

ผลของภาวะในกระบวนการพอลิเมอร์ไรเซชัน ต่อค่าความว่องไวของตัวเร่งปฏิกิริยา  
และสมบัติของพอลิเมอร์ โดยใช้ตัวเร่งปฏิกิริยาเมทัลโลซีนที่มีตัวรองรับ



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บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)

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THE EFFECT OF POLYMERIZATION CONDITIONS ON CATALYST ACTIVITY AND  
POLYMER PROPERTIES USING SUPPORTED METALLOCENE CATALYST

The emblem of Chulalongkorn University, featuring a central figure holding a sword, surrounded by a sunburst and a tiered base.

Miss Phakairat Supaphan

จุฬาลงกรณ์มหาวิทยาลัย  
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ผกายรัตน์ ศุภพันธุ์ : ผลของภาวะในกระบวนการพอลิเมอไรเซชัน ต่อค่าความว่องไวของตัวเร่งปฏิกิริยา และสมบัติของพอลิเมอร์ โดยใช้ตัวเร่งปฏิกิริยาเมทัลโลซีนที่มีตัวรองรับ. (THE EFFECT OF POLYMERIZATION CONDITIONS ON CATALYST ACTIVITY AND POLYMER PROPERTIES USING SUPPORTED METALLOCENE CATALYST) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. บรรเจิด จงสมจิตร, 109 หน้า.

ในวิทยานิพนธ์ฉบับนี้ได้ทำการศึกษาผลของภาวะในกระบวนการพอลิเมอไรเซชัน โดยใช้ตัวเร่งปฏิกิริยาเมทัลโลซีนที่มีตัวรองรับ ต่อค่าความว่องไวของตัวเร่งปฏิกิริยา และสมบัติของพอลิเมอร์ ทั้งในระบบโฮโม และ โคพอลิเมอไรเซชันแบบสเลอรี ซึ่งในส่วนแรกทำการศึกษาผลของอุณหภูมิ, ความดันของเอทิลีน และการตอบสนองของไฮโดรเจน ในกระบวนการพอลิเมอไรเซชัน นอกจากนี้ในส่วนที่สองยังทำการศึกษาเพิ่มเติมโดยศึกษาผลของปริมาณ 1-เฮกซีน ที่เติมในเครื่องปฏิกรณ์ จากผลการทดลองพบว่าค่าความว่องไวของตัวเร่งปฏิกิริยา มีค่าเพิ่มขึ้นเมื่อเพิ่มอุณหภูมิและความดันของเอทิลีนในกระบวนการพอลิเมอไรเซชัน เช่นเดียวกับผลการตอบสนองของไฮโดรเจนแสดงค่าความว่องไวของตัวเร่งปฏิกิริยาเพิ่มสูงขึ้น ที่ความเข้มข้นไฮโดรเจนต่ำ นอกเหนือจากนี้เมื่อทำการเติมปริมาณ 1-เฮกซีนมากขึ้น แสดงค่าความว่องไวของตัวเร่งปฏิกิริยาเพิ่มสูงขึ้นอย่างต่อเนื่องที่อุณหภูมิต่ำ ซึ่งให้ผลตรงกันข้ามที่อุณหภูมิสูง นอกเหนือจากนี้ยังทำการศึกษาสมบัติของพอลิเมอร์ที่ได้พบว่า น้ำหนักโมเลกุลของพอลิเมอร์ถูกควบคุมได้โดยอุณหภูมิและการตอบสนองของไฮโดรเจน ในกระบวนการพอลิเมอไรเซชัน ในทางตรงกันข้ามผลความดันของเอทิลีน และผลของปริมาณ 1-เฮกซีน ที่เติม ไม่ส่งผลกระทบต่อน้ำหนักโมเลกุลของพอลิเมอร์ อย่างไรก็ตามที่อุณหภูมิในการหลอมเหลว และ เปอร์เซนต์ความเป็นผลึกของพอลิเอทิลีนนั้นมีค่าลดลง เมื่อค่าการรวมตัวของปริมาณ 1-เฮกซีนในโคพอลิเมอร์เพิ่มสูงขึ้น

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ภาควิชา วิศวกรรมเคมี

ลายมือชื่อนิสิต .....

สาขาวิชา วิศวกรรมเคมี

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CONDITIONS

PHAKAIRAT SUPAPHAN: THE EFFECT OF POLYMERIZATION CONDITIONS ON  
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In this study, the effects of polymerization conditions were evaluated on polyethylene produced by a supported metallocene catalyst for the catalytic activity and polymer properties in the slurry homo and copolymerization of ethylene. In the first part, the polymerization conditions were carried out to examine the effect of the polymerization temperatures, ethylene pressures and hydrogen response. Moreover, in the second part, we investigated more effect on 1-hexene loaded in the reactor. The results indicated that the catalytic activity was enhanced with increasing polymerization temperatures and ethylene pressures. Also, effect of hydrogen response was study. It was found that the activity increased at low hydrogen concentration. Apart from that at higher 1-hexene loading, the catalytic activity was steadily increasing at low temperature. Moreover, our studies have been found that molecular weight (MW) of polymer were controlled by polymerization temperatures and hydrogen response. However ethylene pressures and 1-hexene loading did not significantly affect. In addition, the melting temperature ( $T_m$ ) and percent crystallinity ( $X_c$ ) of polyethylene decrease with increasing 1-hexene incorporation in the copolymer.

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## CHAPTER I

### INTRODUCTION

Today, polymers and plastics, especially polyethylene (PE), are playing the important role on the material industry and have an influence on daily life. According to their physical properties such as strength, lightness, toughness and resistance to corrosion, polyethylene is used to replace metal in the construction of many household tools and create comforts [1]. Thus, the demand for the polyethylene, is the worldwide annual total polyethylene production by catalytic polymerization processes is approximately 32 million tons of high-density polyethylene (HDPE) [2]. Most polyethylene products are used for packaging including film, bags, sealing, bottles, drums etc. due to its low cost price and process ability, well defined molecular structures and properties [3].

The first generation of ethylene polymerization, polyethylene could be performed. In 1953 Ziegler revealed that high density polyethylene at low pressure with binary mixture of metal alkyls and transition metal salts, and in the next year Natta and his coworkers demonstrated the ability of the same type of catalysts to form isotactic polymers based on alpha-olefins [4]. This technology allows the geometry of the catalyst around the metal center to control the polymer structure. In homogeneous polymerization, the ligand of a catalyst largely controls the geometry of an active metal center in which the polymerization reaction occurs [5]. However, one of the disadvantages of heterogeneous Ziegler–Natta catalysts used for the commercial production of polyolefins is that they have several types of active sites that produce polymer chains with different average properties. It is very difficult to control the behavior of these sites separately. Consequently, polyolefins made with

heterogeneous Ziegler–Natta catalysts have broad distributions of molecular weight (MWD) and chemical composition (CCD) [6].

The new development that may change the polyolefins industry was the introduction of metallocene catalysts. In 1976, Kaminsky and Sinn (Kaminsky 1996) obtained a highly active catalyst with a metallocene complex and MAO. The polymers produced with metallocene catalysts have narrower molecular weight distributions and more uniform incorporation of comonomers than polymers produced with Ziegler catalysts [7]. This opens the door to the production of polyolefins with entirely new improved properties.

In polymer processing, the molecular weight ( $M_w$ ), and the molecular weight distribution (MWD) display basic properties. It is generally accepted that the  $M_w$  is a major determinant of mechanical properties, while MWD is largely responsible for rheological properties. Although high- $M_w$  polyethylene has superior physical properties, it is difficult to process. On the other hand, an increase in MWD tends to improve flowability at high shear rates, which is an important factor in blowing and extrusion techniques. Therefore, it is necessary to control the  $M_w$ , as well as the MWD of polymers in order to optimize both mechanical and rheological properties [8].

Because of the polymerization conditions have influence very much in control of the catalyst activity and polymer properties. Both Ziegler Natta and single site catalysts have responded to conditions in the polymerization The polymerization parameters are such as polymerization temperatures, ethylene pressures, hydrogen, cocatalyst, comonomer and residence time in the reactor etc.

Therefore, in this thesis, study of the relationship between polymerization conditions on catalyst performance in terms of catalyst activity and polymer properties on the homo and copolymerization of ethylene was investigated. So, it has been particularly interesting. This will lead to a catalyst with optimal performance and tailor-made polyolefin product with special properties.

## 1.1 Objectives

1. To investigate the effect of polymerization temperatures, ethylene pressures and hydrogen response on catalytic activity and polymer properties in the slurry of ethylene homopolymerization.
2. To investigate the effect of polymerization temperatures, ethylene pressures and comonomer response on catalytic activity and polymer properties in the slurry of ethylene/1-hexene copolymerization.

## 1.2 Research scopes

The scopes of this research are to study the effect of polymerization conditions by a supported metallocene catalyst on the catalytic activity and polymer properties for homo and copolymerization of ethylene. The scopes are summarized in the detail as follows:

### 1.1.1 Investigate the optimum conditions in the polymerization of ethylene

- 1.2.1.1 Determine the effect of polymerization temperatures at 3 different temperatures i.e. 70°C, 80°C and 90°C on catalytic activity.
- 1.2.1.2 Determine the effect of ethylene pressures at 2 different pressures i.e. 6 barg and 8 barg on catalytic activity.

- 1.2.1.3 Determine the effect of hydrogen response at 3 different hydrogen concentrations i.e. absence of hydrogen, 480 ml and 960 ml on catalytic activity.
- 1.2.1.4 Characterize polyethylene obtained with scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and gel permeation chromatography (GPC)

### 1.1.2 Investigate the optimum conditions in the copolymerization of ethylene/1-hexene

- 1.2.1.1 Determine the effect of polymerization temperature at 3 different temperatures i.e. 60°C, 70°C and 80°C on catalytic activity.
- 1.2.1.2 Determine the effect of ethylene pressures at 2 different pressures i.e. 6 barg and 7 barg on catalytic activity.
- 1.2.1.3 Determine the effect of comonomer response at 3 different volumes 1-hexene i.e. absence of 1-hexene, 10 ml and 15 ml on catalytic activity.
- 1.2.1.4 Characterize polyethylene obtained with scanning electron microscopy (SEM), differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and fourier transforms infrared spectroscopy (FTIR)

### 1.3 Research methodology

The methodology of this research is shown in Figure 1.1.

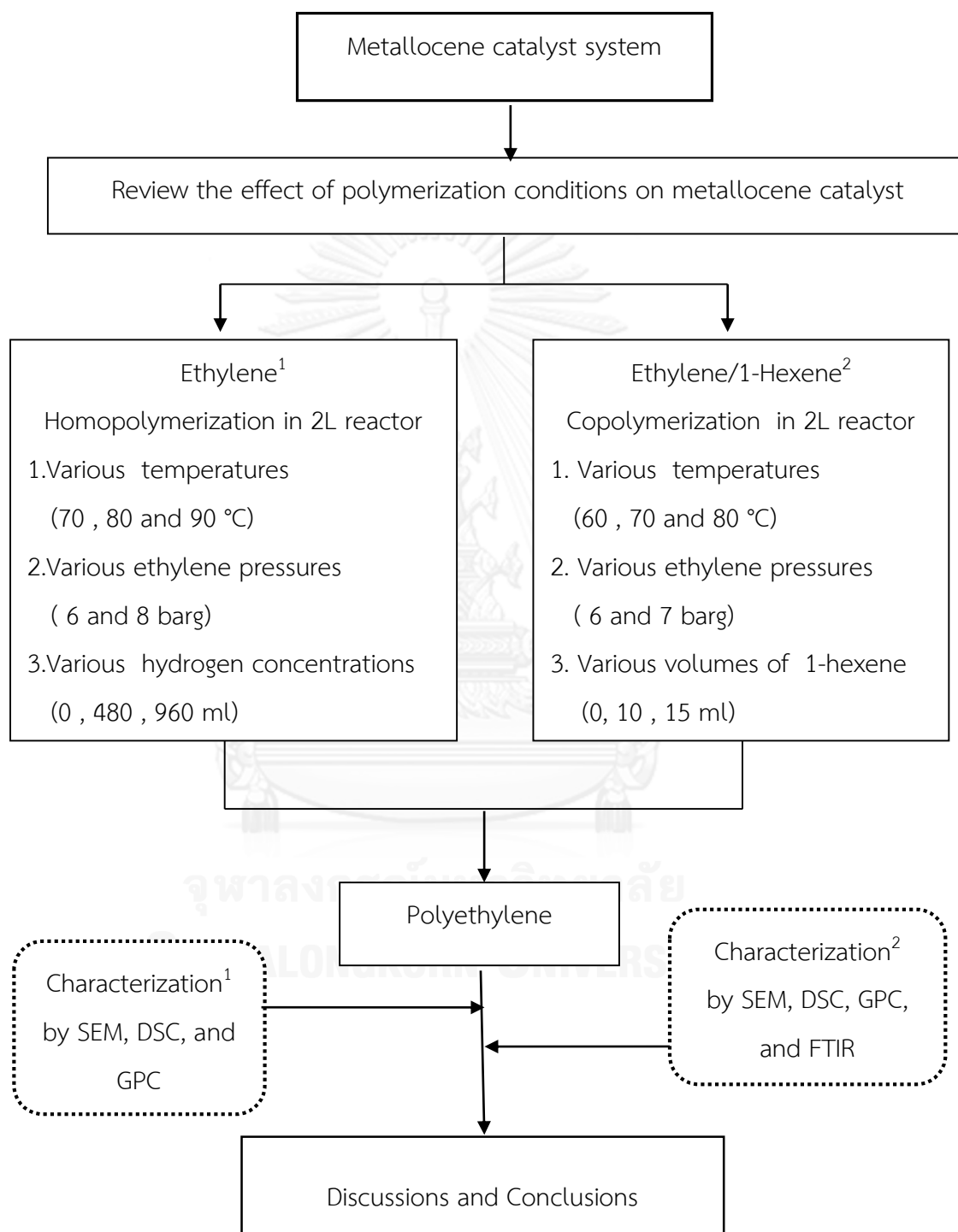


Figure 1. 1 Flow diagram of research methodology

## CHAPTER II

### THEORY AND LITERATURE REVIEWS

#### 2.1 Polyolefins

Polyolefins are the largest group of thermoplastics, often referred to as commodity thermoplastics. They are polymers made of simple olefins such as ethylene, propylene. The two most common polyolefins are polyethylene (PE) and polypropylene (PP); they have a wide range of applications due to their low cost and versatility. Polyolefins are polymer produced from alkene as a monomer. In organic chemistry, an alkene, olefin or olefine is unsaturated chemical compound containing at least one carbon to carbon double bond. The simplest alkene is ethylene. A special family of these olefins is  $\alpha$ -olefines, which have a double bond at the primary or  $\alpha$ -position, (Figure 2.1). This location of a double bond enhances the reactivity of the compound and makes it useful for a number of applications [9, 10].

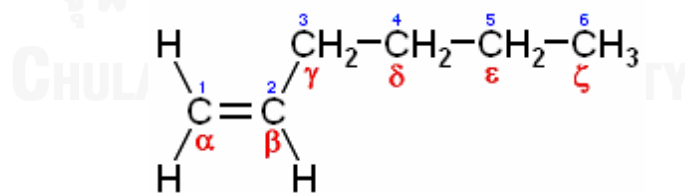


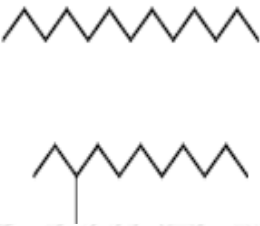
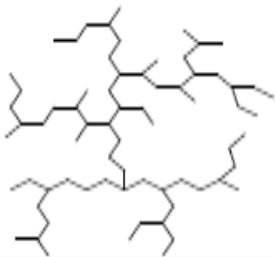
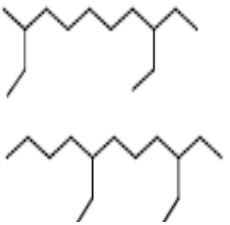
Figure 2. 1 Structures of polyolefins [10].

## 2.2 Classification of polyethylene

Polyethylene (PE) accounts for about one-third of the world's total production of synthetic thermoplastics. PE can be divided into two families: high density and low density PE. When there is no branching off the main backbone of the polymer, the polymer is called linear polyethylene or high density polyethylene (HDPE). When branching occurs off the backbone of the main polymer chain, the branched polymer is called low density polyethylene (LDPE). Low density polyethylene can be further divided into normal LDPE and linear low density polyethylene (LLDPE), based on the microstructures of the polyethylene chains. LDPE contains both short-chain and long-chain branching, which results in low crystallinity, melting point and density compared to HDPE. LDPE is therefore more flexible and has higher impact strength. HDPE is an essentially linear polymer with few chain branches, resulting in close chain packing in the solid state and high crystallinity, making it a rigid thermoplastic. LLDPE is produced by the copolymerization of ethylene with  $\alpha$ -olefin (most commonly 1-butene, 1-hexene and 1-octene). The short-chain branching resulting from the incorporation of  $\alpha$ -olefin unit into the main chain leads to a lowering in polymer melting point and crystallinity. Although the density of LLDPE is in the same range as LDPE, it has much improved impact strength, puncture resistance and tear strength [11].



**Table 2. 1** Density range , molecular structure, synthesis and application of various type polyethylenes [12].

Type of PE	Density (g/cm <sup>3</sup> )	Molecular structure	Synthesis	Application
HDPE	0.941-0.965		Polymerization of ethylene on Philips, Ziegler-Natta and Metallocene catalyst	<ul style="list-style-type: none"> <li>- Plastic bottle</li> <li>- Bottle cap</li> <li>- Food storage Container</li> <li>- Pipeline</li> </ul>
LDPE	0.910-0.940		Free radical polymerization of ethylene at high temperature and high pressure	<ul style="list-style-type: none"> <li>- Plastic bag</li> <li>- Plastic wrap</li> <li>- Tubing</li> </ul>
LLDPE	0.915-0.925		Copolymerization of ethylene with $\alpha$ -olefin on Ziegler-Natta and Metallocene catalyst	<ul style="list-style-type: none"> <li>- Plastic bag</li> <li>- Plastic wrap</li> <li>- flexible tubing</li> </ul>

## 2.3 Catalysts for Polyethylene Polymerization

Today polyethylene are commercially produced using free-radical initiators, Ziegler-Natta catalysts, chromium oxide (Phillips) catalysts and more recently metallocene Each type of catalyst will be discussed briefly below.

### 2.3.1 Ziegler- Natta Catalysts

In general, a Ziegler- Natta catalyst is a complex of a metal cation from groups I-III in the periodic table, such as triethylaluminum,  $\text{Al}(\text{C}_2\text{H}_5)_3$ , and a transition metal compound from groups IV-VIII, such as titanium tetrachloride ( $\text{TiCl}_4$ ). The former component is usually known as the co-catalyst or activator and the latter as the catalyst. For industrial use, most Ziegler- Natta catalysts are based on titanium salts and aluminum alkyls. These types of catalysts have improved considerably since their discovery by K. Ziegler and G. Natta in the late fifties. The first commercial Ziegler-Natta catalyst was a  $\text{TiCl}_3/\text{Et}_2\text{AlCl}$  system with low polymer yield requiring a step for removing the catalyst residue for the commercial production of polyolefins. Modern Ziegler-Natta catalysts are  $\text{TiCl}_4$  supported on  $\text{MgCl}_2$  and use  $\text{Et}_3\text{Al}$  as activator. These catalysts are more active and have better control of active sites and particle morphology, enabling them to meet the increasing demands of high performance polyolefin materials. Nevertheless, due to their multi-sited nature, the polymer structure can be controlled only to a limited degree [13].

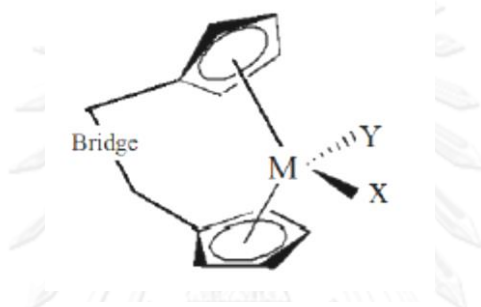
### 2.3.2 Phillips Catalysts

A traditional Phillips catalyst is based on chromium (VI) oxide supported on silica ( $\text{SiO}_2$ ) or aluminosilicates (mixed  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ). The support is sometimes modified with titania ( $\text{TiO}_2$ ). The ability of Phillips catalysts to polymerize ethylene it does not necessarily require a cocatalyst for activation. makes them unique among the olefin polymerization catalyst family. Activation is carried out by heat treatment (calcination) which fixes the  $\text{CrO}_3$  on the support surface. This catalyst is very stable and useful in gas-phase polymerization but unable to polymerize propane to isotactic polypropylene [14]. Due to their multi-sited nature, both Phillips and Ziegler- Natta catalysts produce ethylene homo- and copolymers with broad MWD and broad chemical composition distribution.

### 2.3.3 Metallocene Catalysts

Metallocene catalysts are as old as Ziegler-Natta catalysts, but they were found to have very low activity when alkylaluminums were used as cocatalysts [15, 16]. Their potential was fully realized when methylaluminoxane (MAO) was used as a cocatalyst in the early 1980s [17]. In contrast to heterogeneous Ziegler-Natta catalysts, most metallocenes have only one type of active site and are, therefore, classified as single site catalysts. They offer superior control over the polymer molecular architecture and produce chains with narrow MWD and polydispersity index close to 2 . In addition, their catalytic activity is higher than that of classical Ziegler-Natta systems; for instance, for a standard zirconocene/MAO catalyst system, the activity is 10 to 100 times higher than that of a typical Ziegler-Natta catalysts [18].

Metallocene catalysts have a sandwich structure in which a  $\pi$ -bonded metal atom is situated between two aromatic rings, but this definition has been expanded to include structures having only one  $C_5$  ring. (Figure 2.2) shows the general structure of a bridged metallocene catalyst precursor. In the  $Cp_2MX_2$  complex shown, M, is the transition metal and X and Y are usually Cl or  $CH_3$ . The  $\eta_5$ -bonded “tilted sandwich” cyclopentadienyl (Cp) ligands can be substituted and/or connected by an inter-annular bridge.



**Figure 2. 2** General structure of a bridged metallocene catalyst precursor [9].

Slight structural variations of the bridging groups and ring constituents, as well as transition metal type, can significantly affect the activity and stereoselectivity of olefin polymerization catalysts [19, 20]. Generally, zirconium catalysts are more active than hafnium or titanium systems. The first metallocene catalysts were unsubstituted or substituted bis-cyclopentadienyl ligands and they were activated by methylalumoxane (MAO). Today, numerous families of different single-site catalysts have been developed for the production of polyethylenes and other polyolefins [21-25].

## 2.4 Co-catalyst or Activators

The role played by the co-catalysts or activators in metallo-organic catalyst systems is very important. Activators are essential to produce active sites, and the catalyst precursor must be contacted with an effective activator during catalyst supporting or/and polymerization. The activator type is very important if we are to achieve high catalyst activity, and specific activators are generally matched with a specific catalyst system. Typically, during the activation step, the co-catalyst will become an anion, which is very important in catalytic active cation-anion ion pair. The electro negativity of the catalyst system may have a significant influence on polymerization characteristics and polymer properties. Many studies have been conducted in this area with different catalysts and co- catalysts, including both homogeneous and heterogeneous systems

### 2.4.1 Alkylaluminium

An aluminoxane is a compound produced from an alkylaluminium under controlled hydrolysis. There are many types of aluminoxane available on the market, including ethylaluminoxane and isobutylaluminoxane. However, the consensus from the literature and from polymer producers is that the highest activity could be obtained with methylaluminoxane as a co-catalyst for most metallocene polymerizations. Despite the importance and relatively widespread use of MAO in metallocene polymerizations, and even with the extensive research done in this area, the exact composition and structure of the MAO is still unknown]. MAO is produced by hydrolysis trimethylaluminum under controlled conditions. This reaction will produce a compound in which aluminum and oxygen are arranged alternatively and

the free valences are saturated with methyl groups [26, 27]. Some of the proposed structures of the MAO in the literature are shown in Figure 2.3.

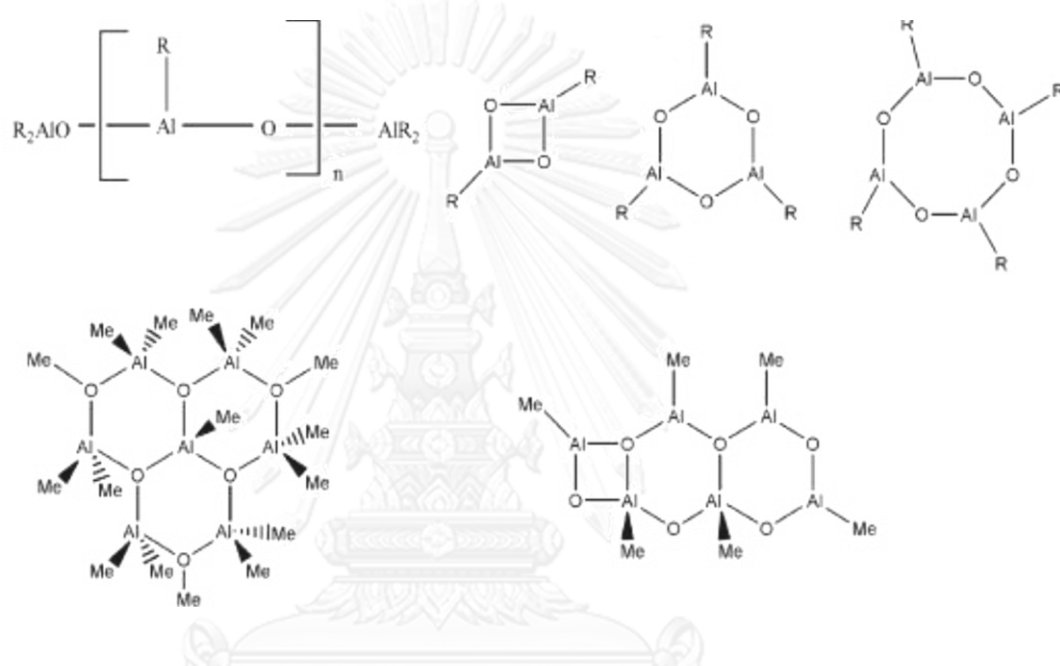


Figure 2. 3 Some of the possible structures of MAO [26]

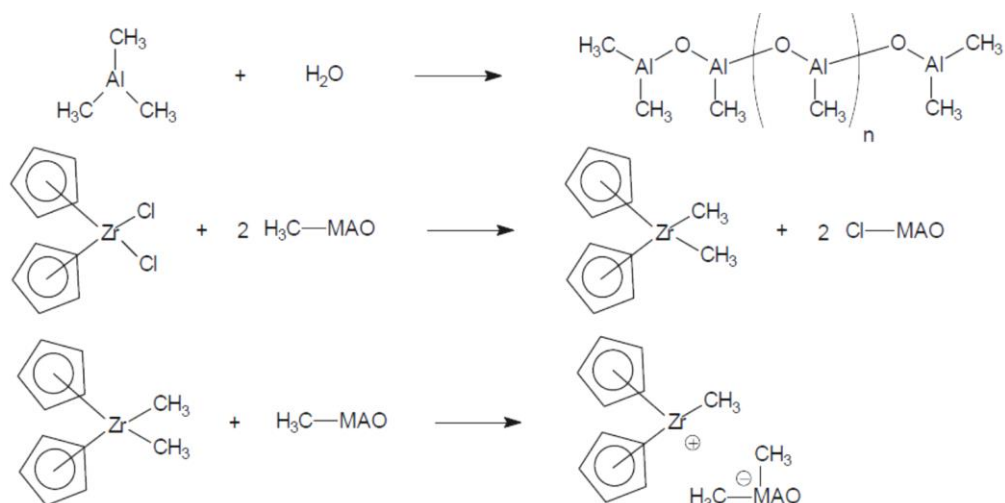


Figure 2. 4 Activation of metallocene by methylaluminoxane [27].

## 2.5 Mechanisms of polymerization using metallocene catalyst systems

Understanding the mechanisms and kinetics involved in the polymerization process enables one to predict the structure of the polymer formed. Propagation and termination rates determine molecular weight, molecular weight distribution, and in copolymerization, comonomer content and distribution. The catalyst initiation and deactivation processes have an influence on the kinetics [28].

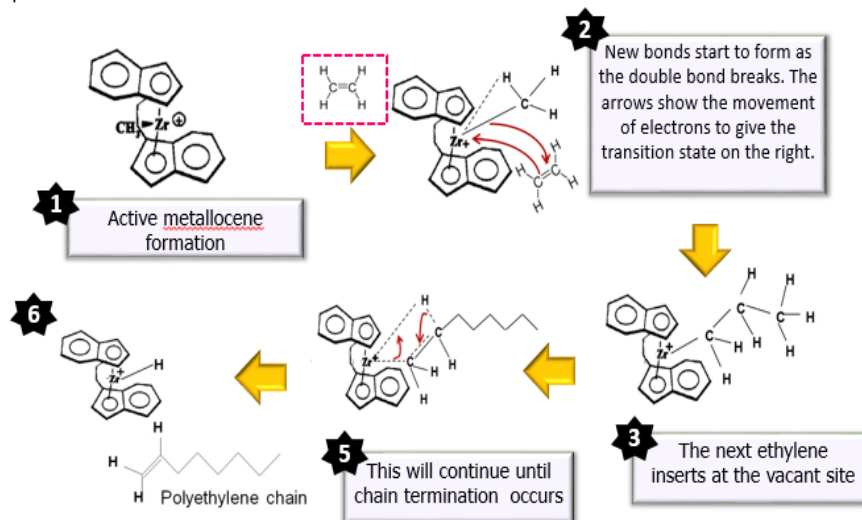


Figure 2. 5 Mechanisms of ethylene polymerization using metallocene catalyst [28].

### 2.5.1 Initiation and propagation reactions

A simplified scheme for the catalyst activation and propagation mechanism in metallocene catalyzed polymerizations is shown in Table 2.2. Neutral metallocene compound ( $L_2MCl_2$ ) is inactive without an activator and requires a strong Lewis acid (i.e. methylaluminoxane) to form a cationic metal center, which is active in 1-olefin polymerization

Propagation then proceeds by 1-olefin coordination and insertion via a transition state. The exact route for the monomer insertion is not completely understood. Agostic interactions appear to have an important role in the chain growth process. Kinetic studies have shown that the polymerization rate  $R_p$ , does not always follow a simple first order relationship ( $\alpha = 1$ ), but often depends on the monomer concentration to the power 1.2-1.4, indicating complex reaction pathways. Different kinetic models have been proposed to describe this kind of polymerization behavior.

**Table 2. 2** Schematic activation and propagation reactions and the kinetic equation for propagation. Propagation constant includes the active site concentration ( $k_p = k_p' \times [C^*]$ ). L = ligand; MAO = methylaluminoxane; M = Ti, Zr, or Hf [28].

Reaction	Mechanisms Reaction	Kinetic Expression
Activation	$L_2MCl_2 + MAO \rightarrow L_2M^+ - CH_3 + [MAO - Cl_2]^-$	
Propagation	$L_2M^+ - CH_2CH_2R + CH_2=CH_2 \rightarrow L_2M^+ - CH_2CH_2CH_2CH_2R$	$R_p = k_p \times [M]^\alpha$



### 2.5.2 Chain transfer reactions

The most common chain transfer mechanisms identified in metallocene catalyzed ethylene polymerization and the corresponding end group types have been collected in Table 2.3

$\beta$ -H elimination (chain transfer to the metal) and chain transfer to the monomer are generally believed to be the dominant chain transfer reactions in the olefin homopolymerization.. They lead to the formation of vinyl ( $\text{CH}_2=\text{CH}-\text{R}$ ) or vinylidene ( $\text{CH}_2=\text{C}(\text{R}')-\text{R}$ ) bond in ethylene or 1-olefin polymerization, respectively. There is some theoretical and experimental evidence that chain transfer may take place via alkene C-H activation ( $\sigma$ -bond metathesis) for some polymerization systems. In that case, vinyl bond is at the beginning of a chain .

Chain transfer to the aluminum (cocatalyst) is usually of minor importance in ethylene polymerization. However, it appears to be more important in propene polymerization . Chain transfer to the aluminum leads to the formation of an  $\text{Al}-\text{CH}_2-\text{R}$  compound. The aluminum-alkyl bond is highly reactive and the treatment with  $\text{HCl}/\text{EtOH}$  standard laboratory washing procedure results in a saturated end-group in the polymer .

Chain transfer to an external chain transfer agent, for example hydrogen, results in a saturated chain end. The introduction of hydrogen significantly increases the productivity of some metallocene catalysts, especially in propene polymerization . Hydrogen is far more reactive in metallocene-catalyzed polymerizations than in Ziegler-Natta polymerizations .

In the copolymerization of ethylene and  $\alpha$ -olefin, vinylidenes and trans-vylenes ( $\text{CH}_3\text{-R}'\text{-CH=CH-R}$ ) account for a significant part of the end-groups. Both  $\beta$ -H elimination and chain transfer to the  $\alpha$ -olefin after 1,2-insertion of the  $\alpha$ -olefin results in the formation of a vinylidene bond.  $\beta$ -H elimination or chain transfer to the monomer after 2,1-insertion results in the formation of a trans-vylyene bond in the polymer chain. In  $\alpha$ -olefin (co)polymerizations a  $\beta$ -alkyl elimination analog to the  $\beta$ -H elimination may take place as termination reaction.

Isomerization reactions play an important role in the formation of regio- and stereoerrors in propene polymerization and in chain termination. The isomerization reactions contribute not only to the formation of stereo errors but also to the chain transfer. The catalyst structure and monomer concentration have a major influence on the extent of the isomerization reaction leading to the formation of the stereo errors. In ethylene polymerization, isomerization reactions have a less important role [29].

**Table 2. 3** Chain transfer reactions, schematic reaction path, and the kinetic equations in ethylene polymerization. Chain transfer constant include the active site concentrations ( $k_{tr} = k_{tr}' \times [C^*]$ ). Ligands have been omitted for clarity [28].

Chain transfer reaction	Reaction components	→	End-groups	Kinetic Expression
Chain transfer to monomer	$M^+ - CH_2CH_2R + CH_2=CH_2$	$\rightarrow$	$M^+ - CH_2CH_3 + CH_2=CHR$	$R_{tr,M} = k_{tr,M}[M]$
$\beta$ -H elimination	$M^+ - CH_2CH_2R$	$\rightarrow$	$M^+ - H + CH_2=CHR$	$R_{tr,\beta-H} = k_{tr,\beta-H}$
Chain transfer to aluminum	$M^+ - CH_2CH_2R + AlR'_3$	$\rightarrow$	$M^+ - R' + R'_2AlCH_2CH_2R$	$R_{tr,Al} = k_{tr,Al}[Al]$
Chain transfer to hydrogen	$M^+ - CH_2CH_2R + H_2$	$\rightarrow$	$M^+ - H + CH_3CH_2R$	$R_{tr,H_2} = k_{tr,H_2}[H_2]$
$\sigma$ -bond metathesis	$M^+ - CH_2CH_2R + CH_2=CH_2$	$\rightarrow$	$M^+ - CH=CH_2 + CH_3CH_2R$	$R_{tr,\sigma} = k_{tr,\sigma}[M]$

### 2.5.3 Catalyst deactivation

The reason for catalyst decay is not well understood. There are many hypotheses [10] :

- 2.5.3.1. One of the most widely supported hypotheses for catalyst activity decay is the over-reduction of the active centers,  $Zr^{4+}$ , into an inactive form,  $Zr^{3+}$ , by the cocatalyst.
- 2.5.3.2. The formation of dormant sites.
- 2.5.3.3. Reaction of active sites with polar impurities.

2.5.3.4. Physical deactivation. It is based on the formation of a polymer shell, surrounding the catalyst, during the polymerization reaction. This shell introduces mass transfer limitations of the monomer molecules that lead to the observed catalyst decay.

2.5.3.5. Two active sites form stable complex that is inactive for monomer polymerization. This type of bimolecular intermediate is favored at high catalyst concentrations and is reversible.

## 2.6 The Influence of the polymerization conditions

Because of the polymerization conditions have influence very much in control of the catalyst activity and polymer properties. Both Ziegler Natta and single site catalysts have responded to conditions in the polymerization, the polymerization parameters such as polymerization temperatures, ethylene pressures, hydrogen and comonomer etc. [30].

### 2.6.1 The Influence of Temperature

The polymerization temperature is one of the most important parameters in all polyolefin processes. Increasing the temperature can increase or decrease both the polymerization rate and yield, and usually changes all the polymer properties discussed in this work: molecular weight, melting temperature, crystallinity, and particle morphology depend on effective control of reaction temperature.

Dos santos et al. 1998 [31] studied the effects of polymerization conditions were evaluated on the production of polyethylene by silica-supported ( $n$ -BuCp)<sub>2</sub>ZrCl<sub>2</sub> grafted under optimized conditions and cocatalyzed by methylaluminoxane (MAO). The influence of the polymerization temperature (with other parameters constant and using 1025 mol of Zr as catalyst). Although the catalyst showed activity at moderate temperatures (318 K), better activity results were achieved at 333 K. Higher temperatures (348 K) decreased activities, probably by deactivating the supported catalyst system. It seems that the silica surface stabilizes the active species, affording higher polymerization activities at temperatures close to 333 K.

J. B. P. Soares et al. 2011 [32] studied the effect of polymerization temperature on the in situ polymerization of ethylene with clay-supported metallocenes. The polymerization temperature was also found to affect the clay exfoliation. Higher polymerization temperatures favor clay exfoliation and dispersion within the polyethylene matrix, provided that the temperature is kept low enough to avoid polymer and/or active site extraction from the clay surface.

Patinya Pipatpratanporn et al. 2007 [33] studied properties of polypropylene (PP) derived from the supported Ziegler-Natta (ZN) catalyst (MgCl<sub>2</sub>/TiCl<sub>4</sub>/DEP) and the supported metallocene (MC) catalyst (SiO<sub>2</sub>/MAO/Et[Ind]<sub>2</sub>ZrCl<sub>2</sub>). Activity profiles based on the polymerization temperatures for cat. A (ZN) and B (MC). It was found that cat. B exhibited higher activities than cat. A. It can be seen that activities increased with increasing the polymerization temperatures from 40 to 60 °C. However, activities decreased with increasing the temperature to 70°C. This can be described

from the stability of the  $\pi$ -complex in cat. B arising from the indenyl ligands at low temperatures.

### 2.6.2 The Influence of Ethylene Pressure

Productivity, product quality, costs and the safety of industrial polymerization processes depend strongly on ethylene pressure. Most researchers simplify the polymerization rate as follows:

$$R_p \approx k_p C_{C_2}^n \approx k_p P_{C_2}^n \quad (2.1)$$

where,  $C_{C_2}$  is the bulk concentration of ethylene,  $P_{C_2}$  is ethylene pressure and  $n$  is the order of reaction related to ethylene. Depending on the type of catalyst and the conditions around the active sites,  $n$  has been found to vary between 1 and 2.

Anna Pietruszka et al. 2012 [34] studied Ethylene polymerization with a titanium complex [N,N-ethylenebis (3-methoxysalicylideneiminato)titanium dichloride] immobilized on the magnesium support is highly active in ethylene polymerization, and its activity increases with increasing temperature and monomer pressure. Pressure of ethylene feed made another factor which was verified for its effect on the activity of the investigated supported catalyst. Increasing monomer pressure within 1–5 atm turned out to cause a considerable growth in the catalyst productivity.

J. B. P. Soares et al. 2000 [35] studied effects of experimental conditions on polymerization kinetics, and molecular weight distribution of the produced polyethylene made with this *in-situ*-supported metallocene catalyst. The polymerization rate is proportional to ethylene pressure. Catalytic activity (measured in g of polyethylene/gmol Zr. atm. hr) is nearly independent of ethylene pressure, which indicates that the polymerization rate is first order with respect to monomer pressure. Monomer pressure has minimal effect on the molecular weights and polydispersity indices of produced polyethylene. The little sensitivity of ethylene pressure on the molecular weight of polyethylene made with  $\text{Et}[\text{Ind}]_2\text{ZrCl}_2$  has been observed before for supported and unsupported systems and been linked to transfer to monomer mechanisms.

### 2.6.3 The Influence of Hydrogen

The molecular weight and MWD of polyethylene produced using metallocene catalysts can be controlled and regulated by many variables such as catalyst, co-catalyst, monomer, hydrogen, and temperature. Hydrogen is the strongest and fastest chain transfer agent for controlling the MWD and can significantly affect the reaction rate of ethylene polymerization. Some other hydrogen effects on polymer properties, such as crystallinity, melting temperature and molecular weight have also been reported in the literature.

Garoff et al., 2002 [36] studied the deactivation effect of hydrogen in ethylene polymerization with different types of Ziegler-Natta catalyst. The aim of their research was to investigate the effect of hydrogen compared with Kissin's theory. According to this theory, hydrogen formed Ti-H bond and generated  $\beta$ -agostic interaction at active centers around 90% as revealed in Figure 2.6. Only 10% of Ti

centers could continue the polymerization. The activity was also decreased. This effect was observed when small amounts of hydrogen were used in their study.

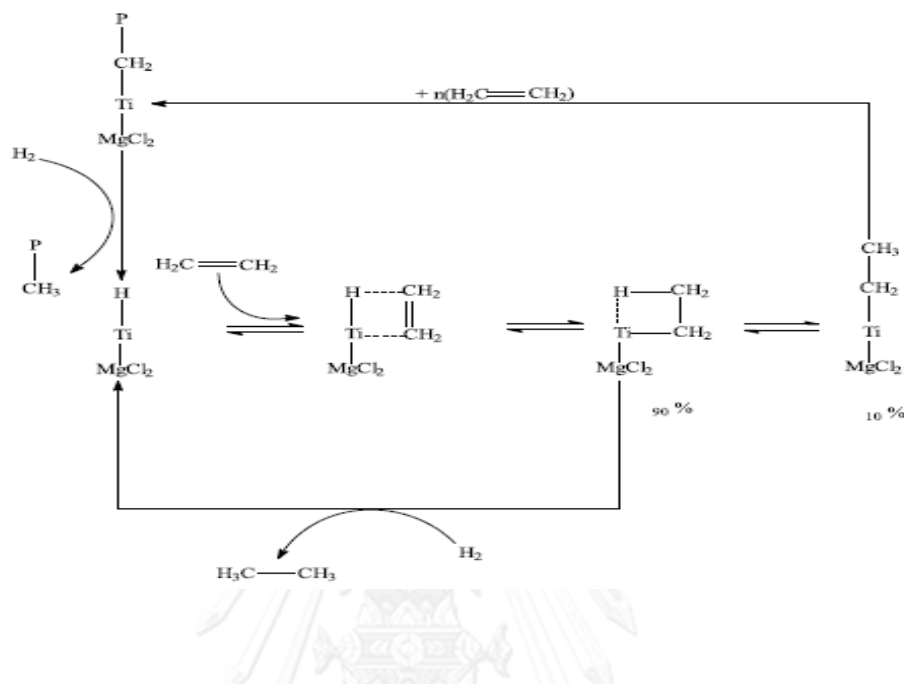


Figure 2. 6 Deactivation effect by hydrogen in ethylene polymerization [36].

Zohuri G. et al. 2005 [37] studied Bis(cyclopentadienyl) zirconium dichloride ( $\text{Cp}_2\text{ZrCl}_2$ ) as a homogeneous metallocene catalyst was under highly controlled conditions. Ethylene polymerization was carried out using this catalyst. Addition of hydrogen as a chain transfer agent up to  $120 \text{ cm}^3/\text{L}$  solvent, increased the activity of the catalyst. Polymerization activity was increased with increasing temperature to  $60^\circ\text{C}$  and slightly decreased with more increase in temperature. particularly when polymerization temperature was higher than  $50^\circ\text{C}$ . This increase could be due to high rate of polymerization which at high temperature could affect catalyst activity. Increase in polymerization temperature and  $\text{H}_2$  concentration decreased  $M_v$  of polymer obtained.



Joao B. P. Soares et al. 2000 [38] to investigate the effect of hydrogen on ethylene polymerization using these novel in-situ supported metallocene catalysts. The catalytic activity of two different insitu supported metallocene catalysts ( $\text{Et}[\text{Ind}]_2\text{ZrCl}_2$  and  $\text{Cp}_2\text{ZrCl}_2$ ) as a function of hydrogen pressure the polymerization rate of ethylene with in-situ supported  $\text{Et}[\text{Ind}]_2\text{ZrCl}_2$  increases steadily with increasing the partial pressure of hydrogen. On the other hand, the polymerization rate of ethylene with in-situ supported  $\text{Cp}_2\text{ZrCl}_2$  passes through a maximum in the range of 10 to 30 psig. Further increase of hydrogen pressure seems to decrease polymerization rate of this catalyst. reactivated for propagation by insertion of a monomer unit. Hydrogen may coordinate to the metal atom and make more metal hydride complexes resulting in a lower propagation rate. In addition, hydrogen can cause reduction of ethylene concentration around active sites because of its characteristics (hydrogenation of olefinic monomer).

#### 2.6.4 The Influence of comonomer

The copolymerization of ethylene with higher  $\alpha$ -olefins such as 1-hexene is a very important production of olefins polymerization. This process produces commercially elastomers and linear low-density polyethylene (LLDPE) with metallocene catalysts is to incorporate the comonomer mainly into the low molecular weight chains. The preferred catalysts for LLDPE are those that have a relatively uniform active center distribution, there has been a growing increase which give copolymers with narrow molecular weight and chemical composition distributions.

The “comonomer effect” is the rate change in ethylene polymerization from  $\alpha$ -olefin incorporation to the backbone which depends on the catalyst system and the comonomer employed. In metallocene catalyst system, the “comonomer

effect” includes the active sites’ modification and increase in the number of active sites by The comonomer activation effect is easier monomer diffusion, monomers through less crystalline polymer (which is due to the incorporation of comonomer).which also leads to an increase of monomer concentration at active sites.. The influence of the comonomer on the copolymerization kinetics can be rationalized in terms of the formation, stability, and behavior of the active centers in the presence of the comonomer [39, 40].

R. Quijada. et al. 1996 [41] studied The effect of ethylene pressure on the copolymerization of ethylene with 1-hexene .The results show an increasing of productivities (g of polymer/ $n_{Zr}$  h) with pressure.When varing the pressure, the characteristics and properties of the formed copolymers are in accordance with the expectation for changes in the monomer concentration; increasing the pressure causes a decrease in comonomer incorporation. At higher ethylene pressure, the polymer is more crystalline due to less incorporation of 1-hexene and the molecular weight is higher. The density of the copolymers also decreases with comonomer incorporation into the copolymer.

Rafael van Grieken et al. 2007 [42] investigated the synthesis of ethylene/1-hexene copolymers with  $(nBuCp)_2ZrCl_2/MAO/SiO_2-Al_2O_3$  catalytic system, studying the influence of 1-hexene concentration on catalytic activity and polymer properties.The activity of  $(nBuCp)_2ZrCl_2/MAO/SiO_2-Al_2O_3$  catalytic system in the 1-hexene/ethylene copolymerization increases with comonomer concentration up to 0.194 mol/L. The initial enhancement in the catalyst activity is related with better monomer diffusion. At higher concentrations of 1- hexene the activity decreases due to the lower insertion rate of the larger comonomer in the polymer chain. The 1-hexene incorporation

increases with the concentration in the polymerization reactor, obtaining ethylene/1-hexene copolymers with broader chemical composition distributions, lower molecular weights and crystallinity than ethylene homopolymer.

Ye et al. 2005 [43] studied Ethylene/1-hexene was copolymerized by an unbridged zirconocene,  $(2\text{-PhInd})_2\text{ZrCl}_2/\text{MAO}$  (methyl aluminoxane) at 0 °C and 50 °C respectively. High copolymerization activity and 1-hexene incorporation were observed at 0 °C, with the copolymer formed having random sequence distribution and narrow molecular weight distribution. Ethylene polymerization at 50 °C showed high activity, but copolymerization at 50 °C showed much lower activity, which decreased sharply with increasing 1-hexene concentration in the monomer feed. Copolymer formed at 50 °C showed blocky sequence distribution and broad molecular weight distribution. A mechanism model based on ligand rotation hindered by the propagation chain has been proposed to qualitatively explain the observed phenomena.

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Chemicals

The chemicals used in this study were specified as below:

1. Chemically pure grade of ethylene ( $C_2H_4$ ) was used as received from Thai Polyethylene Co., Ltd..
2. Chemically purity nitrogen gas ( $N_2$ ) was used as received from Thai Polyethylene Co., Ltd.
3. Ultra high purity hydrogen ( $H_2$ ) was purchased from Thai Industrial Gas Co., Ltd. and used without further purification
4. Commercial grade of n-hexane was supported from Thai Polyethylene Co., Ltd.
5. Commercial grade of 1-hexene was supported from Thai Polyethylene Co., Ltd.
6. Triethylaluminum (TEA) diluted in hexane solution 200 mmol/l, supplied from Thai Polyethylene Co., Ltd.
7. Supported Metallocene Catalyst was supplied from Thai Polyethylene Co., Ltd.

n-Hexane, 1-Hexene, TEA and a commercial catalyst were received as solvent, comonomer, cocatalyst and catalyst, respectively. They were kept and operated under argon and nitrogen atmosphere via glove box and Schlenk line, respectively.

## 3.2 Polymerization

### 3.2.1 Ethylene homopolymerization

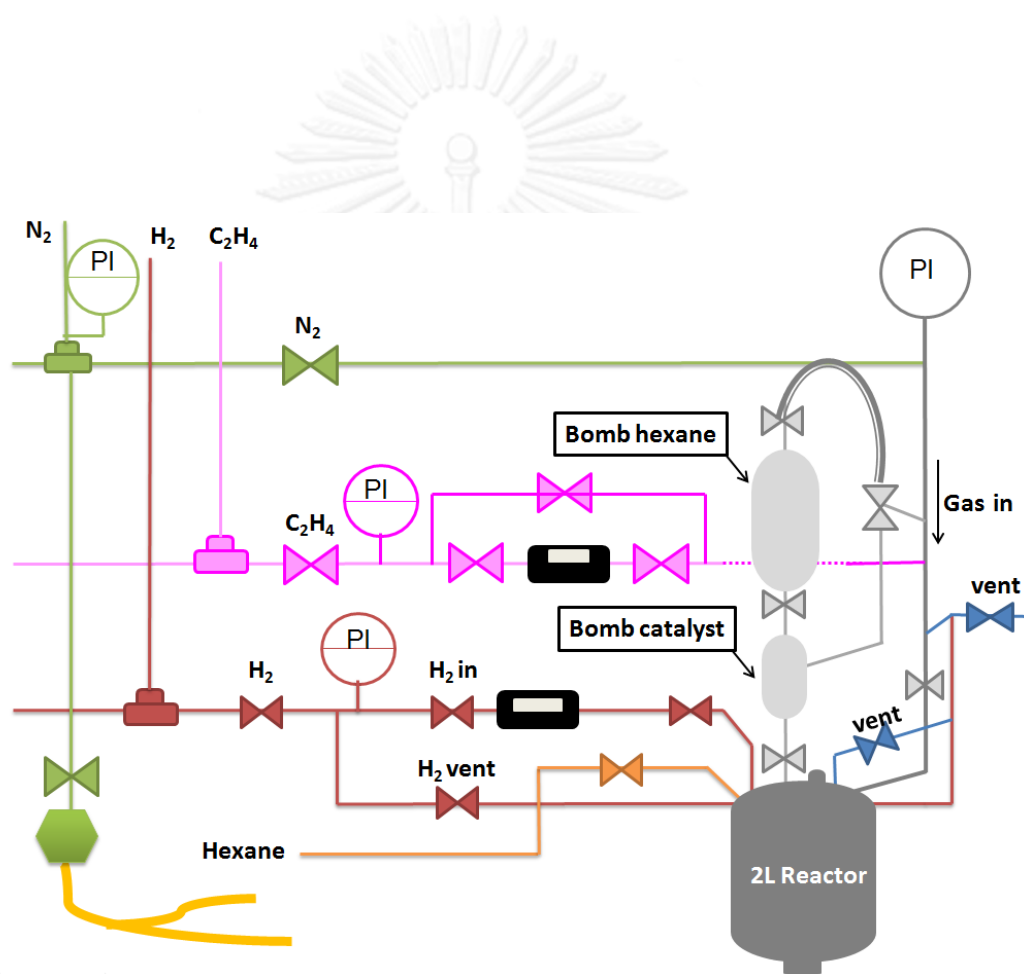
Polymerization of ethylene was carried out in a 2 L semi-batch stainless steel autoclave reactor connected with the lines of nitrogen, ethylene and hydrogen gases and also the hexane feed line. The reactor was equipped with mechanical stirring (670 rpm) and mass flow meter and a temperature control unit comprising of a cooling coil and an electric heater. The polymerization temperature was maintained within  $\pm 2$  °C of the set-point and total pressure was maintained within  $\pm 0.2$  barg of the set-point. The reactor was evacuated and purged by dried nitrogen for 1 h while it was warmed up to 75°C. Then the temperature was reduced to ambient temperature. 150 mL of hexane was charged into sampling hexane vessel and 850 mL of hexane was charged into the reactor by deep line and under 0.2 bar nitrogen pressure 0.5 mmol TEA was charged by pipette and the catalyst was prepared in a glove box (containing 30 mg of catalyst dissolved with 30 ml of hexane were added into schlenk tube) and fed into the specified sampling catalyst vessel connected to the reactor under nitrogen atmosphere. Next displacement nitrogen gas by ethylene gas 3 barg for 3 times and keeping ethylene gas 3 barg within reactor. Then, the stirrer was being started. When the reactor was heated to difference -5°C from the set point of temperature. The ball valve below this sampling hexane vessel and sampling catalyst vessel were opened. Next, the catalyst was injected into the reactor by ethylene pressure flushed with hexane. Together with opened ball valve of hydrogen gas fed continuous at various hydrogen concentrations (0 , 480 ml(4ml/min) and 960 ml (8ml/min) ). After that ethylene was introduced until the total pressure in the reactor reached set point at various pressures (6 and 8 barg). And the feeding process began through mass flow

controllers. The temperature was controlled at various temperatures (70 , 80 and 90°C) set point for 2 h and feeding rate was recorded. Polymerization was terminated, Reactor was depressurized and cooled down and resulting mixture was poured into tray. The polymer was dried at room temperature for overnight.

### 3.2.2 Ethylene/1-Hexene copolymerization

Polymerization of ethylene was carried out in a 2 L semi-batch stainless steel autoclave reactor connected with the lines nitrogen, ethylene and hydrogen gases and also the hexane feed line. The reactor was equipped with mechanical stirring (670 rpm) and mass flow meter and a temperature control unit comprising of a cooling coil and an electric heater. The polymerization temperature was maintained within  $\pm 2$  °C of the set-point and total pressure was maintained within  $\pm 0.2$  barg of the set-point. The reactor was evacuated and purged by dry nitrogen for 1 h while it was warmed up to 75°C. Then the temperature was reduced to ambient temperature. 150mL of hexane was charged into sampling hexane vessel and 850 mL of hexane was charged into the reactor by deep line and under 0.2 bar nitrogen pressure 0.5 mmol TEA ,varied volume 1-hexene (0,10 and 15 ml ) was charged by pipette and the catalyst was prepared in a glove box (containing 30 mg of catalyst dissolved with 30 ml of hexane were added into schlenk tube) and fed into the specified sampling catalyst vessel connected to the reactor under nitrogen atmosphere. Next displacement nitrogen gas by ethylene gas 2 barg for 3 times and keeping ethylene gas 2 barg within reactor. Then the stirrer was being started. When the reactor was heated to difference -10°C from the set point of temperature. The ball valve below this sampling hexane vessel and sampling catalyst vessel was opened next the catalyst was injected into the reactor by ethylene pressure flushed with hexane. After that ethylene was introduced until the total pressure in the reactor reached set point at various pressures (6 and 7 barg). And the

feeding process began through mass flow controllers. The temperature was controlled at various temperatures (60 , 70 and 80°C) set point for 2 h and feeding rate was recorded. Polymerization was terminated Reactor was depressurized and cooled down and resulting mixture was poured into tray. The polymer was dried at room temperature for overnight.



**Figure 3.1** Diagram of 2L Polymerization

### 3.3 Characterization

#### 3.3.1 Differential scanning calorimetry (DSC)

The melting temperature ( $T_m$ ) and percentage of crystallinity ( $X_c$ ) of polyethylene were determined by Perkin-Elmer diamond DSC. The characterizations were performed at a heating rate of 20 °C/ min in the temperature range of 50–170 °C. The samples were heated and cooled to room temperature in the first scan. Then, heated the sample again at the same rate. Due to avoidance of any impurities in samples of first scan. So that the result of the second scan was only reported. The crystallinity of polymers was calculated by the heat of fusion parameter as shown in the equation (3-1) ;

$$X_c = \frac{H_m}{H_p} \times 100 \quad (3-1)$$

Where,  $H_m$  is the enthalpy of the samples

$H_p$  is the enthalpy of a totally crystalline polyethylene, was assumed to be 269.9 J/g [44].

$X_c$  is the percent crystallinity of the samples

#### 3.3.2 Gel permeation chromatography (GPC)

Molecular weight and molecular weight distributions of polymers were determined by using a high temperature GPC (Waters 150 °C) equipped with a viscometric detector. The characterization was performed at 160°C and used 1, 2, 4-trichlorobenzene as a solvent.



### 3.3.3 Fourier transforms infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FT-IR) were used to evaluate the quantitative measurement volume of 1-Hexene from peak showing that it is characteristic of 1-hexene relative to standard calibration curve. The measurements were in the range of 1378.1-1377.9  $\text{cm}^{-1}$ . Absorbance FT-IR spectra were recorded by a Bruker Tensor37 spectrometer with 16 scans at resolution of 4  $\text{cm}^{-1}$ .

### 3.3.4 Scanning electron microscopy (SEM)

SEM was used to determine the morphologies. The SEM of JEOL mode JSM-6400 was applied. The samples were coated with gold particles by ion sputtering device to provide electrical contact to the specimen.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1) Ethylene polymerization on Catalyst

##### 4.1.1) The Effect of Polymerization Temperature on the Catalytic Activity

The influence of polymerization temperatures was investigated with different polymerization temperatures in the range from 70 to 90 °C. The polymerization conditions were performed in hexane solvent using ethylene pressure of 6 and 8 barg , hydrogen concentrations at 0, 480 and 960 ml , using 30 mg of supported metallocene catalyst , triethylaluminum (TEA) concentration of 0.5 mmol/L as a scavenger and polymerization time was fixed at 2 h. Table 4.1 and 4.2 display the results for the influence of temperature on the catalyst activity.

**Table 4. 1** Effect of polymerization temperature on the catalyst activity at ethylene pressure of 6 barg<sup>a</sup>

Ethylene pressure (barg)	Temperature (°C)	hydrogen concentrations (ml)	Yield (g)	Catalyst Activity (kg PE/g cat·h)
6	70	0	134.10	2.2350
	80		218.61	3.6435
	90		211.65	3.5276
	70	480	135.81	2.2635
	80		223.41	3.7235
	90		244.96	4.0827
	70	960	60.07	1.0012
	80		73.39	1.2232
	90		210.16	3.5027

<sup>a</sup> Slurry ethylene polymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

**Table 4. 2** Effect of polymerization temperature on the catalyst activity at ethylene pressure of 8 barg<sup>a</sup>

Ethylene pressure (barg)	Temperature (°C)	hydrogen concentrations (ml)	Yield (g)	Catalyst Activity (kg PE/g cat·h)
8	70	0	193.38	3.2230
	80		364.83	6.0805
	90		297.01	4.9502
	70	480	210.36	3.5060
	80		400.18	6.6697
	90		409.65	6.8275
	70	960	170.84	2.8473
	80		241.06	4.0177
	90		291.52	4.8587

<sup>a</sup> Slurry ethylene polymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

Tables 4.1 and 4.2 show the results that the activity was enhanced with increasing polymerization temperature. It shows a maximum activity value at 80 °C for experimental conditions. It can be explained by widely accepted mechanism of propagation in Metallocene catalyst which involves the initial formation of a  $\pi$ -complex of an olefin with the catalyst metal, followed by chain migratory insertion [45]. In the low polymerization temperature, the  $\pi$ -olefin complex is more stable which is associated to process of activated insertion. Although, the olefin polymerization rate is expected to increase of activity with increasing polymerization temperature, on the other hand, at high temperature (90°C) activity decreased because the activation energy for the catalyst deactivation step ( $E_d$ ) is always higher than the activation energy for propagation ( $E_p$ ). According to increase in the rates of both

propagation (Eq.4.1) and catalyst deactivation (Eq.4.2) with increasing temperature. And ethylene solubility in hexane  $[C_E]$  (Eq.4.3) decreased with increasing temperature.

Moreover, it was probably due to severe deactivation of the catalyst occurs. Several researchers have reported on the possible mechanism for deactivation. One possibility is a slow dissociation of stable active species to form inactive forms or formation of local thermal decomposition at active site. A second possible deactivation mechanism is by  $\beta$ -hydride elimination to give metallocene hydride, which has very low monomer insertion. Apart from that, polymerization constants depend on the temperature according to Arrhenius law.

Assuming the Arrhenius-type temperature dependence of the modified propagation constant is given in equation (4.1).

$$k_p = A \exp(-E_{a,p} / RT) \quad (4.1)$$

$$k_d = A \exp(-E_{a,d} / RT) \quad (4.2)$$

When	$k_p$	=	Propagation rate constant.
	$k_d$	=	Deactivation rate constant.
	$E_{a,p}$	=	Activation energy of the propagation.
	$E_{a,d}$	=	Activation energy of the deactivation.
	A	=	Frequency factor.
	R	=	The gas constant.
	T	=	Kelvin temperature.

Working under isobaric–isothermal reaction conditions and assuming a very rapid monomer mass transfer between all relevant phases, we can rewrite equation (4.3):

$$R_p = k_p [C_E^*] [C_E] \quad (4.3)$$

$$[C_E^*] = [C_E^*]_0 \exp(-k_d t) \quad (4.4)$$

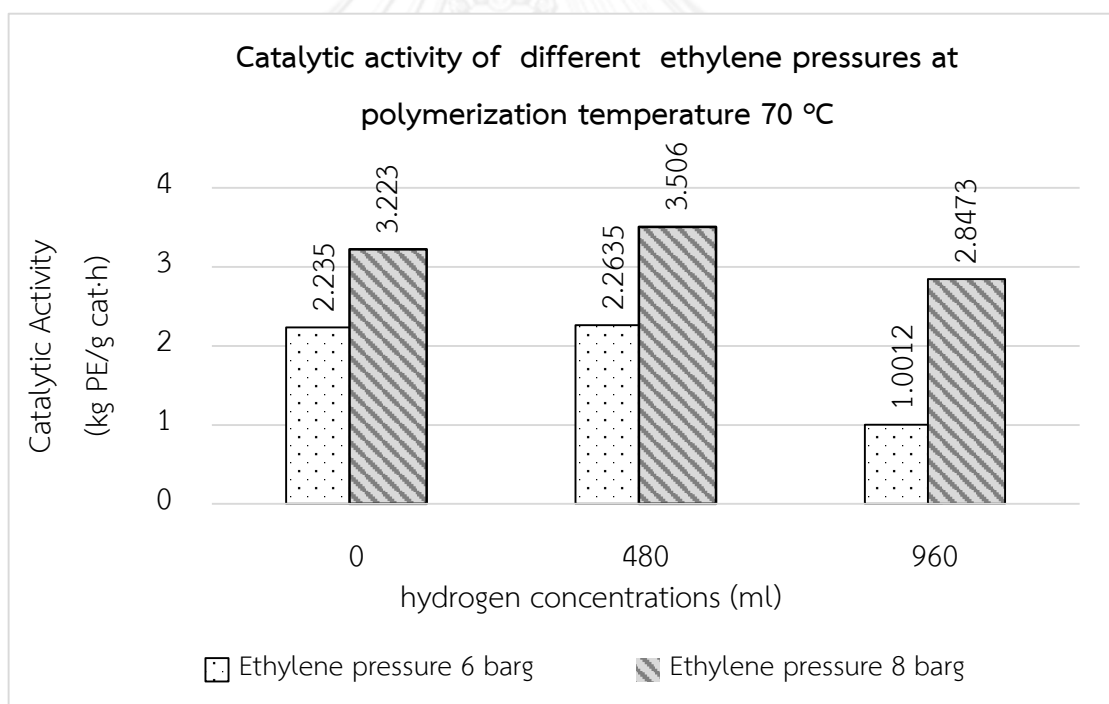
$R_p$  is the polymerization rate,  $C_E^*$  is the active species concentration of ethylene,  $C_{E0}^*$  is the active species initial concentration of ethylene,  $t$  is polymerization time,  $C_E$  is the concentration of ethylene and substituting it in equation (4.1), one can derive Equation (4.5)

$$\frac{R_p}{[C_E^*][C_E]} = A \exp(-E_{a,p} / RT) \quad (4.5)$$

From equation (4.5), productivity is proportional to the polymerization rate which is related to polymerization temperature. Increasing of polymerization temperature improves the polymerization rate, leading to the rise of the catalytic activity. However in the presence of hydrogen, the catalyst was not deactivated at high temperature (90°C), probably due to the effect of hydrogen response.

#### 4.1.2) The Effect of Ethylene Pressure on the Catalytic Activity

The influence of polymerization ethylene pressures was investigated with different polymerization ethylene pressures at 6 and 8 barg. The polymerization conditions were performed in hexane solvent, using polymerization temperature at 70 , 80 and 90 °C , hydrogen concentrations at 0, 480 and 960 ml, using 30 mg of supported metallocene catalyst , triethylaluminum (TEA) concentration 0.5 mmol/L as a scavenger and polymerization time was fixed at 2 h. Figure 4.1 - 4.3 exhibited the results for the influence of ethylene pressures on the catalyst activity.



**Figure 4. 1** Catalytic activity of different ethylene pressures at polymerization temperature of 70 °C

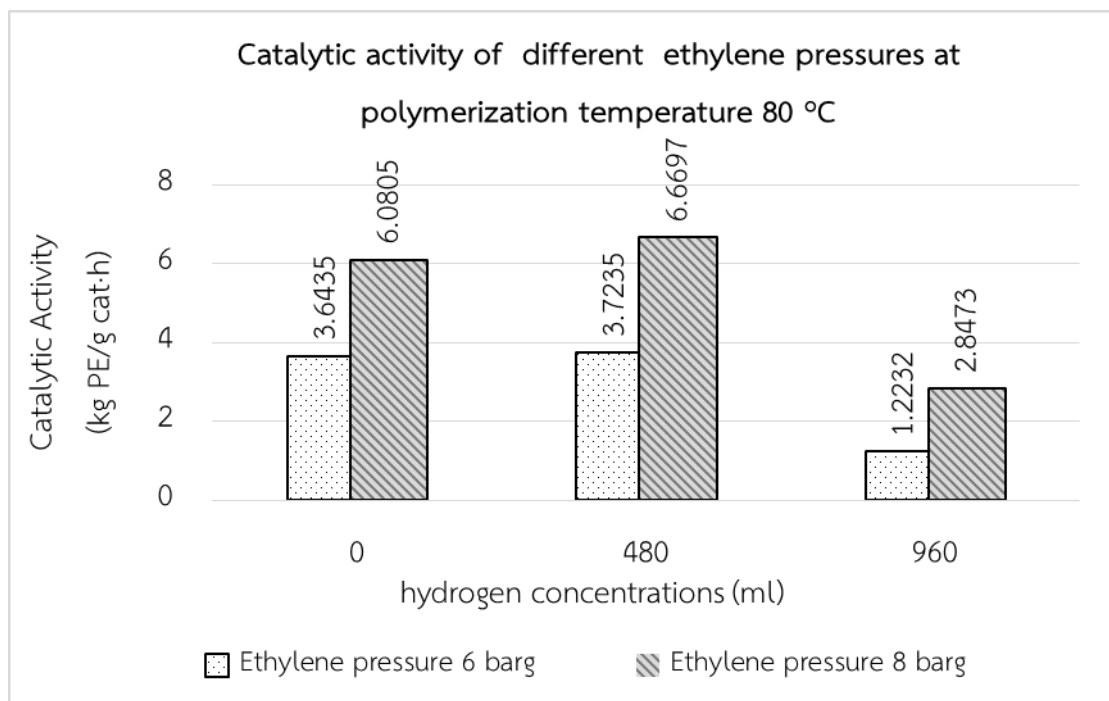


Figure 4. 2 Catalytic activity of different ethylene pressures at polymerization temperature of 80 °C

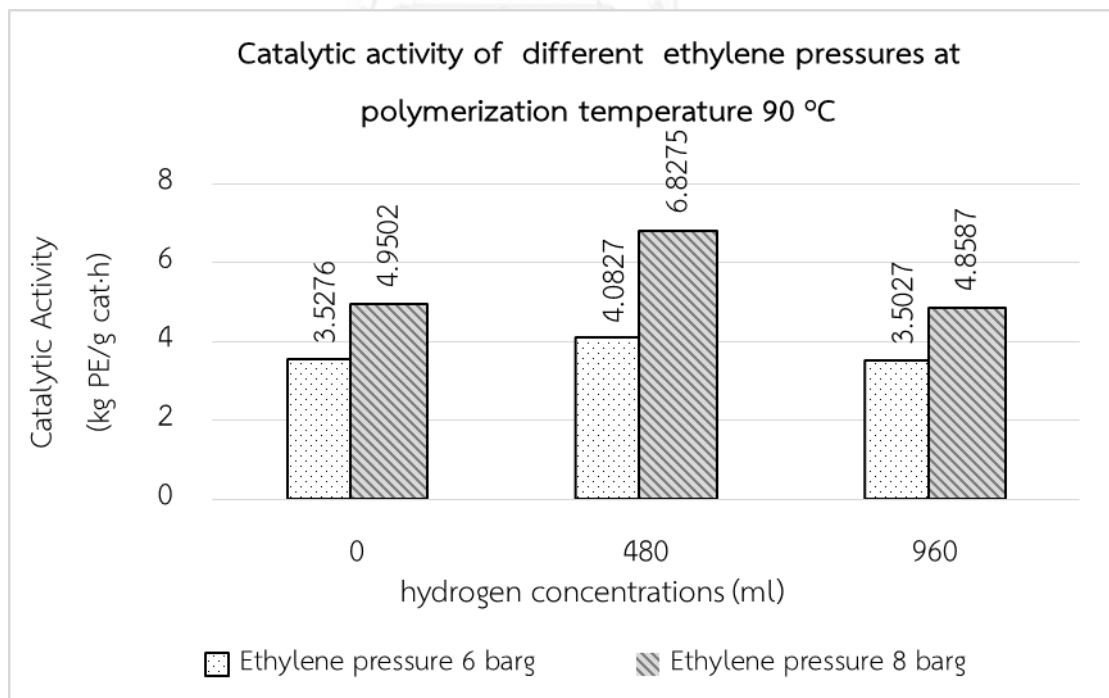


Figure 4. 3 Catalytic activity of different ethylene pressures at polymerization temperature of 90 °C



The influence of ethylene pressure on catalyst activity is shown in Figures 4.1-4.3. The higher monomer pressure renders higher activity suggesting that the propagation step is first order relative to monomer concentration, according with most researchers who simplify the polymerization as follows:

$$\text{Rate of propagation} = k_p [\text{Cat}^*][\text{M}]$$

where  $[\text{Cat}^*]$  is the concentration of active sites. The rate of propagation depends on the propagation rate constant ( $k_p$ ), the number of active sites, and the monomer concentration ( $[\text{M}]$ ) [46].

#### 4.1.3) The Effect of Hydrogen response on the Catalytic Activity

The influence of hydrogen response was investigated with different polymerization condition, i.e. hydrogen concentrations at 0 , 480 and 960 ml. The polymerization conditions were performed in hexane solvent, using polymerization temperature at 70 , 80 and 90 °C , ethylene pressure 6 and 8 barg, using 30 mg of supported metallocene catalyst , triethylaluminum (TEA) concentration 0.5 mmol/L as a scavenger and polymerization time were fixed at 2 h. Tables 4.3 and 4.4 display the results for the influence of hydrogen response on the catalyst activity.

**Table 4. 3** Effect of hydrogen response on the catalyst activity at ethylene pressure of 6 barg<sup>a</sup>

Ethylene pressure (barg)	Temperature (°C)	hydrogen concentration (ml)	Yield (g)	Catalyst Activity (kg PE/g cat·h)
6	70	0	134.10	2.2350
		480	135.81	2.2635
		960	60.07	1.0012
	80	0	218.61	3.6435
		480	223.41	3.7235
		960	73.39	1.2232
	90	0	211.66	3.5276
		480	244.96	4.0827
		960	210.16	3.5027

<sup>a</sup> Slurry ethylene polymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

**Table 4. 4** Effect of hydrogen response on the catalyst activity at ethylene pressure of 8 barg<sup>a</sup>

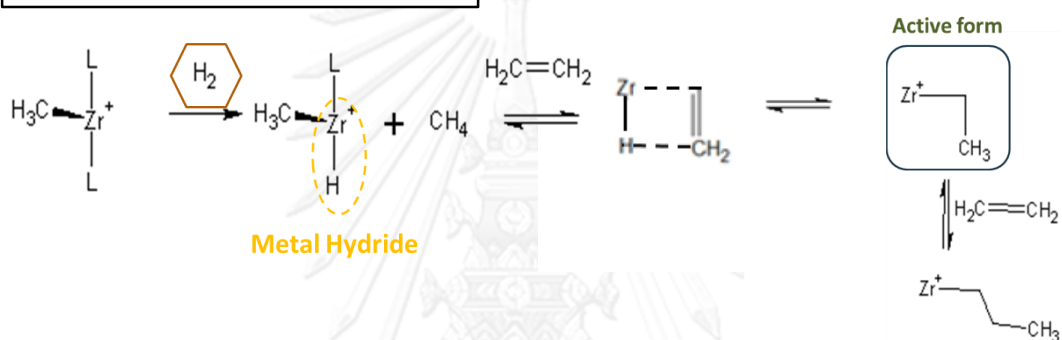
Ethylene pressure (barg)	Temperature (°C)	hydrogen concentration (ml)	Yield (g)	Catalyst Activity (kg PE/g cat·h)
8	70	0	193.38	3.2230
		480	210.36	3.5060
		960	170.84	2.8473
	80	0	364.83	6.0805
		480	400.18	6.6697
		960	241.06	4.0177
	90	0	297.01	4.9502
		480	409.65	6.8275
		960	291.52	4.8587

<sup>a</sup> Slurry ethylene polymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

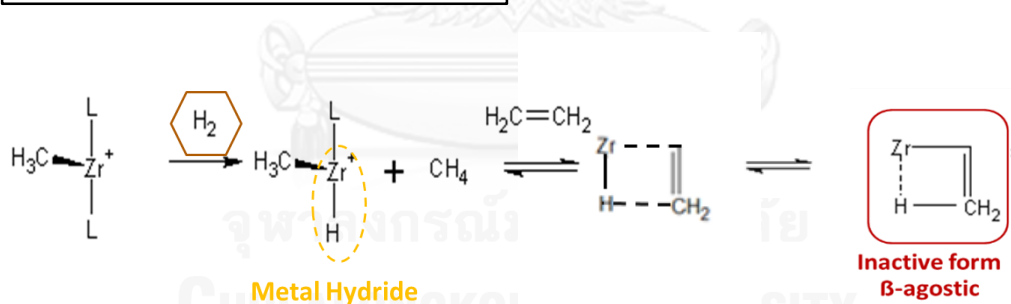
Tables 4.3 and 4.4 compare the catalytic activity of three different polymerization temperatures and two different ethylene pressures as a function of hydrogen concentrations. The results indicated that the activity increased at 480 ml of hydrogen concentration. On the other hand, the activity decreased at 960 ml of hydrogen concentration. Previous reports concerning the effects of hydrogen on olefin polymerization have shown a decrease in catalytic activity in the presence of hydrogen. According to Kissin's theory (in figure 2.6), the more hydrogen that the more hydrogen terminations take place and more metal hydride complexes ( $Zr^+ - H$ ). After the first insertion of ethylene could form the  $Zr-CH_2-CH_3$  groups that tend to more in  $\beta$ -agostic complexation. This  $\beta$ -agostic form resulting in lower catalytic activity.

However, In the presence of hydrogen at low concentration rendered the surface metal hydride formed on the inorganic support. This could be increasing the number of coordinative unsaturated active sites that could effectively coordinate to ethylene in open ethyl form. Therefore, it seems that small concentration hydrogen could be rate enhancement, but at higher concentration hydrogen leading to reduce catalytic activity [37].

Increase in activity cause by  $H_2$



Decrease in activity cause by  $H_2$



## 4.2) Characterization of the Ethylene polymer

### 4.2.1) Melting Temperature ( $T_m$ ) and Crystallinity ( $X_c$ )

The melting temperatures and crystallinities of ethylene polymer using supported metallocene catalysts were determined by differential scanning calorimeter. The results of various effects, such as polymerization temperatures, ethylene pressures and hydrogen concentrations on melting temperatures and crystallinities of produced copolymer are shown in Table 4.5-4.6. The DSC curves of these polymer were also demonstrated in Appendix A.

**Table 4. 5** Melting temperature and crystallinity of ethylene polymer with various polymerization temperatures at ethylene pressure of 6 barg<sup>a</sup>.

Ethylene pressure (barg)	Temperature (°C)	Hydrogen concentration (ml)	$T_m^b$ (°C)	$X_c^b$ (%)
6	70	0	131	42.0
	80		130	44.6
	90		130	43.8
	70	480	134	59.4
	80		133	62.3
	90		135	58.6
	70	960	133	55.1
	80		133	62.3
	90		134	58.6

<sup>a</sup> Slurry ethylene polymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

<sup>b</sup> Determined by DSC, the crystallinity was calculated from heat of crystalline formation based on HDPE.

**Table 4. 6** Melting temperature and crystallinity of ethylene polymer with various polymerization temperatures at ethylene pressure of 8 barg<sup>a</sup>.

Ethylene pressure (barg)	Temperature (°C)	Hydrogen concentration (ml)	T <sub>m</sub> <sup>b</sup> (°C)	X <sub>c</sub> <sup>b</sup> (%)
8	70	0	130	41.5
	80		131	41.2
	90		130	44.6
	70	480	132	56.5
	80		131	49.5
	90		132	51.7
	70	960	134	62.3
	80		134	62.1
	90		131	58.2

<sup>a</sup> Slurry ethylene polymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

<sup>b</sup> Determined by DSC, the crystallinity was calculated from heat of crystalline formation based on HDPE.

#### 4.2.1.1) The melting temperature and crystallinity of ethylene polymer with various polymerization temperatures

The melting temperature and crystallinity were found to have no direct relation between polymerization temperatures in the absence and presence of hydrogen in polymerization systems. The melting temperatures were in the range of 130 - 135 °C and crystallinities were in the range of 41.2 – 62.3 %. All results are presented in Tables 4.5 and 4.6.

#### **4.2.1.2) The melting temperature and crystallinity of ethylene polymer with various ethylene pressures**

The melting temperature and crystallinity were found to have no direct relation between ethylene pressures for absence and presence of hydrogen in polymerization systems. The melting temperatures were in the range of 130 - 135 °C and crystallinity were in the range of 41.2 – 62.3 %. All results are presented in Tables 4.5 and 4.6.

#### **4.2.1.3) The melting temperature and crystallinity of ethylene polymer with various hydrogen concentrations**

The melting temperature and crystallinity were found to have no direct relation between hydrogen concentrations in the presence of hydrogen. The melting temperatures were in the range of 131 - 135 °C and crystallinity were in the range of 49.5 – 62.3 %. All results are presented in Tables 4.5 and 4.6. But the melting temperature and crystallinity in presence of hydrogen higher than the melting temperature and crystallinity in absence of hydrogen because of effect of chain transfer by Hydrogen resulted in an increase of number of short chain (lower molecular weight). It makes short chain polymer easily align to form crystalline polymer due to longer molecules have difficulty organizing into layer become tangled.

#### 4.2.2) Average Molecular Weight and Molecular Weight Distribution

The molecular weight (Mw) and molecular weight distribution (MWD) using supported metallocene catalyst were determined by gel permeation chromatography. The results of various effects, such as polymerization temperatures, ethylene pressures and hydrogen concentrations of produced polymer are shown in Tables 4.7 and 4.8 .

**Table 4. 7** Mw and MWD of ethylene polymer with various polymerization temperatures at ethylene pressure of 6 barg<sup>a</sup>.

Ethylene pressure (barg)	Temperature (°C)	Hydrogen concentration (ml)	Mw <sup>c</sup> (g/mol)	Mn <sup>c</sup> (g/mol)	MWD <sup>c</sup>
6	70	0	342,038	67,380	5.08
	80		180,931	46,460	3.94
	90		148,014	34,432	4.30
	70	480	84,802	8,803	9.63
	80		113,173	12,608	8.98
	90		127,250	11,647	10.93
	70	960	29,513	3,026	9.75
	80		43,368	4,276	10.14
	90		54,593	6,431	8.49

<sup>a</sup> Slurry ethylene polymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

<sup>c</sup> Determined by GPC.



**Table 4. 8** Mw and MWD of ethylene polymer with various polymerization temperatures at ethylene pressure of 8 barg<sup>a</sup>.

Ethylene pressure (barg)	Temperature (°C)	Hydrogen concentration (ml)	Mw <sup>c</sup> (g/mol)	Mn <sup>c</sup> (g/mol)	MWD <sup>c</sup>
8	70	0	347,344	90,546	3.84
	80		178,904	46,715	3.83
	90		150,482	38,987	3.86
	70	480	128,900	13,516	9.54
	80		161,658	17,902	9.03
	90		119,305	13,343	8.94
	70	960	54,434	5,702	9.56
	80		92,647	7,273	12.74
	90		101,842	8,882	11.47

<sup>a</sup> Slurry ethylene polymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

<sup>c</sup> Determined by GPC.

#### 4.2.2.1) The Molecular Weight and Molecular Weight Distribution of ethylene polymer with various polymerization temperatures

The molecular weight and molecular weight distribution at different polymerization temperatures are reported by the data in Tables 4.7 and 4.8. In the absence of hydrogen, it was found that molecular weight decreased with increasing polymerization temperatures. It can be regarded as both propagation and termination rates are produced as a result by temperatures due to termination reactions (especially,  $\beta$ -H elimination chain transfer reaction) need higher activation energies. Therefore, propagation is favored over termination at low temperatures, thus

resulting in polymers with increasing molecular weights. With increasing temperature, activation energy for chain transfer becomes available, leading to a decrease in polymer molecular weight [47-49]. On the other hand, in the presence of hydrogen was found that these data indicates slightly higher molecular weight with increasing temperatures. Consequently, the effect of temperature on the solubility of hydrogen in hexane decreased as the increasing temperature of reactor[30]. Therefore, the capability of chain transfer agent by hydrogen was worse than upon higher polymerization temperatures leading to increment of molecular weight. In contrast, molecular weight distribution did not appear at different polymerization temperatures. The MWD was broader owing to the interactions between the metallocene and the support, which leads to the formation of active sites differing in electronic and steric character [50].

#### **4.2.2.2) The Molecular Weight and Molecular Weight Distribution of ethylene polymer with various ethylene pressures**

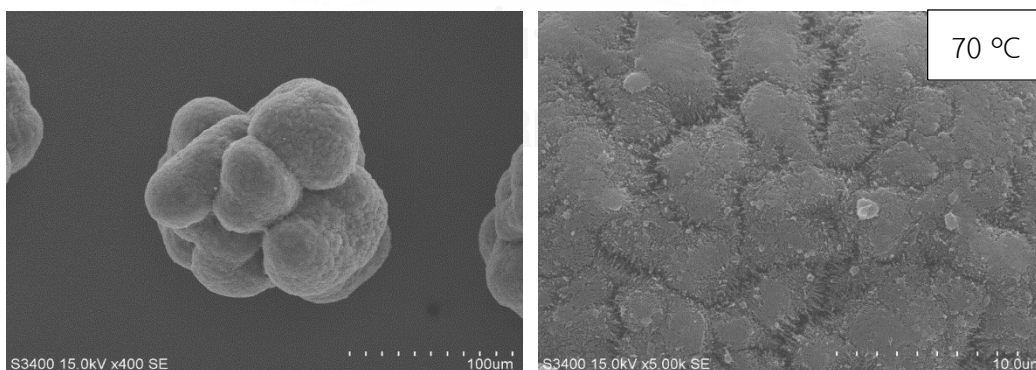
The molecular weight and molecular weight distribution at different ethylene pressures are reported by the data in Table 4.7 and 4.8. In the absence of hydrogen had not shown remarkable effects on molecular weight and molecular weight distribution with increasing ethylene pressures. But in the presence of hydrogen was found that these data indicates slightly higher molecular weight with increasing ethylene pressures . Due to concentration of ethylene pressures increased in spite of total concentration of hydrogen was fixed in reactor. Resulting concentration of hydrogen decreased. Therefore, the capability of chain transfer agent by hydrogen was worse than upon higher ethylene pressures leading to increment of molecular weight.

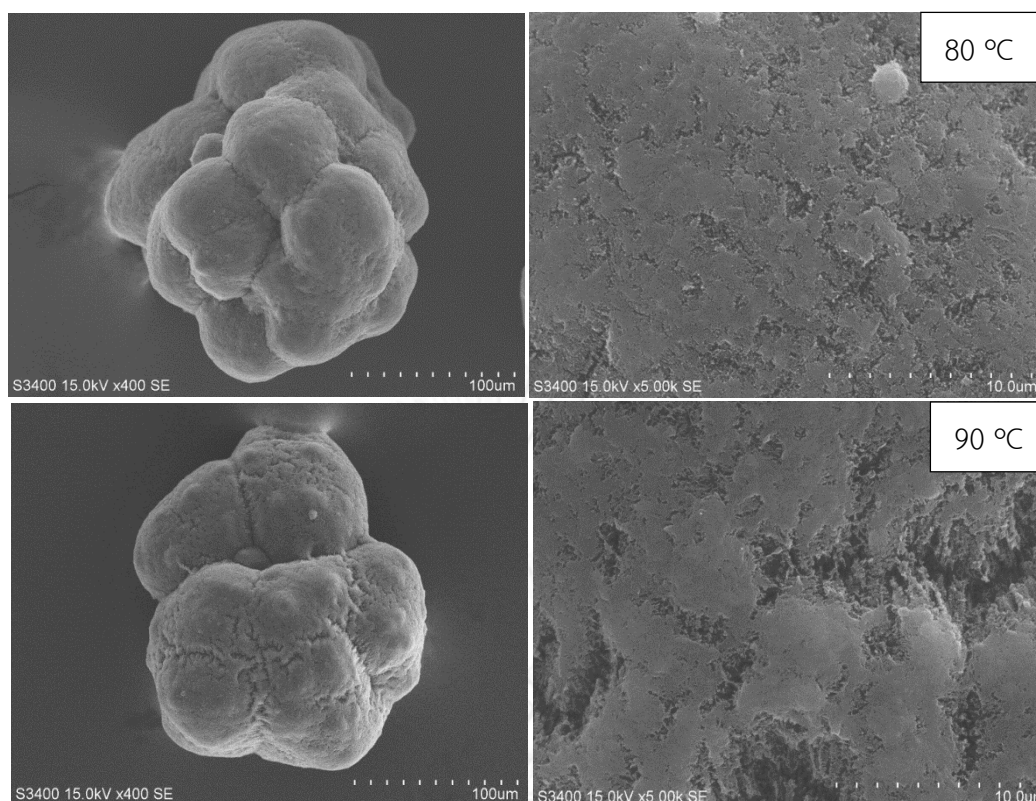
#### 4.2.2.3) The Molecular Weight and Molecular Weight Distribution of ethylene polymer with various hydrogen concentrations

The molecular weight and molecular weight distribution at different hydrogen concentrations are reported by the data in Table 4.7 and 4.8. Hydrogen shows a similar role as strong effect on the molecular weight of the polymer. In the presence of hydrogen, from the result, it revealed slightly lower molecular weights with increasing hydrogen concentrations indicating that these hydrogen terminations or chain transfer agent lead to saturated end-groups, and then decreased in molecular weights. The MWD of in the presence of hydrogen was higher than in the absence of hydrogen. This is because growth of the number of short chains was produced from higher termination rate by hydrogen [51].

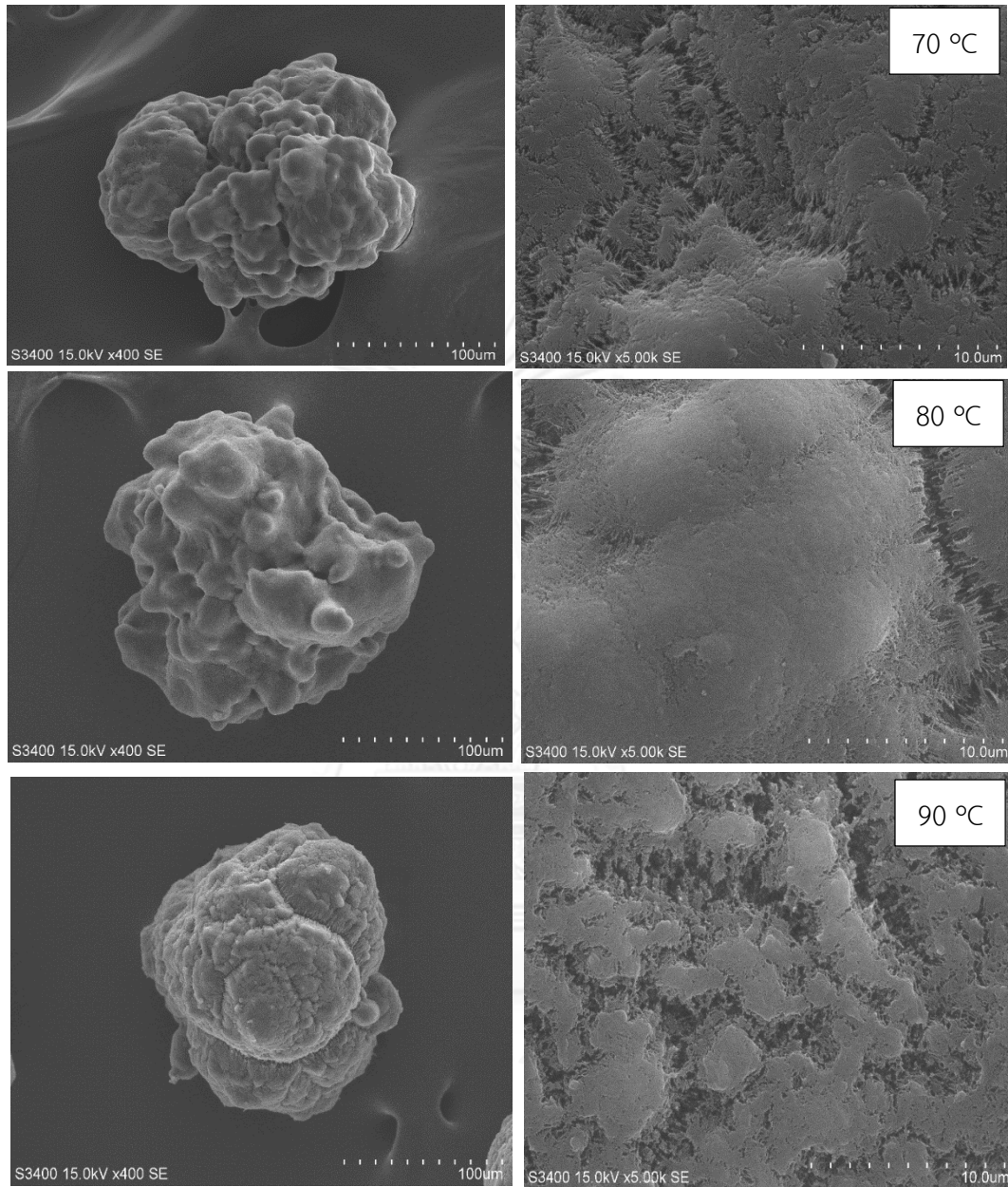
#### 4.2.3) Morphology

The obtained polymer in this study was observed by scanning electron microscopy. It could determine morphology as shown in Figures 4.4 – 4.6.

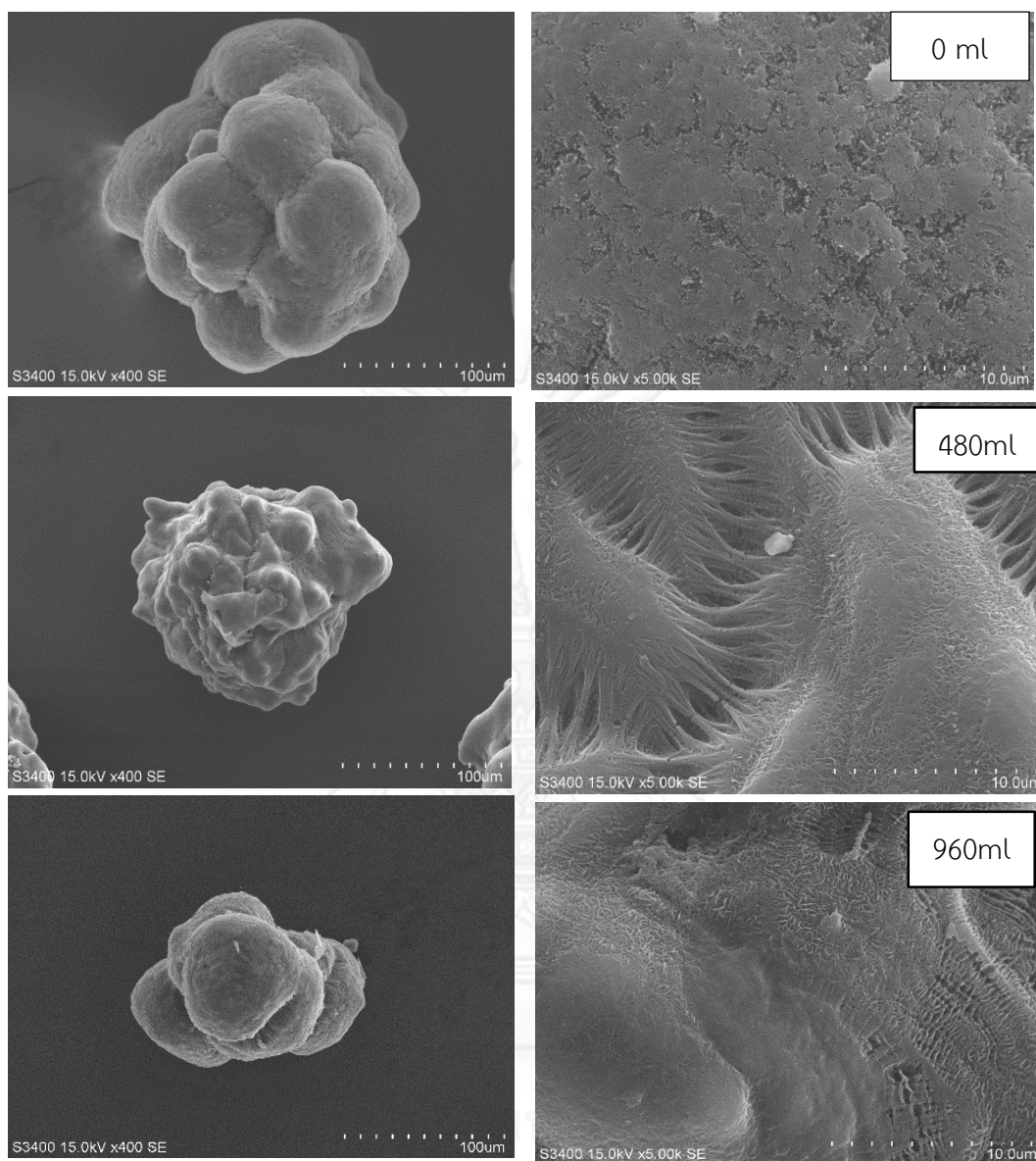




**Figure 4. 4** Scanning electron micrographs of the polyethylene particles without hydrogen at different polymerization temperatures having ethylene pressure of 6 barg



**Figure 4. 5** Scanning electron micrographs of the polyethylene particles without hydrogen at different polymerization temperatures having ethylene pressure of 8 barg



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**Figure 4. 6** Scanning electron micrographs of the polyethylene particles with polymerization temperature at 80 °C at different hydrogen concentrations having ethylene pressure of 6 barg

#### **4.2.3.1) Morphology of ethylene polymer with various polymerization temperatures**

Figure 4.4 and Figure 4.5 show the SEM images of the polymer produced without hydrogen at different polymerization temperatures. It was found that most of the polymer particles were unusual spherical shape and some more broken fragments on the surface polymer with increasing temperatures. It can be seen that there was no significant change in morphologies of the polyethylene produced by changing the polymerization temperatures.

#### **4.2.3.2) Morphology of ethylene polymer with various ethylene pressures**

Figure 4.4 and Figure 4.5 show the SEM images of the polymer produced without hydrogen at different ethylene pressures. It was found that most of the polymer particles were unusual spherical shape. Moreover, It can be seen that the polymer particles growing when higher ethylene pressures.

#### **4.2.3.3) Morphology of ethylene polymer with various hydrogen concentrations**

Figure 4.6 show the SEM images of the polymer produced at different hydrogen concentrations. In the presence of hydrogen, it can be observed that most of the polymer smaller size compares to polymer particle in the absence of hydrogen. Thus, polymer was fine generation in the presence of hydrogen.

### 4.3) Ethylene / 1-Hexene Copolymerization on Catalyst

#### 4.3.1) The Effect of Polymerization Temperature on the Catalytic Activity

The influence of copolymerization temperatures were investigated with different copolymerization temperature in the range from 60 to 80 °C. The copolymerization conditions were performed in hexane solvent using ethylene pressure of 6 and 7 barg , 1-hexene loaded in the reactor at 0, 10 and 15 ml , using 30 mg of supported metallocene catalyst , triethylaluminum (TEA) concentration 0.5 mmol/L as a scavenger and polymerization time was fixed at 2 h. Tables 4.9 and 4.10 reveal the results for the influence of temperature on the catalyst activity.

**Table 4. 9** Effect of polymerization temperature on the catalyst activity at ethylene pressure of 6 barg<sup>a</sup>

Ethylene pressure (barg)	Temperature (°C)	1-hexene loaded in the reactor (ml)	Yield (g)	Catalyst Activity (kg PE/g cat·h)
6	60	0	45.46	0.7577
	70		130.10	2.1683
	80		218.61	3.6435
	60	10	167.36	2.7893
	70		315.20	5.2533
	80		334.05	5.5675
	60	15	210.12	3.5020
	70		312.70	5.2117
	80		325.02	5.4170

<sup>a</sup> Slurry ethylene/1-hexene copolymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.



**Table 4. 10** Effect of polymerization temperature on the catalyst activity at ethylene pressure of 7 barg<sup>a</sup>

Ethylene pressure (barg)	Temperature (°C)	1-hexene loaded in the reactor (ml)	Yield (g)	Catalyst Activity (kg PE/g cat·h)
7	60	0	64.62	1.0770
	70		152.76	2.5460
	80		297.99	4.9665
	60	10	202.38	3.3730
	70		382.83	6.3805
	80		395.64	6.5940
	60	15	250.22	4.1703
	70		373.95	6.2325
	80		375.04	6.2507

<sup>a</sup> Slurry ethylene polymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

Tables 4.9 and 4.10 show the results that the activity is enhanced with increasing polymerization temperature. The highest activity was attained at 80 °C for both homo and copolymerization system. From results, it can be explained by a widely accepted mechanism of propagation in Metallocene catalysis involves the initial formation of a  $\pi$ -complex of an olefin with the metal catalyst, followed by a chain migratory insertion [45]. The increase of activity with the polymerization temperature is related to the increased kinetic by Arrhenius equation.

Assuming the Arrhenius-type temperature dependence of the modified propagation constant given in equation (4.1).

$$k_p = A \exp(-E_{a,p} / RT) \quad (4.1)$$

When	$k_p$	=	Propagation rate constant.
	$E_{a,p}$	=	Activation energy of the propagation.
	A	=	Frequency factor.
	R	=	The gas constant.
	T	=	Kelvin temperature.

Working under isobaric–isothermal reaction conditions and assuming a very rapid monomer mass transfer between all relevant phases, we can rewrite equation (4.2):

$$R_p = k_p [C_E^*] [C_E] \quad (4.2)$$

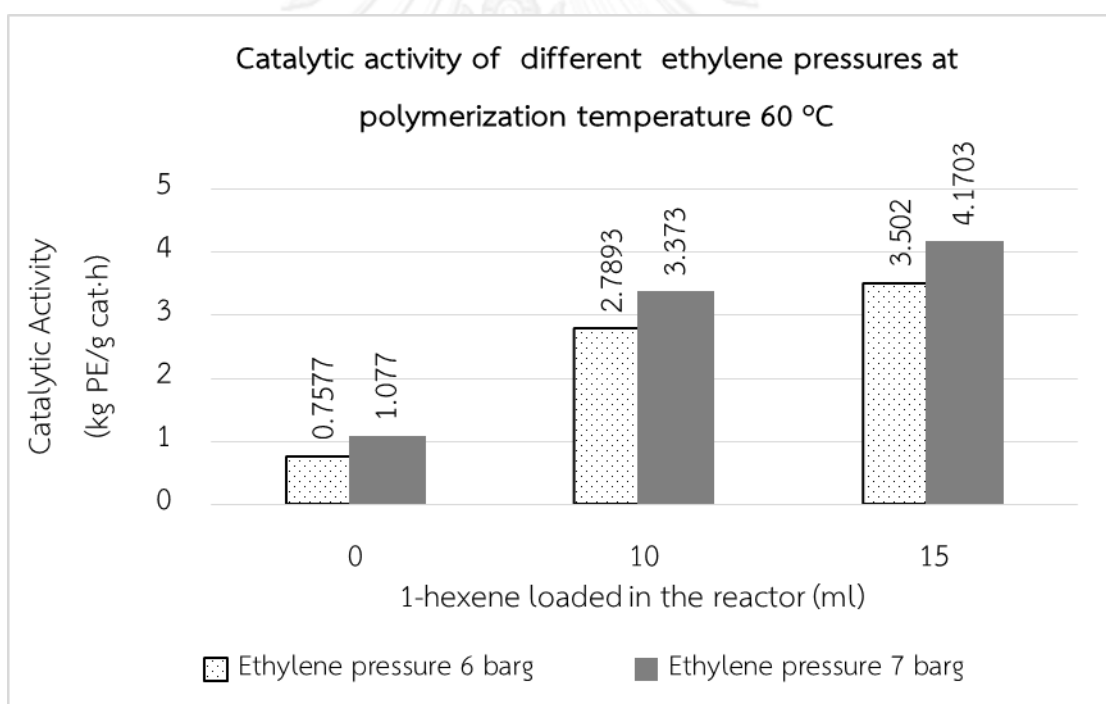
$R_p$  is the polymerization rate,  $C_E^*$  is the active species concentration of ethylene,  $C_E$  is the concentration of ethylene and substituting it in equation (4.1), one can derive Equation (4.3)

$$R_p / C_E = A \exp(-E_{a,p} / RT) \quad (4.3)$$

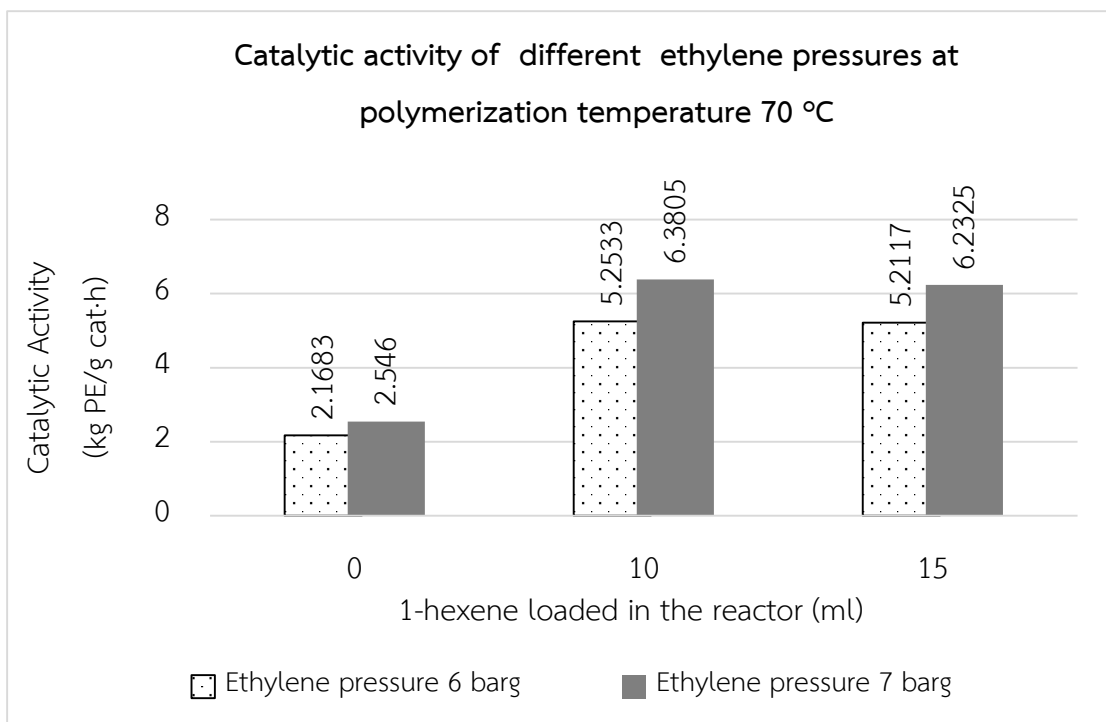
From equation (4.3), productivity is proportional to the polymerization rate which is related to polymerization temperature. Increasing of polymerization temperature improves the polymerization rate, leading to the rise of the catalytic activity.

#### 4.3.2) The Effect of Ethylene Pressure on the Catalytic Activity

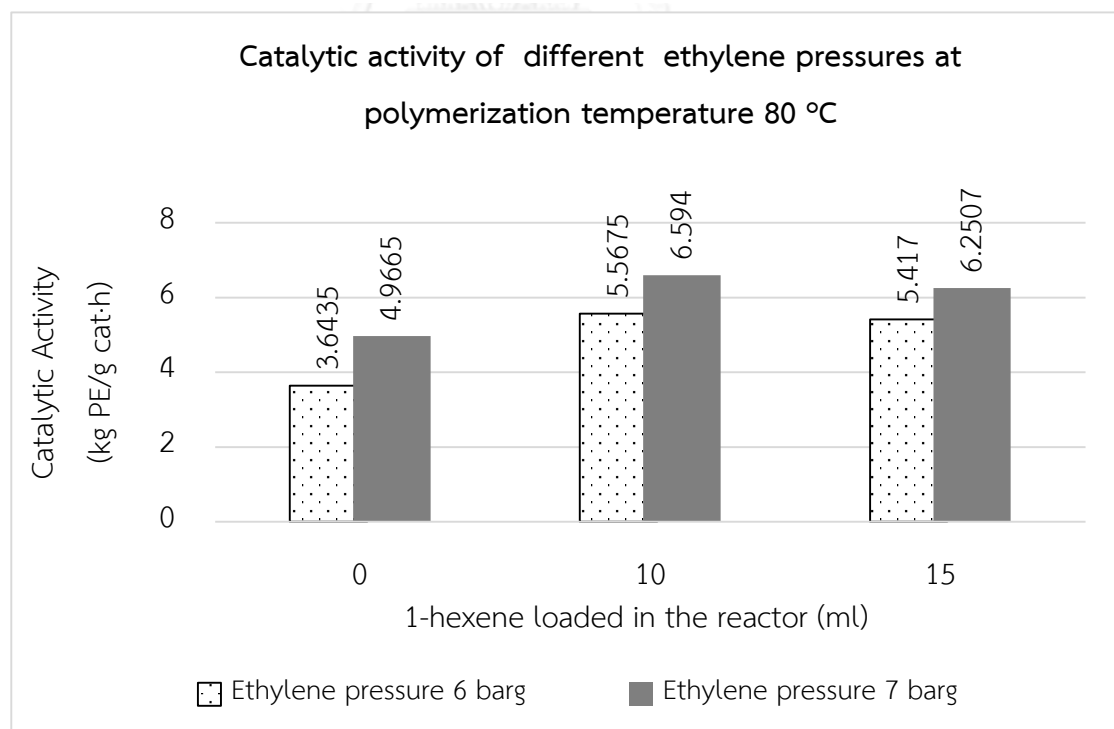
The influence of ethylene pressures on copolymerization was investigated with different ethylene pressures at 6 and 7 barg. The copolymerization conditions were performed in hexane solvent, using copolymerization temperature at 60 , 70 , 80 °C , 1-hexene loaded in the reactor 0, 10 and 15 ml , using 30 mg of supported metallocene catalyst , triethylaluminum (TEA) concentration 0.5 mmol/L as a scavenger and polymerization time were fixed at 2 h. Figures 4.7 -4.9 show the results for the influence of ethylene pressures on the catalytic activity.



**Figure 4. 7** Catalytic activity of different ethylene pressures at polymerization temperature 60 °C



**Figure 4. 8** Catalytic activity of different ethylene pressures at polymerization temperature 70 °C



**Figure 4. 9** Catalytic activity of different ethylene pressures at polymerization temperature 80 °C

The influence of the ethylene pressure on the activity at constant polymerization temperature and volume 1-hexene was investigated. to explain the behavior in slurry polymerization by the chain propagation reaction and kinetic equations.

Copolymerization of the two monomers brings to two types of propagating species with  $E$  at the ethylene propagating end and  $H$  at the 1-hexene propagating. These can be represented by  $C_E^*$  and  $C_H^*$  where the asterisk represents either a radical as the propagating species depending on the particular case. It was assumed that the reactivity of the propagating species was dependent only on the monomer unit at the end of the chain, four propagation reactions were then possible.  $E$  and  $H$  can each add either to a propagating chain ending in  $E$  or to one ending in  $H$ , that the chain propagation reactions were described in equation (4.1) – (4.4) :



Where  $k_{11}$  = rate constant for a propagating chain ending in ethylene adding to ethylene monomer.

$k_{12}$  = rate constant for a propagating chain ending in ethylene adding to 1-hexene monomer.

$k_{21}$  = rate constant for a propagating chain ending in 1-hexene adding to ethylene monomer.

$k_{22}$  = rate constant for a propagating chain ending in 1-hexene adding to 1-hexene monomer.

Ethylene monomer disappears by Reactions 4.1 and 4.3, while 1-hexene monomer disappears by Reactions 4.2 and 4.4. The rates of disappearance of the two monomers, which were synonymous with their rates of entry into the copolymer, The kinetic equation could be utilized following equation (4.5) :

$$R_p = k_{11}[C_E^*][E] + k_{21}[C_H^*][E] + k_{12}[C_E^*][H] + k_{22}[C_H^*][H] \quad (4.5)$$

When  $R_p$  = polymerization rate.

$[E]$  = ethylene concentration.

$[H]$  = 1-hexene concentration.

$C_E^*$  = active center of ethylene concentration.

$C_H^*$  = active center of 1-hexene concentration.

By equation (4.5), productivity was proportional to the polymerization rate which was related to the ethylene concentration and the 1-hexene concentration. As ethylene concentration was relative to the ethylene pressure, increasing of ethylene pressure enhanced the polymerization rate due to increasing the ethylene concentration of ethylene diffused into the active center. It leads to the rise of the catalytic activity. As shown in Figures 4.7 – 4.9 , there were a tendency of the activity to increase with increasing ethylene pressure [40].

#### 4.3.3) The Effect of Comonomer response under various volumes of 1-hexene on the Catalytic Activity

The influence of comonomer response was investigated with different volumes of 1-hexene at absence of 1-hexene, 10 ml and 15 ml. The copolymerization conditions were performed in hexane solvent, using copolymerization temperature at 60 , 70 , 80 °C , ethylene pressure 6 and 7 barg, using 30 mg of supported metallocene catalyst , triethylaluminum (TEA) concentration 0.5 mmol/L as a scavenger and polymerization time was fixed at 2 h. Tables 4.11 and 4.12 reveal the results for the influence of comonomer response on the catalyts activity.

**Table 4. 11** Effect of comonomer response on the catalyst activity at ethylene pressure of 6 barg<sup>a</sup>

Ethylene pressure (barg)	Temperature (°C)	1-hexene loaded in the reactor (ml)	Yield (g)	Catalyst Activity (kg PE/g cat·h)
6	60	0	45.46	0.7577
		10	167.36	2.7893
		15	210.12	3.5020
	70	0	130.10	2.1683
		10	315.20	5.2533
		15	312.70	5.2117
	80	0	218.61	3.6435
		10	334.05	5.5675
		15	325.02	5.4170

<sup>a</sup> Slurry ethylene/1-hexene copolymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

**Table 4. 12** Effect of comonomer response on the catalyst activity at ethylene pressure of 7 barg<sup>a</sup>

Ethylene pressure (barg)	Temperature (°C)	1-hexene loaded in the reactor (ml)	Yield (g)	Catalyst Activity (kg PE/g cat·h)
7	60	0	64.62	1.0770
		10	202.38	3.3730
		15	250.22	4.1703
	70	0	152.76	2.5460
		10	382.83	6.3805
		15	373.95	6.2325
	80	0	297.99	4.9665
		10	395.64	6.5940
		15	375.04	6.2507

<sup>a</sup> Slurry ethylene/1-hexene copolymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.



According to Tables 4.11 and 4.12 , it was illustrated that the productivity of polymerization increased until certain value of 1-hexene loading was reached (15 ml at 60 °C, 10 ml at 70 and 80 °C for both ethylene pressure). For higher 1-hexene loading, the activity was steadily increasing at 60 °C and even a decrease was detected working at 70 and 80 °C. The copolymerization catalytic activity is higher than that for homopolymerization. This behavior was known as the “comonomer effect” that the addition of comonomer increased the catalytic activity could be related with a easier diffusion of the monomers through a less crystalline of the growing polymer around the active sites during the reaction. Therefore, enhanced the copolymerization activity. The reduction in catalyst activity was for higher 1-hexene concentrations. It was probably due to the increase in the 1-hexene inserted active species which was more sterically hindered around active site thus less reactive than the ethylene inserted [52]. Also leading to a reduction in the propagation rate with the presence of higher 1-hexene loading.

#### 4.4) Characterization of the Ethylene /1-Hexene Copolymer

##### 4.4.1) 1-hexene incorporation in the Copolymer (%wt)

The copolymer of ethylene/1-hexene using supported metallocene catalyst were determined by Fourier transforms infrared spectroscopy (FTIR). The results of various effects, such as polymerization temperatures, ethylene pressures and 1-hexene volumes loaded in the reactor on 1-hexene incorporation of produced copolymer are shown in Tables 4.13-4.14 and Figures 4.4-4.6, respectively.

**Table 4. 13** 1-hexene incorporation of copolymer with various polymerization temperatures at ethylene pressure of 6 barg<sup>a</sup>

Ethylene pressure (barg)	Temperature (°C)	1-hexene loaded in the reactor (ml)	1-hexene in the Copolymer <sup>d</sup> (%wt)	Catalyst Activity (kg PE/g cat·h)
6	60	0	-	0.7577
	70		-	2.1683
	80		-	3.6435
	60	10	1.94	2.7893
	70		1.57	5.2533
	80		1.49	5.5675
	60	15	2.51	3.5020
	70		1.95	5.2117
	80		1.86	5.4170

<sup>a</sup> Slurry ethylene/1-hexene copolymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

<sup>d</sup> Determined by FTIR measurement.

**Table 4. 14** 1-hexene incorporation of copolymer with various polymerization temperatures at ethylene pressure of 7 barg<sup>a</sup>.

Ethylene pressure (barg)	Temperature (°C)	1-hexene loaded in the reactor (ml)	1-hexene in the Copolymer <sup>d</sup> (%wt)	Catalyst Activity (kg PE/g cat.h)
7	60	0	-	1.0770
	70		-	2.5460
	80		-	4.9665
	60	10	1.79	3.3730
	70		1.33	6.3805
	80		1.36	6.5940
	60	15	2.20	4.1703
	70		1.82	6.2325
	80		1.65	6.2507

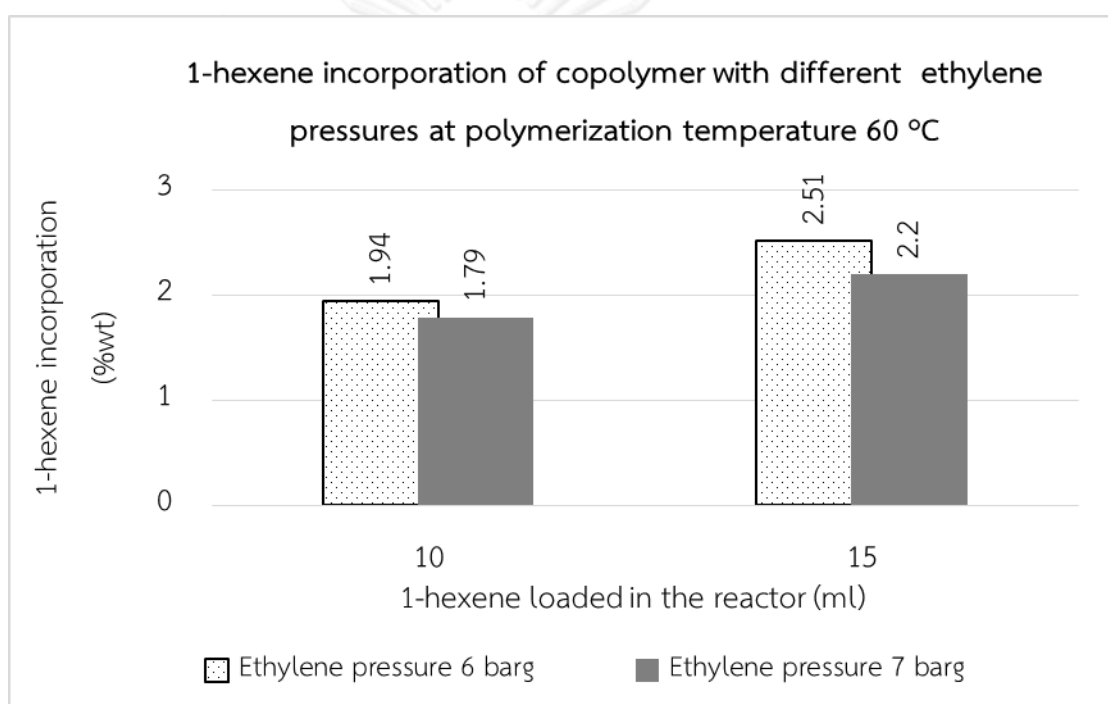
<sup>a</sup> Slurry ethylene/1-hexene copolymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

<sup>d</sup> Determined by FTIR measurement.

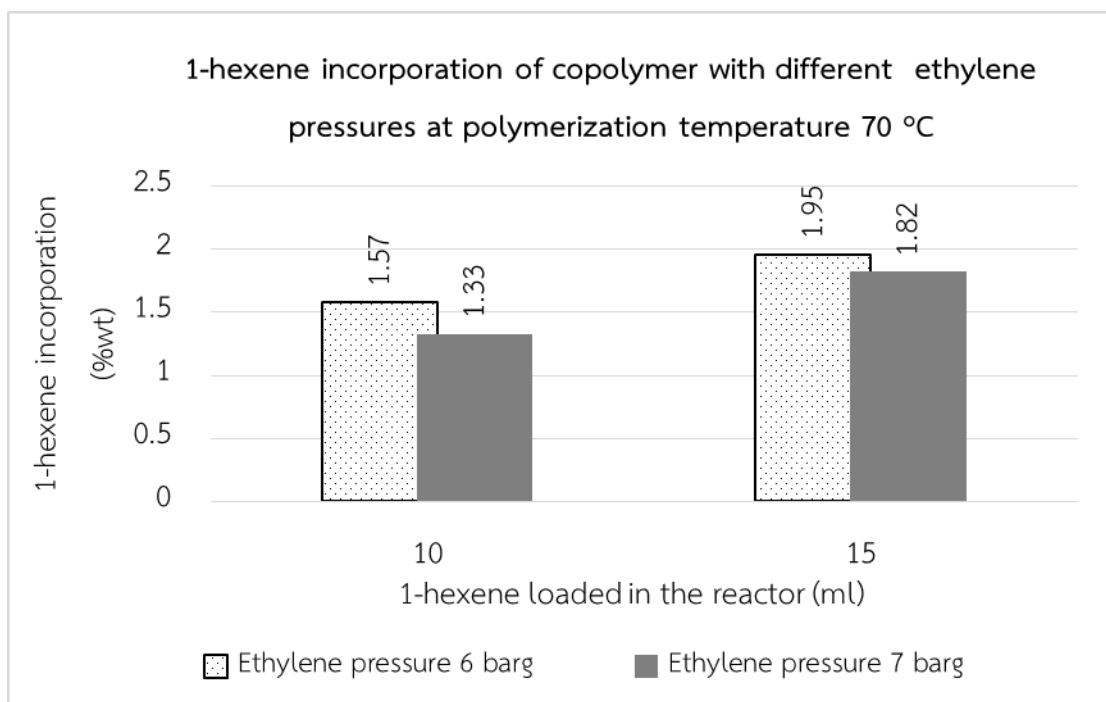
#### 4.4.1.1) The Effect Polymerization Temperatures various volumes of 1-hexene on the 1-hexene incorporation of copolymer

It can be observed from Tables 4.13 and 4.14 that the 1-hexene incorporation observed when decreasing the polymerization temperatures could be related to the different influence on the insertion rate for both ethylene and 1-hexene monomer. As a result above, it shows that the decrease polymerization temperatures from 80 to 60 °C led to a higher amount of 1-hexene in copolymer at both ethylene pressure since ethylene was rapidly inserted in the growing polymer

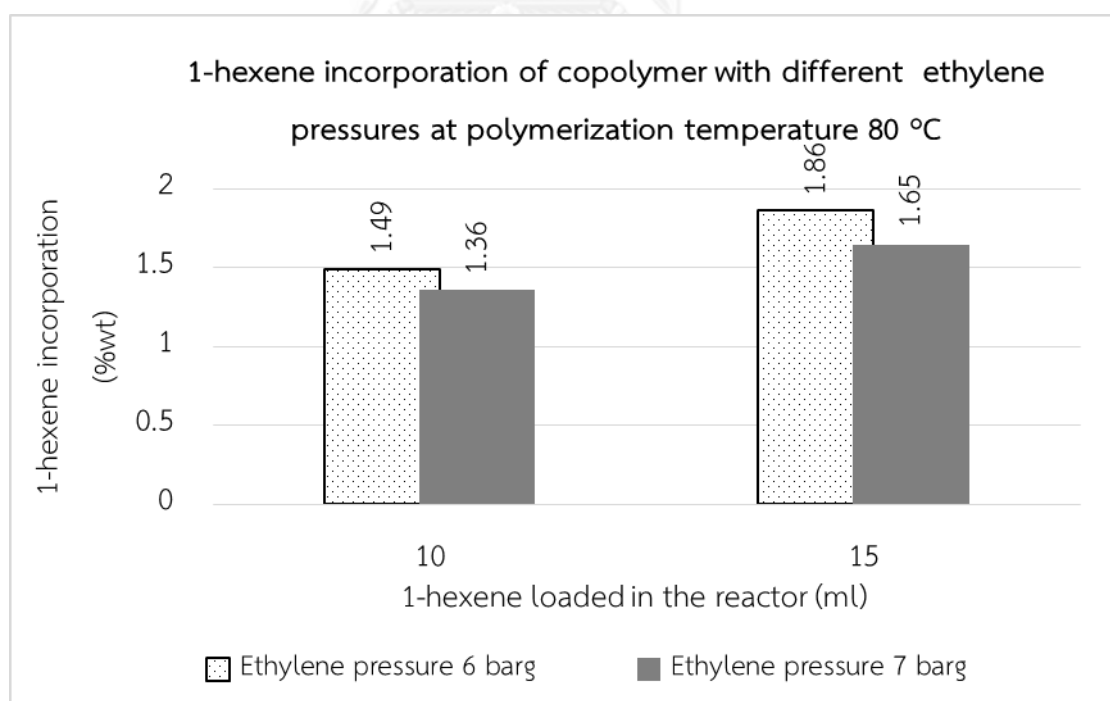
chain than 1-hexene. When the last inserted monomer was an ethylene unit, this means that the copolymerization insertion was decreased with increasing polymerization temperatures. Moreover, temperature can change diffusivities differently for the 1-hexene which can modify the chemical composition around active centers. Leading to different the 1-hexene incorporation [53].



**Figure 4. 10** 1-hexene incorporation of copolymer with different ethylene pressures at polymerization temperature of 60 °C



**Figure 4. 12** 1-hexene incorporation of copolymer with different ethylene pressures at polymerization temperature of 70 °C



**Figure 4. 11** 1-hexene incorporation of copolymer with different ethylene pressures at polymerization temperature of 80 °C

#### 4.4.1.2) The Effect ethylene pressures various volumes of 1-hexene on the 1-hexene incorporation of copolymer

Figures 4.10 - 4.12 show the tendency of copolymerization for a 6 and 7 barg ethylene pressures, giving relation between the incorporated 1-hexene and the ethylene pressures. It could be seen that at lower ethylene pressure more 1-hexene was incorporated into the copolymer. This phenomenon was considered to be due to the incorporation of 1-hexene is favored at low ethylene pressures. It may be attributed to at higher ethylene pressures, the concentration of ethylene in the solution is higher and favors the reaction of ethylene with ethylene in the copolymerization [40].

#### 4.4.2) Melting Temperature ( $T_m$ ) and Crystallinity ( $X_c$ )

The melting temperatures and crystallinities of ethylene/1-hexene copolymer using supported metallocene catalysts were determined by differential scanning calorimeter. The results of various effects, such as polymerization temperatures, ethylene pressures and and 1-hexene volumes loaded in the reactor on melting temperatures and crystallinities of produced copolymer are shown in Tables 4.13 - 4.14 . The DSC curves of these polymer were also demonstrated in Appendix A.

**Table 4. 15** Melting temperature and crystallinity of ethylene/1-hexene copolymer with various polymerization temperatures at ethylene pressure of 6 barg<sup>a</sup>.

Ethylene pressure (barg)	Temperature (°C)	1-hexene loaded in the reactor (ml)	1-hexene in the Copolymer <sup>d</sup> (%wt)	T <sub>m</sub> <sup>b</sup> (°C)	X <sub>c</sub> <sup>b</sup> (%)
6	60	0	-	133	46.1
	70		-	131	42.0
	80		-	130	46.6
	60	10	1.94	123	33.8
	70		1.57	126	34.6
	80		1.49	126	35.2
	60	15	2.51	121	29.6
	70		1.95	124	30.2
	80		1.86	124	35.7

<sup>a</sup> Slurry ethylene/1-hexene copolymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

<sup>b</sup> Determined by DSC, the crystallinity was calculated from heat of crystalline formation based on HDPE.

<sup>d</sup> Determined by FTIR measurement.

**Table 4. 16** Melting temperature and crystallinity of ethylene/1-hexene copolymer with various polymerization temperatures at ethylene pressure of 7 barg<sup>a</sup>.

Ethylene pressure (barg)	Temperature (°C)	1-hexene loaded in the reactor (ml)	1-hexene in the Copolymer <sup>d</sup> (%wt)	T <sub>m</sub> <sup>b</sup> (°C)	X <sub>c</sub> <sup>b</sup> (%)
7	60	0	-	131	41.7
	70		-	134	46.8
	80		-	134	49.3
	60	10	1.79	124	33.6
	70		1.33	126	34.6
	80		1.36	127	37.7
	60	15	2.2	122	27.6
	70		1.82	124	32.2
	80		1.65	124	32.1

<sup>a</sup> Slurry ethylene/1-hexene copolymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

<sup>b</sup> Determined by DSC, the crystallinity was calculated from heat of crystalline formation based on HDPE.

<sup>d</sup> Determined by FTIR measurement.



#### **4.4.2.1) The melting temperature and crystallinity of ethylene/1-hexene copolymer with various polymerization temperatures**

The melting temperature and crystallinity were found to have little effect on polymerization temperatures for both homo and copolymerization. In the homopolymerization system, melting temperatures were in the range of 130 - 134 °C and crystallinity were in the range of 42.0 – 49.3 % . In the copolymerization system, melting temperatures were in the range of 120.69 – 126.86 °C and crystallinity were in the range of 27.6 – 37.7 % . All results are presented in Tables 4.15 and 4.16.

#### **4.4.2.2) The melting temperature and crystallinity of ethylene/1-hexene copolymer with various ethylene pressures**

The melting temperature and crystallinity were found to have little effect on ethylene pressures for both homo and copolymerization. In the homopolymerization system, melting temperatures were in the range of 130 - 134°C and crystallinity were in the range of 42.0 – 49.3 % . In the copolymerization system, melting temperatures were in the range of 120.69 – 126.86 °C and crystallinity were in the range of 27.6 – 37.7 % . All results are presented in Table 4.15 and 4.16.

#### **4.4.2.3) The melting temperature and crystallinity of ethylene/1-hexene copolymer with various 1-hexene volumes loaded in the reactor**

The melting temperature and crystallinity of the obtained copolymer were decreased with increasing 1-hexene incorporation in the copolymer with similar as shown in Tables 4.15 and 4.16. This is because of the reduced difficulty of crystal formation caused by the incorporation of 1-hexene that produced branches and disturbed the polymeric chain packing [54].

#### 4.4.3) Average Molecular Weight and Molecular Weight Distribution

The molecular weight (Mw) and molecular weight distribution (MWD) using the supported metallocene catalyst were determined by gel permeation chromatography. The results of various effects, such as polymerization temperatures, ethylene pressures and 1-hexene volumes loaded in the reactor on 1-hexene incorporation of produced copolymer are shown in Tables 4.17 and 4.18 .

**Table 4. 17** Mw and MWD of ethylene/1-hexene copolymer with various polymerization temperatures at ethylene pressure of 6 barg.

Ethylene pressure (barg)	Temperature (°C)	1-hexene loaded in the reactor (ml)	Mw <sup>c</sup> (g/mol)	Mn <sup>c</sup> (g/mol)	MWD <sup>c</sup>
6	60	0	381,305	88,515	4.31
	70		342,038	67,380	5.08
	80		180,931	46,460	3.94
	60	10	194,504*	64,627*	3.01*
	70		195,255*	55,386*	3.53*
	80		173,908*	52,807*	3.29*
	60	15	208,878*	63,884*	3.27*
	70		210,510*	49,236*	4.28
	80		170,799*	41,867*	4.08*

<sup>a</sup> Slurry ethylene/1-hexene copolymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

<sup>c</sup> Determined by GPC.

\* Sample in preparation before analysis with GPC by dissolving the polymer at a temperature of 160 °C and then filtered polymer to prevent clogging. In GPC measurement.

**Table 4. 18** Mw and MWD of ethylene/1-hexene copolymer with various polymerization temperatures at ethylene pressure of 7 barg.

Ethylene pressure (barg)	Temperature (°C)	1-hexene loaded in the reactor (ml)	Mw <sup>c</sup> (g/mol)	Mn <sup>c</sup> (g/mol)	MWD
7	60	0	369,519	81,154	4.55
	70		250,798	66,472	3.77
	80		172,987	51,954	3.33
	60	10	218,648*	64,947*	3.37*
	70		218,011*	61,669*	3.54*
	80		153,441*	64,511*	3.54*
	60	15	212,403*	63,100*	3.37*
	70		228,639*	64,511*	3.54*
	80		165,846*	48,871*	3.39*

<sup>a</sup> Slurry ethylene/1-hexene copolymerization conditions were performed in hexane using 30 mg of supported metallocene catalyst and reaction time: 2 hr.

<sup>c</sup> Determined by GPC.

\* Sample in preparation before analysis with GPC by dissolving the polymer at a temperature of 160 °C and then filtered polymer to prevent clogging. In GPC measurement.

#### 4.4.3.1) The Molecular Weight and Molecular Weight Distribution of ethylene/1-hexene copolymer with various polymerization temperatures

The molecular weight and molecular weight distribution at different polymerization temperatures are reported by the data in Tables 4.17 and 4.18. In the homopolymerization system, it was found that the molecular weight decreased with increasing polymerization temperatures. It can be regarded as both

propagation and termination rates are produced as a result by temperatures due to termination reactions (especially,  $\beta$ -H elimination chain transfer reaction) need higher activation energies. Therefore, propagation is favored over termination at low temperatures, thus resulting in polymers with increased molecular weights. With increasing temperature, activation energy for chain transfer becomes available, leading to a decrease in polymer molecular weight [47-49]. However, in the copolymerization system, it was found that these data indicated no direct relation between molecular weight and polymerization temperatures at 60-70 °C. In addition, higher temperatures (80°C) resulted in slightly decreased molecular weight. It could be associated with homopolymerization system. In contrast, molecular weight distribution did not appear at different polymerization temperatures. All polymers show MWD in the interval of 3.01-5.08. The MWDs were broader owing to the interactions between the metallocene and the support, which leads to the formation of active sites differing in electronic and steric character [54].

#### **4.4.3.2) The Molecular Weight and Molecular Weight Distribution of ethylene/1-hexene copolymer with various ethylene pressures**

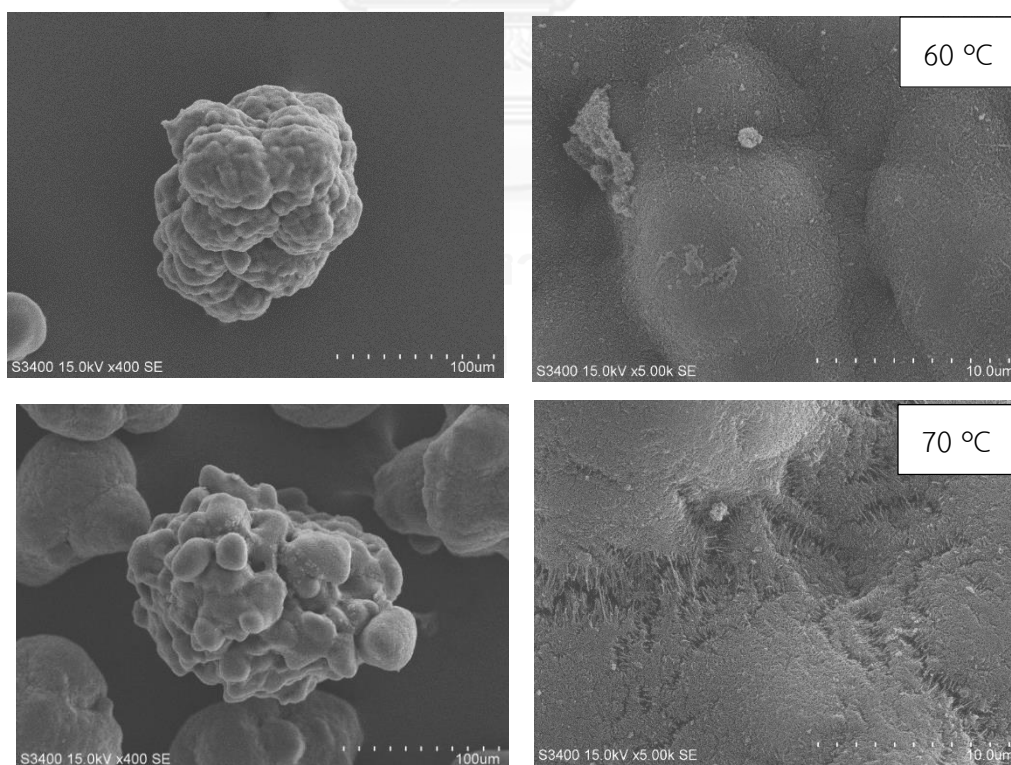
The molecular weight and molecular weight distribution at different ethylene pressures are reported by the data in Tables 4.17 and 4.18. It had not shown remarkable effects on molecular weight and molecular weight distribution with increasing ethylene pressures.

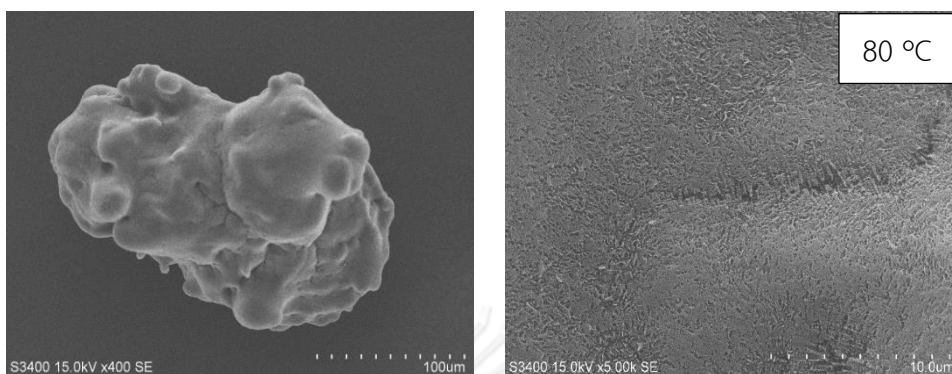
#### 4.4.3.3) The Molecular Weight and Molecular Weight Distribution of ethylene/1-hexene copolymer with various volumes of 1-hexene loaded in the reactor

The molecular weight and molecular weight distribution at different volumes of 1-hexene loaded in the reactor are reported by the data in Tables 4.17 and 4.18. It did not suffer important changes in molecular weight and molecular weight distribution using different 1-hexene initial loaded.

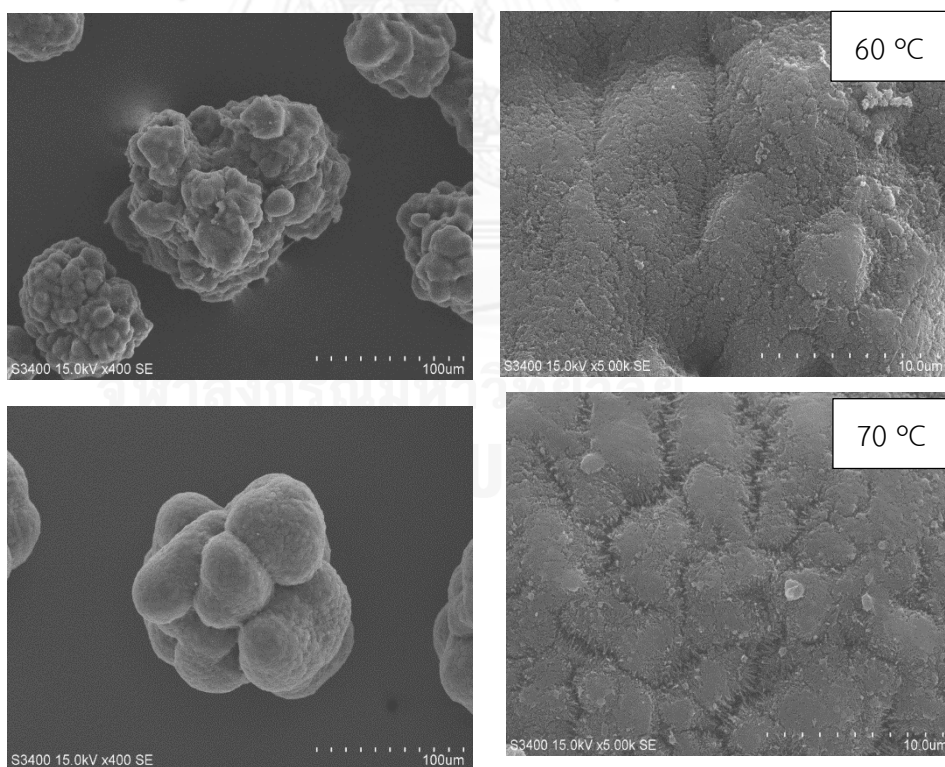
#### 4.4.4) Morphology

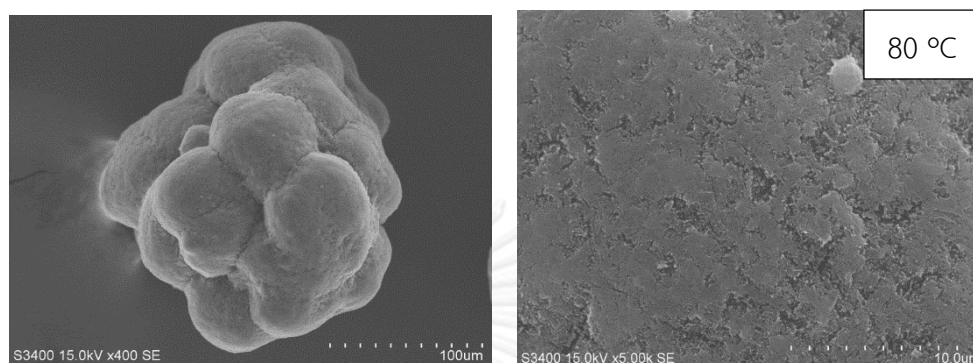
The obtained polymer in this study was observed by scanning electron microscopy. It could determine the morphology as shown in Figure 4.13 – 4.15.



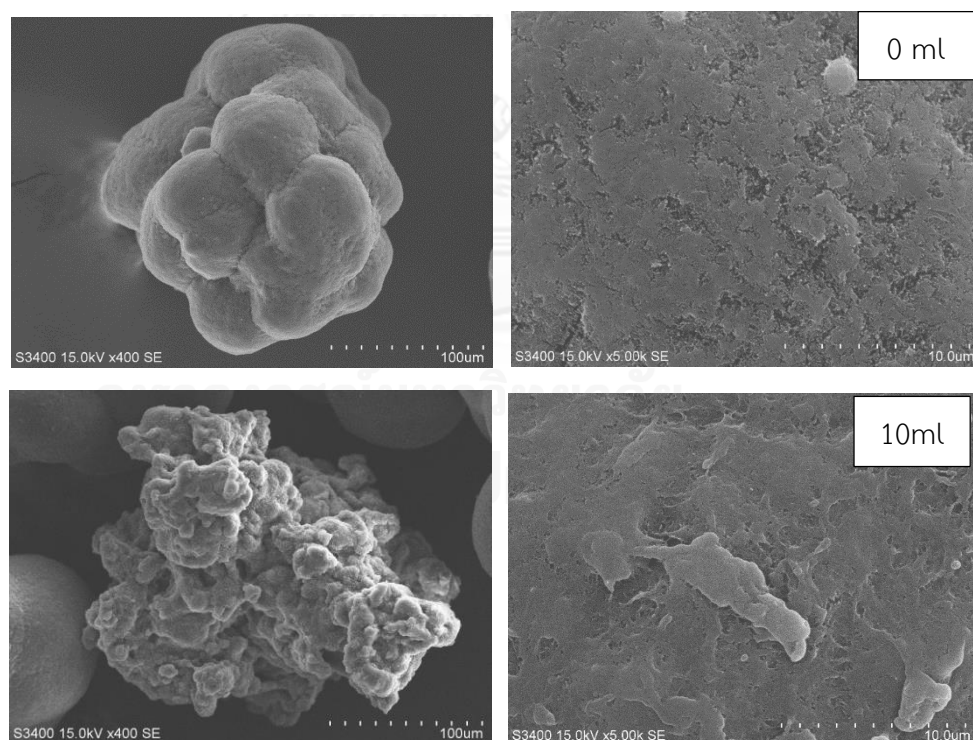


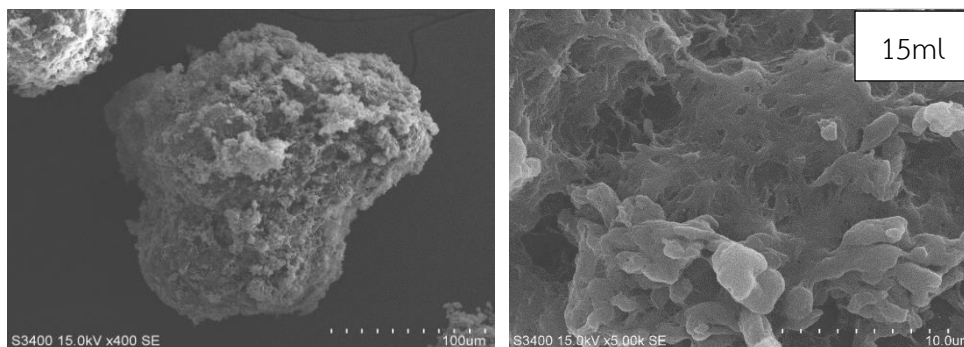
**Figure 4. 13** Scanning electron micrographs of the polyethylene particles without 1-hexene with different polymerization temperatures at ethylene pressure of 7 barg





**Figure 4. 14** Scanning electron micrographs of the polyethylene particles without 1-hexene with different polymerization temperatures at ethylene pressure of 6 barg





**Figure 4. 15** Scanning electron micrographs of the polyethylene particles with polymerization temperature at 80 °C with different volumes of 1-hexene loaded in the reactor at ethylene pressure of 6 barg

#### 4.4.4.1) Morphology of ethylene/1-hexene polymer with various polymerization temperatures

Figure 4.13 and Figure 4.14 show the SEM images of the polymer produced without 1-hexene at different polymerization temperatures. It was found that most of the polymer particles were unusual spherical shape and also more broken fragments on the surface polymer with increased temperatures. It can be seen that there was no significant change in morphologies of the polyethylene produced by changing the polymerization temperatures.

#### 4.4.4.2) Morphology of ethylene/1-hexene polymer with various ethylene pressures

Figure 4.13 and Figure 4.14 show the SEM images of the polymer produced without 1-hexene at different ethylene pressures. It was found that most of the polymer particles were unusual spherical shape. Moreover, it can be seen that the polymer particles growing when higher ethylene pressures were applied.



#### 4.4.4.3) Morphology of ethylene/1-hexene polymer with various volumes of 1-hexene loaded in the reactor

Figure 4.15 shows the SEM images of the polymer produced as comparison the homopolymers and copolymers at different 1-hexene concentrations. The images selected were representative of a general trend observed, where the use of 1-hexene as comonomer. The copolymer had better fragmentation during polymer particle growth that was accelerated by the presence of 1-hexene. Their presence have been associated with diffusion limitations. In this sense, increasing 1-hexene content of polymers that could be related to a lower mass transfer limitation.

## CHAPTER V

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

In the first part, this research was focused on the effect of polymerization conditions by supported metallocene catalyst on the catalytic activity and polymer properties for the slurry ethylene polymerization. In particular, the polymerization conditions were examined under various polymerization temperatures (70, 80 and 90°C), ethylene pressures (6 and 8 barg) and hydrogen concentrations (0, 480 and 960 ml). A number of conclusions may be summarized as follows:

- 1.1 The optimum polymerization conditions of supported metallocene catalyst system for the highest activity of 6.8275 kg PE/g cat·h is observed at polymerization temperature of 90 °C, ethylene pressure of 8 barg and hydrogen concentration of 480 ml.
- 1.2 Based on effect of polymerization temperature in the absence of hydrogen, the activity is enhanced with increasing polymerization temperature. However, catalyst activity decreased at high temperature (90°C) due to severe deactivation of the catalyst. But in the presence of hydrogen the catalyst was not deactivated at high temperature (90°C) probably from the effect of hydrogen response.
- 1.3 The effect of ethylene pressure was found to be at higher monomer pressure, it renders higher activity.

- 1.4 Base on the effect of hydrogen response, it was that the activity increased at 480 ml of hydrogen concentration. On the other hand, the activity decreased at 960 ml of hydrogen concentration.
- 1.5 The melting temperature and crystallinity are not affected by polymerization temperatures, ethylene pressures and hydrogen concentrations.
- 1.6 The molecular weight and molecular weight distribution of the polyethylene are controlled by polymerization temperatures and hydrogen concentrations, whereas ethylene pressures are not affect.
- 1.7 Morphology of polymer are unusual spherical shape. It revealed some more broken fragments on the surface polymer with increasing temperatures and polymer particles growing when higher ethylene pressures. Moreover, polymer are fine generation in the presence of hydrogen.

In the second part, this research was focused on the effect of polymerization conditions by supported metallocene catalyst on the catalytic activity and polymer properties for the slurry ethylene/1-hexene copolymerization. In particular, the polymerization conditions were examined under various polymerization temperatures (60, 70 and 80°C) , ethylene pressures (6 and 7 barg) and 1-hexene loaded in the reactor (0, 10 and 15 ml) . A number of conclusions may be summarized as follows:

- 2.1 The optimum copolymerization conditions of supported metallocene catalyst system for the highest activity of 6.5940 kg PE/g cat·h is observed at polymerization temperature of 80 °C , ethylene pressure of 7 barg and 1-hexene loaded in the reactor of 10 ml.

- 2.2 Based on effect of polymerization temperature, it was found that the activity is enhanced with increasing polymerization temperature. The highest activity was attained at 80 °C for both homo and copolymerization system.
- 2.3 Based on effect of ethylene pressure, it was found that the activity increased with increasing ethylene pressure.
- 2.4 Based on effect of comonomer response, it was found that for higher 1-hexene loading, the activity steadily increased at 60 °C and even a decrease was detected working at 70 and 80 °C.
- 2.5 For 1-hexene incorporation in copolymer, the decreased polymerization temperatures led to a higher amount of 1-hexene in copolymer. Moreover, at lower ethylene pressure more 1-hexene was incorporated into the copolymer.
- 2.6 The melting temperature and crystallinity do not affect by polymerization temperatures and ethylene pressures. In contrast, they decreased with increasing 1-hexene incorporation in the copolymer.
- 2.7 The molecular weight and molecular weight distribution of the copolymer are controlled by polymerization temperatures. However, ethylene pressures and volumes 1-hexene loaded in the reactor are not affect.
- 2.8 Morphology of copolymer are unusual spherical shape. . It revealed some more broken fragments on the surface polymer with increasing temperatures and polymer particles growing when higher ethylene pressures. Moreover, in the presence of 1-hexene copolymer, it has better fragmentation during polymer particle growth is accelerated.

## 5.2 Recommendations

1. The effect of ethylene pressures in this study was discussed only 2 different pressures. It should be studied ethylene pressure in more detail until the optimum condition of ethylene pressure.
2. It can be observed the effect of comonomer response. For higher 1-hexene loading, the activity was steadily increased at 60 °C and even a decrease was detected working at 70 and 80 °C. Therefore, the optimum condition of 1-hexene loading should be considered in the further study polymerization temperature at 60 °C.
3. Proving the phenomenon of hydrogen response on catalyst surface in deep details, it is interesting especially that the activity increased at low hydrogen concentration. Some of our explanation needed the characterization data for more reliability. For example, Find the occurrence of chain end by FTIR or NMR to confirm formation of mechanism reaction in reaction and determine the amount number of active center in this condition by ESR to confirm number of active center has changed or fixed. Thus, they should be studied in more detail.

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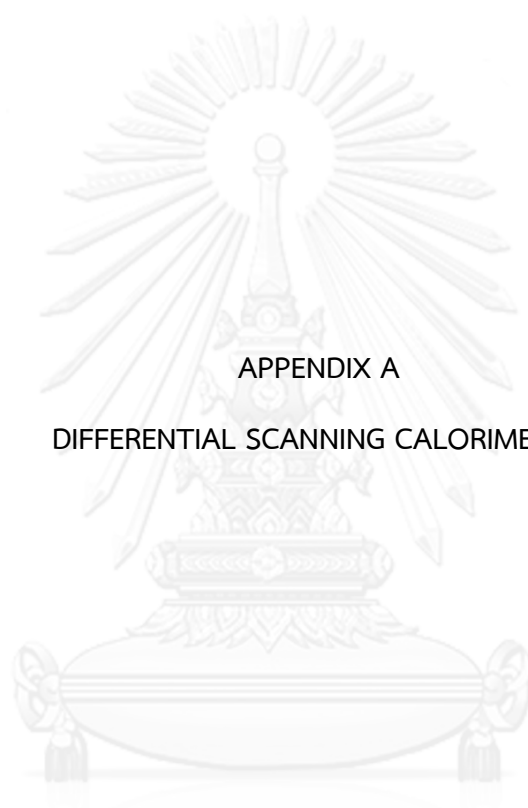


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APPENDIX

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APPENDIX A

DIFFERENTIAL SCANNING CALORIMETRY

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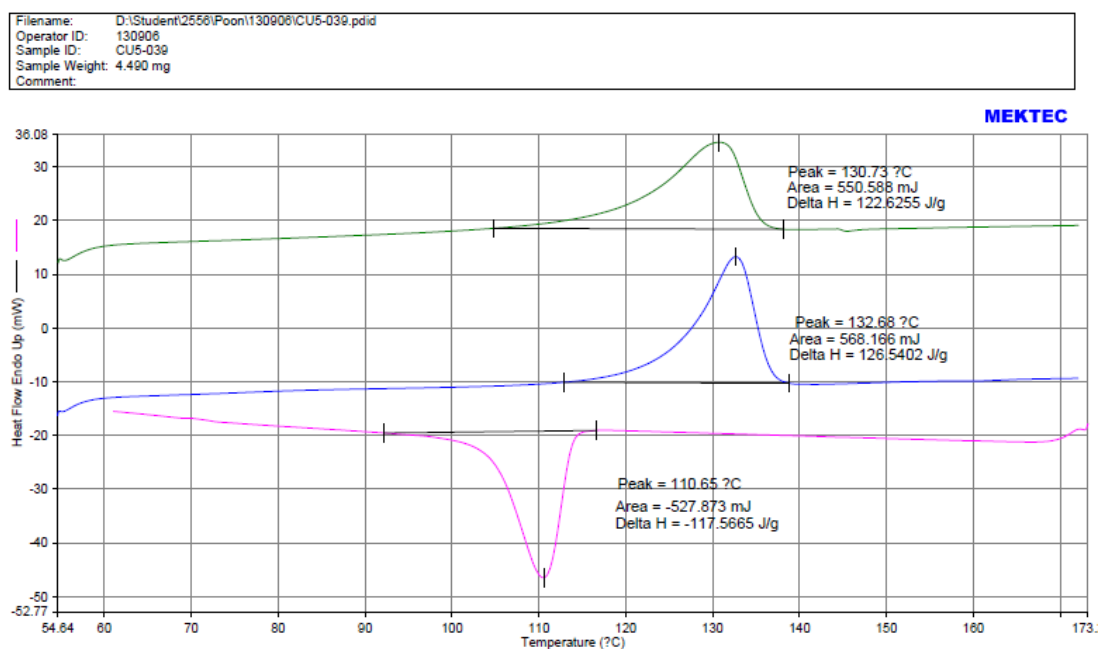


Figure A. 1 DSC curve of polyethylene produced without hydrogen at polymerization temperature of 70 °C having ethylene pressure of 6 barg

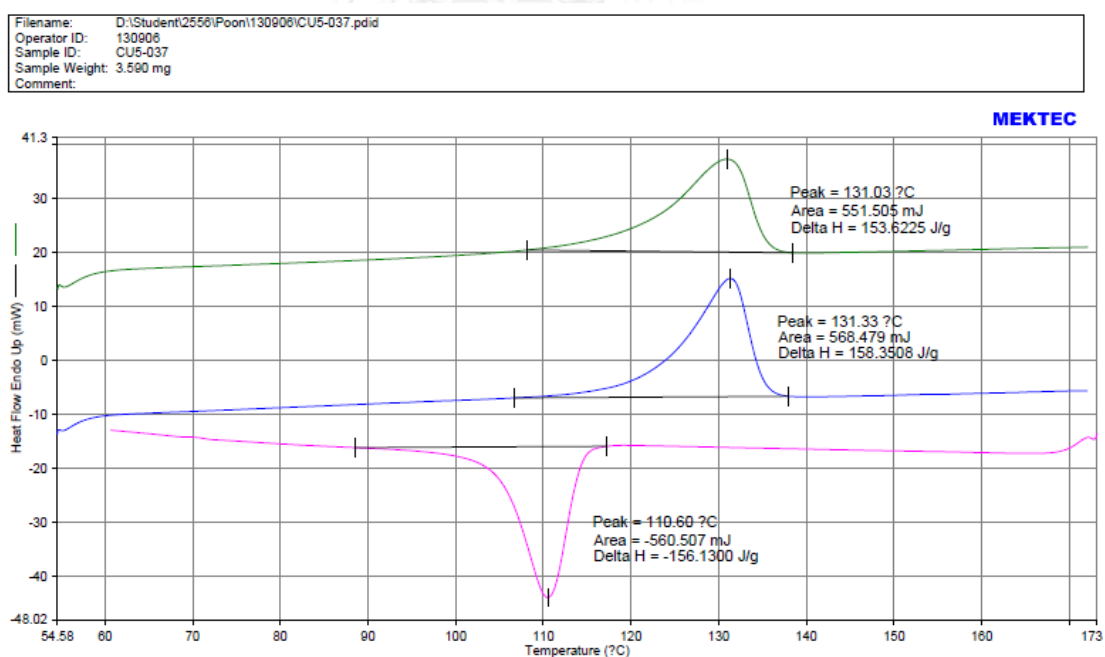


Figure A. 2 DSC curve of polyethylene produced without hydrogen at polymerization temperature of 80 °C having ethylene pressure of 6 barg



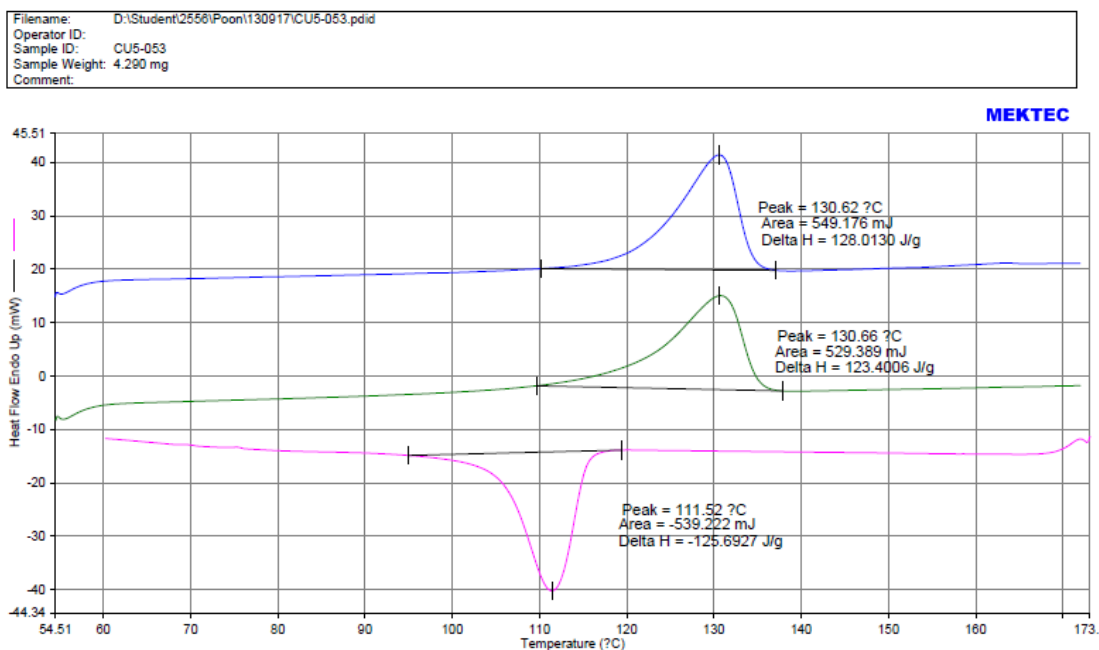


Figure A. 3 DSC curve of polyethylene produced without hydrogen at polymerization temperature of 90 °C having ethylene pressure of 6 barg

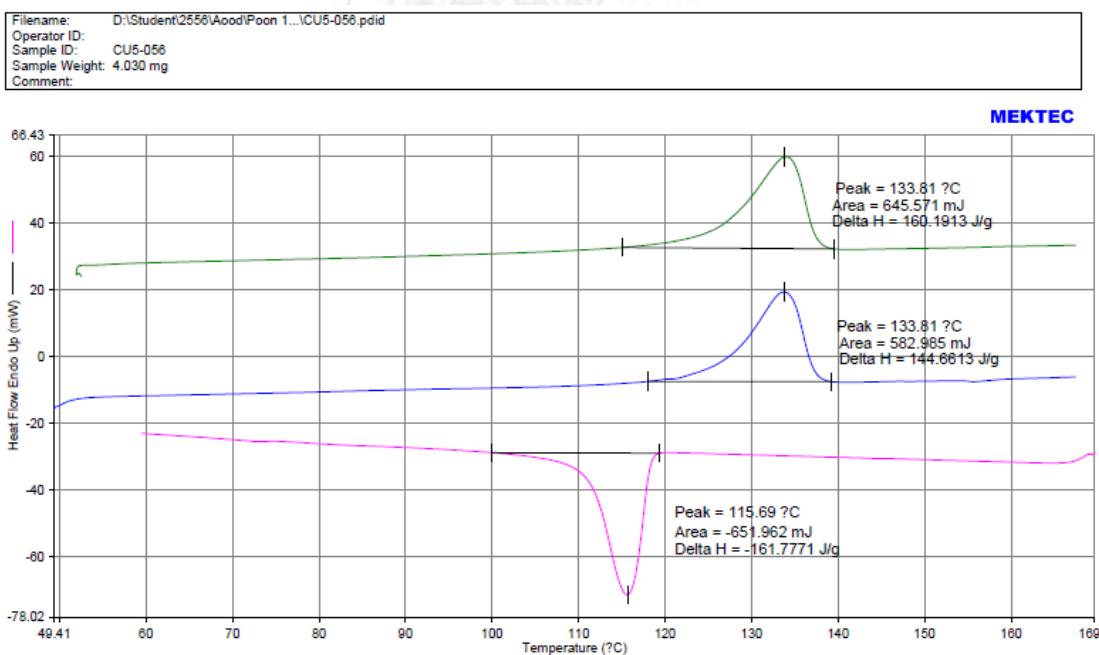


Figure A. 4 DSC curve of polyethylene produced with hydrogen concentrations at 480 ml and polymerization temperature of 70 °C having ethylene pressure of 6 barg

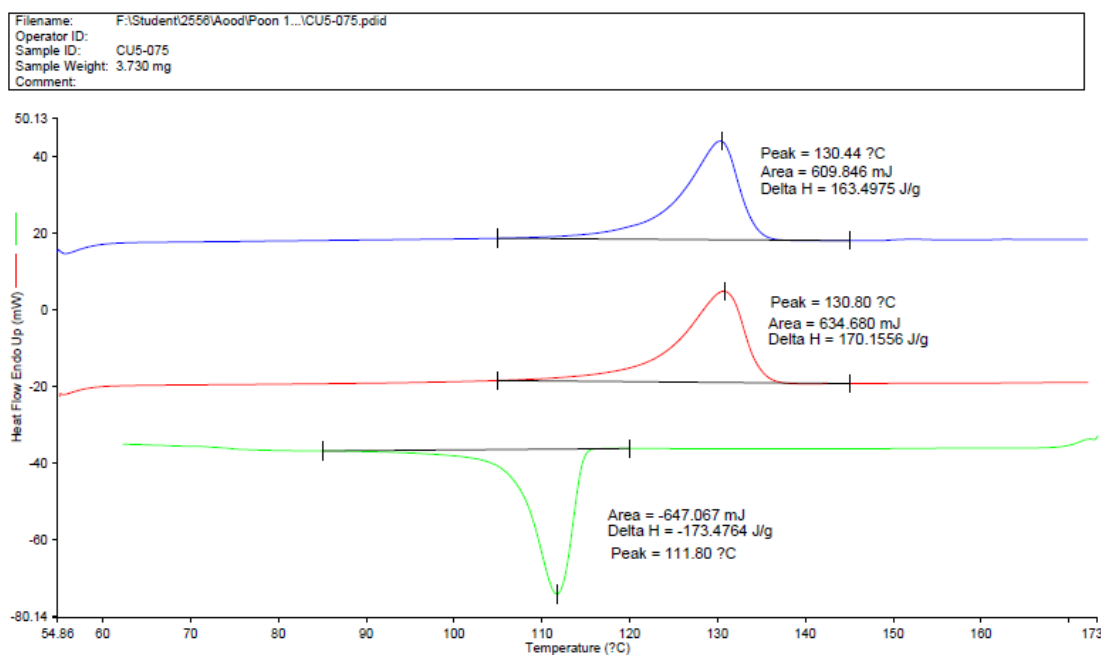


Figure A. 5 DSC curve of polyethylene produced with hydrogen concentrations at 480 ml and polymerization temperature of 80 °C having ethylene pressure of 6 barg

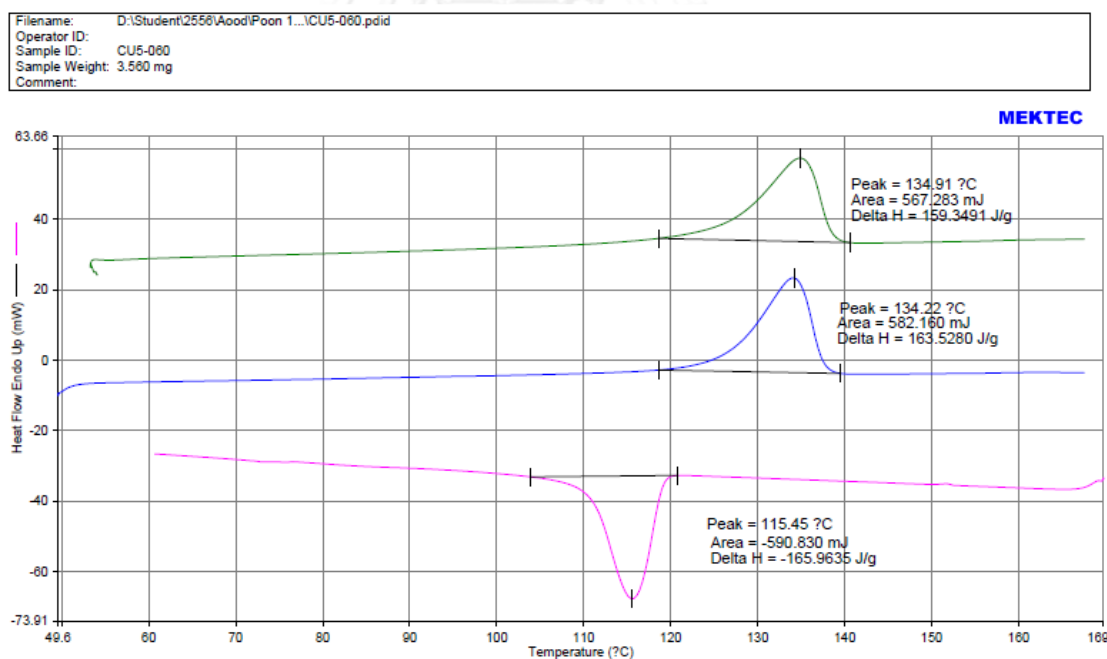


Figure A. 6 DSC curve of polyethylene produced with hydrogen concentrations at 480 ml and polymerization temperature of 90 °C having ethylene pressure of 6 barg

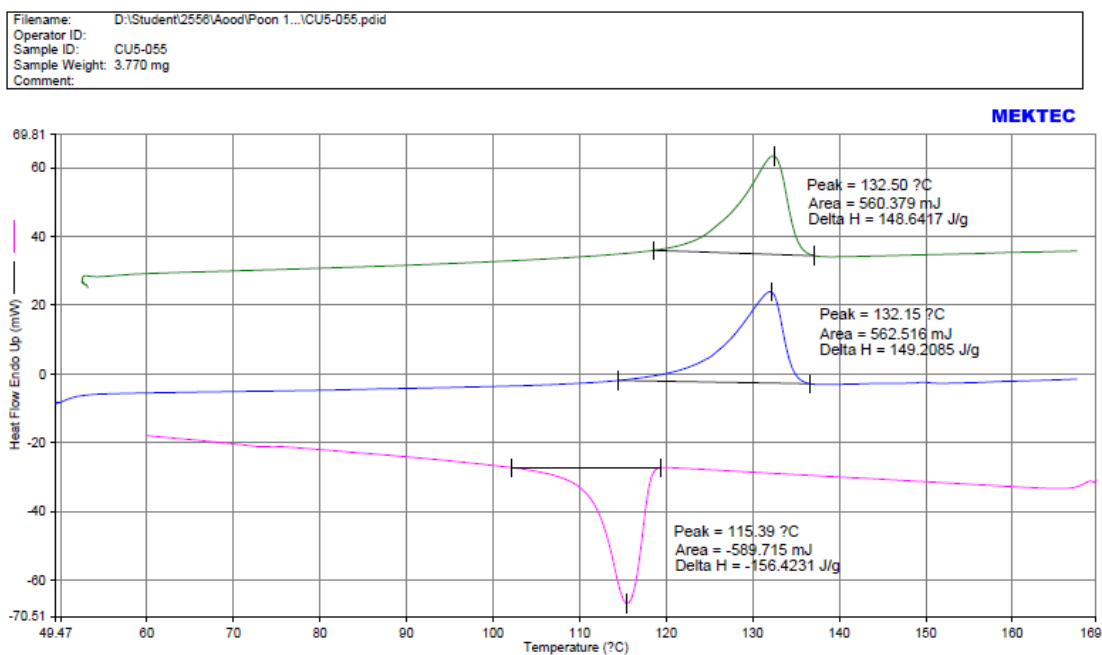


Figure A. 7 DSC curve of polyethylene produced with hydrogen concentrations at 960 ml and polymerization temperature of 70 °C having ethylene pressure of 6 barg

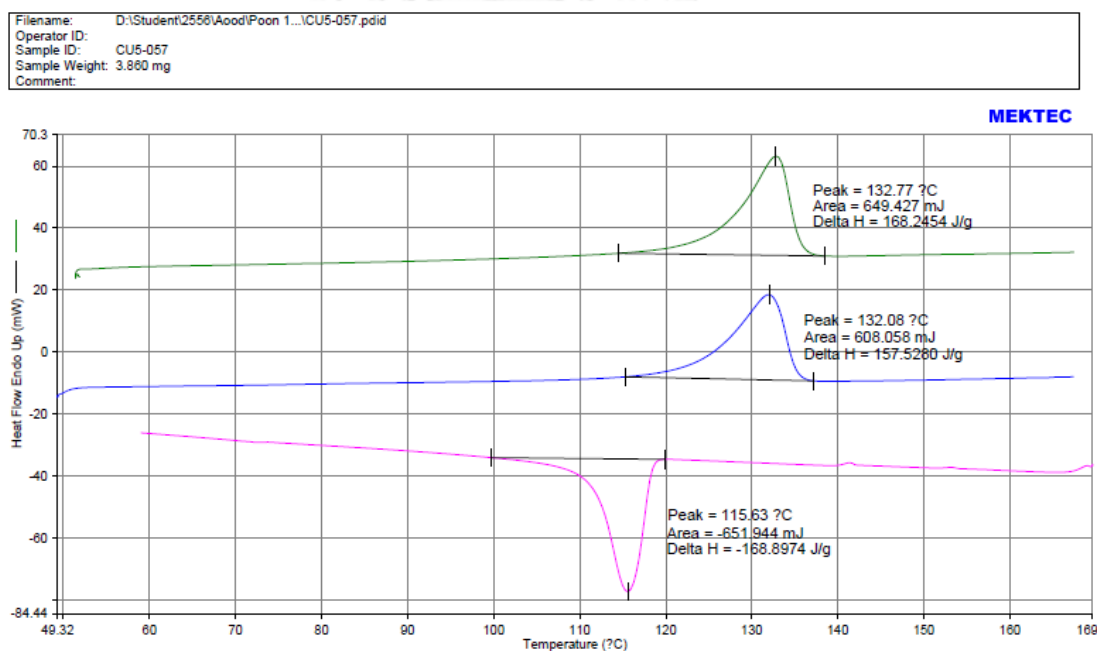
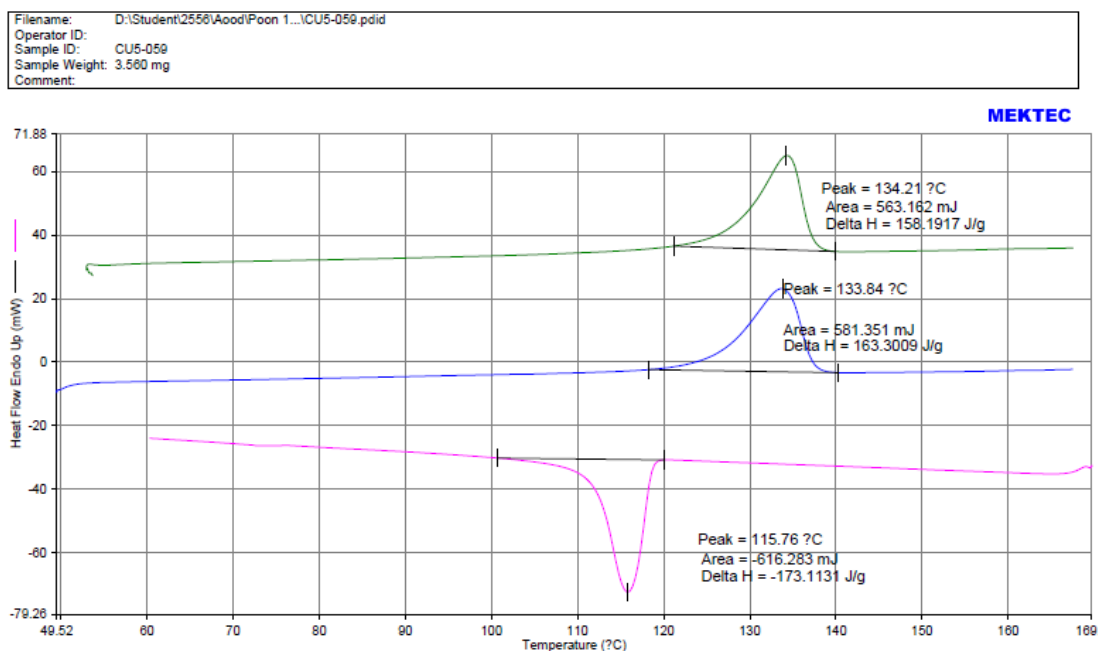
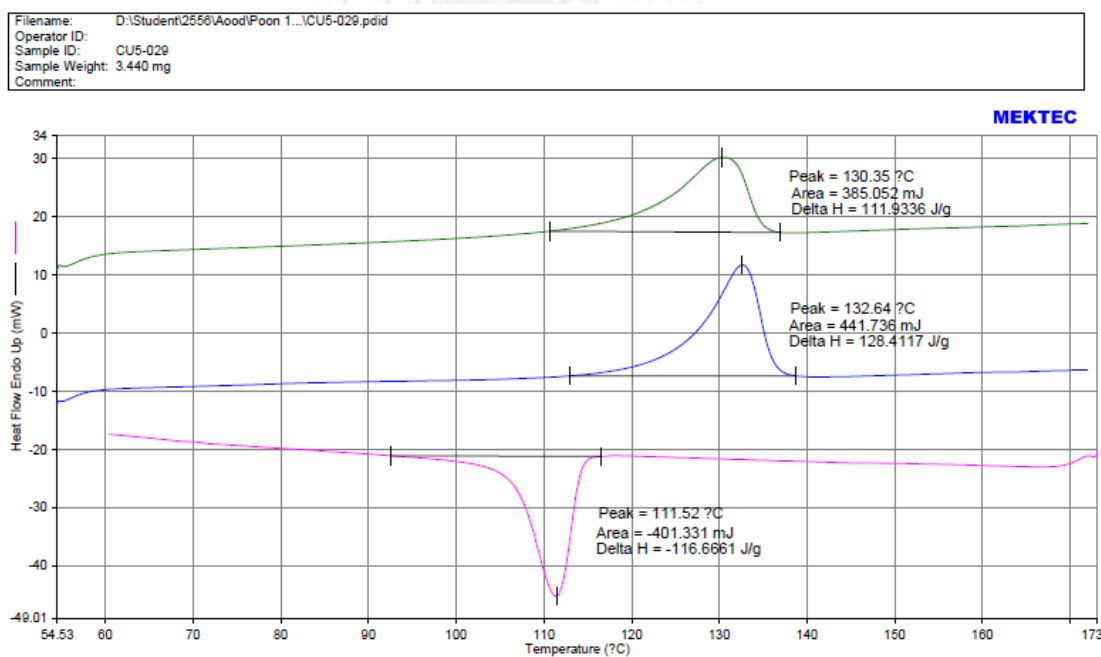


Figure A. 8 DSC curve of polyethylene produced with hydrogen concentrations at 960 ml and polymerization temperature of 80 °C having ethylene pressure of 6 barg



**Figure A. 9** DSC curve of polyethylene produced with hydrogen concentrations at 960 ml and polymerization temperature of 90 °C having ethylene pressure of 6 barg



**Figure A. 10** DSC curve of polyethylene produced without hydrogen at polymerization temperature of 70 °C having ethylene pressure of 8 barg

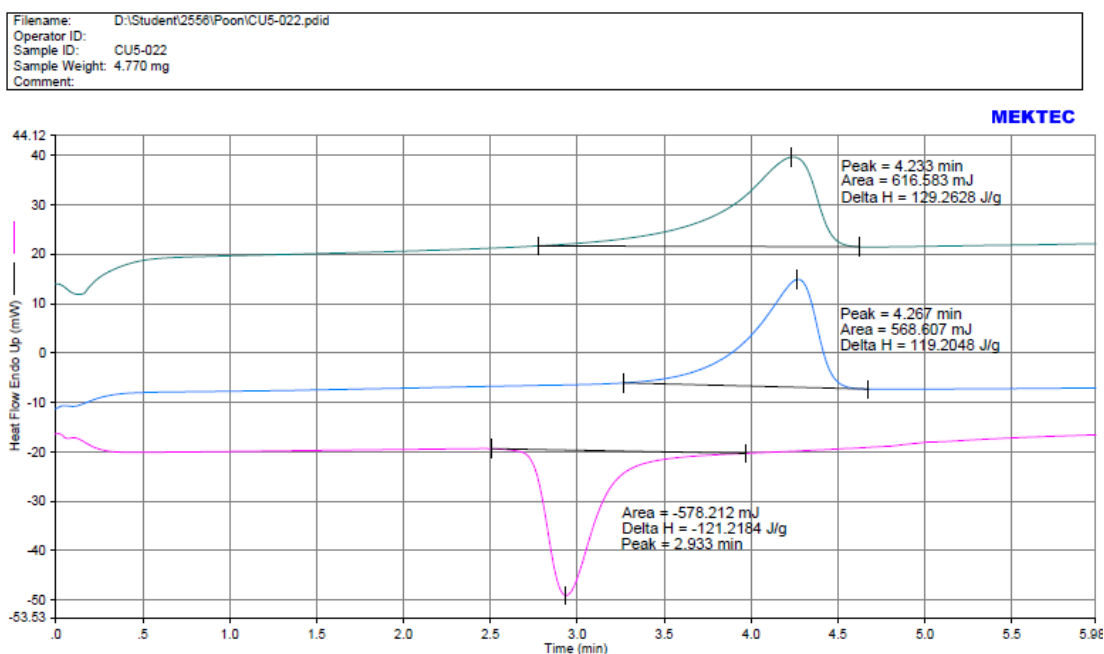


Figure A. 11 DSC curve of polyethylene produced without hydrogen at polymerization temperature of 80 °C having ethylene pressure of 8 barg

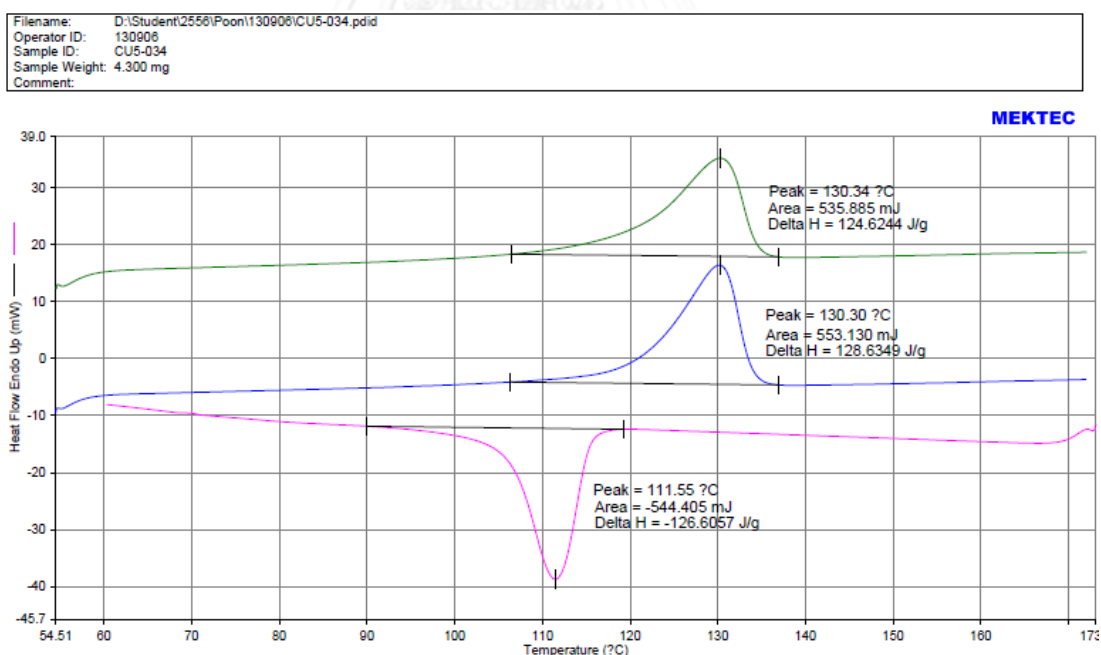
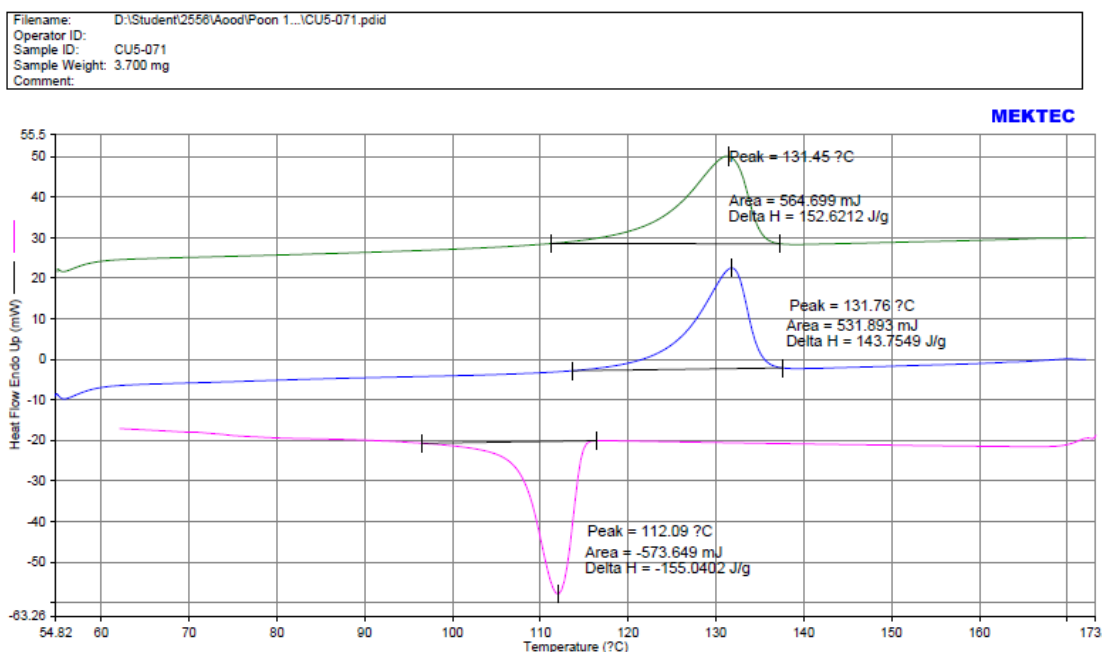
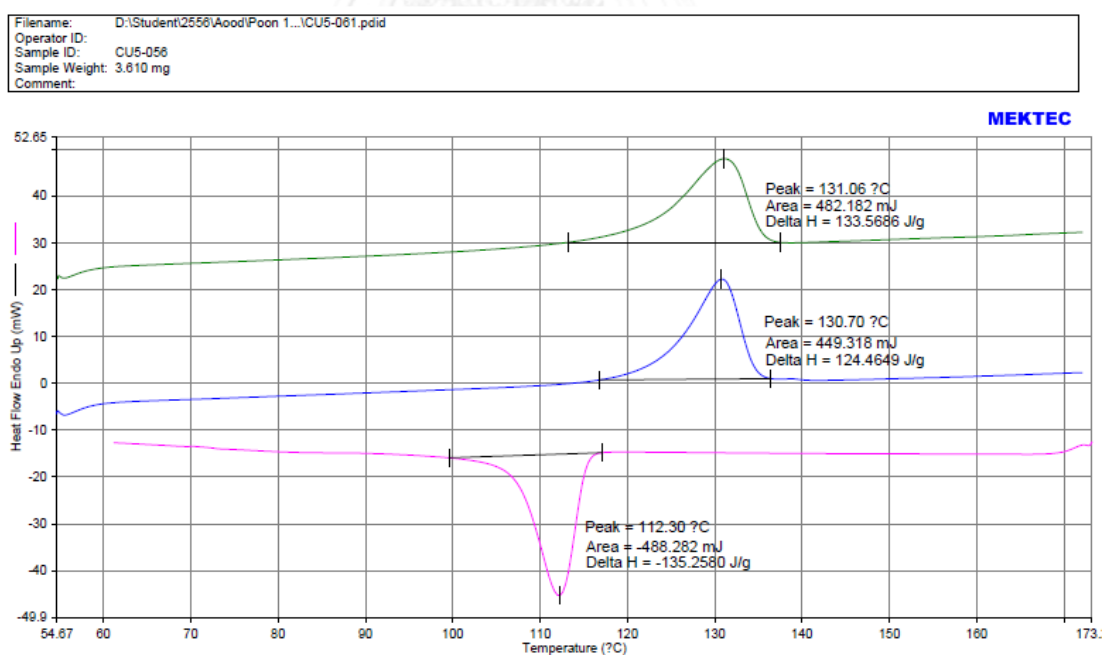


Figure A. 12 DSC curve of polyethylene produced without hydrogen at polymerization temperature of 80 °C having ethylene pressure of 8 barg



**Figure A. 13** DSC curve of polyethylene produced with hydrogen concentrations at 480 ml and polymerization temperature of 70 °C having ethylene pressure of 8 barg



**Figure A. 14** DSC curve of polyethylene produced with hydrogen concentrations at 480 ml and polymerization temperature of 80 °C having ethylene pressure of 8 barg

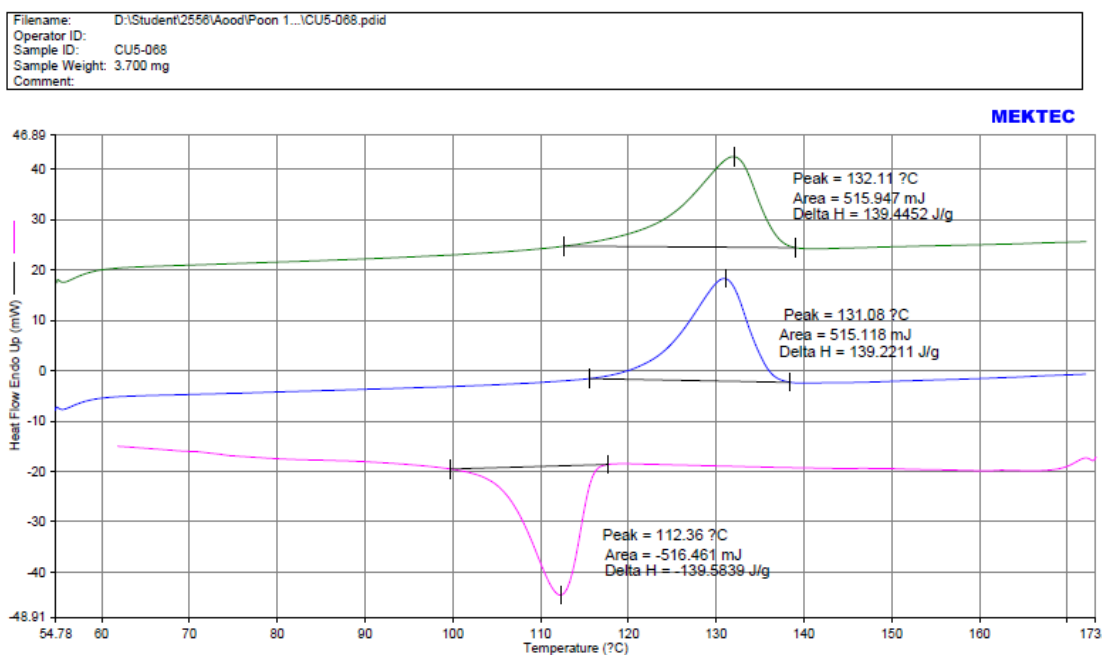


Figure A. 15 DSC curve of polyethylene produced with hydrogen concentrations at 480 ml and polymerization temperature of 90 °C having ethylene pressure of 8 barg

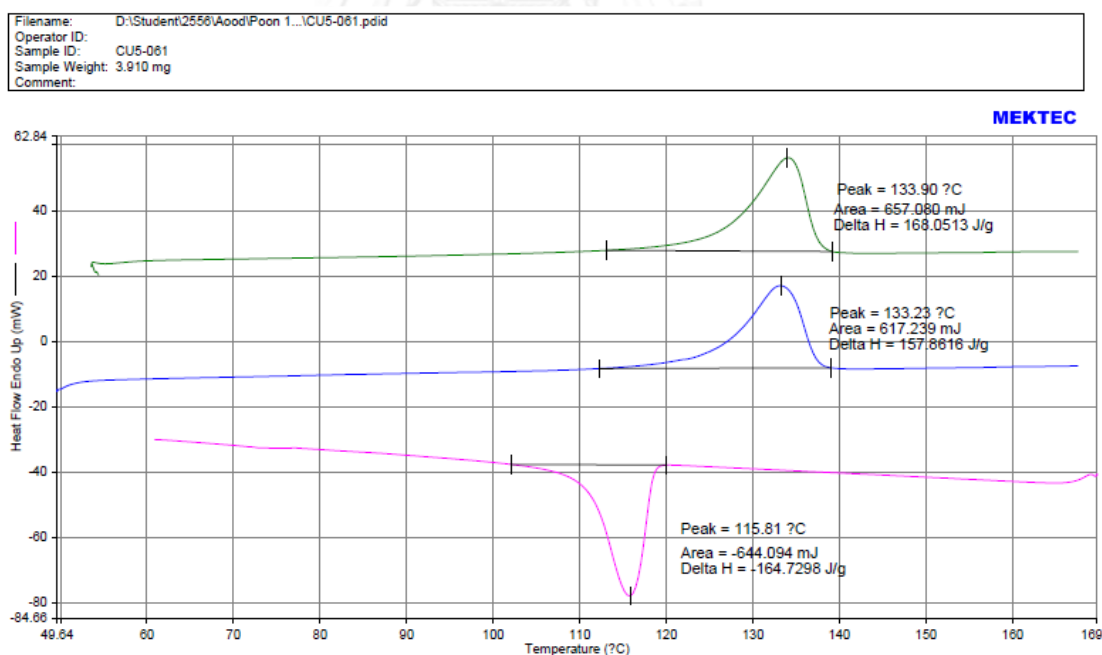
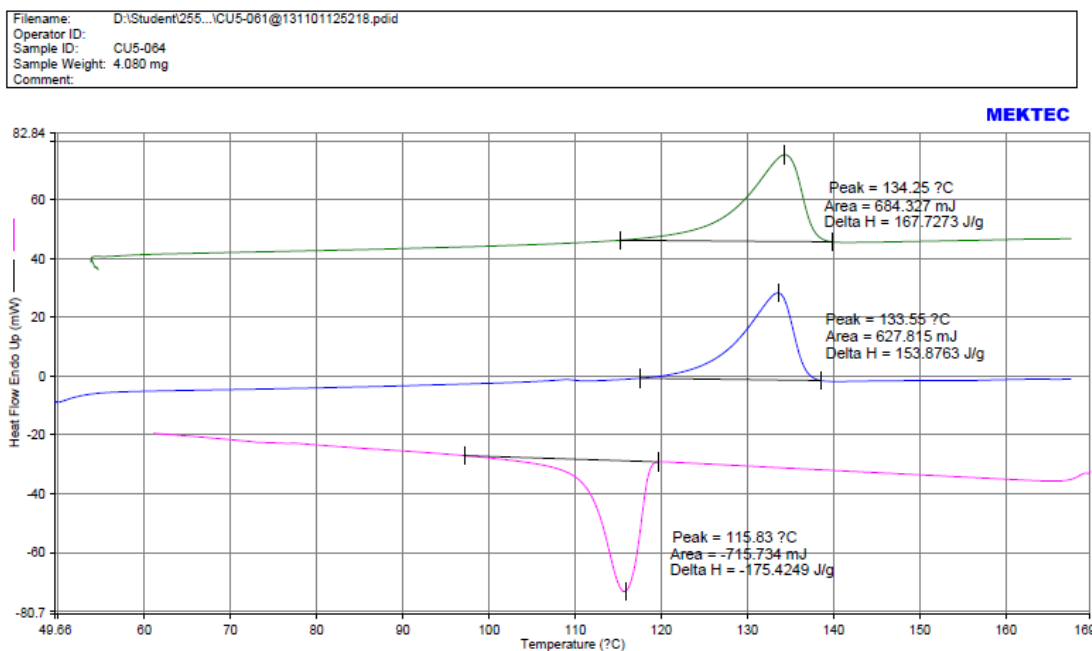
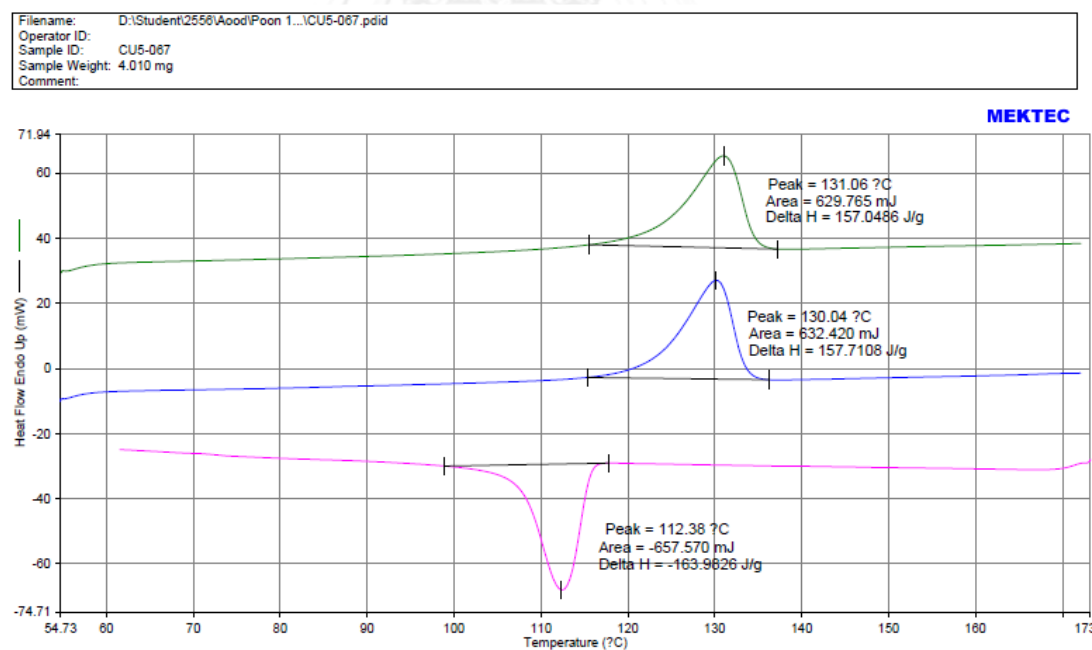


Figure A. 16 DSC curve of polyethylene produced with hydrogen concentrations at 960 ml and polymerization temperature of 70 °C having ethylene pressure of 8 barg



**Figure A. 17** DSC curve of polyethylene produced with hydrogen concentrations at 960 ml and polymerization temperature of 80 °C having ethylene pressure of 8 barg



**Figure A. 18** DSC curve of polyethylene produced with hydrogen concentrations at 960 ml and polymerization temperature of 90 °C having ethylene pressure of 8 barg



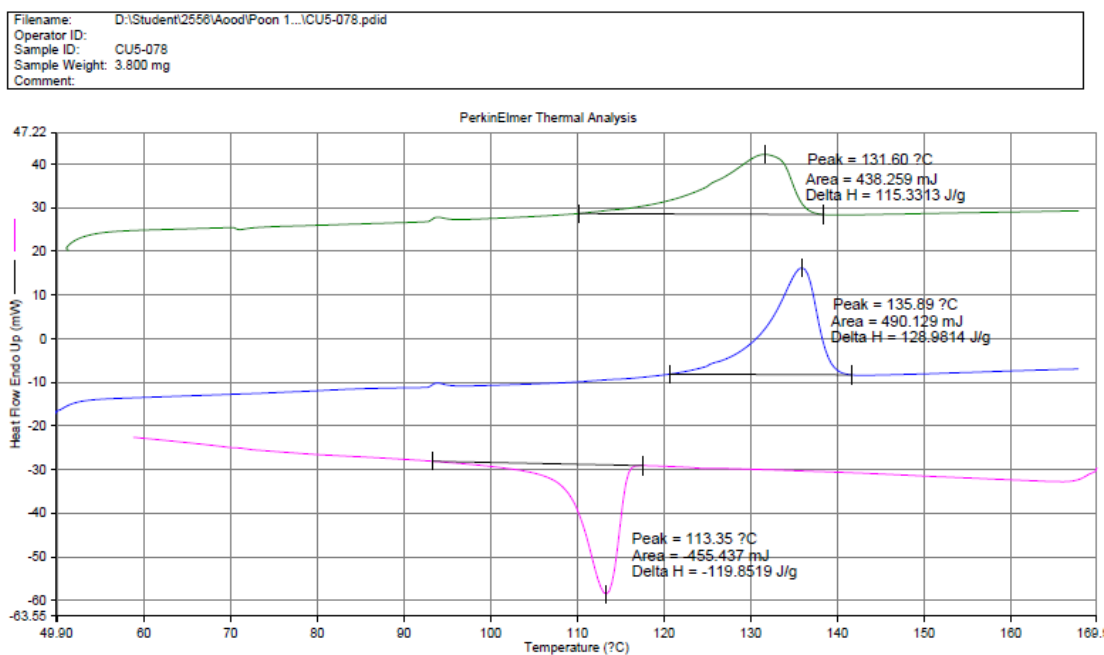


Figure A. 19 DSC curve of polyethylene produced without 1-hexene at polymerization temperature of 60 °C having ethylene pressure of 6 barg

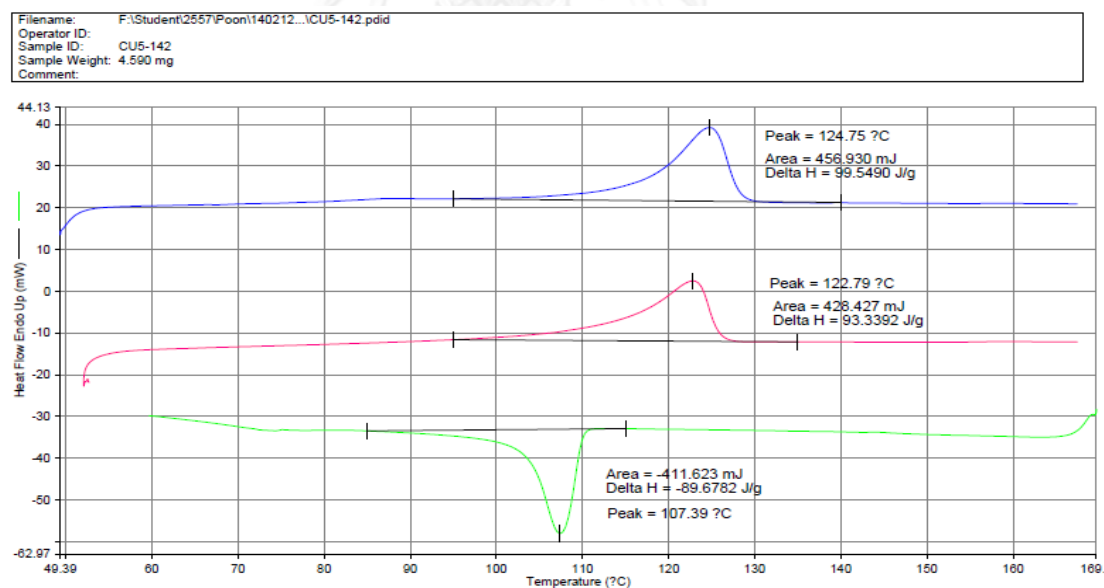
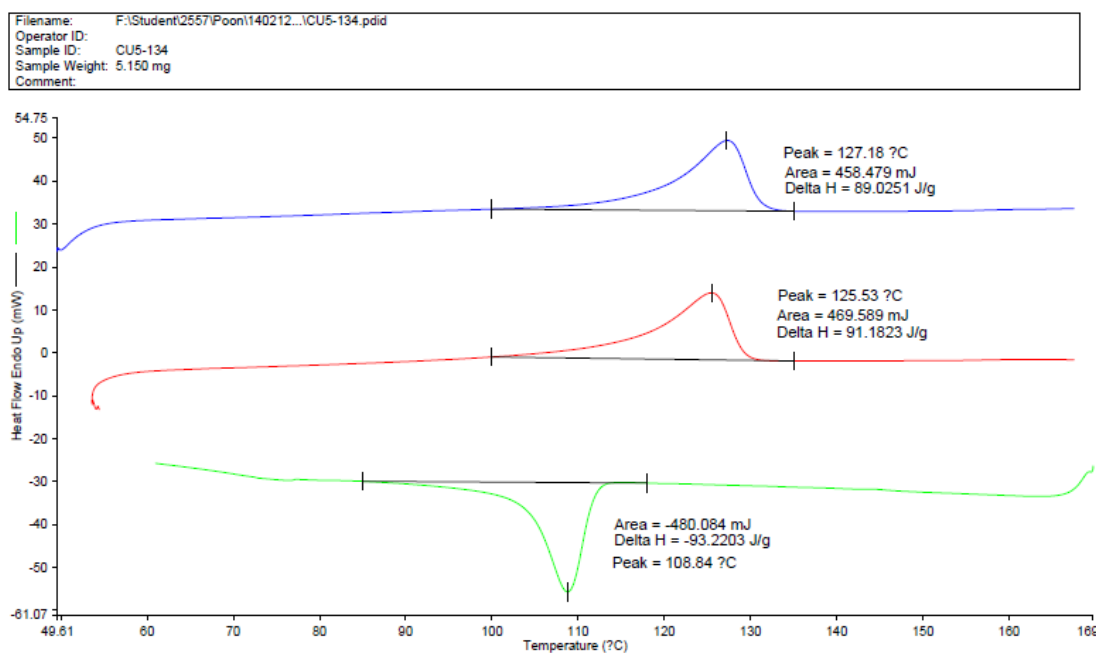
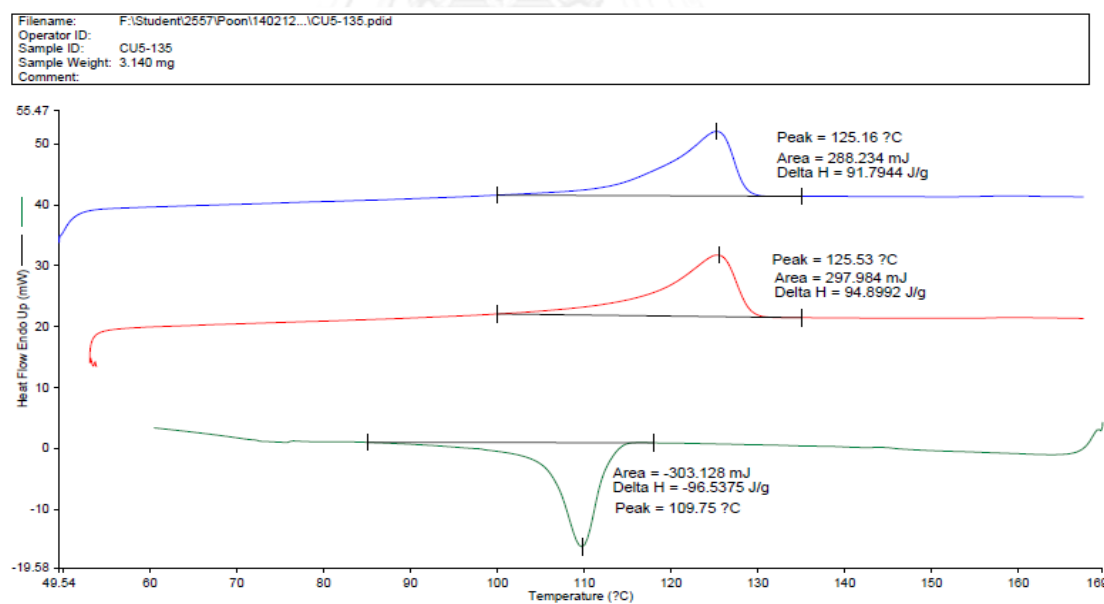


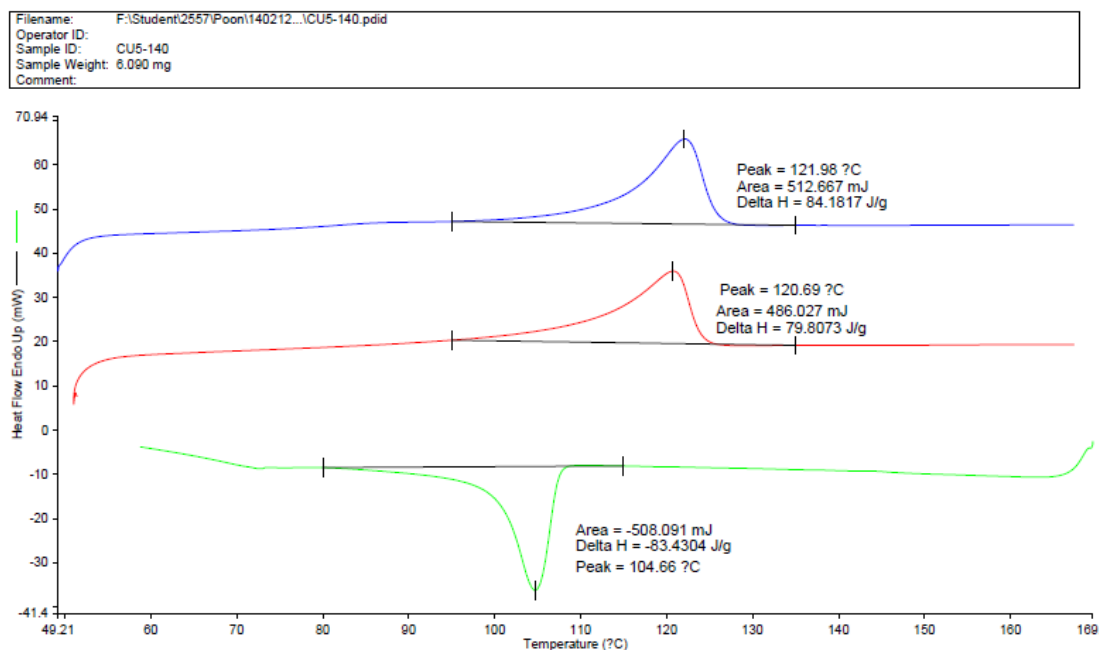
Figure A. 20 DSC curve of polyethylene produced with volume of 1-hexene 10 ml at polymerization temperature of 60 °C having ethylene pressure of 6 barg



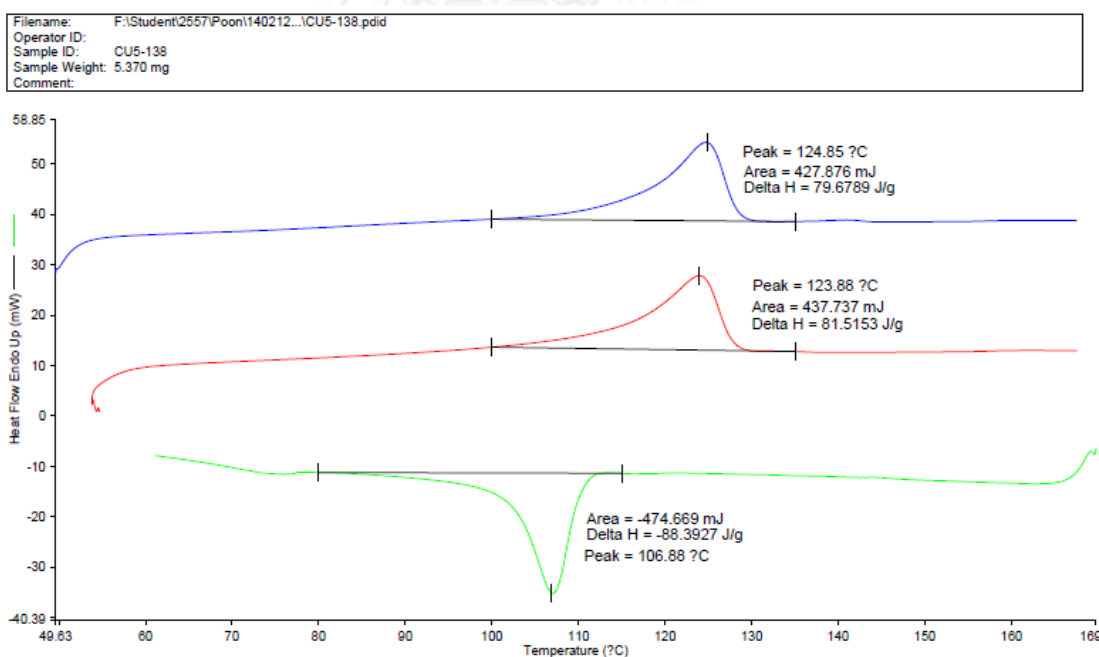
**Figure A. 21** DSC curve of polyethylene produced with volume of 1-hexene 10 ml at polymerization temperature of 70 °C having ethylene pressure of 6 barg



**Figure A. 22** DSC curve of polyethylene produced with volume of 1-hexene 10 ml at polymerization temperature of 80 °C having ethylene pressure of 6 barg



**Figure A. 23** DSC curve of polyethylene produced with volume of 1-hexene 15 ml at polymerization temperature of 60 °C having ethylene pressure of 6 barg



**Figure A. 24** DSC curve of polyethylene produced with volume of 1-hexene 15 ml at polymerization temperature of 70 °C having ethylene pressure of 6 barg

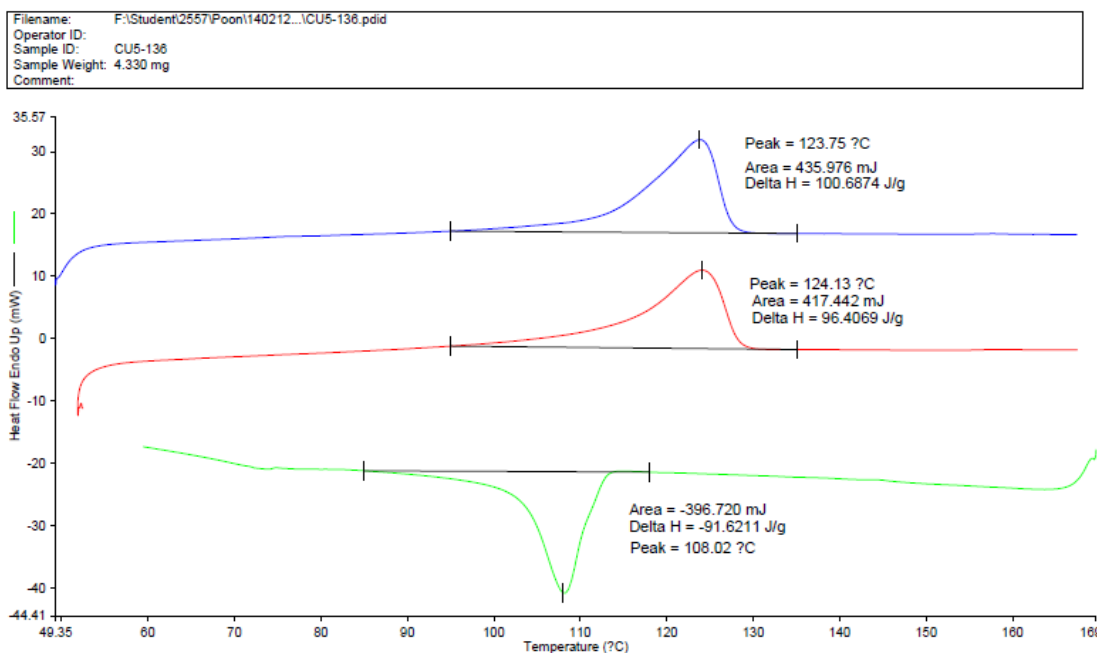


Figure A. 25 DSC curve of polyethylene produced with volume of 1-hexene 15 ml at polymerization temperature of 80 °C having ethylene pressure of 6 barg

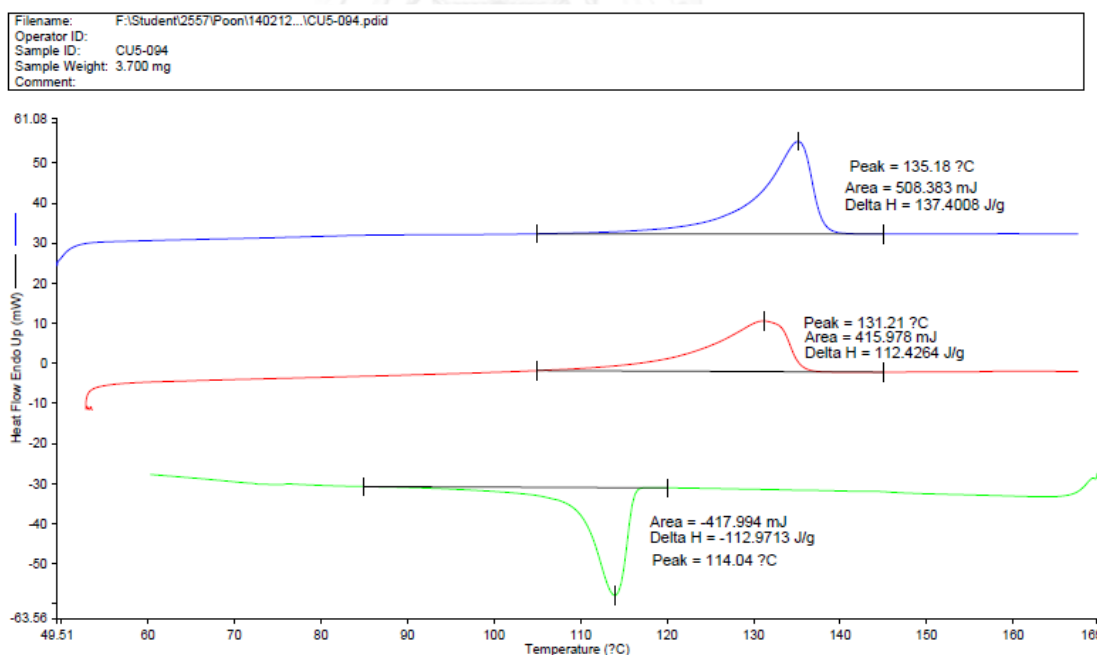
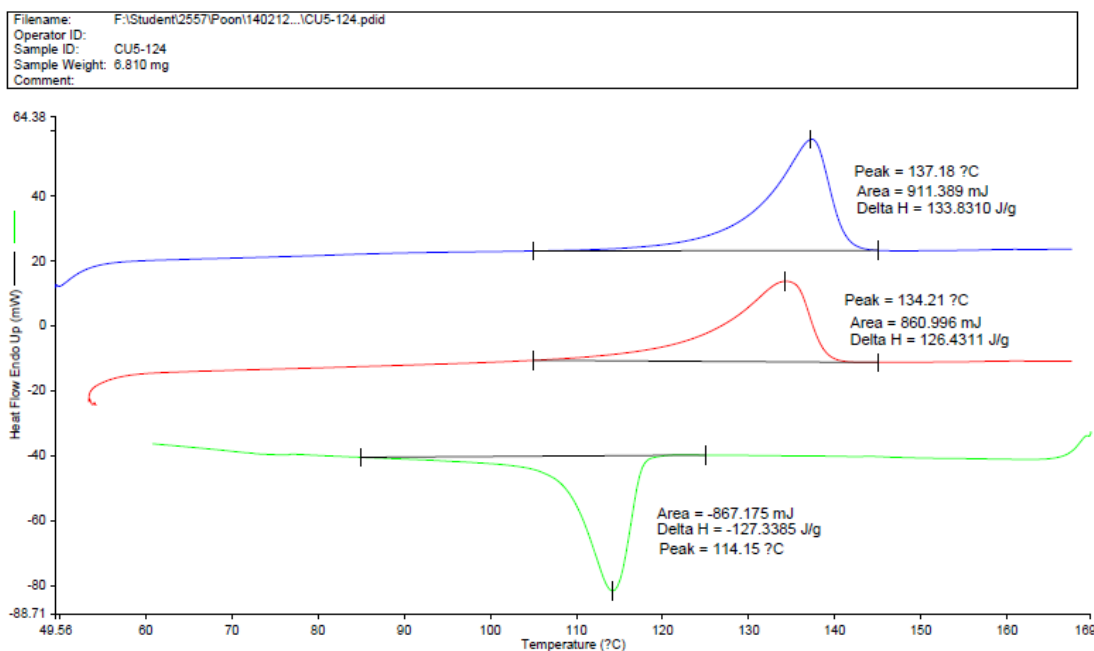
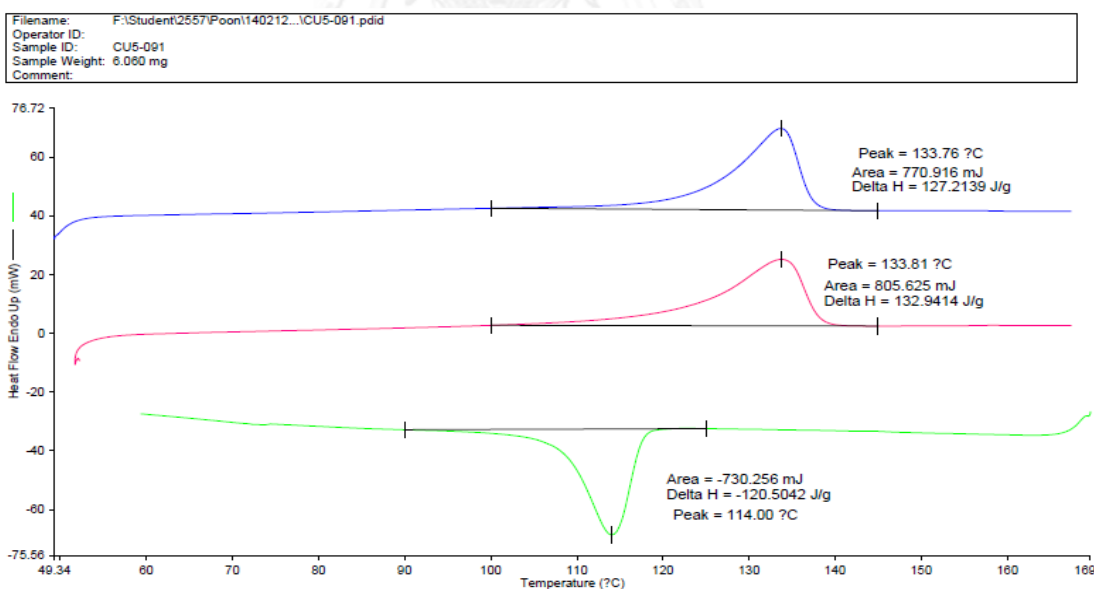


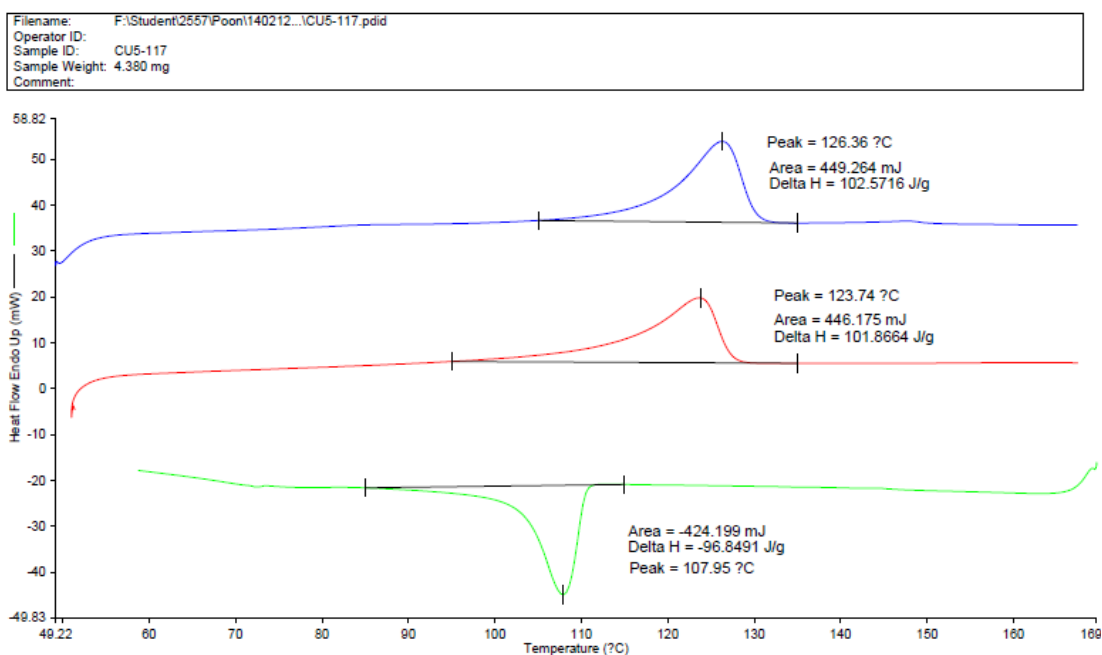
Figure A. 26 DSC curve of polyethylene produced without 1-hexene at polymerization temperature of 60 °C having ethylene pressure of 7 barg



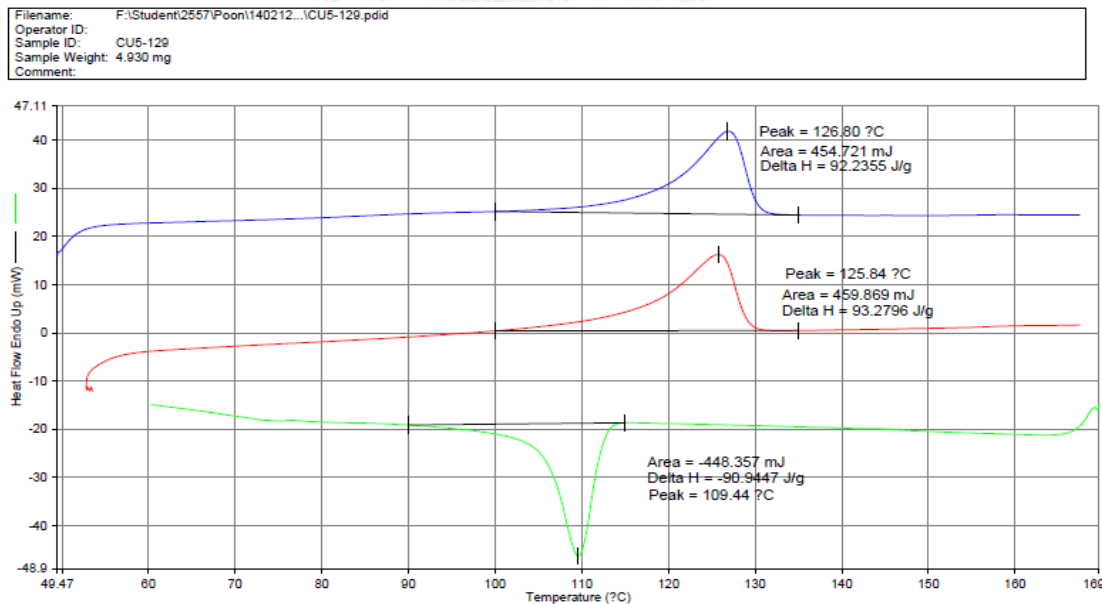
**Figure A. 27** DSC curve of polyethylene produced without 1-hexene at polymerization temperature of 70 °C having ethylene pressure of 7 barg



**Figure A. 28** DSC curve of polyethylene produced without 1-hexene at polymerization temperature of 80 °C having ethylene pressure of 7 barg



**Figure A. 29** DSC curve of polyethylene produced with volume of 1-hexene 10 ml at polymerization temperature of 60 °C having ethylene pressure of 7 barg



**Figure A. 30** DSC curve of polyethylene produced with volume of 1-hexene 10 ml at polymerization temperature of 70 °C having ethylene pressure of 7 barg

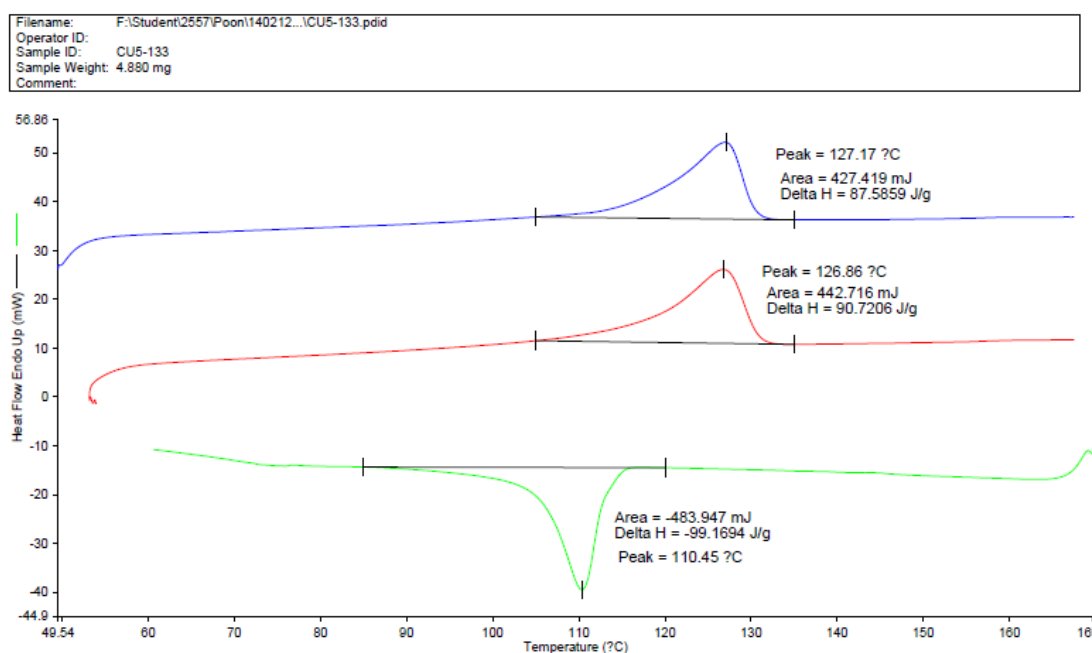


Figure A. 31 DSC curve of polyethylene produced with volume of 1-hexene 10 ml at polymerization temperature of 80 °C having ethylene pressure of 7 barg

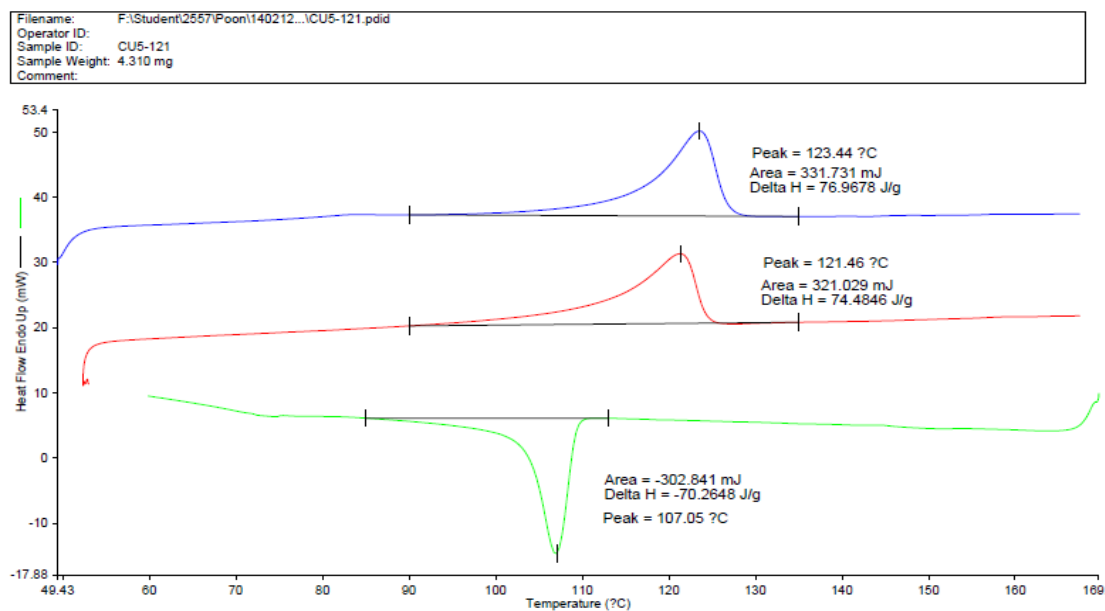
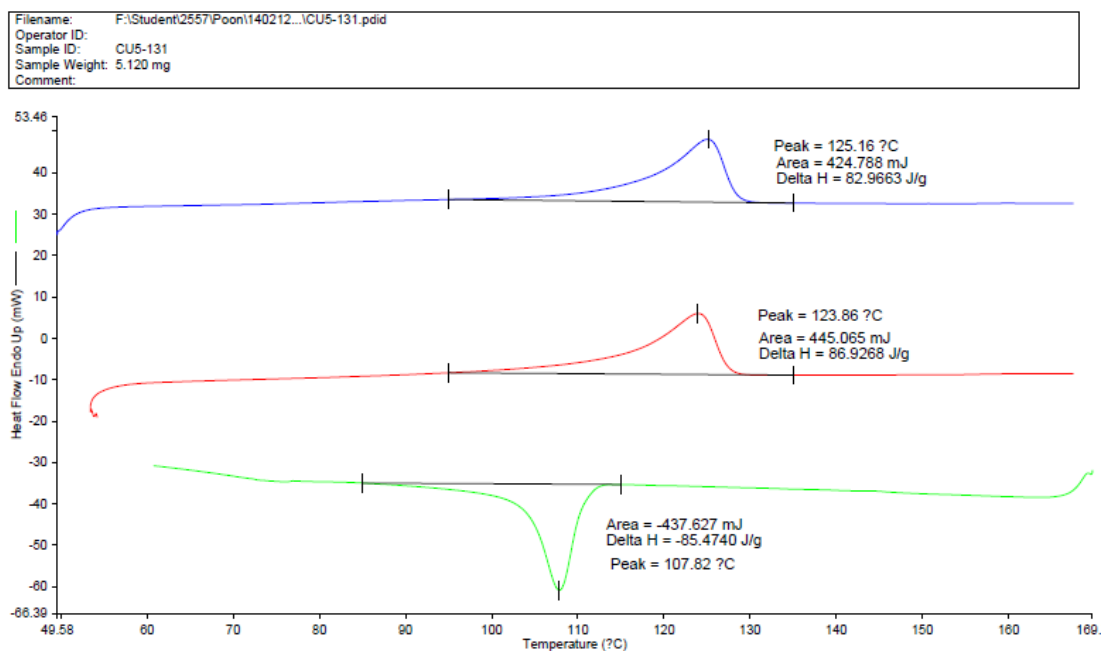
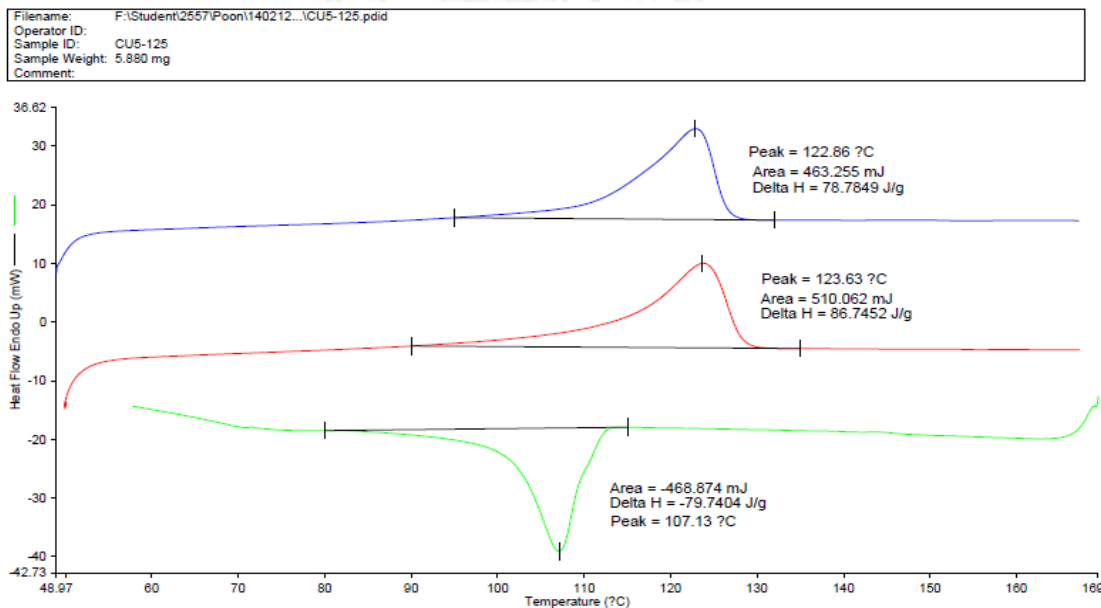


Figure A. 32 DSC curve of polyethylene produced with volume of 1-hexene 15 ml at polymerization temperature of 60 °C having ethylene pressure of 7 barg



**Figure A. 33** DSC curve of polyethylene produced with volume of 1-hexene 15 ml at polymerization temperature of 70 °C having ethylene pressure of 7 barg



**Figure A. 34** DSC curve of polyethylene produced with volume of 1-hexene 15 ml at polymerization temperature of 80 °C having ethylene pressure of 7 barg





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## VITA

Ms.Phakairat Supaphan was born on May 26, 1990 in Bangkok, Thailand. She graduated with a Bachelor's degree of Science, majoring in Chemical Technology, Chulalongkorn University in 2011. Afterward she has continued her study in Master's degree, majoring in Chemical Engineering at Chulalongkorn University and joined the Center of Excellence on Catalysis and Catalytic Reaction Engineering. Then finished her study in 2013.

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