โคพอลิเมอไรเซชันของเอทิลีนกับแอลฟาโอเลฟินใช้เมทิลอะลูมินอกเซนบนตัวรองรับแบบออกไซด์ผสมบนระบบตัวเร่งปฏิกิริยาเซอร์โคโนซีน

นาย สุทธิ งามโพธิ์ศรี

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ETHYLENE/α-OLEFIN COPOLYMERIZATION USING MIXED OXIDES-SUPPORTED METHYLALUMINOXANE WITH ZIRCONOCENE CATALYST

Mr. Sutti Ngamposri

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for the Degree of Master of Engineering in Chemical Engineering
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คำสำคัญ : ตัวเร่งปฏิกิริยาแบบมีตัวรองรับ / ปฏิกิริยาโคพอลิเมอร์ของเอทิลีนกับแอลฟาโอเลฟิน

นายสุทธิ งามโพธิ์ศรี: โคพอลิเมอไรเซชันของเอทิลีนกับแอลฟาโอเลฟินใช้เมทิลอะลูมินอกเซนบนตัวรองรับแบบออกไซด์ผสมบนระบบตัวเร่งปฏิกิริยาเซอร์โคโนซีน (ETHYLENE/α-OLEFIN COPOLYMERIZATION USING MIXED OXIDES-SUPPORTED METHYLALUMINOXANE WITH ZIRCONOCENE CATALYST) อ.ที่ปรึกษา : อ.ดร. บรรเจิด จงสมจิตร, 115 หน้า ISBN 974-17-6445-6

ในการค้นคว้าวิจัยนี้เนื่องมาจากทางธุรกิจมีความสนใจในการใช้ตัวเร่งปฏิกิริยาเมทัลโลซีนสำหรับการเกิดพอลิเมอร์ในอุตสาหกรรมพอลิโอเลฟินและสาเหตุนี้เองทำให้มีการค้นคว้าเกี่ยวกับการใช้ตัวเร่งปฏิกิริยานี้ให้มีประสิทธิภาพมากขึ้น ระบบตัวเร่งปฏิกิริยาแบบเอกพันธ์มีข้อเสียอย่างชัดเจนอยู่สองข้อคือไม่สามารถควบคุมโครงสร้างของพอลิเมอร์และปัญหาการสูญเสียพอลิเมอร์ที่สังเคราะห์ได้เนื่องจากการติดอยู่ข้างถังปฏิกรณ์ ปฏิกิริยาของเอทิลีนกับแอลฟ่าโอเลฟินทำให้เกิดพอลิเมอร์ซึ่งมีสมบัติเฉพาะเรียกว่าพอลิเมอร์สายโซ่ที่มีความหนาแน่นต่ำ อุณหภูมิในการสังเคราะห์พอลิเมอร์ต่อการเตรียมพอลิเมอร์แบบผสมของเอทิลีน/1-ออกทีนด้วยระบบตัวเร่งปฏิกิริยาเอทิลีนบิสอินดีนิลเซอร์โคเนียมไดคลอไรด์-ไตรเมทิลอะลูมินัม (TMA) บนตัวรองรับแบบออกไซด์ผสมซึ่งมีการปรับปรุงด้วยเมทิลอะลูมินอกเซน (MAO) โดยการเปลี่ยนแปลงอัตราส่วนของตัวรองรับแบบออกไซด์ผสมจากการทดลองพบว่าความว่องไวของตัวเร่งปฏิกิริยาปฏิกิริยาก่อนการเกิดปฏิกิริยา ในปฏิกิริยาการเตรียมโคพอลิเมอร์ของเอทิลีน/แอลฟา-โอเลฟิน (1-เฮกซีน 1-ออกทีน และ 1-เดกซีน) พบว่าการใช้ตัวรองรับออกไซด์ผสมที่ถูกปรับปรุงด้วยเมทิลอะลูมิ-นอกเซน มีค่าความว่องไวในการเกิดปฏิกิริยาสูงสุดที่อัตราส่วนของตัวรองรับออกไซด์ไททาเนียซิลิกา20:80โดยน้ำหนักที่ความเข้มข้นของตัวเร่งปฏิกิริยา คือ 5.00 x10^{-5} โมลต่อลิตร และอุณหภูมิที่ใช้ในการสังเคราะห์พอลิเมอร์คือ 70 องศาเซลเซียส ผลการศึกษาคุณสมบัติอื่นของพอลิเมอร์ถูกศึกษาในการวิจัยนี้ด้วย

ภาควิชา…………..วิศวกรรมเคมี………… ลายมือชื่อนิสิต…………………………………….

สาขาวิชา…………วิศวกรรมเคมี………… ลายมือชื่ออาจารย์ที่ปรึกษา……………………..….

ปีการศึกษา……….2547………………….

##4670560221 : MAJOR CHEMICAL ENGINEERING
KEY WORD : SUPPORTED METALLOCENE CATALYST / COPOLYMERIZATION OF ETHYLENE/ALPHA-OLEFINS / ZIRCONOCENE

SUTTI NGAMPOSRI : ETHYLENE/α-OLEFIN COPOLYMERIZATION USING MIXED OXIDES-SUPPORTED METHYLALUMINOXANE WITH ZIRCONOCENE CATALYST. THESIS ADVISOR : BUNJERD JONGSOMJIT, Dr.Ing. 115 pp. ISBN 974-17-6445-6

In this research, due to the commercial interest of using metallocene catalysts for olefin polymerization, it has led to extensive efforts to utilize metallocene catalysts efficiently. However, it was found that homogeneous metallocene catalysts have two major disadvantages; (i) the lack of morphology control and (ii) reactor fouling. Therefore, binding these metallocene catalysts onto inorganic supports as supported metallocene catalysts can overcome those drawbacks. Copolymerization of ethylene with higher 1-olefins is a commercial importance for production of elastomer and linear low-density polyethylene (LLDPE). Metallocene catalysts have been studied for such a purpose because an excellence of comonomer insertion can be achieved. However, using a metallocene catalyst can result in a narrow molar mass distribution (MMD) with poor processibility. Thus, broader MMD of polymers is preferred in terms of processability. This could be achieved using mixed oxide supports to generate different natures of active sites. In this present study, mixed supports between TiO_2 and SiO_2 with various ratios of TiO_2:SiO_2 were used as supported methylaluminoxane (MAO) cocatalyst for ethylene/1-octene copolymerization using zirconocene catalyst. The polymers obtained with various ratios of mixed supports were further characterized. It was found that using TiO_2:SiO_2 (20:80 by weight) could result in an increased activity compared to SiO_2 or even TiO_2 itself. Effect of the TiO_2:SiO_2 ratios of mixed supports on the polymer properties were also discussed.

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CHAPTER I

INTRODUCTION

In plastic industries, polyolefin is one of the largest businesses with a lot of worldwide production per years and only polyethylene alone in excess of two part three of all production. Despite this size, polyolefin are a fast growing segment of the polymer industry with the highest amount of nearly 4 million tons a year. The productions of polyolefin are more and more estimated to be around 140 million tons in 2010 [1]. Because of increasing section of the polymer new catalysts, especially, by metallocene and other metal complexes which are able to control the polymer structure and the other properties have been developed.

In 1957 Natta and Breslow discovered the first homogeneous metallocene catalyst. The ethylene polymerization with the titanocene catalyst Cp_2TiCl_2 and the triethylaluminum(TEA) as cocatalyst was reported by Natta, it used admission in Ziegler-Natta olefin polymerization systems [2]. The activity of the metallocene with the Ziegler-Natta cocatalyst was very low and showed little commercial promise. In the 1980's, new cocatalyst was discovered by Walter Kaminsky. While studying a homogeneous $Cp_2ZrCl_2/Al(CH_3)_3$ polymerization system, water was unexpected introduced into the reactor leading to an utmost active ethylene polymerization system. The hydrolysis of the trimethylaluminum, $Al(CH_3)_3$ is cause of formation the cocatalyst methylaluminoxane (MAO) which precede to the high activity [3]. It has proven to be a major breakthrough for the polyolefin industry.

When the high activity Cp_2ZrCl_2/MAO ethylene polymerization system was discovered by Kaminsky, metallocene catalysts have slowly evolved as producers propel to commercialize the technology. The metallocene catalyst required excessive molar Al to transition metal ratios (Al:M) of between 1000-15000:1 in order to achieve the high activities. Such ratios are commercially unacceptable in terms of the cost and the amount of residues left in the polymer (commercial Ziegler-Natta systems typically require Al to M ratios of between 50-200:1). A significant effort has been put into reducing the amount of MAO required and this has led to the development of many systems with non-aluminum cocatalysts, such as $[B(C_6F_5)_4]$-

and $[CH_3B(C_6F_5)_3]$-. Other developments include the mono-Cp constrained geometry catalysts which have been primarily developed by Dow and Exxon. Significant effort has also gone into heterogenizing the catalyst system by supporting the metallocene and cocatalyst onto an inorganic support such as silica, alumina, magnesium chloride, starch, zeolites, and polymers [4].

Therefore, heterogeneous catalysts offer several additional advantages important to industry; they improved product morphology and reactor fouling and the ability to be used in gas and/or slurry phase synthesis methods more compatible with existing technology. Supported metallocene have a lower catalytic activity than their reciprocal homogeneous metallocene systems. To overcome the preparation complexities of traditionally supported metallocene catalysts, metallocene can be supported in situ, which eliminates the need for a supporting step before polymerization. These systems have a good catalytic activity, produce polymers with a good morphology and high bulk density and do not cause reactor fouling. Additionally, they can be activated with trimethylaluminum (TMA) alone in the nonexistence of soluble methyl aluminoxane (MAO) in the polymerization reactor [5].

Copolymer of ethylene with 1-alkenes such as propene, 1-butene, 1-hexene, and 1-octene are very important commercial products classified as linear low density polyethylene (LLDPE) and/or very low density polyethylene (VLDPE) [4]. Rheological and mechanical properties of polymers do not depend only on their average molecular weights, but also on their molecular weight distribution (MWD) and short chain branching distribution (SCBD). Even though the control of MWD and SCBD is very important, conventional heterogeneous Ziegler-Natta catalysts have limitations in controlling MWD and SCBD, their polymers produced by these catalysts show broad MWD and SCBD, due to the multiple types of nature active sites on the catalyst. Metallocene catalyst permits the synthesis of polymers with narrow and well controlling MWD and SCBD at high polymerization rates [6].

Many inorganic supports such as SiO_2, Al_2O_3 and $MgCl_2$ have been investigated [4]. It was reported SiO_2 is perhaps the most attractive support so far. However, the properties of SiO_2 itself may not be completely satisfied for all purposes based on the polymer produced. Thus, a modification of SiO_2 properties is required. Preparation of TiO_2–SiO_2 mixed oxides using new reaction parameters, in order to obtain materials potentially useful as catalysts and catalyst supports. Such Ti/Si materials would not only take advantage of both TiO_2 (an n-type semiconductor and active catalyst support) and SiO_2 (high thermal stability and excellent mechanical strength), but would also extend their applications through the generation of new catalytic active sites due to the interaction of TiO_2 with SiO_2 [7].

The objectives of this investigation was to study and characterize effects of mixed oxides supported MAO with zirconocene catalyst on catalytic property during the copolymerization of ethylene with α-olefins such as 1-hexene, 1-octene, 1-decene including develop a better understanding on how mixed oxide supports may change the nature of active site on the catalyst.

This thesis was divided into five chapters. Chapter I involved an overview of the use of metallocene catalyst for the polyolefin industry. In Chapter II, knowledge and open literature dealing with metallocene catalysis for olefin polymerization were presented. The literature review was accentuated metallocene catalyst system used for copolymerization of ethylene with α-olefins. The experimental procedure as well as the instrument and techniques used for characterizing the resulting polymers were also described in Chapter III.

In Chapter IV, the results on ethylene and α-olefins copolymerization were presented. Effects of various mixed oxides conditions in ethylene/1-octene, comonomer impact on nature of active site on the catalyst content in the copolymer. Effect of system between homopolymer and copolymer can be changed other polymer properties. The characteristics support and catalyst precursors using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectrometer (EDX) and obtained copolymer using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and ^{13}C-nuclear magnetic resonance (^{13}C –NMR).

Finally, conclusions of this work and some recommendations for future research work were provided in Chapter V.

CHAPTER II

LITERATURE REVIEW

2.1. Background on Polyolefin Catalysts

Polyolefins can be produced with free radical initiators, Phillips type catalysts, Ziegler-Natta catalysts and metallocene catalysts. Ziegler-Natta catalysts have been most widely used because of their broad range of application. However, Ziegler-Natta catalyst provides polymers having broad molecular weight distribution (MWD) and composition distribution due to multiple active sites formed [8].

Metallocene catalysts have been used to polymerize ethylene and α-olefins commercially. The structural change of metallocene catalysts can control composition distribution, incorporation of various comonomers, MWD and stereoregularity [9].

2.1.1. Catalyst Structure

Metallocene is a class of compounds in which cyclopentadienyl or substituted cyclopentadienyl ligands are π-bonded to the metal atom. The stereochemistry of biscyclopentadienyl (or substituted cyclopentadienyl)-metal bis (unibidentate ligand) complexes can be most simply described as distorted tetrahedral, with each η^5-L group (L = ligand) occupying a single co-ordination position, as in Figure 2.1 [10].

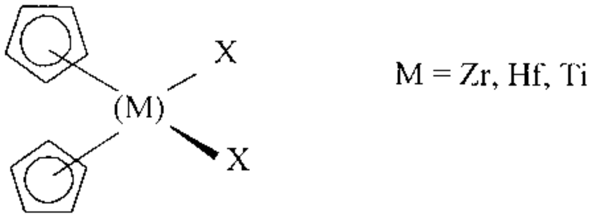

Figure 2.1 Molecular structure of metallocene

Representative examples of each category of metallocenes and some of zirconocene catalysts are shown in Table 2.1 and Figure 2.2, respectively.

Table 2.1 Representative Examples of Metallocenes [10]

Category of metallocenes	Metallocene Catalysts
[A] Nonstereorigid metallocenes	1) Cp_2MCl_2 (M = Ti, Zr, Hf) 2) Cp_2ZrR_2 (M = Me, Ph, CH_2Ph, CH_2SiMe_3) 3) $(Ind)_2ZrMe_2$
[B] Nonstereorigid ring-substituted metallocenes	1) $(Me_5C_5)_2MCl_2$ (M = Ti, Zr, Hf) 2) $(Me_3SiCp)_2ZrCl_2$
[C] Stereorigid metallocenes	1) $Et(Ind)_2ZrCl_2$ 2) $Et(Ind)_2ZrMe_2$ 3) $Et(IndH_4)_2ZrCl_2$
[D] Cationic metallocenes	1) $Cp_2MR(L)^+[BPh_4]^-$ (M = Ti, Zr) 2) $[Et(Ind)_2ZrMe]^+[B(C_6F_5)_4]^-$ 3) $[Cp_2ZrMe]^+[(C_2B_9H_{11})_2M]^-$ (M = Co)
[E] Supported metallocenes	1) Al_2O_3-$Et(IndH_4)_2ZrCl_2$ 2) $MgCl_2$-Cp_2ZrCl_2 3) SiO_2-$Et(Ind)_2ZrCl_2$

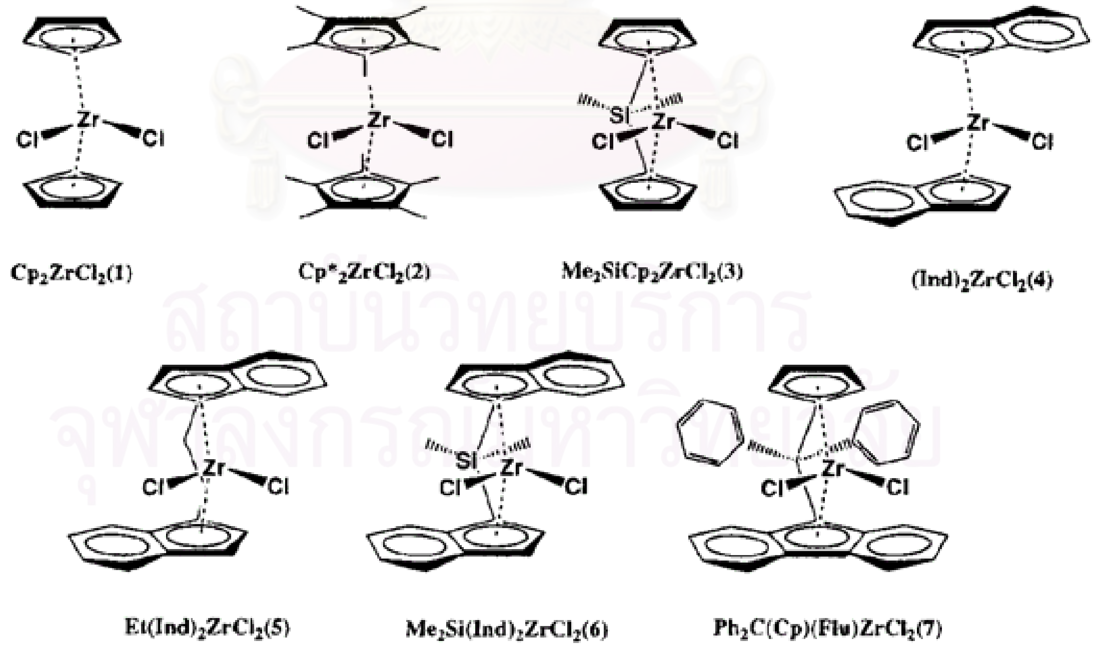

Figure 2.2 Some of zirconocene catalysts structure [11]

Composition and types of metallocene have several varieties. When the two cyclopentadienyl (Cp) rings on either side of the transition metal are unbridged, the metallocene is nonstereorigid and it is characterized by C_{2v} symmetry. The Cp_2M (M = metal) fragment is bent back with the centroid-metal-centroid angle θ about 140^o due to an interaction with the other two σ bonding ligands [12]. When the Cp rings are bridged (two Cp rings arranged in a chiral array and connected together with chemical bonds by a bridging group), the stereorigid metallocene, so-called ansa-metallocene, could be characterized by either a C_1, C_2, or C_s symmetry depending upon the substituents on two Cp rings and the structure of the bridging unit as schematically illustrated in Figure 2.3[10].

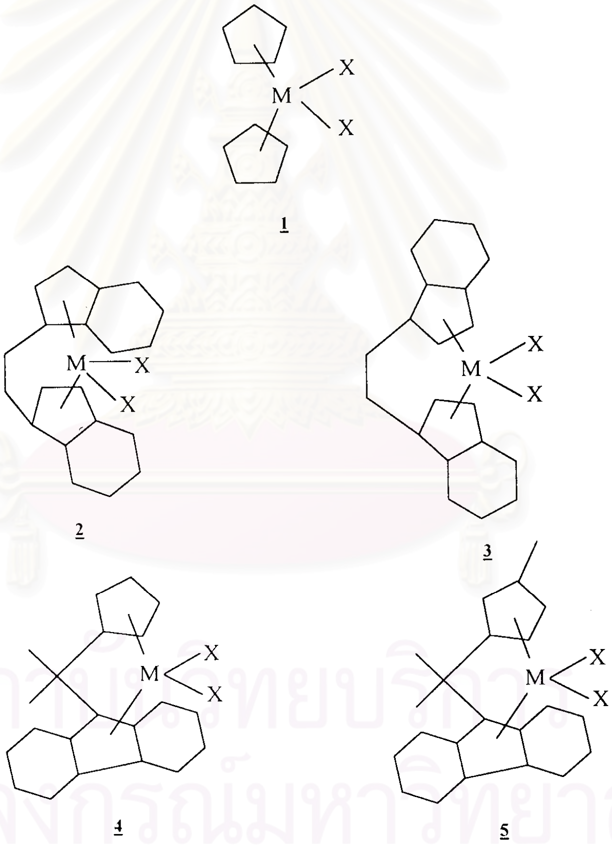

Figure 2.3 Scheme of the different metallocene complex structures [10]. Type 1 is C_{2v}-symmetric; Type 2 is C_2-symmetric; Type 3 is C_s-symmetric; Type 4 is C_s-symmetric; Type 5 is C_1-symmetric.

2.1.2. Polymerization Mechanism

The mechanism of catalyst activation is not clearly understood. However, alkylation and reduction of the metal site by a cocatalyst (generally alkyl aluminum or alkyl aluminoxane) is believed to generate the cationic active catalyst species.

First, in the polymerization, the initial mechanism started with formation of cationic species catalyst that is shown below.

Initiation

$$Et(Ind)_2ZrCl_2 + Al(CH_3)_3 \longrightarrow Et(Ind)_2ZrClMe + Al(CH_3)_2Cl$$

Propagation proceeds by coordination and insertion of new monomer unit in the metal carbon bond. Cossee mechanism is still one of the most generally accepted polymerization mechanism (Figure 2.4) [13]. In the first step, monomer forms a complex with the vacant coordination site at the active catalyst center. Then through a four-centered transition state, bond between monomer and metal center and between monomer and polymer chain are formed, increasing the length of the polymer chain by one monomer unit and generating another vacant site.

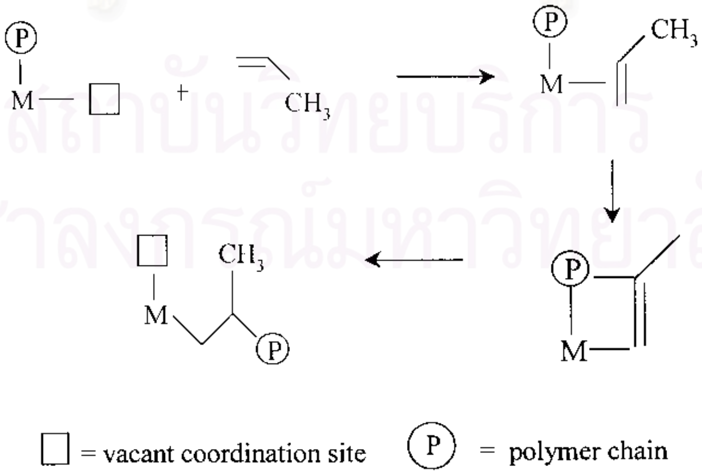

Figure 2.4 Cossee mechanism for Ziegler-Natta olefin polymerization [13].

The trigger mechanism has been proposed for the polymerization of α-olefin with Ziegler-Natta catalysts [1]. In this mechanism, two monomers interact with one active catalytic center in the transition state. A second monomer is required to form a new complex with the existing catalyst-monomer complex, thus trigger a chain propagation step. No vacant site is involved in this model. The trigger mechanism has been used to explain the rate enhancement effect observed when ethylene is copolymerized with α-olefins.

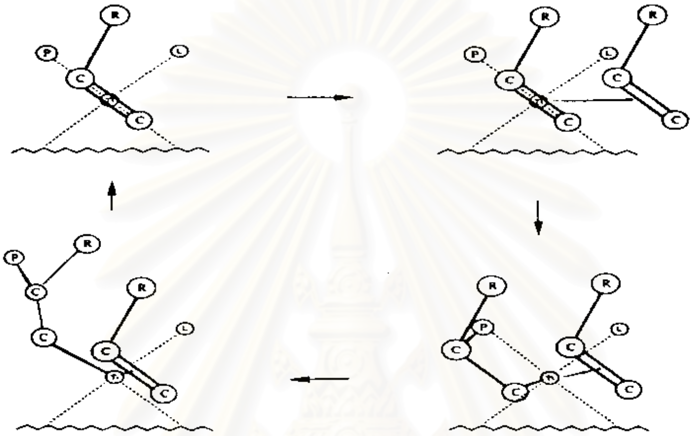

Figure 2.5 The propagation step according to the trigger mechanism [1].

After that , the propagation mechanism in polymerization shown in Figure 2.6.

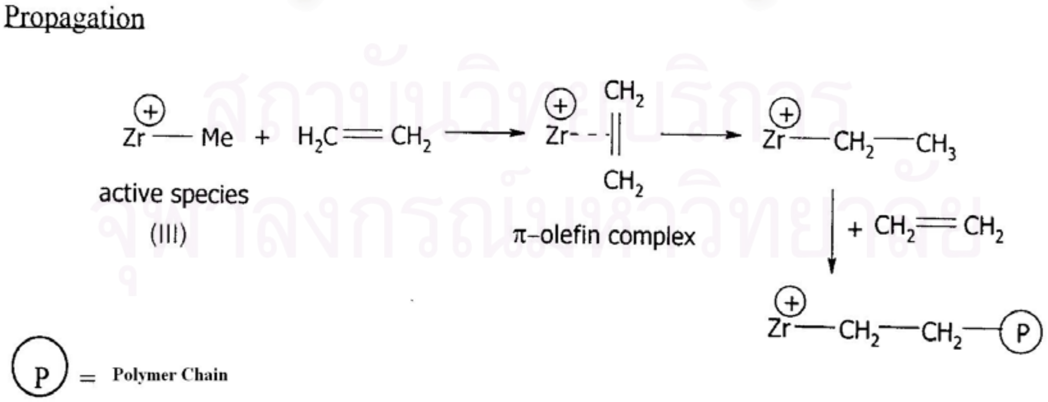

Figure 2.6 Propagation mechanism in polymerization

Finally, the termination of polymer chains can be formed by 1) chain transfer via β-H elimination, 2) chain transfer via β-Me elimination, 3) chain transfer to aluminum, 4) chain transfer to monomer, and 5) chain transfer to hydrogen (Figure 2.7-2.11)[10]. The first two transfer reactions form the polymer chains containing terminal double bonds.

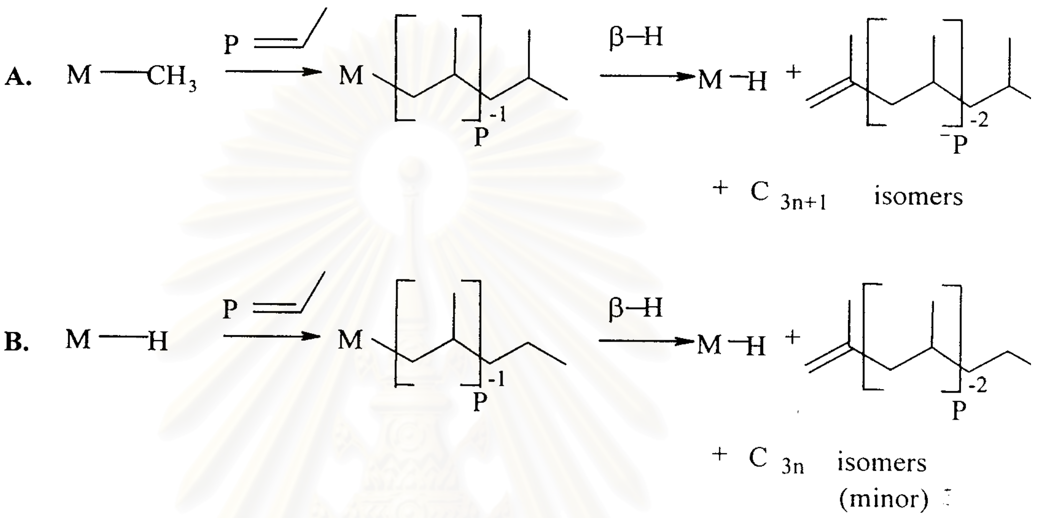

Figure 2.7 Chain transfer via β-H elimination [10]

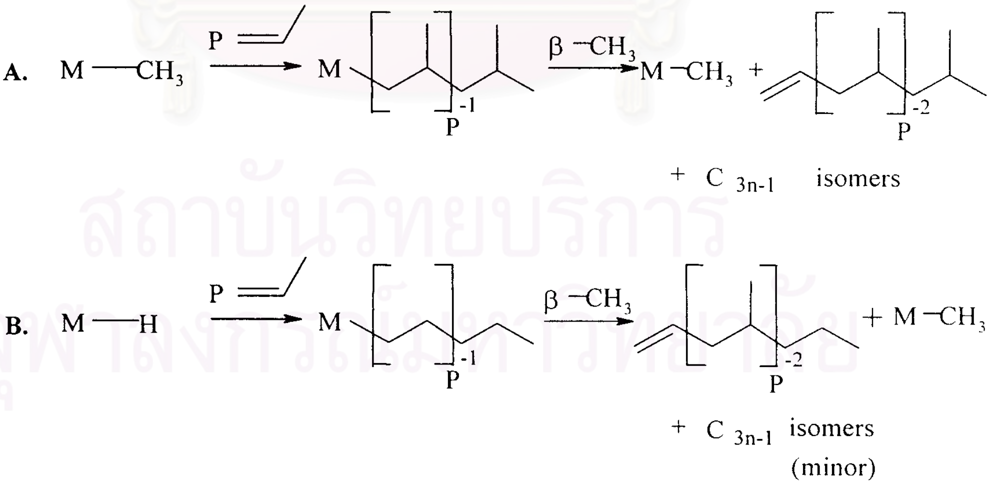

Figure 2.8 Chain transfer via β-CH_3 elimination [10]

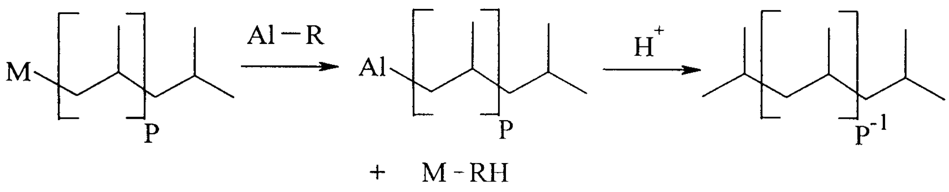

Figure 2.9 Chain transfer to aluminum [10]

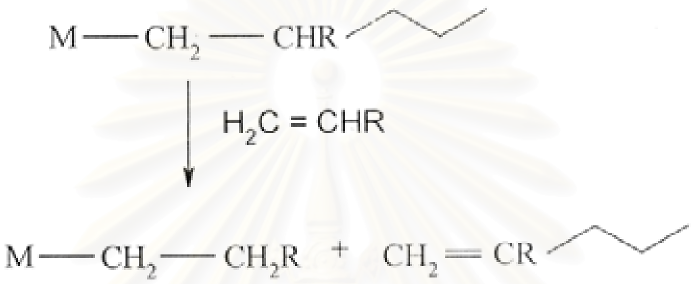

Figure 2.10 Chain transfer to monomer [10]

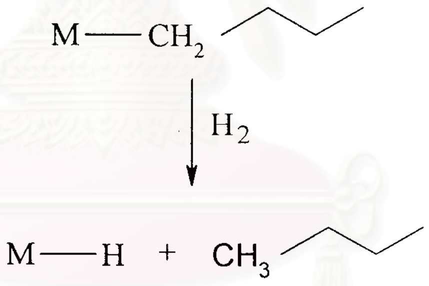

Figure 2.11 Chain transfer to hydrogen [10]

2.1.3. Cocatalysts

Metallocene catalysts have to be activated by a cocatalyst. The most common types of cocatalysts are alkylaluminums including methylaluminoxane (MAO), trimethylaluminum (TMA), triethylaluminum (TEA), triisobutylaluminum (TIBA) and cation forming agents such as $(C_6H_5)_3C^+(C_6F_5)_4B^-$ and $B(C_6F_5)_3$ [14].

Among these, MAO is a very effective cocatalyst for metallocene. However, due to the difficulties and costs involved in the synthesis of MAO, there has been considerable effort done to reduce or elimination the use of MAO. Due to difficulties in separation, most commercially available MAO contains a significant fraction of TMA (about 10-30%) [15]. This TMA in MAO could be substantially eliminated by toluene-evaporation at 25°C.

Indeed, the difficulties encountered to better understand the important factors for an efficient activation are mainly due to the poor knowledge of the MAO composition and structure. Several types of macromolecular arrangements, involving linear chains, monocycles and/or various three-dimensional structures have been successively postulated. These are shown in Figure 2.12. In recent work, a more detailed image of MAO was proposed as a cage molecule, with a general formula $Me_{6m}Al_{4m}O_{3m}$ (m equal to 3 or 4) [16].

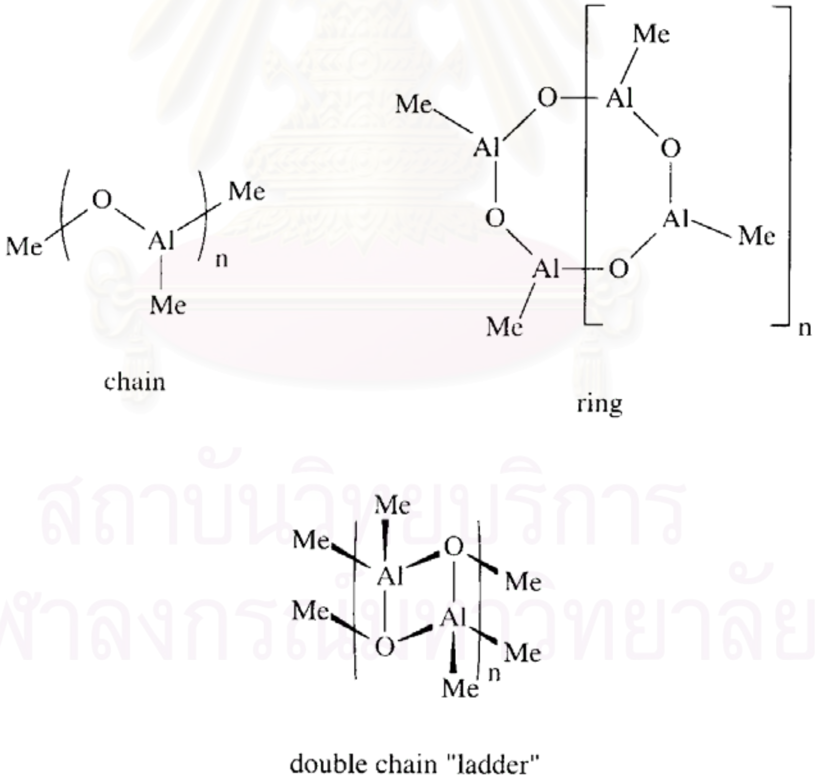

Figure 2.12 Early structure models for MAO [16]

In the case of rac-Et(Ind)$_2$ZrMe$_2$ as precursor, the extracted methyl ligands do not yield any modification in the structure and reactivity of the MAO counter-anion, thus allowing zirconium coordination site available for olefin that presented in Figure 2.13 [17].

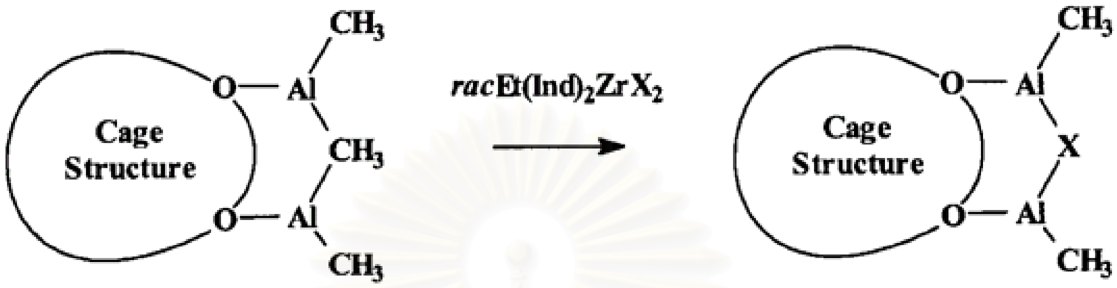

Figure 2.13 Representation of MAO showing the substitution of one bridging methyl group by X ligand extracted from racEt(Ind)$_2$ZrCl$_2$ (X = Cl, NMe$_2$, CH$_2$Ph) [17].

Cam and Giannini [18] investigated the role of TMA present in MAO by a direct analysis of Cp$_2$ZrCl$_2$/MAO solution in toluene-d$_8$ using ^{1}H-NMR. Their observation indicated that TMA might be the major alkylating agent and that MAO acted mainly as a polarization agent. However, in general it is believed that MAO is the key cocatalyst in polymerizations involving metallocene catalysts. The role of MAO included 1) alkylation of metallocene, thus forming catalyst active species, 2) scavenging impurities, 3) stabilizing the cationic center by ion-pair interaction and 4) preventing bimetallic deactivation of the active species.

The homogeneous metallocene catalyst cannot be activated by common trialkylaluminum only. However, Soga *et al.*[19] were able to produce polyethylene with modified homogeneous Cp$_2$ZrCl$_2$ activated by common trialkylaluminum in the presence of Si(CH$_3$)$_3$OH. Their results show that for an “optimum” yield aging of the catalyst and Si(CH$_3$)$_3$OH mixture for four hours is required. However, MWD of the produced polymers is bimodal although the polymers obtained in the presence of MAO have narrow MWD.

Ethylene/α-olefins copolymers with bimodal CCD were produced with homogeneous Cp$_2$ZrCl$_2$ with different cocatalysts such as MAO and mixture of

TEA/borate or TIBA/borate [20]. It seemed that the active species generated with different cocatalysts have different activities and produce polymers with different molecular weights.

2.1.4. Catalyst Activity

The ethylene polymerization rate of the copolymerization reaction with the catalyst system SiO_2/MAO/rac-Me_2Si [2-Me-4-Ph-lnd]$_2ZrCl_2$ was studied by Fink *et al.* [21]. The temperature was varied from 40 to 57^oC. Small amount of hexene in the reaction solution increased the polymerization rate. The extent of the "comonomer effect" depended on the polymerization temperature. At 57^oC the maximum activity of the ethylene/hexene copolymerization was 8 times higher than the homopolymerization under the same conditions. At 40^oC the highest reaction rate for the copolymerization is only 5 times higher than that for the ethylene homopolymerization. For the polymer properties of the ethylene/α-olefin copolymerization, the molecular weights of the polymers decreased with increasing comonomer incorporation. Ethylene/hexene copolymers produced by a metallocene catalyst also have the same melting point and glass transition temperature.

Series of ethylene copolymerization with 1-hexene or 1-hexadecene over four different siloxy-substituted ansa-metallocene/methylaluminoxane (MAO) catalyst systems were studied by Seppala *et al.* [22]. Metallocene catalysts rac-Et[2-(t-$BuMe_2SiO$)Ind]$_2ZrCl_2$ (1), rac-Et[l-(t-$BuMe_2SiO$)Ind]$_2ZrCl_2$ (2), rac-Et[2-(i-Pr_3SiO)Ind]$_2ZrCl_2$ (3) and rac-Et[l-(i-Pr_3SiO)Ind]$_2ZrCl_2$ (4) were used. The effects of minor changes in the catalyst structure, more precisely changes in the ligand substitution pattern were studied. They found that series of polymerization with siloxy-substituted bis(indenyl) ansa-metallocene are highly active catalyst precursors for ethylene-α-olefins copolymerizations. The comonomer response of all four catalyst precursors was good. Under the same conditions the order of copolymerization ability of the catalyst was rac-Et[2-(i-Pr_3SiO)Ind]$_2ZrCl_2$ > rac-Et[2-(t-$BuMe_2SiO$)Ind]$_2ZrCl_2$ and rac-Et[l-(i-Pr_3SiO)Ind]$_2ZrCl_2$ > rac-Et[l-(t-$BuMe_2SiO$)Ind]$_2ZrCl_2$. These catalysts are able to produce high molecular weight copolymers.

2.1.5. Copolymerization

By adding a small amount of comonomer to the polymerization reactor, the final polymer characteristics can be dramatically changed. For example, the Unipol process for linear low density polyethylene (LLDPE) uses hexene and the British Petroleum process (BP) uses 4-methylpentene to produce high-performance copolymers [23]. The comonomer can be affected the overall crystallinity, melting point, softening range, transparency and also structural, thermochemical, and rheological properties of the formed polymer. Copolymers can also be used to enhance mechanical properties by improving the miscibility in polymer blending [24].

Ethylene is copolymerized with α-olefin to produce polymers with lower densities. It is commonly observed that the addition of a comonomer generally increases the polymerization rate significantly. This comonomer effect is sometimes linked to the reduction of diffusion limitations by producing a lower crystallinity polymer or to the activation of catalytic sites by the comonomer. The polymer molecular weight often decreases with comonomer addition, possibly because of a transfer to comonomer reactions. Heterogeneous polymerization tends to be less sensitive to changes in the aluminum/transition metal ratio. Chain transfer to aluminum is also favored at high aluminum concentrations. This increase in chain transfer would presumably produce a lower molecular weight polymer. In addition, some researchers observed the decrease, and some observed no change in the molecular weight with increasing aluminum concentration [25].

The effect of polymerization conditions and molecular structure of the catalyst on ethylene/α-olefin copolymerization have been investigated extensively. Pietikainen and Seppala [26] investigated the effect of polymerization temperature on catalyst activity and viscosity average molecular weights for low molecular weight ethylene/propylene copolymers produced with homogeneous Cp_2ZrCl_2. Soga and Kaminaka [27] compared copolymerizations (ethylene/propylene, ethylene/1-hexene, and propylene/l-hexene) with $Et(H_4Ind)_2ZrC1_2$ supported on SiO_2, Al_2O_3 or $MgCl_2$. Broadness of MWD was found to be related to the combination of support types and types of monomers. The effect of silica and magnesium supports on copolymerization characteristics was also investigated by Nowlin *et al.* [28]. Their results indicated that comonomer incorporation was significantly affected by the way that support was treated based on the reactivity ratio estimation calculated with simplified Finemann Ross method. However, it should be noted that Finemann Ross method could be misleading due to linear estimation of nonlinear system.

Copolymer based on ethylene with different incorporation of 1-hexene,1-octene, and 1-decene were investigated by Quijada [6]. The type and the concentration of the comonomer in the feed do not have a strong influence on the catalytic activity of the system, but the presence of the comonomer increases the activity compared with that in the absence of it. From ^{13}C-NMR it was found that the size of the lateral chain influences the percentage of comonomer incorporated, 1-hexene being the highest one incorporated. The molecular weight of the copolymers obtained was found to be dependent on the comonomer concentration in the feed, showing that there is a transfer reaction with the comonomer. The polydispersity (Mw/Mn) of the copolymers is rather narrow and dependent on the concentration of the comonomer incorporation.

Soga *et al.* [29] noted that some metallocene catalysts produce two-different types of copolymers in terms of crystallinity. They copolymerized ethylene and 1-alkenes using 6 different catalysts such as Cp_2ZrCl_2, Cp_2TiCl_2, Cp_2HfCl_2, $Cp_2Zr(CH_3)_2$, Et(Ind $H_4)_2ZrCl_2$ and i-Pr(Cp)(Flu)$ZrCl_2$. Polymers with bimodal crystallinity distribution (as measured by TREF-GPC analysis) were produced with some catalytic systems. Only Cp_2TiCl_2-MAO and Et$(H_4Ind)_2ZrCl_2$-MAO produced polymers that have unimodal crystallinity distribution. The results seem to indicate that more than one active site type are present in some of these catalysts. However, it is also possible that unsteady-state polymerization conditions might have caused the broad distributions since the polymerization times were very short (5 minutes for most cases).

Marques *et al.*[30] investigated copolymerization of ethylene and 1-octene by using the homogeneous catalyst system based on Et$(Flu)_2ZrCl_2$/MAO. A study was performed to compare this system with that of Cp_2ZrCl_2/MAO. The influence of different support materials for the Cp_2ZrCl_2 was also evaluated, using silica, $MgCl_2$, and the zeolite sodic mordenite NaM. The copolymer produced by the $Et(Ind)_2ZrCl_2$/MAO system showed higher molecular weight and narrower molecular weight distribution, compared with that produced by Cp_2ZrCl_2/MAO system. Because of the extremely congested environment of the fluorenyl rings surrounding the transition metal, which hinders the beta hydrogen interaction, and therefore, the chain transference. Moreover, the most active catalyst was the one supported on SiO_2, whereas the zeolite sodic mordenite support resulted in a catalyst that produced copolymer with higher molecular weight and narrower molecular weight distribution. Both homogeneous catalytic systems showed the comonomer effect, considering that a significant increase was observed in the activity with the addition of a larger comonomer in the reaction medium.

The effect of different catalyst support treatments in the 1-hexene/ethylene copolymerization with supported metallocene catalyst was investigated by Soares *et al.* [31]. The catalysts in the study were supported catalysts containing SiO_2, commercial MAO supported on silica (SMAO) and MAO pretreated silica (MAO/silica) with Cp_2HfCl_2, $Et(Ind)_2HfCl_2$, Cp_2ZrCl_2 and $Et(Ind)_2ZrCl_2$. All the investigated supported catalysts showed good activities for the ethylene polymerization (400-3000 kg polymer/mol metal.h). Non-bridged catalysts tend to produce polymers with higher molecular weight when supported on to SMAO and narrow polydispersity. The polymer produced with Cp_2HfCl_2 supported on silica has only a single low crystallinity peak. On the other hand, Cp_2HfCl_2 supported on SMAO and MAO/silica produced ethylene/1-hexene copolymers having bimodal CCDs. For the case of Cp_2ZrCl_2 and $Et(Ind)_2ZrCl_2$, only unimodal CCDs were obtained. It seems that silica-MAO-metallocene and silica-metallocene site differ slightly in their ability to incorporate comonomer into the growing polymer chain, but not enough to form bimodals CCDs.

Soares *et al.* [4] studied copolymerization of ethylene and 1-hexene. It was carried out with different catalyst systems (homogeneous $Et(Ind)_2ZrCl_2$, supported $Et(Ind)_2ZrCl_2$ and in-situ supported $Et(Ind)_2ZrCl_2$). Supported $Et(Ind)_2ZrCl_2$: an $Et(Ind)_2ZrCl_2$ solution was supported on SMAO. It was used for polymerization of ethylene and 1-hexene. In-situ supported $Et(Ind)_2ZrCl_2$: an $Et(Ind)_2ZrCl_2$ solution was directly added to SMAO in the polymerization reactor, in the absence of soluble MAO. Homogeneous Et(Ind)$_2$ZrCl$_2$ showed higher catalytic activity than the corresponding supported and in-situ supported metallocene catalysts. The relative reactivity of 1-hexene increased in the following order: supported metallocene ≈ in-situ supported metallocene < homogeneous metallocene catalysts. The MWD and short chain branching distribution (SCBD) of the copolymer made with the in-situ supported metallocene were broader than those made with homogeneous and supported metallocene catalysts. They concluded that there are at least two different active species on the in-situ supported metallocene catalyst for the copolymerization of ethylene and 1-hexene.

Soares *et al.* [5] investigated copolymerization of ethylene and 1-hexene with different catalysts: homogeneous Et(Ind)$_2$ZrCl$_2$, Cp$_2$HfCl$_2$ and [(C$_5$Me$_4$)SiMe$_2$N(tert-Bu)]TiCl$_2$, the corresponding in-situ supported metallocene and combined in-situ supported metallocene catalyst (mixture of Et(Ind)$_2$ZrCl$_2$ and Cp$_2$HfCl$_2$ and mixture of [(C$_5$Me$_4$)SiMe$_2$N(tert-Bu)]TiCl$_2$. They studied properties of copolymers by using ^{13}C-NMR, gel permeation chromatography (GPC) and crystallization analysis fractionation (CRYSTAF) and compared with the corresponding homogeneous metallocene. The in-situ supported metallocene produced polymers having different 1-hexene fractions, SCBD and MDW. It was also demonstrated that polymers with broader MWD and SCBD can be produced by combining two different in-situ supported metallocenes.

In addition, Soares *et al.*[32] studied copolymerization of ethylene and 1-hexene with an in-situ supported metallocene catalysts. Copolymer was produced with alkylaluminum activator and effect on MWD and SCBD was examined. They found that TMA exhibited the highest activity while TEA and TIBA had significantly lower activities. Molecular weight distributions of copolymers produced by using the different activator types were unimodal and narrow, however, short chain branching distributions were very different. Each activator exhibited unique comonomer incorporation characteristics that can produce bimodal SCBD with the use of a single activator. They used individual and mixed activator system for controlling the SCBDs of the resulting copolymers while maintaining narrow MWDs.

2.2 Heterogeneous System

The new metallocene/MAO systems offer more possibilities in olefin polymerization compared to conventional Ziegler-Natta catalysts, such as narrow stereoregularity, molecular weight and chemical composition distributions (CCDs) through ligand design. However, only heterogeneous catalysts can be practically used for the existing gas phase and slurry polymerization processes. Without using a heterogeneous system, high bulk density and narrow size distribution of polymer particles cannot be achieved. The advantages of supporting catalysts include improved morphology, less reactor fouling, lower Al/metal mole ratios required to obtain the maximum activities in some cases the elimination of the use of MAO, and improved stability of the catalyst due to much slower deactivation by bimolecular catalyst interactions. Therefore, developing heterogeneous metallocene catalysts, that still have all the advantages of homogeneous systems, became one of the main research objectives of applied metallocene catalysis.

Steinmetz *et al*. [33] examined the particle growth of polypropylene made with a supported metallocene catalyst using scanning electron microscopy (SEM). They noticed formation of a polymer layer only on the outer surface of catalyst particles during the initial induction period. As the polymerization continued, the whole particle was filled with polymer. Particle fragmentation pattern depended on the type of supported metallocene.

2.2.1. Catalyst Chemistry

The nature of the active sites affects the polymer morphology, catalyst stability and activity, and the characteristics of the polymer produced. However, structure and chemistry of the active sites in supported catalysts are not clearly understood. Catalytic activities for supported metallocene are usually much lower than that of their counterpart homogeneous system. Formation of different active species, deactivation of catalyst during supporting procedure, and mass transfer resistance may contribute to decreased catalyst activity.

Tait *et al.* [34] reported general effects of support type, treatment, supporting procedure, and type of diluents on reaction kinetics and physical properties of polymer produced. Although the activities of supported catalysts are much lower compared to homogeneous systems. The activity of catalysts increased slightly when o-dichlorobenzene was introduced in toluene

The catalytic activities of supported catalyst depended on the percentage of the incorporated metallocene was reported by Quijada *et al.* [35]. However, in the case of metallocenes supported on MAO pretreated silica, depending on how the surface bound MAO complex with the catalyst, the activity can be as high as that of homogeneous system. According to the experiment by Chein *et al.* [36], if a single MAO is attached to silica, it would complex with zirconocene and lowers its activity. On the other hand, if multiple MAOs are attached to the surface silanol, the supported zirconocene will not be further complexed with MAO and have activity.

2.2.2. Supporting Methods

In the case of carriers like silica or other inorganic compounds with OH group on the surface, the resulting catalyst displayed very poor activities even combined with MAO. The reaction of metallocene complexes with the Si-OH groups might cause the decomposition of active species. Such decomposition could be suppressed by fixing MAO on the silica surface and then reacting with metallocenes [37]. Therefore, silica must be pretreated before the interaction with metallocene, to reduce the OH concentration and to prepare an adequate surface for metallocene adsorption and reaction in a non-deactivating way [38]. Metallocene immobilization methods can be divided in to three main groups. The first method is the direct support of catalyst onto an inert support. The second method involves the pretreatment of the inert support with MAO or other alkylaluminum followed by metallocene supporting. The third method, the catalyst is chemically anchored to the support, which often involves in-situ catalyst synthesis. These methods produce catalysts with distinct activities, comonomer reactivity ratios, and stereospecificities.

2.2.2.1 Direct Supporting of Inert Material

Collins *et al.* [39] reported that Et(Ind)$_2$ZrCl$_2$, when supported on partially dehydrated silica, reacted with surface hydroxyl groups during adsorption to form inactive catalyst precursors and free ligands (Fig 2.14.). Therefore, the activity is lower compared to the case of using dehydrated silica. Figure 2.15 shows the proposed structure Et(Ind)$_2$ZrCl$_2$ supported on alumina. For the case of alumina, the activity of catalyst supported on dehydrated alumina in lower than the one supported on partially dehydrated alumina. The high Lewis acidity of aluminum sites on dehydrated alumina facilitates the formation of Al-Cl bonds and Zr-O bonded species when the metallocene compound is adsorbed on these sites. However, the metal sites in this case remain inactive even after MAO addition.

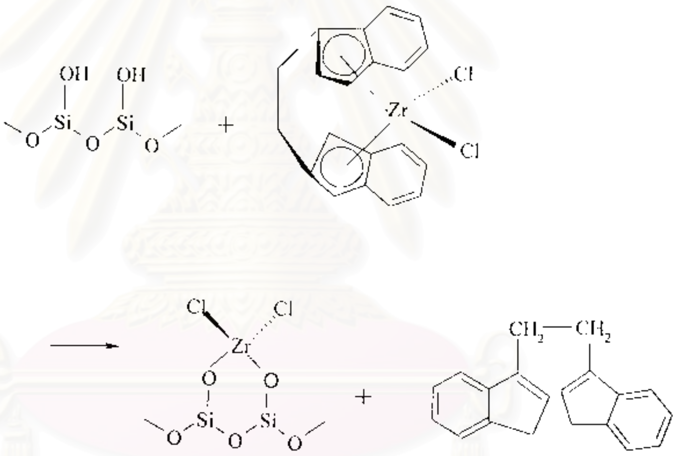

Figure 2.14 Structure of Et(Ind)$_2$ZrCl$_2$ supported on silica [39]

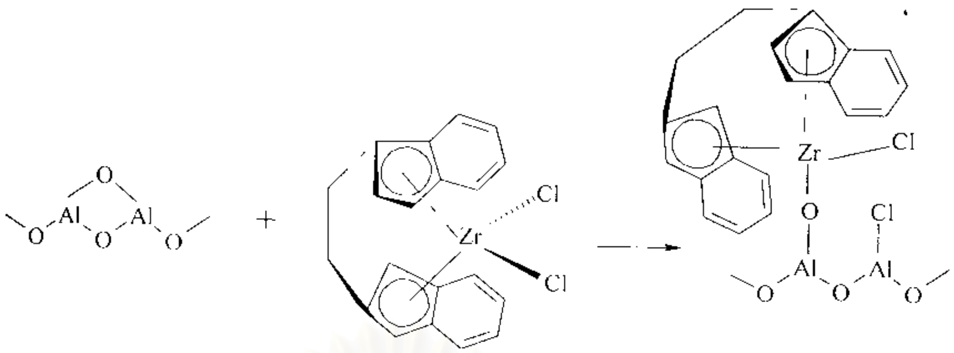

Figure 2.15 Structure of Et(Ind)$_2$ZrCl$_2$ supported on alumina [39]

Kaminsky *et al*. [40] proposed a possible explanation for the different behavior of metallocene supported directly on to silica, homogeneous systems, or supported onto MAO-pretreated silica. It is assumed that the supporting of metallocenes on silica takes place in three stages. First, the metallocene reacts with OH groups of the silica as shown in Figure 2.16.

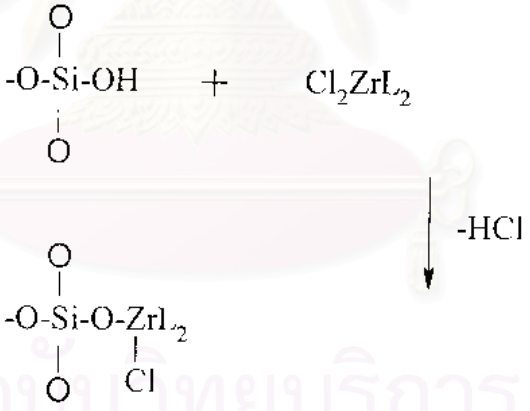

Figure 2.16 Reaction of silica and metallocene during catalyst supporting [40], where L is a ligand (Cp, Ind).

The second step is the alkylation by MAO as shown in Figure 2.17:

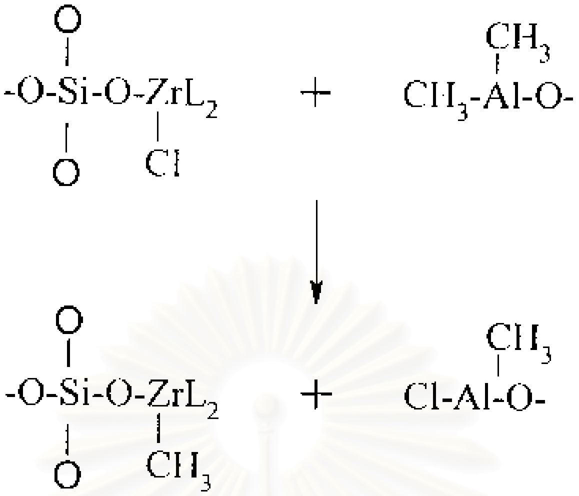

Figure 2.17 Alkylation of supported metallocene by MAO [40]

The third step is the dissociation of the $–SiO_2$-O-Zr- bond to an ion pair to form the cation active center $(SiO)^-(Zr)^+$. The polydispersity of polymers produced with these supported metallocenes are reported to be relatively high (5≈8) due to different electronic and steric interactions between the silica surface and the metal active sites. The immobilization of the zirconocene on silica inhibits bimolecular deactivation processes because the active sites are separated from each other.

As a consequence less use of MAO is required, increased molecular weights are achieved due to the reduction of β-hydrogen transfer by a second zirconocene center, and polypropylene of higher isotacticity and melting point is formed.

2.2.2.2. Supporting Catalyst on Materials Treated with Alkylaluminum

When silica is pretreated with MAO, the supporting mechanism is different. The zirconocene is complexed to MAO supported on silica, which will make the catalyst similarly to a homogeneous system. The polymers produced in this way have lower molecular weights.

Hiatky and Upton [41] reported that supporting of the aluminum-alkyl free catalysts can formed 2 complexes as shown in Figure 2.18, (a) deactivation through coordination of Lewis- basic surface oxides to the electrophilic metal center or (b) reaction of the ionic complex with residual surface hydroxyl groups.

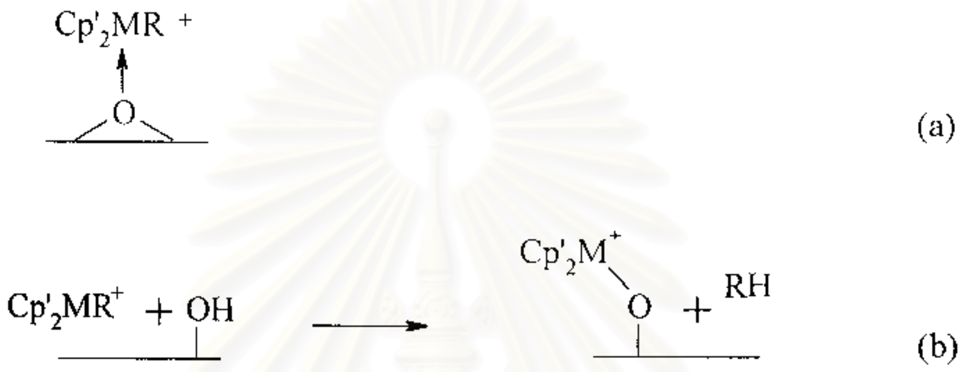

Figure 2.18. Effect of surface hydroxyl groups on ionic metallocene catalysts [41]

However, highly active supported ionic metallocene catalysts for olefin polymerization can be prepared by pretreating the support with scavenger. It is assumed that pretreatment of the support with a scavenger serves to activate the support and compatibilize it with the ionic metallocene complex.

Lee *et al*. [42] used TMA pretreated-silica as the support for metallocene catalysts. The activity of supported catalysts showed dependency to H_2O content in silica, H_2O/TMA ratio, metallocene, and cocatalyst. The supported catalyst was also able to polymerize ethylene in the absence of MAO when common alkyl aluminum was used as the cocatalyst.

The surface aluminum and metallocene loading was studied by Santos *et al.* [43]. About 7 wt% of MAO can be supported on silica when the initial amount of MAO in mixture of silica was ca. 10 wt%. Depending on silica types, saturation of MAO supported on silica can occur at lower MAO contents.

Harrison *et al*. [44] compared a variety of silica and alumina supports with different degrees of surface hydroxylation as the supports. It was shown that as the concentration of OH groups on the surface of the support increased, more MAO could be impregnated and thus catalyst with more metallocene content could be produced. The most obvious benefit of supported catalyst with more metallocene was increased activities compared to catalysts with lower concentration of surface hydroxyl groups (increased activities both in kg PE/mol Zr/hr and kg PE /g-support/h). However, at high polymerization temperatures, leaching of catalyst from the support was observed. In lower polymerization temperatures, leaching was less significant, however, the morphology and bulk density of the polymer formed were still unsuitable for use in gas-phase polymerization.

For the case of propylene polymerization, a decrease in syndiotacticity was observed by Xu *et al.* [45] when the metallocene catalyst was supported on pretreated silica.

2.2.2.3. Chemically Anchoring Catalyst on Support

Soga *et al*. [46] described a method to support zirconocenes more rigidly on SiO_2. The supporting steps are as follows: 1) Silica was treated with $SiCl_4$ to substitute the OH groups with chlorine atoms. 2) The resulting silica was filtered and washed with tetrahydrofuran (THF). 3) The solid was re-suspended in THF and a lithium salt of indene, dissolved in THF, was added drop-wise. 4) The resulting solid was filtered and washed again with THF. And to re-suspended solid in THF, $ZrCl_4$ 2THF dissolved in THF was added. The final solid part was separated by filtration, washed with THF and diethyl ether, and dried under vacuum. The supported catalyst produced in this way showed higher isospecificity than the corresponding homogenous system for propylene polymerization. MAO or ordinary alkylaluminums were used as cocatalysts. The yield was higher when MAO was used as the cocatalyst, but the molecular weight of the polypropylene was half of the molecular weight obtained when TIBA was used as the cocatalyst ($3.4x10^5$ g/mol and $7.2x10^5$ g/mol, respectively). Figure 2.19 shows the structure of the silica supported metallocenes.

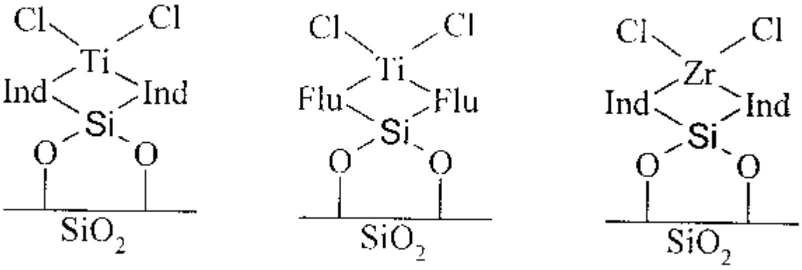

Figure 2.19. Structure of some silica supported metallocene catalysts [46]

Lee *et al.* [47] used spacer molecules in supporting metallocene catalysts onto silica to eliminate the steric hindrance near the active site caused by the silica surface (Figure 2.20).

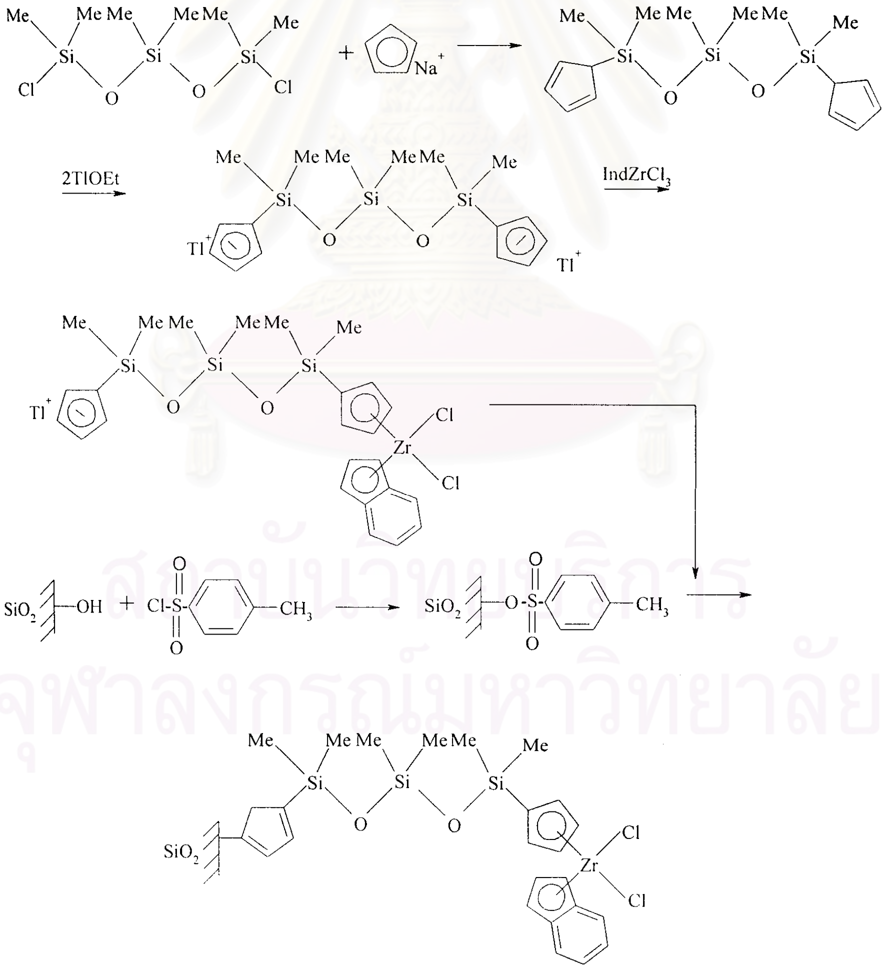

Figure 2.20. Mechanism for supporting metallocene catalysts on silica using spacer molecules [47].

By distancing the active site from the silica surface, higher catalytic activities but lower polymer molecular weights were obtained in comparison with analogous silica-supported catalysts without spacer between silica and $CpIndZrCl_2$.

Iiskola *et al*. [48] treated the surface of partially dehydroxylated silica with a silane coupling agents, $Cp(CH_2)_3Si(OCH_2CH_3)_3$, and then immobilized $CpZrCl_3$ onto cyclopentadienyl surface formed on the silica to obtain a highly active catalyst (Figure 2.21) for ethylene polymerization in the presence of MAO. Depending on the calcination temperature and the modification methods, the catalysts show different activities and produced polymers with different molecular weights. In general, when compared to homogeneous Cp_2ZrCl_2 systems, all the supported catalysts showed lower activities, but the polymers produced had higher molecular weights. On the other hand, when compared to homogeneous Cp_2ZrC1_2 systems, the activities of the supported catalysts were similar but molecular weights of polymer produced were lower and depended on the silica surface modification method used. The polydispersity index of the polymers ranged from 2.2 to 2.8.

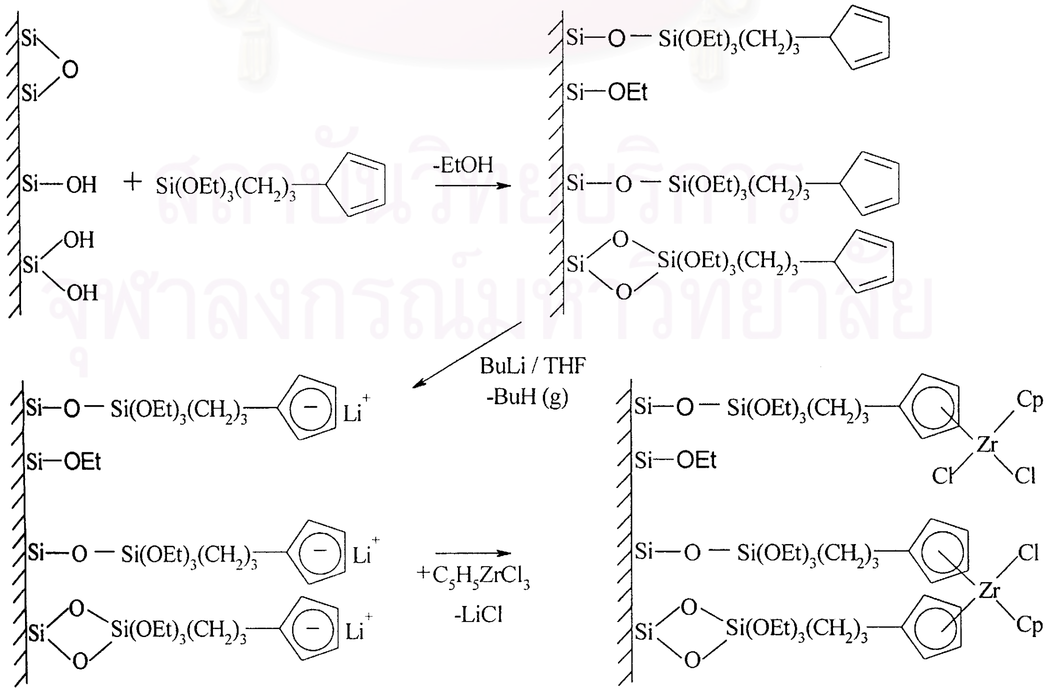

Figure 2.21. Modification of silica with $Cp(CH_2)_3Si(OCH_2CH_3)_3$ and preparation of supported metallocene catalysts [48].

2.2.2.4. Supporting on Other Supports

Lee and Yoon [49] studied ethylene and styrene homopolymerization initiated by cyclodexrin (CD) supported Cp_2ZrCl_2 or Cp^*TiCl_3 catalyst. The effect of CD pretreatment with MAO or TMA on catalyst behaviors was shown that either TMA or MAO could be used as cocatalyst for ethylene polymerization while only MAO could initiate the styrene polymerization with α-CD supported catalysts.

Marques *et al.*[50] investigated ethylene polymerization by using Y zeolite-supported Cp_2ZrCl_2 catalysts. These system produced polyethylene with higher molecular weight and as narrow a molecular weight distribution as the homogeneous precursor, however, at relatively lower activity. The main characteristic that makes a zeolite a good support for metallocene catalyst seems to be a high Si/Al value and therefore a low Al density on the surface of the zeolite. This suggests that the presence of isolated aluminium atoms favors the fixation of zirconocene.

Moreover, Michelotti *et al.* [51] studied copolymerization of ethylene with higher α-olefins, such as 4-methyl-1-pentene, 1-hexene, 1-octene and 1-dodecene. The catalytic behavior of various metallocene (Cp_2ZrCl_2, Ind_2ZrCl_2, $Et(Ind)_2ZrCl_2$, and $Et(Ind)_2HfCl_2$) supported on methylalumoxane-pretreated HY zeolite (SiO_2/Al_2O_3=5.7) were compared.

Meshkova *et al.* [52] investigated ethylene polymerization in the presence of ZSM-5(H_2O)/TMA-$Et(Ind)_2ZrCl_2$. They found that the synthesis of MAO directly on the zeolite support and the absence of free MAO may be one of the way of the reduction of supported zirconocene catalyst leaching. The positive temperature coefficiency of polymerization rate as well as the increase of molecular weight and melting point of PE obtained with the zeolite supported zirconocene catalyst developed in this work compared to PE produced by homogeneous zirconocene system confirms this view.

Weiss *et al.* [53] investigated the clay minerals kaolin and montmorillonite as inorganic carriers for the polymerization of ethylene and propylene with Cp_2ZrCl_2, Cp_2ZrHCl or Cp_2TiCl_2 catalyst and TMA as cocatalyst. The heterogeneous catalysts on kaolin were less active in ethylene polymerization than comparable homogeneous catalysts. But the heterogeneous catalysts on montmorillonite are often more active in ethylene or propylene polymerization than comparable homogeneous catalysts.

Looveren *et al.* [54] studied methylalumoxane (MAO)-MCM-41 as support in the co-oligomerization of ethene and propene with $[C_2H_4(Ind)_2Zr(CH_3)_2]$. They were found that the MAO-MCM-41 was catalytically more active than the corresponding silica-based MAO derivative or the homogeneous system.

CHAPTER III

EXPERIMENTAL

In the present study of the copolymerization of ethylene/α-olefin with the TiO_2-SiO_2 mixed oxides supported zirconocene catalysts, the experiments were divided into four parts:

(i) Preparation of TiO_2-SiO_2 Mixed oxides
(ii) Preparation of catalyst precursor mixed oxides/MAO
(iii) Ethylene and α-olefins copolymerization Procedure
(iv) Characterization of ethylene and α-olefin copolymer products and catalyst precursor mixed oxides/MAO

The details of the experiments are explained as follows.

3.1 Chemicals

The chemicals used in these experiments were analytical grade, but only major materials are specified as follows:

1. rac-Ethylenebis(indenyl)zirconium dichloride ($Et(Ind)_2ZrCl_2$) was supplied from Aldrich Chemical Company, Inc. and used without further purification.

2. Ethylene gas (99.96%) was devoted from National Petrochemical Co., Ltd., Thailand and used as received.

3. 1-Hexene (99+%) was purchased from Aldrich Chemical Company, Inc. and purified by distilling over sodium under argon atmosphere before use.

4. 1-Octene (98%) was purchased from Aldrich Chemical Company, Inc. and used as received.

5. 1-Decene (≥ 97%) was purchased from Fluka Chemie A.G. Switzerland. and used as received.

6. Methylaluminoxane (MAO) 2.667 M in toluene was donated from Tosoh Akso, Japan and used without further purification.

7. Trimethylaluminum [$Al(CH_3)_3$] 2.0 M in toluene was supplied from Nippon Aluminum Alkyls Ltd., Japan and used without further purification.

8. Silica gel from Fuji Silasia Chemical Ltd., (Cariact P-10, surface area 300 m^2/g) was calcined at 400 ^oC for 6 hours under vacuum.

9. JRC-TIO-1 (pure anatase, grade japan reference catalyst) from Department of Material science, shimane university catalysts and chemicals Ind.co., Ltd

10. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma.

11. Ethylene gas (polymerization grade) was devoted from National Petrochemical Co., Ltd., Thailand.

12. Methanol (Commercial grade) was purchased from SR lab.

13. Toluene was devoted from EXXON Chemical Ltd., Thailand. This solvent was dried over dehydrated $CaCl_2$ and distilled over sodium/benzophenone under argon atmosphere before use.

14. Ultra high purity argon gas (99.999%) was purchased from Thai Industrial Gas Co., Ltd., and further purified by passing through columns packed with molecular sieve 3 A, BASF Catalyst R3-11G, sodium hydroxide (NaOH) and phosphorus pentaoxide (P_2O_5) to remove traces of oxygen and moisture.

3.2 Equipments

All types of equipments used in the catalyst precursor preparation and polymerization are listed below:

3.2.1 Cooling system

The cooling system was in the solvent distillation in order to condense the freshly evaporated solvent.

3.2.2 Inert gas supply

The inert gas (argon) was passed through columns of BASF catalyst R3-11G as oxygen scavenger, molecular sieve 3×10^{-10} m to remove moisture. The BASF catalyst was regenerated by treatment with hydrogen at 300 ^oC overnight before flowing the argon gas through all the above columns. The inert gas supply system is shown in Figure 3.1.

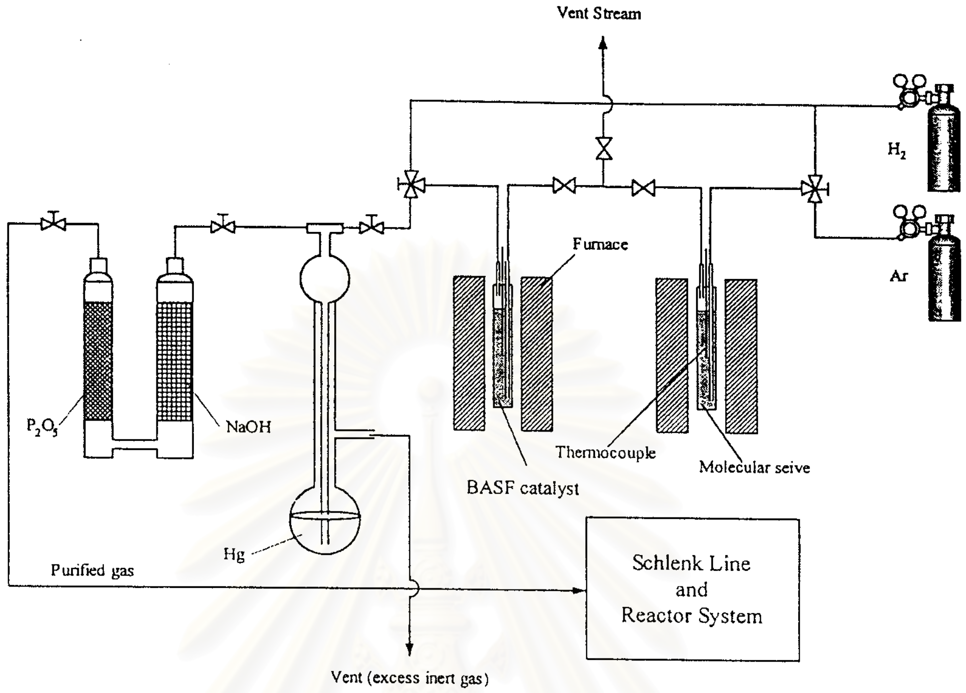

Figure 3.1 Inert gas supply system

3.2.3 Magnetic stirrer and heater

The magnetic stirrer and heater model RTC basis from IKA Labortechnik were used.

3.2.4 Reactor

A 100 ml stainless steel autoclave was used as the copolymerization reactor.

3.2.5 Schlenk line

Schlenk line consists of vacuum and argon lines. The vacuum line was equipped with the solvent trap and vacuum pump, respectively. The argon line was connected with the trap and the mercury bubbler that was a manometer tube and contain enough mercury to provide a seal from the atmosphere when argon line was evacuated. The Schlenk line was shown in Figure 3.2.

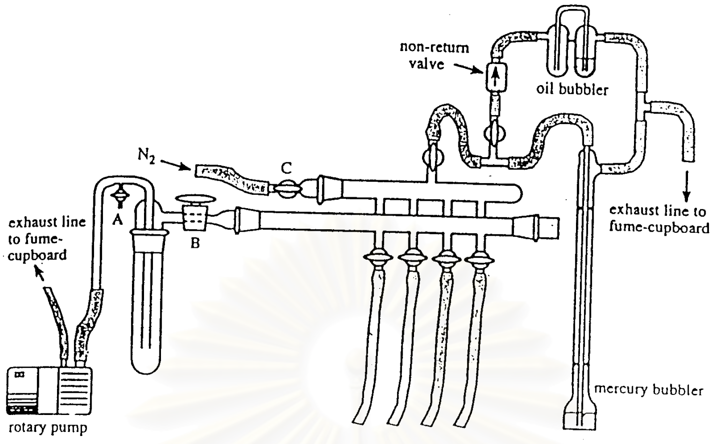

Figure 3.2 Schlenk line

3.2.6 Schlenk tube

A tube with a ground glass joint and side arm, which was three-way glass valve as shown in Figure 3.3. Sizes of Schlenk tubes were 50, 100 and 200 ml used to prepare catalyst and store materials which were sensitive to oxygen and moisture.

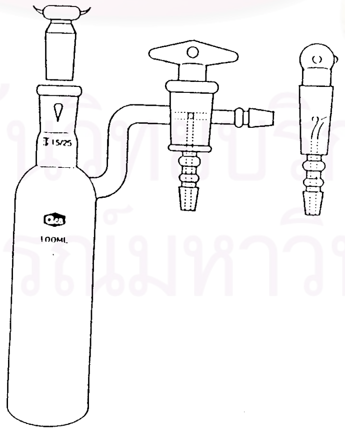

Figure 3.3 Schlenk tube

3.2.7 Vacuum pump

The vacuum pump model 195 from Labconco Corporation was used. A pressure of 10^{-1} to 10^{-3} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

3.2.8 Polymerization line

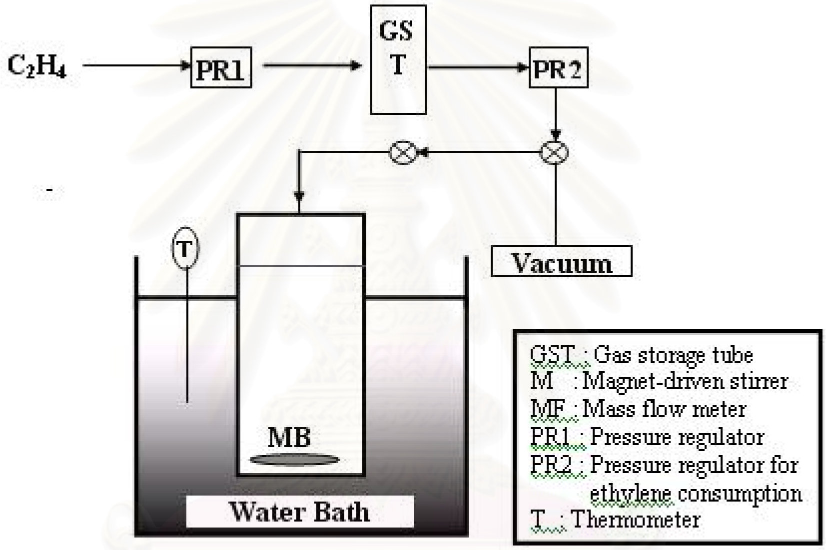

Figure 3.4 diagram of system in slurry phase polymerization

3.3 Characterizing instruments

The instruments used for characterizing catalysts and ethylene/α-olefin copolymer products are specified below.

3.3.1 Differential scanning calorimetry (DSC)

The melting temperature of ethylene/α-olefin copolymer products was determined with a Perkin-Elmer diamond DSC from MEKTEC, at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical

Engineering, Chulalongkorn University. The analyses were performed at the heating rate of 20 °C/ min in the temperature range of 50-150 °C. The heating cycle was run twice. In the first scan, samples were heated and the cooled to room temperature. In the second, samples were reheated at the same rate, but only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of samples.

3.3.2 Gel permeation chromatography (GPC)

Molecular weight and molecular weight distribution of the produced ethylene/α-olefin copolymer were measured at 150 °C using 1,2-dichlorobenzene as solvent by a gel permeation chromatography at Thai Petrochemical Industry Public Company Limited. The GPC instrument was equipped with a PL-GPC 220 Differential refractometer (DRI), PL-BV 400 capillary bridge viscometer (Visc) and 2xPLgel 10 um MIXED-B (300x7.5mm) with PLgel 10 um guard (50 x 7.5 mm). The columns were calibrated with standard narrow molar mass distribution polystyrenes and linear low density polyethylene and polystyrene.

3.3.3 Nuclear magnetic resonance (NMR)

The ^{13}C-NMR spectra were recorded at 100°C using JEOL JNM-A500 operating at 125 MHz. Copolymer solutions were prepared using 1,2 -dichlorobenzene as solvent and benzene-d_6 for internal lock.

3.3.4 Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

SEM observation with a JSM-5800 LV Scanning Microscope, Microspec WDX at Scientific Technological Research Equipment Center, Chulalongkorn University was employed to investigate the morphology of catalyst precursor and polymer. The polymer samples for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimen. EDX was performed using Link Isis series 300 program.

3.3.5 Fourier Transformed Infrared Spectroscopy (FT-IR)

The infrared spectroscopic technique was widely used to characterize polymer structure. Comparison of the position of absorption in the IR spectrum of a polymer sample with the characteristic absorption led to the identification of the bands and functional groups presented in the polymer. The IR spectrum of a polymer was unique which can be considered as a 'fingerprint'. Perkin-Elmer FT-IR series 2000 instrument at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University was employed to study the chemical structure of polyethylene products.

3.3.5 X-ray diffraction (XRD)

XRD was performed to determine the bulk crystalline phases of sample. It was conducted using a SIEMENS D-5000 X-ray diffractometer with $CuK_\alpha(\lambda = 1.54439 \times 10^{-10}$ m). The spectra wrer scanned at a rate 2.4 degree/min in the range $2\theta = 20$-80 degrees.

3.4 Supporting Procedure

All reactions were conducted under argon atmosphere using Schlenk techniques and glove box.

3.4.1 Preparation of Mixed oxides

Mixed TiO_2-SiO_2 supported will be prepare by impregnation as referred in [55]. TiO_2-SiO_2 were impregnated by physical force and were stirred by equipped with magnetic stirrer. The mixture was separated and washed 5 times with 20 ml of toluene, followed by drying in vacuum at room temperature to obtain the catalyst support precursor mixed TiO_2-SiO_2 oxides.

3.4.2. Preparation of Catalyst Precursor Mixed oxides/MAO

Mixed support was heated under vacuum at 400 °C for 6 hours. 1 g of calcined silica was reacted with the desired amount of MAO in 10 ml of toluene at room temperature for 30 minutes. The solid part was separated and washed 5 times with 20 ml of toluene, followed by drying in vacuum at room temperature to obtain the catalyst support precursor mixed oxides/MAO.

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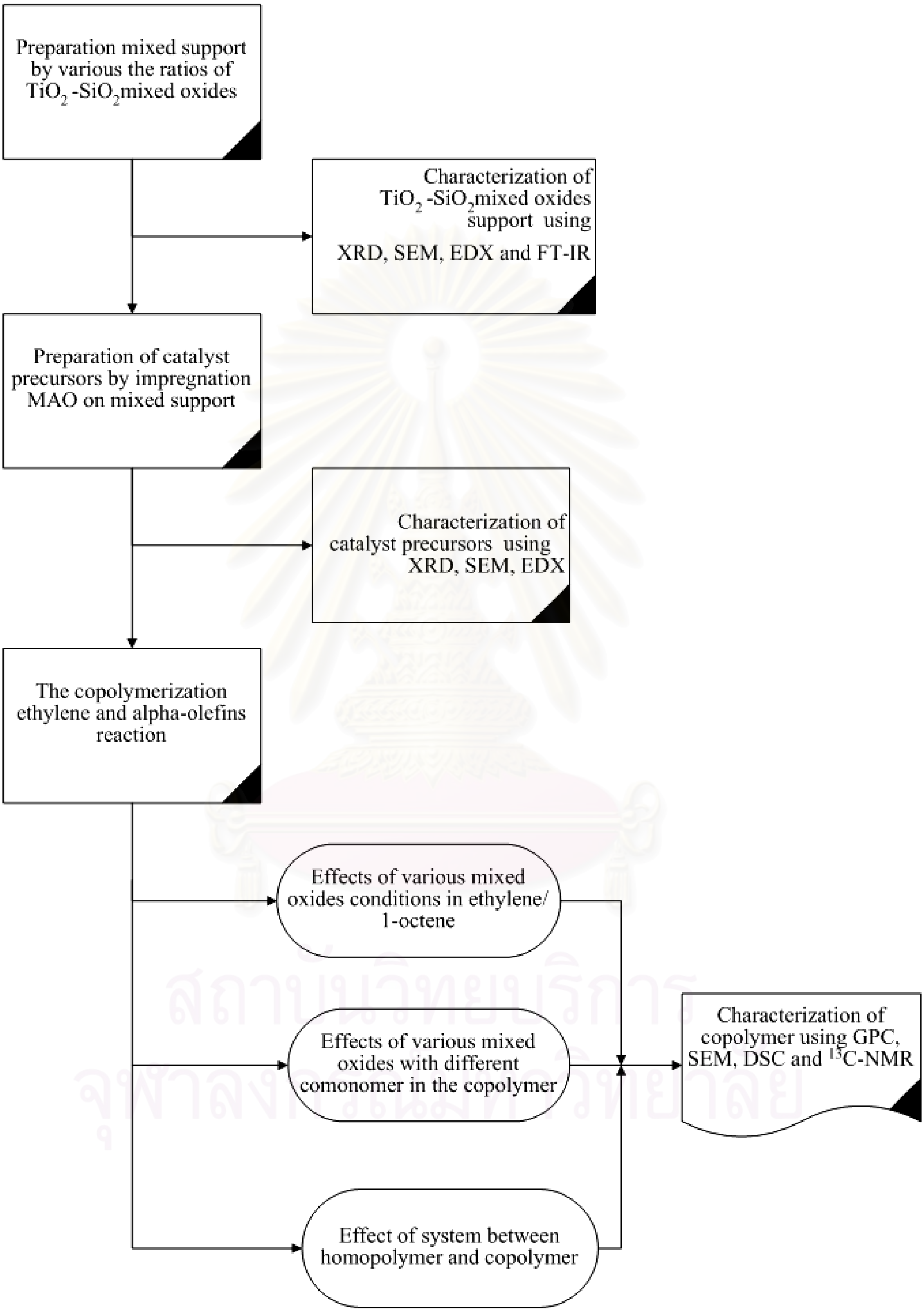
3.5 Ethylene and α-olefin Copolymerization Procedure

The ethylene and α-olefins (1-hexene, 1-octene and 1-decene) copolymerization reactions were carried out in a 100 ml semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. The autoclave and magnetic bar were dried in oven at 110 °C for 30 minutes and purged with argon 5 times in glove box before use in copolymerization of ethylene and α-olefins. Toluene (to make a total volume of 30 ml), 100 mg of catalyst precursor, 3 ml of α-olefins were introduced into the autoclave in the glove box. The amount of $Et(Ind)_2ZrCl_2$ and TMA were mixed and stirred for 5 minutes at room temperature. After that, the mixture of metallocene and TMA was injected into the reactor. The reactor was frozen in liquid nitrogen to stop reaction and then the autoclave was evacuated to remove the argon. After that, the reactor was heated up to polymerization temperature and the polymerization was started by feeding ethylene gas (total pressure 50 psi) until the consumption of ethylene 0.018 mol (6 psi was observed from pressure gauge). The small amount of ethylene was used to avoid the mass transfer effect and increase the homogeneity of polymer. If the amount of comonomer remained higher than 90% after the reaction, the obtained polymer is homogeneous. The reaction of polymerization was terminated by addition of acidic methanol. The time of reaction was recorded for purposes of calculating the activity. The precipitated polymer was washed with methanol and dried in room temperature.

The various effects on the ethylene/α-olefins copolymerization with silica-supported metallocene catalyst and optimized condition were investigated. The effects of copolymerization on production of ethylene/α-olefins copolymer were systematically varied as follow.

Research Methodology



3.6 Characterization of Catalyst Precursor

3.6.1 Morphology and elemental disribution

Scanning electron microscopic (SEM) technique was the effective method to investigate catalyst precursor morphologies. The term of morphology was referred to shape, texture or form of catalyst precursor.

3.6.2 The Amount of Al and Zr on Catalyst Precursors

Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) method was used to investigate amount of Al and Zr that were supported on surface of SiO_2/MAO and SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$, respectively.

3.7 Characterization of Ethylene and α-olefins Copolymer Products

3.7.1 Chemical Structure Determination

The nuclear magnetic resonance technique was widely used for characterizing incorporated comonomer. Comparison of the position of peak in the ^{13}C-NMR spectrum of polymer sample led to identification of the sequences of the comonomer incorporation.

3.7.2 Morphology

The morphology of ethylene/α-olefins copolymer obtained was observed with scanning electron microscopy (SEM).

3.7.3 Melting Temperature (T_m)

Differential scanning calorimetry (DSC) was an instrument designed to measure the thermal properties especially melting temperature (Tm). The melting temperature of ethylene/α-olefins copolymers were determined from the critical point of DSC curve.

3.7.4 Average Molecular Weight and Molecular Weight Distribution

One of the most widely used methods for the routine determination of molecular weight (Mw) and molecular weight distribution (MWD) was gel permeation chromatography (GPC), which employed the principle of size exclusion chromatography (SEC) to separate samples of polydispersed polymers into fractions of narrower molecular weight distribution.

CHAPTER IV

RESULTS AND DISCUSSION

The purpose of this work is to investigate and characterize effects of mixed oxides supported MAO with zirconocene catalyst on catalytic property during the copolymerization of ethylene with α-olefins including develop a better understanding on how mixed oxide supports may change the nature of active site on the catalyst.

4.1 Characterization of supports and catalyst precursors

4.1.1 Characterization of supports and catalyst precursors with X-ray diffraction (XRD)

The mixed oxide supports containing various amounts of titania and silica were characterized before and after impregnation with MAO. It was observed that the pure silica exhibited a broad XRD peak assigning to the conventional amorphous silica. Similar to the pure silica, the XRD patterns of the pure titania indicated only the characteristic peaks of anatase titania at 25^o (major), 37^o, 48^o, 55^o, 56^o, 62^o, 71^o, and 75^o. XRD patterns of the mixed oxide supports containing various amounts of titania and silica revealed the combination of titania and silica supports based on their content. It can be seen that the intensity of XRD characteristic peaks for both supports was changed based on the ratios of TiO_2/SiO_2. It was found that XRD patterns for the supports after impregnation with MAO were almost identical with those before impregnation with MAO. XRD patterns of the mixed oxide supports are shown in Figure 4.1.

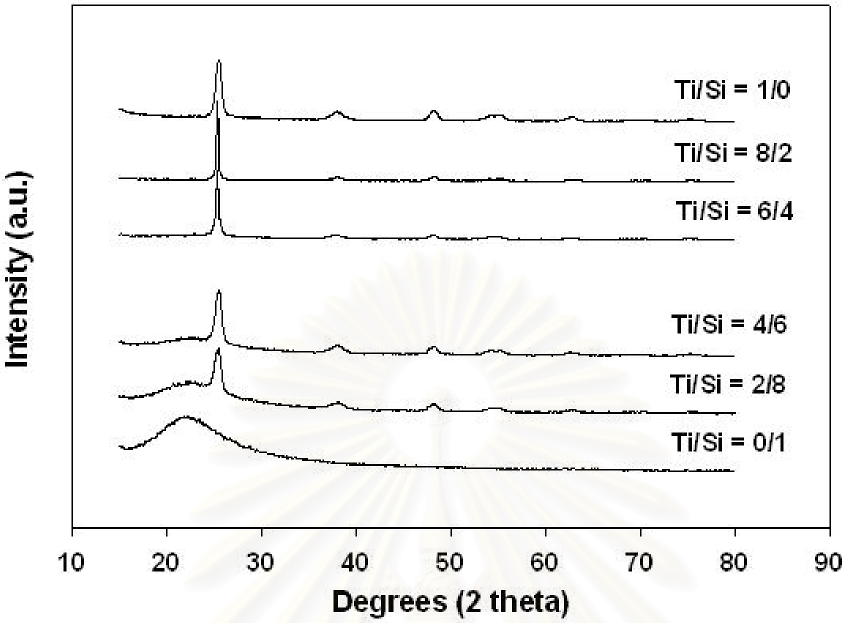


Figure 4.1 The XRD patterns of various TiO_2-SiO_2 mixed oxide supports

4.1.2 Characterization of supports and catalyst precursors with Scanning electron microscope(SEM) and energy dispersive X-ray spectroscopy (EDX)

In order to determine the morphologies and elemental distributions of the supports before and after impregnation, SEM and EDX were performed, respectively. The SEM micrographs showed that silica was appeared in larger particles than titania. It also indicated that at the low content of titania ranged between 20 and 60%, titania was found to decorate on the silica surface as seen in the SEM micrographs. However, at high content of titania, it revealed that titania, essentially isolated from the silica surface. This was probably because the adsorption ability of silica surface with titania was limited by the titania contents in the mixed oxide supports. The SEM micrographs of the supports after impregnation with MAO are shown in Figure 4.2 indicating similar results as before the MAO impregnation in Figure 4.3.

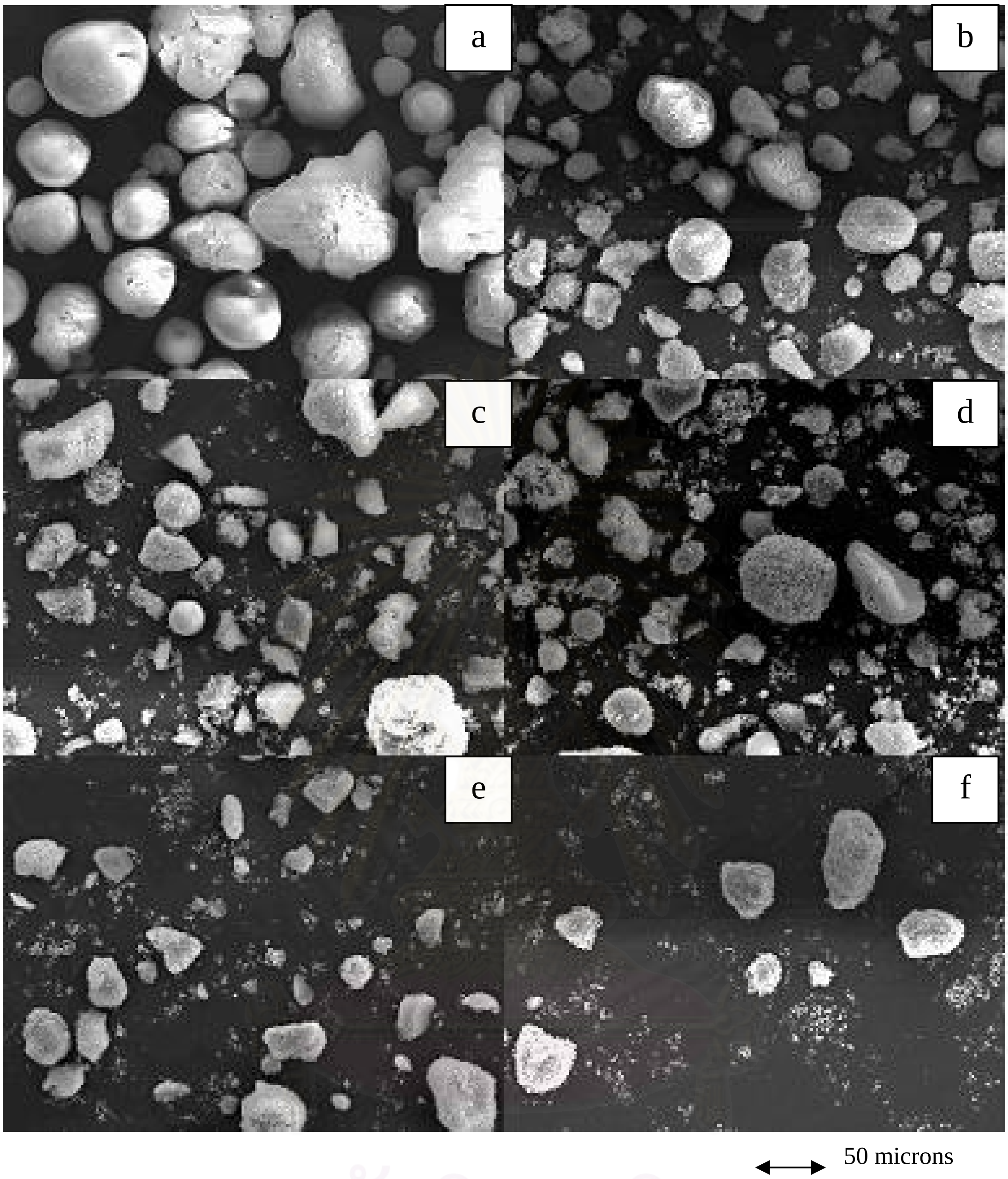


Figure 4.2 SEM micrographs of various TiO_2-SiO_2 mixed oxide supports before MAO impregnation; a: Ti/Si = 0/1, b: Ti/Si = 2/8, c: Ti/Si = 4/6, d: Ti/Si = 6/4, e: Ti/Si = 8/2, f: Ti/Si = 1/0

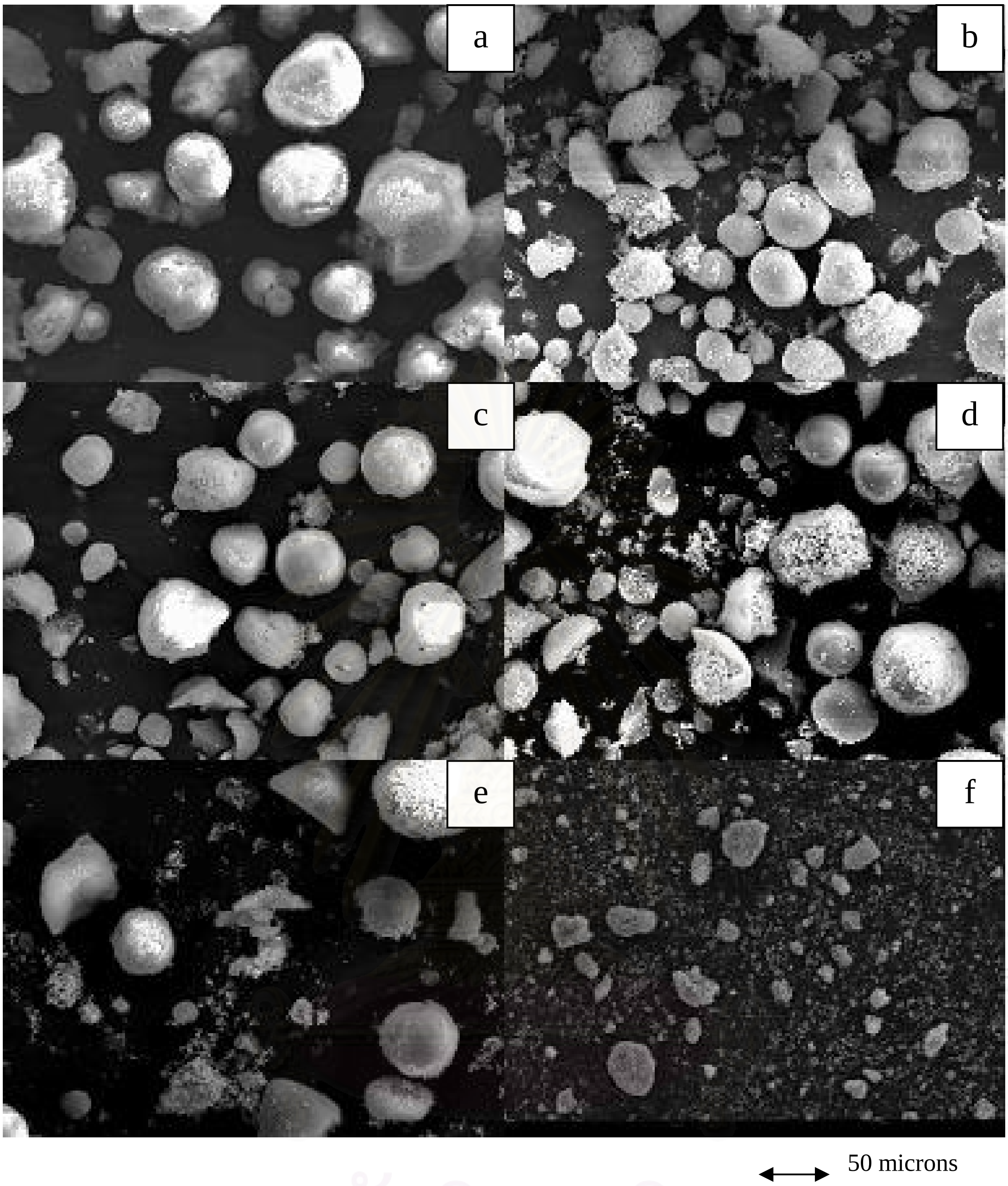


Figure 4.3 SEM micrographs of various TiO_2-SiO_2 mixed oxide supports after MAO impregnation; a: Ti/Si = 0/1, b: Ti/Si = 2/8, c: Ti/Si = 4/6, d: Ti/Si = 6/4, e: Ti/Si = 8/2, f: Ti/Si = 1/0

The distribution of all elements (Si, Ti, and O) obtained from EDX was similar in all samples. The EDX mapping images of the supports can provide more information about the distribution of MAO as seen for Al distribution mapping on each support. It was found that MAO was well distributed all over the support granules. The typical EDX mapping images for the mixed oxide supports after impregnation with MAO are shown in Figure 4.4.

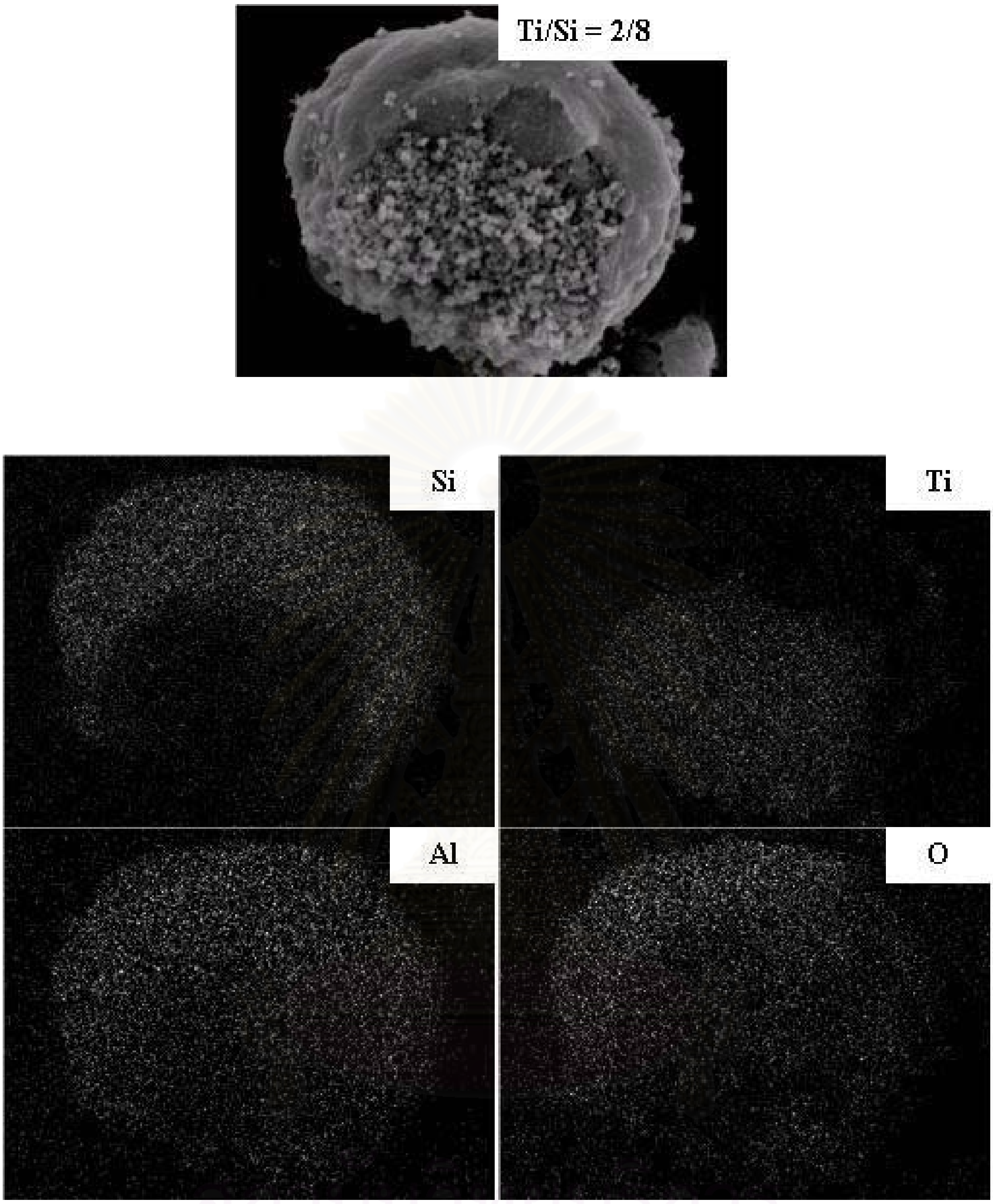


Figure 4.4 EDX mapping of various TiO_2-SiO_2 mixed oxide supports after MAO impregnation

4.1.3 Characterization of supports and catalyst precursors with Fourier Transformed Infrared Spectroscopy (FT-IR)

The IR spectra of samples are shown in Figure 4.5. It revealed that at low concentrations of titania, the IR band at ca. 980 cm-1 assigning to Si-O-Ti connectivity was observed as also reported by Dutoit et al. [7]. The strong IR bands were also seen at ca. 1100 cm-1 assigning to asymetric stretching vibration.

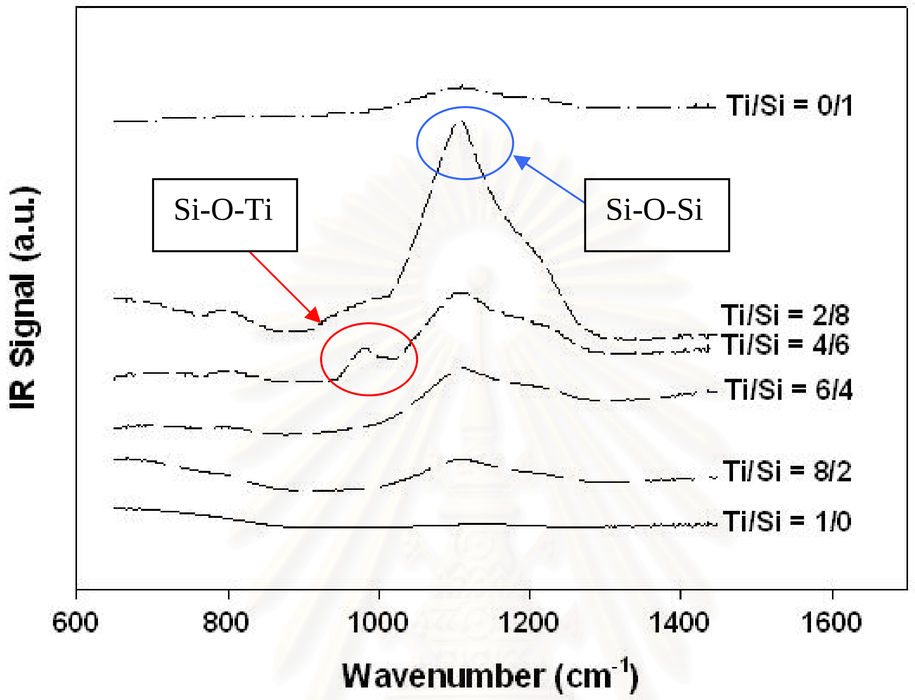


Figure 4.5 IR spectra of various TiO_2-SiO_2 mixed oxide supports

4.2 Effect of TiO_2-SiO_2 mixed oxide supports in ethylene/1-octene copolymerization system

4.2.1 The Effect of TiO_2-SiO_2 mixed oxide supports on the Catalytic Activity

Then, the various TiO_2-SiO_2 mixed oxide supports after impregnation with MAO were used and investigated for catalytic activities. Copolymerization of ethylene/1-octene via various TiO_2-SiO_2 mixed oxides-supported MAO with zirconocene catalyst was performed in order to determine the catalytic activities influenced by the various supports. Methylaluminoxane (MAO) was used as cocatalyst which the molar ratio of Al $_{(MAO)}$/Zr was 1135. The copolymerization were performed in toluene solvent at 70^{o}C using ethylene consumption of 0.018 mol (pressure in reactor 50 psi), 0.018 ml of α-olefin, 100 mg of catalyst precursor and zirconium concentration 5.0x10^{-5} M with total solution volume of 30 ml. The results of the study are shown in Table 4.1 and Figure 4.6.

Table 4.1 Catalytic activity of different ratio mixed oxide in ethylene/1-octene

Weight Ratio (TiO_2-SiO_2)	Yield (g)	Polymerization Time (sec)	Catalytic Activity[a] (kgCopolymer/molZr.h)
Homogenous	1.1347	87	31302
0/100	1.1854	152	18717
20/80	1.1428	116	23644
40/60	1.1940	132	21709
60/40	1.1754	149	18933
80/20	1.1691	157	17871
100/0	1.1254	161	16776

[a] copolymerization conditions: $Al_{(MAO)}/Zr$ = 1135, $Al_{(TMA)}/Zr$ = 2500, precursor = 100 mg ,reaction temperature 70°C, 0.018 mol of ethylene consumption,0.018 mol of 1-octene, total volume = 30 ml, and [Zr] = 5 x 10^{-5} M.

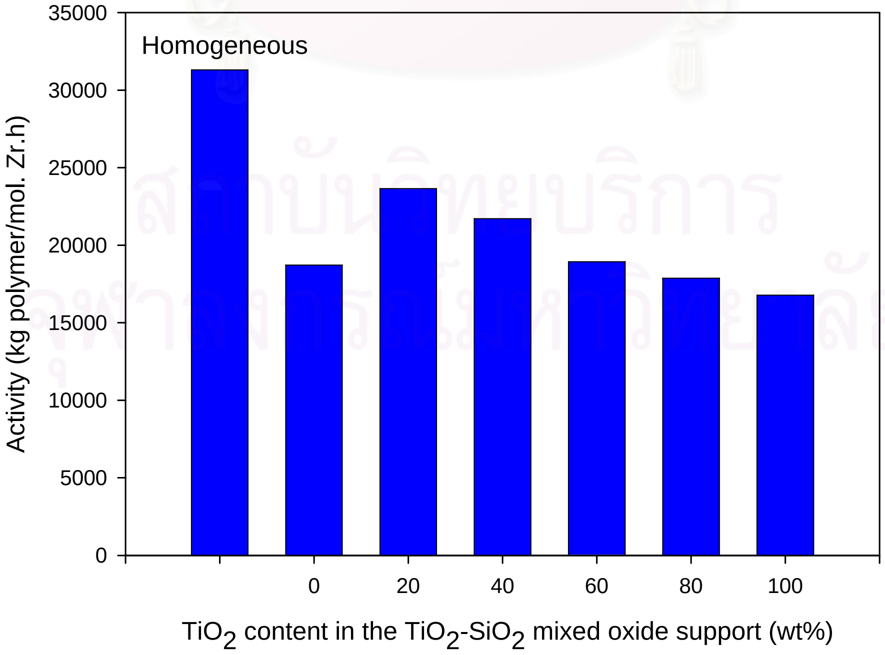


Figure 4.6 Catalytic activity of different ratio mixed oxide in ethylene/1-octene

The activities of the supported system were much lower than the homogeneous one as expected. However, considering only the supported system, it was found that activities dramatically increased with increasing the amounts of titania up to 60% in the supports compared with those for the pure silica support. The maximum activity can be obtained with the presence of 20% titania in the mixed support. However, with increasing the amounts of titania more than 60% resulted in lower activities compared to the pure silica. It was also found that the activity for the pure titania is the lowest because the strong support interaction [7] between MAO and titania was more pronounced. Based on the resulted activities, the role of titania in TiO_2-SiO_2 mixed oxide supports can be proposed. In order to give a better understanding for the role of titania, a conceptual model for titania effect is illustrated in Figure 4.7. As known, when the heterogeneous system was conducted, activities decreased significantly compared to the homogeneous one as also seen in Figure 4.6.

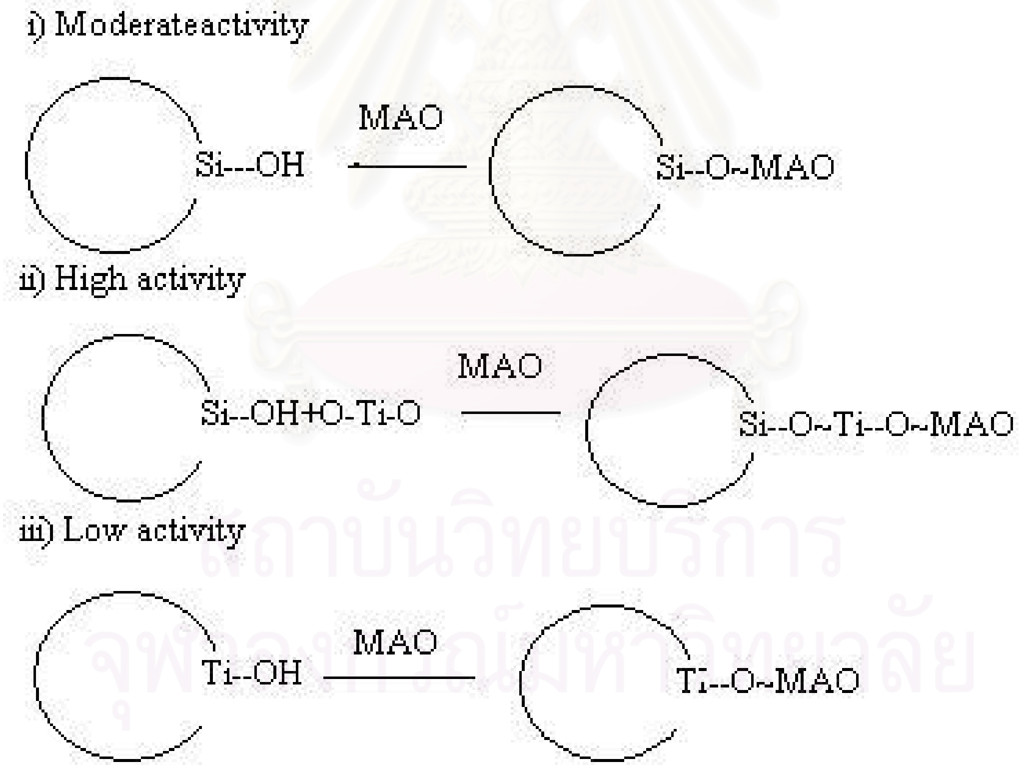


Figure 4.7 Conceptual model in role of titania in TiO_2-SiO_2 mixed oxide

This should be due to a loss of active species by support interaction and/or the steric hindrance arising from the support.

Considering Figure 4.7, activity on the heterogeneous system can be divided into three levels; (i) moderate activity with the conventional pure silica support, (ii) high activity with the certain amounts of titania present in the mixed oxide support, (iii) low activity with the pure titania support (due to strong support interaction [57]). In Figure 4.7, it showed that the presence of certain amounts (20 to 60 wt%) of titania dramatically enhanced activities. The contribution of titania can be drawn as MAO anchored on silica with titania as a spacer group. It can be also seen from SEM and EDX that at low content of titania, it was apparently decorated on silica surface and acted as a spacer to anchor MAO to the silica support. Thus, activities increased about 15 to 25% with the presence of titania between 20 and 40% in the mixed oxide supports. It should be mentioned that increased activities with the presence of titania as a spacer were observed because of less steric hindrance and less interaction on the support surface when a spacer was introduced. Thus, this was suggested to be more homogeneous-like system. Investigation of a spacer such as silane in copolymerization of ethylene/1-olefins was also reported [58, 59]. However, when high amounts of titania were added, activities decreased because the strong support interaction as seen in Figure 4.7 (ii) can occurred resulting in a combination between Figure 4.7 (i) and (iii) where titania started to isolate from silica as segregated titania.

4.2.2 The Effect of TiO_2-SiO_2 mixed oxide supports on the Catalytic reactivity

The various TiO_2-SiO_2 mixed oxide supports after impregnation with MAO were used and investigated for catalytic reactivities. At initial period, the catalyst activation rate was higher than the deactivation rate, so the ethylene consumption rate increased after reach the turn over point. The deactivation rate gradually increased while the activation rate decreased, so the ethylene consumption reduced. The catalytic reactivities influenced by the various supports had the similar trend.

4.2.3 The Effect of TiO_2-SiO_2 mixed oxide supports on the morphologies of copolymers

Morphologies of polymers produced via various supports were also investigated. It indicated that there was no significant change in polymer morphologies upon various mixed oxide supports used.

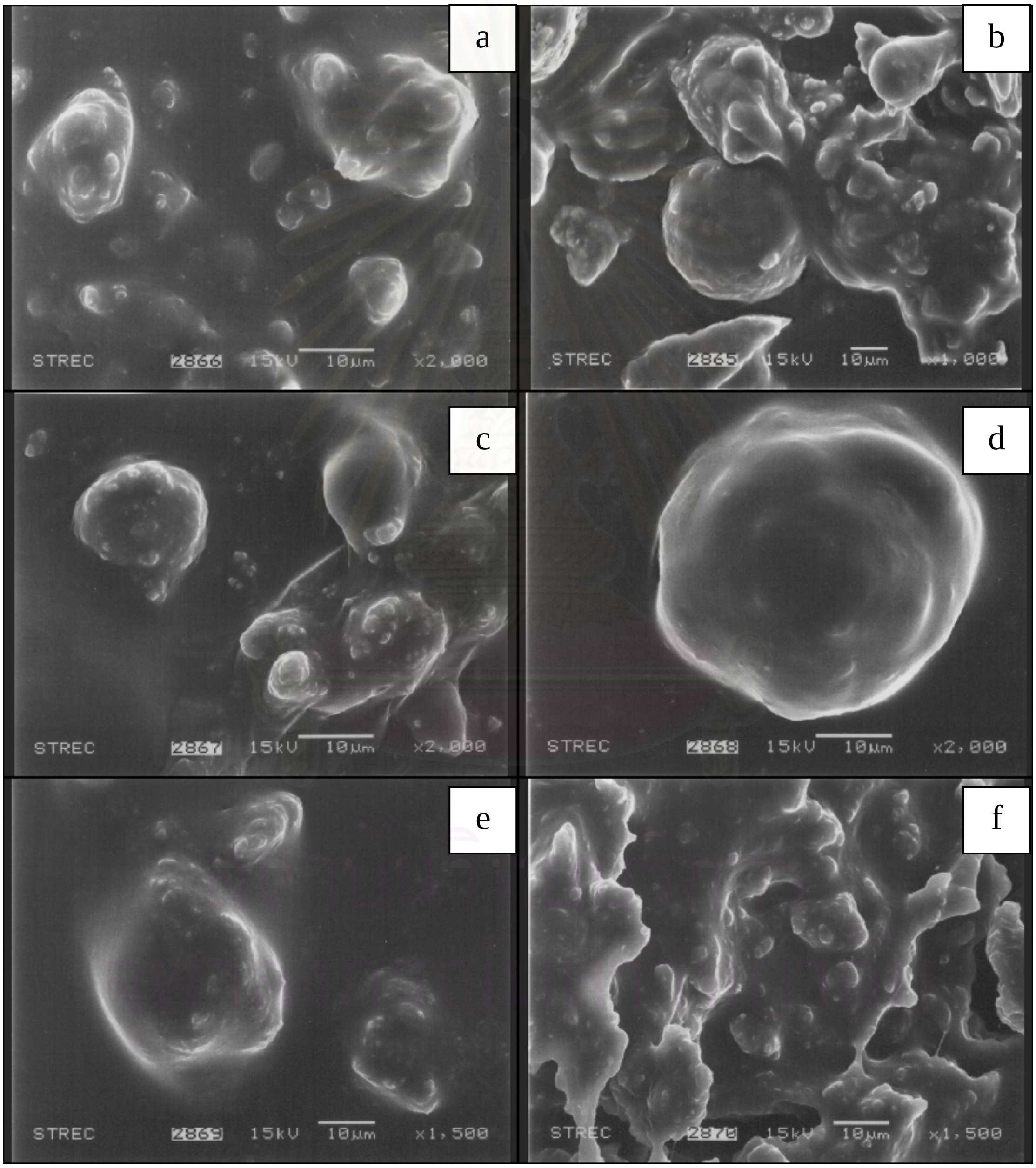


Figure 4.8 Scanning electron microscope image of ethylene/1-octene copolymer; a: Ti/Si = 0/1, b: Ti/Si = 2/8, c: Ti/Si = 4/6, d: Ti/Si = 6/4, e: Ti/Si = 8/2, f: Ti/Si = 1/0

4.2.4 The Effect of TiO_2-SiO_2 mixed oxide supports on the molecular weight of copolymers

The molecular weight based on weight average (M_w) and based on number average (M_n), and molecular weight distribution (MWD) of polymers obtained by a gel permeation chromatography are shown in Table 4.2. and GPC curves of the copolymer are also shown in Appendix B.

Table 4.2 Molecular weight and molecular weight distribution of different ratio mixed oxide in ethylene/1-octene

Weight Ratio (TiO_2-SiO_2)	M_w[a] ($x10^{-4}$g/mole)	M_n[a] ($x10^{-4}$g/mole)	MWD[a]
0/100	3.61	1.06	3.4
20/80	3.42	1.08	3.2
40/60	2.91	1.13	2.6
60/40	2.60	0.96	2.7
80/20	2.65	0.93	2.8
100/0	2.41	0.59	4.1

[a] Obtained from GPC and MWD was calculated from M_w/M_n

It indicated that the addition of TiO_2 resulted in decreased molecular weight of polymer compared to those of pure SiO_2. However, the narrower molecular weight distribution was observed with the addition of TiO_2 except for the one with pure TiO_2.

4.2.5 The Effect of TiO_2-SiO_2 mixed oxide supports on the melting temperatures of copolymers

The melting temperatures (T_m) of copolymer were evaluated by Differential Scanning Calorimeter (DSC) are shown in Table 4.3. DSC curves of the copolymer are also shown in Appendix C.

Table 4.3 Melting temperatures of different ratio mixed oxide in ethylene/1-octene

Weight Ratio (TiO_2-SiO_2)	Tm(^oC)
Homogenous	103.76
0/100	85.78
20/80	87.90
40/60	90.89
60/40	92.06
80/20	89.86
100/0	99.11

Form the characterization of copolymer in Table 4.3, it exhibit that, the melting temperatures (T_m) of copolymer was increase by the amount of Ti in support the copolymerization of ethylene with 1-octene by metallocene catalysis. A small amount of comonomer incorporation of 1-octene leads to linear low density polyethylene (LLDPE), a product of great industrial interest. One effect of the comonomer incorporation is a decrease in crystallinity. As a result, polymers with a lower melting point and density, and an increased flexibility and processibility are obtained [55].

4.2.6 The Effect of TiO_2-SiO_2 mixed oxide supports on the incorporation of polymers

Table 4.4 Incorporation of different ratio mixed oxide in ethylene/1-octene

Weight Ratio (TiO_2-SiO_2)	Insertion (%)
Homogenous	n.a.
0/100	19
20/80	16
40/60	14
60/40	11
80/20	n.a.
100/0	n.a.

Table 4.5 Triad distribution of ethylene /1-octene

Weight Ratio (TiO_2-SiO_2)	**EEE**	**OEE+EEO**	**OEO**	**EOE**	**OOE+EOO**	**OOO**
0/100	0.63	0.18	-	0.19	-	-
20/80	0.69	0.15	-	0.16	-	-
40/60	0.72	0.14	-	0.14	-	-
60/40	0.79	0.10	-	0.11	-	-

E refers to ethylene and **O** refers to corresponding comonomers: 1-octene

^{13}C NMR spectroscopy was used to determine comonomer incorporation and polymer microstructure. Chemical shift were referred internally to the major backbone methylene resonance and calculated according to the method of Randall [67]. The result obtained for the triad sequence distribution of copolymer shown in Table 4.5. The result suggested that the copolymer had a random distribution of comonomer insertion with very low amount of comonomer triad in the polymer chain. comonomer incorporation was decrease by the amount of Ti in support the copolymerization of ethylene with 1-octene by metallocene catalysis.

4.3 Effect of TiO_2-SiO_2 mixed oxide supports with different comonomer

4.3.1 The Effect of TiO_2-SiO_2 mixed oxide supports with different comonomer on the Catalytic Activity

Then, the various TiO_2-SiO_2 mixed oxide supports after impregnation with MAO were used and investigated for catalytic activities. Copolymerization of ethylene/1-decene and ethylene/1-hexene via various TiO_2-SiO_2 mixed oxides-supported MAO with zirconocene catalyst was performed in order to determine the catalytic activities influenced by the various supports. . Methylaluminoxane (MAO) was used as cocatalyst which the molar ratio of $Al_{(MAO)}/Zr$ was varied in the range of

160 to 1135. The copolymerizations were performed in toluene solvent at 70°C using ethylene consumption of 0.018 mol (pressure in reactor 50 psi), 0.018 ml of α-olefin, 100 mg of catalyst precursor and zirconium concentration 5.0×10^{-5} M with total solution volume of 30 ml. The resulted reaction study is shown in Table 4.6- 4.7.

Table 4.6 Catalytic activity of different ratio mixed oxide in ethylene/1-decene

Weight Ratio (TiO_2-SiO_2)	Yield (g)	Polymerization Time (sec)	Catalytic Activity[a] (kgCopolymer/molZr.h)
Homogenous	1.1141	98	27284
0/100	1.1254	162	16672
20/80	1.1187	141	19041
40/60	1.1090	172	15676
60/40	1.1235	179	14869
80/20	1.1161	181	14799
100/0	1.1154	194	13798

[a] copolymerization conditions: $Al_{(MAO)}/Zr = 1135$, $Al_{(TMA)}/Zr = 2500$, precursor = 100 mg ,reaction temperature 70°C, 0.018 mol of ethylene consumption,0.018 mol of 1-decene, total volume = 30 ml, and $[Zr] = 5 \times 10^{-5}$ M.

Table 4.7 Catalytic activity of different ratio mixed oxide in ethylene/1-hexene

Weight Ratio (TiO_2-SiO_2)	Yield (g)	Polymerization Time (sec)	Catalytic Activity[a] (kgCopolymer/molZr.h)
Homogenous	1.1325	81	33555
0/100	1.1931	148	19347
20/80	1.1638	109	25624
40/60	1.1831	128	22183
60/40	1.1653	142	19695
80/20	1.1514	151	18300
100/0	1.1578	165	16840

[a]copolymerization conditions: $Al_{(MAO)}/Zr = 1135$, $Al_{(TMA)}/Zr = 2500$, precursor = 100 mg ,reaction temperature 70°C, 0.018 mol of ethylene consumption,0.018 mol of 1-hexene, total volume = 30 ml, and [Zr] = 5×10^{-5} M.

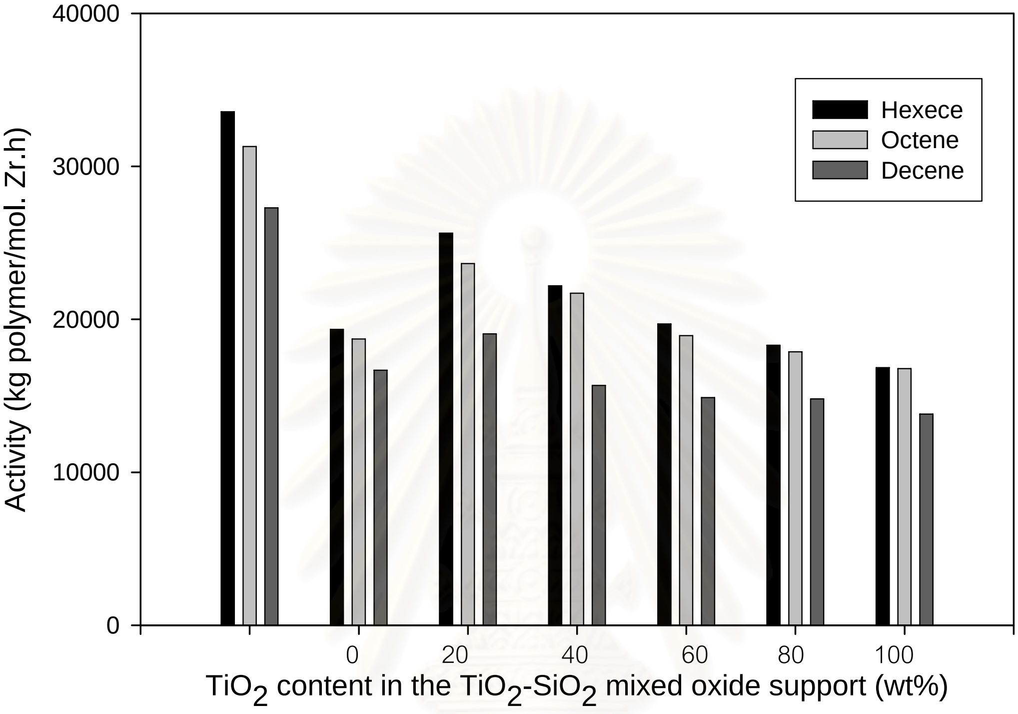


Figure 4.6 Catalytic activity of different ratio mixed oxide and comonomer

In copolymerization of ethylene with three different comonomers, the catalytic activities continuously decrease with carbon atom in comonomers (1-hexene> 1-octene> 1-decene). The activities of the supported system were much lower than the homogeneous one as expected. However, considering only the supported system, it was found that activities dramatically increased with increasing the amounts of titania up to 60% in the supports compared with those for the pure silica support. The maximum activity can be obtained with the presence of 20% titania in the mixed support in all comonomer.

4.3.2 The Effect of TiO_2-SiO_2 mixed oxide supports on the morphologies of copolymers

Morphologies of polymers produced via various supports were also investigated. It indicated that there was no significant change in polymer morphologies upon various mixed oxide supports used but copolymerization of ethylene with three different comonomers the morphology of obtained polymers are seem similar.

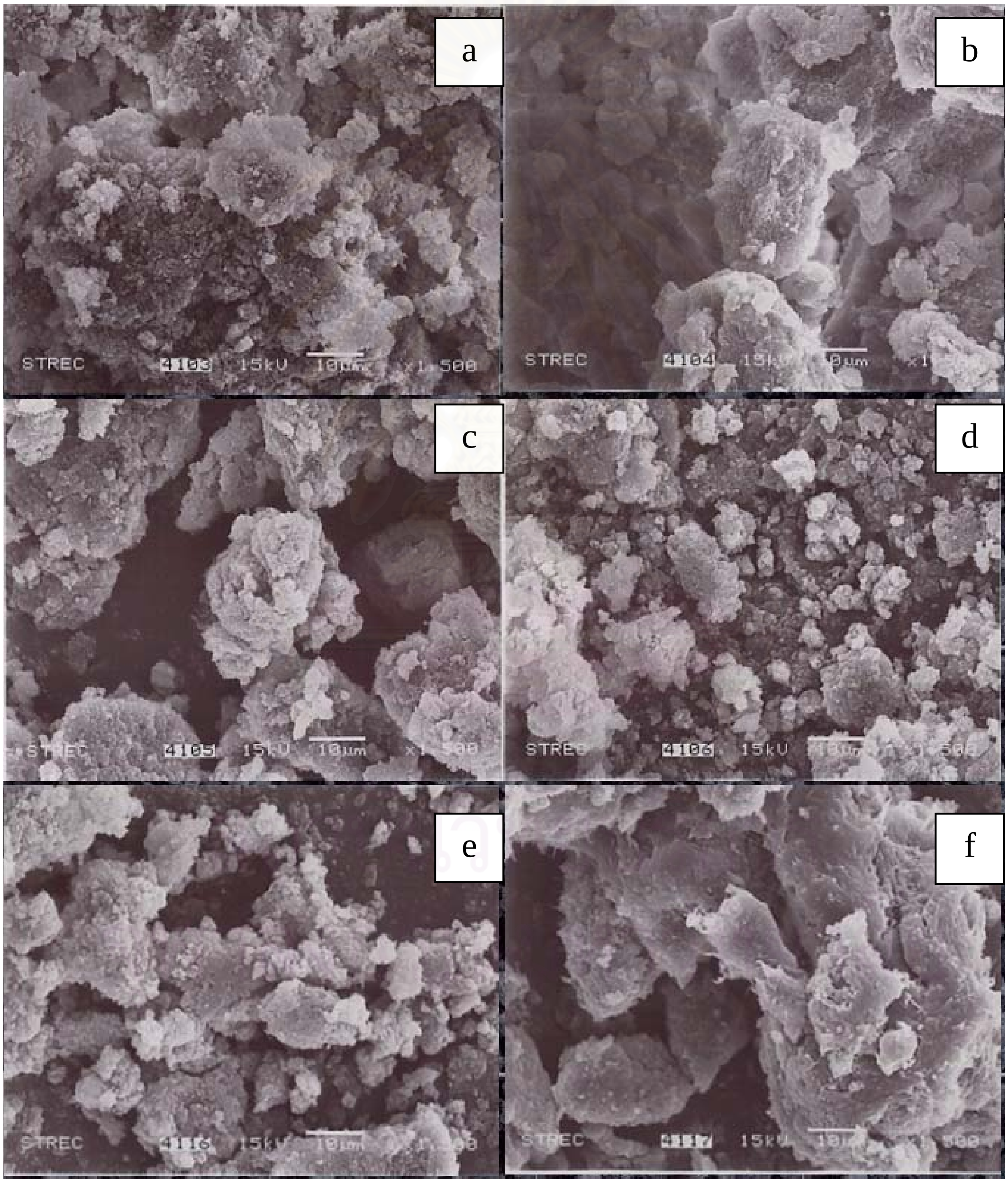


Figure 4.9 Scanning electron microscope image of ethylene/1-decene copolymer; a: Ti/Si = 0/1, b: Ti/Si = 2/8, c: Ti/Si = 4/6, d: Ti/Si = 6/4, e: Ti/Si = 8/2, f: Ti/Si = 1/0

4.3.3 The Effect of TiO_2-SiO_2 mixed oxide supports on the melting temperatures of copolymers with different comonomer

The melting temperatures (T_m) of copolymer were evaluated by differential scanning calorimeter (DSC) are shown in Table 4.7 and Table 4.8. DSC curves of the copolymer are also shown in Appendix C.

Weight Ratio (TiO_2-SiO_2)	Tm(°C)
Homogenous	104.93
0/100	100.68
20/80	101.25
40/60	104.12
60/40	n.a.
80/20	105.07
100/0	n.a.

Table 4.8 Melting temperatures of different ratio mixed oxide in ethylene/1-decene

Weight Ratio (TiO_2-SiO_2)	Tm(°C)
Homogenous	104.43
0/100	88.81
20/80	88.94
40/60	91.29
60/40	94.22
80/20	94.53
100/0	100.28

Table 4.9 Melting temperatures of different ratio mixed oxide in ethylene/1-hexene

Form the characterization of copolymer in Table 4.7-4.8, it exhibit that, the melting temperatures (T_m) of copolymer was increase by the amount of TiO_2 in support the copolymerization of ethylene with 1-decene, 1-hexene by metallocene catalysis. It also that ethylene/1-decene, ethylene/1-hexene have decreased in corporation by the amount of Ti in each support.

4.4 Effect of homopolymer and copolymer

4.4.1 The Effect of TiO_2-SiO_2 mixed oxide supports with polyethylene

Then, the various TiO_2-SiO_2 mixed oxide supports after impregnation with MAO were used and investigated for catalytic activities. Polymerization of ethylene via various TiO_2-SiO_2 mixed oxides-supported MAO with zirconocene catalyst was performed in order to determine the catalytic activities influenced by the various supports. The resulted reaction study is shown in Table 4.10.

Weight Ratio (TiO_2-SiO_2)	Yield (g)	Polymerization Time (sec)	Catalytic Activity[a] (kgpolymer/molZr.h)
Homogenous	0.4895	436	2694
0/100	0.4882	694	1688
20/80	0.4960	621	1917
40/60	0.4939	728	1628
60/40	0.4920	798	1480
80/20	0.4892	810	1449
100/0	0.4884	902	1299

[a] polymerization conditions: $Al_{(MAO)}/Zr = 1135$, $Al_{(TMA)}/Zr = 2500$, precursor = 100 mg ,reaction temperature 70°C, 0.018 mol of ethylene consumption, total volume = 30 ml, and $[Zr] = 5 \times 10^{-5}$ M.

Table 4.10 Catalytic activity of different ratio mixed oxide in polyethylene

The catalytic activities in ethylene polymerization were low active due to the nature of catalyst.

4.4.2 The Effect of TiO_2-SiO_2 mixed oxide supports on polyethylene

Morphologies of polymers produced via various supports were also investigated. It indicated that there was no significant change in polymer morphologies.

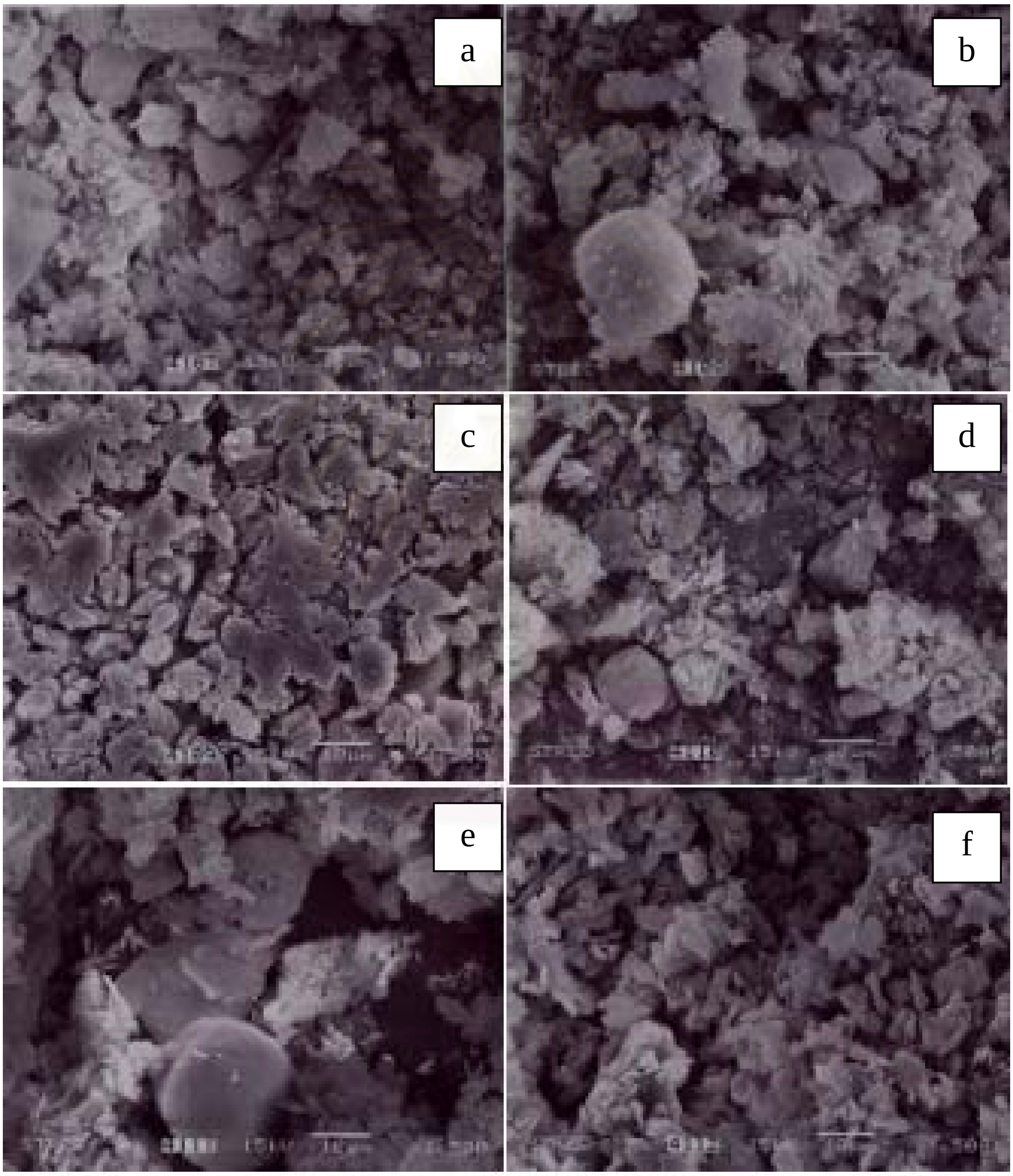


Figure 4.10 Scanning electron microscope image of ethylene/1-decene copolymer; a: Ti/Si = 0/1, b: Ti/Si = 2/8, c: Ti/Si = 4/6, d: Ti/Si = 6/4, e: Ti/Si = 8/2, f: Ti/Si = 1/0

4.4.3 The Effect of TiO_2-SiO_2 mixed oxide supports on the molecular weight of polyethylene

The molecular weight based on weight average (M_w) and based on number average (M_n), and molecular weight distribution (MWD) of polymers obtained by a gel permeation chromatography are shown in Table 4.10. and GPC curves of the copolymer are also shown in Appendix B.

Weight Ratio (TiO_2-SiO_2)	M_w^a ($x10^{-4}$g/mole)	M_n^a ($x10^{-4}$g/mole)	MWD[a]
0/100	3.39	1.21	2.9
20/80	6.20	2.80	2.2
40/60	5.39	3.57	1.5
60/40	2.46	1.13	2.2
80/20	1.29	0.58	2.3
100/0	2.74	0.77	3.6

[a] Obtained from GPC and MWD was calculated from M_w/M_n

Table 4.10 Molecular weight and molecular weight distribution of different ratio mixed oxide in polyethylene

The narrower molecular weight distribution was observed with the addition of TiO_2 except for the one with pure TiO_2.

CHAPTER V

CONCLUSIONS & RECOMMENDATION

5.1 CONCLUSIONS

The first part of this thesis investigate influence of various TiO_2-SiO_2 mixed oxides supported-MAO on the catalytic activities during copolymerization of ethylene/1-octene. It was found that at certain contents of titania ranged between 20 and 60 wt% in the mixed oxide support, activities dramatically increased by 15 to 25% compared to those with the conventional pure silica support. It was proposed that titania added acted as a spacer to anchor MAO to the silica support resulting in less steric hindrance and less interaction on the support surface. However, larger amounts of titania resulted in lower activities because the strong support interaction between titania and MAO was more pronounced. The molecular weights of polymer were found to decrease with the addition of TiO_2 whereas narrower molecular weight distribution can be observed in the mixed TiO_2-SiO_2 supports.The melting temperatures (T_m) of ethylene /1-octene copolymer increased with the amounts of TiO_2 in the supports. It also indicated that comonomer incorporation decreased with increasing the amount of TiO_2 in support.

The effect of different comonomers on the catalytic activities during copolymerization was as follows [ethylene/1-hexene] > [ethylene/1-octene] >[ethylene/1-decene]. The morphologies of polymers produced via various supports were investigated. It indicated that there was slightly change in polymer morphologies. It was observed that morphologies of [ethylene/1-hexene] and [ethylene/1-octene] polymer was similar, but different from those of [ethylene/1-decene] and homo polyethylene. The melting temperatures (T_m) of [ethylene/1-hexene] and [ethylene/1-decene] was found to be similar with those of copolymers.

The catalytic activities in ethylene polymerization was low due to the nature of catalyst. However the narrower molecular weight distribution was observed with the addition of TiO_2 except for the one with pure TiO_2.

5.2 RECOMMENDATION

The other types of mixed oxide supports along with the effect of phase in TiO_2 should be further investigated in the near future.

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APPENDICES

APPENDIX A
(Catalytic reactivity of TiO_2-SiO_2)

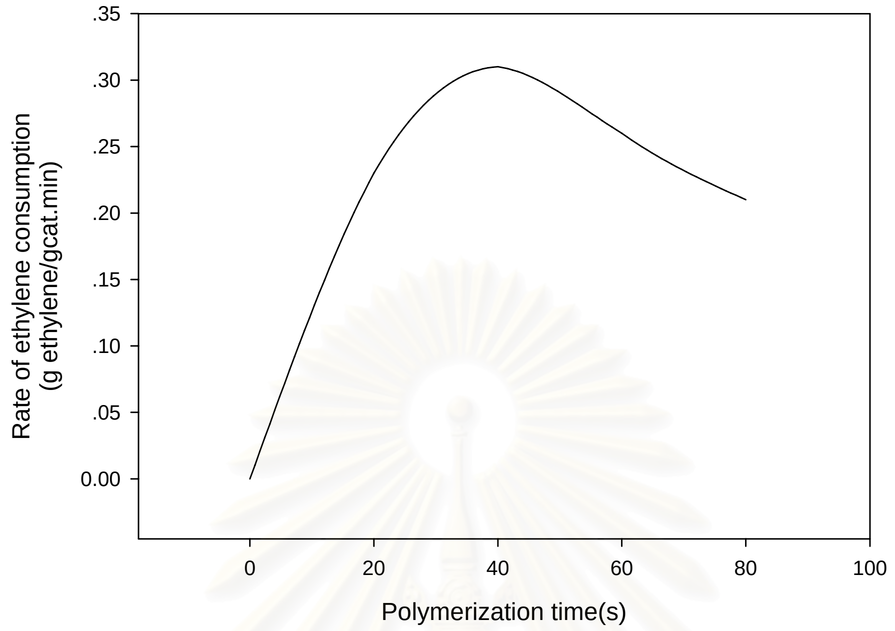


Figure A-1 Catalytic reactivity of homogenous in ethylene/1-octene

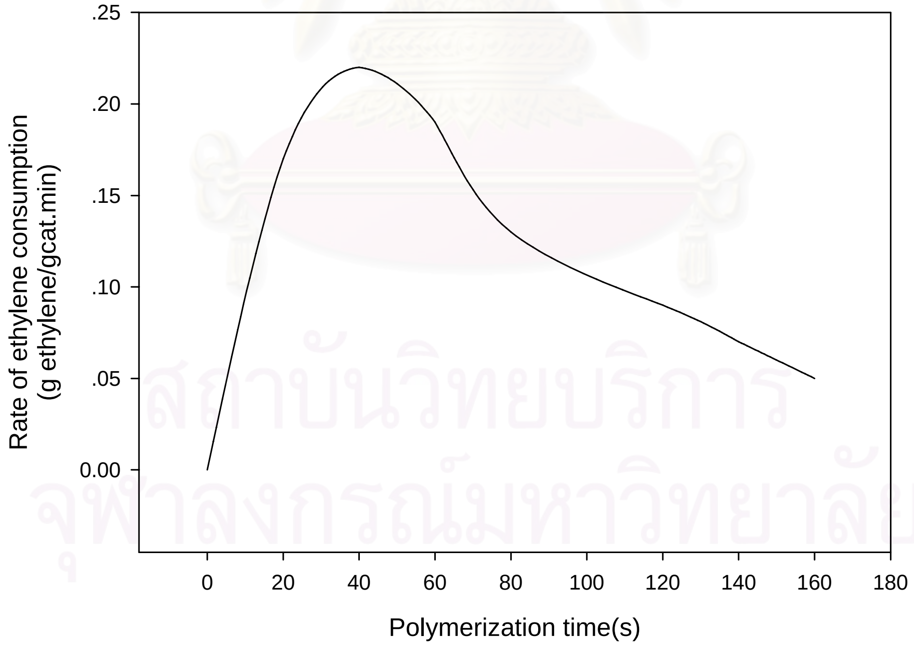


Figure A-2 Catalytic reactivity of SiO_2 support in ethylene/1-octene

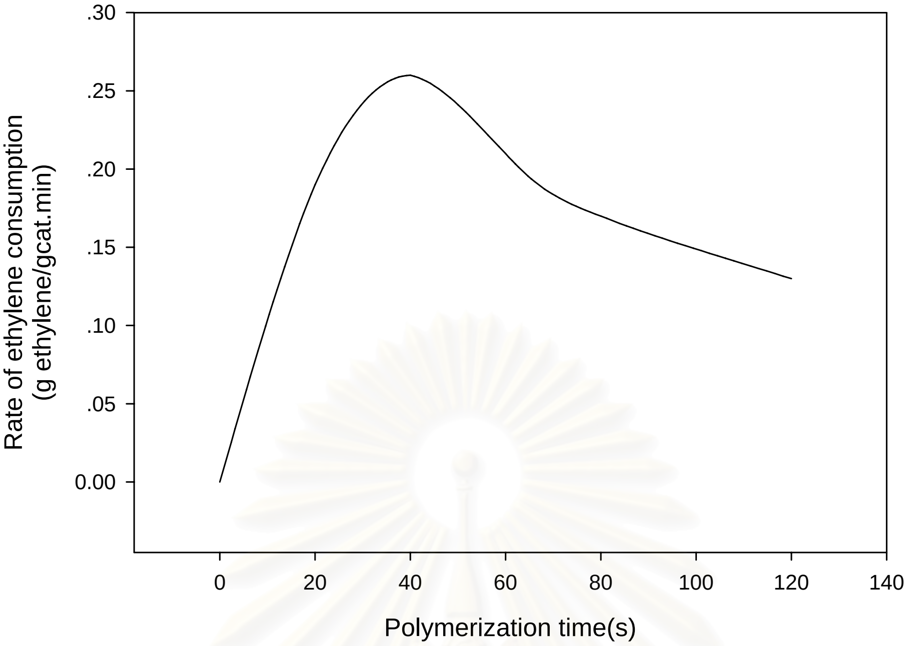


Figure A-3 Catalytic reactivity of TiO_2-SiO_2 (20/80) support in ethylene/1-octene

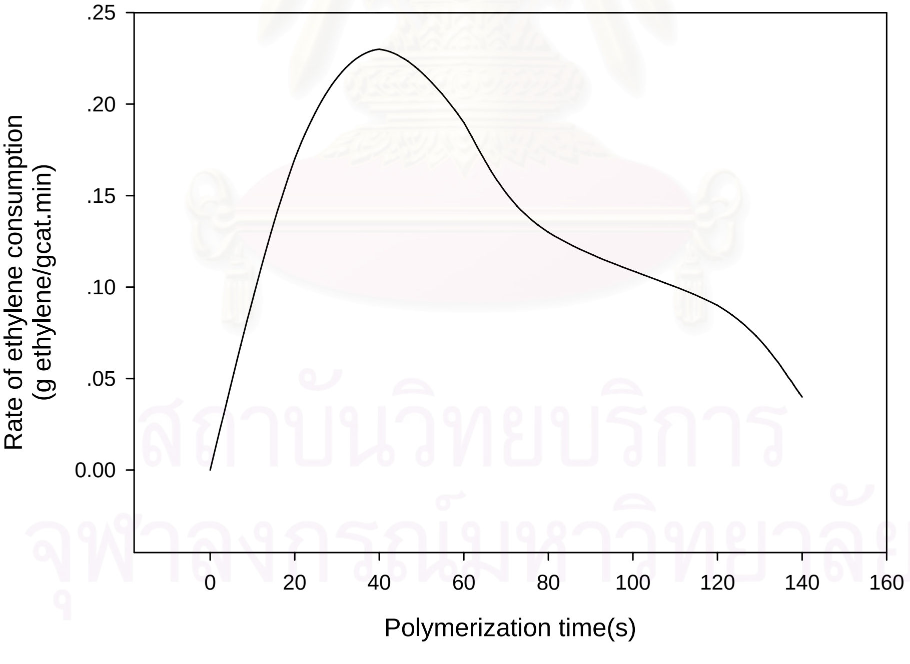


Figure A-4 Catalytic reactivity of TiO_2-SiO_2 (40/60) support in ethylene/1-octene

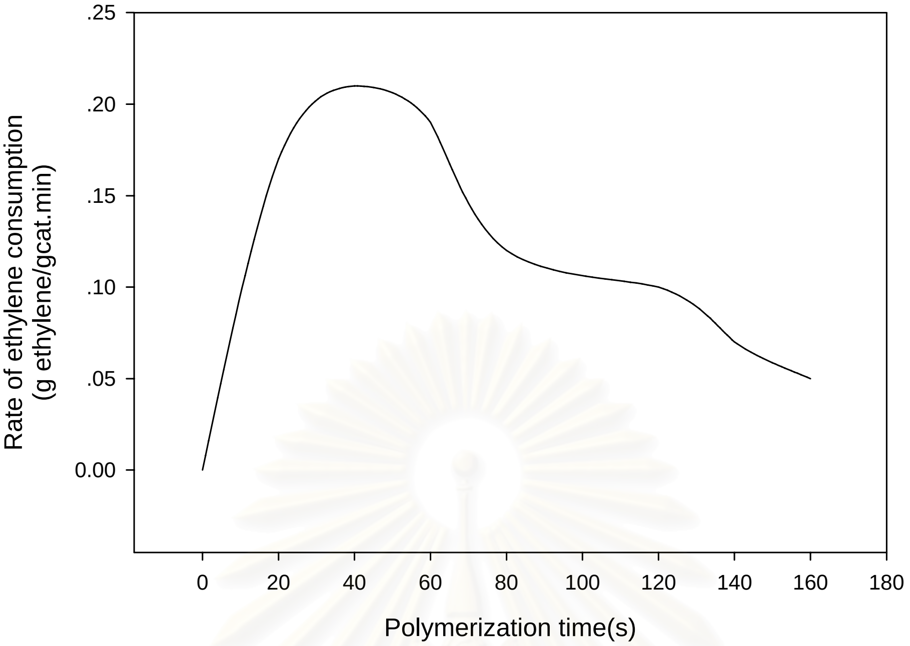


Figure A-5 Catalytic reactivity of TiO_2-SiO_2 (60/40) support in ethylene/1-octene

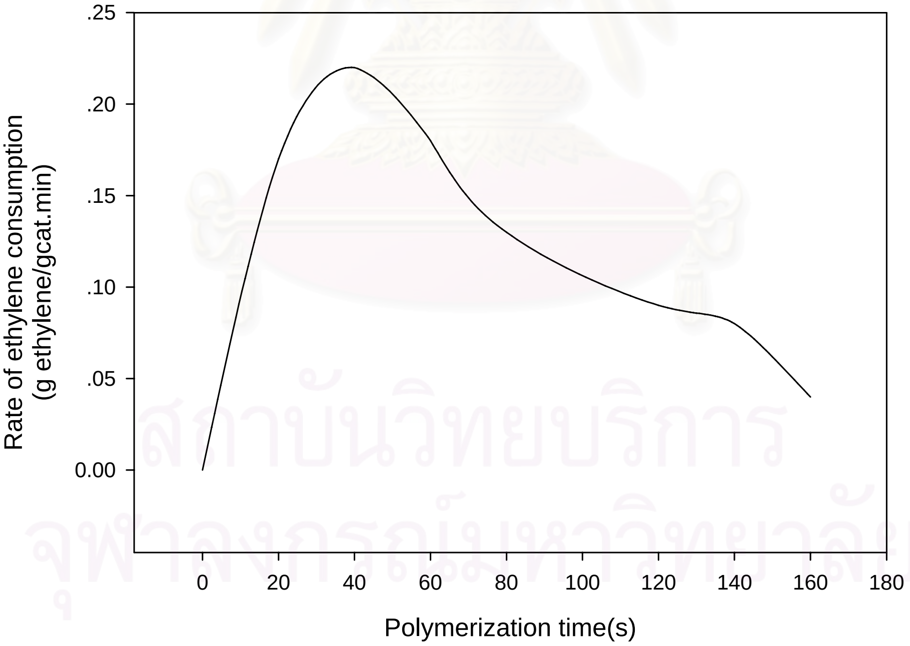


Figure A-6 Catalytic reactivity of TiO_2-SiO_2 (80/20) support in ethylene/1-octene

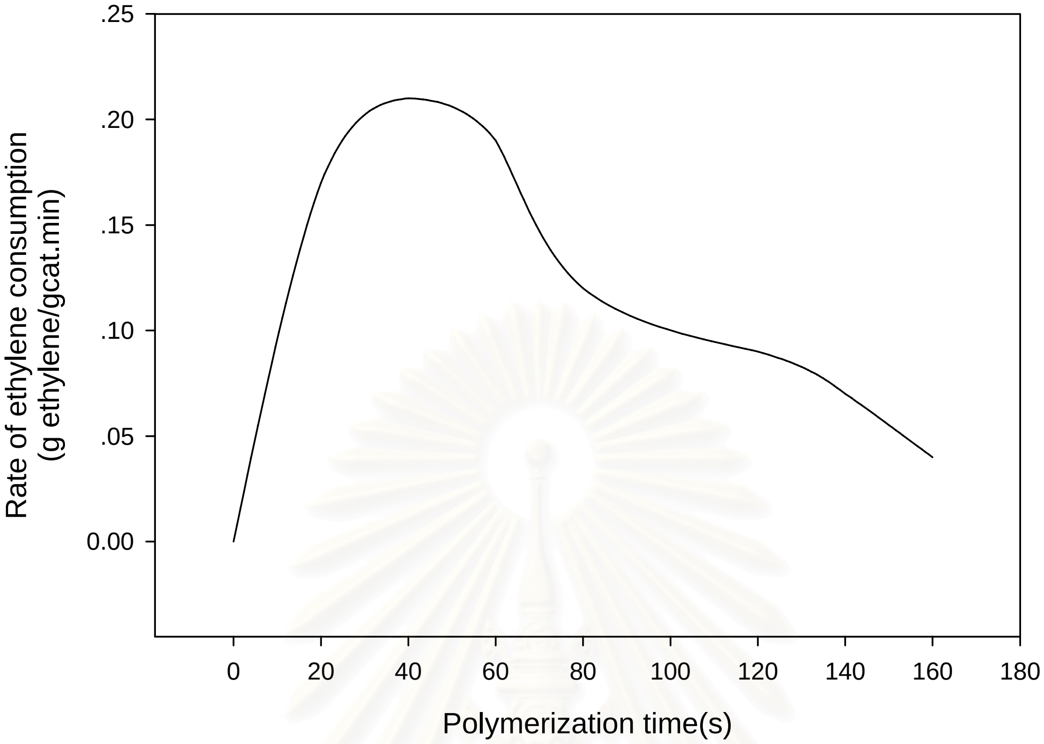


Figure A-7 Catalytic reactivity of TiO_2 support in ethylene/1-octene

APPENDIX B
(Gel permeation chromatography)

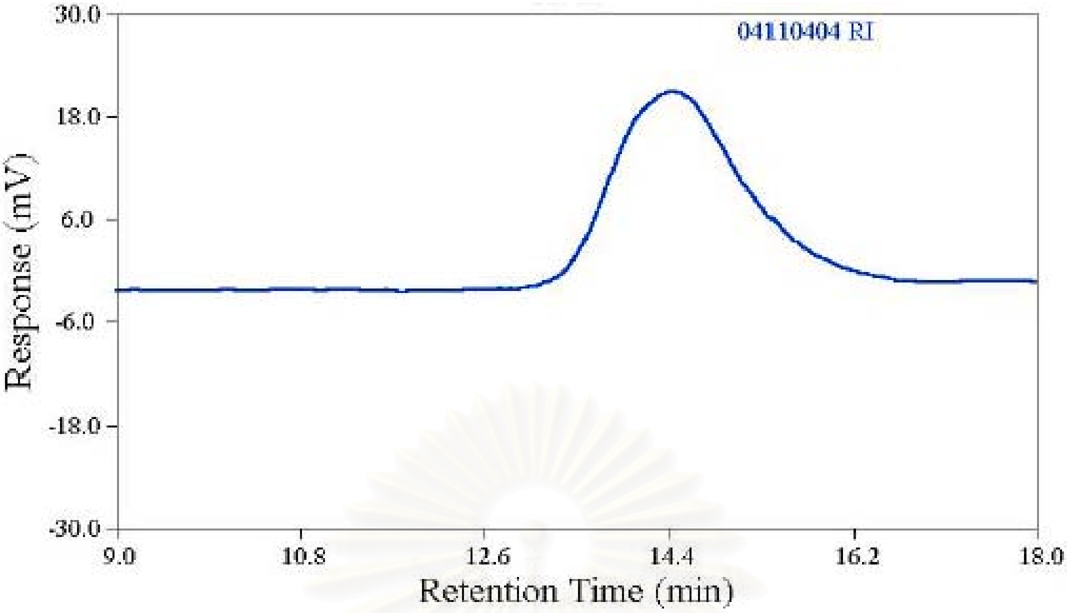


Figure B-1. GPC curve of ethylene polymer produce with TiO_2/SiO_2 = 0/100

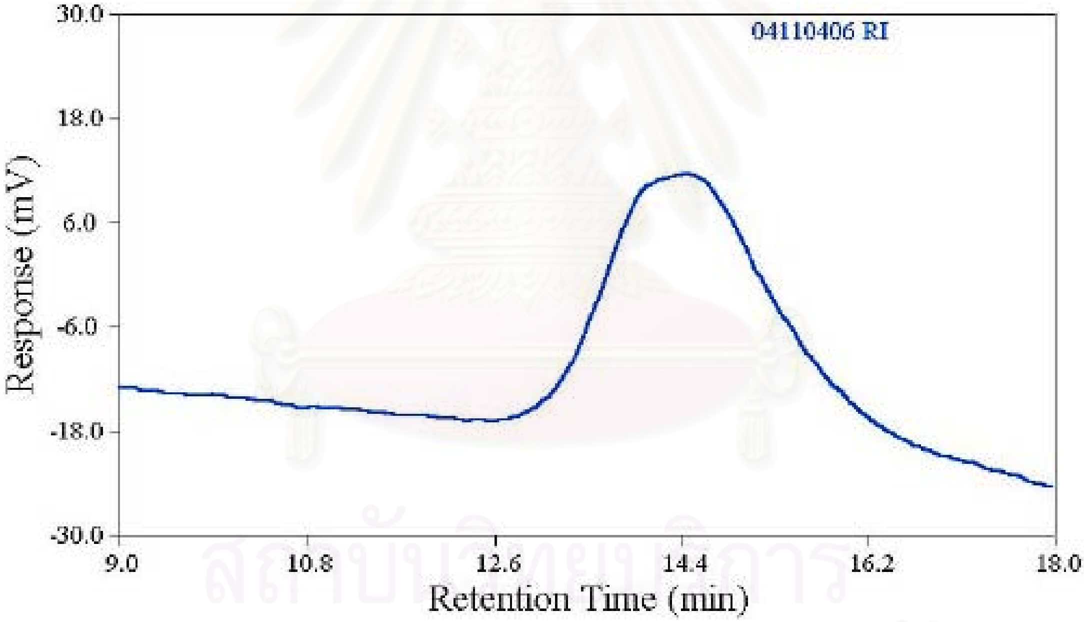


Figure B-2. GPC curve of ethylene polymer produce with TiO_2/SiO_2 = 20/80

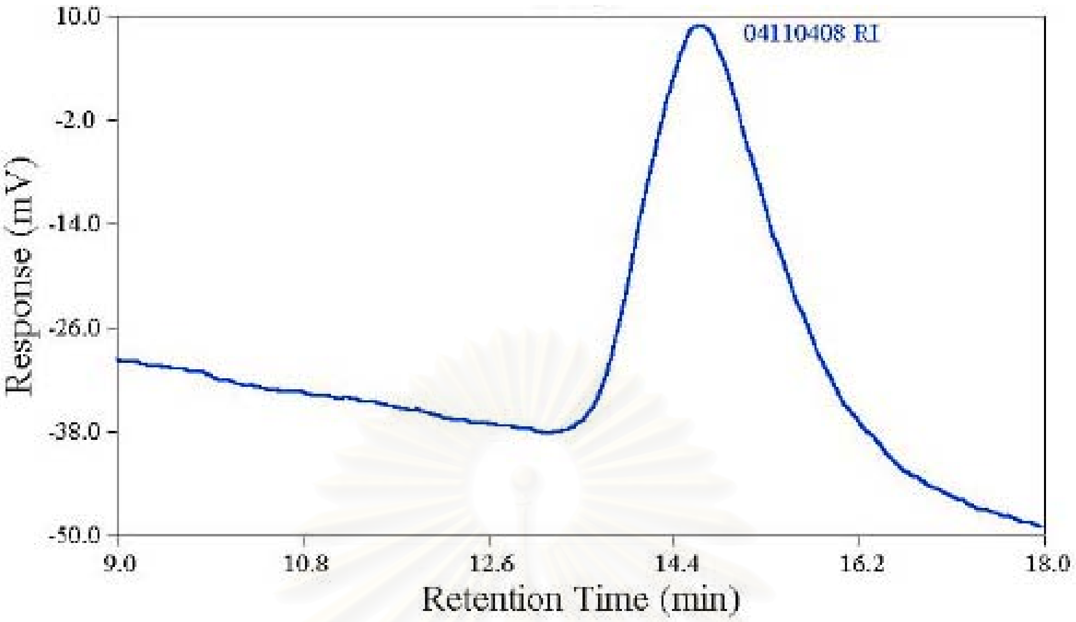


Figure B-3. GPC curve of ethylene polymer produce with TiO_2/SiO_2 = 40/60

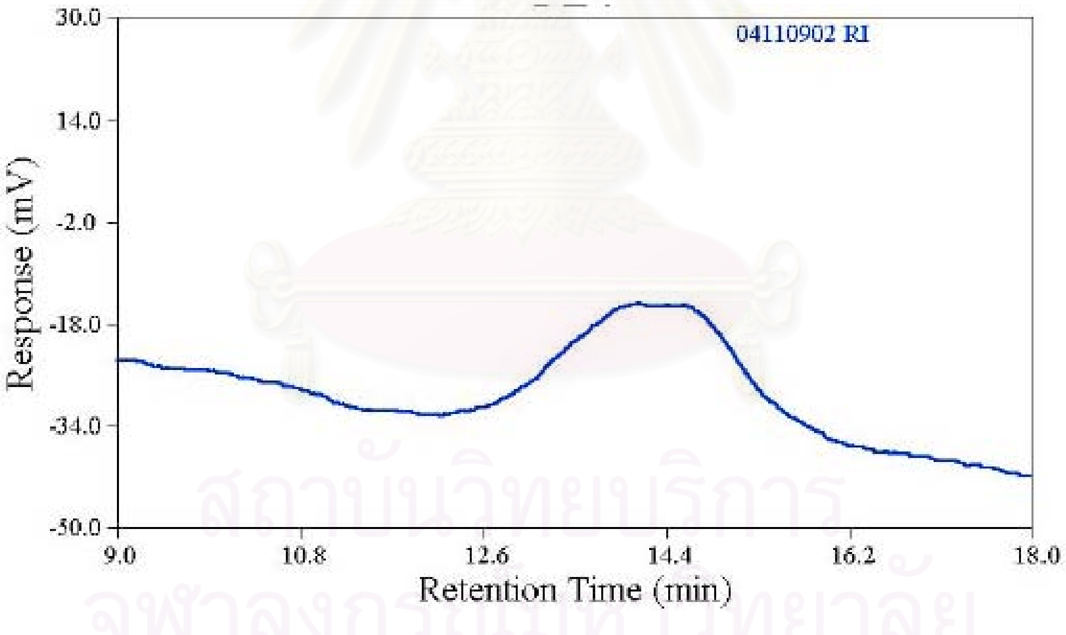


Figure B-4. GPC curve of ethylene polymer produce with TiO_2/SiO_2 = 60/40

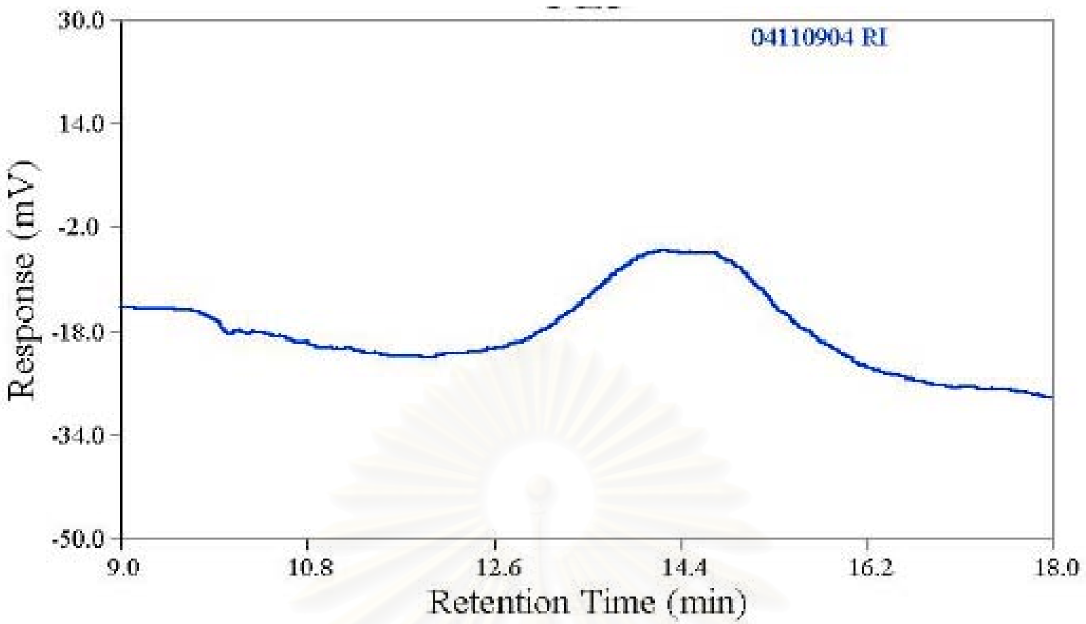


Figure B-5. GPC curve of ethylene polymer produce with TiO_2/SiO_2 = 80/20

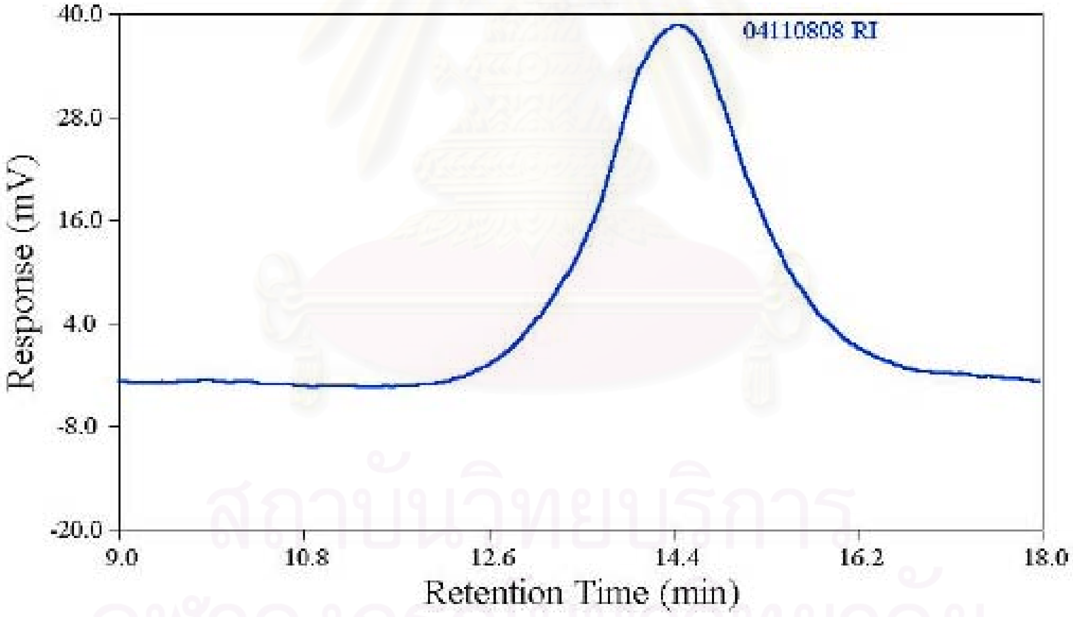


Figure B-6. GPC curve of ethylene polymer produce with TiO_2/SiO_2 = 100/0

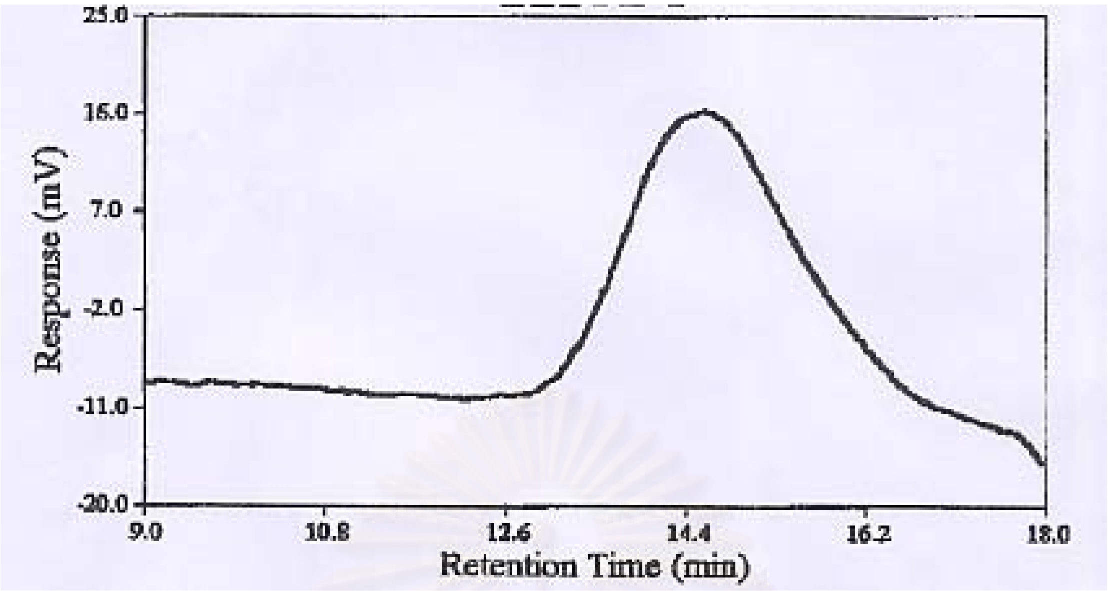


Figure B-7. GPC curve of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 0/100

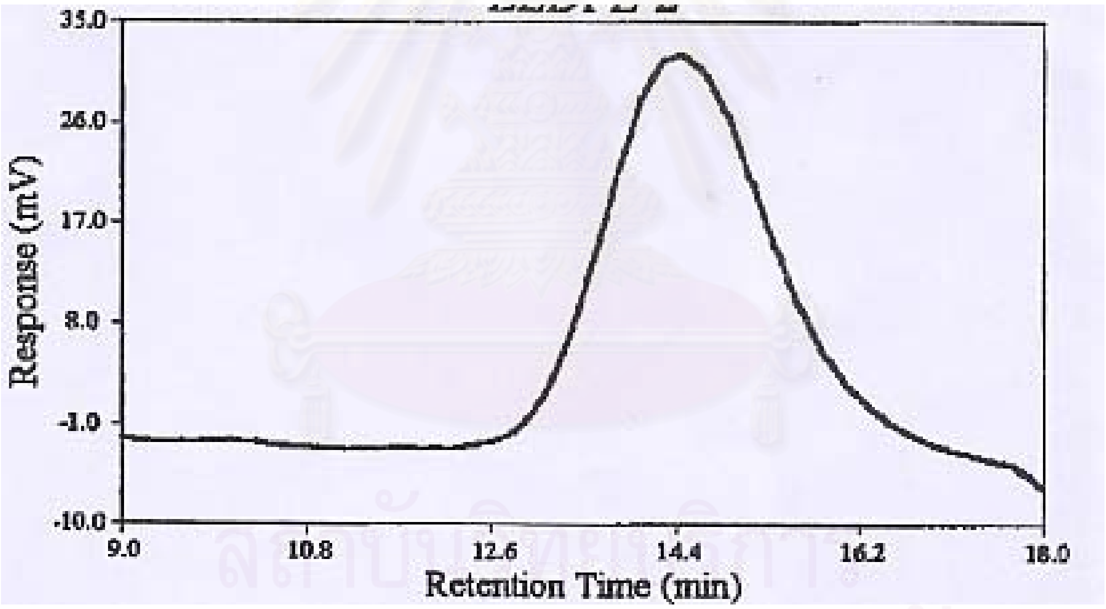


Figure B-8. GPC curve of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 20/80

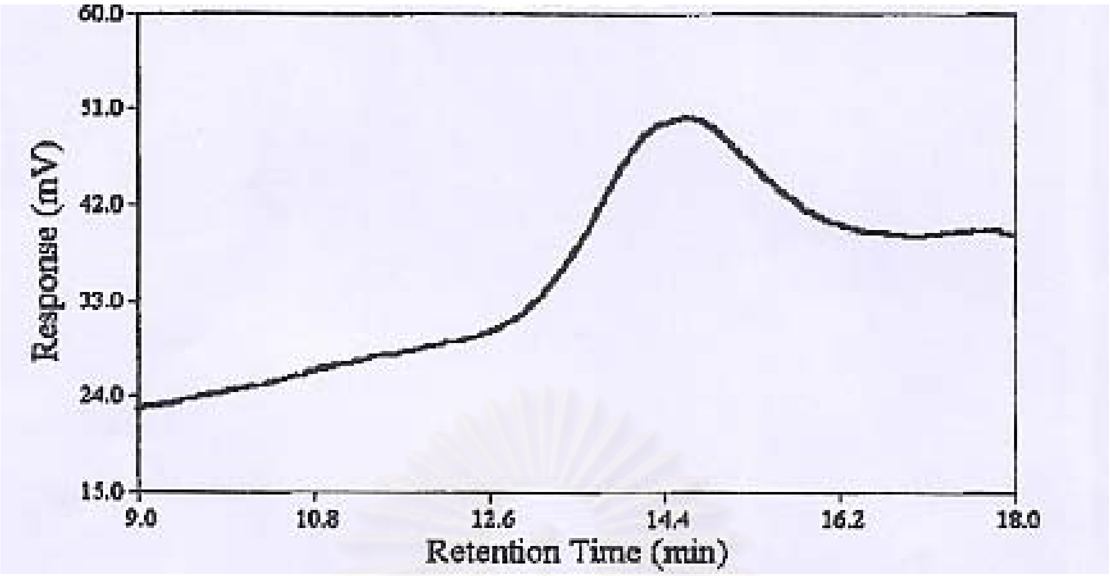


Figure B-9. GPC curve of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 40/60

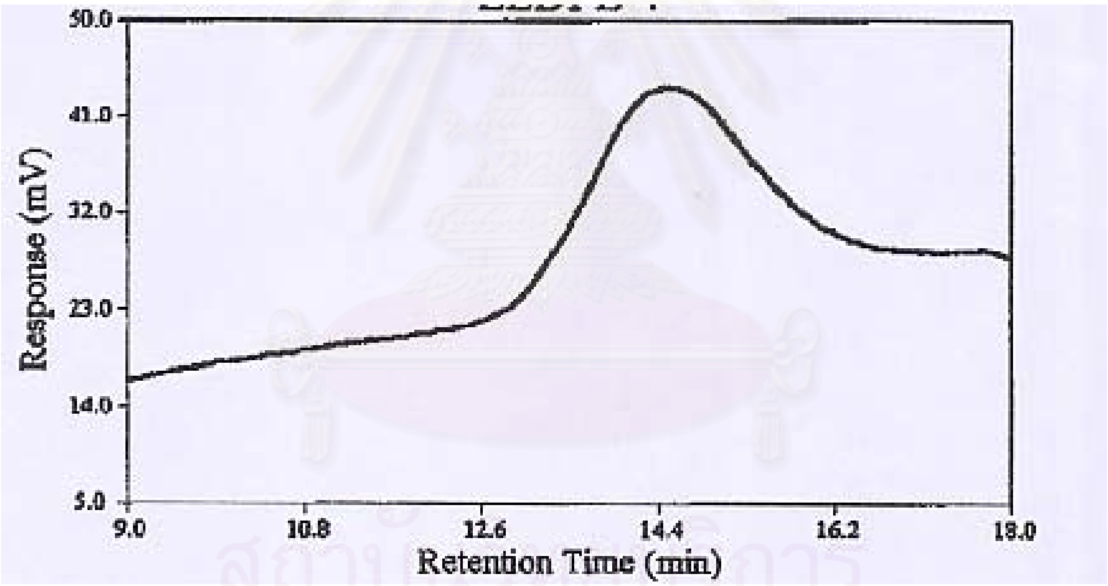


Figure B-10. GPC curve of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 60/40

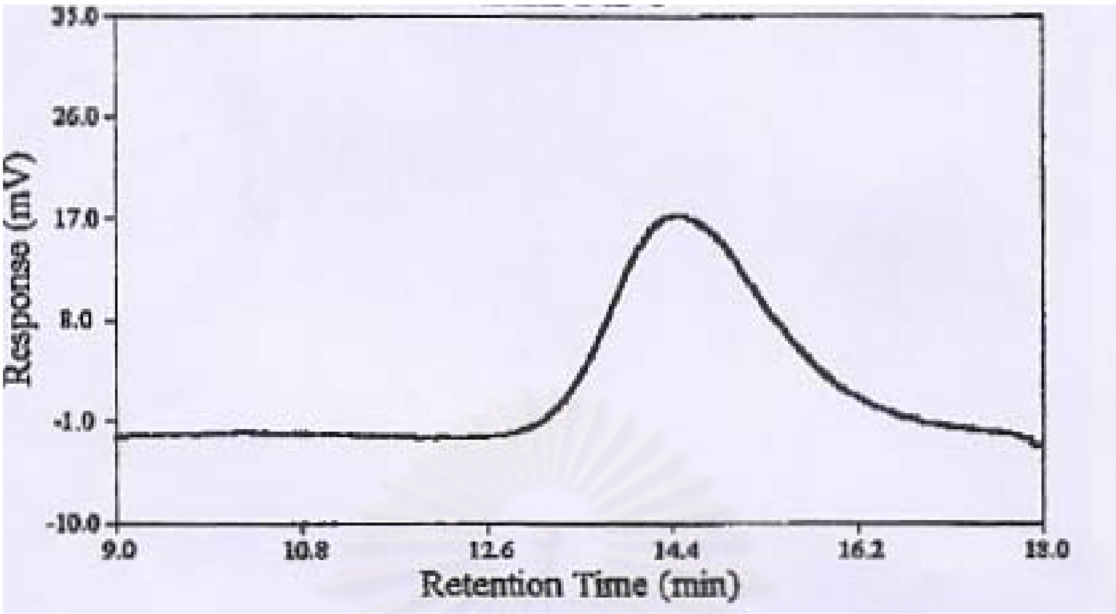


Figure B-11. GPC curve of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 80/20

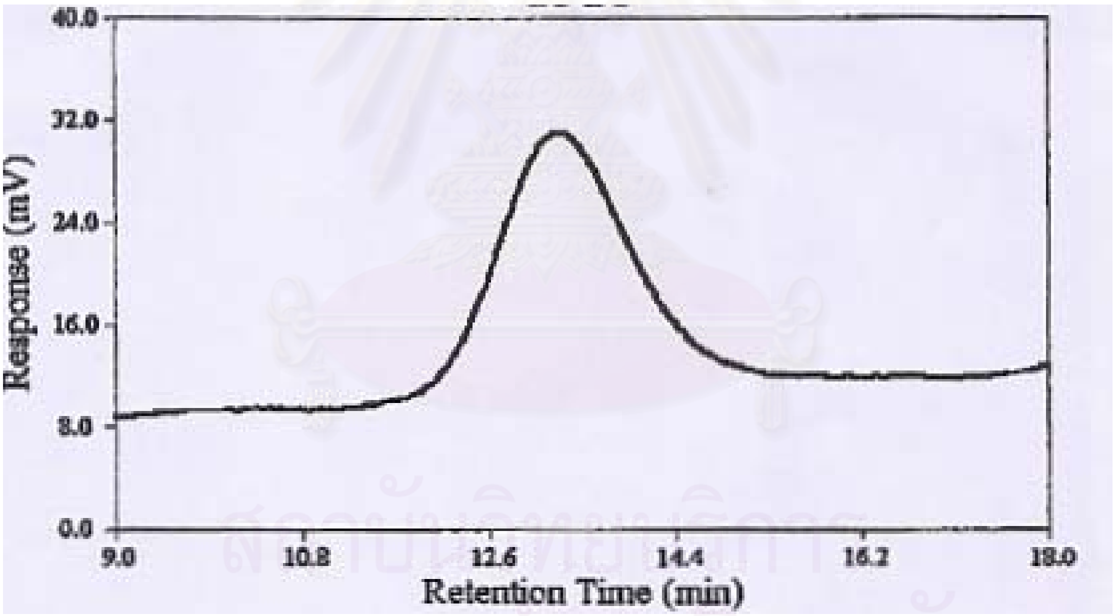


Figure B-12. GPC curve of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 100/0

APPENDIX C
(Differential Scanning Calorimeter)

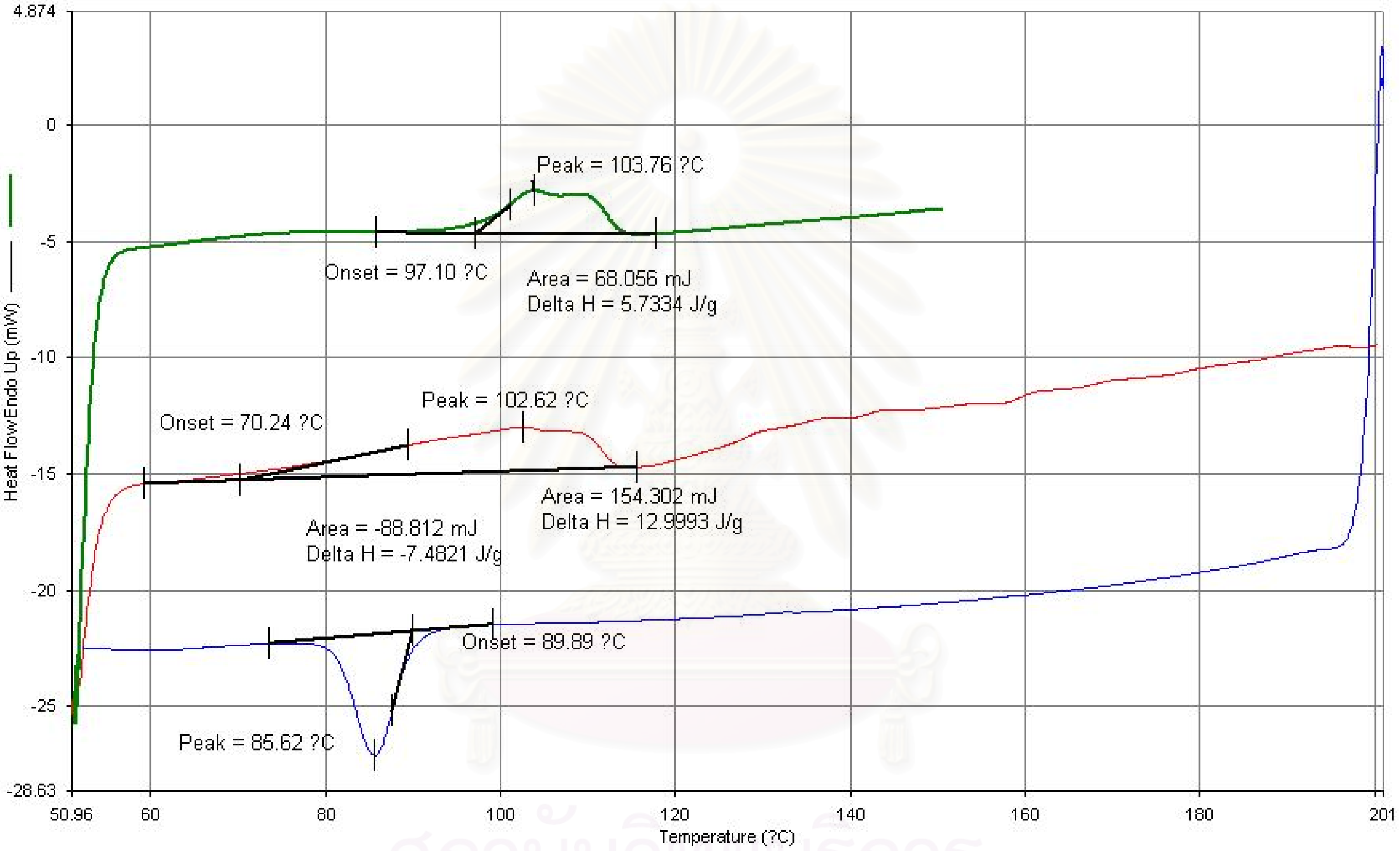


Figure C-1. DSC curve of ethylene/1-octene copolymer produce with homogenous

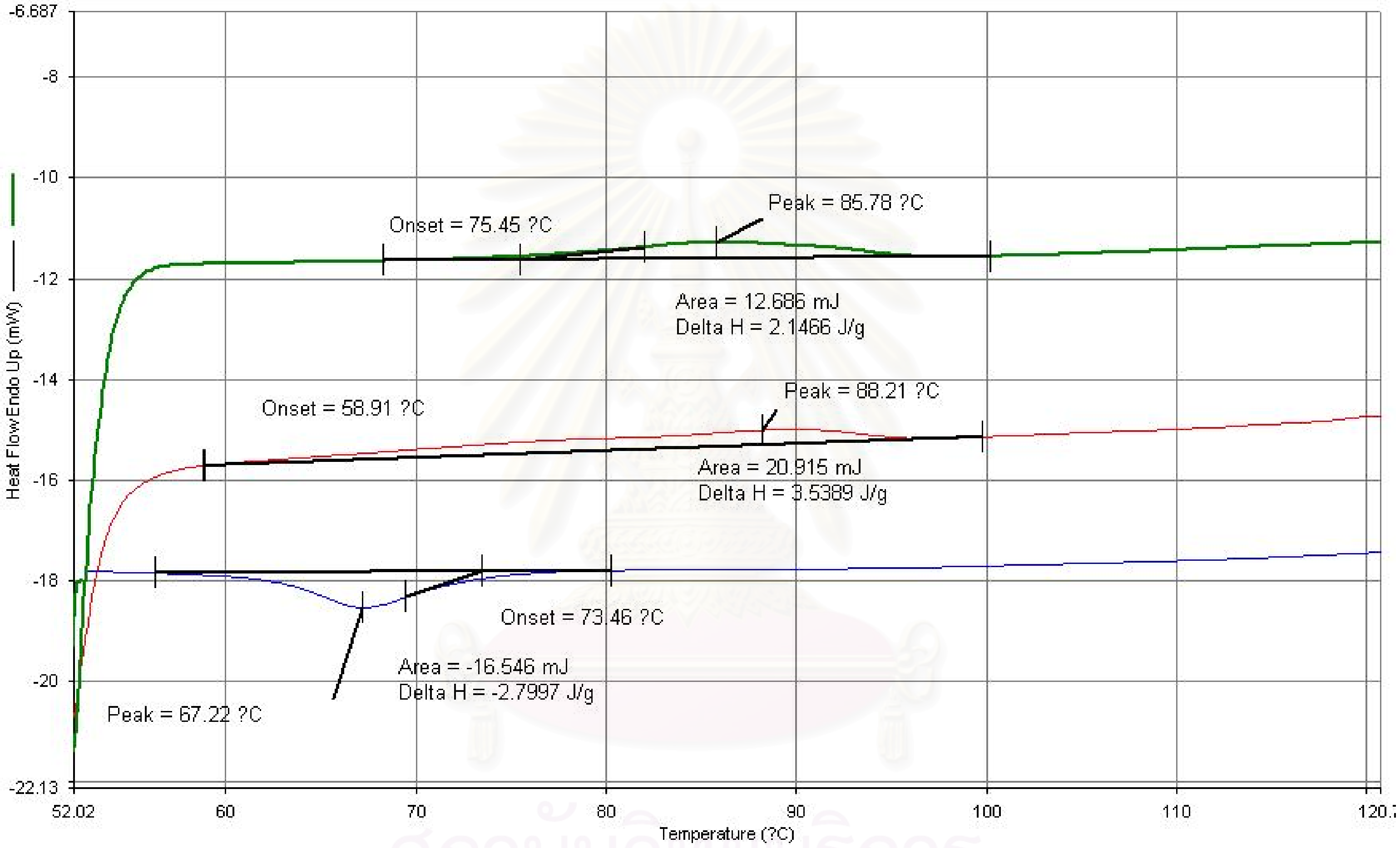


Figure C-2. DSC curve of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 0/100

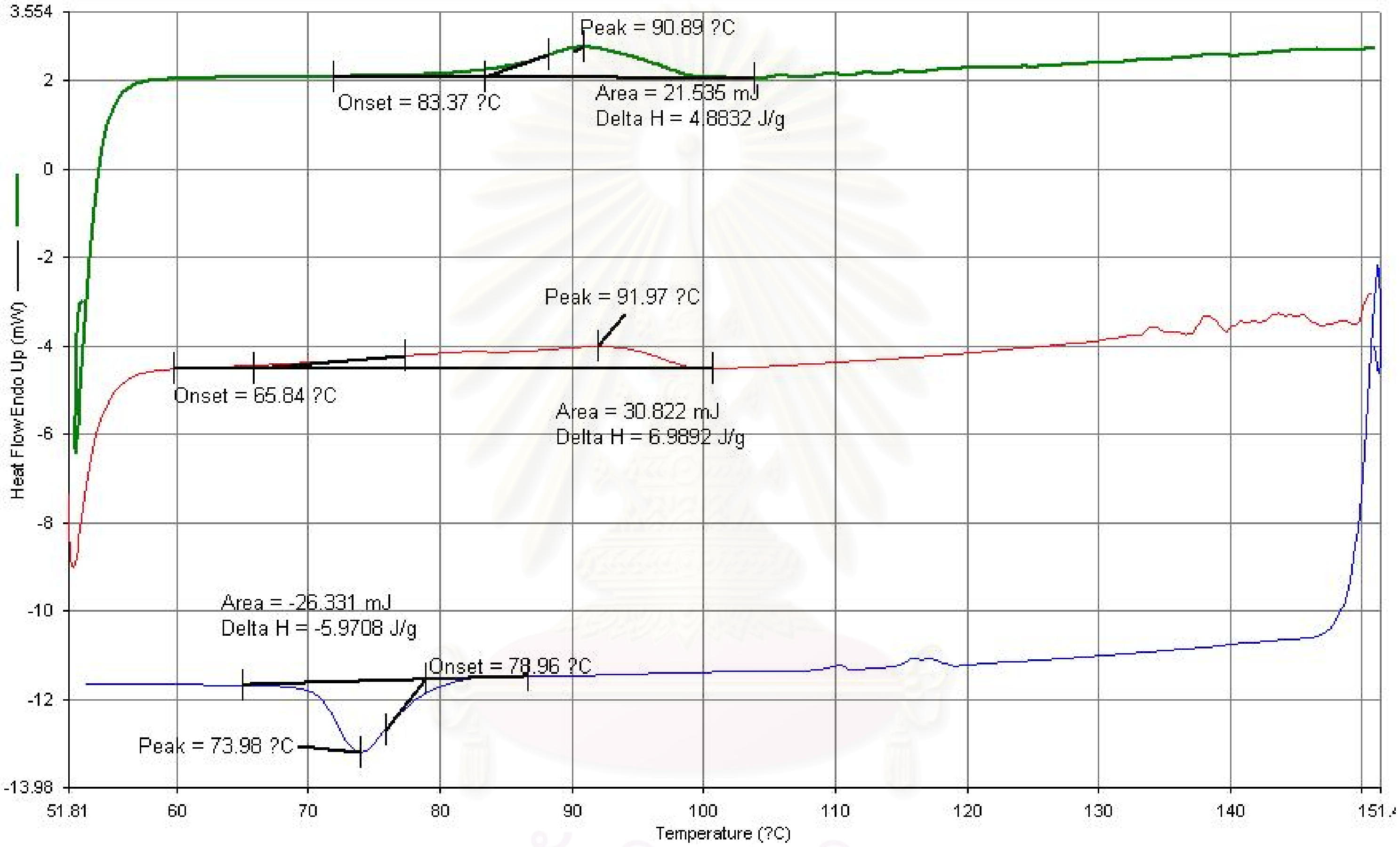


Figure C-3. DSC curve of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 20/80

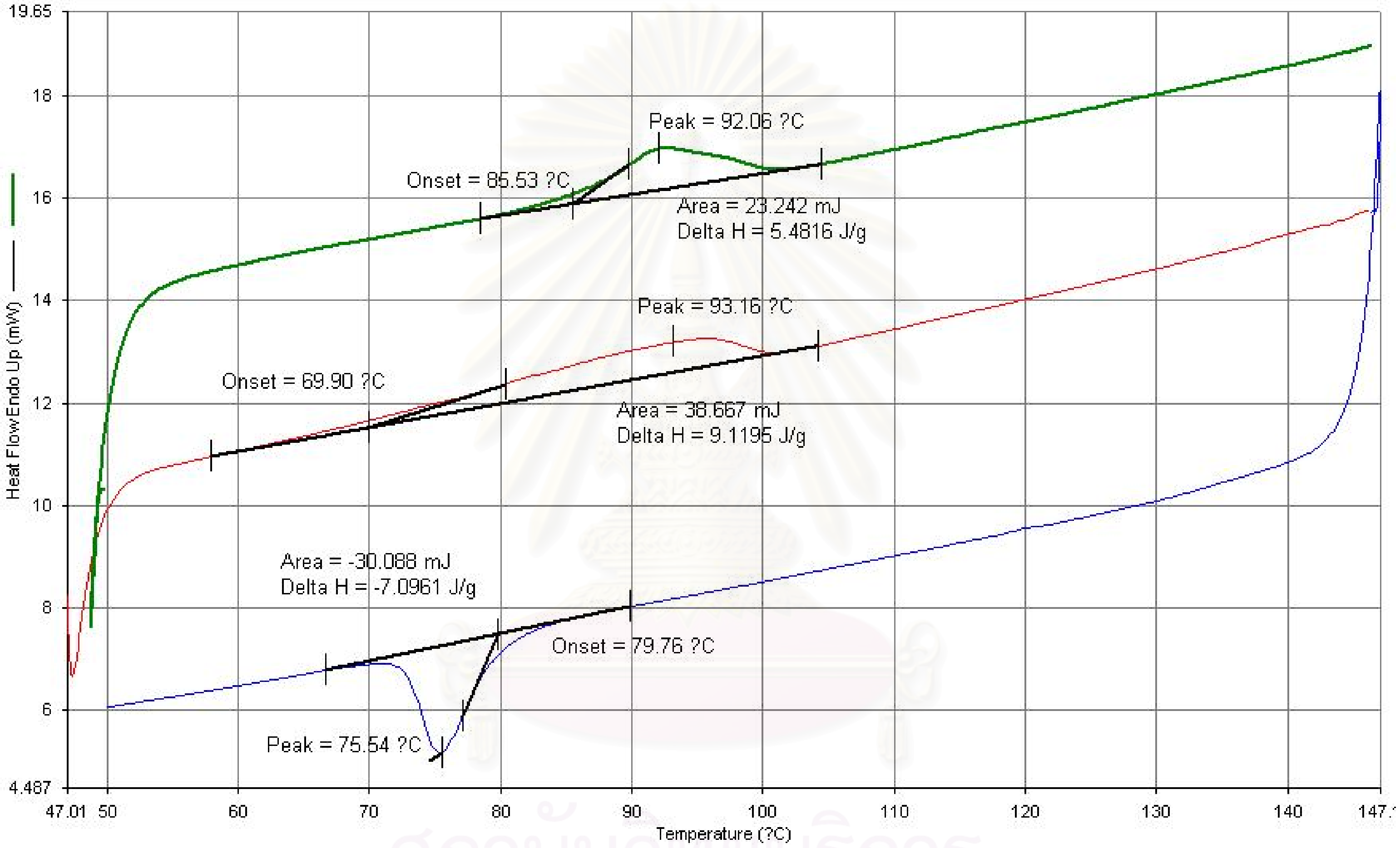


Figure C-4. DSC curve of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 40/60

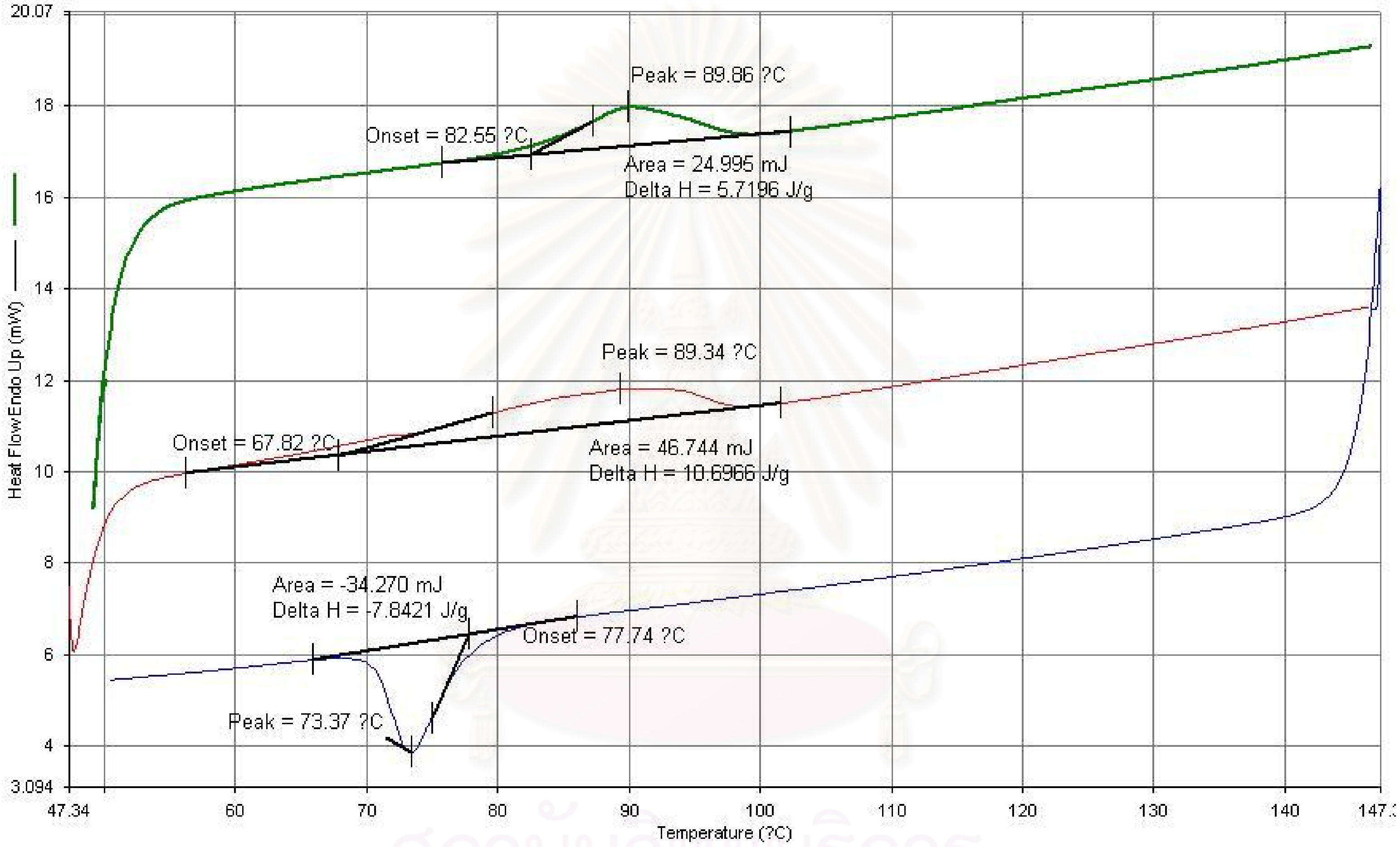


Figure C-5. DSC curve of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 60/40

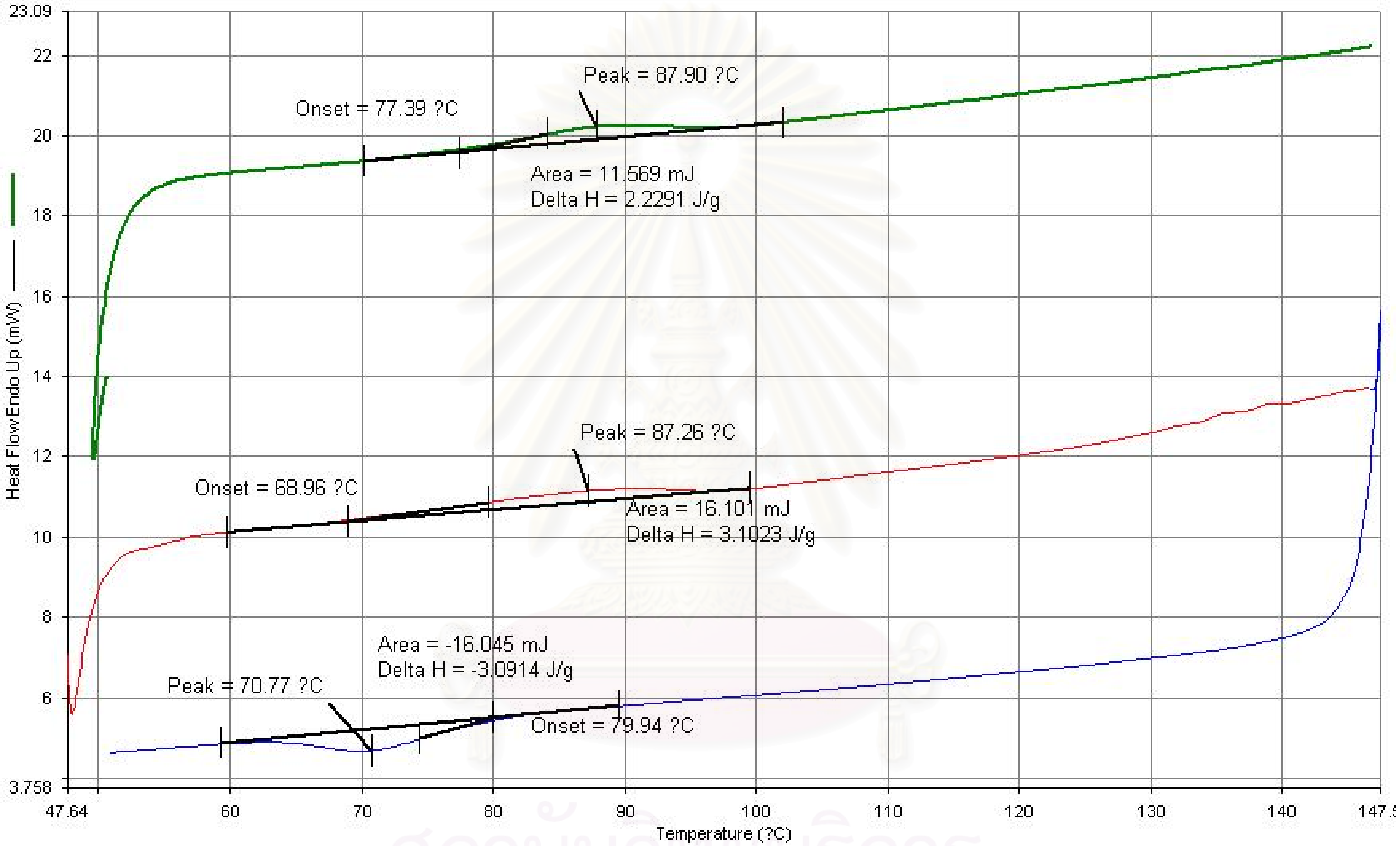


Figure C-6. DSC curve of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 80/20

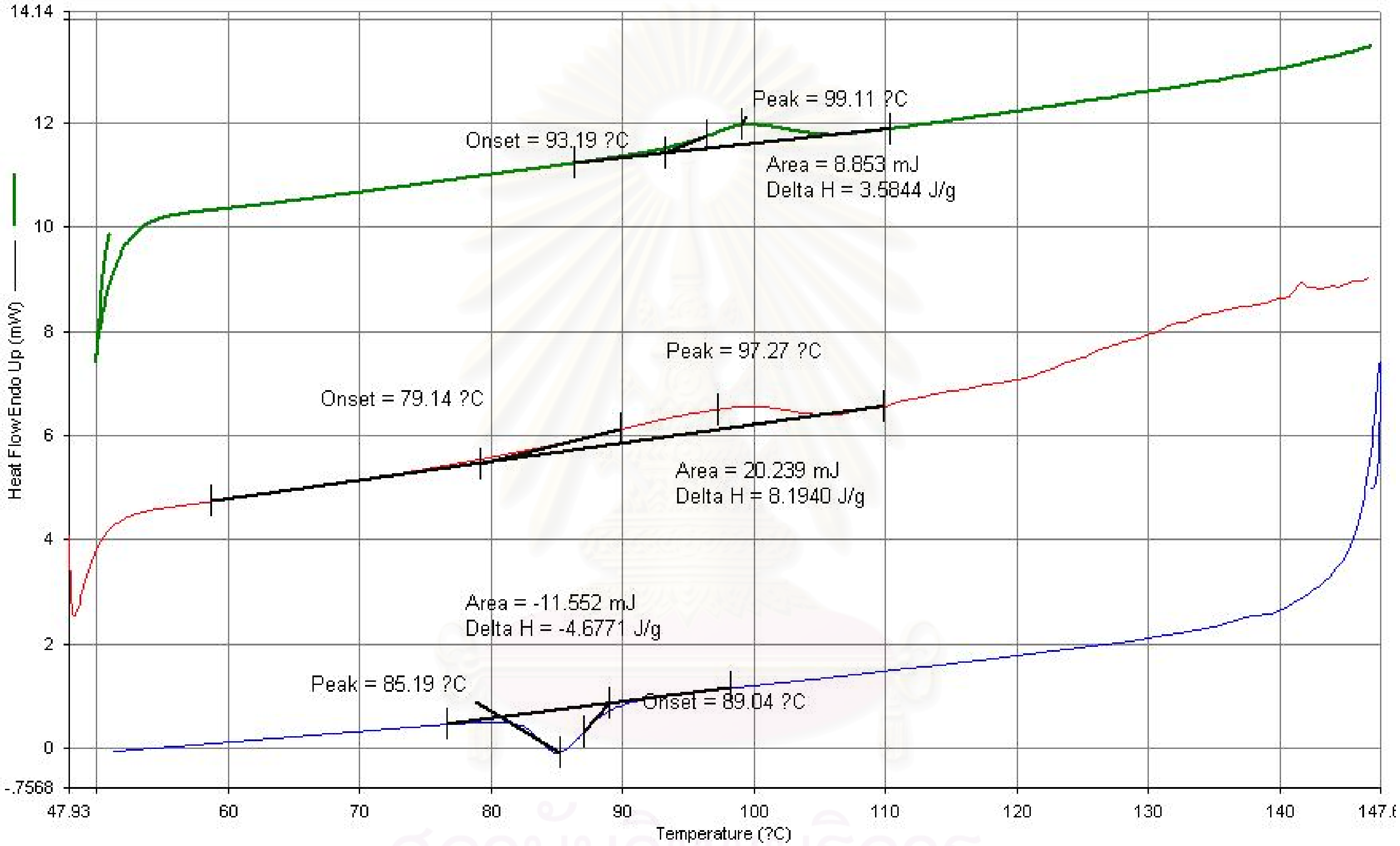


Figure C-7. DSC curve of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 100/0

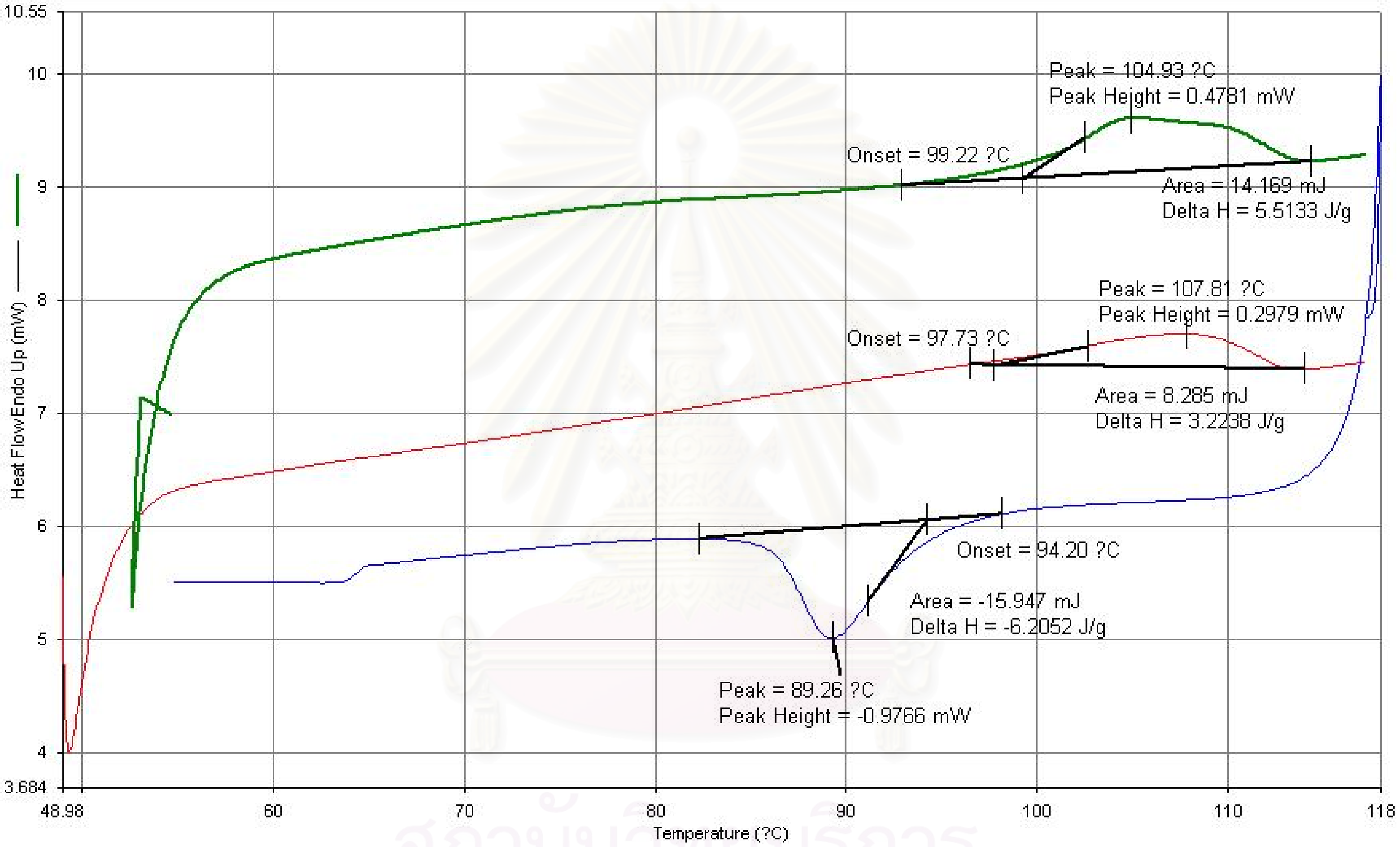


Figure C-8. DSC curve of ethylene/1-decene copolymer produce with homogenous

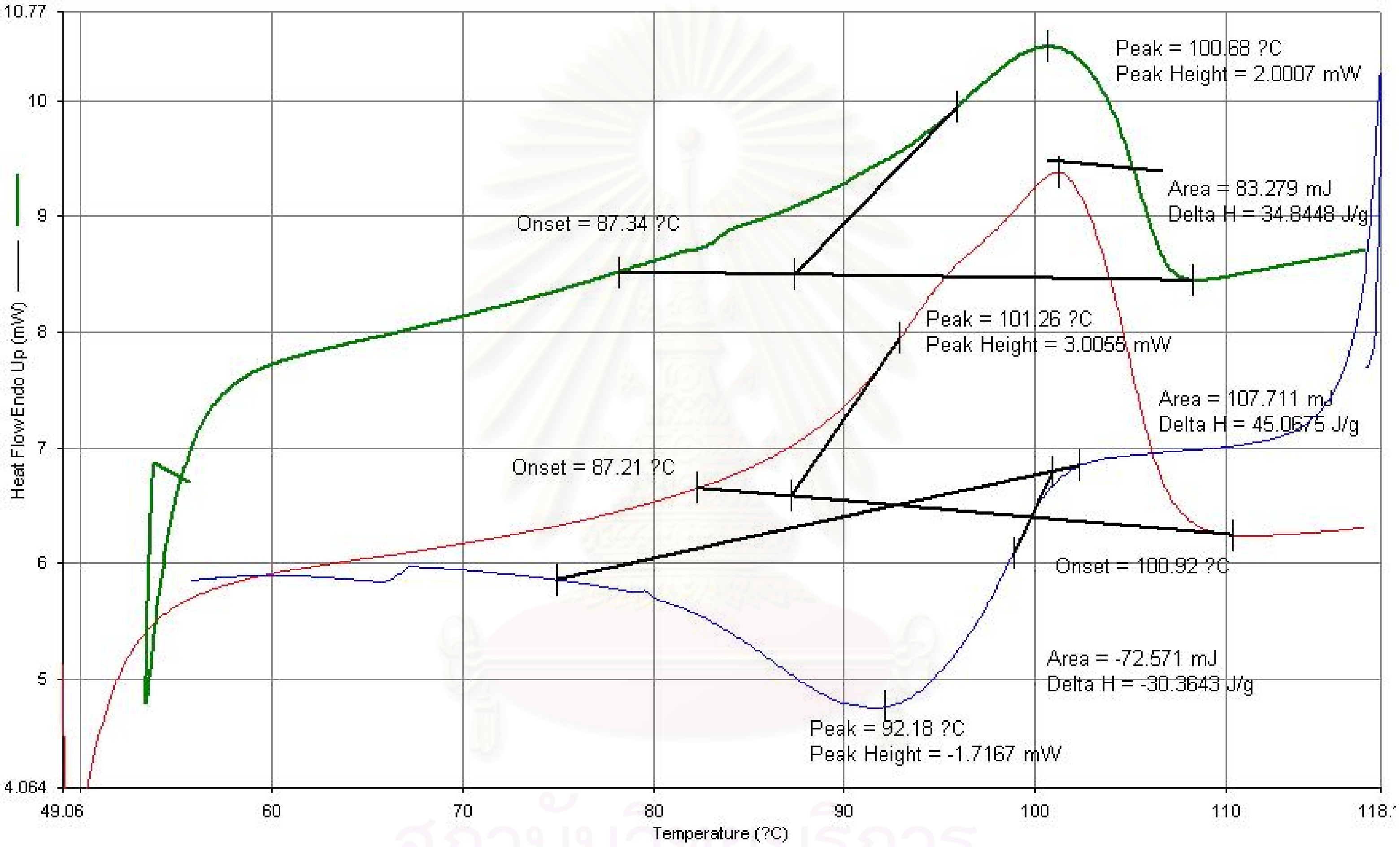


Figure C-9. DSC curve of ethylene/1-decene copolymer produce with TiO_2/SiO_2 = 0/100

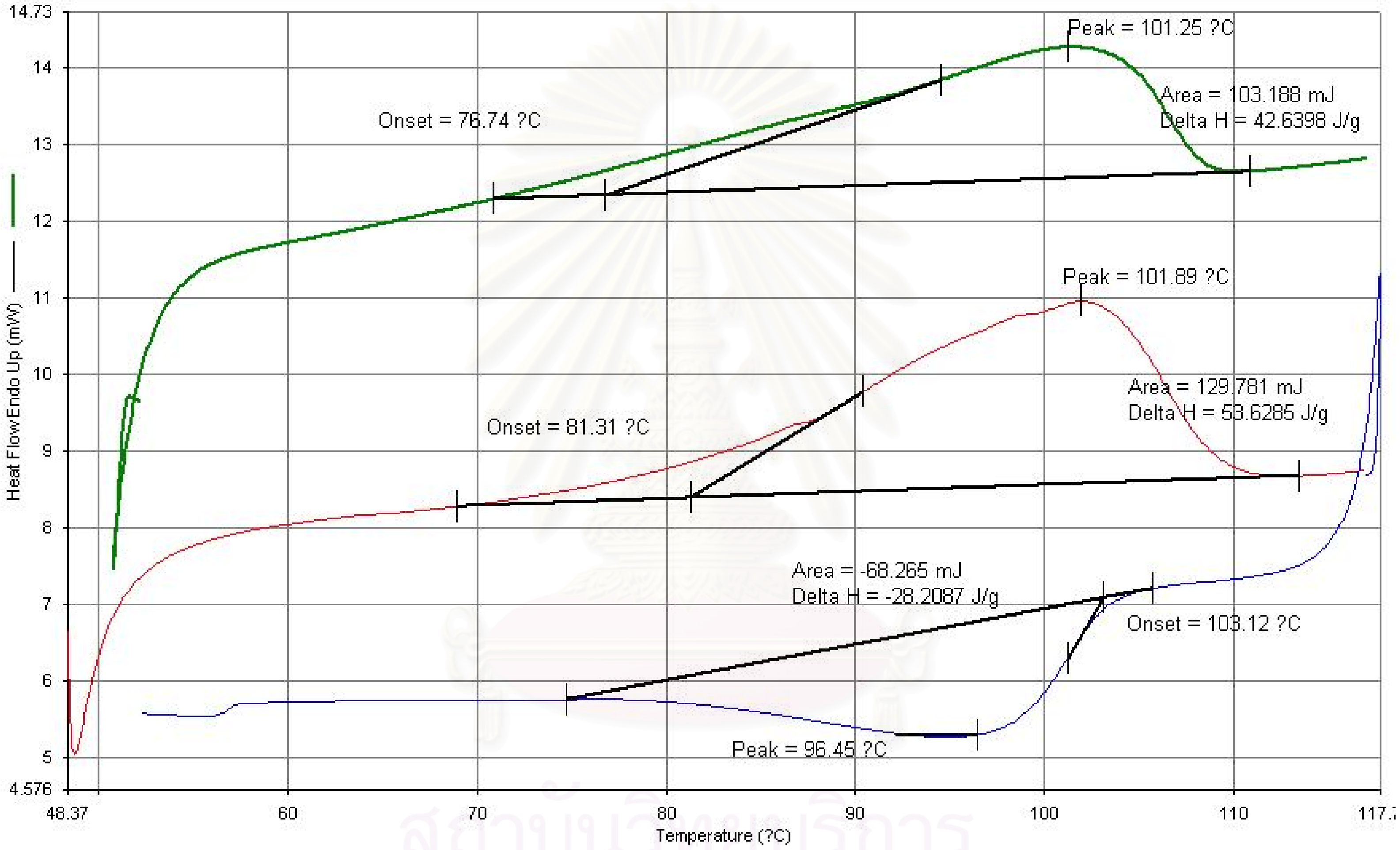


Figure C-10. DSC curve of ethylene/1-decene copolymer produce with TiO_2/SiO_2 = 20/80

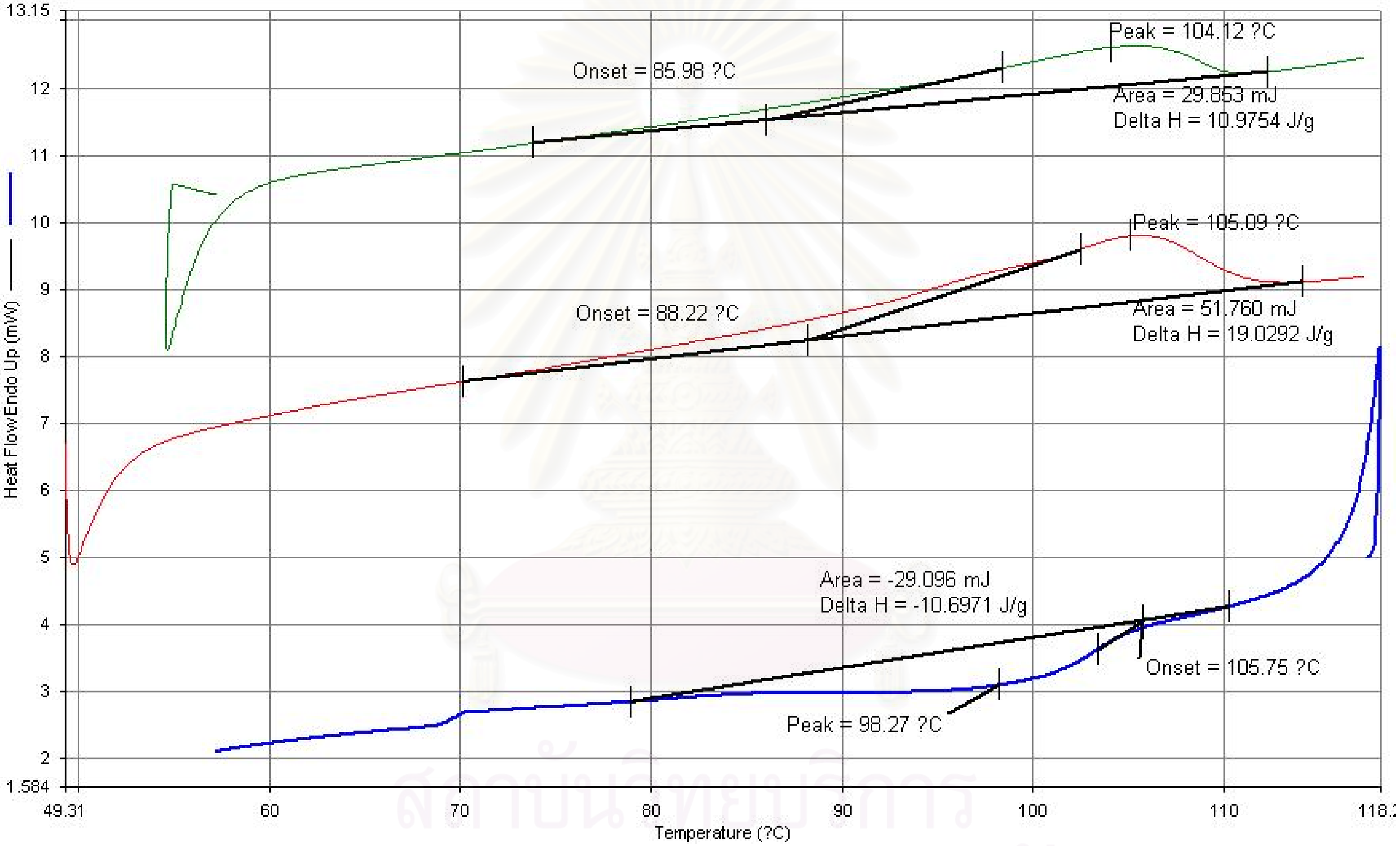


Figure C-11. DSC curve of ethylene/1-decene copolymer produce with TiO_2/SiO_2 = 40/60

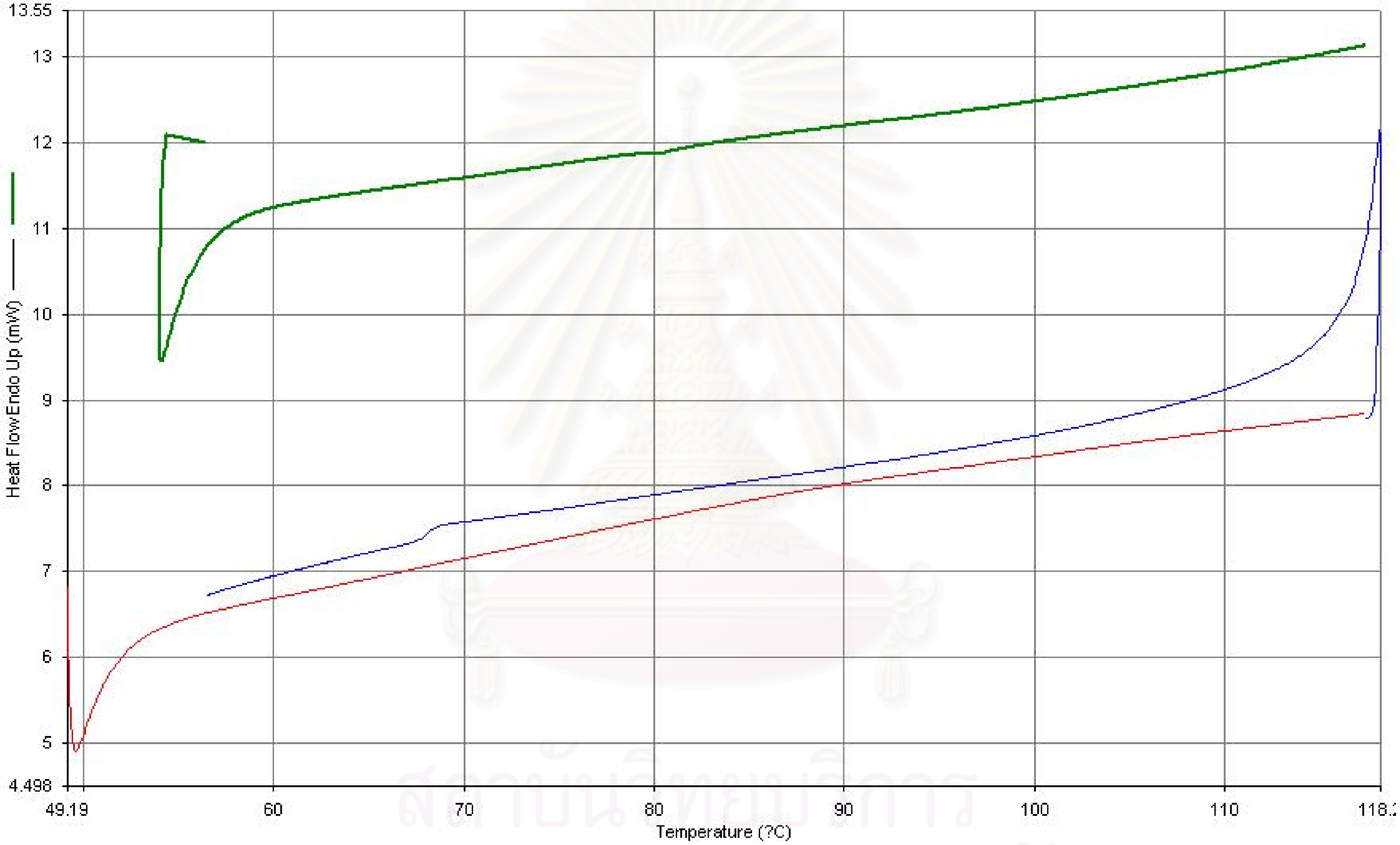


Figure C-12. DSC curve of ethylene/1-decene copolymer produce with TiO_2/SiO_2 = 60/40

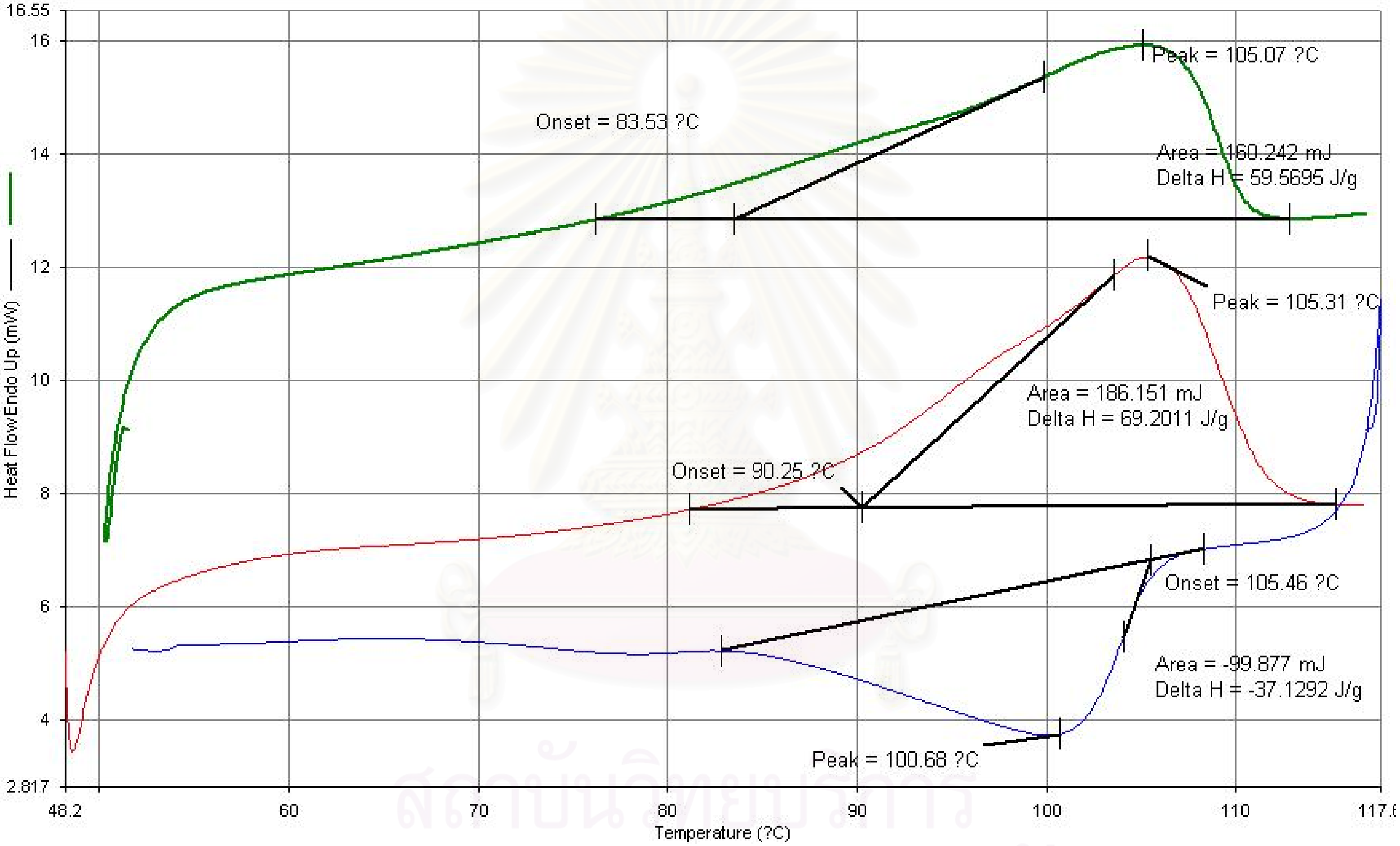


Figure C-13. DSC curve of ethylene/1-decene copolymer produce with TiO_2/SiO_2 = 80/20

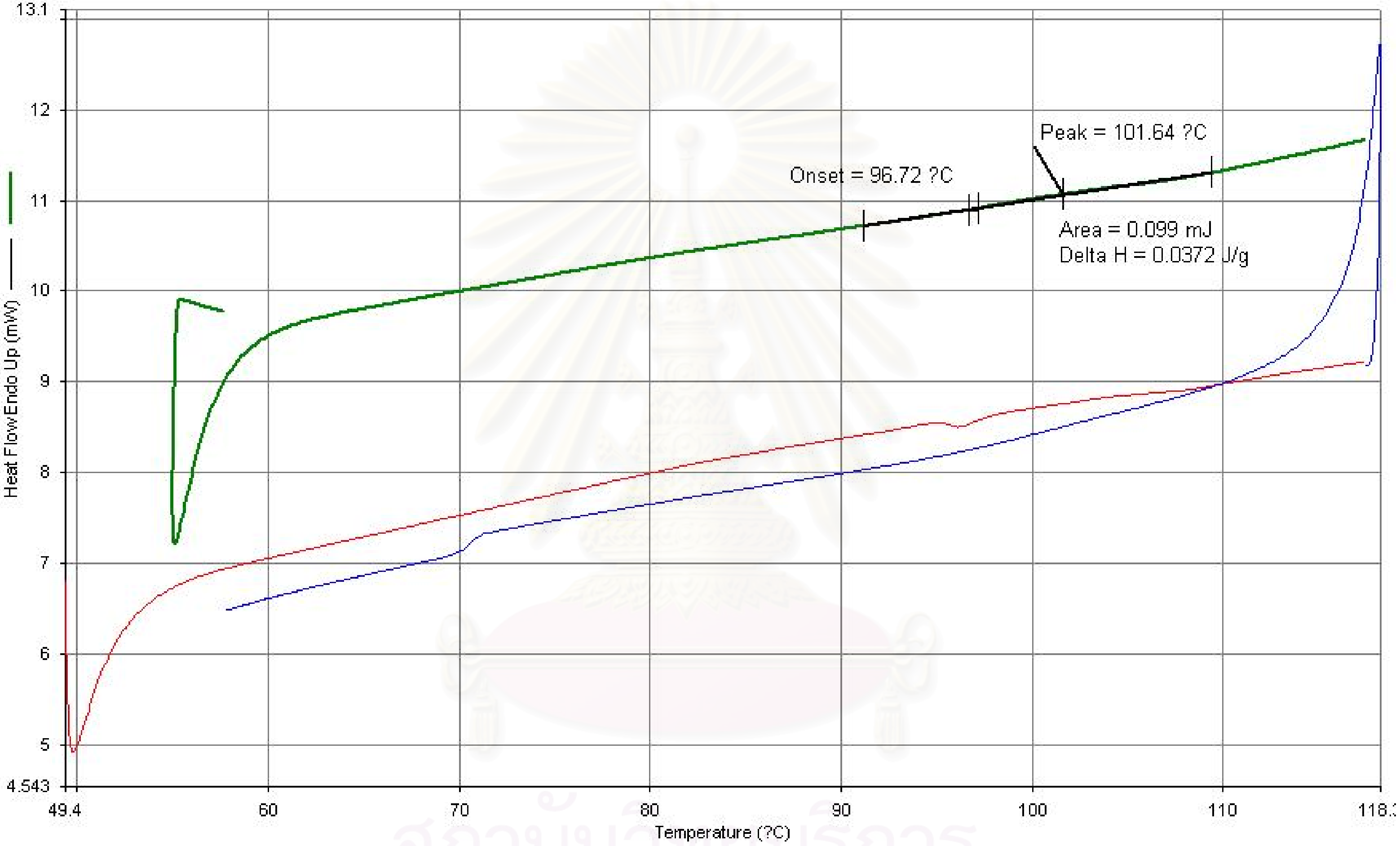


Figure C-14. DSC curve of ethylene/1-decene copolymer produce with TiO_2/SiO_2 = 100/0

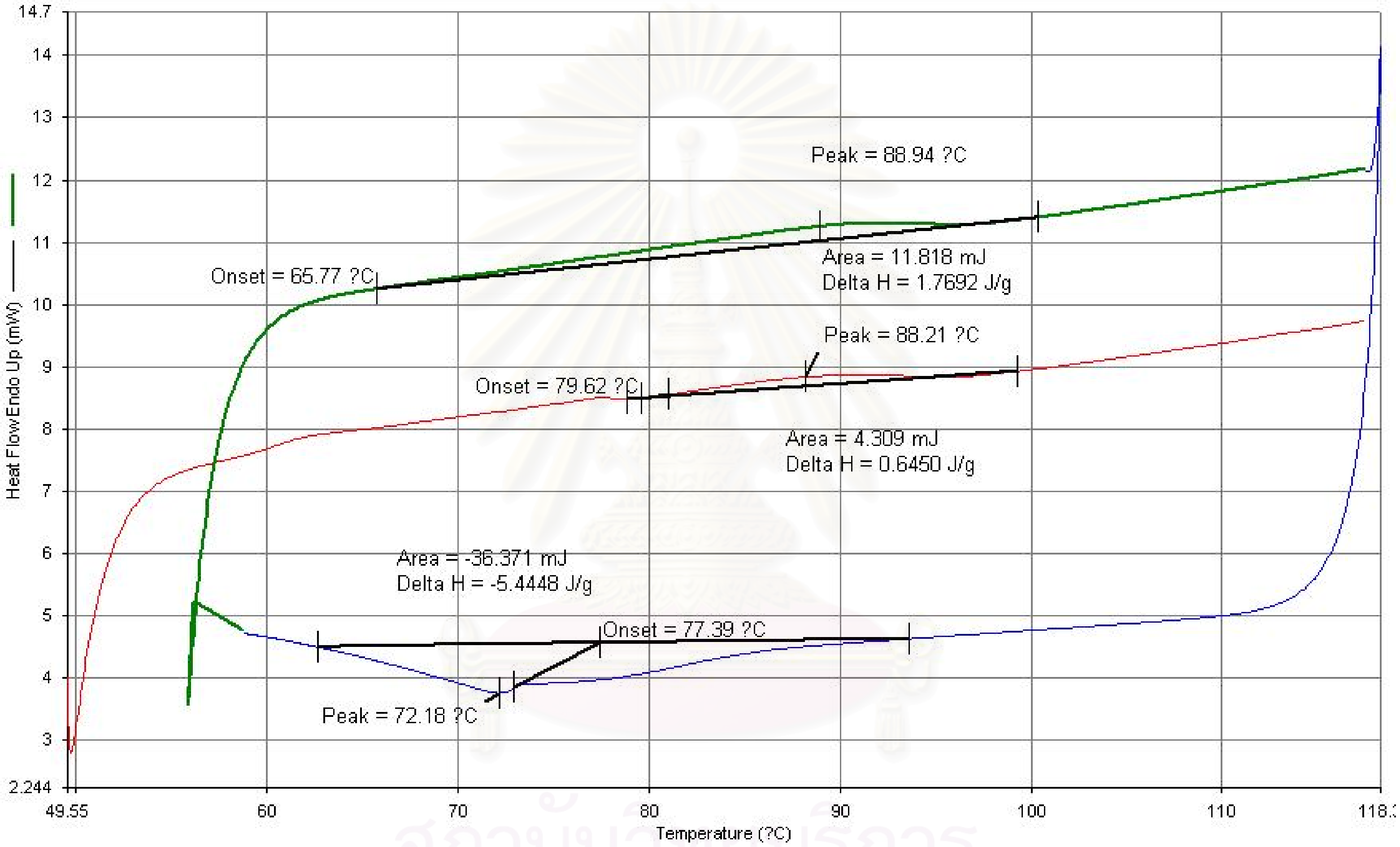


Figure C-15. DSC curve of ethylene/1-hexene copolymer produce with homogenous

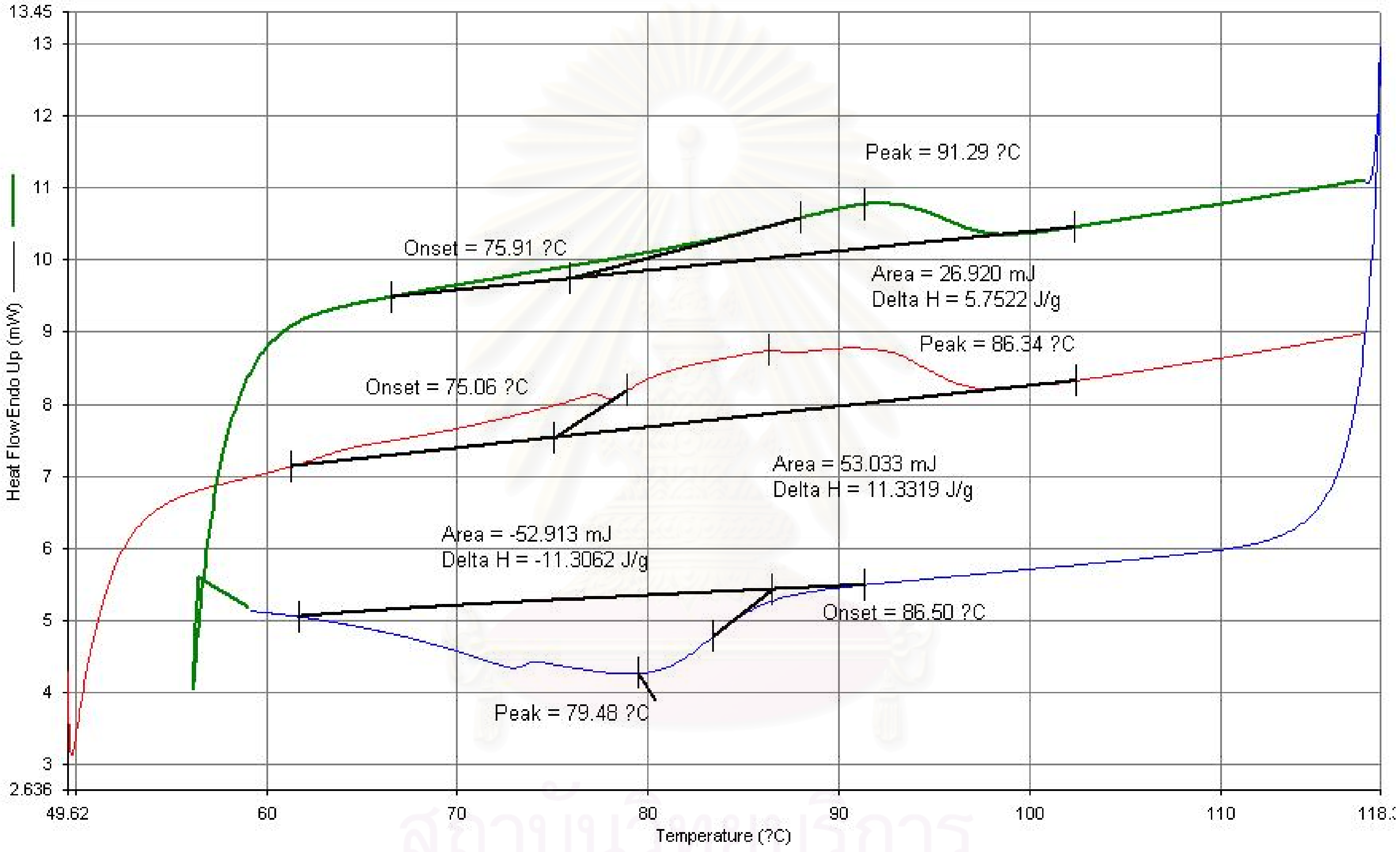


Figure C-16. DSC curve of ethylene/1-hexene copolymer produce with TiO_2/SiO_2 = 0/100

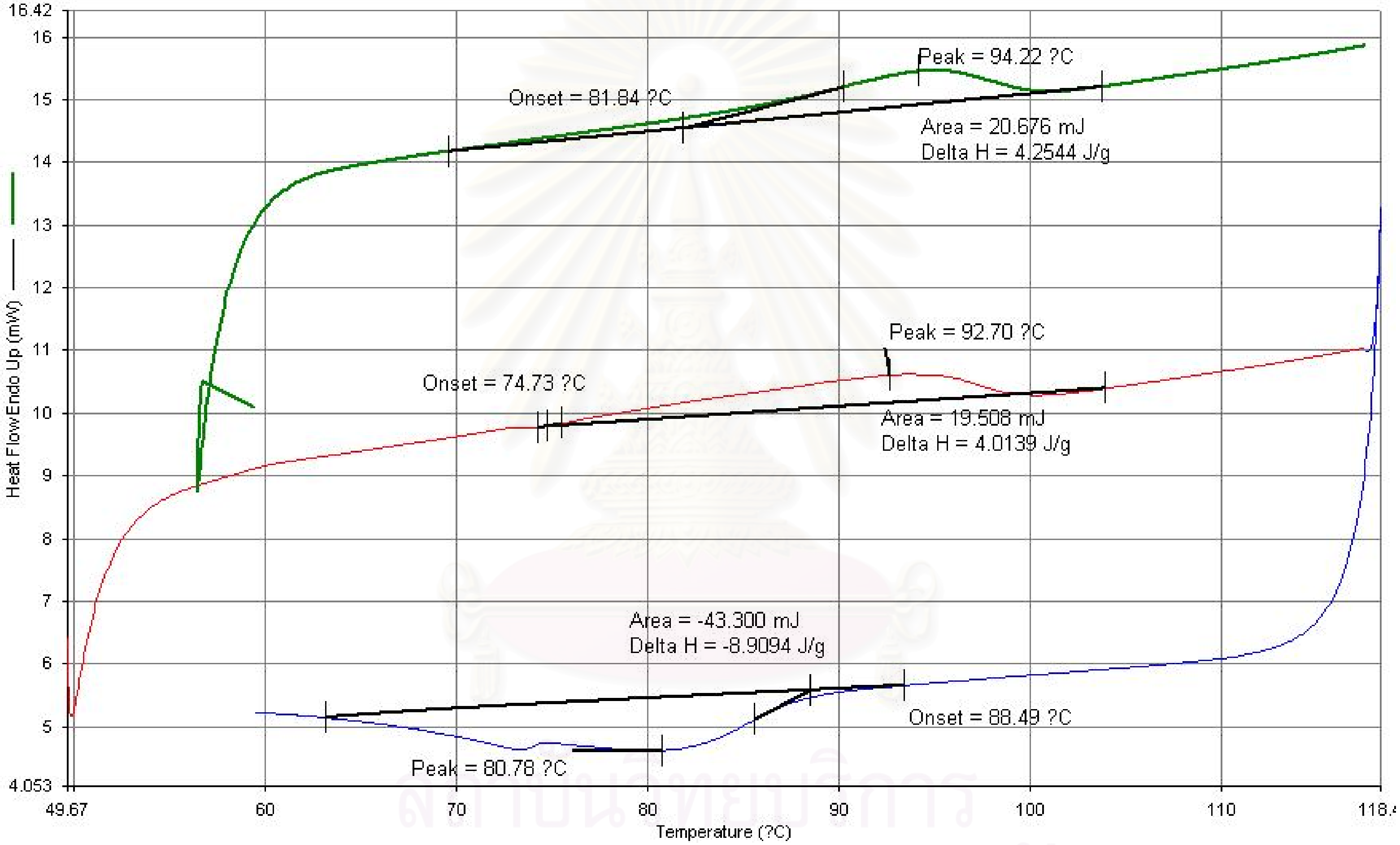


Figure C-17. DSC curve of ethylene/1-hexene copolymer produce with TiO_2/SiO_2 = 20/80

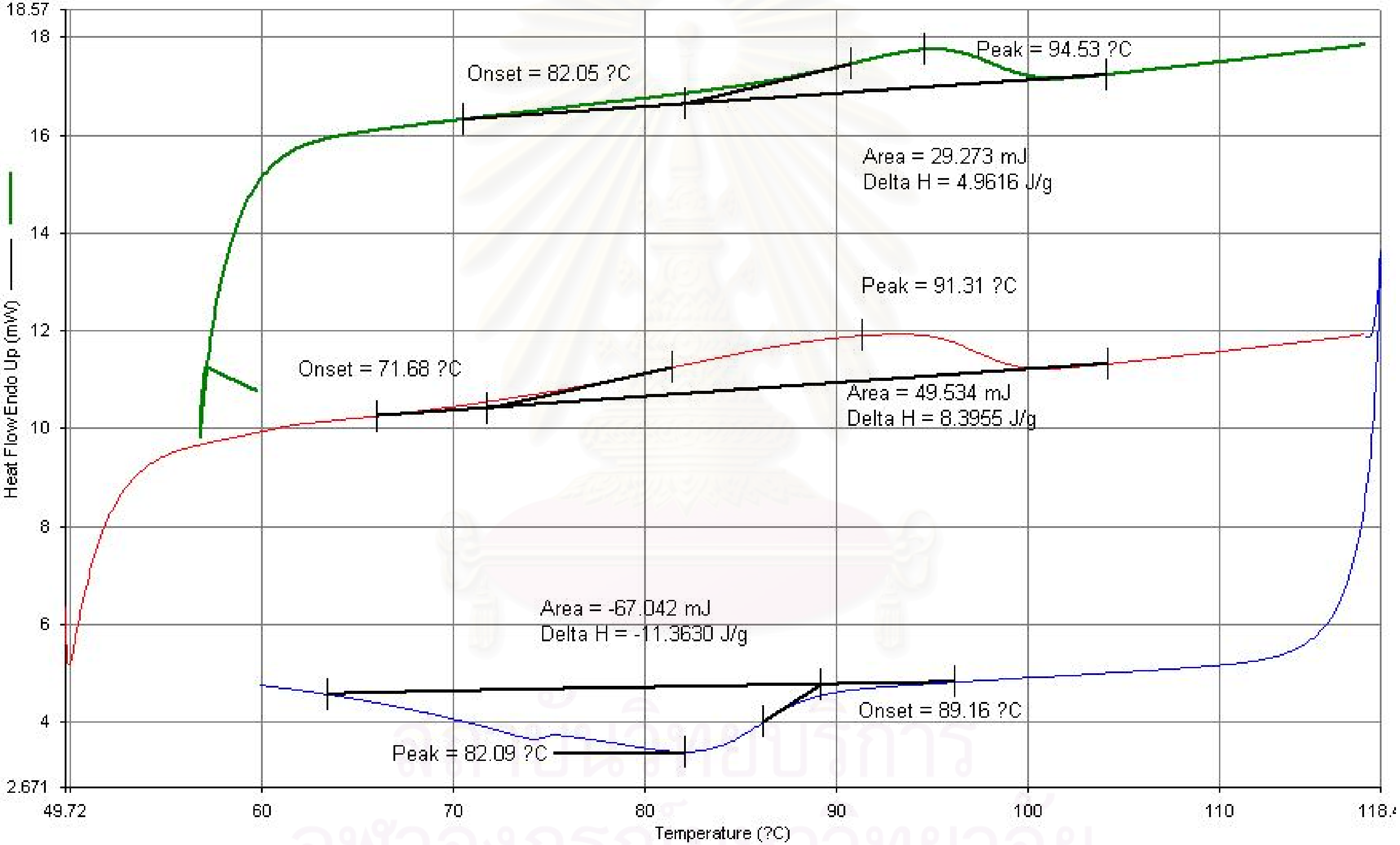

18.57
18
16
14
12
10
8
6
4
2.671
Heat Flow Endo Up (mW)
49.72
60
70
80
90
100
110
118.
Temperature (?C)
Onset = 82.05 ?C
Peak = 94.53 ?C
Area = 29.273 mJ
Delta H = 4.9616 J/g
Peak = 91.31 ?C
Onset = 71.68 ?C
Area = 49.534 mJ
Delta H = 8.3955 J/g
Area = -67.042 mJ
Delta H = -11.3630 J/g
Onset = 89.16 ?C
Peak = 82.09 ?C

Figure C-18. DSC curve of ethylene/1-hexene copolymer produce with TiO_2/SiO_2 = 40/60

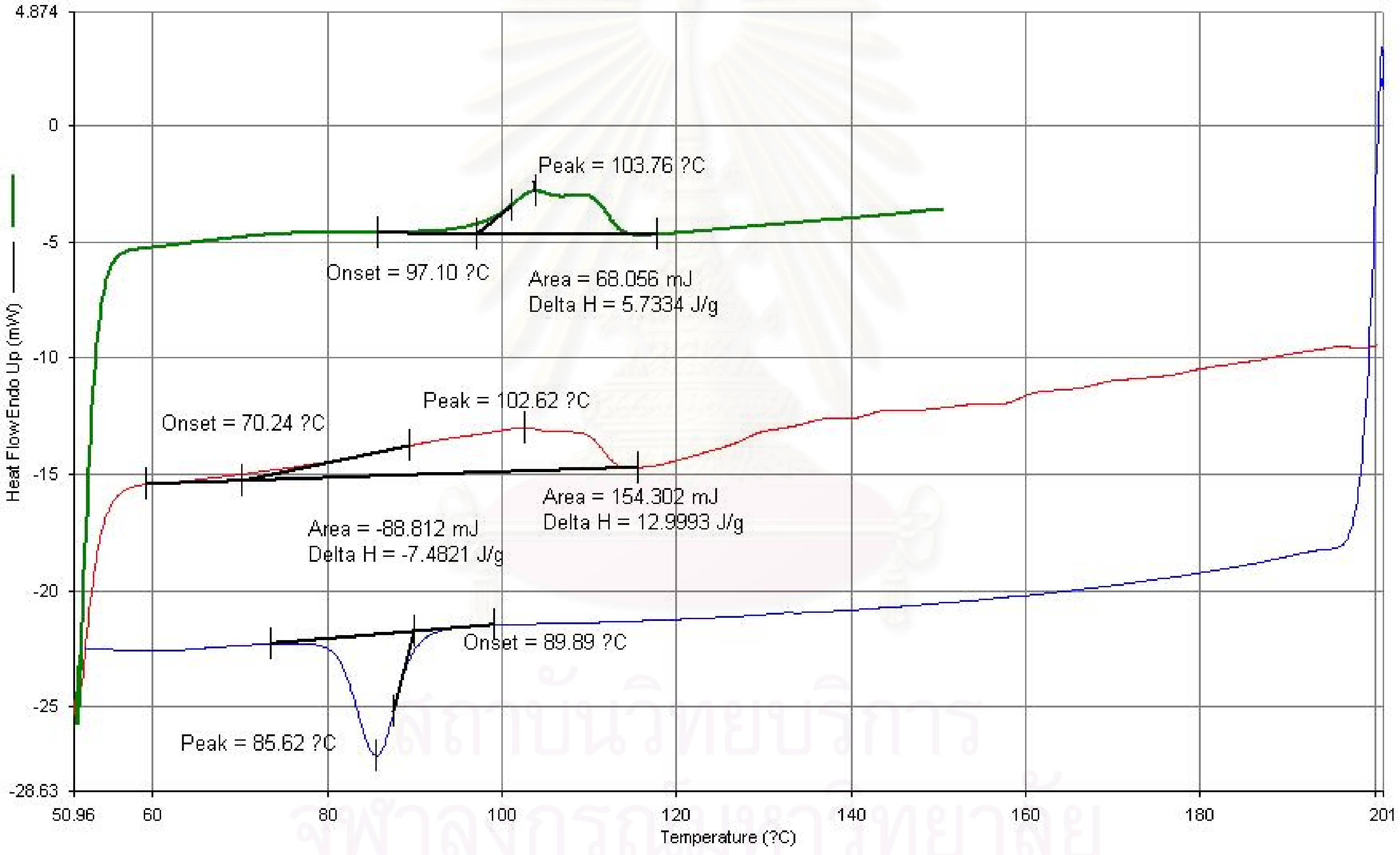


Figure C-19. DSC curve of ethylene/1-hexene copolymer produce with TiO_2/SiO_2 = 60/40

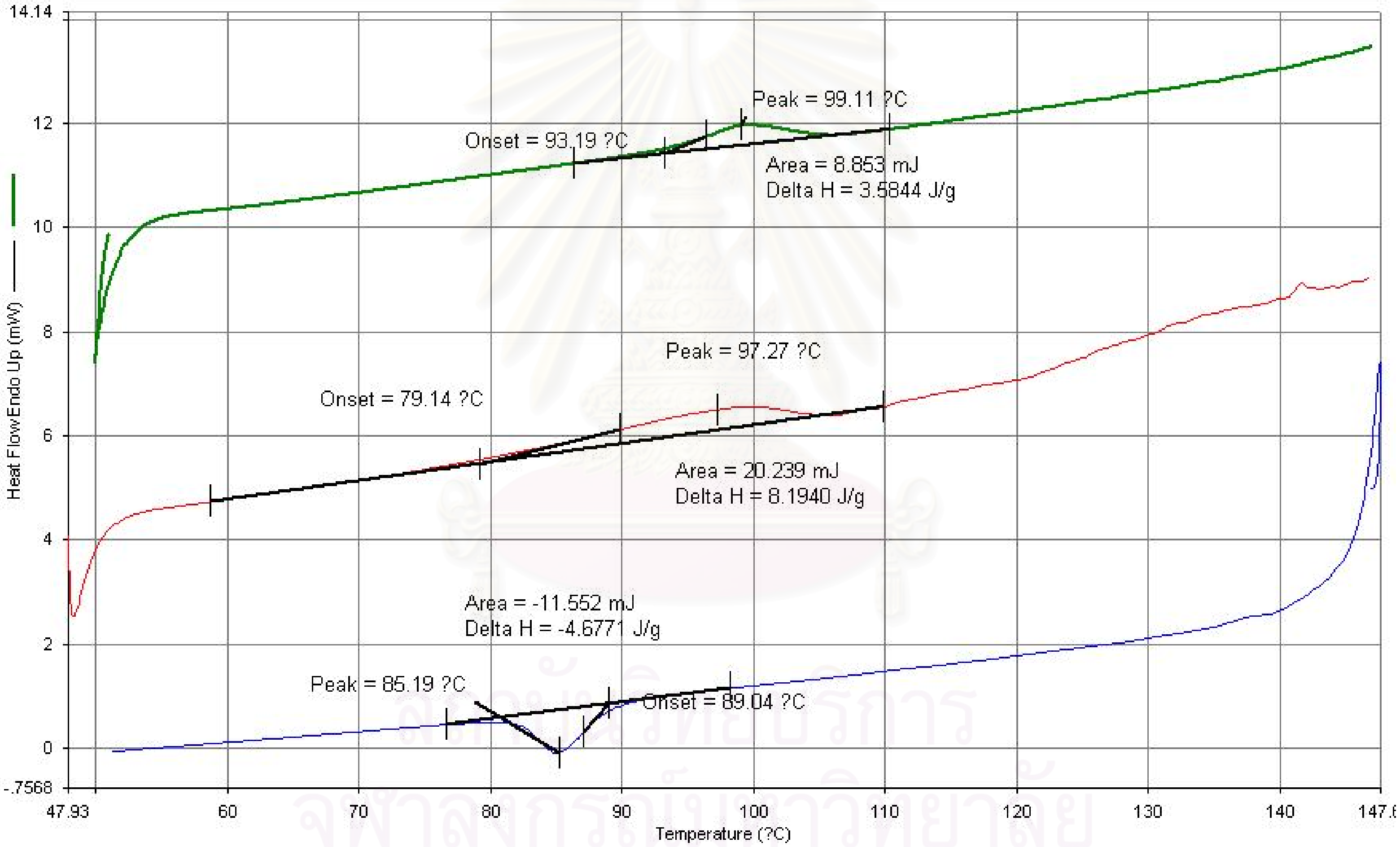
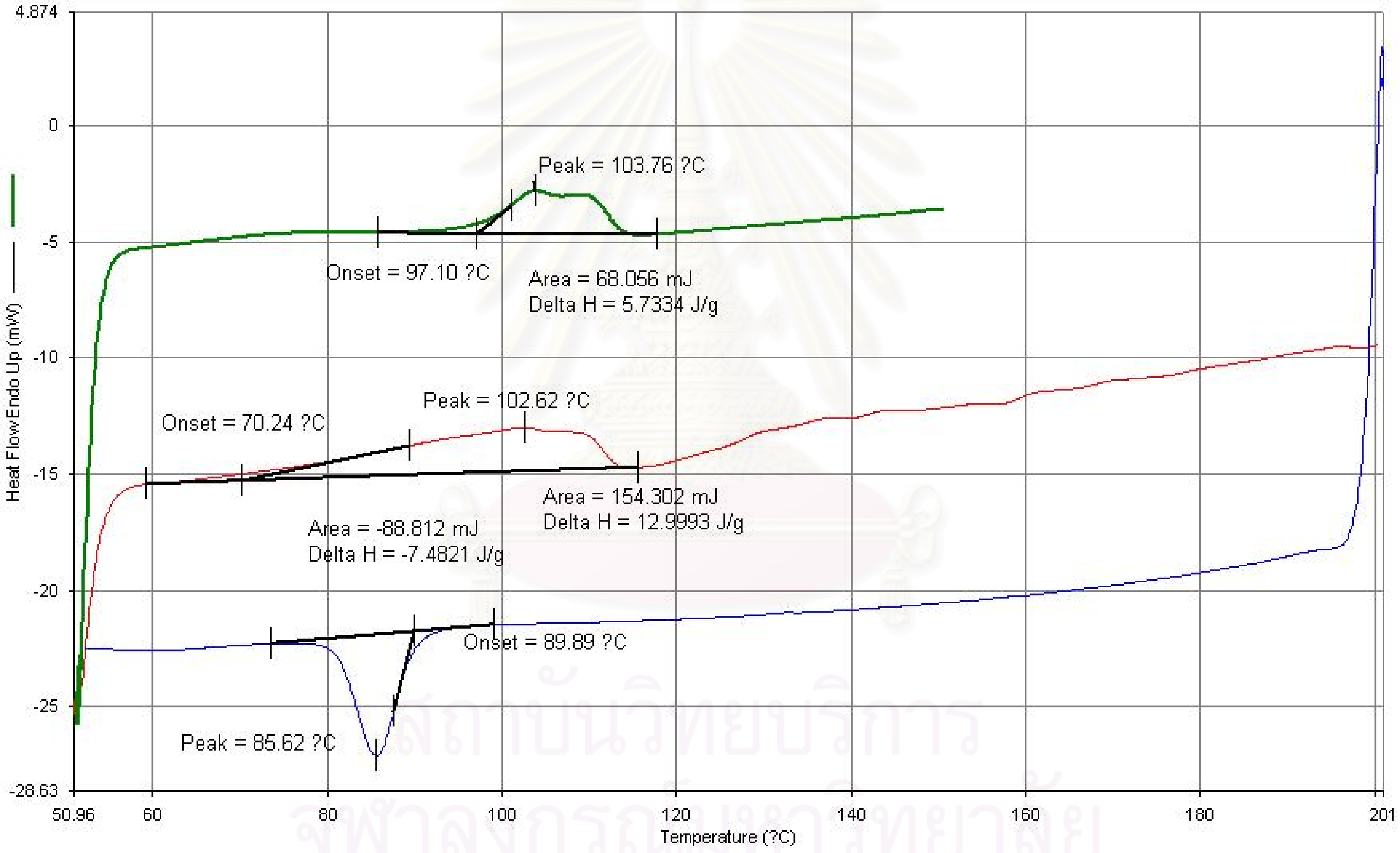
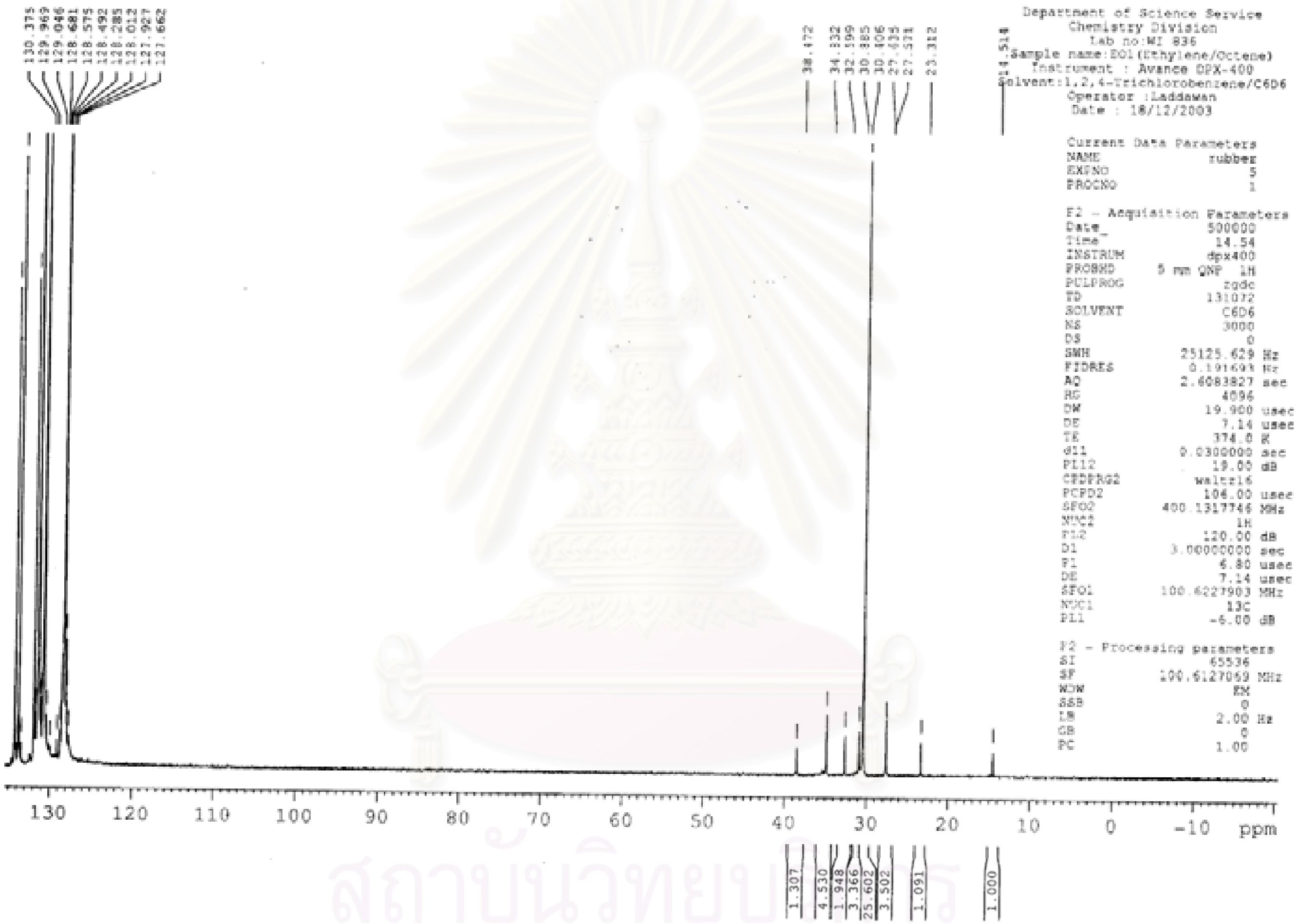


Figure C-20. DSC curve of ethylene/1-hexene copolymer produce with TiO_2/SiO_2 = 80/20



APPENDIX D
(Nuclear Magnetic Resonance)



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Department of Science Service
       Chemistry Division
          Lab no:WI 836
Sample name:EO1(Ethylene/Octene)
   Instrument : Avance DPX-400
Solvent:1,2,4-Trichlorobenzene/C6D6
       Operator :Laddawan
        Date : 18/12/2003

Current Data Parameters
NAME                 rubber
EXPNO                     5
PROCNO                    1

F2 - Acquisition Parameters
Date_                500000
Time                  14.54
INSTRUM              dpx400
PROBHD        5 mm QNP  1H
PULPROG                zgdc
TD                   131072
SOLVENT                C6D6
NS                     3000
DS                        0
SWH               25125.629 Hz
FIDRES             0.191693 Hz
AQ                2.6083827 sec
RG                     4096
DW                   19.900 usec
DE                     7.14 usec
TE                    374.0 K
d11              0.03000000 sec
PL12                  19.00 dB
CPDPRG2             waltz16
PCPD2                104.00 usec
SFO2            400.1317746 MHz
NUC2                     1H
PL2                  120.00 dB
D1               3.00000000 sec
P1                     6.80 usec
DE                     7.14 usec
SFO1            100.6227903 MHz
NUC1                    13C
PL1                   -6.00 dB

F2 - Processing parameters
SI                    65536
SF              100.6127069 MHz
WDW                      EM
SSB                       0
LB                     2.00 Hz
GB                        0
PC                     1.00
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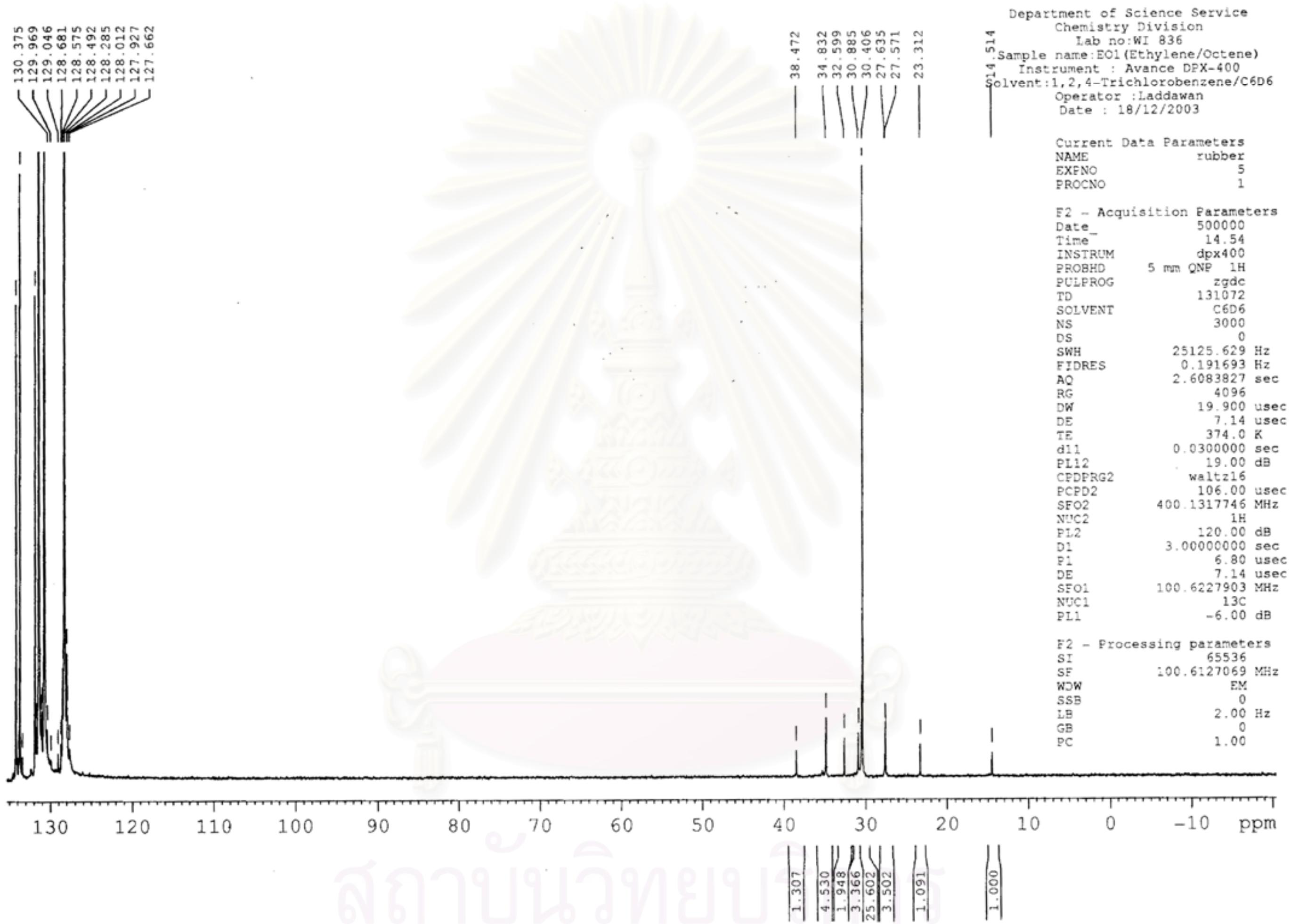
Figure D-1. ^{13}C-NMR spectrum of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 0/100



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Department of Science Service
      Chemistry Division
        Lab no:WI 836
Sample name:EO1(Ethylene/Octene)
  Instrument : Avance DPX-400
Solvent:1,2,4-Trichlorobenzene/C6D6
      Operator :Laddawan
      Date : 18/12/2003

Current Data Parameters
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EXPNO                      5
PROCNO                     1

F2 - Acquisition Parameters
Date_                 500000
Time                   14.54
INSTRUM               dpx400
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PULPROG                 zgdc
TD                    131072
SOLVENT                 C6D6
NS                      3000
DS                         0
SWH                25125.629 Hz
FIDRES              0.191693 Hz
AQ                 2.6083827 sec
RG                      4096
DW                    19.900 usec
DE                      7.14 usec
TE                     374.0 K
d11                0.0300000 sec
PL12                   19.00 dB
CPDPRG2              waltz16
PCPD2                 106.00 usec
SFO2             400.1317746 MHz
NUC2                      1H
PL2                   120.00 dB
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P1                      6.80 usec
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SFO1             100.6227903 MHz
NUC1                     13C
PL1                    -6.00 dB

F2 - Processing parameters
SI                     65536
SF               100.6127069 MHz
WDW                       EM
SSB                        0
LB                      2.00 Hz
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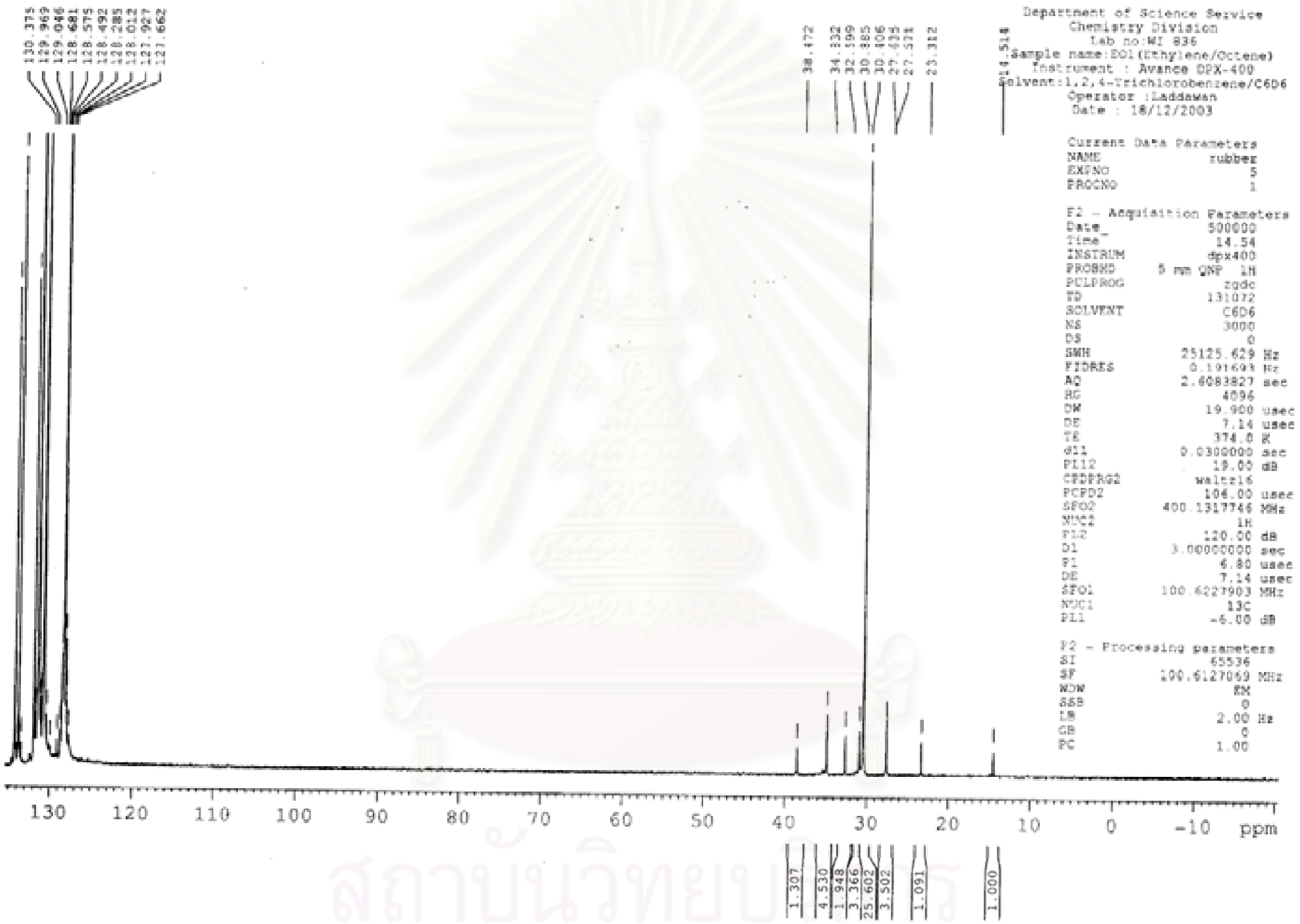
Figure D-2. ^{13}C-NMR spectrum of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 20/80



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Department of Science Service
       Chemistry Division
         Lab no:WI 836
Sample name:EO1(Ethylene/Octene)
   Instrument : Avance DPX-400
Solvent:1,2,4-Trichlorobenzene/C6D6
       Operator :Laddawan
        Date : 18/12/2003

       Current Data Parameters
       NAME               rubber
       EXPNO                   5
       PROCNO                  1

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       DS                      0
       SWH             25125.629 Hz
       FIDRES           0.191693 Hz
       AQ              2.6083827 sec
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       DE                   7.14 usec
       TE                  374.0 K
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       PCPD2              104.00 usec
       SFO2          400.1317746 MHz
       NUC2                   1H
       PL2                120.00 dB
       D1             3.00000000 sec
       P1                   6.80 usec
       DE                   7.14 usec
       SFO1          100.6227903 MHz
       NUC1                  13C
       PL1                 -6.00 dB

       F2 - Processing parameters
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       WDW                    EM
       SSB                     0
       LB                   2.00 Hz
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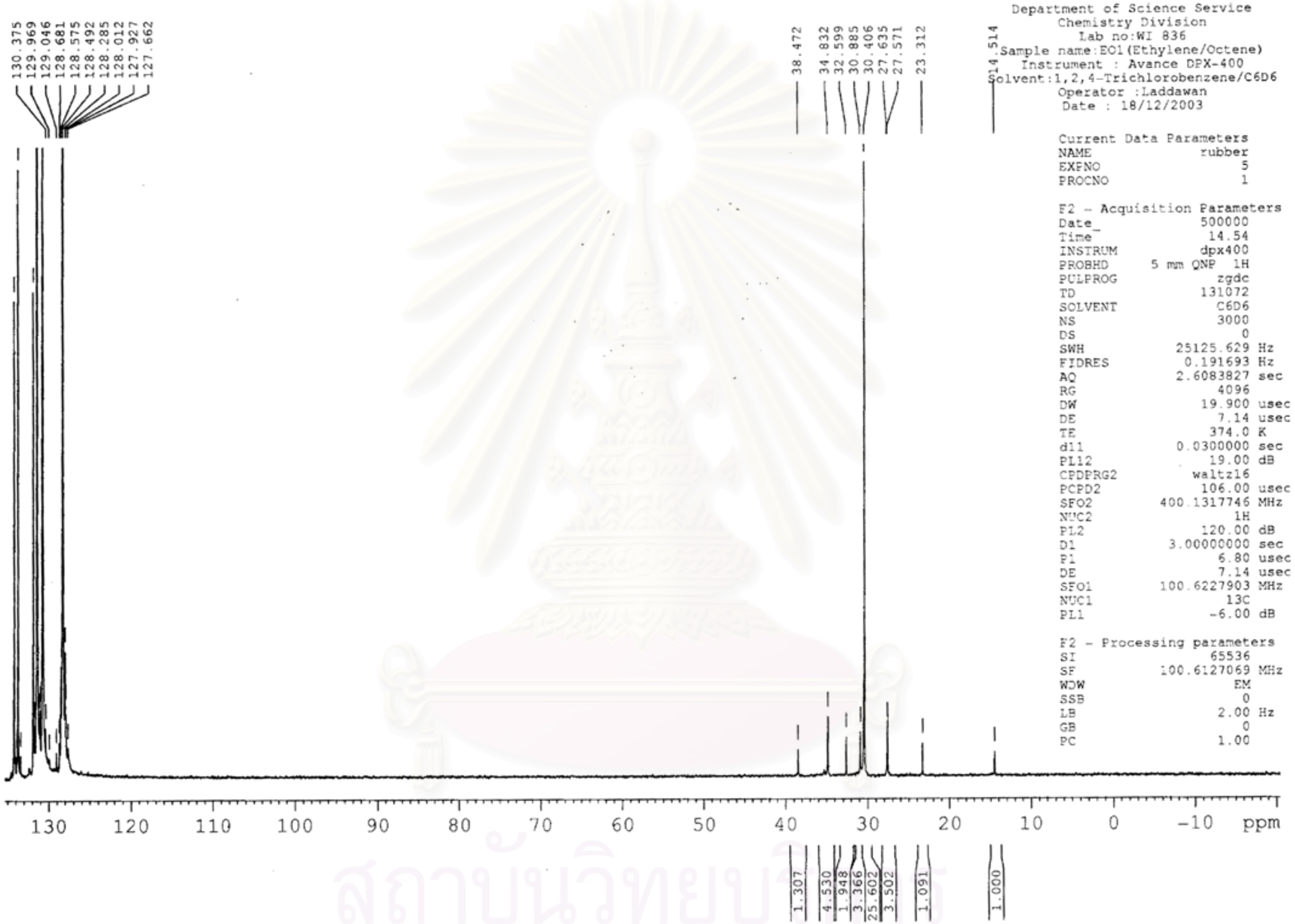
Figure D-3. ^{13}C-NMR spectrum of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 40/60



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Department of Science Service
     Chemistry Division
        Lab no:WI 836
Sample name:EO1(Ethylene/Octene)
   Instrument : Avance DPX-400
Solvent:1,2,4-Trichlorobenzene/C6D6
     Operator :Laddawan
      Date : 18/12/2003

Current Data Parameters
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EXPNO                     5
PROCNO                    1

F2 - Acquisition Parameters
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Time                  14.54
INSTRUM              dpx400
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PULPROG                zgdc
TD                   131072
SOLVENT                C6D6
NS                     3000
DS                        0
SWH              25125.629 Hz
FIDRES            0.191693 Hz
AQ               2.6083827 sec
RG                     4096
DW                   19.900 usec
DE                     7.14 usec
TE                    374.0 K
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PL12                  19.00 dB
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PCPD2                106.00 usec
SFO2            400.1317746 MHz
NUC2                     1H
PL2                  120.00 dB
D1               3.00000000 sec
P1                     6.80 usec
DE                     7.14 usec
SFO1            100.6227903 MHz
NUC1                    13C
PL1                   -6.00 dB

F2 - Processing parameters
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SF              100.6127069 MHz
WDW                      EM
SSB                       0
LB                     2.00 Hz
GB                        0
PC                     1.00
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Figure D-4. ^{13}C-NMR spectrum of ethylene/1-octene copolymer produce with TiO_2/SiO_2 = 60/40

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Role of titania in TiO_2–SiO_2 mixed oxides-supported metallocene catalyst during ethylene/1-octene copolymerization

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Received 29 September 2004; accepted 11 December 2004

The present study showed enhanced activities of ethylene/1-octene copolymerization via TiO_2–SiO_2 mixed oxides-supported MAO with a zirconocene catalyst. It was proposed that titania was decorated on silica surface and acted as a spacer to anchor MAO to the silica support resulting in less steric hindrance and less interaction on the support surface.

KEY WORDS: mixed oxides; silica; supported catalyst; titania; zirconocene catalyst.

1. Introduction

Because of the commercial interest of using metallocene catalysts for olefin polymerization, it has led to an extensive effort for utilizing metallocene catalysts more efficiently. It is known that the copolymerization of ethylene with higher 1-olefins is a commercial importance for productions of elastomer and linear low-density polyethylene (LLDPE). Metallocene catalysts with MAO have been studied for such a copolymerization. In fact, zirconocene catalysts along with MAO have been reported for a potential use to polymerize ethylene with 1-olefins [1–2].

However, it was found that homogeneous metallocene catalytic system has two major disadvantages; the lack of morphology control of polymers produced and reactor fouling. Therefore, binding these metallocene catalysts onto inorganic supports can provide a promising way to overcome these drawbacks. It has been reported that many inorganic supports such as SiO_2, Al_2O_3, and $MgCl_2$ have been extensively studied [3–13]. It has been mentioned that silica is perhaps the most widely used support for metallocene catalysts so far. Unfortunately, due to the support effect, it is found that the catalytic activity of catalysts in heterogeneous system is usually lower than the homogeneous one. Therefore, a modification of the support properties is required in order to maintain high activity as in the homogeneous system or even closer. TiO_2–SiO_2 mixed oxide has been considered to be very attractive as catalysts and supports, which have brought much attention in recent years. It was reported that TiO_2–SiO_2mixed materials have been used as catalysts and supports for various reactions [14]. This TiO_2–SiO_2 mixed oxide would lead to robust catalytic supports of metallocene catalysts for olefin polymerization.

In this present study, the ethylene/1-octene copolymerization using TiO_2–SiO_2 mixed oxides supported-MAO with a zirconocene catalyst was investigated for the first time. The ratios of TiO_2/SiO_2 used were varied. The mixed oxide supports and catalyst precursors were prepared, characterized and tested for ethylene/1-octene copolymerization. The role of TiO_2 in the mixed oxide supports was also further discussed.

2. Experimental

All chemicals [TiO_2 (anatase, Ishihara), SiO_2 (Cariact P-10), toluene, rac-ethylenebis (indenyl) zirconium dichloride [$Et(Ind)_2ZrCl_2$], methylaluminoxane (MAO), trimethylaluminum (TMA) and 1-octene] were manipulated under an inert atmosphere using a vacuum glove box and/or Schelenk techniques.

2.1. *Materials*

2.1.1. *Preparation of TiO_2–SiO_2 mixed oxides support*

TiO_2–SiO_2 mixed oxide supports [surface areas of SiO_2 = 300 $m^2\ g^{-1}$ and TiO_2 (anatase form) = 70 $m^2\ g^{-1}$] for MAO were prepared according to the method described by Conway *et al.* [15]. The TiO_2:SiO_2 ratios were varied from 0:1, 2:8, 4:6, 6:4, 8:2, and 1:0. The supports were heated under vacuum at 400 °C for 6 h.

2.2. *Preparation of TiO_2–SiO_2 mixed oxides-supported MAO*

One gram of the TiO_2–SiO_2 mixed oxide support obtained from 2.1.1 was reacted with the desired amount of MAO at room temperature and stirred for

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E-mail: bunjerd.j@chula.ac.th

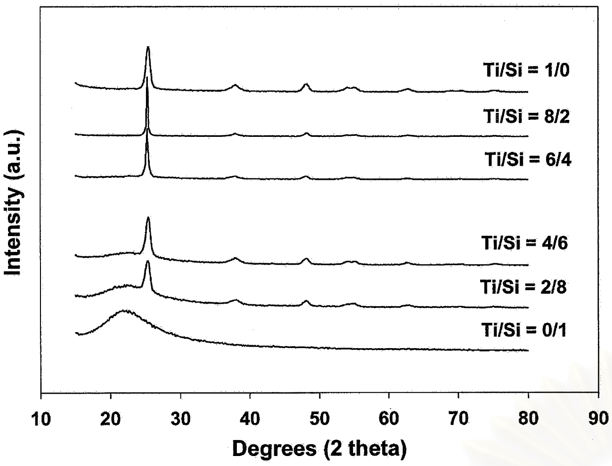


Figure 1. XRD patterns of various TiO_2–SiO_2 mixed oxide supports before MAO impregnation.

30 min. The solvent was then removed from the mixture. About 20 mL of toluene was added into the obtained precipitate, stirred the mixture for 5 min, and then removed the solvent. This procedure was done for 5 times to ensure the removal of impurities. Then, the solid part was dried under vacuum at room temperature to obtain white powder of TiO_2–SiO_2 mixed oxides-supported MAO.

2.3. Polymerization

The ethylene/1-octene copolymerization reaction was carried out in a 100 mL semi-batch stainless steel autoclave reactor equipped with a magnetic stirrer. At first, 0.1 g of the supported MAO ($[Al]_{MAO}/[Zr]$ = 1135) and 0.018 mol of 1-octene along with toluene (to make the total volume of 30 mL) were put into the reactor. The desired amount of $Et(Ind)_2ZrCl_2$ (5×10^{-5} M) and TMA ($[Al]_{TMA}/[Zr]$ = 2500) was mixed and stirred for 5-min aging at room temperature, separately, then was injected into the reactor. The reactor was frozen in liquid nitrogen to stop reaction for 15 min and then the reactor was evacuated to remove argon. The reactor was heated up to polymerization temperature (70 °C). By feeding the fixed amount of ethylene (0.018 mol ~6 psi) into the reaction mixtures, the ethylene consumption can be observed corresponding to the ethylene pressure drop. The polymerization reaction was stopped and the reaction time used was recorded when all ethylene

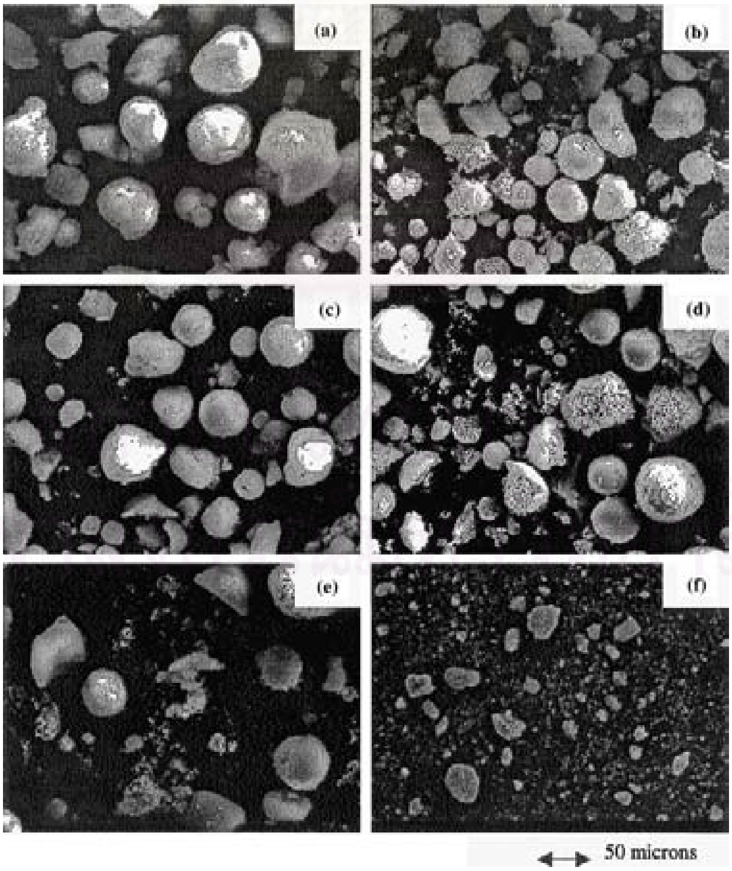


Figure 2. SEM micrographs of various TiO_2–SiO_2 mixed oxide supports before MAO impregnation; (a) Ti/Si = 0/1, (b) Ti/Si = 2/8, (c) Ti/Si = 4/6, (d) Ti/Si = 6/4, (e) Ti/Si = 8/2, (f) Ti/Si = 1/0.

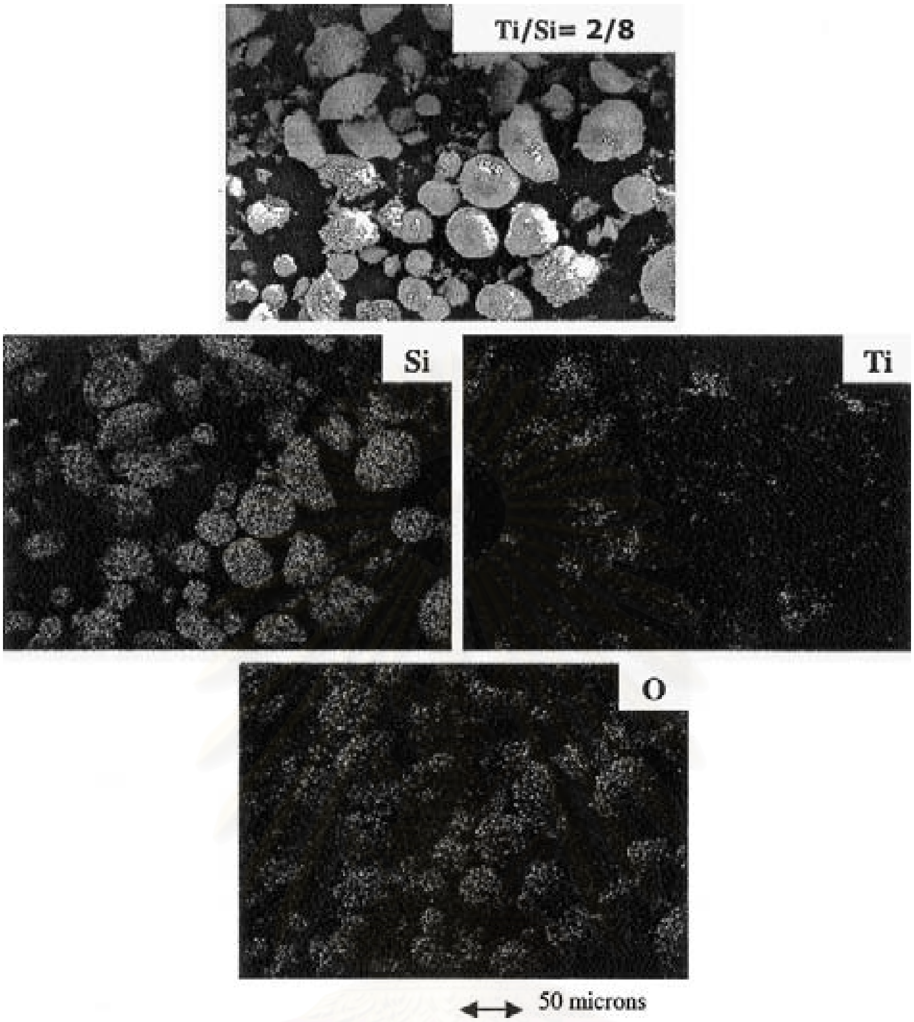


Figure 3. EDX mapping of a typical TiO_2–SiO_2 mixed oxide supports before MAO impregnation.

(0.018 mol) was totally consumed. To start reaction, 0.018 mol of ethylene was fed into the reactor containing the comonomer and catalyst mixtures. After all ethylene was consumed, the reaction was terminated by addition of acidic methanol (0.1% HCl in methanol) and stirred for 30 min. After filtration, the obtained copolymer (white powder) was washed with methanol and dried at room temperature.

2.4. Characterization

2.4.1. Characterization of supports and catalyst precursors

X-ray diffraction: XRD was performed to determine the bulk crystalline phases of samples. It was conducted using a SIEMENS D-5000 X-ray diffractometer with $CuK_\alpha(\lambda = 1.54439$ Å). The spectra were scanned at a rate of 2.4° min^{-1} in the range $2\theta = 20$–80°.

Scanning electron microscopy and energy dispersive X-ray spectroscopy: SEM and EDX were used to determine the sample morphologies and elemental distribution throughout the sample granules, respectively. The SEM of JEOL mode JSM-5800LV was

Table 1
Catalytic activities during ethylene/1-octene copolymerization via TiO_2–SiO_2 mixed oxides supported-MAO with zirconocene catalyst

TiO_2–SiO_2 Weight ratios	wt% of TiO_2 in mixed support	Polymer yield (g)	Polymerization time (s)	Catalytic activity[a] ($\times 10^{-4}$ kg polymer mol^{-1} Zr. h)
Homogeneous	0	1.13	87	3.1
0/100	0	1.19	152	1.9
20/80	20	1.14	116	2.4
40/60	40	1.19	132	2.2
60/40	60	1.18	149	1.9
80/20	80	1.17	157	1.8
100/0	100	1.13	161	1.7

[a] Activities were measured at polymerization temperature of 70 °C, [ethylene] = 0.018 mol, [1-octene] = 0.018 mol, $[Al]_{MAO}/[Zr]$ 1135, $[Al]_{TMA}/[Zr] = 2500$, in toluene with total volume = 30 mL, and $[Zr] = 5 \times 10^{-5}$ M.

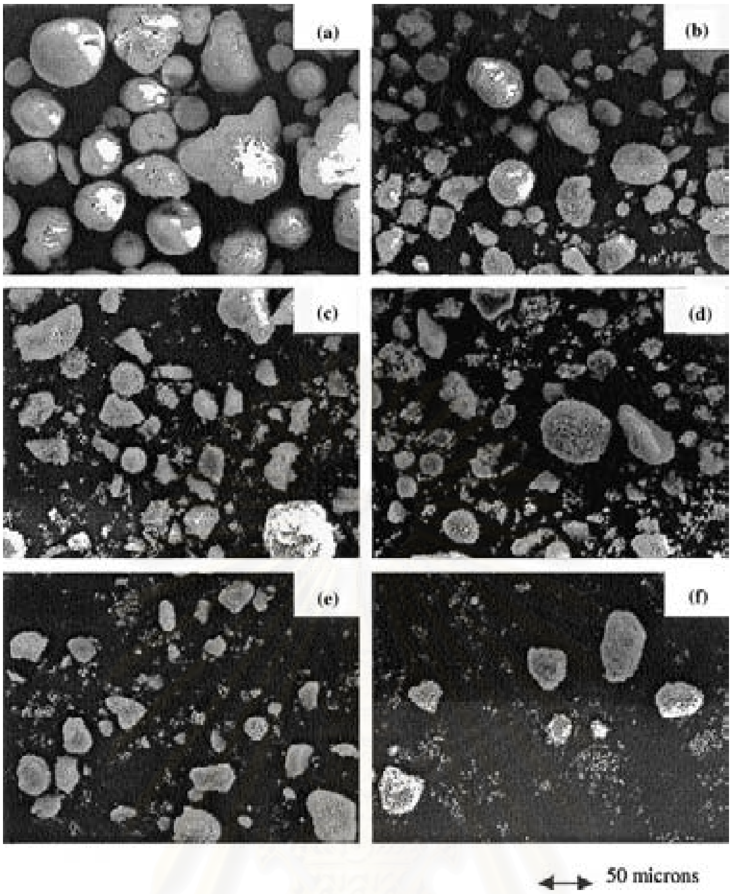


Figure 4. SEM micrographs of various TiO_2–SiO_2 mixed oxide supports after MAO impregnation; (a) Ti/Si = 0/1, (b) Ti/Si = 2/8, (c) Ti/Si = 4/6, (d) Ti/Si = 6/4, (e) Ti/Si = 8/2, (f) Ti/Si = 1/0.

applied. EDX was performed using Link Isis series 300 program.

FTIR spectroscopy: FTIR was conducted on a Perkin-Eelmer series 2000 instruments. The supports (1 mg) were mixed with 100 mg dried KBr. The sample cell was purged with oxygen. About 400 scans were accumulated for each spectrum in transmission with a resolution of 4 cm^{-1}. The spectrum of dried KBr was used as a background subtraction.

2.4.2. *Characterization of polymer*

Scanning electron microscopy: SEM was performed to study morphologies of polymers produced. The same equipment as mentioned above was employed.

Gel permeation chromatography (GPC): A high temperature GPC (Waters 150-C) equipped with a viscometric detector, differential optical refractometer and four Styragel HT type columns (HT3, HT4, HT5, and HT6) with a 1×10^7 exclusion limit for polysyrene was used to determined the molecular weight and molecular weight distributions of the copolymers produced. The analyses were performed at 135 °C using 1,2,4-trichlorobenzene as the solvent. The columns were calibrated with standard narrow molecular weight distribution polystyrene and LLDPE.

3. Results and discussion

The present study showed influences of TiO_2–SiO_2 mixed oxide supports on catalytic activities in heterogeneous metallocene catalytic system. The mixed oxide supports containing various amounts of titania and silica were characterized before and after impregnation with MAO. XRD patterns of the supports before impregnation with MAO are shown in figure 1. It was observed that the pure silica exhibited a broad XRD peak assigning to the conventional amorphous silica. Similar to the pure silica, the XRD patterns of the pure titania indicated only the characteristic peaks of anatase titania at 25° (major), 37°, 48°, 55°, 56°, 62°, 71°, and 75°. XRD patterns of the mixed oxide supports containing various amounts of titania and silica revealed the combination of titania and silica supports based on their content. It can be seen that the intensity of XRD characteristic peaks for both supports was changed based on the ratios of TiO_2/SiO_2. After impregnation with MAO, the mixed oxide supports were again identified using

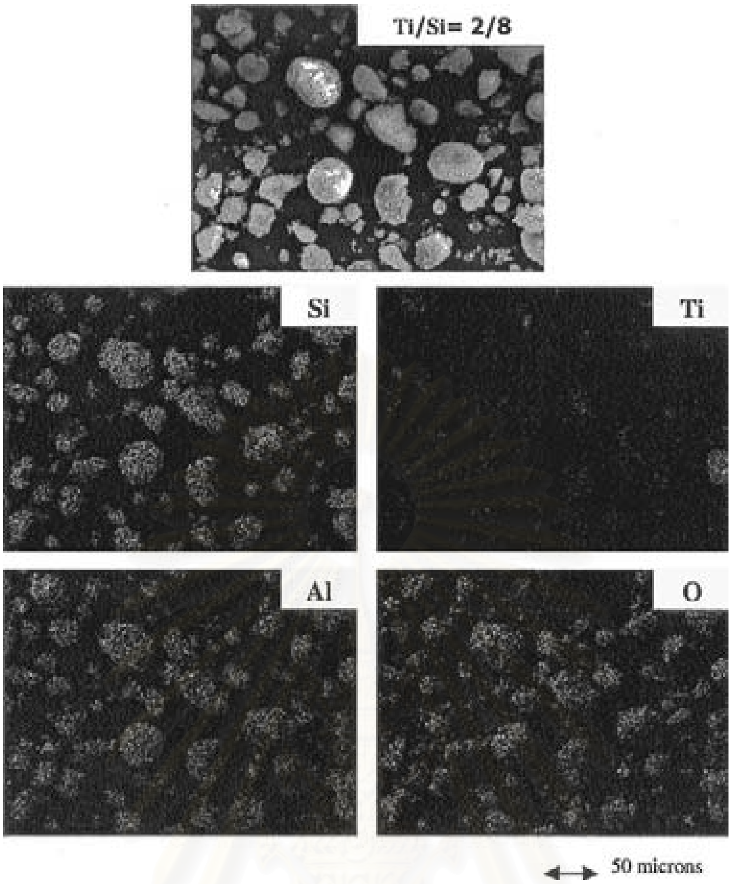


Figure 5. EDX mapping of a typical TiO_2–SiO_2 mixed oxide supports after MAO impregnation.

XRD. It was found that XRD patterns for the supports after impregnation with MAO were identical with those before impregnation with MAO indicating highly dispersed MAO species. In order to determine the morphologies and elemental distributions of the supports before and after impregnation, SEM and EDX were performed, respectively. The SEM micrographs of the supports before impregnation with MAO were shown in figure 2. It showed that silica was appeared in larger particles than titania. It also indicated that at the low content of titania ranged between 20 and 60%, titania was found to decorate on the silica surface as seen in the SEM micrographs. However, at high content of titania, it revealed that titania, essentially isolated from the silica surface. This was probably because the adsorption ability of silica surface with titania was limited by the titania contents in the mixed oxide supports. The distribution of all elements (Si, Ti, and O) obtained from EDX was similar in all samples. The typical EDX mapping images for the mixed oxide support are shown in figure 3 indicating titania located on the silica outer surface. After impregnation with MAO, SEM and EDX of the supports were also conducted. The SEM micrographs of the supports after impregnation with MAO are shown in figure 4 indicating similar results as seen in figure 2. The EDX mapping images of the supports can provide more information about the distribution of MAO as seen for Al distribution mapping on each support. It was found that MAO was well distributed all over the support granules. The typical EDX mapping images for the mixed oxide supports after impregnation with MAO are shown in figure 5. Figure 6 apparently shows SEM and EDX mapping of titania located on the outer surface of silica support. IR spectroscopy was also performed in order to identify chemical species and bonding of the mixed oxide supports. The IR spectra of samples are shown in figure 7. It revealed that at low concentrations of titania, the IR band at ca. 980 cm^{-1} assigning to Si–O–Ti connectivity was observed as also reported by Dutoit *et al.* [16]. The strong IR bands were also seen at ca. 1100 cm^{-1} assigning to asymetric Si–O–Si stretching vibration. Then, the various TiO_2–SiO_2 mixed oxide supports after impregnation with MAO were used and investigated for catalytic activities. Copolymerization of ethylene/1-octene via various TiO_2–SiO_2 mixed oxides-supported MAO with zirconocene catalyst was performed in order to determine the catalytic activities influenced by the various supports. The resulted reaction study is shown in table 1 and figure 8. The activities of the supported system were much

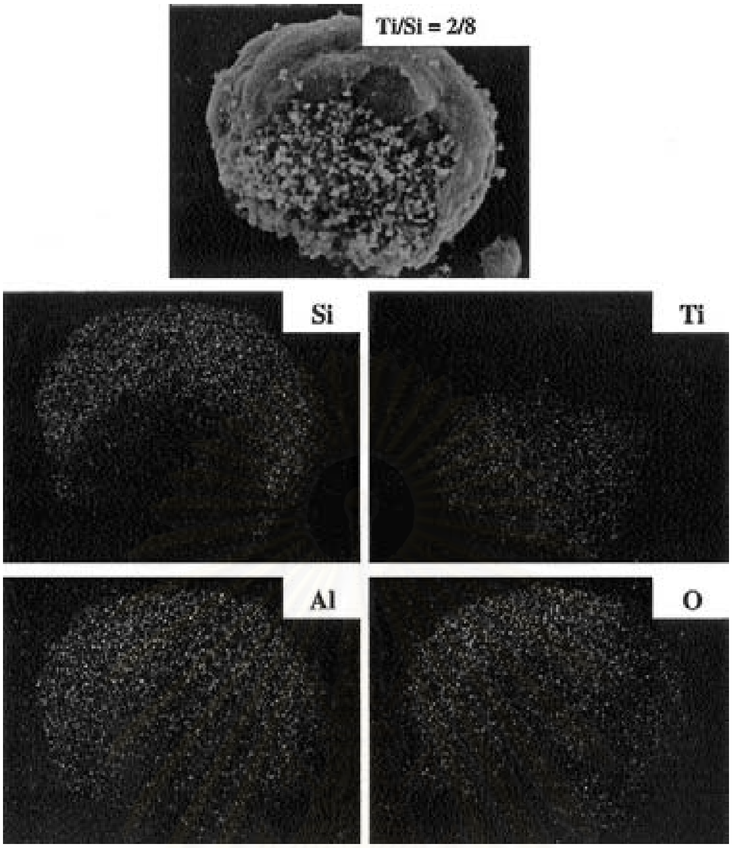


Figure 6. SEM and EDX mapping of titania located on the mixed support granule.

lower than the homogeneous one as expected. However, considering only the supported system, it was found that activities dramatically increased with increasing the amounts of titania up to 60% in the supports compared with those for the pure silica support. The maximum activity can be obtained with the presence of 20% titania in the mixed support. However, with increasing the amounts of titania more than 60% resulted in lower activities compared to the pure silica. It was also found that the activity for the pure titania is the lowest because the strong support interaction [17] between MAO and titania was more pronounced. Based on the resulted activities, the role of titania in TiO_2–SiO_2 mixed oxide supports can be proposed. In order to give a better understanding for the role of titania, a conceptual model for titania effect is illustrated in Scheme 1. As known,

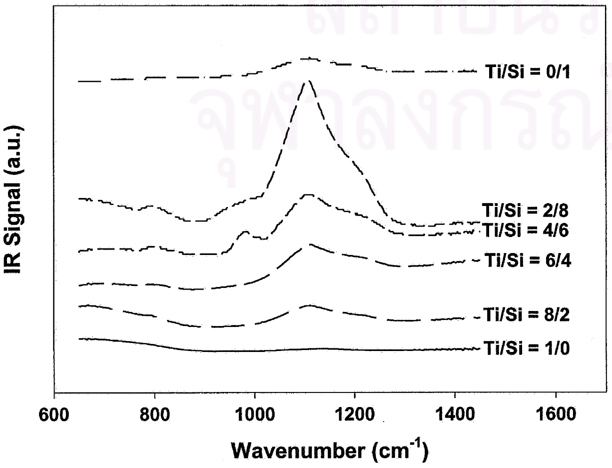


Figure 7. IR spectra of various mixed oxide supports.

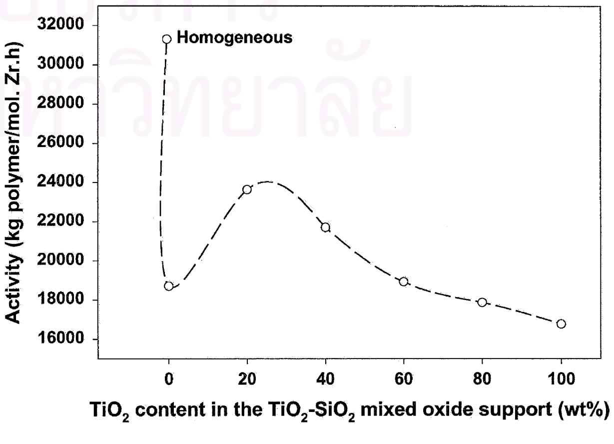
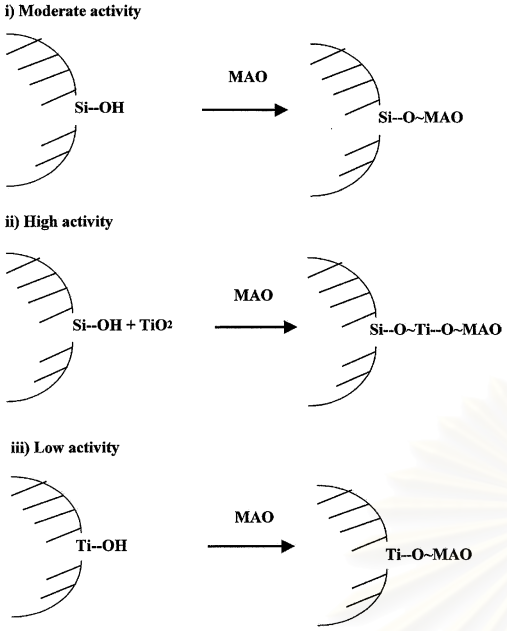


Figure 8. Activities of ethylene/1-octene copolymerization via various TiO_2–SiO_2 mixed oxides-supported MAO with a zirconocene catalyst.



Scheme 1. A conceptual model for evaluation of activities via various TiO_2–SiO_2 mixed oxide supports.

when the heterogeneous system was conducted, activities decreased significantly compared to the homogeneous one as also seen in figure 8. This should be due to a loss of active species by support interaction and/or the steric hindrance arising from the support. Considering Scheme 1, activities on the heterogeneous system can be divided into three levels; (i) moderate activity with the conventional pure silica support, (ii) high activity with the certain amounts of titania present in the mixed oxide support, (iii) low activity with the pure titania support (due to strong support interaction [17]). In Scheme 1 (ii), it showed that the presence of certain amounts (20–60 wt%) of titania dramatically enhanced activities. The contribution of titania can be drawn as MAO anchored on silica with titania as a spacer group. It can be also seen from SEM and EDX that at low content of titania, it was apparently decorated on silica surface and acted as a spacer to anchor MAO to the silica support. Thus, activities increased about 15–25% with the presence of titania between 20 and 40% in the mixed oxide supports. It should be mentioned that increased activities with the presence of titania as a spacer were observed because of less steric hindrance and less interaction on the support surface when a spacer was introduced. Thus, this was suggested to be more homogeneous-like system. Investigation of a spacer such as silane in copolymerization of ethylene/1-olefins was also reported [18,19]. However, when high amounts of titania were added, activities decreased because the strong support interaction as seen in Scheme 1 (iii) can occurred resulting in a combination

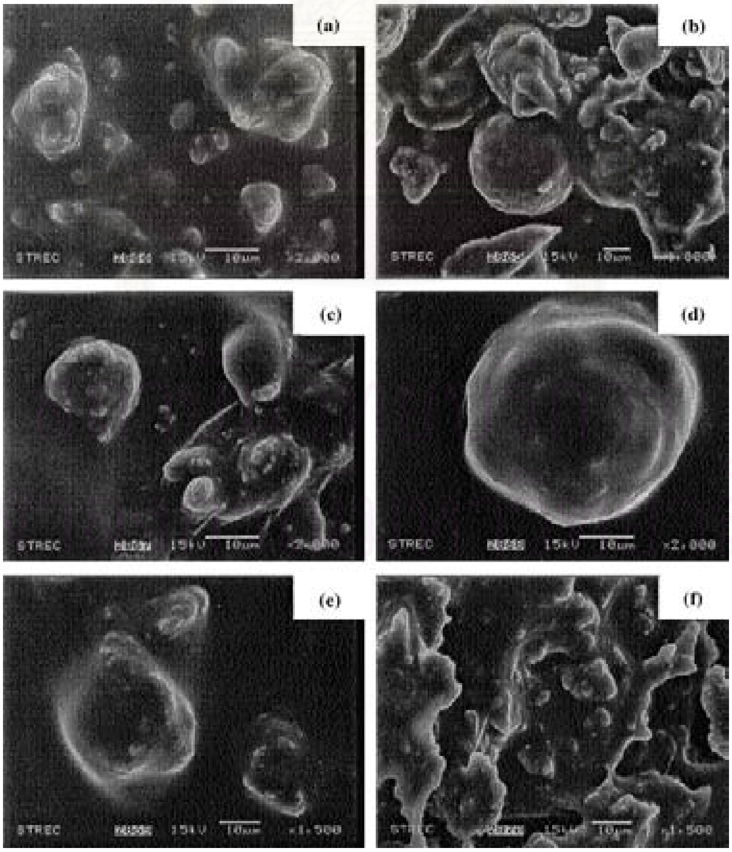


Figure 9. SEM micrographs of polymers obtained with various TiO_2–SiO_2 mixed oxide supports; (a) Ti/Si = 0/1, (b) Ti/Si = 2/8, (c) Ti/Si = 4/6, (d) Ti/Si = 6/4, (e) Ti/Si = 8/2, (f) Ti/Si = 1/0.

Table 2
Molar weight and molecular weight distribution of polymers obtained via TiO_2–SiO_2 mixed oxides supported-MAO with zirconocene catalyst

TiO_2–SiO_2 weight ratios	wt% of TiO_2 in mixed support	M_w^a ($\times 10^{-4}$ g mol^{-1})	M_n^a ($\times 10^{-4}$ g mol^{-1})	MWD[a]
0/100	0	3.61	1.06	3.4
20/80	20	3.42	1.08	3.2
40/60	40	2.91	1.13	2.6
60/40	60	2.60	0.96	2.7
80/20	80	2.65	0.93	2.8
100/0	100	2.41	0.59	4.1

[a] Obtained from GPC and MWD was calculated from M_w/M_n.

between Scheme 1 (i) and (iii) where titania started to isolate from silica as segregated titania. Morphologies of polymers produced via various supports were also investigated. The SEM micrographs of polymers are shown in figure 9. It indicated that there was no significant change in polymer morphologies upon various mixed oxide supports used. The molecular weight based on weight average (M_w) and based on number average (M_n), and molecular weight distribution (MWD) of polymers obtained are shown in table 2. It indicated that the addition of TiO_2 resulted in decreased molecular weights of polymers compared to those of pure SiO_2. However, the narrower molecular weight distribution was observed with the addition of TiO_2 except for the one with pure TiO_2.

4. Conclusions

The present study revealed influence of various TiO_2–SiO_2 mixed oxides supported-MAO on the catalytic activities during copolymerization of ethylene/1-octene. It was found that at certain contents of titania ranged between 20 and 60 wt% in the mixed oxide support, activities dramatically increased by 15–25% compared to those with the conventional pure silica support. It was proposed that titania added acted as a spacer to anchor MAO to the silica support resulting in less steric hindrance and less interaction on the support surface. However, larger amounts of titania resulted in lower activities because the strong support interaction between titania and MAO was more pronounced. The molecular weights of polymers were found to decrease with the addition of TiO_2 whereas narrower molecular weight distribution can be observed in the mixed TiO_2–SiO_2 supports.

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