ผลของตัวจ่ายอิเลคตรอนภายนอกต่อความว่องไวของตัวเร่งปฏิกิริยา และมวลโมเลกุลของพอลิเมอร์สำหรับเอทิลีนพอลิเมอไรเซชัน

นางสาวอนุสรา บัวเจริญ

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EFFECTS OF THE EXTERNAL ELECTRON DONOR ON THE CATALYST ACTIVITY AND POLYMER MOLECULAR WEIGHT FOR THE ETHYLENE POLYMERIZATION

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อ.ที่ปรึกษาวิทยานิพนธ์หลัก : ศ.ดร. ปิยะสาร ประเสริฐธรรม, 119 หน้า.

งานวิจัยนี้ได้ศึกษาผลของการเติมตัวจ่ายอิเลคตรอนภายนอกลงในเอทิลีนพอลิเมอไรเซชัน โดยใช้ตัวเร่งปฏิกิริยาซิเกลอร์-แนตตาที่มีแมกนีเซียมคลอไรด์เป็นตัวรองรับซึ่งสังเคราะห์ด้วยวิธีการตกผลึกซ้ำ (recrystallization) ตัวจ่ายอิเลคตรอนภายนอกที่ศึกษาแบ่งออกเป็น 4 กลุ่มได้แก่ แอลกอฮอล์ คีโตน เอสเทอร์ และอีเทอร์ เพื่อศึกษาชนิดของตัวจ่ายอิเลคตรอนภายนอกและอิทธิพลของโครงสร้างที่แตกต่างกันต่อความว่องไวในการเกิดปฏิกิริยาและสมบัติของพอลิเมอร์เปรียบเทียบกับระบบที่ไม่มีการเติมตัวจ่ายอิเลคตรอนภายนอก ผลการทดลองชี้ให้เห็นว่าตัวจ่ายอิเลคตรอนภายนอกสามารถเพิ่มและลดความว่องไวในการเกิดปฏิกิริยาได้ทั้งนี้ขึ้นอยู่กับชนิดของตัวจ่ายอิเลคตรอนภายนอก โดยลำดับของความว่องไวในการเกิดปฏิกิริยาแสดงได้ดังนี้ di-ether > none > ester > alcohol > ketone นอกจากนี้ลักษณะโครงสร้างของตัวจ่ายอิเลคตรอนภายนอกยังส่งผลกระทบต่อความว่องไวในการเกิดปฏิกิริยาซึ่งพบว่าโครงสร้างที่มีกิ่งก้านมีผลกระทบต่อการลดลงของปฏิกิริยาน้อยกว่าโครงสร้างแบบเส้นตรงเมื่อพิจารณาที่จำนวนคาร์บอนในโครงสร้างเท่ากัน สำหรับมวลโมเลกุลของพอลิเมอร์ที่ได้หลังจากการเติมตัวจ่ายอิเลคตรอนภายนอกขึ้นอยู่กับความว่องไวในการเกิดปฏิกิริยา จากการศึกษาผลของตัวจ่ายอิเลคตรอนภายนอกในระบบเอทิลีนพอลิเมอไรเซชันสามารถสรุปได้ดังนี้ ตัวจ่ายอิเลคตรอนภายนอกที่ลดความว่องไวของตัวเร่งปฏิกิริยาจะลดมวลโมเลกุลของพอลิเอทิลีนด้วยขณะที่ตัวจ่ายอิเลคตรอนชนิดอีเทอร์ที่เพิ่มความว่องไวของตัวเร่งปฏิกิริยาจะเพิ่มมวลโมเลกุลของพอลิเอทิลีน ดังนั้นงานวิจัยนี้จึงเป็นแนวทางหนึ่งในการพัฒนาสมบัติของตัวเร่งปฏิกิริยาซิเกลอร์-แนตตารวมถึงการควบคุมสมบัติของพอลิเอทิลีนทางด้านมวลโมเลกุลให้เหมาะสมกับความต้องการใช้งานในอุตสาหกรรมของโอเลฟิน

ภาควิชา……วิศวกรรมเคมี……....ลายมือชื่อนิสิต………อนุสรา บัวเจริญ……………………..
สาขาวิชา…..วิศวกรรมเคมี………ลายมือชื่ออ.ที่ปรึกษาวิทยานิพนธ์หลัก………………………..
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ANUSARA BUAJAROEN: EFFECTS OF THE EXTERNAL ELECTRON DONOR ON THE CATALYST ACTIVITY AND POLYMER MOLECULAR WEIGHT FOR THE ETHYLENE POLYMERIZATION. ADVISOR: PROF. PIYASAN PRASERTHDAM, Dr.Ing., 119 pp.

In the present study, investigate effects of external electron donors on the ethylene polymerization with $MgCl_2$-supported Ziegler-Natta catalysts synthesized by recrystallization method. External donors can be divided into 4 grouped such as alcohols, ketones, esters and di-ethers. The effects of the different kind of functional groups and molecular structure of external donors on catalytic activity and polymer properties were investigated and also compared with and without any donor. The results indicated that external electron donors remarkably affected on the catalytic activity not only improvement, but also deactivation, depending on the nature of each functional groups. The activities of catalysts are in the following order: di-ether > none > ester > alcohol > ketone. In addition, molecular structures of alcohol carbon were found to be effected; more bulkiness produced an evident deactivation effect lower than linear structures in comparison with the same numbers of carbon. The obtained polymer molecular weight after external electron donors is addition depending on the catalytic activity. It can be proposed that external electron donors decreased the catalyst activity leading to the reduction of polyethylene molecular weight. Furthermore, it was found that di-ether which acts as an external donor increased the catalyst activity and also enhanced polyethylene molecular weight. Therefore, this research plays an important role in developing catalyst efficiently and molecular weight desire of polymer for in olefin industries.

Department : ……Chemical Engineering... Student's Signature : …Anusara Buajaroen…
Field of Study : ...Chemical Engineering… Advisor's Signature : ……………………
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Finally, I would like to dedicate this thesis to my family for their edification support and overwhelming encouragement over the year spent on this study.

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CHAPTER I

INTRODUCTION

Polyethylene is the major polymer and the largest of production in plastic industry, because there are many properties that make polyethylene attractive, such as excellent chemical resistance to solvents, acids and alkalis, high impact strength and stiffness even at low temperatures (Boor, 1979; Chen *et al.*, 2006). Ziegler-Natta catalysts are used for produce polyethylene more than forty years. Up to now, commercial manufacture of polyethylene is still based on modifications and improvements of the original Ziegler-Natta system (Bhaduri, Mukhopadhyay, and Kulkarni, 2006). Many studies concerning the influence of molecular weight on the various properties of polyethylene have been performed due to its scientific interest and industrial importance (Mori, 1999). Moreover, the molecular weight (MW) of polyethylene is also a crucial determinant of mechanical properties, although high MW has superior physical properties which are difficult to process. Therefore, requirement to control the MW plays an important role in both processability and mechanical properties (Chen, 2006; Fukuda, 2003). Various methods for controlling the MW and the molecular weight distribution (MWD) of polymers are available. Control the MW of polyethylene industrial production lines by using Ziegler-Natta catalysts in the presence of some compounds (so-called Lewis bases compound) like water, alcohol, etc.; containing active hydrogen, which is capable of terminating a Ziegler-Natta polymerization reaction is interest (Ahn *et al.*, 1998; Cho *et al.*, 2000; Singh and Merrill, 1971). Generally, the Lewis base have several functions, such as to make a complex or to react with $MgCl_2$, $TiCl_4$, and cocatalyst, to stabilize $MgCl_2$ crystallites, and to deactivate astereospecific polymerization sites or to convert astereospecific sites to stereospecific ones, thus increasing the isotactic index (Ma *et al.*, 2005) for propylene polymerization. In addition, it has been also stated that these compounds can be regarded to influence on the catalyst activity on both the directions in activation and deactivation. Nevertheless, the capability of their compounds that affect on the activity of catalyst and polymer properties have not been well understood and also have been addressed by a few approaches for the ethylene polymerization.

The purpose of this study, we have compared the several Lewis bases compounds, which added during ethylene polymerization in order to elucidate a possible correlation of different kinds and the molecular structures of electron donor on the catalytic activity and polymer properties. This investigation was carried out with $MgCl_2$-alcohol adduct/$TiCl_4$/external donors/$AlEt_3$, which is a typical Ziegler-Natta catalyst in the slurry phase for ethylene polymerization.

1.1 Objectives of the Thesis

The objective of this research is to investigate the effects of Lewis bases as external electron donors which were added during polymerization of ethylene with Ziegler-Natta catalyst, on the catalytic activities and polymer properties.

1.2 Scopes of the Thesis

1. Preparation of Ziegler-Natta catalysts by recrystallization method.
2. Characterization of support and catalysts using N_2 physisorption, X-ray diffraction (XRD), inductively coupled plasma (ICP), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).
3. Synthesize polyethylene by using Ziegler-Natta catalyst in the presence of external electron donors such as alcohols, ketones, esters, and di-ethers groups which were introduced into the system during polymerization of ethylene.
4. Study the effects of electron donors on catalyst activity and polymer properties for the ethylene polymerization.
5. Characterization of polyethylene properties using differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and u-tube viscometer.

1.3 Benefits

Catalytic activity of Ziegler-Natta catalyst and molecular weight of polyethylene can be controlled by external electron donors.

1.4 Research Methodology

The flow diagram research methodology is given in **Figure 1.1**.

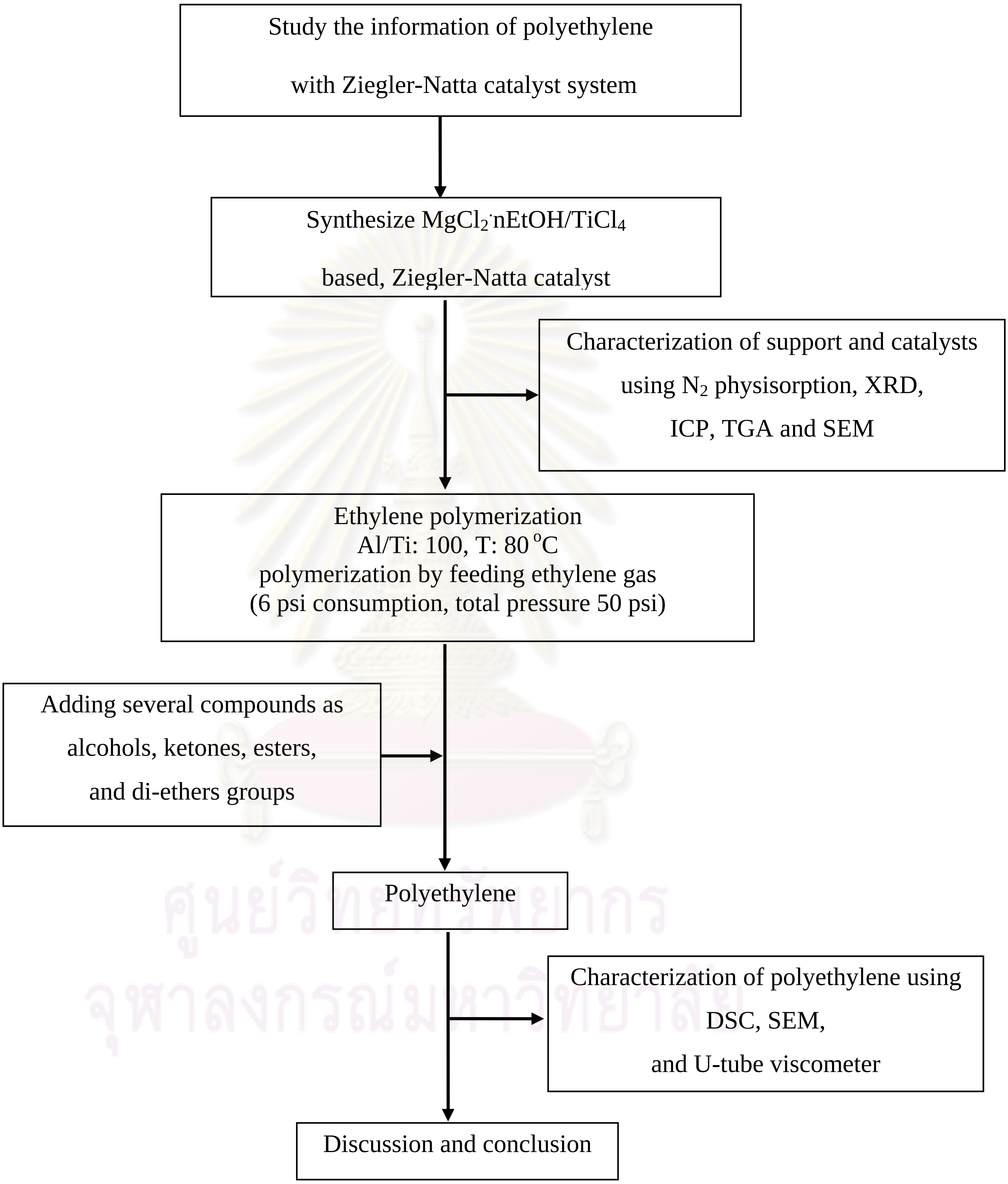


Figure 1.1 Flow diagram of research methodology

This thesis can be divided into five chapters. Chapter I provide the general introduction to lead the objective and scope of this research. Chapter II knowledge and open literature dealing with Ziegler-Natta catalysis for olefin polymerization were presented. 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 polymerization using Ziegler-Natta catalyst with in the presence of different external electron donors were presented. The influences of introduction of electron donors during the polymerization of ethylene on the catalytic activity and polymer properties were investigated. The characteristics support and catalyst using N_2 physisorption, inductively coupled plasma (ICP), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) and obtained polymer using differential scanning calorimetry (DSC) and dilute solution viscosity by u-tube viscometer.

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

CHAPTER II

LITERATURE REVIEWS

2.1 Catalysts and Polymerizations

Heterogeneous Ziegler-Natta catalysts for the synthesis of polyolefins have been markedly improved through several generations of catalysts. The first-generation catalysts, based on $3TiCl_3 \cdot AICl_3$ and $Al(C_2H_5)Cl$, gave polypropene (PP) containing 90 wt% of boiling heptane-insoluble fractions (isotactic index, *II*) with a productivity of only 5 kg per g of Ti. The introduction of a Lewis base into the catalyst system gave rise to the second-generation catalysts which were more active and stereospecific. However, most of the titanium salt involved in the catalyst was inactive and was left as a polluting residue in the polymer, which needed to be removed. A drastic innovation was achieved with the development of the third generation of catalysts, essentially composed of $TiC1_4$ supported on $MgC1_2$, with trialkylaluminum as a co-catalyst and one or two Lewis bases as electron donors. The new catalyst system has presented many advantages for the polyolefin industry. Among these is an extremely high catalyst performance (>2400 kg PP/g Ti, *II* > 98%) which eliminates the process of catalyst removal. Since the heterogeneous supported catalysts are able to replicate their morphology in the morphology of the produced polymer particles, the polymer can be made to be spherical with a controlled diameter, particle-size distribution and compactness according to the specific architectures of the catalysts. In addition, a variety of polymeric materials can be obtained during the same polymerization process by replacing the initial monomer with other monomers.

In the past 10 years (Soga and Shiono, 1997), highly active $MgCl_2$-supported catalysts have played a key role in the introduction of simplified polymerization processes and also in the development of a broader range of tailor-made polyolefins. A great deal of research effort has also been devoted to obtaining a better understanding of the effects of $MgCl_2$-supported catalysts and Lewis bases on the activities and polymer properties of third-generation catalysts.

2.2 Heterogeneous Ziegler-Natta Catalysts

2.2.1 $MgC1_2$- Supported Catalysts

Two crystalline modifications are known for $MgCl_2$, the commercial α form and the less stable β form. Similar to the γ-$TiCl_3$, the α-form has a layer structure of the $CdCl_2$ type and shows a cubic close-packed stacking (ABC…ABC…) of double chlorine layers with interstitial Mg^{2+} ions in six fold coordination (Bruni and Ferrari, 1925). The β-form, on the contrary, shows a hexagonal close packing like that of α-$TiCl_3$ (Bassi *et al.*, 1982). The layer structure of α-$MgCl_2$ displays an X-ray diffraction spectrum with a strong (104) reflection at d = 2.56 Å as a result of the cubic close-packed arrangement of the Cl ions. The internal structures of hexagonal layers in both cases are almost equivalent since van der waals interaction between layers is weak.

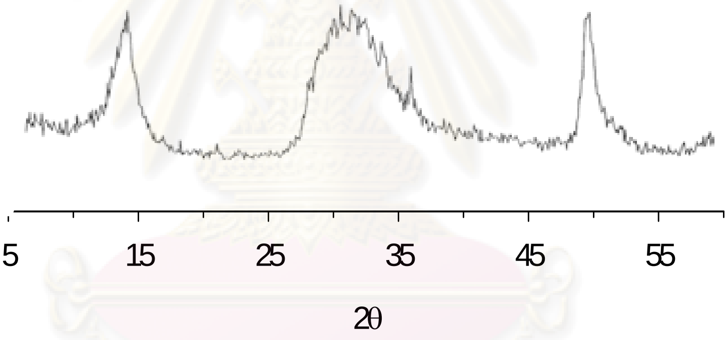


Figure 2.1 Powder X-ray diffraction pattern of δ-$MgCl_2$.

The key ingredient of the catalysts is the "activated" or δ-$MgCl_2$, which exhibits a disordered structure arising from the translation and rotation of the structural Cl-Mg-Cl layers with respect to one another that destroy the crystal order in the stacking direction (Giannini, 1981). In consequence, the X-ray spectrum shows a gradual disappearance of the (104) reflection and its replacement by a broad "halo" centered at d = 2.65 Å. As shown in the **Figure 2.1**, the structurally disordered δ-$MgCl_2$ exhibited broad bands centered at 2θ = 15, 32 and 50.5^o. Moreover, it is believed that the outstanding success of $MgCl_2$ is because δ-$MgCl_2$ and δ-$TiCl_3$ have the same crystal structure and the nearly identical ionic radii and lattice distances (see **Table 2.1**). Such a dramatic increase in activity was revealed to be caused by marked increases in the propagation rate constant (k_p) as well as the number of active species [C*] (Giannini, 1981). The latter effect is easily understood in terms of a high dispersion of the active titanium species on the large surface of $MgCl_2$.

Table 2.1 Crystallographic data for δ-$MgCl_2$ and δ-$TiCl_3$

δ-$MgCl_2$	**δ-$TiCl_3$**
hexagonal close packing of the Cl ions	
a = b = 3.63Å	a = b = 3.54Å
c = 5.93Å	c = 5.86Å
Cation coordination: octahedral	
Mg–Cl = 1.23Å	Ti–Cl = 1.25Å
Mg^{2+} = 0.65Å	Ti^{4+} = 0.68Å
	Ti^{3+} = 0.76Å

Experimental data suggest that preferential lateral cuts correspond to the (100) and (110) planes (Giannini, 1981), and theoretical calculations of the lattice electrostatic energies give a lower energy for the (110). The activation processes (mechanical or chemical) of the $MgCl_2$ increase the portion of (100) and (110) surfaces on the $MgCl_2$ surface (Moore, 1996). These two lateral cuts contain coordinatively unsaturated Mg^{2+} ions, with coordination number 4 on the (110) cut and 5 on the (100) cut, as shown in **Figure 2.2** (Albizzati, 1993). That is to say, the magnesium atoms are coordinated with 4 or 5 chlorine atoms, as opposed to 6 chlorine atoms in the bulk of the crystal.

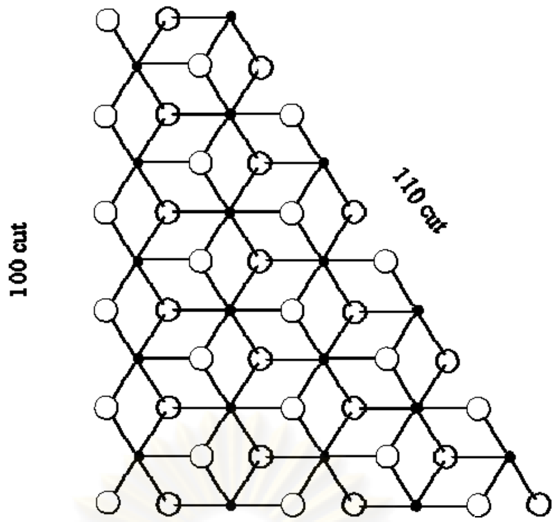


Figure 2.2 Model of $MgCl_2$ layer showing the (100) and (110) cuts.

The situation on crystal edges and corners could present additional differences, so that the presence on the $MgCl_2$ surface of Lewis acidic sites with different acid strength and steric requirements is likely to occur and actually has been verified through interaction with Lewis bases of different strength and steric hindrance. The “activated” $MgCl_2$ support, as it exists in the catalyst, can thus be envisaged as an agglomerate of very small crystallites (primary units) bearing on their side surfaces a variety of exposed Mg^{2+} ions with different degrees of unsaturation, Lewis acidic strength and steric hindrance, and thus potentially able to coordinate with the other catalytic components.

2.2.2 Catalyst Chemistry

It is well known that neither $TiCl_4$ nor the internal donor can be easily removed from the catalyst unless severe thermal treatments or strongly coordinating solvents are used. Thus, it seems that the catalyst components lose their identity and become strongly linked together, forming new complexes. A considerably amount of work has been aimed at elucidating the nature of this bonding mainly by means of spectroscopic observations (IR, NMR) and thermogravimetric (TG) analyses carried out on both the true catalyst and model combinations of its components (i.e., $MgCl_2$/ID, $TiCl_4$/ ID, $TiCl_4/MgCl_2$, $TiCl_4$/ID/$MgCl_2$ complexes or comilled mixtures).

A great deal of IR data is available for catalysts containing ethylbenzoate (EB) as internal donor (Galli *et al.*, 1981; Yano *et al.*, 1988; Chien *et al.*, 1983) for which a shift of the C═O stretching frequency from 1725 cm^{-1} in the free ester to 1680 cm^{-1} to 1700 cm^{-1} is most commonly observed in both the catalyst and the comilled EB/$MgCl_2$ mixtures. This result has been interpreted as an indication that a complexation of EB through the carbonyl oxygen takes place to Mg and not to Ti. The concomitant broadening of the C═O absorption band has been attributed to the presence of a variety of coordination complexes with different bond strengths (Albizzati *et al.*, 1991).

Solid state CP MAS (cross polarization with magic angle spinning) ^{13}C NMR investigations on both the catalyst (Chien *et al.*, 1990; Terano *et al.*, 1992) and model $TiCl_4$·EB complexes or EB/$MgCl_2$ comilled mixtures also led to the conclusion that EB is prevailingly complexed to $MgCl_2$. Possible structures for EB complexed to the (100) and (110) faces of $MgCl_2$ have been proposed by Chien *et al.* (Chien *et al.*, 1990) and are shown in **Figure 2.3**.

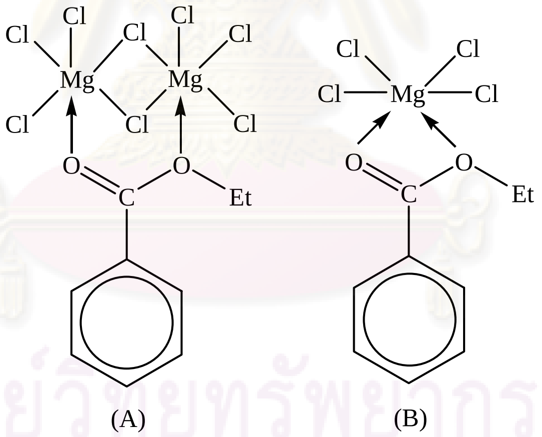


Figure 2.3 Possible models for EB coordination on the (100) (A) and (110) (B) faces of $MgCl_2$.

According to some authors (Ewen *et al.*, 1998; Guyot *et al.*, 1986), however, a slight difference can be noticed in the infrared C═O absorption frequency of the catalyst (~1680 cm^{-1}) and that of the EB/$MgCl_2$ mixture (~1690 cm^{-1}) and this would suggest that in the former, EB is in some way complexed to both Mg and Ti. On the other hand, from electron spin resonance (ESR) analysis of the catalyst after interaction with TEA, some evidence for the presence of small amounts of EB or phthalates complexed to Ti^{3+} has been reported as well (Sergeev *et al.*, 1985; Chien and Hu, 1989).

The information concerning bifunctional donors (phthalates, diethers) is not as abundant. For phthalic acid esters, however, IR observations show a shift of the C═O stretching frequency from ~1730 cm^{-1} in the free ester to 1685 cm^{-1} to 1700 cm^{-1} in both the catalyst and the $MgCl_2$/ester complex. Similarly, the C–O stretching frequency of diethers (1113 cm^{-1}) is shifted to a doublet at 1059 cm^{-1} and 1024 cm^{-1} in both the catalyst and the $MgCl_2$/diether mixture, with no bands from the $TiCl_4$·diether complex being detectable in the former (Albizzati *et al.*, 1995). The same indication is provided by ^{13}C NMR observations on catalyst containing either diethers (Albizzati *et al.*, 1995) or phthalates (Sormunen, Hjertberg, and Iiskola, 1995), though in the latter case a considerable line narrowing observed in binary ester/$MgCl_2$ mixture after treatment with $TiCl_4$ would suggest, according to the authors (Sormunen *et al.*, 1995), that a separate crystalline phase is formed on the support surface.

From all the above, it seems possible to conclude that both monofunctional and bifunctional donors are essentially complexed to Mg rather than to Ti. The structure of the complexes could, however, be different for the different donor types. As a matter of fact, bifunctional Lewis bases could form either 1:1 chelate complexes with tetracoordinated Mg ions on the (100) face (Albizzati *et al.*, 1995).

As far as the $TiCl_4$ bonding is concerned, the most widely accepted models, supported by energy calculations, are those based on epitaxial adsorption on the different $MgCl_2$ faces. According to Corradini and his group (Busico *et al.*, 1985; Busico *et al.*, 1986), for instance, the (100) cut is more basic than the (110) one as far as $TiCl_4$ coordination is concerned. Also, calculations suggest that $TiCl_4$ coordination as a Ti_2Cl_8 dimer on the former face and as a monomer on the latter are energetically favored. Similar models were proposed by Chien (Chien, Weber, and Hu, 1989) who, however, assumed the presence of tetracoordinated rather than hexacoordinated monomeric species on the (110) face, both in clusters and in isolated form. As a consequence of the presence of $TiCl_4$ to coordinate on the (100) face, the situation in the catalyst, before and after reduction with the Al-alkyl, can be roughly represented as in **Figure 2.4**, with the (100) face being prevailingly occupied by Ti_2Cl_8 dimers and the (110) face by the Lewis base.

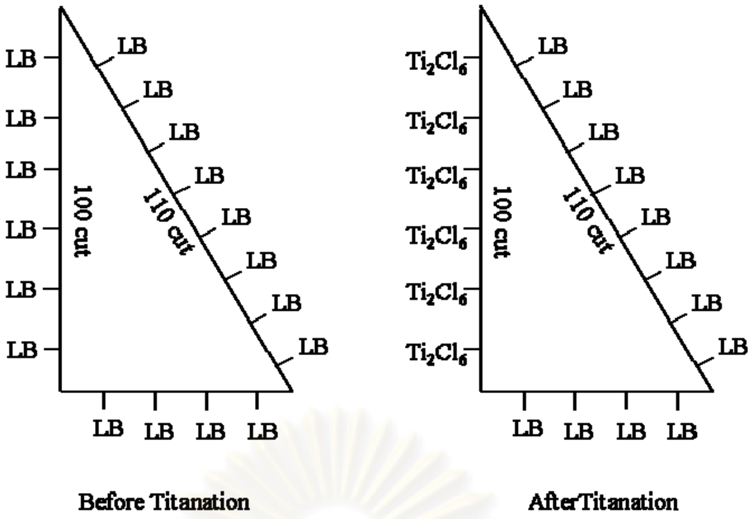


Figure 2.4 Schematic drawing of the Lewis base and Ti halide distribution on the (110) and (100) cuts $MgCl_2$: (left) = support, (right) = catalyst activated with the Al-alkyl.

However, recent spectroscopic studies using FT-Raman have provided evidence for strong adsorption of $TiCl_4$ on the (110) lateral cut of $MgCl_2$, giving a monomeric species with octahedrally coordinated titanium, which can be the precursor for active and stereospecific sites (Brambilla *et al.*, 2004; Brambilla *et al.*, 2007) as shown in **Figure 2.5**.

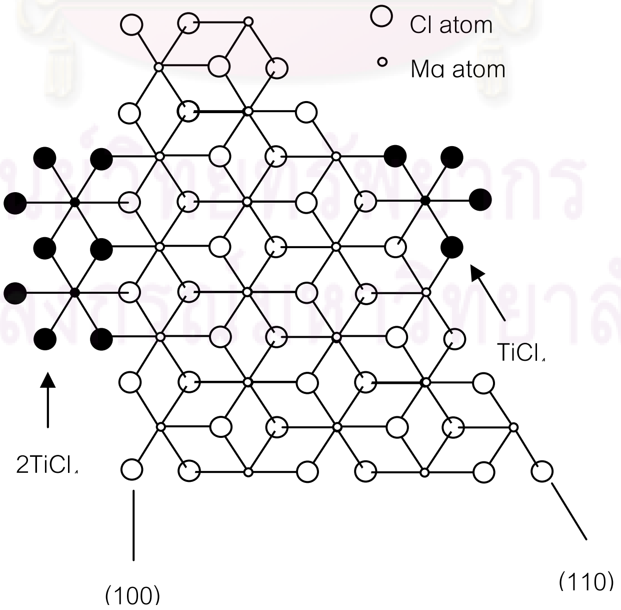


Figure 2.5 Epitaxial binding of $TiCl_4$ on to the surface of δ-$MgCl_2$.

2.2.3 Cocatalyst Chemistry

The cocatalysts used with $MgCl_2$-supported catalysts are invariably Al-trialkyls, triethyl aluminium (TEA) and triisobuthyl aluminium (TIBA) being by far the most preferred ones. Al-alkyl-chlorides, in fact, afford a much poorer performance and can be used only in combination with trialkyls (Barbé, Cecchin, and Noristi, 1986).

On the other hand, the external donor which can be used appears to be dependent on the type of internal donor. If ID is an aromatic monoester (EB is the most usual), esters of the same type are normally required, such as methyl-*p*-tolulate (MPT), ethylanisate (EA), *p*-ethoxy-ethylbenzoate (PEEB) and the like, whereas alkoxysilanes are required with phthalates (or diethers). Hindered piperidines, such as 2,2,6,6-tetramethylpiperidine (TMP), on the other hand, seem to work well with diethers, but not as well with monoesters. Whichever is the external donor, however, owing to its basic nature and the acidic nature of the AlR_3, a more or less complex interaction between the two components takes place.

Most of the literature deals with the interaction between TEA or TIBA and aromatic monoesters, whose chemistry has recently been reviewed by several authors. According to most of the findings, the interaction involves first the formation of an acid-base complex through the carbonyl oxygen, as demonstrated by the shift of the infrared C═O stretching frequency from ~1725 cm^{-1} in the free ester to 1655 cm^{-1} to 1670 cm^{-1} in the AlR_3/ED mixture. The complex is most often assumed to exist in a 1:1 ratio, but on the basis of spectroscopic evidence (Spitz, Lacombe, Primet, 1984) and calorimetric studies (Albizzati *et al.*, 1991), complexes involving two moles of AlR_3 per mole of ED also have been hypothesized. Structures such as those represented in **Figure 2.6** have been proposed by Spitz *et al.* (Spitz *et al.,* 1984), while not very different structures were assumed by Chien and Wu (1982) and Tashiro *et al.* (1984). The complex formation is very fast even at low temperature and in dilute solutions.

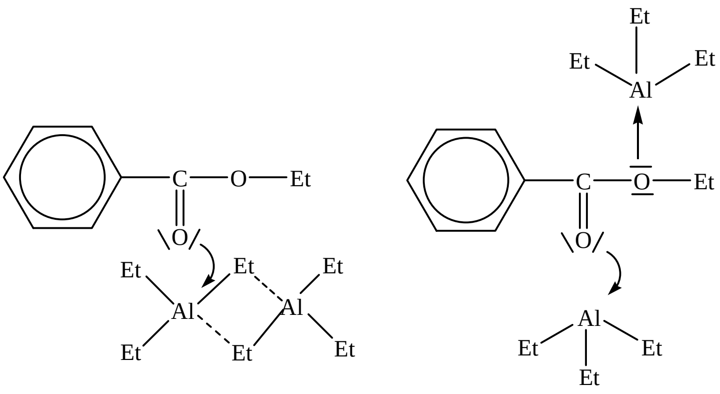


Figure 2.6 possible structures of 1:2 EB/TEA complexes.

As regards alkoxysilanes, the formation of a 1:1 complex between TEA and phenyltriethyoxysilane (PES) has been indicated by means of ^{13}C NMR spectroscopy, at least at relatively high TEA concentrations (0.5 mol/L) (Vähäsarja *et al.*, 1987). The complex seems to involve the O atom from only one OR group, irrespective of the number of OR groups attached to Si.

The above complexes can undergo a further reaction, especially in the presence of excess AlR_3 as is usual for polymerization. In the case of aromatic monoesters, such as EB, a nucleophilic attack of free AlR_3 on the carbonyl group complexed with AlR_3 has been postulated. The reaction leads finally to the formation of two moles of dialkylaluminium alkoxide per one mole of ester, according to the **Figure 2.7** (Barbé *et al.*,1986; Spitz *et al.*, 1988; Jeong *et al.*, 1991).

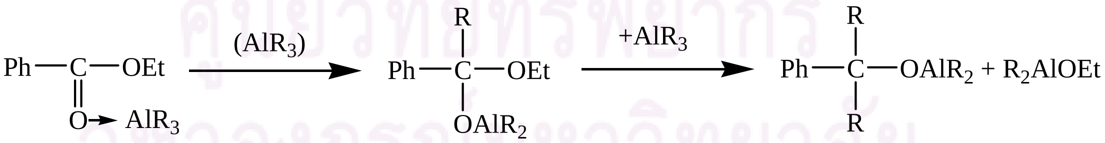


Figure 2.7 The formation of EB and AlR_3 complexation.

Reduction of the C═O group, rather than alkylation, prevails with TIBA with the concomitant elimination of isobutene. The reaction rate is higher for TEA than TIBA and is greatly enhanced in concentrated solutions. Even at the mild conditions used in the polymerization and in the presence of the monomer, however, the reaction proceeds to a considerable extent.

Silyl ethers, in turn, can undergo an exchange reaction with the Al-alkyl, with the formation of alkylated silylethers and dialkyl-Al-alkoxides. The reaction rate is appreciable for silanes containing three or four OR groups and at high concentrations of the Al-alkyl. Starting from $PhSi(OMe)_3$ and TEA, for instance, the reaction at 75^oC can proceed up to the formation of $PhEt_2SiOMe$, according to the scheme of **Figure 2.8** (Vähäsarja *et al.*, 1987).

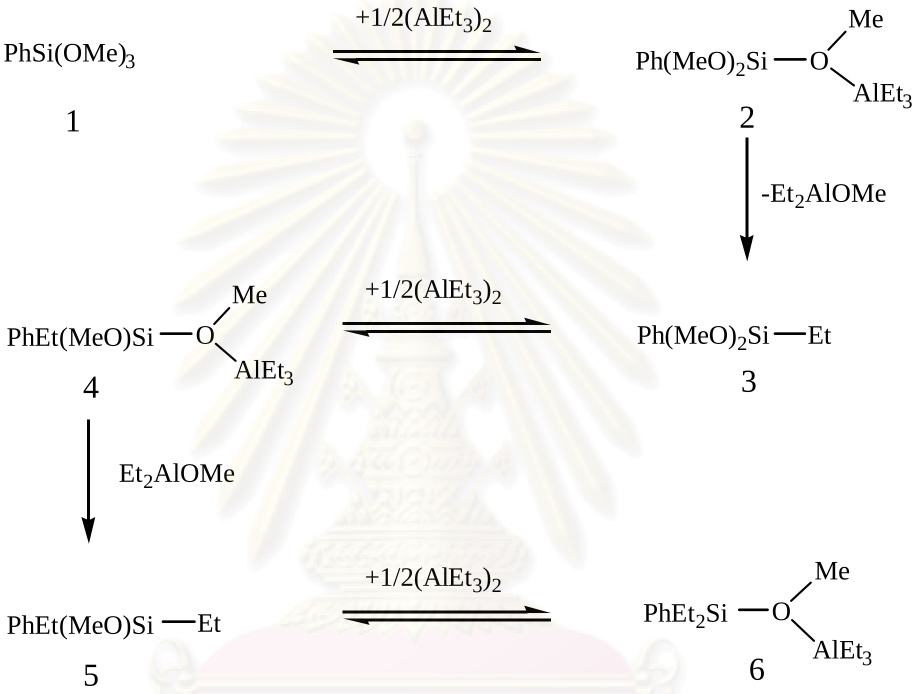


Figure 2.8 Pathway of the reaction between TEA and $PhSi(OMe)_3$.

Under the much more diluted polymerization conditions, however, the reaction is much slower and only 20% of PES, for example, is converted in 1 hour at 70^oC, with TEA = 5 mmol/L and PES = 0.5 mmol/L (Albizzati, 1991).

The reaction is even slower, and sometimes absent for dialkoxysilanes and practically absent at all for monoalkoxysilanes (Vähäsarja *et al.*, 1987). On the other hand, in the case of trialkoxysilanes the main reaction product besides the Al-alkoxide is a dialkoxy-Si derivative which, differently from the aromatic ester derivatives, still behaves as a good stereoregulating agent.

In conclusion, it can be stated that all types of external donor easily form complexes with the AlR_3 cocatalyst. These complexes are rather stable for silanes, whereas in the case of aromatic esters, they further react, leading to the partial destruction of the ester and its replacement with significantly less stereoregulating products. The true cocatalyst is, in this case, a mixture including free AlR_3, unconverted AlR_3/ester complex, and a mixture of Al-alkoxides of different bulkiness. Some free ED also can be present if the Al/ED ratio is very low.

2.3 Catalyst Preparation Methods

The efficiency of olefin polymerization catalysts can be improved by several methods. Since the excellent properties of $MgCl_2$ supported Ziegler-Natta catalysts for production of polyolefins were discovered, many studies on treating methods of $MgCl_2$ have been carried out in order to improve the yield of catalysts through the increase of the surface area and through a better interaction between $MgCl_2$ and $TiCl_4$. These treatments have been the ball-milling, the chemical reaction and the recrystallization methods (Parada, Rajmankina, and Chirinos, 1999). Three main industrially viable synthetic routes have been followed to fulfill the requirements. A short description is given below.

2.3.1 Ball milling

The ball-milling method allows reducing the size of MgCl2 crystallites increasing, as a consequence, the surface area of the catalyst and its activity. Nevertheless, its major disadvantage is a prevalent difficulty in controlling the polymer morphology (Parada *et al.*, 1999).

2.3.2 Recrystallization

A further development has been the use of an alcoholate of $MgCl_2$, allowing the preparation of spherically shaped support and hence catalyst particles (European Patent 0086288, 1983). This important advance resulted from the establishment of catalyst particle replication during polymerization (Galli, 1981; Galli, Ciardelli, and Giusti, 1981) which is an important consideration both for slurry and gas phase commercial polymerization. The method consists of a chemical activation by reaction of crystalline $MgCl_2$ with alcohol to form $MgCl_2 \cdot n$ROH adducts, followed by a controlled regeneration of the active support through recrystallization by removing the added compound (quick cooling, solvent evaporation or titanation). In consequence, the assemblies of spherically fined $MgCl_2$ crystallites with highly distort and high number of uncoordinated magnesium sites is produced.

2.3.3 Chemical reaction

Catalysts prepared from the reaction between $TiCl_4$ and magnesium alkoxides such as $Mg(OEt)_2$ show a very high activity for the polymerization of ethylene and propylene. Such catalysts were successfully developed for ethylene polymerization by Hoechst AG (British Patent 1286867, 1968) and Solvay and Cie (Belgian Patent 743325, 1969) during the late 1960s and early 1970s. Further advances have been achieved by the Toho Titanium Company (U.S. Patent 4829037, 1989) in the preparation of a high activity catalyst for the polymerization of propylene. Magnesium alkoxide compounds consist of crystals with layers of magnesium cations and alkoxy anions with loose layers of alkyl chains of the alkoxy groups in between (Turowa *et al*., 1969). Solvent can penetrate into these loose layers. These layers swell and the bonds are weakened. During the reaction with $TiCl_4$, hydrocarbon solvents are incorporated and a reaction with $TiCl_4$ takes place in this layer to form $MgCl_2$ and $TiCl_{4-n}(OEt)_n$ compounds. The in petrol suspended magnesium ethoxide is transformed into the $MgCl_2$ support and at the same time, $TiCl_4$ is absorbed. The soluble $TiCl_{4-n}(OEt)_n$ compounds are removed by washing with petrol. A catalyst particle with spherical shape, high porosity and high specific surface area is achieved.

2.4 Mechanisms of Olefin Polymerization

Usually, Ziegler-Natta catalyst consists of two components (i.e., a transition metal salt such as a $TiCl_3$ or $TiCl_4$ (catalyst) and main-group metal compounds involving alkyl-Al (cocatalyst). It is generally accepted that the formation of active sites on Ziegler-Natta catalysts for olefin polymerization is accomplished through reduction and alkylation of surface Ti species by interaction of the catalyst with Al-alkyl cocatalyst (Dusseault and Hsu, 1993).

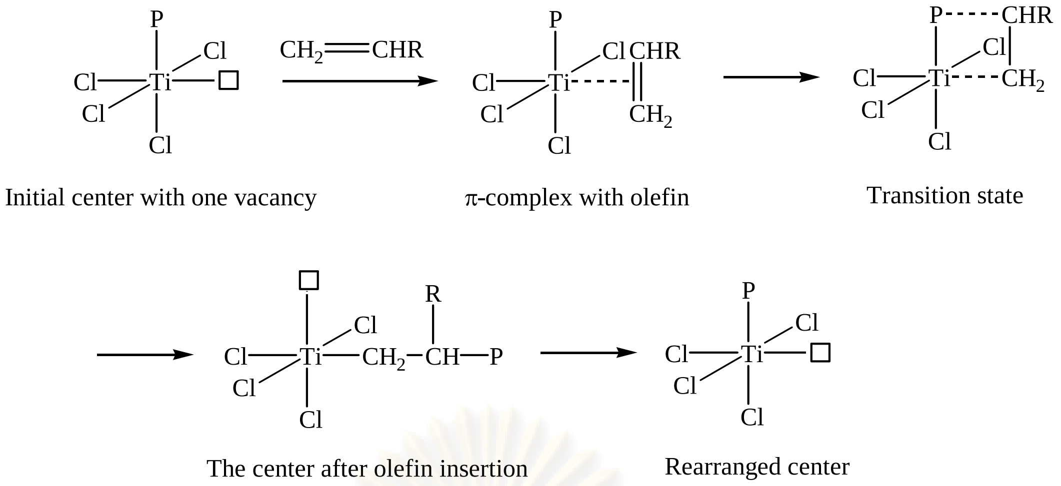


Figure 2.9 Monometallic polymerization mechanism.

The mechanisms of chain propagation can be divided into two groups (i.e., monometallic and bimetallic mechanism) according to the role of the cocatalyst. In monometallic mechanism proposed by Cossee and Arlman (1964), the cocatalyst generates the active species from the transition metal but is not involved in the chain growth reaction itself (**Figure 2.9**). The Ti atom is in an octahedral coordination environment with one vacant site and an adjacent coordination site bonded to an alkyl group of polymer chain. For $MgCl_2$-supported catalysts this structure is created when bound $TiCl_4$ reacts with alkyl-Al. The two-step mechanism for propagation involves π-coordination of an incoming monomer by the Ti atom at its vacant coordination site, followed by insertion, via a four-center transition state, into the Ti-polymer bond. An insertion reaction takes place, shifting the vacant octahedral position. Then migration of the polymer chain occurs to reestablish the vacant site on the original position. The weakness of this mechanism is that active Ti^{3+} has only one outer shell electron available for the formation of π back-bonding, which is a requirement for metal-olefin π-bond formation (Cossee, 1964; Burfield, 1984).

Bimetallic mechanism proposed by Rodrigues and van Looy (1966), involves initial π complexation of monomer to Ti atom that is bridged through alkyl groups to an Al atom (**Figure 2.10**). This is followed by ionization of the transition metal-alkyl bond, formation of a six-membered cyclic transition state, then insertion. In both mechanisms, the polymer chain grows from the catalyst surface by successive insertion reactions of complexed monomer, and the alkyl group originally present in the cocatalyst ends up as one of the terminal group of the polymer chain.

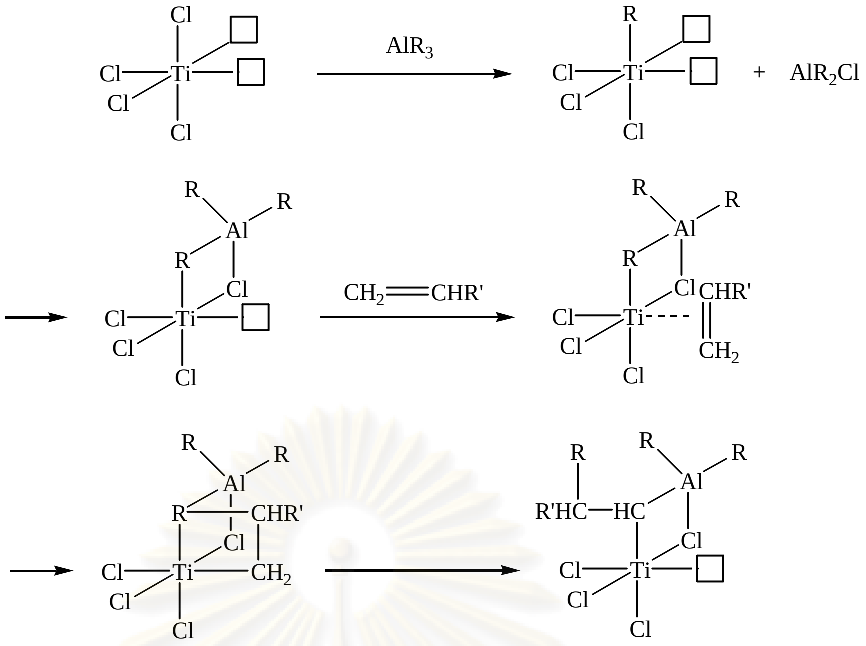


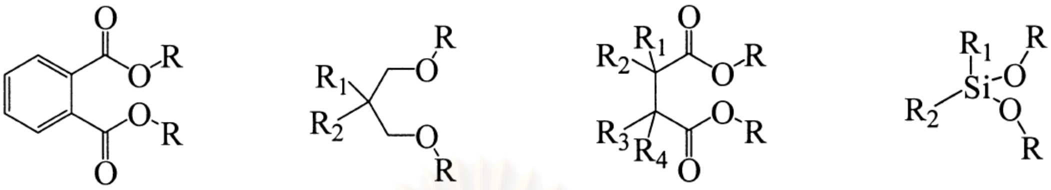
Figure 2.10 Bimetallic polymerization mechanism.

2.5 Modification of Ziegler-Natta catalysts by Lewis Bases

Various types of Lewis bases were employed as additives in the solid catalyst (called “internal donor”) and also in the polymerization system (called “external donor”). Electron donors play a fundamental role in modern Ziegler-Natta catalyst system for propylene and ethylene polymerization which can be explained as follow.

2.5.1 Propylene Polymerization

Lewis base or electron donors are major component in propylene polymerization catalysts; not only is the enhancement of catalyst activity but also control of the catalyst stereospecificity of great importance. A high stereospecificity is required to produce the isotactic polypropylene. The addition of Lewis base compounds often increased catalyst stereospecificity but was accompanied by a significant decrease in catalyst activity. Surprisingly, some aromatic esters like ethyl benzoate were found to increase not only catalyst stereospecificity but catalyst activity as well (Luciani *et al.*, 1977). Much effort has been expended so far in finding better combinations of internal and external donors, and the combination of dialkyl phthalate and alkoxysilane as internal and external donor, respectively, was found to be most efficient (Parodi *et al.,* 1981; Albizzati *et al.*, 1987). More recently, some hindered diethers were claimed to function as excellent internal donors that do not require any external donor (Giovani *et al.*, 1990; Albizzati *et al.*, 1990). General formulas of internal and external donors were shown in **Figure 2.11**.



Phthalate Diether Succinate Silane

Figure 2.11 General formulas of internal and external donors.

A number of papers have been published concerning the role of Lewis bases on propylene polymerization (Pino and Miilhaupt, 1980; Barbé *et al.*, 1987). The complexity of the catalyst system, however, has hindered an understanding of the precise mechanism of how to control the catalyst stereospecificity. The generally accepted explanations for the roles of internal and external donors are summarized in **Table 2.2** as follows.

Table 2.2 The roles of internal and external donors

Role of internal donor	Role of external donor
1. To prevent the coagulation of $MgC1_2$ particles during the milling process, resulting in an enhancement of the effective surface area.	1. To poison non-stereospecific sites selectively.
2. To prevent the formation of non-stereospecific sites by adsorbing on the $MgC1_2$ surface, where $TiCl_4$ is supported to form non-stereospecific sites.	2. To convert non-stereospecific sites into highly isospecific sites.
3. To take part in the formation of highly isospecific sites.	3. To convert isospecific sites into more highly isospecific sites.
4. To be replaced by external donors, resulting in the formation of more isospecific sites.	4. To increase the reactivity of the isospecific sites.

2.5.2 Ethylene Polymerization

In the case Lewis base effects for ethylene polymerization, not only the effect of catalyst activity but also control of the molecular weight and molecular weight distribution are of great importance for the processability and mechanical properties of the polymer (Chen *et al*., 2006; Seth and Ziegler, 2003)

Puhakka *et al*. (1997) studied the coordination of electron donors were alcohols, ketones, esters, and their model compounds to the various coordinatively unsaturated magnesium sites of the $MgCl_2$ support. Examination of the interaction energies indicated that the alcohols bind more strongly to the five-coordinated magnesium atom on the (101) surface than to the four-coordinated magnesium atom on the (110) surface. This stability on the (101) surface can be explained in terms of hydrogen bonding between the complexed alcohol and a chloride ion of the surface. Like the alcohols, the esters form the most stable complexes on the (101) surface. In contrast, the ketones coordinate preferably to the (110) surface. The coordination geometries of the ketones and esters do not depend on the number of electron donors on the same magnesium atom, unlike the situation for the alcohols.

Liu *et a.l.* (2004) had investigated the effects of alkyl-Al co-catalysts on MWD with SiO_2-supported Ziegler-Natta catalyst for ethylene polymerization. The catalysts modified by various alkyl-Al cocatalysts were studied such as TEA, DEAC, EADC, DEAB and DEAI. The differences in molecular weight MW and MWD of the polymers obtained depending on the type of co-catalyst used caused by different states of active sites. The results showed that TEA was observed a broad and multi-modal MWD (MW=900,000; Mw/Mn=30) while for DEAC, the MWD of PE was demonstrated to be vary narrow and unimodal (MW=1,400; Mw/Mn=1.6). Therefore, the catalyst system using TEA produced various types of active sites, while using DEAC has uniform type active sites.

Chen *et al.* (2006) investigated the molecular weight and molecular weight distribution of ethylene polymerization by $MgCl_2$-supported/external electron donor (diphenyldimethoxysilane, DDS)/ $TiCl_4$, based Ziegler-Natta catalyst. Addition of external donor was affected on the MW and MWD. It was found that the polydispersity index of polyethylene decreased with increasing of external donor/Ti molar ratio, on the contrary, the MW increased with increasing of external donor/Ti molar ratio. The addition of external donor did not change the number of active center types, but changed the distribution of Flory components in the whole MWD curve. In addition, the catalyst activity decreased, because nonstereospecific sites on catalyst are selectively poisoned by DDS as external donor.

However, these fundamental matters concerning the activation/deactivation behaviors of ethylene polymerization have not yet been fully elucidated and still open for discussion as a consequence of the complexities of the catalytic system. No detailed studies have so far been carried out to investigate the kinds of electron donor relating to the activity of catalyst and their polymer properties.

2.6 Roles of Electron donors

2.6.1 Aromatic monoesters

Busico *et al.* (1986) proposed a plausible model for the active sites on the $MgCl_2$ crystal surfaces (**Figure 2.12**); i.e. Ti^{3+} atoms located on the (1 0 0) cuts of

$MgCl_2$ produce isotactic polymer, whereas isolated Ti^{3+} atoms on the (1 0 0) and (1 1 0) cuts give atactic polymer. They also proposed that internal ethyl benzoate (EB) predominantly adsorbs on more acidic sites, the (1 1 0) faces, to prevent $TiCl_4$ from forming non-stereospecific site-III, while the external EB prevents the extraction of internal EB as well as deactivates the non-stereospecific site-I selectively.

Kashiwa and Yoshitake (1988, 1983) investigated the effect of external EB on the polymerization activity and molecular weight of PP by using the $TiCl_4/MgCl_2$-$AlEt_3$ catalyst system. Based on the results obtained, they suggested that addition of an appropriate amount of external EB can kill the non-stereospecific sites and also causes an increase in the propagation rate constant of isotactic polymerization.

By using a temperature raising fractionation technique, Kakugo *et al.* (1988) fractionated isotactic PP produced with the $TiCl_4/MgCl_2$-$AlEt_3$ catalyst system in the absence or presence of methyl *p*-toluate (MT) (**Figure 2.13**). Each fraction was characterized by DSC and ^{13}C NMR, the results of which indicated that addition of MT produces a more highly isotactic PP. Similar results have also been reported by other researchers (Sacchi, Tritto and Locatelli, 1988) However, it is not clear whether such highly isospecific sites originate from isospecific sites or non-stereospecific sites. One of the factors which hinder our understanding of the precise role of a Lewis base arises from the fact that the $MgCl_2$-supported $TiCl_4$ catalyst gives about 20 wt% of isotactic PP without any electron donor.

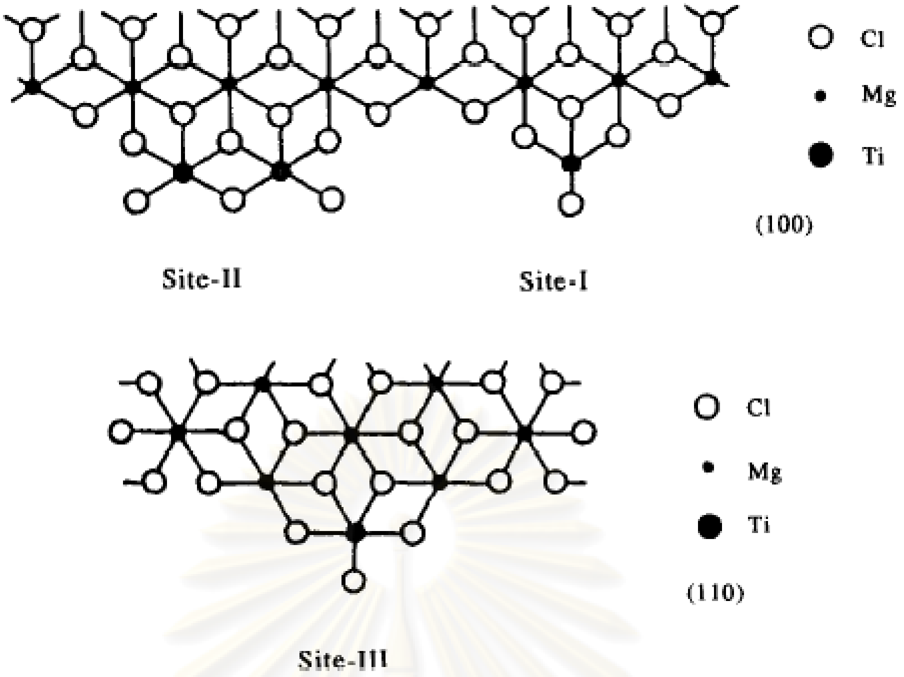


Figure 2.12 Plausible active Ti^{3+} species on the $MgC1_2$ surfaces as proposed by Busico *et al.* (1986).

Utilizing the information proposed by Busico *et al.* (1986), i.e. the mononuclear Ti^{3+} species are non-stereospecific, we prepared an absolutely non-stereospecific catalyst by loading a far smaller amount of $TiC1_3$ on $MgC1_2$ (Shiono, Uchino, and Soga, 1989). The catalyst selectively gave boiling-heptane-soluble PP with a considerably high activity. It was demonstrated that addition of external EB to the non-stereospecific catalyst affords to produce boiling-heptane-insoluble PP up to 94 wt%. The isotactic pentad (mmmm) of boiling-heptane-insoluble polymer was found to reach approximately 95% (**Table 2.3**). These results strongly suggest that the EB molecule directly takes part in the formation of a highly isospecific site. From the results together with some additional observations, we proposed a model as shown in **Scheme 1**. The roles of internal and external donors might be explained in terms of the following mechanism. The internal EB coordinates also on the (1 0 0) surface of $MgCl_2$ to form the highly isospecific site-Ie, which has only one vacant site. As a consequence, the formation of bi- or multinuclear Ti species, which easily transform to non-stereospecific sites by the migration of a bridged Cl ligand, is inhibited. However, the trialkylaluminum (Lewis acid) left in the polymerization system extracts the internal EB result in reforming the non-stereospecific site-I. A large amount of external EB is necessary to prevent the internal EB from such an extraction. Several researchers also reported that internal EB is easily replaced with external MT (Norisuti, 1991; Sacchi, 1991) suggesting the Lewis bases dynamically participate in the formation of active sites owing to the presence of acidic alkylaluminums as co-catalysts.

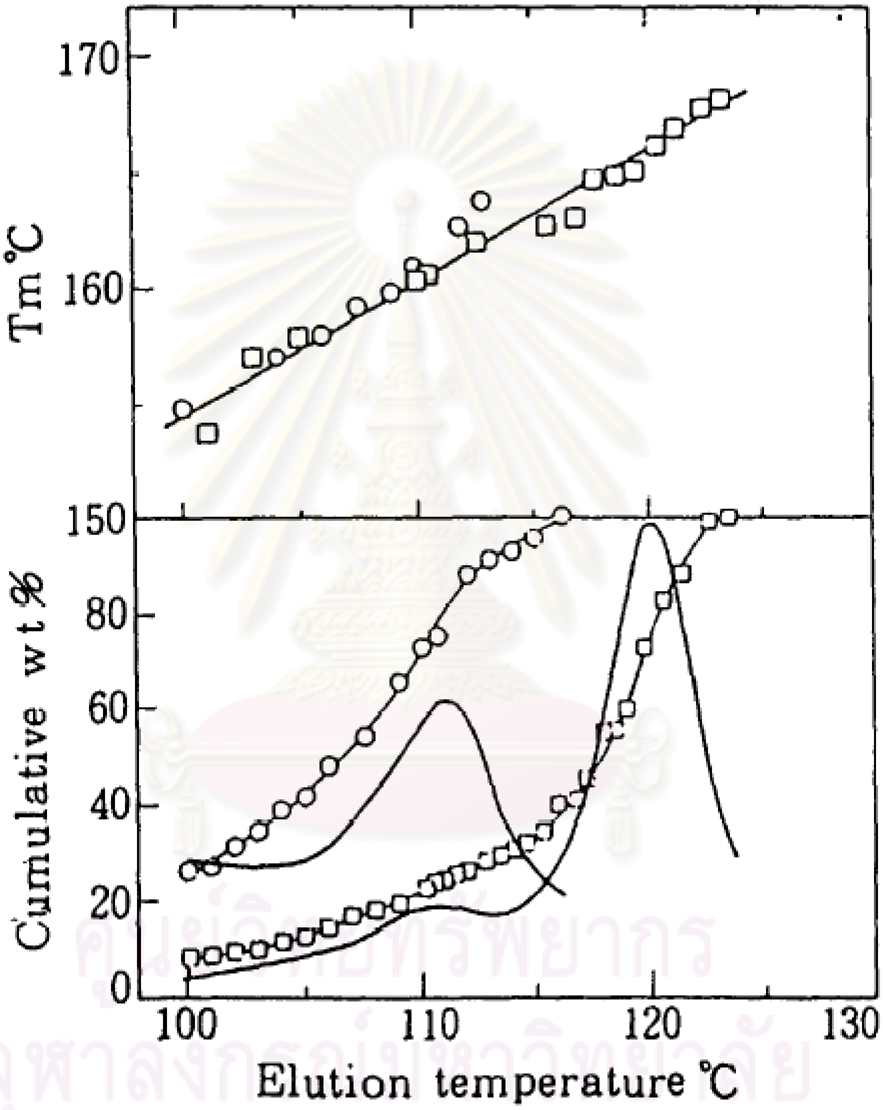


Figure 2.13 Cumulative and differential fractionation curves and the melting temperatures of isotactic PP (Kakugo, 1988). Catalyst system: O, MgC1$_2$-supported Ti catalyst-A1Et$_3$; , MgC1$_2$-supported Ti catalyst-A1Et$_3$/methyl *p*-toluene.

Table 2.3 Effects of aromatic esters and PES on propylene polymerization with $TiC1_3/MgC1_2\text{-}AlEt_3$ catalyst system (Shiono *et al.*, 1989; Soga *et al.*, 1990; Soga *et al.*, 1992)

Electron donor*	ED/Al (mol/mol)	Activity (kg PP/g Ti h)	*II*† (wt%)	mmmm‡ (%)
-	-	20.1	0	34.7
EB	0.02	23.0	2	-
	0.05	15.1	24	-
	0.10	9.5	78	-
	0.20	7.6	86	95.5§
	0.30	6.1	94	93.2§
DBP	0.02	8.8	32	-
	0.05	4.5	65	-
	0.10	2.9	62	-
	0.20	1.1	58	-
PES	0.02	8.1	29	-
	0.05	3.7	46	-
	0.10	1.7	61	-
	0.20	0.9	n.d.π	-

Polymerization conditions: Ti = 0.005 mmol, heptane = 100 ml, $AlEt_3$ = 1.0 mmol, propylene pressure = 1 atm, at 4O°C, 1 h.

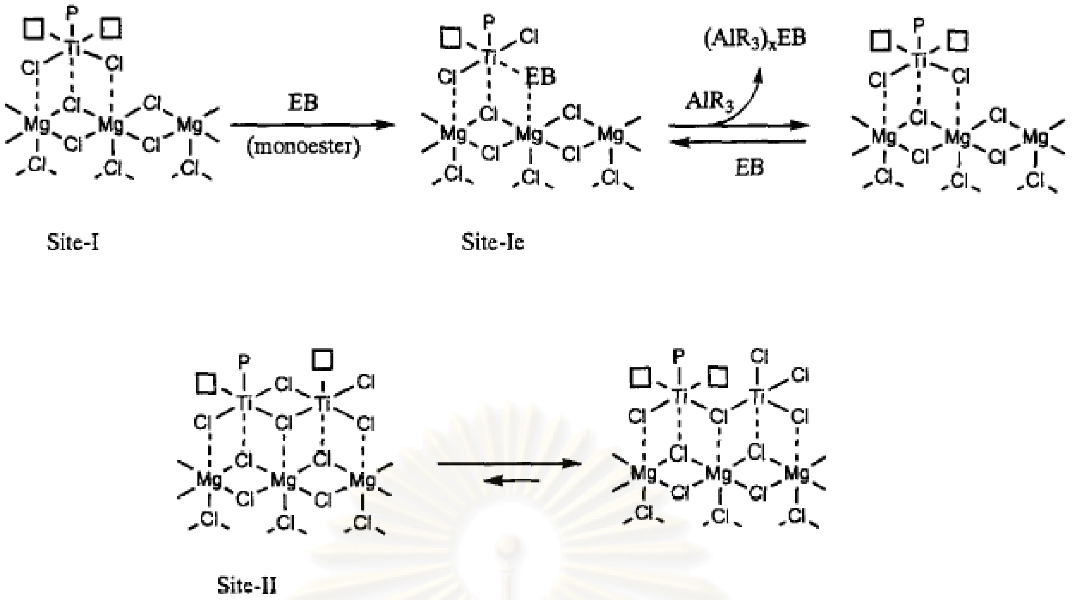
*EB, DBP and PES denote ethyl benzoate, dibutyl phthalate and phenyltriethoxysilane, respectively.

†Weight fraction of boiling-heptane-insoluble part.

‡Isotactic pentad determined by ^{13}C NMR.

§Boiling-heptane-insoluble part.

πNot determined owing to very low yields.



Scheme 1.

2.6.2 Dialkyl phthalates and Alkoxysilanes

Investigations were extended to the catalyst systems containing a dialkyl phthalate (DP) and an arylalkoxysilane as internal and external donors. The biggest difference between EB and DP as an external donor is observed when the polymerization of propylene is conducted in the absence of external donor (Soga *et al.*, 1988; Barbé, Norisuti, and Baruzzi, 1992). The isospecificity of the EB-containing catalyst is generally lower than that of the DP-containing catalyst, and the isotacticity of PP obtained with the former catalyst decreases to a greater extent upon increasing either the polymerization time (Busico *et al.*, 1985) or the concentration of a trialkylaluminum. Such a decrease in the catalyst isospecificity is attributed to the extraction of internal EB with an alkylaluminum (Soga *et al.*, 1988, Keii *et al.*, 1982). Norisuti *et al.* (1991) reported that DP is also extracted by an alkylaluminum. Taking these facts into consideration, DP might improve the isospecificity indirectly, probably by converting the active Ti species from a mononuclear type to more clathrates.

Sacchi *et al.* (1991) *investigated* the stereochemistry of both the first inserted monomer and the main chain of isotactic PP obtained with the $MgCl_2/TiCl_4$, $MgCl_2/EB/TiCl_4$ and $MgCl_2/DP/TiCl_4$ catalysts in the absence and presence of some external donors such as EB, tetramethylpiperidine (TMPip) and phenyltriethoxysilane (PES). They found that the stereospecificity of the isospecific sites increases in the order $MgCl_2/TiC1_4$ < $MgC1_2/DP/TiC1_4$ < $MgC1_2/EB/TiC1_4$, when the polymerization is conducted without using any external donor. The result suggests that there are different kinds of isospecific sites, depending on the catalyst system. It was also observed that the stereospecificity of isospecific sites in the $MgCl_2/EB/ TiC1_4$ catalyst increases more or less upon adding any type of external donor although the productivity of isotactic PP depends upon the external donor, whereas the stereospecificity of isospecific sites in the $MgC1_2/DP/TiC1_4$ catalyst is markedly increased only when PES is used as external donor. They also reported that the internal DP promotes the adsorption of a silane compound on the solid catalyst accompanied by the adsorptions of DP, when an alkylaluminum is present in the system (Norisuti *et al.*, 1991; Sacchi *et al.*, 1991; Sacchi *et al.*, 1992).

There is no doubt that silane compounds used as external donors function as deactivators of non-stereospecific sites and also as promoters for generating highly isospecific sites (Soga *et al.*, 1988; Sacchi *et al.*, 1991; Barbé *et al.*, 1992; Sacchi *et al.*, 1992; Proto *et al.*, 1990).

However, we have still very poor information concerning the mechanism of how such highly isospecific sites are formed. The present authors investigated the effects of phenyltriethoxysilane and dibutyl phthalate as external donors with the absolutely nonstereospecific catalyst and found that the change in isotactic PP caused by the addition of those donors is far less compared with that caused by EB (**Table 2.3**) (Soga *et al.*, 1992). Such bidentate ligands are supposed to function only as deactivators. Accordingly, it may be plausible to consider that the silane compounds used as external donors act as modifiers of the originally isospecific sites, i.e. bi- or multinuclear Ti species (site-II), by preventing the migration of the bridged chloride atom (Soga *et al*., 1988).

2.7 New Electron Donors

As described above, the complexity of $MgC1_2$-supported catalyst is derived from the chemical interactions between the Lewis acids ($MgC1_2$, $TiC1_4$, alkylaluminum) and bases (internal and external donors), mostly from the high reactivity of alkylaluminums towards Lewis bases used as internal and external donors. Recently, it was found that some hindered diethers like 2,2-diisobutyl-1,3-dimethoxypropane (DBDMP) and 2,2-dimethoxypropane (DMP) used as internal donor can improve the catalyst isospecificity to a great extent even without using any external donor. Iiskola *et al.* reported an interesting experimental result on this special catalyst system that DBDMP contained in the $MgCI_2$-supported catalyst is hardly removed by the treatment with a triethylaluminum (Iiskola *et al.*, 1933). The influence of the addition of DMP to the $MgC1_2$-supported catalyst including DP was also reported (Gupta *et al.*, 1992). The data indicate that an increase of the DMP/Al molar ratio up to 0.10 results in a marked improvement in the isotactic index. Further increases in the ratio merely decreased the polymer yield.

2.8 Effects of Electron Donors

2.8.1 Isotactic crystallinity

Different donors or reactants show their affect on isotactic crystallinity in propylene and 1-butebe polymerization. For propylene and higher α-olefins, crystallinity or some property related to crystallinity was measured. The more crystalline a polymer, the higher was its tensile strength, the higher were the insoluble fractions in boiling heptane, the lower was the xylene soluble fraction, and higher was the flexural modulus. Electron donors usually increased the isotactic-regulating ability of a catalyst, but not always.

2.8.2 Activity

Most frequently a claim is made that the activity of catalyst is increased. A variety of reactants or donors have been reported. Organic nitro compounds ($C_6H_5NO_2$) increased the activity of the catalysts $Al_2Et_3Cl_3$-$VOCl_3$, VO $(OBu)_3$ or $V(acac)_3$ for the polymerization of ethylene or copolymerization of ethylene and propylene. Silicon hydrides added to the $AlEt_3/TiCl_4$ catalyst increased its activity for polymerization of ethylene. The activity of the CH_3TiCl_3-$TiCl_3$ catalyst for polymerizing propylene was increased by n-Bu_3N. The presence of ethylorthosilicate in a catalyst prepared by reduction of TiCl4 with $AlEtCl_2$ and activated with $AlEtCl_2$ was reported to increase its activity, and a highly crystalline polypropylene having a high bulk density was formed. More active catalysts for ethylene were formed when transition metal salts were complexed with amines and then combined with Al-i-Bu_2Cl. Similarly, complexes with $CrCl_3$ with ammines, alcohols and ketones were said to lead to a more active catalyst for ethylene when combined with $AlEt_2Cl$. A salt made by reacting vanadium oxides and phenyl phosphonic acid at 80 ^{o}C was combined with $AlEt_2Cl$ to make an active catalyst for polymerization of ethylene. Dienes were very effective in lowering the activity of the $AlEt_3$-$\alpha TiCl_3$ catalyst for the polymerization of ethylene; for example, butadiene > isoprene > styrene > isobutylene > methyl styrene. Higher rates were claimed for polymerization of propylene when peroxides were added to $AlEt_3$-$TiCl_4$.

2.8.3 Molecular Weight

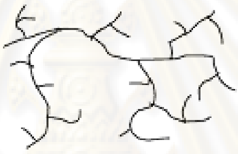
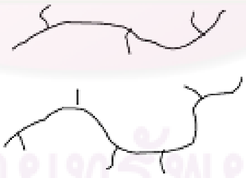
As early as 1956, Dost and co-workers (1960) recognized that electron donor can increase or lower molecular weights of formed polyethylene when added to Ziegler-Natta catalysts; for example, aldehyde, esters, and amines were added to the AlR_3-$TiCl_4$ catalysts. Since then, many other examples have been reported for olefins and diolefins. Typically, the electron donor increases the molecular weight of the formed polymer. Claims have also been made that the molecular weight distribution can be altered by presence of donors. A narrowing was reported by Erofeev in the “width” of the molecular weight distribution by the presence of anisole in the $AlEt_2Cl$-$TiCl_4$ catalyst. Kicheva and co-workers noted that the polyethylene product had a narrower molecular weight distribution when $Ti(OR)_4$ (where R= Et, i-Pr, or Bu) or alcohols were added to the $AlEt_2Cl$-$TiCl_4$ catalyst. Hirooka and co-workers, however, did not significantly affect the molecular weight distribution of polypropylene by addition donors (pyridine, hexamethylphosphoramide, CS_2, etc.) to $AlEt_3$-$TiCl_3H$, $AlEt_2Cl$-$TiCl_3AA$, and $AlEtCl_2$-$TiCl_3AA$ catalysts (Boor, 1979)

Relative to heterogeneous catalyst, soluble catalysts produce polymers consisting of chains whose molecular weights are not significantly different from one another. They have a narrow molecular weight distribution. While the gel permeation chromatography (GPC) has been used to measure molecular weight distribution, most of their literature refers to the ratio Q=Mw/Mn as a measure of dispersity of molecular weights (Mw and Mn are the weight average and number average molecular weights, respectively). For soluble Ziegler-Natta catalysts, Q values in the range of 2 to 4 have been reported for polyethylene. In contrast, heterogeneous catalysts produce polymers that have much wider molecular weight distribution, for example, Q>4 to 20 or higher. Beyond recognizing that soluble catalysts led to narrower molecular weight distribution than obtained with heterogeneous catalyst, not much else of significant importance has been reported on the control of molecular weight distribution. Workers have, however, recognized that changes in molecular weight distribution take place during polymerization (Puhakka *et al*., 1997).

2.9 Polyethylene

The explosion in the dynamic development of polyethylene (PE) started mainly in the 1970s which has the highest production volumes of all synthetic polymers. Polyethylene (PE) is the most important material in plastic and polymer type. Normally, polyethylene can be divided into three categories according to its density and structure; high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) as shown in **Table 2.4**.

Table 2.4 Density range, molecular structure, synthesis, and applications of several types of polyethylene (Richards, 1998).

Type of polyethylene	**Density (g/cm^3)**	**Molecular structure**	**Synthesis**	**Applications**
HDPE	0.945-0.965		Polymerization of polyethylene on Philips, Ziegler-Natta and metallocene catalyst	Gas pipe, car gas tanks, bottles rope and fertilizer bag
LDPE	0.89-0.94		Free radical polymerization of ethylene at high temperature and high pressure	Packing film, bag, wire sheathing, pipes, waterproof membrane
LLDPE (VLDPE,ULDPE)*	0.91-0.925		Copolymerization of ethylene with α-olefins on Ziegler-Natta and metallocene catalysts	Shopping bag, strech wrap, greenhouse film

*A family of LLDPE with density of 0.87-0.915 g/cm^3

From **Table 2.4** summarized the characteristic of three type of polyethylene. The different in structure of polymer affects to the physical properties of polymer such as density of polymer and hence the application of polymer. HDPE is the polymer that has very less or does not have any branch in the polyethylene backbone. From this microstructure HDPE has very high crystalline phase in polymer morphology and highest density about 0.96 g/cm^3. This microstructure results in better packing of polymer chains in solid state, as a result, HDPE is a rigid thermoplastic which is more useful as a structural material due to its rigidity. Applications of HDPE include formed packaging (such as milk bottles), pipe, and molded pieces such as kitchenware and toys. In addition, the considerable industrial interest in HDPE is due to the economics allowed by the low pressure production processes as to its suitability in field where it can be replaced conventional LDPE.

In most cases, normal LDPE is made by a free-radical polymerization process. As a result, LDPE contains short-chain branches, as well as long-chain branches in the polymer chains. LDPE refers to the polyethylene of density between 0.89 g/cm^3 to 0.940 g/cm^3; it has flexible and high impact strength (Xie *et al.*, 1994; Suphchokchai, 1990) The characteristics determining the advantages of LDPE for some particular use are excellent processability at relatively low temperatures, excellent optical characteristics, impact and tearing resistance, and flexibility. These are the properties which lead to the utilization of LDPE in industrial packaging films.

In case of, linear low-density polyethylene (LLDPE) known as branched polyethylene is mainly produced by ethylene copolymerization with α-olefin comonomer, such as 1-butene, 1-hexene, and 1-octene. The properties of LLDPE such as, thermal, physical and mechanical properties depend on the distribution of short chain in the copolymer and polymer microstructure (triad and dyad distribution). Thus, the several LLDPE grades are classified by the primarily result via microstructure of polymer and molecular weight of polymer. LLDPE seems to fit these requirements as a polymer suitable for several fields (Zhanxia *et al.*, 2006).

The knowledge of polyethylene properties are percent crystallinity, average molecular weight, and molecular weight distribution play an important role in processability and mechanical properties (Boor, 1979). There are six properties that make polyethylene attractive: (1) toughness, (2) excellent chemical resistance to solvents, acids, and alkalis, (3) good barrier to gases, (4) outstanding dielectric characteristics, (5) adaptability to various fabrication techniques, and (6) facile adjustment of properties by tailoring branching and molecular weight and by incorporating additives.

Generally, polyethylene has a wide molecular weight distribution are easier to process, which is important in molding and extrusion processes. In contrast, polymers that have a narrow molecular weight distribution have a higher impact resistance, better low temperature toughness, and better resistance to environmental stress cracking. In case of the high molecular weight polyethylenes have better properties than do low molecular weight polymers, such as greater impact resistance (toughness) and chemical resistance. Processing, however, becomes more difficult as their molecular weight increase [20].

2.10 Molecular Weight and Molecular Weight Distribution Control

Many studies concerning the influence of molecular weight (MW) and the molecular weight distribution (MWD) on the various properties of polyethylene have been performed. Various methods for controlling the MW and MWD for ethylene polymerization can be summarized as below (Ahn *et al.*, 1998; Cho *et al.*, 2000; Singh *et al.*, 1971).

(i) Physical blending of the polymers with different average MW, however, this method contains high gel levels result in miscibility problems can arise.

(ii) Cascade reactor process and using composite of different transition metal catalysts in a single reactor polymerization process which can be produced polymers with different Mw ranges but this method more or less has some defects such as gelation, high cost, and complex manipulation.

(iii) Using a series of reactors, each of which supports polymerization under different conditions such as temperature, pressure, and hydrogen partial pressure, etc.

(iv) The presence of some compounds (so-called Lewis bases compound) like water, alcohol, etc.; containing active hydrogen is capable of terminating a Ziegler-Natta polymerization reaction. It has been widely employed to control the Mw of polyethylene industrial production lines by using Ziegler-Natta catalysts (Chen *et al.*, 2006; Seth, 2003)

2.11Average Molecular Weight Technique

Measurement of average molecular weight using the dilute-solution viscosity of polymer solutions provides one of the most easily obtained and widely used items of information about the molecular structure of the samples. Since the dilute-solution viscosity of a given sample depends upon the type of solvent used and the temperature of the measurement, it is necessary that both these be specified (and the concentration also unless the intrinsic viscosity is calculated) for all measurements. Provided that it is known that the polymer is linear rather than branched, empirical correlations can be developed between the intrinsic viscosity and the molecular weight of the sample. The Ubbelodhe viscometer utilized in this experiment operates independent of the total volume of solution over a considerable range. It is therefore useful as a dilution viscometer, in which solutions having several different concentrations can be prepared and measured in situ. This facility results from its construction in which the solution emerging from the lower end of the capillary flows down the walls of bulb A in a manner which is independent of the liquid level in the main reservoir B. This mode of action is referred to as a suspended level.

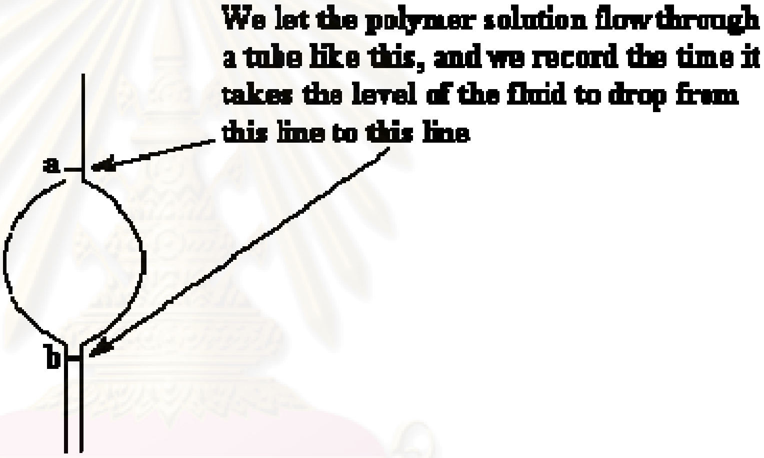


Figure 2.14 Measurement of efflux time of U-tube viscometer

The simplicity of the measurement and the usefulness of the viscosity-molecular weight correlation are so great. Several mathematical equations are available in the literature for determining the intrinsic viscosity [η] of a polymer solution, by graphical extrapolation. In this study, intrinsic viscosity was determined from Kraemer Equation (1938)

$$\frac{\ln \eta_r}{c} = [\eta] + k''[\eta]^2 c \qquad (2\text{-}1)$$

where k" is constant, ηr is relative viscosity, c is concentration in g/dl and [η] is determined from [(ln ηr)/c]c=0. According to the Mark-Houwink-Sakurada relation, the correlation between intrinsic viscosity and molecular weight, the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = K'M^{a} \tag{2-2}$$

where K´ and a are constants related to the stiffness of the chain and depend on the type of polymer, solvent and temperature (Billmeyer, 1984).

CHAPTER III

EXPERIMENTAL

In this chapter, the materials and chemicals, equipments, catalyst preparation, polymerization procedure, characterization instruments will be explained.

3.1 Materials and Chemicals

The chemicals used in these experiments, carried out at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, were specified as follows:

1. Polymerization-grade ethylene (C_2H_4) was used as received from PTT Chemical Plc. (Thailand)
2. Ultra high purity argon (99.999%) was purchased from Thai Industrial Gas Co., Ltd. (TIG) and was further purified by passing through the column packed with molecular sieve 3Å, BASF Catalyst R3-11G (copper catalyst), sodium hydroxide (NaOH) and phosphorus pentoxide (P_2O_5) in order to remove traces of oxygen and moisture.
3. Anhydrous magnesium chloride ($MgCl_2$, >98%) was donated from Tosoh Finechem, Japan and was vacuum dried at 120^oC for 6 h before use.
4. Ethanol (C_2H_5OH >99%) was purchased from Merck Ltd.
5. Titanium tetrachloride ($TiCl_4$, > 99%) was purchased from Merck Ltd.
6. Diethyl aluminum chloride (DEAC) was donated from Tosoh Finechem, Japan
7. Triethylaluminum ($Al(C_2H_5)_3$) in hexane solution, was donated from PTT Chemical Plc., (Thailand).
8. *n*-Butanol ($CH_3(CH_2)_3OH \geq 99.5\%$) was purchased from Merck Ltd.
9. *n*-Octanol ($CH_3(CH_2)_7OH \geq 99.5\%$) was purchased from Merck Ltd.
10. *t*-Butanol ($C_4H_{10}O \geq 99\%$) was purchased from Fluka Ltd.
11. Dibutyl ketone ($CH_3COCH_3 \geq 99.8\%$) was purchased from Merck Ltd.
12. Heptyl acetate ($CH_3COOC_2H_5 \geq 99.5\%$) was purchased from Sigma.
13. Dibutyl ether ($C_8H_{18}O$ >99%) was purchased from Merck Ltd.
14. Dipentyl ether ($(CH_3(CH_2)_4)_2O$>99%) was purchased from Sigma.
15. Dihexyl ether ($CH_3(CH_2)_5O(CH_2)_5CH_3$>97%) was purchased from Sigma.

16. Polymerization-grade *n*-hexane (C_6H_{14}) was donated from Exxon chemical Thailand Ltd. It was dried over dehydrated $CaCl_2$ and was purified by refluxing over sodium/benzophenone under argon atmosphere prior to use.
17. *n*-Heptane (C_7H_{14}, 99.84%) was supplied from Carlo Erba. It was dried over dehydrated $CaCl_2$ and was purified by refluxing over sodium/benzophenone under argon atmosphere prior to use.
18. Toluene was donated from EXXON Chemical Ltd., Thailand. This solvent was dried over dehydrated $CaCl_2$ and distilled over sodium/benzophenone under argon atmosphere before use.
19. Benzophenone (purum 99.0%) was obtained from Fluka Chemie A.G. Switzerland.
20. Sodium (lump in kerosene, 99.0%) was supplied from Aldrich chemical Company, Inc.
21. Calcium chloride (Dehydrated) was manufactured from Fluka Chemie A.G. Switzerland.
22. Xylene (99.8%) was purchased from Merck.
23. Commercial-grade methanol was purchased from SR lab.
24. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma-Aldrich Inc.

3.2 Equipments

Due to the Ziegler-Natta system is extremely sensitive to the oxygen and moisture. Thus, the special equipments were required to handle while the preparation and polymerization process. All of the equipments used in this experiment are listed as below**.**

3.2.1 Gas Purification System

Argon (UHP) was further purified by passing through the column packed with molecular sieve 3Å, BASF Catalyst R3-11G, sodium hydroxide (NaOH) and phosphorus pentoxide (P_2O_5) in order to remove traces of oxygen and moisture prior to use. The BASF catalyst was treated with mixed Ar/H_2 (H_2 3%) at 300^oC overnight in order to regenerate the catalyst. The inert gas purification system is given in **Figure 3.1**.

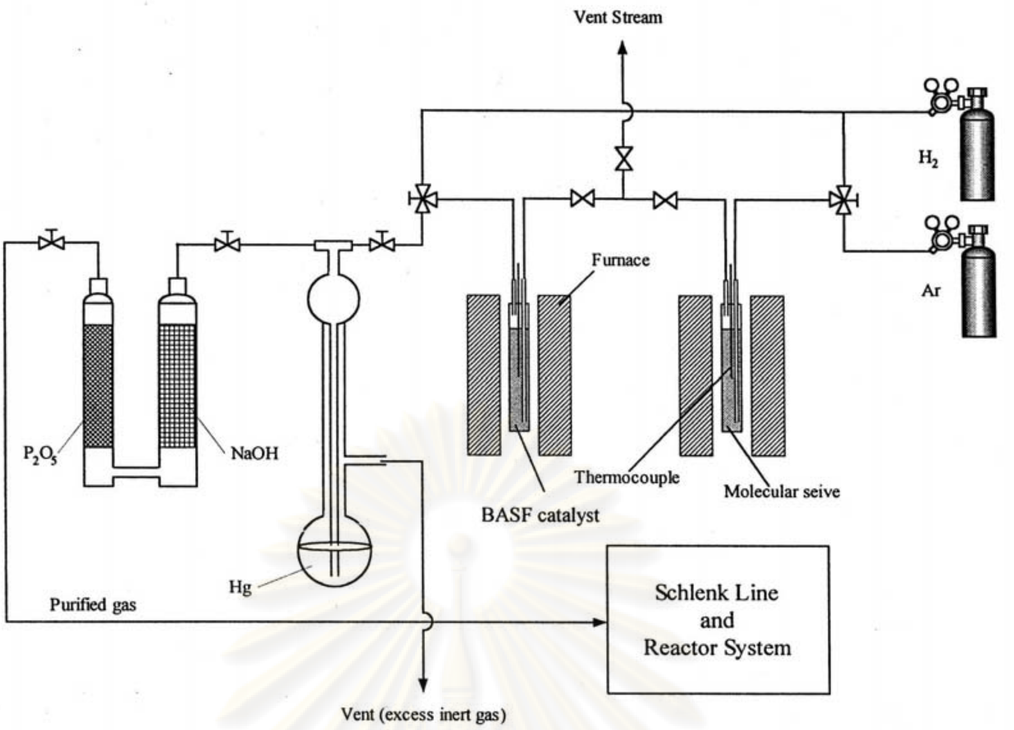


Figure 3.1 The inert gas purification system.

3.2.2 Glove Box

Glove Box System 30905C manufactured Vacuum Atmospheres Company, USA. The VAC Glove box which is a controlled atmosphere apparatus provides an inert environment for handling highly reactive materials. It comprises gas purification system and closed loop gas recirculation to remove O_2 and H_2O. Moreover, oxygen and moisture analyzer is equipped to monitor trace oxygen and moisture content of which acceptable level is less than 5 ppm. The glove box is shown in **Figure 3.2**.

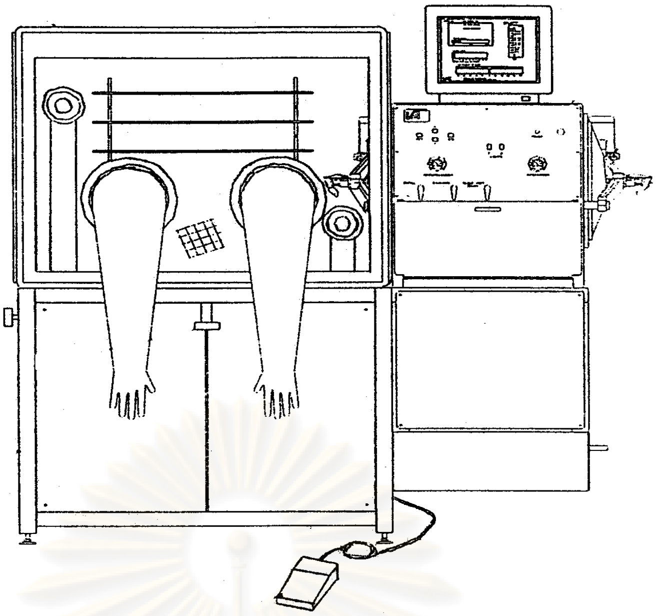


Figure 3.2 Glove box

3.2.3 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. The vacuum pump is shown in **Figure 3.3**.

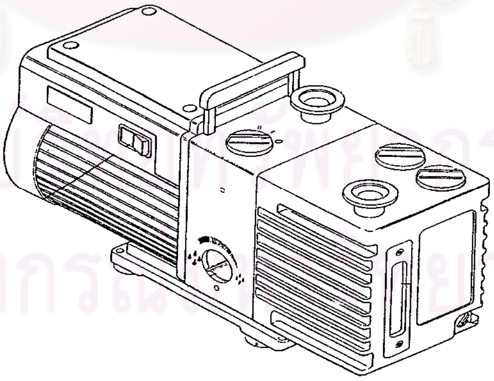


Figure 3.3 Vacuum pump

3.2.4 Schlenk Line

A dual manifold design model of Schlenk line as illustrated in **Figure 3.4**., which is consisted of one manifold for vacuum and another for inert gas, is used as a workhouse item for the manipulation of air-sensitive materials. The argon line is connected with mercury bubbler at which a manometer tube is contained enough mercury to provide a seal from the atmosphere when argon line is evacuated.

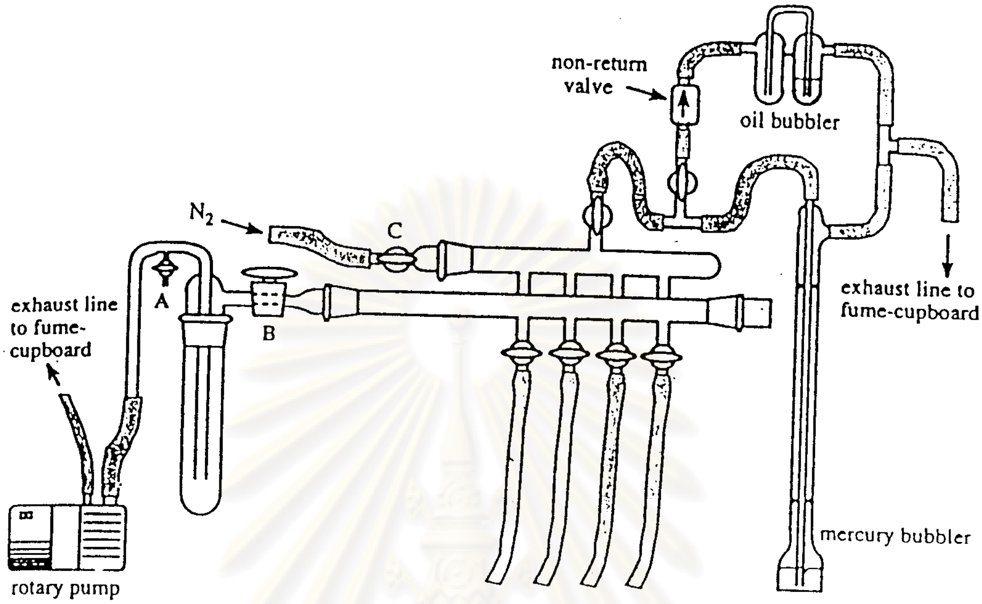


Figure 3.4 Schlenk line

3.2.5 Schlenk Tube

A tube with a ground glass joint and side arm, which is three-way glass valve as illustrated in **Figure 3.5**. It permits the user to pull a vacuum on the tube or to fill it with an inert atmosphere. Sizes of Schlenk tubes are 50, 100 and 200 ml used to prepare catalyst and store materials which are sensitive to oxygen and moisture.

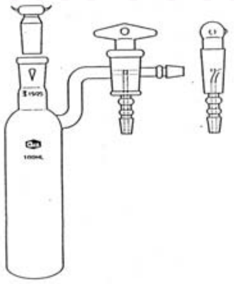


Figure 3.5 Schlenk tube.

3.2.6 Cooling system

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

3.2.7 Magnetic stirrer and heater

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

3.2.8 Reactor

A 100 ml stainless steel autoclave was used as the polymerization reactor for high pressure systems.

3.2.9 Polymerization line

The polymerization line consists of ethylene gas, pressure regulator, and valve system. It use for polymer synthesis, control pressure and type of gas for polymerization. The polymerization line is shown in **Figure 3.6**.

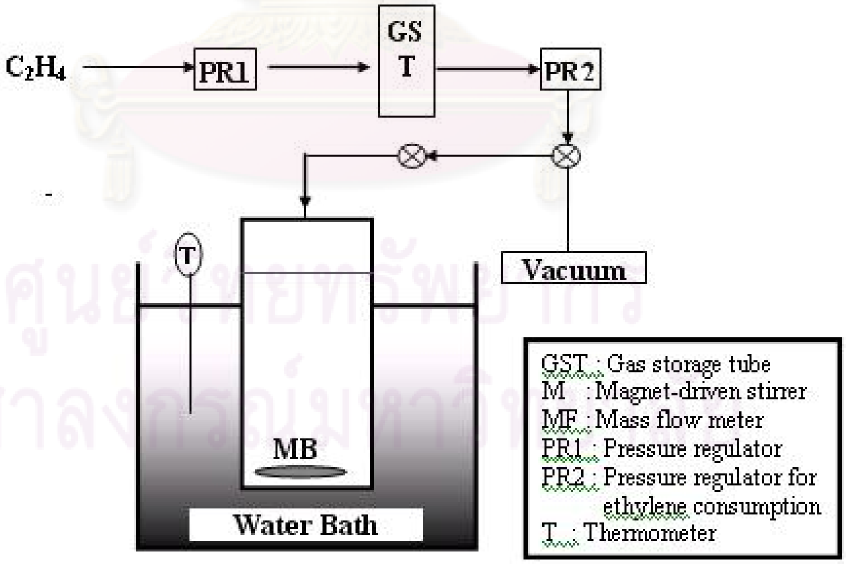


Figure 3.6 diagram of system in slurry phase polymerization

3.2.10 Syringe, Needle and Septum

The syringes were used in the experiment had a volume of 50, 20 and 10 ml and the needle were No. 17, 18 and 20, respectively. The septum was a silicone rod. It was used to prevent the surrounding air from entering into glass bottle by blocking at the needle end. The solvent, catalyst and cocatalyst were transferred to a glass reactor by using needles.

3.2.11 Digital Hot Plate Stirrer

A Cole-Parmer digital hot plate stirrer was used for blending the polymers. The hot plate stirrer is programmable. All functions can be set from digital panel and display their status on LCD. The plate temperature, stirrer speed and time are controllable.

3.3 Catalyst Preparation

3.3.1 Catalyst A

Catalyst A was carried out according to the reported procedure by Mitsui Petrochemical Industries Ltd (U.S. Patent 4071674, 1978) by the recrystallization method. Anhydrous magnesium dichloride 2 g (0.0210 moles) was suspended in 100 ml of heptane and 0.1259 moles of ethanol was added dropwise at room temperature. After the end of addition, the solution was stirred for 2 h. Then, 28 moles of aluminum compound was introduced dropwise and heated up to 90^{o}C for 2 h. Thereafter, 0.0255 moles of titanium tetrachloride was added and the mixture was stirred for 2 h. Finally, the obtained catalyst was washed with heptane for several times.

3.3.2 Catalyst B

Catalyst B is commercial catalyst.

3.4 Ethylene Polymerizations

The ethylene polymerization reaction was carried out in a 100 mL semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. First, the required amounts of hexane (30 ml), TEA (Al/Ti molar ratio = 100) and follow by adding amount of electron donors/Ti molar ratio of 0.1 by a syringe technique. Thereafter, a given amount of catalyst was charged into the reactor. The reactor was then immersed in liquid nitrogen. After that, the autoclave was evacuated to remove the argon. Then, the reactor was adjusted to the polymerization temperatures (80 ^{o}C). Polymerization was started by feeding ethylene gas (total pressure 50 psi) at 0.018 mol (6 psi was observed from pressure gaute). Ethylene pressure and temperature were kept constant during the polymerization, and the consumption rate of ethylene was monitored by mass flow meter. Polymerization was terminated with acidic methanol. The polymers obtained were precipitated in acidic methanol, filtered, adequately washed with methanol, and finally dried under vacuum at 60 ^{o}C for 6 h.

3.5 Characterizations Instruments

3.5.1 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_{α}(λ = 1.54439 Å). The spectra were scanned at a range of 2.4° min^{-1} in the range 2θ = 10-80°. The paraffin film was used to protect of samples from air.

3.5.2 N_2 physisorption

Measurement of BET surface area of catalysts was determined by N_2 physisorption using a Micromeritics ASAP 2000 automated system.

3.5.3 Thermogravimetric Analysis (TGA)

TGA was performed using TA Instruments SDT Q 600 analyzer. The samples of 10-20 mg and a temperature ramping from 40 to 800^{o}C at 10^{o}C/min were used in the operation. The carrier gas was N_2 UHP.

3.5.4 Scanning electron microscope (SEM)

SEM observation with a JEOL mode JSM-6400 will be 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.

3.5.5 Differential Scanning Calorimetry (DSC)

The melting temperature (T_m) and crystallinity (X_c) of ethylene polymer products will be 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 as shown in **Figure 3.7**. The analyses were performed at the heating rate of 10^{o}C min^{-1} in the temperature range of 50-200 °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. The overall crystallinity was calculated from the heat of fusion values using the formula

$$X_C = H_m/H_p \tag{3-1}$$

Where H_m is the enthalpy of the tested samples and H_p, the enthalpy of a totally crystalline PE, was assumed to be 293 J/g (Welsh, 1996; Brandrup and Immergut, 1989).

Figure 3.7 Perkin-Elmer Diamond DSC

3.5.6 U-tube viscometer

One of the most widely used methods for the routine determination of molecular weight (Mw) was solution viscosity. Samples were dissolved in 1,2,4-trichlorobenzene as the solvent at initial concentration of approximately 2g/l and measured at 150 °C by u-tube viscometer are given in **Figure 3.8**. The efflux time was recorded. The data used for viscosity calculations and converted to average molecular weight.

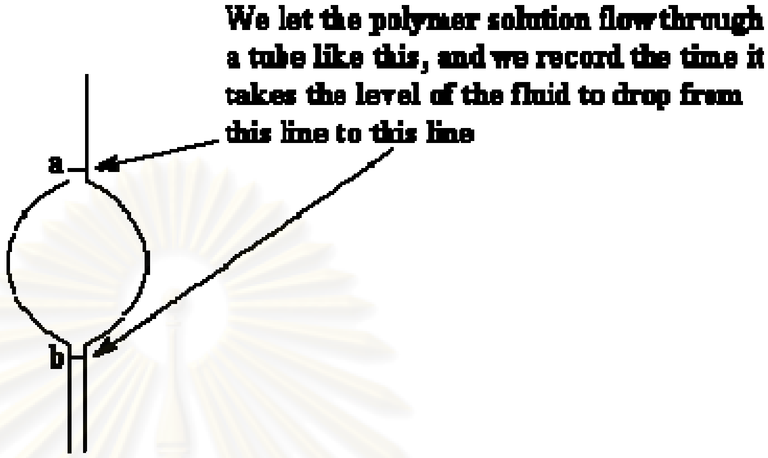


Figure 3.8 Measurement of efflux time of U-tube

CHAPTER IV

RESULTS AND DISCUSSION

The main topic of this study is to investigate and characterize effect of various external electron donors which were introduced into the system during ethylene polymerization on the catalytic activity and polymer properties with Ziegler-Natta catalysts.

4.1 Characterization of supports and catalysts

In this part, there are two catalysts were used; catalyst A was prepared according to a reported procedure by Mitsui Petrochemical Industries Ltd (U.S. Patent 4071674, 1978) and commercial catalyst B, name as, cat-A and cat-B, respectively. All of catalysts were then characterized using ICP, N_2 physisorption, XRD, TGA and SEM.

4.1.1 Titanium content with inductively coupled plasma (ICP)

In **Table 4.1** exhibits the results in terms of the titanium content of both catalysts. The titanium content of cat-A was 3.6 %wt and 4.6 %wt for cat-B. It was observed that commercial catalyst (cat-B) is higher titanium content than synthesized catalyst (cat-A).

4.1.2 BET specific surface area with N_2 physisorption

The BET specific surface areas were characterized by N_2 physisorption method is given in **Table 4.1**. Both of catalysts showed a similar tendency of specific surface areas which cat-A was 124 m^2/g and cat-B was 122 m^2/g respectively.

Table 4.1 Ti content and BET specific surface areas of catalysts.

Name	Ti content (% wt)[a]	BET surface area (m^2/g)[b]
Cat-A	3.6	124
Cat-B	4.6	122

[a] Ti content (%wt) were determined by ICP

[b] specific surface area (m^2/g) were determined by N_2 physisorption

4.1.3 Crystalline phases with X-ray diffraction (XRD)

Many researchers have reported XRD patterns of anhydrous $MgCl_2$ crystal structure has a cubic close packing (ccp) structure, which gives strong XRD patterns at $2\theta = 15^o$ (0 0 3 plane), 30^o (0 0 6 plane), 35^o (0 0 4 plane) and 50^o (1 1 0 plane) (Cho and Lee, 2003; Kashiwa, 2004).

As shown in **Figure 4.1** show XRD pattern of both catalysts after treatment of $MgCl_2$ with $TiCl_4$. It can be seen that both of catalysts exhibited the similar XRD patterns. The peak intensity of XRD patterns of the recrystallized $MgCl_2$ decreased, while remained unchanged patterns with anhydrous $MgCl_2$ (Cho and Lee, 2003; Kashiwa, 2004).

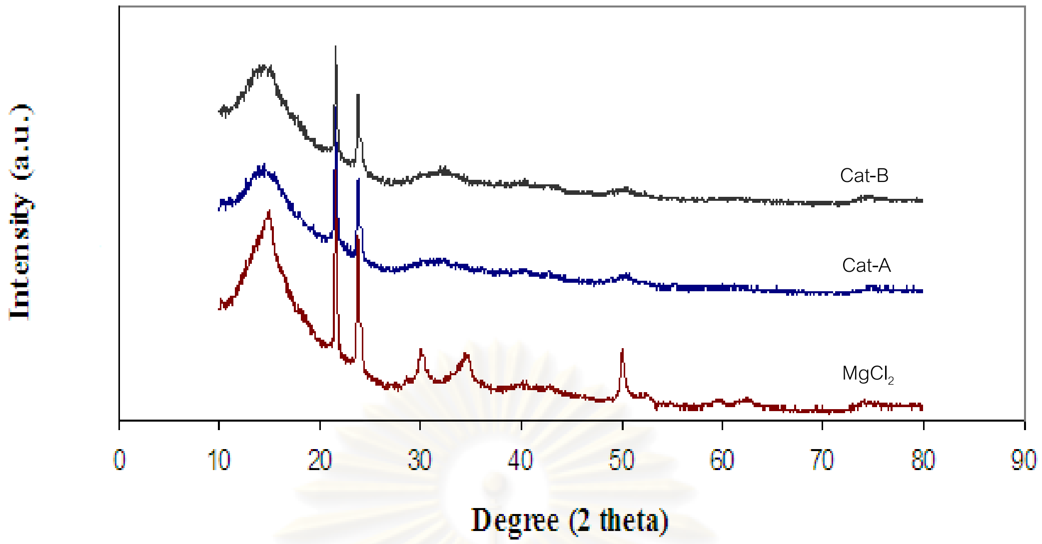


Figure 4.1 XRD patterns of two catalysts

4.1.4 Weight loss with Thermogravimetric analysis (TGA)

In this study, $TiCl_4$ was dispersed by treatment onto the support in order to identify the interaction of $TiCl_4$ on support, the TGA measurement was performed to prove the degree of interaction between the support and the catalyst ($TiCl_4$). The TGA provide information on the degree of interaction for $TiCl_4$ bound to the supports in term of weight loss and removal temperature. The TGA profiles of cat-A and cat-B are shown in **Figure 4.2.** On the previous study (Kashiwa and Yoshitake, 1984), based on TGA patterns, the weight loss was around 213 ^{o}C, which is attributed to the removal of $TiCl_4$ from the crystalline $MgCl_2$ matrix. It was observed that the weight loss of $TiCl_4$ present on cat-A higher than cat-B. This indicated that $TiCl_4$ of cat-B had the stronger interaction on supports than cat-A at 213 ^{o}C.

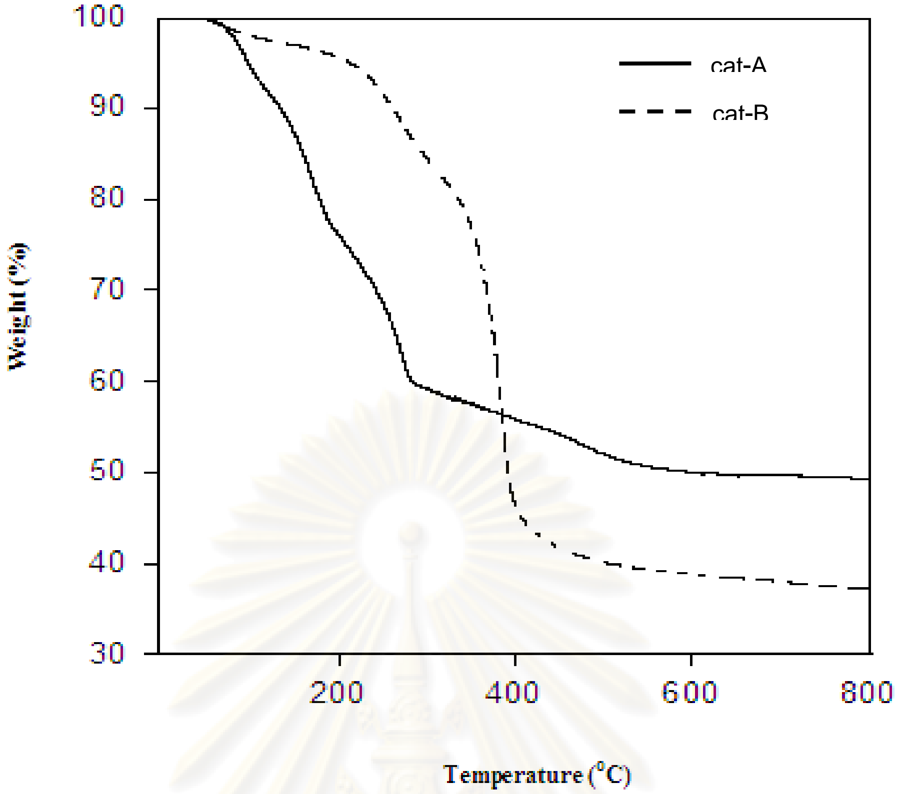
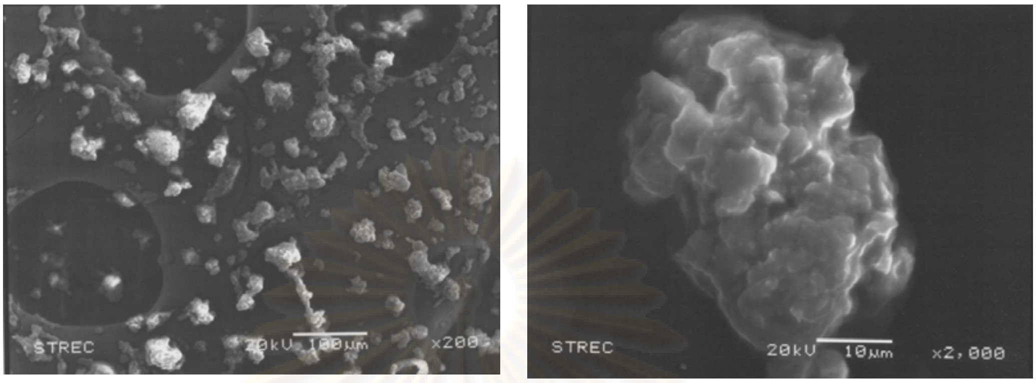


Figure 4.2 TGA profiles of cat-A and cat-B

4.1.5 Morphology with Scanning Electron Microscopy (SEM)

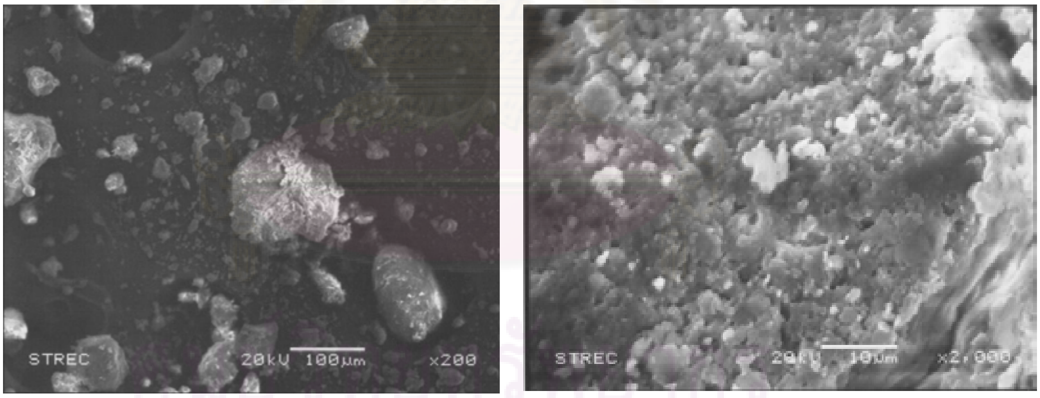
Scanning electron microscopy was also used to determine the morphology of both catalysts. **Figure 4.3 (a)** is the SEM micrograph of cat-A and **Figure 4.3 (b)** is the SEM micrograph of cat-B. It was observed that the particle size of cat-A is smaller than cat-B.

(a)



(1) 200X (2) 2000X

(b)



(1) 200X (2) 2000X

Figure 4.3 SEM micrograph of catalysts morphologies obtained; (a) cat- A (b) cat-B

4.2 External electron donor effecting on ethylene polymerization

4.2.1 The effects of external electron donor on the catalytic activity

This study was intended to evaluate effects of Lewis bases as external electron donor which were added during ethylene polymerization on the catalytic activity with Ziegler-Natta catalysts. From the results, it was observed that the properties of donors are remarkably affected on the catalyst activity which can be divided into 4 parts:

(1) Effect of different kinds of donor on the catalytic activity

Our study was conducted in an attempt to study the effects of several kinds of donor having differing in functional groups on the catalytic activity for ethylene polymerization. This study investigated four different functional groups of donor, such as alcohol, ketone, ester and di-ether while the number of carbon in their molecular structure is essentially the same. In fact, *n*-octanol, dibutyl ketone, heptyl acetate and dibutyl ether, respectively, are represented for each functional groups. All of compounds were introduced into system at donors/Ti molar ratio 0.1. It can be seen molecular structures in **Figure 4.4**

(a) *n*-octanol **(b) dibutyl ketone**

(c) heptyl acetate **(d) dibutyl ether**

Figure 4.4 Molecular structure of different kinds of donor: alcohol, ketone, ester and di-ether (a) *n*-octanol (b) dibutyl ketone (c) heptyl acetate (d) dibutyl ether

Table 4.2 Catalytic activities at different kinds of donor

Catalsyts	**Materials**[a]	**Polymer yield (g)**[b]	**Polymerization time(s)**	**Activity**[c] **(kg PE/mol Ti·h)**
Cat-A	none	0.4157	145	1,638
	n-octanol	0.4924	215	1,309
	dibutyl ketone	0.2656	127	1,195
	heptyl acetate	0.4998	208	1,373
	dibutyl ether	0.4739	103	2,629
Cat-B	none	0.4228	119	2,030
	n-octanol	0.4492	173	1,484
	dibutyl ketone	0.4850	284	976
	heptyl acetate	0.4897	186	1,504
	dibutyl ether	0.4344	112	2,216

[a] Addition of donor to a Poison/Ti mole fraction of 0.1

[b] The polymer yield was fixed [limited by ethylene fed used (0.018 mole equally)]

[c] Slurry ethylene polymerization was carried out with catalyst 10 mg, cocatalyst : TEA ,Al/Ti (mol/mol) = 100 in hexane, temperature of polymerization : 80 °C, [ethylene] =0.018 mole

The result of catalytic activity of cat-A and cat-B obtained with several kinds of donor which differing in functional groups as shown in **Table 4.2**. It was obvious that the activity of cat-B showed higher than cat-A in the absent any donor. The interaction between support and $TiCl_4$ active species seems to play an important role in the formation of the active species. It is possible, cat-B had the stronger interaction that exhibit high polymerization activity than cat-A.

The effect on the activity in the presence of *n*-octanol, dibutyl ketone and heptyl acetate as external donors exhibited lower activity than the absence of these compounds. Conversely, the introduction of dibutyl ether was found the highest value of catalyst activity with both catalysts.

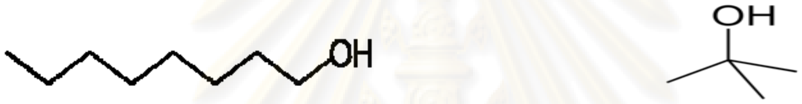
In order to give a better understanding, the effect of di-ether in polymerization activity can be proposed based on the work reported by Costa *et al.* (1998). They revealed that the use of dibutyl ether as internal donor in propylene polymerization remarkably improves the activity of catalyst than the catalyst synthesized without dibutyl ether due to it produced δ-$TiCl_3$, which is described in the literature as a mixed system (cubic and hexagonal) and consequently presents a higher number of crystalline defects than the other crystalline structures (α-, β- and γ-$TiCl_3$). Therefore, δ- $TiCl_3$ is considered to be more active. That could support the reason for the activity of dibutyl ether higher than in the absence or presence of any external donor. It can also be said that, the addition of dibutyl ether helps to increase hexagonal crystalline of catalyst. Moreover, it is found that, when dibutyl ether is used as external donor in cat-A the catalyst activity is higher than cat-B. From this result, it can be considered that interaction of $TiCl_4$ on support which indicated that $TiCl_4$ of cat-A had the weaker interaction on supports than cat-B, is the key factor caused dibutyl ether strongly influenced in activity of cat-A than in cat-B. In addition, it can be said that, using dibutyl ether can improve the catalyst active sites of cat-A is synthesized catalyst than commercial catalyst (cat-B). A possible reason is that cat-A contains more sites that are not active, but also activated after promoted by dibutyl ether external donor.

Conversely, in the presence of *n*-octanol, dibutyl ketone and heptyl acetate as external donors produced a stronger deactivation effect on the catalyst activity. From our results, deactivation of catalyst activity can alter in the following order: ester < alcohol < ketone and also followed the same trend as in both cat-A and cat-B. The use of these compounds as external donors could poison effects on the active center through the decrease in catalyst activity.

(2) Effect of number and bulkiness of alcohols carbon on the catalytic activity

In this part, we have compared the influences of alcohol group in order to discuss the effect of molecular structure aspect on number and bulkiness of alcohol carbon on catalytic performance for ethylene polymerization. The represent of alcohol compounds such as ethanol, *n*-butanol, *n*-octanol and *t*-butanol were investigated. Their molecular structures are shown in **Figure 4.5**.

(a) ethanol **(b) *n*-butanol**



(c) *n*-octanol **(d) *t* –butanol**

Figure 4.5 Molecular structure of alcohols (a) ethanol (b) *n*-butanol (c) *n*- octanol (d) *t*-butanol

The results of ethylene polymerization of alcohol compounds differing in number and bulkiness structures of carbon can be observed from **Table 4.3**. It can be seen that, all compounds produced an evident deactivation effect on the catalyst activity comparing with the absence of these compounds. From our results, it can be noticed that, the use of high number of linear alcohol carbon as external electron donor has led to substantial advances in activity of catalyst. Comparison these results with ethanol and *n*-butanol have shown that *n*-octanol which has the highest number of carbon give the highest values activity. Puhakka *et at.* (1997) explained that the small alcohol is able to produce a stronger evident deactivation of catalyst activity than other alcohol complex because the stability of the alcohol depends on O-H bond length. The small alcohol gives O-H bond length longer than other alcohol complexs which is able to produce a stronger evident deactivation of catalyst activity. In this case, ethanol is smallest alcohol structure which produced the lowest activity of catalyst. Moreover, by comparison of different structure of carbon bearing bulkiness, it became clear that *t*-butanol produced an evident deactivation effect lower than *n*-butanol. It indicated that the stability of the complexes increased with steric bulkiness of alcohol (Puhakka *et at.*, 1997).

Beside, it can be seen that catalytic activity of cat-A has a resistance on small alcohol compounds better than in cat-B. From this result is also consistent with the evidence of the interaction of $TiCl_4$ on support which indicated that $TiCl_4$ of cat-B had the stronger interaction on supports than cat-A resulted into the influence of small structure of alcohol on the catalyst deactivation of cat-B higher than cat-A. Therefore, it is obvious that, the interaction weakness between $TiCl_4$ and support in cat-A could be decreasing the deactivation effects on the catalyst activity from small alcohols.

Table 4.3 Catalytic activities at different in number and bulkiness of alcohol carbon

Catalsyts	**Materials**[a]	**Polymer yield (g)**[b]	**Polymerization time(s)**	**Activity**[c] **(kg PE/mol Ti·h)**
Cat-A	none	0.4157	145	1,638
	ethanol	0.3410	170	1,146
	n-butanol	0.4230	200	1,209
	n-octanol	0.4924	215	1,309
	t-butanol	0.5000	206	1,386
Cat-B	none	0.4228	119	2,030
	ethanol	0.4023	581	396
	n-butanol	0.3848	410	536
	n-octanol	0.4492	173	1,484
	t-butanol	0.4566	223	1,170

[a] Addition of donor to a Poison/Ti mole fraction of 0.1

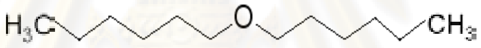
[b] The polymer yield was fixed [limited by ethylene fed used (0.018 mole equally)]

[c] Slurry ethylene polymerization was carried out with catalyst 10 mg, cocatalyst : TEA ,Al/Ti (mol/mol) = 100 in hexane, temperature of polymerization : 80 ^{o}C, [ethylene] =0.018 mole

(3) Effect of molecular structure of di-ether carbon on the catalytic activity

On the basis of first section, di-ether group has attracted a great deal of attention on the activity of catalyst. From this point of view, molecular structure types of di-ether carbon should be also taken into consideration in order to elucidate a possible correlation between molecular structures and catalytic performance. For comparison, there are three types of di-ethers structure to evaluate more obvious, such as dibutyl ether, dipentyl ether and dihexyl ether which differing in number of carbon, molecular structures are shown in **Figure 4.6**.

(a) dibutyl ether **(b) dipentyl ether**



(c) dihexyl ether

Figure 4.6 Molecular structure of diethers as poisoning material (a) dibutyl ether (b) dipentyl ether (c) dihexyl ether

The correlation of molecular structures and catalytic activity are summarized in **Table 4.4**. Comparing their molecular structure in Figure 4.6, the structure of electron donor plays an important role and makes it more effective in catalytic activity. It can be observed that, dibutyl ether exhibited the highest activity while dipentyl and dihexly ether rendered lower activity with both cat-A and cat-B. It is apparent that dibutyl ether is small enough to place adjacent to the catalyst, has a strong electron-donating ability, and exhibited effective influence to the activation more active sites lead to the following increase the catalyst activity.

Table 4.4 Catalytic activities at different molecular structure of di-ether carbon

Catalsyts	**Materials**[a]	**Polymer yield (g)**[b]	**Polymerization time(s)**	**Activity**[c] **(kg PE/mol Ti·h)**
Cat-A	none	0.4157	145	1,638
	dibutyl ether	0.4739	103	2,629
	dipentyl ether	0.4440	157	1,602
	dihexyl ether	0.4357	165	1,509
Cat-B	none	0.4228	119	2,030
	dibutyl ether	0.4344	112	2,216
	dipentyl ether	0.4296	136	1,805
	dihexyl ether	0.4520	137	1,885

[a] Addition of donor to a Poison/Ti mole fraction of 0.1

[b] The polymer yield was fixed [limited by ethylene fed used (0.018 mole equally)]

[c] Slurry ethylene polymerization was carried out with catalyst 10 mg, cocatalyst : TEA ,Al/Ti (mol/mol) = 100 in hexane, temperature of polymerization : 80 °C, [ethylene] =0.018 mole

(4) Effects of dibutyl ether /Ti molar ratio on the catalytic activity

According to many researchers mentioned that di-ethers is excellent internal donor for propylene polymerization, which is able to improve stereospecific and also enhance the activity of catalyst (Andoni et al., 2008; Boor, 1979; Soga, 1997). In this part, we have also extended the study to evaluation of dibutyl ether as especially external donors by varying the molar ratio of dibutyl ether/Ti for ethylene polymerization. The data is shown in **Table 4.5** indicating the polymer yield, polymerization time and polymerization activity obtained from different dibutyl ether/Ti molar ratio, such as 0, 0.05, 0.1, 0.2 and 10. It was obvious that, the highest value of activity was achieved at dibutyl ether/Ti of 0.1 in both cat-A and cat-B. Further increasing the molar ratio, a gradual decreasing in activity of catalysts could be observed. It is possible that, when dibutyl ether/Ti molar ratio increases to an optimal ratio, it is able to promote the activation of active sites on the solid catalyst and enhancement the catalyst activity. Still increasing dibutyl ether/Ti molar ratio, the stable active site is also replaced by donor caused the decrease of the number of active site, the catalytic activity reduces. In addition, one possible point to explain the effect of using a suitable amount of dibutyl ether as external donor with regard to produced hexagonal crystalline highly active, as describe before.

Table 4.5 Influence of dibutyl ether/Ti mole ratio on the catalytic activities.

Catalsyts	**dibutyl ether/Ti molar ratio**	**Polymer yield (g)[a]**	**Polymerization time(s)**	**Activity[b] (kg PE/mol Ti·h)**
Cat-A	0	0.4157	145	1,638
	0.05	0.3900	120	1,857
	0.1	0.4739	103	2,629
	0.2	0.4002	130	1,759
	10	0.3629	128	1,620
Cat-B	0	0.4228	119	2,030
	0.05	0.4660	214	1,244
	0.1	0.4344	112	2,216
	0.2	0.4279	230	1,063
	10	0.4344	158	1529

[a] The polymer yield was fixed [limited by ethylene fed used (0.018 mole equally)]

[b] Slurry ethylene polymerization was carried out with catalyst 10 mg, cocatalyst : TEA ,Al/Ti (mol/mol) = 100 in hexane, temperature of polymerization : 80 ^{o}C, [ethylene] =0.018 mole

4.2.2 The effects of external electron donor on the characteristics of polymer

Many researchers have reported that a given amount of Lewis bases compounds are remarkably affected on catalyst activity and also polymer properties (Andoni *et al.*, 2008; Boor, 1979; Chirinos *et al.*, 2005; Singh and Merrill, 1971). In order to confirm this presumption, all of polymers obtained were characterized using U-tube viscometer, SEM and DSC.

(1) Solution viscosity of polyethylene

Molecular weight of polyethylene was determined by solution viscosity instead of gel permeation chromatography (GPC) because of the difficulty in dissolving these high molecular weight polymers. We obtained the viscosity by using u-tube viscometer and interpreted intrinsic viscosity data to obtain the average-molecular weight (MW). There are many mathematical equations are available in the literature for determining the correlation between intrinsic viscosity [ŋ] and molecular weight of a polymer solution. In this research Kraemer Equation and Mark-Houwink-Sakurada relations (Fred, 1984) were used to evaluate the valuation of intrinsic viscosity [η]and molecular weight (MW), which are summarized in **Table 6**.

Table 4.6 Molecular weight (MW) and viscosity (ŋ) obtained with the solution viscosity[a].

Catalysts	**Entry**	**Materials**	**[ŋ]**	**Mw(x10^{-4})**
cat-A	1	none	2.867	49.83
	2	*n*-octanol	2.455	18.16
	3	dibutyl ketone	2.347	13.54
	4	heptyl acetate	2.470	18.89
	5	dibutyl ether	2.987	65.14
cat-B	6	none	2.666	31.05
	7	dibutyl ether	2.684	32.40

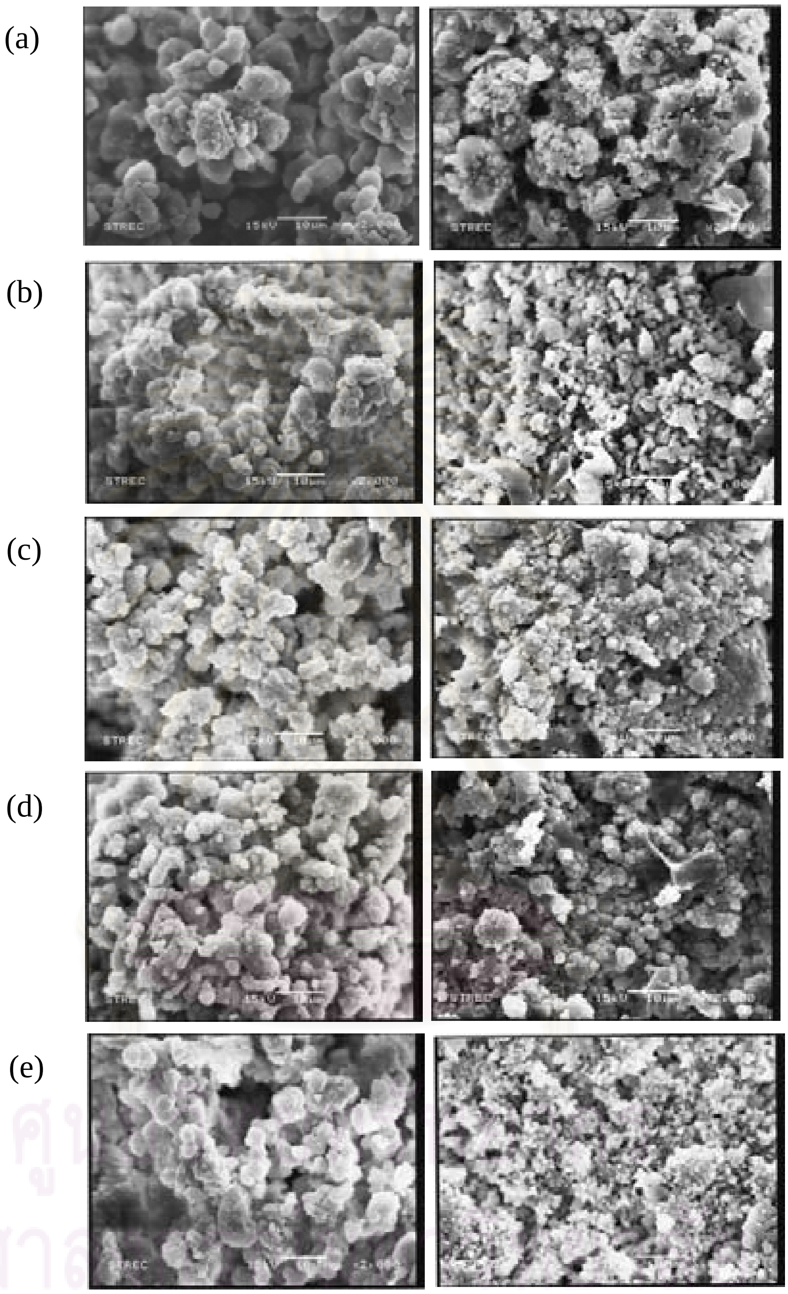
[a] Solvent : 1,2,4 trichlorobenzene, measured at 150 ^{o}C.

In general, ethylene polymerization synthesized with the absent external donor has the molecular weight varies inversely to the catalyst activity (Chirinos *et al.*, 2005). In this work their molecular weight are shown in **Table 4.6**. It was demonstrated that, polymer molecular weight from cat-A (entry 1) are higher than the one obtained with cat-B (entry 3) consistent with the fact that catalyst activity of cat-A are also lower than cat-B. In contrast, the introduction of dibutyl ether as external donor led not only to higher proportions of catalyst activity, but also to the increased polymer molecular weight, showed a similar tendency both cat-A and cat-B. These results accompanied with the observation from previous studies (Chen *et al*., 2006) that the presence of external donor (diphenyldimethoxysilane, DDS or tetrahydrofuran, THF) were influenced on the increase of MW. From these results, it is of interest that the catalyst activity and polymer molecular weight from cat-A, containing dibutyl ether (entry 5) was found to be apparently higher than cat-B (entry 7). Because of using dibutyl ether is directly correlated with activation or/and increasing of active sites in cat-A, as can be seen the polymer molecular weight from that one is higher value with increasing catalyst activity. Including, the deactivation effects from ethylene consumption profile (see in appendix D) exhibited the deactivation rate from cat-A is lower than cat-B. This result can be explain why the cat-A is more active and more polymer molecular weight than the cat-B.

On the other hand, in the presence of *n*-octanol, dibutyl ketone and heptyl acetate produced a stronger deactivation effect on the catalytic activity. Because of these compounds could poison effects on the active sites through the decrease in catalyst activity, which are remarkably affected on decreasing of polymer molecular weight (entry 2-4). It is obvious that, decreasing of polymer molecular weight followed the same trend as in catalyst activity in the following order: ester < alcohol < ketone.

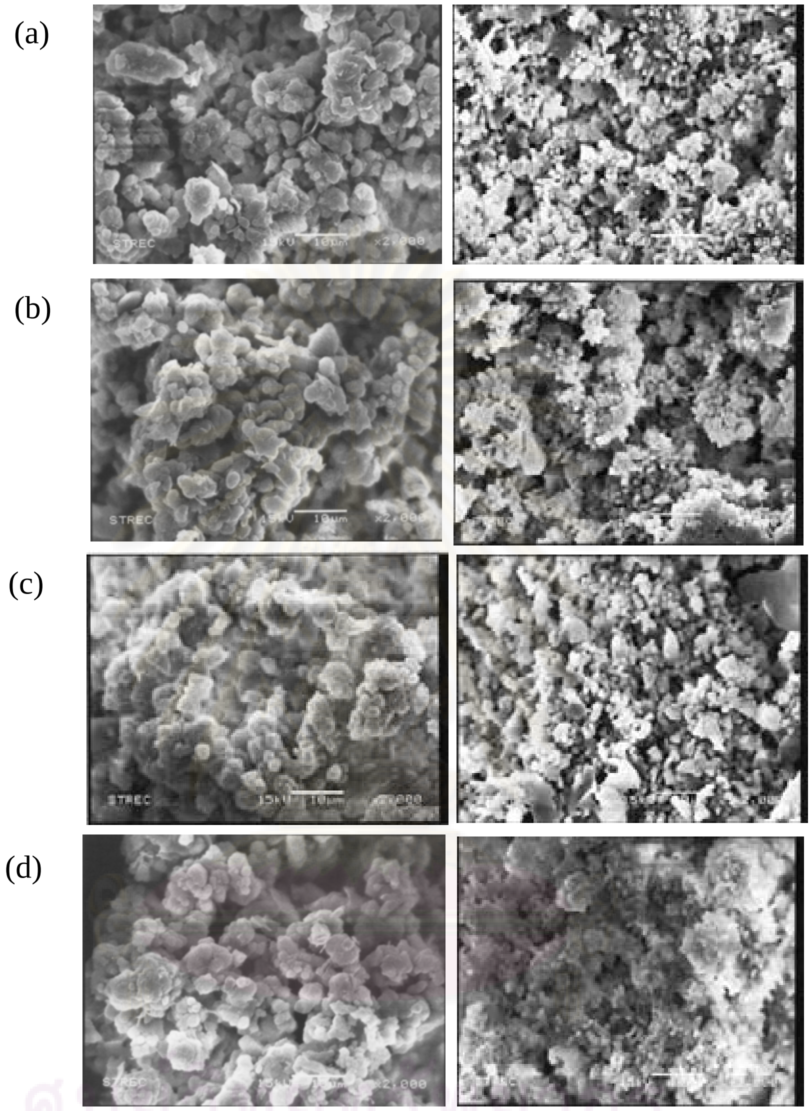
(2) Morphologies of polymers

All of polymers obtained with the addition of electron donors during ethylene polymerization were determined by SEM as shown in **Figures 4.7** to **4.10**. The polyethylenes produced by Ziegler-Natta catalyst which was introduced with electron donors display morphologies with well-defined particles. In addition, it can be seen that, the polymers obtained with cat-B had smaller particle morphology than polymers from cat-A**.**



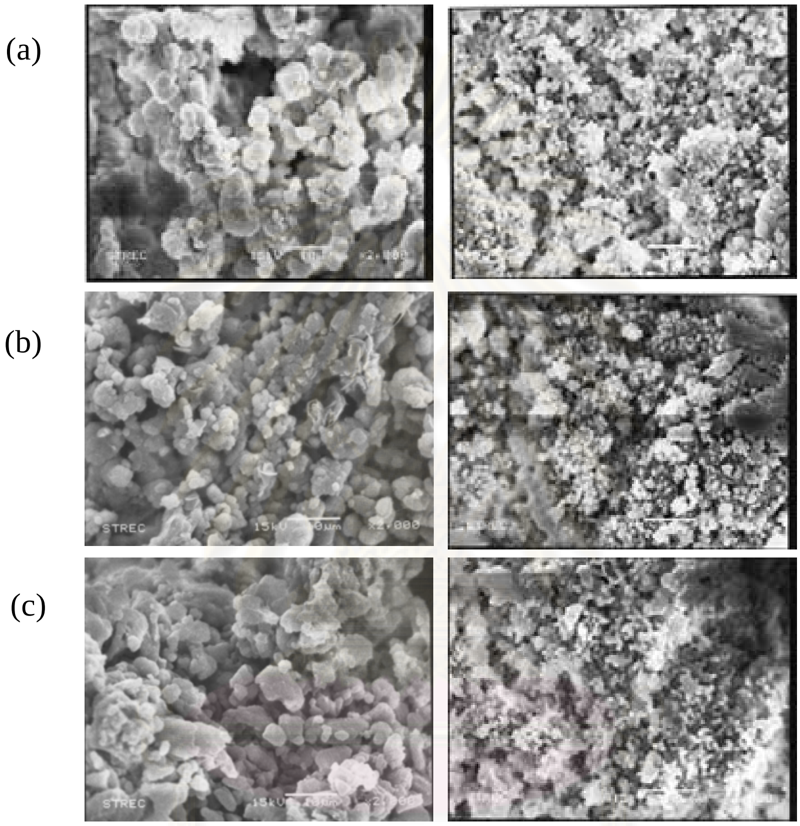
(1) obtained with cat-A (2) obtained with cat-B

Figure 4.7 SEM micrographs of polyethylene particles obtained with cat-A and B prepared with different kinds of donor (a) none (b) octanol (c) dibutyl ketone (d) heptyl acetate (e) dibutyl ether



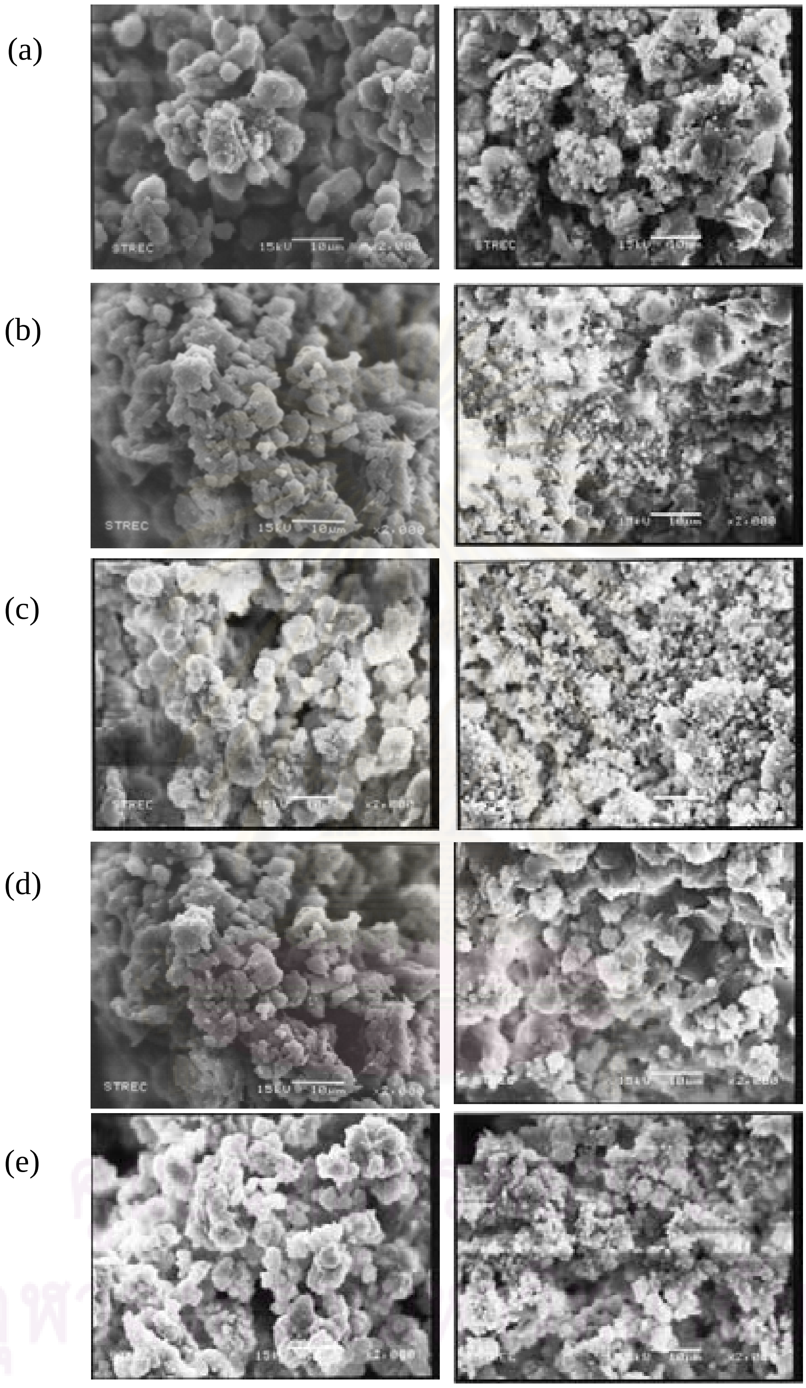
(1) obtained with cat-A (2) obtained with cat-B

Figure 4.8 SEM micrographs of polyethylene particles obtained with cat-A and B prepared with differing in number and bulkiness of alcohol carbon (a) ethanol (b) *n*-butanol (c) *n*-octanol (d) *t*-butanol



(1) obtained with cat-A (2) obtained with cat-B

Figure 4.9 SEM micrographs of polyethylene particles obtained with cat-A and B prepared with different molecular structure of di-ether carbon (a) dibutyl ether (b) dipentyl ether (c) dihexyl ether



(1) obtained with cat-A (2) obtained with cat-B

Figure 4.10 SEM micrographs of polyethylene particles obtained with cat-A and B prepared with with at different dibutyl ether /Ti molar ratio (a) [0] (b) [0.05] (c) [0.1] (d) [0.2] (e) [10]

(3) Thermal properties

The melting temperatures (T_m) and percent of crystallinity of polymer were evaluated by the differential scanning calorimeter (DSC). The melting temperature (T_m) of polymers obtained with cat-A is in the range 129–134 ^{o}C and 130-134 ^{o}C for polymer obtained with cat-B. The degree of crystallinity was calculated by comparison with heat of fusion (ΔH_f) of a perfectly crystalline polyethylene, i.e., 293 J/g. Percent crystallinity of polyethylene are summarized in **Table 4.7**. DSC curves of the polymer are also shown in Appendix A.

It is believed that polymers having the highest molecular weight; higher entanglement of the polymer chains occurs in polymers showed lower crystallinity. Boor (1979) and Chirinos *et al.* (2005), they demonstrated that there was a striking difference in the crystallinity of the polymers obtained with external electron donor. They mentioned that the presence of external donor was influenced on the increase of MW, but did not show the lowest degree of crystallinity when compared with the absence of donor. This is also consistent with the consequence of this work that all of polymers obtained with external donors showed the higher crystallinity than the absent one. It has stronger tendency to be more MW (compared with none and dibutyl ether compound) as already mentioned in part of solution viscosity. As the crystallization increased (Boor, 1979) (decreasing the degree of branching), it is possible for the following properties to increase, such as rigidity, tensile strength, hardness, chemical resistance and opacity. However, there is some different point of polymer obtained from the higher of dibutyl ether/Ti molar ratio up to 0.2 and 10 showed minimum value of crystallinity than absent donor. Therefore, it might be presumed that the amount of external donor increases can contribute to decreasing crystallinity. Morover, Chirinos (2005) stated that polymer crystalline might have some relation to a different PDI (polydispersity index) of polymers formed with respect to having electron donors and absent one.

Table 4.7 Melting temperatures and percent crystallinity of polymer obtained different external electron donors compound

Systems	**Materials**	**$T_m(^oC)^a$**	**$\chi_c,^b$**
Cat-A	none	129	59.00
	ethanol	130	60.25
	n-butanol	129	60.29
	n-octanol	132	61.32
	t-butanol	130	61.66
	dibutyl ketone	132	60.84
	heptyl acetate	131	60.40
	dibutyl ether	132	59.56
	dipentyl ether	132	60.77
	dihexyl ether	131	60.71
	dibityl ether [0.05][c]	132	59.81
	dibityl ether [0.2][d]	131	58.67
	dibityl ether [10][e]	133	58.20
Cat-B	none	133	59.73
	ethanol	132	60.13
	n-butanol	133	60.26
	n-octanol	130	60.58
	t-butanol	133	60.66
	dibutyl ketone	132	60.86
	heptyl acetate	132	61.00
	dibutyl ether	131	59.81
	dipentyl ether	131	60.66
	dihexyl ether	131	60.49
	dibityl ether [0.05][c]	131	60.46
	dibityl ether [0.2][d]	130	59.48
	dibityl ether [10][e]	132	58.93

[a] T_m and crystallinity were determined by DSC.

[b] calculated from heat of crystalline formation based on HDPE.

[c] [dibutyl ether/Ti] = 0.05

[d] [dibutyl ether/Ti] = 0.2

[e] [dibutyl ether/Ti] = 10

4.3 Discussion

In this research, investigate the effects and roles of external electron donors for the ethylene polymerization on the catalytic activity and polymer properties with Ziegler-Natta catalysts. Two catalysts were performed to determine the effects of external donors. The characteristics of both catalysts showed commercial catalyst (cat-B) is higher titanium content which corresponds to the stronger with support interaction than synthesized catalyst (cat-A).

Effects of different external electron donors, having differing in functional groups were study on the catalytic activity. In the absent any donor it demonstrates that the activity of cat-B higher than cat-A. This can be rationalized by the fact that, cat-B contains more sites which are active than cat-A. In the presence of external donors an activation and deactivation effect on the catalyst activity are observed. It is found that, the use of dibutyl ether has led to substantial advances in catalyst activity for both catalysts. Catalytic activity of cat-A after promoted with dibutyl ether are shown higher than promoted cat-B. It can be said that, dibutyl ether can improve the active sites of cat-A than cat-B. A possible reason why catalytic activity of cat-A is higher than cat-B is, cat-A contains more sites that are not active, and have be easier to promoted by dibutyl ether as external donor. From these results, it is consequently demonstrated that the activation effect are remarkably affected on cat-A which has $TiCl_4$ and support weaker interaction than cat-B.

On the contrary, in the presence of *n*-octanol, dibutyl ketone and heptyl acetate as external donors, a deactivation effect on the catalyst activity are observed. The catalytic activity is influenced by the nature of functional group in the following order: ester < alcohol < ketone. This suggests that, these compounds can poison on the active center of catalyst. It can be seen that, heptyl acetate shows the catalytic activity higher than dibutyl ketone. These results support the recognition from the previous study (Tangjituabun, 2008) stated that, ethyl acetate, ethyl benzoate (EB) like structure, could give rise to the electron density of cationic metal center and make the catalytic sites kinetically more stable and active comparing to acetone. In the case of alcohol, is accepted that, $TiCl_4$ is readily reacted with alcohol to produce alkoxide complex which is inactive polymerization and HCl (Garoff *et al*., 1987). In addition, HCl must react with cocatalyst to reduce its activation power and the titanium chloride alkoxides produced on the catalyst surface might have some negative effects on the catalyst activity. Furthermore, Puhakka (1997) explained that stability of the alcohols depends on the possibility of forming hydrogen bonding between the complexes alcohol and a chloride ion. As a result, it was found the catalyst activity of n-octanol higher than dibutyl ketone but lower than heptyl acetate. The results obviously demonstrated that the effectiveness of the catalytic activity depends on kind of external electron donors and nature of functional groups. The interaction mechanism of electron donor on the catalyst surface is shown in **Figure 4.11**.

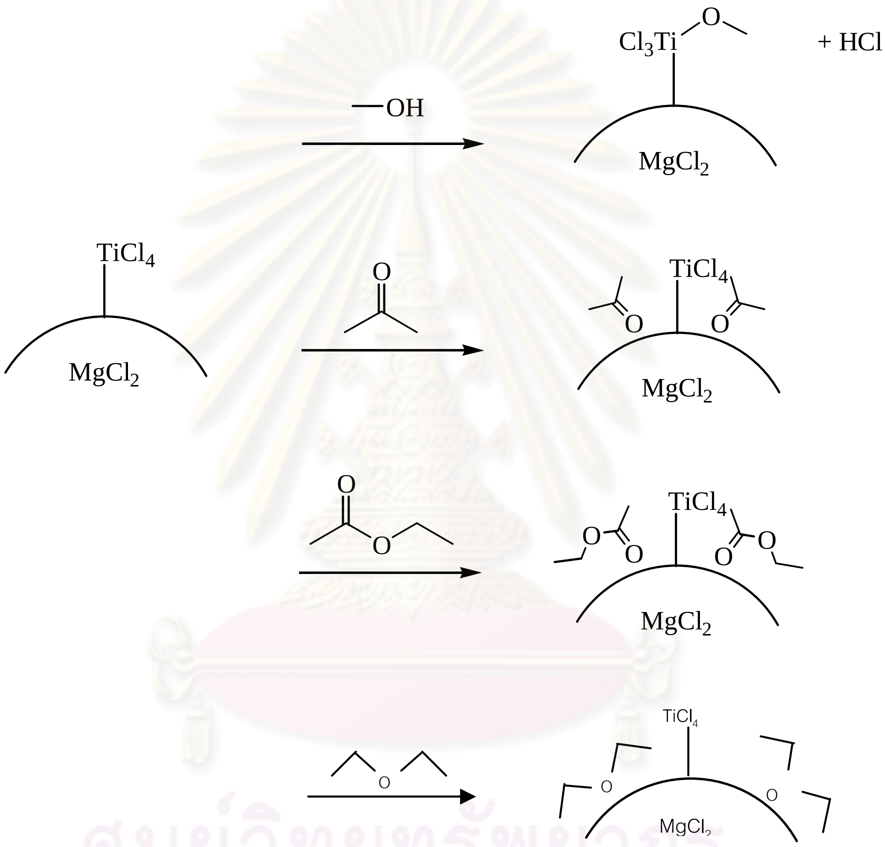


Figure 4.11 Purposed mechanism of the interaction between solid catalyst and electron donors.

To compared the effect of external donors with observed differences in number and bulkiness of alcohols carbon. High number of alkyl chain of alcohol lead to substantial advances in catalyst activity. By comparison of different structure of carbon, it reveals that, more bulkiness produced an evident deactivation effect lower than linear structures in comparison with the same numbers of carbon in molecule. Furthermore, catalyst deactivation of cat-B are higher than cat-A. It may propose that the deactivation or poison effect have influence on cat-B than cat-A due to stronger interaction of $TiCl_4$ and support of cat-B.

The di-ethers structures of electron donor play an important role and make it more effective in catalytic activity. Dibutyl ether exhibited the most effective influence on active sites. Due to it has a strong electron-donating ability, and exhibited effective influence to the activation more active sites leading to increasing the catalyst activity. In addition, the effect of using a suitable amount of dibutyl ether are important to produced hexagonal crystalline which is believe to be active sites. It was obvious that, the highest value of activity was achieved at molar ratio of dibutyl ether/Ti equal to 0.1 in both cat-A and cat-B.

Moreover, the introduction of dibutyl ether as external donor leads not only to high catalytic activity, but also increases polymer molecular weight for both cat-A and cat-B. On the contrary, *n*-octanol, dibutyl ketone and heptyl acetate exhibit a deactivation effect on the catalytic activity, which are remarkably affected on decreasing of polymer molecular weight. All polymers obtained with external donors showed the higher crystallinity than the absent one. In contradiction, the crystallinity changes in opposite direction as external donor.

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

Effects of external electron donors into the ethylene polymerization are investigated. The results indicate that external electron donors remarkably affecte on the catalytic activity not only improvement, but also deactivation depend on the different kinds of each functional group. The molecular weight of polyethylene changes in the same direction of catalytic activity. The activity of catalysts is in the following order: di-ether > none > ester > alcohol > ketone, the same numbers of carbon in their molecular structure. It is found that dibutyl ether which is represented of di-ether group exhibits apparently highest catalyst activity in both cat-A and cat-B. The presences of heptyl acetate, n-octanol and dibutyl ketone, respectively, become gradually lower than the absent of these donors. In addition, molecular structures of alcohol carbon are interpreted in terms of number and bulkiness of alcohol on the catalytic activity. It is demonstrated that increasing the number of alcohol carbon of linear structure reducing the ability in catalyst deactivation. In addition, the bulkiness molecule with the same carbon atom shows lower deactivation effect. It can be seen that dibutyl ether can improve catalyst activity at molar ratio dibutyl ether/Ti molar ratio up to 0.1.

Moreover, in the presence of external donor, it can contribute to polymer molecular weight control. In this research, dibutyl ether is of interesting external donor that not only enhancement catalyst activity and also increase polyethylene molecular weight. On the contrary, *n*-octanol, dibutyl ketone and heptyl acetate exhibit a deactivation effect on the catalyst activity, which are remarkably affected on decreasing of polymer molecular weight. Therefore, the obtained polymer molecular weight after external electron donors is added depending on the catalytic activity.

5.2 Recommendations

1. For the case of external electron donor effect explanation, more detailed study on the polymer properties including the distribution of polyethylene should be further investigated in order to answer the question what and how active sites have been altered by external electron donor to confirm whether such compounds could poison the active site.

2. It is difficult to clarify the polymers properties obtained with external electron donor additive, because there is problems the difficulty in dissolving these high molecular weight polymers. The presence of hydrogen in the polymerization system as an approach to overcome that problems to control molecular weight or terminating polymerization reaction in order to measure polymer properties by GPC.

3. The results showed interestingly for the case of addition ketone which has an influence on the lowest of catalyst activity. More detail study on the result should be further investigated.

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APPENDICES

APPENDIX A

(Differential Scanning Calorimeter)

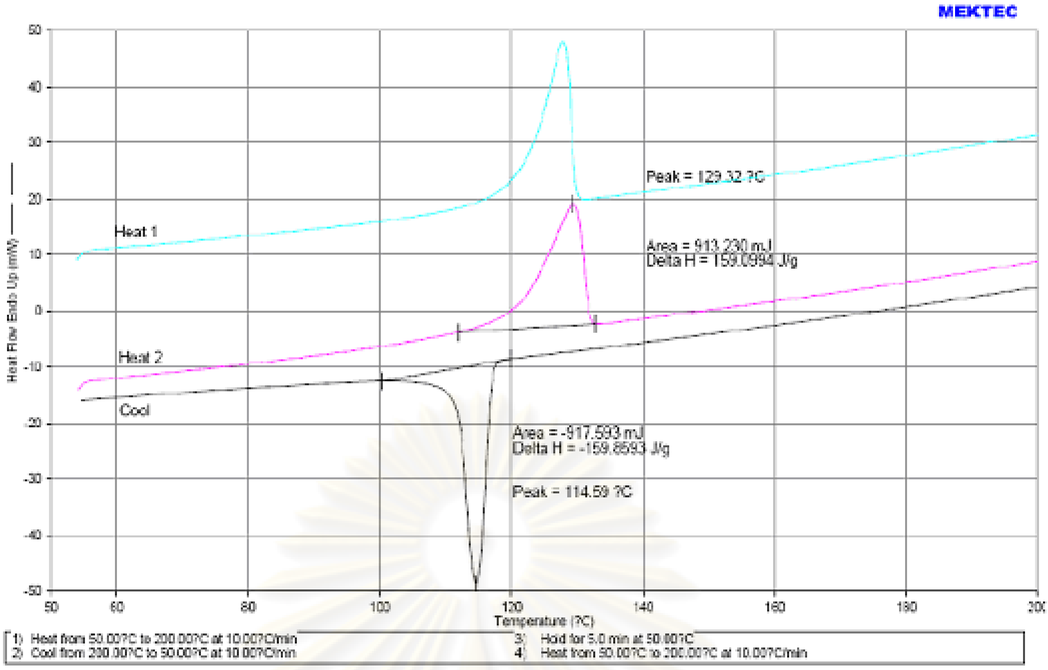

Figure A-1. DSC curve of polyethylene produce from cat-A

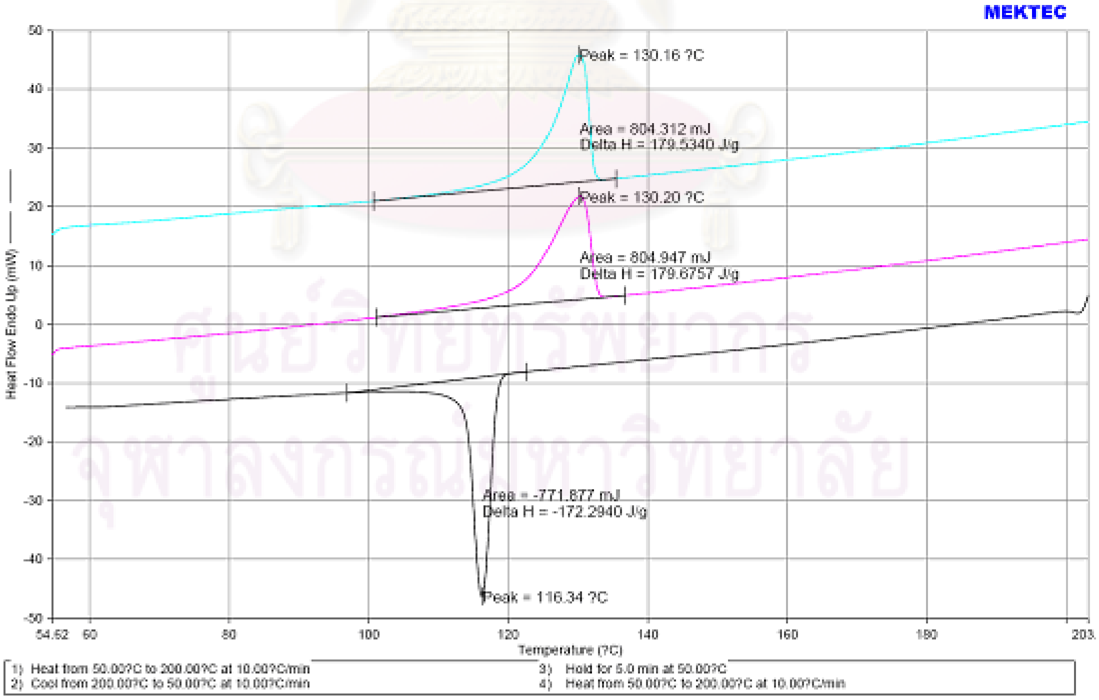

Figure A-2. DSC curve of polyethylene produce from cat-A with ethanol additive

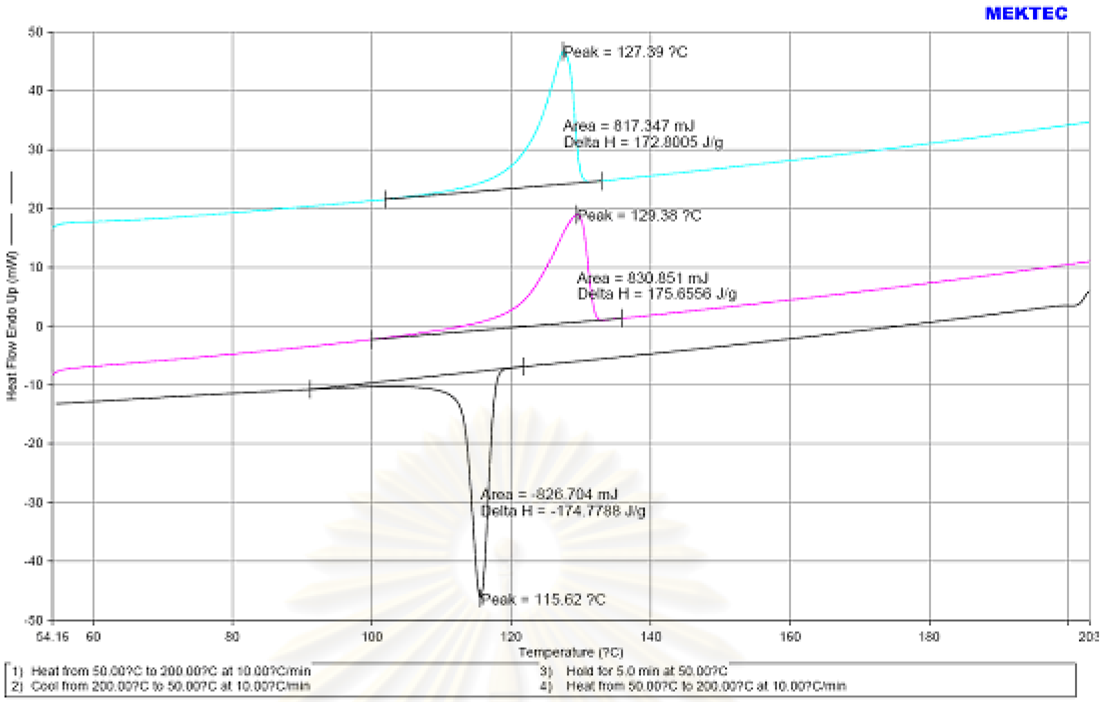

Figure A-3. DSC curve of polyethylene produce from cat-A with butanol additive

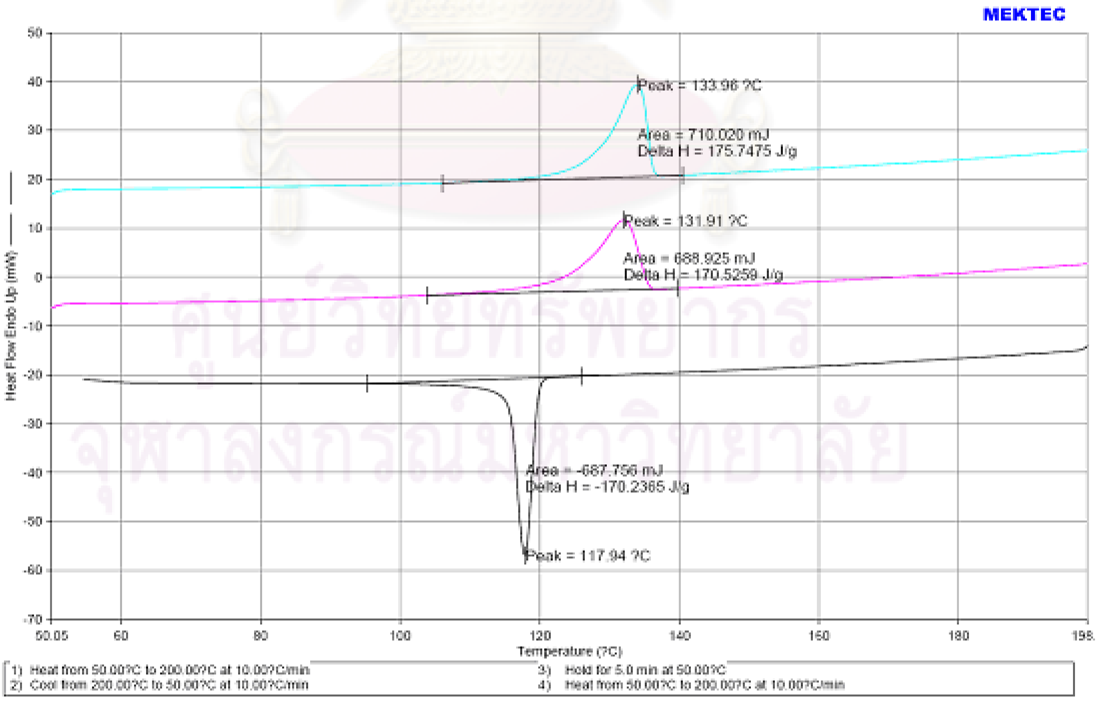

Figure A-4. DSC curve of polyethylene produce from cat-A with octanol additive

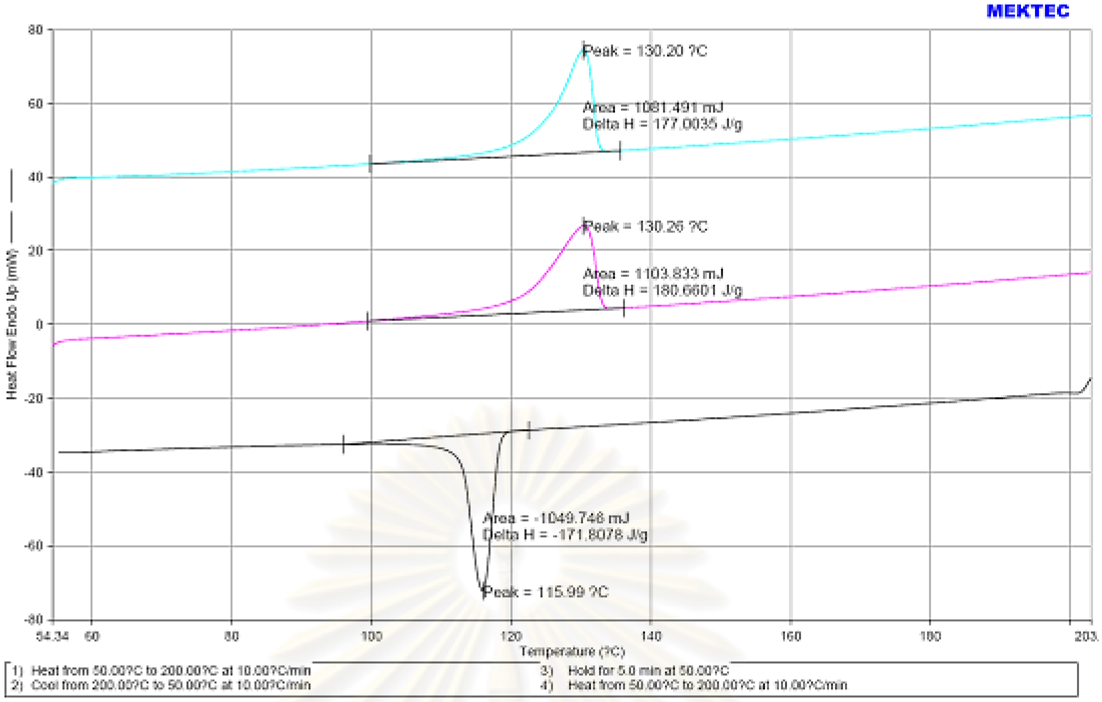

Figure A-5. DSC curve of polyethylene produce from cat-A with *t*-butanol additive

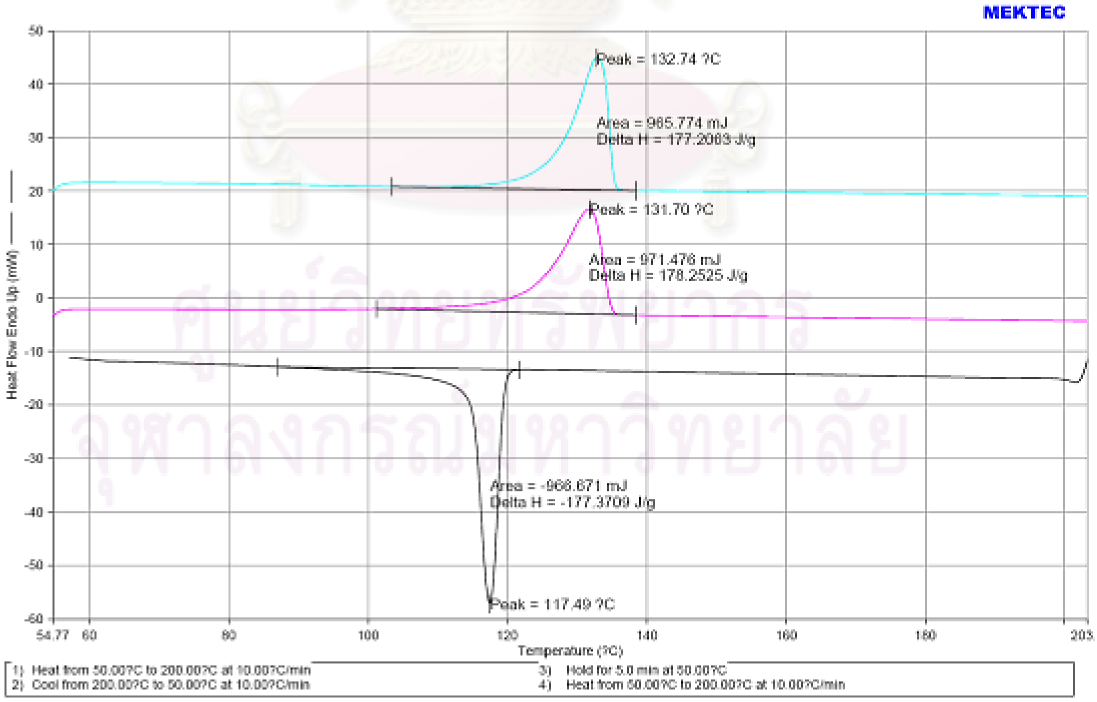

Figure A-6. DSC curve of polyethylene produce from cat-A with dibutyl ketone additive

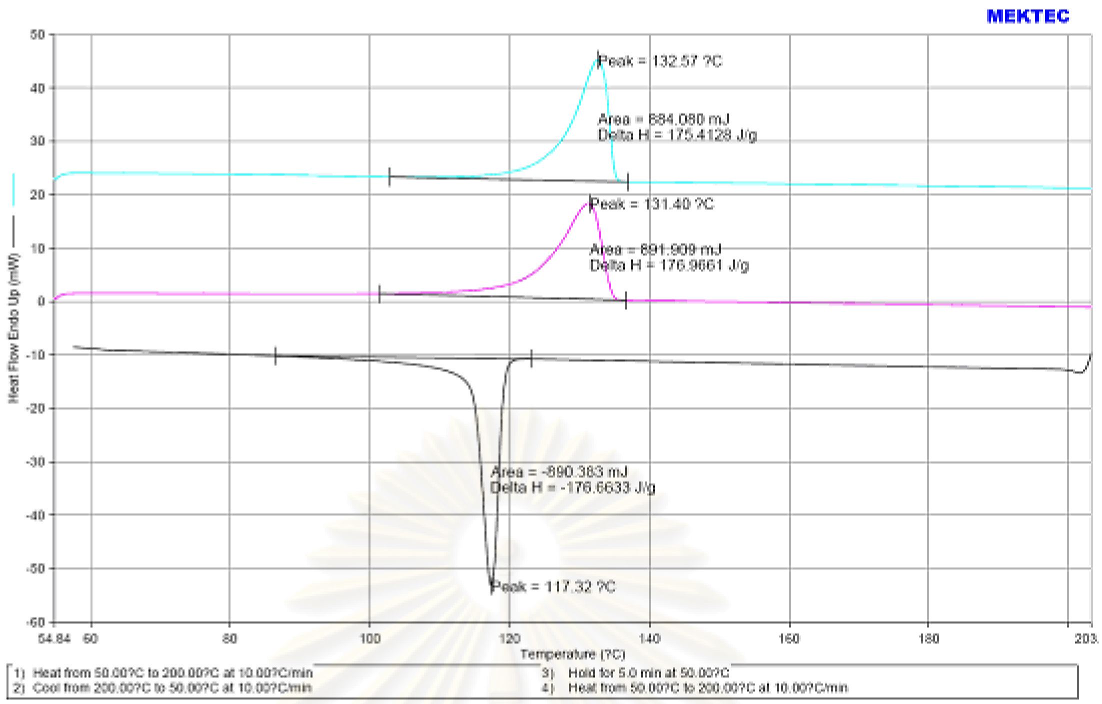

Figure A-7. DSC curve of polyethylene produce from cat-A with heptyl acetate additive

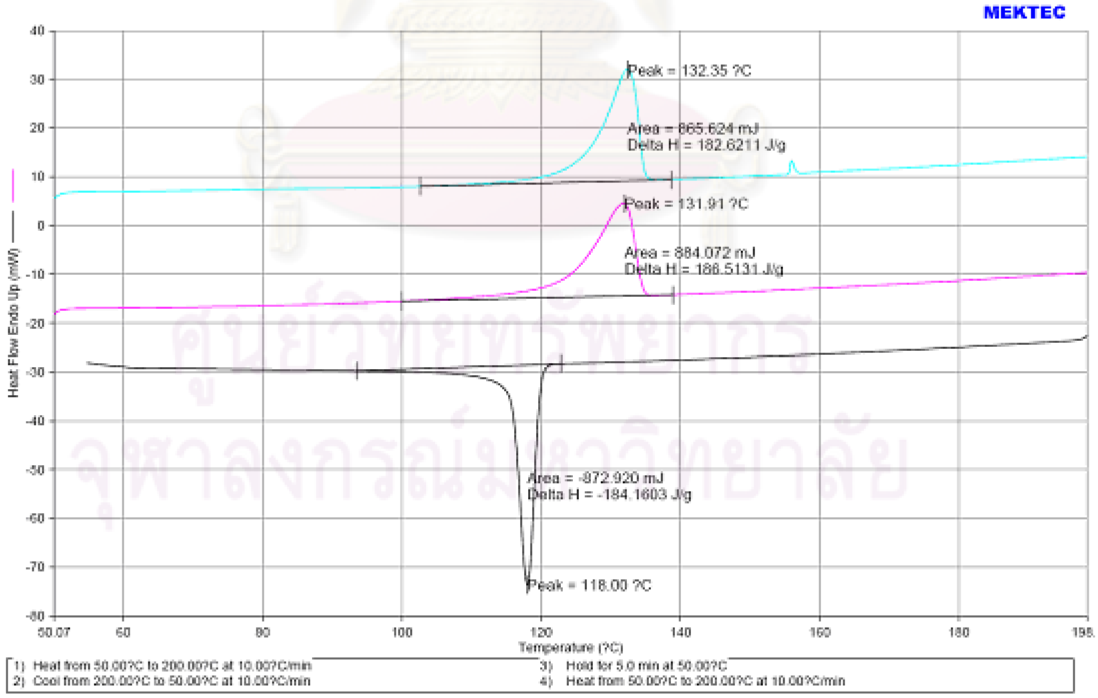

Figure A-8. DSC curve of polyethylene produce from cat-A with dibutyl ether additive

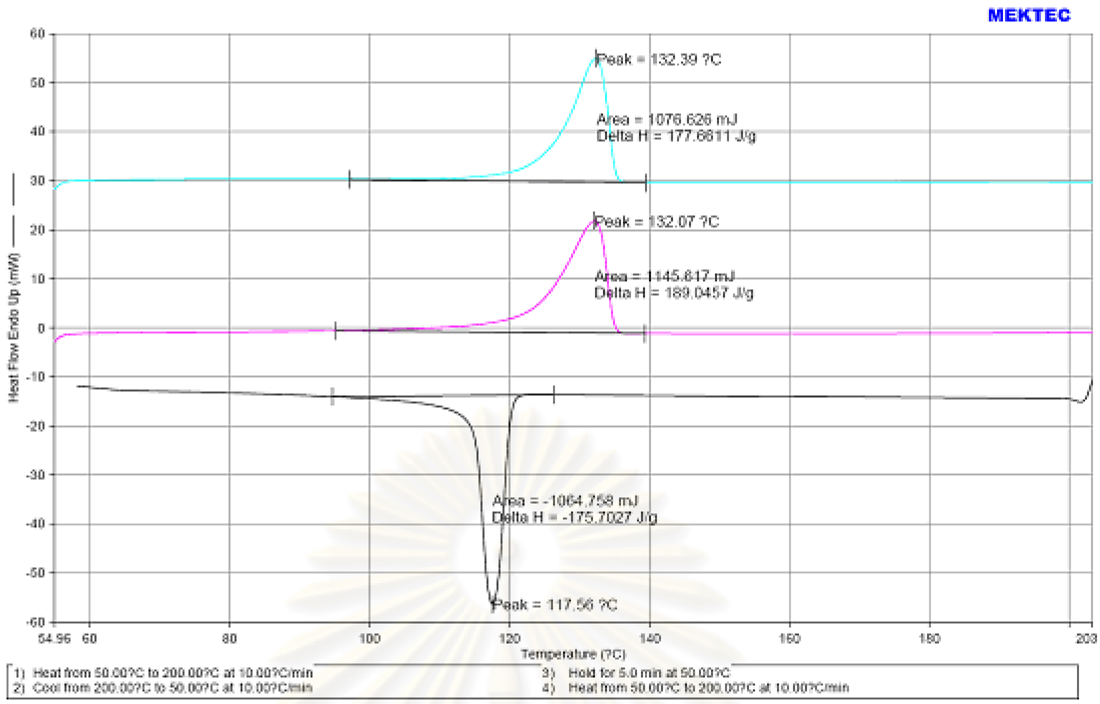

Figure A-9. DSC curve of polyethylene produce from cat-A with dipentyl ether additive

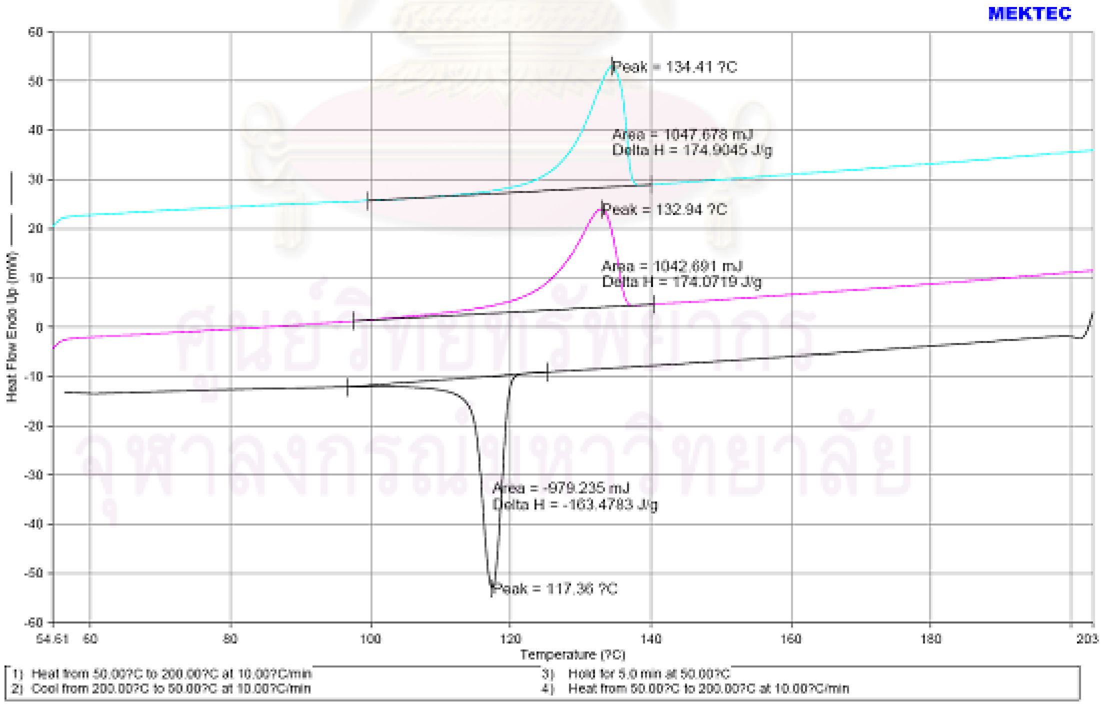

Figure A-10. DSC curve of polyethylene produce from cat-A with dihexyl ether additive

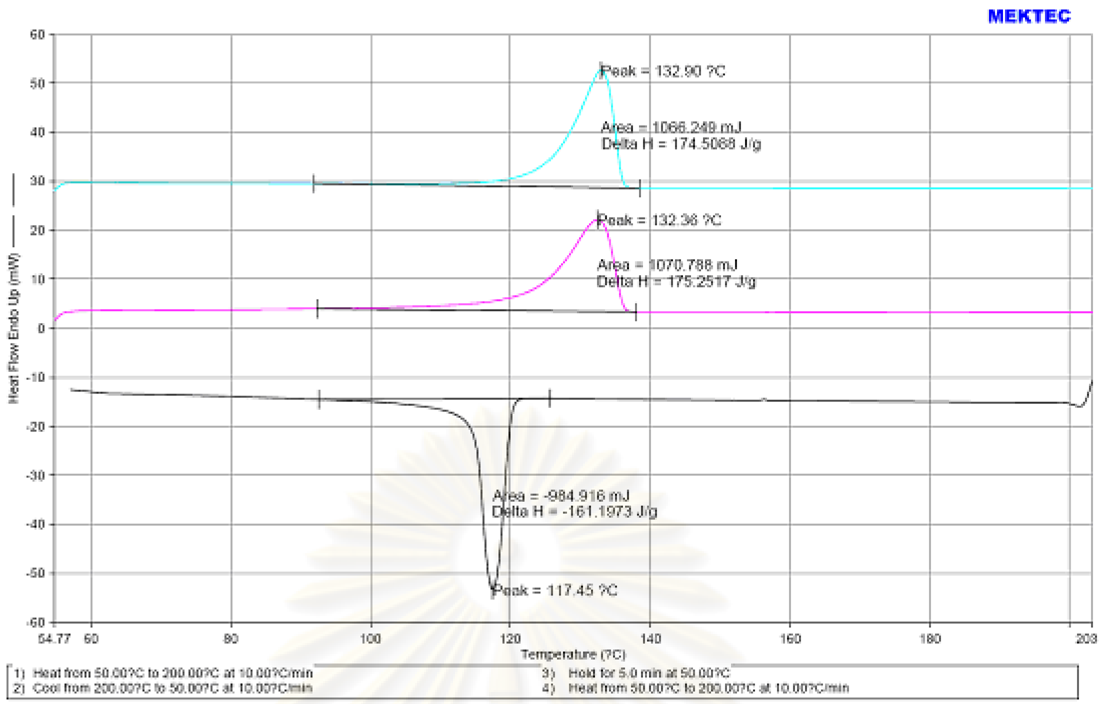

Figure A-11 DSC curve of polyethylene produce from cat-A with [dibutyl ether /Ti] = 0.05

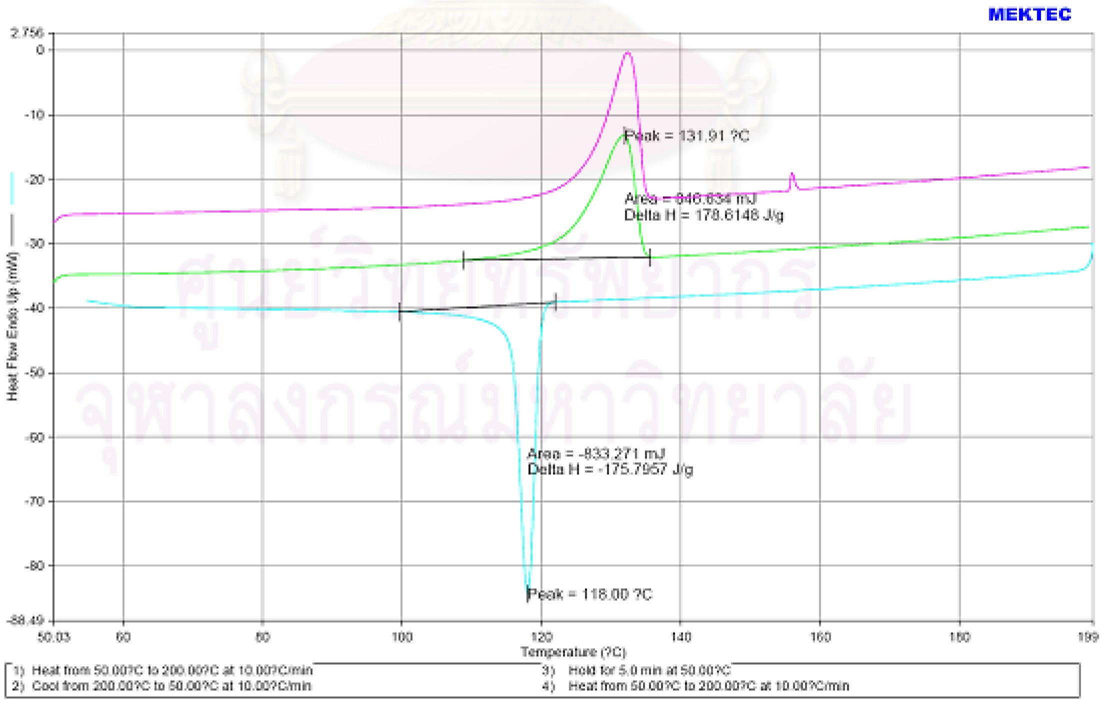

Figure A-12. DSC curve of polyethylene produce from cat-A with [dibutyl ether /Ti] = 0.2

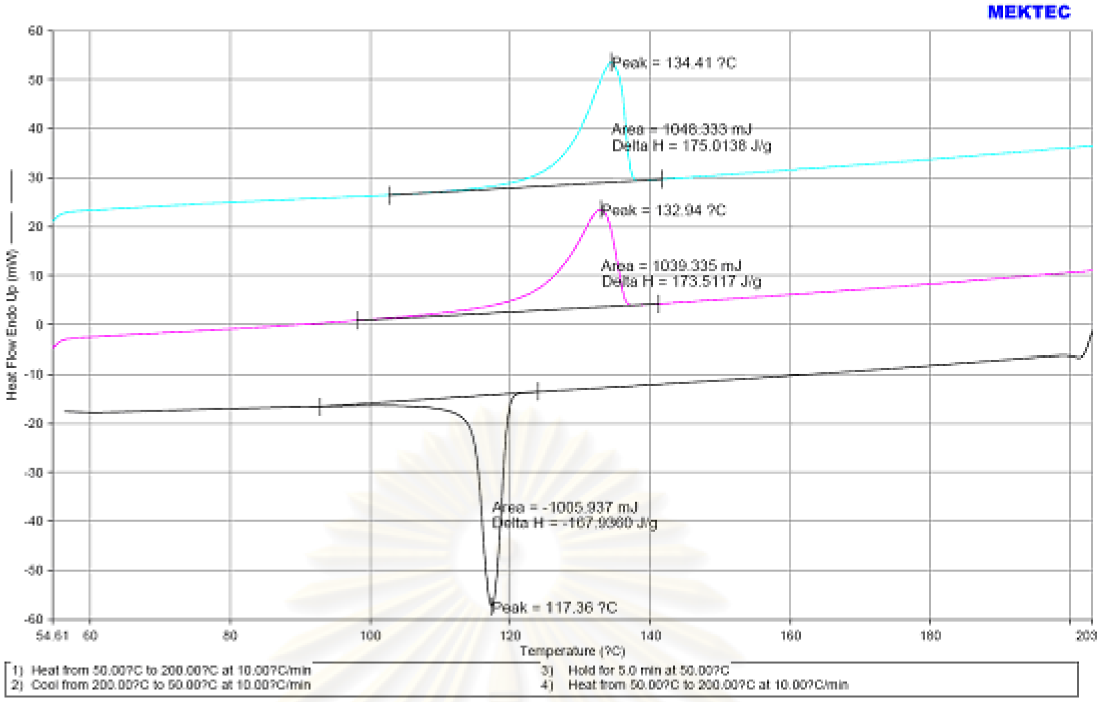

Figure A-13. DSC curve of polyethylene produce from cat-A with [dibutyl ether /Ti] = 10.

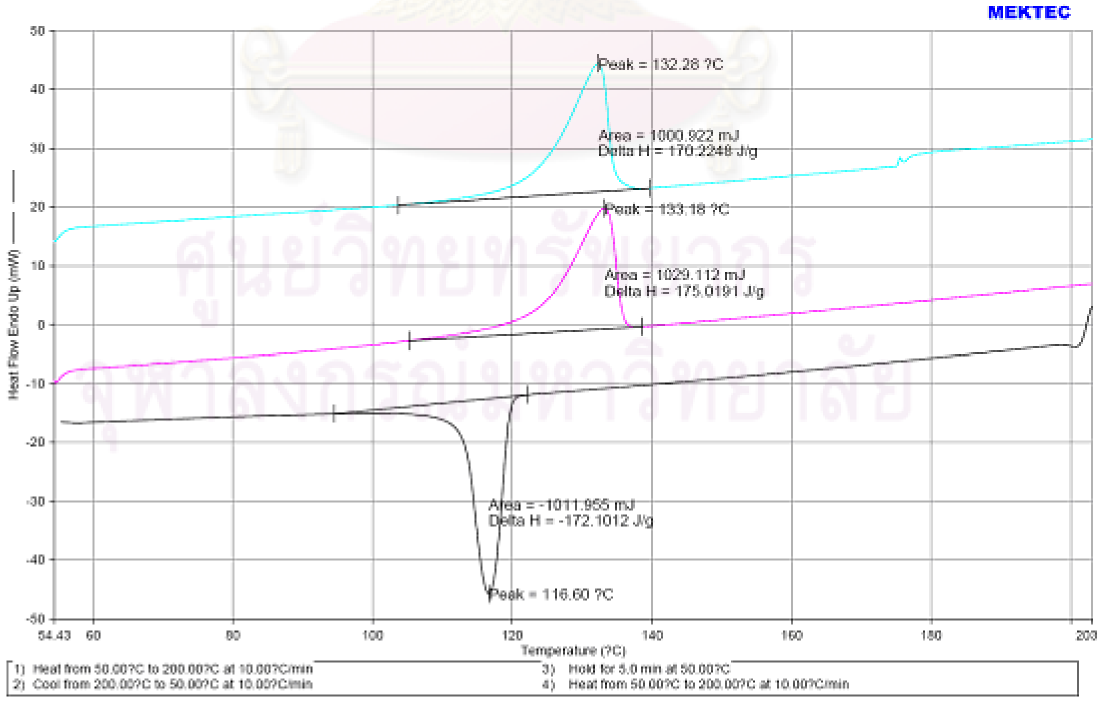

Figure A-14. DSC curve of polyethylene produce from cat-B

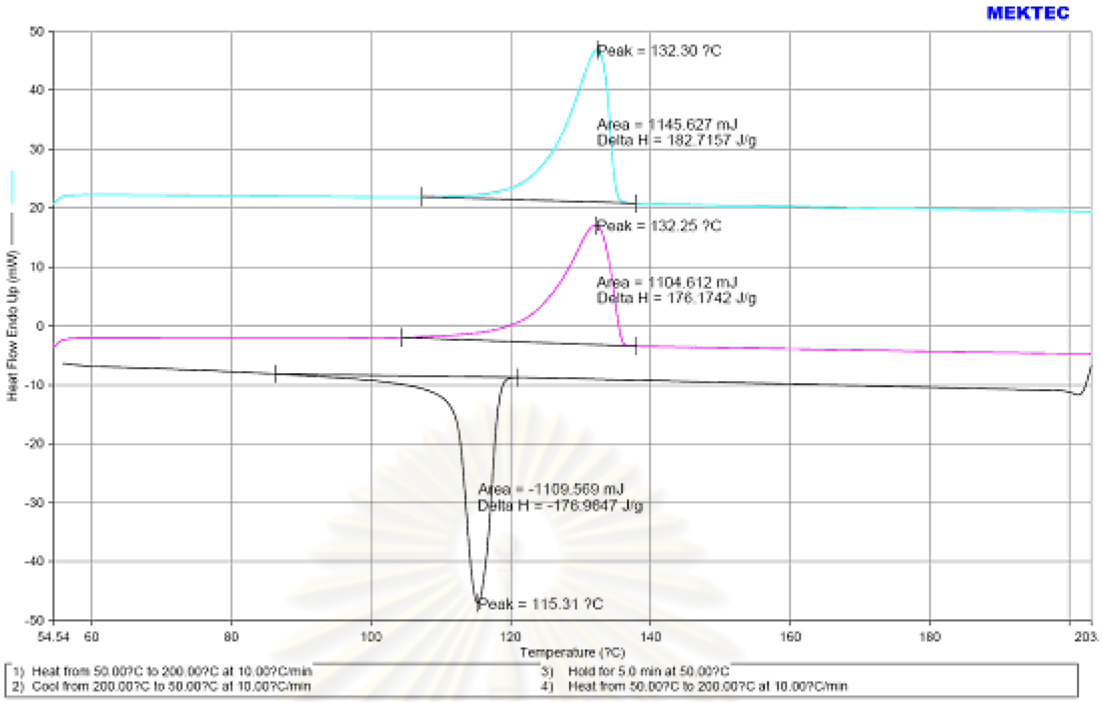

Figure A-15. DSC curve of polyethylene produce from cat-B with ethanol additive

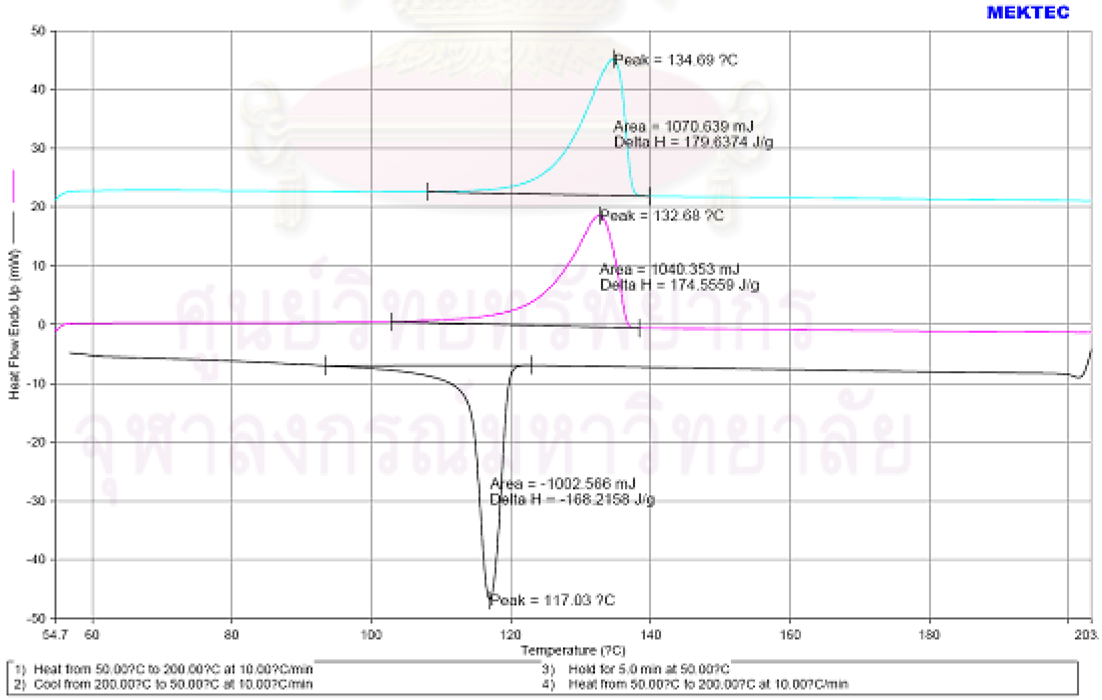

Figure A-16. DSC curve of polyethylene produce from cat-B with butanol additive

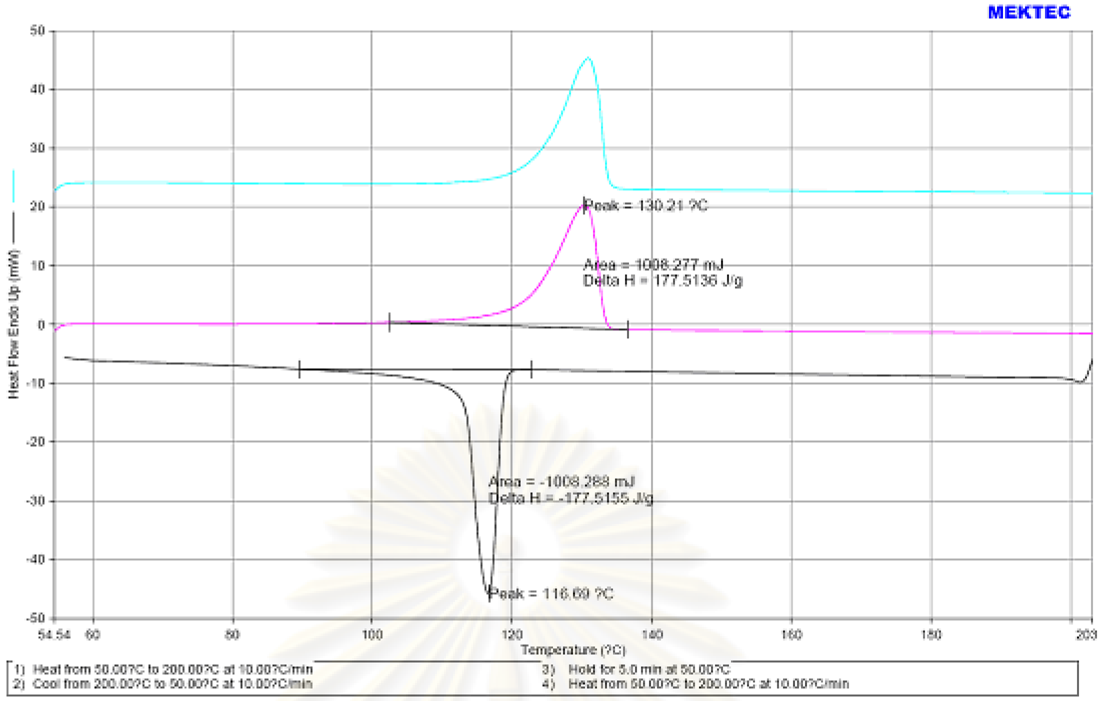

Figure A-17. DSC curve of polyethylene produce from cat-B with octanol additive

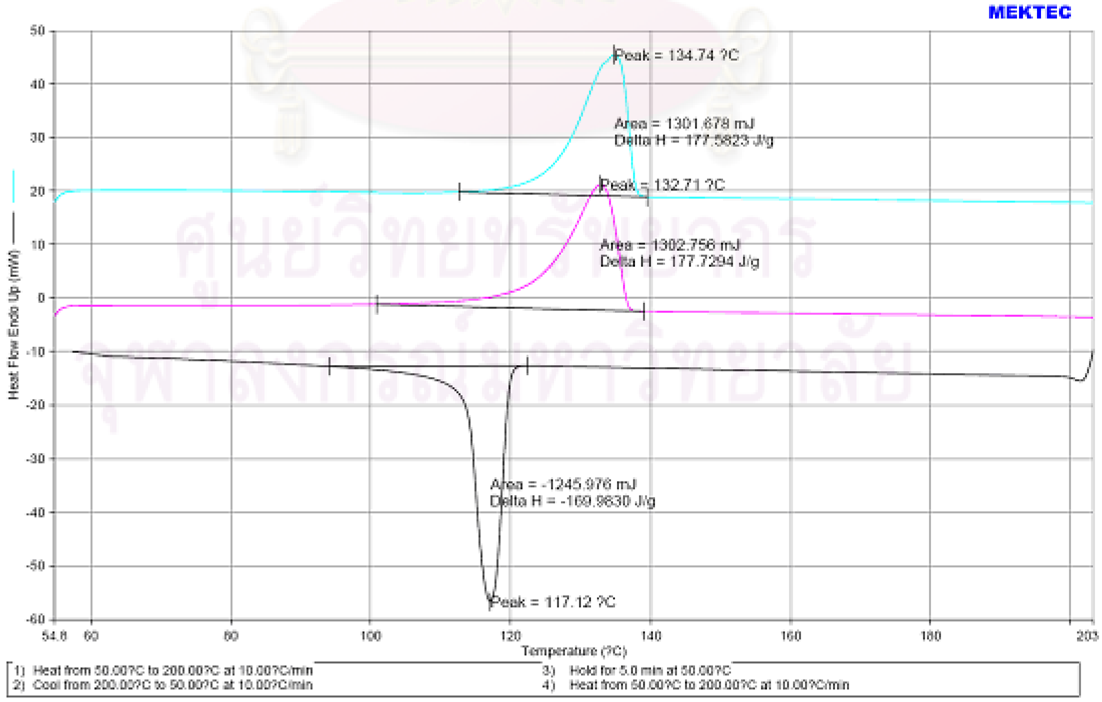

Figure A-18. DSC curve of polyethylene produce from cat-B with *t*-butanol additive

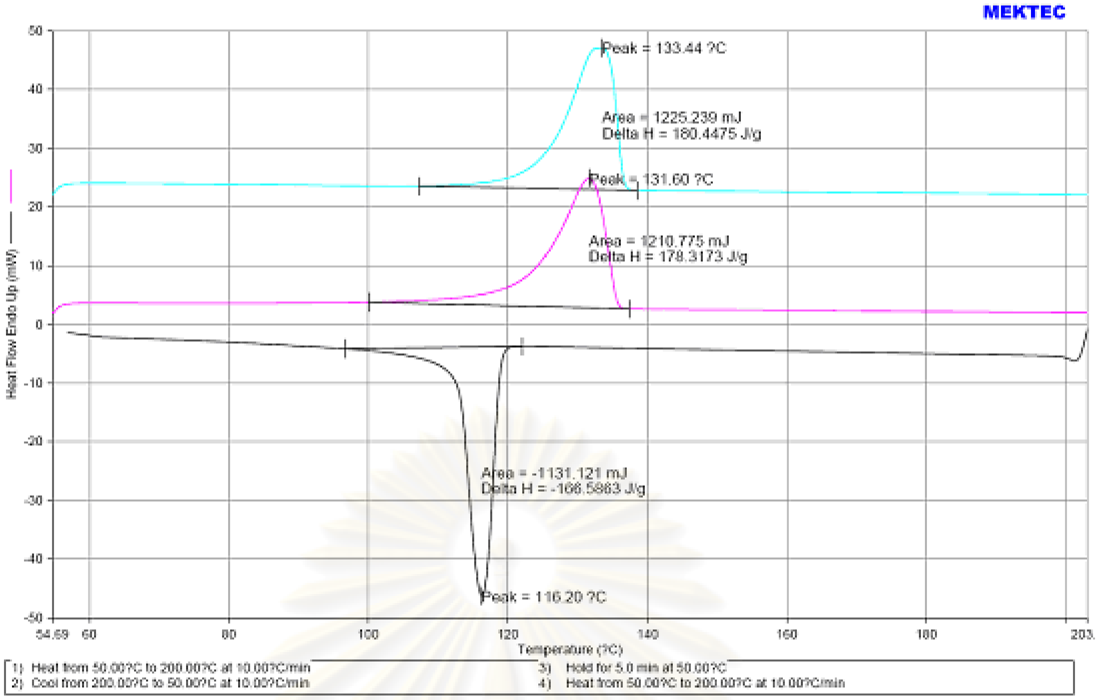

Figure A-19. DSC curve of polyethylene produce from cat-B with dibutyl ketone additive

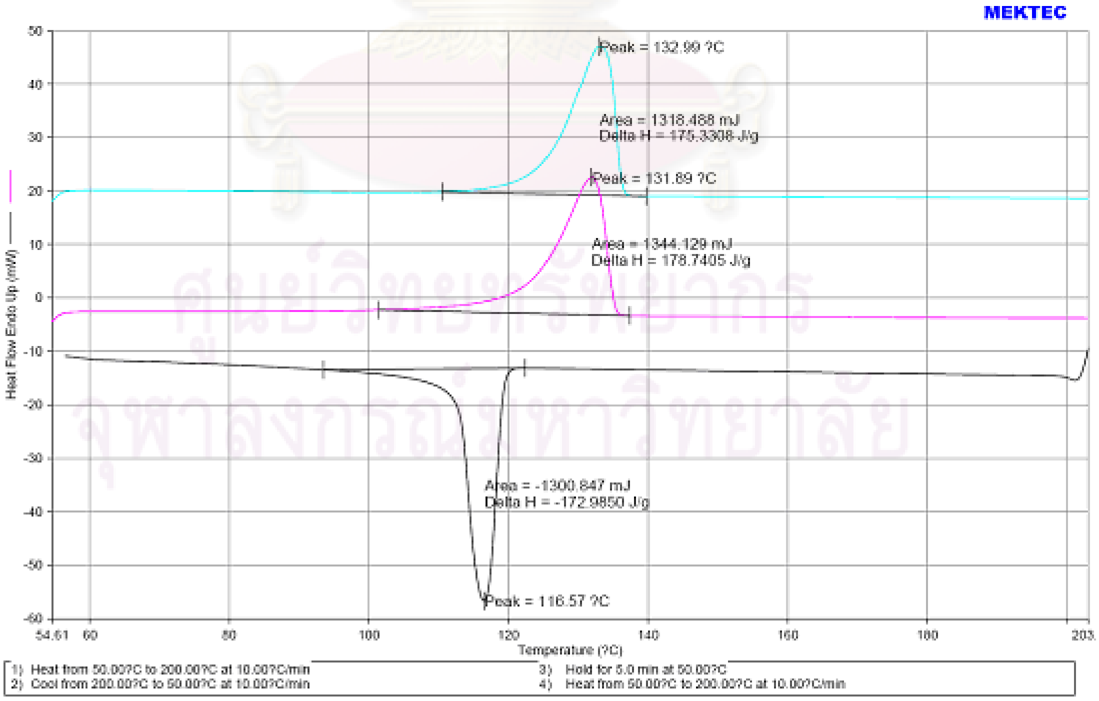

Figure A-20. DSC curve of polyethylene produce from cat-B with heptyl acetate additive

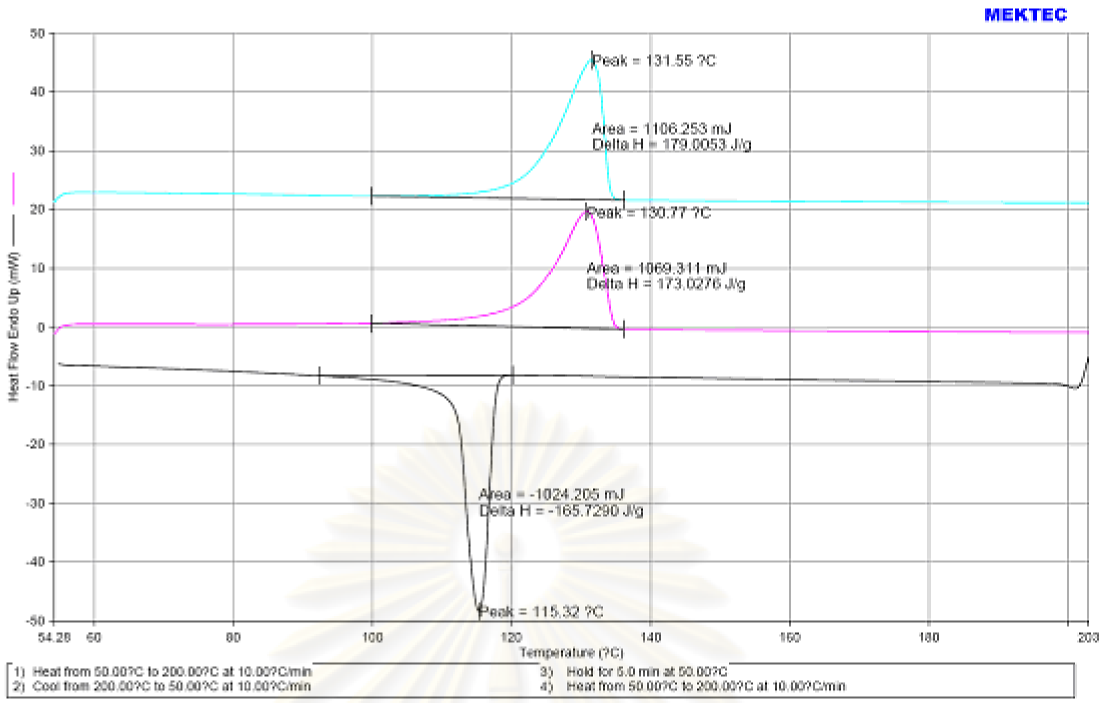

Figure A-21. DSC curve of polyethylene produce from cat-B with dibutyl ether additive

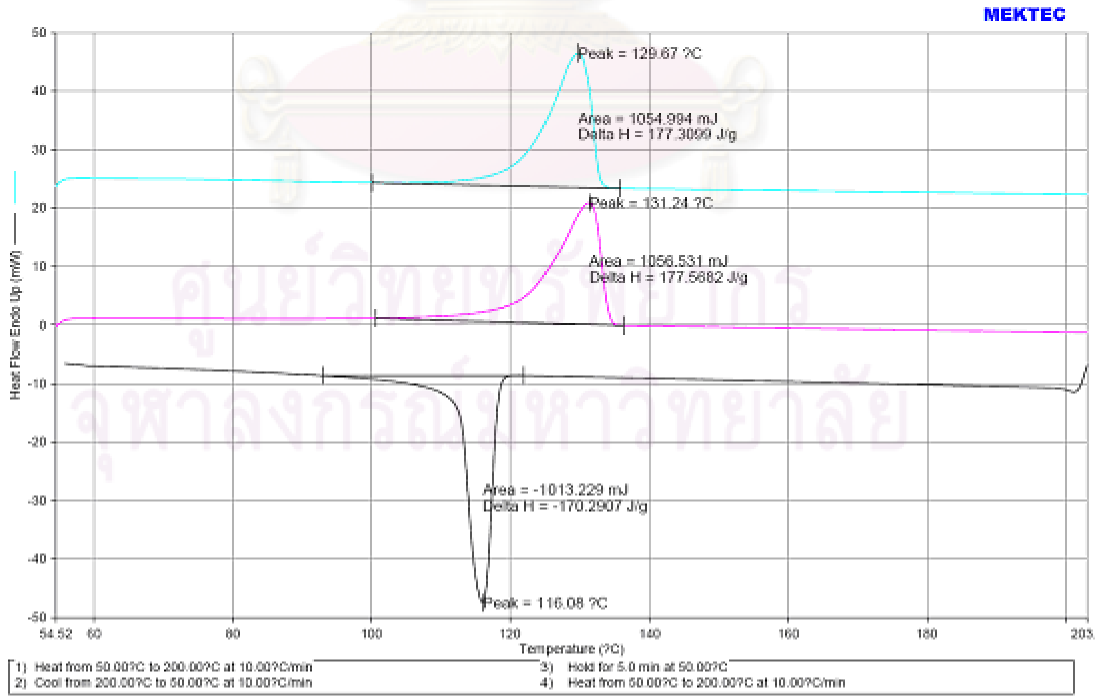

Figure A-22. DSC curve of polyethylene produce from cat-B with dipentyl ether additive

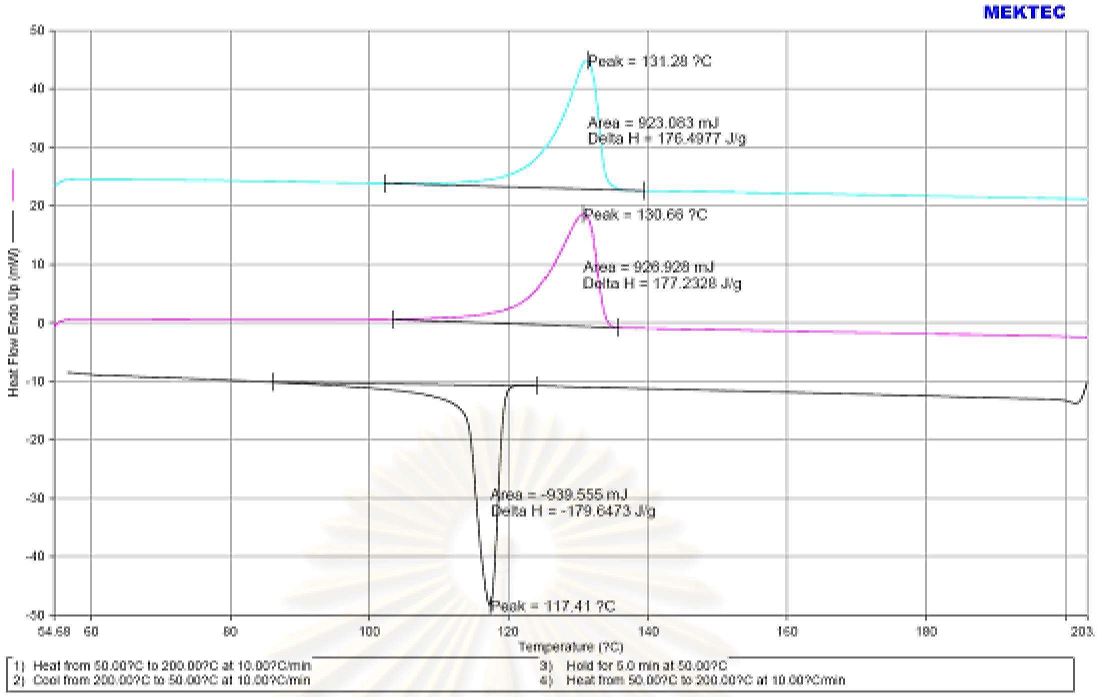

Figure A-23. DSC curve of polyethylene produce from cat-B with dihexyl ether additive

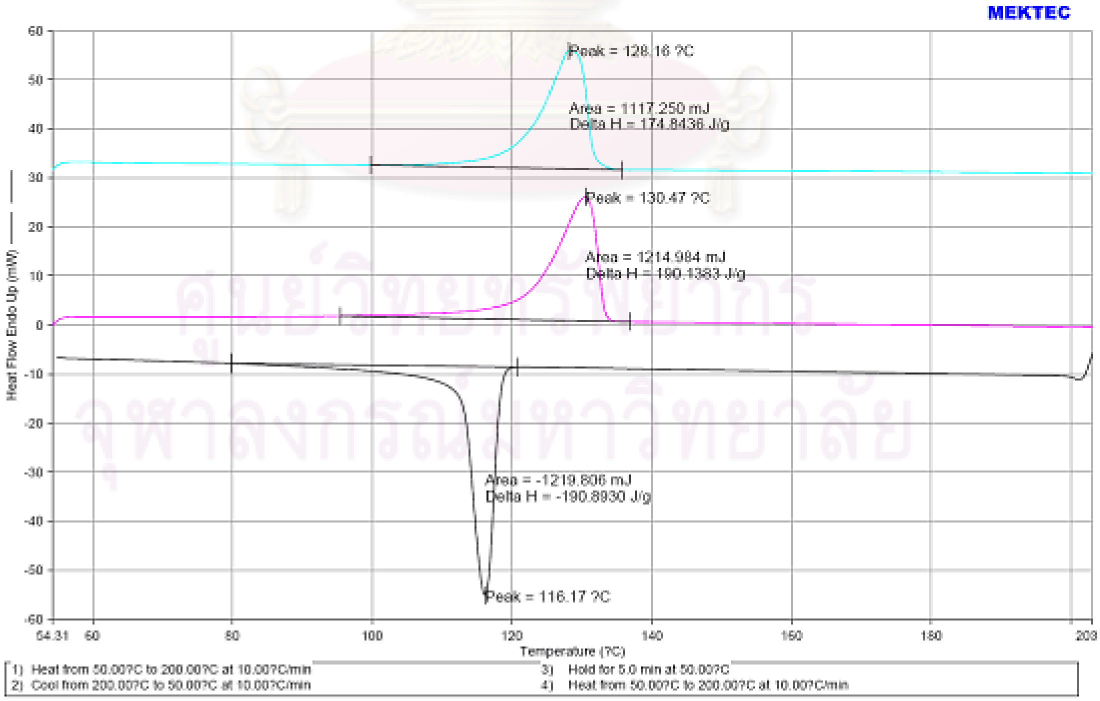

Figure A-24. DSC curve of polyethylene produce from cat-B with [dibutyl ether /Ti] = 0.05

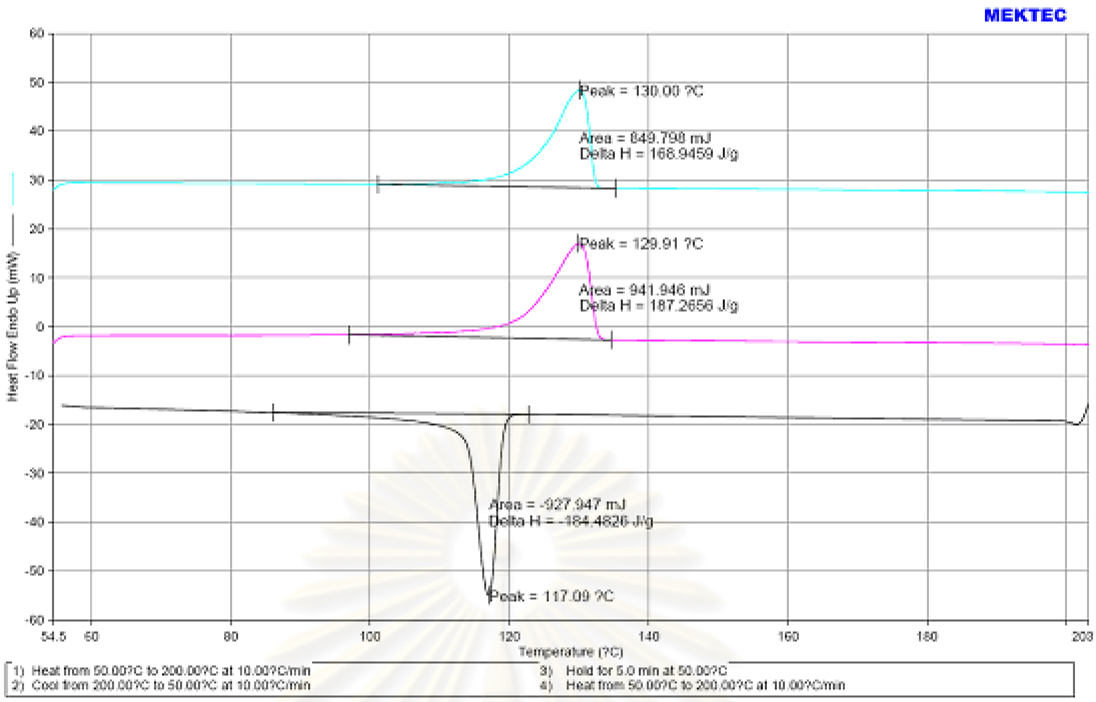

Figure A-25. DSC curve of polyethylene produce from cat-B with [dibutyl ether /Ti] = 0.2

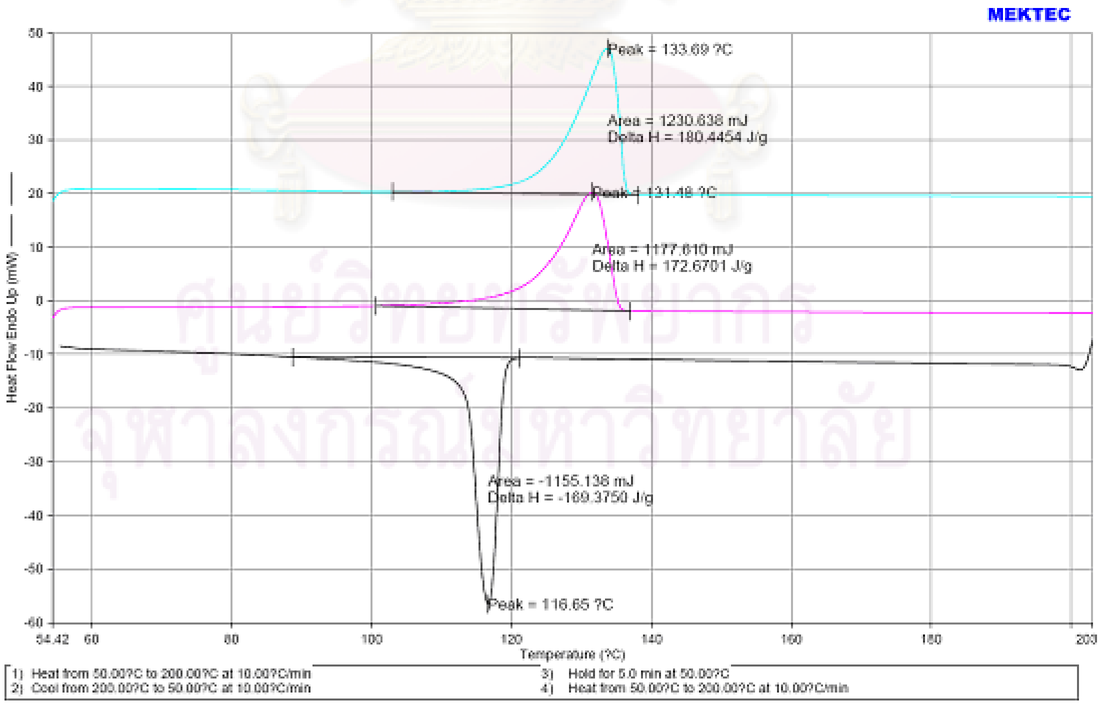

Figure A-26. DSC curve of polyethylene produce from cat-B with [dibutyl ether /Ti] = 10.

APPENDIX B

(Calculation of Polymer Properties)

B.1 Calculation of crystallinity for polymer

The crystallinities of polymers were determined by differential scanning calorimeter. % Crystallinity of polymer is calculated from equation (Liu *et al*., 1997).

$$\chi\ (\%) = \frac{\Delta \boldsymbol{Hm}}{\Delta \boldsymbol{H^{\circ}m}} \times 100$$

Where χ (%) = %crystallinity

$\Delta \boldsymbol{Hm}$ = the heat of fusion of sample (J/g)

$\Delta \boldsymbol{H^{\circ}m}$ = the heat of fusion of perfectly crystalline polyethylene (293 J/g)

APPENDIX C

(The Data of Solution Viscosity)

C-1 The Experimental Data

C-1.1 Polystyrene (PS) Standard-100,000

Initial concentration : 0.1g/50 ml

Solvent : 1,2,4 Trichlorobenzene

Temperature : 150 ^{o}C

Table C-1 The experimental data of 100,000-polystyrene standard

No.	**Conc. (g/100ml)**	**Time (sec)**			
		1	**2**	**3**	**average**
0	0.000	58.78	58.81	58.88	58.82
2	0.025	62.60	62.66	62.41	62.56
3	0.050	63.19	63.15	63.15	63.17
4	0.100	65.47	65.50	65.31	65.43
5	0.200	65.91	65.72	65.91	65.82

No.	**Conc. (g/100ml)**	$\eta_r = t/t_0$	$\eta = \eta_0\eta_r$	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	$\ln \eta_r$	$\ln (\eta_r)/c$	η_{sp}/c
0	0.000	1.000	1.284	0.000	0.000	-	-
2	0.025	1.063	1.366	0.063	0.062	2.461	2.54
3	0.050	1.074	1.379	0.074	0.071	1.426	1.48
4	0.100	1.112	1.428	0.112	0.106	1.064	1.12
5	0.200	1.119	1.437	0.119	0.112	0.562	0.59

C-1.2 Polystyrene (PS) Standard -700,000

Initial concentration : 0.1g/50 ml

Solvent : 1,2,4 Trichlorobenzene

Temperature : 150 ^{o}C

Table C-2 The experimental data of 700,000-polystyrene standard

No.	**Conc. (g/100ml)**	**Time (sec)**			
		1	**2**	**3**	**average**
0	0.000	58.78	58.81	58.88	58.82
2	0.025	63.53	63.66	63.47	63.55
3	0.050	65.37	65.66	65.82	65.62
4	0.100	68.87	68.72	68.69	68.76
5	0.200	69.22	69.15	69.22	69.20

No.	**Conc. (g/100ml)**	$\eta_r = t/t_0$	$\eta = \eta_0\eta_r$	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	$\ln \eta_r$	$\ln (\eta_r)/c$	η_{sp}/c
0	0.000	1.000	1.284	0.000	0.000	-	-
2	0.025	1.080	1.388	0.080	0.077	3.094	3.22
3	0.050	1.115	1.433	0.115	0.109	2.186	2.31
4	0.100	1.169	1.501	0.169	0.156	1.561	1.69
5	0.200	1.176	1.511	0.176	0.162	0.812	0.88

C-1.3 Polyetylene obtained from catalyst A

Initial concentration : 0.1g/50 ml

Solvent : 1,2,4 Trichlorobenzene

Temperature : 150 ^oC

Table C-3 The experimental data of polyethylene from catalyst A

No.	**Conc. (g/100ml)**	**Time (sec)**			
		1	2	3	average
0	0.000	58.78	58.81	58.88	58.82
2	0.025	62.91	62.78	62.78	62.85
3	0.050	67.59	67.2	67.00	67.26
4	0.100	74.47	74.16	74.28	74.30
5	0.200	83.57	83.50	83.50	83.52

No.	**Conc. (g/100ml)**	$\eta_r = t/t_0$	$\eta = \eta_0\eta_r$	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	$\ln \eta_r$	$\ln (\eta_r)/c$	η_{sp}/c
0	0.000	1.000	1.284	0.000	0.000	-	-
2	0.025	1.068	1.372	0.068	0.066	2.645	2.735
3	0.050	1.143	1.469	0.143	0.134	2.682	2.870
4	0.100	1.263	1.622	0.263	0.234	2.336	2.632
5	0.200	1.420	1.824	0.420	0.351	1.753	2.100

C-1.4 Polyetylene from catalyst A with *n*-octanol additive

Initial concentration : 0.1g/50 ml

Solvent : 1,2,4 Trichlorobenzene

Temperature : 150 ^oC

Table C-4 The experimental data of polyethylene from catalyst A with *n*-octanol additive

No.	**Conc. (g/100ml)**	**Time (sec)**			
		1	**2**	**3**	**average**
0	0.000	58.78	58.81	58.88	58.82
2	0.025	62.53	62.56	62.56	62.55
3	0.050	66.41	66.28	66.47	66.39
4	0.100	74.31	74.38	74.31	74.33
5	0.200	93.54	93.53	93.56	93.54

No.	**Conc. (g/100ml)**	$\eta_r = t/t_0$	$\eta = \eta_0\eta_r$	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	$\ln \eta_r$	$\ln (\eta_r)/c$	η_{sp}/c
0	0.000	1.000	1.284	0.000	0.000	-	-
2	0.025	1.063	1.366	0.063	0.061	2.457	2.534
3	0.050	1.129	1.449	0.129	0.121	2.419	2.572
4	0.100	1.264	1.623	0.264	0.234	2.340	2.637
5	0.200	1.590	2.042	0.590	0.464	2.319	2.951

C-1.5 Polyetylene from catalyst A with dibutyl ketone additive

Initial concentration : 0.1g/50 ml

Solvent : 1,2,4 Trichlorobenzene

Temperature : 150 °C

Table C-5 The experimental data of polyethylene from catalyst A with dibutyl ketone additive

No.	**Conc. (g/100ml)**	**Time (sec)**			
		1	**2**	**3**	**average**
0	0.000	58.78	58.81	58.88	58.82
2	0.025	62.22	62.41	62.55	62.39
3	0.050	64.22	64.63	64.44	64.43
4	0.100	68.47	68.56	68.35	68.46
5	0.200	72.59	70.19	70.44	71.07

No.	**Conc. (g/100ml)**	$\eta_r = t/t_0$	$\eta = \eta_0\eta_r$	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	$\ln \eta_r$	$\ln (\eta_r)/c$	η_{sp}/c
0	0.000	1.000	1.284	0.000	0.000	-	-
2	0.025	1.061	1.362	0.061	0.059	2.357	2.428
3	0.050	1.095	1.407	0.095	0.091	1.821	1.906
4	0.100	1.164	1.495	0.164	0.152	1.517	1.638
5	0.200	1.208	1.552	0.208	0.189	0.946	1.041

C-1.6 Polyetylene from catalyst A with heptyl acetate additive

Initial concentration : 0.1g/50 ml

Solvent : 1,2,4 Trichlorobenzene

Temperature : 150 ^{o}C

Table C-6 The experimental data of polyethylene from catalyst A with heptyl acetate additive

No.	**Conc. (g/100ml)**	**Time (sec)**			
		1	**2**	**3**	**average**
0	0.000	58.78	58.81	58.88	58.82
2	0.025	62.35	62.93	62.35	62.54
3	0.050	66.25	66.22	66.25	66.24
4	0.100	73.57	73.78	73.12	73.49
5	0.200	89.34	89.91	89.91	89.72

No.	**Conc. (g/100ml)**	$\eta_r = t/t_0$	$\eta = \eta_0\eta_r$	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	$\ln \eta_r$	$\ln (\eta_r)/c$	η_{sp}/c
0	0.000	1.000	1.284	0.000	0.000	-	-
2	0.025	1.063	1.366	0.063	0.061	2.453	2.530
3	0.050	1.126	1.446	0.126	0.119	2.375	2.522
4	0.100	1.249	1.605	0.249	0.223	2.226	2.493
5	0.200	1.525	1.959	0.525	0.422	2.111	2.626

C-1.7 Polyetylene from catalyst A with dibutyl ether additive

Initial concentration : 0.1g/50 ml

Solvent : 1,2,4 Trichlorobenzene

Temperature : 150 ^{o}C

Table C-7 The experimental data of polyethylene from catalyst A with dibutyl ether additive

No.	**Conc. (g/100ml)**	**Time (sec)**			
		1	**2**	**3**	**average**
0	0.000	58.78	58.81	58.88	58.82
2	0.025	63.28	63.13	63.03	63.15
3	0.050	67.09	67.25	67.65	67.33
4	0.100	73.85	73.5	73.09	73.48
5	0.200	82.50	82.32	82.72	82.51

No.	**Conc. (g/100ml)**	$\eta_r = t/t_0$	$\eta = \eta_0\eta_r$	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	**ln** η_r	**ln** $(\eta_r)/c$	η_{sp}/c
0	0.000	1.000	1.284	0.000	0.000	-	-
2	0.025	1.073	1.379	0.073	0.071	2.837	2.940
3	0.050	1.145	1.470	0.145	0.135	2.701	2.892
4	0.100	1.249	1.604	0.249	0.222	2.225	2.492
5	0.200	1.403	1.802	0.403	0.338	1.692	2.014

C-1.8 Polyetylene obtained from catalyst B

Initial concentration : 0.1g/50 ml

Solvent : 1,2,4 Trichlorobenzene

Temperature : 150 ^{o}C

Table C-8 The experimental data of polyethylene from catalyst B

No.	**Conc. (g/100ml)**	**Time (sec)**			
		1	**2**	**3**	**average**
0	0.000	58.78	58.81	58.88	58.82
2	0.025	62.47	62.87	62.81	62.72
3	0.050	66.62	66.28	66.72	66.54
4	0.100	74.81	74.72	74.00	74.51
5	0.200	86.50	86.53	86.53	86.52

No.	**Conc. (g/100ml)**	$\eta_r = t/t_0$	$\eta = \eta_0\eta_r$	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	**ln** η_r	**ln** $(\eta_r)/c$	η_{sp}/c
0	0.000	1.000	1.284	0.000	0.000	-	-
2	0.025	1.066	1.369	0.066	0.064	2.564	2.647
3	0.050	1.131	1.453	0.131	0.123	2.465	2.624
4	0.100	1.267	1.627	0.267	0.236	2.364	2.667
5	0.200	1.471	1.889	0.471	0.386	1.929	2.354

C-1.9 Polyetylene from catalyst B with dibutyl ether additive

Initial concentration : 0.1g/50 ml

Solvent : 1,2,4 Trichlorobenzene

Temperature : 150 ^{o}C

Table C-9 The experimental data of polyethylene from catalyst B with dibutyl ether additive

No.	Conc. (g/100ml)	Time (sec)			
		1	2	3	average
0	0.000	58.78	58.81	58.88	58.82
2	0.025	62.78	62.69	62.72	62.73
3	0.050	66.25	66.6	66.71	66.52
4	0.100	73.00	73.35	73.66	73.34
5	0.200	83.88	83.69	83.66	83.74

No.	Conc. (g/100ml)	$\eta_r = t/t_0$	$\eta = \eta_0\eta_r$	$\eta_{sp} = (\eta-\eta_0)/\eta_0$	ln η_r	ln $(\eta_r)/c$	η_{sp}/c
0	0.000	1.000	1.284	0.000	0.000	-	-
2	0.025	1.066	1.370	0.066	0.064	2.572	2.657
3	0.050	1.131	1.452	0.131	0.123	2.459	2.617
4	0.100	1.247	1.601	0.247	0.221	2.205	2.467
5	0.200	1.424	1.828	0.424	0.353	1.766	2.118

C-2 Graph information

C-2.1 Polystyrene (PS) Standard-100,000

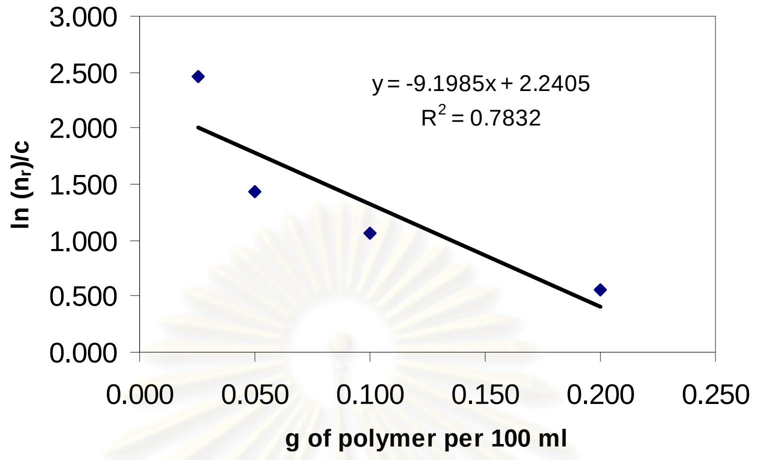

Figure C-1 Intrinsic viscosity of polystyrene-100,000

C-2.2 Polystyrene (PS) Standard -700,000

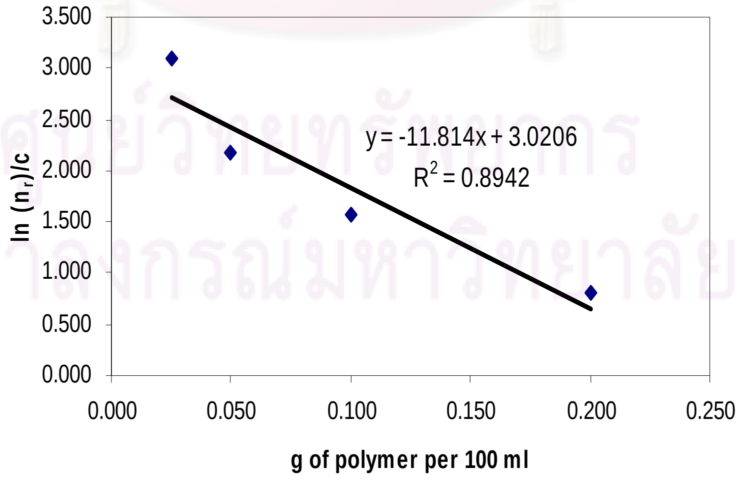

Figure C-2 Intrinsic viscosity of polystyrene-700,000

C-2.3 Polyetylene obtained from cat-A

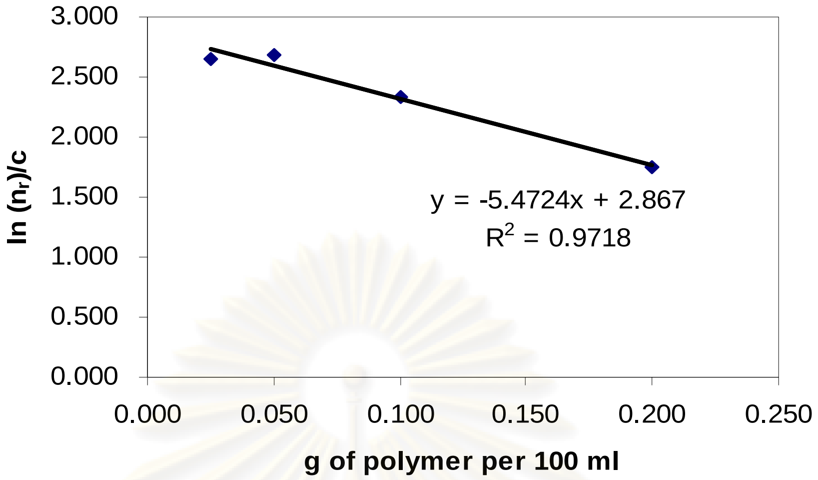

Figure C-3 Intrinsic viscosity of polyetylene obtained from cat-A

C-2.4 Polyetylene from cat-A with *n*-octanol additive

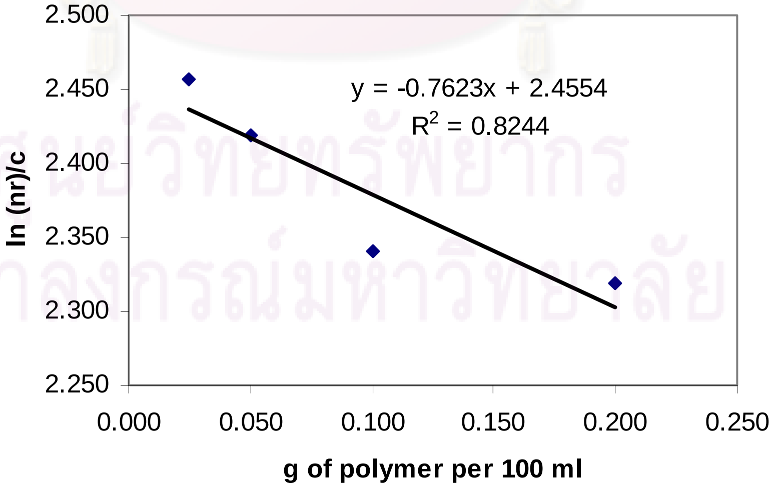

Figure C-4 Intrinsic viscosity of polyetylene obtained from cat-A with *n*-octanol additive

C-2.5 Polyetylene from cat-A with dibutyl ketone additive

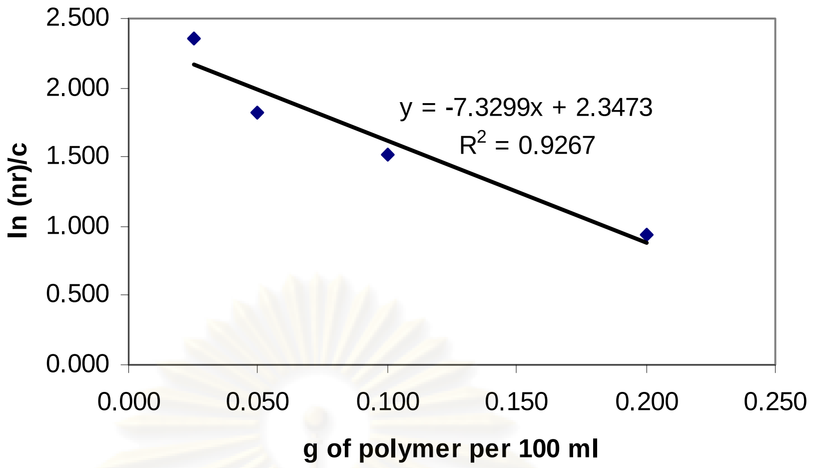

Figure C-5 Intrinsic viscosity of polyetylene obtained from cat-A with dibutyl ketone additive

C-2.6 Polyetylene from cat-A with heptyl acetate additive

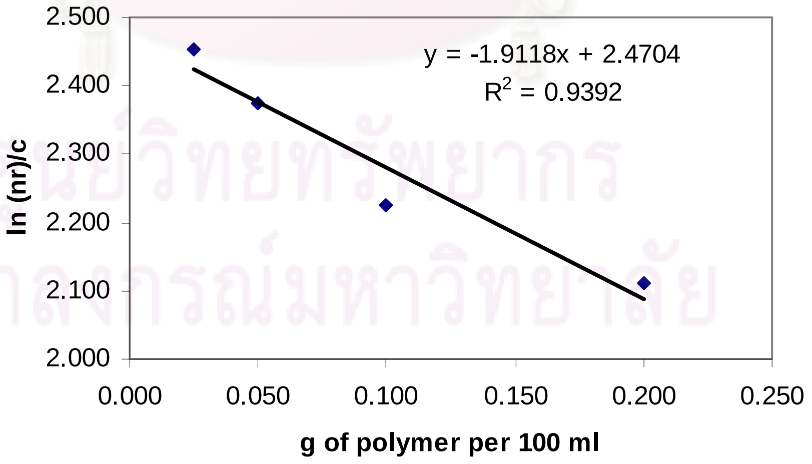

Figure C-6 Intrinsic viscosity of polyetylene obtained from cat-A with heptyl acetate additive

C-2.7 Polyetylene from cat-A with dibutyl ether additive

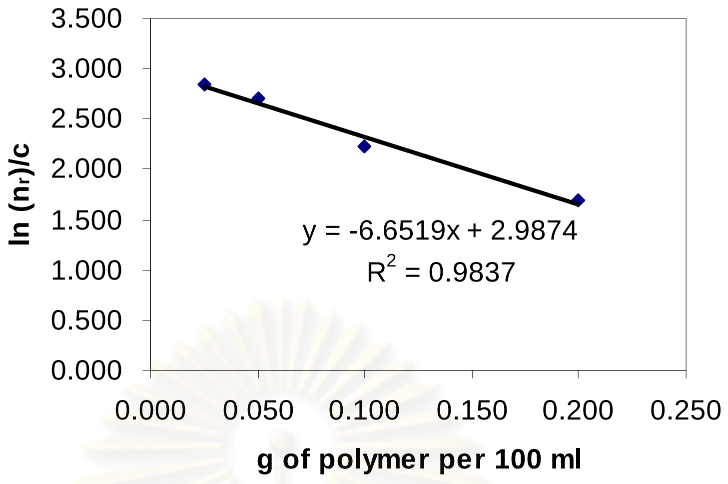

Figure C-7 Intrinsic viscosity of polyetylene obtained from cat-A with dibutyl ether additive

C-2.8 Polyetylene obtained from cat-B

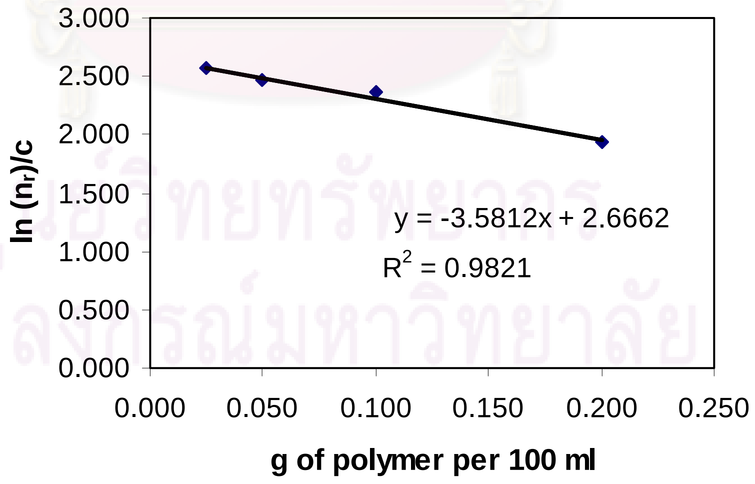

Figure C-8 Intrinsic viscosity of polyetylene obtained from cat-B

C-2.9 Polyetylene from cat-B with dibutyl ether additive

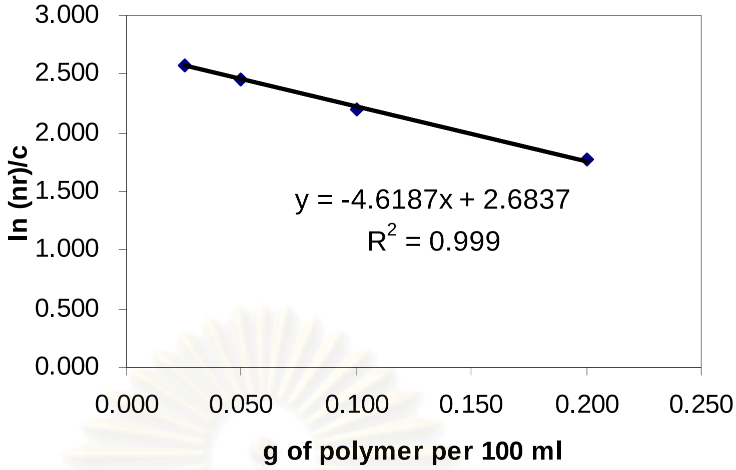

Figure C-9 Intrinsic viscosity of polyetylene obtained from cat-B with dibutyl ether additive

C-3 Calculation of molecular weight (Mw) of polyethylene

In this study, intrinsic viscosity was determined from Kraemer equation (1938)

$$\frac{\ln \eta_r}{c} = [\eta] + k''[\eta]^2 c$$

where k” is constant

ηr is relative viscosity

c is concentration in g/dl

[η] is determined from the extrapolation of $[(\ln \eta r)/c]_{c=0}$ at zero concentration. From plotting between [(ln ηr)/c] and c, the [η] value was determined and shown below:

Table C-10 Intrinsic viscosity and average molecular weight of resulting polyethylene

Sample	**[η]**	**Mw**
PS 100,000	2.240	100,000
PS 700,000	3.020	700,000
Cat-A_none	2.867	498,275
Cat-A_*n*-octanol	2.455	181,586
Cat-A_dibutyl ketone	2.347	135,432
Cat-A_heptyl acetate	2.470	188,934
Cat-A_dibutyl ether	2.987	651,381
Cat-B_none	2.666	310,506
Cat-B_dibutyl ether	2.683	324,023

APPENDIX D

(RATE OF ETHYLENE CONSUMPTION PROFILES)

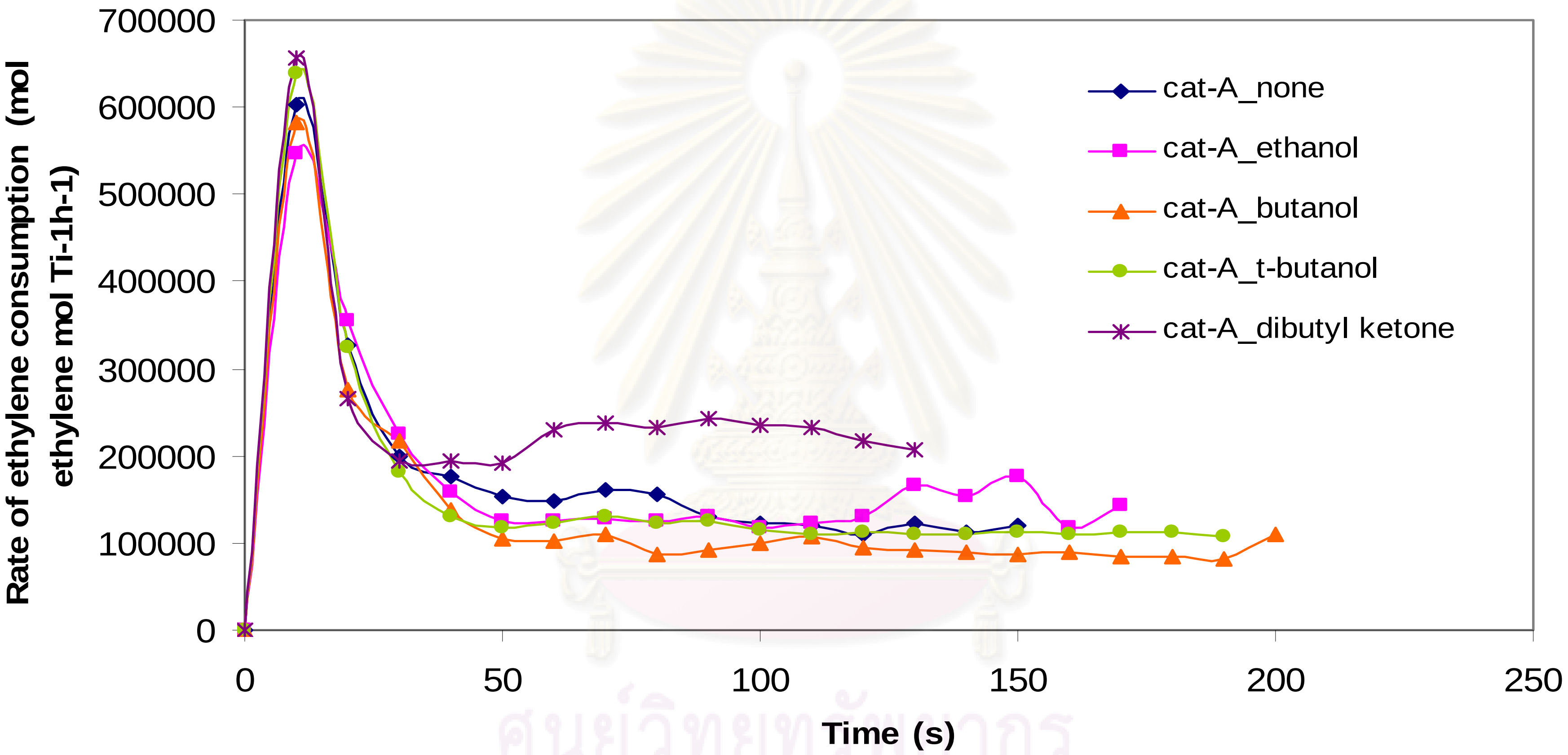

Figure D-1. Rate of ethylene consumption profiles of cat-A with electron donors additive

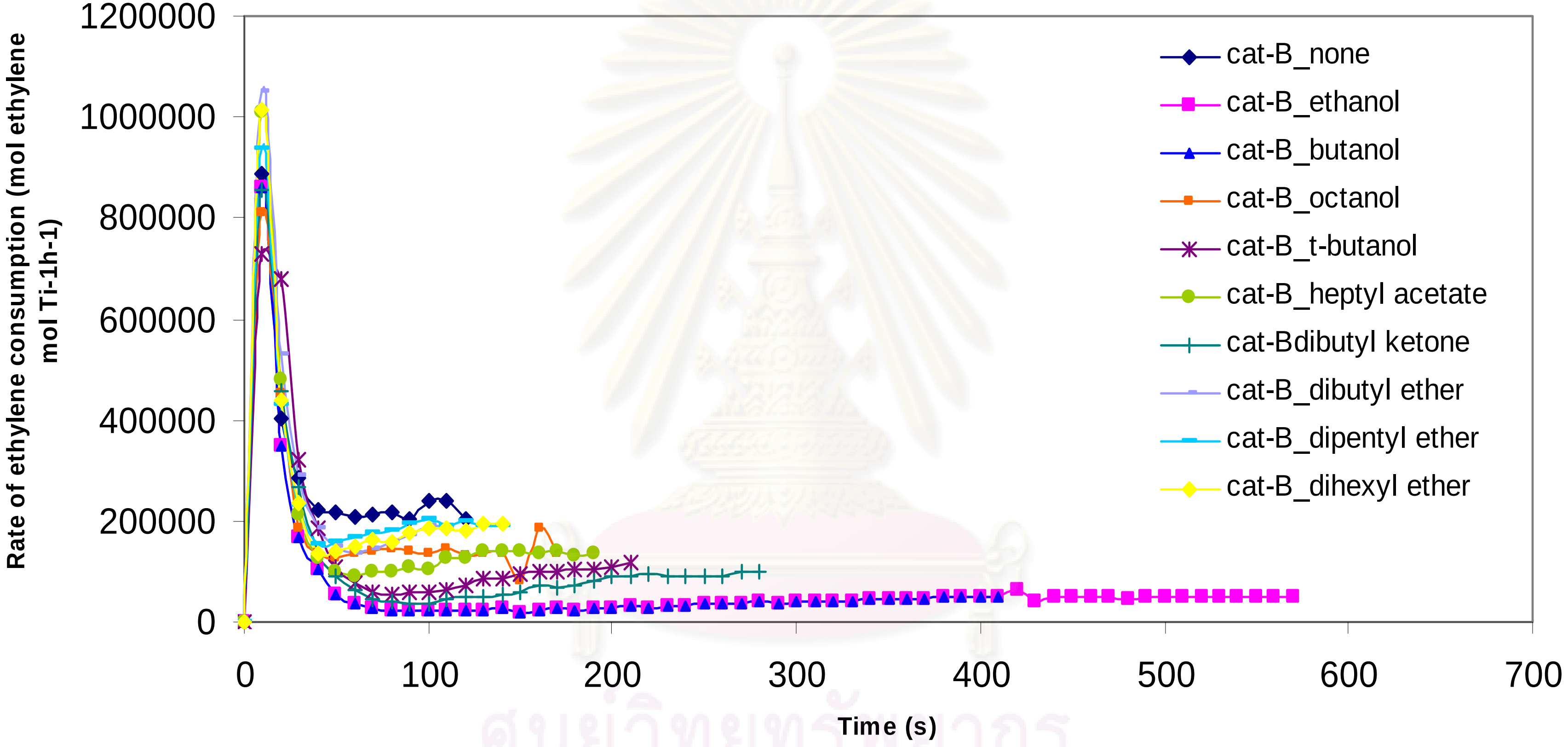

Figure D-2. Rate of ethylene consumption profiles of cat-B with electron donors additive

APPENDIX E
(LIST OF PUBLICATION)

Buajaroen, A.; Praserthdam, P. “Investigation of the poisoning effects on the catalytic activity for the ethylene polymerization” (The Proceeding of 18th Thailand Chemical Engineering and Applied Chemistry Conference, TIChe 2008, Pattaya)

VITA

Miss Anusara Buajaroen was born on May 18, 1985 in Bangkok, Thailand. She received the bachelor’s degree from the Department of Chemical Engineering, Faculty of Engineering, Mahanakorn University of Technology in May, 2007. She continued his Master’s Degree study at Chulalongkorn University in June, 2009.