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ETHYLENE-PROPYLENE-DIENE TERPOLYMERIZATION USING METALLOCENE CATALYSTS

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Field of Study	Chemical Engineering
Thesis Advisor	Professor Piyasan Praserthdam, Dr. Ing.
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จริยา แซ่จาว: เทอร์พอลิเมอไรเซชันของเอทิลีน โพรพิลีนและ ไดอีน โดยใช้ตัวเร่งปฏิกิริยาเมทัลโลซีน (ETHYLENE-PROPYLENE-DIENE TERPOLYMERIZATION USING METALLOCENE CATALYSTS)
อ. ที่ปรึกษา: ศ.ดร. ปิยะสาร ประเสริฐธรรม, อ. ที่ปรึกษาร่วม: Prof. Garry L. Rempel, 148 หน้า ISBN 974-17-1554-4

งานวิจัยนี้ได้ศึกษาการพอลิเมอไรเซชันเอทิลีน และ โพรพิลีน โดยตัวเร่งปฏิกิริยาเมทัลโลซีนชนิดต่างๆ ในเครื่องปฏิกรณ์ 3 ชนิดได้แก่ ชนิดไม่มีสายป้อน (batch) ชนิดมีสายป้อนแก๊สเข้าสายเดียว (semibatch) และชนิดป้อนแก๊สเข้าและออกที่อัตราการไหลคงที่ (continuous gas flow) ได้รวบรวมผลของภาวะการพอลิเมอไรเซชันของโพรพิลีน กล่าวคือ ความเข้มข้นของตัวเร่งปฏิกิริยา ปริมาณตัวเร่งปฏิกิริยาร่วม และอุณหภูมิในการทำปฏิกิริยา จากการทดลองทำเทอร์พอลิเมอไรเซชันของเอทิลีน โพรพิลีนและ ไดอีน พบว่าตัวเร่งปฏิกิริยา เอทิลีนบิส(อินดีนิล)เซอร์โคเนียมไดคลอไรด์ให้ความว่องไวสูงที่สุด พบปรากฏการณ์การเพิ่มขึ้นของความว่องไวจากการเติมโคโมโนเมอร์กับตัวเร่งปฏิกิริยาชนิดนี้ เมื่อเปรียบเทียบชนิดของไดอีน 3 ชนิดคือ ENB, HD และ VCH ไม่พบความแตกต่างของความว่องไวในการเกิดปฏิกิริยา การเติมไดอีนให้ทั้งผลดีและผลเสียต่อความว่องไวโดยเร่งปฏิกิริยาการต่อสายโซ่พอลิเมอร์ และ การเสื่อมสภาพของตัวเร่งปฏิกิริยา จากผลการทดลองพบว่าการลดลงของความว่องไวเมื่อเติมไดอีนเห็นได้ชัดเมื่อการพอลิเมอไรเซชันทำที่ความดันต่ำ ในระบบที่ใช้ซิลิกาเป็นตัวรองรับพบการเพิ่มขึ้นของความว่องไวเมื่อเติมไตรเมทิลอลูมินัม (TMA) และ เมทิลอะลูมินอกเซน (MAO) โดยไตรเมทิลอลูมินัมน่าจะเป็นตัวกำจัดสิ่งปนเปื้อน (impurities) ในระบบในขณะที่เมทิลอะลูมินอกเซนทำหน้าที่เป็นตัวเร่งปฏิกิริยาร่วมในการเกิดหมู่ว่องไว (active species) ผลของ TMA และ MAO ต่อน้ำหนักโมเลกุลเฉลี่ยของโคพอลิเมอร์มีเพียงเล็กน้อยแสดงว่าการเกิด chain transfer ไปยังอัลคิลอลูมินัมไม่ใช่ปฏิกิริยา chain transfer หลักของระบบตัวเร่งปฏิกิริยานี้ การเติมตัวเร่งปฏิกิริยาเมทัลโลซีนในเครื่องปฏิกรณ์โดยตรงให้ความว่องไวที่สูงกว่าจึงเป็นอีกวิธีการหนึ่งที่น่าสนใจสำหรับการทำปฏิกิริยาแบบมีตัวรองรับ เมื่อทำการปรับปรุงตัวรองรับด้วยซิลิกอนเตตระคลอไรด์พบว่าให้ความว่องไวที่สูงขึ้น โดยโคพอลิเมอร์ที่ได้มีน้ำหนักโมเลกุลเฉลี่ยต่ำลง แต่ไม่พบความเปลี่ยนแปลงของการจัดเรียงโครงสร้างในสายโซ่พอลิเมอร์

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KEY WORD: metallocene catalyst / silica supported / copolymerization / methylaluminoxane

CHARIYA CHAO: ETHYLENE-PROPYLENE-DIENE TERPOLYMERIZATION USING METALLOCENE CATALYSTS
THESIS ADVISOR: PROF. PIYASAN PRASERTHDAM, Dr.Ing.,
THESIS COADVISOR: PROF. GARRY L. REMPEL, Ph.D. 148 pp. ISBN 974-17-1554-4

Ethylene and propylene homopolymerization were carried out using different metallocene catalysts in three types of reactor systems i.e. semibatch, batch, and continuous gas flow system. Effects of reaction conditions i.e. catalyst concentration, $[Al]_{MAO}/[Metal]$ ratio, reaction temperature in propylene polymerization are summarized. The ansa-metallocene catalyst $Et[Ind]_2ZrCl_2$ showed the highest activity in ethylene/propylene/diene terpolymerization among the commercially available metallocene catalysts chosen. Rate enhancement from the comonomer addition or so-called comonomer effect was observed in this metallocene catalyst system. No significant effect of the types of diene i.e. ENB, HD, VCH on the activity was observed. Diene addition has both positive and negative effect on the catalytic activity by enhancing the propagation reaction or promoting the deactivation process. More adverse effect was observed in the reaction carried out under lower pressure. In silica-supported system, effect on activity of MAO was more obvious than TMA. TMA may be useful as a scavenger while MAO is required in forming the active species. An increase of TMA and MAO in the system reduced Mw only slightly; this suggested that chain transfer to alkylaluminum is not the major chain transfer reaction for this copolymerization system. In-situ supported system, in which the metallocene catalyst was injected directly to the reactor, exhibit higher activity than preformed supported system without effect on the copolymer properties suggesting another promising heterogeneous process. The modification of silica with silicon tetrachloride increased the copolymerization activity. The copolymer produced had lower molecular weight but no significant effect on the microstructure of the copolymer chain was observed.

Department…..Chemical Engineering …. Student's signature…………………………
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NOMENCLATURE

CGC-Ti	Constrained geometry titanium catalyst
ENB	5-Ethylidene-2-norbornene
EP	Ethylene/propylene copolymer
EPDM	Ethylene/propylene/diene terpolymer
EH	Ethylene/1-hexene copolymer
HD	1,4 Hexadiene
MAO	Methylaluminoxane
Mn	Number average molecular weight
Mw	Weight average molecular weight
MWD	Molecular weight distribution, = Mw/Mn
n/d	Not determined
P	Pressure
T	(polymerization) temperature
Tg	Glass transition temperature
Tm	Melting temperature
TMA	Trimethylaluminum
VCH	4-Vinyl-1-cyclohexene
i-Bu$_3$Al	Triisobutylaluminum
Oct$_3$Al	Trioctylaluminum
Me$_3$Al	Trimethylaluminum
Et$_3$Al	Triethylaluminum
TIBA	Triisobutylaluminum

CHAPTER I

INTRODUCTION

Group 4 metallocenes with methylaluminoxane as cocatalyst form well defined active species for olefin polymerization. Their single site character combined with the possibility to vary their polymerization behaviour by tuning the ligand structure caused an enormous interest in the scientific community as well as in industry (Scheirs and Kaminsky, 2000). Depending on the metallocene ligands and symmetry, these catalysts permit a strong control of the regio- and stereoregularities and of the molecular weight distribution (MWD) of homopolymers with higher activity.

Propylene polymers containing small amounts of ethylene exhibit lower crystallinity and higher impact strength than isotactic homopolypropylene. Copolymerization of propylene with larger amounts of ethylene or their terpolymerization together with 0.1-5.0 wt% of dienes as third monomers results in amorphous rubbery materials, a rapidly growing class of elastomers, referred as EPDM. Copolymers of ethylene and propylene are of great industrial interest especially in the automotive industry (e.g., hoses, gaskets, wipers, bumpers, belts) and in the housing industry (roofing). Because there is no double bond in the backbone of the polymer chain, EPDM is not very sensitive to oxygen and ozone, as well as to acids and alkalis. Amorphous ethylene-propylene copolymers are widely used as impact-strength modifiers in blends with isotactic polypropylene.

In most technical processes for the production of EPDM rubbers, soluble or highly dispersed vanadium compounds, such as $V(acac)_3$ [acac = acetylacetonate], $VOCl_3$, $VO(OR)_3$, cocatalyzed by alkylaluminum chloride in the presence of organic halogen promoters, have been used. One inconvenience of this metal is that the residual vanadium content in the polymer must not exceed 10 ppm to avoid coloring, aging, and toxicity. Moreover, these vanadium-based systems present a drastic catalyst productivity loss in the presence of dienes, besides chain branching and crosslinking in the course of the terpolymerization.

The EPDM worldwide production based on vanadium catalyst systems is presently about 6.5×10^5 tons/year. A projection for metallocenes catalyzed EPDM demand will be 5.0×10^5 tons/year within 10 years. This value, although small, is significant for this product and illustrates that metallocenes are facilitating the penetration of hydrocarbon polymers into areas currently served by high-cost engineering thermoplastics (M.C.Haag 1999).

The key feature of metallocenes that marks a dramatic change with respect to the traditional vanadium catalysis and, actually, to the whole past state of the art is the nature of the catalytic centers. The active species characterized not only by the high homogeneous nature but also, most of all, by the presence of π- ligands of defined chemical structure that remain coordinated to the transition metal atom during the course of the polymerization. This allows one to steer the behavior of the copolymerization and the characteristics of the copolymer by playing with the structure of the ligands.

A commercially useful zirconocene catalyst system should possess the following attributes: (a) high activity and efficient incorporation of diene; (b) random distribution of monomers; (c) good control of molecular weight and molecular weight distribution; (d) low tendency to side reactions (branching or cyclization of the diene). Furthermore, for commercial applications, metallocene catalysts should be immobilized so that they can be used for 'drop-in' technology. It is desireable to immobilize metallocene catalysts on supports to replace the conventional Ziegler-Natta catalysts used in industrial slurry and gas phase processes.

Methods for immobilizing metallocenes fall largely into two categories: (1) MAO-mediated systems, in which impregnation of the support with MAO is followed by addition of a metallocene catalyst, and (2) directly impregnated metallocene onto the support (Chien, 1999; Kaminsky and Winkelbach, 1999; Kristen, 1999; Santos *et al.*,2000). In general, supported metallocenes have a lower catalytic activity than their corresponding homogeneous metallocene systems.

The objective of this study is to investigate the effect of the reaction conditions on the activity of metallocene catalysts in ethylene/ propylene and diene terpolymerization.

In Chapter II, some of background knowledge and reports about the metallocene catalyst system are provided. The literature review is separated into three parts i.e. metallocene catalysts, ethylene/propylene/diene terpolymerization, and the heterogeneous system.

The experimental procedure as well as the instrument and the reactor systems used in this work are described in Chapter III. Because of the highly air-sensitive nature of these compounds, special equipment and methods are required in order to get the reproducible results.

In Chapter IV, the types of reactor system i.e. a semibatch low-pressure polymerization system equipped with the gas uptake monitoring system, a batch system, and a continuous gas flow system, for use in polymerization are discussed. Effects of various reaction conditions and the types of metallocene catalysts on the activity in ethylene and propylene homopolymerization are summarized.

Copolymerization of ethylene and propylene was carried out in continuous gas flow system and batch system using homogeneous metallocene catalysts. Results of the variation in ethylene/propylene feed ratio and types of metallocenes are presented in Chapter V. Results of EPDM terpolymerization using different types of diene are investigated in Chapter VI. Activities of different types of metallocene catalyst and initial ethylene/propylene ratio are also illustrated.

Ethylene/propylene copolymerization with the heterogeneous system, using silica as support, was investigated (Chapter VII). The effect of TMA and MAO on the activity and the copolymer properties using different supporting procedure i.e. the preformed SiO_2/MAO supported Et[Ind]$_2$ZrCl$_2$, and in-situ SiO_2/MAO supported Et [Ind]$_2$ZrCl$_2$ was studied. In Chapter VIII, modification of SiO_2 by $SiCl_4$ prior to MAO impregnation was attempted in ethylene/propylene copolymerization.

Finally, conclusions of this work and some remarks for the future research work are provided in Chapter IX.

CHAPTER II

LITERATURE REVIEW

2.1. Metallocene Catalysts

The first catalytic studies of metallocene complexes provided detail information on the ability of Cp_2TiCl_2/ DEAC and Cp_2TiCl_2/ TEA to polymerize ethylene (Natta *et al.*, 1957). Due to their marginal activity and inability to polymerize propylene, these systems received little attention. However, since the advent of polymethylalumoxane (MAO) as a cocatalyst in 1980, they have found renewed interest (Sinn and Kaminsky, 1980). Dramatic improvements in activity along with the discovery of stereospecific metallocene systems have fueled an intense research effort in the field. The proposed mechanism of metallocene-catalyzed polymerization is shown in Figure 2.1.

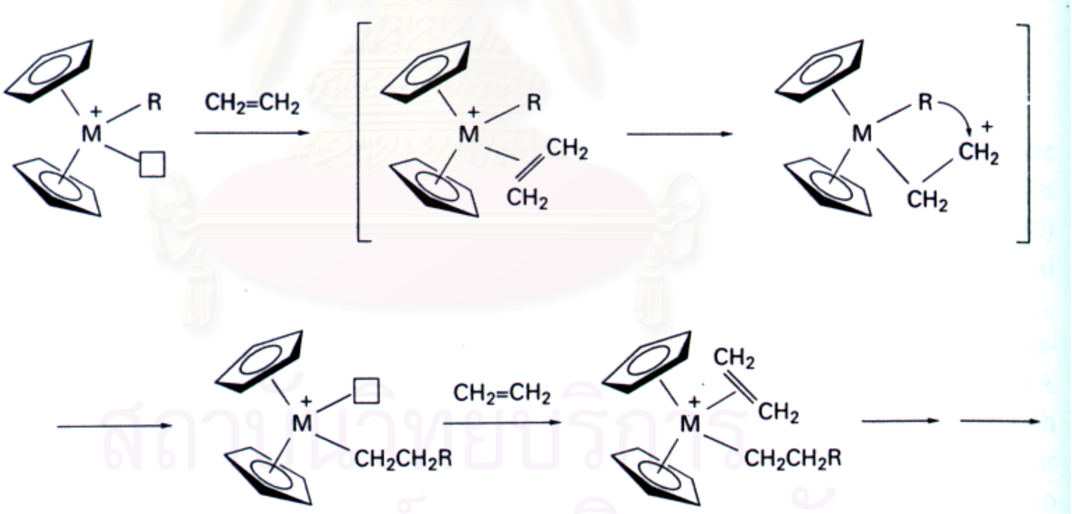


Figure 2.1. The mechanism of olefin polymerization using metallocene catalysts. (Long, 1998)

2.1.1. ‘Tailoring’ of metallocene catalysts

Extensive research has been devoted towards ‘catalytic tailoring’, via the ligand modification of the catalyst system. This leads to the specific changes in the catalytic activity and properties of the product. The important factors affecting catalytic performance are as follows:

(a) Transition metal-olefin interaction. The olefin has a Lewis basic character with respect to the metal and therefore acts as an electron donor. The σ- and π-bonds formed between the metal and olefin destabilize and activate the olefin for insertion into the polymer propagating chain. Olefin co-ordination also destabilizes the M-R (R=alkyl) bond. The stability of olefin co-ordination to M decreases with increasing olefin size.

(b) Metal-alkyl bond stability. Fine adjustment of the M-R bond is possible by variation of ligand electronic effects. The M-R bond should be relatively weak to permit facile opening and olefin insertion to form a new metal-alkyl bond but also strong enough to favor catalytic lifetimes. The strength of this bond depends on R itself and the stability decreases in the order Me> Et> $(CH_2)_nCH_3$. Olefin co-ordination is also another method of weakening the M-R bond in preparation for migratory insertion.

(c) Influence of other ligands. Considering the Cp rings and substituents attached to them, then if the ligand system used is a good electron donor it will reduce the positive charge on the metal. This weakens the bonding between the metal and all other ligands, particularly the already relatively weak M-R bond, making insertion more facile. Conversely, this will also stabilize high oxidation state complexes and make co-ordination of the incoming olefin more unfavorable and so a balance must be found between these effects.

(d) Steric effects of the other ligands. Bulky ligands will aid stereospecific olefin co-ordination and polymerization (Figure 2.2.). Steric effects influence the position of bulky monomers when coordinated with the metal center therefore the stereospecific insertion can be obtained throughout the polymerization time. The coordination site can be opened or closed by controlling the angle that the cyclopentadienyl rings tilt away from each other. Shortening or lengthening the bridge in ansa-metallocenes can lead to much improved monomeric stereoselectivity (Long, 1998).

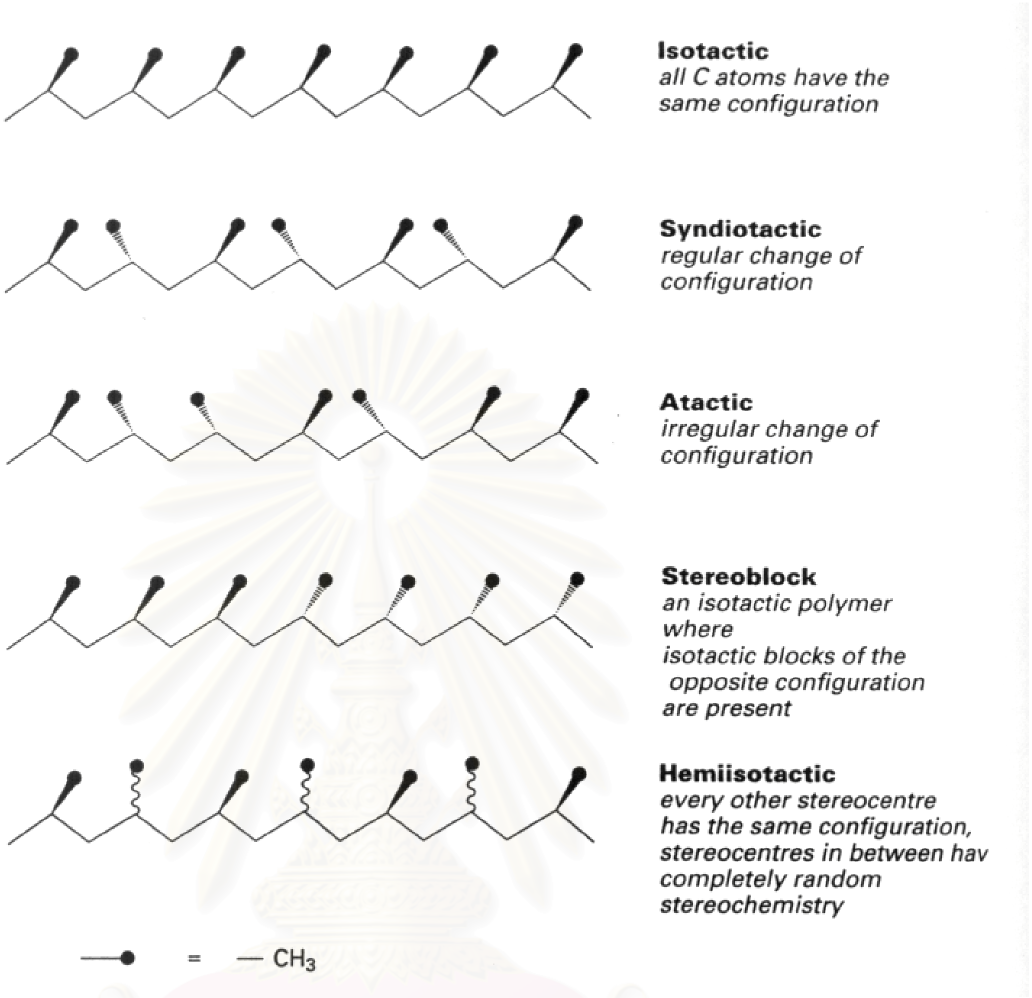


Figure 2.2. Different types of polymer tacticity. (Long, 1998)

2.1.2. Isotactic polymers using metallocene catalysts

The modification of group 4 metallocenes to produce catalysts capable of isospecific polymerization developed slowly however dramatic successes were reported in the mid-1980s. Prior to this time, catalysts using achiral [Cp_2MCl_2] systems could only produce atactic polypropylene. Then Ewen (1984) reported the use of metallocene-based catalysts for the isospecific polymerization of propylene using Brintzinger chiral ansa-metallocenes. It was shown that using a combination of meso and racemic ansa-metallocenes, a mixture of atactic and isotactic polymer chains were produced and soon it was recognized that the isotacticity of the polymer was directly related to the chirality of the metallocene that produced it. This was confirmed when isotactic polypropylene was formed using an isomerically pure sample of a chiral zirconocene analogue.

Corradini has carried out studies on conformational modeling and found that the polymer chain is forced into an open region of the metallocene thus relaying the chirality of the metallocene to the incoming monomer through the orientation of the β-carbon of the alkyl chain (Corradini *et al.*, 1995). These chiral metallocenes have C_2 symmetry with both possible reaction sites being homotropic and therefore selective for the same alkene enantioface. The result is a polymerization reaction that yields an isotactic polyalkene (Figure 2.3).

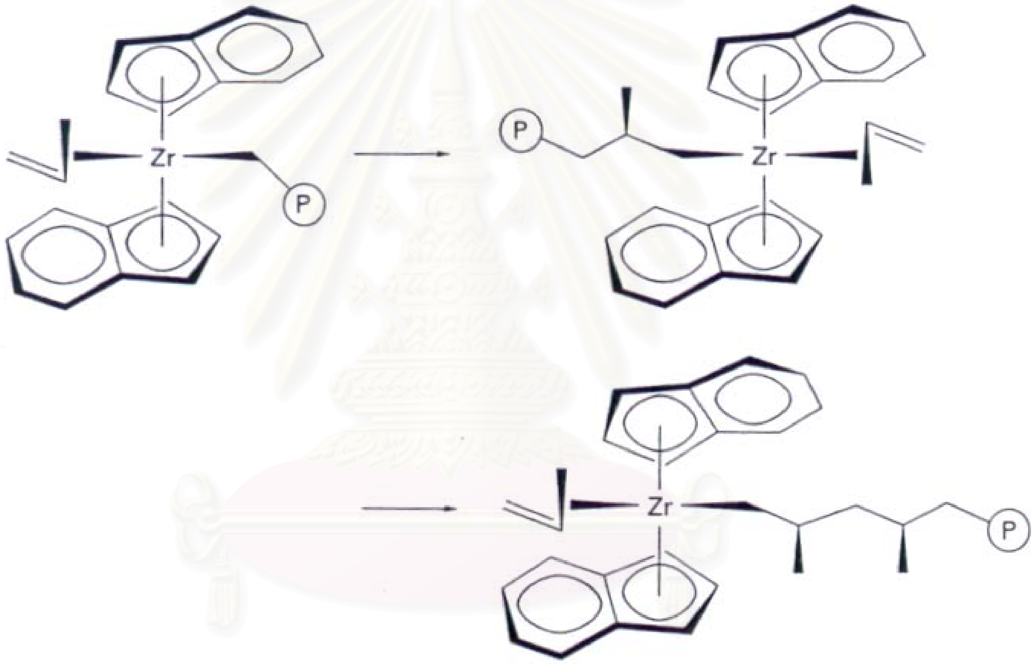


Figure 2.3. The production of isotactic polymers using chiral metallocene catalysts. (Long, 1998)

2.1.3. Syndiotactic polymers using metallocene catalysts

The first case of production of a syndiotactic polymer came in 1962 when Natta and Zambelli reported a heterogeneous vanadium-based catalyst mixture, which produced partially syndiotactic polypropylene. In 1988, Ewen reported the use of zirconium metallocene catalysts to bring about the syndiospecific polymerization of propylene and higher aliphatic α-alkenes. The regularly alternating insertion of alkenes at the heterotropic sites of the C_s-symmetric (achiral) Zr complex results in the formation of a syndiotactic polymer. There is a chance of defect incorporation, as with isospecific C_2-symmetric catalysts through occasional mis-insertion of the incorrect enantioface (Figure 2.4.). The syndiotactic polymer was more transparent than isotactic polypropylene but less stiff.

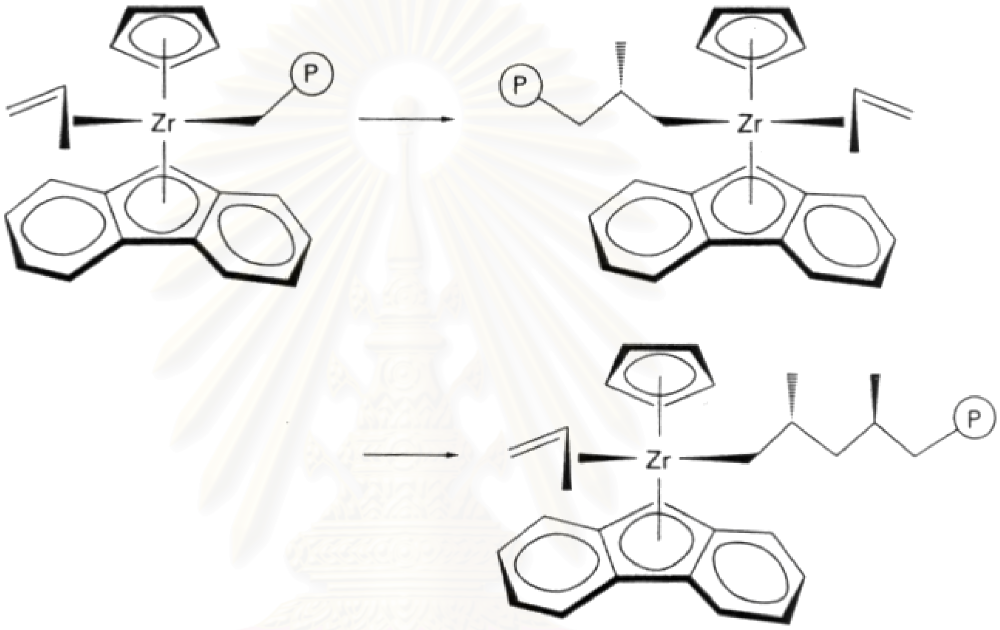
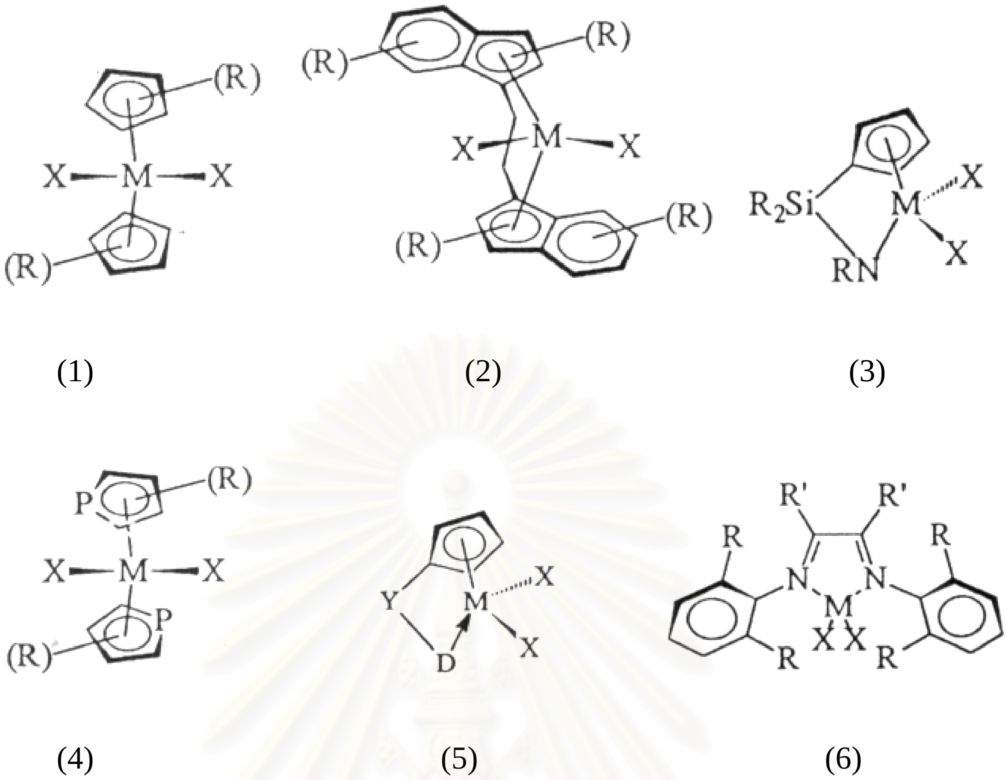


Figure 2.4. The production of a syndiotactic polymer using zirconocene catalysts. (Long, 1998)

2.1.4. Single-Center Catalysts

The demonstrated potential of the metallocene/MAO system has paved the way to the discovery of many other organometallic complexes suitable for olefin polymerization. They are represented in Figure 2.5.



(1) (2) (3)

(4) (5) (6)

Figure 2.5. Organometallic complexes employed in olefin polymerization. (Scheirs, 1999, p.310)

The catalytic systems based on these complexes are: (1) single-center i.e. the catalytic centers responsible for the chain propagation have the same nature, (2) soluble in most aliphatic and aromatic solvents and, nevertheless, active also in liquid monomers and in the gas phase and (3) in many cases endowed with high catalytic activity. Furthermore, (4) the organometallic complexes have a well-defined chemical structure and (5) the π ligands remain coordinated to the transition metal atom during the course of the polymerization.

Nowadays, all these families of single-center catalysts are used for the preparation of polyolefins, to a different extent also on the industrial scale. As far as the performances of the single-center catalysts are concerned, it is possible to say that (1) only metallocenes are, at present, mature catalysts for the synthesis of stereoregular polyolefins and (2) any of the single-center catalysts can be in principle suitable for preparing ethylene-based homo- and copolymers. In fact, in this case the catalyst need not necessarily be stereospecific. This explains the wide application of complexes other than metallocenes e.g. (3) and (5) in Figure 2.5., for the preparation of ethylene-based polymers, from HDPE (high-density polyethylene) to EP(D)M (elastomeric copolymers of ethylene and propylene with a diene).

2.1.5. Cocatalytic Systems for Metallocene-Based Catalysis (MBC)

Cocatalyst alternatives to MAO have appeared on the scene and have been proved able to promote the homo- and copolymerization of ethylene and 1-olefins, e.g., in the first instance, boron containing compounds (Hlatky, 1989). Montell scientists have discovered and developed cocatalysts based on AlR_3 and H_2O (Resconi *et al.*, 1993). They can be prepared and isolated as a tetraalkylalumoxane or can be formed in situ, during the process, adopting a suitable Al: H_2O ratio.

In the scientific literature, the performances of different metallocenes are usually compared adopting MAO-based polymerization tests. As a consequence, any difference, for example, as far as the catalytic activity, is completely attributed to the structure of the metallocene. Different aluminum-based cocatalysts give rise to different catalytic activities and an MAO-based system is not necessarily the most active one. This suggests the need for the new approach to the evaluation of the metallocene-based results.

Several comprehensive reviews about metallocene catalysts have been published (Alt and Koppl, 2000; Brintzinger *et al.*, 1995; Chen and Marks, 2000; Coates, 2000; Fink *et al.*, 2000; Gupta *et al.*, 1994; Hamielec and Soares, 1996; Hlatky, 1999; Hlatky, 2000; Huang and Rempel, 1995; Kaminsky, 1996; Kaminsky, 1999; Keii and Soga, 1990; Long, 1998; Olabisi *et al.*, 1997; Reddy and Sivaram, 1995; Scheirs and Kaminsky, 1999; Soga and Shiono, 1997).

2.2. Ethylene/ Propylene/ Diene terpolymerization

Propylene polymers containing small amounts of ethylene exhibit lower crystallinity and higher impact strength than isotactic homopolypropylene. Copolymerization of propylene with larger amounts of ethylene or their terpolymerization with 0.1-5.0 wt% of dienes as third monomers results in amorphous rubbery materials, a rapidly growing class of elastomers. The family of ethylene, propylene and diene terpolymers, referred as EPDM, possesses certain outstanding properties not shared by other types of elastomers. The ethylene-propylene-diene (EPDM) elastomers present excellent physical, mechanical, and chemical properties that guarantee a wide range of applications especially in the automotive industry (e.g., hoses, gaskets, wipers, bumpers, belts) and in the housing industry (roofing). Because there are no double bonds in the backbone of the polymer chain, EPDM is not very sensitive to attack by oxygen and ozone, as well as to acids and alkalis. Other excellent properties of this rubber are its high and low temperature performance. Some very recent applications comprehend its use in composites and in blends with polyolefins, with carboxylated nitrile rubbers, and in microcellular rubbers.

The incorporation of a small percentage of ethylenic unsaturations (introduced by a diene termonomer) provides reactive sites, which allow curing by peroxides or sulfur derivatives. The necessary amount for subsequent vulcanization are 2-3 mol% (0.1-5.0 wt%). The production of EPDM grades can be modulated, among other parameters (monomer ratio, reaction temperature, catalyst precursor, catalysts and cocatalysts), by the proper choice of the diene, as well as by its relative concentration. EPDM materials available from industry are mostly based on 2-ethylidenebi-cyclo [2.2.1]hept-5-ene (ENB), the preferred cyclic termonomer, or 1,4 hexadiene. For both technical and economical reasons, these termonomers are incorporated in ethylene/propylene chains only in very low concentration (<2 mol%) (Haag *et al.*, 2000).

The properties and performance of an olefin copolymer are determined by the comonomer content and, most importantly, by the comonomer distribution within and between single polymer chains. An amorphous polymer results if the comonomers are distributed randomly, whereas crystalline polymers could be obtained when the monomers are segregated into long sequences.

The search for new catalysts for the EPDM synthesis is primarily motivated by the low activities of the conventional systems compared with those of HDPE and PP syntheses. Some vanadium catalysts have the disadvantage to form more than one active center, thus leading to a broad molecular weight distribution. Another problem is that all vanadium compounds are toxic, thus restricting application of the products in certain applications, e.g. medicine.

2.2.1. Traditional Ziegler-Natta Technology

2.2.1.1. Vanadium catalysts

In most technical processes for the production of EPDM rubbers, soluble or highly dispersed vanadium compounds, such as $V(acac)_3$ [acac = acetylacetonate], $VOCl_3$, $VO(OR)_3$, cocatalyzed by alkylaluminum chloride in the presence of organic halogen promoters, have been used (Haag *et al.*, 1999). With perhaps exception to the metallocenes systems, these Ziegler-Natta complexes demonstrate superior monomer sequencing and diene incorporation. They are capable of high molecular weights and respond well to modifiers when in the presence of chlorinated activators.

One inconvenience of this metal is that the residual vanadium content in the polymer must not exceed 10 ppm to avoid coloring, aging, and toxicity (Datta *et al.*, 1996). Moreover, these vanadium-based systems present a drastic catalyst productivity loss in the presence of dienes, besides chain branching and crosslinking in the course of the terpolymerization (Soga *et al.*, 1989). At elevated temperatures, vanadium systems demonstrate undesirable activity and a rapid, second order deactivation. In addition to these facts, even an organoaluminum cocatalyst is capable of reducing the active V(III) species to an inactive V(II) one. Accordingly, successful developments in vanadium technology have centered not on ligand design but on new chlorinated additives to enhance the stability and number of active sites. Concerning this aspect, the immobilization of such vanadium complexes on various solids was recently shown to increase the resistance to reduction by aluminum cocatalysts (Czaja and Bialek, 1998).

The kinetic model of EPDM terpolymerization using $VOCl_3$-$Al_2Et_3Cl_3$, and 2-ethylidenebicyclo[2.2.1] hept-5-ene (ENB) as diene was developed by Haag *et al.* (1998). At the Al/V ratios lower than 2, no reaction occurred whereas between 2 and 8, yield increases until it reaches a plateau for ratio over 8. Increase in Al/V ratio from 8.5 to 15.0 leads to a decrease of Mw due to the increase in alkyl aluminum transfer reaction. Increase of diene concentration resulted in the decrease of reaction yield. Glass transition temperature (Tg) is practically constant, except for very high diene concentration where Tg value becomes higher because of branching. Polydispersity changes from 3.8 to 30.0 with the increase in diene concentration. V/C and Al/V ratios in EPDM films, prepared with $VOCl_3/Al_2Et_3Cl_3$ catalyst at various Al/V ratios and diene concentrations, were determined by Rutherford backscattering spectrometry (Haag *et al.*, 1998). It was reported that Al/V molar ratio in the terpolymers is roughly constant independent of the initial Al/V molar ratio in the reaction mixture. However, the amount of V increased while Al/V ratio constant leads to the conclusion that Al remains coordinated to V in the terpolymer. Haag *et al.* (1999) also produced EPDM with the $Et(Ind)_2ZrCl_2$/ MAO catalyst system. Metallocene catalyst gave higher activity, lower Mw, narrower MWD, and the highest activity guaranteed lower residual metal content (10^{-5} Zr/C, 10^{-4} V/C). Only about 4% of MAO remained in the polymer (Al/Zr = 3000) while in the case of vanadium-based, all the Al remained in the polymer.

2.2.1.2 Titanium catalysts

The use of titanium chlorides is in large part limited to the synthesis of various grades of polyethylene and polypropylene. Copolymerizations employing this technology therefore use relatively little comonomer and are designed to modify homopolymer properties such as impact strength or low temperature behavior. Their lack of utility for elastomeric EPDM is due to difficulty in uniformly incorporating dienes and their propensity for creating a blocky, semi-crystalline comonomer structure (Busico *et al.*, 1985; Avella *et al.*, 1986). Cure efficiencies are therefore inferior to standard vanadium catalysts. However, the $TiCl_3$ and $MgCl_2$/ $TiCl_4$

systems, with their superior activity and stability at high temperatures, could substantially reduce the cost of EPDM production (Corbelli *et al.*, 1981).

2.2.2. Metallocene Catalyzed EPDM Polymerization

Several properties of metallocenes are of interest to EPDM production. Notably, their unique activity could allow metal loadings to be reduced to the degree that recovery is not required. Production costs may be further reduced by operating at temperatures at which vanadium catalysts deactivate excessively. Metallocene catalyzed terpolymerizations produce narrow chemical composition and molecular weight distributions and monomer sequencing that is equal or superior to that created by industrial catalysts.

From a commercial standpoint, molecular structure is the primary variable governing the crystallinity, mechanical properties and oxidative stability of EPDM. To produce useful elastomer therefore places demands on a potential catalyst in regard to monomer incorporation. In the first place, the degree of monomer insertion must be flexible enough to produce a variety of compositions. Irrespective to this target composition, the sequencing of monomer within the polymer chain must be sufficiently random so as to minimize ethylene crystallization. In addition, the diene must be incorporated uniformly to ensure efficient curing behavior and show low tendency to side reactions (branching or cyclization of the diene).

The key feature of metallocenes that marks a dramatic change with respect to the traditional vanadium catalysis and, actually, to the whole past state of the art is thus the nature of the catalytic centers, characterized not only by the high homogeneous nature but also, most of all, by the presence of π- ligands of defined chemical structure that remain coordinated to the transition metal atom during the course of the polymerization. This allows one to steer the behavior of the copolymerization and the characteristics of the copolymer by playing with the structure of the ligands. A correlation between the structure and the performances of the organometallic complex can be established or, at least, attempted.

2.2.3. Summary Comparing Metallocene-Based Catalysts with Traditional Titanium- and Vanadium-Based Catalytic Systems

The product of the reactivity ratios for most heterogeneous titanium catalysts is typically greater than 1, which is consistent with the tendency of these types of catalysts to form long crystallizable ethylene sequences. Vanadium-based catalysts give a more random distribution of comonomers; r_er_p is close to unity in most cases. While for most of the studied metallocenes systems the product of the reactivity ratios is smaller than 1, indicating a tendency toward alternation of ethylene and propylene units.

Tables 2.1 and 2.2 summarize the major differences in metallocene-based, traditional titanium-based and vanadium-based catalytic systems.

Table 2.1. Main features of catalytic systems for ethylene-propylene (-diene) copolymerization (Scheirs, 1999)

	Catalytic system based on		
	Metallocenes	Vanadium	Titanium
Catalytic center	Single center	Single- or multi-center	Multi-center
Catalytic activity	High	Low	High
Chemical Structure	Defined	Unknown	Unknown

Table 2.2. Catalytic activity (kg polymer/gmetal) in ethylene-propylene copolymerizations as a function of catalytic system and polymerization process* (Scheirs,1999)

Process	T (^oC)	Catalytic system based on		
		Metallocene	Vanadium	Titanium
Solution	50	600	80	-
Slurry	40	1000	100	500
Gas phase	50	500	80	150

*Polymerization time = 30 min for solution and slurry, 60 min for gas phase.

In fact, the relative catalytic activity depends on the type of alumoxane, the Al/metal ratio, the polymerization temperature and monomer concentration etc. Upon changing any of them, even slightly, a new list of relative performances would need to be established. However, a reliable order of magnitude can be established.

Koivumaki and Seppala (1994) copolymerized ethylene in liquid propylene with a high activity heterogeneous $MgCl_2.TiCl_4$- triethylaluminum catalyst and with homogeneous $VOCl_3$-diethylaluminumchloride and Cp_2ZrCl_2-MAO catalysts to study the effect of the catalyst system on the properties of the products. The titanium catalyst gave crystallizable ethylene blockies at high ethylene contents and the zirconium catalyst gave the most random distribution of the monomers. Zirconocenes were unable to obtain high Mw copolymers, while $TiCl_4$ and $VOCl_3$ gave a much broader MWD. From DSC measurements, the polyethylene melting peak in the samples made with the $TiCl_4$ system was seen at much lower ethylene contents than in the samples made with the vanadium catalyst. The DMTA analysis revealed that the glass transition was at lower temperatures for samples made with vanadium catalyst and these samples would carry more impact strength at sub-zero temperatures.

2.2.4. Activity and Molecular Properties of E/P Copolymers from Various Types of Metallocenes

Some of the metallocene complexes that have been applied for E/P copolymerization by several authors are summarized in Table 2.3.

A set of molecular properties, which contributes to the determination of E/P copolymer behavior in the elastomeric field, includes molecular mass, chemical composition and their intermolecular distribution.

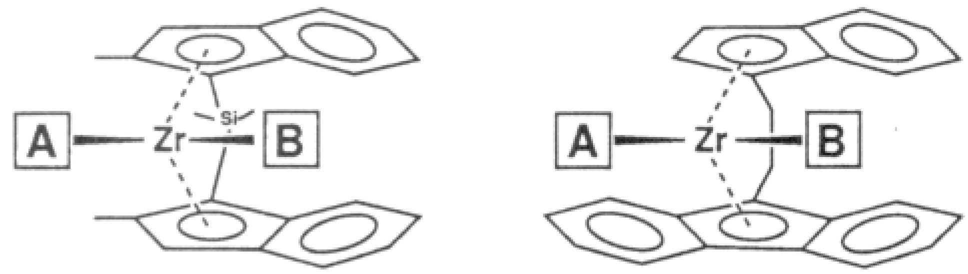
Table 2.3. Metallocene complexes used in ethylene/propylene copolymerization.

Metallocene catalyst system	References
$[Me_2C(3\text{-}RCp)(Flu)]ZrCl_2$; R = H, Me, ^{iso}Pr, ^{tert}Bu / MAO	Arndt and Kaminsky *et al.* (1998)
rac-Me_2Si(2-methyl-4-phenyl-1-indenyl)$_2ZrCl_2$/ MAO	Busico *et al.* (1999)
Ethylene-bis(indenyl)hafnium dichloride, $Et(Ind)_2HfCl_2$/ MAO	Djupfors *et al.* (1997)
rac-isopropylidenebis(3-tert-butylcyclopentadienyl) zirconium dichloride/ MAO	Galimberti *et al.* (1998)
{η^1:η^5-[(tert-butylamido) dimethylsilyl] (2,3,4,5-tetramethyl-1-cyclopentadienyl)} titanium dichloride/ MAO; CGC catalyst	Galimberti *et al.* (1999)
$Me_2SiFlu_2ZrCl_2$, r-$Me_2C(3\text{-}t\text{-}BuCp)_2ZrCl_2$ / MAO	Galimberti *et al.* (1999)
Ethylene (1-indenyl)(9-fluorenyl) zirconium dichloride/ MAO	Jin *et al.* (1998)
unbridged 2-arylindenyl metallocene complexes: bis(2-phenylindenyl) zirconium dichloride/ MAO; Ethylene-bis(indenyl)zirconium dichloride, $Et(Ind)_2ZrCl_2$/ MAO	Kravchenko and Waymouth (1998)
Tetramethyldisiloxanediylbis (cyclopentadienyl) zirconium dichloride and dimethyl derivatives / MAO	Lee *et al.* (1996)
Cp_2MCl_2, rac-$Et(Ind)_2MCl_2$, rac-$Me_2Si(Ind)_2MCl_2$; M = Zr, Hf / MAO	Naga *et al.* (1997)
racemic(1,4-butanediyl)silylene-bis(1-η^5-indenyl)dichlorozirconium with trialkylaluminum and triphenylcarbenium tetrakis(pentafluorophenyl)borate.	Tsai and Chien (1994)
$CpMe_4(SiMe_2N^tBu)]TiMe_2$ (CGC-catalyst)/ MMAO/ tris (pentafluorophenyl)boron (TPFPB)	Wang and Zhu (2000)

Copolymerization of propylene and ethylene with $Et(Ind)_2HfCl_2$/ MAO in toluene at 40 °C and 60 °C using a semi-flow method was carried out by Djupfors *et al.* (1997). ^{13}C-NMR indicated the formation of short ethylene blocks in the polymer chain (more blocks at lower temperature). Addition of ethylene showed an activation effect even for only small amounts. The molar mass was increased but the crystallinity and the melting temperature of the polymer were decreased. Dynamic mechanical analysis (DMA) showed a strong decrease in the stiffness values as a function of increasing ethylene in the copolymer. Almost linear relationship is seen between the amount of ethylene in the feed and the amount in the copolymer. Naga *et al.* (1997) investigated Cp_2MCl_2, rac-$Et(Ind)_2MCl_2$, rac-$Me_2Si(Ind)_2MCl_2$ where M =

Zr or Hf with MAO metallocene systems. Polymerization activity decreased with increase of propene feed ratio in non-bridged non-specific metallocenes, while higher polymerization activities were observed for the copolymerization compared to ethylene and propylene homopolymerization with ansa-isospecific metallocenes. In chain-end analysis by ^{13}C NMR, the value of [PP]/[EP] is smaller than that of $[PP]_t$/ $[EP]_t$ indicates the preference of chain transfer that occurs immediately following an addition of a propylene unit to a proceeding propylene unit. Tetramethyldisiloxanediylbis (cyclopentadienyl) zirconium dichloride was found to give higher content of comonomer incorporated than and tetramethyldisiloxanediylbis (cyclopentadienyl) dimethyl zirconium (Lee *et al.*, 1996). The catalyst activity in copolymerization decreased when propylene was added.

With rac-isopropylidenebis(3-tert-butylcyclopentadienyl)zirconium dichloride, MAO, the EP copolymer with 17%-92% ethylene molar content could be obtained (Galimberti *et al.*, 1998). The isospecific metallocene allowed the preparation of bipolymers composed of ethylene and propylene with regioregular propylene units inserted, with the same enantioface. Narrow distribution of the chemical composition copolymer was produced with long sequences of both comonomers. Jin *et al.* (1998) copolymerized ethylene and propylene at –40°C with ethylene (1-indenyl)(9-fluorenyl) zirconium dichloride/MAO. The copolymer produced is stereoregular and isotactic. This catalyst has two non-equivalent coordination sites i.e. the sterically less hindered site A and the more hindered site B (Figure 2.6.). It may be expected that the more bulky propylene and the less bulky ethylene monomers will preferentially coordinate with the sites A and B, respectively under the condition of [propylene]>> [ethylene]. From ^{13}C NMR, propylene monomers are selectively incorporated into the polymer via 1,2-addition. No [PP] sequence was observed which suggests that the polymer chain or the site A does not migrate to the site B and propylene coordinates only with the site A.



meso-$Me_2Si(2\text{-}Me\text{-}1\text{-}Ind)_2ZrCl_2$ $Et(1\text{-}Ind)(9\text{-}Flu)ZrCl_2$

Figure 2.6. The two non-equivalent coordination sites of ethylene (1-indenyl)(9-fluorenyl) zirconium dichloride: the sterically less hindered site, A and the more hindered site, B (Jin *et al.*, 1998).

Arndt and Kaminsky *et al.* (1998) used $[Me_2C(3\text{-}RCp)(Flu)]ZrCl_2$ (R = H, Me, ^{iso}Pr, ^{tert}Bu) (see Figure 2.7.) in ethylene/propylene copolymerization at 30°C and 60° C. A copolymerization model taking into account the heterotopic nature of the metallocenes has been developed which fits the experimental triad distributions obtained. They concluded that copolymerization proceeds via chain migratory insertion for R = H and Me whereas a retention mechanism is formed for R = ^{tert}Bu.

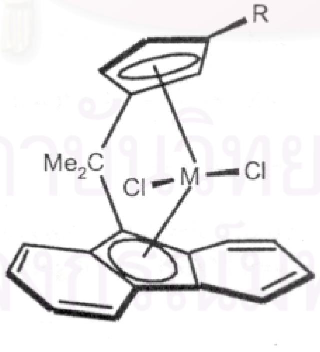


Figure 2.7. Structure of the metallocenes used for ethylene/propylene copolymerization (M = Zr, R = H (I), Me (II), ^{iso}Pr (III), ^{tert}Bu (IV)) (Arndt and Kaminsky *et al.*, 1998)

The data presented imply that the polymerization by [Me_2C(3-MeCp)(Flu)] $ZrCl_2$ proceeds via an alternating mechanism and that the hemiisotactic polypropene produced by using this metallocene is the result of a disturbed stereoselectivity at one of the sites.

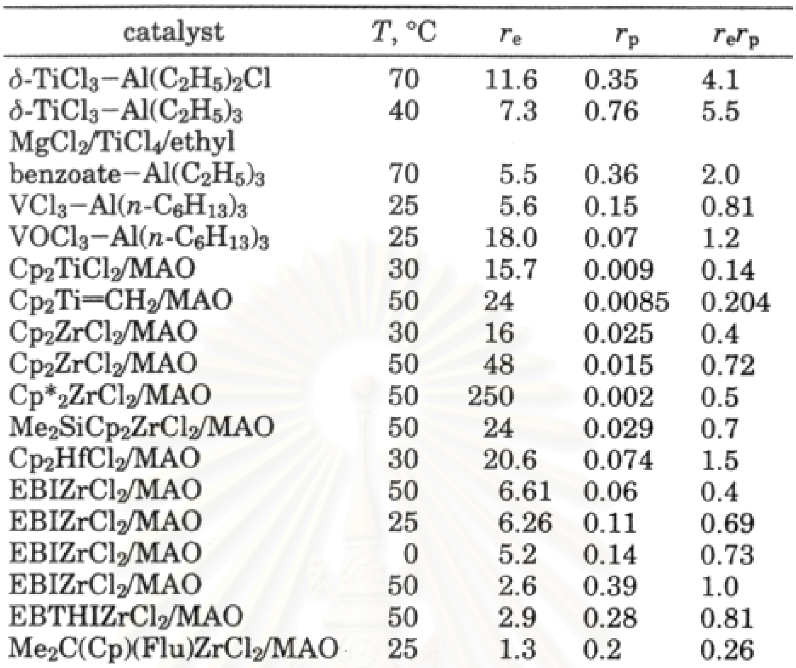
Busico *et al.* (1999) investigated the kinetics of ethylene and propylene polymerization at 20-60°C with rac-Me_2Si(2-methyl-4-phenyl-1-indenyl)$_2ZrCl_2$/ MAO, C_2-symmetric, isotactic-selective, catalytic system by means of stopped-flow techniques. The specific rate of chain propagation turned out to be $\sim 10^2$ times higher for ethene than for propene. They suggested that diffusion limitations through the poly(ethylene) precipitating at longer reaction times may be responsible for the fact that the two monomers polymerize instead at comparable rates under ‘standard’ conditions. It was also found that the concentration of active sites is significantly lower than the analytical Zr concentration.

Ethylene/propylene copolymer produced with “constrained geometry” half-sandwich organometallic complex {η^1:η^5-[(tert-butylamido) dimethylsilyl] (2,3,4,5-tetramethyl-1-cyclopentadienyl)} titanium dichloride/ MAO indicated the random distribution of ethylene and propylene. It gave rise to values of r_P and r_E very similar to each other showing the tendency to an almost ideal copolymerization and the presence of regioirregularities was in a much lower amount with respect to vanadium based copolymers (Galimberti *et al.*, 1999). On the other hand, the ethylene/propylene copolymerization carried out in a continuous-stirred tank reactor (CSTR) at 130-150° C with constrained geometry catalyst, the inverted propylene units were present (Wang and Zhu, 2000). It was demonstrated that the CGC-catalyst did not have much control over the stereoregularity of the propylene insertion. Compared to the vanadium EP, the CGC EP copolymers had fewer alternating comonomer sequences and more consecutive ethylene and propylene units.

Various types of alumoxane i.e. poly(methylalumoxane) (MAO), tetraisobutylalumoxane (TIBAO), and tetraisooctylalumoxane (TIOAO) were used by Galimberti *et al.* (1999). MAO gave higher activities and lower molecular masses of the copolymers. Productivity of TIOAO is higher than TIBAO with the similar copolymer properties. Results of the fractionations clearly show the narrow chemical composition distribution of a copolymer prepared from a metallocene-based catalytic system activated by an alumoxane other than MAO. For TIOAO- and MAO- based samples, similar values are obtained for both isotacticity (pretty far from 100%) and amount of regioirregularity. $Me_2SiFlu_2ZrCl_2$ exhibited almost alternate distribution while *rac*-$Me_2C(3\text{-t-BuCp})_2ZrCl_2$ produced copolymer with long sequences of comonomers. Also in the case of copolymerization characterized by very different product of reactivity ratios, the copolymer microstructure can be correlated with the metallocene used for the copolymerization rather than with the type of the cocatalyst.

Kravchenko and Waymouth (1998) used unbridged 2-arylindenyl metallocene complexes such as bis(2-phenylindenyl)zirconium dichloride/ MAO for synthesis of elastomeric polypropylene. Addition of small amounts of ethylene results in a large and nonlinear increase in the polymerization rate. This increase cannot be explained by the faster rate of ethylene insertion but is likely the result of the activation of dormant catalyst sites by ethylene. This “ethylene effect” is much larger for bis(2-phenylindenyl)zirconium dichloride/MAO [$(2PhInd)_2ZrCl_2$ 1/MAO] and bis(2-(3,5-bis(trifluoromethyl)phenyl) indenyl]-zirconium dichloride/MAO [$(CF_3)_2PhInd)_2ZrCl_2$/ MAO 2/MAO] than $EBIZrCl_2$/MAO (3/MAO). Unbridged 2-arylindene catalysts show a tendency toward random or slightly blocky incorporation of comonomers (r_Er_P = 1.0-1.9 >1) whereas the ansa-metallocene 3/MAO exhibits a tendency toward alternating comonomer distribution (r_er_p = 0.5 <1). The reactivity ratios of ethylene/propylene copolymerization with different catalytic systems reported in the literature are shown in Table 2.4.

Table 2.4. Reactivity ratios of ethylene/propylene copolymerization (Kravchenko and Waymouth, 1998)



catalyst	T, °C	r_e	r_p	r_er_p
δ-$TiCl_3-Al(C_2H_5)_2Cl$	70	11.6	0.35	4.1
δ-$TiCl_3-Al(C_2H_5)_3$	40	7.3	0.76	5.5
$MgCl_2/TiCl_4$/ethyl benzoate$-Al(C_2H_5)_3$	70	5.5	0.36	2.0
$VCl_3-Al(n\text{-}C_6H_{13})_3$	25	5.6	0.15	0.81
$VOCl_3-Al(n\text{-}C_6H_{13})_3$	25	18.0	0.07	1.2
Cp_2TiCl_2/MAO	30	15.7	0.009	0.14
$Cp_2Ti{=}CH_2$/MAO	50	24	0.0085	0.204
Cp_2ZrCl_2/MAO	30	16	0.025	0.4
Cp_2ZrCl_2/MAO	50	48	0.015	0.72
$Cp^*_2ZrCl_2$/MAO	50	250	0.002	0.5
$Me_2SiCp_2ZrCl_2$/MAO	50	24	0.029	0.7
Cp_2HfCl_2/MAO	30	20.6	0.074	1.5
$EBIZrCl_2$/MAO	50	6.61	0.06	0.4
$EBIZrCl_2$/MAO	25	6.26	0.11	0.69
$EBIZrCl_2$/MAO	0	5.2	0.14	0.73
$EBIZrCl_2$/MAO	50	2.6	0.39	1.0
$EBTHIZrCl_2$/MAO	50	2.9	0.28	0.81
$Me_2C(Cp)(Flu)ZrCl_2$/MAO	25	1.3	0.2	0.26

Tsai and Chien (1994) synthesized racemic(1,4-butanediyl)silylene-bis(1-η^5-indenyl)dichlorozirconium and used with trialkylaluminum and triphenylcarbenium tetrakis(penta-fluorophenyl)borate in ethylene and propylene copolymerization. The variations of polymerization activities in ethylene and in propylene for Tp from –55° C to +70°C indicate Michaelis Menton kinetics. This catalyst copolymerizes ethylene and propylene with reactivity ratios of comparable magnitude r_E ~$4r_P$; r_E*r_P ~0.5 indicating random copolymer formation.

As far as the molecular mass of the copolymer is concerned, the following comments can be made, based on results obtained with experimental conditions of industrial significance (Scheirs,1999).

(1) Metallocenes are able to cover a broad range of molecular masses. The molecular mass of an E/P copolymer is indeed a critical parameter that brings about a dramatic selection among the metallocenes: as the molecular mass increases, the number of metallocenes available for their preparation decreases.

(2) For copolymers obtained with the same metallocene and under the same experimental conditions, the molecular mass depends on their chemical composition: the higher the 1-olefin content; the lower the molecular mass. This

result is in agreement with what is traditionally observed with other catalytic systems for copolymers prepared with metallocenes representative of different classes.

(3) With the same metallocene and at the same temperature, higher molecular masses are obtained in slurries rather than in solution and these are essentially due to the higher concentration of monomers.

2.2.5. Terpolymerization of Ethylene and Propylene with a Diene

Several metallocene catalyst systems have been used in EPDM synthesis. Table 2.5 illustrates the types of diene accompanied with the catalytic system applied in terpolymerization, which has been carried out by different authors.

Table 2.5. Metallocene complexes and type of diene used in ethylene/propylene/diene terpolymerization.

Metallocene catalyst system	**Diene Type**	**References**
{[2-(dimethylamino) ethyl] cyclopentadienyl} titanium trichloride (Cp^NTiCl_3)/ MAO; rac-(dimethylsilylene) bis (1-η^5-indenyl)dichlorozirconium/MAO; rac-Et[Ind]$_2$ZrCl$_2$; Cp_2HfCl_2; Cp_2TiCl_2; Cp_2ZrCl_2 / MAO	ethylidene norbornene (ENB) 4-vinylcyclohexene (VCH) 1,4 hexadiene (HD)	Chien *et al.* (1998)
Et[Ind]$_2$ZrCl$_2$/ MAO	ENB	Haag *et al.* (2000)
Et[Ind]$_2$ZrCl$_2$; Et[Ind]$_2$HfCl$_2$ /MAO	ENB, DCPD	Malmberg and Lofgren (1997)
Et[Ind]$_2$ZrCl$_2$/ MAO	cyclooctadiene (COD), VCH	Marques *et al.* (1995)
Et[Ind]$_2$ZrCl$_2$/ MAO	HD, ENB	Yu *et al.* (1995)
ethylene bis(η^5-fluorenyl)zirconium dichloride; rac-dimethylsilylene bis(1-η^5-indenyl)zirconium dichloride/ MAO	ENB	Yu *et al.* (1995)

Haag *et al.* (2000) developed a mathematical model for the homogeneous terpolymerization EPDM with $Et[Ind]_2ZrCl_2$/ MAO using semibatch reactor. They also developed the kinetic model in order to explain the catalyst and EPDM properties such as catalyst activity, weight average molecular weight, and terpolymers composition, which were experimentally and theoretically obtained. Lower ethylene/ propylene feed ratio resulted in lower molecular weight and broader initial MWD. Increase of diene concentration decreased catalytic activity without broadening MWD. In EP copolymerization this ansa-metallocene catalyst incorporate larger amounts of propylene than do nonbridged systems and as a consequence produce lower Mw. A general reaction mechanism and reaction rates for a terpolymerization reaction with metallocene catalysts has also been provided by Haag *et al.* (2000). In their model, they considered only chain transfer to propylene. Chain-transfer reactions can occur preferentially by β-H elimination, followed by transfer to ethylene and to propylene monomers and to MAO. D'Agnillo *et al.* (1998) proposed that there is chain transfer reaction to ethylene in homopolymerization however; through chain-end analysis Naga *et al.* (1997) stated that copolymers of ethylene and propylene mainly terminate with EP and PP sequences.

Chien *et al.* (1998) used {[2-(dimethylamino) ethyl]cyclopentadienyl} titanium trichloride (Cp^NTiCl_3) with MAO in terpolymerization of ethylene, propylene, and diene i.e. ethylidene norbornene (ENB), vinylcyclohexene (VCH), 1,4 hexadiene (HD). Copolymerization of ethylene and propylene has reactivity ratios $r_E = 6.4$, $r_P = 0.29$ at 20°C $r_Er_P = 1.9$. Terpolymerization of E/P/ENB activity = 10^5 gpolymer/mol Ti.h and incorporates up to 14 mol% (~40 wt%) of ENB; Mw = 1-$3x10^5$ insensitive to ENB concentration. In case of VCH, A = 1.3 ± 0.3 x10^5 g/molTi.h and VCH incorporation increases with increasing of VCH concentration. With HD, A was about 1/3 of VCH or ENB, low Mw copolymer was produced and less than 4% HD incorporated.

rac-(dimethylsilylene) bis (1-η^5-indenyl)dichlorozirconium/ MAO is better for E/P/VCH while rac-ethylene bis(1-η^5-indenyl)dichlorozirconium/ MAO superior in E/P/HD. With INSITE technology {(tetramethyl-η^5-cyclopentadienyl)[(N-tert-butylamido) dimethyl-silyl]dichlorotitanium}, activity obtained was 10^7-10^8 g of ethylene-α-olefin copolymer/ molTi.h.

All the nonbridged precursors have r_E>>>r_P by 3-5 orders of magnitude, whereas the differences between r_E and r_P of ansa-zirconocene precursors are in the order of one order of magnitude. Cp_2HfCl_2 produce copolymer with r_Er_P = 1.52 while Cp_2TiCl_2 and Cp_2ZrCl_2 products of reactivity ratio are less than 1.0. This shows the dependence of reactivity ratio on the metal as well as ligand.

Yu *et al.* (1995) carried out the terpolymerization of ethylene/propylene and 1,4-hexadiene using rac-1,2-ethylenebis (1-η^5-indenyl)zirconium(IV)dichloride and methylaluminoxane (Et[Ind]$_2$ZrCl$_2$/ MAO). HD lowers the polymerization activity, the effect is more pronounced for P/HD and E/P/HD using large amount of propylene. Mw is most strongly affected by the temperature of polymerization (Tp), whereas the E/P ratio in the feed has virtually no effect. r_E and r_P are 3.0 and 0.3 at 20°C but r_P becomes larger than r_E at Tp = 70°C r_E~0.5 r_P~1.4. From ^{1}H-NMR, HD is incorporated in the terpolymer only by linear 1,2-addition. Terpolymerization of E/P/ENB with Cp_2ZrCl_2/ MAO exhibits long induction time whereas for Et[Ind] $_2$ZrCl$_2$/ MAO or Et[Ind]$_2$Zr$^+$R, no induction was observed in both solution or for SiO_2 supported system. The amount of diene incorporated in the terpolymer is almost directly proportional to the amount of diene in the feed, up to 40 wt%. A change of Tp from 20 to 50°C almost doubles the diene content in the EPDM.

Marques *et al.* (1995) used rac-Et[Ind]$_2$ZrCl$_2$ to prepare EPDM with 4-vinylcyclohexene (VCH) and cyclooctadiene (COD). They compared the VCH with vinylcyclohexane and concluded that the linear olefinic double bond is more active than the cyclic internal double bond. VCH reduces ethylene polymerization rate but not propylene polymerization rate in copolymerization. In terpolymerization, VCH tends to suppress ethylene incorporation especially at elevated polymerization temperature and lowers the polymer Mw by half. COD has very low activity as a termonomer. They indicates that the overall rate constants are independent of the last inserted monomer i.e. ideally random copolymerization, which is a characteristic of single site metallocene catalysts.

Yu *et al.* (1995) investigated the ethylene bis(η^5-fluorenyl)zirconium dichloride (1) and rac-dimethylsilylene bis(1-η^5-indenyl)zirconium dichloride (2) / MAO catalytic system in EPDM terpolymerization. In copolymerization, (1) produced high Mw rich in ethylene with r_E =1.7 and r_P < 0.01 while (2) produced lower Mw random copolymers with r_E =1.32 and r_P = 0.36. In case of terpolymerization (1)/MAO complexes with ENB but does not undergo insertion in the presence of ethylene and propylene. (2)/MAO undergoes terpolymerization incorporating 9-15 mol% of ENB with slightly lower Mw and activity than copolymerization. The terpolymerization differences between (2) and (1) are largely due to steric effects. If electronic factors play an important role, one might expect (1) to incorporate more ENB than (2) since the fluorenyl ligand is more electron donating which may cause more weakening of the Zr-C bond than the indenyl ligand.

With the $Et[Flu]_2ZrCl_2$/ MAO system; catalytic activity for PE ~10^8 , PP ~ 10^7, and EP ~ $2x10^7$ g/molZr h, at Tp = 70°C so the copolymerization rate lies in between ethylene and propylene homopolymerization but closer to propylene homopolymerization. Whereas for $Me_2Si[Ind]_2ZrCl_2$ / MAO, copolymerization rate is less than both homopolymerization.

Malmberg and Lofgren (1997) used $Et[Ind]_2ZrCl_2$ / MAO ($20x10^3$ kg/molM.h) and $Et[Ind]_2HfCl_2$ /MAO ($5x10^3$ kg/molM.h) in E/P copolymerization and E/P/ENB terpolymerization. Activity decreased with large diene feeds. Glass transition temperature of the copolymers is between -59°C and –55°C; a 1.5°C increase per wt% of ENB in the polymer was found. There may be a slight preference for ENB at higher ethylene feed with $Et[Ind]_2ZrCl_2$. Molar mass decreased with increase of comonomer.

The $Et[Ind]_2ZrCl_2$/MAO catalyst system is by far the most studied metallocene system in the open literature for the production of polyethylene, polypropylene, EP copolymers, and EPDM terpolymers. In EP copolymerizations, this ansa-metallocene catalyst incorporates larger amounts of propylene than do nonbridged systems and, as a consequence, produce lower molecular weights. The terpolymerization of ethylene/ propylene/ ethylidene norbornene by Cp_2ZrCl_2/MAO exhibits long induction time while there is no induction period for the $Et[Ind]_2ZrCl_2$/MAO or the $Et[Ind]_2Zr^+R$ system both in solution and supported in silica. The catalytic activity of a metallocene-based polymerization decreases in the presence of diene. The extent of the decrease depends on the nature of the diene. It appears that ENB and VNB behave similarly and have less effect on the catalyst productivity than DCPD. It is interesting to observe that a highly isospecific metallocene shows the lowest reactivity for ENB. With metallocenes belonging to different classes and only the endocyclic double bond of ENB undergoes an insertion reaction. The presence of a diene in the polymerization bath brings about an appreciable reduction of the molecular mass of the copolymer.

There are also some patents involving the production of ethylene/propylene copolymer and EPDM elastomer using the metallocene catalysts. Floyd and Hoel (1993) presented a process for producing a high molecular weight EPDM elastomer having low crystallinity using a bridged bis-metallocene-alumoxane catalyst. Davis and Grove (1995) provided a catalyst system comprising certain bimetallic metallocenes and an alumoxane together with a process for the preparation of high molecular weight ethylene/α−olefin elastomers and ethylene/α−olefin/nonconjugated diolefin elastomers. Sagane *et al.* (1997) presented the invention to provide an ethylene/α−olefin/nonconjugated polyene random copolymer having good moldability, high vulcanizing speed and excellent mechanical properties such as high vulcanization strength. Gillis and Karpeles (2000) reported a liquid phase polymerization process for producing a polyolefin elastomer from ethylene, α−olefin such as propylene, and optionally a diene employing a metallocene catalyst. The process comprises contacting monomer under liquid phase polymerization conditions with a metallocene catalyst, preferably one containing a bridging group possessing at least two bulky groups. Resconi and Piemontesi (2000) prepared amorphous polymers of propylene modified with ethylene units in high yields, by carrying out the polymerization reaction in the presence of a catalyst based on a metallocene compound that has two bridged fluorenyl ligands. These copolymers produced have glass transition temperatures well below $0^{o}C$ so that the copolymer can be used at low temperatures.

2.3. Heterogeneous System

Metallocene catalysts in dissolved form are in most cases unsuitable for the application in an industrial scale. In order to use them in existing technical processes (drop-in technology) by exchanging the conventional Ziegler-Natta catalysts, metallocenes have to be supported. Different methods are possible by using MAO as cocatalyst (Kaminsky and Winkelbach, 1999; Kaminsky and Laban, 2001).

(1) In the method of direct heterogenization, the metallocene or a mixture of the metallocene and MAO is anchored via physisorption or chemisorption onto the support. In the first case, the metallocene must be activated by external MAO.

(2) The metallocene can be supported by covalent bonding of its ligand environment to the support followed by activation with external MAO. The metallocene can be synthesized gradually as a covalent bonded species direct on the supporting material.

(3) Initial impregnation of MAO onto the support followed by adsorption and simultaneous activation of the metallocene (indirect heterogenization). In analogy to the homogeneous metallocene catalysis, the bonding between the active species $[Cp_2ZrCH_3]^+$ and the supported MAO is ionic. When performing the method of indirect heterogenization, no further MAO has to be added.

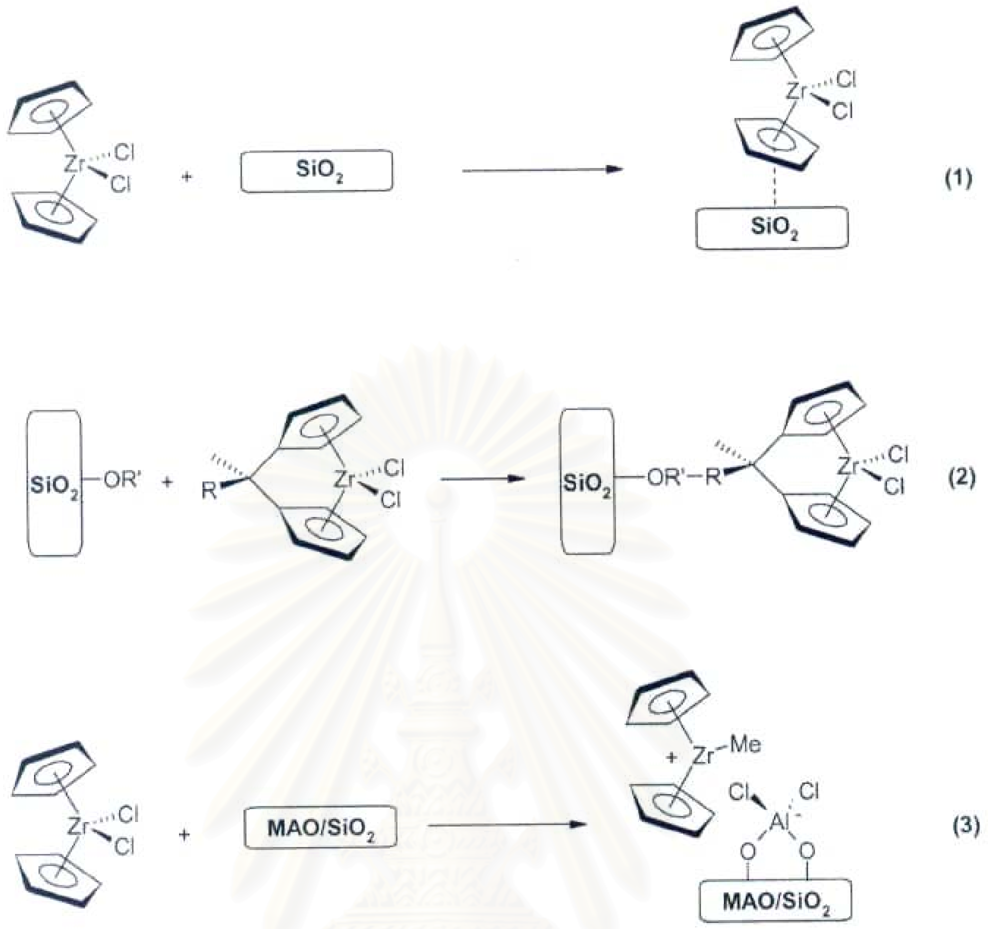


Figure 2.8. Supporting methods of metallocenes: (1) direct heterogenization, (2) covalent bonding on the support, (3) indirect heterogenization (Kaminsky and Laban, 2001)

Metallocenes supported according to the method of direct heterogenization have been known to produce polymers with higher molecular weight than those afforded by the homogeneous catalysts. However, direct heterogenization has also been known to change the polymerization characteristics of the metallocene, possibly by the interaction with surface hydroxyl groups. Sacchi *et al.* (1995) carried out propylene polymerization in the presence of the isospecific Et[Ind]$_2$ZrCl$_2$ and the aspecific [Ind]$_2$ZrCl$_2$ complexes in solution and anchored to SiO$_2$ and SiO$_2$/MAO supports. From the stereochemical analysis of the polypropylene samples obtained it can be deduced that the same active species is formed when a metallocene is in solution and when it is anchored to the SiO$_2$/MAO support and a completely different active species is formed when the metallocene is anchored to the silica.

Difficulties can also be encountered in the covalent bonding of metallocene complexes. If they are successively synthesized on the support, chemically non-uniform anchor groups, such as vicinal and geminal silanol groups, can lead to a mixture of different active species. The most promising method of supporting is indirect heterogenization as the chemical nature of the metallocene is changed, if at all, only to a small degree. The polymers obtained by the method of indirect heterogenization are very similar to those obtained by the homogeneous system. Each metallocene on the support forms an active center and the starting point for the growth of a polymer chain.

The improvements a supported catalyst needs to achieve in order to be accepted in existing manufacturing facilities are the following (Chien, 1999):

(a) The supported catalyst system should have activity approaching those of the homogeneous catalysts.
(b) The supported system needs to be more stable.
(c) The amount of methylaluminoxane has to be greatly reduced for economic viability of the supported catalysts.
(d) The supported catalyst should produce higher Mw polymers at high Tp compared to those produced by homogeneous system.
(e) Polyolefins obtained in homogeneous processes have a very low particle size, as well as a broad size distribution and low bulk density. Supported catalysts must be able to control the polymer morphology.
(f) The supported systems should have the capability of producing polymers having desired broad or bimodal MWD for good rheological and physical properties.
(g) Some supported metallocenes catalysts have been reported to cause fouling of gas-phase reactors. Corrective measures must be found.
(h) The steric control of metallocene catalysts is determined by molecular structure. It would be advantageous if this can be controlled or even altered by the support.

2.3.1. Effects of Support Type

Bonini *et al.* (1995) carried out propylene polymerization with supported metallocene catalyst, prepared by initial reaction of silica gel with methylaluminoxane. The rate-time curves obtained are analyzed to understand the influence of support on the reaction. A partially new particle growth model, based on a shell by shell fragmentation hypothesis (gradual break-up from the outside to the inside of the particle), and a final multigrain structure of the particle was developed. Fragmentation of catalyst particles during polymerization can be circumvented, and maintain the catalyst activity with a method of preparation for such newly designed supported metallocene catalysts (Goretzki *et al.*, 1999), where the active catalyst sites are located exclusively on the particle surface.

Soga and Kaminaka (1994) copolymerized ethylene with 1-hexene, ethylene with propylene and propylene with 1-hexene with SiO_2-, Al_2O_3-, $MgCl_2$- supported metallocene catalysts using common alkylaluminiums as cocatalyst. Random copolymers were obtained ($r_1r_2 \leq 1$). When ethylene was used as a base monomer, the polymer yield markedly increased with increasing comonomer concentration. The molecular weight of the copolymers obtained in this study were found to be much higher than those obtained with homogeneous catalysts. Whereas the polydispersity of the copolymer is dependent on the combination of monomers as well as on the inorganic compounds used as carrier. The content of comonomer incorporated slightly depends on the catalyst carrier ($SiO_2 \sim Al_2O_3 > MgCl_2$).

Harrison *et al.* (1998) compared silica and alumina as supports, which treated with methyl aluminoxane and a variety of metallocene dichloride complexes in polymerizations of ethylene or propylene. In particular, aluminas derived from calcination of sol-gel precursors feature high degrees of surface hydroxylation in comparison with commercially available silica of similar surface area and total porosity. This feature provides a mechanism for increasing the amount of aluminoxane on the supports, such that commercially acceptable productivities (>10 kgPE/g support.hr) are observed at relatively low total levels of aluminoxane. Therefore, the alumina based systems are the most active on a per support basis.

Soga *et al.* (1993) prepared modified SiO_2 by reacting SiO_2 with $Cl_2Si(CH_3)_2$ in toluene, on which MAO was supported to obtain a catalyst precursor. The MAO-free catalyst system composed of the modified SiO_2 and Cp_2ZrCl_2 was surprisingly found to be activated by common trialkylaluminums. Moroz *et al.* (1998) investigated ethylene polymerization with supported catalysts prepared by interaction of metallocene catalysts with silica chemically modified by $(CH_3)_3SiCl$ or trialkylaluminum compounds. The $Cp_2Zr(CH_3)_2/SiO_2$-$(CH_3)_3SiCl$ catalyst showed a fairly high activity in ethylene polymerization (30-300 kgPE/molZr.hr.bar) even in the absence of any cocatalysts specially added.

Dos Santos *et al.* (1997) determined Zr and Al loading on different kinds of commercial silicas by Rutherford backscattering spectrometry and titrometry technique, respectively. In all silicas, a saturation trend was observed with increasing amount of metal in the initial solution.

2.3.2 Effects of supporting procedure

Ferreira and Damiani (2001) described several methods to prepare supported $Et[Ind]_2ZrCl_2$ (EBI) on SiO_2/MAO, varying the washing step durations and washing step temperatures. The activity of the supported catalysts EBI/MAO/SiO_2 decreases to a third of the soluble catalyst EBI/MAO activity with the same Al/Zr molar ratio. Zr contents higher than 0.7% produce catalysts with lower productivities and MAO coverage and SiO_2 that is higher than a monolayer is probably not useful in order to stabilize the zirconocene on the SiO_2/MAO support.

Chu *et al.* (2000) carried out the polymerization of ethylene with a novel in situ supported metallocene catalyst that eliminated the need for a supporting step before polymerization. In the absence of TMA, in situ supported $Et[Ind]_2ZrCl_2$ was not active, but the addition of TMA during polymerization activated the catalyst. Et $[Ind]_2Zr(CH_3)_2$ was active even in the absence of TMA, whereas the addition of TMA during polymerization enhanced the catalytic activity. The polymerization rate profiles of the in situ supported metallocene catalyst did not show rate decay as a function of time. A polymerization mechanism of this system was proposed. The in-situ supported metallocene catalysts may deactivate, but homogeneous metallocene species present in the reactor may form new active sites and compensate for deactivated sites. As the Al/Zr ratio (Al present in SiO_2/MAO) increases, the catalytic activity increases. At high Al/Zr ratios, the ethylene feed rate decrease with time because there are less soluble metallocene species in the reaction medium. Al/Zr molar ratio does not affect Mw and MWD of the polymer. The catalytic active sites are uniform and only one type of active species exists in the reaction system with in situ supported metallocene catalyst. The catalytic activity of the in situ supported Et $[Ind]_2ZrCl_2$ was less sensitive to the TMA/SMAO mole ratio.

Chu *et al.* (1999) carried out the copolymerization of ethylene and 1-hexene with different catalysts (homogeneous $Et[Ind]_2ZrCl_2$, supported $Et[Ind]_2ZrCl_2$, and in-situ supported $Et[Ind]_2ZrCl_2$). The in-situ supported metallocene catalyst showed higher activity than the corresponding supported metallocene catalyst. At the same polymerization conditions, the relative reactivity of 1-hexene increases in the following order: supported metallocene ~ in-situ supported metallocene < homogeneous metallocene. The molecular weights of the produced copolymers with the three different catalysts are similar, but the MWD of the copolymer made with the in-situ supported metallocene is broader than that of those made with the other catalysts. From short chain branching distribution, it indicates that there are at least two different active species with the in-situ supported metallocene catalyst in the copolymerization of ethylene and 1- hexene.

Haag *et al.* (2001) evaluated effects of heterogenization parameters on compositional and catalytic properties of $Et[Ind]_2ZrCl_2$ supported on silica modified with MAO. Both MAO and $Et[Ind]_2ZrCl_2$ concentrations during preparation affected the determination of the final Al/Zr ratio on silica. The catalyst systems were tested in ethylene/propylene copolymerization using external MAO as cocatalyst. Relationship between Al/Zr ratio on silica and the average ethylene incorporation was observed. Catalyst systems with given Al/Zr ratios might yield different crystallites, suggesting a plural distribution of chemical composition.

2.3.3. Effects of polymerization conditions

Dos Santos *et al.* (1999) evaluated the effects of polymerization conditions i.e. Al/Zr molar ratio, reaction temperature, monomer pressure, the age and concentration of the catalyst, on the production of polyethylene by silica supported $(n\text{-}BuCp)_2ZrCl_2$ grafted under optimized conditions and cocatalyzed by methylaluminoxane. In ethylene and propylene copolymerization with $Et[IndH_4]_2ZrCl_2$/ MAO/ SiO_2 – Al $(iC_4H_9)_3$, the polymer yield obtained was found to increase drastically with increasing monomer feed ratio of propene/ ethylene up to a high concentration of propene (Soga and Kaminaka, 1994).

Do couto Junior *et al.* (2002) carried out ethylene polymerization using Cp_2ZrCl_2/MAO system. They obtained the highest value of catalyst activity at 60^{o}C when [Al]/[Zr] molar ratio = 500 was employed. Further increase of this ratio did not show a significant increase in the activity.

Bianchini *et al.* (2002) evaluated the effect of Al content on MAO-modified silicas on catalyst activity, on polymer properties, and on residual metal content in the resulting polyethylenes. MAO-modified silicas were prepared by impregnating MAO toluene solutions over the concentration range of 0.5 to 20.0 wt% Al/SiO_2. Using external MAO as cocatalyst (Al/Zr = 2000), no difference in catalyst activity was observed. Nevertheless, for Al/Zr = 500, catalyst activities were shown to be higher for supported zirconocene systems containing 0.0-2.0 wt% Al/SiO_2 range. Polymers with two Tm peaks were obtained with catalysts prepared with 10.0 wt% Al/SiO_2 and 20.0 wt% Al/SiO_2.

Semikolenova and Zakharov (1997) found that the interaction of supported metallocene catalysts with methylaluminoxane leads to the desorption of the metallocene compound from the surface of the support and the formation of highly active homogeneous complexes.

Xu *et al.* (2001) conducted ethylene homopolymerization and copolymerization with a supported metallocene in a gas-phase reactor for a kinetic study. A reaction rate order close to 2 is obtained for ethylene homopolymerization whereas approximate first order dependence is observed in the presence of propylene.

Liu and Rytter (2001) used the dual site $Cp^*_2ZrCl_2$/ $Et[IndH_4]_2ZrCl_2$ metallocene catalyst system with a mixture of MAO and TMA as the cocatalyst. Polymer properties can be controlled by the amount of TMA added, monomer pressure, polymerization temperature, and the addition of hexane or hydrogen. TMA is suggested to be partly coordinated to the active sites, thereby enhancing termination, increasing comonomer incorporation, but also partially blocking coordination and chain transfer to hydrogen.

Frauenrath *et al.* (2001) investigated the nature of the active species in zirconocene/MAO catalyzed polymerizations. Varying monomer concentration and monomer conversion does not result in any unexpected behavior. However, changing catalyst and cocatalyst concentration leads to broadened, or even bimodal MWD under certain reaction conditions. These results may be interpreted in terms of a coexistence of two active species with different rates of propagation and of termination.

Chirinos *et al.* (2000) synthesized the half-sandwich complex $[\{\eta^5\text{: }\sigma\text{-}C_5H_4(CH_2)_2NEt\}Ti(NEt_2)_2]$ and used it with MAO for homogeneous ethylene polymerization and ethylene/propylene copolymerization. The effect of the Al/Ti molar ratio was studied. A maximum of the catalytic activity was observed at an Al/Ti molar ratio of 2500. No correlation between thermal properties and MAO/Ti ratio was established. The MWD and DSC measurements show the presence of two different catalytic sites.

2.3.4. Effects of TMA and MAO as a cocatalyst

Panchenko *et al.* (1999) used IR spectroscopy to study the interaction of silica with TMA and two methylaluminoxane (MAO) samples differed by trimethylaluminum (TMA) content. Whereas TMA interacts with terminal hydroxyl groups of silica via the protolysis reaction, MAO mainly adsorbs on the surface hydroxyl groups of silica without noticeable protolytical reaction with them. When silica is treated with commercial grade MAO with significant TMA content, the silica surface hydroxyl groups mainly interacts with TMA and MAO adsorbs on the surface of SiO_2/TMA sample.

Ioku et al. (2002) found that dried methylaluminoxane (MAO) which was free of Me_3Al, was more active than the standard MAO system, resulting in a steady polymerization rate and giving higher Mw polypropylenes. Additive effects of trialkylaluminum on the dried MAO system showed that the polymer yield was increased by the addition of i-Bu_3Al and Oct_3Al and decreased by Me_3Al and Et_3Al.

Ferreira *et al.* (2000) studied the MAO-silica interaction experimentally and theoretically by evaluating CH_4 evolution. The conclusion of this work is that OH from a silica surface reacts with MAO and probably with TMA during the MAO treatment. The most probable final species is where the MAO molecule is fixed to the surface by several points, mainly in a linear form. When MAO*TMA is supported, TMA would be associated to MAO on the surface and the reaction of TMA with the surface would be possible.

Ystenes *et al.* (2000) investigated the structure of MAO by Raman and in situ IR spectroscopy. With bis(pentamethylcyclopentadieny) zirconium dichloride ($Cp^*_2ZrCl_2$), MAO and TMA seem to influence chain termination independently. A strong dependence of Mw of the polymer on the TMA concentration was found for the polymerization of ethylene with $Cp^*_2ZrCl_2$/MAO/TMA in toluene, indicating chain transfer to TMA.

Wang et al. (2002) studied propylene polymerization and propylene/1-octene copolymerization using rac-$Me_2SiInd_2ZrCl_2$/ MAO or rac-$Me_2SiInd_2ZrCl_2$/

(MAO+TIBA). The structure distribution of the polymers was characterized by temperature gradient extraction fractionation or precipitation fractionation, as well as by DSC analysis of the thermal segregated samples. It is found that adding TIBA in the catalyst system increases the blockiness of the polymer chain.

Britto *et al.* (2001) carried out ethylene/1-hexene copolymerization in hexane with Et[Ind]$_2$ZrCl$_2$/MAO in presence of TIBA. Increasing the TIBA concentration, the MAO solubility augments in the polymerization milieu. The catalyst activity and the comonomer incorporation also increased with the increase of TIBA. Increasing the Al$_{TOTAL}$/Zr molar ratio, catalyst activity becomes higher, while comonomer incorporation remained constant for molar ratios between 0 and 5000. For Al$_{TOTAL}$/Zr molar ratios higher than 5000, comonomer incorporation increased gradually. Wilmes *et al.* (2002) showed that the nature of the cocatalyst has a significant influence on the productivity and stereoselectivity of the unbridged 2-arylindenyl metallocene complexes. The type of MAO influences the stereoselectivity of propylene polymerization: MAOs containing isobutylaluminum groups yielded higher tacticity polypropylenes than those with only methylaluminum groups.

CHAPTER III

EXPERIMENTAL

3.1. Equipment

3.1.1. Equipment for handling air-sensitive compounds

Since the operations of reagent loading and polymerization involve air-sensitive compounds, special equipment is required to provide inert gas atmosphere protection and to prevent oxygen and moisture from the reaction systems. Such equipment utilized for this purpose are as follows:

(a) Glove box (Vacuum Atmospheres) with oxygen and moisture indicator for transferring solid and liquid reagents under argon atmosphere and for storing air-sensitive reagents. The oxygen and moisture levels are normally below 2 ppm inside the glove box.

(b) Schlenk line composed of vacuum line connected to vacuum pump and argon line for purging when reagents are transferred (Figure 3.1.).

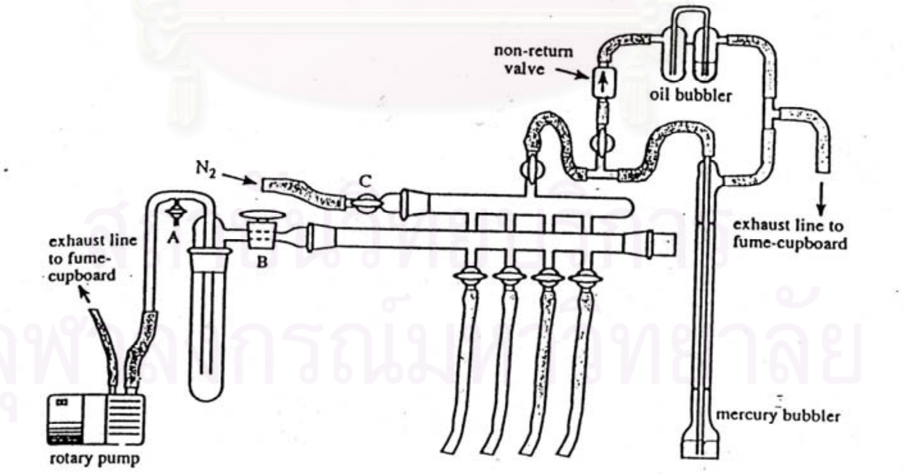


Figure 3.1. Schlenk Line

(c) Schlenk tube (Figure 3.2.) for keeping reagents under argon atmosphere outside the glove box. It was used accompanied with the Schlenk line.

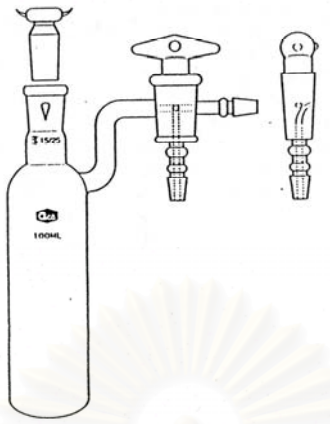


Figure 3.2. Schlenk Tube

(d) Oxygen trap (BASF catalyst), moisture trap (molecular sieve), sodium hydroxide (NaOH) and phosphorus pentaoxide (P_2O_5) for purifying ultra high purity argon before use in schlenk line and solvent distillation column (Figure 3.3.).

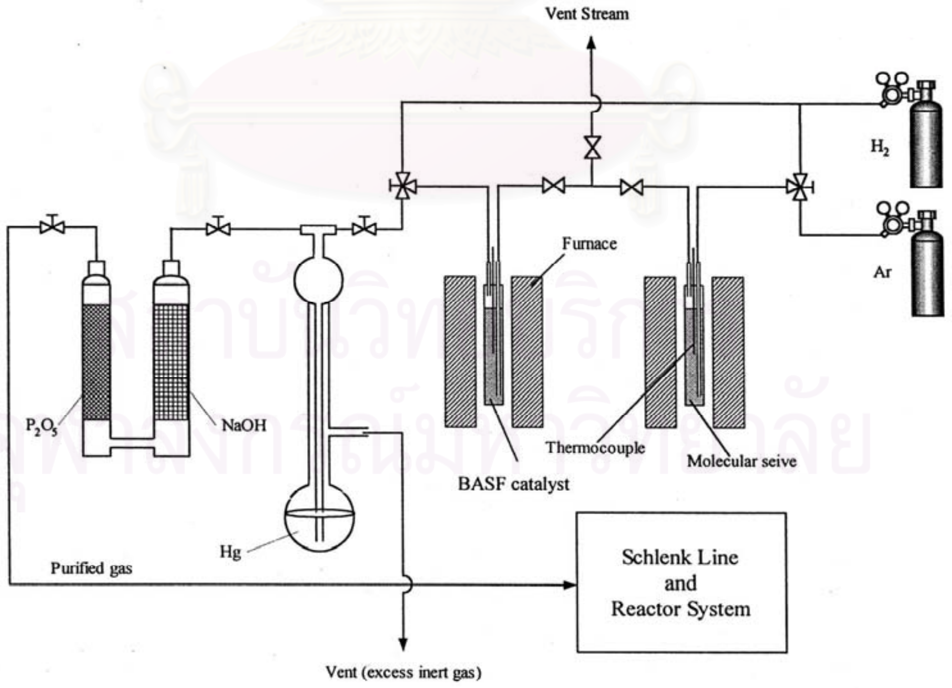


Figure 3.3. Inert gas supply system

3.2. Reagents

The reagents used in the experiments of the present investigation and their sources are summarized in Table 3.1.

Table 3.1. The reagents used in the experiments

Chemicals	Grade	Source
Acetone	Commercial	SR Lab
Benzophenone		Fluka
Ethylene	Polymerization	National Petrochemical Co. Ltd. (NPC)
Propylene	Polymerization	National Petrochemical Co. Ltd. (NPC)
Hydrochloric acid	Fuming 37%	Merck
Methanol	Commercial	SR Lab
Nitrogen	Ultra High Purity (99.999%)	Thai Industrial Gas Co.,Ltd. (TIG)
Argon	Ultra High Purity (99.999%)	Thai Industrial Gas Co.,Ltd. (TIG)
Trimethylaluminum (TMA)	2.0 M in toluene	Nippon Aluminum Alkyls Ltd. Japan
Methylaluminoxane (MAO)	2.857 M in toluene	Tosoh Akzo, Japan
Cp_2ZrCl_2		Japan
$Et[Ind]_2ZrCl_2$		Aldrich
Silica Gel	Cariact P-10, surface area 300 m^2/g	Fuji Silasia Chemical Ltd.
Calcium chloride	Dehydrated	Fluka
4-Vinyl-1-cyclohexene (VCH)	99%	Aldrich
1,4 Hexadiene (HD)	99%	Aldrich

Chemicals	Grade	Source
5-Ethylidene-2-norbornene (ENB)	99%	Aldrich
1-Hexene	99.8%	Fluka
Activated clay		Actochem
Silicon tetrachloride ($SiCl_4$)	99.998%	Aldrich
Sodium hydrogen carbonate ($NaHCO_3$)		Fluka
Toluene	Commercial	Exxon

3.3. Polymerization

3.3.1. Material preparation

Since the solvents were of commercial grade, there might be some undesirable impurities; especially water, which have to be removed before use. Therefore solvents are refluxed in the presence of Na/benzophenone and then distilled under argon atmosphere and kept in schlenk tubes. Ethylene and propylene are polymerization grade. They were purified by passing through a column of LABCLEAR^{TM} gas filter. The ultra high purity argon was further purified by passing through molecular sieve 3 A, BASF catalyst R3-11G, sodium hydroxide (NaOH) and phosphorus pentaoxide (P_2O_5) to remove traces of oxygen and moisture.

3.3.2. Polymerization

3.3.2.1. Batch system

Polymerization was carried out in a 100 mL stainless steel reactor with magnetic stirrer in the following manner. Using Schlenk line, solvent was first added to the reactor in the amount to make the total volume of 30 mL. Cocatalyst solution was then added according to the specified ratio to the catalyst concentration followed by diene. Finally, the metallocene catalyst was injected and immediately the reactor was placed in liquid nitrogen to stop any reaction between the catalyst and cocatalyst. After the solution was frozen for 15 minutes, the reactor was evacuated for 3 minutes then filled with gaseous monomer (ethylene and propylene) while the reactor was still in liquid nitrogen. The amount of gaseous monomer fed into the reactor, was monitored from the pressure drop in the supply cylinders.

The reactor was taken out of liquid nitrogen and put in the water bath at the desired temperature to start the polymerization reaction. To stop reaction, the gaseous monomer was released and the solution was poured into excess methanol. Polymer was filtered and dried. The monomer consumption can be monitored from the pressure gauge connected to the reactor. The sample of gaseous monomer can be taken during the reaction to determine the ratio of ethylene to propylene by gas chromatography.

3.3.2.2. Semibatch system

The semibatch system is the system, in which the gaseous monomer was fed to the reactor during polymerization to compensate its consumption and to keep the pressure of monomer inside the reactor constant (Huang, 1995). The overall system essentially consists of two separate systems: (i) a constant-pressure reactor system, and (ii) a gas monitoring system. A schematic flow diagram is provided in figure 3.4.

A drop in pressure in the reactor (due to gas consumption) is detected by the differential pressure transducer (PT-1) and is compared with the pressure in tube AB. The pressure in tube AB serves as a reference pressure, which can be set using the on/off valve V-1 prior to the start of the reaction. The control valve (CV-1) allows the necessary amount of gas into the reactor and readjusts the pressure accordingly.

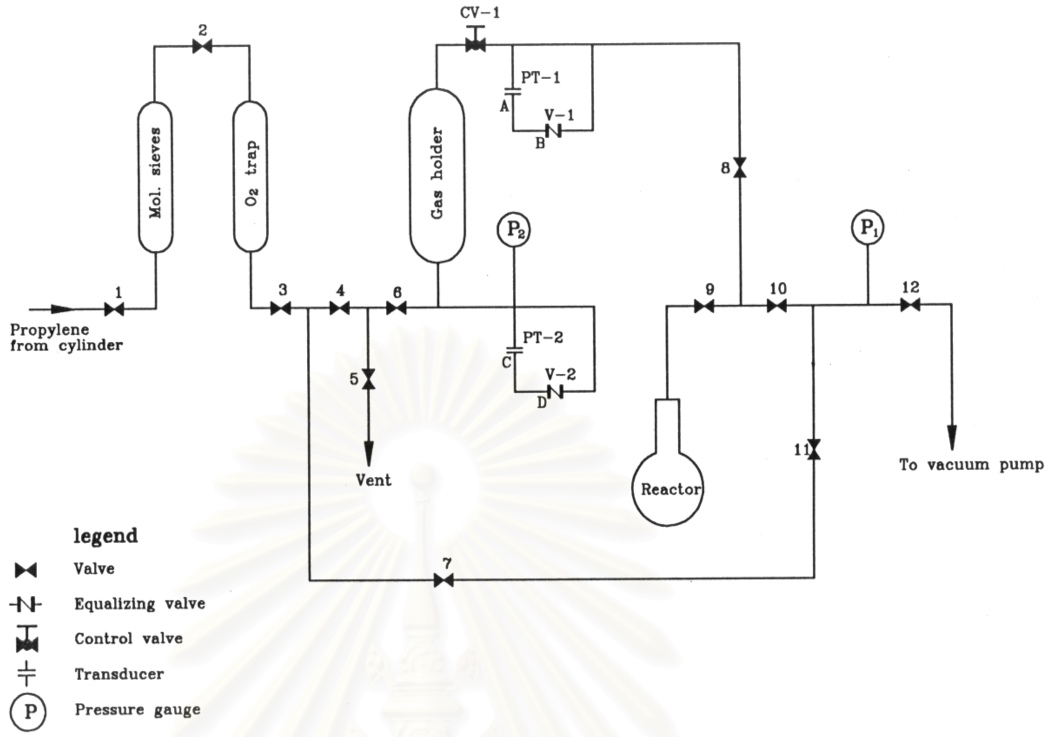


Figure 3.4. Schematic flow diagram of the semibatch or constant pressure reactor system (Huang, 1995).

The gas monitoring system uses a simple principle of measurement of a pressure drop in a gasholder according to the gas consumption. The decrease of pressure in the gasholder is detected by a differential pressure transducer PT-2 and compared with the pressure in tube CD, which can be set using the on/off valve V-2.

The procedure for running polymerization is as follows:

(a) Fill the gasholder with ethylene or propylene. Evacuate and refill several times to get rid of impurities in the gasholder. The pressure can be seen from pressure gauge P_2.

(b) Load reagents in glove box. While certain amount of solvent and cocatalyst were added directly into a special flask reactor, the metallocene catalyst was loaded in the bucket hung with a hook of the reactor (Figure 3.5.).

(c) Degas the solvent: Connect flask to the system and degas by the freeze-thaw technique which is the series of solution frozen in liquid nitrogen and then degas by the vacuum pump followed by heat up until the solution melt.

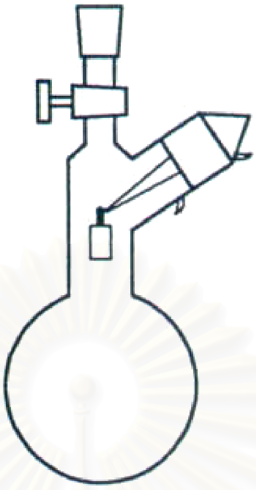


Figure 3.5. The special flask reactor for semibatch system

(d) Set the reference pressure: Fill gas in the reactor by open valve 7 and 11 while open valve V-1 to tube AB for reference (figure 3.4). The reaction mixture is saturated with gas at desired pressure and temperature (pressure in the reactor is constant). Then close the valve to tube AB and CD to set the reference pressure.

(e) Set the computer (put in the file name, pressure, calibration factor, etc.).

(f) Start reaction by turn over the hook in the reactor dropping catalyst-containing bucket into the solution. Computer is immediately started to collect data.

(g) Stop the reaction: shut off the control system therefore the control valve is closed. Open valve V-1 and V-2. Remove the flask from the system. Polymer is collected by normal procedures.

3.3.2.3. The system with gas flow at constant rate

Ethylene and propylene were mixed in a gas cylinder at the desired molar ratio with quantities of the two gases small enough to prevent their condensation. Since the consumption rate of each gaseous monomer could be different, the ethylene/ propylene molar ratio in the reactor of batch or semibatch system could vary during the ethylene/ propylene copolymerization. Therefore, with this system, the mixture of gas was continuously fed through the reactor at a flowrate high enough to maintain the gas composition in the reactor. Pressure in the reactor was controlled by the level of paraffin oil (see figure 3.6).

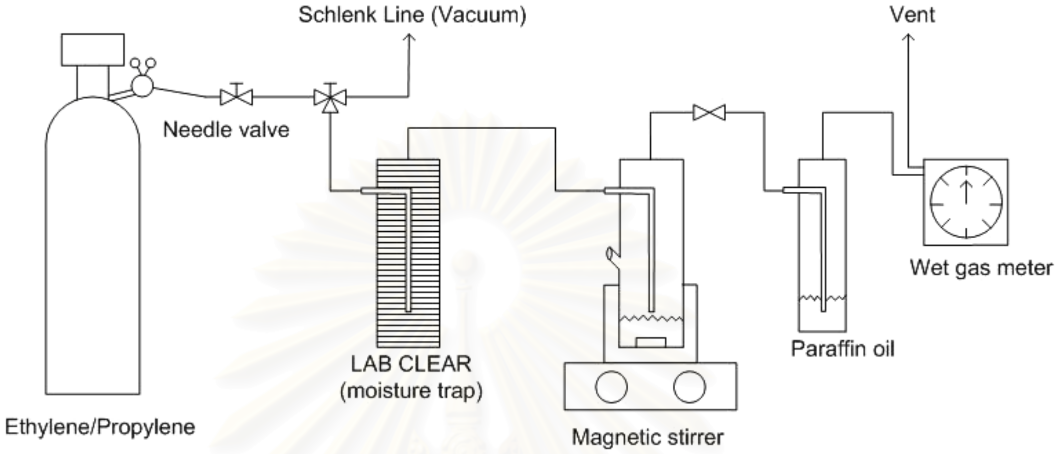


Figure 3.6. Schematic flow diagram of the continuous gas flow system.

The glass reactor is first connected to the gas handling part of the system, and then it was evacuated and filled with the gaseous monomer at the desired composition determined by gas chromatography. The gas flowrate was monitored by the wet gas meter and it was adjusted by the needle valve. Xu *et al.* (2001) showed that the system with a continuous flow of monomer gas (purge mode) provides better results for a kinetic study of ethylene homopolymerization and ethylene/propylene copolymerization than a no-purge mode. An increase in activity and improvement in reproducibility was also observed.

Using the schlenk technique, solvent was then added to make the total volume of 30 mL. Wait until the solvent was saturated with the monomer at the desired temperature. Cocatalyst and/or diene were injected, followed by the metallocene catalyst to start the reaction. The consumption of monomer was monitored by the decrease of the output flowrate. Sample of gas in the reactor can be taken to measure the composition by gas chromatography during the reaction. Reaction was stopped by stopping the feed of monomer and injecting methanol then follow the normal procedure of polymer collection.

3.3.3. Polymer Collection

After the polymerization reaction was stopped, the reaction solution containing produced polymer was poured into the excess methanol. Polymer was precipitated. Then, it was filtered and washed thoroughly several times with methanol. In case of homopolymer, the polymer was dried in the oven at 110^{o}C overnight. While for copolymer, it was dried under vacuum at room temperature overnight to prevent the melting of copolymer at the elevated temperature. Weight of the collected polymer was recorded for the calculation of the activity.

3.4. Procedure for support preparation

3.4.1. Preparation of SiO_2/MAO Catalyst Precursor

Silica gel was calcined under vacuum at 400° C for 6 hours. Calcined silica 1 g was reacted with the desired amount of MAO in 10 mL of toluene at room temperature for 30 minutes. The solid part was separated and washed 5 times with 20 mL of toluene, followed by drying in vacuo at room temperature to obtain the catalyst support precursor SiO_2/MAO.

3.4.2. Preparation of Supported SiO_2/MAO/Et[Ind]$_2$ZrCl$_2$

The catalyst support precursor SiO_2/MAO was stirred at room temperature with the desired amount of Et[Ind]$_2$ZrCl$_2$ solution in toluene for 30 minutes. The solid part was washed with toluene and then dried in vacuo at room temperature.

3.4.3. Preparation of the Modified Silica Gel

Silica gel was calcined under vacuum at 400° C for 6 hours. Calcined SiO_2 2 g and 2 mmol of $SiCl_4$ in 20 mL toluene were refluxed at 110^o C for 7 hours while stirring with a magnetic stirrer under an argon atmosphere. The resulting silica gel was washed 5 times with 40 mL of toluene and then 0.038 mL of 1.5 N aqueous sodium bicarbonate ($NaHCO_3/H_2O$) was added to the silica gel in 20 mL of toluene.

The mixture was stirred at room temperature for 7 hours. The solid part was separated, washed 5 times with 40 mL of toluene and dried in vacuo at room temperature to obtain the modified silica gel.

3.4.4. Preparation of the $SiO_2/SiCl_4$/MAO Catalyst Precursor

The modified silica gel prepared above was reacted with MAO 34 mmol in 20 mL of toluene at room temperature for 30 minutes. The solid part was separated and washed 5 times with 40 mL of toluene, followed by drying in vacuo at room temperature to obtain the catalyst precursor.

3.5. Polymer Characterization

3.5.1. ^{13}C-Nuclear Magnetic Resonance (^{13}C-NMR)

^{13}C-NMR spectroscopy was used to determine propylene incorporation and polymer microstructure. Chemical shifts were referenced internally to the major backbone methylene resonance (taken as 30 ppm from Me_4Si) and calculated according to the method of Randall (1989). Sample solutions were prepared in o-dichlorobenzene and benzene-d_6 (20 vol%) for internal lock signal. The ^{13}C-NMR spectra were obtained at 80^{o}C using JEOL JNM-A500 operating at 125 MHz (at the Technological Research Equipment Centre, Chulalongkorn University). Spectra were taken with a 70^{o} flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s (Haag *et al.*, 2001; Galland *et al.*, 1999).

NMR is an absolute method that does not require calibration. The locations of the resonance peaks identify type of branches or end groups. ^{13}C-NMR was used for studying the incorporation of the α-olefins in the polymeric chain. Tritto *et al.* (1995) investigated ^{13}C NMR of EP copolymers at high ethylene content, prepared with highly isospecific, highly syndiospecific, and aspecific catalysts. The assignment of new sequences is based on (1) correlation of chemical shifts of homo- and copolymers performed with the same catalysts. (2) comparison of spectral intensities for samples of different compositions, (3) comparison with chemical shift values predicted by calculations Cheng's CALMOD program. Their detailed information obtained on comonomer and tactic sequences opens the possibility of describing the chain growth mechanism for the various catalytic systems and of correlating chain structure and copolymer physical and mechanical properties.

Kolbert and Didier (1999) extended the methods for sequencing ethylene-propylene copolymers (EPMs) by ^{13}C-NMR to account for third monomer effects. The equations for calculating the ethylene content and monomer sequence distribution in EPMs were corrected for the presence of the third monomers, 1,4-hexadiene, 2-ethylidene-5-norbornene, and 5,8-dicyclopentadiene that display resonances that overlap with the main chain EPM carbons. These corrections dramatically reduce the standard deviation among equivalent calculation methods. They also examined the effects of experimental conditions on the sequencing data including the choice of solvent, Cr^{3+} doping, and the presence of the nuclear Overhauser effect. In the choosing of a solvent for the NMR of EPDM, one must consider possible reactions with the double bonds that are introduced into the system by the presence of the third monomer. The diene concentration can be easily calculated by integrating the olefinic region and the aliphatic region from 0 to 3.3 ppm and taking the appropriate ratios after subtracting the contribution of the third monomer to the aliphatic intensity.

The solvent of choice for EPM is 1,1,2,2-tetrachloroethane-d_4 (TCE). TCE is an excellent solvent for EPDM as well and displays a triplet of ^{13}C resonances centered at 74 ppm, which is well out of the spectral region of either the main chain EP lines or the third monomer resonances. Unfortunately TCE is an extremely reactive solvent at the temperature necessary to dissolve EPDM, and it rapidly attacks the double bonds in the third monomer leading to crosslinking and, perhaps, chloride addition to the double bond. O-Dichlorobenzene is much less reactive, showing only a slight loss in double bonds after 24 h at 125°C.

3.5.2. Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) is also known as the size exclusion chromatography (SEC). The molecular weight and molecular weight distribution of the polymer samples were determined with a high-temperature GPC instrument (Waters 150-C) equipped with a viscometric detector, differential optical refractometer and four styragel HT type columns (HT3, HT4, HT5 and HT6) with a $1x10^7$ exclusion limit for polystyrene (at Bangkok Polyethylene Public Co, Ltd.). The analyses were performed at 135^o C using 1,2,4-trichlorobenzene as solvent. The columns were calibrated with standard narrow molar mass distribution polystyrene and linear low-density polyethylene.

In this method, the polymer chains are fractionated based on their hydrodynamic volume in solution as they flow through column(s) packed with particles of varying porosity. The MWD obtained by GPC can be modeled as a superposition of polymer chains produced at different catalyst site types. Therefore, by deconvoluting broad MWDs into narrower theoretical distributions, such as Flory’s most probable distribution, information on active center types can be obtained in addition to the information on polymer chain length.

3.5.3. Differential Scanning Calorimetry (DSC)

The melting temperature and glass transition temperature of the copolymers were measured by a Perkin-Elmer DSC 7 at Bangkok Polyethylene Public Co.Ltd. The heating rate of 20^o C/min was employed. The heating cycle was run twice. The first scan, samples were heated up and then cooled down to room temperature. In the second scan, samples were reheated at the same rate. Only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of the samples.

Melting points and melting enthalpies can be measured by DSC. Depending on comonomer presence and polymerization conditions, the melting points of copolymers can change significantly. In addition to measuring melting points and fusion enthalpies, attempts were made to use DSC to get information on the distribution of microstructure of polymer samples. DSC can be used to determine rough chemical composition distributions based on the peak broadness in DSC curve. To enhance this result, polymer samples can be slowly annealed at different temperature ranges before the analysis or by using more sensitive solution phase DSC.

3.5.4. Scanning Electron Microscope (SEM)

Al distribution on the catalyst support precursor and polymer particles were investigated by Scanning Electron Microscope (SEM), JSM-640 Scanning Microscope, Microspec WDX at Technological Research Equipment Center, Chulalongkorn Univeristy, with Energy Dispersive X-ray analysis (EDX).

3.5.5. Temperature Rising Elution Fractionation (TREF)

Chemical composition distribution of the copolymers was analyzed by temperature rising elution fractionation (TREF) at Univerisity of Alberta, Canada. The details of the TREF procedure and the method of data analysis are described by Zhang *et al.* (2000).

Fractionation based on polymer crystallinity in dilute solutions can be used to estimate the distribution of chemical composition and stereoregularity of polyolefins. The primary steps of preparation involved in TREF are 1) dissolution of polymer in a solvent at a high temperature, 2) precipitation of polymer onto an inert support under very slow cooling rate (not more than 0.1^{o}C/hr), and 3) elution and fractionation of polymer under slow heating to re-dissolve the precipitated polymer chains. TREF can be operated in analytical or preparative modes.

An attempt to model the fractionation process on TREF based on thermodynamic model, which was made by Borrajo *et al.* (1995). In addition to Flory-Huggins theory, they considered effects of melting temperature, melting enthalpy, average crystallinity, average crystallizable sequence length, and polymer-solvent interactions. The thermodynamic model divides each chain by crystallizable homopolymer blocks and non-crystallizable highly branched copolymer blocks. Therefore, statistically, every individual chain has distribution of longest to the shortest crystallizable lengths. Since molecular weights of commercial copolymers are large enough for a single chain to form crystallites of different lamella thickness, the effect of chain length is not usually considered in this kind of approach. Their model further assumes that the crystallites have similar thickness. The model predicted the dependence of previously mentioned parameters in reasonable manner when was compared with experimental results.

Zhang *et al.* (2000) presented a new technique for characterization of LLDPE. The LLDPE resins were fractionated by TREF and the TREF fractions were further analyzed by size exclusion chromatography and differential scanning calorimetry (DSC) coupled with successive nucleation annealing (SNA). This technique allowed a direct observation of methylene sequence distribution and thus short chain branch (SCB) distribution. Zhang *et al.* (2001) indicated that the copolymer made with Ziegler-Natta catalyst exhibited a broad bimodal SCB distribution, while the polymer made with the metallocene catalysts had a narrow SCB distribution. They concluded that the SCB distribution has a more significant effect on melting and crystallization behaviors of PE copolymers than the average SCB content.

3.5.6. Gas Chromatography (GC)

Gas chromatography technique was used in order to measure the ratio of ethylene to propylene. Flame ionization detector gas chromatograph Shimadzu GC 14B equipped with column VZ10 was operated using nitrogen (99.999%) as carrier gas at flowrate of 25 ml/min. Both initial and final column temperatures were set to 70^{o}C, detector temperature was set at 150^{o}C and injector temperature was at 100^{o}C.

CHAPTER IV

REACTOR SYSTEM

The purpose of this work is to study copolymerization of ethylene and propylene and to study terpolymerization of ethylene/ propylene and diene. However, it is easier to start investigating the parameters, which have effects on polymerization using metallocene catalyst system, with homopolymerization of ethylene or propylene. Therefore, in this chapter homopolymerizations of ethylene or propylene were carried out to get some preliminary results concerning the reaction conditions such as catalyst concentration [Zr], molar ratio of $[\text{Al}]_{\text{MAO}}/[\text{Zr}]$, reaction temperature, and the characteristics of different reactor systems.

There are many types of reactors, which have been reported in the literature, for studying ethylene/ propylene and/or diene polymerization using metallocene catalysts. The most commonly used reactor system in ethylene or propylene based polymerization is a semibatch system, where the gas consumption can be monitored as a function of time by recording the amount of gas fed to the reactor in order to keep the pressure in the reactor constant. With this reactor system, ethylene/ propylene copolymerization can be carried out in the following ways:

(a) fixed amount of either ethylene or propylene firstly added to the reactor and the other is continuously supplied to the reactor (Kaminsky and Miri, 1985; Koivumaki and Seppala, 1993; Koivumaki and Seppala, 1994; Arndt *et al.*, 1998; Kravchenko and Waymouth, 1998; Arrowsmith *et al.*, 2000; Fan and Waymouth, 2001; Fan *et al.*, 2001),

(b) fixed ratio of premixed ethylene/propylene is fed to the reactor (Koivumaki and Seppala, 1993; Yu *et al.*, 1995; Kaminsky and Drogemuller, 1990; Chien and He, 1991; Galimberti *et al.*, 1998; Galimberti *et al.*, 1999; Chirinos *et al.*, 2000; Galimberti *et al.*, 2001),

(c) using advance online techniques, which can control the ethylene and propylene feed according to the gas composition inside the reactor.

Using batch system, fixed amount of ethylene and propylene along with catalyst and cocatalyst are initially filled into the reactor. As polymerization proceeds, none of these reactants and catalysts is added. The activity is calculated from the polymer weight obtained (Jin *et al.*, 1998). Continuous stirred tank reactor (CSTR) is the system that reactants, catalysts, cocatalysts as well as the products continuously flow out of the reactor at the controlled flow rate according to the desired residence time (Park *et al.*, 2000; Wang and Zhu, 2000; Wang *et al.*, 2000).

Another widely used reactor system in ethylene/propylene copolymerization is the system wherein a fixed ratio of ethylene/propylene gas mixture is supplied to the reactor at constant flow rate (so called purge-mode semibatch system or semiflow method). The constant flow of the gas mixture replaces the gas consumption and also maintains the gas composition in the reactor therefore the comonomer concentration is constant throughout the course of polymerization (Tsutsui *et al.*, 1989; Zambelli *et al.*, 1991; Soga and Kaminaka, 1994; Malmberg and Lofgren, 1997; Lehtinen *et al.*, 1997; Naga *et al.*, 1997; Haag *et al.*, 1998; Djupfors *et al.*, 1998; Galimberti *et al.*, 1998; Haag *et al.*, 1999; Galimberti *et al.*, 1999; Haag *et al.*, 2000; Xu *et al.*, 2001; Galimberti *et al.*, 2001; Bavarian *et al.*, 2001; Haag *et al.*, 2001).

In this work, three reactor systems were used i.e. atmospheric semibatch system, batch system, and continuous gas flow system.

4.1. Atmospheric semibatch system

As described in the experimental part (section 3.3.2.2), this system uses a special designed reactor flask with the catalyst bucket hung above the reaction solution. In order to start the polymerization, this catalyst bucket was dropped into the solution. The monomer pressure inside the reactor was kept constant at 1 atm by continuously feeding monomer to the reactor. The monomer consumption can be monitored by recording the pressure drop in the supply cell (see section 3.3.2.2).

Propylene polymerizations with Cp_2ZrCl_2/MAO were conducted to study the effects of the polymerization conditions i.e. reaction temperature, [Al]/[Zr] ratio and Zr concentration on the rate of polymerization. The solution containing a desired amount of methylaluminoxane (MAO) in toluene 25 mL was first added in the glass reactor under nitrogen atmosphere in the glove box. Then the reactor was degassed by freeze-thaw technique to remove nitrogen. Propylene was introduced until the amount of propylene dissolved in toluene reached equilibrium at the desired temperature and 1 atm of propylene pressure indicated by the level of mercury in a manometer. Polymerization was started by dropping the catalyst bucket containing Cp_2ZrCl_2 into the reaction solution. The computer was immediately started to record the amount of propylene consumption. After 3 hours, the reaction was stopped by pouring the reaction mixture into an excess amount of methanol. The precipitated product was filtered and dried in a vacuum oven at 60°C overnight.

4.1.1. Effect of [Zr] catalyst concentration

Catalyst concentration, [Zr] was varied from 7.5, 15 to 22.5 μM. Propylene consumption and the rate of propylene polymerization are shown in Figure 4.1 and Figure 4.2, respectively. Propylene consumption was faster when higher Zr concentration was used and when this number was divided by the amount of Zr used in terms of moles, the activity of the catalyst or the rate of polymerization were similar for every catalyst concentration studied.

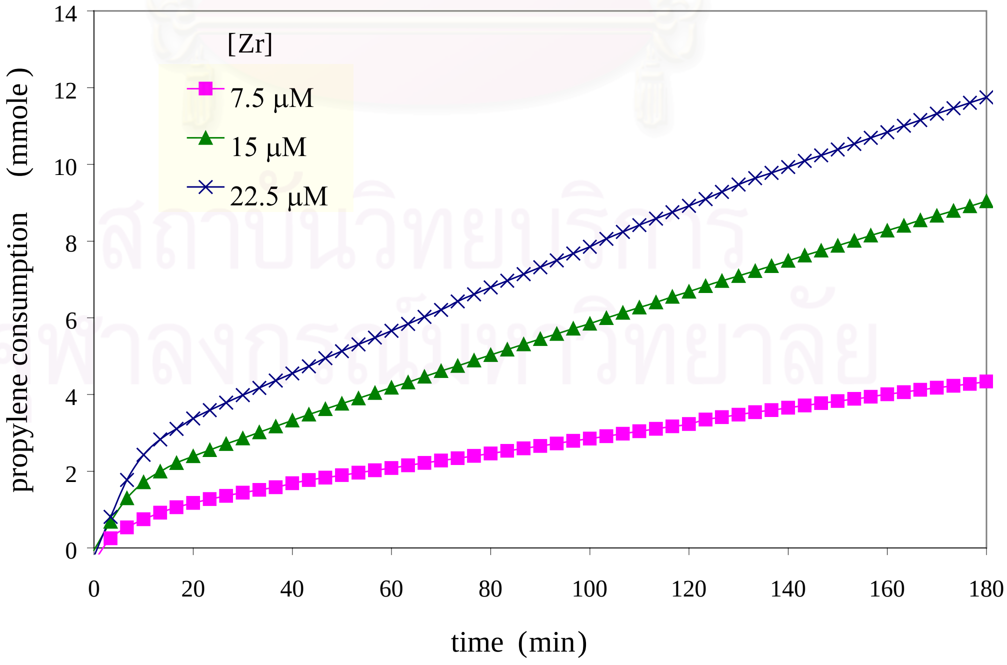


Figure 4.1. Propylene consumption at different [Zr] (using [Al]/[Zr] = 2000, at 40°C)

The changes of [Zr] concentration should not result in the different nature of the active species formed. Only the number of active species should be increased according to the [Zr] concentration. However, when very low [Zr] concentration was applied, only trace of polymer was produced. This might due to the impurities that are still present in the reaction system. Therefore, in order to get rid of the effect coming from these trace impurities, [Zr] concentration selected for the further experiments was high enough, assuming that the impurity level does not change much from one reaction to another.

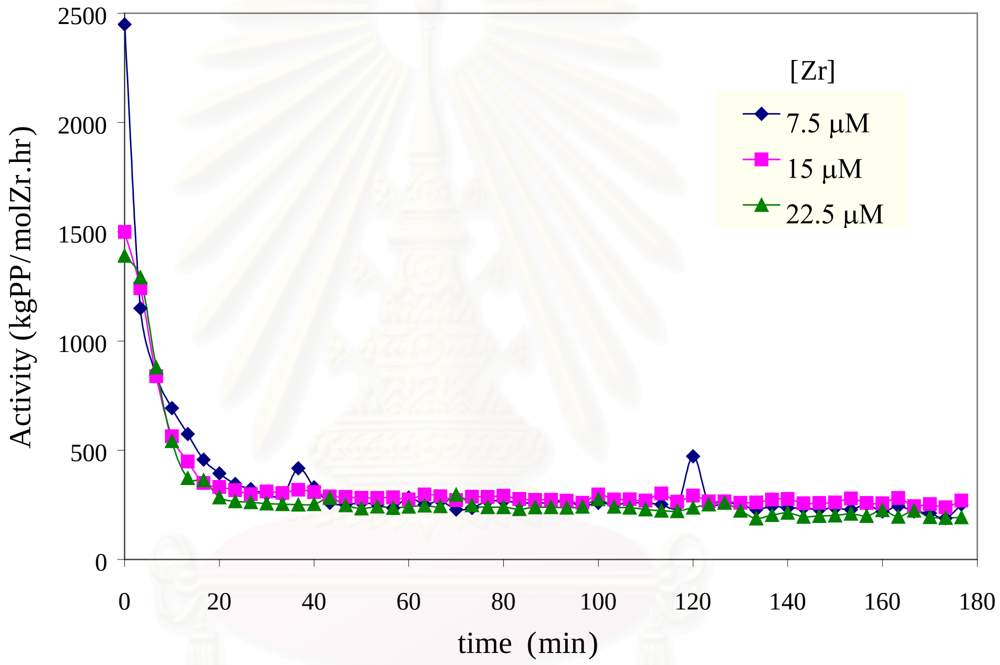
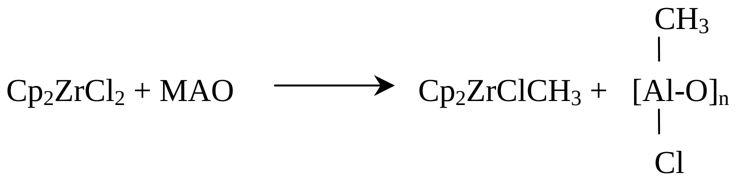


Figure 4.2. Rate of propylene polymerization at different [Zr] (using [Al]/[Zr]=2000, at 40^{o}C)

The rate curves of these three [Zr] concentrations are similar in shape, but when the average rate of reaction is taken into account, the increase in zirconocene concentration resulted in a slight decrease in catalyst activity (350, 340, and 298 kgPP/molZr.hr for [Zr] = 7.5, 15, and 22.5 μM, respectively). The dimerization of the active zirconium complexes forming an inactive species (see equations 4.1 and 4.2), which is favored at higher [Zr] is probably the explanation of this negative effect (Keii and Soga, 1990; Chien and He, 1991).



$$Cp_2ZrCl_2 + MAO \longrightarrow Cp_2ZrClCH_3 + \underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{[Al\text{-}O]_n}}}} \qquad (4.1)$$

$$2\ Cp_2ZrClCH_3 \longrightarrow \underset{\text{Inactive species}}{Cp_2Zr(CH_2)_2ZrCp_2} + 2\ HCl \qquad (4.2)$$

4.1.2. Effect of $[Al]_{MAO}/[Zr]$ ratio

The [Al]/[Zr] ratio was varied from 750 to 4000. Propylene consumption and rate of polymerization of catalyst system with various [Al]/[Zr] ratios are illustrated in Figure 4.3 and Figure 4.4, respectively. It can be seen that the increase in [Al]/[Zr] molar ratio resulted in an increase in the polymerization rate. The average catalytic activity is 381, 340, 262, and 246 kgPP/molZr.hr for the [Al]/[Zr] ratio of 4000, 2000, 1000, and 750, respectively. The most significant enhancement in polymerization rate was observed when the [Al]/[Zr] molar ratio was increased from 1000 to 2000. A further increase of [Al]/[Zr] molar ratio from 2000 to 4000 showed an increase in the polymerization rate but to a lesser extent. The increase of cocatalyst concentration in the polymerization medium may cause an augmentation in the number of active sites. However, in this study a larger amount of MAO ([Al]/[Zr]=4000) was not able to increase significantly the capacity of activation of the metallocene and thus the catalyst activity was not strongly influenced.

It might be concluded that the maximum number of active sites was attained at an [Al]/[Zr] ratio between 2000 and 4000 (Do Couto Junior *et al.*, 2002). The further increase of [Al]/[Zr] ratio higher than 4000 may result in slightly increase of activity but in much less proportional gain and will result in higher amount of Al residual in the polymer produced. The maximum benefit achieved when $[Al]_{MAO}/[Zr]$ increased in the range of 1000-2000.

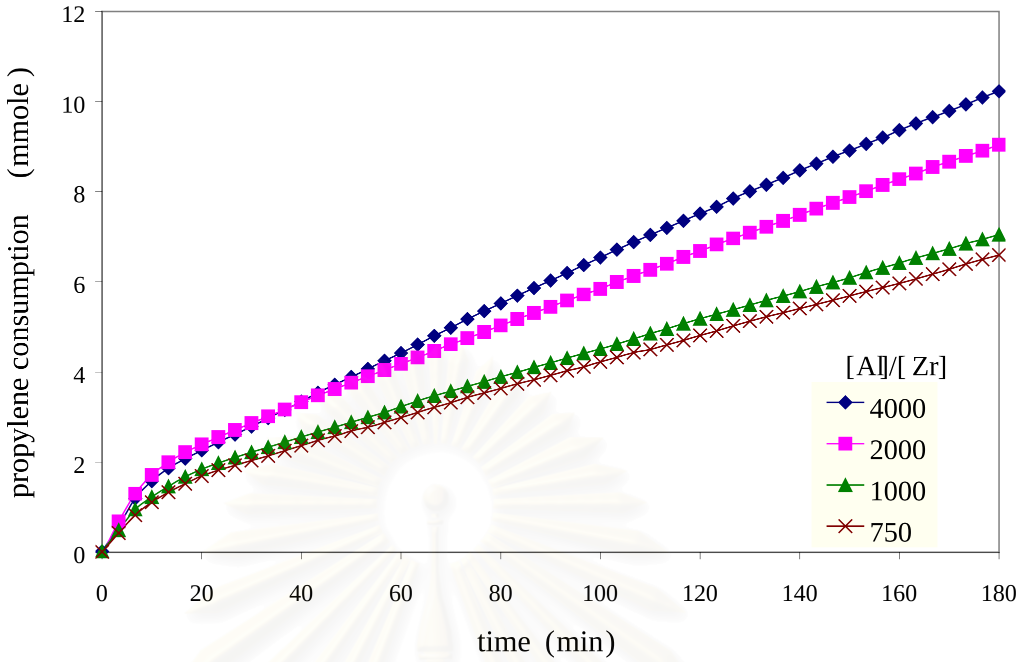


Figure 4.3. Propylene consumption at different [Al]/[Zr] molar ratios (using [Zr]=15 μM at 40°C)

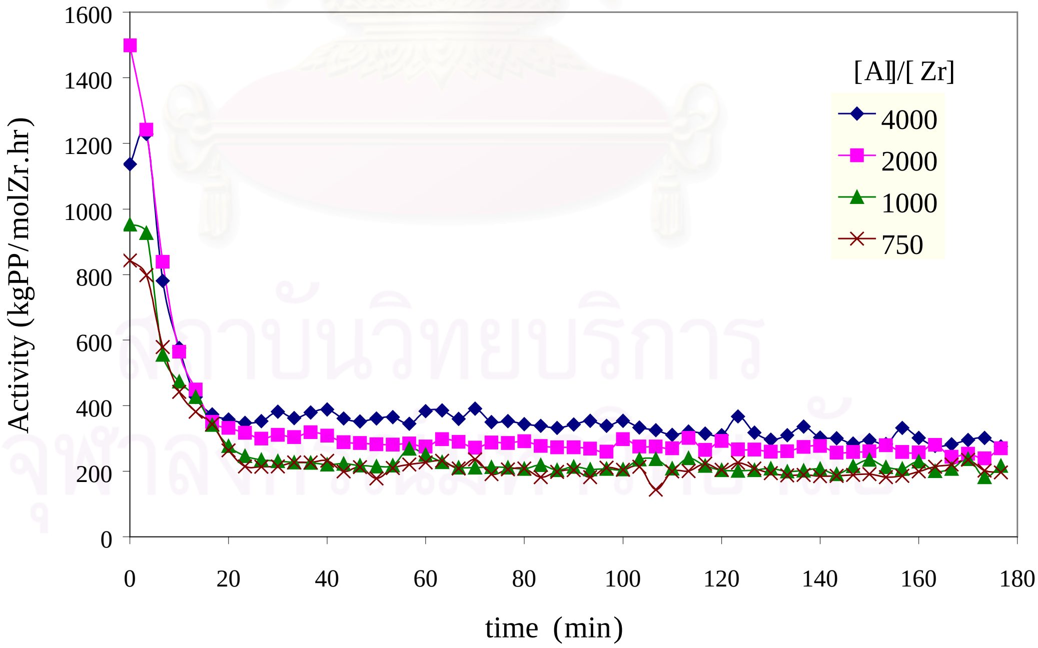


Figure 4.4. Rate of propylene polymerization at different [Al]/[Zr] molar ratios (using [Zr]=15 μM at 40°C)

4.1.3. Effect of reaction temperature

The reaction temperature was varied from 40^{o}C to 60^{o}C for a series of experiments. The results are shown in Figure 4.5 and Figure 4.6. The reaction temperature did not cause any significant difference in the propylene consumption and polymerization rate after it had reached the steady state. Average catalytic activities of these systems are 381, 408, and 399 kgPP/molZr.hr for polymerization temperatures of 40, 50, and 60^{o}C, respectively.

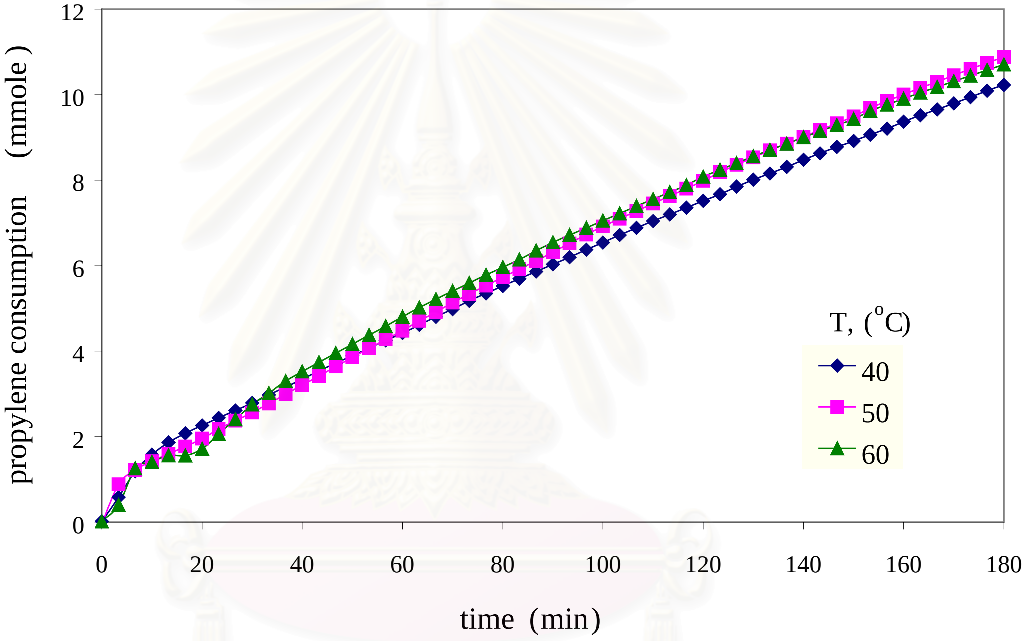


Figure 4.5. Propylene consumption at different reaction temperature (using [Al]/[Zr]=4000, [Zr]=15 μM)

In general, the rate of a chemically controlled reaction increases with the increase of temperature as the rate constant is increased. In Ziegler-Natta catalysis, a widely accepted mechanism of propagation involves the initial formation of a π-complex of an olefin with the catalyst metal, followed by chain migratory insertion (Tsai and Chien, 1994).

$$Zr^{+}\text{-}R_n + C_3H_6 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [\pi C_3H_6 \longrightarrow Zr^{+}\text{-}R_n] \xrightarrow{k_2} Zr^{+}\text{-}R_{n+1} \tag{4.3}$$

At low polymerization temperatures, the π-olefin complex is more stable; its lifetime is longer than the period of insertion. At high temperatures, the complex readily dissociates (dos Santos *et al.*, 1999). The increase of the activity with the increase of reaction temperature may be attributed to the process of activated insertion and the activity is expected to decrease with further increase of reaction temperature because of a shift of equilibrium to the dissociation of the π-complex (Tsai and Chien, 1994).

However, since the activity calculated here does not take into account the solubility of the propylene gas in solvent (toluene), it should be kept in mind that the monomer concentration of these systems are different (higher propylene concentration at lower temperature). Consequently, the results shown in these two figures may be subject to effects of both temperature and monomer concentration at the same time.

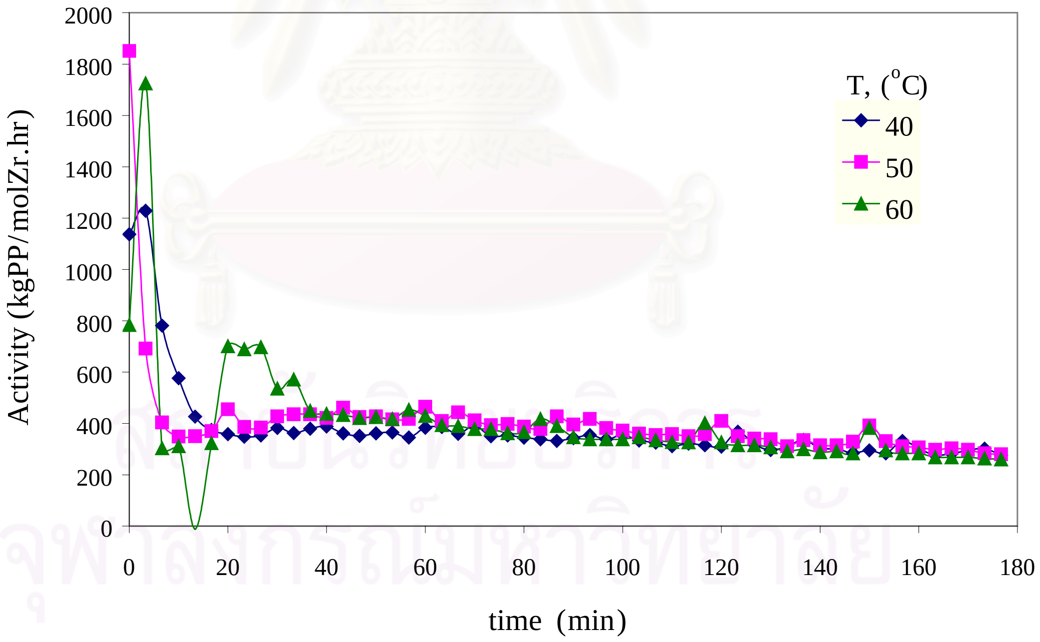


Figure 4.6. Rate of propylene polymerization at different reaction temperature (using [Al]/[Zr]=4000, [Zr]=15 μM)

Table 4.1. Solubility of propylene in toluene at various temperatures (Huang, 1995).

Temperature (^oC)	Solubility (mol/L)
40	0.40
50	0.30
60	0.28

The solubility of propylene in toluene at various temperatures is shown in Table 4.1. The activity defined as kgPP/molZr.[propylene].hr, which takes into account the difference in propylene concentration at different reaction temperatures, shows a linear relationship with reaction temperatures (Figure 4.7).

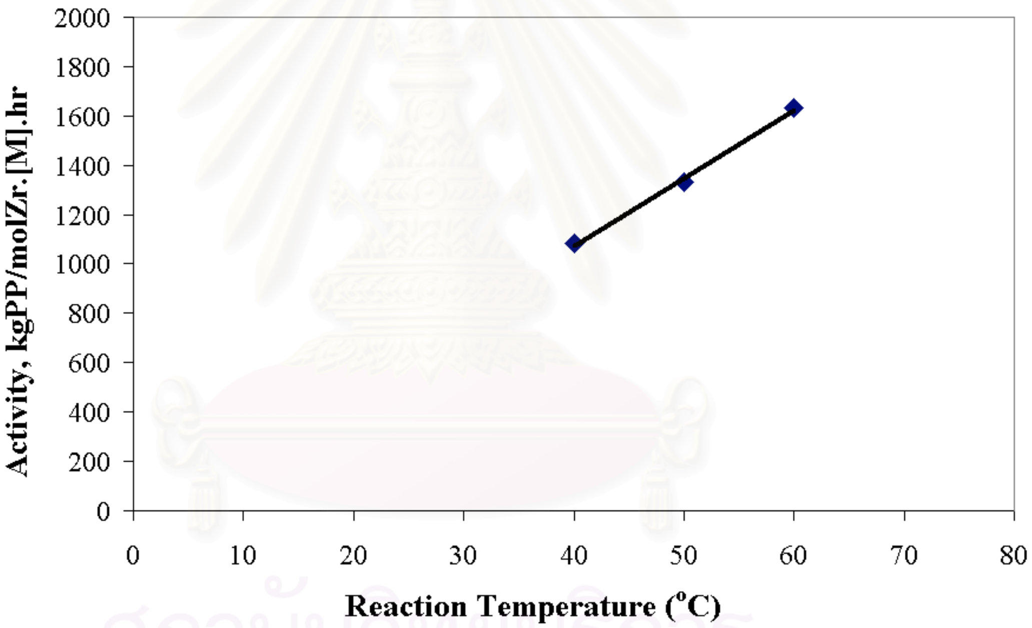


Figure 4.7. Activity of Cp_2ZrCl_2/MAO catalyst system at various reaction temperatures.

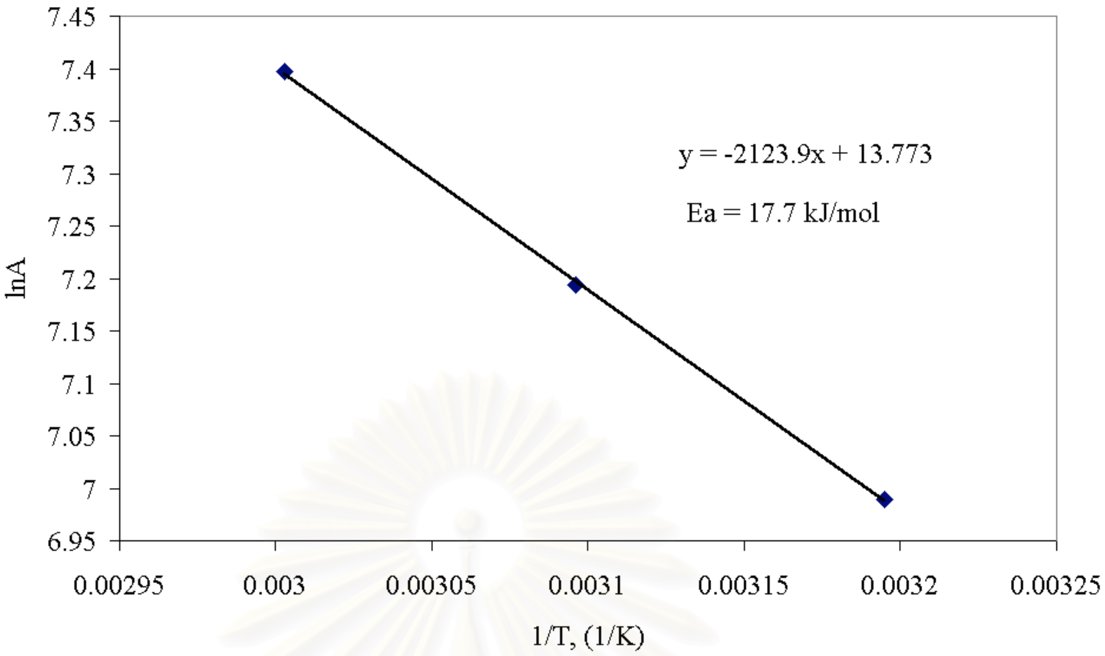


Figure 4.8. Arrhenius plot of Cp_2ZrCl_2/MAO catalyst system.

From Arrhenius plot in Figure 4.8, the activation energy of this system can be estimated. It seems that there is a diffusion limitation of the monomer to the active sites. Diffusion limitations are usually found in ethylene polymerization because of the precipitation of polyethylene, the highly active nature of the catalyst, and low ethylene partial pressure (concentration). In propylene polymerization, this diffusion limitation should be less since no precipitation was observed and this catalyst is not so active as in ethylene polymerization. This reactor system was previously used in kinetic study of propylene polymerization using $Et[H_4Ind]_2ZrCl_2$/ MAO (Huang and Rempel, 1997).

4.1.4. Effect of catalyst type

Propylene polymerization using $Et[Ind]_2ZrCl_2$/MAO catalyst system was carried out (Figure 4.9). With this semibatch system, activity in propylene homopolymerization of $Et[Ind]_2ZrCl_2$/MAO was about twice of Cp_2ZrCl_2/MAO catalyst system. Using [Zr] concentration of 15 μM and [Al]/[Zr] 2000 at 40^oC, activity of $Et[Ind]_2ZrCl_2$ was in the order of 700 kgPP/molZr.hr, while in the case of Cp_2ZrCl_2 was 340 kgPP/molZr.hr.

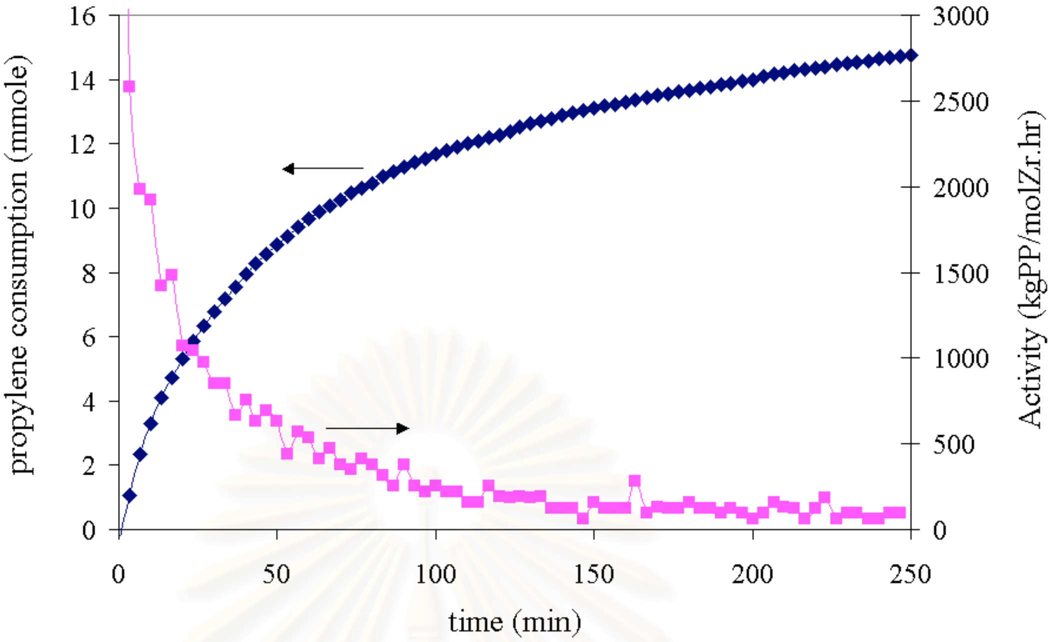


Figure 4.9. Propylene consumption and rate of propylene polymerization with Et[Ind]$_2$ZrCl$_2$/MAO catalyst system, using [Zr]=15 μM, [Al]/[Zr]=2000, in 25 mL reaction solution.

4.2. Batch system

The semibatch system used in this work is an excellent reactor system since it can provide the polymerization rate profile. However, this semibatch system is not suitable for ethylene homopolymerization. Polyethylene usually precipitated from the reaction solution because of its high yield and low solubility in toluene. Therefore, it was difficult to clean the reactor and get all of the polyethylene produced. So the stainless steel reactor used for batch system was chosen to study ethylene homopolymerization instead of the semibatch system. In this section, the activity obtained from different types of metallocene catalyst were compared in ethylene and propylene homopolymerization.

The following tables (Tables 4.2, and 4.3) show yield, and activity of various catalytic systems for ethylene homopolymerization and propylene homopolymerization carried out in a batch system. MAO was used as cocatalyst in all metallocene catalyst systems. Ethylene or propylene 0.0794 mol was initially charged to the reactor. Polymerization procedure is described in the experimental part (section 3.3.2.1). The catalyst concentration applied was 30 μM because when using 15 μM only trace amount of polymer was produced. The higher catalyst concentration required in batch system compared to the semibatch system may result from the impurities in the monomer since a larger amount of monomer was fed into the reactor in the case of the batch system.

Table 4.2. Yield of polyethylene and polypropylene produced with various catalytic systems using batch system; [Metal] 30 μM, [Al]/[Metal] 2000, 40°C, 1 hr.

Catalyst type	PE g	PP g
Cp_2ZrCl_2	1.3875	0.6806
$Et[Ind]_2ZrCl_2$	0.2185	1.7846
Cp_2TiCl_2	0.7408	0.4123
$CpTiCl_3$	0.2595	0.1477

Table 4.3. Catalytic activity of various catalytic systems using batch system; [Metal] 30 μM, [Al]/[Metal] 2000, 40°C, 1 hr.

Catalyst type	PE KgPolymer/molM.hr	PP KgPolymer/molM.hr
Cp_2ZrCl_2	1,542	756
$Et[Ind]_2ZrCl_2$	243	1,983
Cp_2TiCl_2	823	458
$CpTiCl_3$	288	164

From these results, it can be seen that among these catalyst systems, the titanium catalyst showed lower activity than the zirconium one and the half metallocene exhibited much lower activity. Cp_2ZrCl_2/MAO is the most active catalyst system in ethylene homopolymerization, while $Et[Ind]_2ZrCl_2$/MAO is suitable for propylene homopolymerization. Therefore, these two catalysts i.e. Cp_2ZrCl_2 and Et

$[Ind]_2ZrCl_2$ will be used in the following experiments in copolymerization and terpolymerization of ethylene and propylene as representative catalysts, which are good for ethylene and propylene homopolymerization, respectively.

4.3. Continuous gas flow system

Homopolymerization of ethylene and propylene were also carried out using a continuous gas flow system. Xu *et al.* (2001) showed that the system with a continuous flow of monomer gas (purge mode) provides better results for a kinetic study of ethylene homopolymerization and ethylene/propylene copolymerization than a no-purge mode. An increase in activity and improvement in reproducibility was observed.

The glass reactor is first connected to the gas handling part of the system, and then it was evacuated and filled with the gaseous monomer. The gas flow rate was monitored by the wet gas meter and it was adjusted by the needle valve (see experimental part section 3.3.2.3). Using the schlenk technique, solvent was then added to make the total volume 30 mL. After the solvent was saturated with the monomer at the desired temperature, cocatalyst was injected, followed by the metallocene catalyst to start the reaction. The consumption of monomer was monitored by the decrease of the output flow rate.

4.3.1 Ethylene homopolymerization

In the continuous gas flow system, the purge stream may carry some solvent out of the reactor, which resulted in the decrease in the amount of solvent. In order to reduce this effect, the polymerization at lower reaction temperature (20^{o}C) was carried out. Using $Et[Ind]_2ZrCl_2$/MAO catalyst system, ethylene consumption of the polymerization carried out at two reaction temperatures i.e. 40 and 20^{o}C are shown in Figure 4.10. At higher reaction temperature, the solvent (toluene) underwent significant lost with the gas flow due to the increase in vapor pressure at high temperature.

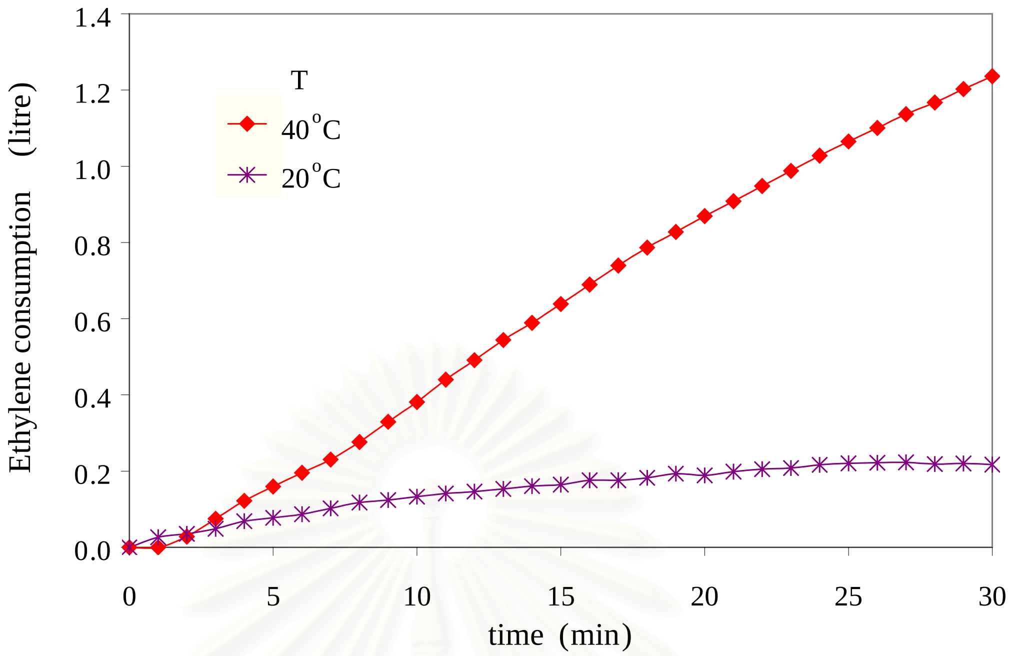


Figure 4.10. Ethylene homopolymerization using Et[Ind]$_2$ZrCl$_2$/MAO catalyst system with [Al]/[Zr] 2000, [Zr] = 15 µM at two reaction temperatures.

Much lower activity was obtained at 20°C compared to 40°C so the reaction temperature of 20°C was too low to produce enough polymer for further characterization.

Ethylene homopolymerization was carried out using Cp$_2$ZrCl$_2$/MAO, and Et [Ind]$_2$ZrCl$_2$/MAO catalyst systems. Representative ethylene consumption profiles for these catalyst systems are shown in Figure 4.11. Cp$_2$ZrCl$_2$/MAO gave very high activity at the beginning and then lost some of its activity as the polymerization proceeded suggesting that deactivation was occurring. In contrast, Et[Ind]$_2$ZrCl$_2$/MAO showed lower activity at the beginning but the activity maintained until the reaction was stopped, only slightly decrease in activity was observed over the time the reaction was followed. This higher activity of Et[Ind]$_2$ZrCl$_2$ system is different from that observed in the batch system. The explanation to this difference should be the higher pressure at the beginning of the batch system, which helps accelerate the rate of polymerization in the case of Cp$_2$ZrCl$_2$ during the initial state. Compare to one point measure of polymer weight in batch system, the consumption profiles were obtained from the continuous gas flow system. It seems that the Et[Ind]$_2$ZrCl$_2$/MAO catalyst system is preferable for ethylene polymerization.

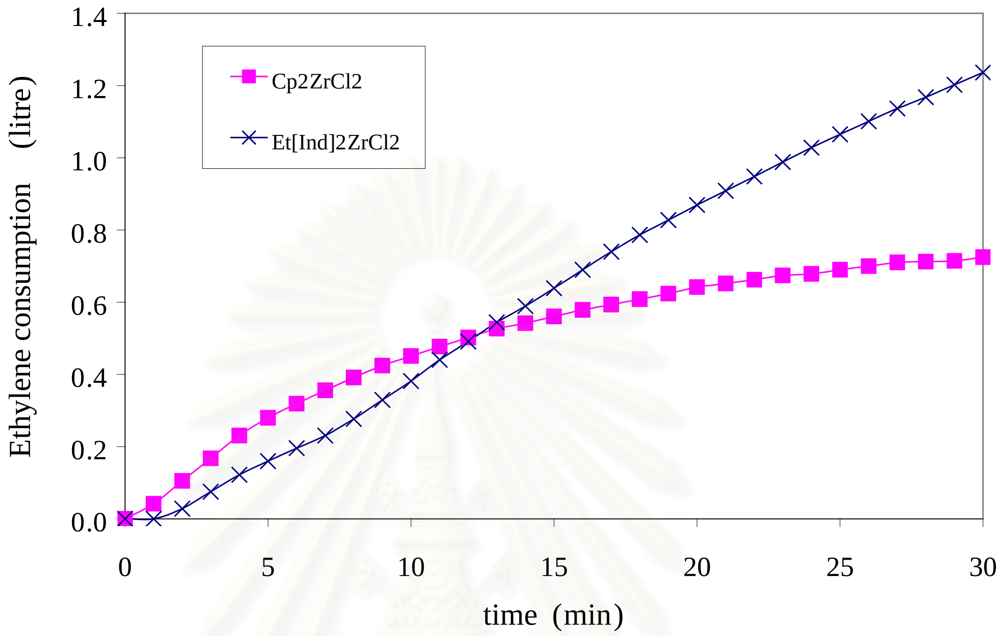


Figure 4.11. Ethylene homopolymerization using two types of metallocene catalysts; [Zr] = 15 μM, T = 40^{o}C, [Al]$_{MAO}$/[Zr] 2000.

4.3.2. Propylene homopolymerization

Propylene homopolymerization was carried out using Et[Ind]$_2$ZrCl$_2$/MAO catalyst system at Zr concentration of 15 μM. Propylene consumption and the activity obtained was very low therefore the Zr concentration was increased to 30 μM (see Figure 4.12). It can be seen that at [Zr] 30 μM, this catalyst showed high and constant activity. Therefore, [Zr] concentration of 15 μM that was used in polymerization carried out in semibatch system, was too low for this continuous gas flow system, where impurities entrained in the gas continuously flow into the reactor.

From Figure 4.13, when compared Et[Ind]$_2$ZrCl$_2$/MAO with Cp$_2$ZrCl$_2$/MAO catalyst system, it can be seen that Et[Ind]$_2$ZrCl$_2$ gave higher activity in propylene homopolymerization. This result is similar to that of the batch system.

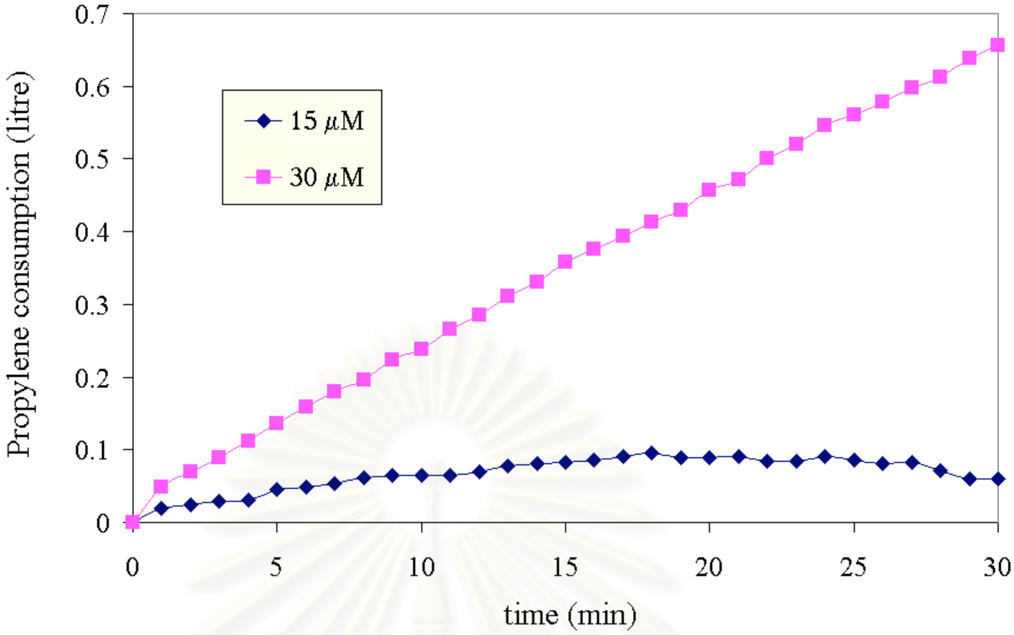


Figure 4.12. Propylene homopolymerization using Et[Ind]$_2$ZrCl$_2$/MAO catalyst system at two [Zr] concentrations; [Al]$_{MAO}$/[Zr] 2000, 40^{o}C.

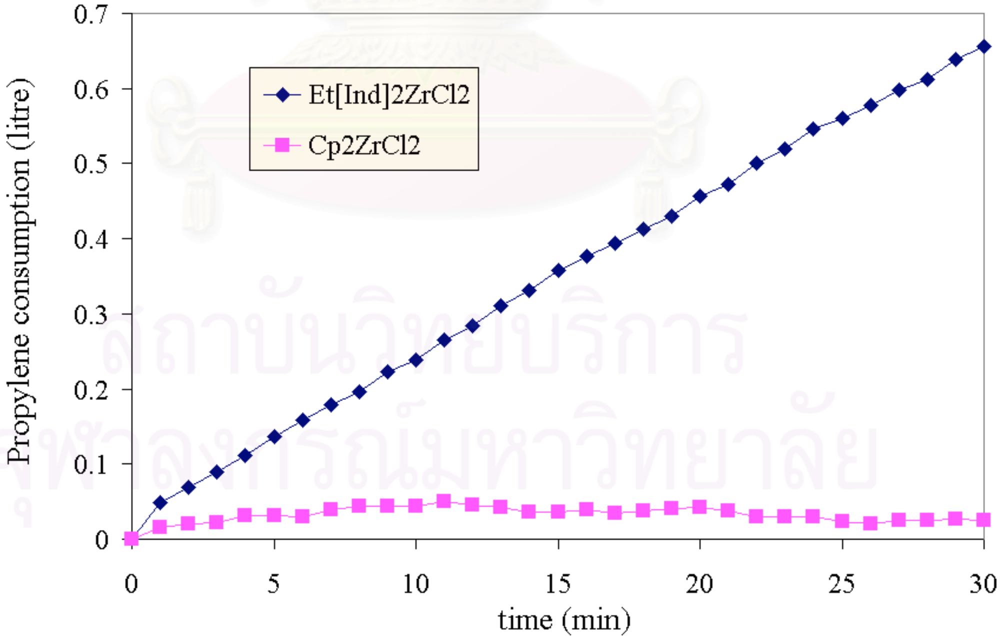


Figure 4.13. Propylene homopolymerization using two types of metallocene catalysts; [Zr] = 30 μM, [Al]$_{MAO}$/[Zr] 2000, 40^{o}C.

4.4. Summary

Important parameters, which have effects on polymerization with the metallocene catalysts, are reaction temperature, catalyst concentration [Zr], $[Al]_{MAO}/[Zr]$. In order to get enough polymer yield for characterization and the accuracy in measuring the polymer yield, the appropriate conditions of these parameters should be selected depending on the reactor systems. $Et[Ind]_2ZrCl_2/MAO$ and Cp_2ZrCl_2/MAO were chosen for the following study in copolymerization and terpolymerization.

CHAPTER V

ETHYLENE/PROPYLENE COPOLYMERIZATION

Ethylene/propylene copolymerization was carried out using batch and continuous gas flow systems. The semibatch system was not used for copolymerization because a sample of gas in the reactor cannot be taken to measure its composition during the polymerization. In the batch system, desired amount of ethylene and propylene were filled into the reactor only once at the beginning. Whereas, in the case of the continuous gas flow system, ethylene and propylene were mixed in a gas cylinder at the desired molar ratio and the gas mixture was continuously fed through the reactor at a flow rate high enough to maintain the gas composition in the reactor. The consumption of monomer was calculated from the decrease of the output flow rate from the feed rate (see experimental part section 3.3.2).

5.1. Effect of the types of metallocene catalyst

5.1.1. Continuous gas flow system

From the results in Chapter 4, Cp_2ZrCl_2/MAO showed the highest activity in ethylene homopolymerization, while Et[Ind]$_2$ZrCl$_2$/MAO exhibited the highest activity in propylene homopolymerization among the metallocenes tested. When ethylene/propylene copolymerization was carried out at ethylene/propylene feed ratio of 50/50 using a continuous gas flow reactor system with these two types of metallocene catalysts, the activity was measured and the results are compared in Table 5.1. Under these reaction conditions, Et[Ind]$_2$ZrCl$_2$/MAO gave higher activity.

Table 5.1. Yield of EP copolymers produced with two metallocene catalysts at [Zr] 30 μM, [Al]/[Zr] = 2000, T=40^{o}C, 30 min, E/P ratio feed 50/50

Catalyst type	Yield (g)	Activity (kgEP/molZr.hr)
$Et[Ind]_2ZrCl_2$	1.8103	4,023
Cp_2ZrCl_2	1.2807	2,846

5.1.2. Batch system

With a batch system, the activity of homogeneous $Et[Ind]_2ZrCl_2$ and Cp_2ZrCl_2 in ethylene/propylene copolymerization are shown in Table 5.2. Similar to the result obtained from the continuous gas flow reactor system, $Et[Ind]_2ZrCl_2$ exhibited higher activity under these reaction conditions. Using semibatch system at 10 psig, Chien and He (1991) also reported that copolymerization activity of $Et[Ind]_2ZrCl_2$ was about 4-5 times higher than Cp_2ZrCl_2 catalyst system. So no matter what type of reactor system is used, $Et[Ind]_2ZrCl_2$/MAO is the better metallocene catalyst for ethylene/propylene copolymerization.

Table 5.2. Yield of EP copolymers produced with different metallocene catalysts; [Zr] 30 μM, [Al]/[Zr] = 2000, T = 40^{o}C, 1 hr, E/P initial molar ratio 50/50

Catalyst type	Yield (g)	Activity (kgEP/molZr.hr)
$Et[Ind]_2ZrCl_2$	1.8500	2,056
Cp_2ZrCl_2	1.1968	1,330

5.2. Effect of ethylene/propylene molar ratio

The Et[Ind]$_2$ZrCl$_2$/MAO catalyst system was then used to investigate the effect of ethylene/propylene feed ratio on the activity of ethylene/propylene copolymerization. Chien and He (1991) observed only slightly increase in copolymerization activity with increasing ethylene/propylene feed ratio in the semibatch reactor system.

5.2.1. Continuous gas flow system

Figures 5.1 and 5.2 show the gas consumption and activity of ethylene/propylene copolymerization using various ethylene/propylene (E/P) feed ratios, respectively. It can be observed that at the highest ethylene ratio, the activity decreased during the polymerization, while the activity was quite constant throughout the polymerization period using higher propylene ratio.

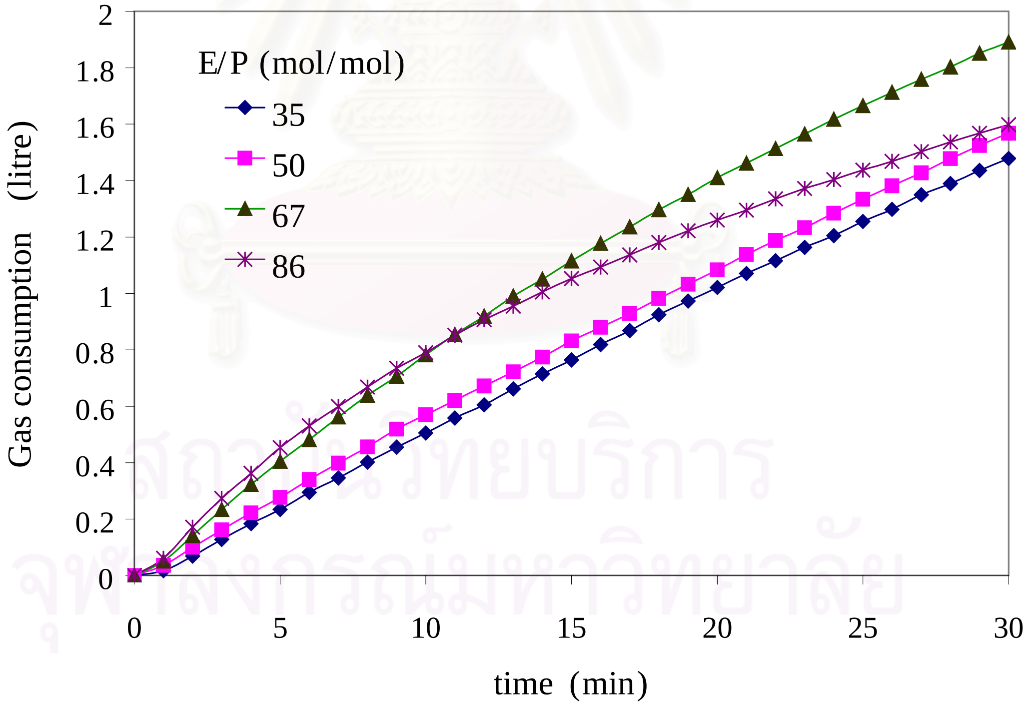


Figure 5.1. Ethylene/propylene copolymerization using various E/P feed ratio with Et[Ind]$_2$ZrCl$_2$/MAO catalyst system at [Al]/[Zr] 2000, 40°C

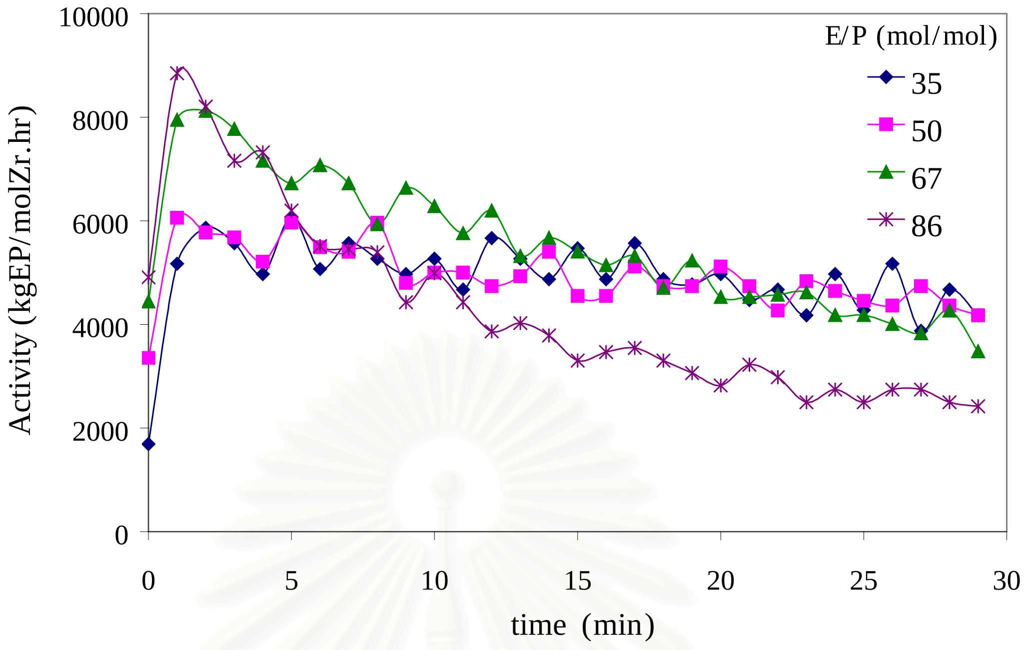


Figure 5.2. Activity of Et[Ind]$_2$ZrCl$_2$/MAO catalyst system in ethylene/propylene copolymerization using various E/P feed ratio at [Al]/[Zr] 2000, 40^{o}C

The average activities of each ethylene/propylene feed ratio are summarized in Table 5.3. The highest activity was obtained at a % ethylene composition in the feed of 67. Figure 5.3 shows that the gas composition during the copolymerization in this flow system was constant throughout the reaction time. Therefore it might be expected that a copolymer having homogeneous composition would be produced.

Table 5.3. Yield of EP copolymers produced with various ratio of ethylene/propylene feed ratio using homogeneous Et[Ind]$_2$ZrCl$_2$/MAO at [Zr] 30 μM, [Al]/[Zr] = 2000, T=40^{o}C, 30 min

Ethylene/Propylene Molar ratio	Yield (g)	Activity (kgEP/molZr.hr)
35/65	2.4361	5414
50/50	2.4365	5414
67/33	2.8754	6390
86/14	2.1889	4864

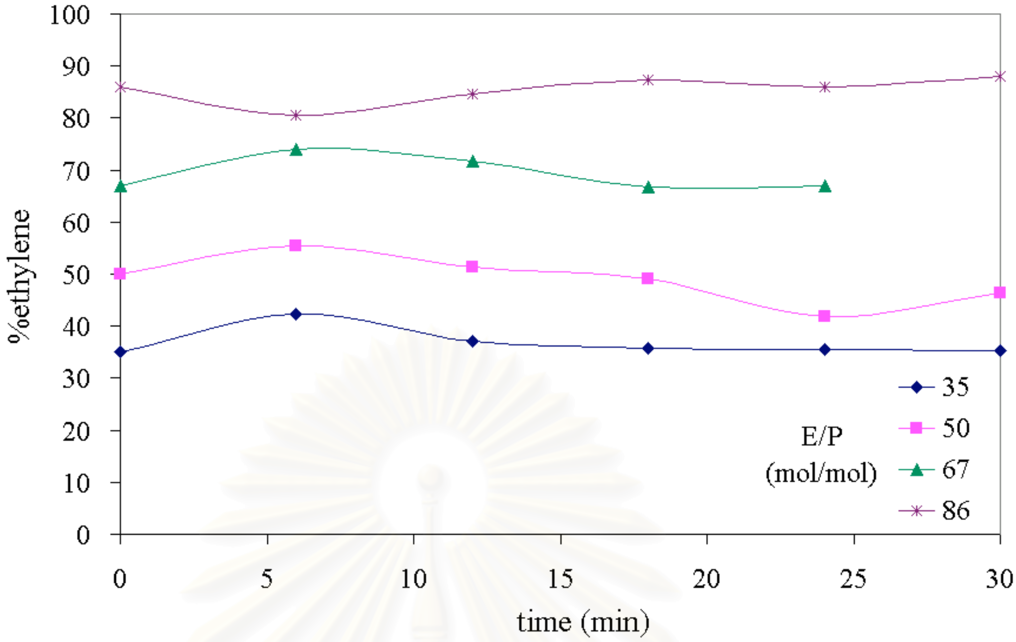


Figure 5.3. % ethylene in the reactor during the ethylene/propylene copolymerization

5.2.2. Batch system

The ethylene/propylene copolymerization was carried out using Et[Ind]$_2$ZrCl$_2$/MAO catalytic system at reaction temperature of 40°C for 1 hr. The ethylene/propylene molar ratio was changed from 0/100, 25/75, 50/50, 75/25 to 100/0. Results are shown in Table 5.4.

Table 5.4. Yield of EP copolymer produced with various ethylene/propylene molar ratios; Et[Ind]$_2$ZrCl$_2$/MAO, [Zr] 30 μM, [Al]/[Zr] 2000, 40^{o}C, 1 hr.

Ethylene/Propylene molar ratio	Ethylene mol	Propylene mol	Polymer Yield g	Activity KgPolymer/molZr.hr
0/100	-	0.0794	1.7846	1,983
25/75	0.0199	0.0596	2.8341	3,149
50/50	0.0397	0.0397	1.8500	2,056
75/25	0.0596	0.0199	1.8353	2,039
100/0	0.0794	-	0.2185	243

Pressure in the reactor was monitored by the pressure gauge connected to the reactor and the ethylene molar ratio was measured by gas chromatography. Results are shown in figures 5.4 and 5.5.

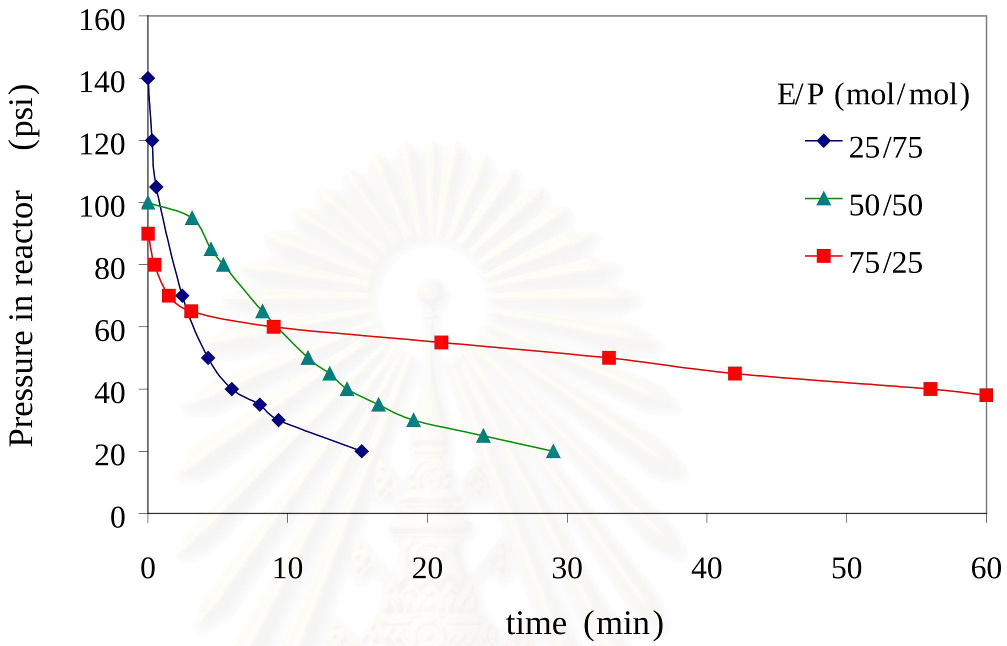


Figure 5.4. Pressure drop in the reactor during polymerization at various initial ethylene/ propylene molar ratios using conditions: Et[Ind]$_2$ZrCl$_2$/MAO, [Zr] = 30 μM, [Al]/[Zr] = 2000, T = 40°C

From Figure 5.4, it can be seen that the highest rate was obtained from the lowest ethylene molar ratio feed where pressure in the reactor decreased more than 60 percent within 10 minutes.

From the results in Table 5.4, activities obtained in copolymerization were higher than both ethylene homopolymerization and propylene homopolymerization. The “ethylene effect”, increase of activity with the presence of ethylene compared to propylene homopolymerization, was also observed by Kravchenko and Waymouth (1998). The addition of small amounts of ethylene results in a large and nonlinear increase in the propylene polymerization rate. They suggested that it is likely the result of the activation of dormant catalyst sites by ethylene. Another type of activation effect has been observed for ethylene polymerization upon addition of small amounts of an α-olefin comonomer, which is usually referred to as a "comonomer effect". Some explanations have been forwarded to explain this phenomenon, including the "trigger" mechanism (Naga *et al.*, 1997) and improved rates of diffusion due to the solubilization of active centers by incorporation of comonomer (Koivumaki and Seppala, 1993).

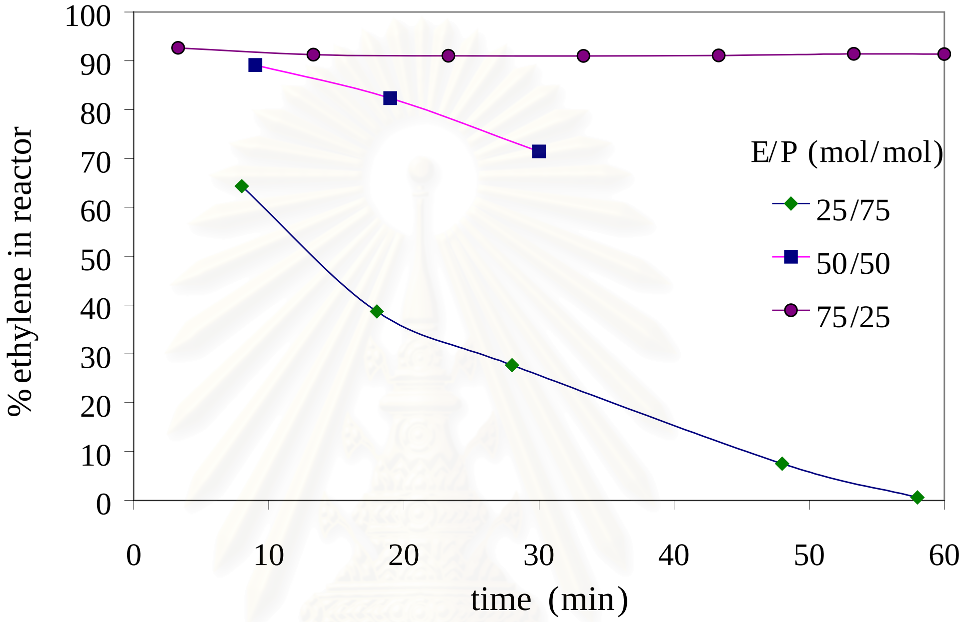


Figure 5.5. Mole %ethylene during polymerization at various initial ethylene/ propylene molar ratio using conditions: Et[Ind]$_2$ZrCl$_2$, [Zr] = 30 μM, [Al]/[Zr] = 2000, T = 40°C

The results shown in Figure 5.5 indicate that with a lower ethylene feed, the gas composition in the reactor changed considerably while it was almost constant with higher ethylene feed ratio. This composition shift may affect the homogeneity of the copolymer obtained.

5.3. Summary

1. In ethylene/propylene copolymerization at E/P molar ratio of 50/50, homogeneous Et[Ind]$_2$ZrCl$_2$/MAO catalyst system gave higher activity compared to Cp$_2$ZrCl$_2$/MAO system both in batch and continuous gas flow systems. So Et[Ind]$_2$ZrCl$_2$/MAO catalyst system is chosen to further investigate ethylene/propylene copolymerization.

2. In a batch system, copolymer produced composed of polymer chains having different chemical composition resulted from different conditions coming from a variation in pressure and comonomer concentration. Whereas, in a continuous gas flow system, gas composition in the reactor is constant throughout the polymerization period. Therefore, to characterize the properties of copolymer produced, it would be better to carry out the copolymerization using a continuous gas flow system.

3. At ethylene/propylene feed ratio of 67/33, the highest activity was achieved with homogeneous Et[Ind]$_2$ZrCl$_2$/MAO catalyst system. The following experiments in ethylene/propylene copolymerization therefore are carried out at ethylene/propylene feed ratio of 70/30.

CHAPTER VI

EPDM TERPOLYMERIZATION

In this chapter, diene was added to the system in order to produce ethylene-propylene- diene elastomer so called EPDM. Terpolymerization was carried out with two metallocene catalysts i.e. Cp_2ZrCl_2/MAO and Et[Ind]$_2$ZrCl$_2$/MAO. Three types of dienes, 5-ethylidene-2-norbornene (ENB), 1,4 hexadiene (HD), and 4-vinyl-1-cyclohexene, were chosen as termonomer. Batch and continuous gas flow systems were used.

6.1. Batch System

6.1.1. Effect of catalyst type

Cp_2ZrCl_2/MAO, and Et[Ind]$_2$ZrCl$_2$/MAO were used in the ethylene/propylene/diene terpolymerization in toluene. Diene used in these experiments was 5-ethylidene-2-norbornene (ENB). Results for the activity of these catalysts over an hour of EPDM production are shown in Table 6.1.

Table 6.1. Activity of EPDM produced with two metallocene catalytic systems; catalyst concentration 30 μM, [Al]/[Zr] 2000, ethylene 0.0397 mol, propylene 0.0397 mol, ENB 0.1 M, 40^oC, 1 hr.

Catalyst type	Polymer Yield G	Activity KgPolymer/molZr.hr
Cp_2ZrCl_2	0.4768	530
Et[Ind]$_2$ZrCl$_2$	2.1127	2,347

The Et[Ind]$_2$ZrCl$_2$/MAO catalyst system gave higher activity than the Cp_2ZrCl_2/MAO catalyst system. Cp_2ZrCl_2/MAO was reported in Chapter 4 as giving very high activity for ethylene polymerization but not for propylene polymerization. For the Et[Ind]$_2$ZrCl$_2$/MAO catalyst system, although the activity observed for the ethylene homopolymerization is not as high as provided by Cp_2ZrCl_2/MAO, it performs very well in the propylene homopolymerization and this might be an important factor for the higher activity in copolymerization at E/P molar ratio of 50/50. It has previously been reported that when using a semibatch system, activities of $Et[Ind]_2ZrCl_2$/MAO in terpolymerization with ENB are higher by one order of magnitude than the terpolymerization catalyzed by Cp_2ZrCl_2/MAO (Yu *et al.*, 1995). In this batch system, $Et[Ind]_2ZrCl_2$ gave about 4 times higher activity than Cp_2ZrCl_2. $Et[Ind]_2ZrCl_2$/MAO catalyst system therefore seems to be more suitable for EPDM terpolymerization than Cp_2ZrCl_2/MAO.

Table 6.2 summarizes the activity of these two catalytic systems in ethylene homopolymerization, propylene homopolymerization, ethylene/propylene copolymerization and ethylene/propylene/diene terpolymerization.

Table 6.2. Catalytic activity of various catalytic systems; catalyst concentration 30 μ M, [Al]/[Metal] 2000, ethylene/propylene molar ratio 50/50 for EP and EPDM, ENB 0.1 M, 40^{o}C, 1 hr.

Catalyst type	PE KgPolymer/molZr.hr	PP KgPolymer/molZr.hr	EP KgPolymer/molZr.hr	EPDM (ENB) KgPolymer/molZr.hr
Cp_2ZrCl_2	1,542	756	1,330	530
$Et[Ind]_2ZrCl_2$	243	1,983	2,056	2,347

It can be seen that in the case of the $Et(Ind)_2ZrCl_2$/MAO system the presence of diene increased the activity, while the results showed a decrease in activity when diene was added in the Cp_2ZrCl_2/MAO catalyst system. When comparing EP copolymerization with ethylene and propylene homopolymerization, it was found that for the Cp_2ZrCl_2/MAO catalyst system, addition of propylene reduce the activity from ethylene homopolymerization, while in the case of $Et(Ind)_2ZrCl_2$/MAO rate enhancement was observed.

Using a continuous flow method, Naga *et al.* (1997) observed that the activity of non-bridged non-specific metallocenes (Cp_2ZrCl_2) in copolymerization at 50 mol% propylene in feed was less than ethylene homopolymerization but higher than propylene homopolymerization. They also reported that higher activities were obtained for the copolymerization compared to ethylene and propylene homopolymerization with ansa-isospecific metallocenes ($Et[Ind]_2ZrCl_2$). This accelerating effect was explained that it might result from an increase in the concentration of active centers and/or an increase of the rate constant of ethylene insertion. This tendency could also be explained by hindrance of monomer diffusion to active species by high crystalline polymers produced.

Using a semibatch system, with both $Et[Flu]_2ZrCl_2$/MAO (C_{2v} symmetric catalyst) and $Me_2Si[Ind]_2ZrCl_2$/MAO (C_2 symmetric catalyst), Yu *et al.* (1995) reported that the copolymerization rates lie in between those of the homopolymerization. The decrease in catalyst activity with the addition of propylene was also observed when using tetramethyldisiloxanediyl$[Cp]_2ZrCl_2$ catalyst system (Lee *et al.*, 1996). When [2-(dimethylamino)ethyl]$CpTiCl_3$/ MAO was used, activity of copolymerization was less than both ethylene and propylene homopolymerization (Chien *et al.*, 1998). Whereas the activities obtained in E/P copolymerization using isopropylidene[Cp][Flu]$ZrCl_2$ and isopropylidene[3-MeCp][Flu]$ZrCl_2$ (C_1 symmetric catalyst) were higher than their analogous ethylene and propylene homopolymerization (Arndt *et al.*, 1998; Arrowsmith *et al.*, 2000). So depending on the type of metallocene catalysts, the rate enhancement effect, which is referred to as the comonomer effect may be observed.

Kaminsky and Miri (1985) carried out E/P/ENB terpolymerization with Cp_2ZrMe_2/ MAO using semibatch system under a total pressure of 9 bar, [ENB] 0.1 M. When comparing the terpolymerization with the diene-free copolymerization, it becomes obvious that the presence of the diene monomer causes lower activities, especially at low ethylene/propylene ratios. Yu *et al.* (1995) also reported that, with Et $[Flu]_2ZrCl_2$/MAO and $Me_2Si[Ind]_2ZrCl_2$/MAO catalyst system, the presence of ENB (0.074 M) significantly reduces the copolymerization activity by 10-20 fold. Diene (ENB) also exhibited the adverse effect on the activity when isopropylidene [3-MeCp][Flu]$ZrCl_2$ was used (Arrowsmith *et al.*, 2000). The activity decreased about 7 fold when diene concentration of 0.2 M was applied. A similar decrease in activity of about 7 fold was also observed with [2-(dimethylamino)ethyl]$CpTiCl_3$/ MAO at [ENB] 0.07-0.15 M (Chien *et al.*, 1998).

Using a semibatch system under reaction pressure of 10 psig, Chien and He (1991) reported that the presence of ENB (0.037 M) decreases the rate of polymerization carried out with $Et[Ind]_2ZrCl_2$ to about a half. In contrast, Malmberg and Lofgren (1997) reported that the termonomer (ENB) did not affect the polymerization yield significantly. Polymerization yields were lower only at the largest diene concentrations (0.6 M). Terpolymerization was carried out using continuous gas flow method and the polymerization pressure was 3 bar. Haag *et al.* (2000) also carried out E/P/ENB terpolymerization with $Et[Ind]_2ZrCl_2$. At low diene concentrations (less than 0.025 M), no significant change can be observed in the activity. Whereas at high diene concentrations (more than 0.1 M), increase in diene concentration leads to a decrease in the catalyst activity. They suggested that there might be a competition between the deactivation of active species and the propagation reaction, both promoted by diene. Thus, in the range of low diene concentration, no significant change was observed. On the other hand, for higher diene concentration, the activity falls probably due to the deactivation mechanism promoted by the diene, which prevails over the active species.

From the results shown in Table 6.2, the concentration of diene (0.1 M of ENB) used might be too low to compete with the propagation reaction in the case of $Et(Ind)_2ZrCl_2$/MAO; therefore a slight increase in activity was observed. Whereas the deactivation of active species, which resulted from the diene at this concentration, is more pronounced with the Cp_2ZrCl_2/MAO catalyst system. Deactivation arising from diene chelating effect or bidentate complex to the active sites and hinder the addition of monomer may occur to greater extent in the case of Cp_2ZrCl_2 than $Et(Ind)_2ZrCl_2$ ansa-metallocene which is more conformation.

6.1.2. Effect of diene type

The EPDM terpolymerization was then carried out using the $Et[Ind]_2ZrCl_2$/MAO catalytic system in toluene to investigate the effect of diene types. Three types of diene i.e. 5-ethylidene-2-norbornene (ENB), 1,4 hexadiene (HD), and 4-vinyl-1-cyclohexene (VCH), were chosen for comparison. Ethylene 0.0397 mol and propylene 0.0397 mol was initially added to the reactor. The results for these terpolymerization are shown in Table 6.3.

Table 6.3. Yield of EPDM produced with various dienes using Et[Ind]$_2$ZrCl$_2$/MAO; [Zr] 30 μM, [Diene] 0.1 M, [Al]/[Zr] 2000, ethylene/propylene ratio 50/50, 40^{o}C, 1 hr

Diene Type	Polymer Yield g	Activity KgPolymer/molZr.hr
5-Ethylidene-2-norbornene (ENB)	2.1127	2,347
1,4 Hexadiene (HD)	2.2272	2,475
4-Vinyl-1-cyclohexene (VCH)	2.2226	2,470

At a diene concentration of 0.1 M, the type of diene used in the present study did not appear to have any sizable effect on the activity within experimental error. Yu *et al.*, (1995) and Marques *et al.*, (1995) however reported that when three types of diene were added to the systems, the activity in terpolymerization was in the order of VCH>ENB~HD. They proposed that both double bonds in HD might chelate to the metal center resulting in a lower activity.

6.1.3. Effect of ethylene/propylene initial molar ratio

The EPDM terpolymerization was carried out using the Et[Ind]$_2$ZrCl$_2$/MAO catalytic system in toluene at a reaction temperature of 40 °C for 1 hr. The ethylene/propylene molar ratio was changed from 25/75, 50/50 to 75/25 with diene (ENB) 0.1 M and the results observed are shown in Table 6.4.

Table 6.4. Yield of EPDM produced with various ethylene/propylene molar ratios; Et [Ind]$_2$ZrCl$_2$/MAO, [Zr] 30 μM, [Al]/[Zr] 2000, 40^{o}C, 1 hr.

Ethylene/Propylene molar ratio	Ethylene mol	Propylene mol	ENB M	Polymer Yield g	Activity KgPolymer/molZr.hr
25/75	0.0199	0.0596	0.1	3.1989	3,554
50/50	0.0397	0.0397	0.1	2.1127	2,347
75/25	0.0596	0.0199	0.1	1.9353	2,150

Since the catalyst used in this set of experiments was Et[Ind]$_2$ZrCl$_2$/MAO, which gave higher activity in propylene polymerization than in ethylene polymerization, the higher activity can be seen from the higher ratio of propylene to ethylene. When compared to ethylene/propylene copolymerization, the same trend was observed (see Table 5.4). The activity was slightly increased when ENB was added for any ethylene/propylene ratio.

6.2. Continuous gas flow system

When diene (ENB) was added to the continuous gas flow system at the concentration of 0.1 mol/L in EPDM terpolymerization, only trace amounts of the polymer were obtained although very high [Zr] concentration (60μM) was applied. This might result from the more pronounced adverse effect of diene to the activity at low ethylene and propylene pressure.

6.3. Summary

1. Et[Ind]$_2$ZrCl$_2$ provided higher catalytic activity. Rate enhancement or comonomer effect was observed in the case of Et[Ind]$_2$ZrCl$_2$, but not for the Cp$_2$ZrCl$_2$ catalyst system. Moreover, significant decrease in activity was observed when diene was added in the case of Cp$_2$ZrCl$_2$, while slight increase in activity was obtained with Et[Ind]$_2$ZrCl$_2$. Therefore when the activity was a concern, Et[Ind]$_2$ZrCl$_2$ is preferred for carrying out EP and EPDM polymerization.
2. In EPDM terpolymerization using Et[Ind]$_2$ZrCl$_2$ in batch system, the type of diene i.e. ENB, HD, and VCH did not exhibited any different effect on the catalytic activity.
3. Diene addition may have both positive and adverse effect on the activity by enhancing the propagation reaction or promoting the deactivation process depending on the type of catalysts and reaction conditions. Deactivation may arise from chelating of diene to the active species, which occurred to a greater extent in non-bridged Cp$_2$ZrCl$_2$ than the bridged Et[Ind]$_2$ZrCl$_2$ catalyst system. Using the same diene concentration, the decrease of activity resulting from the presence of diene was observed at low-pressure reactor system.

CHAPTER VII

HETEROGENEOUS CATALYST SYSTEM

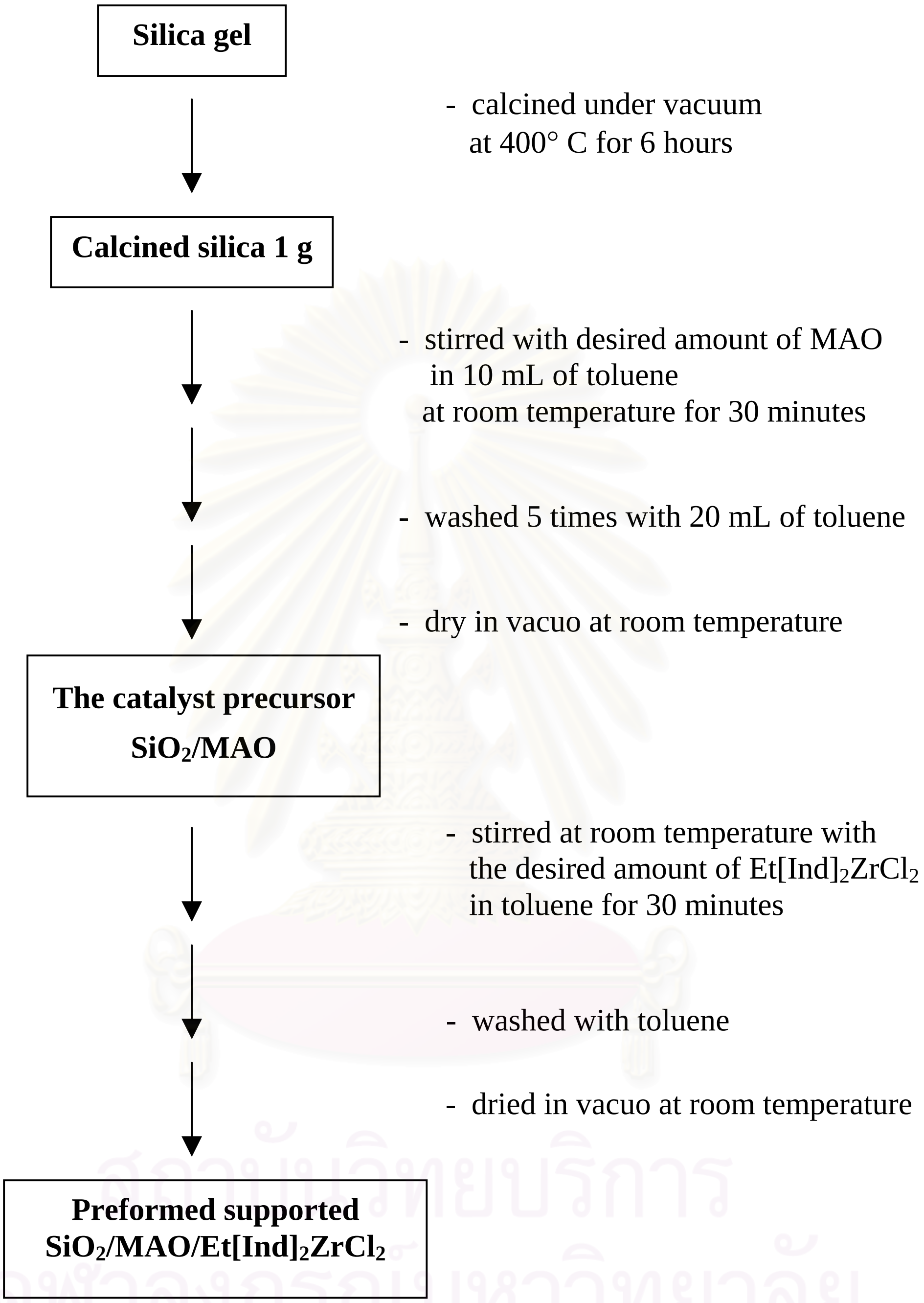
For commercial applications, metallocene catalysts should be immobilized on supports so that they can be used for ‘drop-in’ technology replacing the conventional Ziegler-Natta catalysts used in industrial slurry and gas phase processes. So in this Chapter, E/P copolymerization using a heterogeneous system was studied. Methods for immobilizing metallocenes fall largely into two categories: (1) MAO-mediated systems, in which impregnation of the support with MAO is followed by addition of a metallocene catalyst, and (2) directly impregnated metallocene onto the support (Chien, 1999; Kaminsky and Winkelbach, 1999; Kristen, 1999; Santos *et al.,*2000). In this work, method (1) was applied by using SiO_2 as support and the $Et[Ind]_2ZrCl_2$ as catalyst. From the results in Chapter 5, the continuous gas flow system was then selected for this study and ethylene/propylene ratio in the feed of 70/30 was applied.

Methylaluminoxane (MAO) is synthesized from a hydrolysis reaction of trimethylaluminum (TMA). Previous investigations have shown that there is always some residual TMA in commercially available MAO and, moreover, that this is difficult to remove even under vacuum condition accompanied by heating (Ystenes *et al.*, 2000). Therefore, when MAO is immobilized on silica, both TMA and MAO possibly react with the OH-groups on the silica surface.

According to the IR results, Panchenko *et al.*, 1999 suggested that for the most part of silica, the terminal OH-groups interact particularly with TMA, and some amount of oligomeric MAO molecules strongly adsorb on the SiO_2/TMA surface. The presence of TMA increases the reactivity of MAO on the surface and the stability of the final adsorbed species; therefore MAO without TMA may present lower reactivity. However, the conclusion from the work of Ferreira *et al.* (2000) is that OH from a silica surface reacts with MAO and probably with TMA during the MAO treatment. The most probable final species is one where the MAO molecule is fixed to the surface at several points, mainly in a linear form. When MAO*TMA is supported, TMA would be associated with MAO on the surface.

Apart from the effect of TMA on the active species formed during the preparation of MAO impregnated silica, TMA showed an adverse effect in homogeneous catalyst systems. Dried MAO prepared as reported by Hasan *et al.* (2001), which was free of TMA, was found to be more active than the standard MAO system. The addition of TMA on the dried MAO system resulted in a decrease in polymer yield (Ioku *et al.*, 2002). In ethylene polymerization, quite contradictory conclusions about the effects of TMA and MAO on the polymer properties were drawn in different laboratories. It was reported that the influence of TMA on polymerization and the resulting polymer properties are catalyst-specific (Ystenes *et al.*, 2000).

In this Chapter, the effects of trimethylaluminum (TMA) and methylaluminoxane (MAO) on ethylene-propylene copolymerization with different supporting procedures: preformed SiO_2/MAO supported Et[Ind]$_2$ZrCl$_2$, and in-situ SiO_2/MAO supported Et[Ind]$_2$ZrCl$_2$ were examined. The procedure of preparing preformed supported SiO_2/MAO/Et[Ind]$_2$ZrCl$_2$ is illustrated in Scheme 7.1. For the reaction, when this preformed supported system was carried out, the suspension of SiO_2/MAO/Et[Ind]$_2$ZrCl$_2$ was injected directly to the reactor to start the copolymerization. While in the case of in-situ supported system, the catalyst precursor SiO_2/MAO was primarily injected to the reactor and the solution of Et[Ind]$_2$ZrCl$_2$ was injected to the reactor subsequently to start the reaction.



Scheme 7.1. The procedure of preparing preformed supported SiO_2/MAO/Et[Ind]$_2$ZrCl$_2$

7.1. In-situ supported system

7.1.1. Effects of TMA in SiO_2/MAO in-situ supported system

Ethylene/ propylene copolymerization was carried out with various amounts of TMA (injected directly to the reactor). Table 7.1 shows catalytic activity and copolymer properties for copolymers synthesized using different $[Al]_{TMA}/[Zr]$ mole ratio for the SiO_2/MAO in-situ supported system. When no TMA was present, some activity was observed. However, the activity was found to increase further with increase of TMA up to a $[Al]_{TMA}/[Zr]$ mole ratio as high as 1000. As the $[Al]_{TMA}/[Zr]$ mole ratio was increased further, the activity was found to decrease to some extent. Chu *et al.* (2000) carried out the polymerization of ethylene with in-situ supported metallocene catalyst. In the absence of TMA, in-situ supported $Et[Ind]_2ZrCl_2$ was not active, whereas the $Et[Ind]_2Zr(CH_3)_2$ was active. These results confirm that TMA probably acted as an impurity scavenger, alkylating agent, and/or activator.

TMA as a scavenger helps in reducing the amount of impurities in the system thereby leading to an increase in activity. However, TMA is also able to inhibit certain functions of MAO. Several explanations for this are possible. Since TMA is a stronger alkylating and reducing agent than MAO, TMA could cause the reduction of the zirconocene compound resulting in an inactive species. It may also compete with MAO as a complexing ligand leading to a catalyst of lower polymerization activity. Moreover, addition of TMA can lower the degree of oligomerization of MAO and its overall effectiveness (Chien and He, 1991). Therefore, addition of TMA has both advantages and disadvantages with respect to catalytic activity.

TMA may act as a chain transfer agent leading to the termination of the growing chain, via chain transfer to the alkylaluminum; consequently the reaction results in a decrease in molecular weight when more TMA is added. It was reported that chain termination by transfer to the cocatalyst is an essential part of the termination mechanism for ethylene polymerization with bis(pentamethylcyclopentadienyl) zirconium dichloride $Cp^*_2ZrCl_2$/MAO/TMA. Both

Mw and Mn decrease significantly with the addition of TMA (Ystenes *et al.*, 2000). The results shown in Table 7.1 suggest that the chain transfer to TMA might not be the major chain transfer reaction in this system since no significant change in Mw was observed even when a high excess of TMA was present.

Table 7.1. Activity and properties of copolymer produced with different amount of TMA for the SiO_2/MAO in-situ supported system using catalyst concentration = 60 μM, E/P molar ratio = 70/30, $[Al]_{MAO}/[Zr]$ mole ratio = 215, T = 40^{o}C, reaction time 30 min.

Run	$[Al]_{TMA}/[Zr]$ mole ratio	Activity (kgPolymer/molZr.hr)	Mw	MWD	Ethylene in copolymer %
EP1	0	2364	51000	3.2	70.5
EP2	500	3301	44000	3.0	
EP3	1000	3404	43000	2.8	
EP4	1500	3246	66000	5.0	75.1
EP5	2000	2879	59000	4.9	
EP6	2500	3016	57000	4.8	
EP7	3000	2732	55000	4.7	
EP8	3500	2591	59000	4.8	72.4

MWD broadening likely resulted from the interactions between the metallocene and the support, which leads to the formation of active sites differing in electronic and steric character. Ethylene incorporation in copolymers was found to be close to the ratio of the ethylene to propylene feed ratio. No significant effect of TMA on ethylene incorporation was observed. All the copolymers produced were amorphous with no specific melting temperature.

7.1.2. Effects of MAO in SiO_2/MAO in-situ supported system

MAO has many possible functions in metallocene catalyst systems, such as scavenging of impurities, alkylation, ionization and/or reduction of the transition element, stabilization of the cationic metallocene alkyl and/or the counter ion, and perhaps others. One important role of MAO is apparently to prevent the formation of a $ZrCH_2CH_2Zr$ species (inactive dimeric complex). This is one of the reasons why a very large amount of MAO is needed to realize the maximum catalytic activity of the ansa-metallocene complexes in solution polymerization. One way to lower this large MAO requirement is to immobilize the complex on a support (Chien and He, 1991).

Table 7.2. Activity and properties of copolymer produced with different amounts of MAO in the SiO_2/MAO in-situ supported system using catalyst concentration 60 μM, E/P molar ratio = 70/30, $[Al]_{TMA}/[Zr]$ mole ratio = 2500, T = 40^oC, reaction time 90 min.

Run	$[Al]_{MAO}/[Zr]$ mole ratio	Activity (kgPolymer/molZr.hr)	Mw	MWD	Ethylene in copolymer %
EP9	98	158	23000	3.5	77.8
EP10	118	199	27000	4.4	79.6
EP11	157	507	28000	3.9	
EP12	184	915	25000	3.9	77.7
EP13	215	2075	33000	2.5	

With increased amounts of MAO used for the catalyst precursor, catalytic activity was continuously increased with increase of MAO while no significant effect on molecular weight was observed (Table 7.2.). The increase in activity did not linearly depend on the amount of MAO used but the activity increased more when using a high level of MAO. In homogeneous metallocene systems, there is usually a minimum requirement of the amount of MAO that can stabilize the active species. In a similar fashion, this in-situ supported system requires MAO to activate and increase the number of active species as well as to stabilize them in order to obtain the high activity.

The molecular weight of the copolymer produced, when different amounts of MAO were used in the precursor preparation, did not change significantly under the condition used in this work. However, for the homogeneous catalyst system, it was found that the Mw increased slightly by lowering $[Al]_{MAO}/[Zr]$ ratio (Chien and He, 1991, p.1603).

7.2. Preformed supported system

7.2.1. Effects of TMA in preformed $SiO_2/MAO/Et[Ind]_2ZrCl_2$ supported system

When $Et[Ind]_2ZrCl_2$ was supported on SiO_2/MAO instead of being injected separately into the reactor, TMA showed more adverse effect on the catalytic activity at higher $[Al]_{TMA}/[Zr]$ ratios. In general the activity of the in-situ system was a little higher than for the preformed supported system. This may have resulted from the exposure and activation of new sites formed after catalyst fragmentation which could be reached easier by monomer in the case of in-situ supported system compared to the preformed active sites, which may be covered by a polymer layer in the case of the preformed supported system. Chu *et al.* (1999) compared homogeneous, supported and, in-situ supported $Et[Ind]_2ZrCl_2$ on SiO_2 for ethylene and 1-hexene copolymerization. They found that the in-situ supported system showed higher activity than the supported system. The amount of 1-hexene incorporated in the copolymer of the preformed supported system is similar to the in-situ supported system but less than the homogeneous catalyst system.

Molecular weight of copolymers produced with this preformed supported system decreased when higher amounts of TMA were used (Table 7.3). Supporting metallocenes on silica/MAO possibly prevents deactivation reactions by blocking the α-hydrogen transfer. In some cases, the β-hydrogen transfer is also suppressed so that molecular weight of the obtained polyolefins is much higher for supported than for homogeneous catalysts (Kaminsky and Strubel, 1998). Chu *et al.* (1999) reported that the molecular weight of the copolymer produced did not depend on the supporting procedure while the MWD of the in-situ supported system is broader. They proposed the existence of at least two different active species in the case of in-situ supported system. In this work, both in-situ and preformed supported system produced copolymer having similar MWD value.

Table 7.3. Activity and properties of copolymer produced with different amount of TMA in SiO_2/MAO/ Et(Ind)$_2$ZrCl$_2$ preformed supported system using catalyst concentration = 47.5 μM, $[Al]_{MAO}/[Zr]$ mole ratio = 272, T = 40^{o}C, E/P ratio = 70/30, reaction time 30 min.

Run	$[Al]_{TMA}/[Zr]$ mole ratio	Activity (kgPolymer/molZr.hr)	Mw	MWD	Ethylene in copolymer %
EP14	0	1873	83000	4.0	65.4
EP15	500	2540	57000	3.3	
EP16	1500	3093	59000	5.3	73.5
EP17	2500	2464	51000	4.4	
EP18	3500	1448	49000	4.8	78.4

7.2.2. Effects of MAO in preformed SiO_2/MAO/Et[Ind]$_2$ZrCl$_2$ supported system

When the amount of MAO used was varied with the preformed supported system, the activity continuously increased similar to that of an in-situ system (Figure 7.1.). However, the increase in activity according to MAO added was more pronounced in the in-situ system. Molecular weight of the copolymer increased when the $[Al]_{MAO}/[Zr]$ was increased for the preformed supported system (Table 7.4.). This effect was not observed with the in-situ system. Haag *et al.* (2001) used a SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$ supported system with external MAO added. They found that the optimum $[Al]_{MAO}/[Zr]$ molar ratio to the activity was about 1300. An increase of $[Al]_{MAO}/[Zr]$ resulted in an increase in %ethylene in the copolymer, Tm, and Mw.

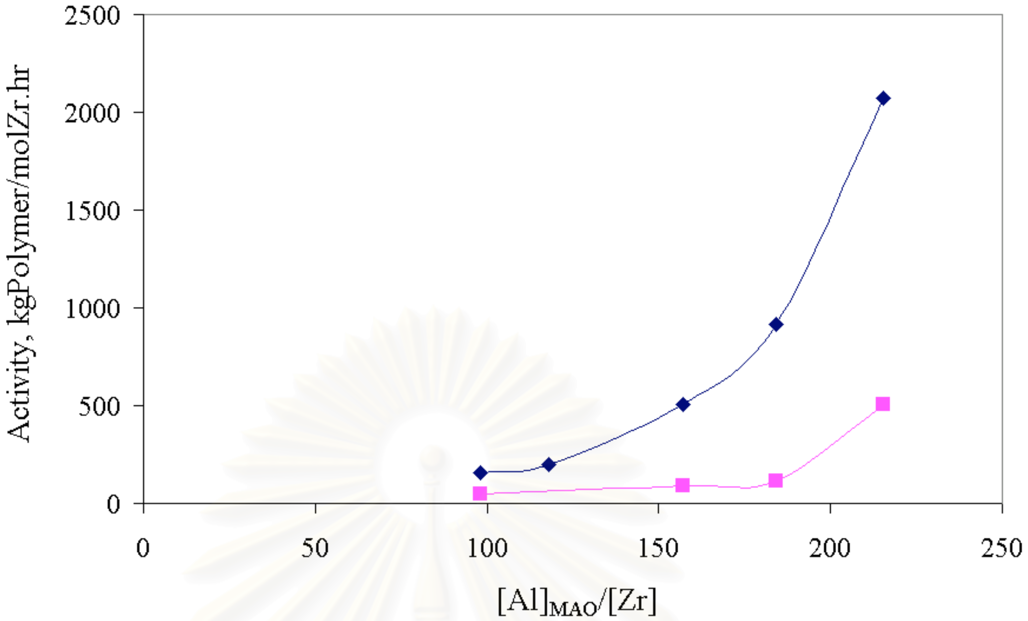


Figure 7.1. Effect of MAO on activity of different supporting system: (♦) in-situ; (■) preformed supported.

Table 7.4. Activity and properties of copolymer produced with different amount of MAO in SiO_2/MAO/ $Et(Ind)_2ZrCl_2$ supported system using catalyst concentration 120 μM, $[Al]_{TMA}/[Zr]$ mole ratio = 2500, T = 40°C, E/P ratio = 70/30, reaction time 90 min.

Run	$[Al]_{MAO}/[Zr]$ mole ratio	Activity (kgPolymer/molZr.hr)	Mw	MWD	Ethylene in copolymer %
EP19	98	46	30000	2.9	78.2
EP20	157	92	39000	2.9	78.4
EP21	184	115	41000	2.9	78.8
EP22	215	505	47000	2.9	

Chien and He (1991) investigated the SiO_2/MAO/$Et(Ind)_2ZrCl_2$ supported system at the [Al]/[Zr] ratio of 50 on the silica with various amounts of additional MAO added in the solution. At a total [Al]/[Zr] ratio in the range of 4390 to 670, the activity was essentially the same, however, markedly higher than the supported system without additional MAO. The copolymers produced had compositions close to the comonomer feed ratio, but when the [Al]/[Zr] molar ratio was reduced to 130, copolymer with higher ethylene incorporation was obtained. It seems that a high level of MAO impregnated on silica is still necessary to obtain the high activity in ethylene/propylene copolymerization with this supported system, while additional MAO in solution had less effect.

7.3. Characterization of the supported catalyst

Considering the correlation between the amount of MAO added to silica in the impregnation step and the aluminium content of SiO_2/MAO precursor obtained, Al on silica increased linearly with Al weight added (Figure 7.2.).

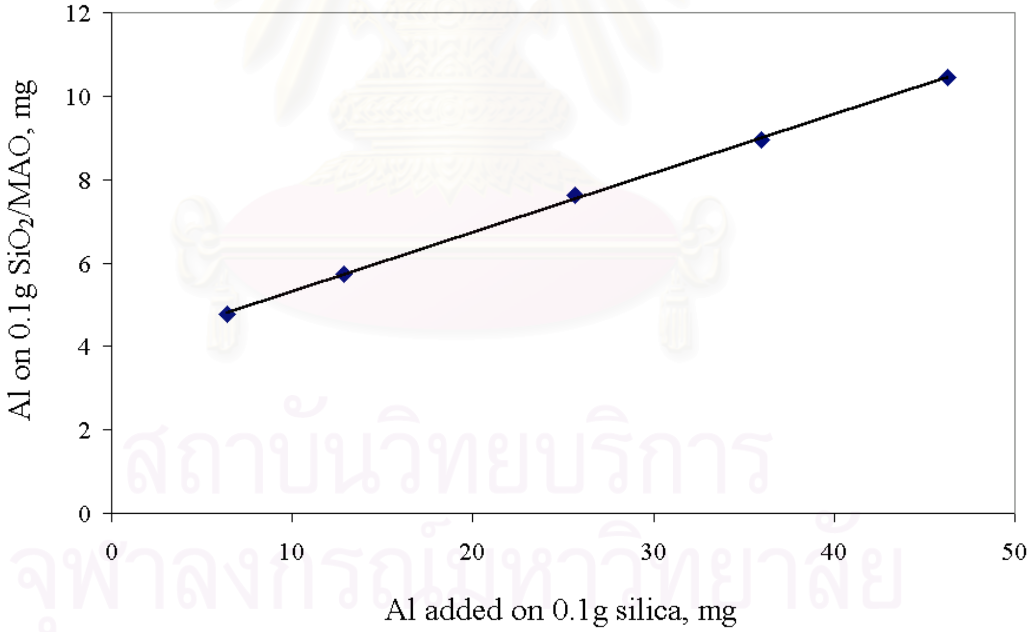


Figure 7.2. Amount of Al impregnated on the silica measured by ICP at various amounts of MAO added.

The zirconium content on the supported catalyst $SiO_2/MAO/Et[Ind]_2ZrCl_2$, which contained different amounts of MAO was further investigated. It can be seen from Figure 7.3 that almost all the loaded Zr was immobilized on the support. A blank reaction was carried out by passing argon through the reactor instead of the comonomer feed. After 30 mins, the reaction solution was evaluated for Zr content. In the in-situ case, 0.00416 mg of Zr was found in the solution compared to 0.164 mg added to reactor suggesting that most of the Zr remained bound to the support. For the preformed supported case, 0.00296 mg of Zr was found in the solution, while 0.13 mg of Zr was initially bound to the support; thus, it can be concluded that no significant leaching occurred during the copolymerization reaction.

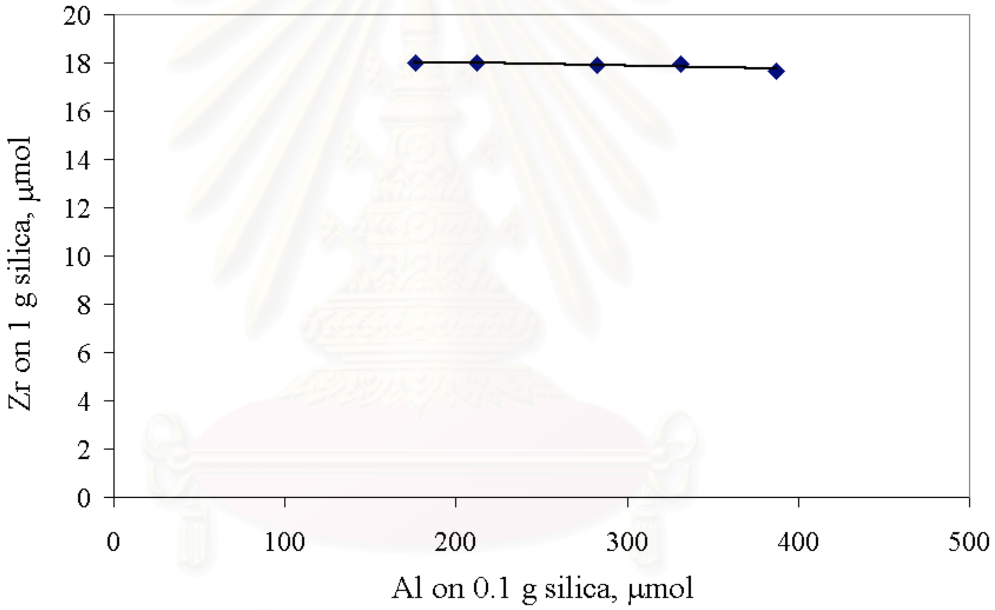
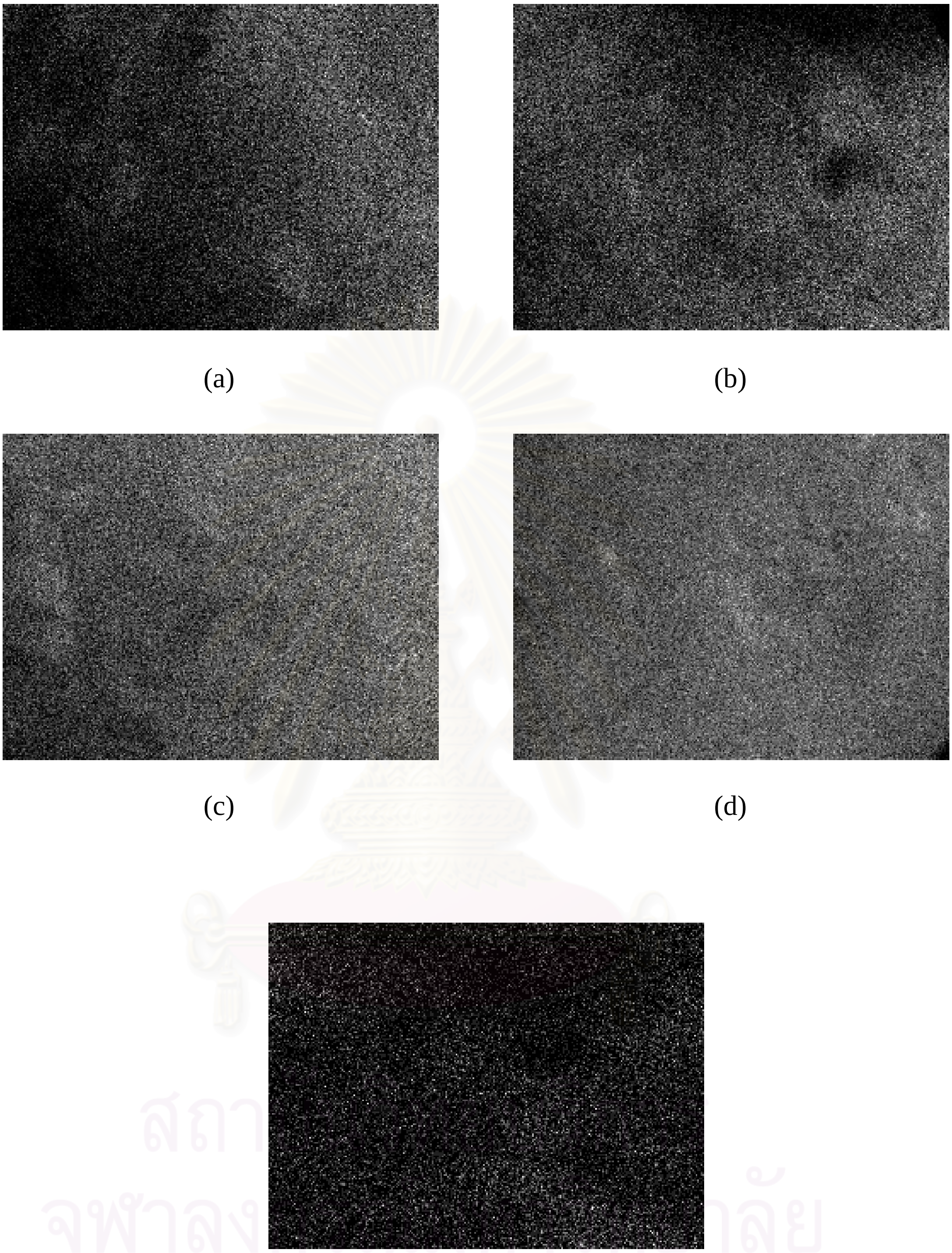


Figure 7.3. Amount of Zr on support measured by ICP at various ratio of Al on silica surface at Zr loading of 18.02 μmol per gram silica.

From EDX analysis in Figure 7.4, Al is well-dispersed throughout the catalyst support precursor. No significant difference of Al distribution can be observed between the catalyst support precursor prior and after metallocene loaded (compare Figure 7.4(a) with 7.4(b) and Fig. 7.4(c) with 7.4(d)). Unfortunately, the Zr distribution cannot be assessed with this method because of the very low Zr amount loaded and the very low intensity detected. In ethylene/propylene copolymer



(a) (b)

(c) (d)

(e)

Figure 7.4. Al distribution from Scanning Electron Micrographs of the catalyst precursor and ethylene/propylene copolymer [3000x] (a) SiO_2/MAO at [Al]/[Zr] = 98, EP9 (b) SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$ at [Al]/[Zr] = 98, EP19 (c) SiO_2/MAO at [Al]/[Zr] = 215, EP13 (d) SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$ at [Al]/[Zr] = 215, EP22 (e) Ethylene/Propylene copolymer produced

produced (Figure 7.4(e)), Al was detected uniformly throughout the polymer particles. This suggested that the catalyst support precursor was fragmented during the polymerization proceeded. If the active catalyst sites are located exclusively on the particle surface, no particle fragmentation occurs (Goretzki *et al.*, 1999).

7.4. Microstructure of the copolymer produced

The results obtained for the triad sequence distribution shown in Table 7.5, indicate a very small amount of [PPP], [PPE], [EPP] triads occur suggesting the greater chance of having isolated propylene [P] in the polymer chain. These catalyst systems seem to provide alternating polymer chains and do not produce blocks of each monomer, which is similar to the nature of this catalyst in the soluble system reported (Chien and He, 1991 p.1585). Immobilization apparently did not alter the polymerization behavior with respect to the microstructure of the copolymer produced.

Table 7.5. Triad sequence distribution of ethylene (E)/propylene (P) copolymers. Triad sequences were calculated from ^{13}C-NMR by the Randall method (Randall, 1989).

Run	Support	$[Al]_{TMA}/[Zr]$ mole ratio	$[Al]_{MAO}/[Zr]$ mole ratio	E	P	EEE	PEE+EEP	PEP	EPE	PPE+EPP	PPP
EP1	SiO_2/MAO	0	215	0.705	0.295	0.312	0.330	0.063	0.173	0.108	0.014
EP4	SiO_2/MAO	1500	215	0.751	0.249	0.392	0.309	0.051	0.169	0.072	0.007
EP8	SiO_2/MAO	3500	215	0.724	0.276	0.336	0.332	0.056	0.170	0.103	0.003
EP9	SiO_2/MAO	2500	98	0.778	0.222	0.449	0.291	0.038	0.149	0.069	0.003
EP10	SiO_2/MAO	2500	118	0.796	0.204	0.486	0.273	0.037	0.147	0.052	0.005
EP12	SiO_2/MAO	2500	184	0.777	0.223	0.446	0.286	0.045	0.157	0.063	0.004
EP14	SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$	0	272	0.654	0.346	0.226	0.345	0.083	0.192	0.126	0.027
EP16	SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$	1500	272	0.735	0.265	0.356	0.331	0.049	0.170	0.089	0.006
EP18	SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$	3500	272	0.784	0.216	0.456	0.290	0.038	0.152	0.062	0.002
EP19	SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$	2500	98	0.782	0.218	0.465	0.270	0.046	0.149	0.065	0.004
EP20	SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$	2500	157	0.784	0.216	0.464	0.278	0.042	0.152	0.059	0.005
EP21	SiO_2/MAO/Et(Ind)$_2$ZrCl$_2$	2500	184	0.788	0.212	0.463	0.287	0.038	0.154	0.055	0.003

7.5. Summary

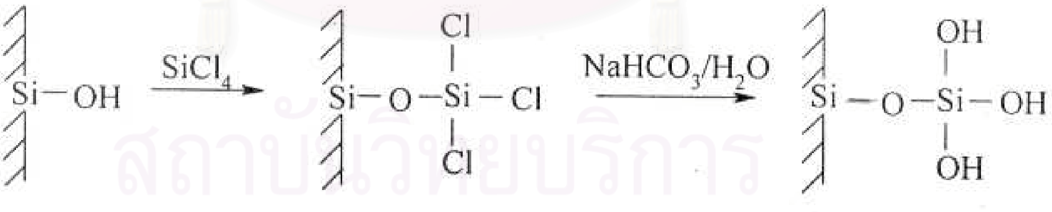
1. Chain transfer to alkylaluminum is not the major chain transfer reaction for this system.
2. Molecular weight distribution of these systems were higher than for the analogous homogeneous system so there might be more than one active species in the system.
3. Effect on activity of MAO was more obvious than TMA. TMA may only have a role as the scavenger while MAO on the support is a cocatalyst for the formation of active species. Therefore the activity increased exponentially with increased level of MAO impregnated on silica.
4. TMA and MAO amount do not have any significant effect on the copolymer microstucture.
5. Al content on catalyst precursor depends linearly on the Al concentration added during the preparation step, while all Zr was immobilized. No significant Al leaching occurred during Zr immobilization.
6. In-situ supported system is another suitable way for providing the heterogeneous system. This system shows higher activity than preformed supported system and it does not require the catalyst immobilization step.

CHAPTER VIII

COPOLYMERIZATION USING SILICONTETRACHLORIDE MODIFIED SiO_2/ MAO WITH $Et[Ind]_2ZrCl_2$

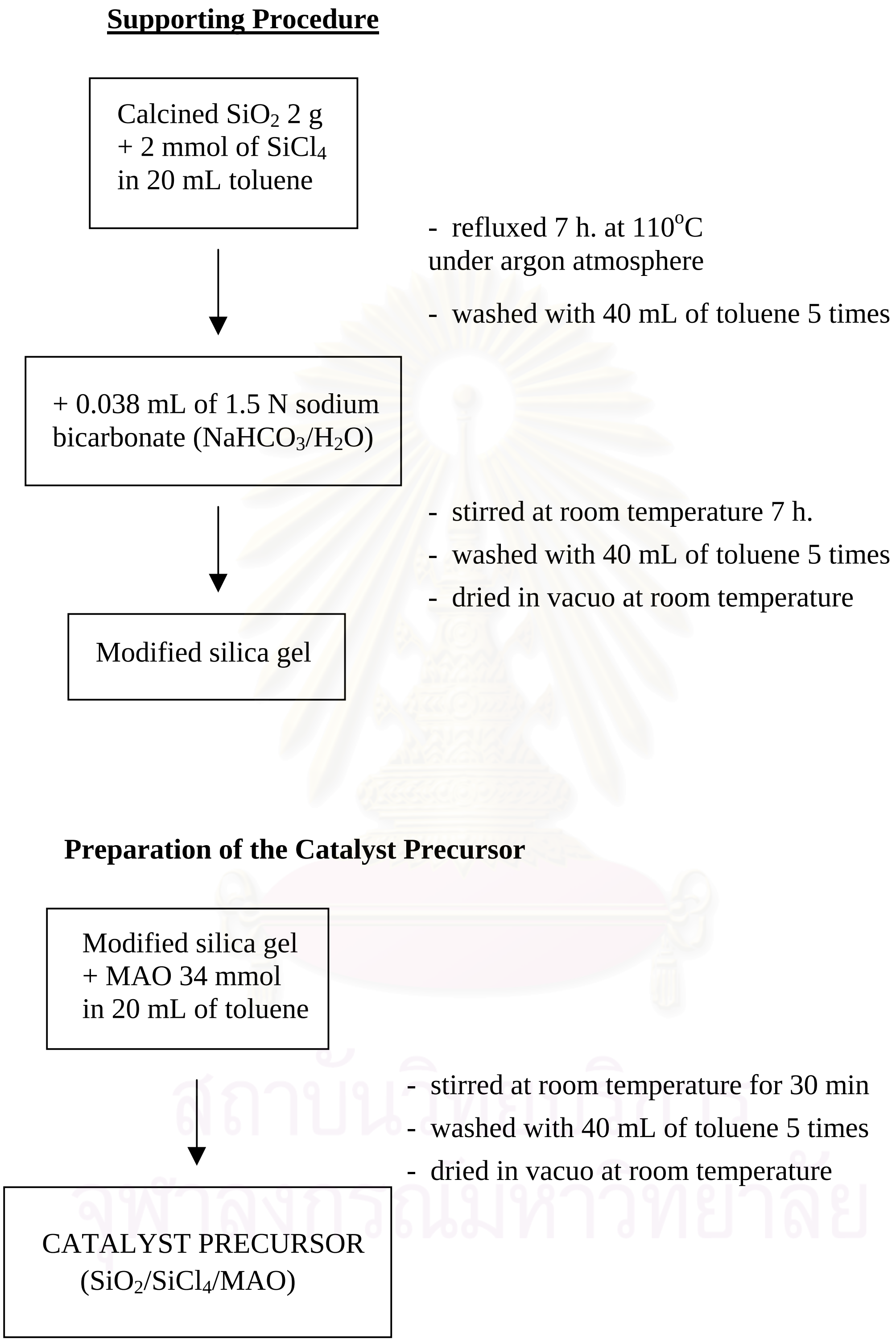
Recently, some researchers have reported that a new immobilization method of introducing a spacer group, such as polysiloxane, between the support and metallocene resulted in higher catalytic activity (Arai *et al.*, 1997; Lee *et al.*, 1997). The $Cp_2Zr(CH_3)_2$/ SiO_2 catalyst modified with $(CH_3)_3SiCl$ showed a fairly high activity in ethylene polymerization even in the absence of any added cocatalysts (Moroz *et al.*, 1998). Another possible way of forming a heterogeneous catalytic system is by adsorption of MAO on silica prior to immobilizing the metallocene catalyst. Soga *et al.* (1993) modified SiO_2 with $Cl_2Si(CH_3)_2$ before treating with MAO and used the resulting material as a support in ethylene polymerization with Cp_2ZrCl_2. With this modified SiO_2, activity increased significantly and when TMA was added as a co-catalyst, the MAO-free catalyst system showed a comparable activity.

In this Chapter, results are reported for the attempted ethylene/propylene copolymerization using SiO_2 modified with $SiCl_4$ as a support (Scheme 8.1).



Scheme 8.1. Modified silica with silicontetrachloride for using as support in copolymerization of ethylene and propylene.

The procedure of preparing SiO_2/$SiCl_4$/MAO catalyst precursor is illustrated in Scheme 8.2. In-situ supported system, i.e. solution of $Et[Ind]_2ZrCl_2$ catalyst was injected directly to the reactor to start the polymerization, was applied to these experiments.



Scheme 8.2. Procedure of $SiO_2/SiCl_4$/MAO catalyst precursor preparation

Copolymerization of ethylene and propylene was carried out in the continuous gas flow reactor system using homogeneous, SiO_2/MAO and $SiO_2/SiCl_4$/MAO systems. The activity obtained for each system is summarized in Table 8.1. In the case of the homogeneous system, the amount of MAO used is similar to that used in preparation for the support precursor 0.1 g (Al_{MAO} 1.7 mmol). It can be seen that when the supported system was applied, the activity was significantly reduced. This might result from loss of the active species or steric effects arising from the support. With the $SiCl_4$ modified system, the copolymerization activity increased by about 30 percent. This could be the result of less steric hindrance on the support surface.

Table 8.1. Activity in copolymerization of ethylene and propylene with different catalytic systems. Reaction conditions: $Et[Ind]_2ZrCl_2$, [Zr] = 60μM, T = 40°C, reaction time 15 mins, catalyst precursor 0.1 g, $[Al]_{TMA}/[Zr]$ 1500, ethylene/propylene feed ratio 70/30.

Run	Catalyst system	Yield (g)	Activity (kgEP/molZr.hr)
EP1	homogeneous	1.4035	3119
EP2	SiO_2/MAO	0.4453	990
EP3	$SiO_2/SiCl_4$/MAO	0.5918	1315

In Table 8.2, the activity of SiO_2/MAO and $SiO_2/SiCl_4$/MAO in-situ supported systems carried out under different reaction conditions from the experiments in Table 8.1 are reported. After a polymerization time of 2 hours, the $SiO_2/SiCl_4$/MAO system still gave higher activity therefore this modification did not increase the rate of deactivation of the metallocene catalyst, compared to the normal supported system.

Table 8.2. Activity for copolymerization of ethylene and propylene with different catalytic systems. Reaction conditions: $Et[Ind]_2ZrCl_2$, [Zr] = 60μM, T = 40^{o}C, reaction time 120 mins, catalyst precursor 0.2 g, $[Al]_{TMA}/[Zr]$ 3000, ethylene/propylene feed ratio 50/50.

Run	Support	Yield (g)	Activity (kgEP/molZr.hr)
EP4	SiO_2/MAO	2.4707	686
EP5	SiO_2/SiC_{l4}/MAO	4.1369	1149

Molecular weight and molecular weight distribution for the ethylene/propylene copolymer are reported in Table 8.3. Molecular weight of obtained EP copolymer using the SiO_2/MAO supported system was much higher than obtained using the homogeneous system. Kaminsky and Strubel (1998) proposed that this increase in molecular weight results from the suppression of β-hydrogen transfer as well as the inhibition of α-hydrogen transfer deactivation reaction. When $SiCl_4$ was added, the molecular weight was reduced to about half. This suggested that the chain transfer reactions, which most likely involve β-hydrogen elimination, are more prevalent when the support surface was treated with $SiCl_4$.

The molecular weight distribution, for the $SiO_2/SiCl_4$/MAO system was lower than for the SiO_2/MAO system. This supports the idea that the $SiO_2/SiCl_4$/MAO system may be more homogeneous like with less effect from the support.

Table 8.3. Properties of ethylene/propylene copolymers obtained.

Run	Catalyst system	Mw	MWD	%ethylene in copolymer
EP1	homogeneous	29000	2.2	n/d
EP2	SiO_2/MAO	66000	5.0	75.1
EP3	$SiO_2/SiCl_4$/MAO	35000	3.9	78.0

n/d = not determined

Copolymerization of ethylene with 1-hexene was carried out at higher pressure using a semibatch reactor system (Pratchayawutthirat, 2001). With the $SiO_2/SiCl_4/MAO$ system, the activity was about 4 times higher than the normal SiO_2/MAO supported system. As was found for ethylene/propylene copolymerization, molecular weight of the copolymer produced with $SiO_2/SiCl_4/MAO$ system is only about half of that of the copolymer from the SiO_2/MAO system. Molecular weight distribution was decreased by the addition of $SiCl_4$.

Table 8.4 shows the triad distribution of the two supported systems calculated from ^{13}C-NMR. Ethylene incorporation of both systems is about the same compared to ethylene/propylene molar ratio feed. Both systems gave a similar triad distribution with less tendency of building block PP, which is characteristic for this zirconocene in the homogeneous system.

Table 8.4. Triad distribution of each supported system in ethylene/propylene copolymerization.

Run	Support	EEE	PEE+EEP	PEP	EPE	PPE+EPP	PPP
EP2	SiO_2/MAO	0.392	0.309	0.051	0.169	0.072	0.007
EP3	$SiO_2/SiCl_4/MAO$	0.447	0.290	0.043	0.159	0.058	0.003

TREF profiles for ethylene/propylene copolymers produced with different catalyst systems are summarized in Figure 8.1. The patterns for the EP samples show that the samples are very amorphous and most of the sample was probably lost at temperatures below 0^oC. Therefore, the samples of ethylene/1-hexene copolymer produced with SiO_2/MAO (EH1) and $SiO_2/SiCl_4/MAO$ (EH2) supported system provided by Pratchayawutthirat (Pratchayawutthirat, 2001) were used to verify the chemical composition distribution of the copolymer produced. In the case of ethylene/1-hexene copolymers, one sharp peak was observed in each supported system.

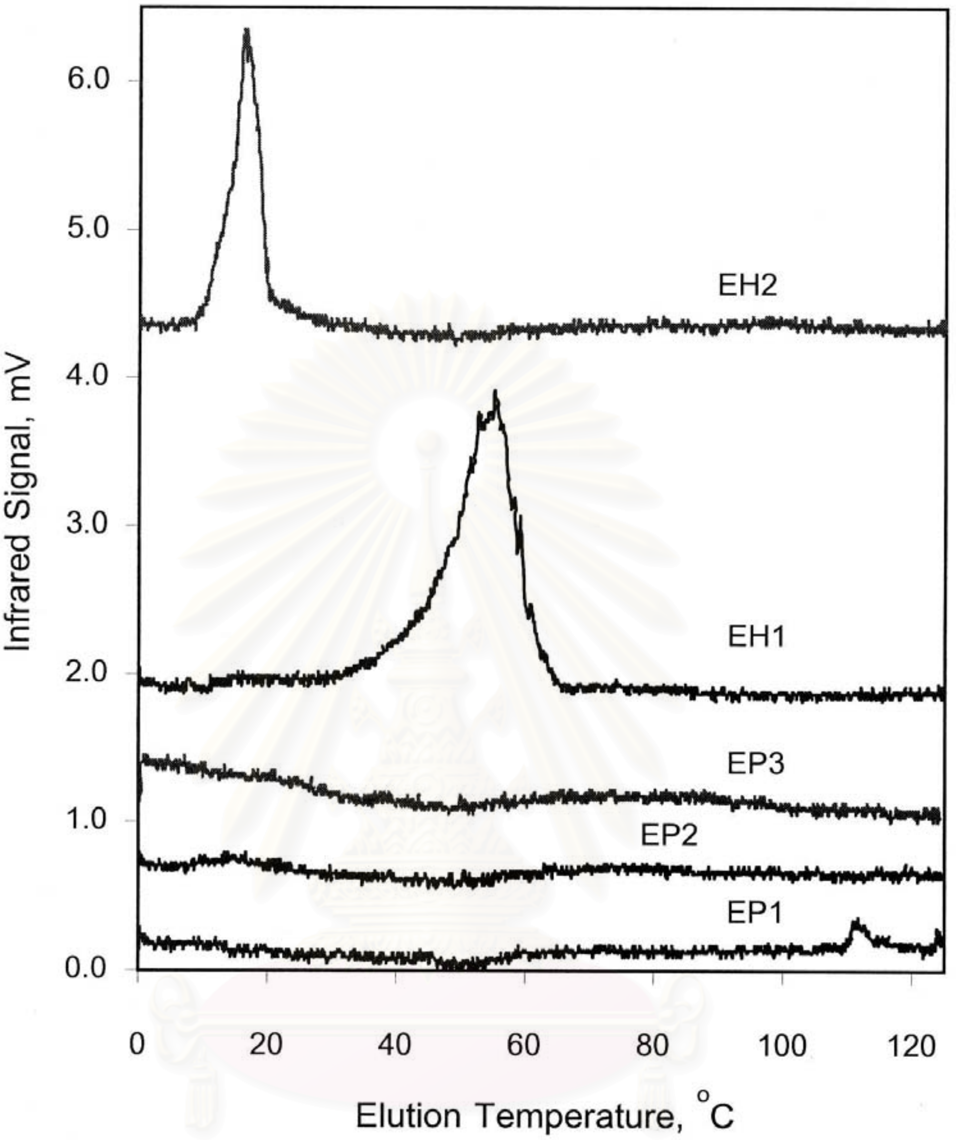


Figure 8.1. TREF profiles for ethylene/propylene and ethylene/1-hexene copolymer produced with different catalyst system. (The patterns have been offset for clarity.)

In Table 8.5, the number and mass average CH_3 per 1000 carbons concentrations (C_n and C_w) as well as the C_w/C_n ratio for the ethylene/1-hexene copolymer are provided. It seems that the level of 1-hexene incorporated in the copolymer produced from $SiO_2/SiCl_4/MAO$ supported system was higher than SiO_2/MAO. From C_w/C_n ratio, it can be seen that both systems have a narrow chemical composition distribution. The details of the TREF procedure and the method of data analysis are described by Zhang *et al.* (2000).

Table 8.5. The number and mass average CH_3 per 1000 carbons concentrations of ethylene/1-hexene copolymer calculated from TREF profiles.

Sample	C_n	C_w	C_w/C_n
EH1	27.4	29.7	1.08
EH2	59.3	59.7	1.01

In Table 8.6, results are provided for activated clay as a support, and compared with silica as a support in ethylene homopolymerization. The BET surface area was determined by nitrogen adsorption in an automatic apparatus ASAP 2000 constructed by Micromeritics, USA. BET surface area of silica is 320 m^2/g, while for the activated clay it is 200 m^2/g. Average pore diameter of silica is 230 A, and for the activated clay is 60 A. This activated clay was analyzed for its composition by XRF. It is composed of SiO_2 70.1%, Al_2O_3 11.6%, Fe_2O_3 2.92%, MgO 0.37%, CaO 2.46%, Na_2O 1.54%, and K_2O 1.45%.

Table 8.6. Ethylene polymerization with activated clay and silica as support with Et $[Ind]_2ZrCl_2$ 60 μM, 0.1 g catalyst precursor, $[Al]_{TMA}/[Zr]$ 2500, T=40°C, 90 min

Support	Yield (g)	Activity (kgPE/molZr.hr)
$SiO_2/SiCl_4/MAO$	1.0150	376
$Clay/SiCl_4/MAO$	1.0346	383

It can be seen that activated clay gave comparable activity as silica in ethylene homopolymerization (Table 8.6) although the BET surface area of these two types of support are much different. Then, the activated clay supported system with and without $SiCl_4$ modification was used for ethylene/propylene copolymerization. Its activity is presented in Table 8.7. The increase of activity in $SiCl_4$ modified support was again observed. It can be concluded that the activity enhancement by $SiCl_4$ can be obtained not only in the SiO_2 system but also another support such as this activated clay.

Table 8.7. Activity in copolymerization of ethylene and propylene using activated clay as support. Reaction conditions: [Zr] = 60μM, T=40^{o}C, 30 min, 0.1 g catalyst precursor, $[Al]_{TMA}/[Zr]$ 2500, E/P molar ratio 70/30.

Support	Yield (g)	Activity (kgEP/molZr.hr)
Clay/MAO	0.3513	390
Clay/$SiCl_4$/MAO	0.5276	586

8.1. Summary

1. Silicontetrachloride reduces the steric effect from the support so that the activity of EP copolymerization with in-situ supported zirconocene catalyst is increased. However, this modification enhanced the chain transfer reaction, which is most likely through β-H elimination, resulting in significant decrease of Mw.
2. Silicontetrachloride modification does not have any significant effect on the microstructure as well as the chemical composition distribution of the copolymer produced.

CHAPTER IX

CONCLUSIONS AND SUGGESTIONS

9.1. CONCLUSIONS

From this work, it can be concluded as follows:

1. Three reactor systems i.e. semibatch, batch, and continuous gas flow system yield a comparable activity of homopolymerization providing that the suitable reaction conditions of each system are applied.
2. When the catalytic activity is of concern, Et[Ind]$_2$ZrCl$_2$/MAO is better than the Cp$_2$ZrCl$_2$/MAO catalyst system for ethylene/propylene copolymerization. The rate enhancement from the ‘comonomer effect’ is observed with Et[Ind]$_2$ZrCl$_2$/MAO catalyst system.
3. Types of diene used in EPDM terpolymerization do not have significant effect on the activity when carried out in batch system using Et[Ind]$_2$ZrCl$_2$. Diene shows both positive effect and adverse effect on the activity by enhancing the rate of propagation and promoting the deactivation reaction, respectively. Deactivation may arise from diene chelating to the active species, which occurred to a greater extent in non-bridged Cp$_2$ZrCl$_2$ than the bridged Et[Ind]$_2$ZrCl$_2$ catalyst system. Therefore Cp$_2$ZrCl$_2$ catalyst is probably more structure sensitive with respect to diene type than is Et[Ind]$_2$ZrCl$_2$ catalyst system. Some further work is required to ascertain the effect of diene type in Cp$_2$ZrCl$_2$ system. The adverse effect is more pronounced when terpolymerization is carried out under lower pressure.
4. In the heterogeneous system, activity of ethylene/propylene copolymerization using in-situ SiO$_2$/SiCl$_4$/MAO > in-situ SiO$_2$/MAO > preformed supported SiO$_2$/MAO/ Et[Ind]$_2$ZrCl$_2$. While microstructure of copolymer produced with these three supported system are similar, the copolymer obtained from the in-situ SiO$_2$/SiCl$_4$/MAO have the lowest Mw.

5. The increase of the amount of MAO impregnated on the support surface can increase the catalytic activity significantly. TMA may have a role as a scavenger in the system whereas MAO is the cocatalyst in the formation of the active species. Molecular weight of the copolymer cannot be altered by the amount of TMA since the chain transfer to alkylaluminum is not the major chain transfer reaction in ethylene/propylene copolymerization. Molecular weight can be decreased by reducing the steric effect from the support i.e. providing a spacer, which increases β-hydrogen elimination.

9.2. SUGGESTIONS

From the results in this work, the further investigation of the following subjects will be useful.

1. The effect of the diene concentration on the catalytic activity in both batch and continuous gas flow reactor system would be of interest. The effect of the ethylene and propylene pressure (total reaction pressure) will be another possible way of varying the comonomer feed ratio.
2. From the conclusions of this study, the presence of diene significantly decreased the activity in EPDM terpolymerization carried out using Cp_2ZrCl_2/ MAO catalyst system. It seems that the type or structure of diene may have different effect on the EPDM terpolymerization activity using Cp_2ZrCl_2/ MAO. So the effect of the type of diene in EPDM terpolymerization with Cp_2ZrCl_2/ MAO should be investigated.
3. It would be interesting to study the effect of diene on the activity in the heterogeneous system since the effect from the support may result in the different behavior from the EPDM terpolymerization carried out in homogeneous system.
4. Further study in the silicon tetrachloride-modified-silica heterogeneous system should be carried out to explain how this modification increases the catalyst activity. Amount of MAO loaded on the surface of the modified silica, the position of immobilized MAO and the possible types of active species should be verified since after the modification there might be different reactive sites for MAO impregnation present.

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APPENDICES

APPENDIX A

NUCLEAR MAGNETIC RESONANCE

A.1. Triad distribution of ethylene/propylene copolymer calculated from ^{13}C-NMR spectrum

Table A.1. ^{13}C-NMR chemical shift and assignments for ethylene/propylene copolymer (Randall, 1989).

Region	Integration range (ppm)	Sequence Assignment
A	45-48	k(PPP+(1/2)[PPE+EEP])
B	36-39	k(PEP+(1/2)[PEE+EEP]+EPE+(1/2)[PPE+EPP])
C	33.3	k(EPE)
D	29.1-31.5	k(2EEE+[PPE+EPP]+(1/2)[PEE+EEP])
E	28-29.5	k(PPP)
F	27-28	k(PEE+EEP)
G	24-25	k(PEP)
H	19-22	k(PPP+[PPE+EPP]+EPE)

The following results are obtained:

$k(EEE) = (1/2)(T_{DEF}+T_A+T_C+3T_G-T_B-2T_H)$

$k(PEE+EEP) = T_H+(1/2)T_B-T_A-2T_G$

$k(PEP) = T_G$

$k(EPE) = T_C$

$k(EPP+PPE) = (1/2)(2T_H+T_B-2T_A-4T_C)$

$k(PPP) = (1/2)(3T_A+2T_C-(1/2)T_B-T_H)$

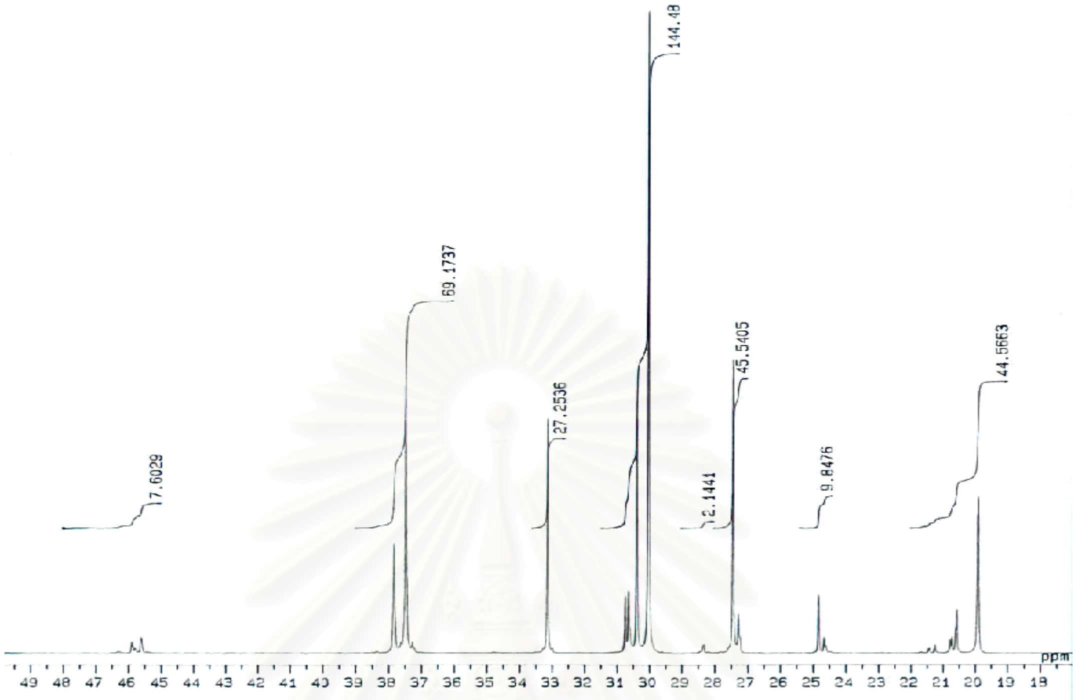


Figure A-1. ^{13}C-NMR spectrum of EP copolymer (EP1, Table 7.5.)

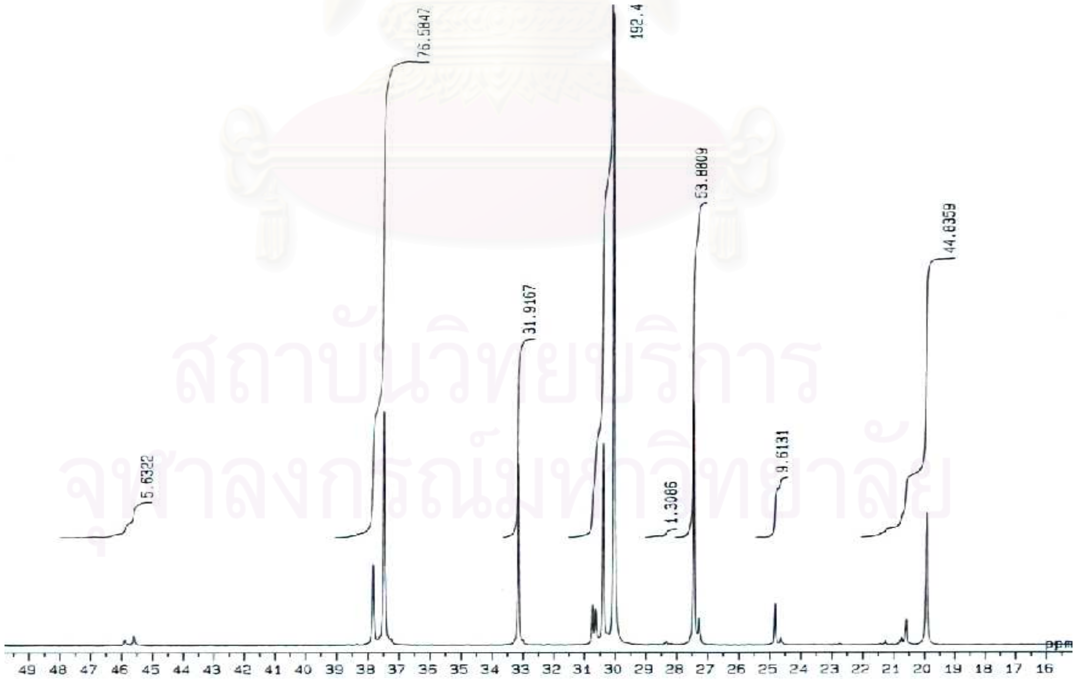


Figure A-2. ^{13}C-NMR spectrum of EP copolymer (EP4, Table 7.5.)

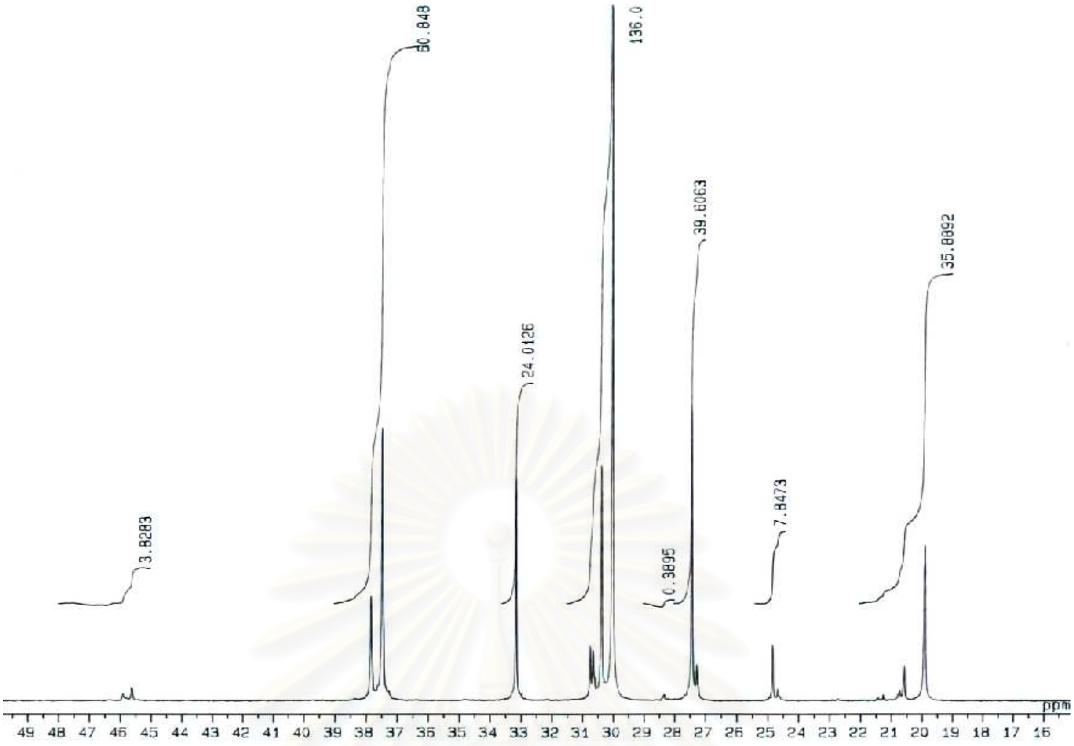


Figure A-3. ^{13}C-NMR spectrum of EP copolymer (EP8, Table 7.5.)

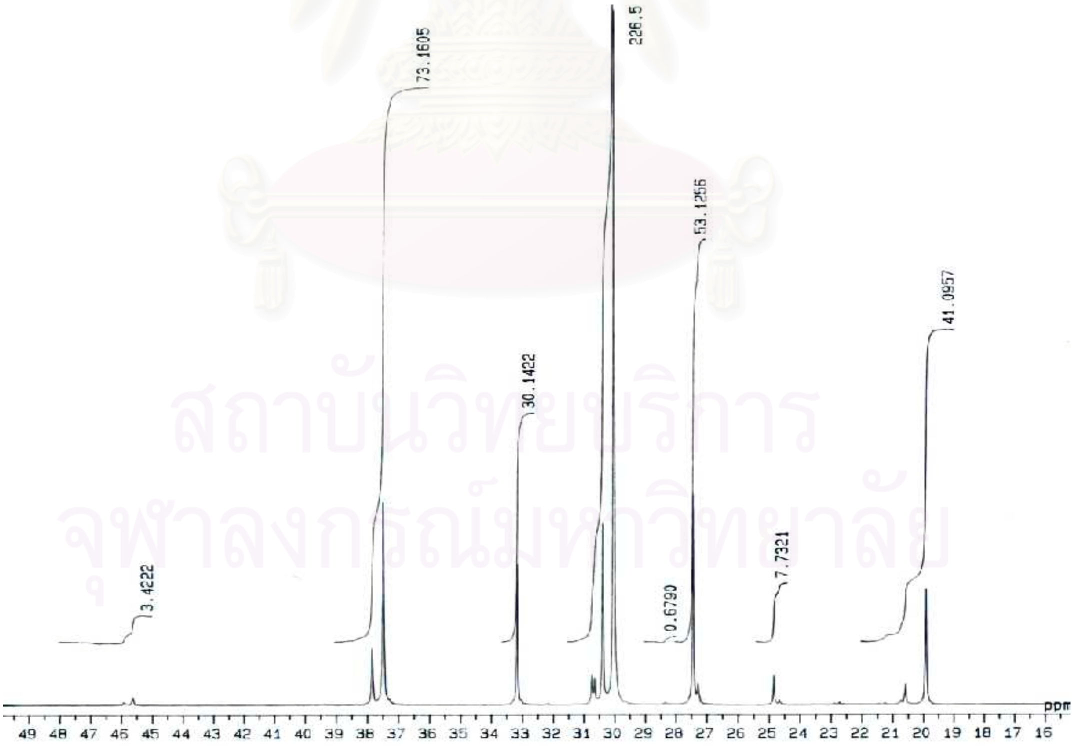


Figure A-4. ^{13}C-NMR spectrum of EP copolymer (EP9, Table 7.5.)

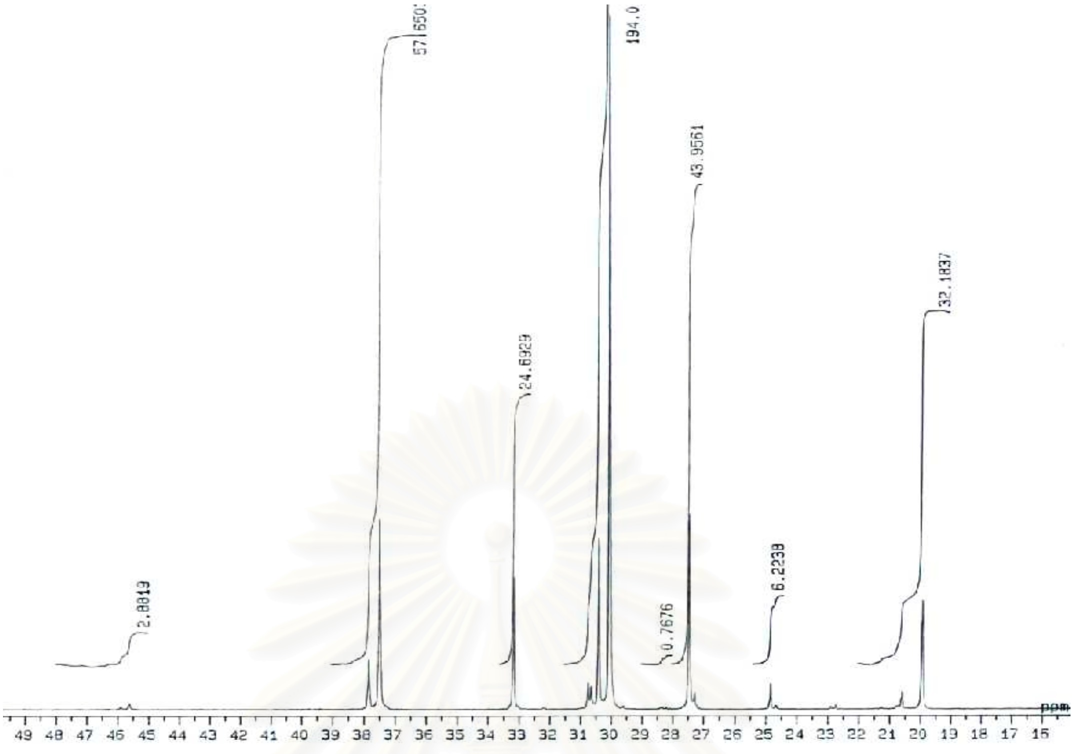


Figure A-5. ^{13}C-NMR spectrum of EP copolymer (EP10, Table 7.5.)

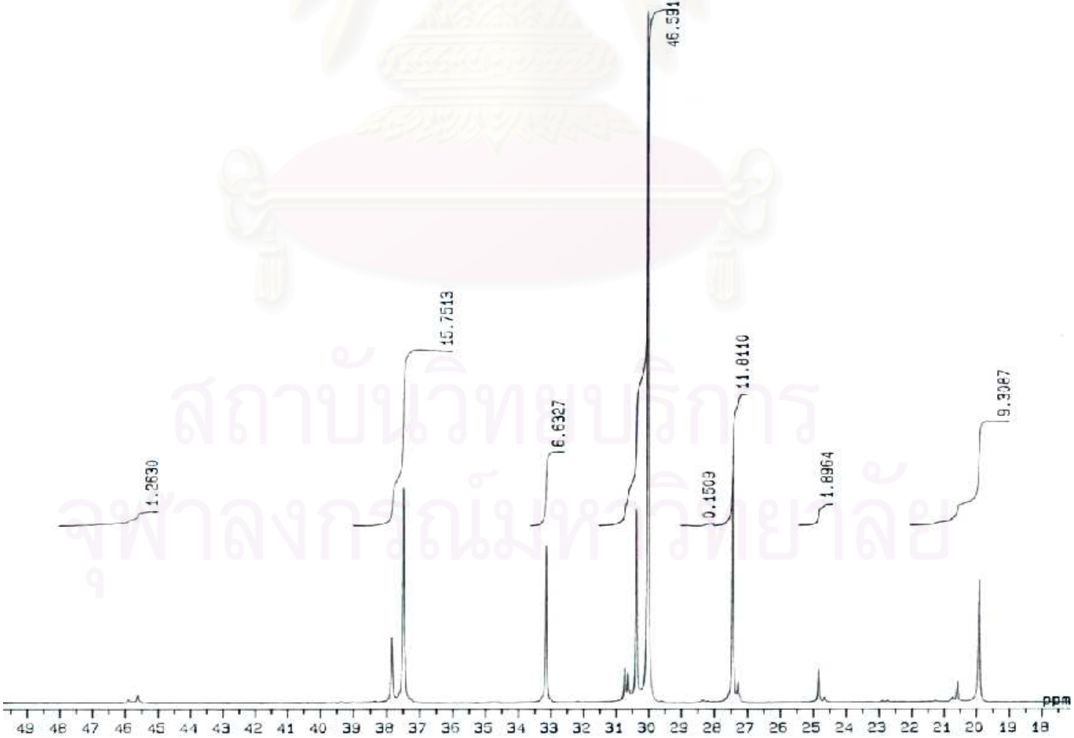


Figure A-6. ^{13}C-NMR spectrum of EP copolymer (EP12, Table 7.5.)

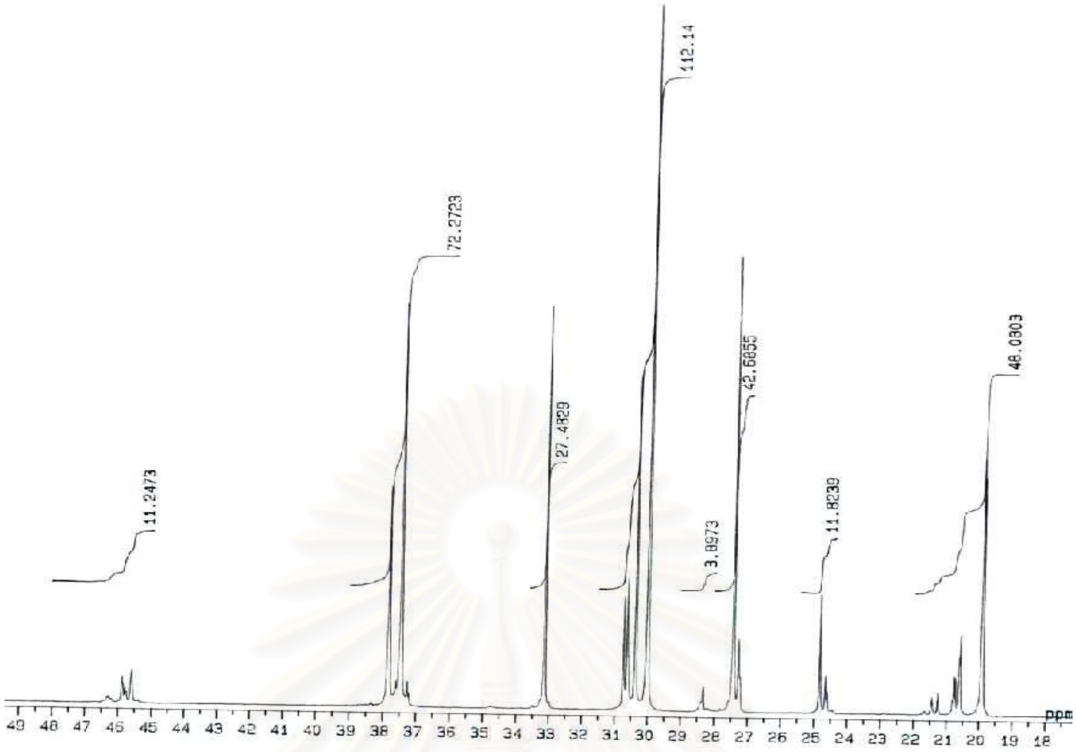


Figure A-7. ^{13}C-NMR spectrum of EP copolymer (EP14, Table 7.5.)

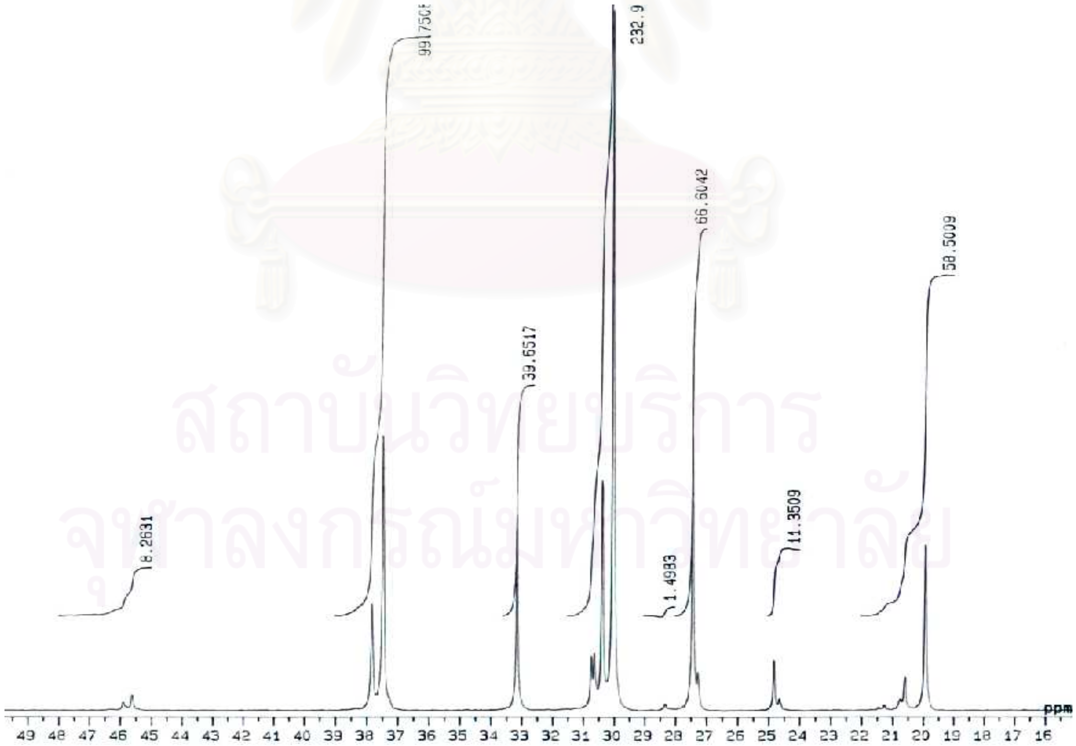


Figure A-8. ^{13}C-NMR spectrum of EP copolymer (EP16, Table 7.5.)

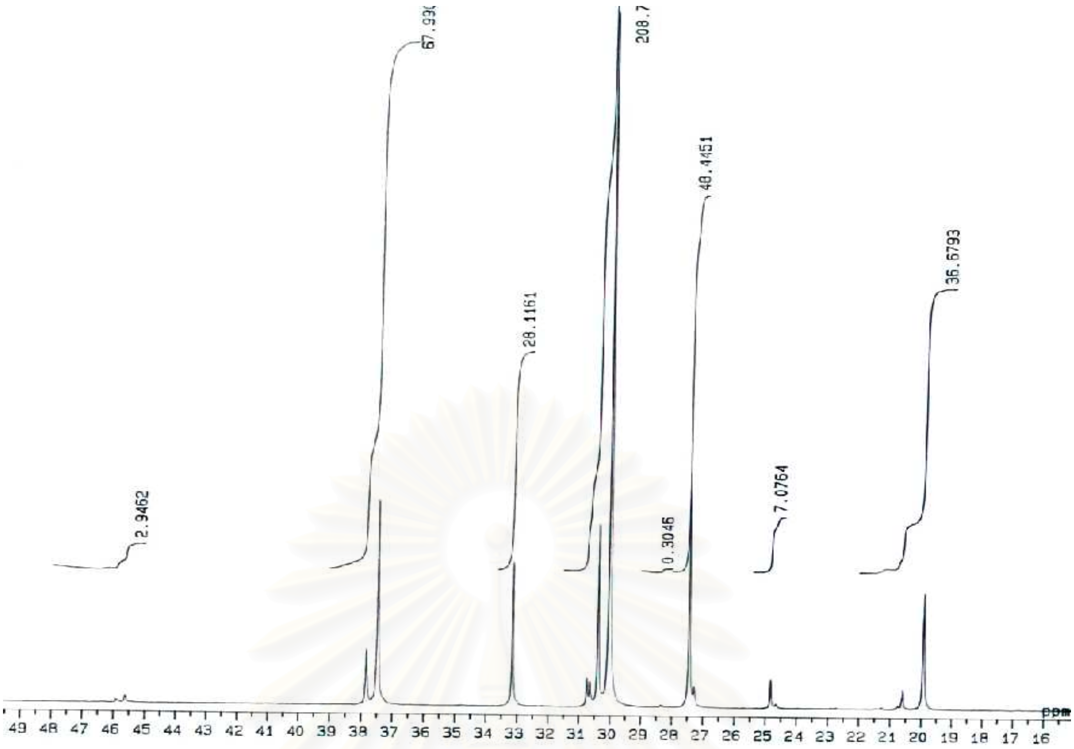


Figure A-9. ^{13}C-NMR spectrum of EP copolymer (EP18, Table 7.5.)

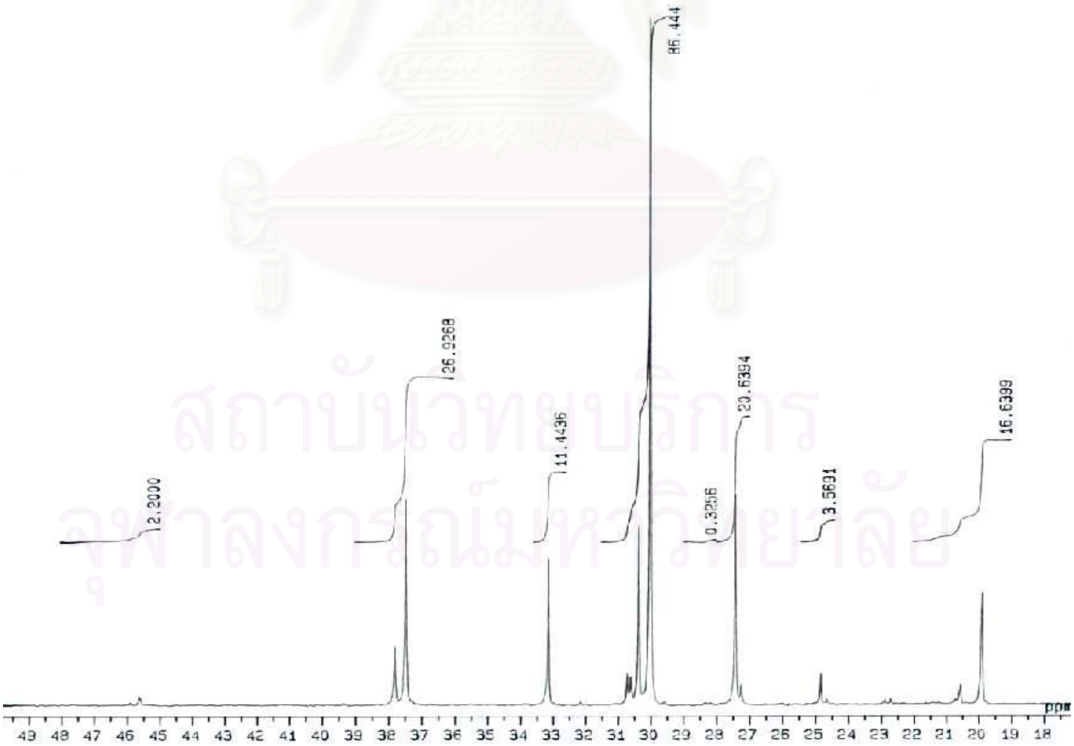


Figure A-10. ^{13}C-NMR spectrum of EP copolymer (EP19, Table 7.5.)

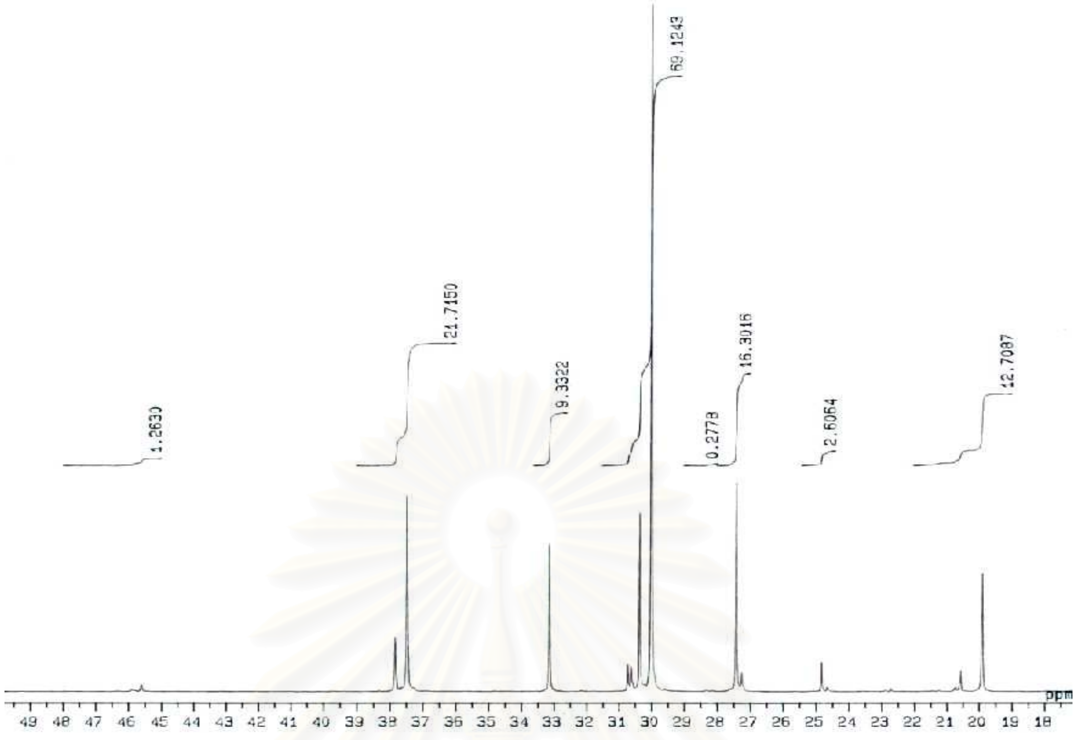


Figure A-11. ^{13}C-NMR spectrum of EP copolymer (EP20, Table 7.5.)

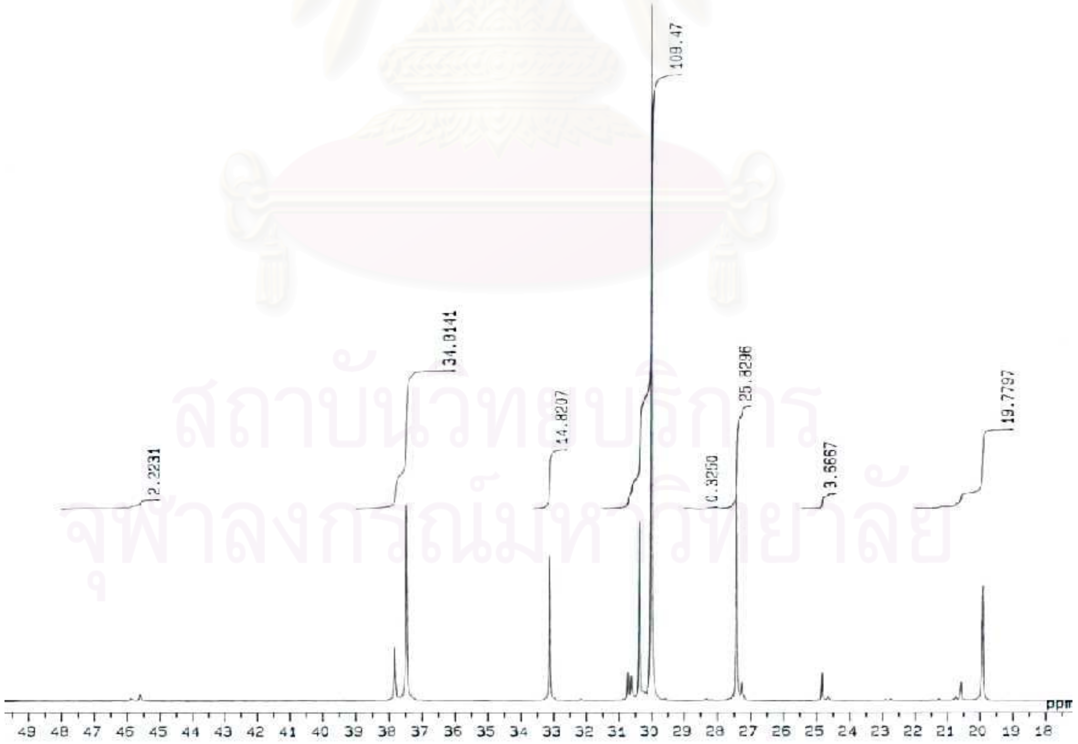


Figure A-12. ^{13}C-NMR spectrum of EP copolymer (EP21, Table 7.5.)

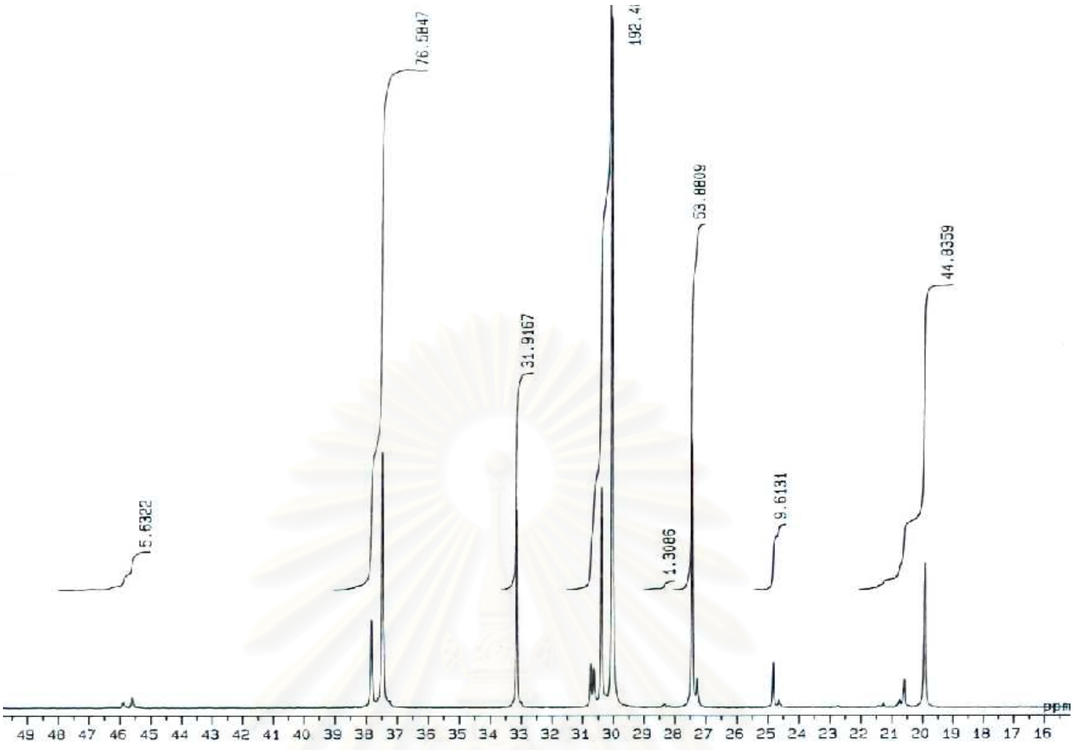


Figure A-13. ^{13}C-NMR spectrum of EP copolymer (EP2, Table 8.5.)

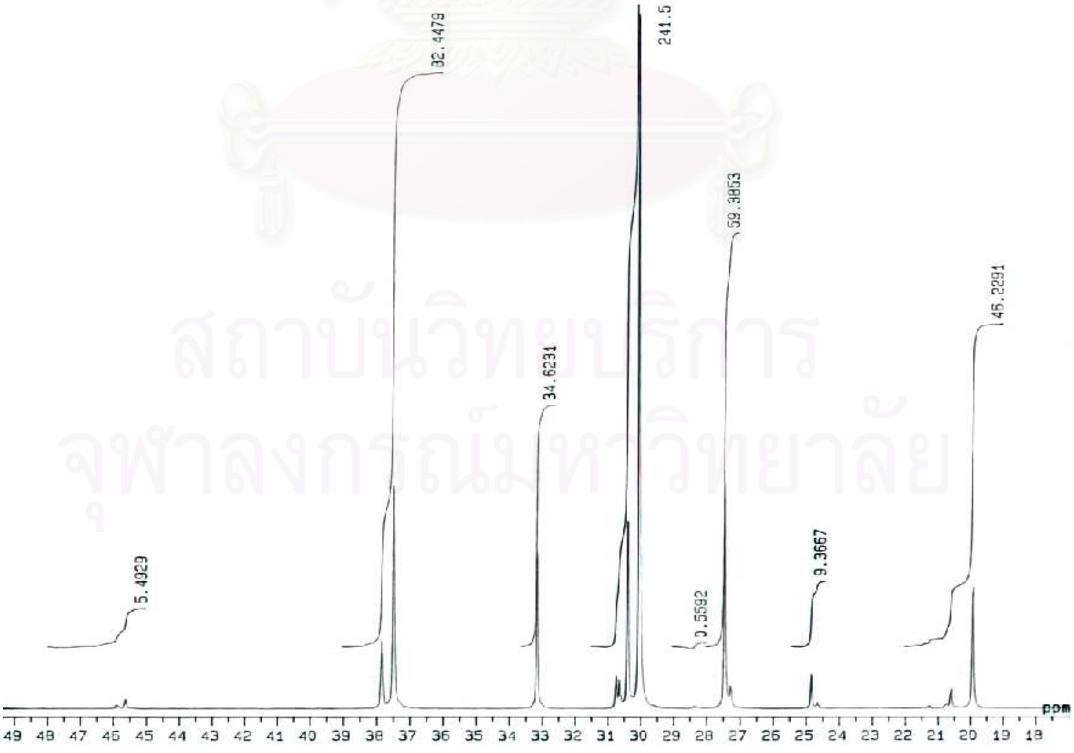


Figure A-14. ^{13}C-NMR spectrum of EP copolymer (EP3, Table 8.5.)

APPENDIX B

GEL PERMEATION CHROMATOGRAPHY

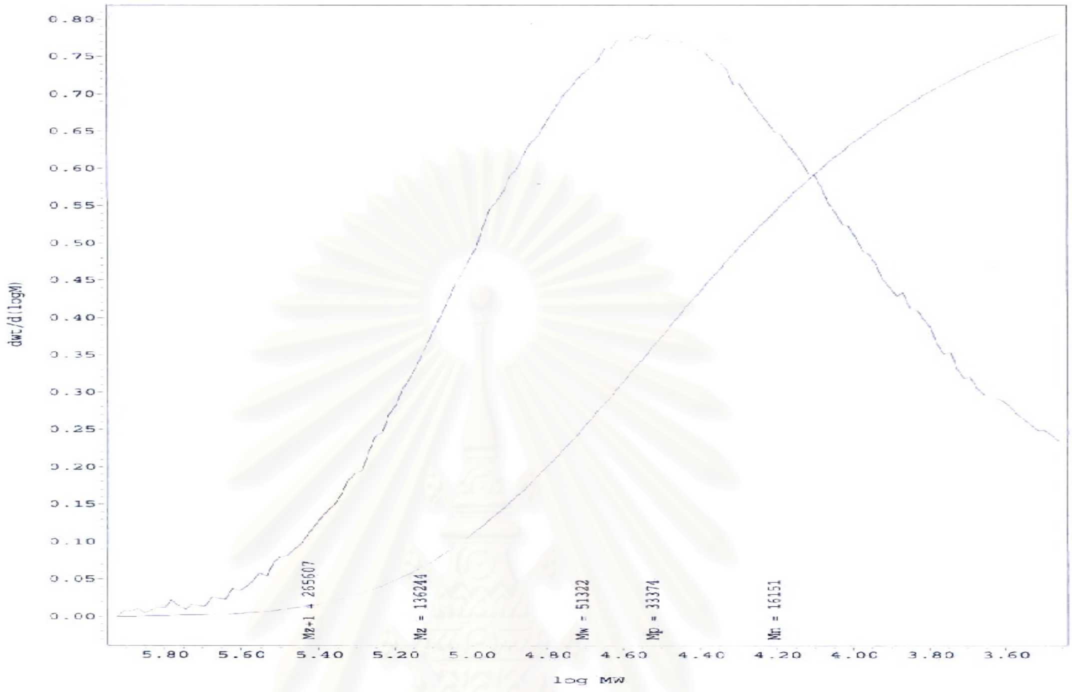


Figure B-1. GPC curve of EP copolymer (EP1, Table 7.1.)

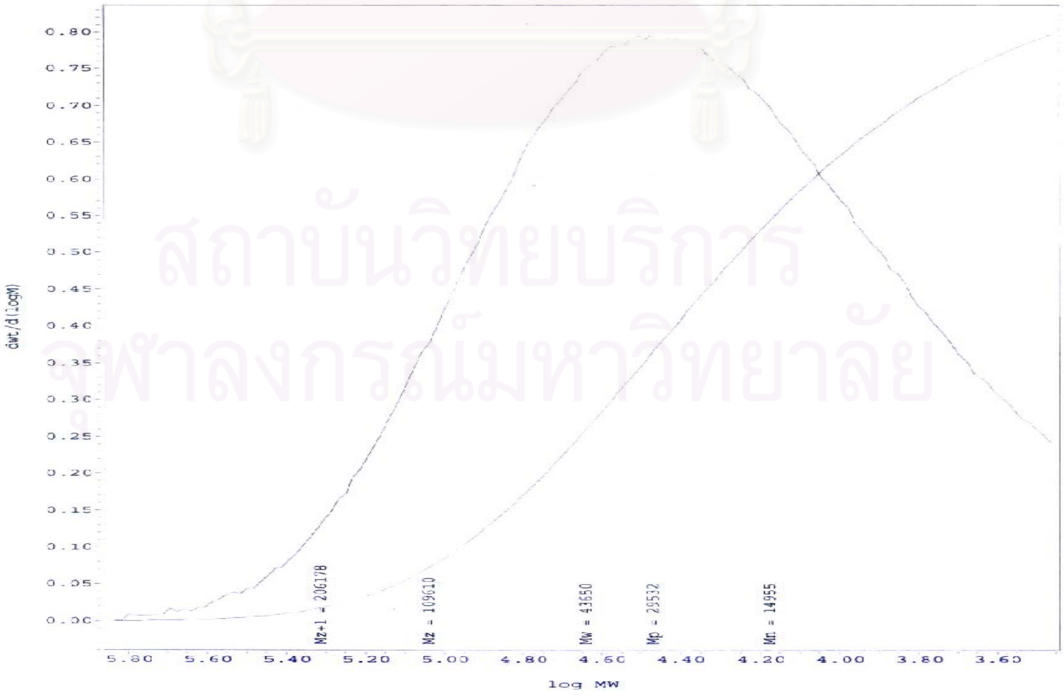


Figure B-2. GPC curve of EP copolymer (EP2, Table 7.1.)

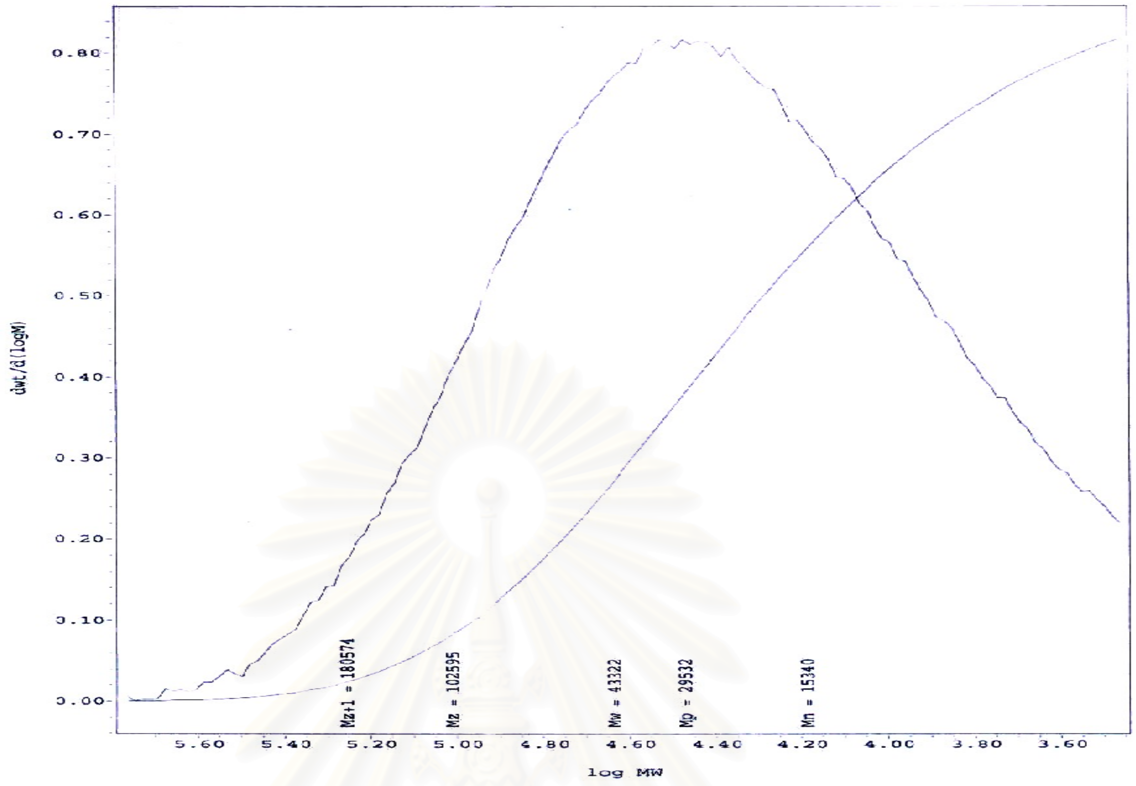


Figure B-3. GPC curve of EP copolymer (EP3, Table 7.1.)

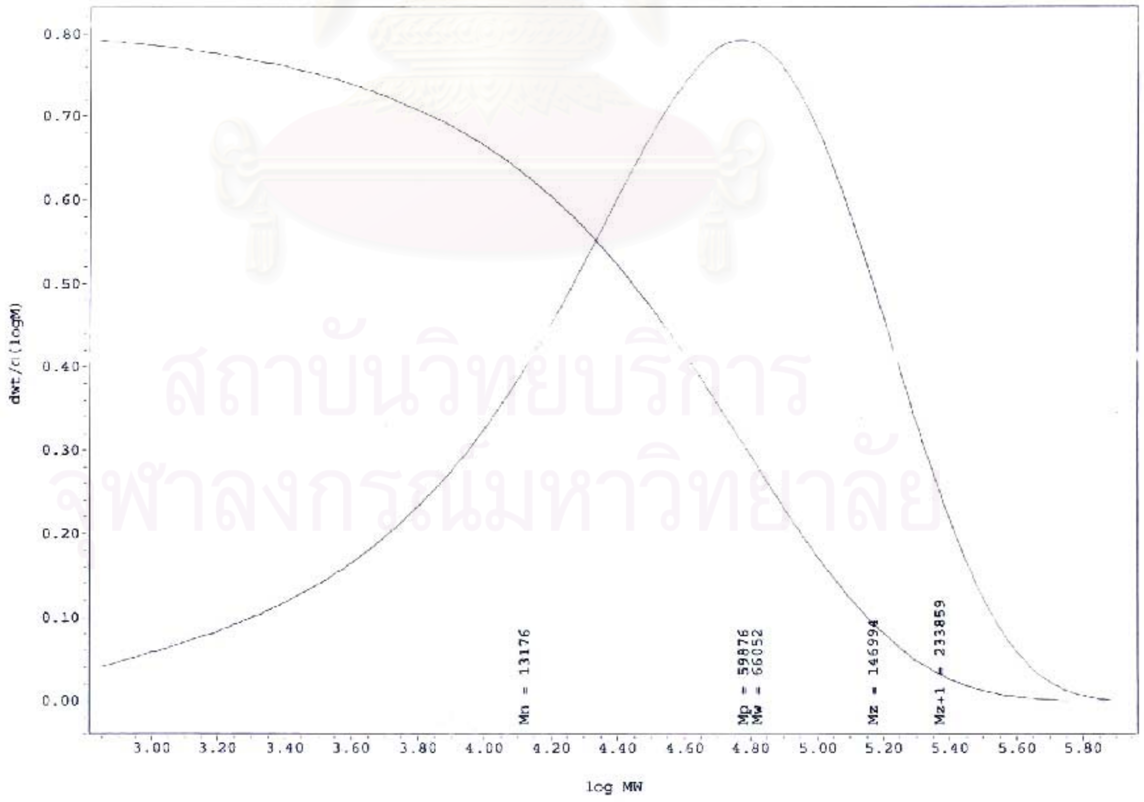


Figure B-4. GPC curve of EP copolymer (EP4, Table 7.1.)

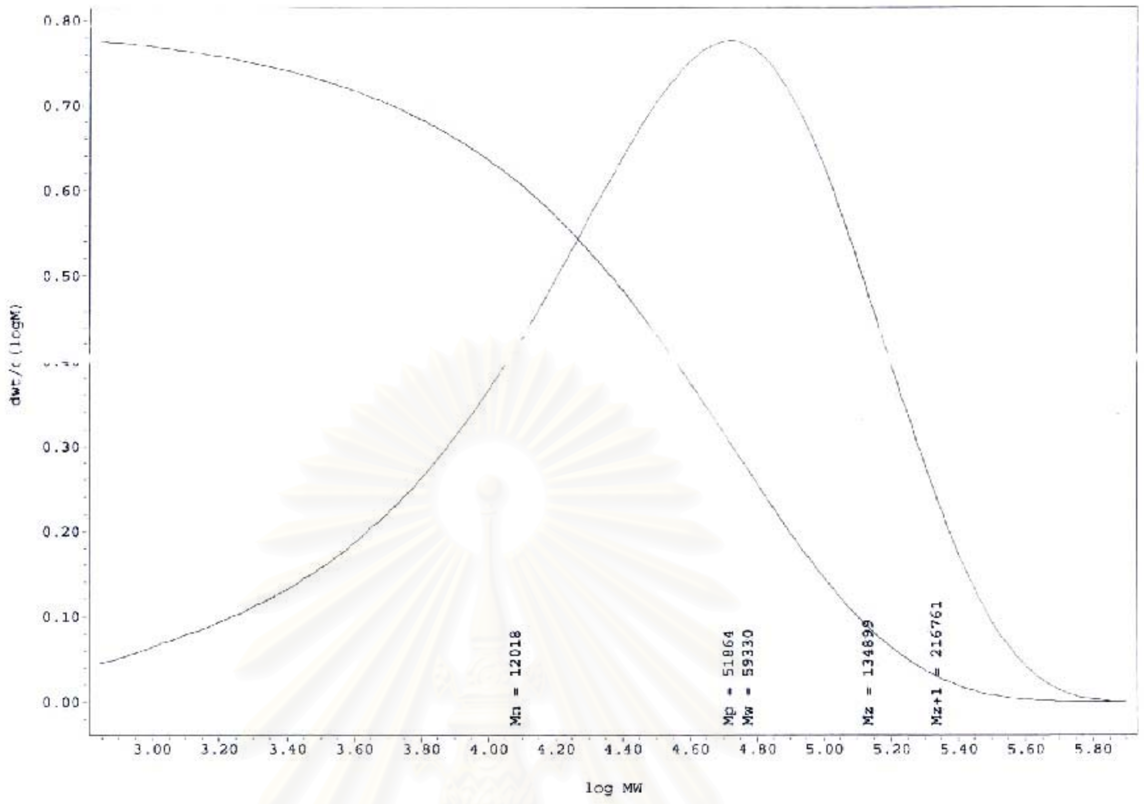


Figure B-5. GPC curve of EP copolymer (EP5, Table 7.1.)

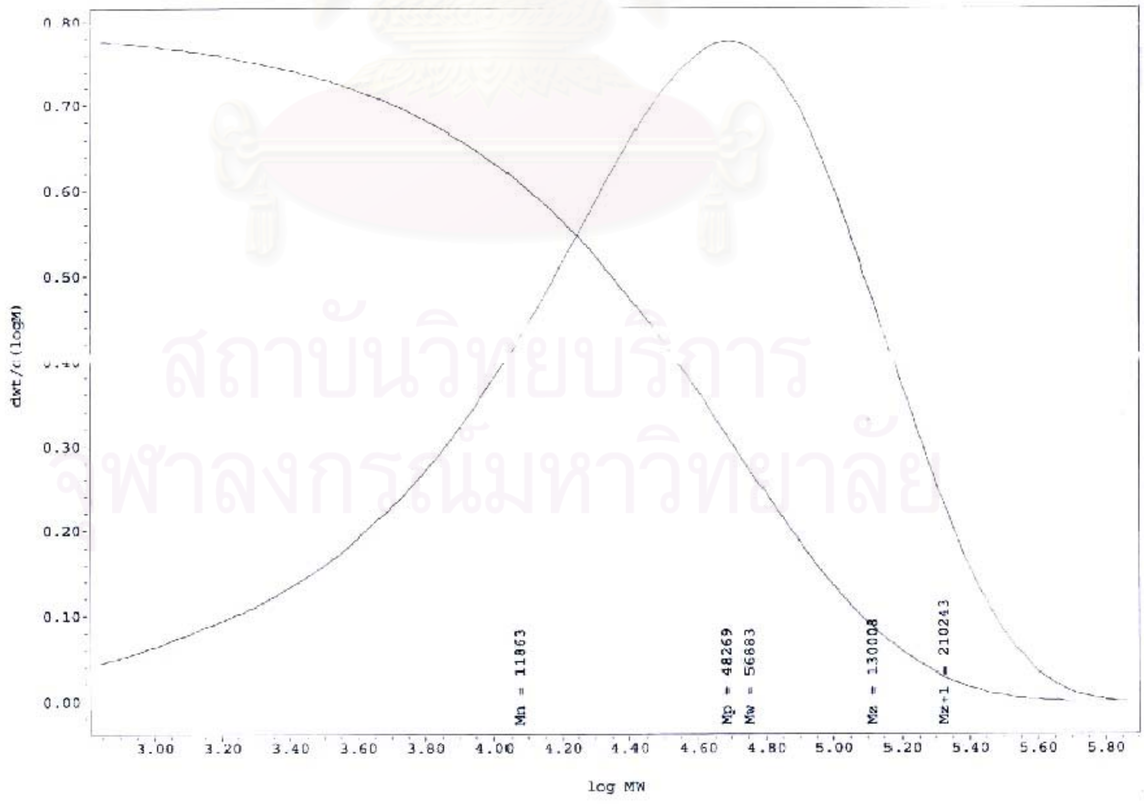


Figure B-6. GPC curve of EP copolymer (EP6, Table 7.1.)

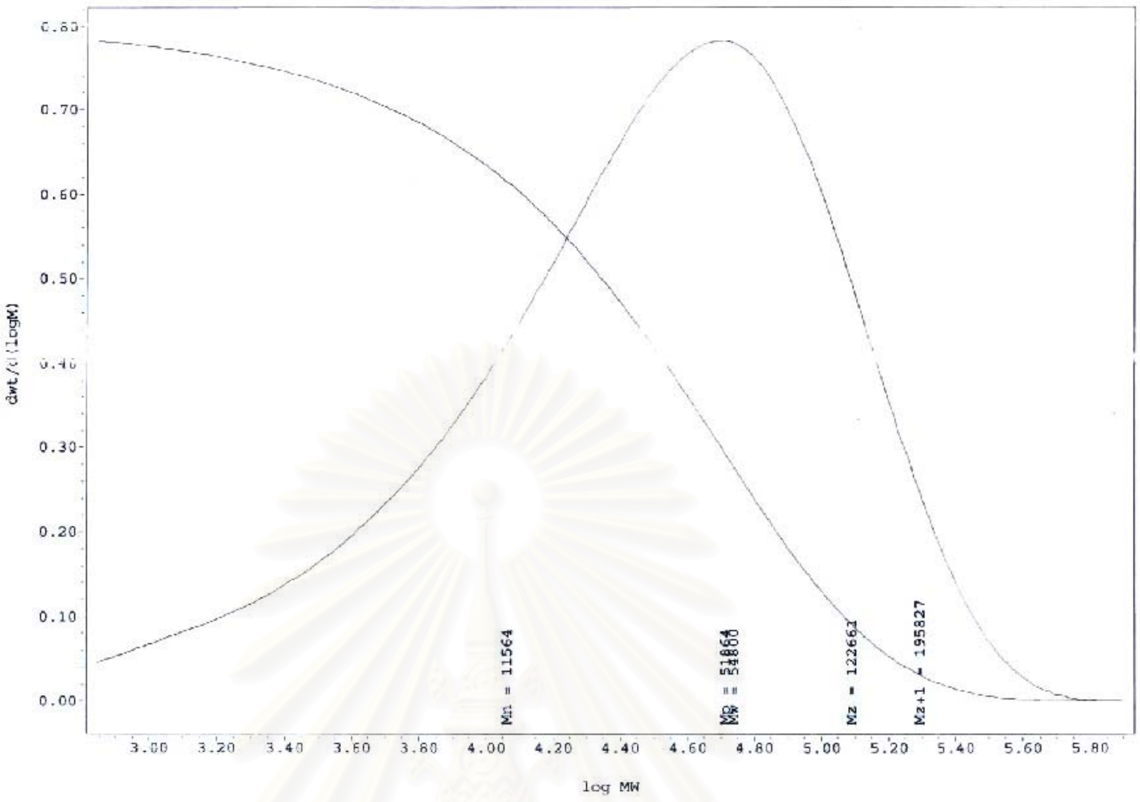


Figure B-7. GPC curve of EP copolymer (EP7, Table 7.1.)

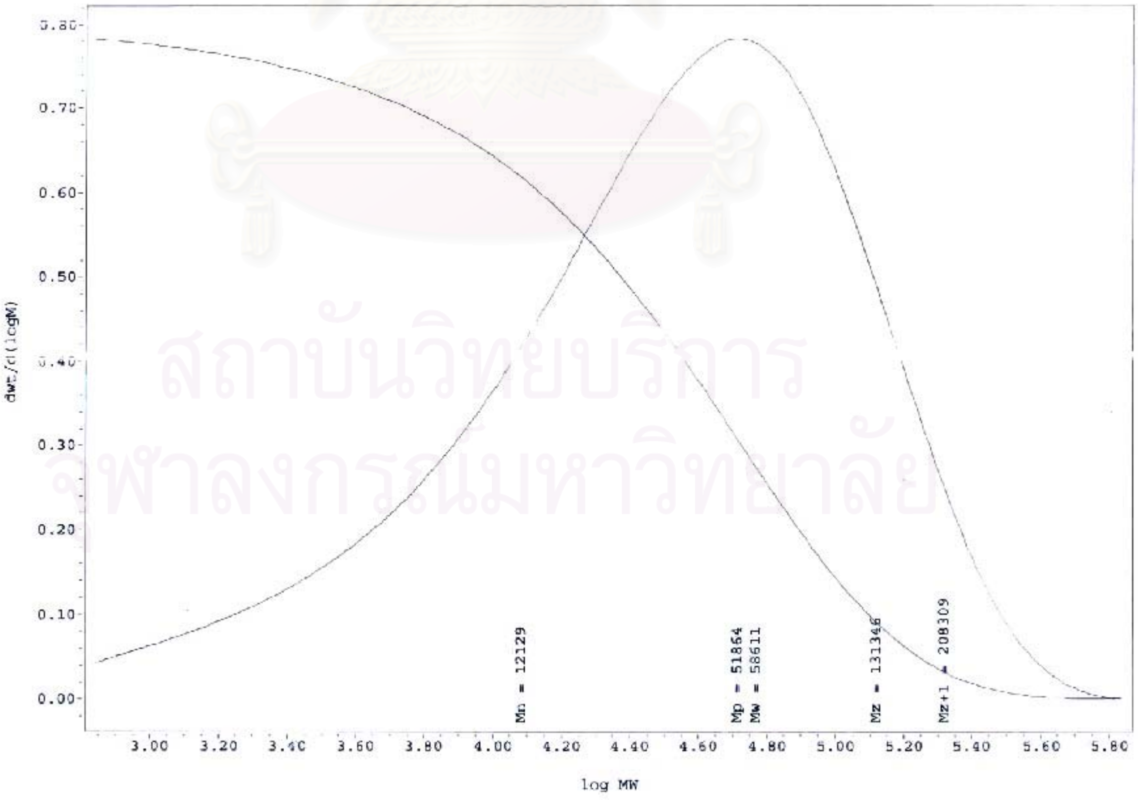


Figure B-8. GPC curve of EP copolymer (EP8, Table 7.1.)

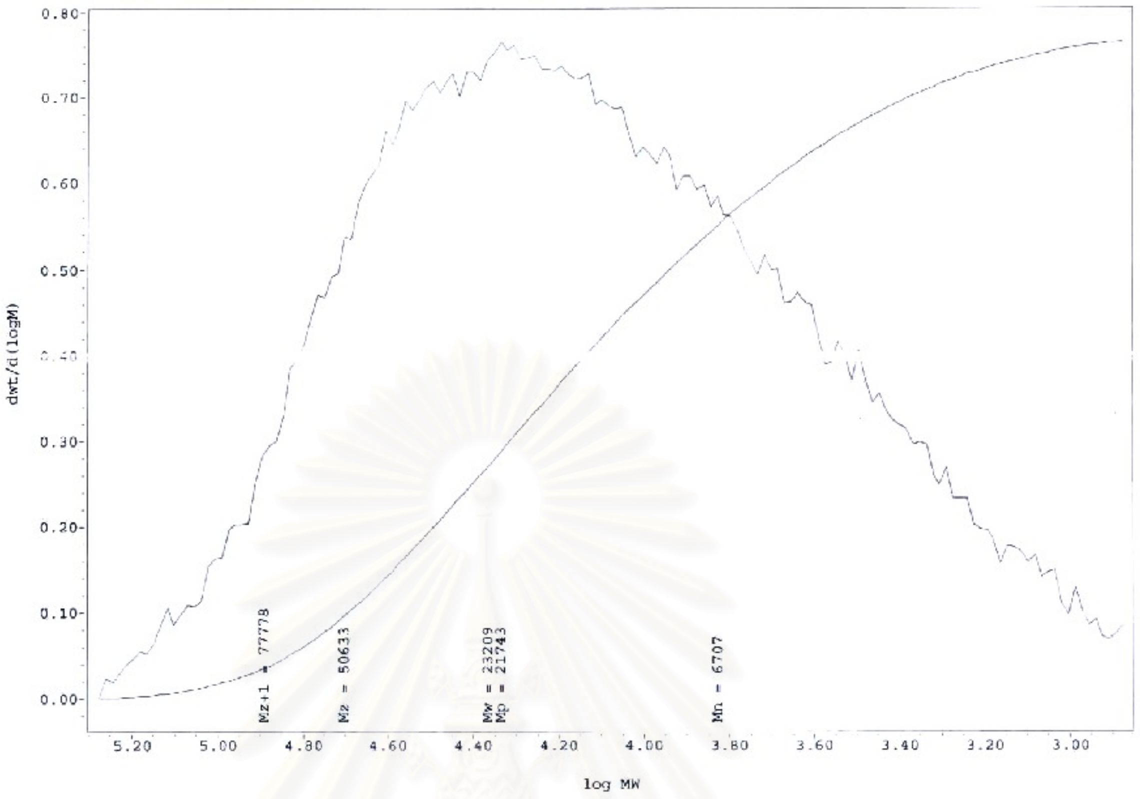


Figure B-9. GPC curve of EP copolymer (EP9, Table 7.2.)

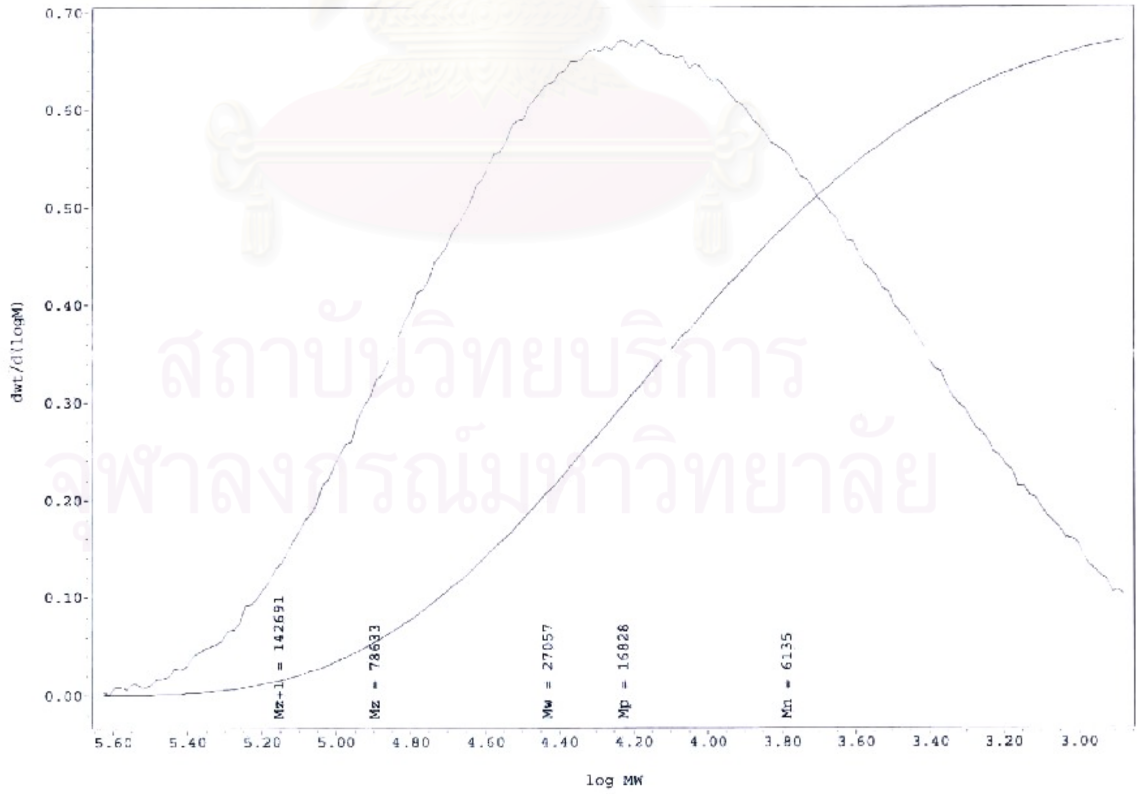


Figure B-10. GPC curve of EP copolymer (EP10, Table 7.2.)

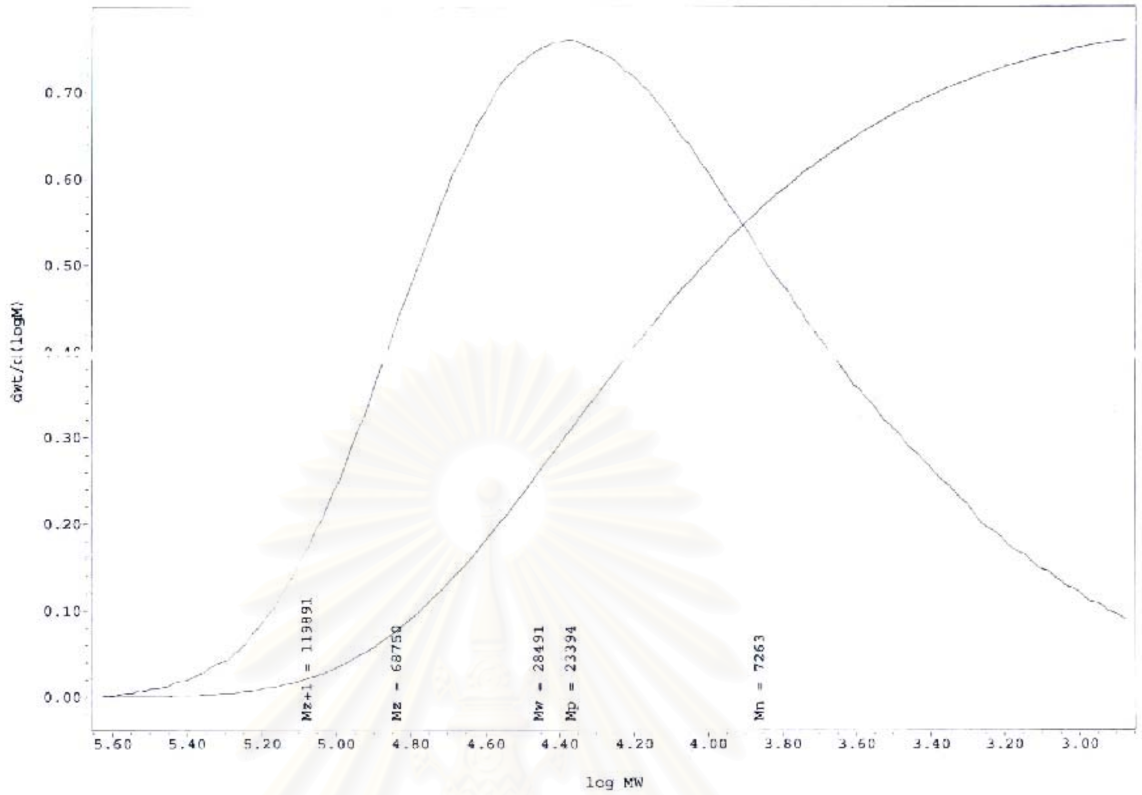


Figure B-11. GPC curve of EP copolymer (EP11, Table 7.2.)

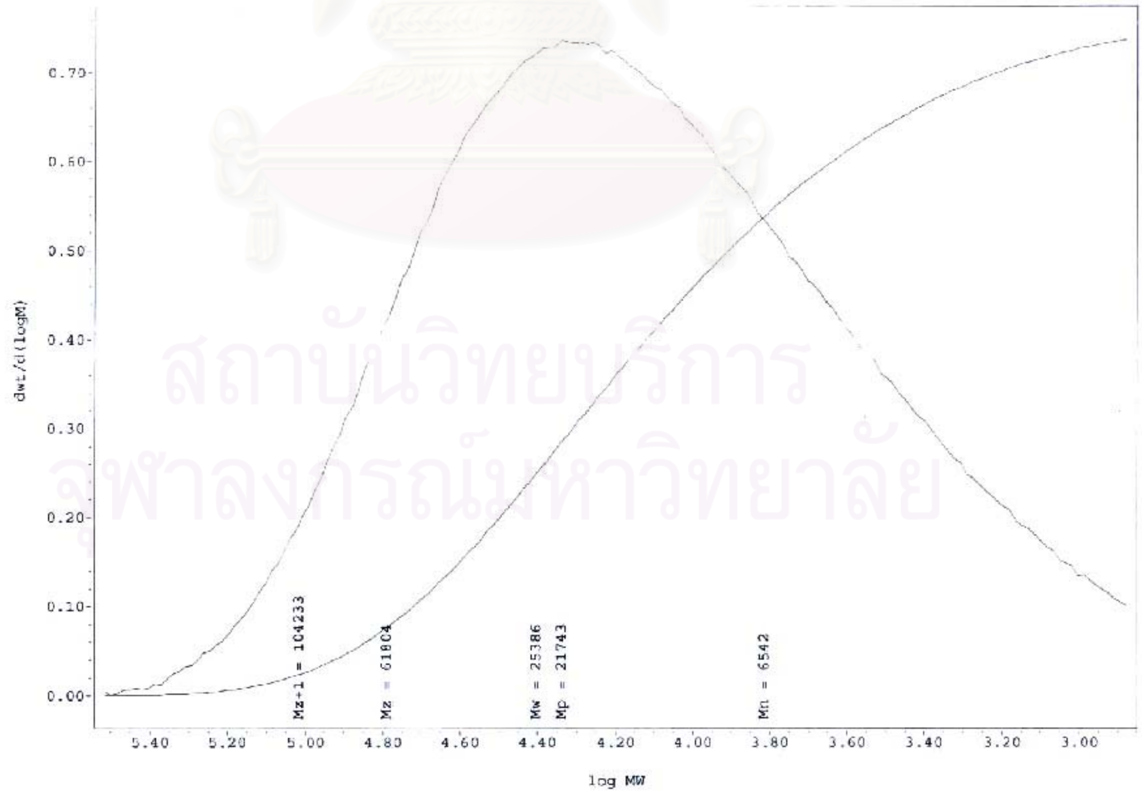


Figure B-12. GPC curve of EP copolymer (EP12, Table 7.2.)

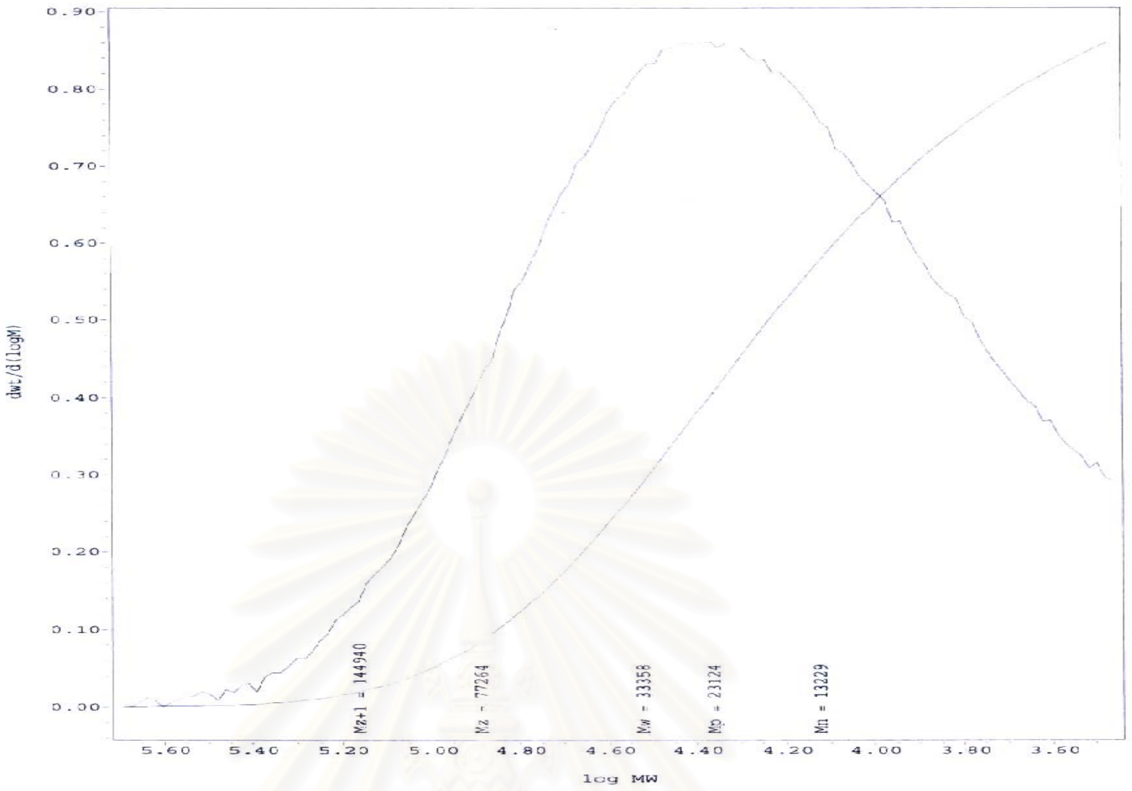


Figure B-13. GPC curve of EP copolymer (EP13, Table 7.2.)

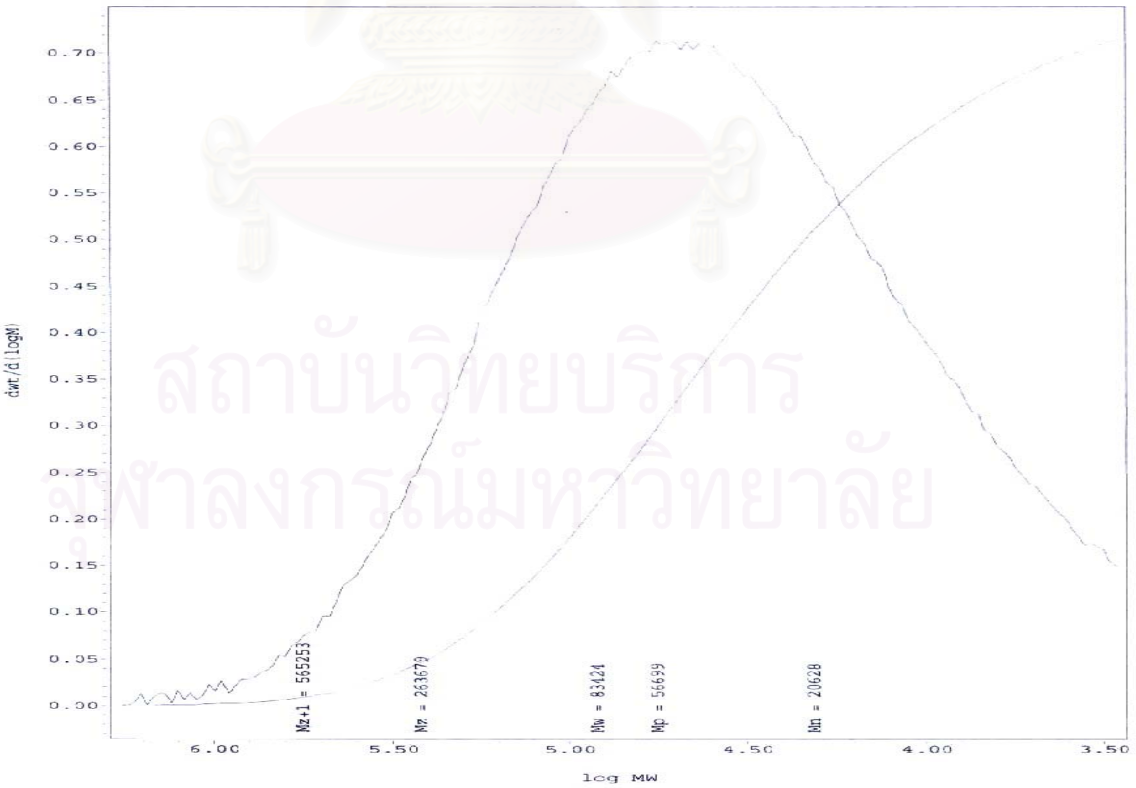


Figure B-14. GPC curve of EP copolymer (EP14, Table 7.3.)

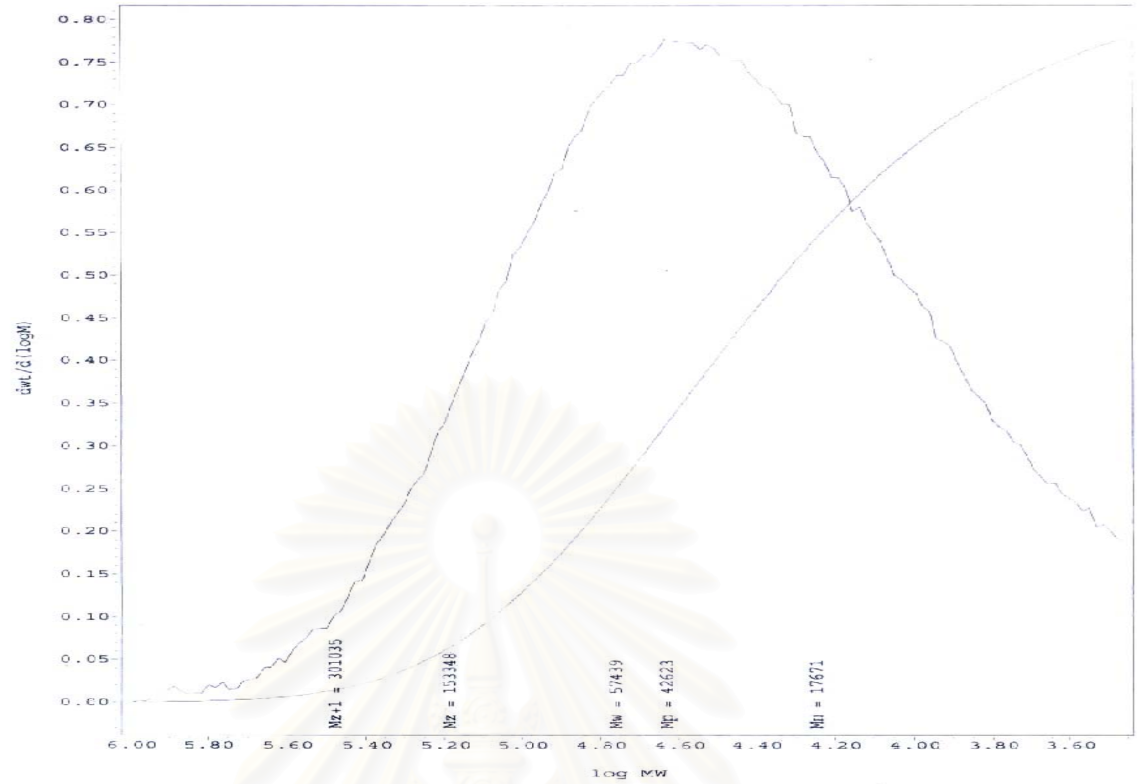


Figure B-15. GPC curve of EP copolymer (EP15, Table 7.3.)

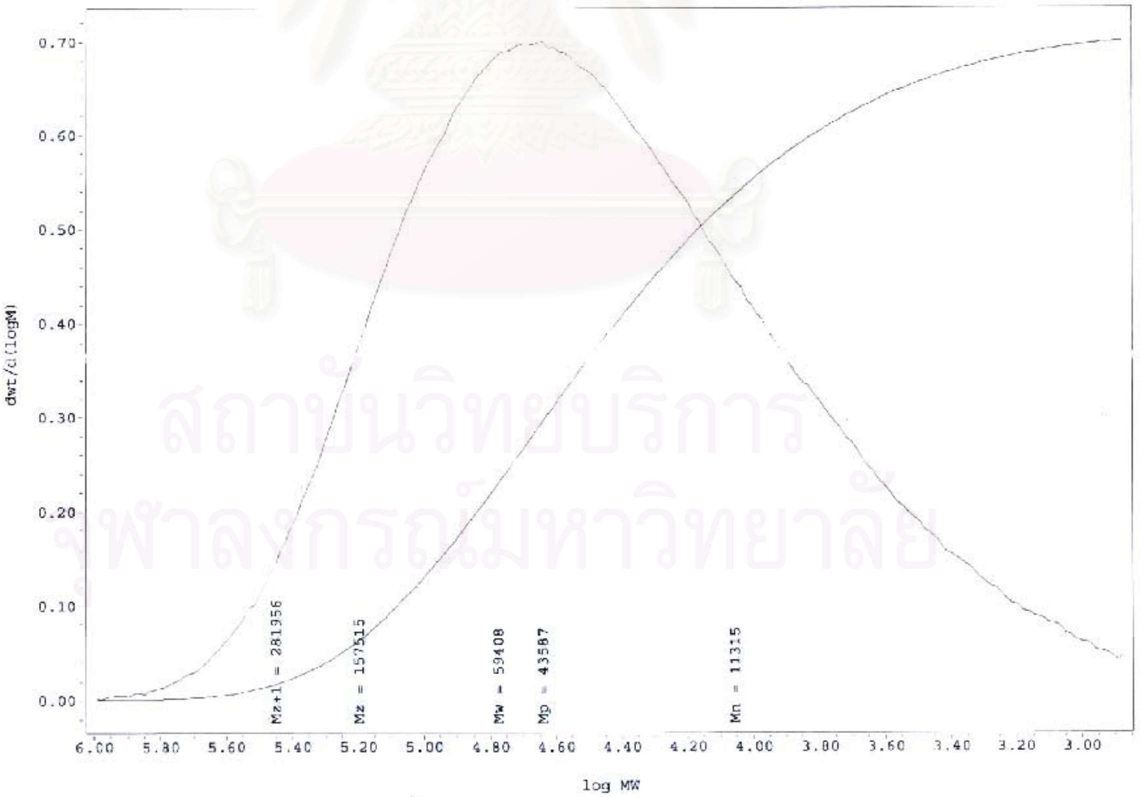


Figure B-16. GPC curve of EP copolymer (EP16, Table 7.3.)

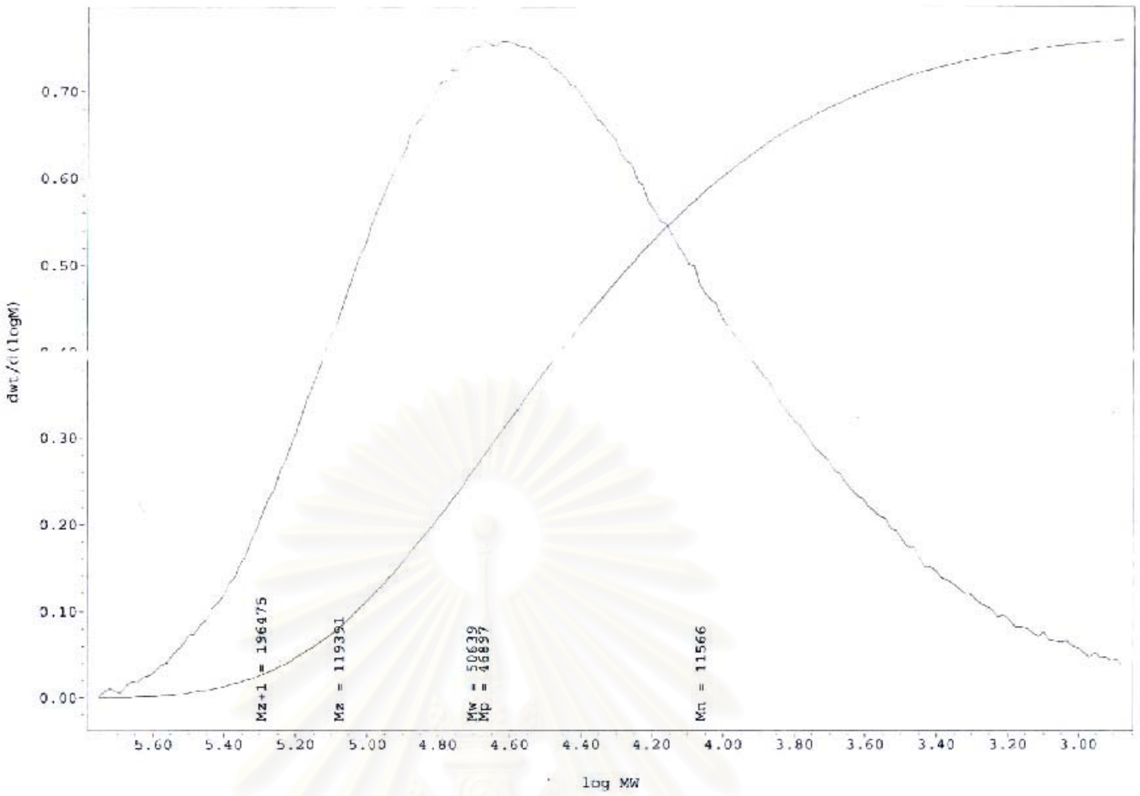


Figure B-17. GPC curve of EP copolymer (EP17, Table 7.3.)

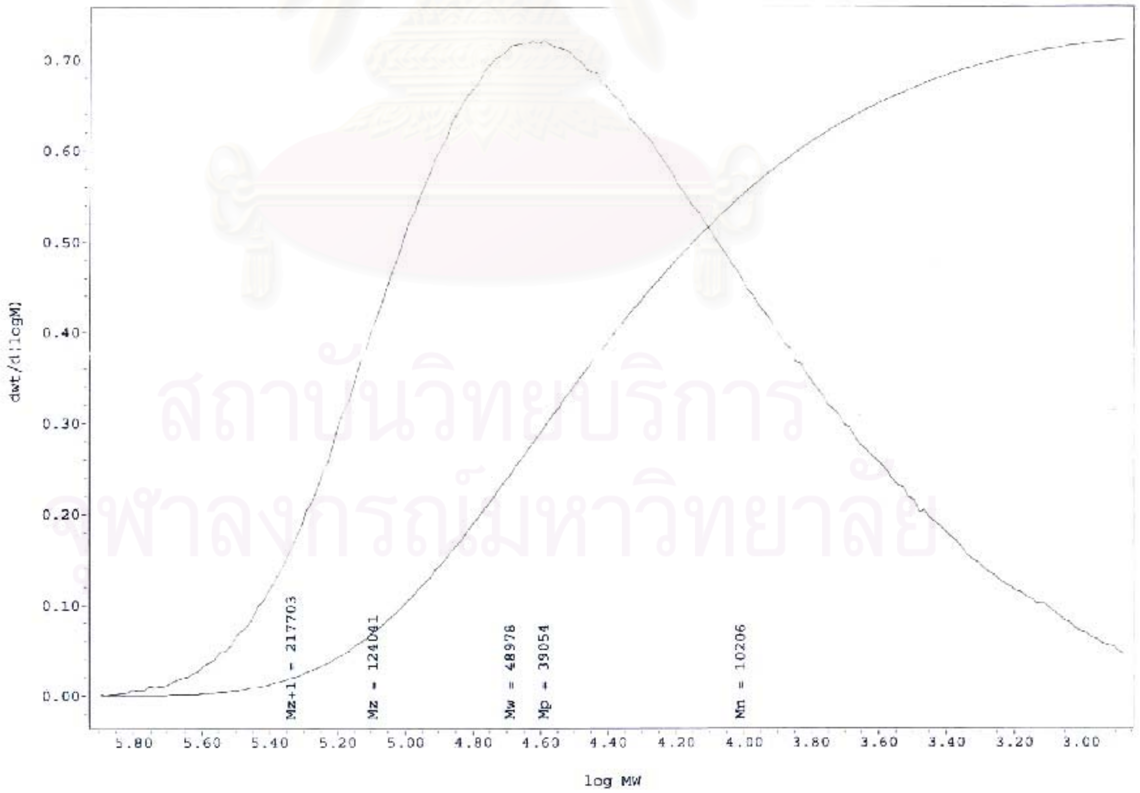


Figure B-18. GPC curve of EP copolymer (EP18, Table 7.3.)

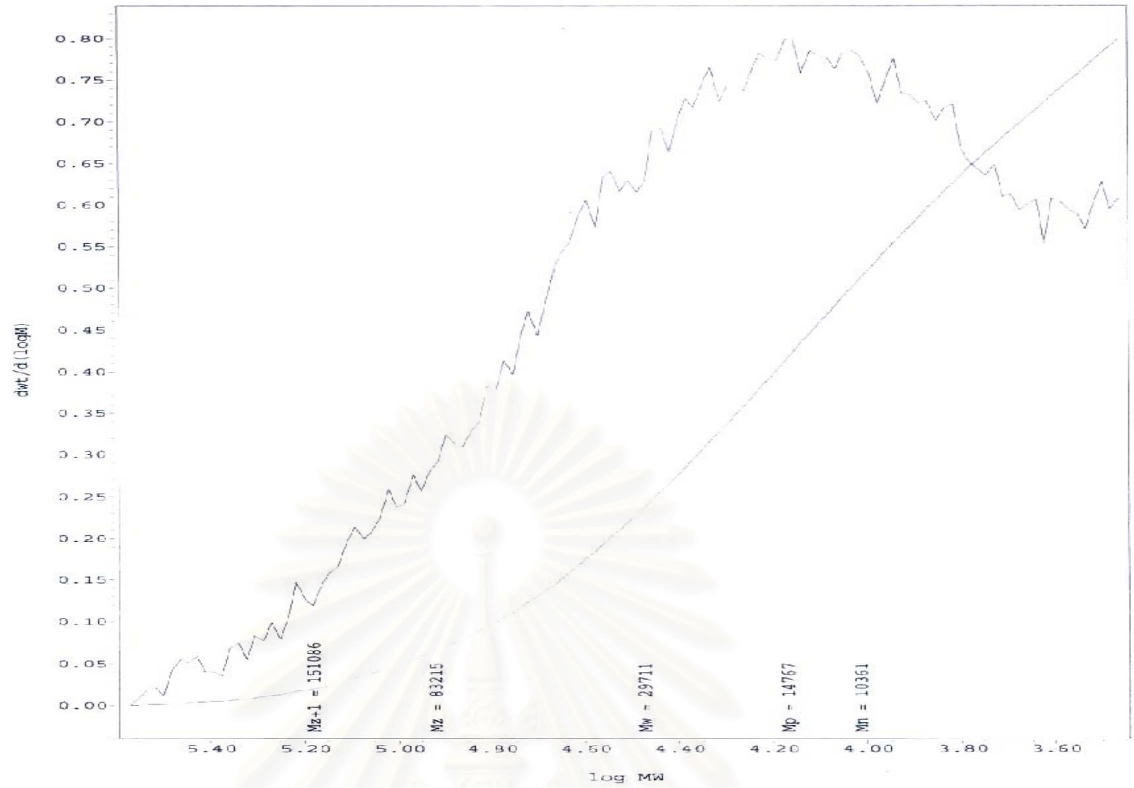


Figure B-19. GPC curve of EP copolymer (EP19, Table 7.4.)

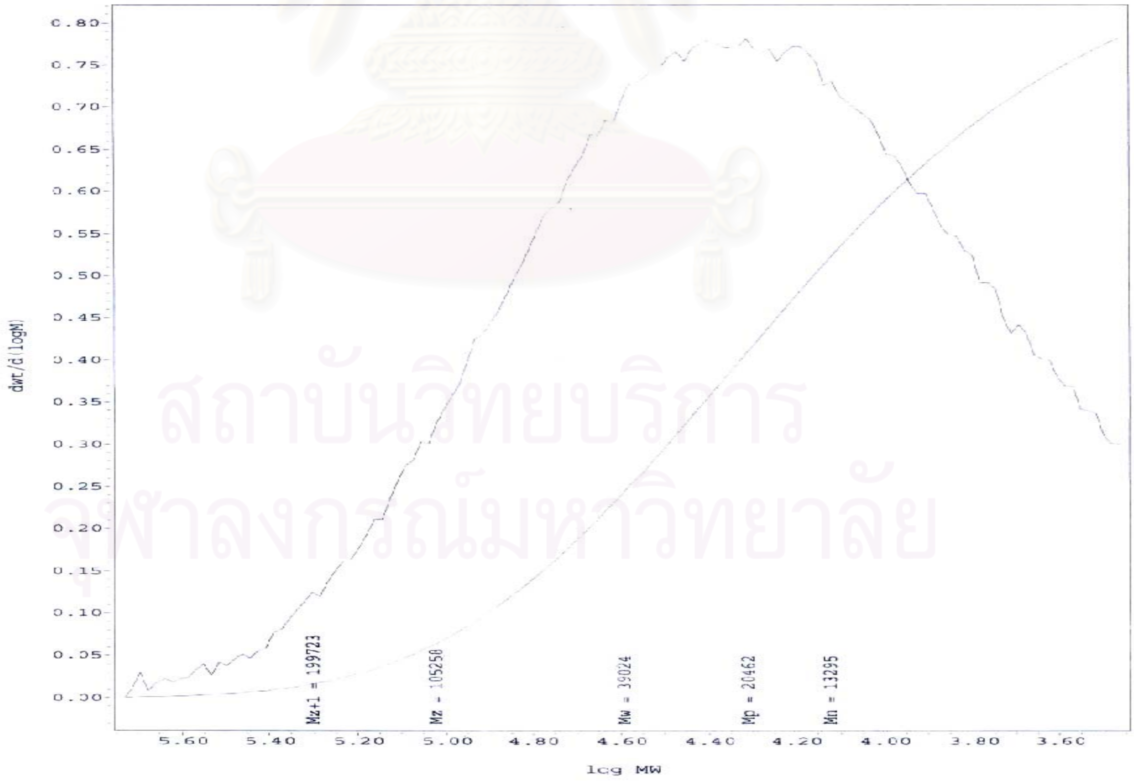


Figure B-20. GPC curve of EP copolymer (EP20, Table 7.4.)

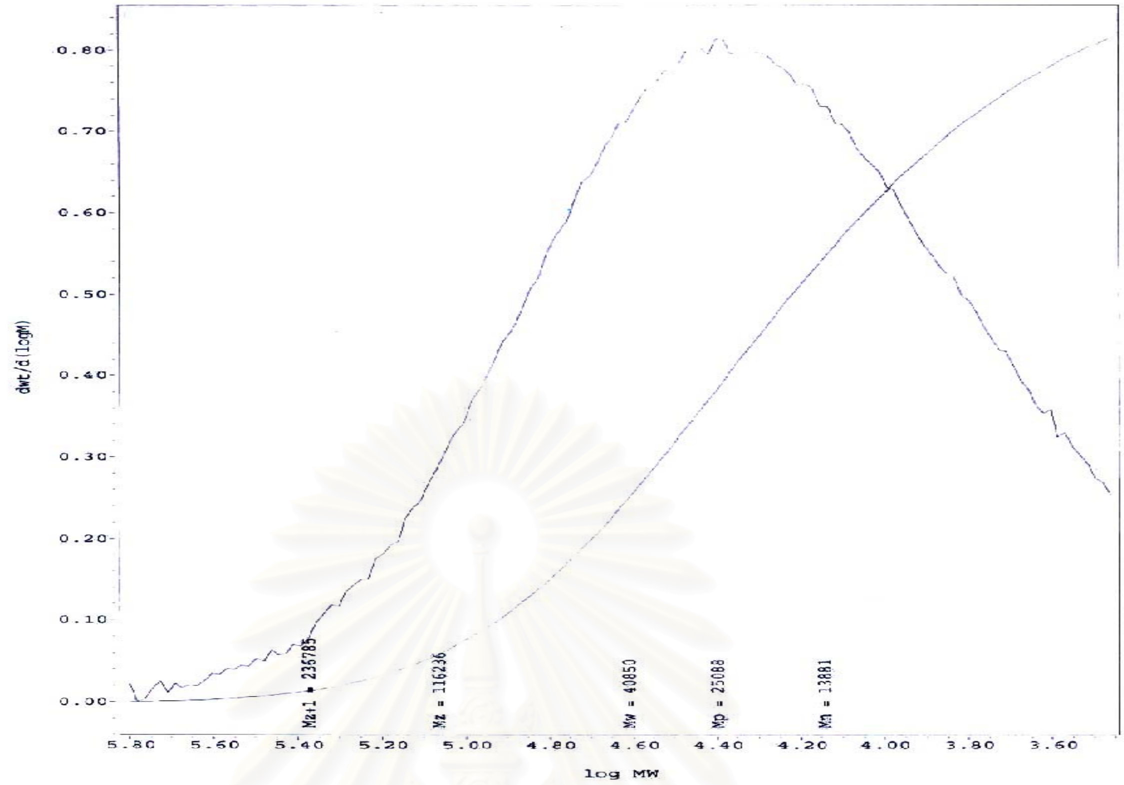


Figure B-21. GPC curve of EP copolymer (EP21, Table 7.4.)

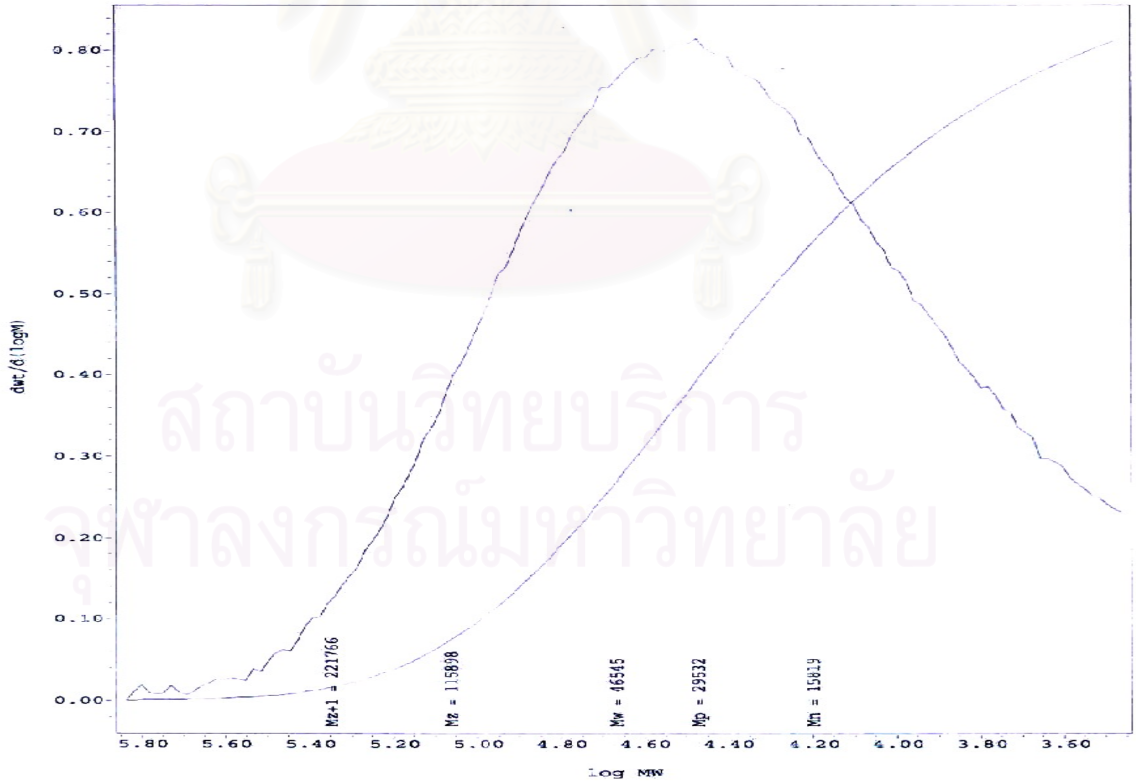


Figure B-22. GPC curve of EP copolymer (EP22, Table 7.4.)

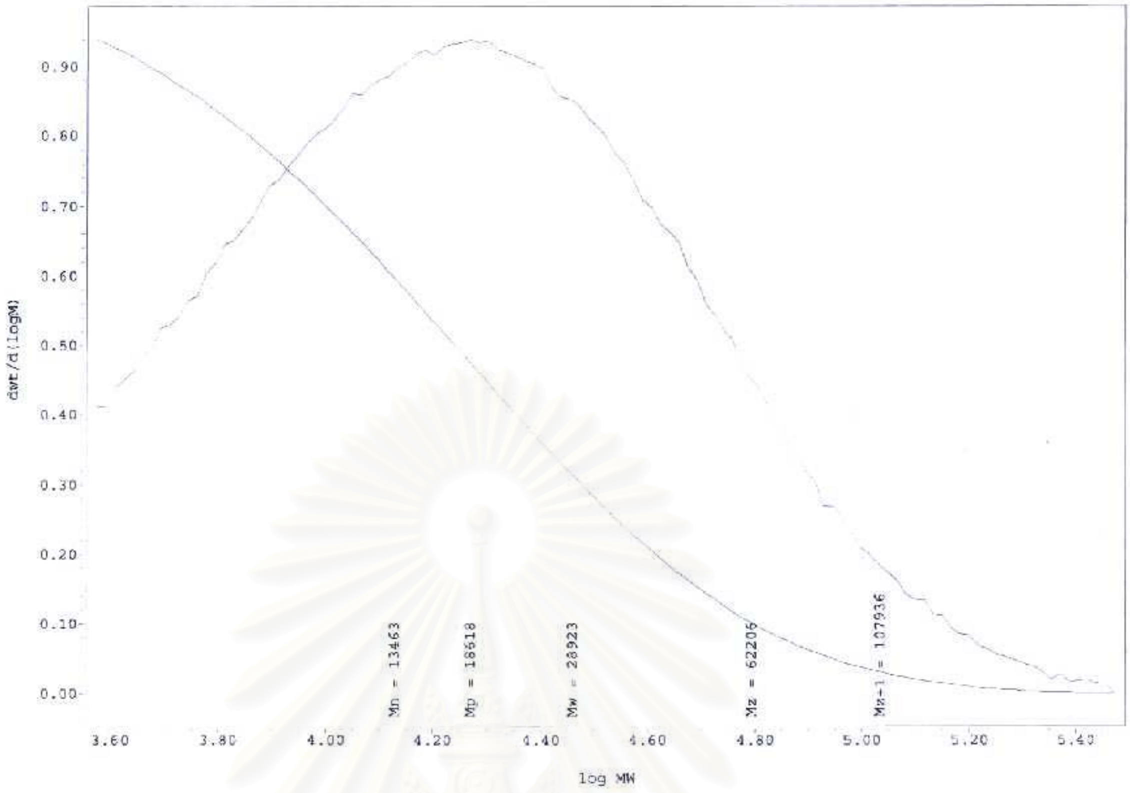


Figure B-23. GPC curve of EP copolymer (EP1, Table 8.3.)

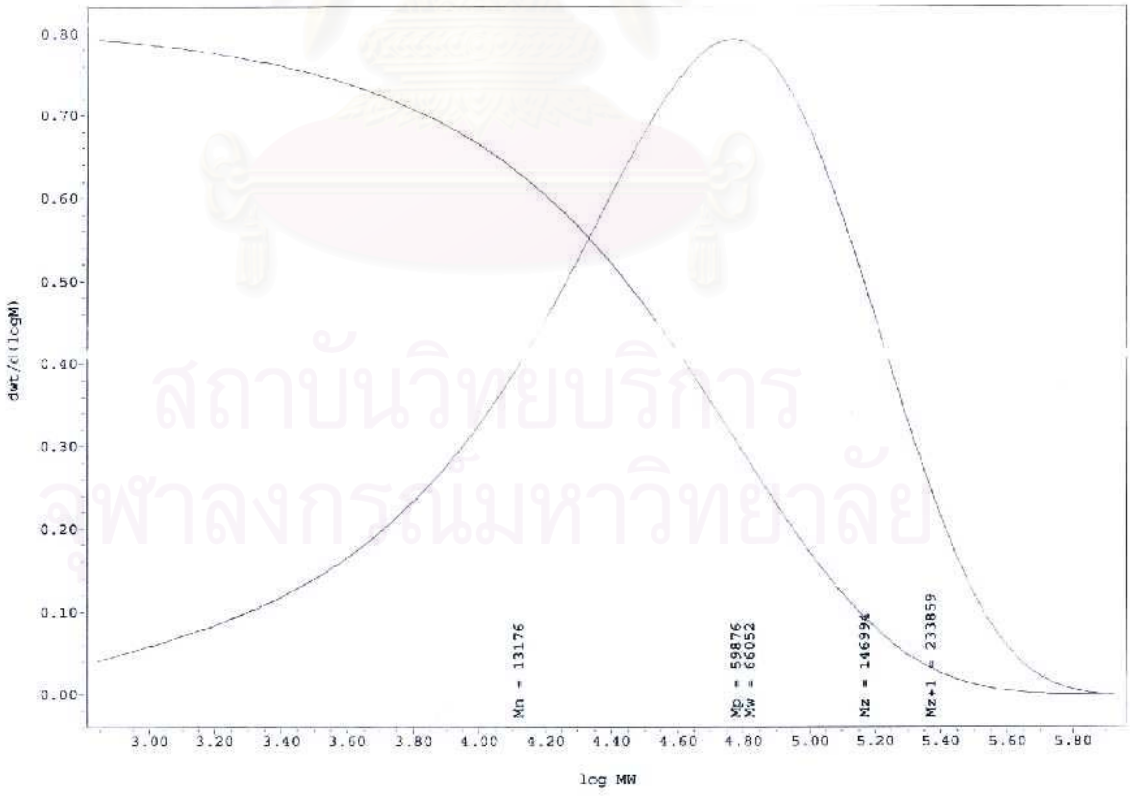


Figure B-24. GPC curve of EP copolymer (EP2, Table 8.3.)

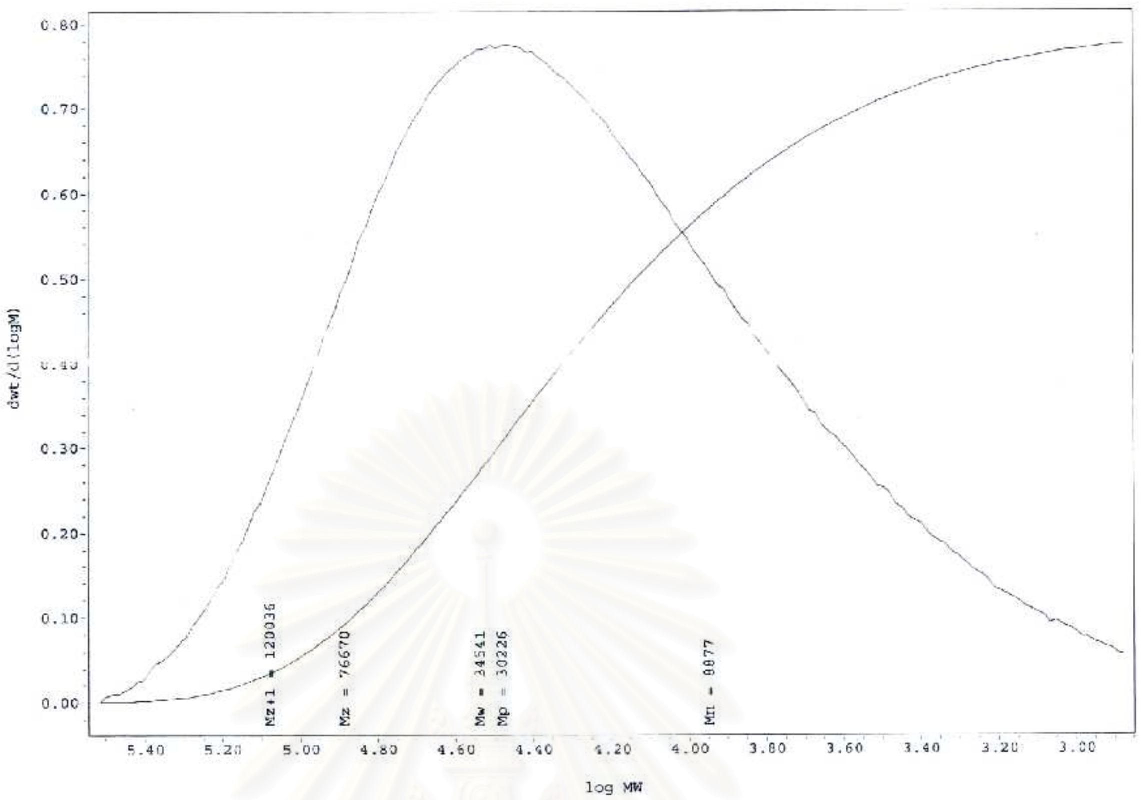


Figure B-25. GPC curve of EP copolymer (EP3, Table 8.3.)

APPENDIX C

DSC CURVES

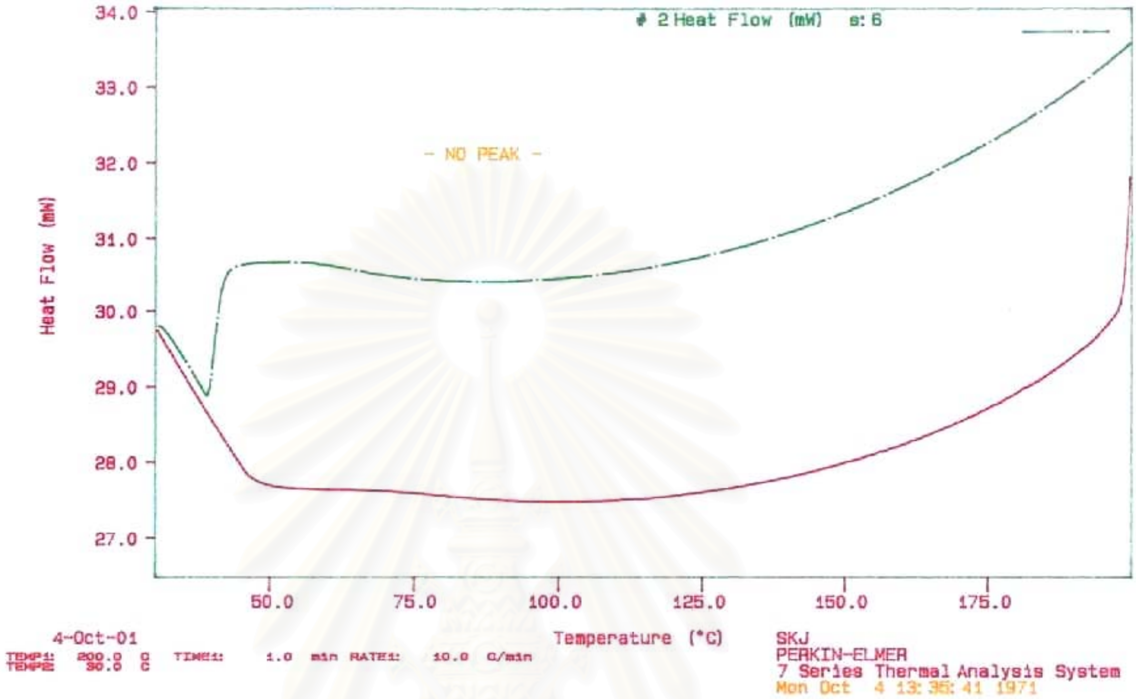


Figure C-1. DSC curves of EP copolymer (EP4, Table 7.1.)

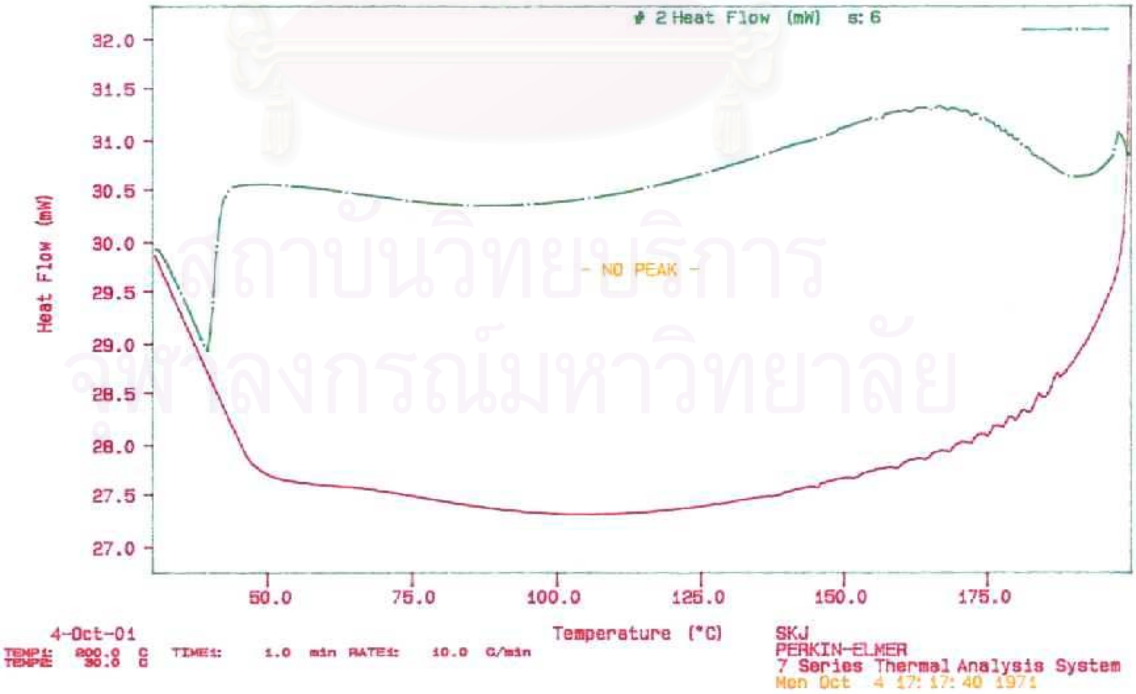


Figure C-2. DSC curves of EP copolymer (EP5, Table 7.1.)

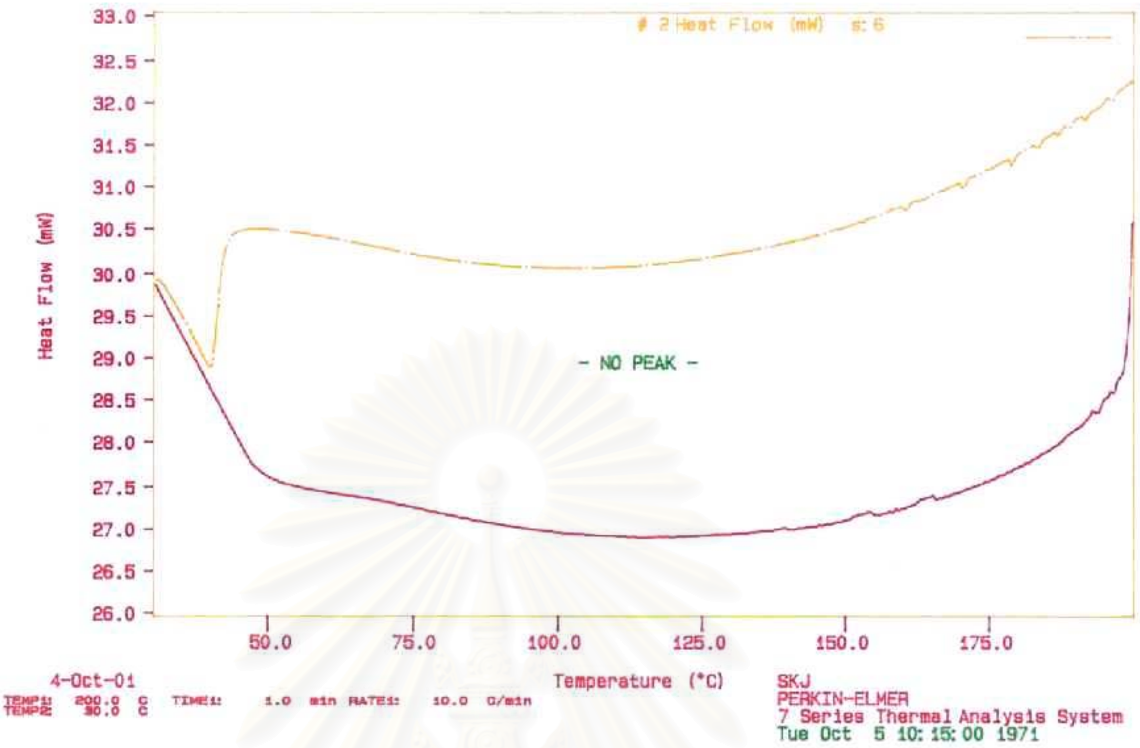


Figure C-3. DSC curves of EP copolymer (EP6, Table 7.1.)

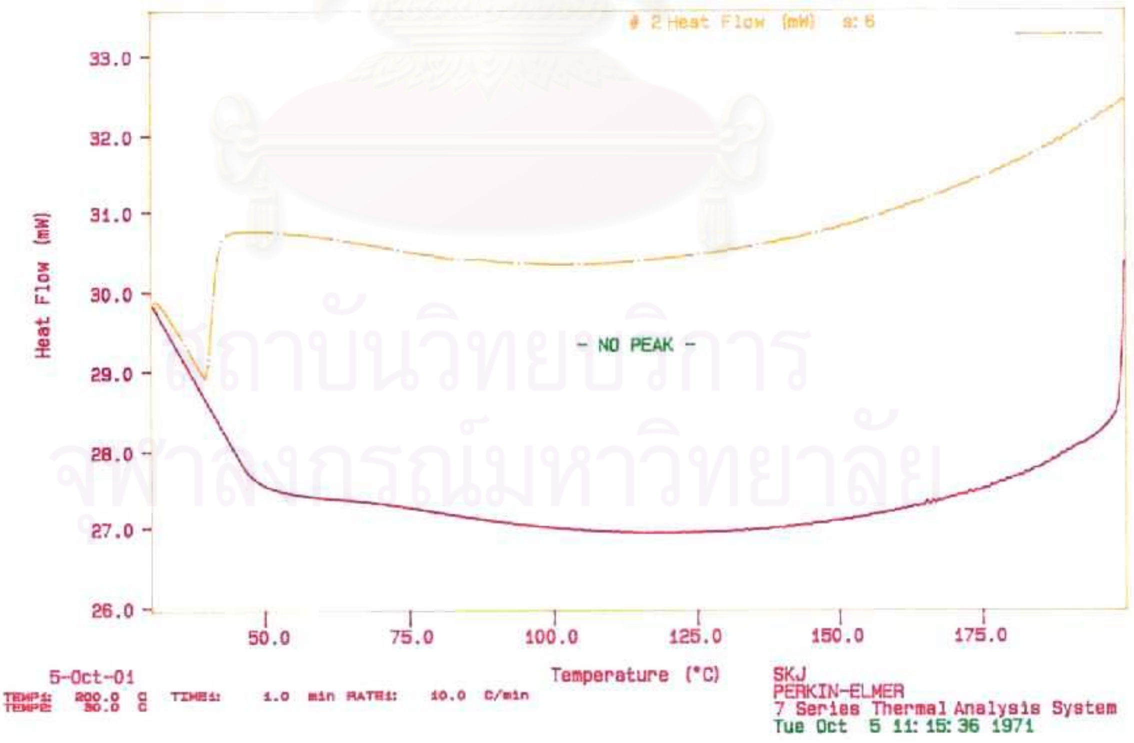


Figure C-4. DSC curves of EP copolymer (EP7, Table 7.1.)

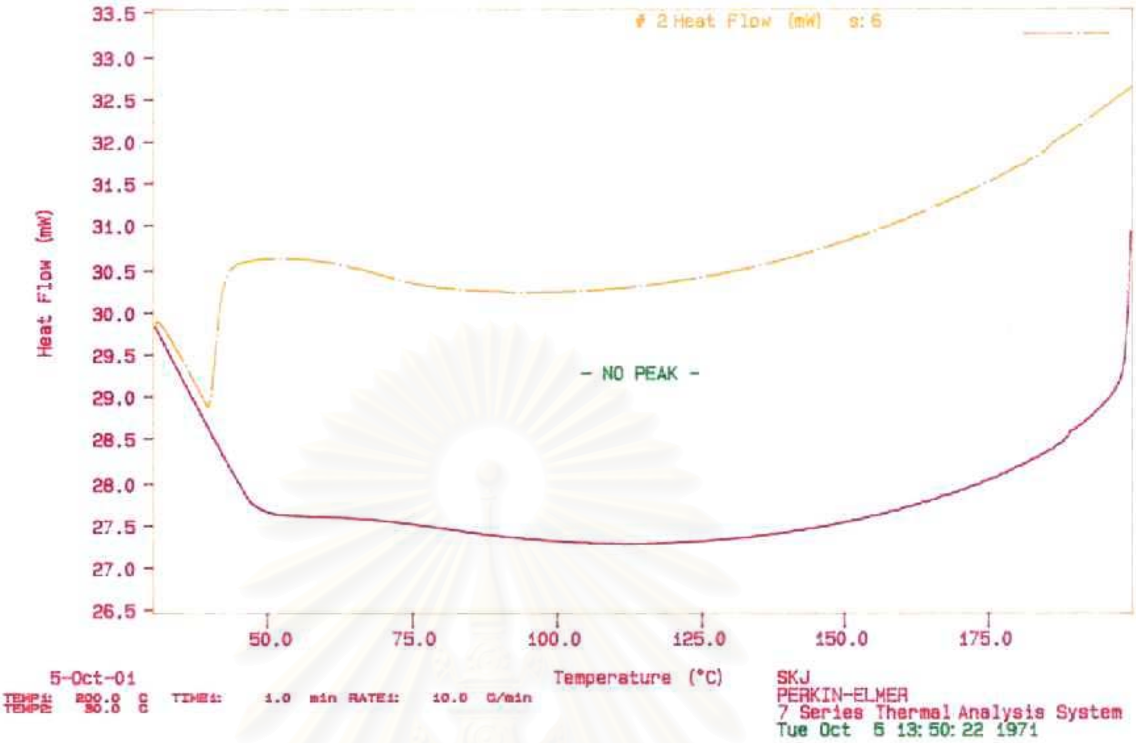


Figure C-5. DSC curves of EP copolymer (EP8, Table 7.1.)

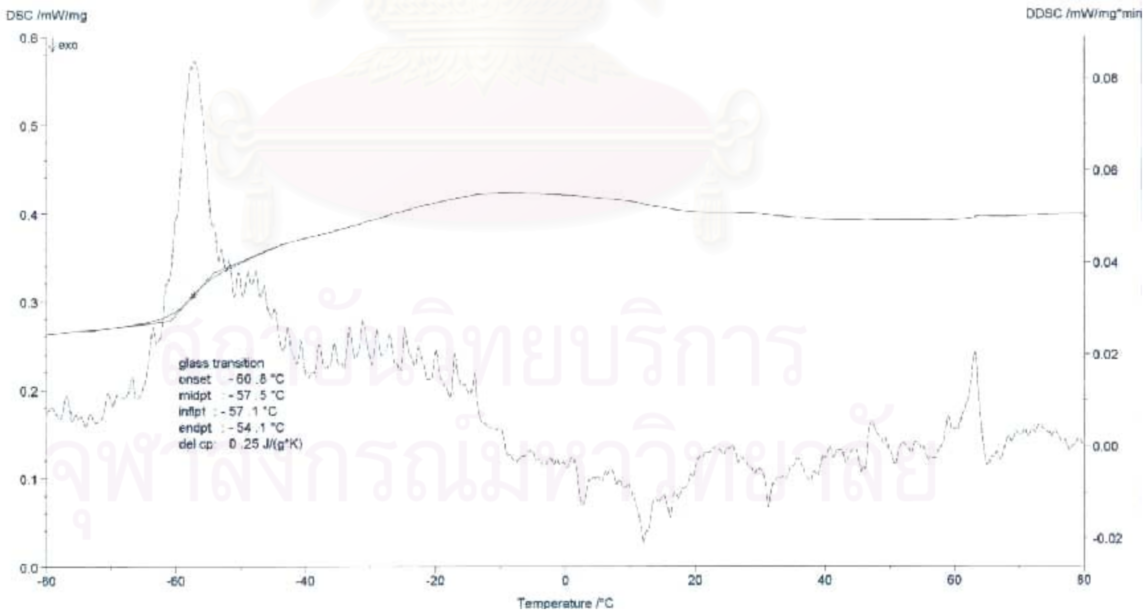


Figure C-6. DSC curves at low temperature range of EP copolymer (EP1, Table 7.1.)

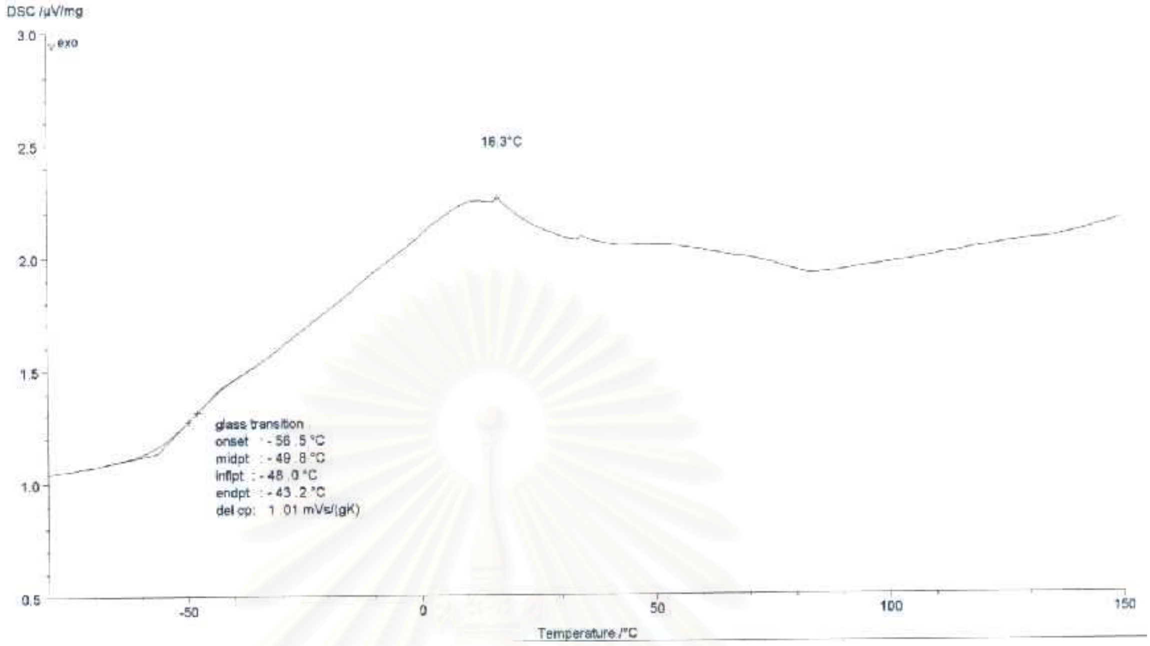


Figure C-7. DSC curves at low temperature range of EP copolymer (EP4, Table 7.1.)

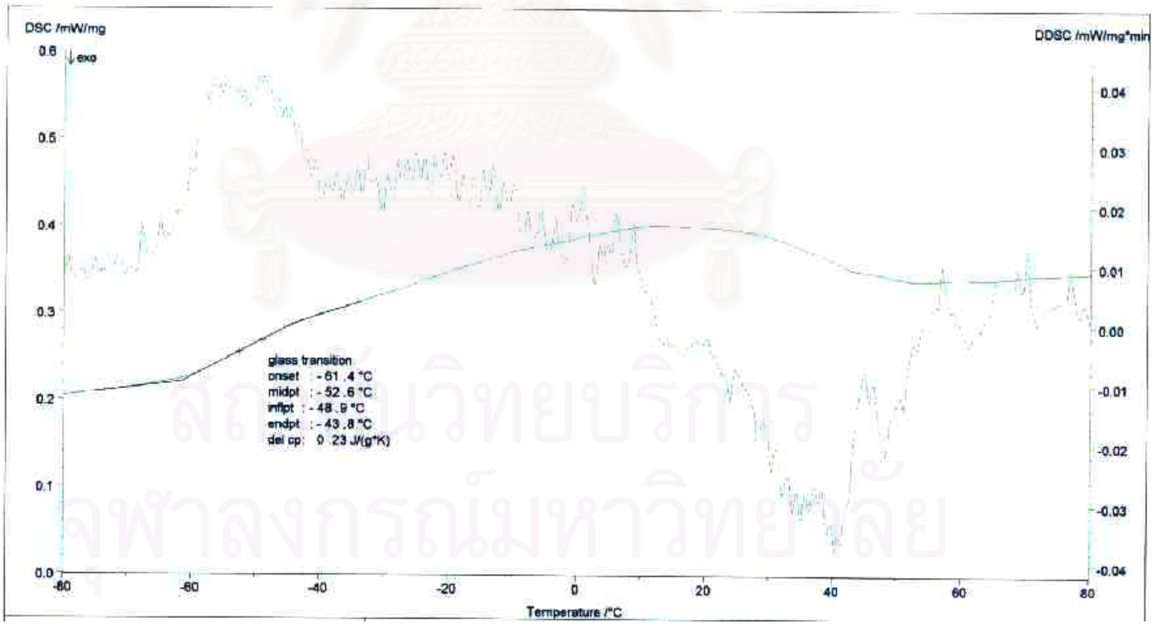
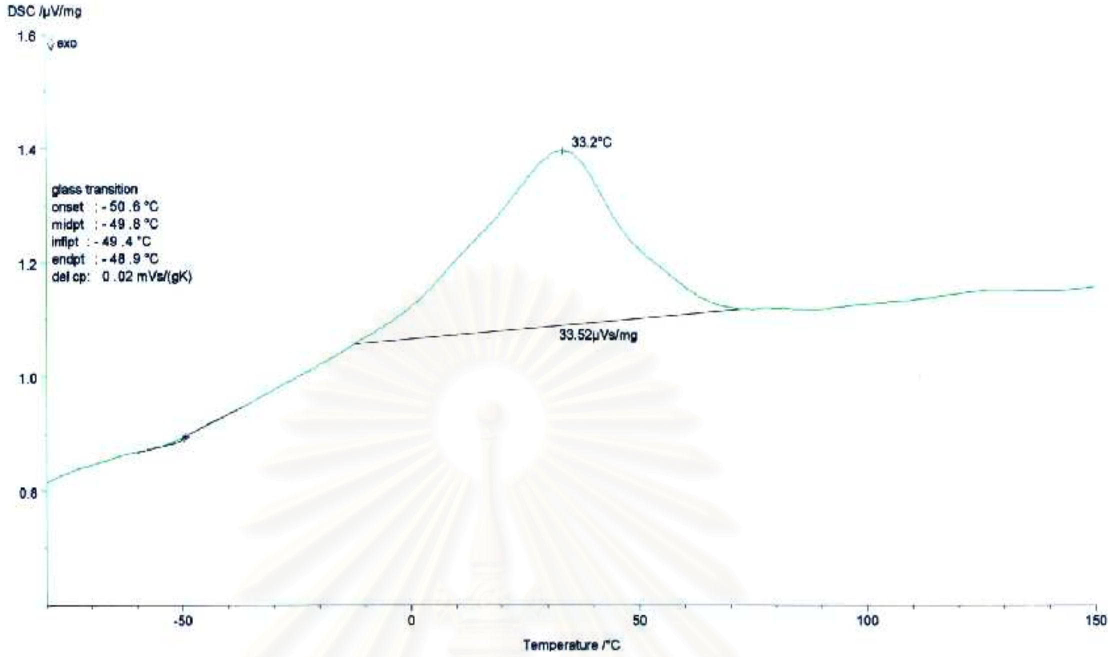
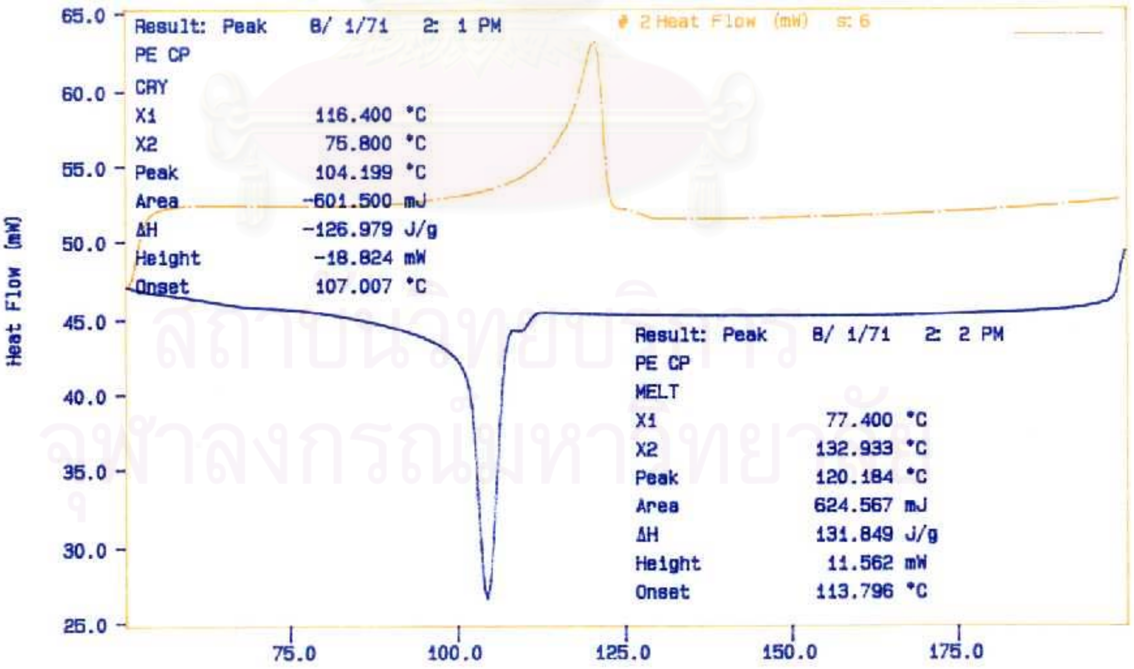


Figure C-8. DSC curves at low temperature range of EP copolymer (EP14, Table7.3.)



```
glass transition
onset  : -50.6 °C
midpt  : -49.8 °C
inflpt : -49.4 °C
endpt  : -48.9 °C
del cp:  0.02 mVs/(gK)
```

Figure C-9. DSC curves at low temperature range of EP copolymer (EP3, Table 8.3.)



```
Result:  Peak     8/ 1/71    2:  1 PM
PE CP
CRY
X1               116.400  °C
X2                75.800  °C
Peak             104.199  °C
Area            -601.500  mJ
ΔH              -126.979  J/g
Height           -18.824  mW
Onset            107.007  °C
```

```
Result:  Peak     8/ 1/71    2:  2 PM
PE CP
MELT
X1                77.400  °C
X2               132.933  °C
Peak             120.184  °C
Area             624.567  mJ
ΔH               131.849  J/g
Height            11.562  mW
Onset            113.796  °C
```

Figure C-10. DSC curves of polyethylene produced by Cp_2ZrCl_2/MAO (Figure 4.11.)

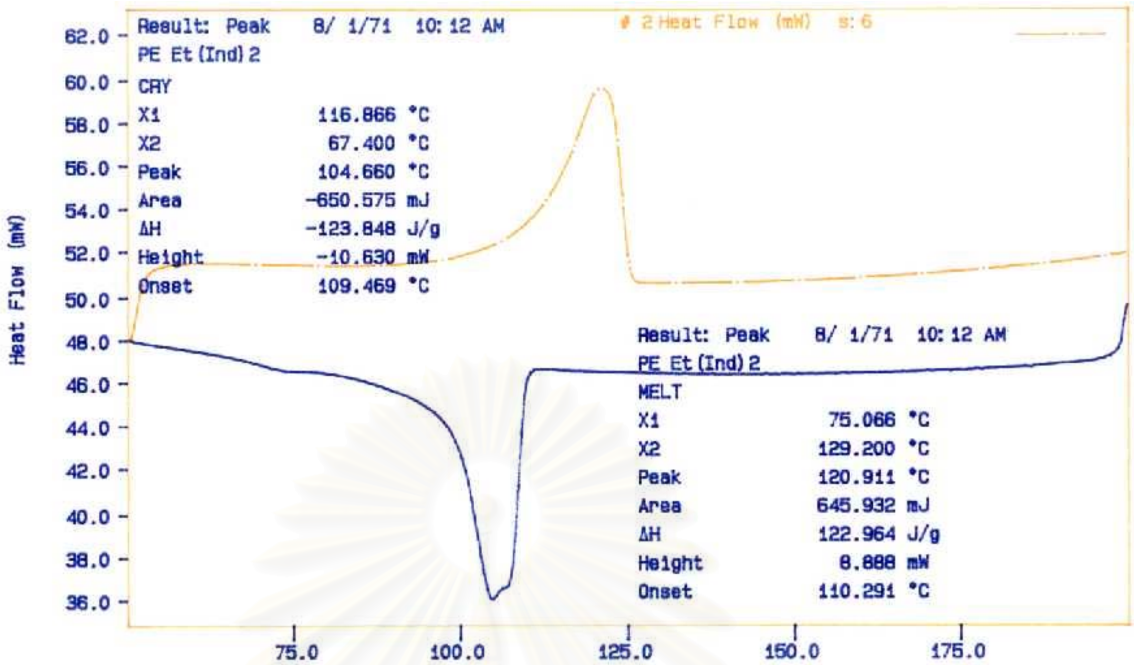


Figure C-11. DSC curves of polyethylene produced by Et[Ind]$_2$ZrCl$_2$/MAO (Figure 4.11.)

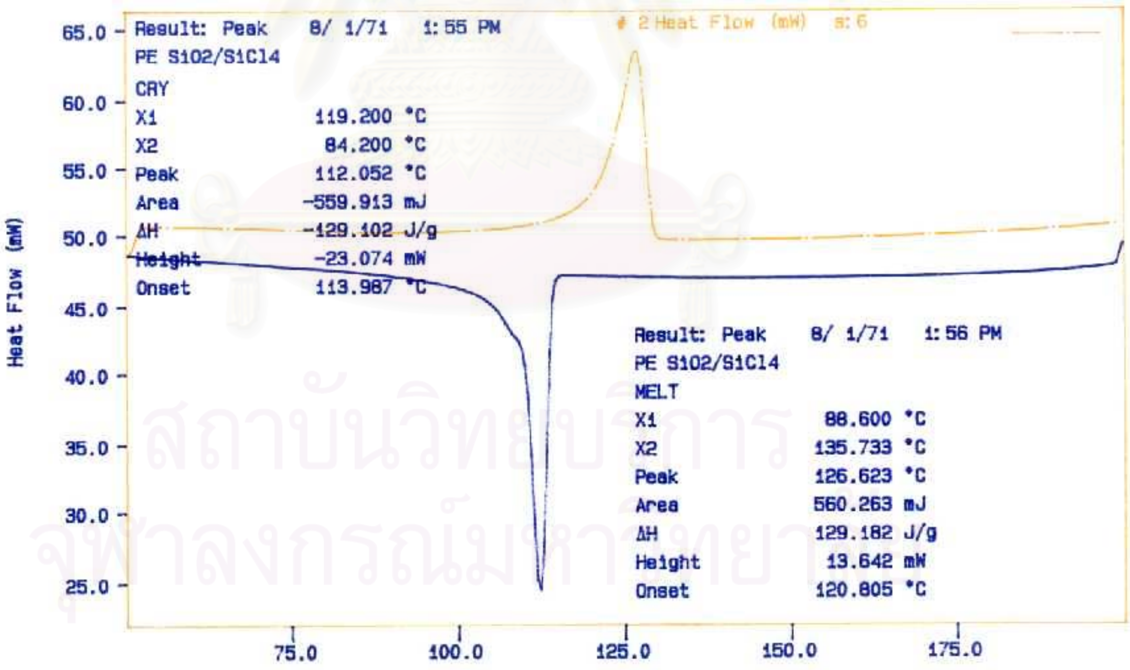


Figure C-12. DSC curves of polyethylene produced with SiO$_2$/SiCl$_4$/MAO-Et[Ind]$_2$ZrCl$_2$ (Table 8.6.)

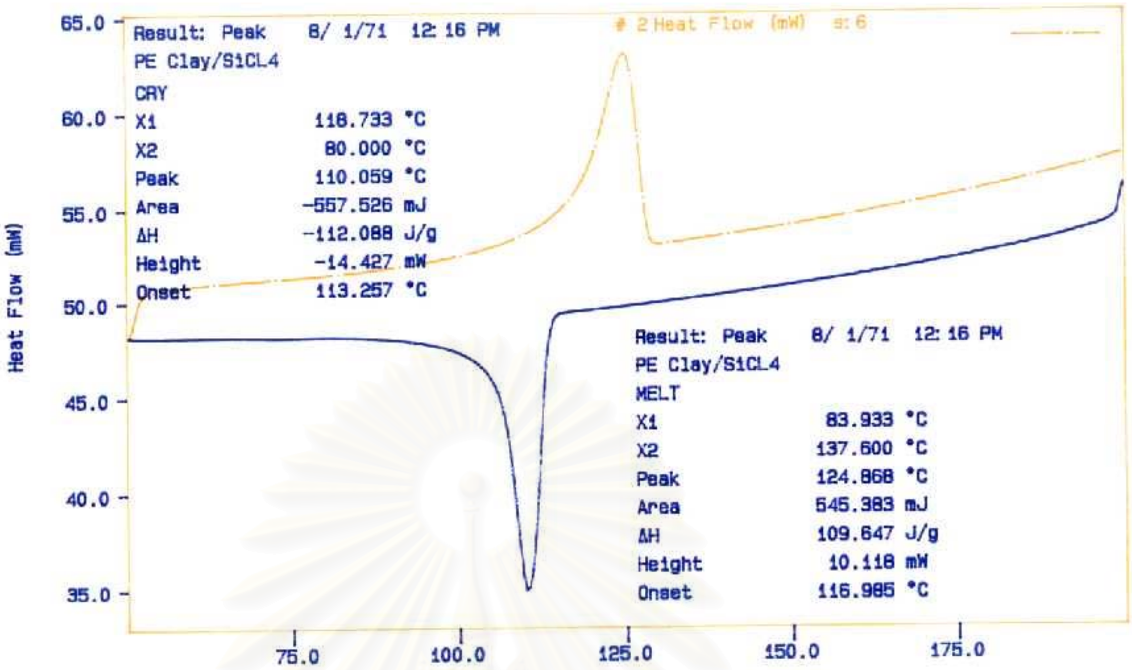


Figure C-13. DSC curves of polyethylene produced with Clay/$SiCl_4$/MAO-Et[Ind]$_2ZrCl_2$ (Table 8.6.)

VITA

Miss Chariya Chao was born in Bangkok, Thailand, on March 6, 1978. She received her Bachelor Degree in Chemical Engineering from Chulalongkorn University in 1997. She continued in Doctoral Degree of Engineering from the Department of Chemical Engineering, Chulalongkorn University in June, 1998.

Presentation

- The international symposium on "Future Technologies for Polyolefin and Olefin Polymerization Catalysis", Tokyo (2001).
- "Bangkok International Conference on Heterogeneous Catalysis", Bangkok (2001).

Publications

- Chariya Chao, Waraporn Pratchayawutthirat, Piyasan Praserthdam, Takeshi Shiono, Garry L. Rempel; "Copolymerization of Ethylene and Propylene Using Silicon Tetrachloride- Modified Silica/ MAO with $Et[Ind]_2ZrCl_2$ Metallocene Catalyst", Macromolecular Rapid Communications, 23 (2002): 672.
- Chariya Chao, Piyasan Praserthdam, Supaporn Khorbunsongserm, Garry L. Rempel; "Effects of TMA and MAO on Ethylene-Propylene Copolymer Using Supported Zirconocene Catalysts", Journal of Macromolecular Science- Pure and Applied Chemistry (accepted).