พอลิเมอร์ไรเซชันของเอทิลีนด้วยตัวเร่งปฏิกิริยาบิส[เอ็น(สามเทิร์ทบิวทิลซาลิไซลิดีน)ไซโคลเฮปทิลเอมีน]ไทเทเนียมไดคลอโรบนตัวรองรับซิลิกา

นายพสุชา ทองอยู่

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ปีการศึกษา 2559

POLYMERIZATION OF ETHYLENE WITH BIS[N-(3-TERT-BUTYLSALICYLIDENE)CYCLOHEPTYLAMINE] TITANIUM DICHLORO-SUPPORTED ON SILICA

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A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Title	POLYMERIZATION OF ETHYLENE WITH BIS[N-(3-TERT-BUTYLSALICYLIDENE)CYCLOHEPTYLAMINE] TITANIUM DICHLORO-SUPPORTED ON SILICA
By	Mr. Pasucha Thongyoo
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(Sasiradee Jantasee, Ph.D.)

พสุชา ทองอยู่ : พอลิเมอร์ไรเซชันของเอทิลีนด้วยตัวเร่งปฏิกิริยาบิส[เอ็น(สามเทิร์ทบิวทิลซาลิไซลิดีน)ไซโคลเฮปทิลเอมีน]ไทเทเนียมไดคลอโรบนตัวรองรับซิลิกา (POLYMERIZATION OF ETHYLENE WITH BIS[N-(3-TERT-BUTYLSALICYLIDENE)CYCLOHEPTYLAMINE] TITANIUM DICHLORO-SUPPORTED ON SILICA) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร.บรรเจิด จงสมจิตร, 71 หน้า.

ตัวเร่งปฏิกิริยาเมทัลโลซีนนั้นเป็นหนึ่งในตัวเร่งปฏิกิริยาที่ถูกนำมาใช้ในการผลิตพอลิเอทิลีนร่วมกับตัวเร่งปฏิกิริยาร่วมคือเมทิลอะลูมินอกเซนซึ่งให้สมรรถนะของตัวเร่งปฏิกิริยาสูง ตัวเร่งปฏิกิริยาเมทัลโลซีนในระบบโฮโมจีเนียสให้สมรรถนะของตัวเร่งปฏิกิริยาสูงแต่ข้อเสียคือเกิดฟาวลิ่งและไม่สามารถควบคุมลักษณะสัณฐานของพอลิเมอร์ได้ ซิลิกาจึงถูกนำมาใช้ในระบบเฮทเทอโรจีเนียสเพื่อแก้ปัญหาข้างต้น ซึ่งในปัจจุบันมีการศึกษาตัวรองรับซิลิกาชนิดต่างๆมากมายร่วมกับตัวเร่งปฏิกิริยาเมทัลโลซีน ในงานวิจัยนี้ได้ศึกษาผลกระทบปริมาณเมทิลอะลูมินอกเซนที่ใช้ในการผลิตพอลิเอทิลีนแบบอินซิตูร่วมกับตัวรองรับซิลิกาชนิดต่างๆได้แก่ SiO_2-LP, SiO_2-SP, SiO_2-MP, SiO_2-VSP และ SSP และศึกษาผลกระทบการปรับปรุงตัวรองรับซิลิกาชนิด SiO_2-MP เพื่อเปรียบเทียบผลที่ได้ก่อนปรับปรุง จากการทดลองเมื่อพิจารณาการใช้ปริมาณเมทิลอะลูมินอกเซนที่ต่ำพบว่าตัวรองรับ SSP ให้สมรรถนะของตัวเร่งปฏิกิริยาสูงที่สุด เมื่อพิจารณาการใช้ปริมาณเมทิลอะลูมินอกเซนที่สูงพบว่าตัวรองรับ SiO_2-LP ให้สมรรถนะของตัวเร่งปฏิกิริยาสูงที่สุด ซึ่งแสดงให้เห็นว่าอนุภาคของซิลิกาที่มีขนาดเล็กให้สมรรถนะของตัวเร่งปฏิกิริยาดี ในทางกลับกันอนุภาคของซิลิกาที่มีขนาดใหญ่จะเกิดปฏิกิริยาบนผิวซิลิกาได้ไม่ดีซึ่งทำให้เกิดโฮโมพอลิเมอร์ไรเซชันและการศึกษาพอลิเอทิลีนที่ใช้ตัวรองรับ SiO_2-MP ที่ผ่านการปรับปรุงเรียบร้อยแล้วพบว่าทำให้สมรรถนะของตัวเร่งปฏิกิริยาดีขึ้นและใช้ปริมาณเมทิลอะลูมินอกเซนน้อยลง ลักษณะของพอลิเอทิลีนที่ได้มีความเป็นผลึกมากกว่าพอลิเอทิลีนที่ใช้ตัวรองรับ SiO_2-MP ที่ไม่ได้ปรับปรุง

ภาควิชา วิศวกรรมเคมี
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ลายมือชื่อนิสิต ....
ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

5870278821 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: POLYETHYLENE / METALLOCENE / POLYMERIZATION / SILICA

PASUCHA THONGYOO: POLYMERIZATION OF ETHYLENE WITH BIS[N-(3-TERT-BUTYLSALICYLIDENE)CYCLOHEPTYLAMINE] TITANIUM DICHLORO-SUPPORTED ON SILICA. ADVISOR: PROF. BUNJERD JONGSOMJIT, Ph.D., 71 pp.

One of the most popular catalysts for ethylene polymerization is metallocene catalyst that is used with methylaluminoxane as cocatalyst because it makes high activity. The metallocene catalysts in a homogeneous system presents very high activity, but major disadvantages of this system are fouling in a reactor and lack of ability to control polymer morphology. Silica is extensively used for heterogeneous system in order to overcome these drawbacks. In the present study, various silica supports are used for supported metallocence catalyst. This research is aimed to study the effect of various amounts of methylaluminoxane with SiO_2-LP, SiO_2-SP, SiO_2-MP, SiO_2-VSP and SSP supports for ethylene polymerization via *in situ*, and to study the effect of $SiCl_4$-modified SiO_2-MP support compared with unmodified SiO_2-MP support. From the experiment, it was found that the SSP support expressed the highest activity at low methylaluminoxane and the SiO_2-LP support showed the highest activity at high methylaluminoxane. The small particles of silica exhibit good activity and big particles show poor reaction on silica surface where high homopolymerization occurred. The polyethylene obtained from modified SiO_2-MP support was observed that the crystallinity is higher than the polyethylene obtained from unmodified SiO_2-MP support and improved catalytic activity with decreased methylaluminoxane used.

Department: Chemical Engineering Student's Signature ....

Field of Study: Chemical Engineering Advisor's Signature ....

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LIST OF ABBREVIATIONS

Abbreviations	
SiO_2	Silica
-LP	Large pore
-SP	Small pore
-MP	Medium pore
-VSP	Very small pore
SSP	Spherical silica particle
3-tert-C7	bis[N-(3-tert-butylsalicylidene) cycloheptylamine] titanium dichloride
MAO	Methylaluminoxane
PE	Polyethylene
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray spectroscopy
DSC	Differential scanning calorimetry
XRD	X-ray diffraction
BET	Surface area and porosity analyzer

CHAPTER I

INTRODUCTION

1.1 Introduction

One of the most popular materials used in daily life is polyethylene. It is used to produce plastic bag, water pipe, bottle, bulletproof vests and etc. Polyethylene has been received high demand because it has a wide range of properties such as high flexible, high strength, very tough at low temperature, resistance to chemical attack, no smell and no taste [1]. The development of polyethylene production having high performance is necessary. Polyethylene can be produced from ethylene monomer reacting over a catalyst to form polymer. Polymerization of ethylene is preferably carried out over Ziegler-natta catalysts and metallocene catalysts. Ziegler-natta catalysts produce polymer with broad molecular weight distribution. However, metallocene catalysts can produce polymer with narrow molecular weight distribution because it has only one type of an active site so called single-site catalyst [2]. Metallocene catalysts not only produce the polymer having specific properties, but also have higher catalytic activity than Ziegler-natta catalysts [3]. Thus, metallocene catalysts have been continuously developed for ethylene polymerization.

In 2001, Matsui and Fujita independently discovered the super active metallocene catalysts, that is FI catalysts [4]. The metal center of FI catalysts is group 4 transition metal. Their structure consist of two phenoxy-imine ligands instead of cyclopentadienyl rings or substituted cyclopentadienyl rings contributing to higher activity and higher molecular weight than the traditional metallocene catalysts [5]. The FI catalysts have to be activated by a cocatalyst to generate active form before polymerization. The popular cocatalyst employed for the FI catalysts are ttiisobutylaluminum (TIBA), triethylaluminum (TEA), trimethylaluminum (TMA) and methylaluminoxane (MAO). Many researchers found that the FI catalyst activated with a MAO cocatalyst provided high activity [6]. Although the FI catalysts in a homogeneous system presents very high activity, major disadvantages of this system are fouling in a reactor and lack of ability to control polymer morphology [7]. Binding these FI catalysts on a support as the supported FI catalysts or the heterogeneous metallocene catalysts has been done to overcome these drawbacks [8].

Generally, the support can be classified into three types including metal filler, organic support such as cyclodextrin, polyamide, and inorganic support such as alumina, zeolite and silica [9, 10]. Various kinds of silicas have received high interest in several applications because of its properties, especially in heterogeneous polymerization [11]. Many researchers revealed that silicas were used as a support for metallocene catalysts because of high surface area and good morphology [12]. Silica supported metallocenes showed lower catalyst activity for ethylene polymerization compared homogeneous metallocene systems [13] and the properties of silicas had a disadvantage about a spacer group on silica surface which difficultly reaction between silica surface and cocatalyst. Contributing to the polymerization activity increase, most researchers reported that treating the silica surface with Ga, BCl_3, $SiCl_4$ and silane for highly efficiency.

In this work, bis[N-(3-tert-butylsalicylidene) cycloheptylamine] titanium dichloride activated with various amounts of MAO are used for the ethylene polymerization. Various kinds of silica are employed as a support of this catalyst. Moreover, the influences of $SiCl_4$-modified silica on the catalytic activity and polymer properties are also investigated and compared the results with silica without modification. The properties of silicas are characterized by SEM/EDX, XRD and BET, and the properties of polyethylene are analyzed by SEM, DSC, and XRD.

1.2 Objectives

1.2.1 To investigate the optimal amounts of MAO for 3-tert-C7 catalyst with various silica supports for *in situ* polymerization of ethylene.

1.2.2 To investigate the effects of $SiCl_4$-modification on the suitable silica support on the catalytic activity of 3-tert-C7 catalyst for *in situ* polymerization of ethylene and polyethylene properties.

1.3 Research scopes

1.3.1 Silica, including SiO_2-LP, SiO_2-SP, SiO_2-MP, SiO_2-VSP, spherical silica particle (SSP) and modified silica with $SiCl_4$ are used to support the catalyst for ethylene polymerization.

1.3.2 The amounts of MAO in toluene solution are 3, 3.25, 3.5 and 3.75 mL.

1.3.3 Silica are characterized by SEM, EDX, XRD and BET method.

1.3.4 Ethylene polymerization carried out to measure the catalytic activity are performed in a 0.5 L of glass reactor equipped with a mechanical stirrer, 250 ml of toluene , polymerization temperature is 50 ^{o}C while stirring at 450 rpm under 1 bar of ethylene pressure.

1.3.5 Polyethylenes are characterized by XRD, DSC and SEM.

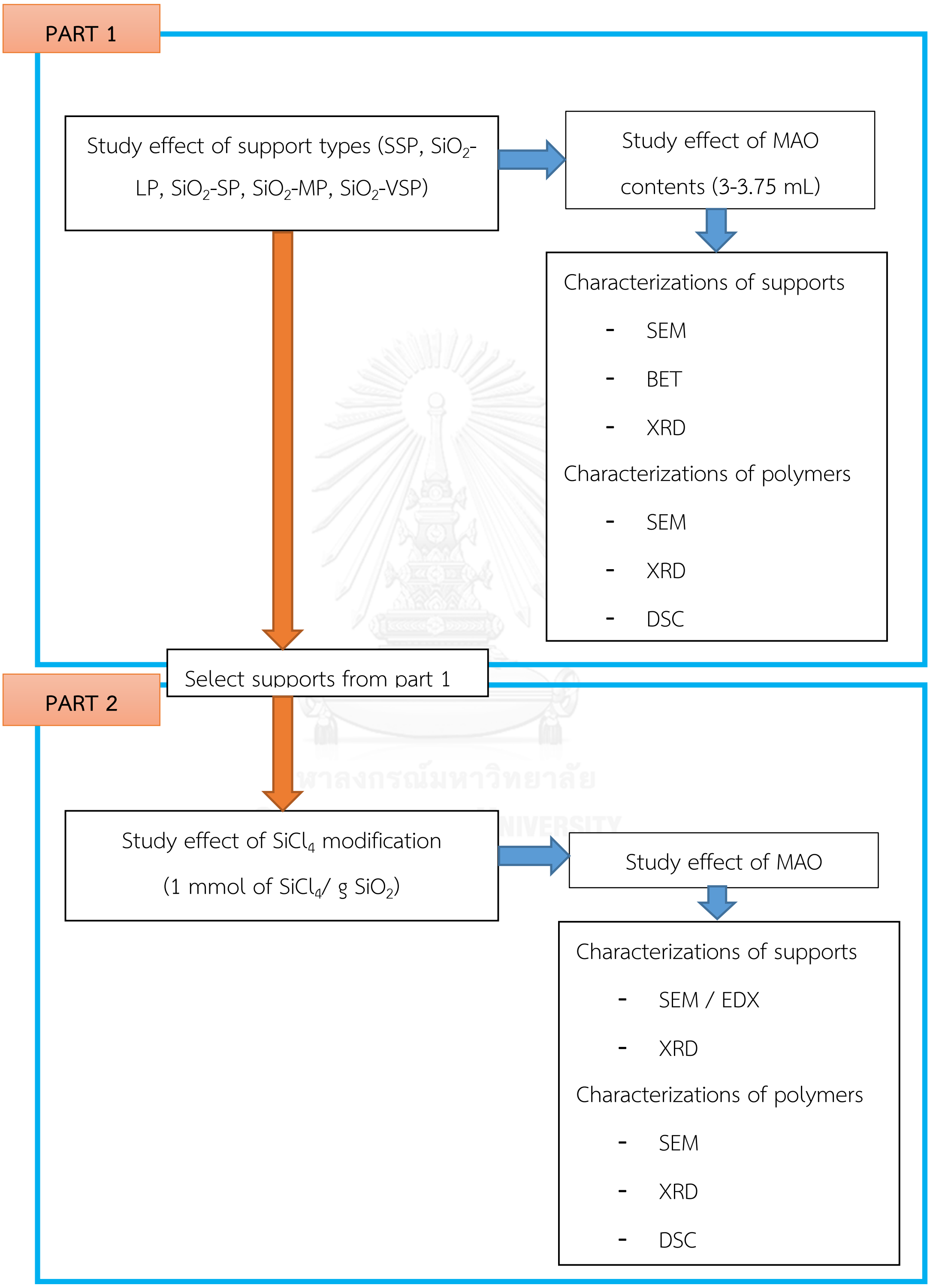
1.4 Benefits

1.4.1 To understand the effects of silica types and amounts of MAO on the catalytic activity of 3-tert-C7 catalyst for *in situ* ethylene polymerization and the polyethylene properties.

1.4.2 To understand the effects of $SiCl_4$-modified silica on the catalytic activity of 3-tert-C7 catalyst for *in situ* polymerization of ethylene and polyethylene properties.

1.4.3 To obtain an optimum amount of MAO and suitable silica type for 3-tert-C7 catalyst for *in situ* ethylene polymerization.

1.5 Research methodology



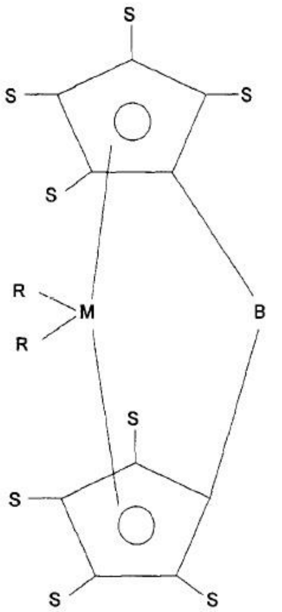
CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 FI catalyst

Metallocene catalysts are organometallic coordination compounds in which one or two cyclopentadienyl rings or substituted cyclopentadienyl rings are bonded to a central transition metal atom (**Figure 2.1**). The cyclopentadienyl ring of a metallocene is singly bonded to the central metal atom by a n-bond. Consequently, the formal valence of the ring-metal bond is not centered on any one of the five carbon atoms in the ring but equally on all of them. The nature and number of the rings and substituents (S); the type of transition metal (M) and its substituents (R); the type of the bridge determine the catalytic behavior of these organometallic compounds towards the polymerization [14].

After the discovery of the group 4 metallocene catalyst systems, transition metal complexes have been intensively investigated as post-metallocene candidates and some excellent new catalysts have been developed. In 2001, Shigekazu Matsui and Terunori Fujita [4] were discovered group 4 transition metal complexes possessing two phenoxy-imine ligands so called FI Catalysts, display exceptionally high activity and high molecular weight from ethylene polymerization.

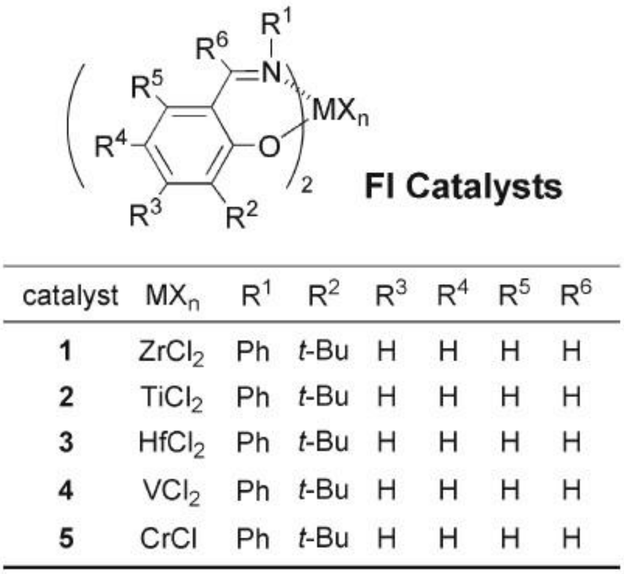


M : transition metal of groups 4b, 5b or 6b
R : hydrocarbyl, alkylidene, halogen radicals
S: hydrogen, hydrocarbyl radicals
B: alkylene, alkyl radicals, heteroatom groups

Figure 2.1 Generic structure of a metallocene catalyst [14].

2.1.1 Structure of FI catalysts

A neutral FI catalyst is an octahedral complex bearing two bidentate phenoxy-imine ligands as seen in **Figure 2.2** and two nonspectator x ligands which most x ligands are halides. The synthesis of phenoxy-imine ligands are very complication and very expensive inventories. Phenoxy-imine ligands have resulted in the versatility of FI catalysts and have also help described in the structure-reactivity relationships and reaction mechanism [1]. The center metal of FI catalyst is transition metal such as Zr, Hf, and Ti. Some researcher reported that Ti was exhibited excellent properties for higher α-olefin polymerization [4].



catalyst	MX_n	R^1	R^2	R^3	R^4	R^5	R^6
1	$ZrCl_2$	Ph	*t*-Bu	H	H	H	H
2	$TiCl_2$	Ph	*t*-Bu	H	H	H	H
3	$HfCl_2$	Ph	*t*-Bu	H	H	H	H
4	VCl_2	Ph	*t*-Bu	H	H	H	H
5	CrCl	Ph	*t*-Bu	H	H	H	H

Figure 2.2 General structure of FI catalysts and structures of FI catalysts 1 – 5 [15].

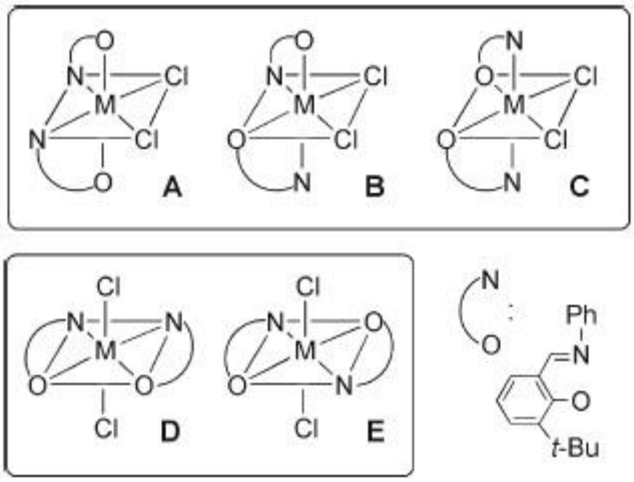
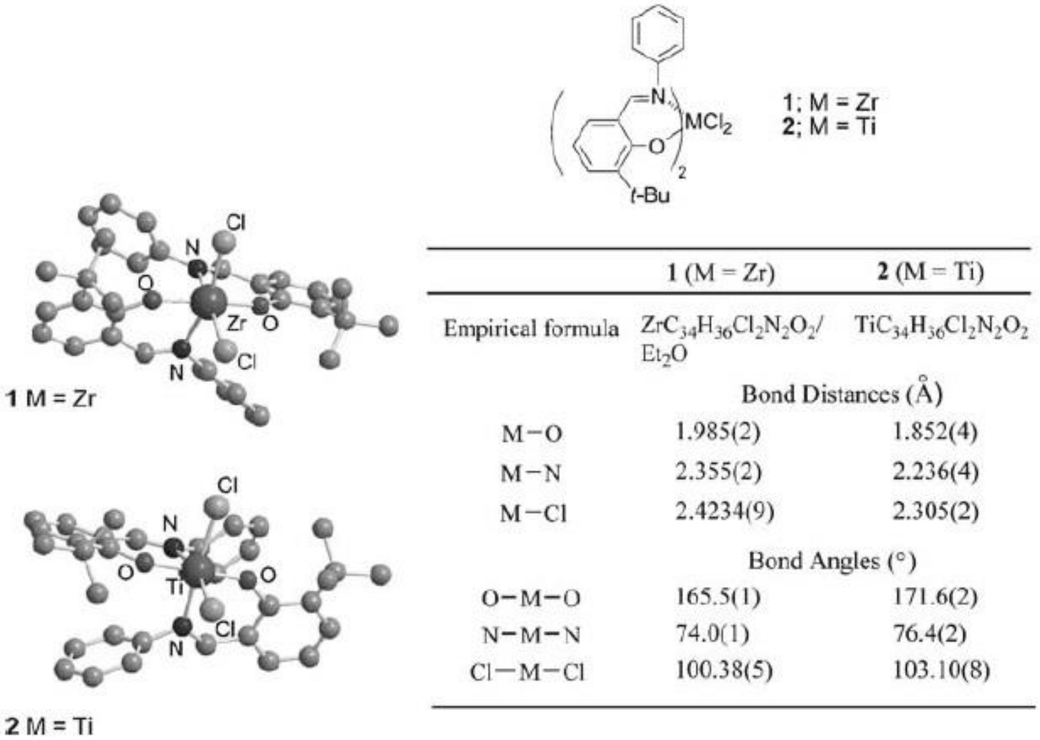


Figure 2.3 Possible isomers of an FI catalyst and phenoxy-imine ligand [15].



	1 (M = Zr)	2 (M = Ti)
Empirical formula	$ZrC_{34}H_{36}Cl_2N_2O_2/Et_2O$	$TiC_{34}H_{36}Cl_2N_2O_2$
	Bond Distances (Å)	
M−O	1.985(2)	1.852(4)
M−N	2.355(2)	2.236(4)
M−Cl	2.4234(9)	2.305(2)
	Bond Angles (°)	
O−M−O	165.5(1)	171.6(2)
N−M−N	74.0(1)	76.4(2)
Cl−M−Cl	100.38(5)	103.10(8)

Figure 2.4 Molecular structures of Zr- and Ti-FI catalysts [15].

2.1.2 Electronic features of FI catalysts

The bearing of FI ligands with heteroatom donors renders a requirement for an active olefin polymerization catalyst. The heteroatom ligation renders the metal-(phenoxy-imine) bonding properties of FI catalysts more ionic or polarized compared to metallocene catalysts. It causes the characteristic differences between these two catalysts because metal-(phenoxy-imine) bonding FI catalysyts are more strongly chemisorbed on the surface than the metallocene catalysts. Another major characteristic of the FI catalyst is a fuctional group tolerance, which the energy differences (ΔE) values of a Ti-FI catalysts are smaller than that of the metallocene catalysts resulting in the FI catalysts viable candidates for the polymerization of polar olefins [1].

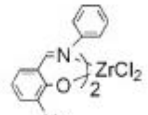
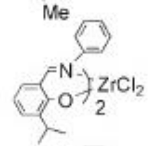
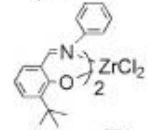
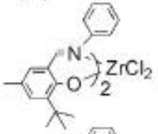
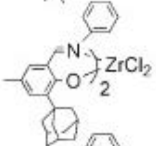
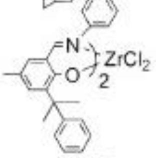
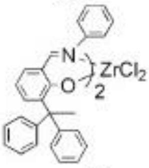
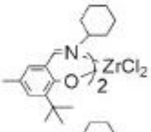
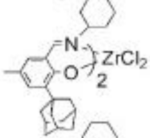
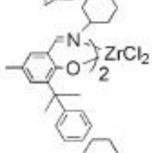
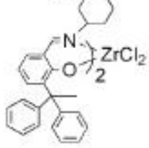
In previous explanation, FI catalysts contain phenoxy-imine ligands that can be enormous structural diversity. It is highly electrophilic, chemically adsorbable and functional group tolerant. Thus, the FI catalysts are interesting in development of olefin polymerization.

2.1.3 FI ligand structure and Ti-FI catalysts

The modification of FI ligand has a significant influence on a catalytic activity for the ethylene polymerization. As can be seen from **Figure 2.5**, if R^2 substituents are sterically smaller than a *t*-Bu group, they significantly reduce the activity. In contrast, if R^2 substituents are sterically larger than the *t*-Bu group, they can enhance the activity.

Moreover, a cyclohexyl group as R^1, *t*-Bu as R^2 position, exhibits 82 kg mmol^{-1} h^{-1} of activity, when the insertion of the 1,1-diphenylethyl group as R^2 (**Figure 2.5**, entry 11) enhanced the activity to 6552 kg mmol^{-1} h^{-1} which displayed the highest catalytic activity. Kawai et al. [15] probably explained about the significant effect of R^2 position with regard to the activity increase is as follows :

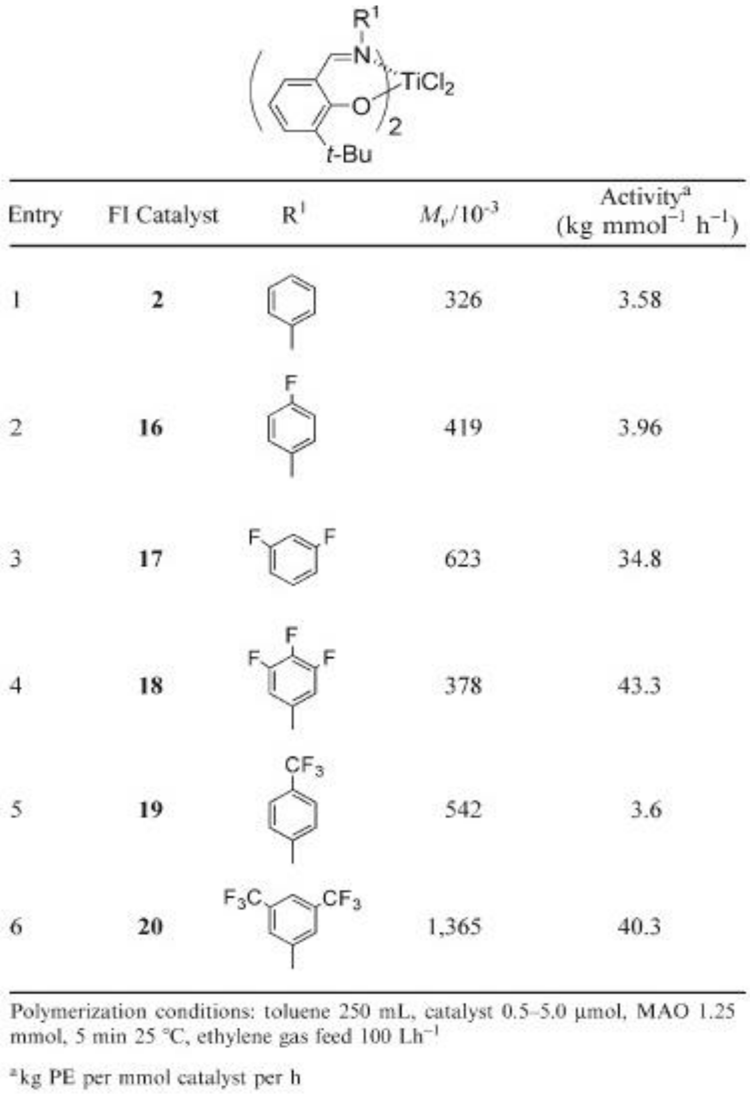
"1. The large R^2 substituents can protect attachment of oxygen donors that are reacted the metal centers from coordination with lewis acids. The coordination increases steric crowed near the polymerization center which encumbered ethylene coordination to the metal.
2. The large R^2 increase space for ethylene coordination to the metal centers which it induce effective ion-separation. The ion separation increases the electrophilicity of cationic species which enhances the ethylene polymerization."

Entry	FI Catalyst	Activity[a] (kg $mmol^{-1}$ h^{-1})
1	**7**; 	0.4
2	**6**; 	0.9
3	**1**; 	519
4	**8**; 	331
5	**9**; 	714
6	**10**; 	2096
7	**11**; 	2383
8	**12**; 	82
9	**13**; 	434
10	**14**; 	4315
11	**15**; 	6552

Polymerization conditions: in toluene (250 mL); atmospheric ethylene (0.1 MPa); 25 °C; 5 or 10 min; MAO (1.25 mmol); Al/Zr = 250 (Entries 1 and 2), 62,500 – 125,000 (Entries 3 -7)

[a] kg PE per mmol Zr per h

Figure 2.5 Ethylene polymerization with Zr-FI catalysts [15].



Entry	FI Catalyst	R¹	$M_v/10^{-3}$	Activity[a] (kg $mmol^{-1}$ h^{-1})
1	**2**		326	3.58
2	**16**		419	3.96
3	**17**		623	34.8
4	**18**		378	43.3
5	**19**		542	3.6
6	**20**		1,365	40.3

Polymerization conditions: toluene 250 mL, catalyst 0.5–5.0 μmol, MAO 1.25 mmol, 5 min 25 °C, ethylene gas feed 100 Lh^{-1}

[a] kg PE per mmol catalyst per h

Figure 2.6 Ethylene polymerization with fluorinated Ti-FI catalysts [15].

As can be seen from **Figure 2.6**, the Ti-FI catalysts displayed higher ethylene polymerization activities more than the early group 4 metallocene catalysts, Cp_2MCl_2 (M=Ti and Zr) with MAO, under the given conditions. The activity enhancement is probably ascribed to an increasing electrophilicity of the active Ti species which the Ti center plays a dominant role in determining the catalytic activity of the Ti-FI catalsts. Thus, it can confirm that the Ti-FI catalysts are interesting in development of ethylene polymerization.

2.2 Cocatalysts for FI catalysts

FI catalysts can exhibit unique catalytic behavior depending on the cocatalyst used for polymerization.

2.2.1 i-$Bu_3Al/Ph_3CB(C_6F_5)_4$ cocatalyst

Ethylene polymerizations using these FI catalysts with i-$Bu_3Al/Ph_3CB(C_6F_5)_4$ as cocatalyst provide could improve molecular weight of polyethylene but presented lower activities compared to FI catalysts using MAO as activator [15]. Figure 2.7 showed the results that the reaction of Zr-FI catalyst with i-$Bu_3Al/Ph_3CB(C_6F_5)_4$ form a bis(phenoxy-amine) complex. Similar review were made for corresponding Ti- and Hf-FI catalysts .

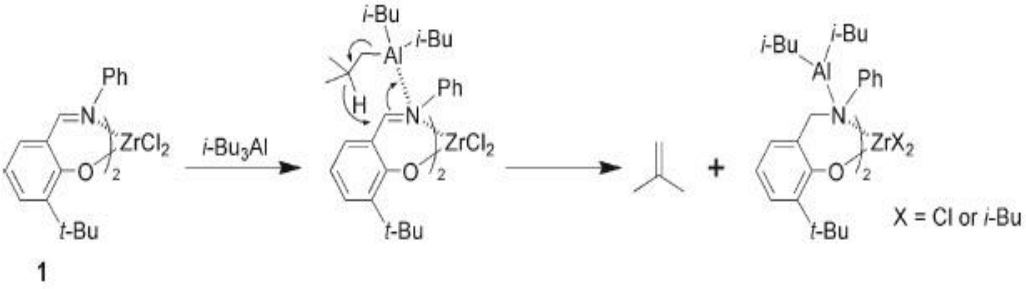


Figure 2.7 Reaction scheme for the formation of a phenoxy-amine complex [15].

2.2.2 Methylaluminoxane (MAO) cocatalyst

In previously, the cocatalytic ability of MAO was discovered as seen in **Figure 2.8**. Its exact structure and functional group are still unknown. Some researcher reported that MAO consists of cage structures [16]. Even if the MAO is very expensive inventory, MAO is always used to be an activator for metallocene catalyst to active form for polymerization because of higher active catalytic system than other cocatalysts. Many researchers reported that MAO is an exceptional activator than other cocatalysts for ethylene polymerization. For example, Gil et al. [17] studied the influence of [Al]/[Ti] molar ratio, reaction temperature, and cocatalyst types (MAO, TMA, TiBA and IPRA) on the activity and polymer properties using tris(pyrazolyl)borate titanium(IV) catalyst. The results were observed that the highest activity of ethylene polymerization used MAO as cocatalyst at 30-60 °C and [Al]/[Ti] is 300.

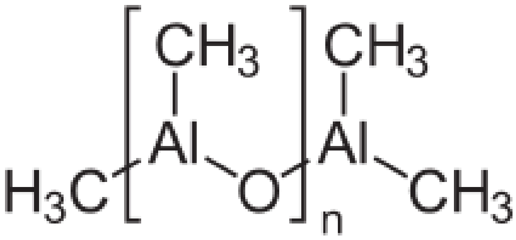


Figure 2.8 Element of MAO structure.

Another research, Park et al. [18] studied the effect of $Al_{(MAO)}$/Zr ratio on the physical properties and chemical composition distributions (CCDs) of ethylene–hexene copolymers produced by a rac-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB catalyst. It was found that the catalytic activity of rac-Et(Ind)$_2$ZrCl$_2$/TiCl$_4$/MAO/SMB was steadily increased with increasing $Al_{(MAO)}$/Zr ratio from 200 to 500.

In previous example, MAO is interesting activator for FI catalyst and metallocene catalyst because it can provide very high catalytic activity compared to other cocatalysts. Therefore, the various amounts of MAO are investigated in this wok.

2.3 Heterogeneous system

Metallocene catalyst in homogeneous system presents very high activity. However, major disadvantages of homogeneous polymerization are fouling in reactor and lack of ability to control polymer morphology [7]. Binding these metallocene catalysts onto a support as the supported metallocene catalysts or heterogeneous metallocene catalysts, has been done to overcome these drawbacks. Generally, the support can be classified into three types including metal filler, organic support such as cyclodextrin, polyamide, and inorganic support such as alumina, zeolite and silica . Variuos kinds of silicas have received high interest in several applications because of its properties, especially in heterogeneous polymerization [11]. Many researchers revealed that silicas were used as a support for metallocene catalysts because of high surface area and good morphology [12].

2.3.1 Silica

Silica contains a large kind of products with the general formular SiO_2 or $SiO_2.xH_2O$. Silica is often used as a support for various transition metals. It has high surface area, porosity stability at high temperature and low cost. It is an excellent morphology control and appropriate to be support or template in supporting system [19, 20].

Sol-gel technique is employed to obtain the silica-type powder. The silica powder from this method is synthesized using hydrolysis and condensation of tetraethyl orthosilicate (TEOS) catalyzed by ammonia [9, 21, 22]. Its advantageous morphology with wide and shallow pores allows to obtain catalytic systems of higher activity in low-pressure ethylene polymerization [13].

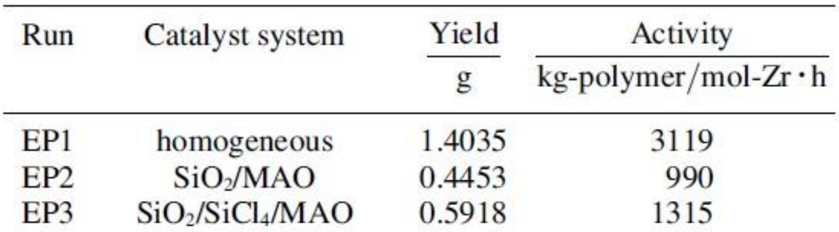
2.4 Modification of silica

Supported metallocenes showed lower catalyst activity for ethylene polymerization compared to homogeneous metallocene system. Nevertheless, it has been discovered that a new immobilization method for introducing a spacer group onto the support resulting in an increasing the catalytic activity. This is because catalyst easily react with the cocatalyst on the support surface [23].

Smit [13] described that the concentration of hydroxyl groups on silica surface are more or less constant for a given drying temperature between 200^{o}C and 1000^{o}C which contains about 4.6 OH/nm^2 and this can be calculate as a physicochemical constant. The results showed that the amounts of hydroxyl groups on the silica materials are available for chemical modification which can successfully be manipulated (1.0-3.2 mmol OH/g silica) in a reproducible manner with calcination.

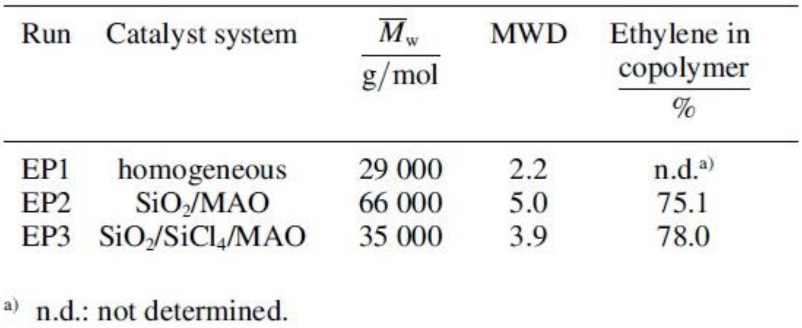
Chao et al. [24] studied the effect of silicon tetrachloride-modified silica support for copolymerization of ethylene and propylene. The result showed that from the $SiCl_4$-modified system, the copolymerization activity increased by about 30%

(**Figure 2.9**) and molecular weight distribution of polymer is smaller than using SiO_2 without treating as a support (**Figure 2.10**).



Run	Catalyst system	Yield g	Activity kg-polymer/mol-Zr·h
EP1	homogeneous	1.4035	3119
EP2	SiO_2/MAO	0.4453	990
EP3	SiO_2/$SiCl_4$/MAO	0.5918	1315

Figure 2.9 Activity in the copolymerization of ethylene and propylene with different catalytic systems [24].



Run	Catalyst system	$\overline{M}_w$ g/mol	MWD	Ethylene in copolymer %
EP1	homogeneous	29 000	2.2	n.d.[a)]
EP2	SiO_2/MAO	66 000	5.0	75.1
EP3	SiO_2/$SiCl_4$/MAO	35 000	3.9	78.0

a) n.d.: not determined.

Figure 2.10 Properties of the ethylene/propylene copolymers obtained [24].

2.5 *In situ* polymerization

Some researchers have reported the immobilization methods for catalysts provided high catalytic activity but these methods might be less attractive in a commercial application. *In situ* polymerization is an interesting method for polyethylene production, which can eliminate the supporting step before polymerization because of this method can be approximate catalytic activity and morphology that the results corresponding with normal method [10, 25].

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

Table 3.1 The chemicals used in the support preparation and the polymerization.

Chemicals	Formula	Supplier
bis[N-(3-tert-butylsalicylidene) cycloheptylamine] titanium dichloride ; (3-tert-C7)	-	PTT RTI
Methylaluminoxane (MAO, 10%)	$(Al(CH_3)O)_n$	Aldrich
Cetyltrimethylammonium bromide (CTAB, 98%)	$C_{19}H_{42}BrN$	Aldrich
Ethanol (99.99%),	C_2H_6O	J.T. Baker
Ammonia (30%)	NH_3	Panreac
Tetraethyl orthosilicate (TEOS, 98%)	$SiC_8H_{20}O_4$	Aldrich
Silicon tetrachloride	$SiCl_4$	Aldrich
Sodium bicarbonate	$NaHCO_3$	Univar
SiO_2-LP	SiO_2	PTT RTI
SiO_2-SP	SiO_2	PTT RTI
SiO_2-MP	SiO_2	PTT RTI
SiO_2-VSP	SiO_2	PTT RTI
Ethylene gas (99.99%)	C_2H_4	PTT RTI
Toluene	C_6H_5-CH_3	PTT RTI

3.2 Experimental

3.2.1 Preparation of supports

3.2.1.1 Synthesis of spherical silica particle (SSP)

The SSP was synthesized according to Jetsadanurak et al. [26]. 3.3 g of CTAB were added into the mixture of 11.46 mL of ammonia, 100.05 mL of ethanol, and 70.56 mL of DI water, and then stirred for 30 minutes. After that, 6.75 mL of TEOS was added into the solution and stirred at a room temperature for 2 hours. The slurry was filtered by a vacuum pump, followed by drying overnight in the oven at 120 ^{o}C to obtain the white powder. The list of chemicals are shown in **Table 3.1**.

3.2.1.2 Calcination

The SSP and the commercial silicas including SiO_2-LP, SiO_2-SP, SiO_2-MP, and SiO_2-VSP were dried at 600 ^{o}C, heating rate 20 ^{o}C/min under nitrogen for 6 hours. Then, they were cooled down to a room temperature and stored in bottle under argon atmosphere.

3.2.1.3 Modification of silica by $SiCl_4$

The silica was modified by a $SiCl_4$ according to Jongsomjit et al. [27]. 2 g of calcined silica was mixed with silicon tetrachloride (2 mmol) in 20 mL of toluene under argon atmosphere. The mixture was refluxed at 110 ^{o}C for 7 hours while stirring with a magnetic stirrer under argon atmosphere. Then, 0.038 mL of the sodium bicarbonate aqueous solution (1.5 N) was added into the mixture, and stirred at a room temperature. The obtained solid was filtered, after that washed with toluene and dried at 60 ^{o}C under vacuum to obtain the white powder of $SiCl_4$-modified silica support.

3.2.2 In situ ethylene polymerization

Ethylene polymerization was conducted under an atmospheric pressure of ethylene gas in a 0.5 L of glass reactor equipped with a mechanical stirrer using toluene as a solvent. The reactor was removed oxygen and moisture by evacuating and purging with argon several times and kept under vacuum at 120 °C for 2 hours. Silica (0.5 g) was introduced into 2 mL of toluene in a bottle under argon atmosphere, and then the desired amount of MAO (3, 3.25, 3.5 or 3.75 mL) was added into the mixture and stirred for 2 hours. After that, 250 mL of toluene was added into a glass reactor at 50 °C. Then, the mixture of silica and MAO and the 4 mL of 3-tert-C7 catalyst solution (3-tert-C7 1 μmol/mL) were injected into a glass reactor respectively while stirring at 450 rpm under a 1 bar of ethylene pressure. After 30 minutes, the ethylene gas was stopped and an acidic ethanol (ethanol/HCl) was introduced in the reactor to terminate the polymerization. The obtained polymer was filtered, washed with ethanol, and dried in vacuum at 60 °C overnight.

3.3 characterization of supports and polmers

3.3.1 Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

Morphology of silica and polyethylene were investigated by of JEOL mode JSM-6400 of SEM. Elemental distribution of chloride were observed by EDX using Link Isis series 300 program to confirm the modification of silica by $SiCl_4$.

3.3.2 N_2 physisorption

Surface area, pore size and pore volume of silica were determined by Brunauer Emmett Teller (BET) analysis via nitrogen adsorption/desorption using a Micromeritics ASAP 2000 automated system.

3.3.3 Differential scanning calorimetry (DSC)

Melting temperature of polyethylene were performed using dsc TA Instrument SDT Q600. The samples of 3.5-3.55 mg was used. Carrier gas was nitrogen UHP. Temperature ramping was operated from 25 to 170 °C at 10 °C/min .

3.3.4 X-ray diffraction (XRD)

The bulk crystalline phases of silica and polyethylene were analyzed using a SIEMENS D-5000 X-ray diffractometer with CuK α radiation with Ni filter in the 2θ range of 20 to 80 degrees.

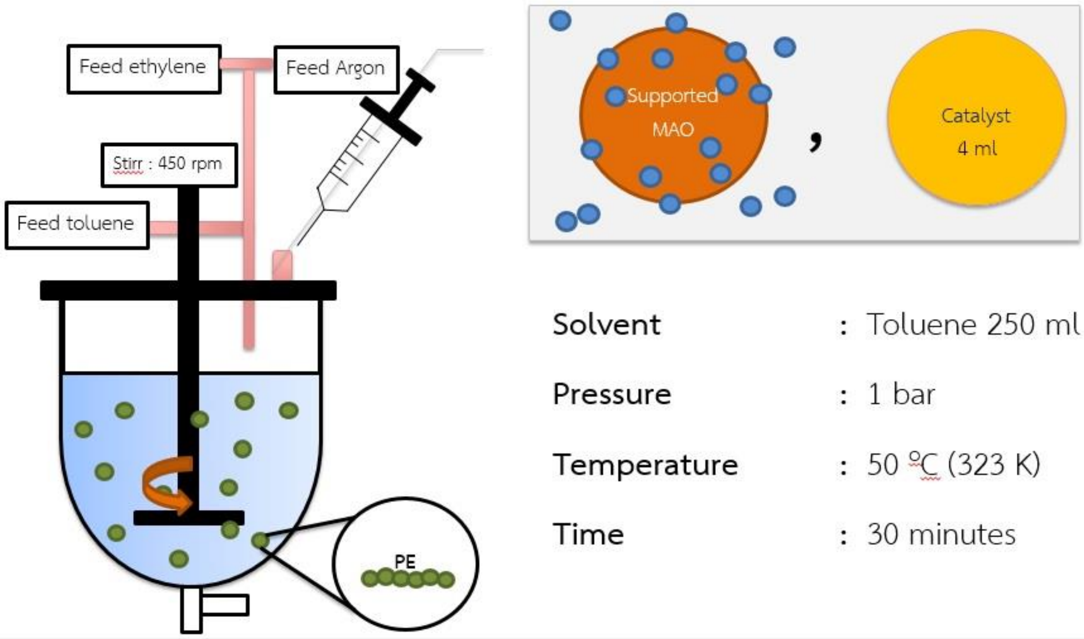


Figure 3.1 Diagram of glass reactor 0.5 L for *in situ* polymerization.

CHAPTER IV

RESULTS AND DISCUSSION

The results and discussion are divided into two parts composing of the effect of various SiO_2-supported 3-tert-C7 on ethylene polymerization (part 1) and the modification effect of silica (SiO_2-MP) modified with $SiCl_4$ for ethylene polymerization (part 2).

PART 1 : Effect of various SiO_2-supported 3-tert-C7 catalyst on ethylene polymerization

In this part, various silica supports without modification were investigated including SiO_2-LP, SiO_2-SP, SiO_2-MP, SiO_2-VSP and SSP. These were prepared and characterized using BET, XRD and SEM. This part has been focused on the effect of various silica-supported 3-tert-C7 catalyst on ethylene polymerization in term of catalytic activity and polymer properties.

4.1 Characterization of silica supports without modification

4.1.1 Characterization of supports with N_2 physisorption

The silica supports were found to have different surface areas. The silica from commercial (SiO_2-LP, SiO_2-SP, SiO_2-MP and SiO_2-VSP) have the surface area of 355-460 m^2/g, pore size around 95-144 Å and pore volume of 1.06-1.46 cm^3/g. Another silica was the synthesized SiO_2 by chemical method (SSP) has surface area of 999 m^2/g, pore size around 24 Å and pore volume of 0.5 cm^3/g. The particle size of SiO_2-LP, SiO_2-SP, SiO_2-MP, SiO_2-VSP and SSP are 6, 11, 18, 44 and 0.5 µm, respectively. The results are shown in **Table 4.1**.

Figure 4.1 shows the N_2 adsorption-desorption isotherms for various silica supports. The pore structure of commercial SiO_2 supports exhibited the characteristic of mesoporous structure and SSP support exhibited the characteristic of microporous structure according to type IV and type I, respectively, classified by IUPAC (International Union of Pure and Applied Chemistry).

Table 4.1 N_2 physisorption of various silica supports.

Silica	Particle size (μm)	Surface area (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)
SiO_2-LP	6	355	144	1.06
SiO_2-SP	11	460	118	1.46
SiO_2-MP	18	394	120	1.29
SiO_2-VSP	44	433	95	1.40
SSP	0.1-0.5	999	24	0.50

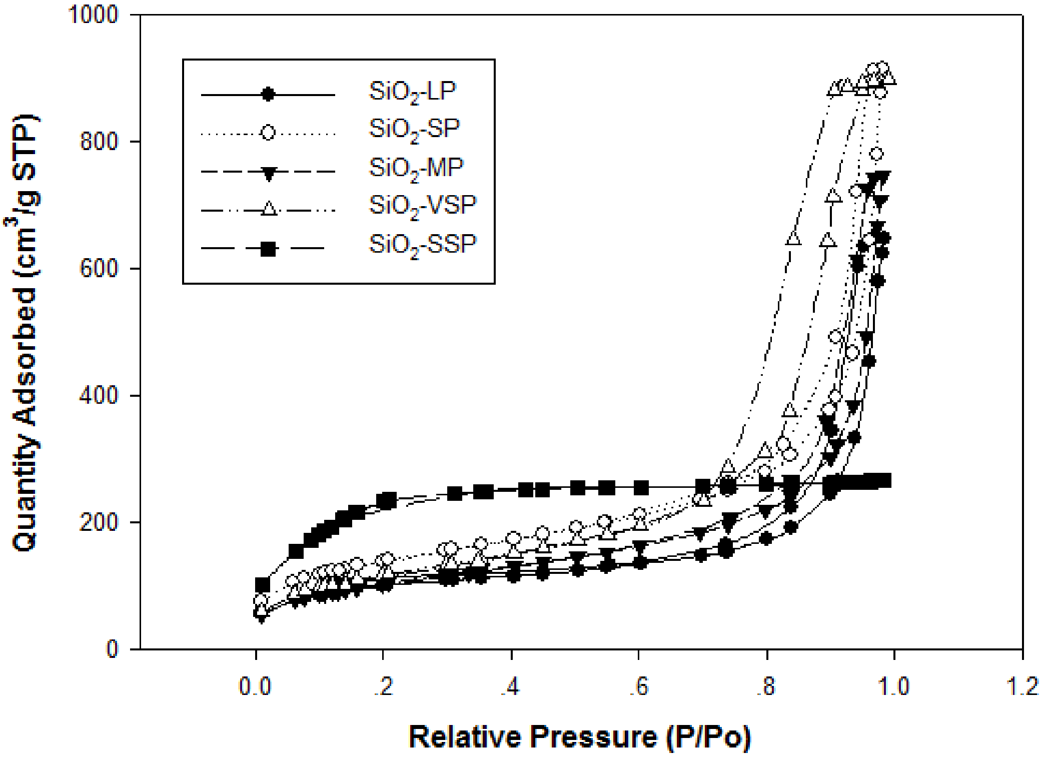


Figure 4.1 The N_2 adsorption-desorption isotherms for all supports.

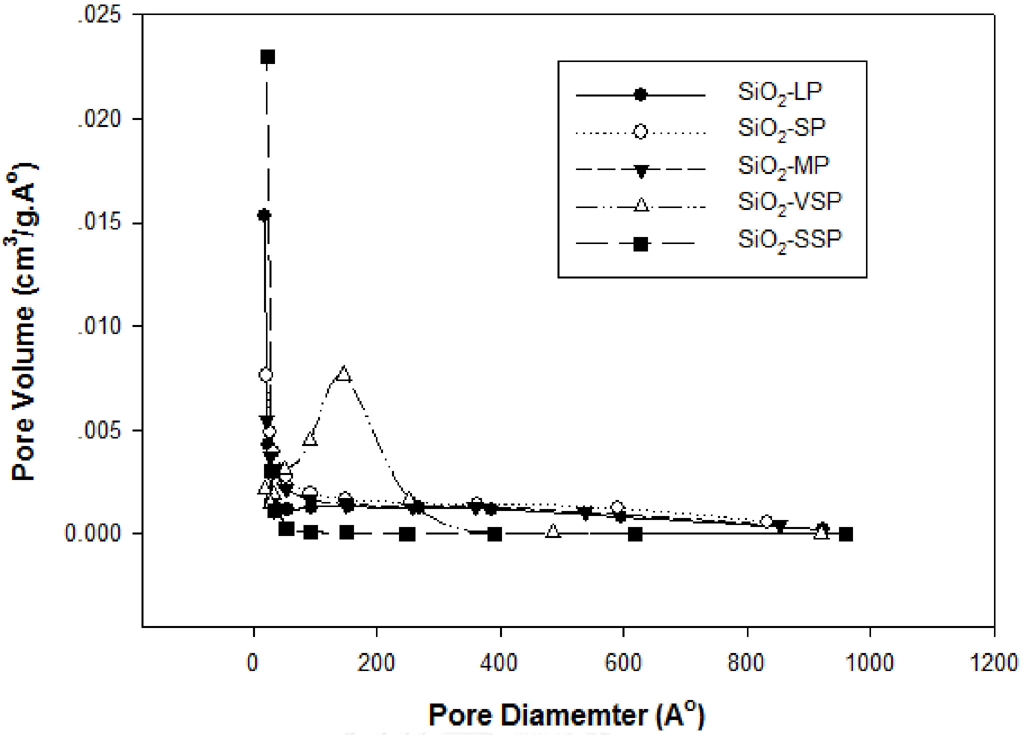


Figure 4.2 The pore size distribution of various of silica supports.

The pore size distributions of various of silica supports are shown in **Figure 4.2**, which were related to the pore structure as discussed from **Figure 4.1**. The average pore diameter of SiO_2-LP, SiO_2-SP, SiO_2-MP, SiO_2-VSP and SSP was 154, 157, 147, 239 and 152 Å, respectively.

4.1.2 Characterization of supports with X-ray diffraction (XRD)

The various SiO_2 supports without modification were characterized with XRD. The XRD patterns of supports are shown in **Figure 4.3**. All silica supports exhibited the similar XRD patterns indicating a board peak between 20 - 25° as commonly seen for the conventional amorphous silica.

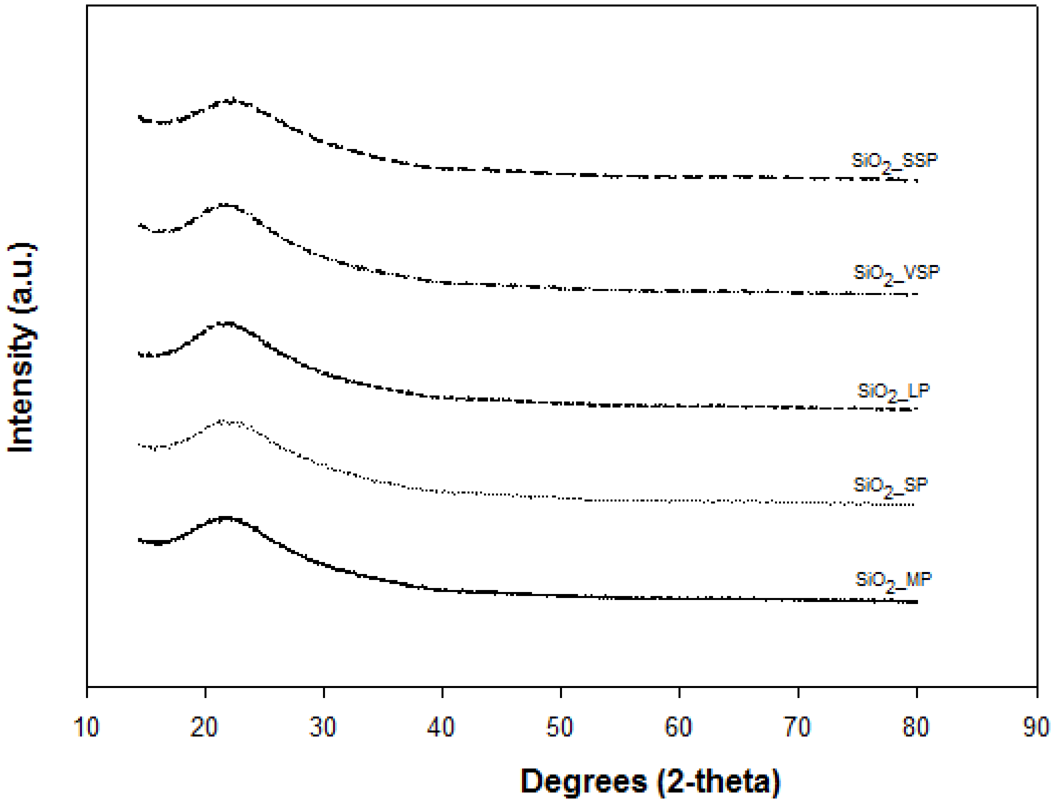


Figure 4.3 XRD patterns of various SiO_2 supports.

4.1.3 Characterization of supports with scanning electron microscope (SEM)

The morphologies of various silica supports are shown in **Figure 4.4**. The shape of SiO_2-LP (**Figure 4.4a**), SiO_2-SP (**Figure 4.4b**) and SiO_2-MP (**Figure 4.4c**) are spherical morphology and smooth surface. On the other hand, SiO_2-VSP (**Figure 4.4d**) is rather spherical morphology and rough surface. Another, SSP (**Figure 4.4e**) has shape like SiO_2-LP, SiO_2-SP, and SiO_2-MP, but it has very small particles (**Figure 4.4f**).

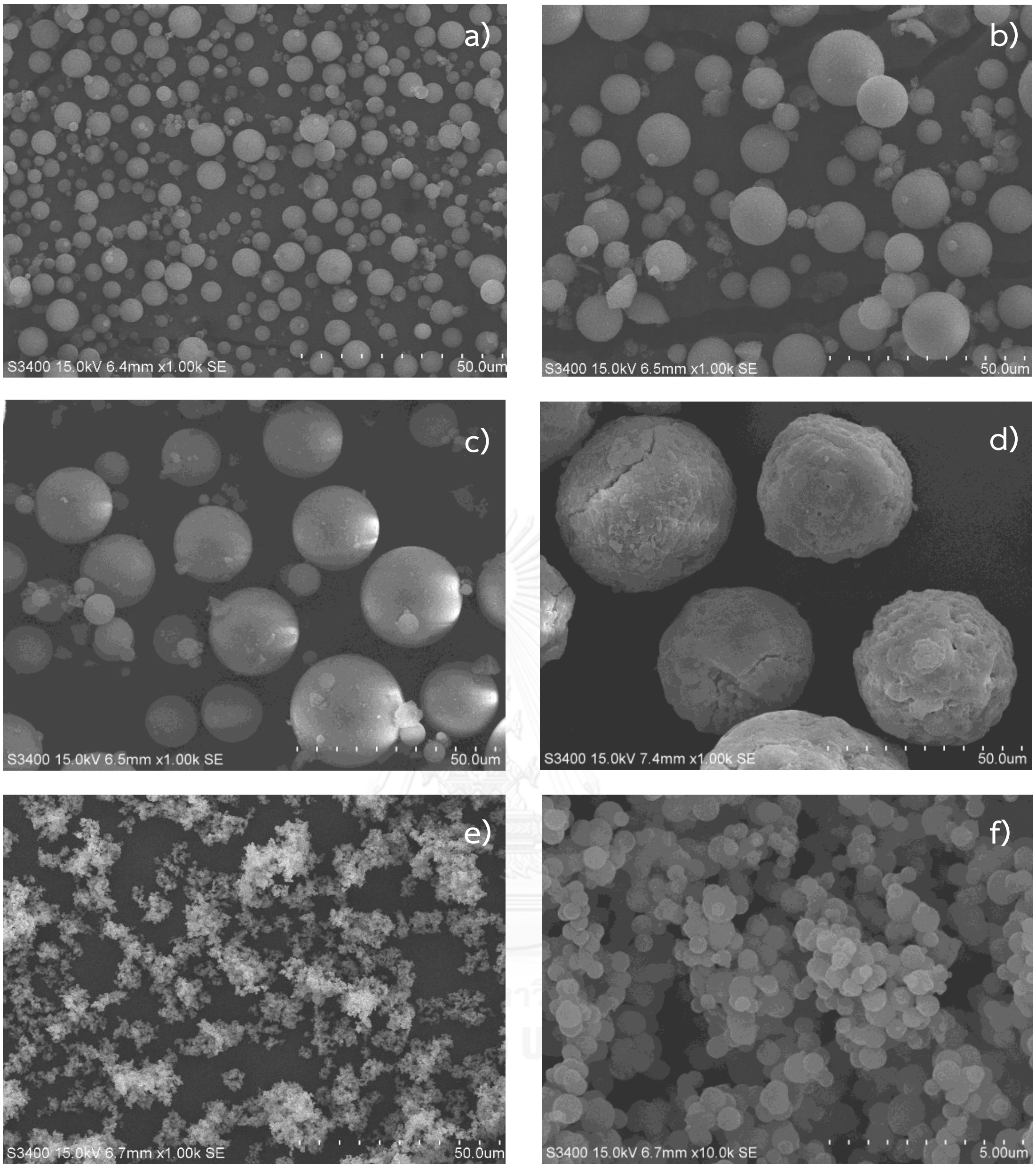


Figure 4.4 SEM micrographs of various SiO_2 supports at scale bar 50 μm; (a) SiO_2-LP, (b) SiO_2-SP, (c) SiO_2-MP, (d) SiO_2-VSP, (e) SSP and (f) SSP is SEM micrograph of various SiO_2 supports at scale bar 5 μm

4.2 Characterization and catalytic properties of polyethylene using silica supports without modification

4.2.1 The effect of silica supports on the catalytic activity

Table 4.2 Ethylene polymerization activities without modification of silica supports.

Silica	MAO (ml)	[Al/Ti]	Yield (g)	Activity (kg PE/mmol cat *hr)[a]
SiO_2-LP	3	1131	2.94	1.22
	3.25	1225	4.44	1.97
	3.5	1320	5.30	2.40
	3.75	1414	7.38	3.44
SiO_2-SP	3	1131	2.16	0.83
	3.25	1225	2.30	0.90
	3.5	1320	2.43	0.97
	3.75	1414	2.25	0.88
SiO_2-MP	3	1131	2.11	0.80
	3.25	1225	2.25	0.88
	3.5	1320	2.39	0.95
	3.75	1414	2.02	0.76
SiO_2-VSP	3	1131	2.37	0.93
	3.25	1225	2.84	1.17
	3.5	1320	3.19	1.34
	3.75	1414	5.13	2.31
SSP	3	1131	4.97	2.24
	3.25	1225	5.74	2.62
	3.5	1320	6.22	2.86
	3.75	1414	6.43	2.97

[a] Activities were measured at polymerization temperature of 50°C via *in situ*, support 0.5 g, 30 minutes, Ethylene pressure 1 bar, toluene 250 ml, 3-tert-C7 4 mL and stirr 450 rpm.

From **Table 4.2**, the activities mostly increase with increasing of MAO. The activity obtained by SiO_2-LP at Al/Ti=1414 (3.44 kg PE/mmol cat *hr) was higher than SSP, SiO_2-VSP, SiO_2-SP and SiO_2-MP, respectively. Based on Al/Ti=1131 and 1225, the activity of SSP expressed the highest activity (2.24 and 2.26 kg PE/mmol cat *hr) when compared with SiO_2-LP, as shown in **Figure 4.5**.

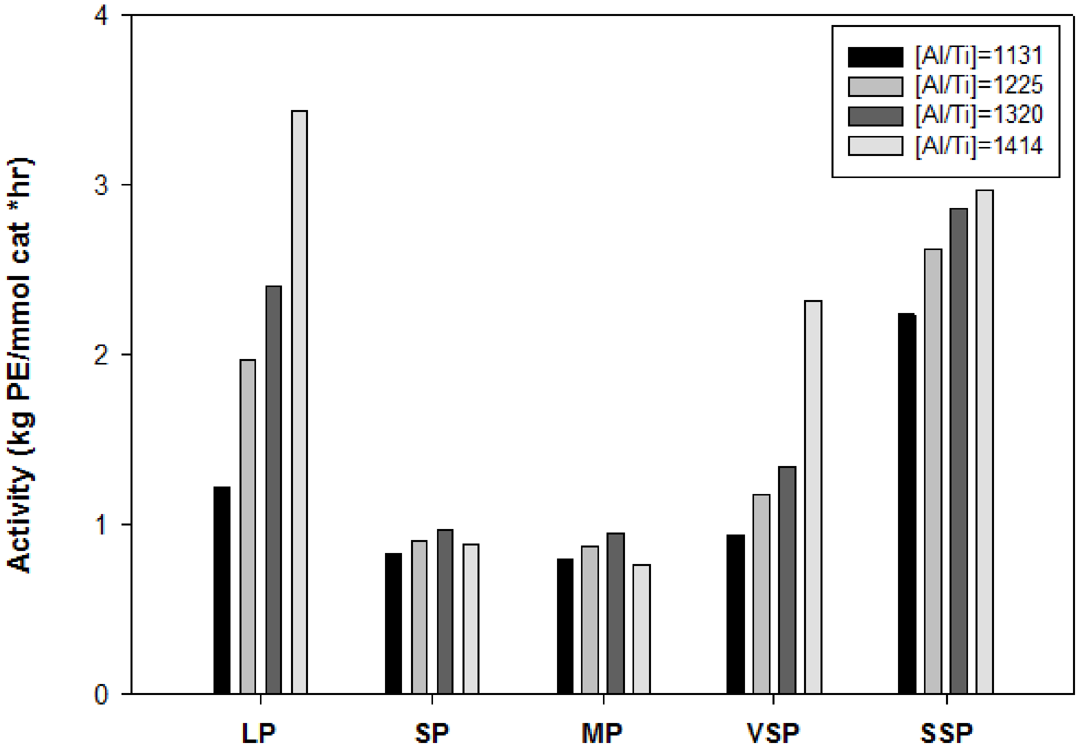


Figure 4.5 Comparison of catalytic activities of various SiO_2 supports without modification.

4.2.2 The effect of silica supports on the melting temperatures of polyethylene

The melting temperatures (T_m) of polymer evaluated by the differential scanning calorimeter (DSC) are shown in **Table 4.3**.

Table 4.3 The effect of various silica supports without modification on the melting temperatures of polymers.

Polymer[a]	MAO (ml)	[Al/Ti]	T_m (°C)	Crystallinity (%)
PE_SiO_2-LP	3	1131	134.5	45.0
	3.25	1225	134.5	49.8
	3.5	1320	134.0	64.1
	3.75	1414	134.1	73.8
PE_SiO_2-SP	3	1131	134.9	34.2
	3.25	1225	134.3	40.4
	3.5	1320	135.1	34.3
	3.75	1414	134.9	38.7
PE_SiO_2-MP	3	1131	132.6	44.2
	3.25	1225	132.0	43.7
	3.5	1320	132.3	51.2
	3.75	1414	133.6	35.8
PE_SiO_2-VSP	3	1131	134.4	33.8
	3.25	1225	134.4	37.9
	3.5	1320	134.8	41.1
	3.75	1414	134.6	49.6
PE_SSP	3	1131	134.1	65.1
	3.25	1225	134.2	65.2
	3.5	1320	134.3	68.3
	3.75	1414	134.4	62.9

[a] PE_SiO_2-LP=polyethylene from SiO_2-LP support, PE_SiO_2-SP= polyethylene from SiO_2-SP support, PE_SiO_2-MP=polyethylene from SiO_2-MP support, PE_SiO_2-VSP= polyethylene from SiO_2-VSP support, PE_SSP= polyethylene from SSP support.

From the characterization of polymer in **Table 4.3**, It was found that the melting temperatures of PE_SiO$_2$-LP, PE_SiO$_2$-SP, PE_SiO$_2$-MP, PE_SiO$_2$-VSP and PE_SSP from *in situ* polymerization were similar (a.134 ^{o}C).

The crystallinity of PE_SiO$_2$-LP at Al/Ti=1414 was the highest (73.8%), but the crystallinity is not constant with increased MAO. The crystallinity of PE_SiO$_2$-SP, PE_SiO$_2$-MP and PE_SiO$_2$-VSP was similar between 34-50 %. The PE_SSP had high crystallinity and rather constant values.

4.2.3 Characterization of polyethylene with X-ray diffraction (XRD)

The polymers obtained from *in situ* polymerization were characterized by XRD as shown in **Figure 4.6** that the example of XRD of polyethylene using MAO 3 ml (Al/Ti=1131). It can be seen that all amounts of MAO and all exhibited the similar XRD patterns expressed the sharp peak at 21° and 24° as seen typically for the polyethylene. While PE_SiO$_2$-MP has very short peak of polyethylene, it indicated that it was amorphous polyethylene.

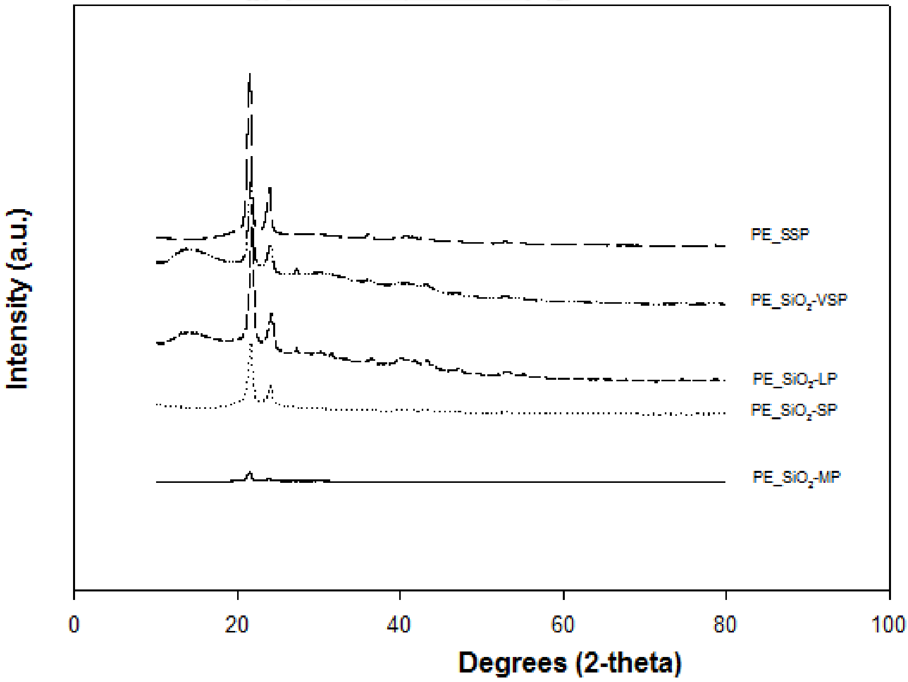
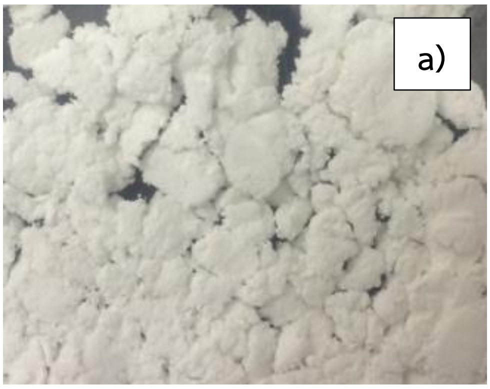
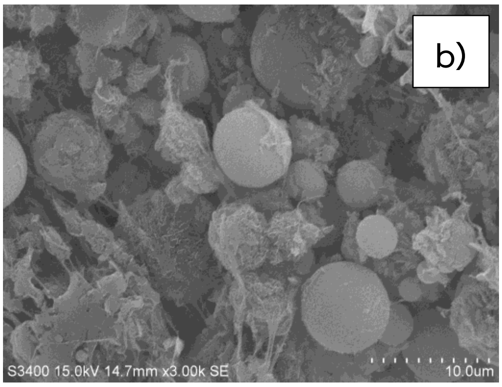


Figure 4.6 XRD pattern of polymers from in situ polymerization without modification SiO$_2$ supports.

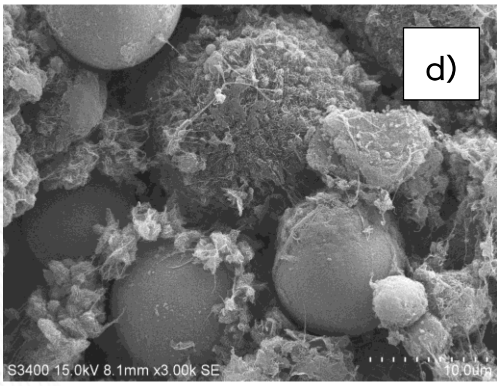
4.2.4 Characterization of polyethylene with scanning electron microscope (SEM)

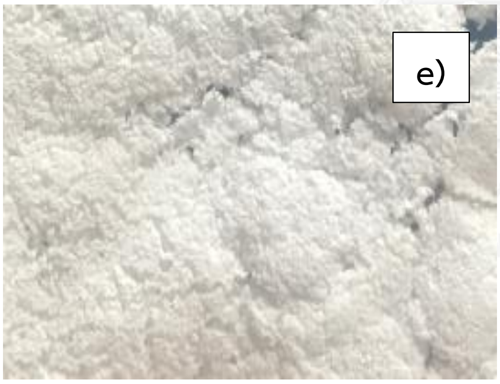
The morphology of polyethylene obtained via *in situ* using various silica support without modification was determined by SEM. From **Figure 4.7**, the SEM images of polyethylene of SiO_2-LP, SiO_2-SP, SiO_2-MP, SiO_2-VSP and SSP using MAO 3ml (Al/Ti=1131) are illustrated in **Figure 4.7a), Figure 4.7c), Figure 4.7e), Figure 4.7g)** and **Figure 4.7i)**, respectively. The SEM micrographs of polyethylene of SiO_2-LP, SiO_2-SP, SiO_2-MP, SiO_2-VSP and SSP that using MAO 3ml (Al/Ti=1131) are shown in **Figure 4.7b), Figure 4.7d), Figure 4.7f), Figure 4.7h)** and **Figure 4.7j)**, respectively. First, the polyethylene using SiO_2-LP (**Figure 4.7a** and **4.7b**) reveals that some polymers occurred on silica surface and other polymers formed by the homogeneous system (fine particles). Polyethylene using SiO_2-SP was similar to that using SiO_2-LP, but the polymer was not fine particles (**Figure 4.7c**). The characteristics of polyethylene using SiO_2-MP was better than that using SiO_2-LP and SiO_2-SP with fine particles and least homopolymerization occurred (**Figure 4.7e** and **4.7f**). Polymer that using SiO_2-VSP support was not fine particles and high homopolymerization occurred (**Figure 4.7g** and **4.7h**). When considered the particles of polymer using SSP support, it showed good fine particle. The SEM micrograph exhibited the fine particles of polymer due to the very small size of SSP. Thus, when polymer formed on SSP, it replicates the morphology of SSP leading to fine particles of polymer produced.

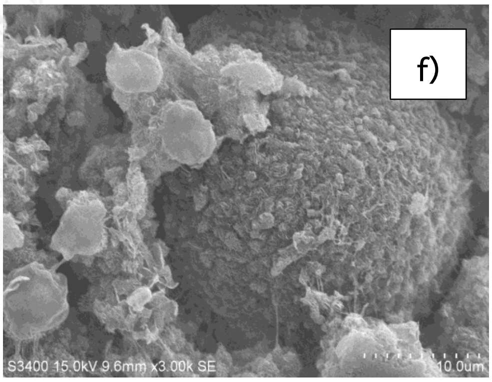

a)


b)
S3400 15.0kV 14.7mm x3.00k SE
10.0um


c)


d)
S3400 15.0kV 8.1mm x3.00k SE
10.0um


e)


f)
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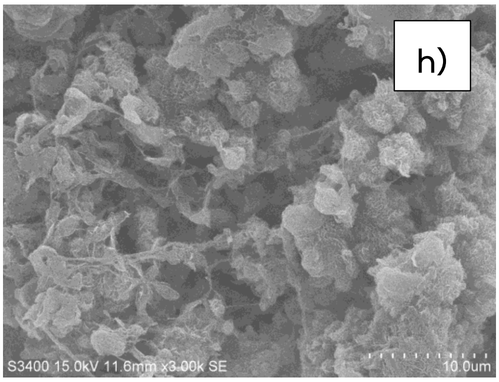
10.0um


g)


h)
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10.0um

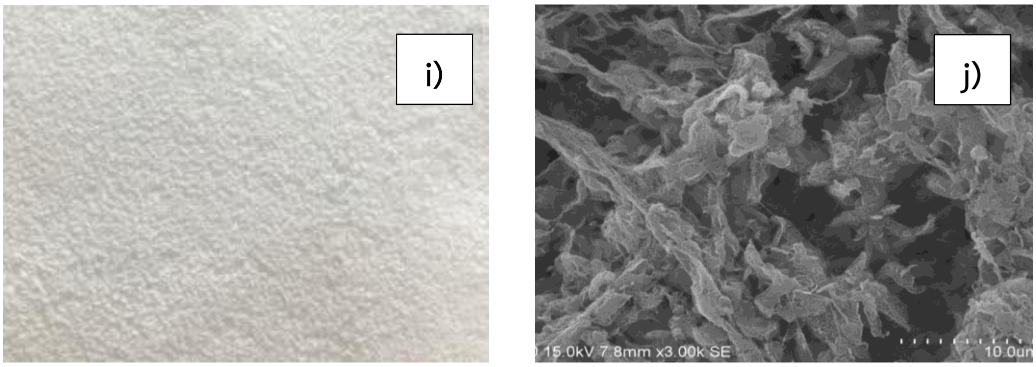

Figure 4.7 images and SEM micrographs at scale bar of 10 μm ; PE_SiO_2-LP (a,b), PE_SiO_2-SP (c,d), PE_SiO_2-MP (e,f), PE_SiO_2-VSP(g,h), PE_SSP (i,j).

PART 2 : Effect of $SiCl_4$ modification on (SiO_2-MP)-supported 3-tert-C7 catalyst during ethylene polymerization

From the results in part 1, The SiO_2-MP support having low activities and low crystallinity indicated that, it was amorphous polyethylene. The hypothesis of part 2 was the modification by $SiCl_4$ make characteristic of SiO_2-MP support better than in part 1, SiO_2-MP support was selected.

This part has been focused on the effect of a modified SiO_2-MP with $SiCl_4$ supported 3-tert-C7 catalyst on ethylene polymerization. In fact, the SiO_2 support was prepared, and sequentially modified with $SiCl_4$ (modified_SiO_2-MP). The modified SiO_2-MP support was characterized using SEM-EDX, TGA and XRD.

4.3 Characterization of a modified SiO_2-MP support

4.3.1 Characterization of the modified SiO_2-MP support with scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

The SEM micrographs of SiO_2-MP supports without modification and modification (modified_SiO_2-MP) are shown in **Figure 4.8** indicating that the silica particles retain the shape like the SiO_2 without modification. However, the SEM images also revealed that some breakage of particles occurred when it is extremely stirred for too long. According to N_2 physisorption, the modified SiO_2-MP support had surface area more than the SiO_2-MP because of cracking of particles.

The elemental distribution of the modified and unmodified SiO_2-MP is shown in **Figure 4.9**. It is clear that with $SiCl_4$ modification, the Si mapping exhibited very high Si distribution compared with the unmodified one.

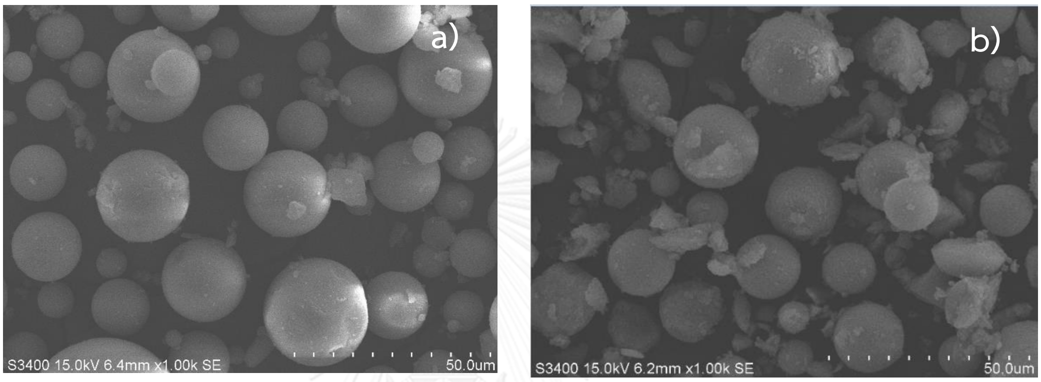

Figure 4.8 SEM micrographs of SiO_2-MP (a) and modified_SiO_2-MP (b) at scale bar of 50 μm.

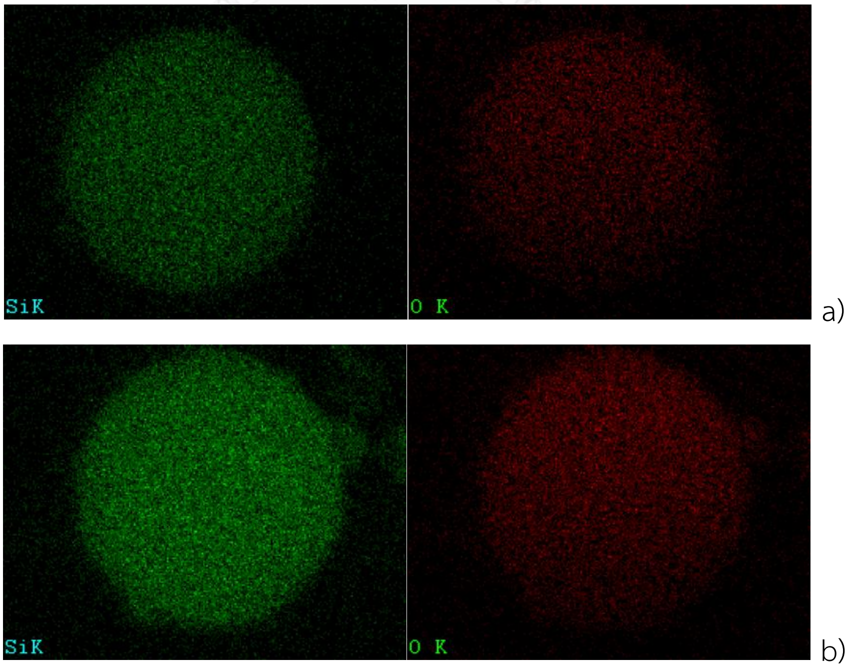

Figure 4.9 EDX of SiO_2-MP (a) and modified_SiO_2-MP (b).

Table 4.4 EDX analysis of Si and O on the silica supports.

		Area(1)	Area(2)	Area(3)	Average
[Si : O]	SiO_2-MP	1.11	1.00	1.13	1.08
	modified_SiO_2-MP	1.13	1.18	1.14	1.15

Besides, the average ratio of Si : O of both SiO_2-MP supports was compared as shown in **Table 4.4**, the results showed that the modified SiO_2-MP support has the average ratio of Si : O (1.15) more than the silica support without modification (1.08). Thus, it was confirmed that the modified SiO_2-MP support has spacer group ($SiCl_4$) distributed on it.

4.3.2 Characterization of the modified SiO_2-MP support with X-ray diffraction (XRD)

The XRD pattern of modified SiO_2-MP support is shown in **Figure 4.10** and was compared with silica support without modification. The silica supports exhibited the similar of XRD patterns as seen from **Figure 4.3,** but the sharp peak of modified silica support has very short peak. Thus, it predicted that it was low crystallinity because cracking of particles when it is extremely stirred.

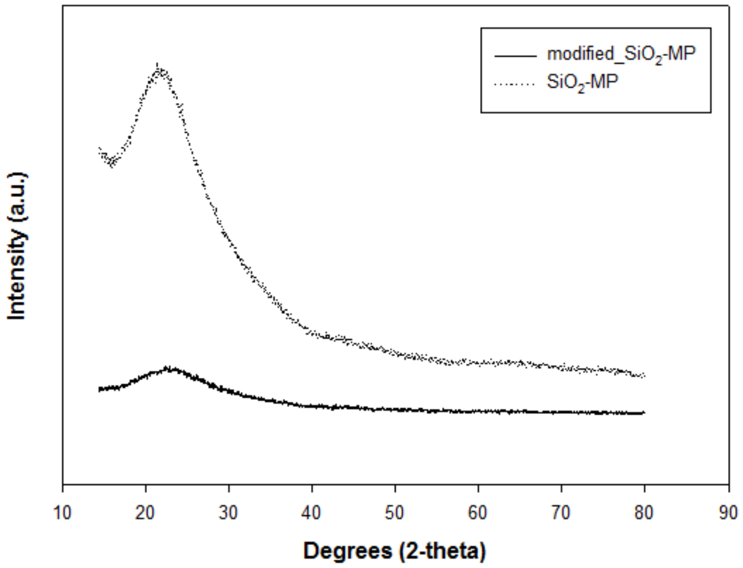

Figure 4.10 XRD patterns of modified SiO_2-MP support and unmodified SiO_2-MP support.

4.4 Characterization and catalytic properties of polyethylene using the modified SiO_2-MP support

4.4.1 The effect of the modified SiO_2-MP support on the catalytic activity

Ethylene polymerization was carried out via modified silica support with 3-tert-C7 catalyst/MAO. First, the modified silica support was used with 3 mL of MAO (Ail/Ti=1131), same condition in part 1. The result showed that the catalytic activity (1.84 kg PE/mmol cat *hr) is higher than using the unmodified silica support with 3 mL of MAO (0.8 kg PE/mmol cat *hr). With increasing MAO of 3.25 mL (Ail/Ti=1225), the catalytic activity (1.88 kg PE/mmol cat *hr) is still higher than unmodified silica support at same condition. Then, decreasing MAO from 3 mL to find the amount of MAO that the catalytic activity was equal using unmodified silica support. After decreasing MAO to 0.25 per time, the use of MAO of 1.75 mL (Ail/Ti=660) still gave catalytic activity (1.34 kg PE/mmol cat *hr) than using unmodified silica support with MAO 3 mL. When using MAO of 1.5 mL (Ail/Ti=566) , the catalytic activity (0.11 kg PE/mmol cat *hr) decreased and was lower than the unmodified silica support with MAO of 3 mL as shown in **Table 4.5**.

Table 4.5 Ethylene polymerization activities with modification of silica support.

Silica	MAO (ml)	[Al /Ti]	Yield (g)	Activity (kg PE/mmol cat *hr)^b
Modified_SiO_2-MP	1.5	566	0.73	0.11
	1.75	660	3.19	1.34
	2	754	3.01	1.25
	2.25	848	2.92	1.21
	2.5	943	3.48	1.49
	2.75	1037	3.86	1.68
	3	1131	4.19	1.84 (0.80)^c
	3.25	1225	4.25	1.88 (0.88)^c

^{a}modified_SiO_2-MP=modification of SiO_2 support (SiO_2-MP) with $SiCl_4$

^{b}Activities were measured at polymerization temperature of 50°C via *in situ*, support 0.5 g, 30 minutes, Ethylene pressure 1 bar, toluene 250 mL, 3-tert-C7 4 mL and stirr 450 rpm.

^{c}( ) refers to the value of unmodified SiO_2-MP

4.4.2 The effect of a modified SiO_2-MP support on the melting temperatures of polyethylene

Table 4.6 shows the effect of modified silica support on the melting temperatures of polymers. From these results with various amounts of MAO in this part, the melting temperatures are 133 °C, which are similar to those in **Table 4.3** in part 1. However, the crystallinity increased (63-68%). On the other hand, the polymer obtained from the modified silica support with MAO 1.5 ml has melting temperature of 130.9 °C and showed the minimum crystallinity of 14 %, which is lower than that obtained from the unmodified silica support .

Table 4.6 The effect of modified silica support on the melting temperatures of polymers.

Polymer[a]	**MAO (ml)**	**[Al/Ti]**	**T_m (°C)**	**Crystallinity (%)**
PE_modified_SiO$_2$-MP	1.5	566	130.9	14.0
	1.75	660	133.6	65.3
	2	754	133.7	65.6
	2.25	848	133.5	63.3
	2.5	943	133.5	68.0
	2.75	1037	133.3	68.4
	3	1131	133.1	68.2
	3.25	1225	133.1	67.8

[a] PE_modified_SiO$_2$-MP=polyethylene from modified silica support (modified_SiO$_2$-MP)

4.4.3 Characterization of polyethylene with X-ray diffraction (XRD)

From the results on **Figure 4.6**, it was found that XRD patterns of polyethylene obtained from SiO$_2$-MP support has very short peak with low crystallinity. According to **Figure 4.11**, The XRD patterns of polyethylene obtained from modified SiO$_2$-MP support with MAO 1.75 and 3 mL have sharper peak than that of using SiO$_2$-MP support. The crystallinity is higher than that in part 1. The XRD patterns of polyethylene obtained from modified SiO$_2$-MP support at MAO 1.5 mL exhibit sharp peak with low intensity, indicating non-crystalline or amorphous polymer.

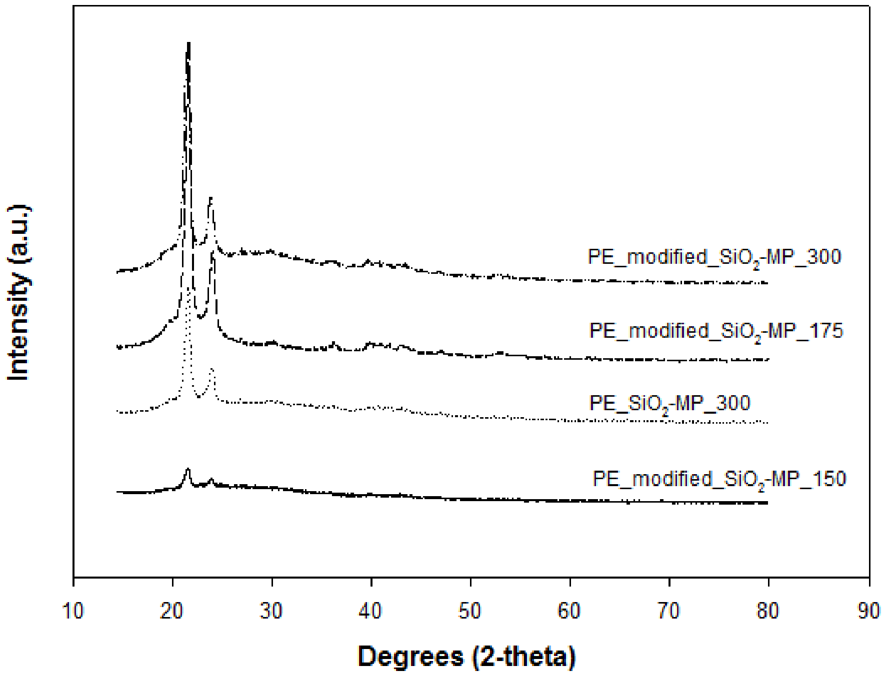

Figure 4.11 XRD patterns of polymers from in situ polymerization with modified SiO$_2$-MP supports and SiO$_2$-MP without modification.

4.4.4 Characterization of polyethylene with scanning electron microscope (SEM)

The polyethylene obtained from the modified SiO$_2$-MP support expressed rather fine particles and the SEM micrograph showed good morphology of polymer on the modified silica surface.

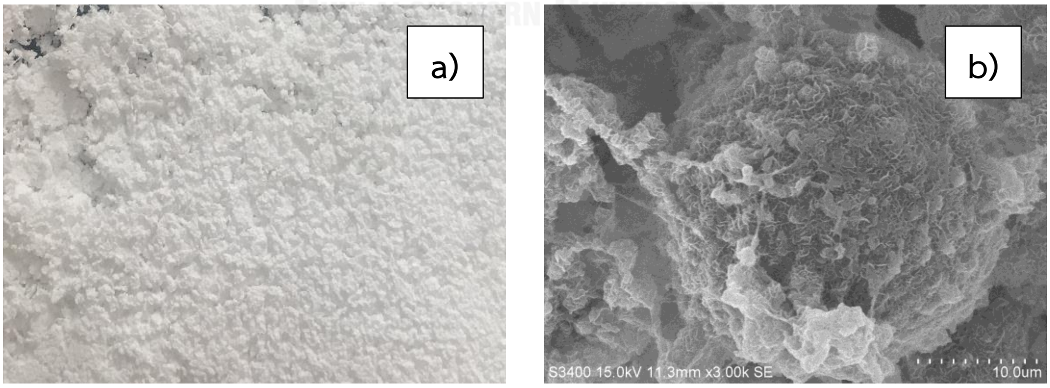

Figure 4.12 image and SEM micrograph at scale bar of 10μm ; PE_modified_SiO$_2$-MP (a,b).

CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The ethylene polymerization via *in situ* using metallocene catalyst/MAO on silica supports from commercial and synthesis by chemical method, is divided into two parts: part 1 was to study the effect of various SiO_2-supported 3-tert-C7 catalyst on ethylene polymerization with varied amounts of MAO and part 2 was to further investigate the effect of $SiCl_4$ modification on (SiO_2-MP)-supported 3-tert-C7 catalyst during ethylene polymerization with various amounts of MAO.

5.1.1 Effect of various SiO_2-supported 3-tert-C7 catalyst on ethylene polymerization

In this part, it can be summarized into two cases : Case 1, the condition at low MAO, the spherical silica particle (SSP) support expressed the highest activity, and then the activity was obtained by SiO_2-LP was higher than all commercial silicas because small particles exhibit good reaction. Case 2, the condition at high MAO, the SiO_2-LP support showed the highest activity. Next sequence, the SSP support was higher than SiO_2-VSP, SiO_2-SP and SiO_2-MP, but the activity obtained by SiO_2-VSP support was high when using high MAO. The SiO_2-VSP support was big particles having poor reaction on silica surface with high homopolymerization occurred.

The commercial process required low cost. Therefore, the SSP support was good support to have high activity that can be used at low MAO. Considering the nature of particles, the polymers obtained by SiO_2-LP did not exhibit fine particles with the highest activity. It is a good advantage to overcome fouling in the reactor. Moreover, the activities obtained by SiO_2-LP have higher reaction rate than the activities that obtained by SSP. It may increase when with MAO added above 3.75 mL.

5.1.2 Effect of $SiCl_4$ modification on (SiO_2-MP)-supported 3-tert-C7 catalyst during ethylene polymerization

In the second part, the polymerization of $SiCl_4$-modified SiO_2-MP support was investigated. It was found that the activities increased with $SiCl_4$ modification. It was proposed that an addition of $SiCl_4$ into support can increase spacer group that improve catalytic activity with decreased cocatalyst (MAO) used, and hence enhance the catalytic activity of polymerization. The polyethylene obtained from modified SiO_2-MP support was observed that the crystallinity is higher than the polyethylene obtained from unmodified SiO_2-MP support in part 1, indicating that $SiCl_4$ modification decreased the formation of branched polyethylene.

5.2 Recommendations

- Investigation of other modified supports should be further studied.
- Investigation of other modifiers should be further studied.
- The polyethylene was obtained by various silica supports in this research that cannot be investigated with Gel Permeation Chromatography (GPC). Then, it should be used Melt Flow Rate (MFR) to study the molecular weight distribution of polymers.

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APPENDICES

APPENDIX A

CALCULATION

A.1 Calculation of amounts of MAO

Amounts of

MAO 3 ml มี density 0.875 g/ml

$$\text{MAO} = 3 \times 0.875 \ \text{g/ml}$$

$$= 2.625 \ \text{g}$$

$$= 2.625 \times \frac{1 \ \text{mol}}{58.02 \ \text{g}} \times \frac{10}{100}$$

$$= 0.00452 \ \text{mol/3ml}$$

$$\text{MAO/ml} = \frac{0.00452 \ \text{mol}}{3 \ \text{ml}} = 0.0015 \ \frac{\text{mol}}{\text{ml}}$$

A.2 Calculation of crystallinity for polyethylene

The crystallinity of polymers were determined by differential scanning calorimeter. %crystallinity of polymers is calculated from equation [Liu *et al*., 1997]

$$\chi(\%) = \frac{\Delta Hm}{\Delta Hmo} \times 100$$

Where :

(%) = %crystallinity

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

ΔHmo = the heat of fusion of perfectly crystalline polyethylene (286 J/g) [28]

APPENDIX B

FOURIER TRANSFORM INFRARED SPECTROSCOPY

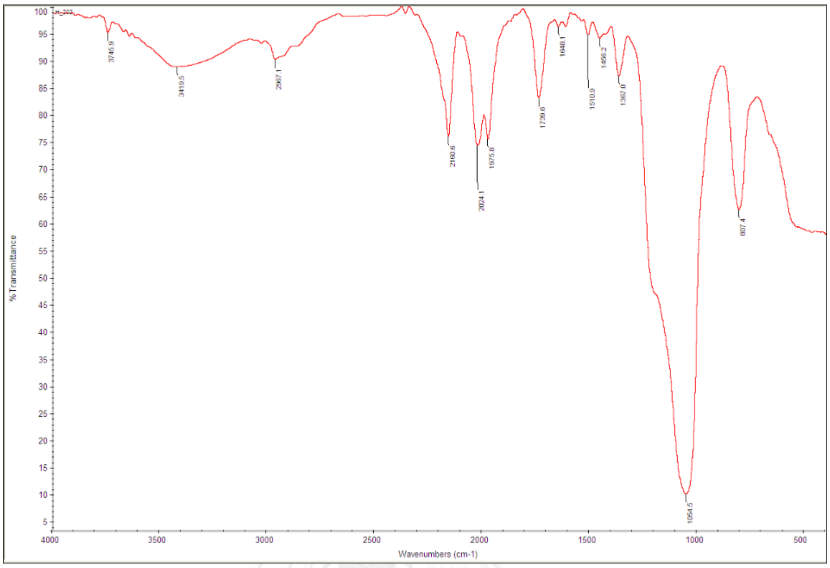

Figure B-1 FT-IR of SiO_2-MP.

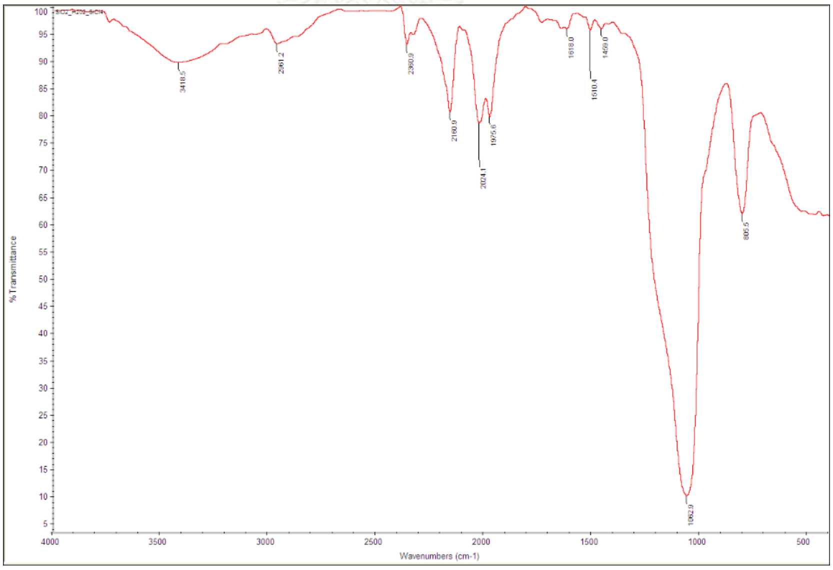

Figure B-2 FT-IR of modified SiO_2-MP.

APPENDIX C

THERMOGRAVIMETRIC ANALYSIS

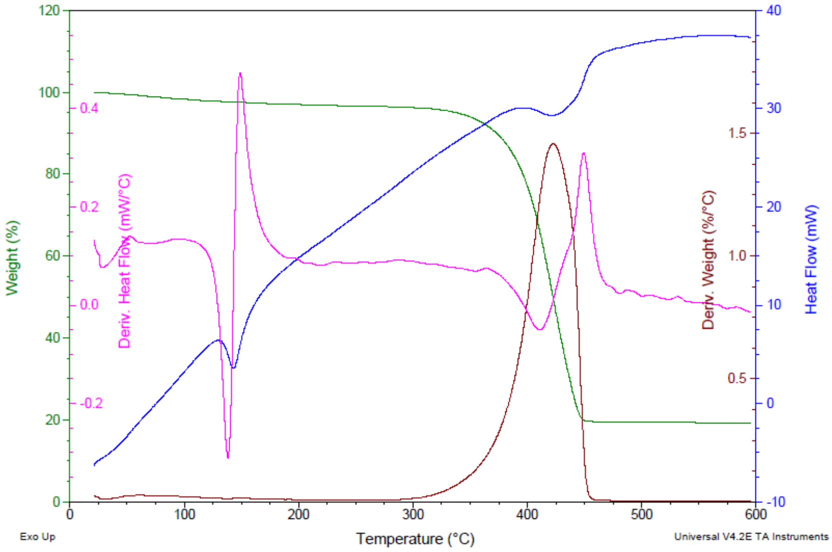

Figure C-1 TGA curve of polyethylene produce with SiO_2-LP at MAO 3 ml.

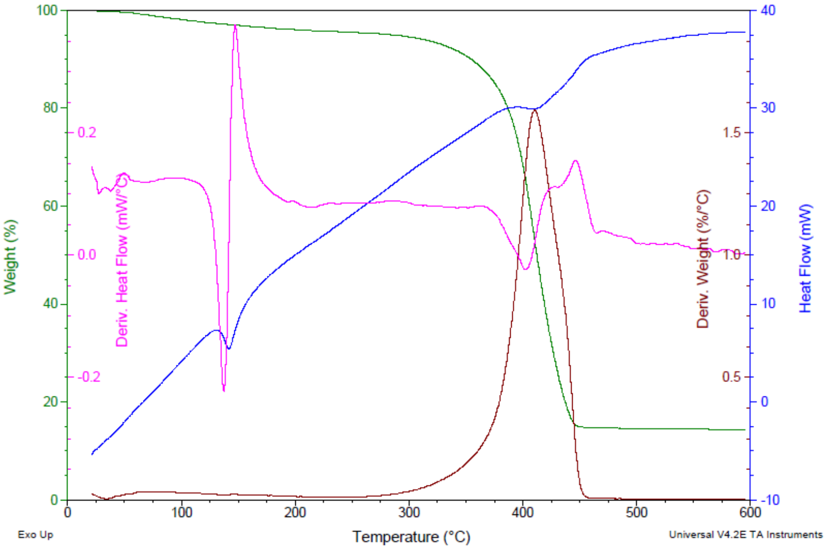

Figure C-2 TGA curve of polyethylene produce with SiO_2-LP at MAO 3.25 ml.

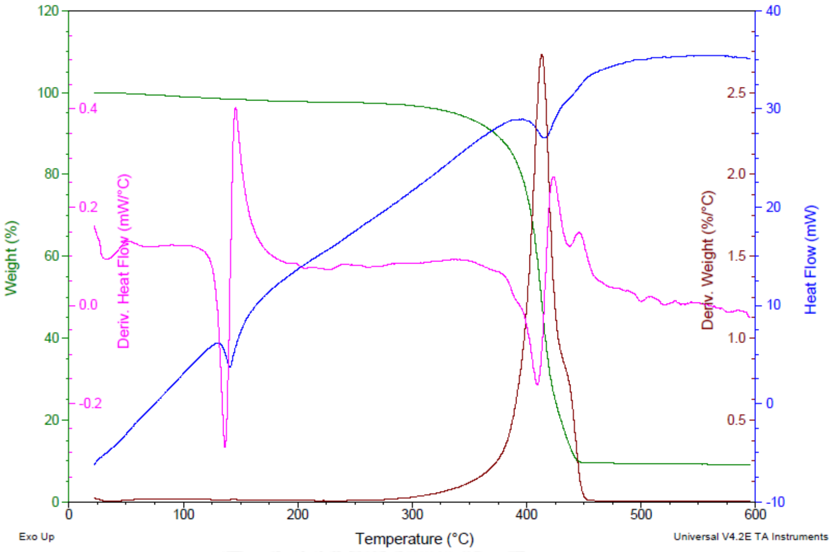

Figure C-3 TGA curve of polyethylene produce with SiO_2-LP at MAO 3.5 ml.

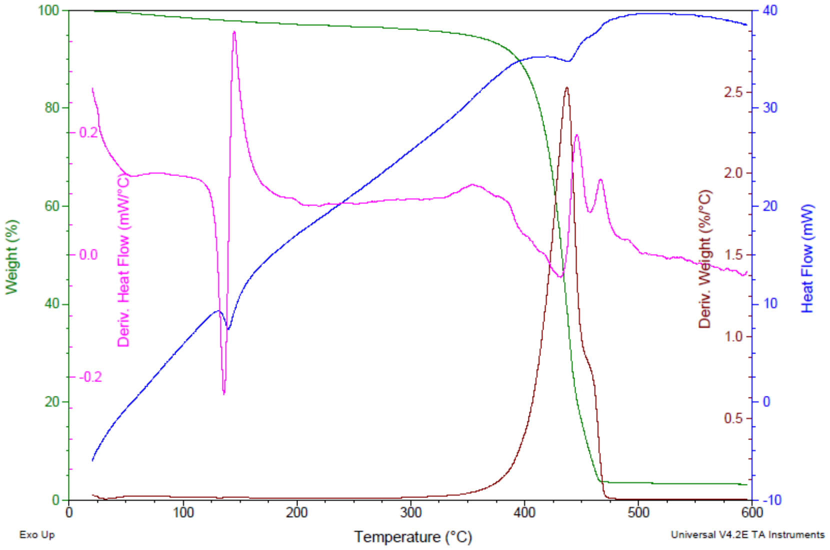

Figure C-4 TGA curve of polyethylene produce with SiO_2-LP at MAO 3.75 ml.

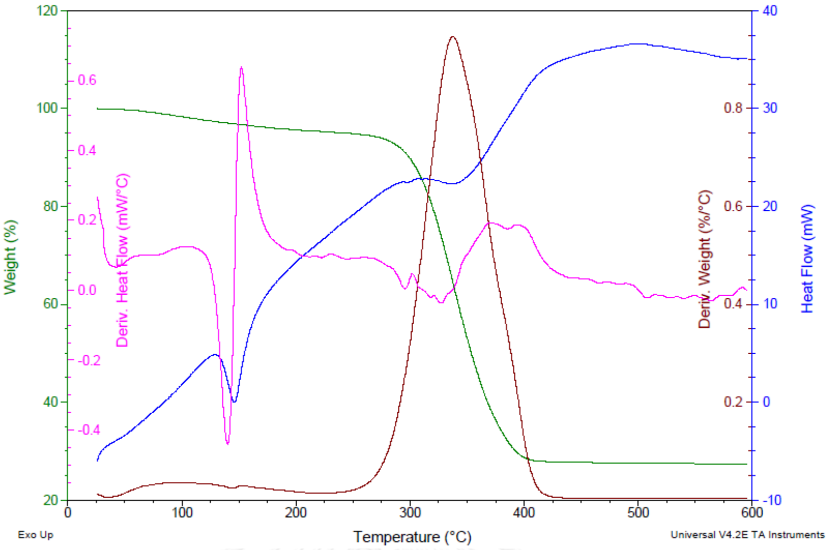

Figure C-5 TGA curve of polyethylene produce with SiO_2-SP at MAO 3 ml.

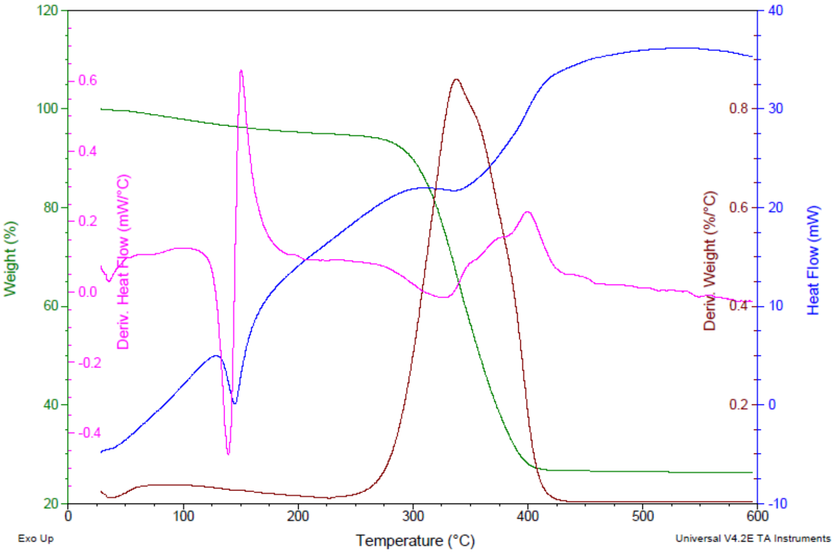

Figure C-6 TGA curve of polyethylene produce with SiO_2-SP at MAO 3.25 ml.

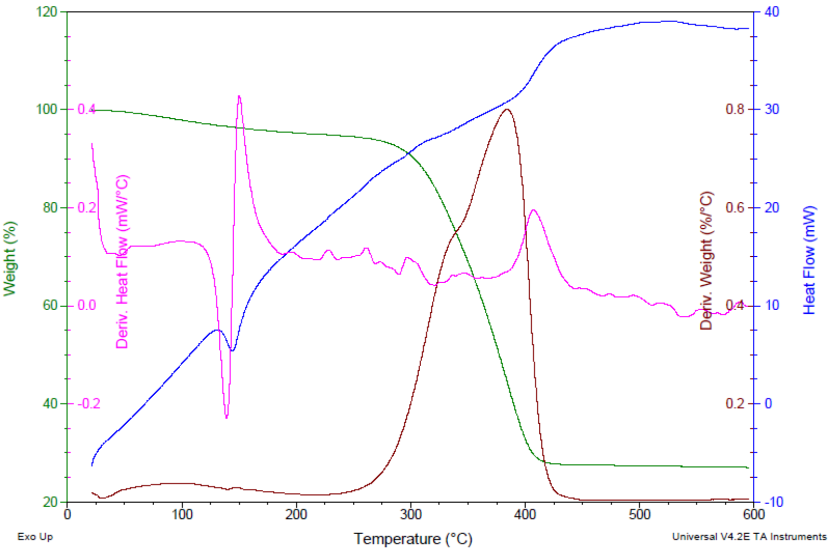

Figure C-7 TGA curve of polyethylene produce with SiO_2-SP at MAO 3.5 ml.

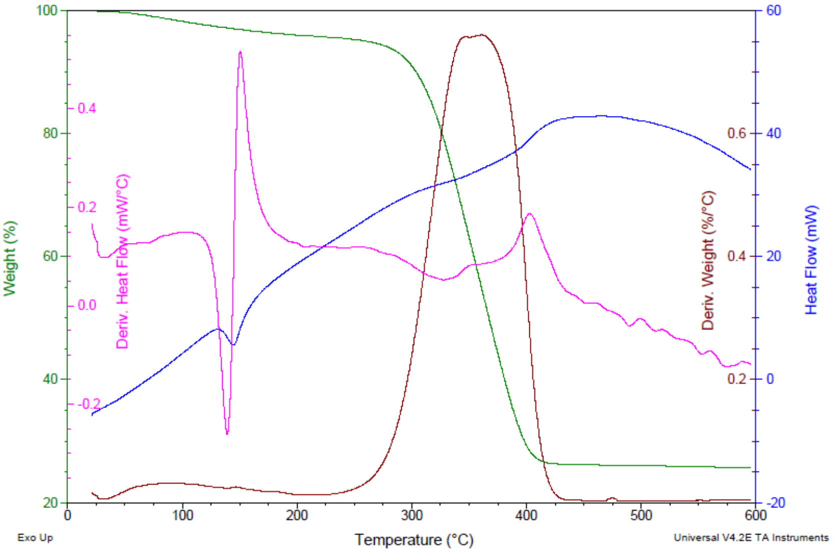

Figure C-8 TGA curve of polyethylene produce with SiO_2-SP at MAO 3.75 ml.

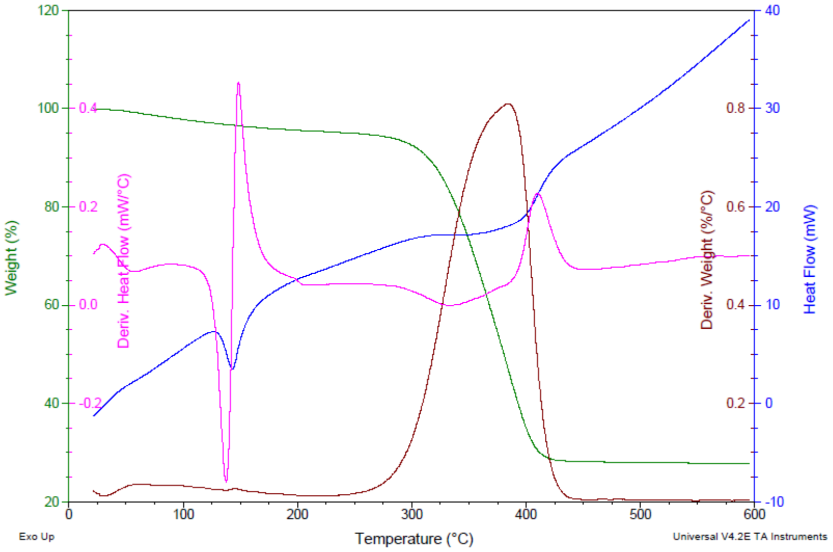

Figure C-9 TGA curve of polyethylene produce with SiO_2-MP at MAO 3 ml.

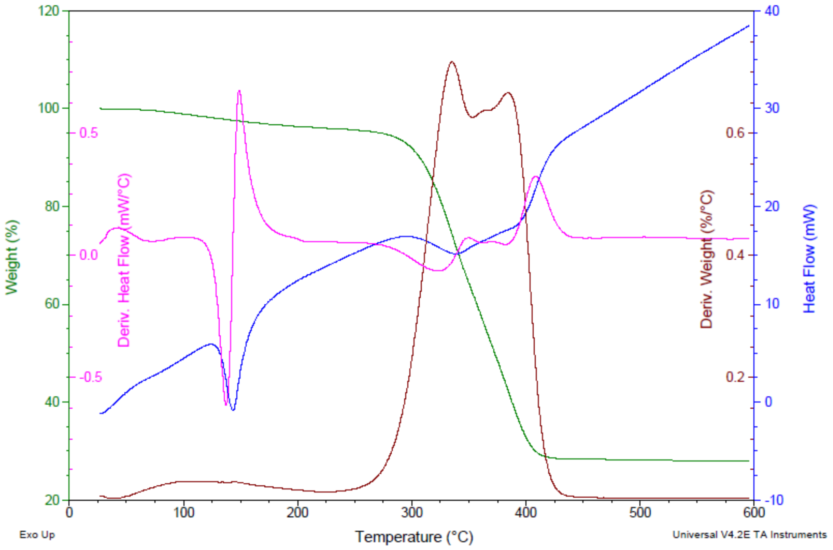

Figure C-10 TGA curve of polyethylene produce with SiO_2-MP at MAO 3.25 ml.

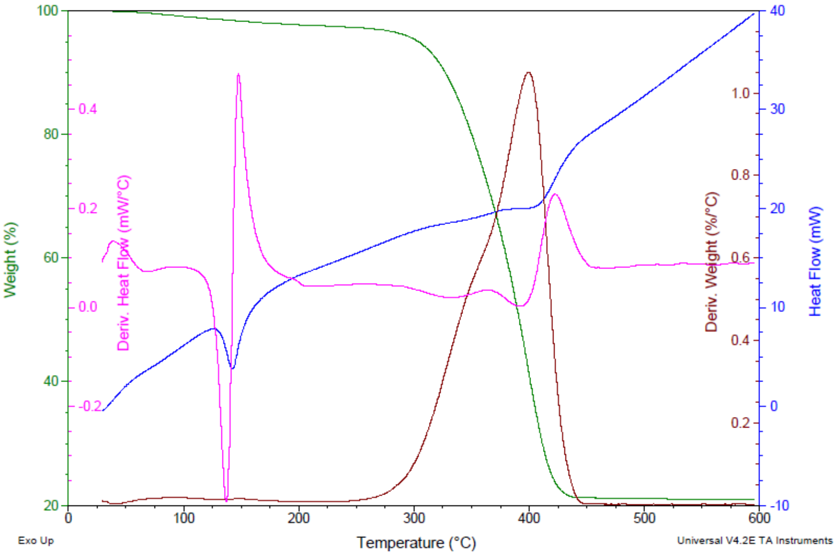

Figure C-11 TGA curve of polyethylene produce with SiO_2-MP at MAO 3.5 ml.

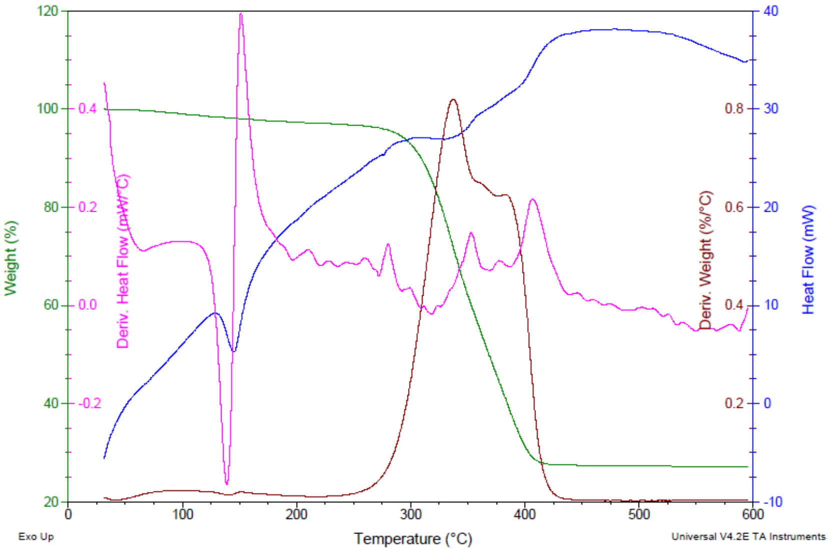

Figure C-12 TGA curve of polyethylene produce with SiO_2-MP at MAO 3.75 ml.

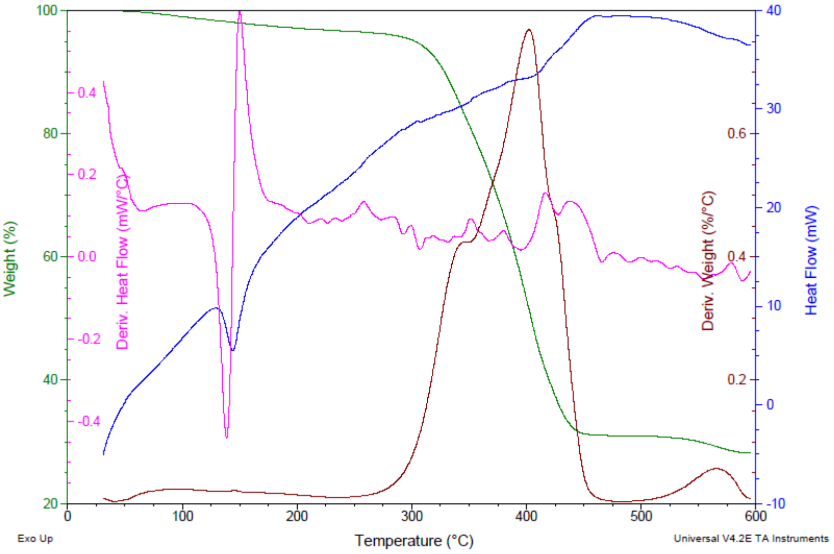

Figure C-13 TGA curve of polyethylene produce with SiO_2-VSP at MAO 3 ml.

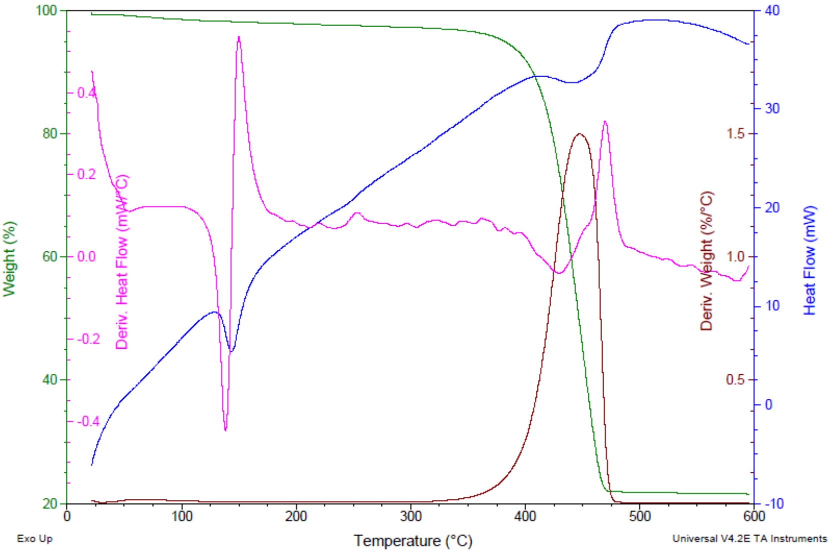

Figure C-14 TGA curve of polyethylene produce with SiO_2-VSP at MAO 3.25 ml.

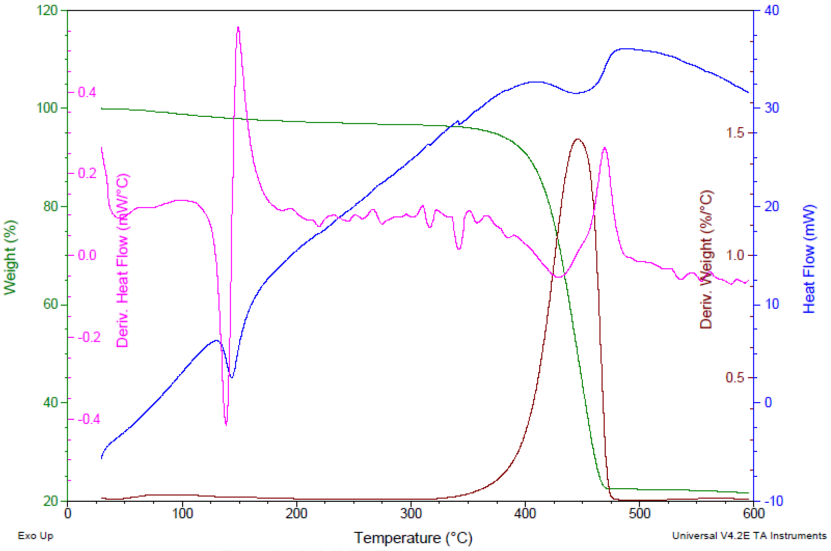

Figure C-15 TGA curve of polyethylene produce with SiO_2-VSP at MAO 3.5 ml.

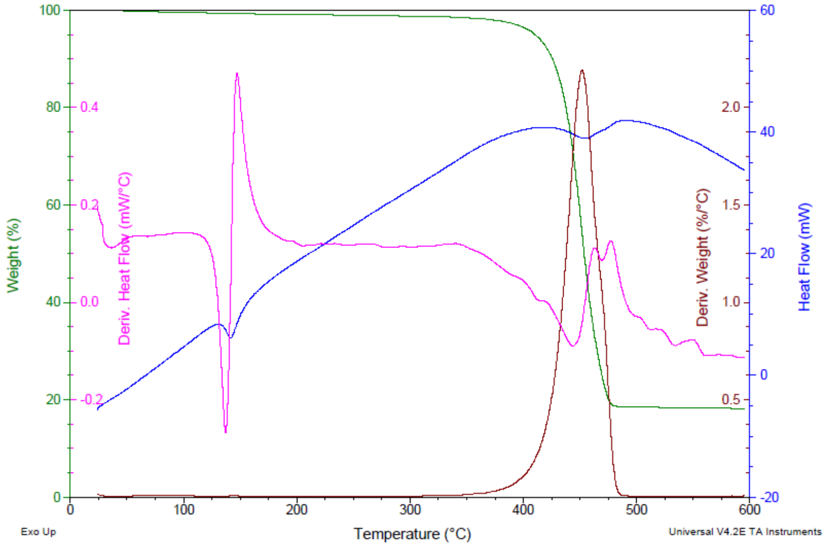

Figure C-16 TGA curve of polyethylene produce with SiO_2-VSP at MAO 3.75 ml.

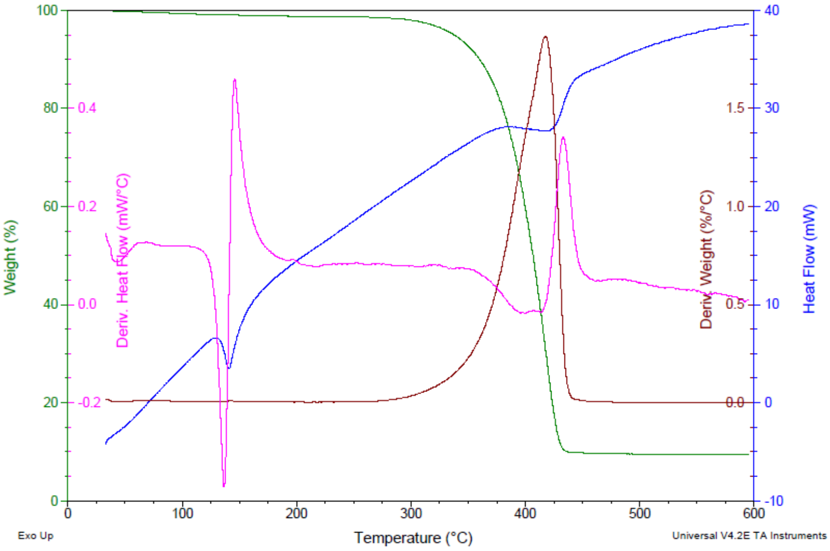

Figure C-17 TGA curve of polyethylene produce with SSP at MAO 3 ml.

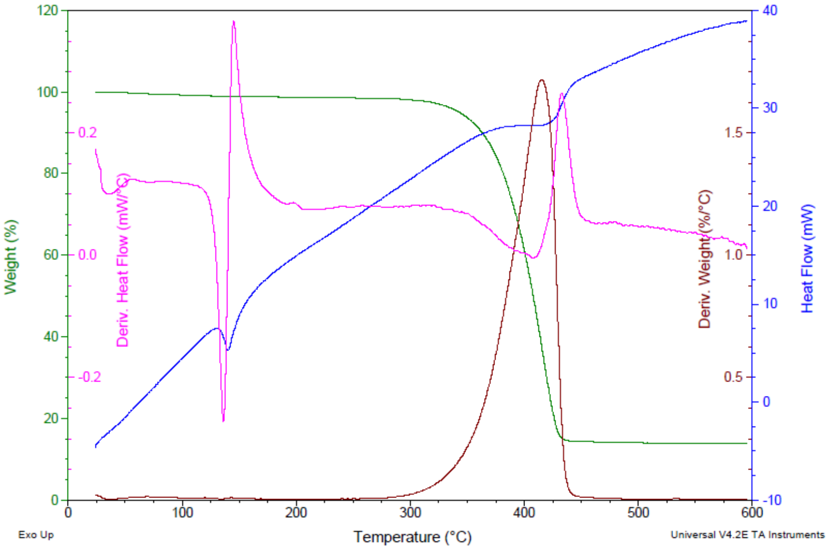

Figure C-18 TGA curve of polyethylene produce with SSP at MAO 3.25 ml.

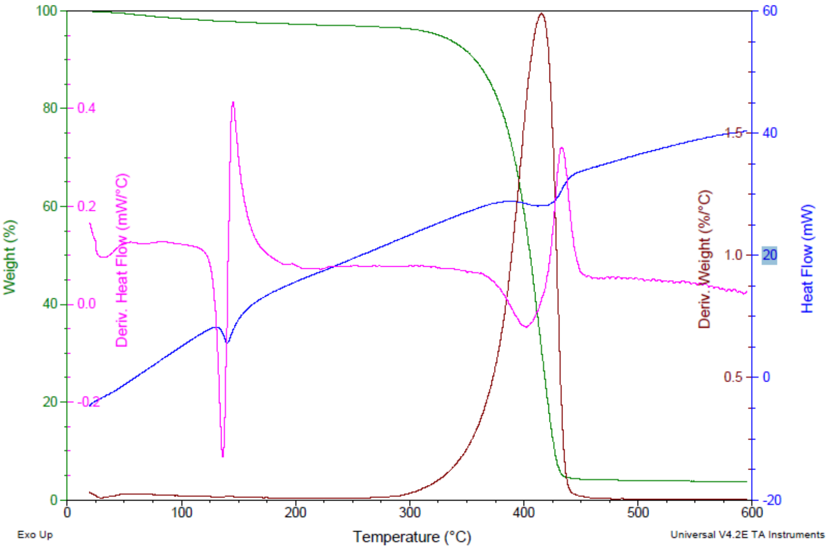

Figure C-19 TGA curve of polyethylene produce with SSP at MAO 3.5 ml.

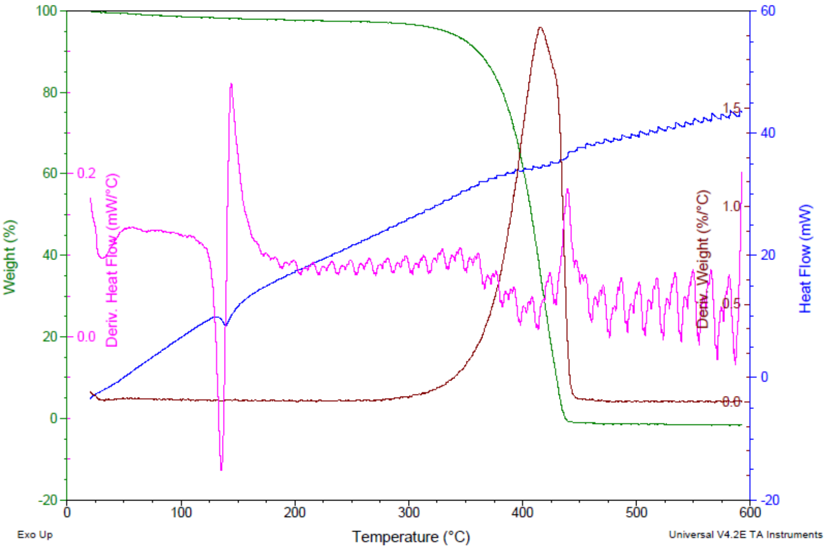

Figure C-20 TGA curve of polyethylene produce with SSP at MAO 3.75 ml.

APPENDIX D

DIFFERENTIAL SCANNING CALORIMETRY

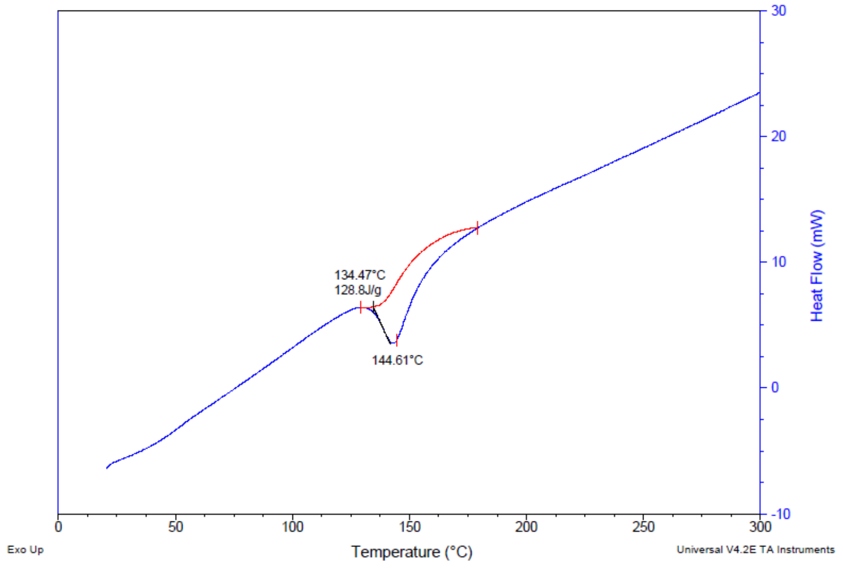

Figure D-1 DSC curve of polyethylene produce with SiO_2-LP at MAO 3 ml.

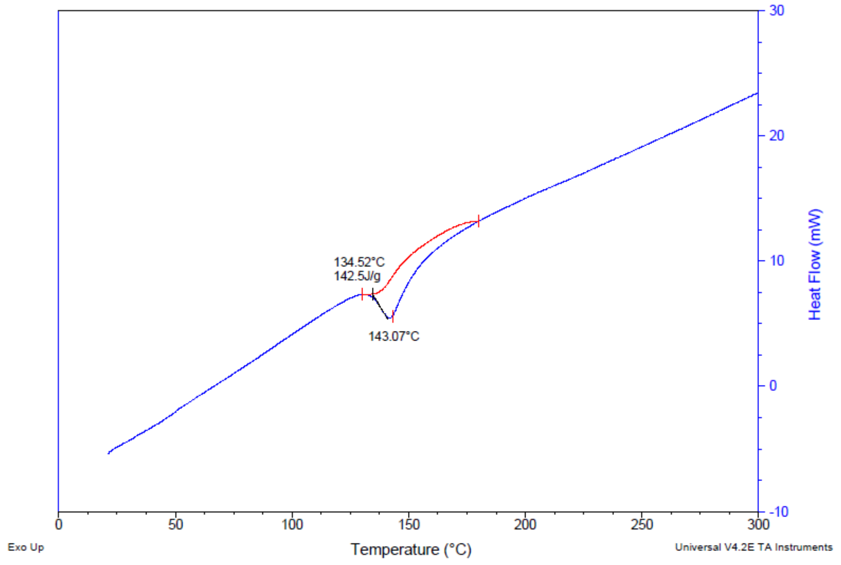

Figure D-2 DSC curve of polyethylene produce with SiO_2-LP at MAO 3.25 ml.

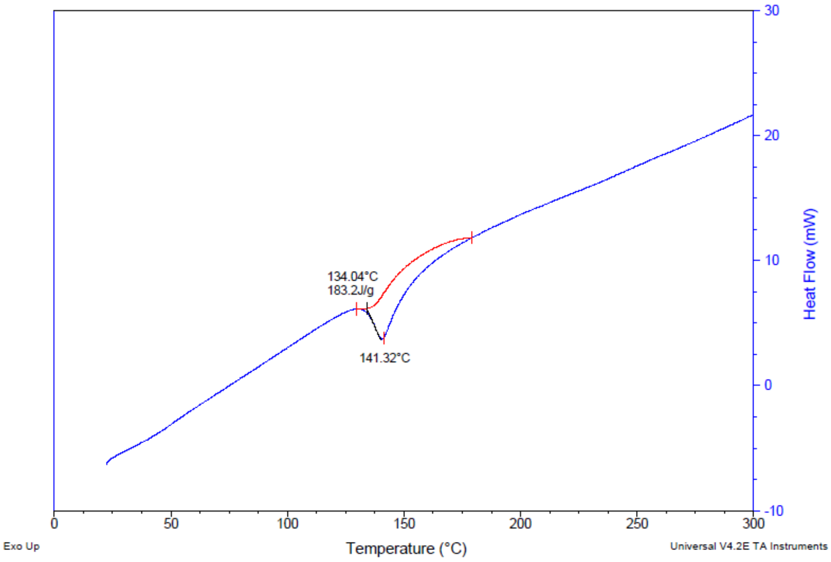

Figure D-3 DSC curve of polyethylene produce with SiO_2-LP at MAO 3.5 ml.

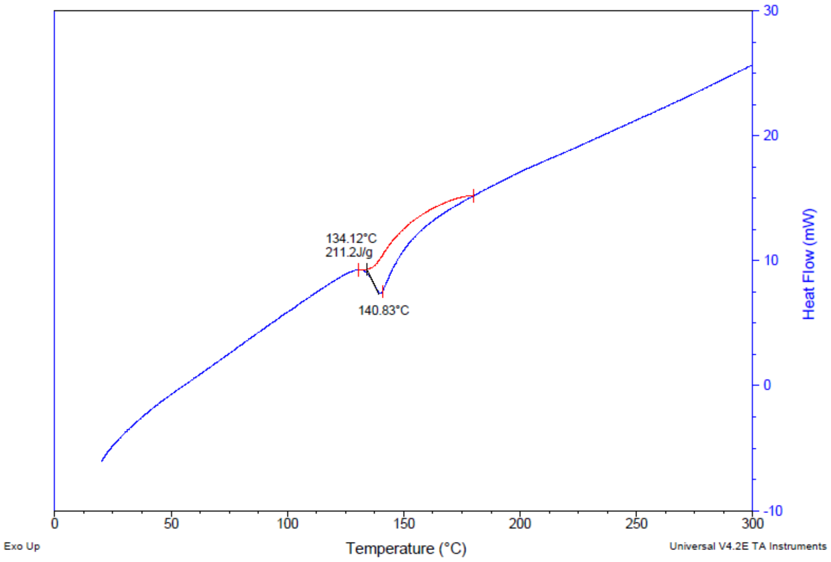

Figure D-4 DSC curve of polyethylene produce with SiO_2-LP at MAO 3.75 ml.

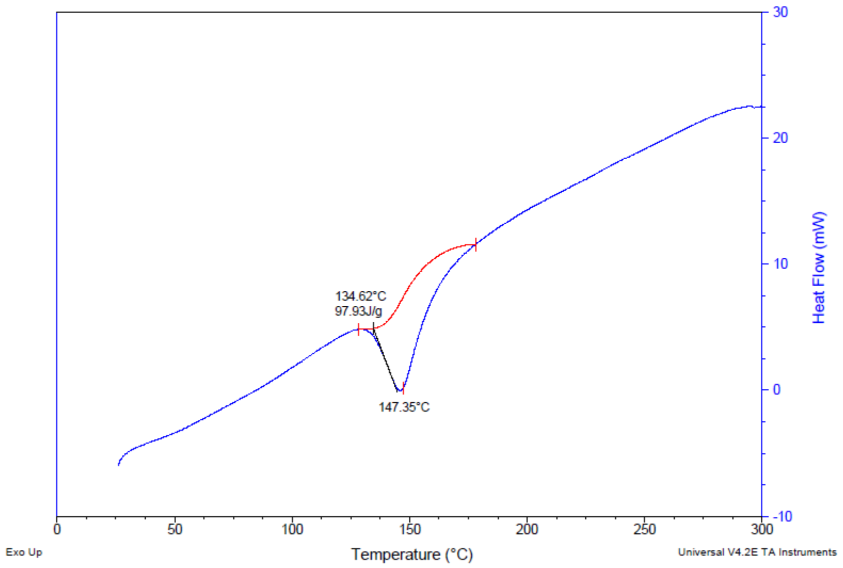

Figure D-5 DSC curve of polyethylene produce with SiO_2-SP at MAO 3 ml.

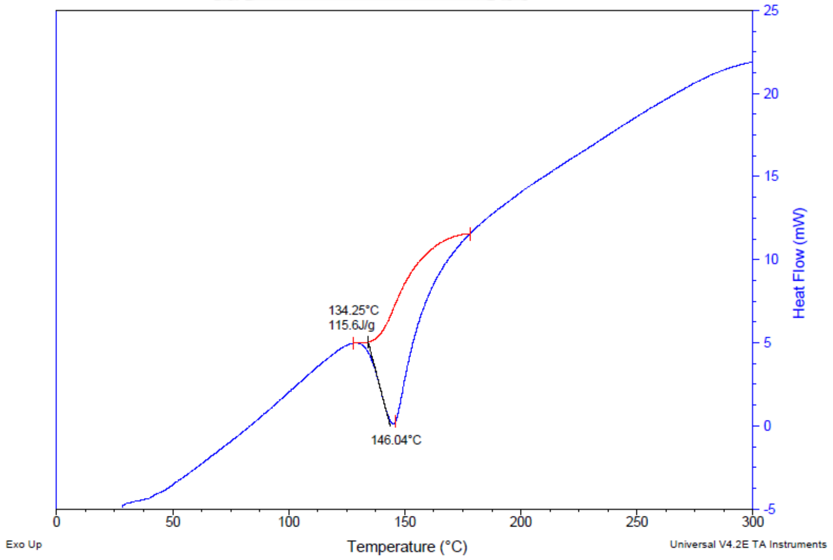

Figure D-6 DSC curve of polyethylene produce with SiO_2-SP at MAO 3.25 ml.

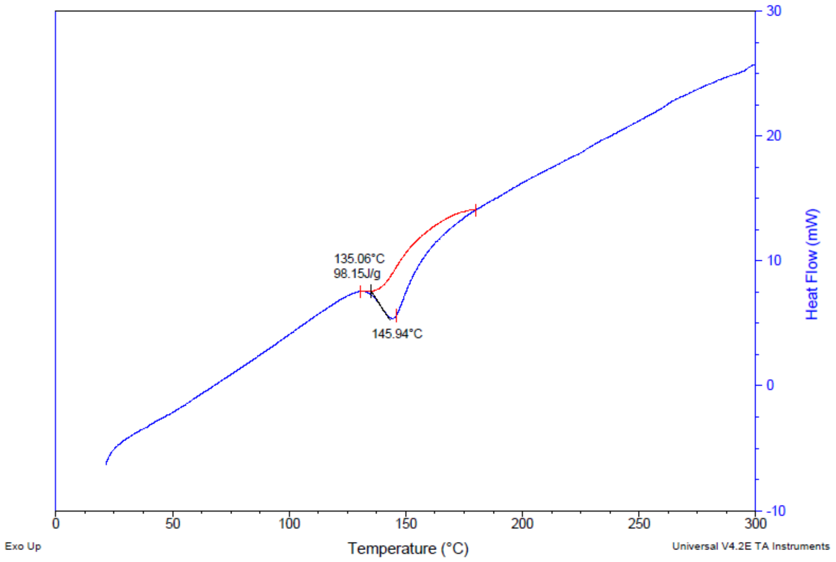

Figure D-7 DSC curve of polyethylene produce with SiO_2-SP at MAO 3.5 ml.

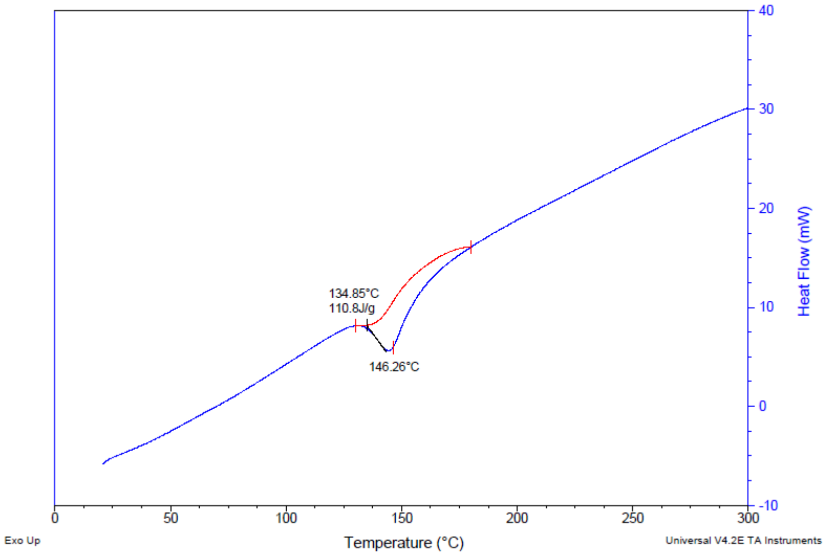

Figure D-8 DSC curve of polyethylene produce with SiO_2-SP at MAO 3.75 ml.

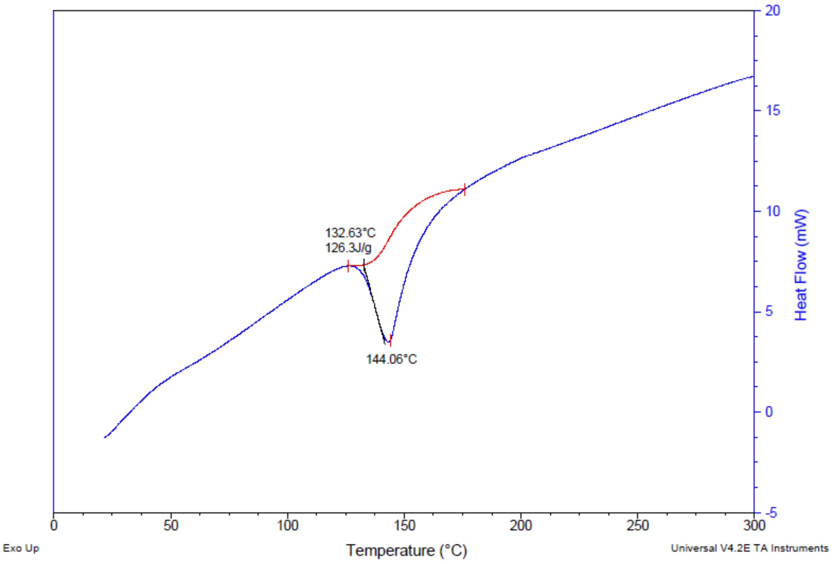

Figure D-9 DSC curve of polyethylene produce with SiO_2-MP at MAO 3 ml.

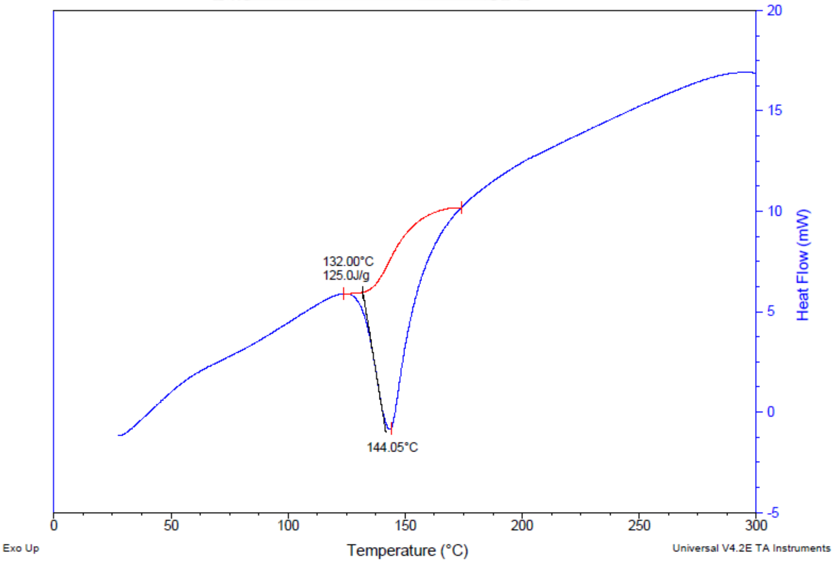

Figure D-10 DSC curve of polyethylene produce with SiO_2-MP at MAO 3.25 ml.

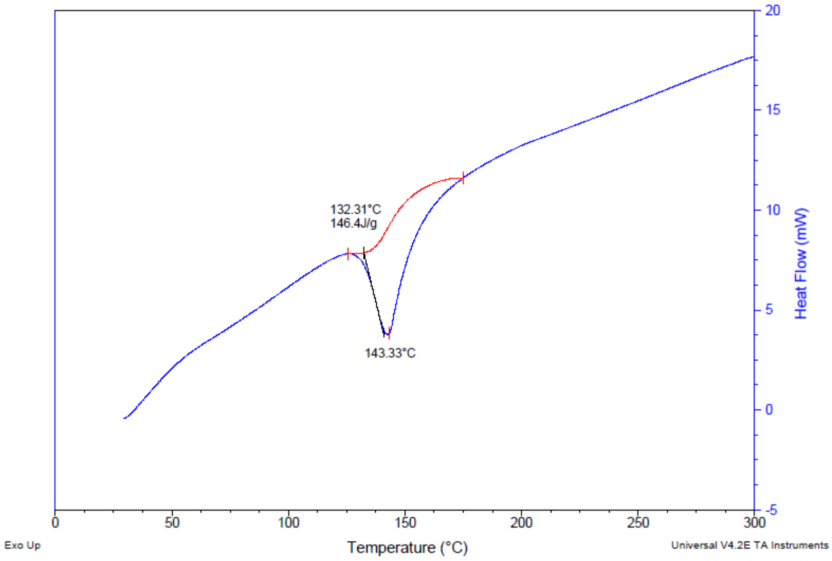

Figure D-11 DSC curve of polyethylene produce with SiO_2-MP at MAO 3.5 ml.

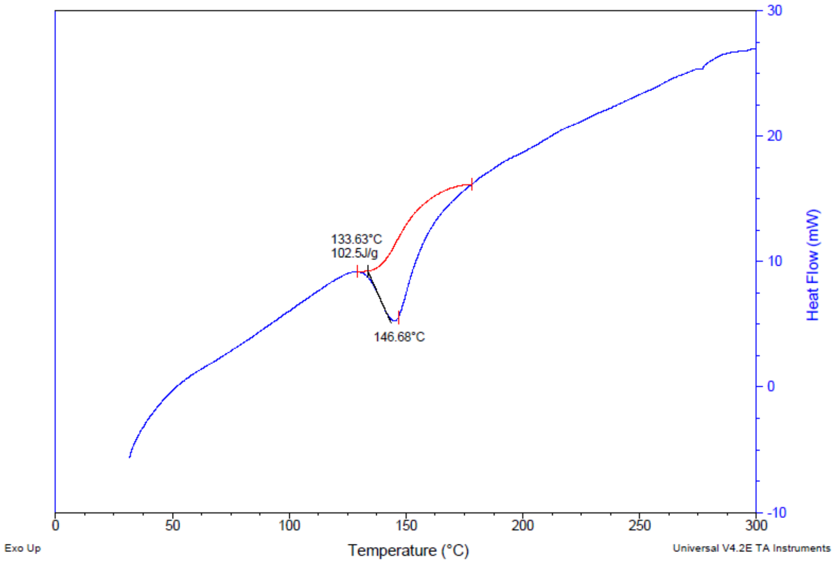

Figure D-12 DSC curve of polyethylene produce with SiO_2-MP at MAO 3.75 ml.

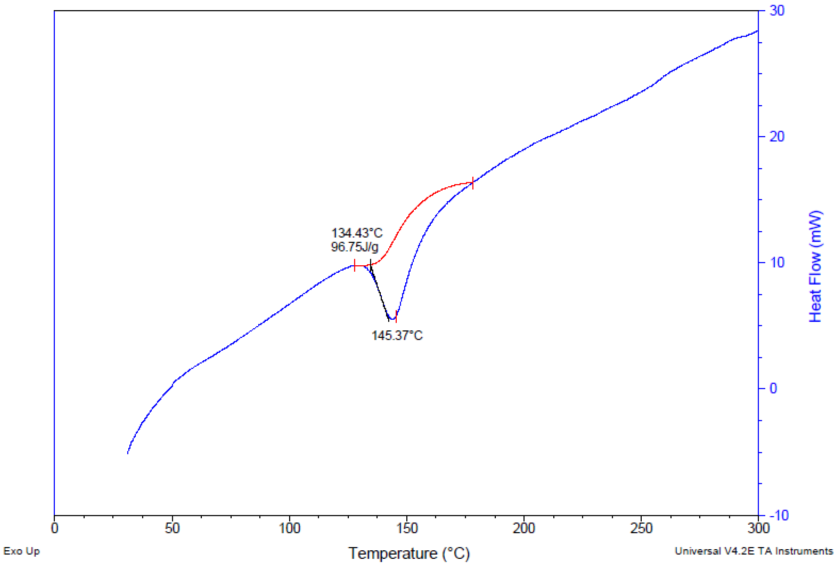

Figure D-13 DSC curve of polyethylene produce with SiO_2-VSP at MAO 3 ml.

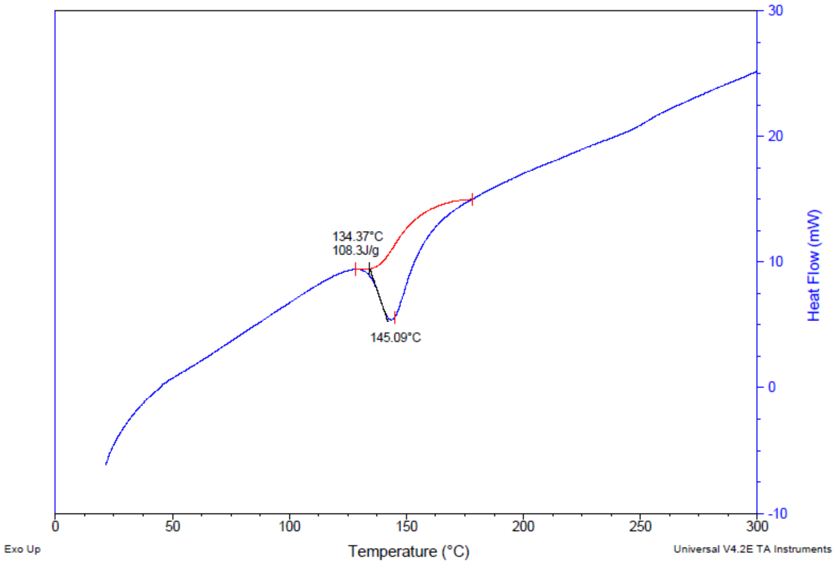

Figure D-14 DSC curve of polyethylene produce with SiO_2-VSP at MAO 3.25 ml.

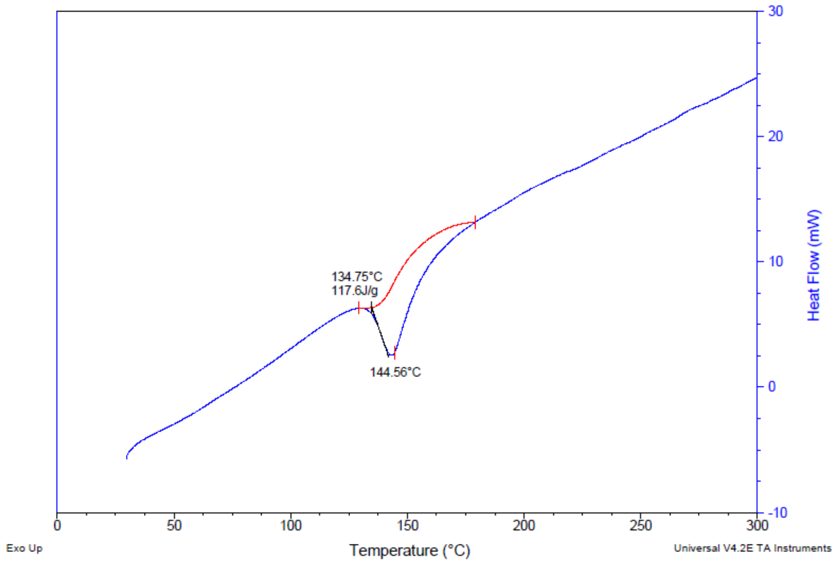

Figure D-15 DSC curve of polyethylene produce with SiO_2-VSP at MAO 3.5 ml.

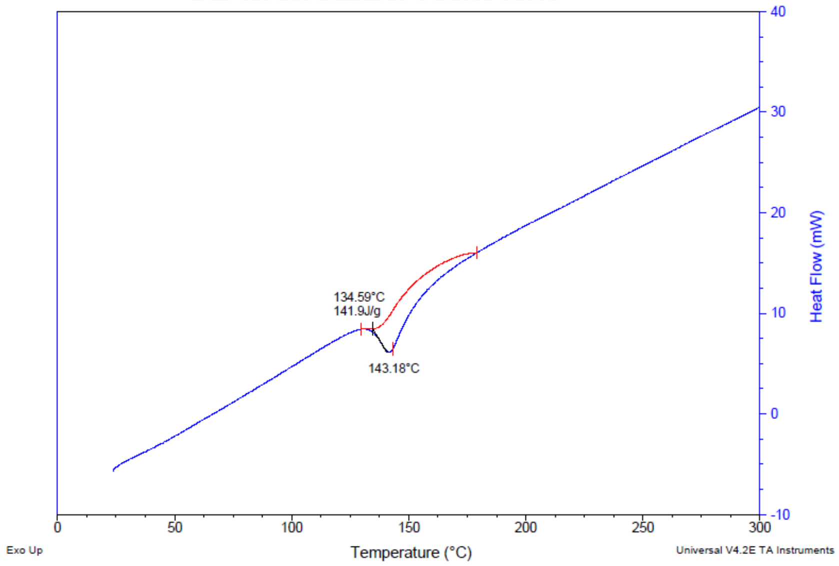

Figure D-16 DSC curve of polyethylene produce with SiO_2-VSP at MAO 3.75 ml.

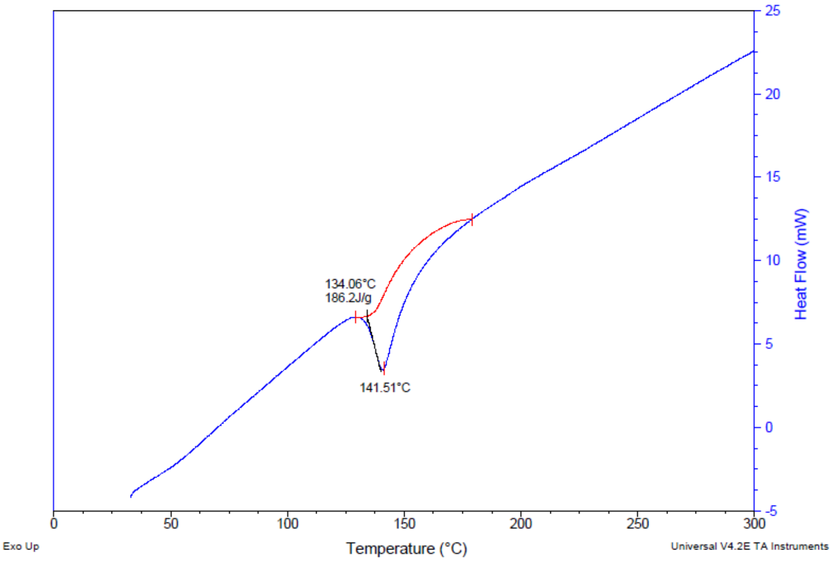

Figure D-17 DSC curve of polyethylene produce with SSP at MAO 3 ml.

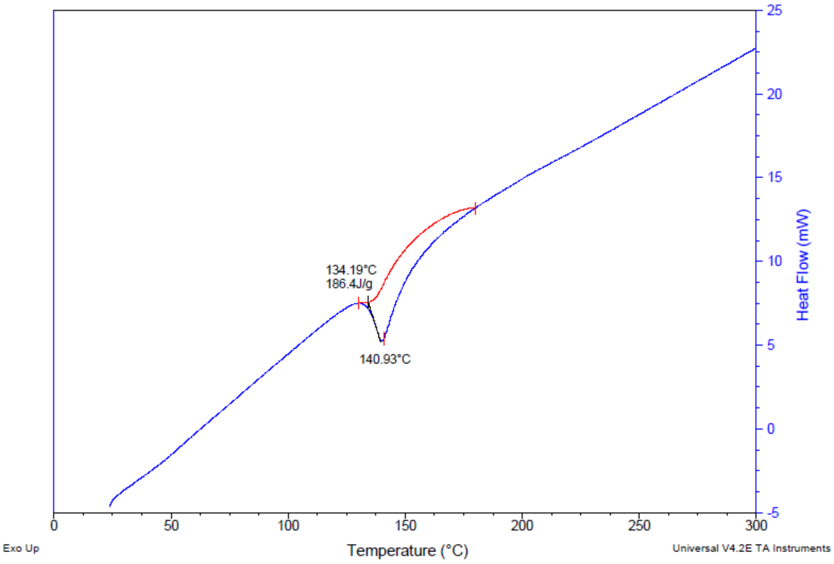

Figure D-18 DSC curve of polyethylene produce with SSP at MAO 3.25 ml.

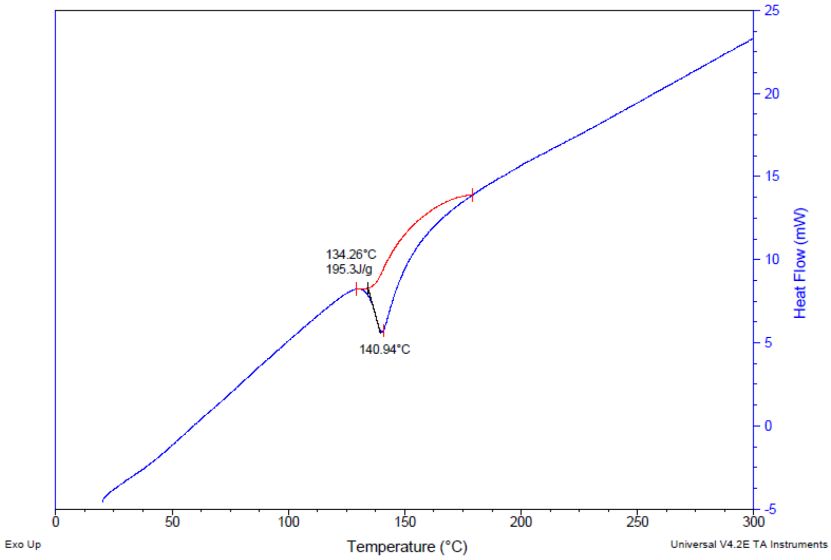

Figure D-19 DSC curve of polyethylene produce with SSP at MAO 3.5 ml.

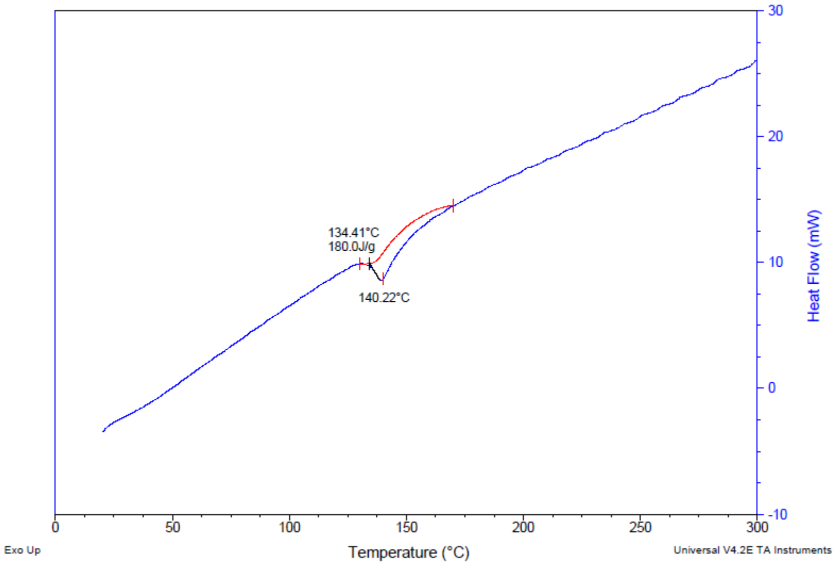

Figure D-20 DSC curve of polyethylene produce with SSP at MAO 3.75 ml.

APPENDIX E

X-RAY POWDER DIFFRACTION

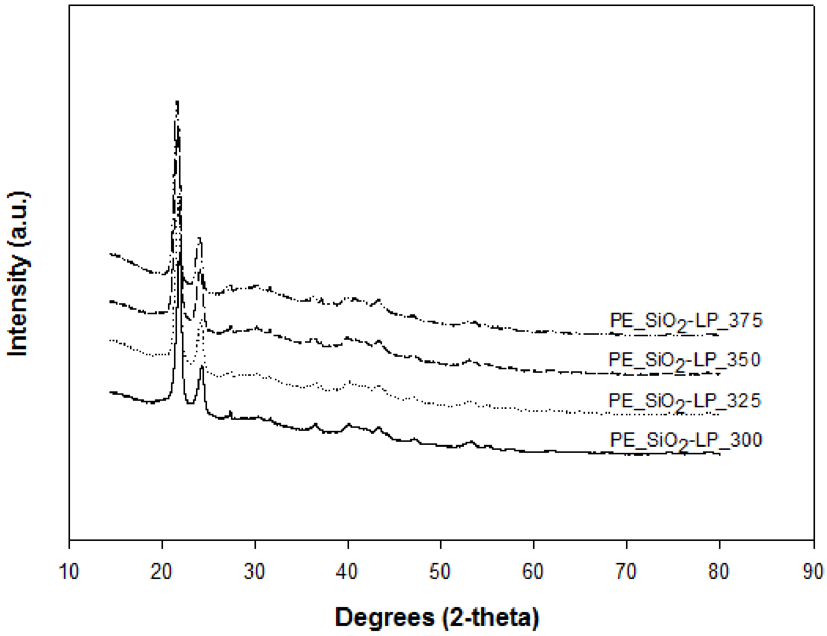

Figure E-1 XRD patterns of polyethylene produce with SiO_2-LP.

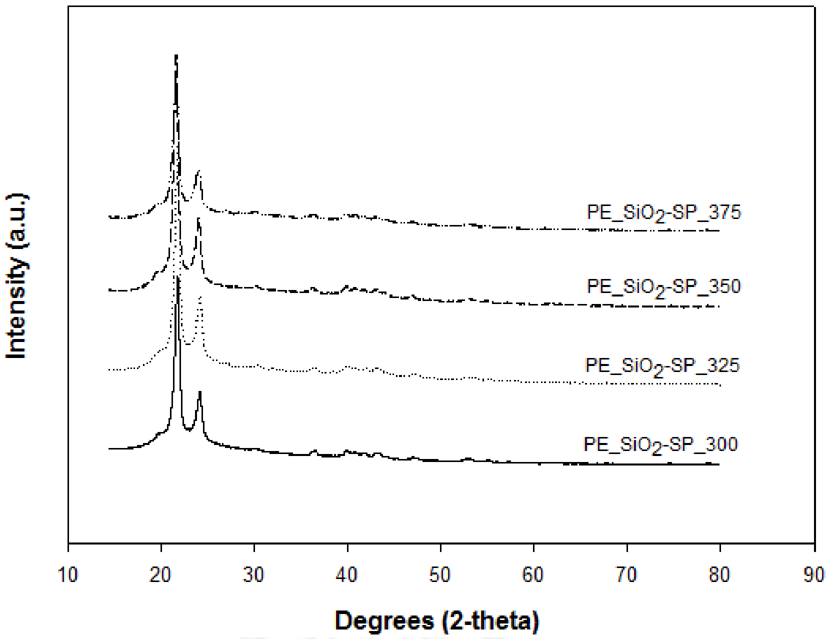

Figure E-2 XRD patterns of polyethylene produce with SiO_2-SP.

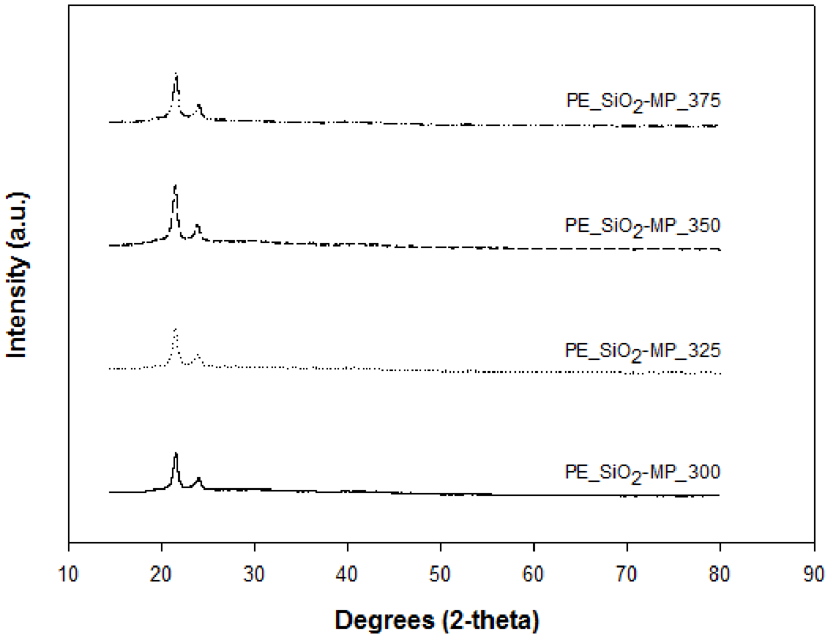

Figure E-3 XRD patterns of polyethylene produce with SiO_2-MP.

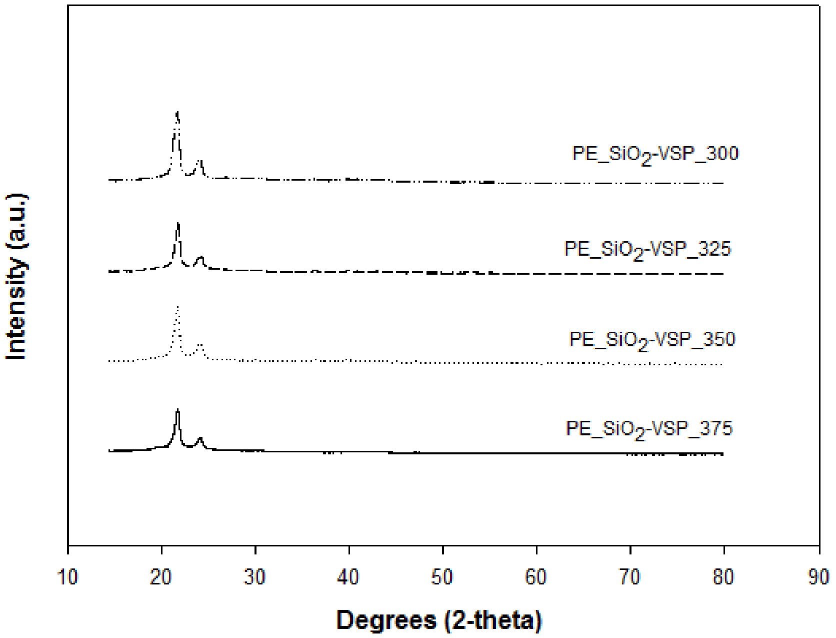

Figure E-4 XRD patterns of polyethylene produce with SiO_2-VSP.

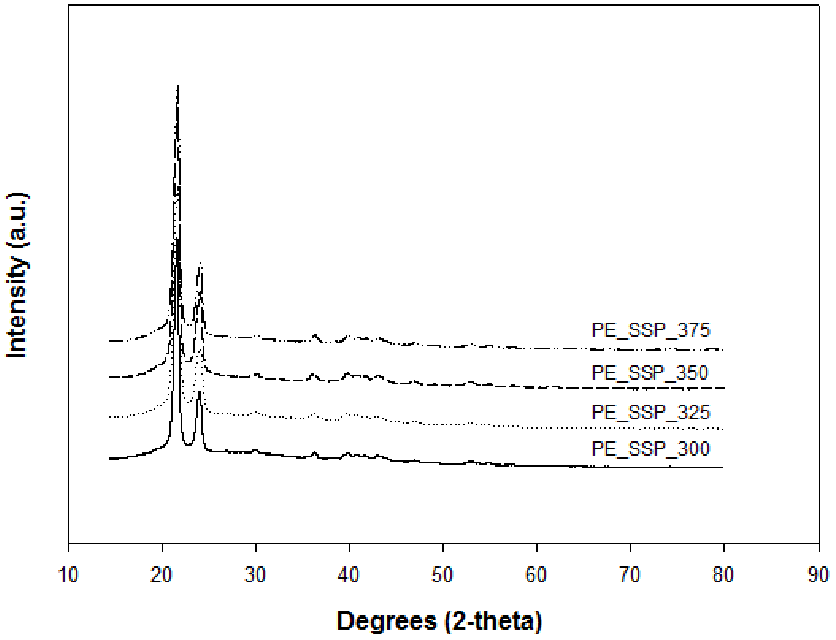

Figure E-5 XRD patterns of polyethylene produce with SSP.

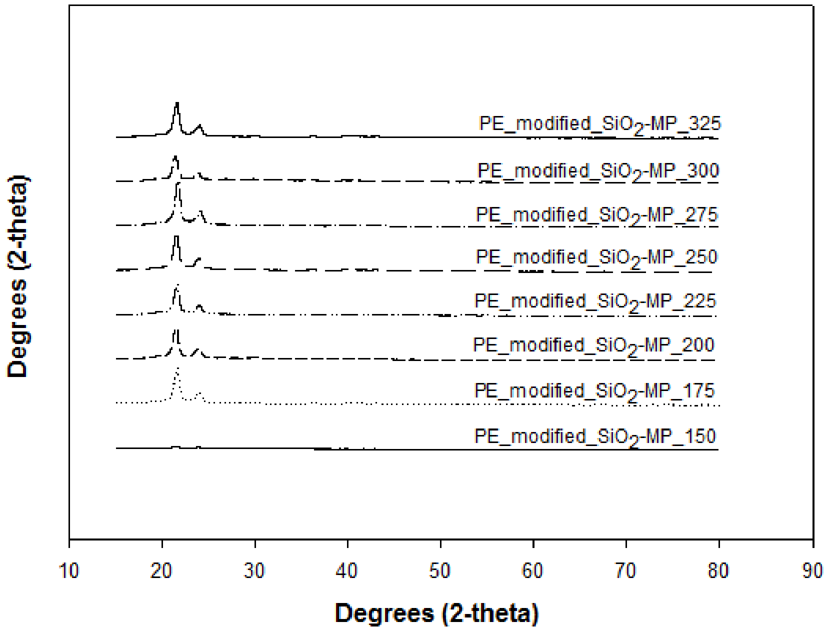

Figure E-6 XRD patterns of polyethylene produce with modified SiO_2-MP.

APPENDIX F

LIST OF PUBLICATION

F.1 List of publication

Pasucha Thongyoo, Supaporn Khubunsongserm, and Bunjerd Jongsomjit "Polymerization of ethylene over titanocene supported on spherical silica" (The 26th National Thai Institute of Chemical Engineering and Applied Science Conference (TIChE2016) and the 6th International Thai Institute of Chemical Engineering and Applied Science Conference (ITIChE2016), Bangkok, Thailand)

VITA

Mr.Pasaucha Thongyoo was born on August 13, 1992 in Prachin Buri, Thailand. He finished his high school from Thanyaburi school in 2011. After that, He received the Bachelor degree of Chemical Technology from Faculty of Science, Chulalongkorn University in August 2015. He continued the master degree of Chemical Engineering from Faculty of Engineer at Chulalongkorn University and participated in the Center of Excellence on Catalysis and Catalytic Reaction Engineering laboratory under the supervision of Prof. Dr. Bunjerd Jongsomjit in August 2015.