

Synthesis of Ziegler-Natta catalysts containing $\text{SiCl}_4/\text{TEOS}/\text{TiCl}_4/\text{MgCl}_2$ for ethylene/1-hexene copolymerization



A Thesis Submitted in Partial Fulfillment of the Requirements
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Department of Chemical Engineering

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การสังเคราะห์ตัวเร่งปฏิกิริยาซีเกลอร์-นัตตาที่มีองค์ประกอบของ $\text{SiCl}_4/\text{TEOS}/\text{TiCl}_4/\text{MgCl}_2$ สำหรับ
โคพอลิเมอไรเซชันของเอทิลีนและหนึ่งเฮกซีน



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สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2562
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

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By Miss Wasinee Ousirisombat
Field of Study Chemical Engineering
Thesis Advisor Professor BUNJERD JONGSOMJIT, Ph.D.

Accepted by the FACULTY OF ENGINEERING, Chulalongkorn University in
Partial Fulfillment of the Requirement for the Master of Engineering

..... Dean of the FACULTY OF
ENGINEERING
(Professor SUPOT TEACHAVORASINSKUN, Ph.D.)

THESIS COMMITTEE

..... Chairman
(Professor MUENDUEN PHISALAPHONG, Ph.D.)

..... Thesis Advisor
(Professor BUNJERD JONGSOMJIT, Ph.D.)

..... Examiner
(Chutimon Satirapipathkul, Ph.D.)

..... External Examiner
(Assistant Professor Ekrachan Chaichana, Ph.D.)

วคินี้ อู่ศิริสมบัติ : การสังเคราะห์ตัวเร่งปฏิกิริยาซีเกลอร์-นัตตาที่มีองค์ประกอบของ $\text{SiCl}_4/\text{TEOS}/\text{TiCl}_4/\text{MgCl}_2$ สำหรับโคพอลิเมอร์ไรเซชันของเอทิลีนและหนึ่งเฮกซีน.
(Synthesis of Ziegler-Natta catalysts containing $\text{SiCl}_4/\text{TEOS}/\text{TiCl}_4/\text{MgCl}_2$ for ethylene/1-hexene copolymerization) อ.ที่ปรึกษาหลัก : ศ. ดร.บรรเจิด จงสมจิตร

พอลิเอทิลีนยังคงมีการผลิตอย่างแพร่หลายทั่วโลกโดยมีการผลิตมากที่สุดที่แถบทวีปเอเชีย โดยหลักๆแล้วพอลิเอทิลีนจะแบ่งเป็น 3 ชนิดหลัก ได้แก่ พอลิเอทิลีนความหนาแน่นสูง (HDPE), พอลิเอทิลีนความหนาแน่นต่ำ (LDPE) และ พอลิเอทิลีนความหนาแน่นต่ำเชิงเส้น (LLDPE) ตัวเร่งปฏิกิริยาซีเกลอร์-นัตตา คือตัวเร่งปฏิกิริยาที่ใช้ในปฏิกิริยาเพื่อเร่งให้เกิดพอลิเมอร์ของอัลฟาโอเลฟิน ซึ่งตัวเร่งปฏิกิริยานี้สามารถนำมาเร่งให้เกิดพอลิเอทิลีนได้ ในงานวิจัยนี้สนใจที่จะศึกษาการสังเคราะห์ตัวเร่งปฏิกิริยาซีเกลอร์-นัตตา $\text{SiCl}_4/\text{TEOS}/\text{TiCl}_4/\text{MgCl}_2$ เพื่อใช้เร่งปฏิกิริยาให้เกิดพอลิเอทิลีน โดยการเติมสารเติมแต่ง (Additive) ที่เป็นสารประกอบซิลิกอน ได้แก่ เตตระเอทิลอโทซิลิเกต (TEOS) และซิลิกอนเตตระคลอไรด์ (SiCl_4) เพื่อปรับปรุงตัวเร่งปฏิกิริยาให้เหมาะสมในแง่การเกิดพอลิเมอร์ไรเซชันในระบบที่เป็นโคพอลิเมอร์ไรเซชันระหว่างเอทิลีนกับ1-เฮกซีน และศึกษาที่ปริมาณของโคพอลิเมอร์ที่ 0%, 3% และ 5% โดยงานวิจัยนี้มีการแบ่งการศึกษาเป็น 2 ส่วน ในส่วนแรกจะศึกษาเปรียบเทียบคุณสมบัติระหว่าง TEOS และ SiCl_4 มีชื่อว่า cat AT และ cat AS ตามลำดับโดยผลที่ได้คือ cat AS ที่มีการเติม SiCl_4 จะให้ค่า comonomer insertion มากกว่าการใช้สารเติมแต่งที่เป็น TEOS และส่วนที่สองของงานวิจัยนี้ได้มีการผสมระหว่างทั้งสองสารประกอบซิลิกอน และมีการปรับเปลี่ยนอัตราส่วนโดยโมล (mol ratio) ของ TEOS/Mg ซึ่งส่วนนี้จะมีการสังเคราะห์มี cat ATS, cat ATS0.15 และ cat ATS0.20 โดย cat ATS จะใช้ mol ratio เท่ากับที่ใช้ในงานวิจัยครั้งแรก, cat ATS0.15 และ cat ATS0.20 จะใช้ TEOS/Mg เท่ากับ 0.15 และ 0.20 ตามลำดับ ผลที่ได้ในครั้งหลังคือเมื่อเพิ่มปริมาณ TEOS/Mg จะยิ่งทำให้ปริมาณของ comonomer insertion ลดลง และ cat ATS ให้ค่า comonomer insertion และ activity ที่ดีที่สุดในทั้งระบบที่ใช้ปริมาณโคพอลิเมอร์เท่ากับ 0%, 3% และ 5% ในระบบเอทิลีน/1-hexene โคพอลิเมอร์ไรเซชัน

สาขาวิชา วิศวกรรมเคมี

ลายมือชื่อนิสิต

ปีการศึกษา 2562

ลายมือชื่อ อ.ที่ปรึกษาหลัก

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Polyethylene (PE) is still worldwide manufacturing, and its most productivity is in Asia. The main categories of PE including high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). Ziegler-Natta catalyst is catalyst that used for α -olefins polymerization and it is widely used in industry because it has good activity with low operating cost. This research studies on synthesized $\text{SiCl}_4/\text{TEOS}/\text{TiCl}_4/\text{MgCl}_2$ Ziegler-Natta catalyst in ethylene/1-hexene copolymerization with added silicon compounds, including tetraethylorthosilicate (TEOS) and SiCl_4 , used as additive in catalyst by varying 1-hexene comonomer at 0%, 3% and 5%. This research is separated into 2 parts, the first one is comparison comonomer insertion and activity between TEOS and SiCl_4 . The results indicated that SiCl_4 addition in cat AS had better comonomer insertion and activity than cat AT that TEOS added. The second part of this research is studied about the synergistic effect of mixed silicon compound between TEOS and SiCl_4 and vary TEOS/Mg. The synthesized catalyst in this part including cat ATS, which is mol ratio of silicon compound is the same as first part and cat ATS 0.15 and cat ATS 0.20 were TEOS/Mg = 0.15 and TEOS/Mg = 0.20. The polymerization by using cat ATS 0.20 illustrated that it is the best comonomer insertion and activity.

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Wasinee Ousirisombat

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Chapter 1 Introduction

1.1 Introduction

Polyethylene (PE) is still demanded in the market. It is main material used to produce plastic beads, packaging and several films. The mechanical properties of polyethylene belong to the type of branching, the crystallinity of structure and the molecular weight. PE has a main category classified by its density and branching including high density polyethylene (HDPE), low density polyethylene (LDPE), and linear low-density polyethylene (LLDPE).

LLDPE occupied about 34% of polyethylene production in the market in 2016 and the most production of LLDPE is films. LLDPE produces from copolymerization of ethylene and α -olefins such as 1-butene, 1-hexene and 1-octene. LLDPEs have linear structure with short chain branching. The structure of LLDPE allows it to have a good tensile and high strength, so the product of LLDPE is mostly used as films [1].

Ziegler-Natta catalysts are known as the catalysts that are used for α -olefins polymerization. At present, Ziegler-Natta catalysts supported on $MgCl_2$ are still achieved highly active for α -olefins polymerization [2]. Ziegler-Natta catalysts with $MgCl_2$ support have many methods for preparation such as ball milling method, alcohol adduct and Grignard reagent [2, 3]. However, the catalyst with supported $MgCl_2$ prepared by Grignard reagent is thermally stable catalyst [3].

In fact, Ziegler-Natta catalyst exhibits the lowest operating cost of catalyst used for polyethylene production. However, it is multisite catalyst and it gives the polymer with broad molecular weight distribution and low insertion of comonomer, which are not suitable to LLDPE production. Therefore, this research aims to adjust the properties of catalyst, especially in comonomer insertion by using silicon compounds including silicon tetrachloride ($SiCl_4$) and tetraethyl orthosilicate (TEOS) as additives to improve the catalyst performance to be able to produce LLDPE. This research study is divided into 2 parts; the first one is focused on comparison of silicon compounds performance and another part is emphasized on the mixed silicon compounds performance in Ziegler-Natta catalyst prepared by Grignard reagent. The comonomer response and activity of catalysts depending on $SiCl_4$ and

TEOS additives in ethylene/1-hexene copolymerization were elucidated and discussed in this study.

1.2 Research objective

To study the effect of silicon compounds such as tetraethyl orthosilicate (TEOS) and SiCl_4 in Ziegler-Natta catalysts containing $\text{SiCl}_4/\text{TEOS}/\text{TiCl}_4/\text{MgCl}_2$ on ethylene/1-hexene copolymerization behaviors including polymerization activity and comonomer insertion

1.3 Research scopes

1.3.1 Synthesis of the Ziegler-Natta catalysts containing $\text{SiCl}_4/\text{TEOS}/\text{TiCl}_4/\text{MgCl}_2$ with different amounts of two silicon compounds.

1.3.2 The molar ratios of $\text{TEOS}/\text{Mg} = 0.07, 0.15$ and 0.20 in the synthesized catalyst were studied.

1.3.3 The ethylene/1-hexene copolymerization was performed according to the condition as follows; polymerization in 2-liter autoclave reactor with condition by using catalyst 0.02 g., TEA as cocatalyst (mol ratio $\text{Al}/\text{Ti} = 60$), ethylene 7 bars and hydrogen 1 bar operated at temperature 80 °c for 1 h.

1.3.4 Variation of comonomer in ethylene/1-hexene copolymerization as follows; 0% 1-hexene, 3% 1-hexene and 5% 1-hexene

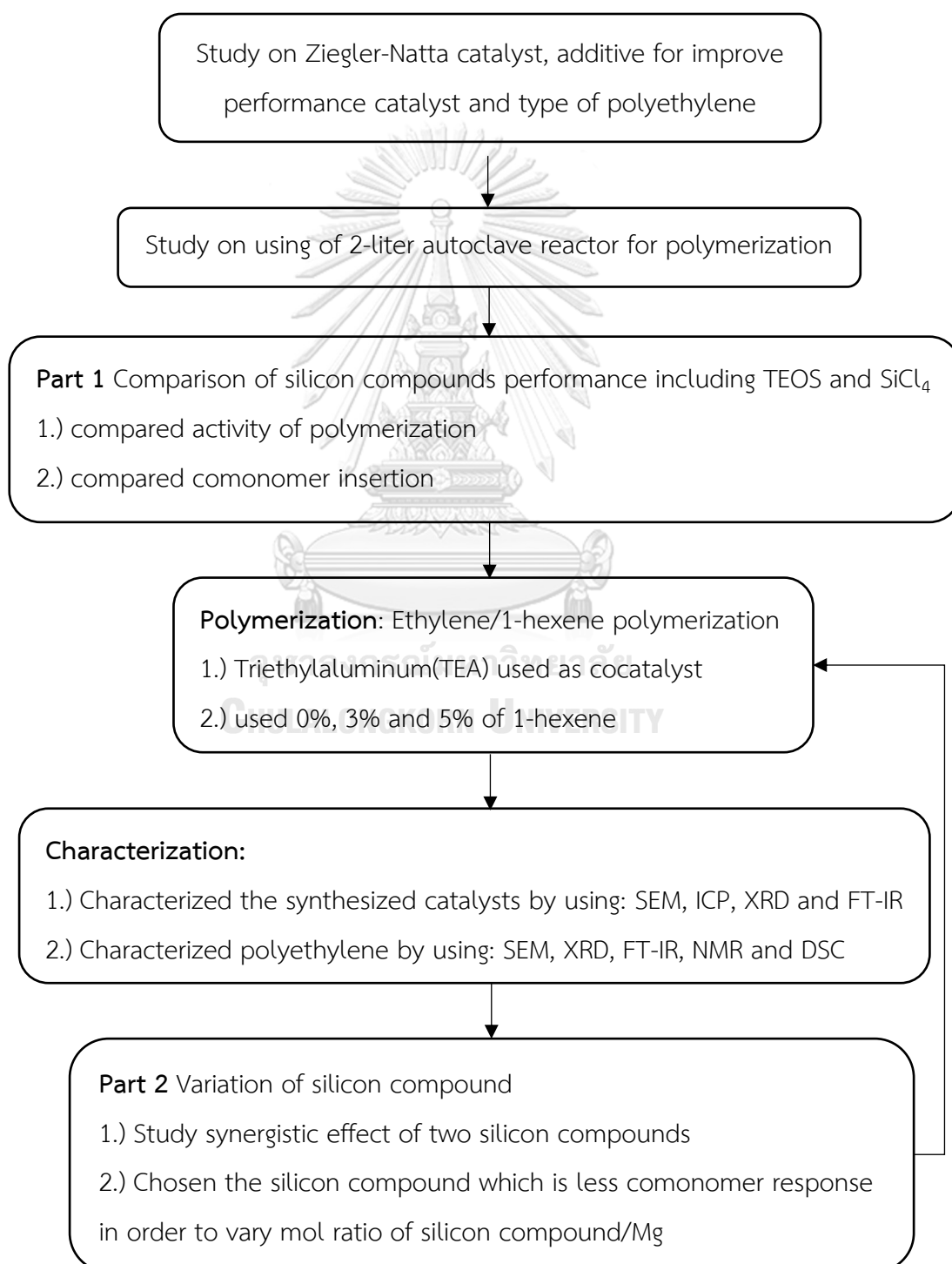
1.3.5 Characterization of synthesized catalyst was as follows; Scanning electron microscopy (SEM): Morphology of catalyst, Inductively coupled plasma (ICP): Ti, Mg and Si content, X-ray diffraction (XRD): XRD pattern of crystal structure of catalyst and Fourier transform infrared spectroscopy (FT-IR): existence of silicon compounds on catalyst crystal structure

1.3.6 Characterization of polymer was as follows; Scanning electron microscopy (SEM): Morphology of polymer, X-ray diffraction (XRD): XRD pattern for study about type of polyethylene, Nuclear magnetic resonance (NMR) or Fourier transform infrared spectroscopy (FT-IR): content of comonomer insertion and Differential scanning calorimetry (DSC): Polymer melting point (T_m) and crystallinity (χ_c)

1.4 Research benefits

To gain a better understanding for effects of silicon compounds on TiCl_4 -Ziegler-Natta catalyst supported on MgCl_2 for ethylene/1-hexene copolymerization such as activity, morphology and comonomer insertion.

1.5 Research Methodology



Chapter 2 Theory and literature review

2.1 Theory

2.1.1 Ziegler-Natta catalyst [4-9]

Ziegler-Natta catalyst was found in around 1950's by Karl Ziegler and Giulio Natta. Ziegler-Natta catalyst is heterogeneous catalyst with group IV-VIII transition metals with a metal alkyl or alkyl halide of Group I-III base metals. The main transition metals including titanium (Ti), vanadium (V) and chromium (Cr). The catalyst has a multi-site catalyst, so that it gives a broad molecular weight distribution polyolefin.

Ziegler-Natta catalyst develop with containing $MgCl_2$ in polyethylene polymerization is the most dominant in production of linear polyethylene, while functions of $MgCl_2$ in propylene polymerization is not only use as a support material but also as a part of the active complex. The catalyst with $MgCl_2$ have shown very high activities and are also give narrower molecular weight and chemical composition distributions of polymers comparing to $TiCl_3$ catalysts. $MgCl_2$ supported catalysts preparation as follow: ball milling, impregnated on silica carrier, alcohol adduct(precipitation), Grignard reagent and spray-drying.

1. Ball milled $MgCl_2$ -based Ziegler Catalysts: $TiCl_4$ or $TiCl_3$ are often co-milled with $MgCl_2$, melding together to form a solid solution. The crystal structure must be changed from the α - $MgCl_2$ to the δ - $MgCl_2$ form, where the closely packed layered structure is strongly interrupted by stacking defects. But today, ball milling of $MgCl_2$ is no longer common in Ziegler-Natta catalyst preparation.

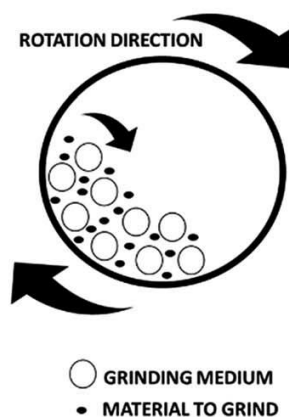


Figure 1 Ball-milling process

2. Impregnation of MgCl_2 -Titanium Catalysts on silica: Silica-based catalysts is especially used in gas-phase processes. The silica support acts like a carrier material, imparting morphology control to the catalyst. A wide variety of catalysts can also be achieved by altering the physical properties of the silica support material (particle size and distribution, pore volume, surface area, etc.). Silica - based catalysts possess improved chemical composition distributions (CCD) in ethylene copolymerization.
3. Alcohol adduct of MgCl_2 -Titanium Catalysts: Adding highly soluble magnesium and or aluminum alcoholates or alkyl to the reaction solution, and then precipitating the catalyst by the addition of a suitable chlorination agent. Titanium can be added as a soluble complex or used as one of the chlorination agents. Precipitated MgCl_2 as an amorphous material, imparting high catalytic activity to the system.
4. MgCl_2 -Titanium Catalysts synthesized via Grignard reagent: Grignard reagent usually start from Mg powder reacting to I_2 and chlorinating agent to synthesize MgCl_2 which is support of Ziegler-Natta catalyst.
5. Spray-drying of MgCl_2 -Titanium Catalysts: Droplets in spray-drying containing a solution or slurry of the catalyst components are sprayed into a chamber under drying conditions in order to remove the solvent or slurry diluent, leaving behind a solid residue. The characteristics of the droplets formed can be used to tailor the particle size of the final catalyst. Spray-drying techniques process like “filler” controlling the shape and composition of the catalyst. Hydrophobic fumed silicas are common use as spray-dried solution, it has a relatively high viscosity to the slurry to be spray-dried, improve the mechanical strength of the catalyst and generate increased porosity in the catalyst.

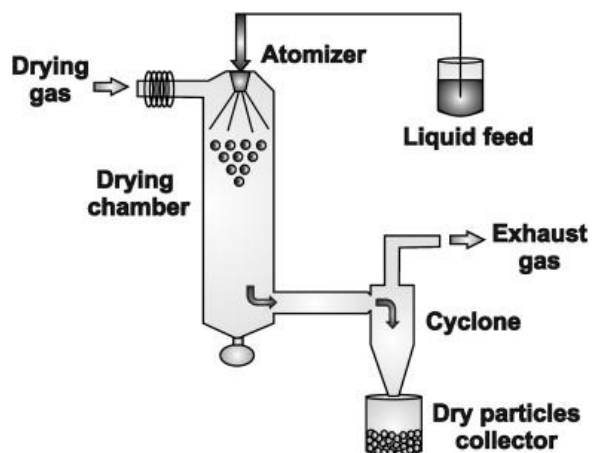


Figure 2 Spray-drying process

2.1.2 Polymerization [4, 10, 11]

Polymerization process with Ziegler-Natta catalyst, for example TiCl_4 Ziegler-Natta catalyst, it wants to fulfil Ti orbital to form active form in order to achieve polymerization by using Alkylaluminium compound as cocatalyst in common such as diethylaluminumchloride (DEAC), triethylaluminum (TEA), triisobutylaluminum (TIBA), and trioctylaluminium (TnOA). The mechanism of cocatalyst as shown in *Figure 3* and *Figure 4*.

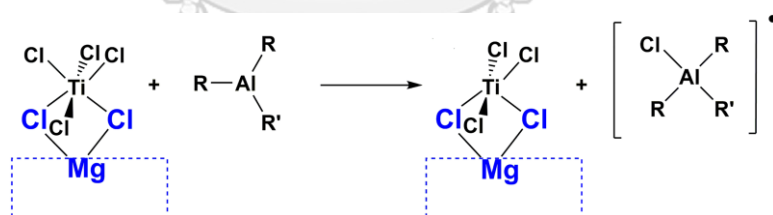


Figure 3 Reduction of TiCl_4 species adsorbed on the MgCl_2 surface in the presence of Al-alkyl cocatalysts

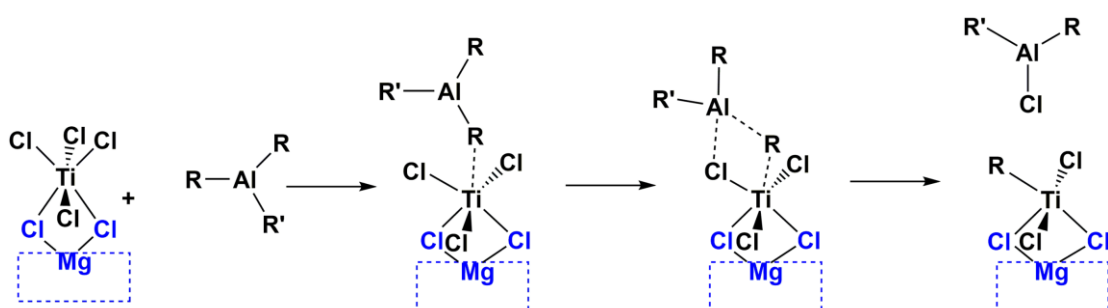


Figure 4 Transalkylation between Al-cocatalysts and Ti center on the MgCl_2 surface

Ziegler-Natta catalyst in polymerization have two main ways including slurry phase and gas phase polymerization

1. Slurry polymerization process contain three-phase including gas bubbles, hydrocarbon diluent with the dissolved alkylaluminum compound, and the solid growing polymer particles loaded with the active sites. Today, the slurry polymerization process is being run all over the world with great success. The current installed capacity for the described process is around 6 million tons per year.

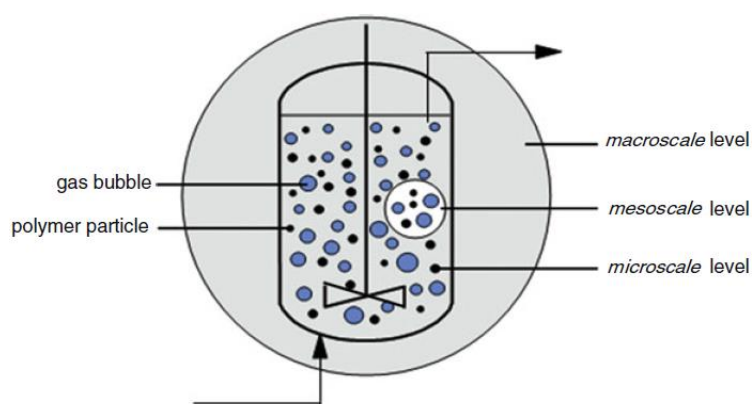


Figure 5 Slurry polymerization process

2. Gas phase polymerization processes prepare an environment that is conducive for olefin polymerization. The remarkable characteristics of gas-phase olefin polymerization lie in the fact that as the system does not involve any liquid phase in the polymerization zone; the gas phase plays a role in the provision of monomers, the integration of polymer particles and removal of the heat of reaction. In this system, polymerization reaction occurs at the interface between the solid catalyst and the polymer matrix, and as can be seen, it is swollen with monomers throughout the polymerization stage. In the gas-phase polymerization process, reactors must work closely to the dew point of the monomer mixture to achieve high monomer concentrations and high yields and the catalyst morphology must be very tightly controlled so that particle melting and agglomeration due to the heat transfer limitation of the gas can be prevented.

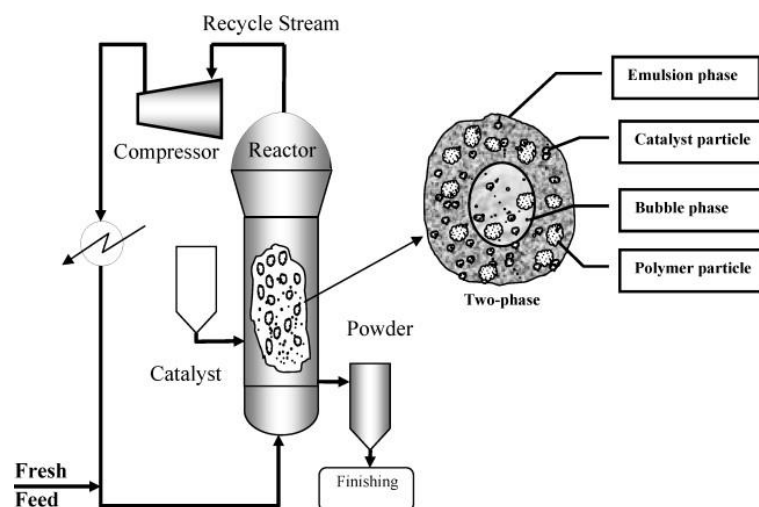


Figure 6 Gas phase polymerization process

2.1.3 Polyethylene [12-14]

Polyethylene (PE) or IUPAC name ethene is a thermoplastic polymer which consist of long chains of the monomer ethylene. PE contains the chemical elements carbon and hydrogen. PE is created through polymerization of ethene. It can be produced through radical polymerization, anionic addition polymerization, ion coordination polymerization or cationic addition polymerization. PE has many applications including films or sheets for packaging, bottles, pipes, pails and insulation for wire and cable. Polyethylene is classified into several different categories based mostly on its density and branching. PE three main type polymer including high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE)

1. High density polyethylene (HDPE) has density greater or equal to 0.941 g.cm^{-3} , it has a low degree of branching and thus stronger intermolecular forces and tensile strength. HDPE products are packaging such as detergent bottles, margarine tubs and garbage containers, water pipes and almost toys are the products from HDPE. HDPE is now produced by catalytic polymerization of ethylene in either slurry or gas phase reactors by using Ziegler-Natta catalysts or metallocene catalysts.
2. Low density polyethylene (LDPE) has a density in range of $0.910 - 0.940 \text{ g.cm}^{-3}$. LDPE has a lower tensile strength and increased ductility. LDPE is more flexible

and lower melting temperature than HDPE. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap.

3. Linear low density polyethylene (LLDPE) has a density in range of $0.915\text{--}0.925\text{ g.cm}^{-3}$. LLDPE is the product of copolymerization of ethylene with alpha-olefins such as 1-butene, 1-hexene, and 1-octene. LLDPE structure is linear polymer with significant numbers of short branches. It has balance of stiffness and toughness. Almost LLDPE products are film.

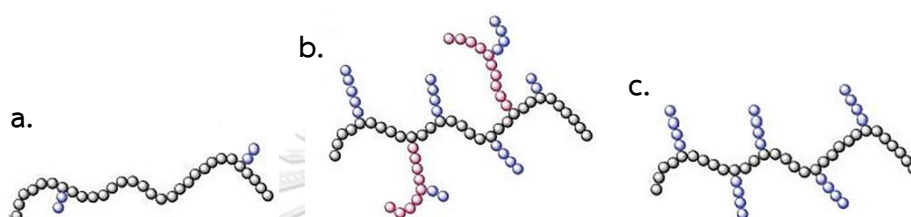


Figure 7 Structures of a. HDPE, b. LDPE, and c. LLDPE respectively

2.2 Literature review

GUO Zifang et.al synthesized a highly performance novel catalyst and used tetrabutylloxsilicane as electron donor in ethylene polymerization and ethylene/1-butene copolymerization to study about morphology of catalyst and polymer, catalytic activity and hydrogen response in these systems. The catalyst morphology has narrower size distribution and less fine content than commercial catalyst that confirmed by the results of scanning electron microscope (SEM). The bulk density of catalyst was higher than commercial catalyst. It indicated that a novel catalyst has better morphology than commercial catalyst, so a novel catalyst produced narrower size distribution of resins than that of commercial catalyst because more uniform of catalyst morphology in a novel catalyst. Furthermore, a novel catalyst has better activity and more stable to hydrogen response than commercial catalyst in ethylene polymerization. The activity in copolymerization of ethylene/1-butene of a novel catalyst also better than that of commercial catalyst but activity was decreased by increased 1-butene insertion. The copolymer obtained from a novel catalyst has a

lower branch degree in low molecular weight fraction and higher branch degree in high molecular weight fraction than that of commercial catalyst [15].

Marina I. Nikolaeva et.al synthesized Titanium-Magnesium catalyst (TMC) by using titanium tetrachloride (TiCl_4) on the support and Triethylaluminum (TEA) as a cocatalyst for copolymerization of ethylene with α -olefins in with and without the presence of hydrogen to study about effect of polymerization duration on comonomer content and the molecular weight distribution of copolymers. The results of the effect of reaction duration on copolymerization of ethylene/1-hexene in the absence of hydrogen illustrated that the activity on copolymerization was higher than homopolymerization but molecular weight (MW) was lower and the increment of polymerization duration on comonomer affected to increasing of yield and molecular weight (MW) and narrowing of molecular weight distribution (MWD) but 1-hexene incorporate is decreased. The increment of comonomer to ethylene ratio (C_6/C_2) 2.3 to 4.6 also gave the same tendency of results. The short chain branching profile of copolymer showed large amount of butyl branches component in low molecular weight fraction at all of polymerization duration and decreased amount of butyl branches at high polymerization duration. The higher polymerization duration gave higher MW, which cause the deactivation of the sites that reduced comonomer insertion, and narrower MWD. The incorporation of butyl branches component in low molecular weight fraction was increased when added up comonomer ratio. After introduced with hydrogen, the activity of ethylene/1-hexene copolymerization (at $C_6/C_2 = 2.3$) was higher than homopolymerization in the same within the case of the absence hydrogen but after the maximum activity at 5 mins of copolymerization was more significant decrease of activity. The increment of copolymerization duration increased yield and MW but decreased MWD and 1-hexene incorporation. The copolymerization experiment is opposite to homopolymer on yield and molecular weight but same tendency in MWD. The short chain branching profile of copolymer showed the same results as absence hydrogen and hydrogen has no effect on comonomer distribution [16].

A. Parada et.al synthesized TiCl_4 catalyst supported on MgCl_2 , by using recrystallization technique with SiCl_4 and subsequently impregnated with TiCl_4 and

used triethylaluminium (TEA) as a cocatalyst. This research study about the effect of the alcohol nature, including 1-hexanol, t-butanol, butanol, iso-propanol, propanol and ethanol, on activity and tacticity control in $\text{TiCl}_4/\text{MgCl}_2/\text{SiCl}_{4-n}(\text{OR})_n$ catalyst for olefins polymerization. The catalytic activities that obtained linear chain alcohol was higher than branched chain alcohol. SiCl_4 produced $\text{MgCl}_2 \cdot \text{Si}(\text{OR})_n\text{Cl}_{4-n}$ adduct (alkoxysilanes) by dealcoholation process and SiCl_4 was used to eliminate alcohol to avoid reaction between alcohol and TiCl_4 during impregnation to produce titanium alkoxides that are inactive in polymerization by blocking active center. The alkoxysilanes can act like internal electron donors, which are important to orientate the insertion of α -olefins to get higher values of isotactic index. The binding of alkoxysilane at surface MgCl_2 can block some vacant sites to form specific sites and possible to stabilize some active isospecific sites. Recrystallization with SiCl_4 by precipitation technique gave the most active catalyst because disorder structure and size of MgCl_2 , which are affect to higher content of Ti loading through impregnation process. The results of Isotactic index (II) and EDS support the idea of alkoxysilane formation during preparation of catalysts through the reaction between alcohol and SiCl_4 [17].

Wanna phiwkliang et.al synthesized the catalyst $\text{TiCl}_4/\text{MgCl}_2/\text{THF}$ and added different additives including ZnCl_2 , SiCl_4 and combined $\text{ZnCl}_2\text{-SiCl}_4$ to study about the effect of additives to catalytic activity for ethylene polymerization. The tetrahydrofuran used as internal electron donors. The addition of Lewis acid was possible to prevent the aggregation of MgCl_2/THF support that lead to increased surface area, confirmed by XRD at lower intensity in MgCl_2/THF peak. or was possible to break the crystal growth that lead to Ti content in bulk was lower than surface, confirmed by ICP and EDX. The SEM/EDX showed more Ti distribution in catalyst with additives. The oxidation state of Ti^{3+} was characterized by ESR, showed that the addition of Lewis acid in catalyst tended to increase the amount of Ti^{3+} species. The phenomena is like to cocatalyst, which a reducing power. On the other hands Ti^{3+} in SiCl_4 was less because its strong Lewis acid similar to strong reducing power caused the over-reduction of Ti^{4+} to Ti^{3+} and Ti^{3+} to Ti^{2+} . Thus, the influence of Lewis acid on the oxidation state may lead to increase or decrease of polymerization activity. The

modified catalyst with ZnCl_2 - SiCl_4 showed higher activity than any other catalyst in this research because the mixture was higher acidity (Lewis acid) that remove THF structure from catalyst. The electron donor lead to reduce catalytic activity. The Zn-Si mixture also gave the highest surface area and Ti content at surface of catalyst that confirm catalytic activity earlier. SiCl_4 is stronger Lewis acid, more surface area and Ti content at surface area than ZnCl_2 , then SiCl_4 was higher catalytic activity. The properties of polyethylene showed that T_m , T_c , and crystallinity of all polymers were similar to the unmodified catalyst as characterized by DSC analysis. The influence of Lewis acid in catalyst showed a trend to give a slight increase in the M_v of polyethylene, excepting catalyst with SiCl_4 . However, the Lewis acid modification did not affect to the overall polymer properties.[18]

Niyomthai T. et.al synthesized the $\text{TiCl}_4/\text{MgCl}_2/\text{THF}$ catalyst (Cat. A) and used triethylaluminium (TEA) as a cocatalyst to study about effect of Lewis acid including AlCl_3 , FeCl_4 and mixed AlCl_3 - FeCl_4 (marked as Cat. A-Al, Cat. A-Fe, Cat. A-Al-Fe respectively) of ethylene polymerization and ethylene/1-hexene copolymerization in catalytic activity, H_2 response and polymer properties. The results of catalytic activity in ethylene polymerization was in the following order: Cat. A-Al > Cat. A-Fe > Cat. A-Al-Fe > Cat. A. The results showed that Cat. A was the lowest activity, though it had the highest Ti/Mg ratio, which contrast with theoretical. Therefore, it must be considered about aggregation of Ti species that can decrease concentration of active site at the surface (from ICP results), which decrease activity in ethylene polymerization. Cat. A-Al was the highest activity because addition of Lewis acid can promote activity of ethylene polymerization by removing THF (as electron donor) and by giving more isolated Ti species. The removal of THF was confirmed by lower intensities of C-O-C stretching of IR band and rarely O-H stretching of IR band in Fourier Transform Infrared Spectroscopy (FTIR). The results of catalytic activity in ethylene/1-hexene copolymerization was in the following order: Cat. A-Al-Fe > Cat. A-Fe > Cat. A-Al > Cat. A. The results also showed the lowest activity in Cat. A. The highest activity was Cat. A-Al-Fe because mixed Lewis acid can make the difference acidity active site that suit for copolymerization. The perspective of activity of copolymerization was lower than homopolymerization because 1-hexene is more

steric hindrance than ethylene, so 1-hexene is difficult to insert into the backbone chain. The addition of Lewis acid can reduce vacant site of MgCl_2 by attract Cl atom to give defect lattice structure of MgCl_2 and then Ti species insertion was lower in bulk catalyst. The addition of Lewis acid also can adjust active center distribution (ACD) through Ti distribution from clustered Ti species to isolated Ti species then Ti can disperse more uniform and then catalyst have higher activity.

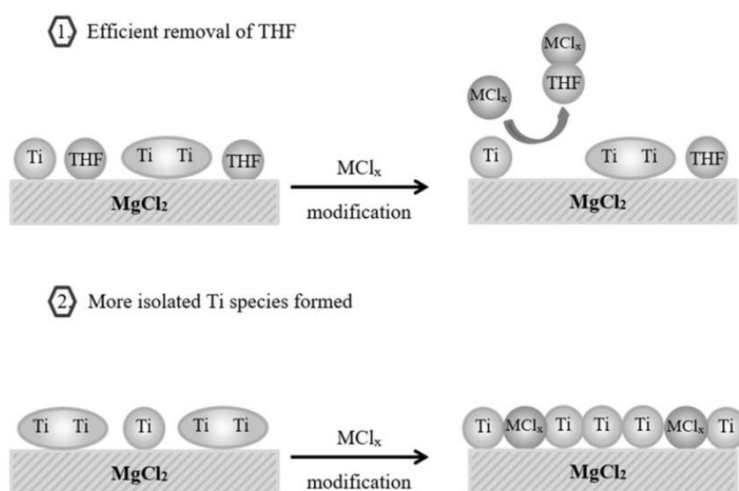


Figure 8 Lewis acid conceptual model roles

Hydrogen response in homopolymerization and copolymerization, addition of Lewis acid resist hydrogen effect on activity by regulating the active center distribution (Ti distribution) on the surface of catalyst. The addition of single or mixed Lewis acid has no significant change in catalytic activity in system with hydrogen because the hydrogen effect depends on the distribution of Ti species [19].

Chapter 3 Experimental

3.1 Materials

TiCl₄, titanium propoxide (Ti(OPr)₄), tetraethyl orthosilicate (TEOS), Butylchloride and 2,6-lutidine from TCL chemicals; I₂ and isobutanol from Sigma-Aldrich; SiCl₄ from Alfa Aesar; ethylene gas, hydrogen gas and nitrogen gas from Linde; Mg powder, triethylaluminum (TEA) in hexane and hexane were supplied from SCG Chemicals, Thailand.

3.2 Equipment

3.2.1 4-necked flask reactor

500 mL 4-necked flask reactor is a reactor used for synthesis of catalyst. The reactor was achieved the reaction under inert atmosphere. 4-necked flask connected with condenser for keeping degree of solvent, connected with Teflon stirring blade, Thermometer and 3 way feeding glass in this system.

3.2.2 Cooling and heating control

Cooling and heating control at reactor were connected to oil bath for controlling temperature in reactor of synthesizing system.

3.2.3 2-liter autoclave reactor

2-liter autoclave reactor was used for polymerization of ethylene and ethylene/1-hexene polymer. The reactor was achieved polymerization reaction under inert atmosphere. It is connected with cooling and heating control for controlling temperature in polymerization.

3.2.4 Vacuum pump

Vacuum pump was used for vac off solvent from 500 mL 4-necked flask after washing in synthesizing system. In polymerization system, it was used for purified reactor before polymerization.

3.2.5 Glove box

Glove box is the box under inert Argon gas system. It was used for prepared compound for synthesis of Ziegler-Natta catalyst, which was operated under inert atmosphere, such as Mg powder and I₂ for synthesis supported MgCl₂ via Grignard

reagent. Glove box was also used for catalyst preparation and cocatalyst for polymerization of ethylene and ethylene/1-hexene polymer.

3.3 Synthesis of $\text{TiCl}_4/\text{MgCl}_2$ -Ziegler-Natta catalysts

3.3.1 Synthesis of $\text{TiCl}_4/\text{MgCl}_2$ -Ziegler-Natta catalysts with silicon compound

Synthesis of $\text{TiCl}_4/\text{MgCl}_2$ -Ziegler-Natta catalysts was conducted under procedure, which was modified from patent [20] in nitrogen atmosphere. MgCl_2 Support was synthesized via Grignard reagent by filling 3.99 g. of Mg powder, 0.41 g. of I_2 , 0.46 mL of *iso*-butanol and 0.73 mL of butylchloride in 500 mL 4-necked round bottom flask connected with teflon stirring blade, condenser and thermometer, set stirring speed at 150 rpm and used 250 mL hexane as solvent, then heated up to 67°C and reaction time for 1 hour. Then, 0.07 mol of TEOS or 0.27 mol of SiCl_4 in mol ratio to Mg was subsequently added and stirred for 20 minutes. After that, 5.76 mL of $\text{Ti}(\text{OPr})_4$ and 2.29 mL of TiCl_4 were added and stirred for 30 minutes followed by adding of 2.44 mL of 2,6-lutidine into reactor. Then, 26.66 mL of butylchloride was slowly added for 30 minutes, and was hold for 2 hours for reaction. Finally, the catalyst was washed by hexane at first time at 50°C , then washed by hexane for 4 times at room temperature and dried by vacuum pump. The nomenclature of catalysts was given as follows; cat A is a catalyst without silicon compound, cat AT is a catalyst with TEOS and cat AS is a catalyst with SiCl_4 .

3.3.2 Variation of TEOS in synthesise $\text{TiCl}_4/\text{MgCl}_2$ -Ziegler-Natta catalysts

Condition of synthesis catalyst in part 2 was similar to part 1, but in this part, mixed silicon compounds catalyst was performed for synergistic performance by fixing mol ratio of SiCl_4/Mg at 0.27, but varied TEOS/Mg at 0.07, 0.15 and 0.20 and their nomenclatures are denoted as cat ATS0.07, cat ATS 0.15 and cat ATS 0.20, respectively.

3.4 Polymerization

Ethylene polymerization was conducted in 2-liter autoclave reactor. The reactor was purified by evacuating and by heating up to 75°C for 30 minutes, then evacuated and purged by N_2 for 5 times. After purification system, the reactor was cooled down to

45°C, then filled with 1 liter of hexane into the reactor and fed TEA as a cocatalyst (Al/Ti = 60) and catalyst 0.02 g. into the reactor. The pressure of hydrogen of 1 bar and ethylene of 7 bars was subsequently fed into the reactor. Polymerization temperature was operated at 80°C for 1 hour. Variation of copolymer amount (vol%) in ethylene/1-hexene copolymerization was varied at 3% and 5% of 1-hexene.

3.5 Characterization

3.5.1 Scanning Electron Microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

Scanning Electron Microscope (SEM) was used to study the morphology of catalyst and polymer. Energy dispersive X-ray spectroscopy (EDX) was used to study elemental distribution on the catalyst by mapping element on catalyst.

3.5.2 Inductively couple plasma (ICP)

Inductively couple plasma (ICP) was used to measure Ti, Mg and Si content in catalyst.

3.5.3 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to determine melting temperature (T_m) of polymer and heat of fusion (ΔH) of polymer to calculate crystallinity of polymer (χ_c).

3.5.4 X-ray diffraction (XRD)

X-ray diffraction (XRD) was used to obtain XRD patterns of catalyst with and without silicon compound addition at 2θ in range 0° to 80° and XRD pattern of polymer to approximately infer the type of polyethylene.

3.5.5 Fourier-transform infrared spectroscopy (FT-IR)

- Fourier-transform infrared spectroscopy (FT-IR) was used to identify the functional group of catalyst in order to prove existence of Si from silicon compounds on the crystal structure of catalyst.
- Fourier-transform infrared spectroscopy (FT-IR) was used to determine the amount of 1-hexene incorporation in polymer by compressing size of polymer in the mold for keep thickness of sample and then compare 1-hexene content with standard.

3.5.6 Nuclear Magnetic Resonance (^{13}C -NMR)

Nuclear Magnetic Resonance (^{13}C -NMR), which was operated at high temperature, was used to determine the amount of 1-hexene incorporation in polymer.

Table 1 The characterization data equipment

Technique	Characterization	Contact
SEM-EDX	SEM: morphology of catalyst EDX: metal element of sample surface	Center of Excellence on Catalysis and Catalytic Reaction Engineering
ICP	elemental composition analysis in bulk catalyst	Center of Excellence on Catalysis and Catalytic Reaction Engineering
DSC	determine melting temperature (T_m) of polymer and heat of fusion (ΔH) of polymer to calculate crystallinity of polymer (χ_c).	Center of Excellence on Catalysis and Catalytic Reaction Engineering
XRD	XRD patterns of catalyst and polymer	Center of Excellence on Catalysis and Catalytic Reaction Engineering
FT-IR	functional group of catalyst	Center of Excellence on Catalysis and Catalytic Reaction Engineering
	1-hexene incorporation in polymer	Thai Polyethylene Co., Ltd. SCG Chemicals
^{13}C -NMR	1-hexene incorporation in polymer	Thai Polyethylene Co., Ltd. SCG Chemicals

3.6 Research plan

No.	Operation	2019					2020						
		8	9	10	11	12	1	2	3	6	7	8	
1.	Literature review	←											→
2.	Synthesis catalyst by various component ratio	←					→						
3.	Characterization of catalyst	←							→				
4.	Synthesis polyethylene and ethylene/ 1- hexene copolymer			←						→			
5.	Characterization of polymer				←						→		
6.	Results and discussion	←											→
7.	Thesis writing								←				→

Chapter 4 Results and Discussion

4.1 Comparison of silicon compounds performance

4.1.1. Characterization

4.1.1.1 Catalyst characterization

4.1. 1.1.1 Scanning electron microscopy and energy dispersive X-ray spectrometer (SEM-EDX)

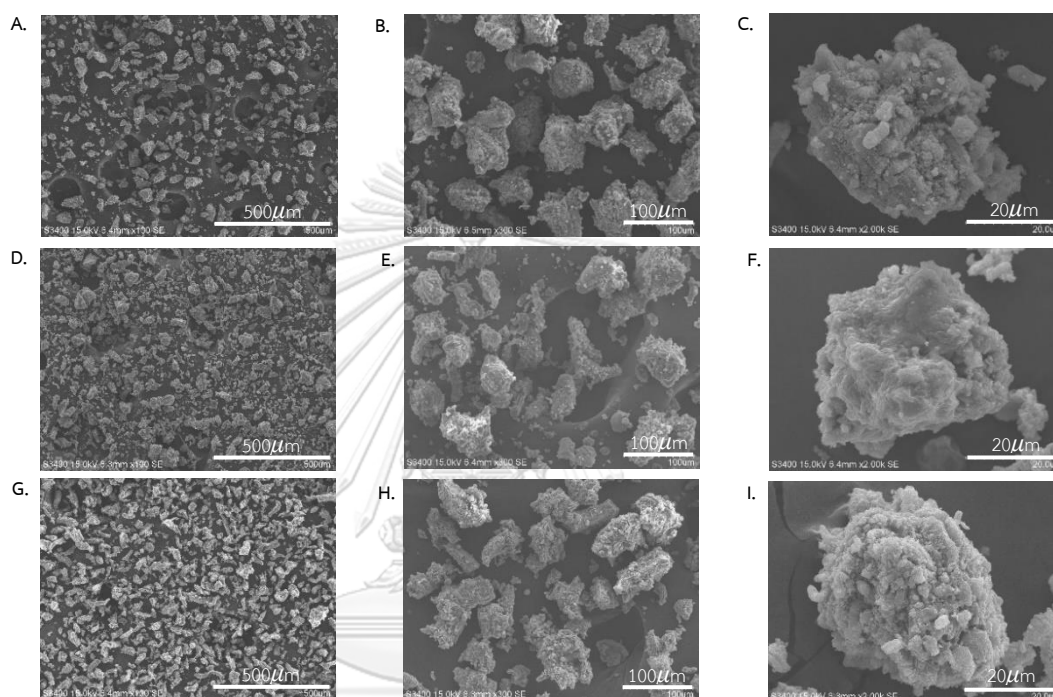


Figure 9 SEM characterization at 100x, 300x and 2000x magnification of cat A are A., B. and C.; cat AT are D., E. and F. and cat AS are G., H. and I. respectively.

The morphologies of synthesized Ziegler-Natta catalyst including cat A, cat AT and cat AS are similar appearing in irregular shape (granules) as shown in **Figure 9** obtained SEM characterization at 100x, 300x and 2000x. However, cat AT consisting of TEOS gave more fine particle of catalyst as shown in **Figure 9D. – 9F.**. The average particle size of cat A is ca. 50 μm, cat AT is ca. 54 μm and cat AS is ca. 74 μm. Thus, silicon compound addition resulted in larger size catalyst than that obtained from cat A without silicon compound addition.

From the results of EDX, the distribution of Ti and Si on the surface of synthesized Ziegler-Natta catalyst are illustrated in **Figure 10**. The elemental distribution (as EDX mapping) in cat A, cat AT and cat AS are similar having good distribution of Ti on external surface of catalyst, which is good for polymerization as shown in **Figure 10B., 10D.** and **10G.** In addition, cat AT and cat AS also have a good distribution of Si on the surface of the catalyst as shown in **Figure 10E.** and **10H.**

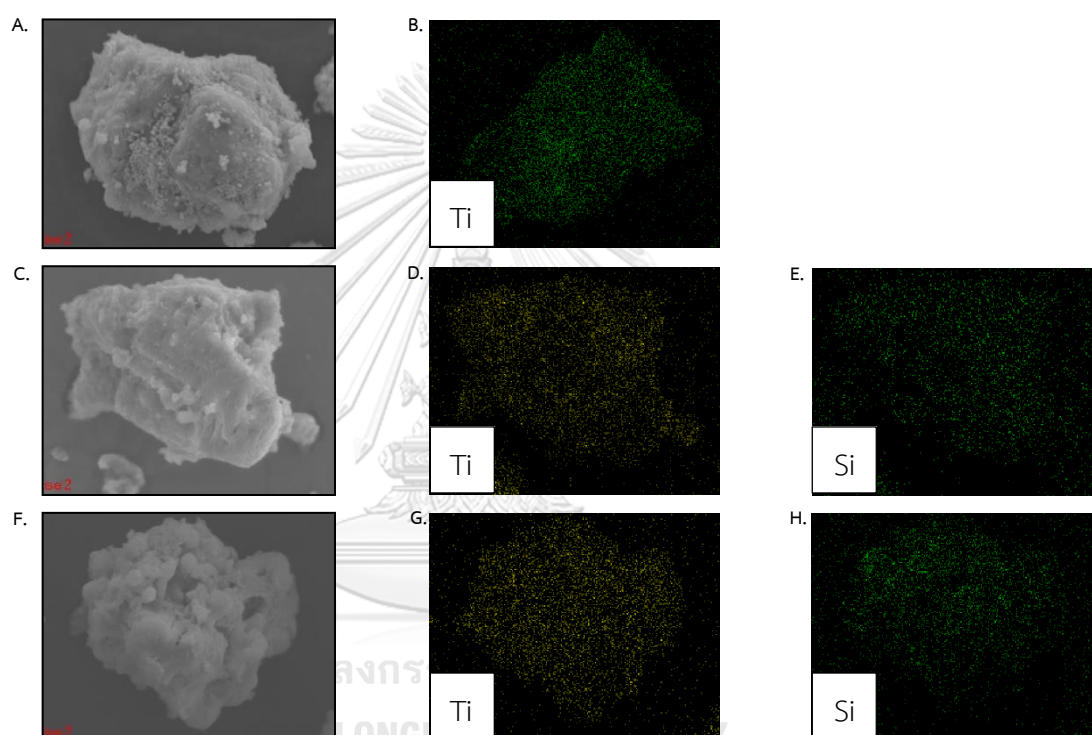


Figure 10 EDX mappings of cat A are A. (granule) and B. (Ti distribution); cat AT are C (granule), D. (Ti distribution) and E (Si distribution) and cat AS are F. (granule), G. (Ti distribution) and H. (Si distribution), respectively.

4.1.1.1.2 Inductively coupled plasma (ICP)

The composition of elements obtained by inductively coupled plasma of cat A, cat AT and cat AS are shown in **Table 2** indicating that amount of Ti in bulk catalyst of cat AS > cat A > cat AT, corresponding to activity in polymerization using these synthesized catalysts. Thus, the more amount of Ti in catalyst, the better activity in polymerization it can be obtained. The results of ICP showed that amount of Ti in cat A is not significantly different to cat AS, but TEOS made cat AT had different amount of Ti from cat A because a nature of TEOS is bulky compound and it may make the Ti hard to attach on the surface of catalyst.

Table 2 Inductively coupled plasma measurement of cat A, cat AT and cat AS in unit of mmol/mL

Catalyst	Ti	Mg	Ti/Mg	Si/Mg
cat A	4.21	11.43	0.37	-
cat AT	3.79	11.06	0.34	0.04
cat AS	4.34	11.30	0.38	0.17

4.1.1.1.3 Fourier transform infrared spectroscopy of catalysts (FT-IR)

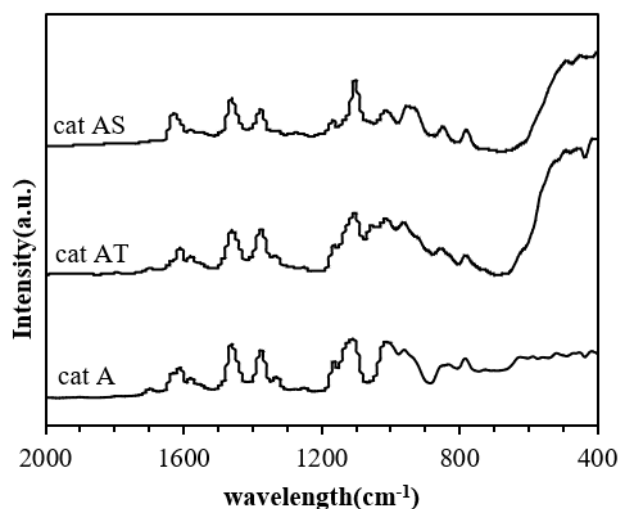


Figure 11 IR spectra of cat A, cat AT and cat AS

From the results of FT-IR of cat A, cat AT and cat AS as shown in **Figure 11**, the absorption peak of the titanium species on MgCl_2 support is located at $430\text{--}450\text{ cm}^{-1}$ for all synthesized catalysts[21]. It can be observed that cat A, cat AT and cat AS exhibited the IR band at $\sim 445\text{ cm}^{-1}$ assigned to Ti atom on MgCl_2 (110) crystal surface[21]. The FT-IR spectrum of cat AT showed the IR bands at 1163.0 cm^{-1} and 962.2 cm^{-1} and 1052.7 cm^{-1} assigned to the Si-alkoxy compound and at 473.0 cm^{-1} assigned to O-C-C band[22, 23]. These spectra essentially confirmed that the synthesized catalyst contained TEOS in structure of catalyst. The FT-IR spectrum of cat AS exhibited the IR band at 489.8 cm^{-1} and 450.0 cm^{-1} assigned to the Si-Cl band from the addition of SiCl_4 existing in the cat AS structure[22].

4.1.1.1.4 X-ray diffraction of catalyst

From the results of X-ray diffraction characterization of cat A, cat AT and cat AS as shown in **Figure 12**, it can be observed MgCl_2 peaks at $2\theta = 12.5^\circ$, 31° and 50° for all catalysts[19]. The XRD patterns of cat AT and cat AS were similar to cat A illustrated that TEOS and SiCl_4 did not affect the formation of MgCl_2 and did not destroy the crystal structure of catalyst. However, TEOS addition in cat AT was found to decrease the crystallinity of catalyst.

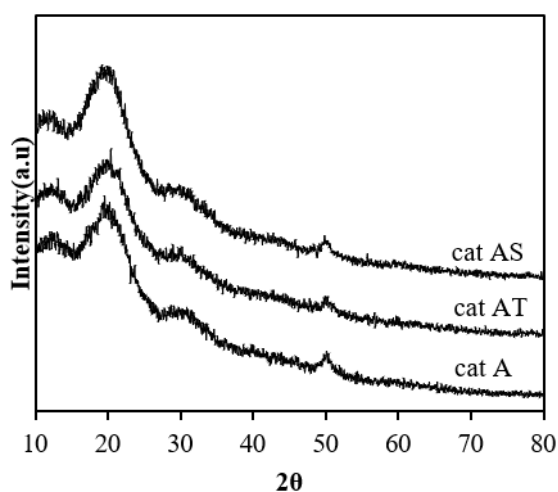


Figure 12 XRD patterns of cat A, cat AT and cat AS

4.1.1.2 Polymer characterization

4.1.1.2.1 X-ray diffraction of polymer

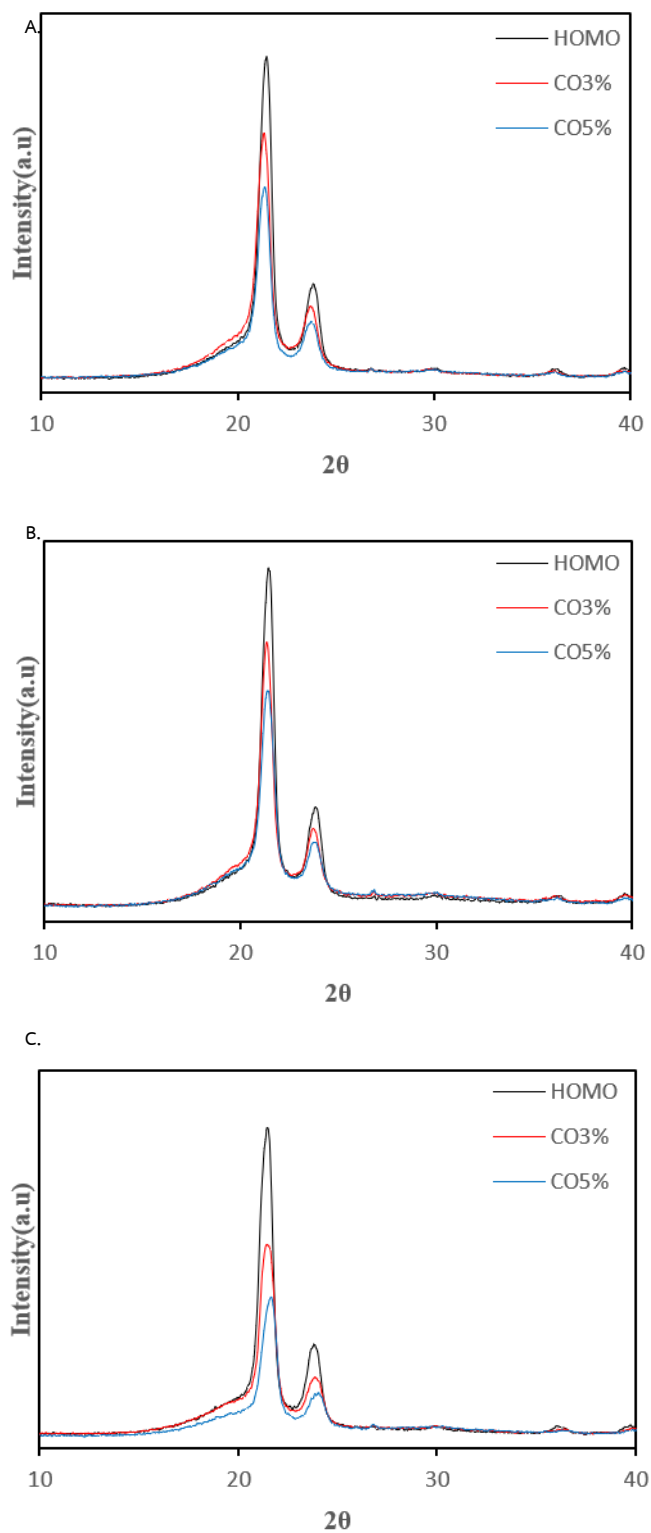


Figure 13 XRD patterns of polyethylene from cat A is A., cat AT is B. and cat AS is C.

From the results of X-ray diffraction characterization, it showed the (110) and (200) lattice planes of orthorhombic form of polyethylene at peaks $2\theta = 21.4^\circ$ and 23.8° and also observed the broad peak at $2\theta = 19.8^\circ$ is an amorphous for all polyethylene (homopolymer) and ethylene/1-hexene (LLDPE) samples obtained from cat A, cat AT and cat AS indicating the characteristics of PE and LLDPE (semi-crystalline)[24]. All polymer samples obtained from each catalyst exhibited the similar characteristic XRD peaks. It is obvious that the homopolyethylene had the highest crystallinity (strongest sharp peak), while the copolymers (LLDPE) exhibited lower crystallinity. This is because the incorporation of comonomer (1-hexene) essentially leads to lower degree of crystallinity. In addition, increased comonomer insertion apparently results in more decrease in crystallinity when compared LLDPE having comonomer 3% and 5%. Thus, the intensity of sharp peak for CO5% is lower than CO3%.

4.1.1.2.2 Differential scanning calorimetry (DSC)

From the results of differential scanning calorimetry as shown in **Table 3**, it reveals the melting temperature (T_m) and crystallinity in polymer obtained from cat A, cat AT and cat AS. It was found that T_m of polymers produced by cat A, cat AT and cat AS decreased when amount of incorporated 1-hexene comonomer increased, which is basically related to the results of ^{13}C nuclear magnetic resonance. The crystallinities that were calculated from ΔH_f of all polymers in homopolymerization system were not significantly different, but for those values in copolymerization system, the crystallinity decreased with increasing amount of comonomer. The incorporation of 1-hexene into backbone of polymer can result in chains of polymer did not pack so well leading to decreasing in crystallinity and then decreased T_m [25].

4.1.1.2.3 ^{13}C Nuclear magnetic resonance (^{13}C -NMR)

From the results of ^{13}C -NMR characterization, 1-hexene incorporations in polymer obtained from cat AT is not significantly different from that produced by cat A at 3% v/v of comonomer. They were equally 1-hexene incorporation at 5% v/v of comonomer as shown in **Table 3**. This indicated that TEOS cannot facilitate the incorporation of comonomer. The highest 1-hexene incorporation was found in copolymers produced by cat AS in both parts of 3% v/v and 5% v/v of comonomer. Thus, the better additive with good in comonomer response for copolymerization system is SiCl_4 .

Table 3 Differential scanning calorimetry and ^{13}C Nuclear magnetic resonance Characterization data of polymer catalyzed by cat A, cat AT and cat AS

Polymer of catalyst	comonomer (%)	ΔH_f (J/g)	crystallinity (%)	T_m ($^{\circ}\text{C}$)	1-hexene incorporation (%wt)
cat A	0	162.4	56.75	131.29	-
	3	150.5	52.59	126.13	0.56
	5	136.1	47.56	121.27	1.14
cat AT	0	159.3	55.66	130.76	-
	3	139.7	48.81	126.76	0.62
	5	129.1	45.11	125.62	1.14
cat AS	0	170.6	59.61	125.94	-
	3	142.3	49.72	115.73	1.95
	5	106.9	37.35	113.82	3.29

4.1.2 Catalytic activity

The polymerization activity obtained for all catalysts is shown in **Table 4**. Considering, the polymerization of cat AT, the catalytic activity in copolymerization with 3% v/v of 1-hexene comonomer increased because of the comonomer effect leading to increase ethylene diffusion causing the higher activity of polymerization. However, the copolymerization with 5% v/v of 1-hexene decreased because of steric hindrance effect of comonomer arising from diffusion limitation. For polymerization of cat AS, the catalytic activity increased when comonomer increased because of comonomer effect as well. The activity values are shown in **Table 4**.

Activity of cat AT in polymerization was lower than cat A because TEOS acted as spacer group but its bulky group that can prevent coordinating of $TiCl_4$ on the surface of catalyst and TEOS can also act like internal donor group, which occupied some active site [17, 26, 27]. Thus, it decreased Ti on surface of catalyst, and consequently activity decreased. Activity of cat AS in polymerization was higher than cat A because $SiCl_4$ in cat AS acted as spacer group leading to increased catalytic activity. From all results in **Table 4**, the highest activity was found in homopolymerization and copolymerization using cat AS.

Table 4 Activity of synthesized Ziegler-Natta catalyst

catalyst	comonomer (%)	activity ($kgPE.gcat^{-1}.h^{-1}$)	activity ratio
cat A	0	3.08	1.00
	3	3.13	1.02
	5	2.56	0.83
cat AT	0	2.30	1.00
	3	2.93	1.07
	5	2.46	1.28
cat AS	0	7.34	1.00
	3	6.46	0.88
	5	5.54	0.75

4.2 Mixed silicon compound performance

4.2.1 Characterization

4.2.1.1 Catalyst characterization

4.2.1.1.1 Scanning electron microscopy and Energy Dispersive X-ray Spectrometer (SEM-EDX)

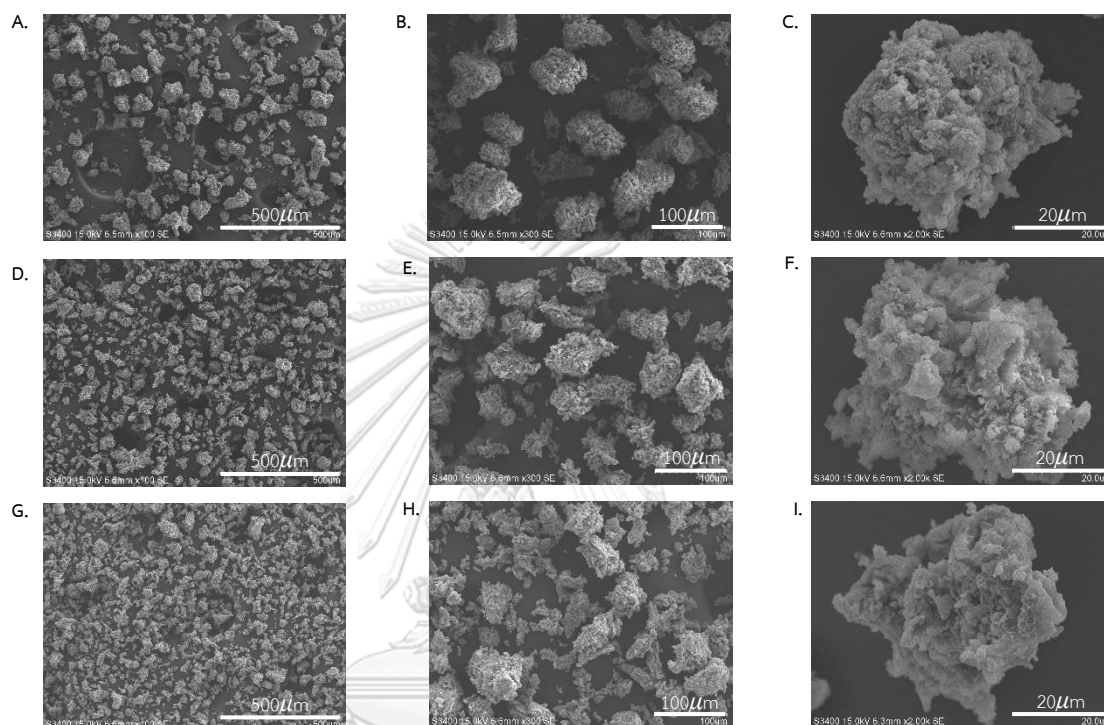


Figure 14 SEM characterization at 100x, 300x and 2000x magnification of cat ATS0.07 are A., B. and C.; cat ATS0.15 are D., E. and F. and cat ATS0.20 are G., H. and I. respectively.

The morphologies of synthesized Ziegler-Natta catalyst as shown in SEM characterization in **Figure 14**, cat ATS0.07, cat ATS0.15 and cat ATS0.20 have the same irregular shape and it showed that the more molar ratio of TEOS/Mg, the more fine particle of synthesized catalyst. Thus, TEOS did not affect to shape of catalyst, but make more fine particle in synthesized catalyst. The catalyst approximated size of cat ATS0.07 is 66 μm , cat ATS0.15 is 61 μm and cat ATS0.20 is 58 μm .

From the results of EDX, the distribution of Ti and Si on the surface of synthesized Ziegler-Natta catalyst as shown in **Figure 15**. cat ATS0.07, cat ATS0.15 and cat ATS0.20 are similar in a good distribution of Ti on surface of catalyst that is good for polymerization, as shown in **Figure 15B., 15E.** and **15H.**. All of the synthesized catalysts have a good distribution of Si on the surface of the catalyst as shown in **Figure 15C., 15F.** and **15I.**

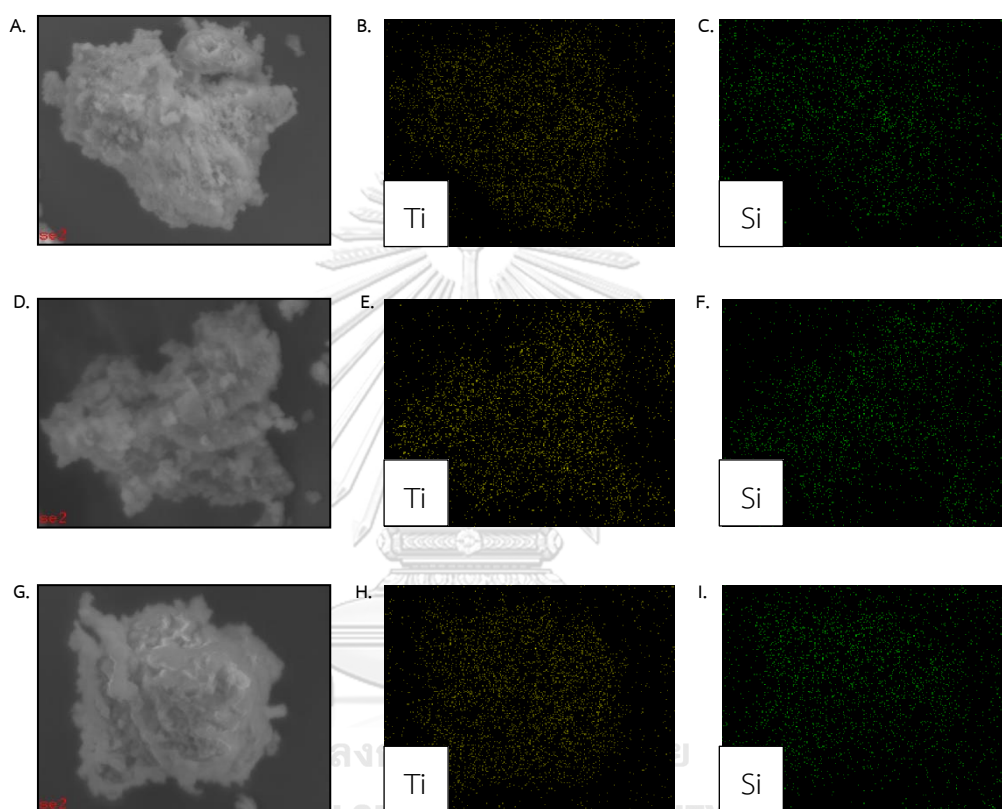


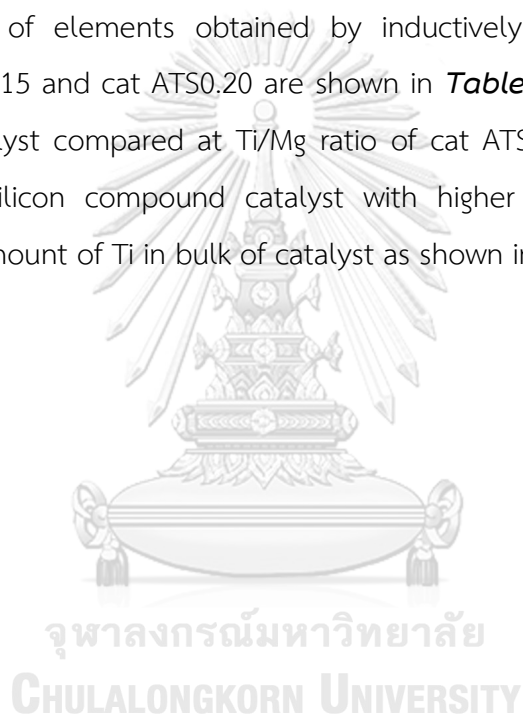
Figure 15 EDX characterization of cat ATS0.07 are A., B. And C.; cat ATS0.15 are D., E. and F. and cat ATS0.20 are G., H. and I. respectively.

4.2.1.1.2 Inductively coupled plasma (ICP)

Table 5 Inductive couple plasma characterization of cat ATS0.07, cat ATS0.15 and cat ATS0.20 in unit of mmol/mL

Catalyst	Ti	Mg	Ti/Mg	Si/Mg
cat ATS0.07	3.84	12.26	0.31	0.11
cat ATS0.15	5.99	12.10	0.49	0.12
cat ATS0.20	5.58	10.65	0.52	0.09

The composition of elements obtained by inductively coupled plasma of cat ATS0.07, cat ATS0.15 and cat ATS0.20 are shown in **Table 5**, indicating that amount of Ti in bulk catalyst compared at Ti/Mg ratio of cat ATS0.20 > cat ATS0.15 > cat ATS0.07, mixed silicon compound catalyst with higher amount of TEOS is not associated with amount of Ti in bulk of catalyst as shown in **Table 5**.



4.2.1.1.3 Fourier transform infrared spectroscopy of catalysts (FT-IR)

From the results of cat ATS0.07, cat ATS0.15 and cat ATS0.20 as shown in **Figure 16**, They exhibited the IR bands at 1163 cm^{-1} and 962 cm^{-1} and 1052.7 cm^{-1} indicating the Si-alkoxy compound and at 473.0 cm^{-1} assigned to O-C-C band[22, 23]. These confirmed that contained TEOS in structure of synthesized catalyst and the IR band at 489.8 cm^{-1} and 450.0 cm^{-1} were assigned to the Si-Cl band from the addition of SiCl_4 [22, 23]. The absorption peaks at $430\text{--}450\text{ cm}^{-1}$ are the peak of the titanium species on supported MgCl_2 [21], IR band in range of $430\text{--}450\text{ cm}^{-1}$, which overlapping to silicon compounds including Si-Cl band of SiCl_4 and O-C-C band of TEOS, assigned to Ti atom on MgCl_2 (110) crystal surface.

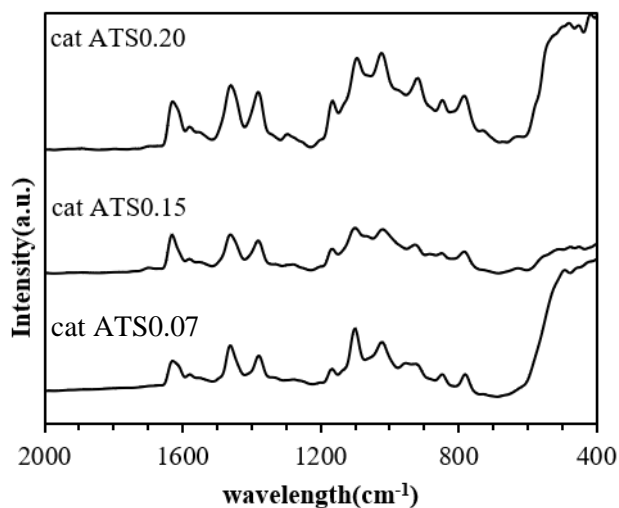


Figure 16 IR spectra of cat ATS0.07, cat ATS0.15 and cat ATS0.20

4.2.1.1.4 X-ray diffraction of catalyst (XRD)

From the results of X-ray diffraction as shown in **Figure 17** of cat ATS0.07, cat ATS0.15 and cat ATS0.20, it can be observed MgCl_2 peaks at $2\theta = 12.5^\circ$, 31° and 50° for all catalysts and XRD patterns of cat ATS0.07, cat ATS0.15. Cat ATS0.20 illustrated that mixing of silicon compounds including TEOS and SiCl_4 did not destroy the crystal structure of catalyst but amount of Si elemental composition in catalyst as shown in **Table 5**, corresponding to crystallinity that is shown on XRD patterns indicating that cat ATS0.15 had the highest amount of Si elemental composition. Thus, it had the lowest intensity of XRD pattern, then the crystallinity is lower than any other synthesized catalysts.

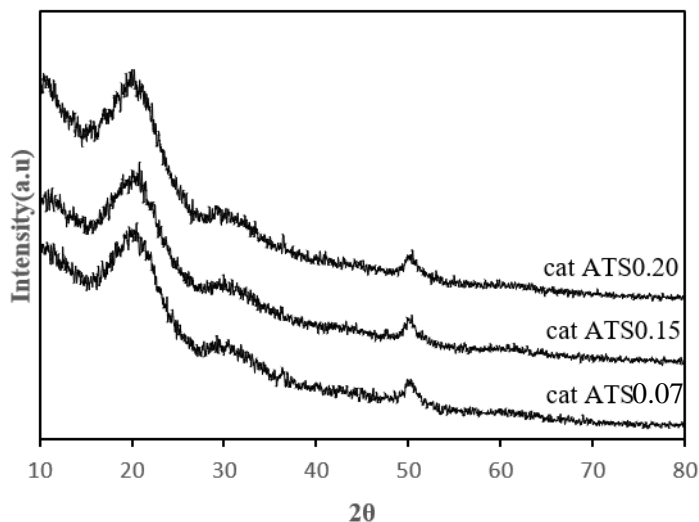


Figure 17 XRD patterns of cat ATS0.07, cat ATS0.15 and cat ATS0.20

4.2.1.2 Polymer characterization

4.2.1.2.1 Differential scanning calorimetry (DSC)

From the results of differential scanning calorimetry as shown in **Table 6**, the study of polymer was investigated regarding to melting temperature (T_m) and crystallinity of cat ATS0.07, cat ATS0.15 and cat ATS0.20. It was found that T_m of polymer of cat ATS0.07, cat ATS0.15 and cat ATS0.20 decreased with increasing amount of incorporated 1-hexene comonomer, which corresponding to the results of Fourier transform infrared spectroscopy. The crystallinity of cat ATS0.07, cat ATS0.15 and cat ATS0.20, which was calculated from ΔH_f in copolymerization system decreased with increasing amount of comonomer. However, in homopolymerization system, it was not significantly different. The incorporation of 1-hexene into backbone of polymer can result in chains of polymer did not pack so well leading to decreasing in crystallinity and then decreased T_m .

4.2.1.2.2 Fourier transform infrared spectroscopy (FT-IR)

In the part of FT-IR characterization, 1-hexene incorporations in polymer obtained from cat ATS0.07, cat ATS0.15 and cat ATS0.20 increased when % comonomer in copolymerization system increased. The more TEOS molar ratio using in synthesis catalyst is high, the more of 1-hexene incorporation is low. As shown in **Table 6**, cat ATS0.07 exhibited the best of comonomer response in ethylene/1-hexene copolymerization system. Comonomer response of mixed silicon compound addition is better than that of synthesized catalyst of part 4.1 as shown in **Table 3** including cat A, cat AT and cat AS because mixing of silicon compound between TEOS and SiCl_4 , which spacer group. Differences structure of silicon compound that anchored on surface of catalyst make catalyst have active site proper to copolymerization.

Table 6 Differential scanning calorimetry and Fourier transform infrared spectroscopy Characterization data of polymer catalyzed by cat ATS0.07, cat ATS0.15 and cat ATS0.20

Polymer of catalyst	comonomer (%)	ΔH_f (J/g)	crystallinity (%)	T_m (°C)	1-hexene incorporation (%wt)
cat ATS0.07	0	165.30	57.76	129.36	-
	3	120.80	42.21	117.18	1.50
	5	91.99	32.14	111.50	3.56
cat ATS0.15	0	152.90	53.43	128.77	-
	3	105.40	36.83	117.52	1.43
	5	84.07	29.38	115.66	2.25
cat ATS0.20	0	136.40	47.66	127.70	-
	3	99.71	34.84	119.11	1.29
	5	82.97	28.99	117.59	2.21

4.2.2 Catalytic activity

The polymerization activity is shown in **Table 7**. Considering, the polymerization of cat ATS0.07 and cat ATS 0.20, the catalytic activity decreasing with amount of 1-hexene comonomer increased because of steric hindrance effect of bulky of silicon compound on catalyst surface and comonomer arising from diffusion limitation. For polymerization of cat ATS0.15 with 3% v/v of 1-hexene comonomer, the activity decreased when compared with homopolymerization, whereas at 5% v/v of 1-hexene comonomer the activity slightly increased when compared with copolymerization with 3% v/v of 1-hexene comonomer. This is probably because of the system being proper to polyhexene polymerization. Thus, at 5% v/v of 1-hexene comonomer, it gives higher activity than at 3% v/v of 1-hexene comonomer in ethylene/1-hexene copolymerization system. The mixing of silicon compound in synthesized catalyst gives an active site being proper to polymerization because difference structure of silicon compounds, which acted as spacer group that make monomer easier to diffuse to active site, so overall activity of synthesized catalyst with mixed silicon compound is higher than activity of catalyst in part 4.1.

Table 7 Activity of synthesized Ziegler-Natta catalyst

catalyst	comonomer (%)	activity (kgPE.gcat ⁻¹ .h ⁻¹)	activity ratio
cat ATS0.07	0	7.99	1.00
	3	4.60	0.58
	5	3.92	0.49
cat ATS0.15	0	6.08	1.00
	3	5.31	0.87
	5	5.62	0.92
cat ATS0.20	0	6.27	1.00
	3	5.60	0.89
	5	5.38	0.86

Chapter 5 Conclusion and recommendation

5.1 Conclusion

From the first part of synthesized Ziegler-Natta catalyst by using silicon compound as additive including TEOS and SiCl_4 with TEOS had added in cat AT and SiCl_4 had added in cat AS, it revealed that addition of additive did not affect to morphologies of catalyst. However, TEOS addition in cat AT gave more fine particle than cat A and cat AS and TEOS addition in cat AT made catalyst less Ti content because of its bulky. The elemental distribution of Ti and Si on the surface of synthesized Ziegler-Natta catalyst exhibited good distribution on catalyst surface for both cat A, cat AT and cat AS. The TEOS addition in cat AT decreased crystallinity of catalyst, but did not destroy the crystal structure of catalyst and SiCl_4 added in cat AS also did not destroy the crystal structure of catalyst. The FT-IR spectra of cat AT and cat AS were found the peak that confirmed silicon compound in catalyst structure. Cat AS achieved the highest activity in homopolymerization and copolymerization in the part of comparison of silicon compounds and the better additive with good in comonomer response for copolymerization system is SiCl_4 . It indicated that cat AS is the best comonomer response catalyst that confirmed by ^{13}C -NMR characterization. Another part of synthesized Ziegler-Natta catalyst was studied on the mixed silicon compounds between TEOS and SiCl_4 with various TEOS/Mg molar ratio, but fixed SiCl_4 /Mg molar ratio. At the same TEOS/Mg molar ratio with part 1, the nomenclature was cat ATS0.07. Variation of TEOS/Mg, mol ratio at 0.15 is cat ATS0.15 and at 0.20 TEOS/Mg is cat ATS0.20. cat ATS0.07, cat ATS0.15 and cat ATS0.20 exhibited the same irregular shape and it showed that increasing of molar ratio of TEOS/Mg, it had more fine particle of synthesized catalyst. However, at higher TEOS/Mg, it is not associated with amount of Ti in bulk of catalyst. The elemental distribution of Ti and Si are good distributed on synthesized catalyst. The crystallinity of catalyst, mixing with silicon compounds including TEOS and SiCl_4 , varied by Si elemental composition content in bulk catalyst. Mixing of silicon compound did not destroy the crystal structure of catalyst, which confirmed by XRD patterns in **Figure 10.** The catalytic activity of cat ATS0.07 and cat ATS 0.20 decreased with increasing of 1-hexene

comonomer because of steric hindrance effect of bulky of silicon compound on catalyst surface and comonomer arising from diffusion limitation. However, the catalytic activity of cat ATS0.15 is not following the trend probably because the catalyst is proper to polyhexene polymerization.

The perspective of cat ATS0.07 achieved the best comonomer response because the appropriated ratio of silicon compound between TEOS/Mg and SiCl_4/Mg , which acted like spacer group, including that TEOS and SiCl_4 give an active site being proper to copolymerization.

5.2 Recommendation

1. Catalyst should characterized by solid state Nuclear magnetic resonance (Si-NMR) or X-ray photoelectron spectroscopy (XPS) in under out of oxygen system to determine structure of catalyst.
2. Polymers that of synthesized catalyst should characterized by Gel permeation chromatography (GPC) to determine molecular weight and molecular weight distribution of polymer and classify type of polyethylene and it should characterized by ^{13}C -Nuclear magnetic resonance (^{13}C -NMR) to determine type of copolymer.
3. Operating in gas phase system



APPENDIX

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CHULALONGKORN UNIVERSITY

APPENDIX A

A-1 Calculation of activity

$$\text{Activity} = \frac{\text{weight polymer (kgPE)}}{\text{weight catalyst (gcat)} \times \text{time (h.)}} \text{ kgPE.gcat}^{-1} \text{ .h}^{-1}$$

Example A-1 Polymer that of polymerized by synthesized catalyst is 120 g.

$$\text{Activity} = \frac{0.12 \text{ kgPE}}{0.02 \text{ gcat} \times 1 \text{ h.}} = 6.00 \text{ kgPE.gcat}^{-1} \text{ .h}^{-1}$$

(Polymerization condition: 20 mg of catalyst and polymerization 1 hour)

A-2 Calculation of %crystallinity (χ_c)

$$\% \text{Crystallinity } (\chi_c) = \frac{\Delta H \text{ of experimental (J/g)}}{\Delta H \text{ of polyethylene (J/g)}} \times 100$$

Note: ΔH is heat of fusion

Example A-2 ΔH of polymer that of synthesized catalyst is 162.4 J/g.

$$\% \text{Crystallinity } (\chi_c) = \frac{162.4 \text{ J/g}}{286.2 \text{ J/g}} \times 100 = 56.8$$

(ΔH of polyethylene is 286.2 J/g)

APPENDIX B

B-1 Scanning electron microscopy (SEM)

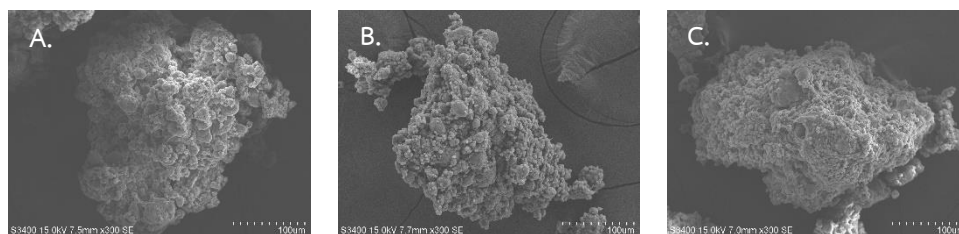


Figure B-1 SEM characterization at 300x magnification of polyethylene that of cat A: 0% comonomer is A., 3% comonomer B. and 5% comonomer is C. respectively.

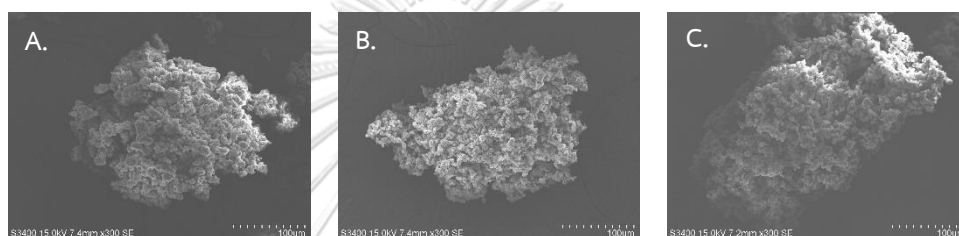


Figure B-2 SEM characterization at 300x magnification of polyethylene that of cat AT: 0% comonomer is A., 3% comonomer B. and 5% comonomer is C. respectively.

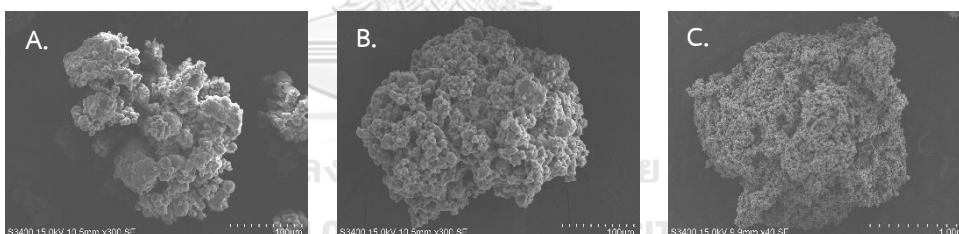


Figure B-3 SEM characterization at 300x magnification of polyethylene that of cat AS: 0% comonomer is A., 3% comonomer B. and 40x magnification of 5% comonomer is C. respectively.

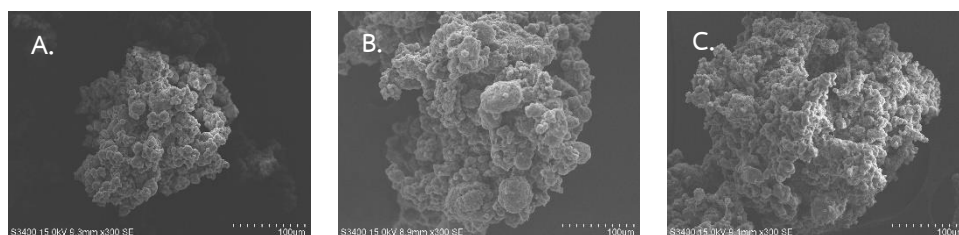


Figure B-4 SEM characterization at 300x magnification of polyethylene that of cat ATS: 0% comonomer is A., 3% comonomer B. and 5% comonomer is C. respectively.

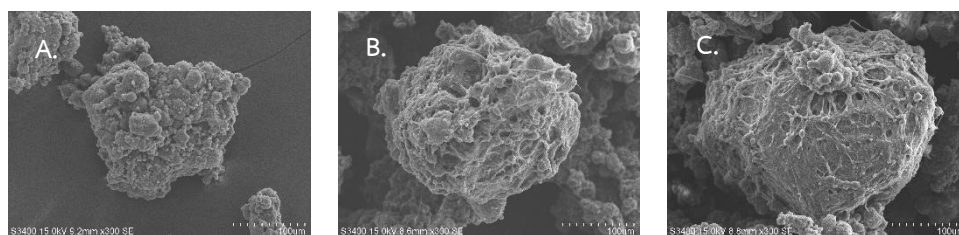


Figure B-5 SEM characterization at 300x magnification of polyethylene that of cat ATS0.15: 0% comonomer is A., 3% comonomer B. and 5% comonomer is C. respectively.

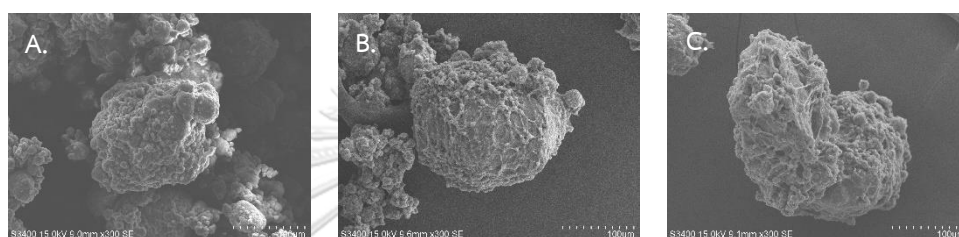


Figure B-6 SEM characterization at 300x magnification of polyethylene that of cat ATS0.20: 0% comonomer is A., 3% comonomer B. and 5% comonomer is C. respectively.

B-2 X-ray diffraction (XRD)

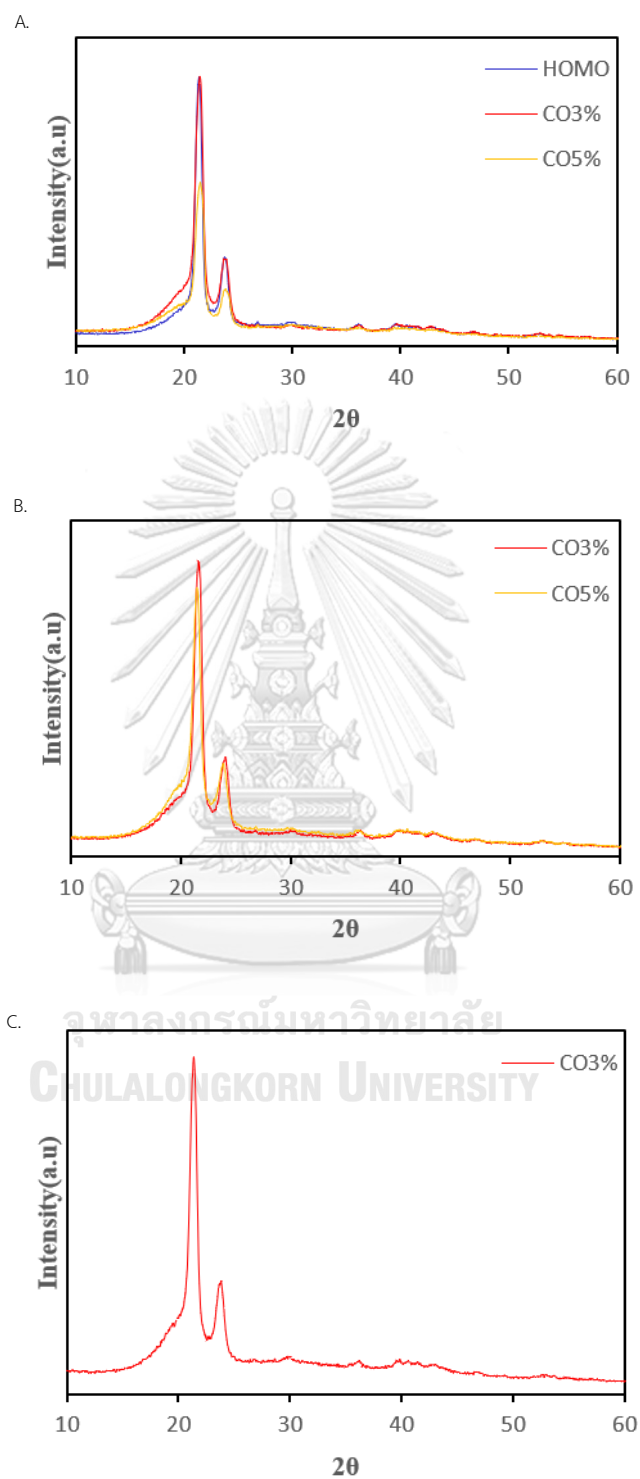
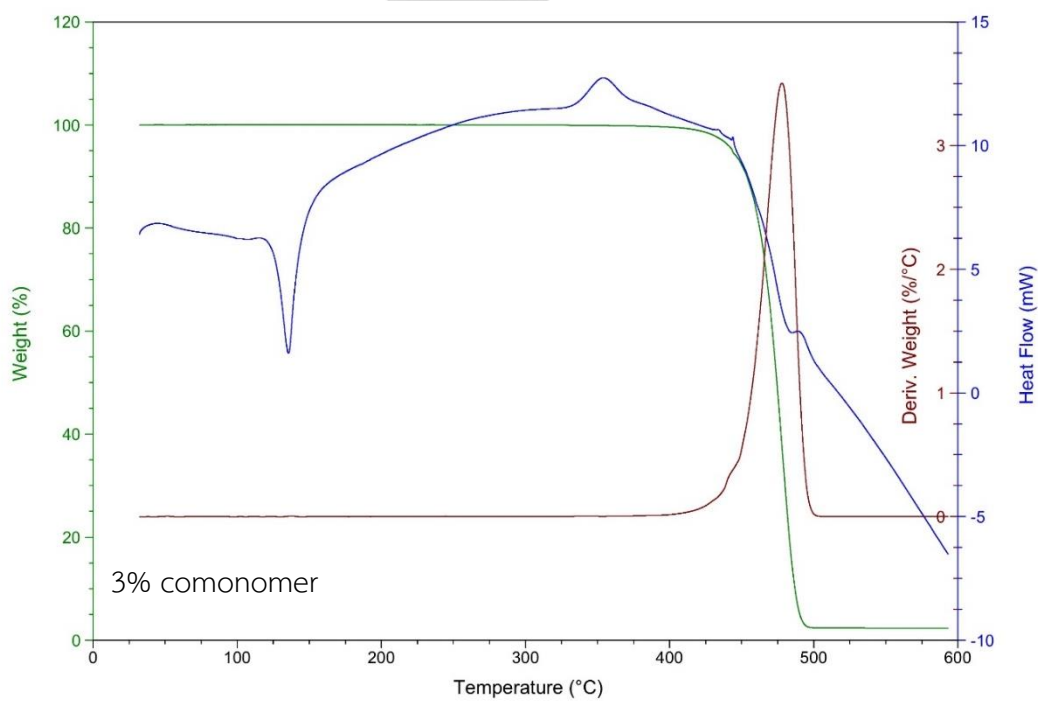
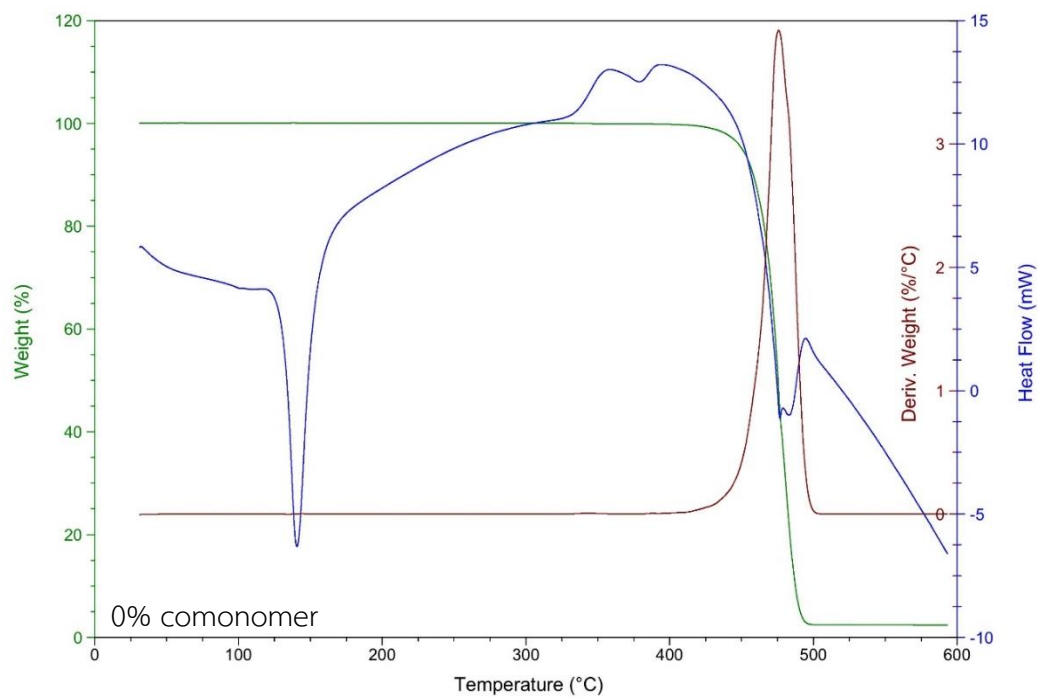
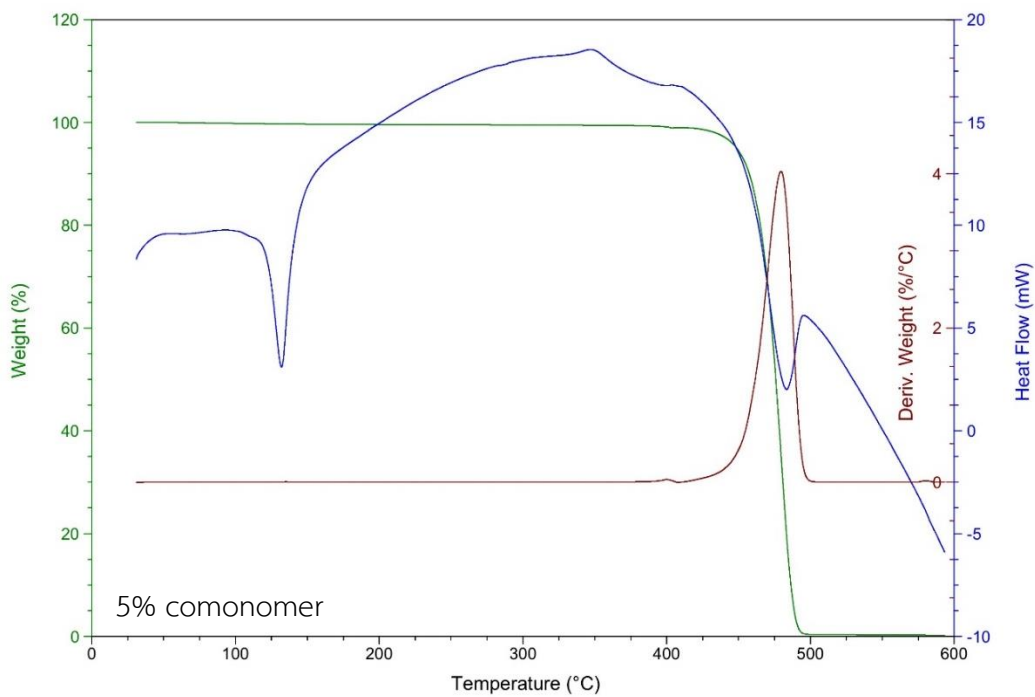


Figure B-7 XRD patterns of polyethylene that of cat ATS is A., cat ATS0.15 is B. and cat ATS0.20 is C. at 0% comonomer (HOMO), 3% comonomer B (CO3%) and 5% comonomer (CO5%) respectively.

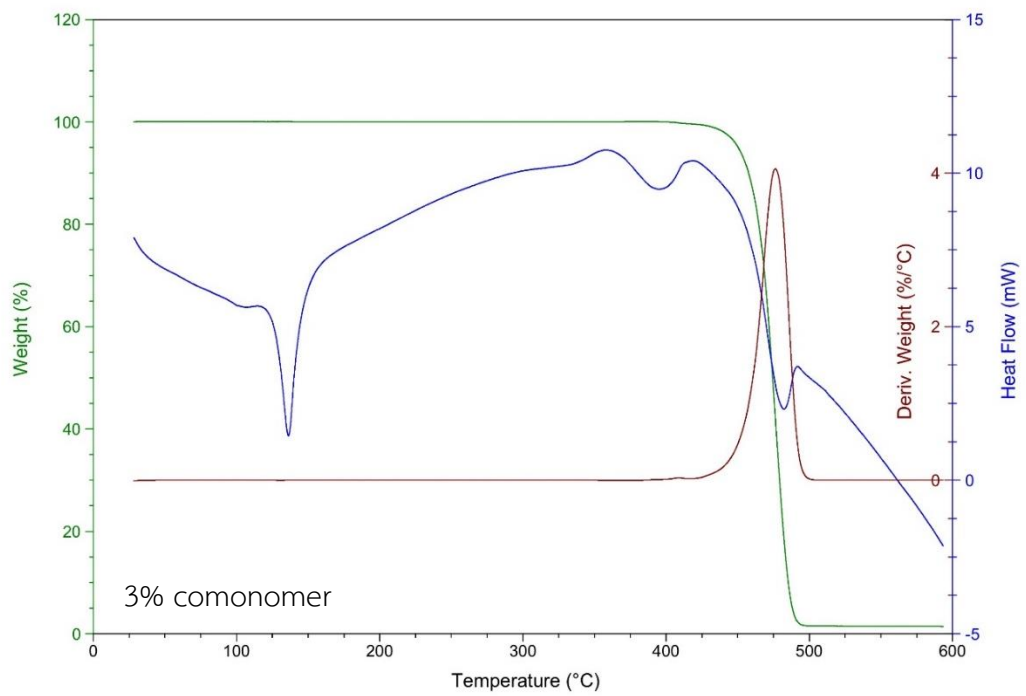
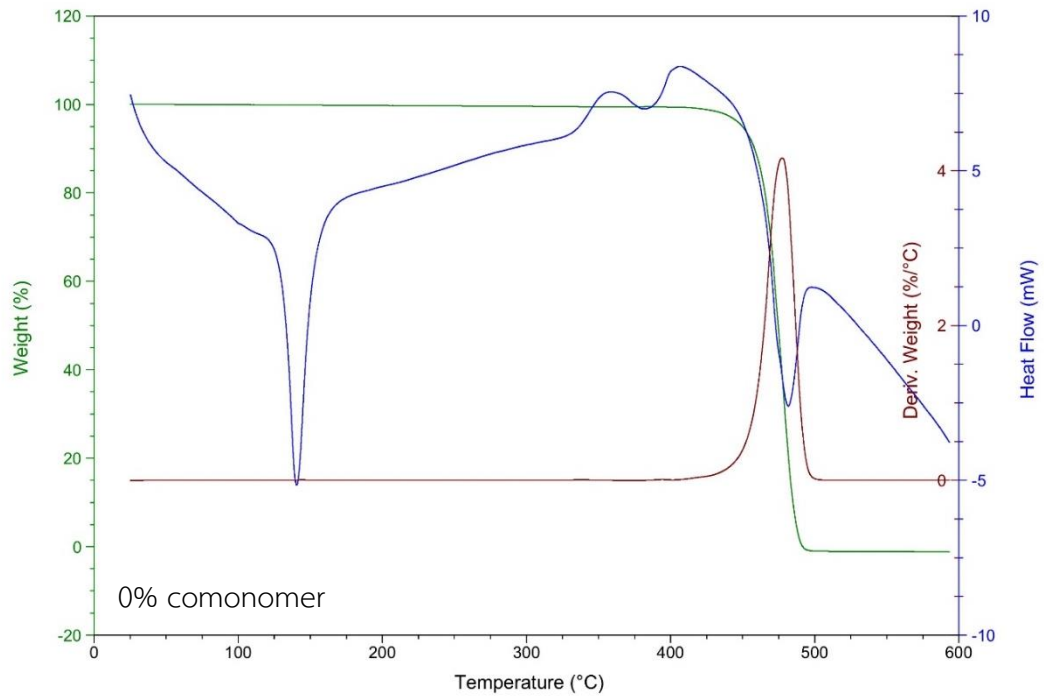
B-3 Thermogravimetric analysis (TGA)

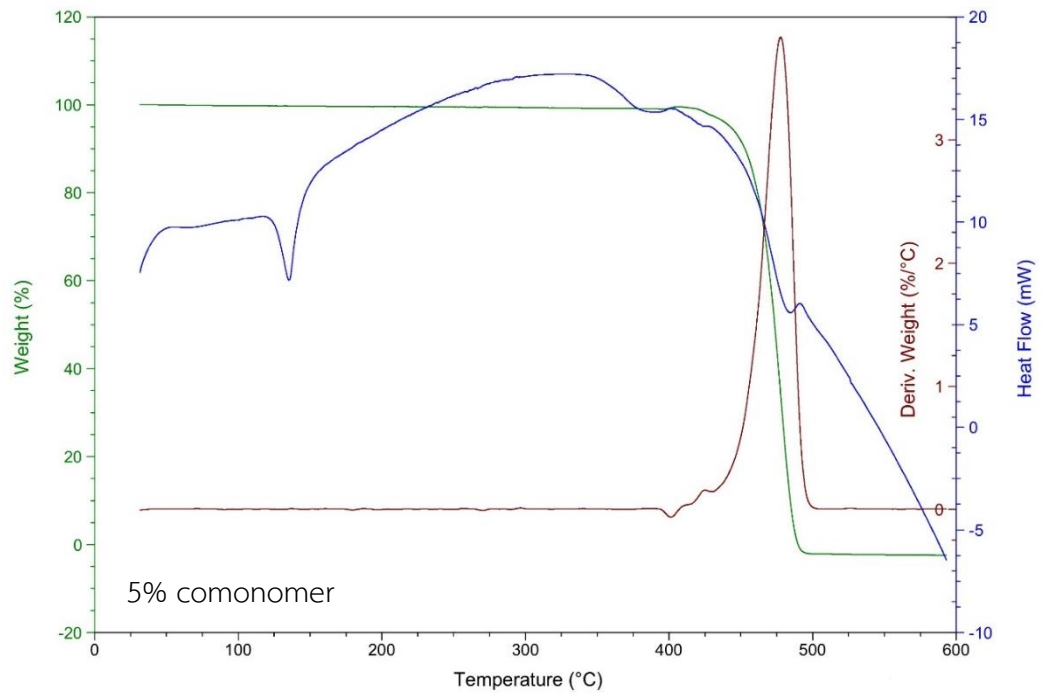
B-3.1 cat A



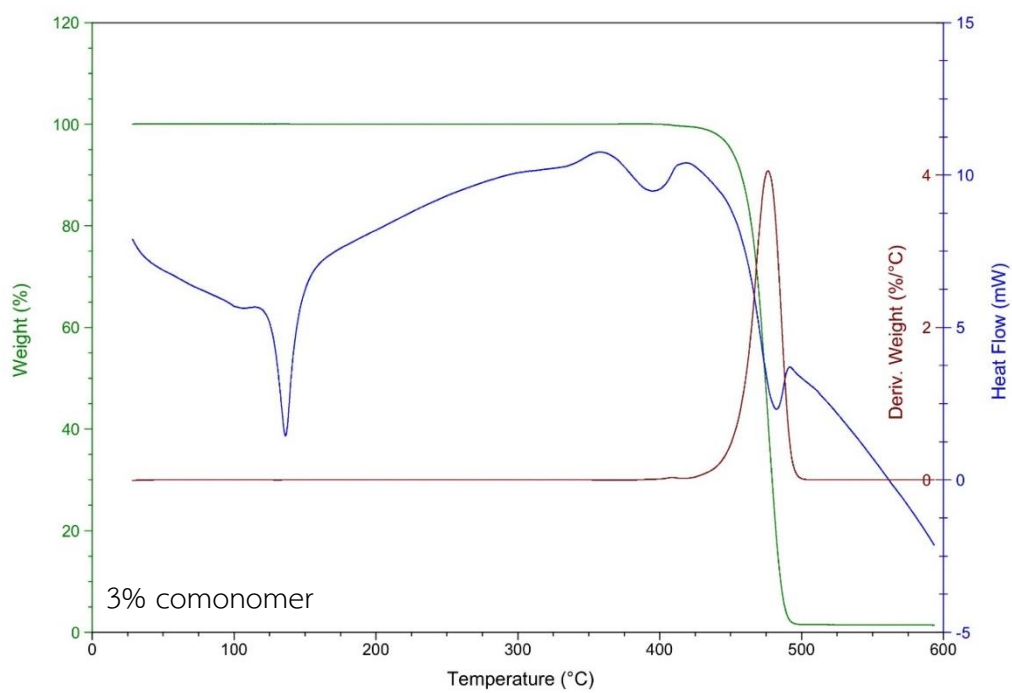
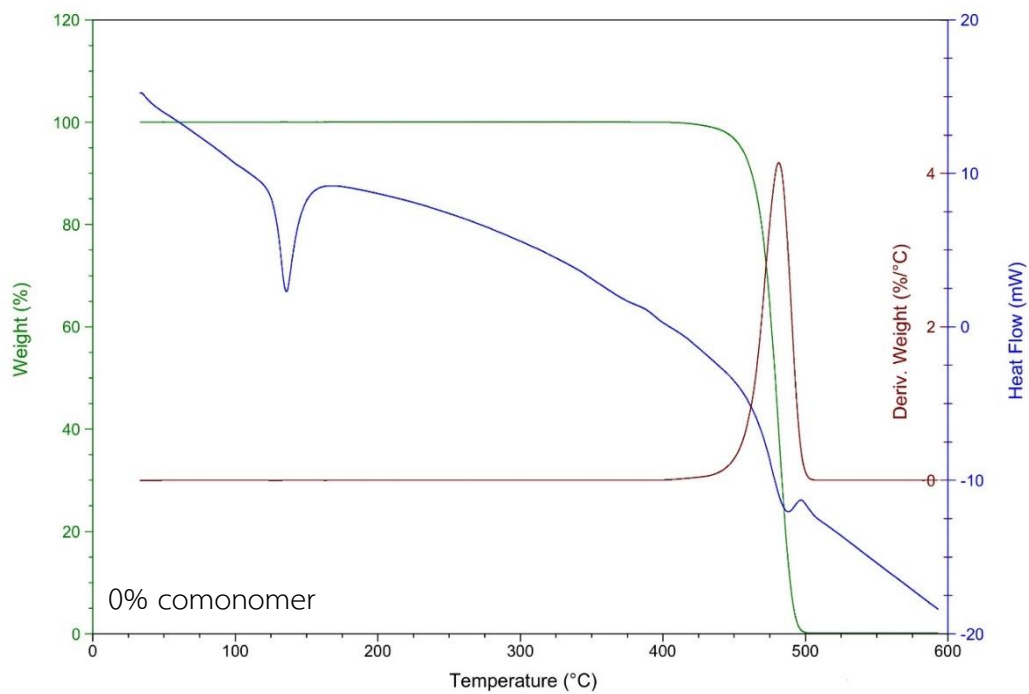


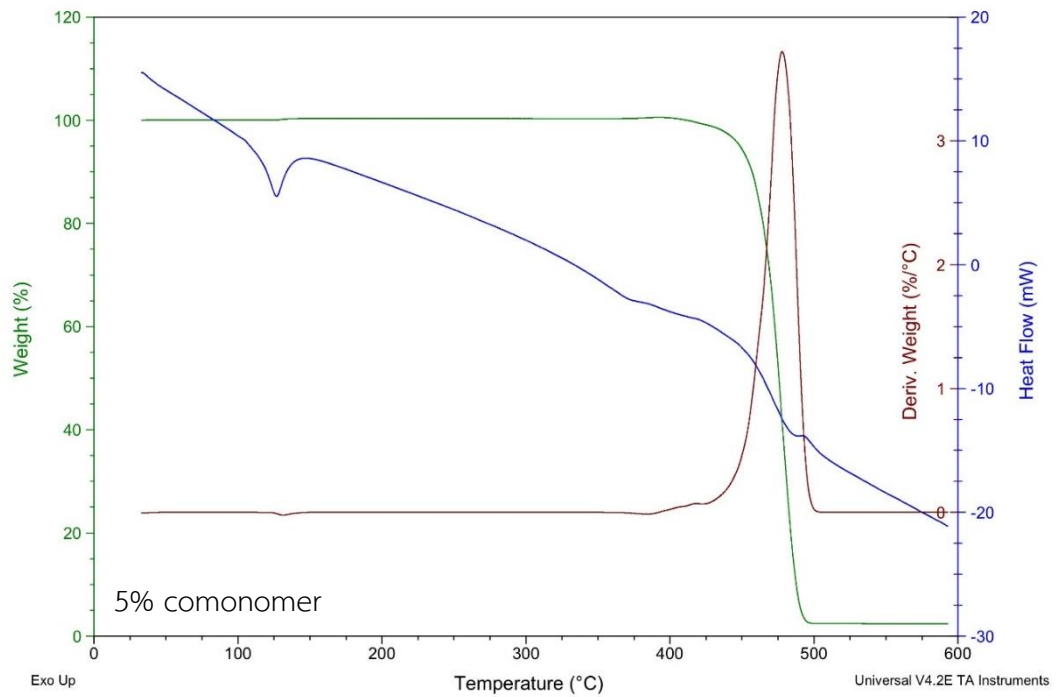
B-3.2 cat AT



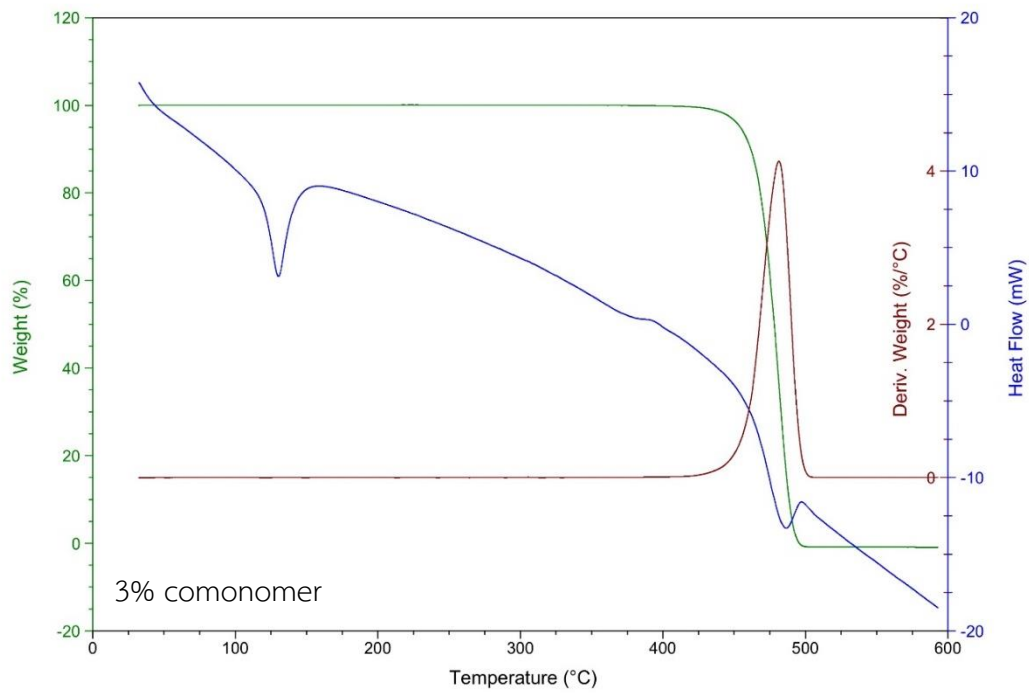
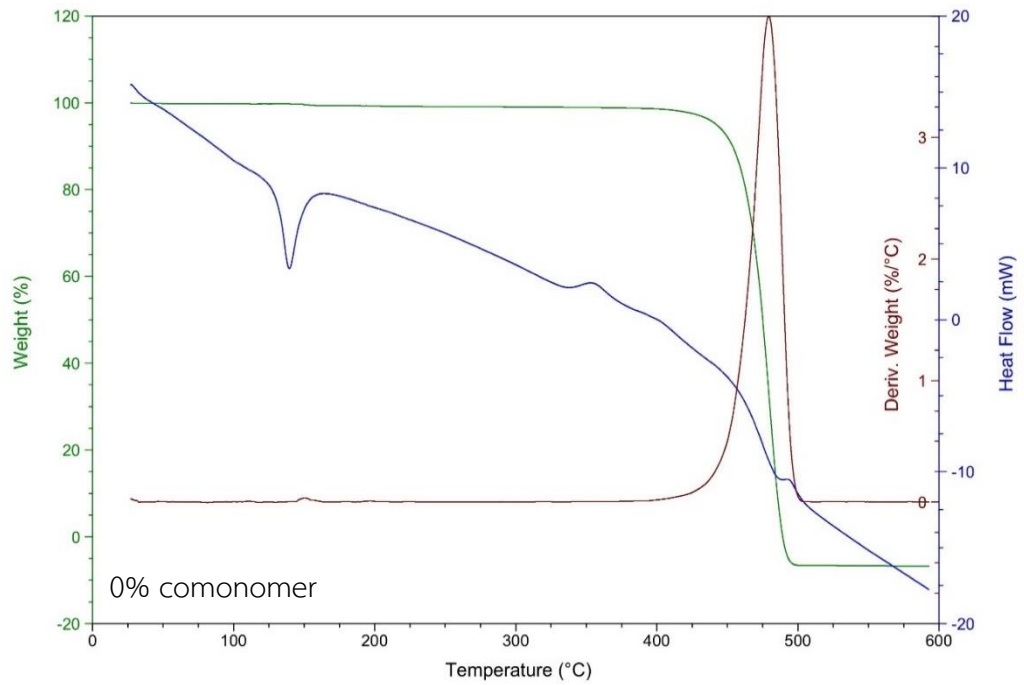


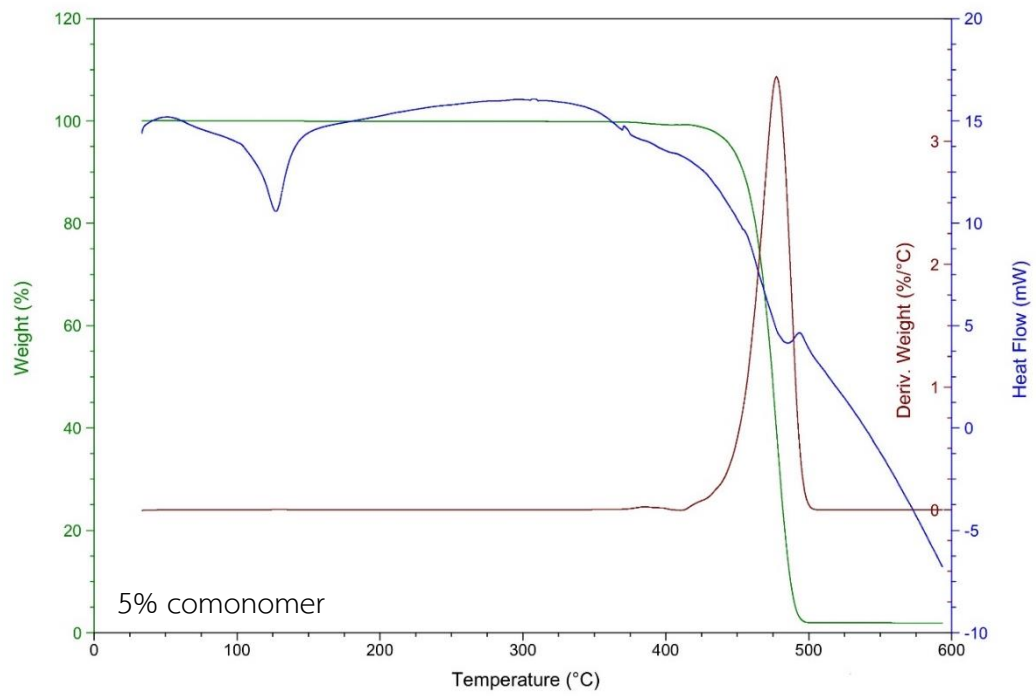
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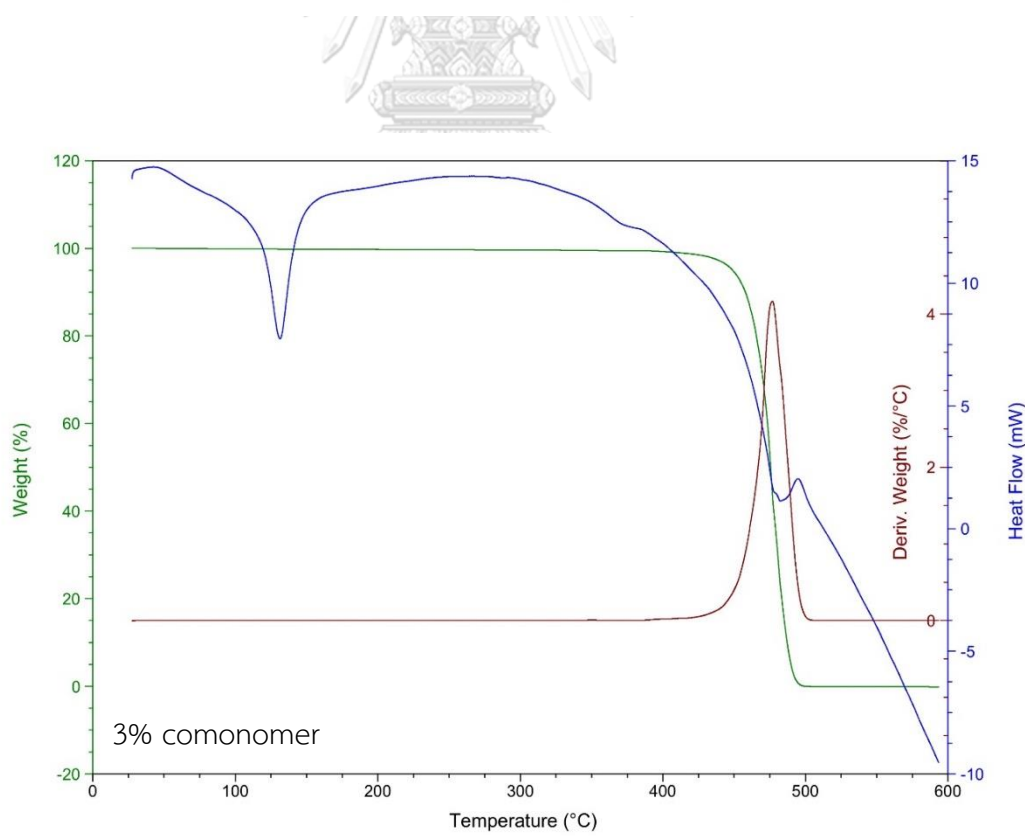
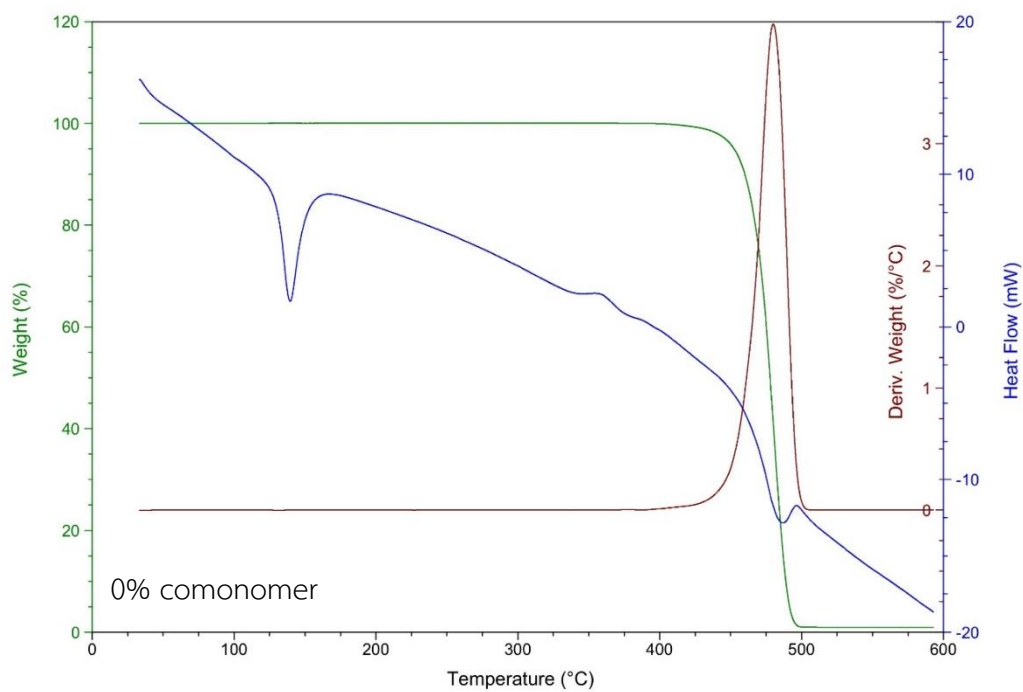


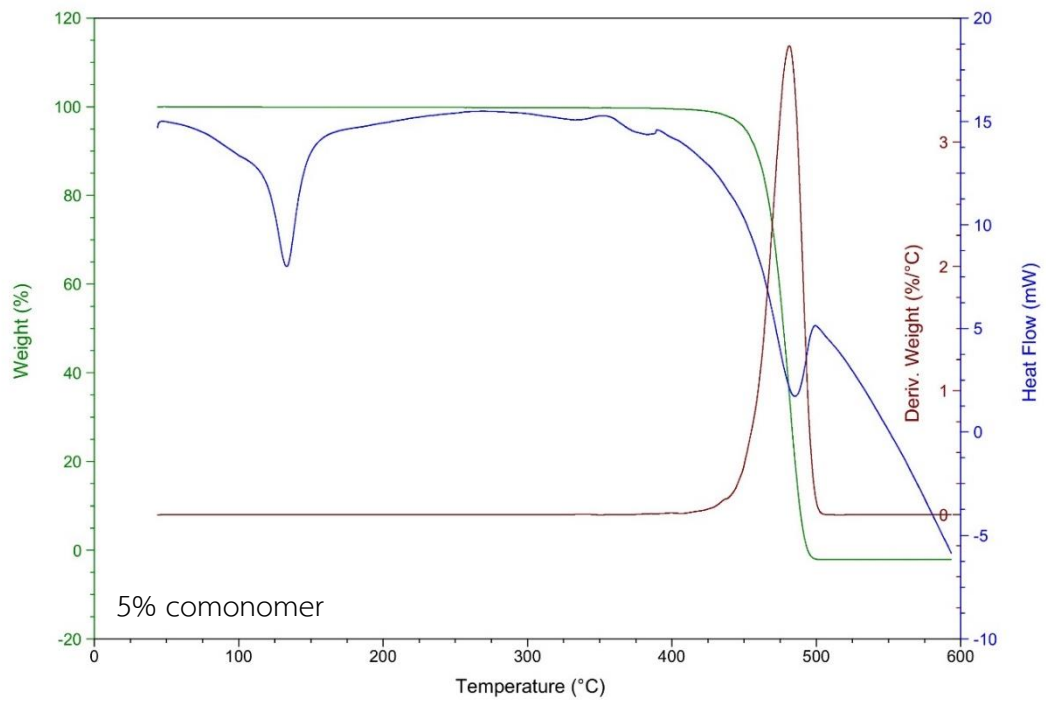
B-3.4 cat ATS



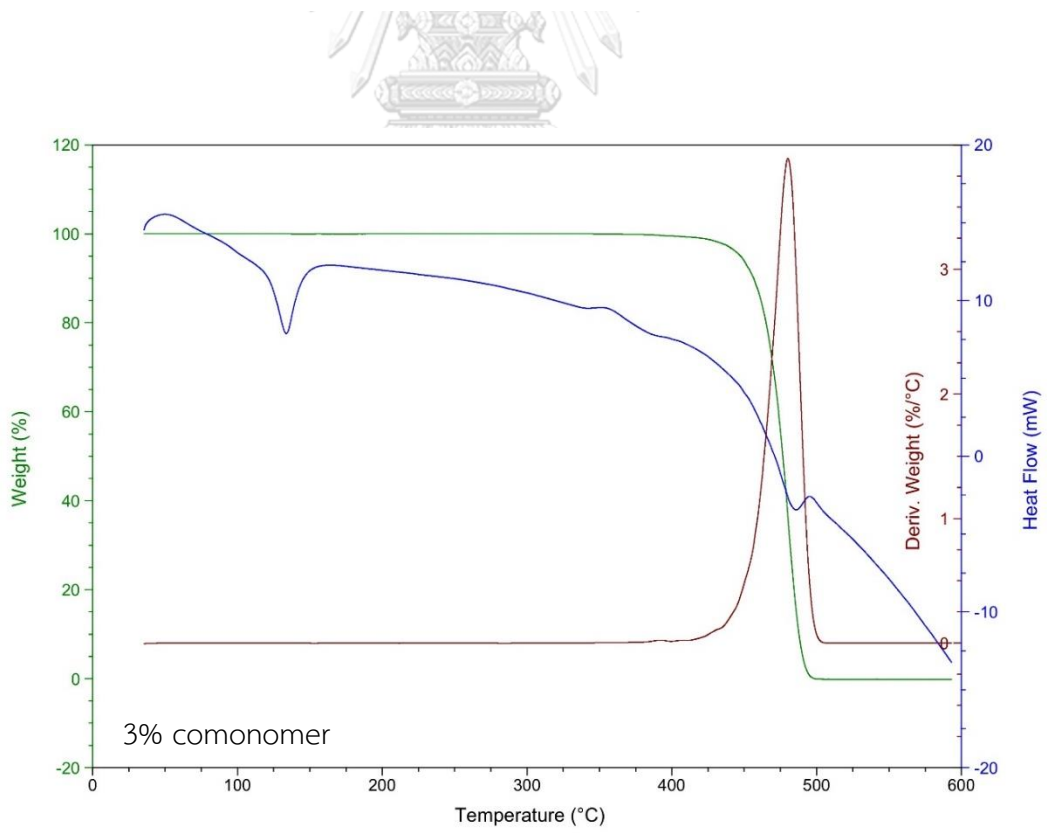
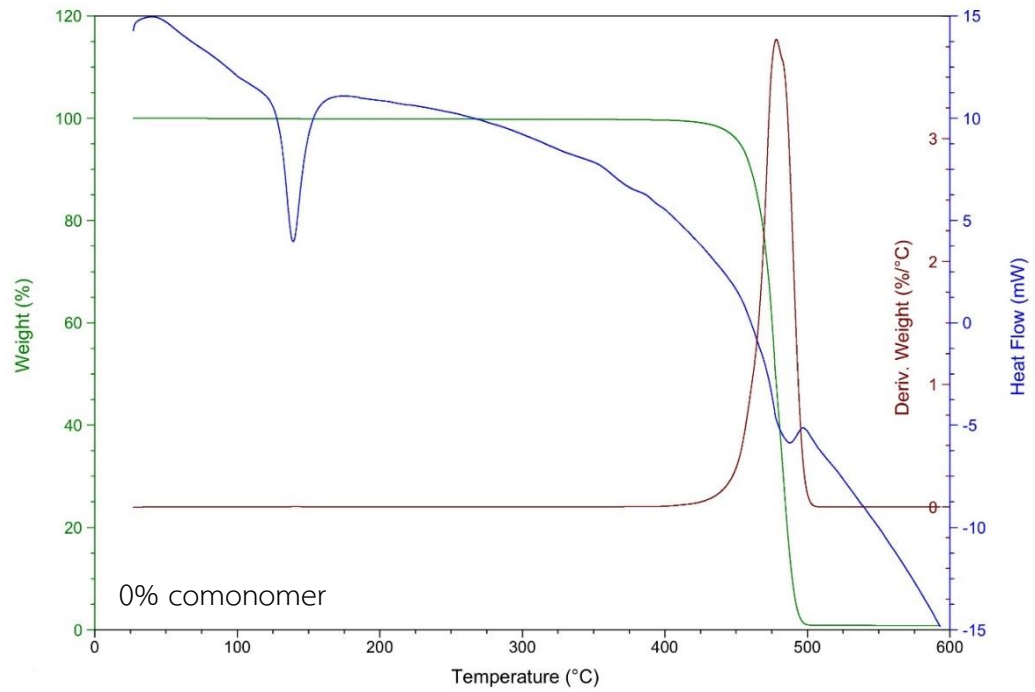


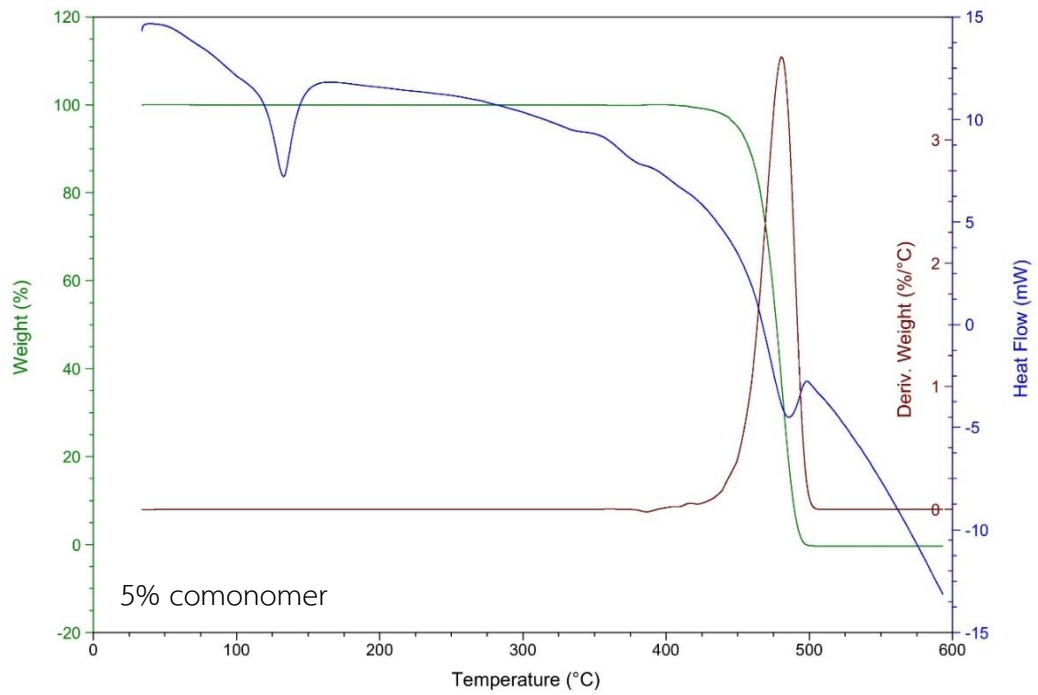
B-3.5 cat ATS0.15





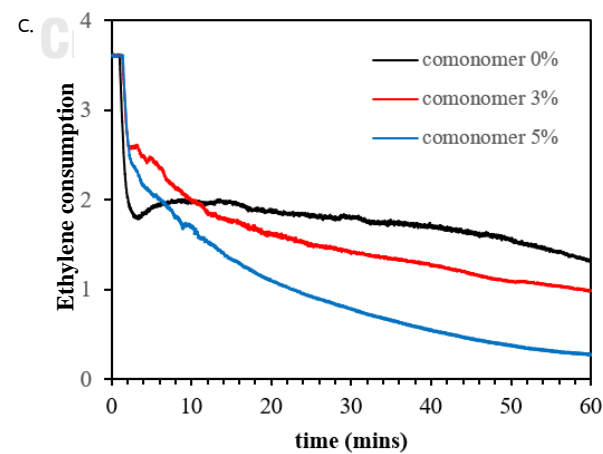
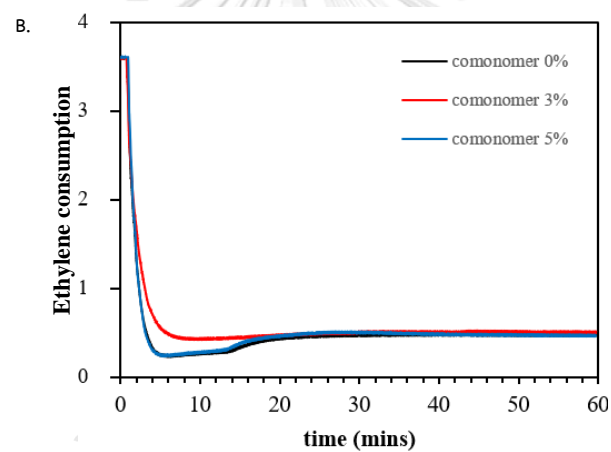
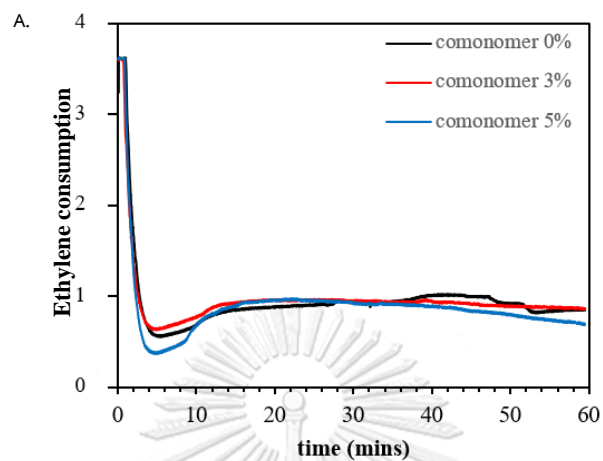
B-3.6 cat ATS0.20



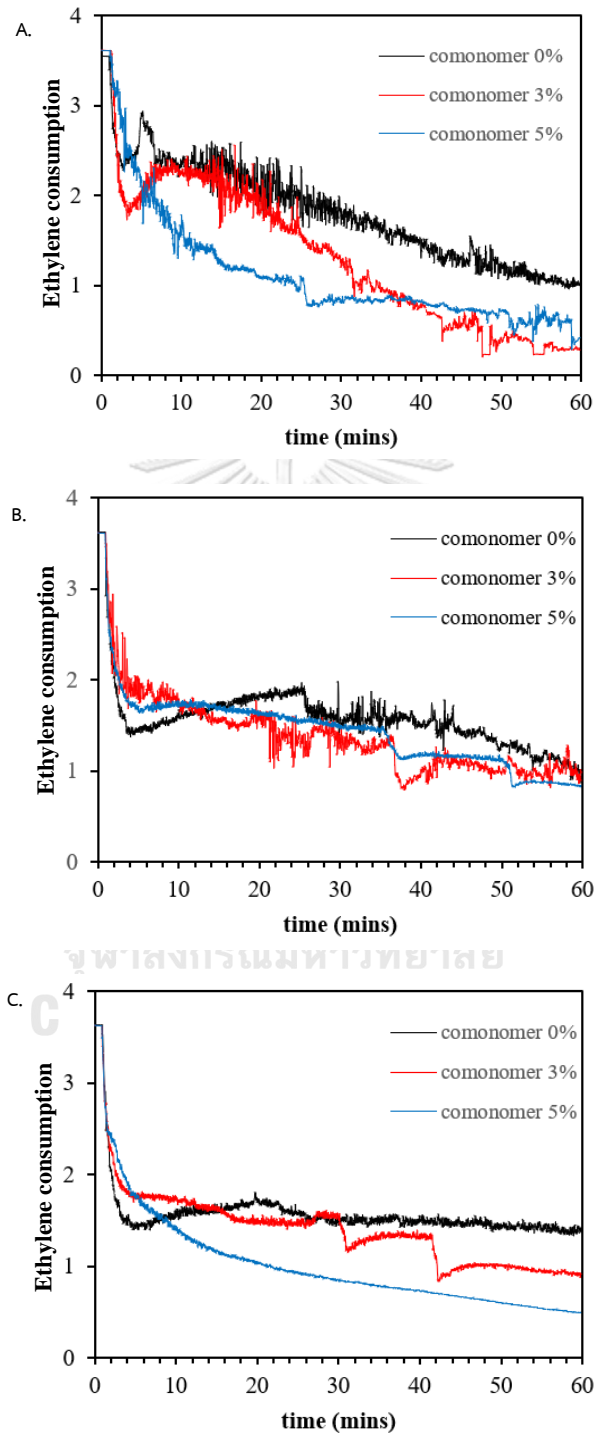


B-4 Ethylene consumption

B-4.1 Ethylene consumption of cat A is A., cat AT is B. and cat AS is C. in ethylene and ethylene/1-hexene polymerization



B-4.2 Ethylene consumption of cat ATS0.07 is A., cat ATS0.15 is B. and cat ATS0.20 is C. in ethylene and ethylene/1-hexene polymerization



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จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

VITA

NAME Wasinee Ousirisombat

DATE OF BIRTH 7 Feb 1996

PLACE OF BIRTH Lampang, Thailand

INSTITUTIONS ATTENDED The Bachelor of Science Degree in Chemistry

HOME ADDRESS 224 Bunyawat road Suandok subdistrict Mueang district
Lampang Thailand 52100

