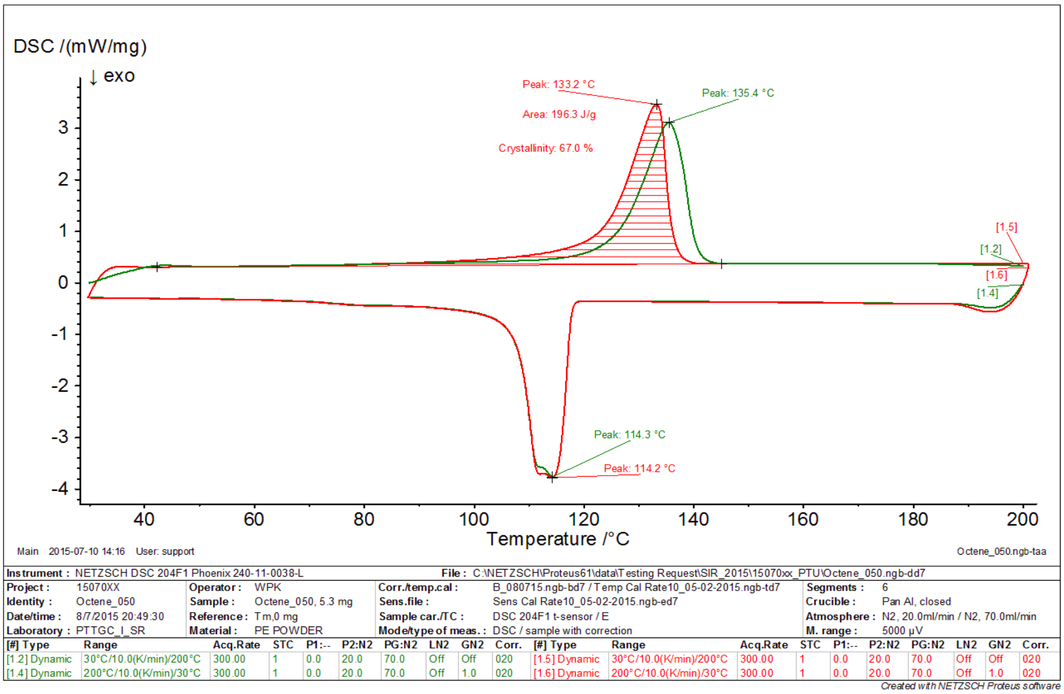
Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\15070xx_PTU\Octene_025.ngb-dd7

Project :	15070XX	**Operator :**	WPK	**Corr./temp.cal :**	B_080715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7	**Segments :**	6
Identity :	Octene_025	**Sample :**	Octene_025, 5.5 mg	**Sens.file :**	Sens Cal Rate10_05-02-2015.ngb-ed7	**Crucible :**	Pan Al, closed
Date/time :	8/7/2015 19:29:02	**Reference :**	Tm,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Atmosphere :**	N2, 20.0ml/min / N2, 70.0ml/min
Laboratory :	PTTGC_I_SR	**Material :**	PE POWDER	**Mode/type of meas. :**	DSC / sample with correction	**M. range :**	5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 46 DSC of ethylene polymer (Cat.A 1-octene 0.25 mol).



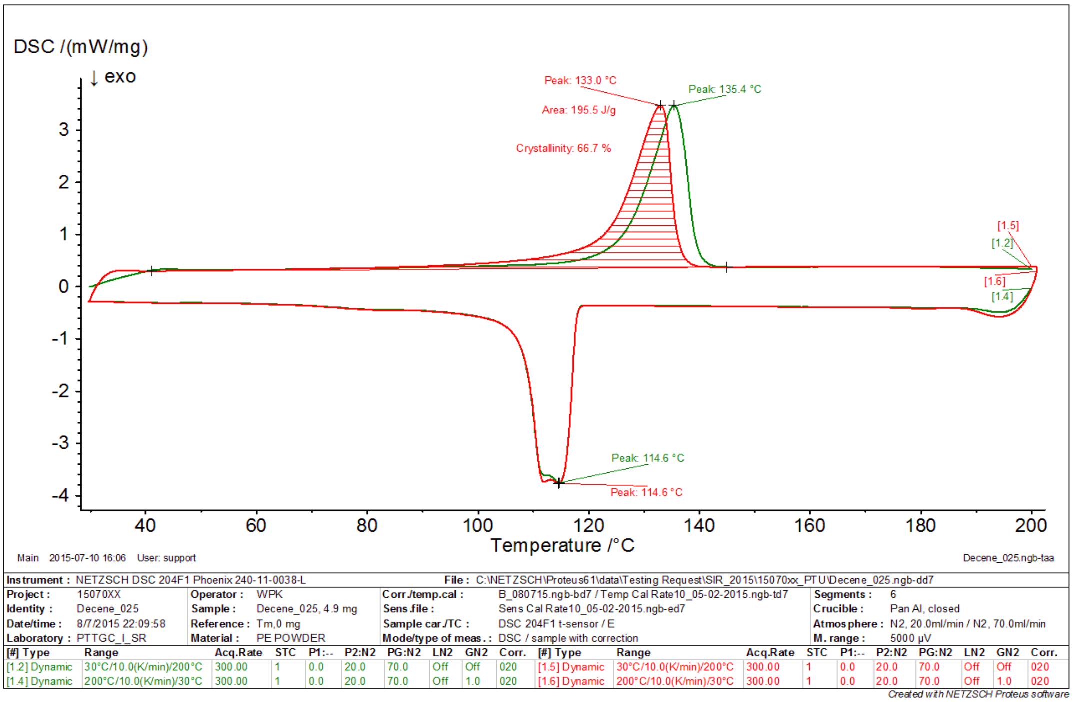
Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L
File : C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\15070xx_PTU\Octene_050.ngb-dd7

Project :	15070XX	**Operator :**	WPK	**Corr./temp.cal :**	B_080715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7	**Segments :**	6
Identity :	Octene_050	**Sample :**	Octene_050, 5.3 mg	**Sens.file :**	Sens Cal Rate10_05-02-2015.ngb-ed7	**Crucible :**	Pan Al, closed
Date/time :	8/7/2015 20:49:30	**Reference :**	Tm,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Atmosphere :**	N2, 20.0ml/min / N2, 70.0ml/min
Laboratory :	PTTGC_I_SR	**Material :**	PE POWDER	**Mode/type of meas. :**	DSC / sample with correction	**M. range :**	5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020
[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 47 DSC of ethylene polymer (Cat.A 1-octene 0.5 mol).



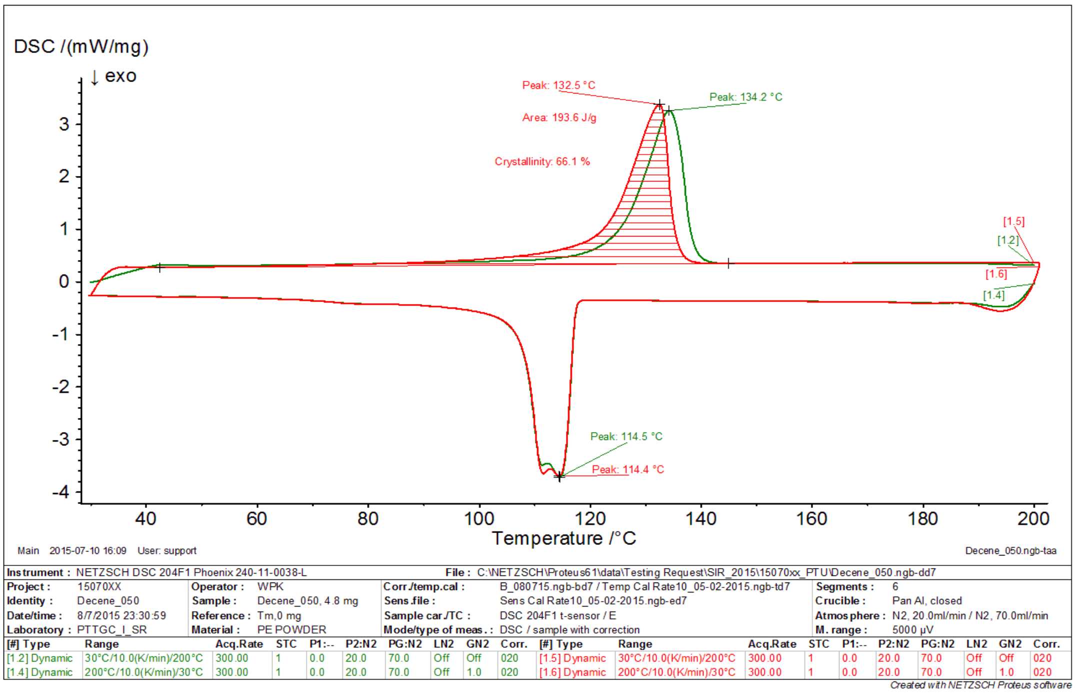
Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L
File : C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\15070xx_PTU\Decene_025.ngb-dd7

Project :	15070XX	**Operator :**	WPK	**Corr./temp.cal :**	B_080715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7	**Segments :**	6
Identity :	Decene_025	**Sample :**	Decene_025, 4.9 mg	**Sens.file :**	Sens Cal Rate10_05-02-2015.ngb-ed7	**Crucible :**	Pan Al, closed
Date/time :	8/7/2015 22:09:58	**Reference :**	Tm,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Atmosphere :**	N2, 20.0ml/min / N2, 70.0ml/min
Laboratory :	PTTGC_I_SR	**Material :**	PE POWDER	**Mode/type of meas. :**	DSC / sample with correction	**M. range :**	5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020
[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 48 DSC of ethylene polymer (Cat.A 1-decene 0.25 mol).



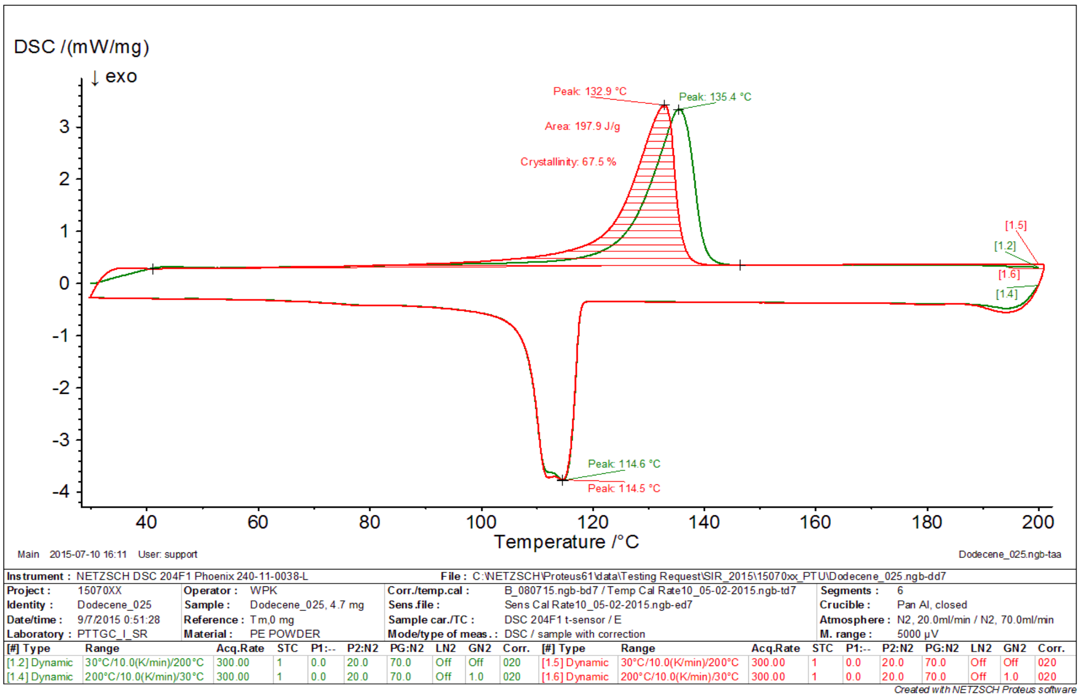
Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\15070xx_PTU\Decene_050.ngb-dd7

Project : 15070XX
Identity : Decene_050
Date/time : 8/7/2015 23:30:59
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Decene_050, 4.8 mg
Reference : Tm,0 mg
Material : PE POWDER
Corr./temp.cal : B_080715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction
Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 49 DSC of ethylene polymer (Cat.A 1-decene 0.5 mol).



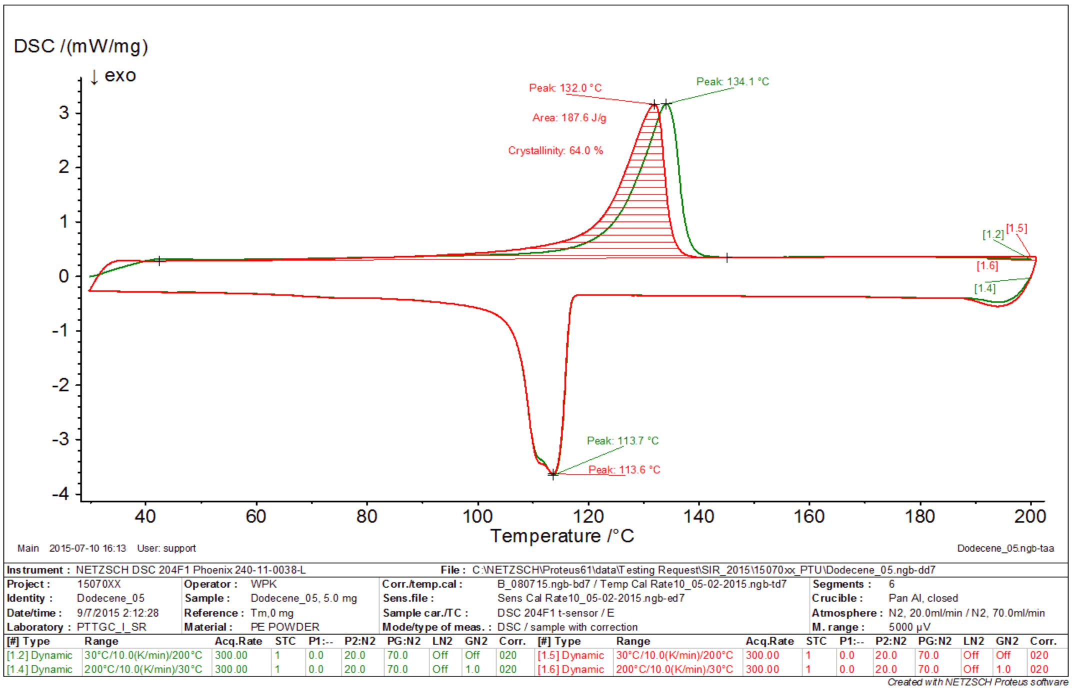
Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\15070xx_PTU\Dodecene_025.ngb-dd7

Project : 15070XX
Identity : Dodecene_025
Date/time : 9/7/2015 0:51:28
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Dodecene_025, 4.7 mg
Reference : Tm,0 mg
Material : PE POWDER
Corr./temp.cal : B_080715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction
Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 50 DSC of ethylene polymer (Cat.A 1-dodecene 0.25 mol).



Main 2015-07-10 16:13 User: support

Dodecene_05.ngb-taa

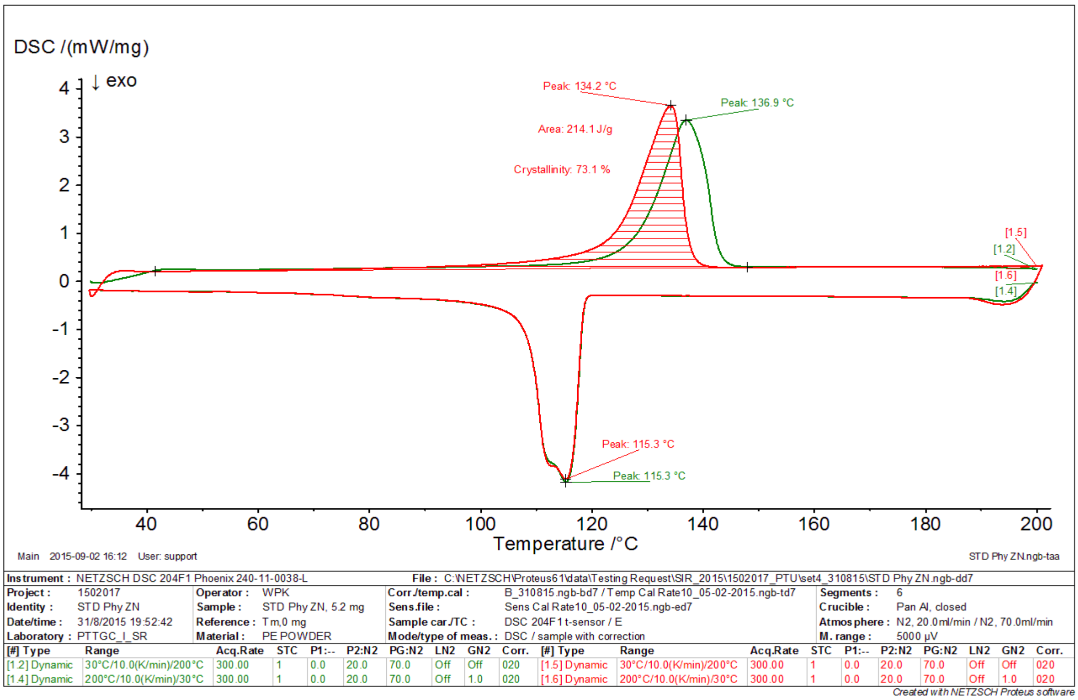
Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\15070xx_PTU\Dodecene_05.ngb-dd7

Project :	15070XX	**Operator :**	WPK	**Corr./temp.cal :**	B_080715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7	**Segments :**	6
Identity :	Dodecene_05	**Sample :**	Dodecene_05, 5.0 mg	**Sens.file :**	Sens Cal Rate10_05-02-2015.ngb-ed7	**Crucible :**	Pan Al, closed
Date/time :	9/7/2015 2:12:28	**Reference :**	Tm,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Atmosphere :**	N2, 20.0ml/min / N2, 70.0ml/min
Laboratory :	PTTGC_I_SR	**Material :**	PE POWDER	**Mode/type of meas. :**	DSC / sample with correction	**M. range :**	5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 51 DSC of ethylene polymer (Cat.A 1-dodecene 0.5 mol).



Main 2015-09-02 16:12 User: support

STD Phy ZN.ngb-taa

Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set4_310815\STD Phy ZN.ngb-dd7

Project :	1502017	**Operator :**	WPK	**Corr./temp.cal :**	B_310815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7	**Segments :**	6
Identity :	STD Phy ZN	**Sample :**	STD Phy ZN, 5.2 mg	**Sens.file :**	Sens Cal Rate10_05-02-2015.ngb-ed7	**Crucible :**	Pan Al, closed
Date/time :	31/8/2015 19:52:42	**Reference :**	Tm,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Atmosphere :**	N2, 20.0ml/min / N2, 70.0ml/min
Laboratory :	PTTGC_I_SR	**Material :**	PE POWDER	**Mode/type of meas. :**	DSC / sample with correction	**M. range :**	5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

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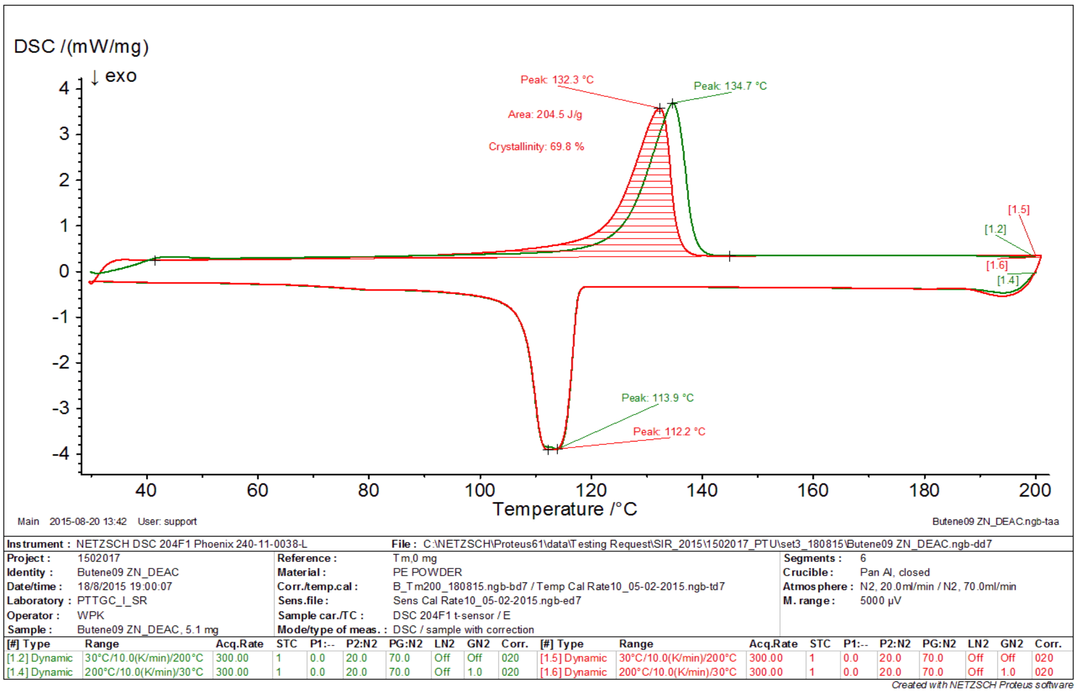
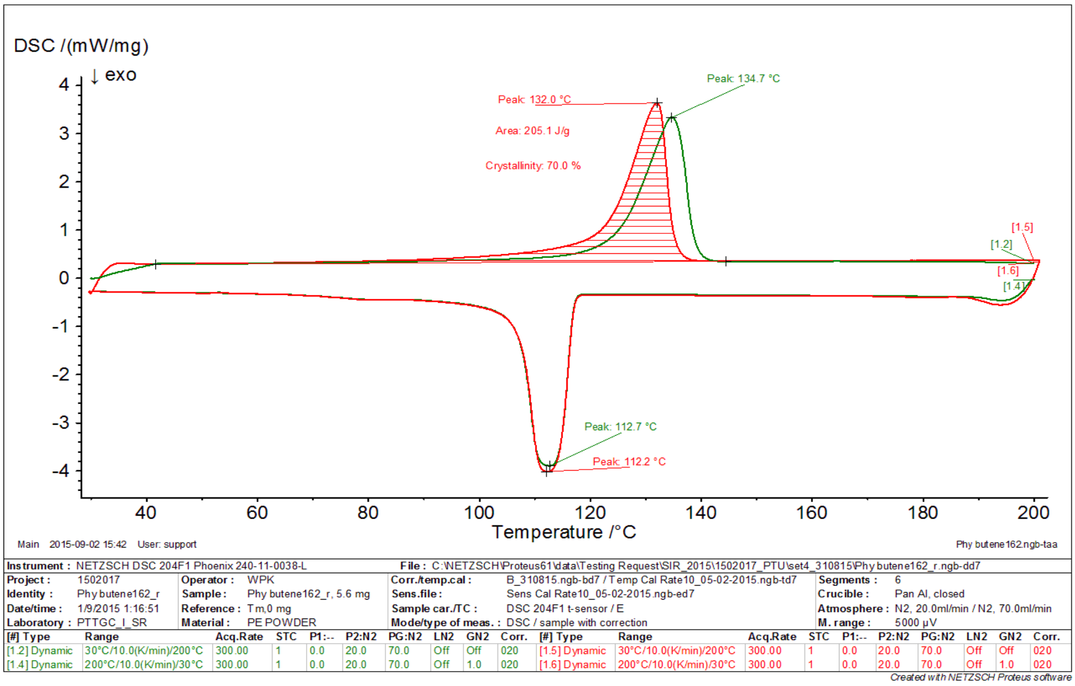
Figure 52 DSC of ethylene polymer (Cat.B nocomonomer).



Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L
File : C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set3_180815\Butene09 ZN_DEAC.ngb-dd7
Project : 1502017
Identity : Butene09 ZN_DEAC
Date/time : 18/8/2015 19:00:07
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Butene09 ZN_DEAC, 5.1 mg
Reference : Tm,0 mg
Material : PE POWDER
Corr./temp.cal : B_Tm200_180815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction
Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

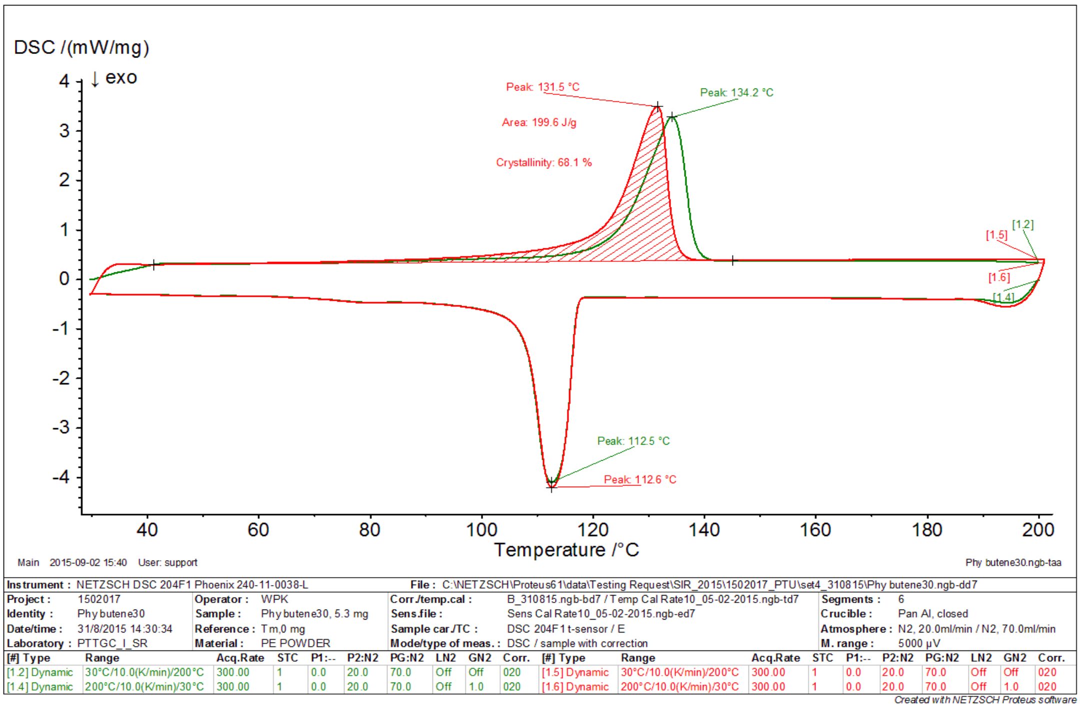
Figure 53 DSC of ethylene polymer (Cat.B 1-butene 0.9 mol%).



Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L
File : C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set4_310815\Phy butene162_r.ngb-dd7
Project : 1502017
Identity : Phy butene162_r
Date/time : 1/9/2015 1:16:51
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Phy butene162_r, 5.6 mg
Reference : Tm,0 mg
Material : PE POWDER
Corr./temp.cal : B_310815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction
Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Figure 54 DSC of ethylene polymer (Cat.B 1-butene 1.8 mol%).



Main 2015-09-02 15:40 User: support

Phy butene30.ngb-taa

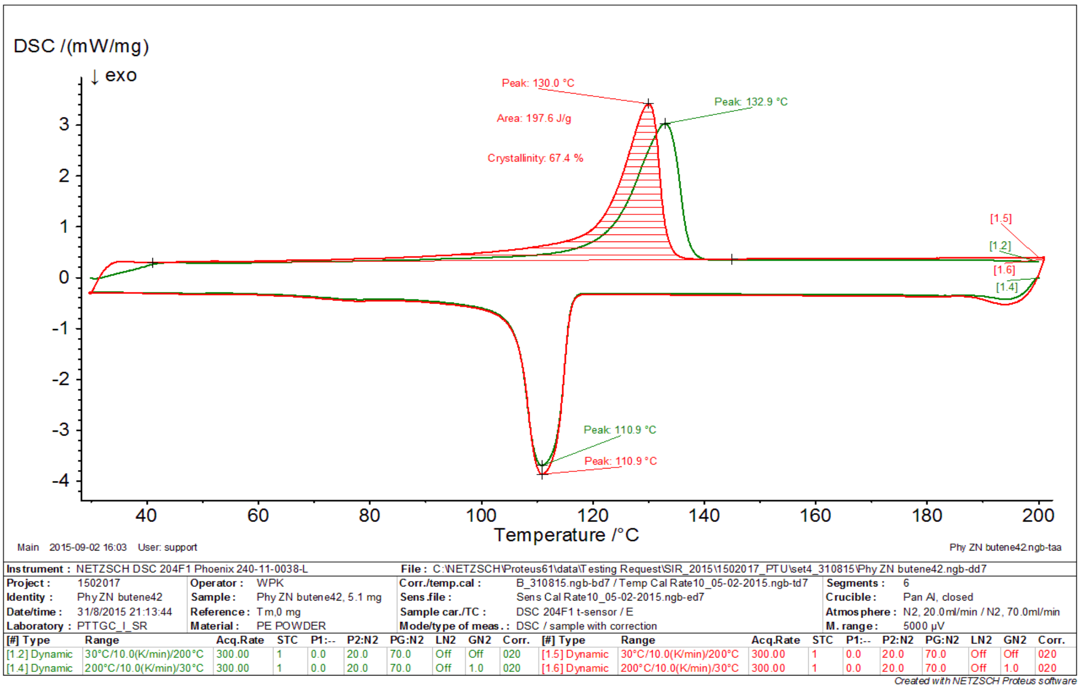
Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set4_310815\Phy butene30.ngb-dd7

Project : 1502017
Identity : Phy butene30
Date/time : 31/8/2015 14:30:34
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Phy butene30, 5.3 mg
Reference : Tm,0 mg
Material : PE POWDER
Corr./temp.cal : B_310815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction
Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020
[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 55 DSC of ethylene polymer (Cat.B 1-butene 3.0 mol%).



Main 2015-09-02 16:03 User: support

Phy ZN butene42.ngb-taa

Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set4_310815\Phy ZN butene42.ngb-dd7

Project : 1502017
Identity : Phy ZN butene42
Date/time : 31/8/2015 21:13:44
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Phy ZN butene42, 5.1 mg
Reference : Tm,0 mg
Material : PE POWDER
Corr./temp.cal : B_310815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction
Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020
[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

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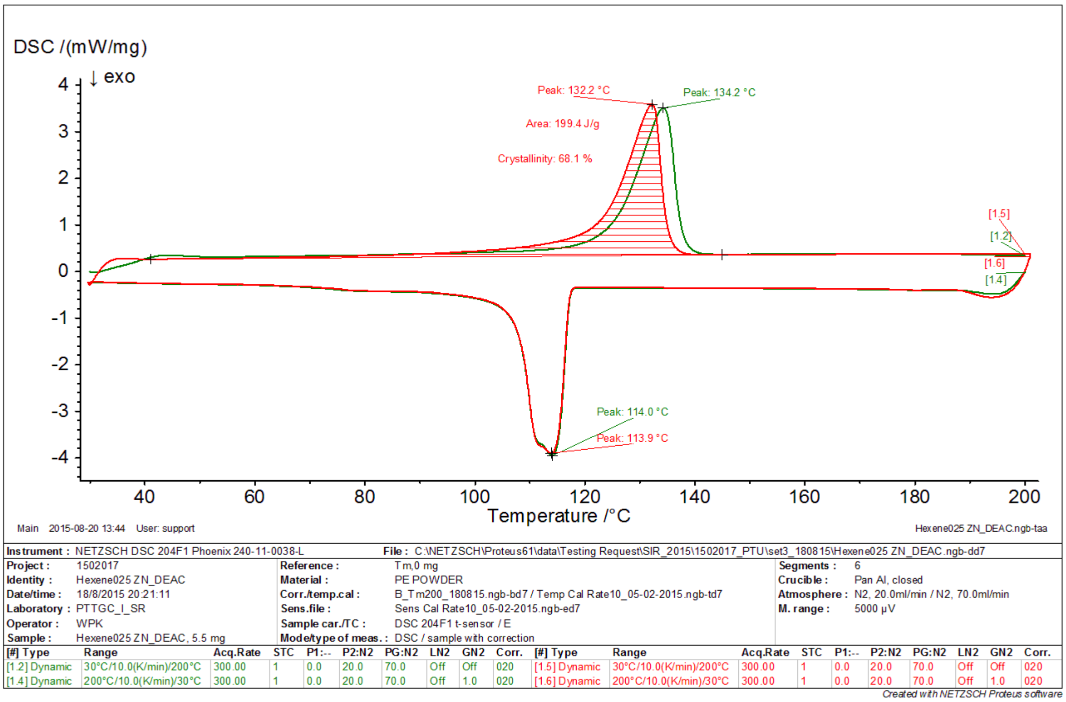
Figure 56 DSC of ethylene polymer (Cat.B 1-butene 4.2 mol%).



Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L
File : C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set3_180815\Hexene025 ZN_DEAC.ngb-dd7

Project : 1502017
Identity : Hexene025 ZN_DEAC
Date/time : 18/8/2015 20:21:11
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Hexene025 ZN_DEAC, 5.5 mg

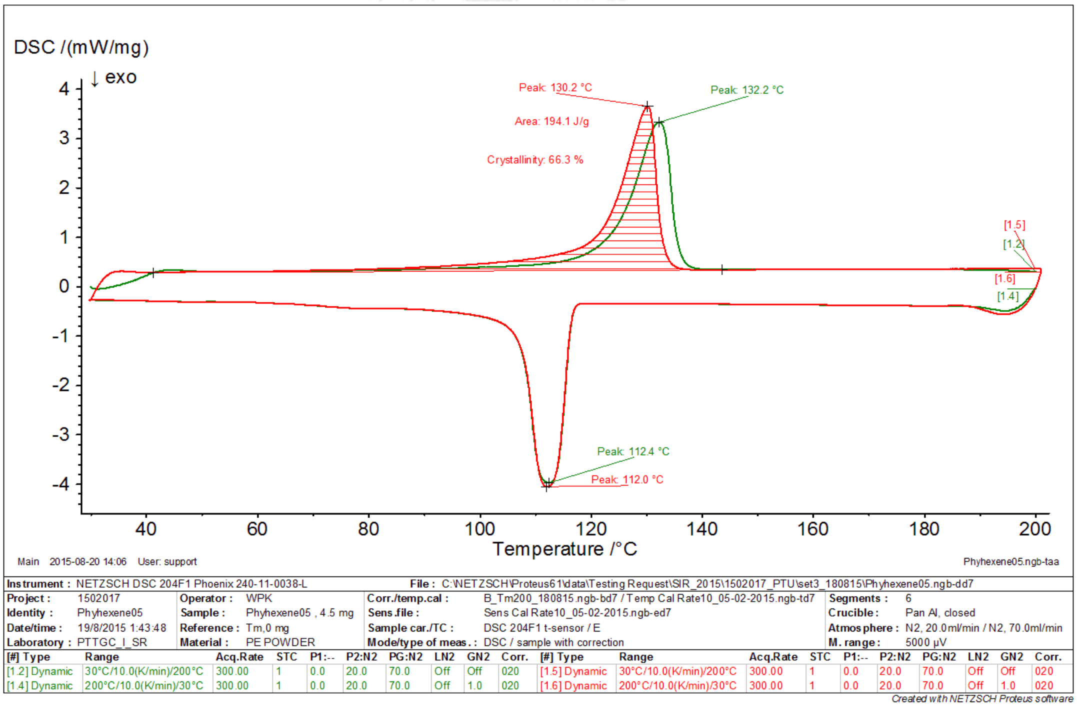
Reference : Tm,0 mg
Material : PE POWDER
Corr./temp.cal : B_Tm200_180815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction

Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 57 DSC of ethylene polymer (Cat.B 1-hexene 0.25 mol).



Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L
File : C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set3_180815\Phyhexene05.ngb-dd7

Project : 1502017
Identity : Phyhexene05
Date/time : 19/8/2015 1:43:48
Laboratory : PTTGC_I_SR

Operator : WPK
Sample : Phyhexene05 , 4.5 mg
Reference : Tm,0 mg
Material : PE POWDER

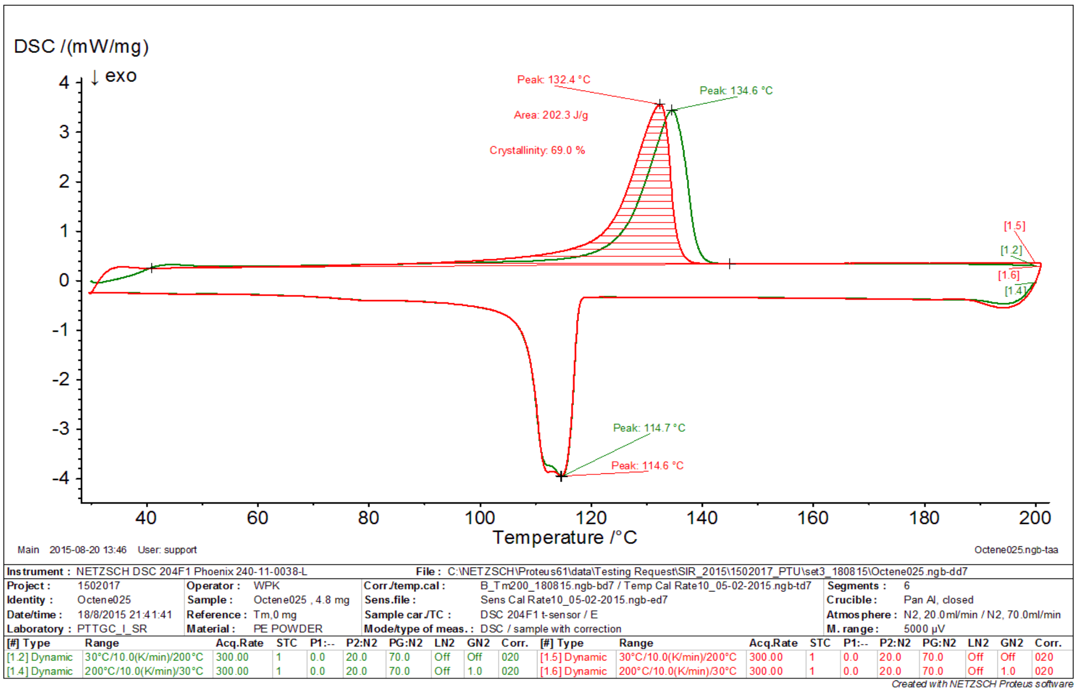
Corr./temp.cal : B_Tm200_180815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction

Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 58 DSC of ethylene polymer (Cat.B 1-hexene 0.5 mol).



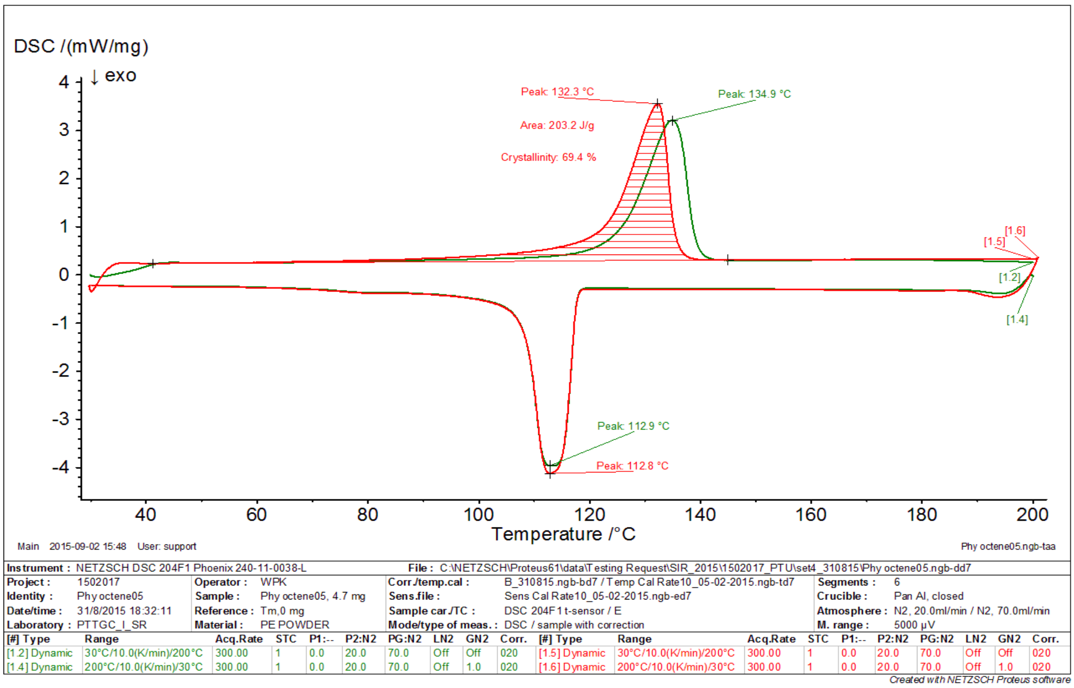
Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set3_180815\Octene025.ngb-dd7

Project :	1502017	**Operator :**	WPK	**Corr./temp.cal :**	B_Tm200_180815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7	**Segments :**	6
Identity :	Octene025	**Sample :**	Octene025 , 4.8 mg	**Sens.file :**	Sens Cal Rate10_05-02-2015.ngb-ed7	**Crucible :**	Pan Al, closed
Date/time :	18/8/2015 21:41:41	**Reference :**	Tm,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Atmosphere :**	N2, 20.0ml/min / N2, 70.0ml/min
Laboratory :	PTTGC_I_SR	**Material :**	PE POWDER	**Mode/type of meas. :**	DSC / sample with correction	**M. range :**	5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 59 DSC of ethylene polymer (Cat.B 1-octene 0.25 mol).



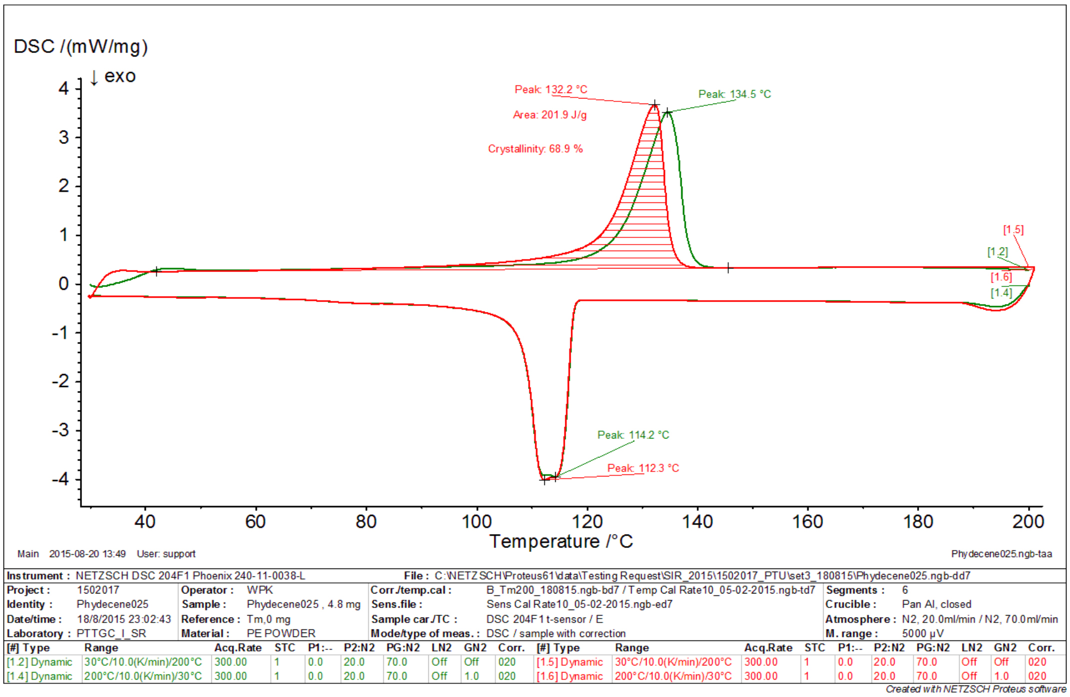
Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set4_310815\Phy octene05.ngb-dd7

Project :	1502017	**Operator :**	WPK	**Corr./temp.cal :**	B_310815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7	**Segments :**	6
Identity :	Phy octene05	**Sample :**	Phy octene05, 4.7 mg	**Sens.file :**	Sens Cal Rate10_05-02-2015.ngb-ed7	**Crucible :**	Pan Al, closed
Date/time :	31/8/2015 18:32:11	**Reference :**	Tm,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Atmosphere :**	N2, 20.0ml/min / N2, 70.0ml/min
Laboratory :	PTTGC_I_SR	**Material :**	PE POWDER	**Mode/type of meas. :**	DSC / sample with correction	**M. range :**	5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 60 DSC of ethylene polymer (Cat.B 1-octene 0.5 mol).



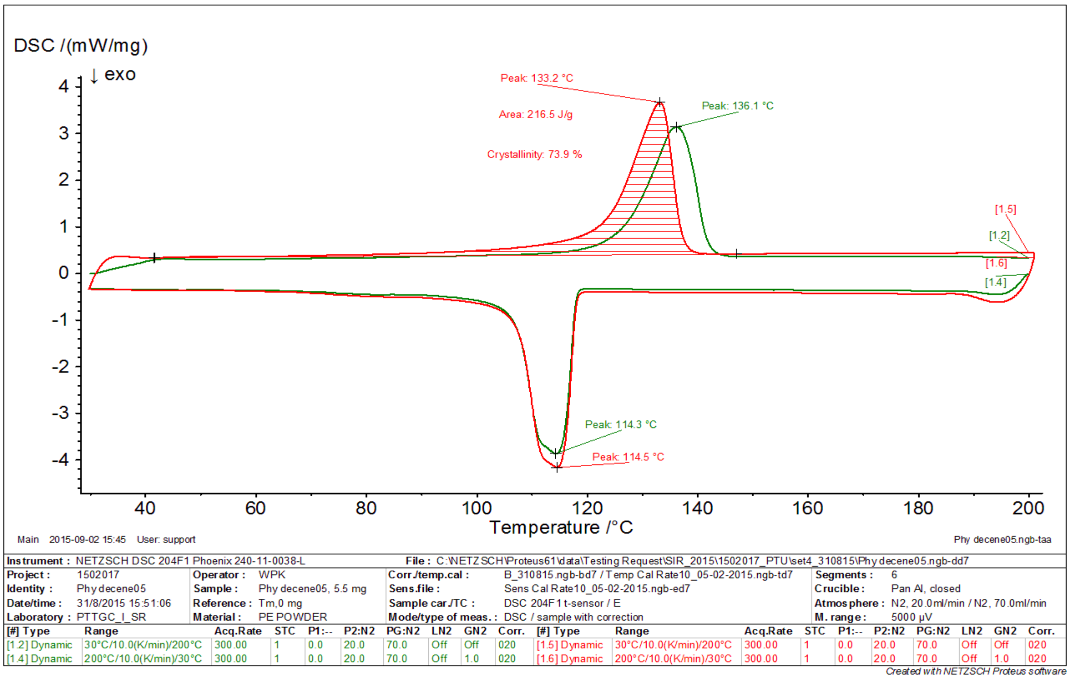
Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set3_180815\Phydecene025.ngb-dd7

Project : 1502017 **Operator :** WPK **Corr./temp.cal :** B_Tm200_180815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7 **Segments :** 6
Identity : Phydecene025 **Sample :** Phydecene025 , 4.8 mg **Sens.file :** Sens Cal Rate10_05-02-2015.ngb-ed7 **Crucible :** Pan Al, closed
Date/time : 18/8/2015 23:02:43 **Reference :** Tm,0 mg **Sample car./TC :** DSC 204F1 t-sensor / E **Atmosphere :** N2, 20.0ml/min / N2, 70.0ml/min
Laboratory : PTTGC_I_SR **Material :** PE POWDER **Mode/type of meas. :** DSC / sample with correction **M. range :** 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 61 DSC of ethylene polymer (Cat.B 1-decene 0.25 mol).



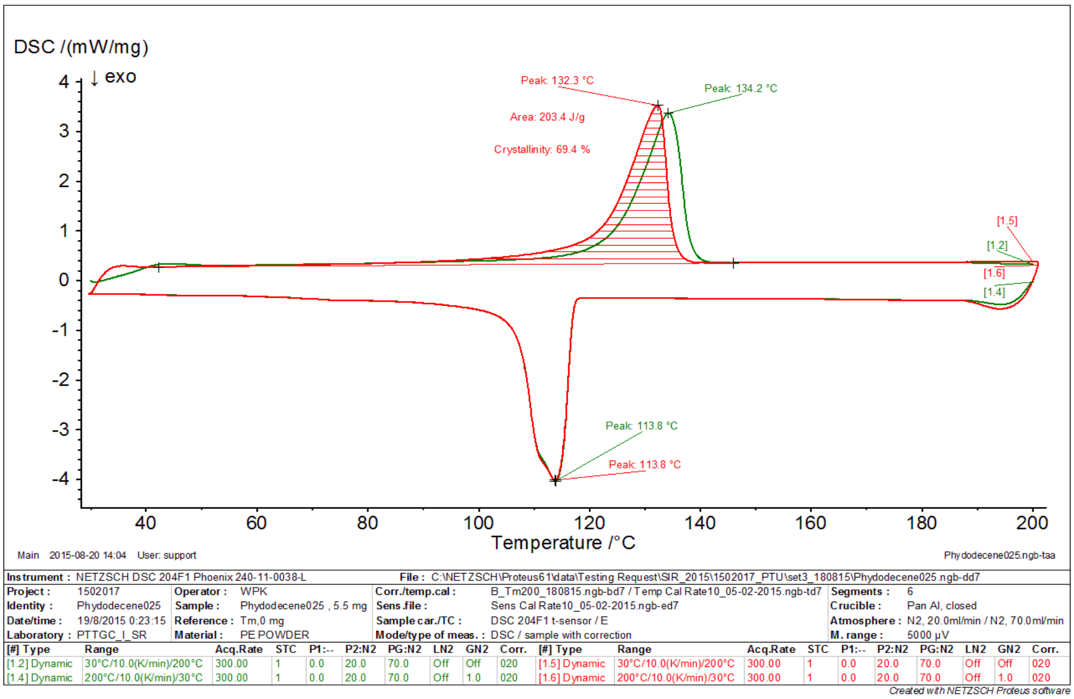
Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set4_310815\Phy decene05.ngb-dd7

Project : 1502017 **Operator :** WPK **Corr./temp.cal :** B_310815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7 **Segments :** 6
Identity : Phy decene05 **Sample :** Phy decene05, 5.5 mg **Sens.file :** Sens Cal Rate10_05-02-2015.ngb-ed7 **Crucible :** Pan Al, closed
Date/time : 31/8/2015 15:51:06 **Reference :** Tm,0 mg **Sample car./TC :** DSC 204F1 t-sensor / E **Atmosphere :** N2, 20.0ml/min / N2, 70.0ml/min
Laboratory : PTTGC_I_SR **Material :** PE POWDER **Mode/type of meas. :** DSC / sample with correction **M. range :** 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 62 DSC of ethylene polymer (Cat.B 1-decene 0.5 mol).



Main 2015-08-20 14:04 User: support

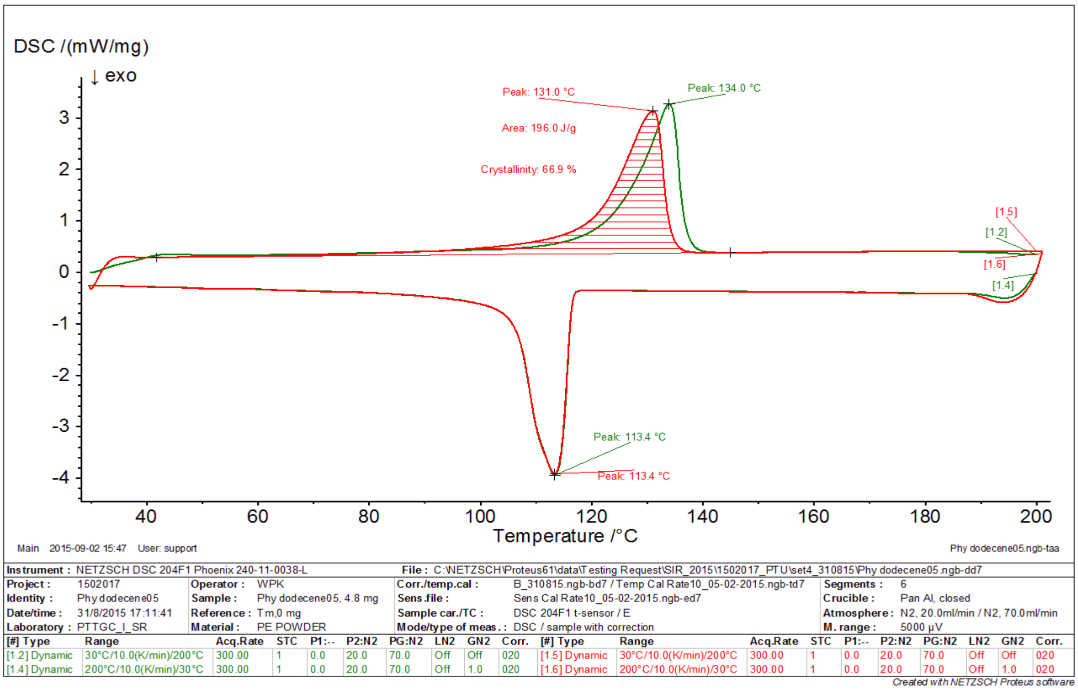
Phydodecene025.ngb-taa

Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L
File : C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set3_180815\Phydodecene025.ngb-dd7
Project : 1502017
Identity : Phydodecene025
Date/time : 19/8/2015 0:23:15
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Phydodecene025 , 5.5 mg
Reference : Tm,0 mg
Material : PE POWDER
Corr./temp.cal : B_Tm200_180815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction
Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020
[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 63 DSC of ethylene polymer (Cat.B 1-dodecene 0.25 mol).



Main 2015-09-02 15:47 User: support

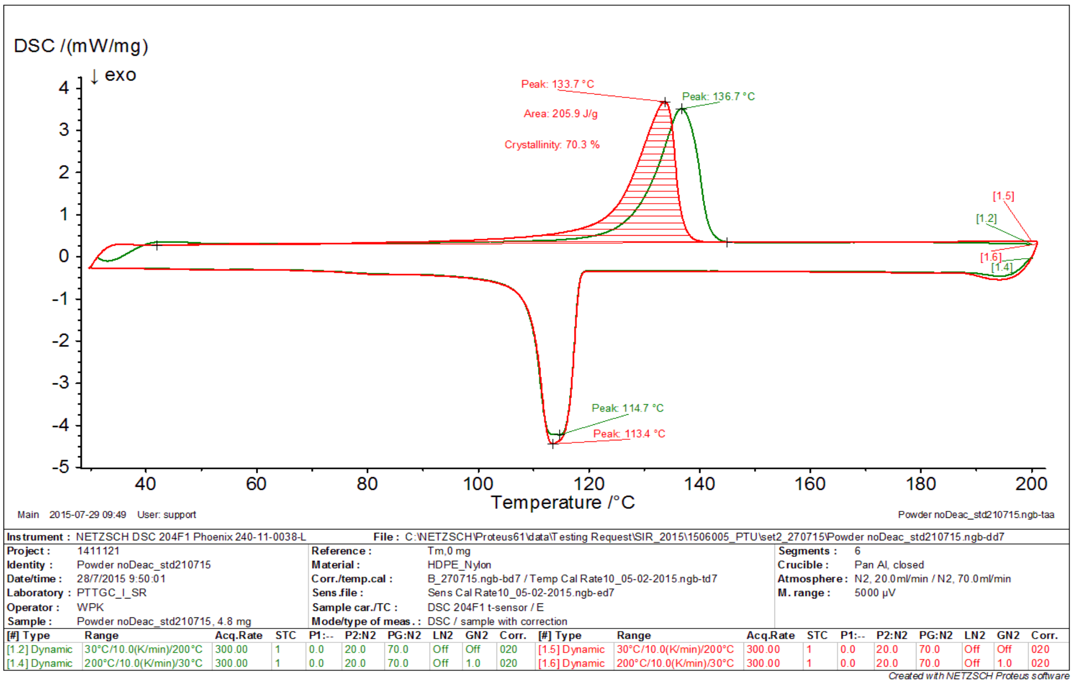
Phy dodecene05.ngb-taa

Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L
File : C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set4_310815\Phy dodecene05.ngb-dd7
Project : 1502017
Identity : Phy dodecene05
Date/time : 31/8/2015 17:11:41
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Phy dodecene05, 4.8 mg
Reference : Tm,0 mg
Material : PE POWDER
Corr./temp.cal : B_310815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction
Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020
[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 64 DSC of ethylene polymer (Cat.B 1-dodecene 0.5 mol).



Main 2015-07-29 09:49 User: support

Powder noDeac_std210715.ngb-taa

Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1506005_PTU\set2_270715\Powder noDeac_std210715.ngb-dd7

Project : 1411121
Identity : Powder noDeac_std210715
Date/time : 28/7/2015 9:50:01
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Powder noDeac_std210715, 4.8 mg

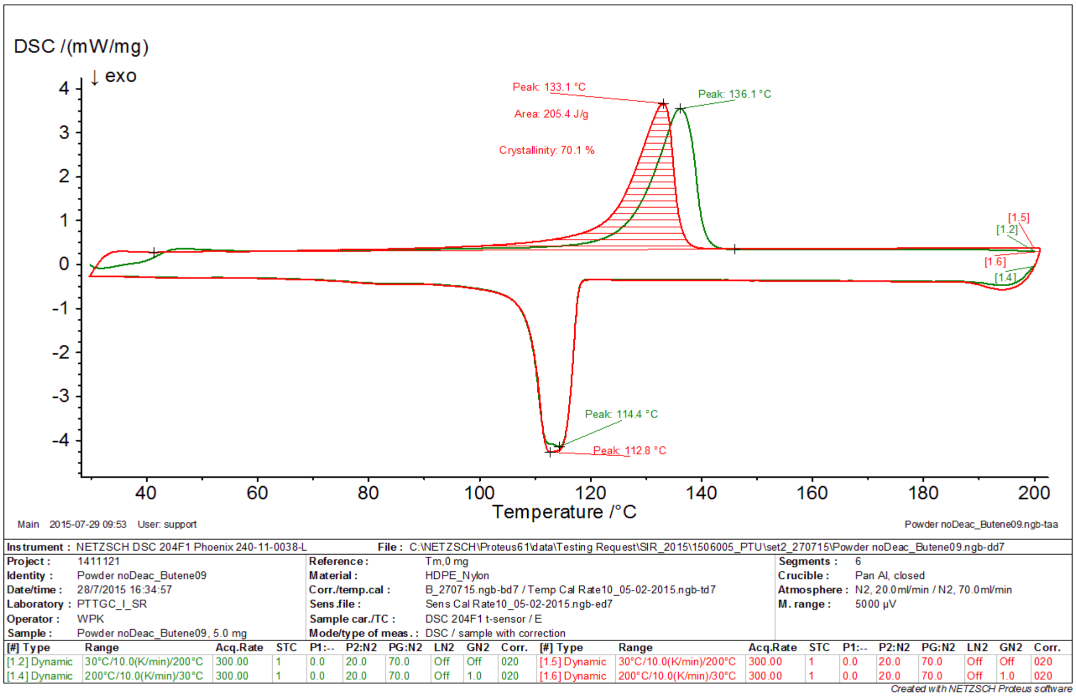
Reference : Tm,0 mg
Material : HDPE_Nylon
Corr./temp.cal : B_270715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction

Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 65 DSC of ethylene polymer (Cat.C nocomonomer).



Main 2015-07-29 09:53 User: support

Powder noDeac_Butene09.ngb-taa

Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1506005_PTU\set2_270715\Powder noDeac_Butene09.ngb-dd7

Project : 1411121
Identity : Powder noDeac_Butene09
Date/time : 28/7/2015 16:34:57
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Powder noDeac_Butene09, 5.0 mg

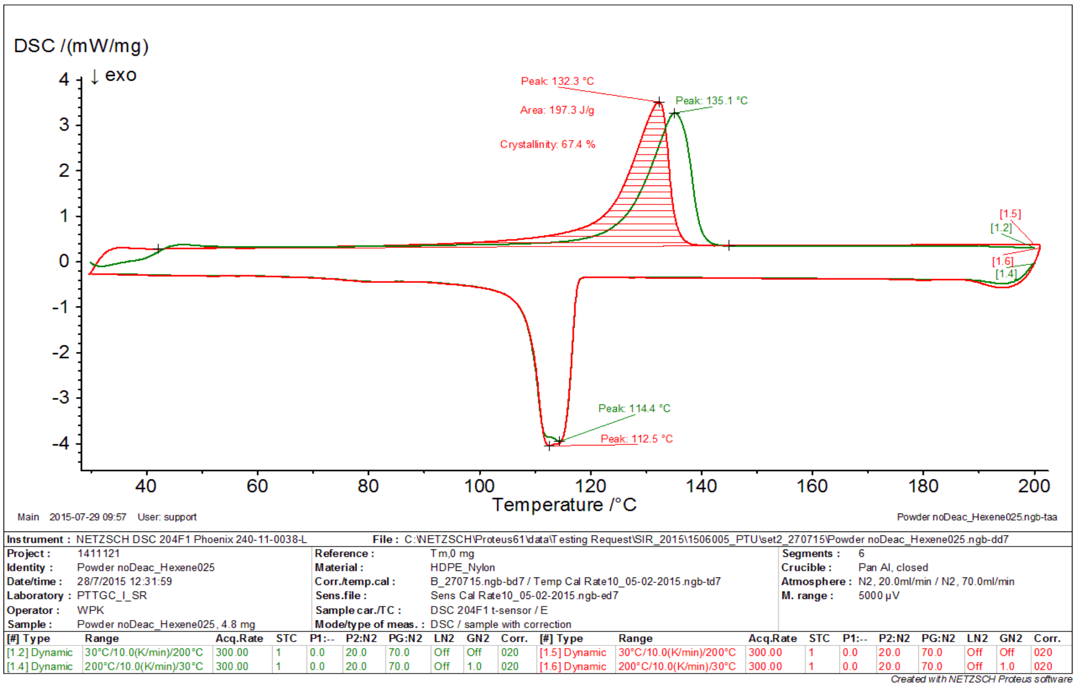
Reference : Tm,0 mg
Material : HDPE_Nylon
Corr./temp.cal : B_270715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction

Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 66 DSC of ethylene polymer (Cat.C 1-butene 0.9 mol%).



Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1506005_PTU\set2_270715\Powder noDeac_Hexene025.ngb-dd7

Project : 1411121
Identity : Powder noDeac_Hexene025
Date/time : 28/7/2015 12:31:59
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Powder noDeac_Hexene025, 4.8 mg

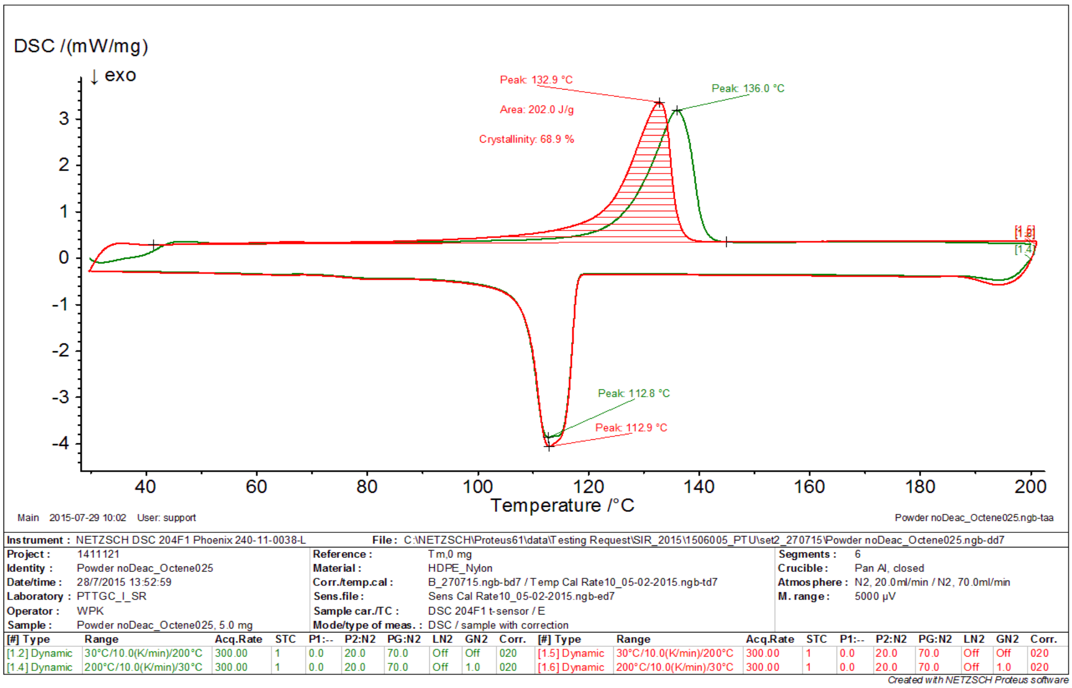
Reference : Tm,0 mg
Material : HDPE_Nylon
Corr./temp.cal : B_270715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction

Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 67 DSC of ethylene polymer (Cat.C 1-hexene 0.25 mol).



Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1506005_PTU\set2_270715\Powder noDeac_Octene025.ngb-dd7

Project : 1411121
Identity : Powder noDeac_Octene025
Date/time : 28/7/2015 13:52:59
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Powder noDeac_Octene025, 5.0 mg

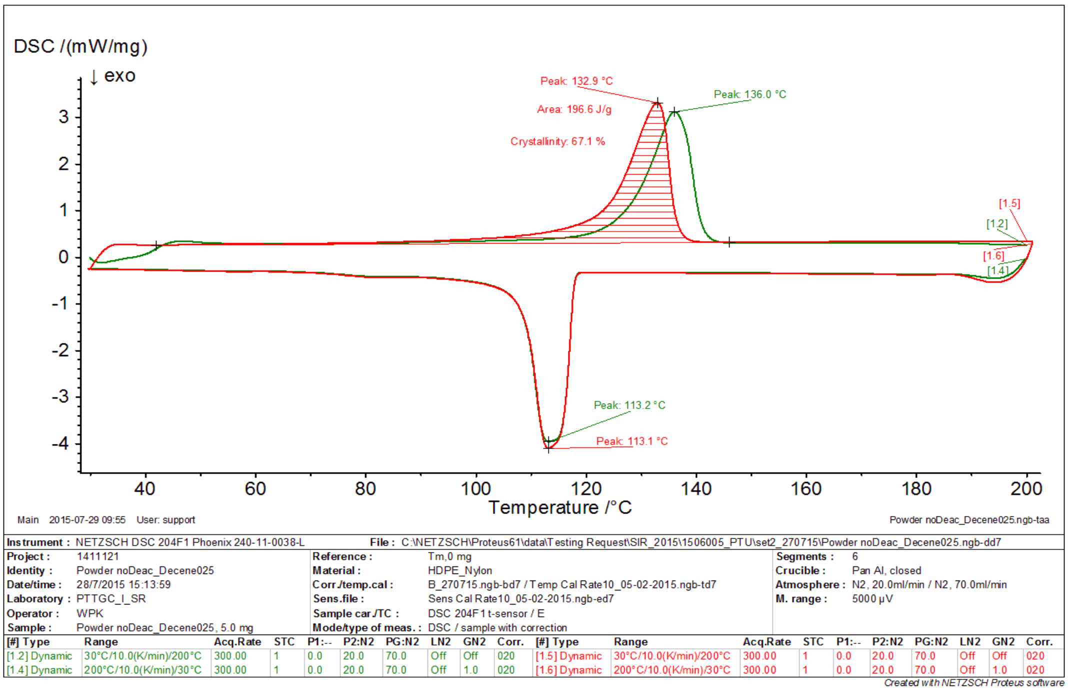
Reference : Tm,0 mg
Material : HDPE_Nylon
Corr./temp.cal : B_270715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction

Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 68 DSC of ethylene polymer (Cat.C 1-octene 0.25 mol).



Main 2015-07-29 09:55 User: support

Powder noDeac_Decene025.ngb-taa

Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1506005_PTU\set2_270715\Powder noDeac_Decene025.ngb-dd7

Project : 1411121
Identity : Powder noDeac_Decene025
Date/time : 28/7/2015 15:13:59
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : Powder noDeac_Decene025, 5.0 mg

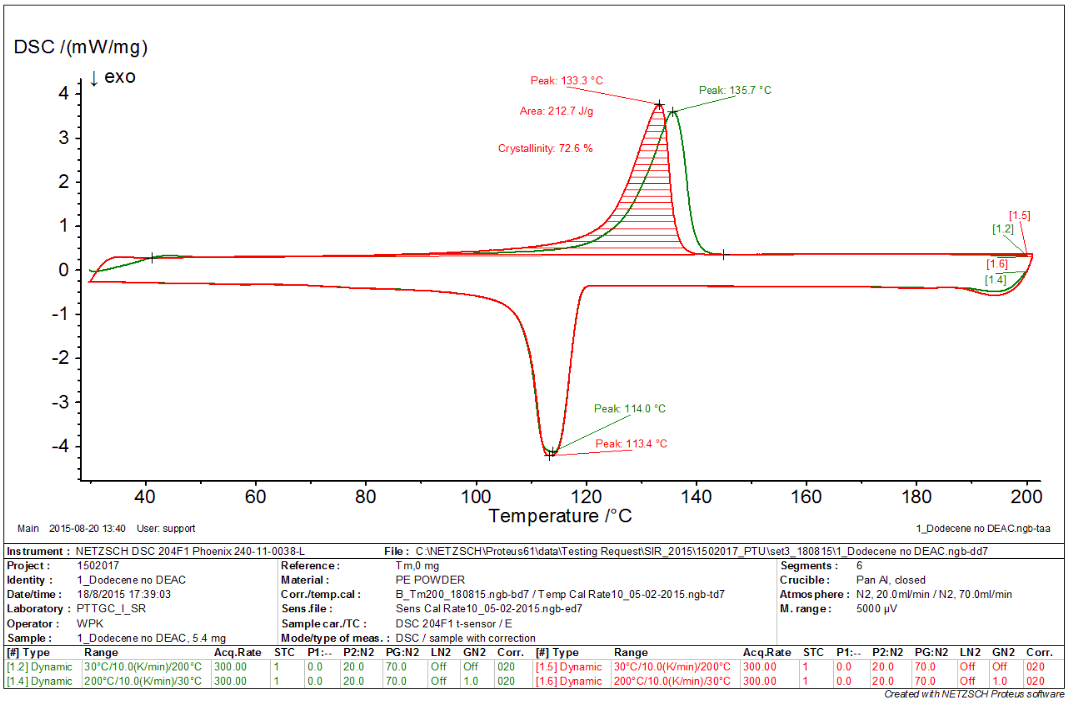
Reference : Tm,0 mg
Material : HDPE_Nylon
Corr./temp.cal : B_270715.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction

Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 69 DSC of ethylene polymer (Cat.C 1-decene 0.25 mol).



Main 2015-08-20 13:40 User: support

1_Dodecene no DEAC.ngb-taa

Instrument : NETZSCH DSC 204F1 Phoenix 240-11-0038-L **File :** C:\NETZSCH\Proteus61\data\Testing Request\SIR_2015\1502017_PTU\set3_180815\1_Dodecene no DEAC.ngb-dd7

Project : 1502017
Identity : 1_Dodecene no DEAC
Date/time : 18/8/2015 17:39:03
Laboratory : PTTGC_I_SR
Operator : WPK
Sample : 1_Dodecene no DEAC, 5.4 mg

Reference : Tm,0 mg
Material : PE POWDER
Corr./temp.cal : B_Tm200_180815.ngb-bd7 / Temp Cal Rate10_05-02-2015.ngb-td7
Sens.file : Sens Cal Rate10_05-02-2015.ngb-ed7
Sample car./TC : DSC 204F1 t-sensor / E
Mode/type of meas. : DSC / sample with correction

Segments : 6
Crucible : Pan Al, closed
Atmosphere : N2, 20.0ml/min / N2, 70.0ml/min
M. range : 5000 µV

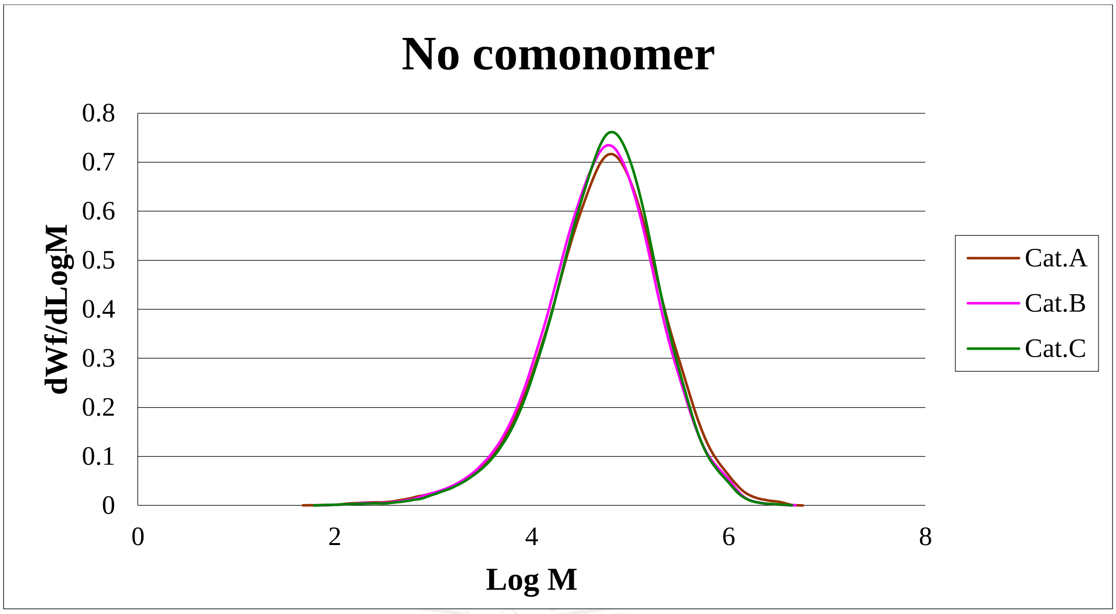
[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.	[#] Type	Range	Acq.Rate	STC	P1:--	P2:N2	PG:N2	LN2	GN2	Corr.
[1.2] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020	[1.5] Dynamic	30°C/10.0(K/min)/200°C	300.00	1	0.0	20.0	70.0	Off	Off	020
[1.4] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020	[1.6] Dynamic	200°C/10.0(K/min)/30°C	300.00	1	0.0	20.0	70.0	Off	1.0	020

Created with NETZSCH Proteus software

Figure 70 DSC of ethylene polymer (Cat.C 1-dodecene 0.25 mol).

Appendix E

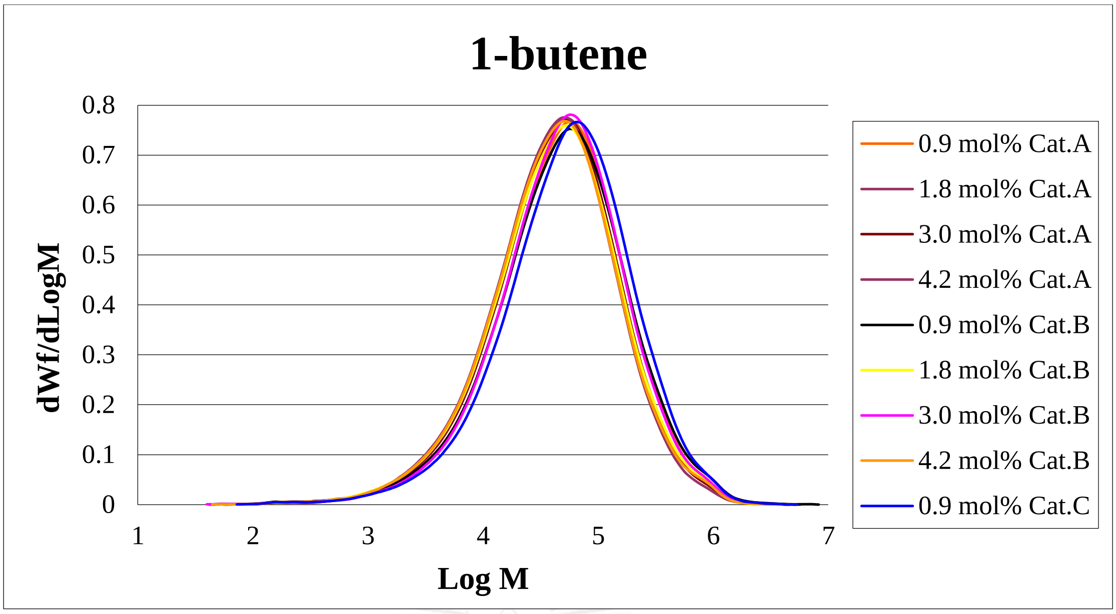
Gel permeation chromatography



	Cat.A nocomonomer	Cat.B nocomonomer	Cat.C nocomonomer
Mw (g/mol)	113016	111059	128216
Mn (g/mol)	15744	14351	13737
MW / Mn	7.18	7.74	9.33
Mz (g/mol)	406992	419833	569494
Mz1 (g/mol)	1058314	1053293	1530977
Mp (g/mol)	65199	60702	63917
Mv (g/mol)	90977	88196	99631
IV (dL/g)	1.3662	1.3371	1.455
Bulk CH_3/1000C	3.7	3.7	3.7
Bulk SCB/1000C	2	2.2	1.6

Remark: GPC-IR condition: Solvent = 1,2,4-trichlorobenzene, T = 140 °C
Polymerization condition: Reactor 5 L, solvent = hexane 2.5 L, T = 80°C, time = 70 min, PH2 = 3.5 bar, Ptotal = 8 bar, Cocat = TEA 1mmol/L, Cat = 0.01 mmol/L

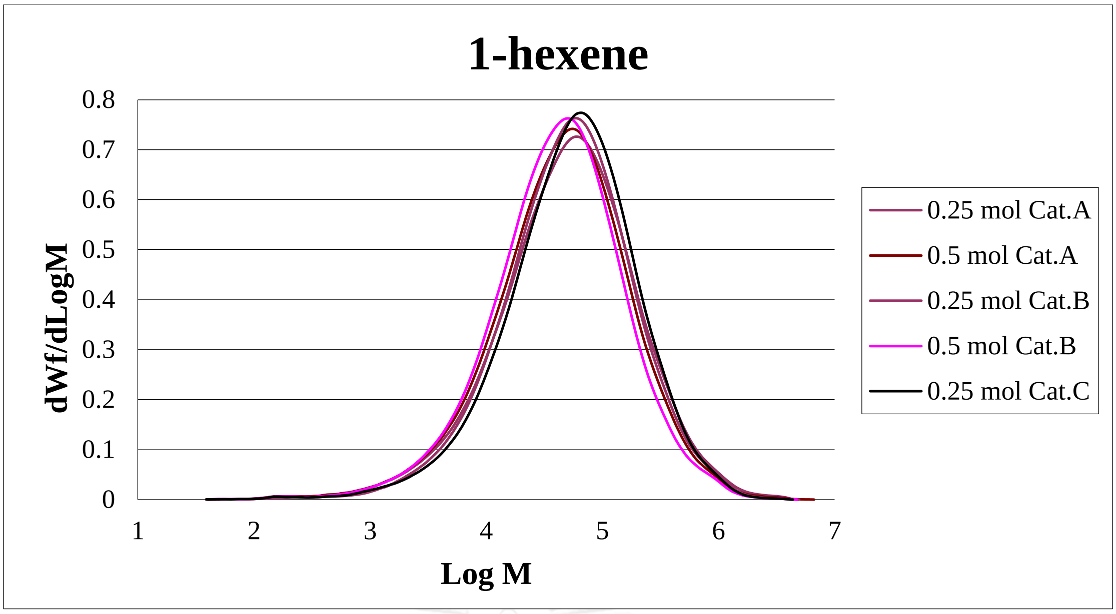
Figure 71 GPC of polyethylene with no comonomer synthesized by the three catalysts.



	Cat.C Butene 0.9	Cat.B Butene 4.2	Cat.B Butene 3.0	Cat.B Butene 1.8	Cat.B Butene 0.9	Cat.A Butene 4.2	Cat.A Butene 3.0	Cat.A Butene 1.8	Cat.A Butene 0.9
Mw (g/mol)	113667	87067	98739	91397	107347	83565	91161	91275	100618
Mn (g/mol)	15946	12631	14203	13441	13766	13145	13092	14279	13342
MW / Mn	7.13	6.89	6.95	6.8	7.8	6.36	6.96	6.39	7.54
Mz (g/mol)	397161	323381	345847	337329	477983	319084	367171	361432	387680
Mz1 (g/mol)	1003526	814803	868313	814210	1765660	938360	1148844	1067102	1059753
Mp (g/mol)	65450	51265	57714	52876	57907	50931	53535	52859	57624
Mv (g/mol)	91855	69778	79869	73069	84723	67280	72937	73081	80516
IV (dL/g)	1.3753	1.1368	1.2483	1.1737	1.3004	1.1084	1.1722	1.1738	1.2553
Bulk CH_3 / 1000C	4.3	5.7	5.2	4.7	4.5	7.1	6.5	6.1	5.6
Bulk SCB / 1000C	2.5	3.5	3.2	2.6	2.5	5	4.3	4.1	3.5

Remark: GPC-IR condition: Solvent = 1,2,4-trichlorobenzene, T = 140 °C
Polymerization condition: Reactor 5 L, solvent = hexane 2.5 L, T = 80°C, time = 70 min, PH2 = 3.5 bar, Ptotal = 8 bar, Cocat = TEA 1mmol/L, Cat = 0.01 mmol/L

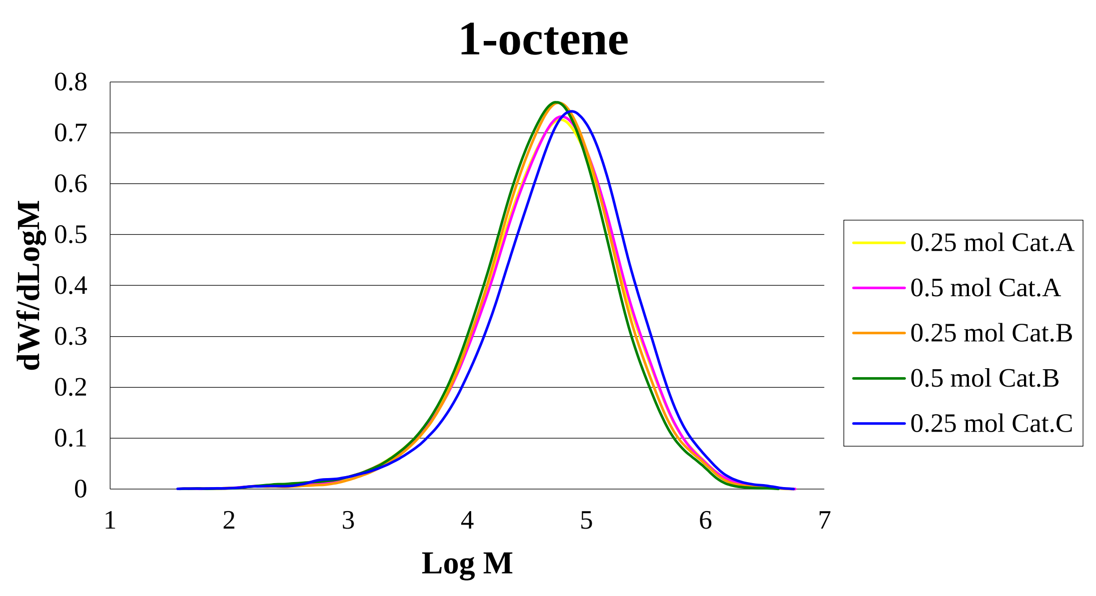
Figure 72 GPC of polyethylene with various concentration of 1-butene comonomer synthesized by the three catalysts.



	Cat.C Hexene 0.25	Cat.B Hexene 0.5	Cat.B Hexene 0.25	Cat.A Hexene 0.5	Cat.A Hexene 0.25
Mw (g/mol)	112760	90918	108396	103667	117651
Mn (g/mol)	14934	12142	15367	12392	13332
MW / Mn	7.55	7.49	7.05	8.37	8.82
Mz (g/mol)	394719	394475	419430	487417	539462
Mz1 (g/mol)	1002829	1179113	1093396	1539705	1505277
Mp (g/mol)	65099	50366	58909	55290	60094
Mv (g/mol)	91239	71756	86373	80884	91360
IV (dL/g)	1.3689	1.159	1.3179	1.2593	1.3702
Bulk CH_3 / 1000C	4.2	5.3	4.7	6	4.8
Bulk SCB / 1000C	2.3	3	2.8	3.8	3.8

Remark: GPC-IR condition: Solvent = 1,2,4-trichlorobenzene, T = 140 °C
Polymerization condition: Reactor 5 L, solvent = hexane 2.5 L, T = 80°C, time = 70 min, PH2 = 3.5 bar, Ptotal = 8 bar, Cocat = TEA 1mmol/L, Cat = 0.01 mmol/L

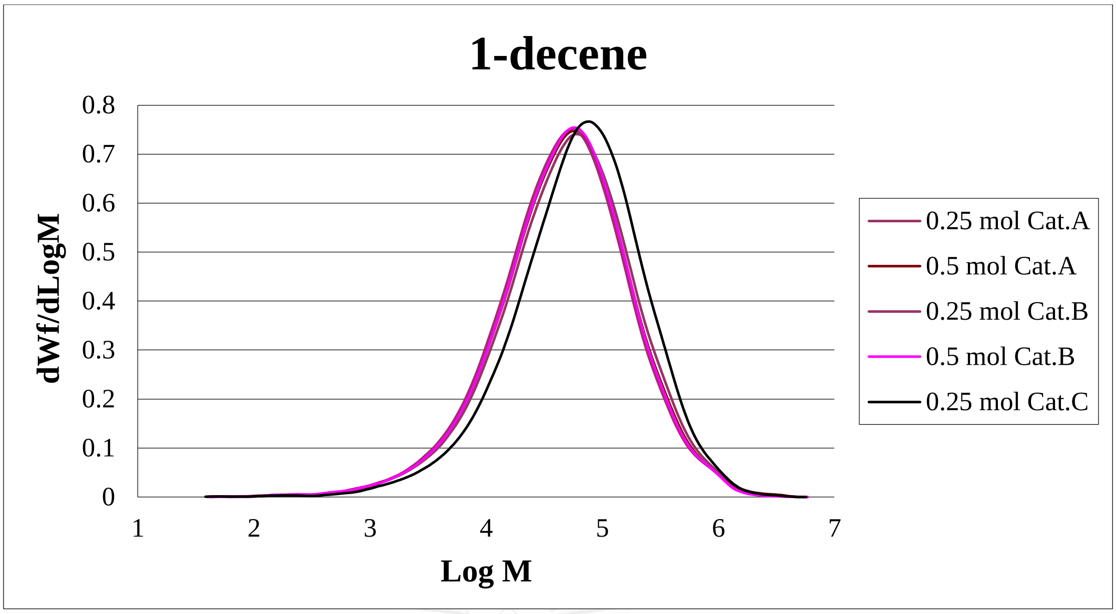
Figure 73 GPC of polyethylene with various concentration of 1-hexene comonomer synthesized by the three catalysts.



	Cat.C Octene 0.25	Cat.B Octene 0.5	Cat.B Octene 0.25	Cat.A Octene 0.5	Cat.A Octene 0.25
Mw (g/mol)	137272	98310	108999	118039	116799
Mn (g/mol)	13730	12218	13978	13440	14057
MW / Mn	10	8.05	7.8	8.78	8.31
Mz (g/mol)	552185	370193	452753	511903	506712
Mz1 (g/mol)	1487711	950555	1293910	1455077	1396148
Mp (g/mol)	75149	55925	58622	62204	60628
Mv (g/mol)	108657	78492	86310	92547	91324
IV (dL/g)	1.5451	1.2333	1.3172	1.3825	1.3698
Bulk CH_3 / 1000C	4.2	4.2	4.2	4.5	4.2
Bulk SCB / 1000C	2.1	1.9	2.2	2.4	2.2

Remark: GPC-IR condition: Solvent = 1,2,4-trichlorobenzene, T = 140 °C
Polymerization condition: Reactor 5 L, solvent = hexane 2.5 L, T = 80°C, time = 70 min, P_{H2} = 3.5 bar, P_{total} = 8 bar, Cocat = TEA 1mmol/L, Cat = 0.01 mmol/L

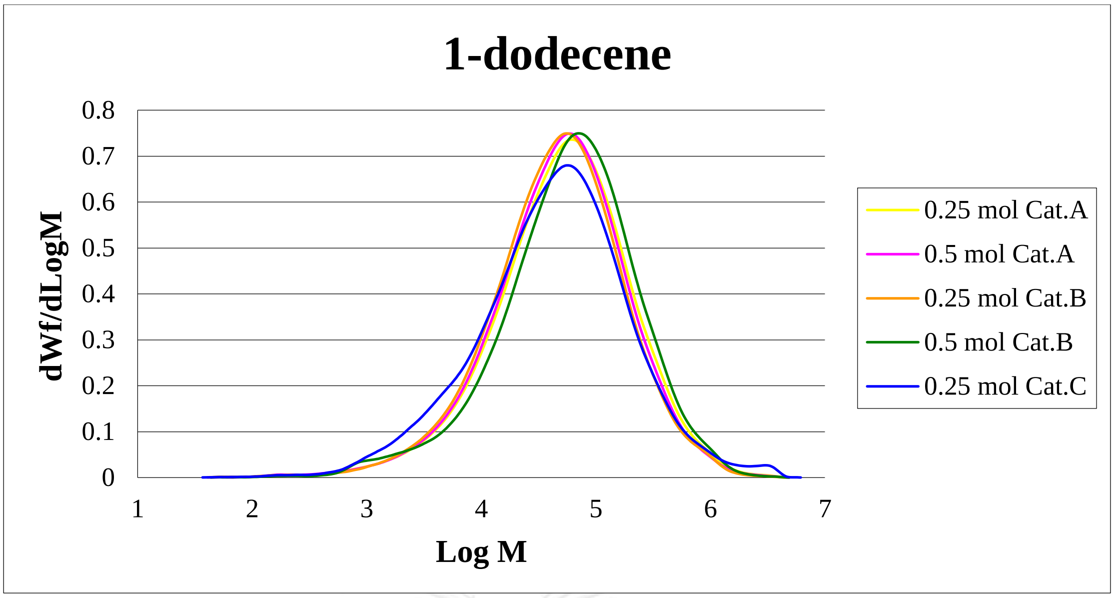
Figure 74 GPC of polyethylene with various concentration of 1-octene comonomer synthesized by the three catalysts.



	Cat.C Decene 0.25	Cat.B Decene 0.5	Cat.B Decene 0.25	Cat.A Decene 0.5	Cat.A Decene 0.25
Mw (g/mol)	130294	103148	101567	108132	114709
Mn (g/mol)	16863	13747	13531	14068	12999
MW / Mn	7.73	7.5	7.51	7.69	8.82
Mz (g/mol)	455088	400178	416633	478930	493267
Mz1 (g/mol)	1175893	1106795	1141490	1384062	1392725
Mp (g/mol)	75818	57427	55152	57157	60276
Mv (g/mol)	105483	82131	80270	84806	90124
IV (dL/g)	1.5137	1.2727	1.2526	1.3013	1.3573
Bulk CH_3 / 1000C	4.1	4.1	4.1	4.3	4.1
Bulk SCB / 1000C	2.5	2	2	2.3	2

Remark: GPC-IR condition: Solvent = 1,2,4-trichlorobenzene, T = 140 °C
Polymerization condition: Reactor 5 L, solvent = hexane 2.5 L, T = 80°C, time = 70 min, P_{H2} = 3.5 bar, P_{total} = 8 bar, Cocat = TEA 1mmol/L, Cat = 0.01 mmol/L

Figure 75 GPC of polyethylene with various concentration of 1-decene comonomer synthesized by the three catalysts.



	Cat.C Dodecene 0.25	Cat.B Dodecene 0.5	Cat.B Dodecene 0.25	Cat.A Dodecene 0.5	Cat.A Dodecene 0.25
Mw (g/mol)	127268	127008	102119	109092	117226
Mn (g/mol)	10270	14660	12413	13031	13201
MW / Mn	12.39	8.66	8.23	8.37	8.88
Mz (g/mol)	914645	460980	416795	458971	487765
Mz1 (g/mol)	2321692	1149254	1127708	1299909	1320017
Mp (g/mol)	56802	71132	55648	59114	61911
Mv (g/mol)	90970	101586	80707	86110	92266
IV (dL/g)	1.3661	1.4747	1.2574	1.3151	1.3796
Bulk CH_3 / 1000C	4	3.8	3.8	4.3	3.8
Bulk SCB / 1000C	1.3	1.8	1.5	2.2	1.6

Remark: GPC-IR condition: Solvent = 1,2,4-trichlorobenzene, T = 140 °C Polymerization condition: Reactor 5 L, solvent = hexane 2.5 L, T = 80°C, time = 70 min, P_{H2} = 3.5 bar, P_{total} = 8 bar, Cocat = TEA 1mmol/L, Cat = 0.01 mmol/L

Figure 76 GPC of polyethylene with various concentration of 1-dodecene comonomer synthesized by the three catalysts

1. Nattapol Samanukul, Supawan Tantayanon, Sutheerawat Samingprai, Worawat Chuencheep “Comonomer incorporation of ethylene polymerization for HDPE using the different preparation technique of Ziegler-Natta catalyst” (The proceedings of pure and applied chemistry international conference, PACCON 2016, Bangkok, Thailand).

VITA

Nattapol Samanukul was born on July 16, 1989 in Saraburi, Thailand. He graduated in a Chemical Engineering major with GPA 3.70 from Thammasat University in March 2012 and he continued his Master's degree in Petrochemistry and Polymer Science, Chulalongkorn University in 2013. He is now working at PTT Global Chemical Public Company Limited.