อิทธิพลของไดอีนต่อการสังเคราะห์เทอร์พอลิเมอไรเซชันของเอทิลีน โพรพิลีน และไดอีน ด้วยตัวเร่งปฏิกิริยา เอทิลีนบีส(อินดินิล)เซอร์โคเนียม ไดคลอไรด์ / เมทิลอะลูมินอกเซน

นางสาว สิริธร ภูวคีรีวิวัฒน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2548

ISBN 974-17-5489-2

DIENES EFFECTS ON TERPOLYMERIZATION OF ETHYLENE PROPYLENE AND DIENE WITH ETHYLENEBIS(INDENYL)ZIRCONIUM DICHLORIDE / METHYLALUMINOXANE CATALYST

Miss Sireethorn Phoowakeereewiwat

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic year 2005

ISBN 974-17-5489-2

Thesis Title	DIENES EFFECTS ON TERPOLYMERIZATION OF ETHYLENE PROPYLENE AND DIENE WITH ETHYLENEBIS(INDENYL)ZIRCONIUM DICHLORIDE/ METHYLALUMINOXANE CATALYST
By	Miss Sireethorn Phoowakeereewiwat
Field of Study	Chemical Engineering
Thesis Advisor	Professor Piyasan Praserthdam, Dr.Ing.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………………Dean of the Faculty of Engineering

(Professor Direk Lavansiri, Ph.D.)

THESIS COMMITTEE

…………………………………………………… Chairman

(Associate Professor Suttichai Assabumrungrat ,Ph.D.)

…………………………………………………… Thesis Advisor

(Professor Piyasan Praserthdam, Dr.Ing.)

……Bunjerd Jongsomjit……………………………… Member

(Assistant Professor Bunjerd Jongsomjit, Ph.D.)

……Chariya Chao…………………………………… Member

(Dr. Chariya Chao, D.Eng.)

สิริธร ภูวคีรีวิวัฒน์ : อิทธิพลของไดอีนต่อการสังเคราะห์เทอร์พอลิเมอไรเซชันของเอทิลีน
โพรพิลีน และไดอีน ด้วยตัวเร่งปฏิกิริยาเอทิลีนบีส(อินดินิล)เซอร์โคเนียม ไดคลอไรด์ /
เมทิลอะลูมินอกเซน (DIENES EFFECTS ON TERPOLYMERIZATION OF
ETHYLENE PROPYLENE AND DIENE WITH ETHYLENEBIS(INDENYL)
ZIRCONIUM DICHLORIDE / METHYLALUMINOXANE CATALYST)
อ.ที่ปรึกษา : ศ.ดร. ปิยะสาร ประเสริฐธรรม, 141 หน้า ISBN 974-17-5489-2

งานวิจัยนี้ศึกษาการโคพอลิเมอไรเซชันของเอทิลีน-โพรพิลีน โดยมีการเติม และไม่เติมไดอีน ด้วยระบบตัวเร่งปฏิกิริยาเอทิลีนบีส(อินดินิล)เซอร์โคเนียม ไดคลอไรด์ และใช้เมทิลอะลูมินอกเซนเป็นตัวเร่งปฏิกิริยาร่วม ในเครื่องปฏิกรณ์ระบบ batch และsemibatch ชนิดของไดอีนที่ศึกษา ได้แก่ 1,4 HD, 1,5 HD, ENB, VCH และCOD ซึ่งปริมาณของไดอีนเพียงเล็กน้อยที่เติมเข้าไปในระบบ จะมีผลต่อพฤติกรรมของการโคพอลิเมอไรเซชันของเอทิลีน-โพรพิลีน สำหรับในระบบ batch พบว่าเมื่อเติมไดอีนเข้าไปในระบบจะให้ค่าความว่องไวลดลง และชนิดของไดอีนที่ศึกษานั้นไม่พบความแตกต่างของความว่องไว นอกจากนี้การเติมไดอีนยังสามารถเปลี่ยนปริมาณการเข้าร่วมของเอทิลีน และโพรพิลีนในพอลิเมอร์ โดยจะเป็นไปตามชนิดของไดอีนที่แตกต่างกัน ซึ่งพบว่า ENB เป็นไดอีนเพียงชนิดเดียวเท่านั้นที่สามารถเข้าไปในพอลิเมอร์ได้ และอุณหภูมิของการหลอมเหลวของพอลิเมอร์ที่ได้มีค่าเพิ่มขึ้นเมื่อเติมไดอีน ส่วนในระบบ semibatch พบว่าในทุกอัตราส่วนของเอทิลีนต่อโพรพิลีน ค่าความว่องไวจะลดลงเมื่อมีการเติมไดอีน และค่าความว่องไวจะเพิ่มขึ้นเมื่อลดอัตราส่วนของเอทิลีนต่อโพรพิลีน โดยไดอีนที่สามารถเข้าไปในพอลิเมอร์ได้นั้น ได้แก่ ENB, 1,4 HD และ1,5 HD สำหรับอุณหภูมิของการหลอมเหลวของพอลิเมอร์ที่ได้จะมีแนวโน้มเพิ่มขึ้นเมื่อเติมไดอีน ซึ่งสมบัตินี้จะขึ้นอยู่กับสัดส่วนของเอทิลีน และโพรพิลีนในพอลิเมอร์ กล่าวโดยสรุปคือ การเติมไดอีนในปริมาณเพียงเล็กน้อยนั้นจะสามารถไปเปลี่ยนพฤติกรรมของการโคพอลิเมอไรเซชันของเอทิลีน-โพรพิลีนได้ โดยเฉพาะอย่างยิ่งการเปลี่ยนพฤติกรรมในการพอลิเมอร์ไรเซชันที่ขึ้นอยู่กับอัตราส่วนของเอทิลีนต่อโพรพิลีน และชนิดของไดอีน

ภาควิชา........วิศวกรรมเคมี...... ลายมือชื่อนิสิต...................................
สาขาวิชา......วิศวกรรมเคมี...... ลายมือชื่ออาจารย์ที่ปรึกษา.............................
ปีการศึกษา.........2548..........

4670557421 : MAJOR CHEMICAL ENGINEERING
KEY WORD : POLYMERIZATION / EP COPOLYMER / ELASTOMERS / METALLOCENE CATALYST / METHYLALUMINOXANE

SIREETHORN PHOOWAKEEREEWIWAT : DIENES EFFECTS OF TERPOLYMERIZATION OF ETHYLENE PROPYLENE AND DIENE WITH ETHYLENEBIS(INDENYL)ZIRCONIUM DICHLORIDE / METHYLALUMINOXANE CATALYST. THESIS ADVISOR : PROF. PIYASAN PRASERTHDAM, Dr.Ing., 141 pp. ISBN 974-17-5489-2.

Copolymerization of ethylene (E) and propylene (P) with and without diene addition were performed using *rac*-ethylenebis(indenyl)zirconium dichloride ($Et[Ind]_2ZrCl_2$) catalyst system in the presence of methylaluminoxane (MAO) as a cocatalyst. Batch and semibatch reactor system were used. The different types of diene i.e. 1,4 HD, 1,5 HD, ENB, VCH and COD were chosen. A small amount of dienes added could have impact on behaviors of ethylene–propylene (EP) copolymerization. In the batch reactor system, the addition of dienes resulted in a slight decrease in polymerization activities. Furthermore, the types of diene did not exhibit any differences in activity. The addition of dienes can alter the incorporation of ethylene and propylene in the polymer backbone according to different types of diene used. The dienes (except for ENB) did not incorporate in the polymer backbone pronouncedly. In addition the melting temperature of EP elastomers increased with the addition of dienes. For the semibatch reactor system, the activities decreased with diene addition in all E/P ratio. However, the activities increased with decreasing the E/P ratio. It was found that only ENB, 1,4 HD and 1,5 HD can incorporate in the polymer backbone. The melting temperature of EP elastomers tended to increase with the addition of dienes. In addition, the thermal properties are also dependent on the fraction of ethylene and propylene in the polymer backbone. It was concluded that the addition of only a small amount of dienes could alter the behaviors of EP copolymerization. In particular, changes in polymerization behaviors were dependent on E/P ratios and types of diene.

Department.....Chemical Engineering .... Student's signature..............................
Field of Study..Chemical Engineering..... Advisor's signature..............................
Academic year............2005..............

ACKNOWLEDGEMENTS

The author would like to express her greatest gratitude and appreciation to her advisor, Professor Piyasan Praserthdam for his invaluable guidance, providing value suggestion and kind supervision throught this study. In addition, she is also grateful to Associate Professor Sutthichai Assabumrunrat, as the chairman of the committee, Assistant Professor Bunjerd Jongsomjit, Ph.D. and Dr. Chariya Chao who were members of the examining committee are acknowledged for their spending time in review my thesis and for their recommendation and advise on my work.

Thanks for the financial support are conveyed to The Thailand Research Fund (TRF) and Graduate School of Chulalongkorn University.

This thesis would not be possible without the kind assistance from Professor Takeshi Shiono, Scientific and Technological Research Equipment Center (STREC), Mectec Manufacturing Corporation for using Differential Scanning Calorimetry (DSC). Chulalongkorn University, for SEM characterization by Ms. Bungon Wattanaaumpi, Department of Science Service for NMR analysis by Ms. Nongnaphat Duangdee, Tosho Akzo (Japan), BASF and Capolactam Thai Co., Ltd., Bangkok Polyethylene Co., Ltd. (BPE) and National Petrochemical (NPC) for chemicals and gases supply.

Sincere thanks to all friends and colleagues in Center of Excellence on Catalysis and Catalytic Reaction Engineering (Petrochemical Engineering Research Laboratory), Department of Chemical Engineering, Chulalongkorn University for their assistance and friendly encouragement.

Finally, I would like to manifest my greatest gratitude to my parents and my families for their tremendous support and overwhelming encouragement, which embodied the completion of this work.

CONTENTS

Page

CHAPTERS

Page

Page

APPENDICES

LIST OF TABLES

Table **Page**

Table **Page**

LIST OF FIGURES

Figure **Page**

Figure **Page**

Figure **Page**

Figure **Page**

Figure **Page**

CHAPTER I

INTRODUCTION

Polyolefins comprise perhaps the most important, and by far the most prevalent, polymer group in the world.; worldwide 53.6×10^6 ton of polyolefins were produced in 1995. This amount makes up 47% of the entire production of plastics. Furthermore, in the past, the extent of production of individual types such as LLDPE or PP doubled in a period of about 5–7 years; this is an outstanding growth rate when compared to that of other materials. Estimates show that this development will continue. In the year 2005, the proportion of polyolefins will climb to 55%, taking into account a simultaneous increase in the entire production of plastics. In turn, this means that polyolefins will displace some of the commercial plastics of today that are less easy to manufacture or pose more problems for recycling or waste disposal (Brintzinger *et al.*,1995).

It is known that the copolymerization of ethylene (E) and propylene (P) can result in a production of rubbery materials called EP elastomers (Allen, 1983 and Kaminsky, 1985). It was found that addition of the third monomer such as dienes could be applied in order to escalate the properties of EP elastomers. the so-called EPDM elastomers continue to be one of the most widely used and fastest growing synthetic rubbers having both specialty and general-purpose applications (Malmberg, 1997 and Deffieux, 1996). Polymerization and catalyst technologies in use today provide the ability to design polymers to meet specific and demanding application and processing needs. Propylene polymers containing small amount 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, Copolymers of ethylene and propylene are of great industrial interest especially in the automotive industry and housing industry (e.g. hoses, gaskets, wipers, bumpers, belts and roofing).

Because there is no double bond in the backbone of the polymer chain, EPDM is not very sensitive to oxygen and ozone. As non-polar elastomers, they have good electrical resistivity, as well as resistance to polar solvents, such as water, acids, alkalies. Some very recent applications comprehend its use in composites and in blends with polyolefins. Amorphous ethylene-propylene copolymers are widely used as impact-strength modifiers in blends with isotactic polypropylene. Every year the production and use of EPDM-elastomer is growing rapidly. The EPDM worldwide production based on vanadium catalyst systems is presently higher than 6.5×10^5 tons/year. Projections for metallocenes catalyzed EPDM demand is about 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).

In most technical processes for the production of EPDM rubbers, with vanadium-based catalyst 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 (M.C.Hagg 1998). As mentioned, EP and EPDM are currently produced with vanadium catalysts, which are low in activities and have toxicity concerns, thus restricting application of the products in certain applications, e.g. medicine. The reduction of vanadium in the presence of linear and cyclic dienes was reported to be the cause of low terpolymerization activity (Kaminsky and Miri, 1985). Moreover, some vanadium catalysts have the disadvantage to form more than one active center, thus leading to a broad molecular weight distribution. Thus, in order to overcome those problems, an alternative way of using the homogeneous metallocene catalysts has been substantially investigated.

Recently homogeneous metallocene catalyst systems have been developed for olefin polymerization with exceedingly high activities and their abilities to effect random distributions of monomers and to provide good control over molecular weight distribution. Therefore, these metallocene catalysts were referred to as single site catalysts and offered potential advantages over traditional multi-site Zigler-Natta catalyst. 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 diene). Nevertheless, the production of EPDM is considered an important matter, the approach of this study was apparently different from the others. Hereby, only a small amount of various dienes was introduced into the system during EP copolymerization, not for the purpose of synthesizing the EPDM as in general, but specifically for altering the behaviors of EP copolymerization.

In this research, the attention was focused on the effect of dienes types and ethylene/propylene ratios on the insertion in polymer chain including catalytic activities of polymerization and properties of polymers produced. This thesis was divided into five chapters. Chapter I involved an overview of the use of metallocene catalyst for the polyolefin industry. In Chapter II, knowledge and open literature dealing with metallocene catalysis for olefin polymerization were present. The literature review was emphasized on the metallocene catalyst system used for copolymerization of ethylene/propylene and terpolymerization of ethylene/ propylene/diene. The experimental procedure as well as the instrument and techniques used for characterizing the resulting polymers were described in Chapter III. In Chapter IV, the types of reactor system i.e. a batch system and a semibatch system for use in polymerization were present. The effects of diene types and the variation in ethylene/propylene feed ratio on the insertion in polymer chain including catalytic activities of polymerization and characteristics of polymers produced are illustrated. Finally, conclusions of this work and some recommendations for future research work are provided in Chapter V.

CHAPTER II

LITERATURE REVIEW

2.1 Metallocene Catalysts

Metallocene catalysts are operative in all existing industrial plants that are presently used for polyolefin manufacture revolutionize the technology for the production of these polymers (Imanishi and Naga, 2001).

Metallocene compounds are becoming an important class of catalyst for the synthesis of organic molecules and polymers.(Poli, 1991; Halterman, 1992; Cardin *et al*.,1986; Thewalt, 1984; Wailes ,1974; Jordan, 1991). These complexes also have good potential to act as catalysts or catalyst precursors for a number of organic reactions. The discovery of group 4 metallocene-aluminoxane systems as catalysts for polymerization reactions has opened up a new frontier in the are of organometallic chemistry and polymer synthesis (Gupta *et al*.,1994).

2.1.1 General structure of Metallocene catalysts

Metallocene are a class of organometallic coordination compounds in which one or two π-carbocylic ligands such as cyclopentadienyl ring, substituted cyclopentadienyl ring, or derivative of cyclopentadienyl ring (such as fluorenyl, indenyl etc.) are chained to a metal central transition atom (Titanium, Zirconium and Hafnium). The typical chemical structure of a metallocene catalyst is represented by Figure 2.1.

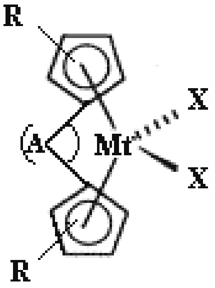
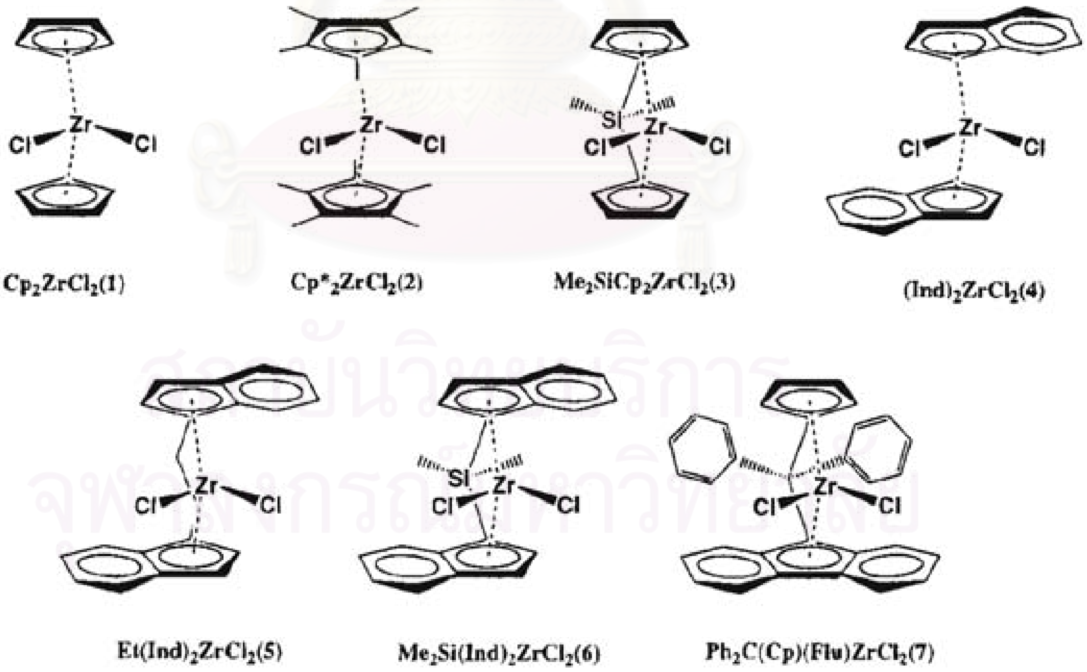


Figure 2.1. Typical chemical structure of a metallocene catalyst [where Mt is the transition metal, normally from Group 4, 5, or 6 e.g. Zr, Ti or Hf, A is an optional bridging unit consisting of 1-3 atoms in the backbone, R is hydrocarbyl substituents or fused ring systems (indenyl, fluorenyl and substituted derivatives) and X is chlorine or other halogens from group 7 or an alkyl group] (Alt, 1999).

Representative examples of zirconocene catalysts are shown in Figure2.2.



Cp_2ZrCl_2(1) $Cp^*_2ZrCl_2$(2) $Me_2SiCp_2ZrCl_2$(3) $(Ind)_2ZrCl_2$(4)

$Et(Ind)_2ZrCl_2$(5) $Me_2Si(Ind)_2ZrCl_2$(6) $Ph_2C(Cp)(Flu)ZrCl_2$(7)

Figure 2.2. Some of zirconocene catalysts structure (Naga *et al*., 2002)

Single site catalysts can be separated into five main symmetry group, which influence on the polymer architectures as shown in Figure 2.3. It is assumed that the polymer rapidly equilibrates with the available coordination site for the purposes of assigning symmetry. Catalysts exhibiting C_{2v} symmetry typically produce atactic polymers or moderately stereoregular polymers by chain-end control mechanisms. C_s-symmetric catalysts that have mirror planes containing the two-diastereotopic coordination sites behave similarly. However, C_s-symmetric catalysts that have a mirror plane reflecting two enantiotopic coordination sites frequently produce syndiotactic polymers. C_2-symmetric complexes, both racemic mixtures and enantiomerically pure ones, typically produce isotactic polymers via a site-control mechanism. Stereoselectivities of asymmetric (C_1) complexes are unpredictable and have been reported to produce polymer architectures ranging from highly isotactic, to atactic, including isotactic-atactic stereoblock and hemiisotactic. Polymer architectures relevant to this modification of ligands are shown in Figure 2.4.

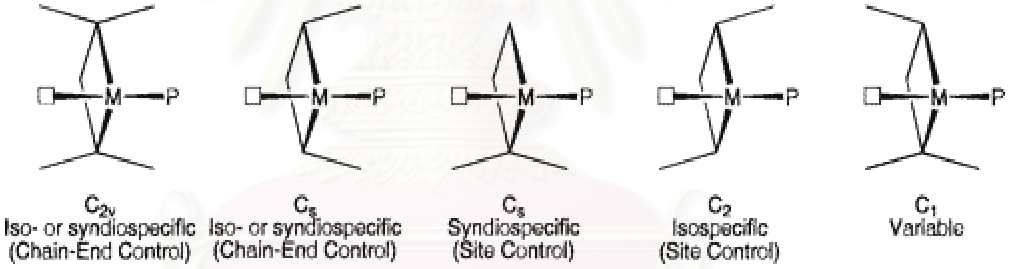


Figure 2.3. General symmetry classifications, based on ligand geometries, of catalysts and their stereoselectivities for polyolefin synthesis (Coates,2000)

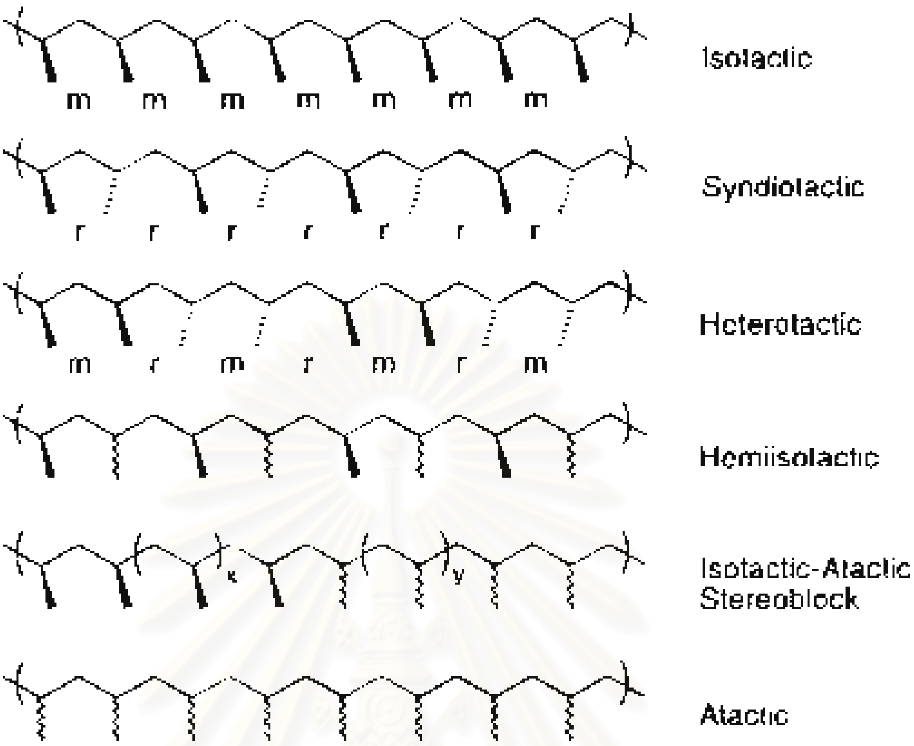


Figure 2.4. Common polymer tacticities (Coates, 2000)

2.1.2 ‘Tailoring’ of Metallocene Catalysts (Long, 1998)

Extensive research has been devoted towards ‘catalytic tailoring’ with modification of the catalyst system leading to specific changes in catalytic activity and product characteristics. This requires an understanding of the physical properties involved in ligand modification and there are several important factors affecting catalytic performance:

(a) Transition metal-olefin interaction. The olefin has a 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. Olefin co-ordination also destabilizes the M-R (R=alkyl) bond. The stability of olefin co-ordination to M decreases with increasing olefin size due to steric factors and the energies of the olefin orbitals involved in bonding to the metal.

(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 unstable 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 unstable 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. Steric effects influence the coordination of bulky monomers and selectivity towards different monomeric species in a polymerization reaction can be maintained. 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.

2.2 Methylaluminoxane Cocatalyst

The importance of cocatalysts in metal-catalyzed polymerization processes can be appreciated as follows. First, to form active catalysts, catalyst precursors must be transformed into active catalysts by an effective and appropriate activating species. Second, a successful activation process requires cocatalysts which retain the nature of the catalytic site and do not have adverse effects on the polymerization kinetics and polymer properties. Finally, the cocatalyst, which becomes an anion after the activation process, is the vital part of catalytically active cation-anion pair and may significantly influence polymerization characteristics and polymer properties (Chen and Marks, 2000).

A metallocene catalyst precursor can be activated with organoalumoxanes, especially methylaluminoxane (MAO), which provides maximum activity. Methylaluminoxane is a compound in which aluminum and oxygen atoms are arranged alternately and free valances are saturated by methyl substitutions. It is prepared by carefully controlled partial hydrolysis of trimethylaluminum (TMA) and according to investigations by Sinn, 1995; Barron *et al.*,1996 and Ystenes *et al.*, 2000. The hydrolysis of AlR_3 (R = Me, Et, iBu) has been shown to proceed via the formation of an alkylaluminum water complex shown in Equation 2.1 (Barron, 1993), which subsequently eliminates an alkane to form a dialkylaluminum hydroxide complex. This rapidly associates to give dimers or larger oligomers in solution as shown in Equation 2.2.

$$AlR_3 + H_2O \longrightarrow AlR_3(H_2O) \qquad (2.1)$$

$$AlR_3(H_2O) \longrightarrow 1/n\,[R_2Al(OH)]_n + RH \qquad (2.2)$$

The structure of MAO consists mainly of units of the basic structure $[Al_4O_3Me_6]$, which contains four aluminum, three oxygen atoms and six methyl groups. Although very extensive research has been carried out in both academia and industry, the exact composition and structure of MAO are still not entirely clear or well understood.

The proposed structures for MAO in the open literature shown in Figure 2.5 include: (1) one-dimensional linear chains; (2) cyclic rings, which contain three-coordinate Al centers; (3) two-dimensional structures and (4) three-dimensional clusters. The three-dimensional structure (4) proposed by Sinn, 1995 is based on structural similarities with tert- butylaluminoxanes,which form isolable and X-ray crystallographically characterizable cage structures (5).

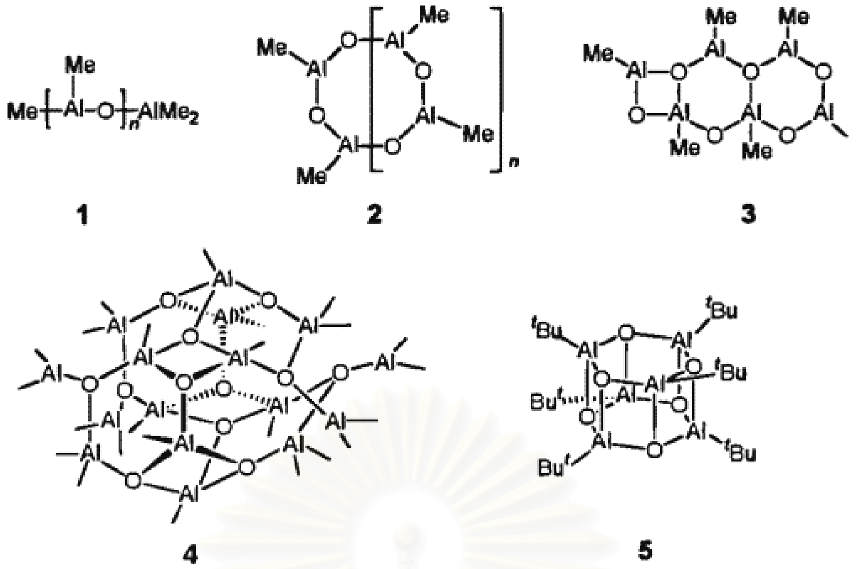


Figure 2.5. The general proposed structure of MAO (Chen and Marks, 2000).

Depending on the nature of the hydrated salt (the H_2O source) used for the MAO synthesis and the exact MAO synthetic reaction conditions, MAO-activated metallocenes may exhibit widely differing activities in olefin polymerization. The MAO structure can hardly be elucidated directly because of the multiple equilibria present in MAO solutions, and residual trimethylaluminum in MAO solutions appears to participate in equilibria that interconvert various MAO oligomers (Giannetti *et al.*, 1985; Resconi *et al.*, 1990). There are two types of TMA present in typical MAO solutions: “free” TMA and “associated” TMA shown in Equation 2.3

$$\left[\!-\mathrm{Al(Me)O}-\!\right]_n \cdot x\,\mathrm{AlMe_3} \rightleftharpoons \left[\!-\mathrm{Al(Me)O}-\!\right]_n \cdot \underset{\text{"Associated"}}{(x\text{-}y)\,\mathrm{AlMe_3}} + \underset{\text{"Free"}}{y\,\mathrm{AlMe_3}} \qquad (2.3)$$

Tritto *et al.* (1997) found that cryoscopy MAO molecular weight decrease after $AlMe_3$ addition according to a linear relationship, which is caused by disproportionate reactions . However, recent in-situ FTIR spectroscopy investigations do not indicate any obvious reaction between TMA and MAO (Kaminsky, 1999). Nevertheless, in light of its complicated, unresolved structural features, MAO is usually represented for the sake of simplicity as having linear chain or cyclic ring structures $[-Al(Me)-O-]_n$, containing three-coordinate aluminum centers.

2.2.1 Interaction of Metallocene with Aluminoxanes and Nature of Active Species

The interaction of metallocene with aluminoxanes has been studied in detail. Metallocene dichloride reacts with methylaluminoxane to yield a methylated compound (Figure 2.6.) It undergoes either methyl or chloride abstraction to generate metallocene methyl cation (Giannetti *et al.*,1985; Chien *et al.*,1988). The research work reported by Marks, Bochmann, Jordan and others gave synthetic and spectroscopic evidence that cationic metallocene $[(Cp_2MR)]^+$ are the active species (Yang *et al.*, 1991; Hlatky *et al.*,1989). The interaction of dichlorozirconocene, methylchlorozirconocene and dimethylzirconocene with MAO has been studied by x-ray photoelectron spectroscopy (Gassman and Callstrom, 1987). The results indicated the formation of cationic metallocene with MAO as the counteranion. Spectroscopic evidence for the formation of cationic species is also reported by Marks *et al.*,1992. The solid-state ^{13}CPMAS-NMR study at different Al/Zr ratios indicated the formation of a cation like the $Cp_2ZrCH_3^+$ species. The data also indicate that the Al:Zr stoichiometry required to form this cation is considerably lower than that in a typical catalyst reaction. Siedle *et al.*, 1990 employed solution ^{13}C-NMR spectroscope to demonstrate that dimethyl metallocene such as $Cp_2Zr(^{13}CH_3)_2$, $(MeCp)_2Zr(^{13}CH_3)_2$, $(Indenyl)_2Zr(^{13}CH_3)_2$, $Me_2Si(C_5H_4)_2Zr(^{13}CH_3)_2$ and $Cp_2Hf(^{13}CH_3)_2$ undergo degenerate methyl exchange with methyl acceptor compounds such as Me_6Al_2 and $(MeAlO)_x$ (see equation 2.4). The kinetics of degenerate methyl exchange indicates that steric effects are important determinants of the free energy of activation as compared to electronic effects in the formation of cationic species.

$$Cp_2Zr(^{13}CH_3)_2 + Me_3Al \longrightarrow Cp_2Zr^{13}CH_3^{(+)}AlMe_4^{(-)} \qquad (2.4)$$

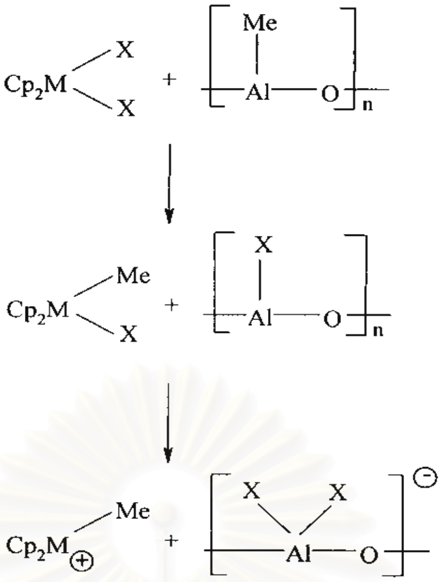


Figure 2.6. Postulated mechanism of formation of the active species in the reaction between metallocene and methylaluminoxane (Zucchini *et al*., 1993)

2.3 Polymerization Mechanism

The mechanism of the polymerization of olefins by zirconocene catalysts has been many theoretical investigations such as Cossee mechanism and the Trigger mechanism. However, alkylation and reduction of the metal site by cocatalyst (generally alkylaluminum or alkylaluminoxane) is believed to generate the active catalyst species, cationic metallocene species.

In the cationic metallocene species, the metal atom is coordinated with the π-ligands and alkyl group (growing polymer chain). During polymerization, the monomer is coordinated with a highly electrophillic and coordinatively unsaturated cationic complex. It is followed by insertion of a monomer in the metal-carbon bond to produce a polymer chain. The migration of the polymer chain and the formation of the metal-carbon bond occur in concert through a four-center transition state. These results in the reaction of a vacant coordination site at the site originally occupied by the polymer chain. This process involving shifting of the growing chain to the position previously occupied by a coordinated monomer continues until termination of the polymer chain. The proposed mechanism of metallocene-catalyzed polymerization is illustrated in Figure 2.7.

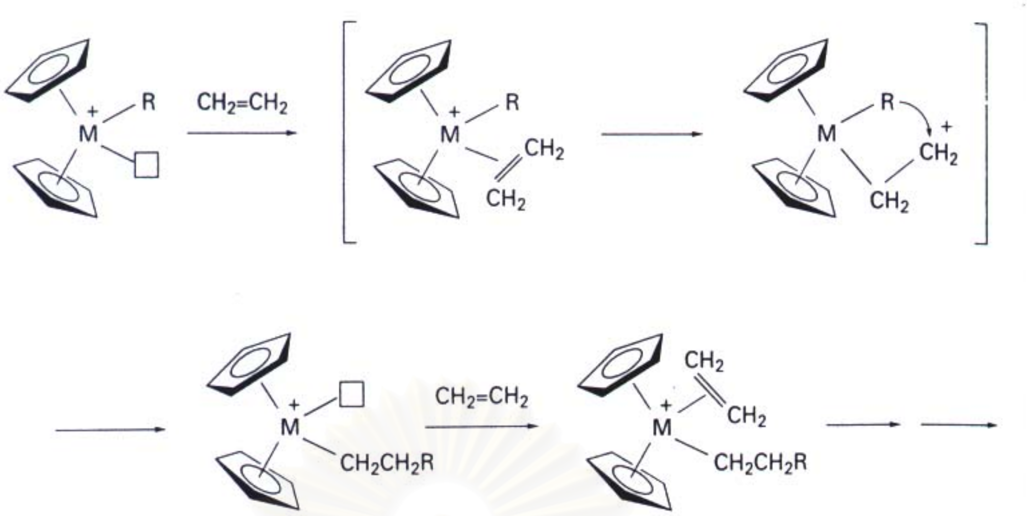


Figure 2.7. The mechanism of olefin polymerization using metallocene catalysts. (Long, 1998)

2.4 Chain Termination and Transfer

Chain termination and transfer mechanisms can have tremendous influences on the nature of the polymer. In metallocene-catalyzed olefin polymerization (Gupta *et al*., 1994), the termination of polymer chain occurs through a chain transfer involving β-H elimination, β-Me elimination, chain transfer to aluminum or chain transfer to monomer or chain transfer to hydrogen were demonstrated in Figure 2.8-2.12 respectively. All of the mechanisms proposed above are dependent on the nature of the metallocene, aluminoxane, and the polymerization conditions. Resconi *et al*. (1992) studied the contribution of various chain transfer processes in the propylene polymerization reaction due to the different metallocenes and reaction conditions. $Cp_2^*MCl_2$/MAO (Cp^* = pentamethylcyclopentadienyl; M = Zr, Hf) gives atactic propylene oligomers and low molecular weight polymer. The GC-MS and ^{1}H-and ^{13}C-NMR analyses of the products show the presence of unsaturated and saturated end groups. The unsaturated end groups contain vinylidine and alkyl groups. Product analysis shows that both M-CH_3 and M-H bonded active species are involved in the chain termination step involving β-CH_3 and β-H elimination.

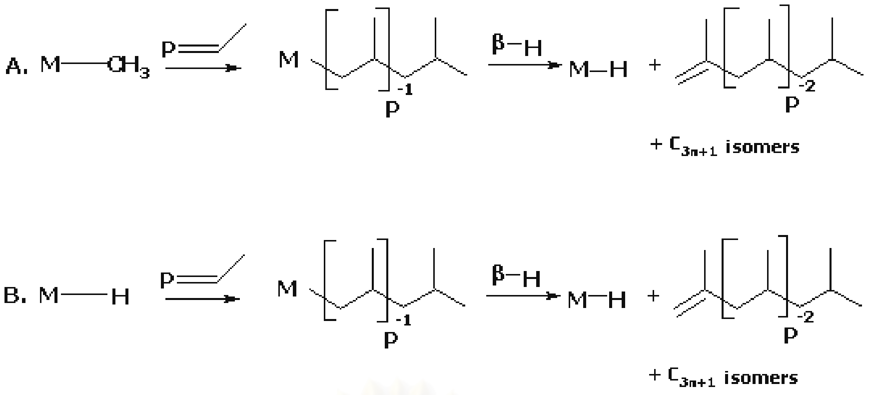


Figure 2.8. Chain transfer via β-H elimination (Resconi *et al.*, 1992)

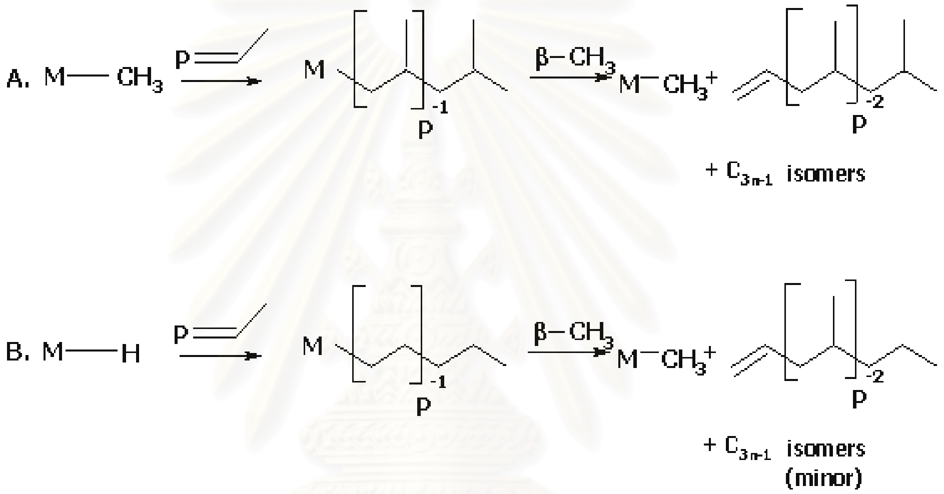


Figure 2.9. Chain transfer via β-Me elimination (Resconi *et al.*, 1992)

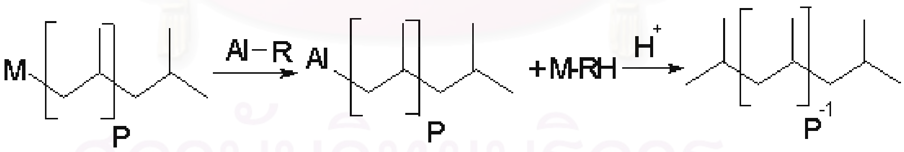


Figure 2.10. Chain transfer to aluminum (Resconi *et al.*, 1992)

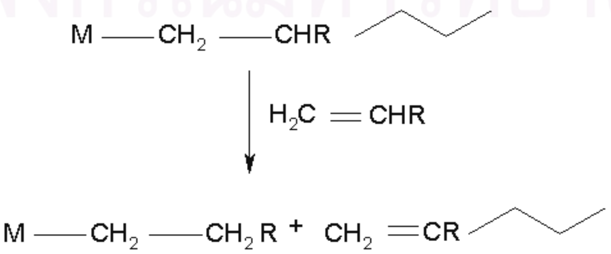


Figure 2.11. Chain transfer to monomer (Gupta *et al.*, 1994)

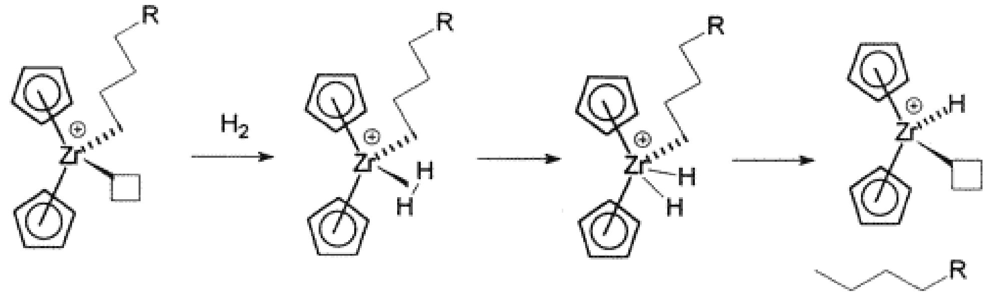
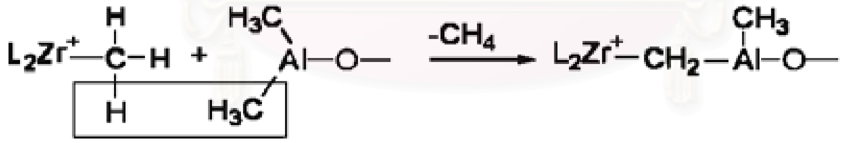


Figure 2.12. Chain transfer to hydrogen (Alt and Gupta , 2000)

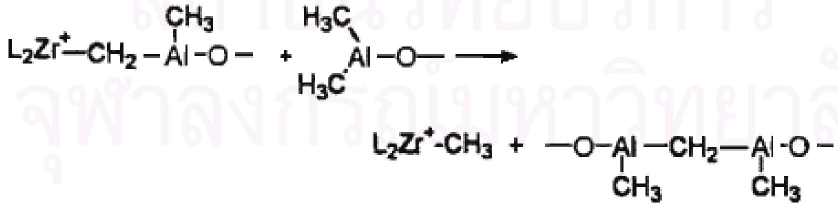
2.5 Deactivation Processes

An important deactivation process for MAO-activated catalytic systems is α-hydrogen transfer, which leads to the production of methane (Kaminsky, 1996). The methane production is much more rapid with MAO than with less Lewis acidic TMA.The deactivation of the metallocenium alkyl + MAO might be attributed to the formation of inactive species with Zr-CH_2-Al or Zr-CH_2-Zr structures in Equation 2.5. Although these inactive species can be reactivated by a transmetallation reaction with MAO and lost Al-CH_2-Al structure at excess MAO, forming $L_2Zr(CH_3)^+$ and Al-CH_2-Al structures in Equation 2.6.



$$L_2Zr^{+}-\overset{H}{\underset{H}{C}}-H \;+\; \overset{H_3C}{\underset{H_3C}{Al}}-O- \xrightarrow{-CH_4} L_2Zr^{+}-CH_2-\overset{CH_3}{Al}-O-$$

(2.5)

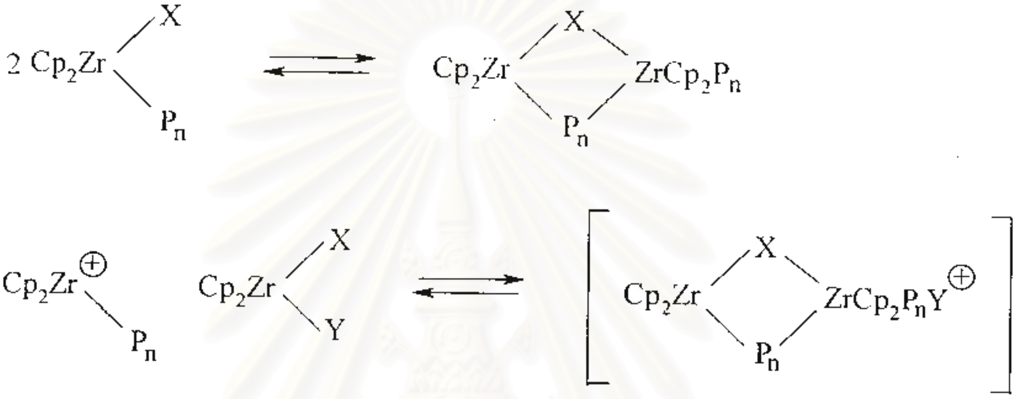


$$L_2Zr^{+}-CH_2-\overset{CH_3}{Al}-O- \;+\; \overset{H_3C}{\underset{H_3C}{Al}}-O- \longrightarrow L_2Zr^{+}-CH_3 \;+\; -O-\underset{CH_3}{Al}-CH_2-\underset{CH_3}{Al}-O-$$

(2.6)

Fischer et al. (1993) found that there is another type of deactivation, which is fast and second-order relative to the active site concentration, in the Cp_2ZrCl_2/MAO catalyst system and subsequently proposed a reversible + irreversible deactivation process kinetic scheme to fit the decay of the polymerization rate as a function of time (Equation 2.7). The mechanism involves reversible second-order deactivation combined with a slower irreversible deactivation of the active and/or dormant zirconium sites, which may involve interactions between active as well as inactive Zr sites (binuclear processes). The reversible conversion of active cationic zirconium sites into dormant neutral zirconium sites is shown in Figure 2.13.

$$\underset{\text{Active}}{2\,C^*} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{Dormant}}{C_1} \xrightarrow{k_2} \underset{\text{Inactive}}{C_2} \qquad (2.7)$$



X, Y : Me, Cl, O-AlMe-MAO; P : polymer

Figure 2.13. Mechanism of reversible second-order deactivation

2.6 Copolymerization of Ethylene and Propylene (EP)

Ethylene- propylene elastomers are synthetic polymers with outstanding resistance to oxygen, ozone and heat. They are used in a large variety of non-tire automotive applications, including radiator and heater hoses, body and chassis parts, car bumpers, weathers trips, seals and mats.

Ethylene-propylene copolymers are saturated, and they require vulcanization with free radical generators. The EP copolymers are produced by solution polymerization using Ziegler-Natta type catalysts. Copolymers containing 1 to 1.5 ethylene units for every propylene unit are most desirable, because long blocks produce undesirable crystallinity (Henri, 1982).

Koivumaki and Seppala (1994) studied copolymerization of ethylene and 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. They studied 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. Zirconocene were unable to obtain high Mw copolymers, while $TiCl_4$ and $VOCl_3$ gave a much broader MWD. From DSC, polyethylene based crystallinity can be seen with $TiCl_4$ system. Glass transition temperature (Tg) was at lower temperature for samples made with vanadium therefore carry more impact strength at sub-zero temperature.

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. The variations of polymerization activities in ethylene and in propylene for Tp from –55°C to +70°C. This catalyst copolymerizes ethylene and propylene with reactivity ratios of comparable magnitude $r_E \sim 4r_P$; $r_E r_P \sim 0.5$ indicating random copolymer formation.

Naga *et al.* (1997) investigated Cp_2MCl_2, rac-Et(Ind)$_2$MCl$_2$, rac-Me$_2$Si(Ind)$_2$MCl$_2$ 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. Tetramethyldisiloxanediylbis (cyclopentadienyl) zirconium dichloride was proved 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.

Djupfors *et al.* (1997) investigated copolymerization of ethylene and propylene with Et(Ind)$_2$HfCl$_2$/MAO in toluene at 40 °C and 60 °C by using a semi-flow method. ^{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 decreased the crystallinity and the melting temperature of the polymer. 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.

Arndt and Kaminsky *et al.* (1998) used [Me$_2$C(3-RCp)(Flu)]ZrCl$_2$ (R = H, Me, ^{iso}Pr, ^{tert}Bu) (see Figure 2.14.) 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.

The data presented imply that the polymerization by [Me$_2$C(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.

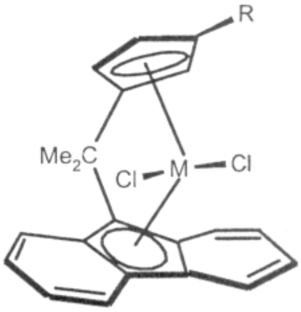


Figure 2.14. Structure of the metallocenes used for ethylene/propylene copolymerization (M = Zr, R = H (I), Me (II), ^{iso}Pr (III), ^{tert}Bu (IV)) (Arndt and Kaminsky *et al.*, 1998)

Jin *et al.* (1998) copolymerized ethylene and propylene at –40°C with ethylene (1-indenyl)(9-fluorenyl) zirconium dichloride/MAO. Copolymer produced is stereoregular and isotactic. This catalyst having two non-equivalent coordination sites i.e. the sterically less hindered site A and the more hindered site B (Figure 2.15). 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.

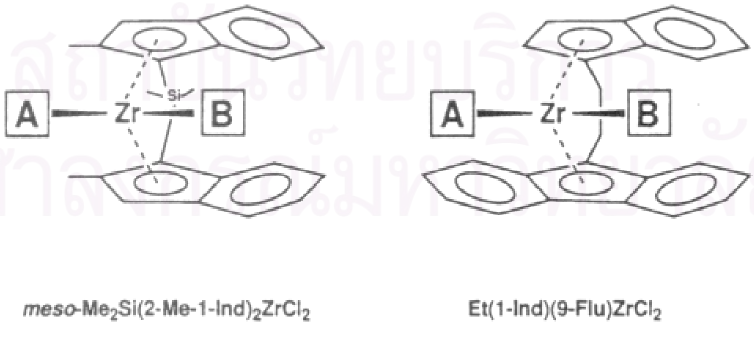


Figure 2.15. The two non-equivalent coordination sites of ethylene (1-indenyl)(9-fluorenyl) zirconium dichloride: the sterically less hindered site, A and the more hindered site, B.

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).

Galimberti *et al.*, (1998) studied rac-isopropylidenebis(3-tert-butylcyclopentadienyl)zirconium dichloride/ MAO, the EP copolymer with 17%-92% ethylene molar content could be obtained. 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 produced with long sequences of both comonomers.

Busico *et al.* (1999) studied 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 ~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.

Galimberti *et al.*, (1999) investigated copolymerization of 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. On the other hand, the ethylene/propylene copolymerization carried out in CSTR at 130-150°C with constrained geometry catalyst, 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.

Wang *et al.*, (2003) polymerized ethylene and propylene by $(n\text{-BuCp})_2\text{ZrCl}_2$ and $rac\text{-Et(Ind)}_2\text{ZrCl}_2$ and ethyl-iso-butylaluminoxanes (EBAO) which displayed as good polymerization activity as MAO. They found the loose ionic pair derived from EBAO prefers the monomer propagation and hinders the interaction between active species, which results in high catalytic activity and molecular weight.

Wang *et al.*, (2004) investigated copolymerization of ethylene/propylene synthesized by constrained geometry catalyst (CGC); $[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{NtBu})]\text{TiMe}_2$ and ansa-zirconocene catalyst; $\text{Et(Ind)}_2\text{ZrCl}_2$/MAO (EBI). It was found that the EBI copolymers had higher polydispersities than the CGC copolymers. From DSC, with the increase of propylene fraction, the copolymer exhibited lower melting point and crystallinity. Dynamic mechanical analysis (DMA) showed storage modulus (E’) for copolymer decreased with an increase of propylene content indicating that the copolymers became less stiff and had lower crystallinity.

2.7 Ethylene/ Propylene/ Diene Terpolymerization (EPDM)

A classic method of activating polyolefins is the introduction of unsaturation. Commercial ethylene-propylene-diene termonomers (EPDM) (Chung, 2002) is a good example that contains several mol % of diene units. The diene units in EPDM are essential for the subsequent crosslinking and functionalization reactions to form the desirable rubber products.

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 and housing industry (e.g., hoses, gaskets, wipers, bumpers, belts and roofing). Because there are no double bonds in the backbone of the polymer chain, EPDM is not very sensitive to oxygen and ozone, as well as to acids and alkalis. Other excellent properties of this rubber are its electrical properties, and 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 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. 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. Necessary for subsequent vulcanization are 2-3 mol% (0.1-5.0 wt%). EPDM 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.

2.7.1 Traditional Ziegler-Natta Technology

2.7.1.1 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).

2.7.1.2 Vanadium Catalysts

For EPDM production, Vanadium salts have been the preeminent catalyst precursors. 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. As a result, soluble vanadium precursors have been widely adopted industrially and carefully studied by researchers in the field.

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. 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).

Haag *et al.*, (1998) developed 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. 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, excepting 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 $Et(Ind)_2ZrCl_2$/ 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 Al remained in the polymer.

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 poisonous, thus restricting application of the products, e.g. in medicine (Kaminsky *et al.*, 1985).

2.7.2 Metallocene Catalyzed EPDM Polymerization

Metallocenes have several properties 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 composition and molecular weight distributions and monomer sequencing that is equal or superior to that created by industrial catalysts.

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.

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. In each of these respects, most metallocene systems have proven to meet or exceed the standards established by vanadium technology.

Theoretically and often in practice, the effect of catalyst exhibits in the copolymerization is reflected in monomer reactivity ratios. These estimates directly correlate the monomer concentrations to copolymer composition and offer a simple assessment of the sequencing of ethylene and propylene.

2.7.3 Comparing Metallocene-based with Traditional Titanium- and Vanadium-based Catalytic Systems.

In comparison with titanium chlorides, vanadium systems demonstrate undesirable activity and a rapid, second order deactivation at elevated temperatures. The use of chlorinated “activators” has minimized these deficiencies. 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. Another approach has sought a positive influence from supporting vanadium complexes on various solids.

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; $r_E r_P$ is close to unity in most cases. 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.

2.7.4 Terpolymerization of Ethylene and Propylene with a Diene (EPDM)

Yu *et al.* (1995) investigated 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, than for E/HD and E/P/HD using feed low in propylene. The polymer molecular weight is most strongly affected by the temperature of polymerization (Tp), whereas the E/P ratio in the feed has virtually no effect. The reactivity ratio 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$_2$ZrCl$_2$/ MAO exhibits long induction time while Et[Ind]$_2$ZrCl$_2$/ MAO or Et[Ind]$_2$Zr$^+$R, no induction was observed in both solution and SiO$_2$ supported. The amount of diene incorporated in 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 double the diene content in the EPDM. The products contains little (<6%) or no cyclopolymerization structures.

Marques *et al.* (1995) investigated 4-vinylcyclohexene (VCH) and cyclooctadiene (COD) as termonomers in EPDM synthesis by using rac-Et[Ind]$_2$ZrCl$_2$ as a catalyst. 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 about 2-fold. 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. The magnitude of reactivity ratio for E/P copolymerization changes with Tp. r_E and r_P have values of about 2.8 and 0.3 at 20°C; they changed to 0.5 and 1.6 at 70°C.

Yu *et al.* (1995) studied the ethylenebis(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 whereas (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. Because 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 $Et[Flu]_2ZrCl_2$/ 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 but closer to propylene. Whereas for $Me_2Si[Ind]_2ZrCl_2$/MAO, copolymerization rate is less than both homopolymerization.

Dynamic mechanical analysis (DMA) showed above glass transition temperature (T_g), the partly crystalline polymer (73 mol% ethylene) retained considerable stiffness at higher temperatures compared with the amorphous copolymer (58 %mol ethylene). Below Tg, terpolymer with diene and 58 %mol ethylene was the stiff terpolymers.

Malmberg and Lofgren (1997) used $Et[Ind]_2ZrCl_2$ / MAO and $Et[Ind]_2HfCl_2$ /MAO in E/P copolymerization and E/P/ENB terpolymerization. The polymerization activity decreased with diene feed, but this effect was significant only at very large diene feeds. Glass transition temperature of the copolymers is between -59°C and –55°C and the terpolymer glass transition temperature rose 1.5°C per wt% of ENB in the polymer. 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 metallocenes 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.

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 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.

Chien *et al.* (1998) studied terpolymerization of ethylene, propylene, and diene i.e. ethylidene norbornene (ENB), vinylcyclohexene (VCH), 1,4 hexadiene (HD) using {[2-(dimethylamino) ethyl]cyclopentadienyl} titanium trichloride (Cp^NTiCl_3) and MAO. 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, activity = $1.3 \pm 0.3 \text{ x } 10^5$ g/molTi.h and VCH incorporation increases with increasing of VCH concentration. With HD, activity was about 1/3 of VCH or ENB, low Mw copolymer was produced and less than 4% HD incorporated.

However, 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. All the nonbridged precursors have $r_E >>> r_P$ by 3-5 order of magnitude, whereas the differences between r_E and r_P of ansa-zirconocene precursors are in the order of tens. Cp_2HfCl_2 produce copolymer with $r_E.r_P = 1.52$ while Cp_2TiCl_2

and Cp_2ZrCl_2 products of reactivity ratio are less than 1.0. This shows the dependent of reactivity ratio on the metal as well as ligand.

Haag *et al.* (2000) developed mathematical model for the homogeneous terpolymerization EPDM with $Et[Ind]_2ZrCl_2$/ MAO using semibatch reactor in order to explain the catalyst and EPDM properties such as catalyst activity, weight average molecular weight, and terpolymers composition, As result 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 nonbrided systems and as a consequence produce lower Mw.

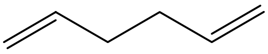
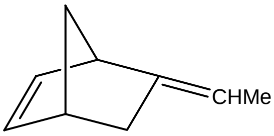
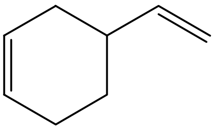
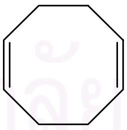
Sobhanmanesh and Hajizadeh (2004) investigated E/P/ENB terpolymerization using homogeneous $VOCl_3$-$Al_2Et_3Cl_3$ and indenyl, rac-$Et[Ind]_2ZrCl_2$/MAO catalyst system to compare their activity and their effects on the MWD and microstructure of the final products. They found that terpolymers prepared with the vanadium-based catalyst were of the higher Mw and random the structure than those obtained with the zirconium catalyst. The latter catalyst system produced comparatively narrower molecular weight distribution.

From the previous study, Chao (2002) studied the ethylene-propylene-diene-terpolymerization using metallocene/MAO catalyst system. The optimum conditions for polymerization were Al/Zr mole ratio of 2000 at zirconium concentration of 30×10^{-6} M, and polymerization temperature of 40 ^{O}C. Moreover, she's work was found to be at ethylene and propylene molar ratio 75/25 gave the unchanged trend in composition of gaseous monomer during the reaction.

2.7.5 Structure of dienes

The structure of dienes using in this investigation are shown in Table 2.1..

Table 2.1. The structure of dienes using in this investigation.

Name of dienes	Types	Structure
1,4-Hexadiene (1,4 HD)	Symmetric aliphatic	
1,5-Hexadiene (1,5 HD)	Asymmetric aliphatic	
5-Ethylidene-2-norbonene (ENB)	Cyclic	
4-Vinyl-1-cyclohexene (VCH)	Cyclic	
Cyclooctadiene (COD)	Cyclic	

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

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

1. Argon gas (Ultra high purity 99.999 %) was purchased from Thai Industrial Gas Co., Ltd. And further purified by passing through column packed with copper catalyst, NaOH, P_2O_5 and molecular sieve 4A to remove traces of oxygen and moisture.

2. Benzophenone (purum 99.0%) was obtained from Fluka Chemie A.G. Switzerland.

3. Calcium chloride (Dehydrated) was manufactured from Fluka Chemie A.G. Switzerland.

4. 1,5 Cyclooctadiene (COD) was purchased from Aldich chemical Company,Inc. and was distilled before use.

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

6. 5-Ethyidene-2-norbonene (ENB) was purchased from Aldich chemical Company, Inc. and was distilled before use,

7. 1,4 Hexadiene (1,4 HD) was purchased from Aldich chemical Company, Inc. and was distilled before use.

8. 1,5 Hexadiene (1,5 HD) was purchased from Aldich chemical Company, Inc. and was distilled before use.

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

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

11. Methylaluminoxane (MAO) 2.534 M in toluene was donated from Tosoh Akso, Japan and used without further purification.

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

13. Sodium (lump in kerosene, 99.0%) was supplied from Aldrich chemical Company, Inc.

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

15. 4-Vinyl-1-cyclohexene (VCH) was purchased from Aldich chemical Company, Inc, and was distilled before use.

3.2 Equipments

All equipments used in the preparation and polymerization of the polymer are listed as below:

3.2.1 Equipment for handling air-sensitive compounds

Since the most of reagents and catalysts were very sensitive to the oxygen and moisture therefore special techniques were taken in the handling of reagents and for loading the catalyst into the reactor. Such equipment utilized for this purpose are as follows:

(a) Glove box (Vacuum Atmospheres) with oxygen and moisture analyzer for transferring solid reagents under inert atmosphere and for storing air-sensitive reagents. The oxygen and moisture levels are normally below 2 ppm inside the glove box. The glove box is shown in Figure 3.1.

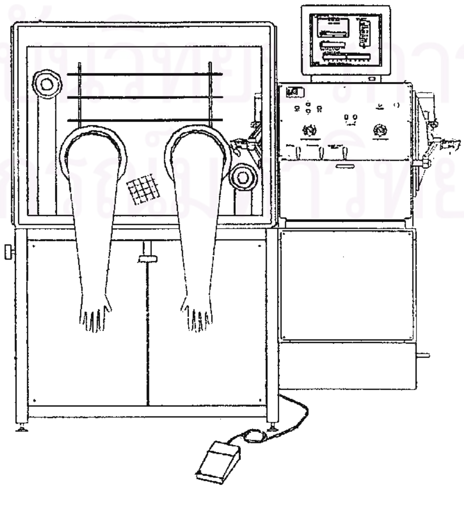


Figure 3.1. Glove box

(b) **Schlenk line** included of vacuum line connected to vacuum pump and argon line for purging when reagents are transferred. The schlenk line was shown in Figure 3.2.

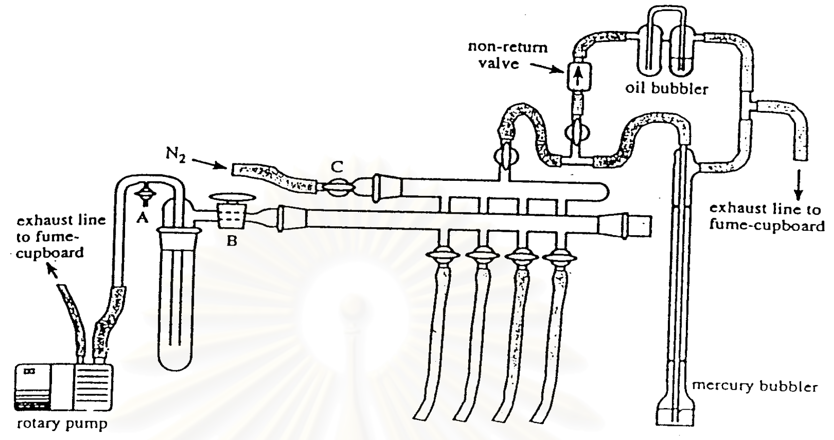


Figure 3.2. Schlenk line

(c) **Schlenk tube** for keeping reagents under argon atmosphere outside the glove box. It was used accompanied with the Schlenk line. Schlenk tube is a tube with a ground joint and side arm which was three way glass valve as shown in Figure 3.3.

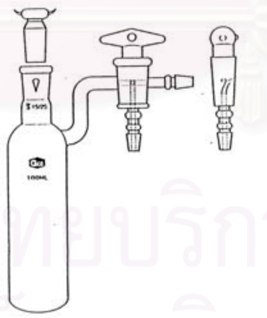


Figure 3.3. Schlenk tube

(d) **The inert gas** (argon) was pass through columns of oxygen trap (BASF catalyst, R3-11G), 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. The inert gas supply system is shown in Figure 3.4.

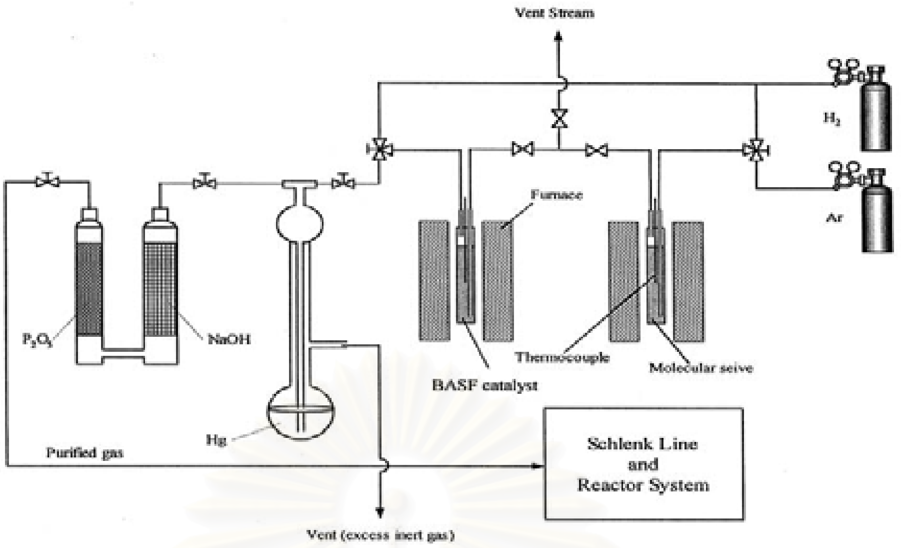


Figure 3.4. Inert gas supply system

(e) **The vacuum pump** model 195 from Labconco Coporation was used. A pressure of 10^{-1} to 10^{-3} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line. The vacuum pump is shown in Figure 3.5.

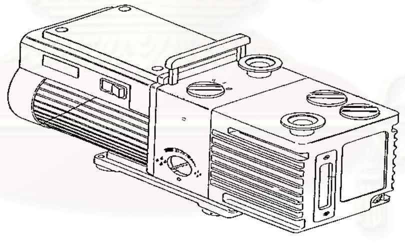


Figure 3.5. Vacuum pump

3.2.2 Cooling System

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

3.2.3 Gas Distribution System

The system consists of an ultra high purity argon feeding lines made of stainless steel pipe with diameter of ¼ inch.

3.2.4 Magnetic Stirrer and Heater

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

3.2.5 Reactor

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

3.3 Polymerization Procedure

3.3.1 Material Preparation

Since the solvents will be used are the commercial grade, there might be some undesired impurities; especially water, which have to be removed before use. Therefore solvents are refluxed in Na/benzophenone and then distilled under argon atmosphere and keep in schlenk tube.

Ethylene and propylene are the polymerization grade which purified by passing through a column of LABCLEAR^{TM} gas filter. The ultra high purity argon was further purified by pass through molecular sieves 3A, BASF catalyst, R3-11G, sodium hydroxide (NaOH) and phosphorus pentaoxide (P_2O_5) to remove traces of oxygen and moisture.

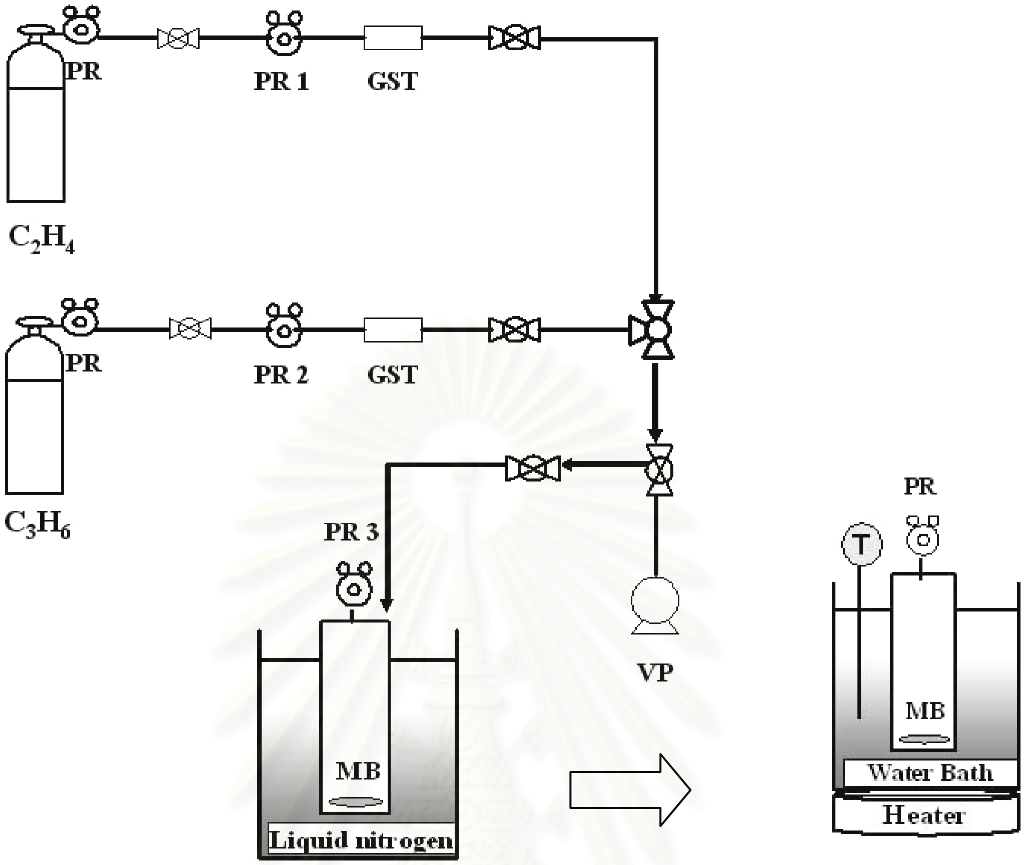
3.3.2. Polymerization

All chemicals were manipulated under purified argon using a vacuum atmosphere glove boxes and/or Schlenk techniques.

3.3.2.1 Batch system

Polymerization was carried out in a 100 mL stainless steel reactor with magnetic stirrer. Using Schlenk line, First, toluene used as a solvent was added to the reactor in the amount to make the total volume of 30 mL. Then, methylaluminoxane (MAO) solution was added according to the specified ratio to the catalyst concentration ([Al]/[Zr] = 2000) followed by diene the addition of 0.1 M of a selected diene [dienes used were 1,4-hexadiene (1,4HD), 5-ethylidene-2-norbonene (ENB) and 4-vinyl-1-cyclohexene (VCH)]. Then, the metallocene catalyst was injected into the system. The reactor was immediately put into liquid nitrogen to stop the reaction between the catalyst and cocatalyst. After the solution was frozen for 15 minutes, the reactor was evacuated for 3 minutes to remove argon then filled with gaseous monomers (ethylene/propylene with a molar ratio of 3) while the reactor was still frozen 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 heated up to polymerization temperature (40^{o}C) to start the polymerization reaction. The polymerizations was kept for 1 hr. In order to stop reaction, the gaseous monomer were released and the reaction mixture was washed with acidic methanol. The polymer obtained was filtered and dried under ambient condition. 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. Schematic diagram of system in slurry phase polymerization of batch system is displayed in Figure 3.6.



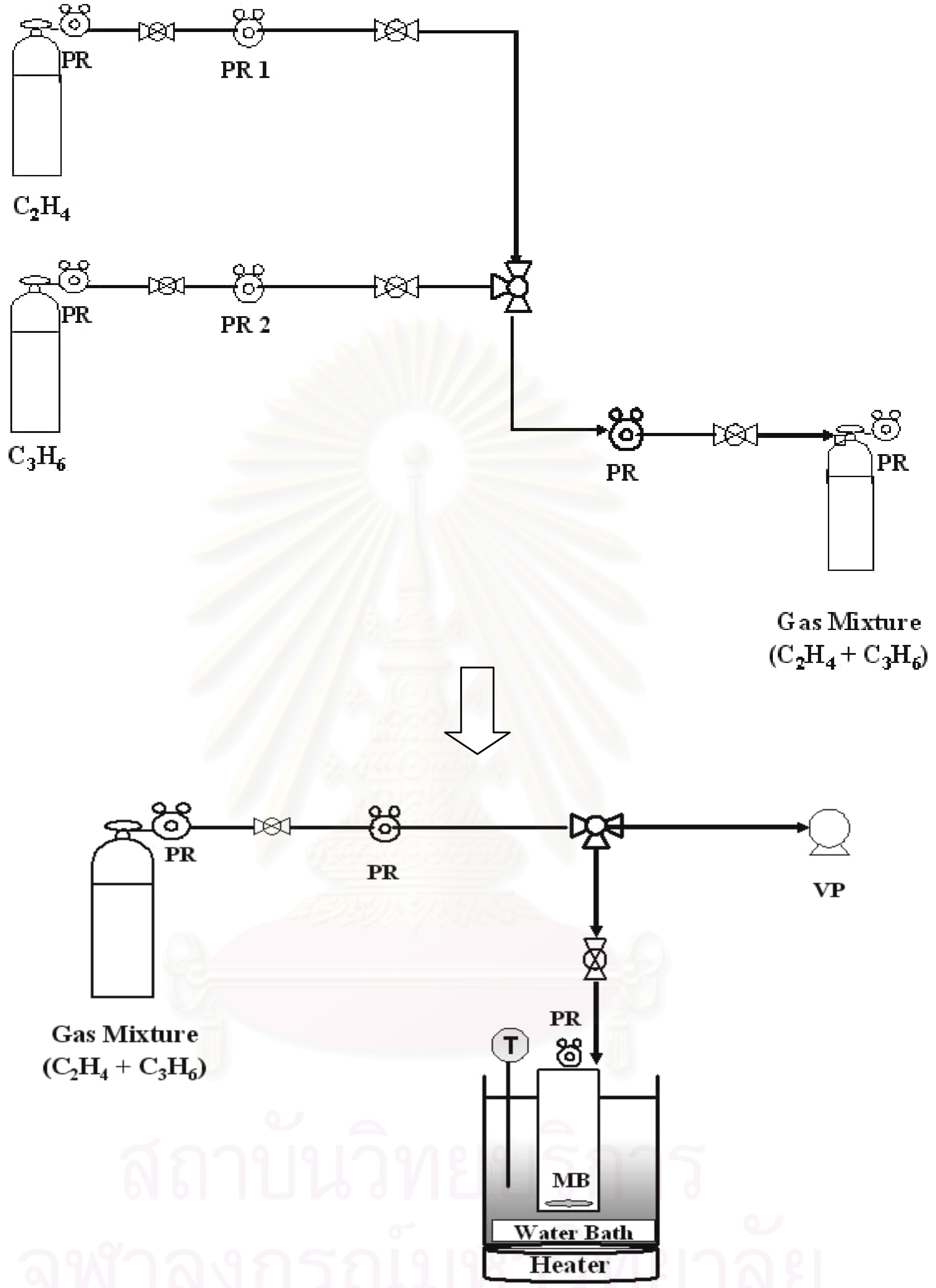
- **MB** : Magnet-Driven Stirrer
- **PR** : Pressure Regulator
- **PR 1** : Pressure Regulator for Ethylene Consumption
- **PR 2** : Pressure Regulator for Propylene Consumption
- **PR 3** : Pressure Regulator for pressure in reactor
- **GST** : Gas Storage Tube
- **VP** : Vacuum Pump
- **T** : Thermometer

Figure 3.6. Schematic diagram of system in slurry phase polymerization of batch system

3.3.2.2 Semibatch system

In this system, ethylene and propylene were premixed in a cylinder at the desired molar ratio (3, 1 and 0.667). The polymerization were carried out in a 100 ml stainless steel autoclave reactor equipped with magnetic stirrer. Toluene used as a 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 a diene the addition of 0.1 M of a selected diene [dienes used were 1,4-hexadiene (1,4HD), 1,5-hexadiene (1,5HD), 5-ethylidene-2-norbonene (ENB), 4-vinyl-1-cyclohexene (VCH) and cyclooctadiene (COD)]. After that, the metallocene catalyst was injected into the reactor immediately. The reactor was frozen in liquid nitrogen to stop reaction between the catalyst and cocatalyst. After the solution was frozen for 15 minutes, the reactor was evacuated for 3 minutes to remove argon then heated up to polymerization temperature at 40^{o}C. The polymerization was started by feeding continuously ethylene/propylene gas mixture to the reactor in order to keep the pressure to be constant at 30 psi.

The reaction of polymerization was terminated after 1 hr by addition of acidic methanol. The precipitated polymer was washed with methanol and dried in room temperature. Schematic diagram of system in slurry phase polymerization of semibatch system is displayed in Figure 3.7.



- **MB** : Magnet-Driven Stirrer
- **PR** : Pressure Regulator
- **VP** : Vacuum Pump
- **T** : Thermometer

Figure 3.7. Schematic diagram of system in slurry phase polymerization of semibatch system

3.4 Polymer Characterization

3.4.1 ^{13}C-Nuclear Magnetic Resonance (^{13}C-NMR)

^{13}C-NMR spectroscopy was widely used to determine comonomer incorporation and polymer structure. Comparison of the positions of peak in the ^{13}C-NMR spectrum of polymer sample with characteristic led to identification of the sequence of the comonomer incorporation. Sample solutions were prepared in *o*-dichlorobenzene and benzene-d_6 (20 vol %) for internal lock single. The ^{13}C-NMR spectra were obtained at 110°C using JEOL JNM-A500 operating at 125 MHz (at the Department of Science Service).

3.4.2 Differential Scanning Calorimetry (DSC)

The melting temperature (Tm) of the polymers were measured by a Perkin-Elmer Diamond DSC 7 at Central Instrument Facility Faculty of Science, Mahidol University and Center of excellent on Catalytic and Catalytic reaction Engineering, Chulalongkorn University. The heating rate of 20^{o}C/min in the temperature range -60 - 100 ^{o}C was employed. The heating cycle were twice operated. 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. Percent crystallinity was computed from enthalpies of melting by Equation 3.1, using the reliable value of Wunderlich.

$$\chi\,(\%) \quad = \quad (\Delta H_m/\Delta H^{\circ}_m) \times 100 \qquad (3.1)$$

Where (ΔH_m) is the heat of fusion of sample and (ΔH°_m) is the heat of fusion of 100% crystalline polyethylene [290 J/g] (Ottani and Porter, 1991).

3.4.3 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) was the effective method to investigate polymer morphology. The term of morphology was referred to shape, texture or form of polymers. The morphology of catalyst and polymers was examined by scanning electron microscopy (SEM) with a JSM-640 scanning microscope, microspec WDX at Scientific Technological Research Equipment Center, Chulalongkorn University using a camera and a Polaroid film. The polymer samples were coated with a thin layer of gold particles by ion sputtering before they were placed in the specimen chamber of the SEM.

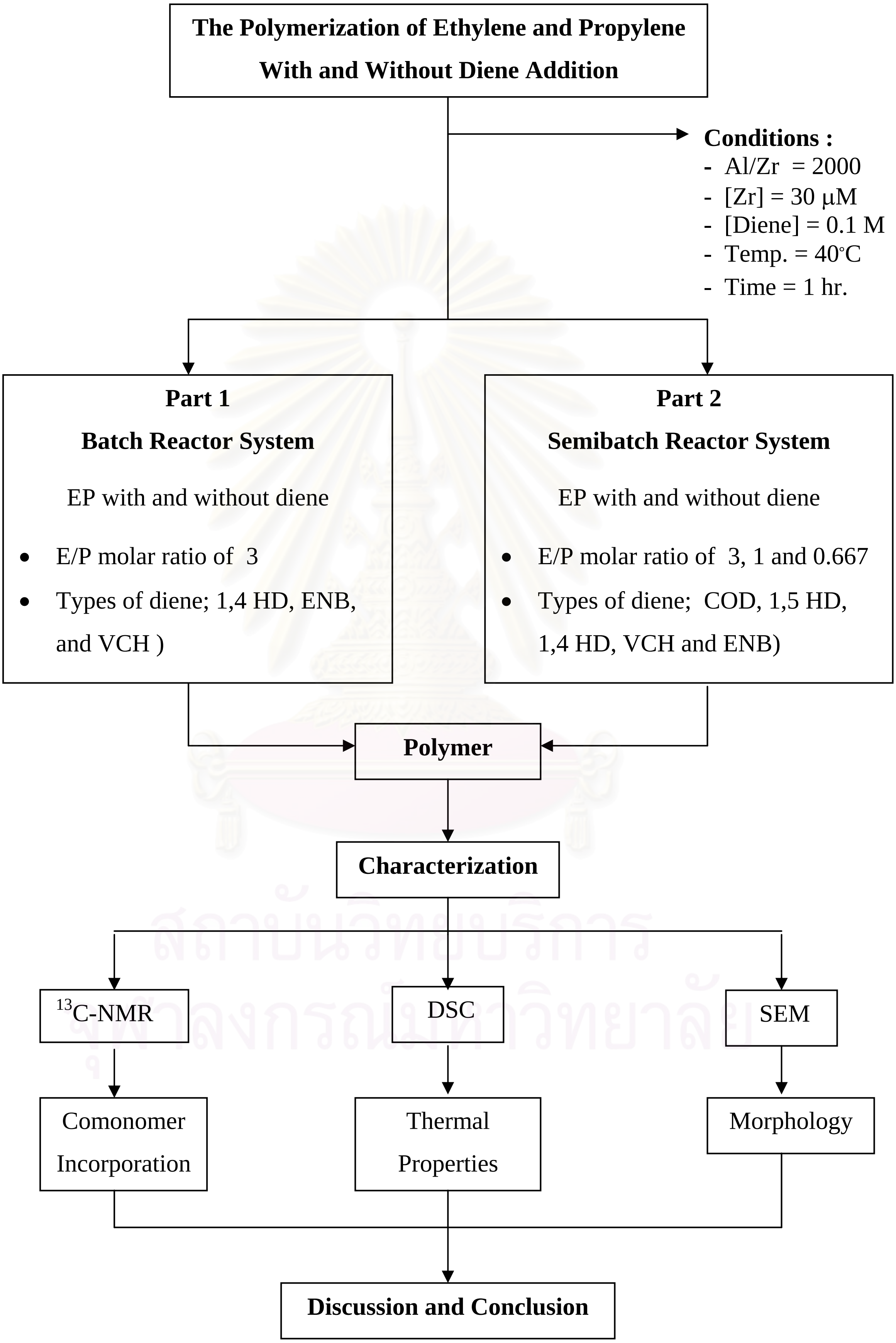
3.4.4 Gas Chromatography (GC)

Gas Chromatography technique was used 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 flow rate of 25 ml/min. Both initial and final column temperature were set to 70°C, detector temperature was set at 150°C and injector temperature was at 100°C.

3.4.5 Gel Permeation Chromatography (GPC)

One of the most widely used methods for the determination of molecular weight (Mw) and molecular weight distribution (MWD) was gel permeation chromatography (GPC). Samples were prepared having approximately concentration of 1.0-2.0 mg/ml in tricholobenzene (mobile phase) by using the sample preparation unit (PL-SP 260) at a temperature of 150°C for approximately hours. The dissolved sampled were transferred into PL-GPC 220. GPC were performed at Thai Petrochemical Industry Public Co., Ltd.

RESEARCH METHODOLOGY CHART



CHAPTER IV

RESULTS AND DISCUSSIONS

The purpose of this work was to study copolymerization of ethylene and propylene with and without diene using racemic-ethylenebis(indenyl)zirconium dichloride (*rac*-Et[Ind]$_2$ZrCl$_2$) catalyst system in the presence of methylaluminoxane (MAO) as a cocatalyst. Therefore, this chapter performed batch and semibatch reactor system used, effect of different types of diene, effect of ethylene/propylene initial molar ratios and characteristics of copolymers obtained.

4.1 Batch System

In the batch system, fixed amount of ethylene and propylene along with catalyst and cocatalyst were initially filled into the reactor only once. As polymerization proceeds, none of these reactants and catalysts was added. The activity was calculated from the polymer weight obtained (Jin *et al.*,1998). In this section, the catalytic activities, comonomer insertion and thermal properties of polymer produced from different types of diene [Three types of dienes i.e. 1,4-hexadiene (1,4 HD), 4-vinyl-1-cyclohexene (VCH) and 5-ethylidene-2-norbonene (ENB)] added in ethylene-propylene (EP) copolymerization were compared in ethylene-propylene copolymerization without diene.

4.1.1 The effect of different types of diene

4.1.1.1 Catalytic activities

This system was investigated using *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst in the presence of methylaluminoxane (MAO) as a cocatalyst. The molar ratio of [Al]$_{MAO}$/[Zr] of 2000. The ethylene/propylene molar ratio of 3 was employed. The copolymerization was performed in toluene at 40°C, 0.1 M of diene and zirconium concentration 30 μM with total solution volume 30 ml. The yields and activities of EP elastomers produced are shown in Table 4.1.

Table 4.1 Yields and activities of EP elastomers produced from with various dienes using *rac*-Et[Ind]$_2$ZrCl$_2$/MAO; [Zr] = 30 μM in toluene, [Al]/[Zr] =2000, [diene] = 0.1 M , ethylene/propylene molar ratio = 3 (ethylene 0.0819 mol, propylene 0.0273 mol), polymerization temperature = 40°C, and polymerization time = 1 hr.

Sample	Diene type[a]	Polymer Yield (g)	Activity (kg polymer/mol Zr.hr)
EP (0)	1,4 HD	2.54	2824
EP (1)	VCH	2.60	2887
EP (2)	ENB	2.40	2671
EP (3)	None added	2.88	3198

[a] 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

The results indicated that a small amount of dienes (1,4 HD, VCH and ENB) added could have impact on behaviors of ethylene-propylene (EP) copolymerization with a metallocene and MAO catalyst. In fact, a large amount of diene addition could result in a decreased activity of polymerization as reported by Malmberg and Lofgren (1997). However, it should be noted that the large amounts (~10-16 mol %) of diene were technically required in order to produce the terpolymer of EPDM. In particular, only a small amount (~3 mol %) of each diene was added during EP copolymerization in this study in order to maintain high activity of polymerization at this specified condition.

Yields and activities of various EP elastomers are shown in Table 4.1. It indicated that the types of diene did not exhibit any significant differences in the catalytic activity. In addition the addition of dienes could result in only slightly decreased activities regardless of the dienes used. The similar trend was found by the other groups (Yu *et al.*,1995 and Marque *et al.*, 1995). However, it was reported that when various types of diene were added to the systems, the activities dramatically decreased compared to the conventional EP copolymerization. They reported that when three types of diene were added to the systems, the activity in terpolymerization was in order of VCH > ENB~HD. They proposed that both double bonds in 1,4HD can chelate to the metal center resulting in a lower activity. Chelation is unlikely for VCH because of low steric flexibility of the double bond in the cyclohexene ring.

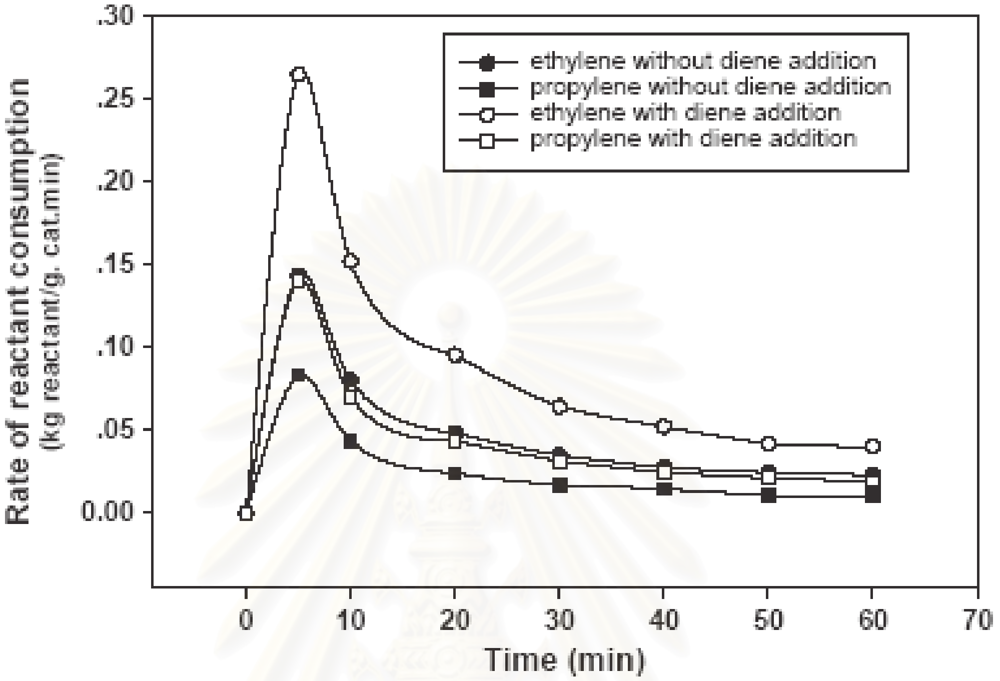


Figure 4.1. Activity profiles based on ethylene and propylene consumption with and without diene addition

Based on the assumption that propylene was in the gas phase and mole of monomer consumption calculated according to the ideal gas law (see Appendix A), the rates of consumption for ethylene and propylene with and without the diene addition are shown in Figure 4.1. It was found that the induction period of the catalyst was also observed at the beginning of polymerization. The consumption rate went to a maximum after 6–7 min, then decreased due to catalyst deactivation. With the diene addition, similar activity profiles can still be observed as also shown in Figure 4.1. It was suggested that the addition of dienes would have no effect on the catalyst performance at all indicating the similar rate profiles. However, the Figure 4.1 showed that ethylene and propylene consumptions with diene addition were higher than those without diene addition. It was found that the ethylene and propylene consumptions with diene addition had some error due to diene effect on pressure in the reactor resulting in partially condensation of propylene during polymerization. The activity profiles of all samples are also shown in Appendix B.

4.1.1.2 Comonomer insertion

The ^{13}C NMR is one of the most powerful techniques used to identify the microstructure of a polymer. The ^{13}C NMR spectra for all polymer samples are shown in Figure 4.2.

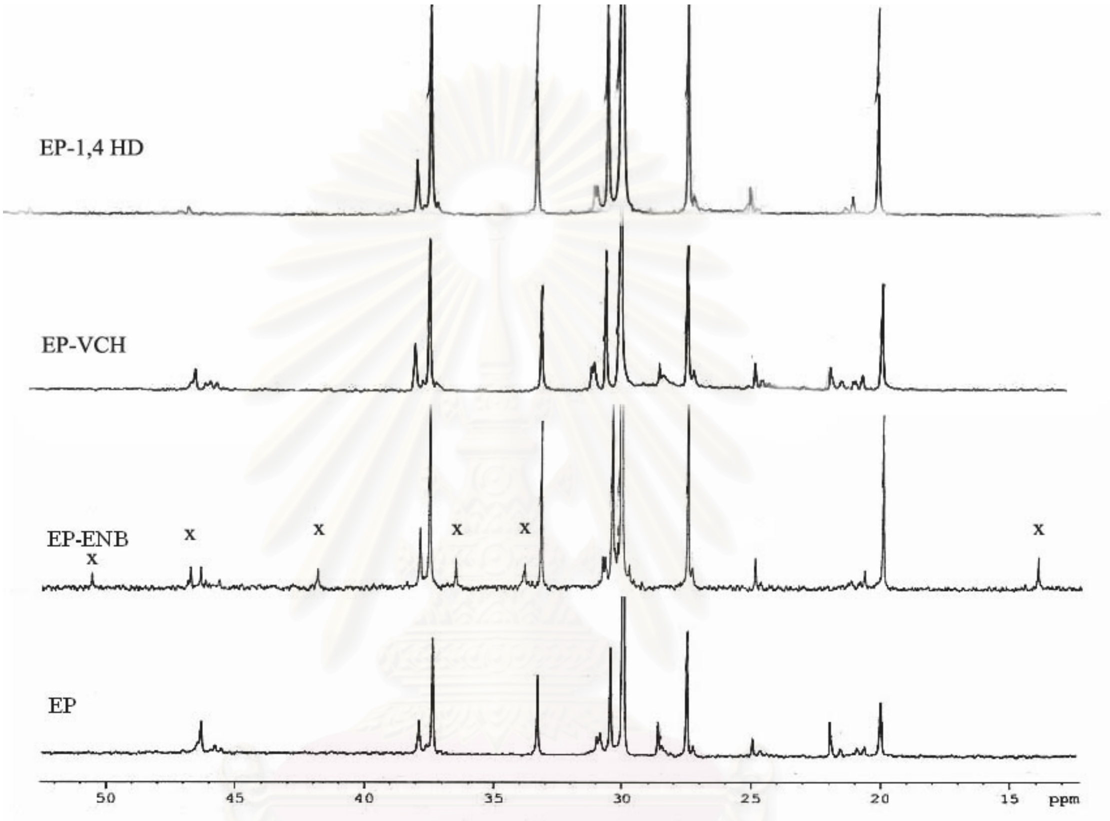


Figure 4.2. The ^{13}C NMR spectra of various EP elastomers with and without diene addition

It can be observed that the ^{13}C NMR spectra of EP, EP-VCH and EP-1,4 HD samples exhibited similar patterns corresponding with those as reported by Randall (1989). These revealed that there was no incorporation of 1,4 HD and VCH in the polymer backbone. The ^{13}C NMR spectrum of EP-ENB sample is also shown in Figure 4.2., which apparently exhibited the slightly different patterns compared with other samples as mentioned before. Besides the characteristic peaks of EP copolymer, the incorporation of ENB can be additionally observed at δ = 14, 34, 36.5, 42, 46.5 and 50 ppm corresponding with those as reported by Andrew (1999). This indicated that only ENB was able to incorporate into the polymer backbone at this specified condition. The ^{13}C-NMR spectra are also shown in Appendix C.

Table 4.2 Triad distribution obtained by ^{13}C NMR measurement of ethylene (E) and propylene (P) in polymers produced.

Sample	Diene type[a]	EEE	PEE+EEP	PEP	EPE	EPP+PPE	PPP
EP (0)	1,4 HD	0.609	0.210	0.032	0.118	0.031	0
EP (1)	VCH	0.505	0.205	0.056	0.114	0.088	0.032
EP (2)	ENB	0.604	0.191	0.023	0.107	0.024	0.051
EP (3)	None added	0.502	0.187	0.045	0.122	0.032	0.112

[a] 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

Table 4.3 Incorporation of ethylene (E), propylene (P) calculated from ^{13}C NMR measurement.

Sample	Diene type[a]	Incorporation (%)	
		E	P
EP (0)	1,4 HD	85	15
EP (1)	VCH	76	24
EP (2)	ENB	82	18
EP (3)	None added	73	27

[a] 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

The triad distribution, % incorporation of ethylene (E) and propylene (P) can be also calculated based on the method described by Randall (1989). The triad distribution of E and P for all samples are shown in Table 4.2. It indicated that the similar triad distribution was observed, except no block PPP in EP (0) sample. However, % incorporation of E and P are shown in Table 4.3. It revealed that upon the addition of a small amount of diene during copolymerization of EP, the incorporation of propylene in the polymer apparently decreased, especially for the ENB and 1,4 HD. The changes in the incorporation of ethylene and propylene upon the diene addition, it can be observed that the insertion of propylene apparently decreased with the diene addition. Therefore, it can be proposed that the addition of diene probably inhibited the propylene insertion catalytic site. Those phenomena resulted in a decreased propylene insertion.

4.1.1.3 Thermal properties

The thermal properties such as crystallization temperature (T_c) and melting temperature (T_m) of polymers obtained from differential scanning calorimeter (DSC) measurement along with % crystallinity can be also calculated based on the method described by Ottani and Porter (1991). The results are displayed in Table 4.4. The DSC curves are also shown in Appendix D.

Table 4.4 Thermal properties of polymers obtained from DSC measurement.

Sample	Diene type[a]	T_c (°C)	T_m (°C)	ΔH_m (J/g)	% Crystallinity (% χ)
EP (0)	1,4 HD	70.0	88.2	49.1	17.0
EP (1)	VCH	65.2	80.5	36.3	12.5
EP (2)	ENB	57.2	73.8	23.8	8.2
EP (3)	None added	59.3	73.6	30.6	10.6

[a] 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

It was found that the crystallization temperature (T_c), melting temperature (T_m) and % crystallinity of EP tended to increase with the addition of dienes. In addition, the various dienes gave different impacts on % crystallinity of EP. It showed that using 1,4HD would result in the largest number of melting temperature, crystallization temperature and % crystallinity. Based on DSC results, it was suggested that dienes can enhance the incorporation of ethylene into the growing polymer resulting higher crystallinity observed.

4.2 Semibatch System

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. Ethylene and propylene were mixed in the desired proportion in a gas cylinder, which was left overnight to ensure homogeneity of the mixture. With this reactor system, EP ratios can be fixed during copolymerization at constant pressure.

In this section, the effects of diene types and variation in ethylene/propylene feed ratios were the focus of this study. Experimentally, types of dienes (Five types of dienes i.e. COD, 1,5 HD, 1,4 HD, VCH and ENB) used and the ratios of E/P at 3, 1 and 0.667 were varied. The resulted activity and characteristics of polymer obtained were also discussed.

4.2.1 The effect of ethylene/propylene initial molar ratio

The ethylene and propylene copolymerization with and without diene addition were carried out using *rac*-Et[Ind]$_2$ZrCl$_2$/MAO catalytic system in toluene at reaction temperature of 40^{o}C for 1 hr. The ethylene/propylene molar ratios were varied at 3 (E > P), 1 (E = P) and 0.667 (E < P).

4.2.1.1 At E/P molar ratio of 3

4.2.1.1.1 Catalytic activities

The results for the effect of ethylene/propylene feed ratio of 3 (E > P) on the yields and activities of EP elastomers produced are given in Table 4.5.

At E/P molar ratio of 3 (E > P), the presence of diene resulted in a slight decrease in polymerization activity. The addition of 1,4 HD resulted in the lowest activity. When compared ethylene and propylene copolymerization, the similar decrease in activity was observed with using a batch system (see Table 4.1).

Table 4.5 Yields and activities of EP elastomers produced using Et[Ind]$_2$ZrCl$_2$/MAO catalyst; [Zr]=30 μM, [Al]/[Zr]=2000, [diene]=0.1 M, E/P molar ratio 3, polymerization temperature = 40°C, and polymerization time = 1 hr.

Sample	Types of diene[a]	Polymer Yield (g)	Activity (Kg Polymer/molZr.hr)
EP (0)	COD	1.97	2192
EP (1)	1,5 HD	1.93	2145
EP (2)	1,4 HD	1.68	1862
EP (3)	VCH	1.99	2210
EP (4)	ENB	1.77	1963
EP (5)	None added	2.26	2505

[a] COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

4.2.1.1.2 Comonomer insertion

Based on results of ethylene/propylene feed ratio of 3 (E > P), the % incorporation of ethylene (E), propylene (P) can be also calculated according to the method described by Randall (1989) as shown in Table 4.6.

In the case of ethylene/propylene feed ratio of 3 when comparing EP copolymerization without diene, it revealed that upon the addition of small amount of dienes during copolymerization of EP affect the incorporation of both ethylene (E) and propylene (P) except when COD was added.

Table 4.6 Incorporation of ethylene (E), propylene (P), E/P molar ratio of 3 calculated from ^{13}C NMR measurement.

Sample	Types of diene[a]	Incorporation (%)	
		E	P
EP (0)	COD	74.3	25.7
EP (1)	1,5 HD	75.9	24.1
EP (2)	1,4 HD	83.7	16.3
EP (3)	VCH	72.8	27.2
EP (4)	ENB	77.2	22.8
EP (5)	None added	74.3	25.7

[a]COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

Table 4.7 Triad distribution obtained by ^{13}C NMR measurement of ethylene (E) and propylene (P) in polymers produced, E/P molar ratio of 3.

Sample	Types of diene[a]	EEE	PEE+EEP	PEP	EPE	EPP+PPE	PPP
EP (0)	COD	0.390	0.291	0.062	0.167	0.082	0.008
EP (1)	1,5 HD	0.407	0.307	0.045	0.172	0.053	0.015
EP (2)	1,4 HD	0.583	0.225	0.028	0.119	0.044	0
EP (3)	VCH	0.357	0.304	0.067	0.166	0.106	0
EP (4)	ENB	0.634	0.112	0.026	0.112	0	0.115
EP (5)	None Added	0.382	0.293	0.068	0.172	0.085	0

[a]COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

Triad distribution of ethylene (E) and propylene (P) for copolymers produced, E/P molar ratio of 3 is shown in Table 4.7 corresponding with those as reported by Randall (1989). It indicated that the similar triad distribution was observed, except for the observation of PPP block in some cases. However, incorporation sequences of monomer depend on E/P ratio and types of dienes

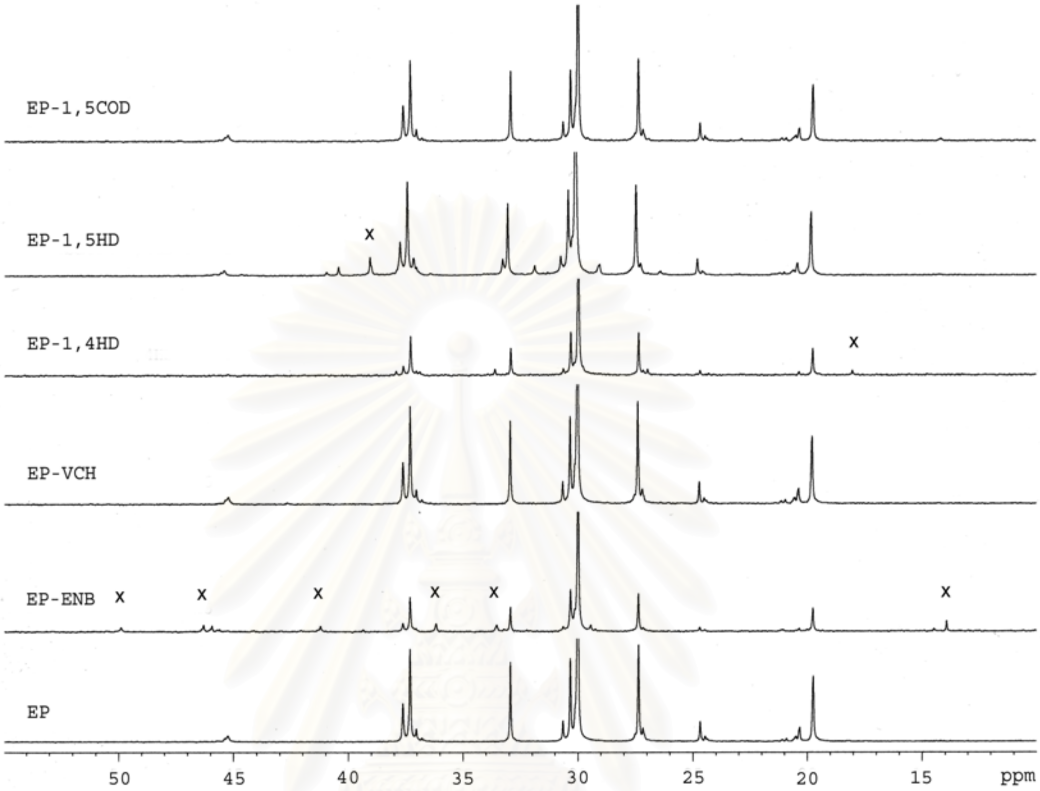


Figure 4.3. ^{13}C NMR spectra of various EP elastomers with and without diene addition at ethylene/propylene molar ratio of 3

The typical ^{13}C NMR spectra for all EP elastomers with various dienes at ethylene/ propylene with a molar ratio of 3 are shown in Figure 4.3. The ^{13}C-NMR spectra are also shown in Appendix C. It revealed that VCH and COD did not incorporate in EP indicating the similar patterns for EP, EP-VCH, and EP-COD corresponding with those as reported by Randall (1989). The ^{13}C spectra of EP-ENB, EP-1,4 HD and EP-1,5 HD are also shown in Figure 4.3, which apparently exhibited the slightly different patterns compared with other samples as mentioned before. Besides the characteristic peaks of EP copolymer, the incorporation of those dienes can be additionally observed at δ = 50, 46, 41, 36, 33.5 and 14 for ENB, at δ = 18 for 1,4 HD and at δ = 39 for 1,5 HD corresponding with those as reported by Andrew (1999). These indicated that only ENB, 1,4 HD and 1,5 HD were able to slightly incorporate into the polymer backbone at the specified condition.

4.2.1.1.3 Thermal property

The thermal property such as the melting temperature (T_m) obtained from DSC measurement is listed in Table 4.8. The DSC curves are also shown in Appendix D. It can be observed that the melting temperature of EP elastomers tended to increase with the addition of dienes. This might result from the addition dienes can enhance the incorporation of ethylene into the growing polymer resulting higher crystallinity observed.

Table 4.8 Thermal property of polymers obtained from DSC measurement, E/P molar ratio of 3.

Sample	Types of diene[a]	T_m (°C)
EP (0)	COD	80
EP (1)	1,5 HD	79
EP (2)	1,4 HD	79
EP (3)	VCH	78
EP (4)	ENB	77
EP (5)	None added	76

[a] COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

4.2.1.2 At E/P molar ratio of 1

4.2.1.2.1 Catalytic activities

The yields and activities of EP elastomers produced at ethylene/ propylene feed ratio of 1 (E = P) are shown in Table 4.9. It was found that diene addition resulted in slightly decreased activities of polymerization, the similar decrease in activity was observed with using E/P molar ratio of 3 (E > P).

Table 4.9 Yields and activities of EP elastomers produced using *rac*-Et[Ind]$_2$ZrCl$_2$/MAO catalyst; [Zr]=30 μM, [Al]/[Zr]=2000, [diene]=0.1 M, E/P molar ratio 1, 40°C, 1 hr.

Sample	Types of diene[a]	Polymer Yield (g)	Activity (Kg Polymer/molZr.hr)
EP (6)	COD	1.99	2209
EP (7)	1,5 HD	2.00	2214
EP (8)	1,4 HD	1.77	1962
EP (9)	VCH	2.00	2226
EP (10)	ENB	1.83	2038
EP (11)	None added	2.40	2665

[a] COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

4.2.1.2.2 Comonomer insertion

The results for ethylene/propylene feed ratio of 1 (E = P), the % incorporation of ethylene (E) and propylene (P) are shown in Table 4.10.

Table 4.10 Incorporation of ethylene (E), propylene (P), E/P molar ratio of 1 calculated from ^{13}C NMR measurement.

Sample	Types of diene[a]	Incorporation (%)	
		E	P
EP (6)	COD	72.1	27.9
EP (7)	1,5 HD	70.9	29.1
EP (8)	1,4HD	77.4	22.6
EP (9)	VCH	68.3	31.7
EP (10)	ENB	76.4	23.6
EP (11)	None added	63.5	36.5

[a] COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

Table 4.11 Triad distribution obtained by ^{13}C NMR measurement of ethylene (E) and propylene (P) in polymers produced, E/P molar ratio of 1.

Sample	Types of diene[a]	EEE	PEE+EEP	PEP	EPE	EPP+PPE	PPP
EP (6)	COD	0.340	0.308	0.072	0.173	0.106	0
EP (7)	1,5 HD	0.286	0.356	0.067	0.200	0.091	0
EP (8)	1,4 HD	0.439	0.284	0.050	0.159	0.068	0
EP (9)	VCH	0.266	0.328	0.090	0.191	0.126	0
EP (10)	ENB	0.423	0.286	0.054	0.157	0.079	0
EP (11)	None added	0.221	0.300	0.113	0.184	0.158	0.023

[a] COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

From Table 4.10, in the case of ethylene/propylene feed ratio of 1 (E = P) when comparing EP copolymerization without diene, it revealed that upon the addition of a small amount of dienes during copolymerization of EP, the incorporation of propylene in the polymer apparently decreased in all the types of diene. Triad distributions of ethylene (E) and propylene (P) at E/P = 1 is shown in Table 4.11 corresponding with those as reported by Randall (1989). It indicated that the similar triad distribution was observed, except for the observation of PPP block in the cases of the diene addition.

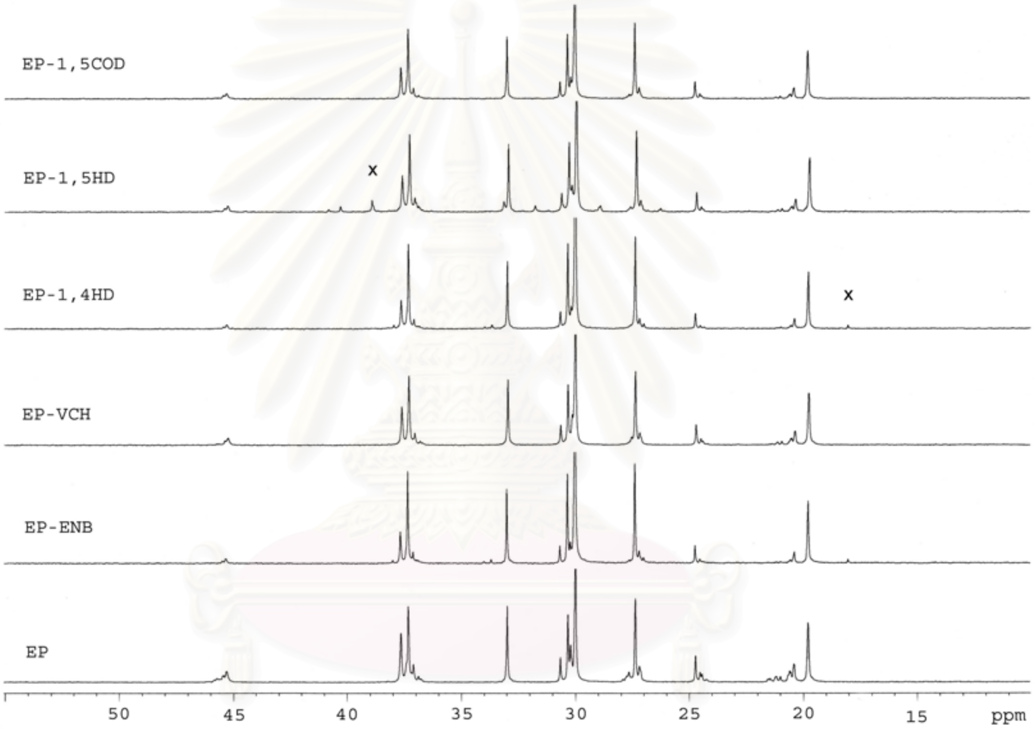


Figure 4.4. ^{13}C NMR spectra of various EP elastomers with and without diene addition at ethylene/propylene molar ratio of 1

The ^{13}C NMR spectra for all polymer samples with E/P ratio of 1 are shown in Figure 4.4. It can be observed that the ^{13}C NMR spectra for all samples exhibited the similar patterns. It revealed that ENB, VCH and COD did not incorporate in EP indicating the similar patterns for EP, EP-ENB, EP-VCH and EP-COD corresponding with those as reported by Randall (1989). The ^{13}C spectra of EP-1,4 HD and EP-1,5 HD are also shown in Figure 4.4, which apparently exhibited the slightly different patterns compared with other samples as mentioned before. These revealed that only 1,4 HD and 1,5 HD were able to slightly incorporate into the polymer backbone at the specified condition. ENB did not incorporated into the polymer backbone. This might result from competition between E and P was negligible. The ^{13}C-NMR spectra are also shown in Appendix C.

4.2.1.2.3 Thermal property

The thermal property such as the melting temperature (T_m) obtained at E/P molar ratio of 1 (E = P) from DSC measurement is listed in Table 4.12. It can be observed that the melting temperature of EP elastomers tended to increase with the addition of dienes., the similar trend was observed with using E/P molar ratio of 3. The DSC curves are also shown in Appendix D.

Table 4.12 Thermal property of polymers obtained from DSC measurement, E/P molar ratio of 1.

Sample	Types of diene[a]	Tm (°C)
EP (6)	COD	60
EP (7)	1,5 HD	58
EP (8)	1,4 HD	70
EP (9)	VCH	60
EP (10)	ENB	60
EP (11)	None added	51

[a]COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

4.2.1.3 At E/P molar ratio of 0.667

4.2.1.3.1. Catalytic activities

The yields and activities of EP elastomers produced at ethylene/propylene feed ratio of 0.667 (E < P) are shown in Table 4.13. It revealed that the presence of diene resulted in a slight decrease in polymerization activity, the similar decrease in activity was observed with in the case of E > P and E = P (see Table 4.5 and Table 4.9).

Table 4.13 Yields and activities of EP elastomers produced using *rac*-Et[Ind]$_2$ZrCl$_2$/MAO catalyst; [Zr]=30 μM, [Al]/[Zr]=2000, [diene]=0.1 M, E/P molar ratio 0.667, 40°C, 1 hr.

Sample	Types of diene	Polymer Yield (g)	Activity (Kg Polymer/molZr.hr)
EP (12)	COD	2.11	2343
EP (13)	1,5 HD	2.10	2332
EP (14)	1,4 HD	1.98	2204
EP (15)	VCH	2.24	2492
EP (16)	ENB	2.10	2330
EP (17)	None added	2.53	2811

[a] COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

4.2.1.3.2. Comonomer insertion

The results ethylene/propylene feed ratio of 0.667 (E < P), the % incorporation of E and P can be also calculated based on the method described by Randall (1989) as shown in Table 4.14. The triad distribution of E and P for all samples are shown in Table 4.15.

Table 4.14 Incorporation of ethylene (E), propylene (P), E/P molar ratio of 0.667 calculated from ^{13}C NMR measurement.

Sample	Types of diene[a]	Incorporation (%)	
		E	P
EP (12)	COD	57.4	42.6
EP (13)	1,5 HD	67.2	32.8
EP (14)	1,4 HD	77.9	22.1
EP (15)	VCH	55.4	44.6
EP (16)	ENB	53.8	46.2
EP (17)	None added	59.4	40.6

[a] COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

Table 4.15 Triad distribution obtained by ^{13}C NMR measurement of ethylene (E) and propylene (P) in polymers produced, E/P molar ratio of 0.667.

Sample	Types of diene[a]	EEE	PEE+EEP	PEP	EPE	EPP+PPE	PPP
EP (12)	COD	0.142	0.301	0.130	0.182	0.198	0.046
EP (13)	1,5 HD	0.233	0.346	0.093	0.205	0.122	0.001
EP (14)	1,4 HD	0.451	0.283	0.045	0.151	0.070	0
EP (15)	VCH	0.114	0.305	0.136	0.183	0.210	0.052
EP (16)	ENB	0.110	0.306	0.122	0.175	0.199	0.088
EP (17)	None added	0.138	0.325	0.131	0.198	0.190	0.018

[a] COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

From Table 4.14, it revealed that upon the addition of a small amount of dienes during copolymerization of EP, The changes in the incorporation of ethylene and propylene upon the diene addition. The addition of 1,4 HD resulted in the lowest % P incorporation. The triad distributions of E and P at E/P = 0.667 is shown in Table 4.15. It indicated that the similar triad distribution was observed, except for the observation of PPP block in some case. However, it revealed that the block EEE was predominant even at E < P.

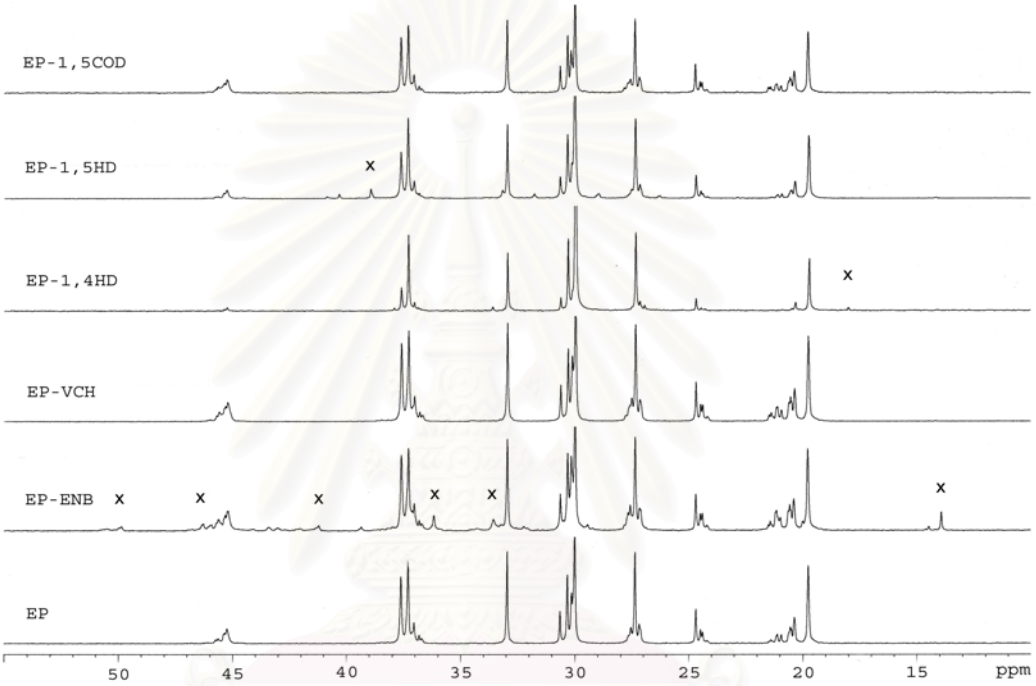


Figure 4.5. ^{13}C NMR spectra of various EP elastomers with and without diene addition at ethylene/propylene molar ratio of 0.667

The typical ^{13}C NMR spectra for all EP elastomers with various dienes at E/P ratio of 0.667 are shown in Figure 4.5. The ^{13}C-NMR spectra are also shown in Appendix C. It revealed that VCH and COD did not incorporate in EP indicating the similar patterns for EP, EP-VCH and EP-COD corresponding with those as reported by Randall (1989). The ^{13}C spectra of EP-ENB, EP-1,4 HD and EP-1,5 HD apparently exhibited the slightly different patterns compared with other samples as mentioned before. It revealed that only ENB, 1,4 HD and 1,5 HD were able to slightly incorporate into the polymer backbone at the specified condition.

4.2.1.3.3. Thermal property

The thermal property such as melting temperature (T_m) obtained from DSC measurement. The DSC curves are also shown in Appendix D. It should be noted that melting temperature increased with increasing the E/P ratios due to the crystallinity of PE. However, with E/P < 1, the disappearance of melting temperature can be observed. Hence, the EP elastomers with the low content of ethylene became absolutely amorphous materials. In addition, the thermal properties are also dependent on the fraction of ethylene and propylene in the polymer backbone.

Table 4.16 Comparison of activities and P incorporation (%) of EP elastomers at various molar ratios of ethylene/propylene.

1. Activities			
Case **Sample**	**E >P**	**E = P**	**E < P**
EP-COD	-	0	+
EP-1,5 HD	-	0	+
EP-1,4 HD	-	0	+
EP-VCH	-	0	+
EP-ENB	-	0	+
EP	-	0	+
2. P incorporation (%)			
Case **Sample**	**E >P**	**E = P**	**E < P**
EP-COD	-	0	+
EP-1,5 HD	-	0	+
EP-1,4 HD	-	0	0
EP-VCH	-	0	+
EP-ENB	-	0	+
EP	-	0	+

\+ increase, 0 unchange, - decrease

[diene types; COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)]

Table 4.17 Propylene incorporation in polymer (% mole)/propylene in feed (% mole) at various molar ratios of ethylene/propylene (see Appendix E).

Sample	E/P	Types of diene[a]	P in feed (% mole)	P incorporation in polymer / P in feed (%)
EP (0)	3	COD	25	100.0
EP (1)	3	1,5 HD	25	96.4
EP (2)	3	1,4 HD	25	65.2
EP (3)	3	VCH	25	100.0
EP (4)	3	ENB	25	91.2
EP (5)	3	None added	25	100.0
EP (6)	1	COD	50	55.8
EP (7)	1	1,5 HD	50	58.2
EP (8)	1	1,4 HD	50	45.2
EP (9)	1	VCH	50	63.4
EP (10)	1	ENB	50	47.2
EP (11)	1	None added	50	73.0
EP (12)	0.667	COD	60	71.0
EP (13)	0.667	1,5 HD	60	54.7
EP (14)	0.667	1,4 HD	60	36.8
EP (15)	0.667	VCH	60	74.3
EP (16)	0.667	ENB	60	77.0
EP (17)	0.667	None added	60	67.7

[a]COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

Comparisons of activities and P incorporation (%) of EP elastomers at various molar ratios of ethylene/propylene are summarized in Table 4.16. Propylene incorporation in polymer (% mole)/propylene in feed (% mole) at various molar ratios of ethylene/propylene are shown in Table 4.17.

Since the catalyst used in this set of experiment was Et[Ind]$_2$ZrCl$_2$/MAO, which gave higher activity in propylene polymerization than in ethylene polymerization (Chao, 2002), the higher activity can be seen from the higher ratio of propylene to ethylene. At lower E/P (E/P < 1), the incorporation of propylene monomer was higher than the ethylene monomer due to higher amounts of propylene added.

In order to focus on the impact of diene addition involving in polymerization activity, the activity profiles at various E/P ratios and various types of dienes were constructed as shown in Figure 4.6.

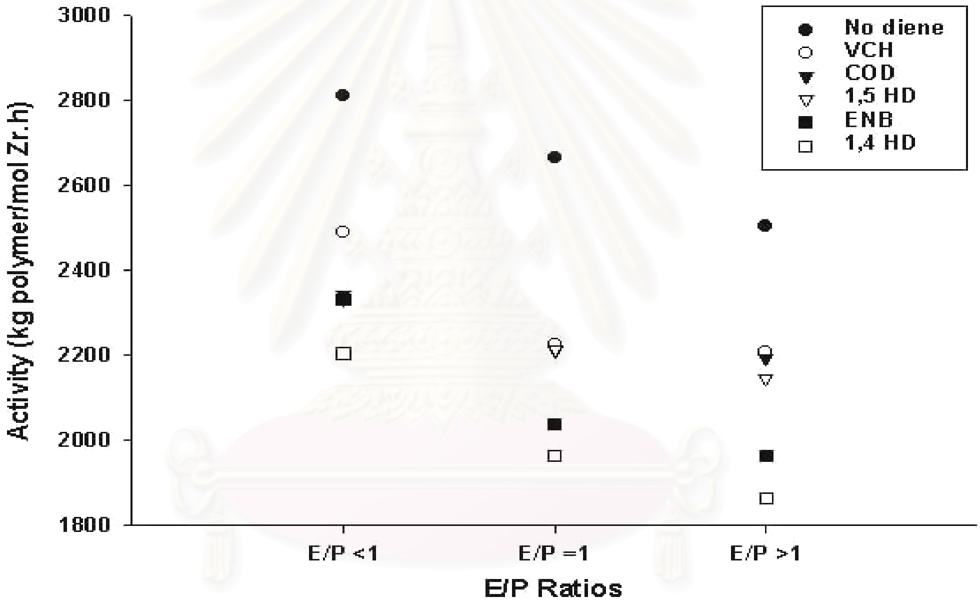


Figure 4.6 The activity profiles at various E/P ratios and various types of dienes

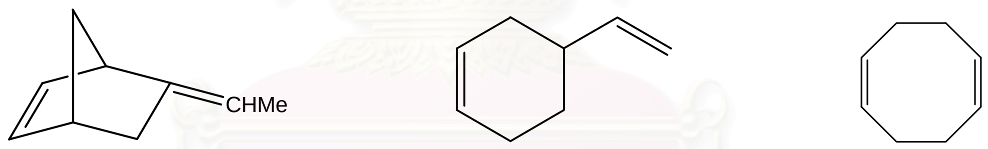
From Figure 4.6., it was found that diene addition resulted in slightly decreased activities of polymerization in regardless to E/P ratios. However, the activities increased with decreasing the E/P ratios. This was probably due to lower activity for ethylene polymerization with the presence of diene under the specified system. It should be mentioned that the activity for EP copolymerization was higher than both ethylene and propylene homopolymerization due to the comonomer effect (Kravchenko and Waymouth, 1998). Some explanations have been forwarded to explain this phenomenon, including the trigger mechanism (Naga,1997) and improved rates of diffusion due to the solubilization of active centers by incorporation of comonomer (Koivumaki and Seppala, 1993). The similar trend was found by the other groups (Yu *et al.*,1995 and Marques *et al.*,1995) using different catalyst system. However, it was reported that when various types of diene were added to the system, the activities dramatically decreased compared to the conventional EP copolymerization.

4.2.2 The effect of different types of diene

The effect of different types of diene were investigated. Five types of dienes such as 1,4 HD, 1,5 HD, ENB, VCH and COD. The structure of dienes using in this investigation are shown in Figure 4.7.

1,4-Hexadiene (1,4 HD)

1,5-Hexadiene (1,5 HD)



5-Ethylidene-2-norbonene (ENB)

4-Vinylcyclohexene (VCH)

Cyclooctadiene (COD)

Figure 4.7. The structure of dienes used in this investigation.

Considering the types of diene employed, it revealed that activities decreased with diene addition. For all cases, the addition of 1,4 HD resulted in the lowest activity among the other dienes added.

At the specified condition, only ENB, 1,4 HD and 1,5 HD can incorporate in the polymer backbone based on ^{13}C NMR results. It revealed that upon the addition of a small amount of dienes during copolymerization of EP, the incorporation of propylene in the polymer apparently decreased, especially for 1,4 HD and 1,5 HD at various ratios of E/P. Hence, the addition of 1,4 and 1,5 HD may inhibit the insertion of propylene.

The thermal property such as melting temperature obtained from DSC measurement. It can be observed that the melting temperature of EP elastomers tended to increase with the addition of dienes. It was suggested that the addition dienes can enhance the incorporation of ethylene into the growing polymer resulting higher crystallinity observed. In addition, the thermal properties are also dependent on the fraction of ethylene and propylene in the polymer backbone. Thus, it is necessary to determine the incorporation of ethylene and propylene in the polymer sample.

Yu *et al.* (1995) also studied terpolymerization of E/P/ENB using Et[Flu]$_2$ZrCl$_2$/MAO at E/P = 4. They found that the presence of ENB significantly reduced the polymerization activity by 10-20 fold from EP copolymerization. The results of terpolymerization with VCH were similar, but somehow the reduction of polymerization activity by VCH was smaller. The polymerization activities in the presence of HD lied in between those of ENB and VCH. The activities for terpolymerization with HD were comparable to the results for ENB as the termonomer. They proposed that both double bonds in HD can chelate to the metal center. Chelation is unlikely for VCH because of low steric flexibility of the double bond in the cyclohexene ring. Marques *et al.* (1995) investigared E/P/diene (VCH and COD) using Et[Ind]$_2$ZrCl$_2$ as a catalyst. They found that the activities of terpolymerization with COD were lower than that of VCH. Kaminsky and Miri (1985) carried out E/P/ENB terpolymerization with Cp$_2$ZrMe$_2$/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. Yu *et al.* (1995) also reported that, with Et[Flu]$_2$ZrCl$_2$/MAO and Me$_2$Si[Ind]$_2$ZrCl$_2$/MAO catalyst system at 70^{o}C, E/P=4. The presence of ENB (0.074 M) significantly reduces the copolymerization activity by 10-20 fold. Arrowsmith *et al.*(2000) using isopropylidene [3-MeCp][Flu]ZrCl$_2$ in E/P/ENB terpolymerization, diene exhibited the adverse effect on the activity. The activity decreased about 7 fold when diene concentration of 0.2 M was applied. The similar decrease in activity of about 7 fold was also observed with [2-(dimethylamino) $CpTiCl_3$/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) decrease the rate of polymerization carried out with $Et[Ind]_2ZrCl_2$ to about a half. The terpolymerization for ENB catalyzed by this catalyst system has an activity, which is about 3-5 times smaller than the copolymerization (Chien and Xu, 1993). In contrast, Malmberg and Lofgren (1997) reported that the termonomer (ENB) did not affect the polymerization yield significantly in ethylene/propylene/ENB terpolymerization using $Et[Ind]_2ZrCl_2$/ MAO catalyst system, the polymerization pressure was 3 bar. Polymerization yields were significantly lower only at the largest diene concentrations (0.6 M). A concentration about 0.167 M of HD lowers the polymerization activity by one order of magnitude; further increase of diene concentration leads to additional but more gradual loss of activity (Yu *et al.*, 1995).

Comparisons of activities and P incorporation (%) of EP with and without diene addition at various molar ratios of ethylene/propylene are summarized in Table 4.18. Based on all experimental data, the effects of E/P ratios along with the types of dienes could be drawn from the resulting polymerization activity and E/P incorporation. It was obvious that the addition of a small amount of dienes could alter the behaviors of EP copolymerization using a zirconocene/MAO catalyst. It can be observed that the effects of diene addition were apparently dependent on the E/P ratios and types of dienes.

Table 4.18 Comparisons of activities and P incorporation (%) of EP with and without diene addition at various molar ratios of ethylene/propylene.

1. Activities

Sample Case	P-COD	EP-1,5 HD	EP-1,4 HD	EP-VCH	EP-ENB	EP
E > P	-	-	-	-	-	0
E = P	-	-	-	-	-	0
E < P	-	-	-	-	-	0

2. P incorporation (%)

Sample Case	P-COD	EP-1,5 HD	EP-1,4 HD	EP-VCH	EP-ENB	EP
E > P	0	-	-	+	-	0
E = P	-	-	-	-	-	0
E < P	+	-	-	+	+	0

+ increase, 0 unchange, - decrease

[diene types; COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)]

4.2.2.1 Morphology

The morphologies of polymer produced were observed using scanning electron microscopy (SEM) technique. SEM micrographs of various EP produced are shown in Figure 4.8. It can be observed that there were some differences in morphologies of the various EP produced. Apparently, the EP produced with the addition of dienes appeared in a larger air gap in the texture compared to those without diene addition.

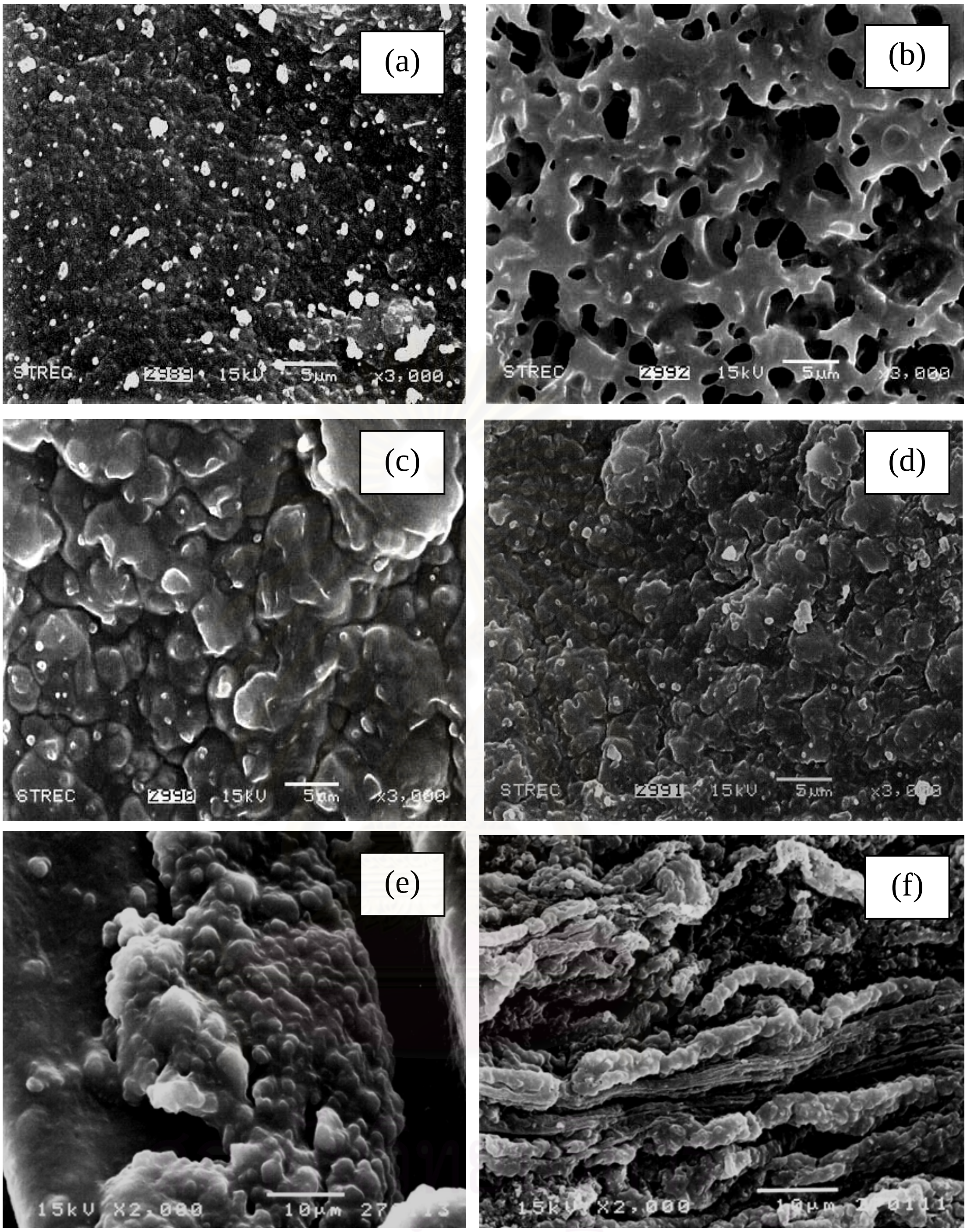


Figure. 4.8. SEM micrographs of various EP elastomers; (a) EP ×3000, (b) EP-ENB ×3000, (c) EP-VCH ×3000, (d) EP-1,4 HD ×3000, (e) EP-1,5 HD ×2000, (f) EP-COD ×2000.

.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The conclusions of this research can be summarized as follows:

1. The addition of only a small amount of dienes under the specified condition could alter the copolymerization behaviors of ethylene and propylene with a Et[Ind]$_2$ZrCl$_2$/MAO catalyst. In particular, changes in polymerization behaviors were dependent on E/P ratios and types of diene. It revealed that activities decreased with diene addition in all E/P ratio. However, the activities increased with decreasing the E/P ratio (E/P = 0.667).
2. The effects of diene addition were apparently dependent on the E/P ratios and types of dienes. Upon the various dienes used, % incorporation of E and P, melting temperature, crystallization temperature, and % crystallinity can be changed significantly.
3. Based on ^{13}C NMR results, with a small amount of diene added in batch system, the dienes (except for ENB) did not incorporate in the polymer backbone pronouncedly. For semibatch system, only ENB, 1,4 HD and 1,5 HD can incorporate in the polymer backbone.
4. The melting temperature of EP elastomers tended to increase with the addition of dienes. It was suggested that the addition dienes can enhance the incorporation of ethylene into the growing polymer resulting higher crystallinity observed. The melting temperature increased with increasing the E/P ratios. However, with E/P < 1, the disappearance of melting temperature can be observed. Hence, the EP elastomers with the low content of ethylene became absolutely amorphous materials. In addition, the thermal properties are also dependent on the fraction of ethylene and propylene in the polymer backbone.

5.2. RECOMMENDATIONS

1. From the results of this study, the addition of only a small amount of dienes under the specified condition was investigated. This indicated that some types of diene did incorporate into the polymer backbone at low content. So the effect of the diene concentrations in polymerization should be further investigated.
2. Further study on other types of diene both in aliphatic and cyclic diene should be considered.
3. The effect of different metallocene catalysts on the catalytic activity and the incorporation of ethylene, propylene and diene should be performed.

REFERENCES

Allen, R.D. **J. Elastomers Plast.** 15 (1983): 19.

Alt, H. "The Heterogenization of Homogeneous Metallocene Catalysts for Olefin Polymerization", **Journal of The Chemical Society; Dalton Transactions** (1999): 1703-1709.

Alt, H. G. and Köppl, A. "Effect of the Nature of Metallocene Complexes of Group IV Metals on Their Performance in Catalytic Ethylene and Propylene Polymerization", **Chemical Reviews** 100 (2000): 1205-1221.

Arndt, M., Kamisky, W., Schauwienold, A. M., and Weingarten, U."Ethene/ propene copolymerization by [Me_2C(3-RCp)(Flu)]$ZrCl_2$/ MAO (R= H, Me, ^{iso}Pr, ^{tert}Bu)", **Macromol. Chem. Phys.** 199 (1998): 1135-1152.

Avella, M.; Martuscelli, E. And Volpe, G. D. **Makromol. Chem.** 187 (1986): 1927-1943.

Barron, A. R.; Mason, M. R.; Smith, J. M., and Bott, S.G. "Hydrolysis of Tri-tert-butylaluminum: The First Structural Characterization of Alkylalumoxanes $[(R_2Al)_2O]_n$ and $(RAlO)_n$", **Journal of the American Chemical Society** 115 (1993): 4971-4984.

Barron, A.R.; Koide, Y. and Bott, S.G. "Alumoxanes as Cocatalysts in The Palladium-catalyzed Copolymerization of Carbonmonoxide and Ethylene: Genesis of A Structure-activity Relationship", **Organometallics** 15 (1996): 2213-2226.

Brintzinger,H.H.; Fischer,D.; Mulhaupt,R. and B. Rieger, **Angew. Chem**. 107 (1995): 1255.

Busico, V., Cipullo, R., and Esposito, V. "Stopped-flow polymerization of ethene and propene in the presence of the catalyst system rac-Me_2Si(2-methyl-4-phenyl-1-indenyl)$_2ZrCl_2$/ methylaluminoxane", **Macromol. Rapid. Commun.** 20 (1999): 116-121.

Cardin, D. J.; Lappert, M. F. and Raston, C.L. **Chemistry of Organo-Zirconium and-Hafnium Compounds.** Wiley, New York (1986).

Chao, C. "The ethylene-propylene-diene terpolymerization using metallocene catalysts." **Master's Thesis, Chem. Eng., Chulalongkorn University,** (2002).

Chen, E. Y. X., and Marks, T. J. “Cocatalysts for Metal-Catalyzed Olefin Polymerization: Activators, Activation Processes, and Structure-Activity Relationships”, **Chem. Rev.** 100 (2000): 1391-1434.

Chien, J. C. W., Yu, Z., Marques, M. M., Flores, J. C., and Rausch, M. D. “Polymerization of Olefins and Diolefins Catalyzed by Monocyclopentadienytitanium Complexes Containing a (Dimethylamino) ethyl substituent and comparison with ansa-zirconocene systems”, **J. Polym. Sci. Part A: Polym. Chem.** 36 (1998): 319-328.

Chung, T. C. **Functionalization of Polyolefins** (2002): 135.

Coates, G. W. Precise “Control of Polyolefin Stereochemistry Using Single-Site Metal Catalysts”, **Chem. Rev.** 100 (2000): 1223-1252.

Corbelli, L.; Milani, F. and Fabbri, R. **Kaut. Gummi Kunstst**. 34 (1981): 11-15.

Czaja, K. and Bialek, M. **Macromol. Rapid Commun.** 19 (1998): 163.

Deffieux, A.; Dolakthani, M. and Cramail, H. **Macromol. Chem. Phys.** 197 (1996): 289.

Djupfors, R., Starck, P., and Lofgren, B. “Copolymerization of propene with ethene by Et(Ind)$_2$HfCl$_2$/ methylaluminoxane catalyst”, **Eur. Polym. J.** 34 (1998): 941-948.

Galimberti, M., Piemontesi, F., Fusco, O., Camurati, I., and Destro, M. “Ethene/Propene Copolymerization with high product of reactivity ratios from a single center, metallocene-based catalytic system”, **Macromolecules** 31 (1998): 3409-3416.

Galimberti, M., Piemontesi, F., Mascellani, N., Camurati, I., Fusco, O., and Destro, M. “Metallocenes for Ethene/Propene Copolymerizations with High Product of Reactivity Ratios”, **Macromolecules** 32 (1999): 7968-7976.

Gassman, P.G. and Callstrom, M.R. “Isolation, and Partial Characterization by XPS, of Two Distinct Catalysts in the Ziegler-Natta Polymerization of Ethylene”, **Journal of the American Chemical Society** 109 (1987): 7875-7876.

Giannetti, E.; Nicolett, G. M. and Mazzocchi, R. **Journal of Polym. Science: Polymer Chemistry** 23 (1985): 2117-2134.

Gupta, V. K., Satish, S., and Bhardwaj, I. S. “Metallocene Complexes of Group 4 Elements in the Polymerization of Monoolefins”, **J.M.S.-Rev. Macromol. Chem. Phys.** C34(3) (1994): 439-514.

Gupta, V.K.; Satish, S. and Bhardwaj, I.S. **Rev. Macromol.Chem. Phys.** 34 (1994).

Haag, M. C., Dos Santos, J. H. Z., Dupont, J., and Secchi, A. R. **"**Dynamic Simulation and Experimental Evaluation of EPDM Terpolymerization with Vanadium-Based Catalyst", **J. Appl. Polym. Sci.** 70 (1998): 1173-1189.

Haag, M.C., Dos Santos, J.H.Z., Stedile, F.C., and Dupont, J. "Residual Metal Content in Ethylene-Propylene-Diene Monomers Synthesized Using Vanadium- and Zirconocene- Based Catalysts. **J. Appl. Polym. Sci.** 74 (1999): 1997-2003.

Haag, M.C., Dos Santos, J.H.Z., Stedile, F.C., De Araujo, M.A., Dupont, J., and Baumvol, I.J.R. "Synthesis and Characterization of EPDM Films", **J. Appl. Polym. Sci.** 68 (1998): 535-541. Halterman, R. L. Ibid., 92 (1992): 965.

Henri, U. **Introduction to Industrial Polymers** (1982): 69.

Hlatky, G.G.; Turner, H.W. and Eckman, R.R. "Ionic, Base-Free Zirconocene Catalysts for Ethylene Polymerization", **Journal of the American Chemical Society** 112 (1989): 2728-2729.

Imanishi, Y. and Naga, N. "Recent Developments in Olefin Polymerizations with Transition Metal Catalysts", **Progress in Polymer Science** 26 (2001): 1147-1198.

Jin, J., Uozumi, T., Sano, T., Teranishi, T., Soga, K., and Shiono, T. "Alternating copolymerization of ethylene and propene with the [ethylene(1-indenyl)(9-fluorenyl)]zirconium dichloride- methylaluminoxane catalyst system", **Macromol. Rapid. Commun**. 19 (1998): 337-339.

Jordan, R. F. Adv. Organomet. Chem. 32 (1991): 325

Kaminsky, W., and Miri, M. "Ethylene Propylene Diene Terpolymers Produced with a Homogeneous and Highly Active Zirconium Catalyst", **J. Polym. Sci.: Polym. Chem.** 23 (1985) 2151-2164.

Kaminsky, W. **Metalorganic Catalysts for Synthesis and Polymerization**, Springer, (1999).

Koivumaki, J. and Seppala, J. V. "Comparison of ethylene-propylene copolymers obtained with Ti, V, and Zr catalyst systems", **Polym. Bull.** 31 (1993): 441-448.

Koivumaki, J., and Seppala, J. V. "Copolymerization of ethene and propene in liquid propene with $MgCl_2/TiCl_4$, $VOCl_3$ and Cp_2ZrCl_2 catalyst systems – A comparison of products", **Eur. Polym. J.** 30 (1994): 1111-1115.

Kravchenko, R., and Waymouth, R. M. "Ethylene-Propylene Copolymerization with

2-Arylindene Zirconocenes”, **Macromolecules** 31 (1998): 1-6.

Lee, D. H., Yoon, K. B., and Lee, E. H. “Polymerization and copolymerization of ethene initiated with disiloxane-bridged biscyclopentadienylzirconium complexes and methylaluminoxane”, **Macromol. Rapid. Commun** 17 (1996): 325-331.Long, N. J. **London: Blackwell Science** (1998**).**

Long, N. J. **Metallocenes: An introduction to sandwich complexes** London, Blackwell Science Ltd., (1998**).**

Malmberg, A., and Lofgren, B. “The production of Ethene/Propene/5-Ethylidene-2-Norbornene Terpolymers Using Metallocene Catalysts: Polymerization, Characterization and Properties of the Metallocene EPDM”, **J. Appl. Polym. Sci.** 66 (1997): 35-44.

Marques, M., Yu, Z., Rausch, M. D. and Chien, J. C.W. “Olefin Terpolymerizations II. 4-Vinylcyclohexene and Cyclooctadiene”, **J. Polym. Sci. Part A: Polym. Chem.** 33 (1995): 2787-2793.

Michelotti, M.; Altomare, A.; Ciardelli, F. and Roland, E. **Journal of Molecular Catalysis A: Chemistry** 129 (1998): 241-248.

Naga, N. and Imanishi, Y. “Copolymerization of Ethylene and Cycopentene with Zirconocene Catalysts: Effects of Ligand Structure of Zirconocenes”, **Macromolecular Chemistry and Physics** 203 (2002): 159-165.

Naga, N., Ohbayashi, Y., and Mizunuma, K. “Study of molecular size in ethylene-propene copolymerization with zirconocene and hafnocene catalysts”, **Macromolecular Rapid Communication** 18 (1997): 837-851.

Natta, G.; Crespi, G.; Valvassori A.; Sartori, G.; Cameli, and Turba, V. **Rubber Plast.** Age 46 (1965): 683.

Ottani, S., and Porter, R. S. “A Calorimetric Investigation on High Molecular Weight Polyethylene Reactor Powders”, **Journal of Polymer Science: Part B: Polymer Physics** 29 (1991): 1179-1188.

Resconi, L.; Bossi, S. and Abis, L. “Study on the Role of Methylalumoxane in Homogeneous Olefin Polymerization”, **Macromolecules** 23 (1990): 4489-4491.

Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L. and Fiorani, T. “Olefin Polymerization at Bis(pentamethylcyclopentadienyl) Zirconium and Hafnium Centers-Chain-Transfer Mechanisms”, **Journal of the American Chemical Society** 114 (3) (1992): 1025-1032.

Sinn, H. Proposals for Structure and Effect of Methylaluminoxane Based on Mass Balances and Phase Separation Experiments. **Macromolecular Symposia** 97 (1995): 27-52.

Sobhanmanesh K. and Hajizadeh A. **Iranian Polymer Journal** 13 (2004): 257-262.

Thewalt, U. **Gmelin Handbook of Inorganic Chemistry**, Part 4,Springer-Verlag, Berlin. (1984).

Tritto, I.; Mealares, C.; Sacchi, M. C. and Locatelli, P. "Methylaluminoxane: NMR Analysis, Cryoscopic Measurements and Cocatalytic Ability in Ethylene Polymerization", **Macromolecular Chemistry and Physics** 198 (1997): 3963-3977.

Tsai, W.M. and Chien, J.C.W. "Silolene-bridge Zirconocenium Polymerization Catalysts", **Journal of Polymer Science: Part A: Polymer Chemistry**: 32 (1994) 149-158.

Wang, Q.; Hong, J.; Fan, Z. and Tao, R. **J. Polym. Sci. Part A: Polym. Chem**. 41(2003): 998-1003.

Wailes, P. C.; Coutts, R. S. P. and Wegold, H. **Organometallic Chemistry of Titanium, Zirconium and Hafnium,** Academic Press, New York.(1974)

Wang, W. J., and Zhu, S. "Structural Analysis of Ethylene/Propylene Copolymers Synthesized with a Constrained Geometry Catalyst", **Macromolecules** 33 (2000): 1157-1162.

Wang, W.J.; Ye, Z.; Fan, H.; Li, B.G.and Zhu, S. **Polymer** 45 (2004): 5497-5504.

Yang, X.; Stern, C.L. and Marks, T.J. **"**Cation-like Homogeneous Olefin Polymerization Catalysts Based upon Zirconocene Alkyls and Tris (pentafluorophenyl) borane", **Journal of the American Chemical Society** 113 (1991): 3623-3625.

Ystenes, M., Eilertsen, J. L., Liu, J., Ott, M., Rytter, E., and Stovneng, J. A. "Experimental and Theoretical Investigations of the Structure of Methylaluminoxane (MAO) Cocatalysts for Olefin Polymerization", **J. Polym. Sci. Part A: Polym. Chem.** 38 (2000): 3106-3127.

Yu, Z., Marques, M., Rausch, M. D., and Chien, J. C.W. "Olefin Terpolymerization I. 1,4-Hexadiene", **J. Polym. Sci. Part A: Polym. Chem.** 33 (1995): 979-987.

Yu, Z., Marques, M., Rausch, M. D., and Chien, J. C.W. “Olefin Terpolymerizations III. Symmetry, Sterics and Monomer Structure in ansa-Zirconocenium Catalysis of EPDM synthesis”, **J. Polym. Sci. Part A: Polym. Chem.** 33 (1995) 2795-2801.

Zucchini, U.; Dallocco, T. and Resconi, L. “Ziegler-Natta Catalysis for The Polyolefin Industry Present Status and Perspectives”, **Indian Journal of Technology** 31 (1993): 247-262.

APPENDICES

APPENDIX A

% MOLE OF REACTANT DURING POLYMERIZATION

The ethylene and propylene molar ratio were measured by gas chromatography

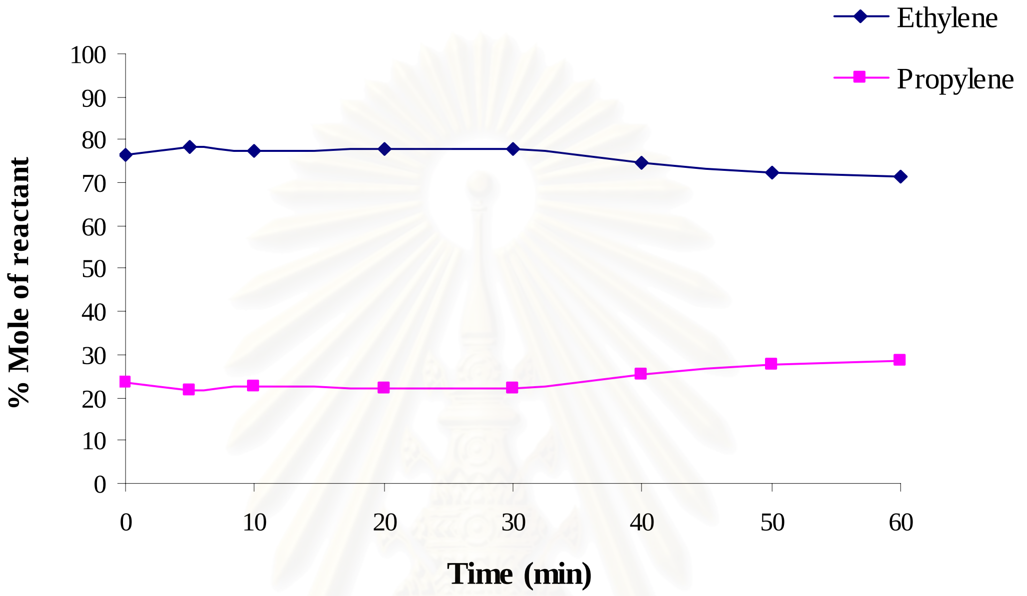


Figure A-1. % Mole of reactant during polymerization of EP copolymer with 1,4HD [EP (0)] at initial ethylene/propylene molar ratio of 3 (batch system).

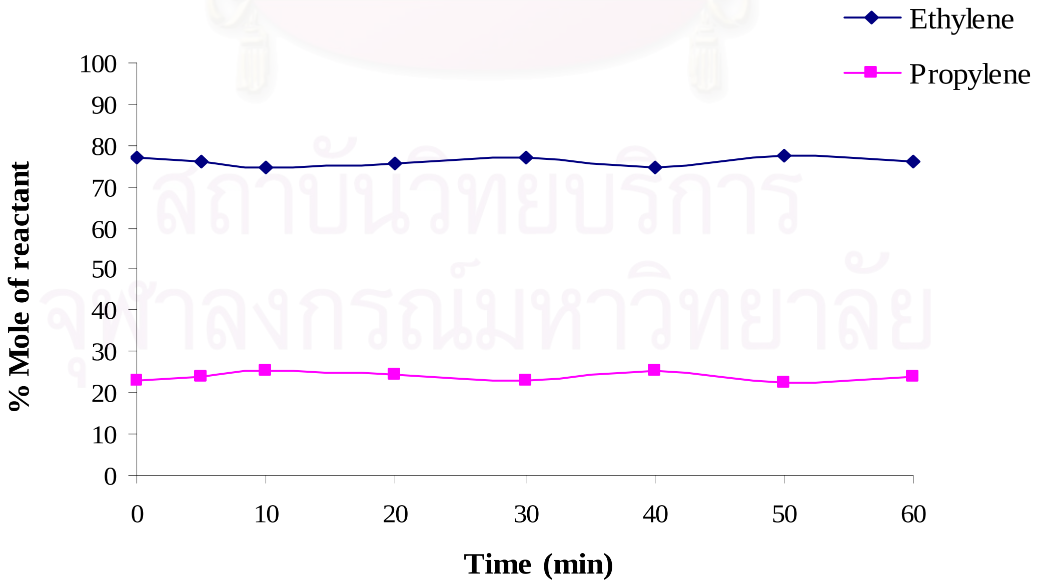


Figure A-2. % Mole of reactant during polymerization of EP copolymer with VCH [EP (1)] at initial ethylene/propylene molar ratio of 3 (batch system).

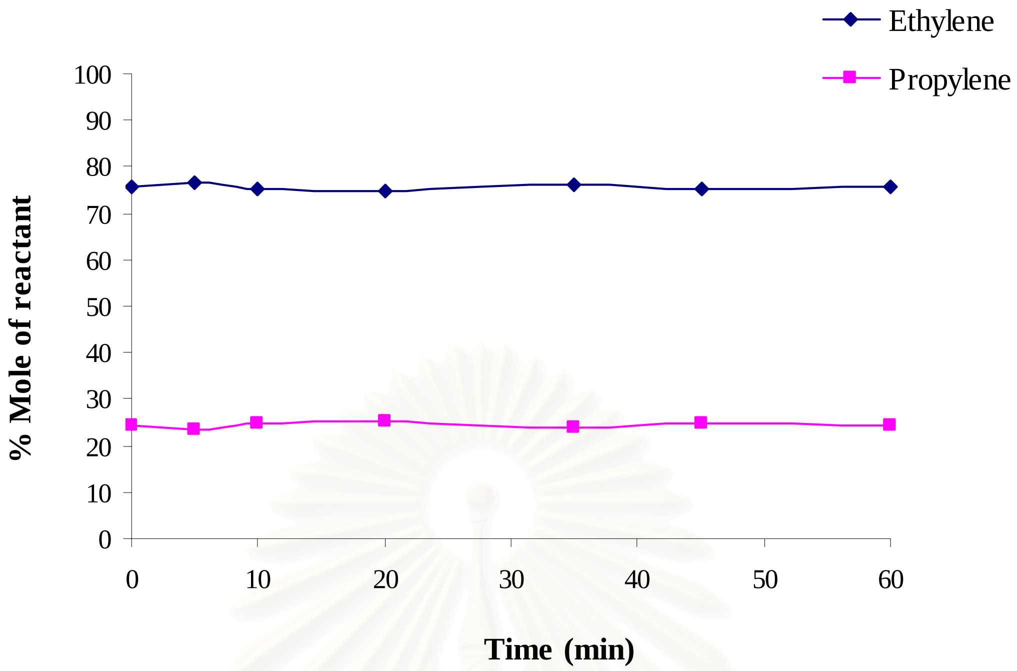


Figure A-3. % Mole of reactant during polymerization of EP copolymer with ENB [EP (2)] at initial ethylene/propylene molar ratio of 3 (batch system).

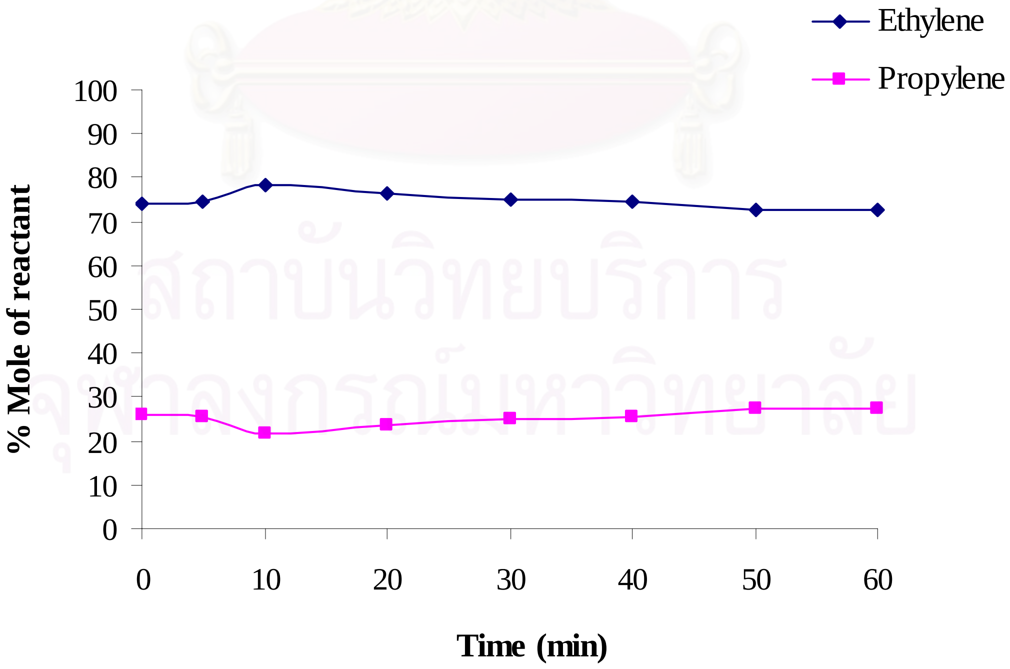


Figure A-4. % Mole of reactant during polymerization of EP copolymer [EP (3)] at initial ethylene/propylene molar ratio of 3 (batch system).

APPENDIX B

ACTIVITY PROFILES

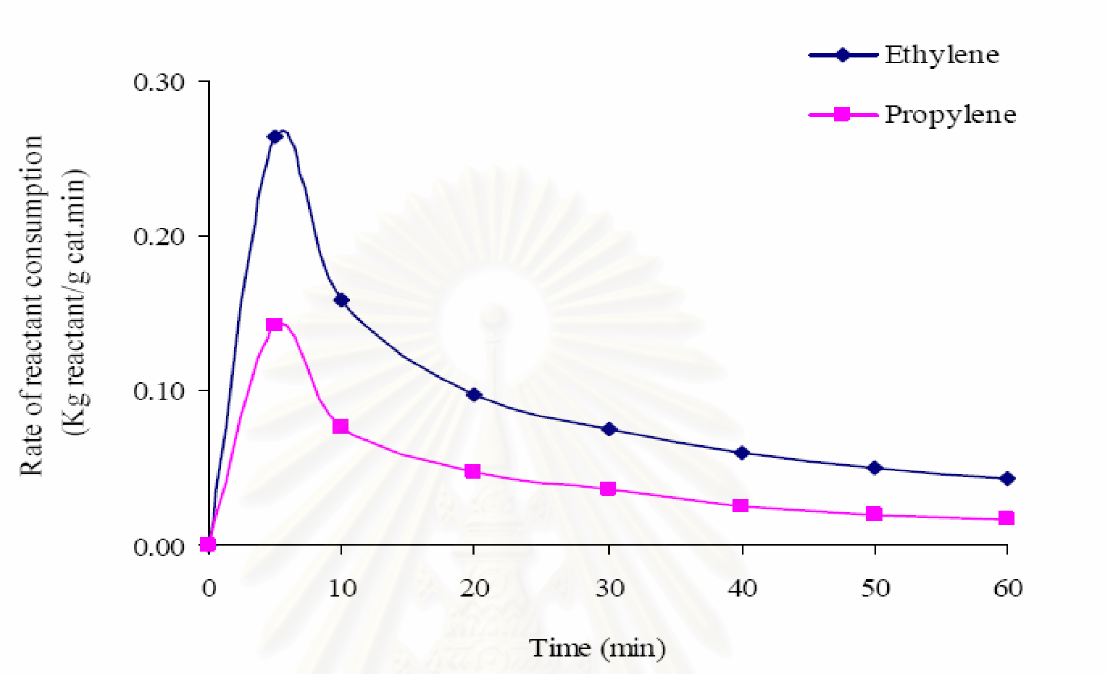


Figure B-1. Activity profiles for EP copolymerization with 1,4HD [EP (0)] at initial ethylene/propylene molar ratio 3 (batch system).

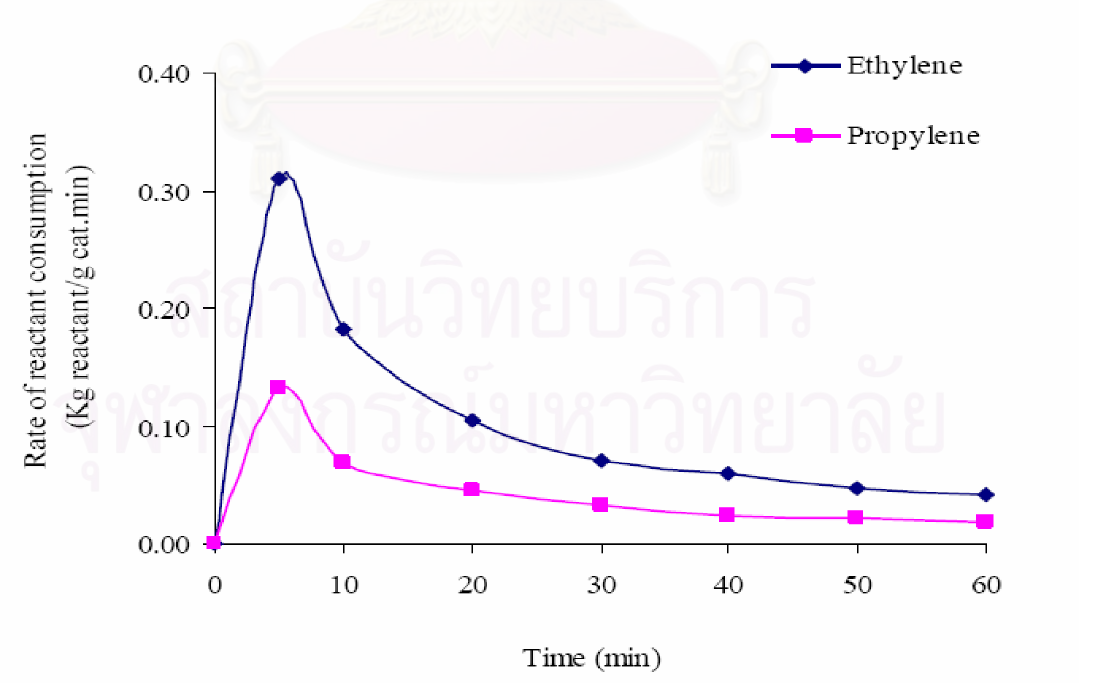


Figure B-2. Activity profiles for EP copolymerization with VCH [EP (1)] at initial ethylene/propylene molar ratio 3 (batch system).

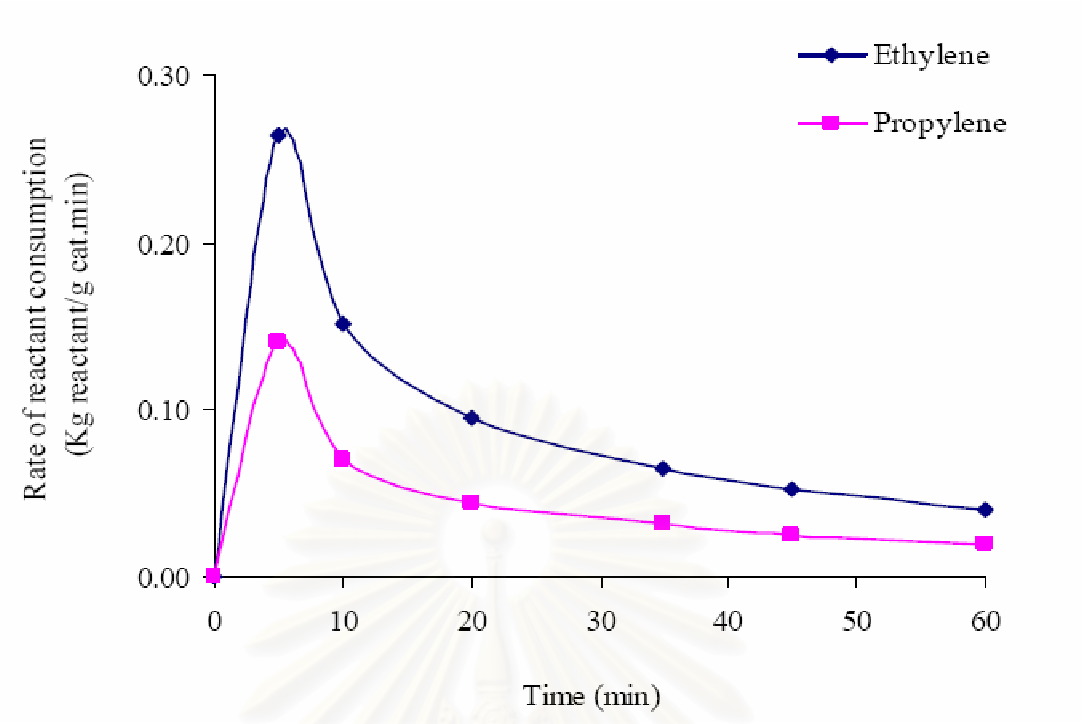


Figure B-3. Activity profiles for EP copolymerization with ENB [EP (2)] at initial ethylene/propylene molar ratio 3 (batch system).

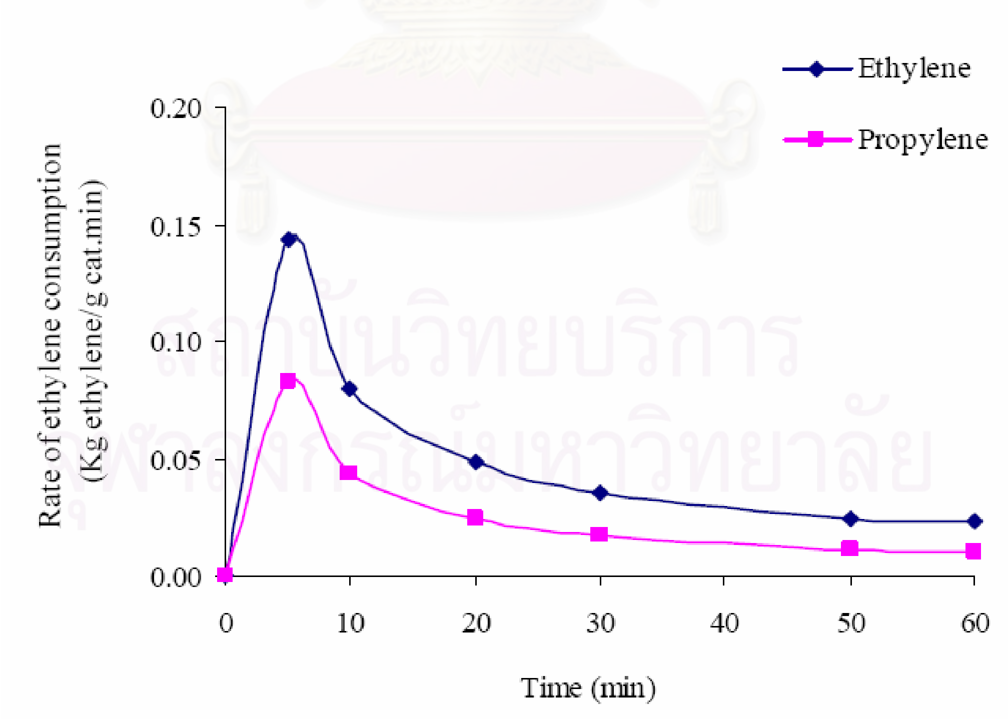


Figure B-4. Activity profiles for EP copolymerization [EP (3)] at initial ethylene/propylene molar ratio of 3 (batch system).

Table B-1. Calculation of Ethylene (E) and Propylene (P) rate consumption for EP copolymerization with 1,4HD [EP (0)] at initial ethylene/propylene molar ratio 3 (batch system).

Time (min)	% Mole		Total pressure (psi)	Partial pressure (psi)		Consumption (psi)		Mole monomer		Ethylene (Kg)	Kg ethylene/ g cat.min	Propylene (Kg)	Kg propylene / g cat.min
	E	P		E	P	E	P	E	P				
0	76.64	23.36	260	199.26	60.74	0	0	0	0	0	0	0	0
5	78.17	21.83	170	132.90	37.10	66.36	23.64	1.76E-02	6.26E-03	4.92E-04	0.264	2.63E-04	0.141
10	77.34	22.66	155	119.88	35.12	79.38	25.62	2.10E-02	6.79E-03	5.89E-04	0.158	2.85E-04	0.076
20	77.85	22.15	130	101.20	28.80	98.06	31.94	2.60E-02	8.46E-03	7.27E-04	0.097	3.55E-04	0.048
30	77.80	22.20	110	85.58	24.42	113.68	36.32	3.01E-02	9.62E-03	8.43E-04	0.075	4.04E-04	0.036
40	74.52	25.48	105	78.25	26.75	121.01	33.99	3.20E-02	9.00E-03	8.97E-04	0.060	3.78E-04	0.025
50	72.23	27.77	100	72.23	27.77	127.03	32.97	3.36E-02	8.73E-03	9.42E-04	0.051	3.67E-04	0.020
60	71.65	28.35	95	68.07	26.93	131.19	33.81	3.47E-02	8.96E-03	9.73E-04	0.043	3.76E-04	0.017

Conditions : Et[Ind]$_2$ZrCl$_2$, [Zr] = 30 µM, [Al]/[Zr] = 2000, Temp. = 40°C, Time 1 hr.

% Mole of E and P obtained from GC
Total pressure in reactor vary with time
Partial pressure = % Mole from GC × Total pressure in reactor
Consumption = Partial pressure at t_i - Partial pressure at t_0 ; ti = 5, 10, 20, 30, 40,50 and 60, t_0 = 0
Mole monomer calculated from ideal gas law (PV = nRT) ; Assumption : Propylene was in gas phase
Ethylene (Kg) = Mole of E monomer × MW of ethylene
Propylene (Kg) = Mole of P monomer × MW of propylene
g cat.min = Mole of Et[Ind]$_2$ZrCl$_2$ × MW of Et[Ind]$_2$ZrCl$_2$

Table B-2. Calculation of Ethylene (E) and Propylene (P) rate consumption for EP copolymerization with VCH [EP (1)] at initial ethylene/propylene molar ratio 3 (batch system).

Time (min)	% Mole		Total pressure (psi)	Partial pressure (psi)		Consumption (psi)		Mole monomer		Ethylene (Kg)	Kg ethylene/ g cat.min	Propylene (Kg)	Kg propylene / g cat.min
	E	P		E	P	E	P	E	P				
0	76.91	23.09	265	203.80	61.20	0	0	0	0	0	0	0	0
5	76.21	23.79	165	125.74	39.26	78.06	21.94	2.07E-02	5.81E-03	5.79E-04	0.310	2.44E-04	0.131
10	74.61	25.39	150	111.92	38.08	91.88	23.12	2.43E-02	6.12E-03	6.81E-04	0.183	2.57E-04	0.069
20	75.75	24.25	130	98.47	31.53	105.33	29.67	2.79E-02	7.86E-03	7.81E-04	0.105	3.30E-04	0.044
30	77.16	22.84	125	96.44	28.56	107.36	32.64	2.84E-02	8.65E-03	7.96E-04	0.071	3.63E-04	0.032
40	74.69	25.31	115	85.90	29.10	117.90	32.10	3.12E-02	8.50E-03	8.74E-04	0.059	3.57E-04	0.024
50	77.44	22.56	110	85.18	24.82	118.62	36.38	3.14E-02	9.64E-03	8.80E-04	0.047	4.05E-04	0.022
60	75.99	24.01	105	79.79	25.21	124.01	35.99	3.28E-02	9.53E-03	9.20E-04	0.041	4.00E-04	0.018

Table B-3. Calculation of Ethylene (E) and Propylene (P) rate consumption for EP copolymerization with ENB [EP (2)] at initial ethylene/propylene molar ratio 3 (batch system).

Time (min)	% Mole		Total pressure (psi)	Partial pressure (psi)		Consumption (psi)		Mole monomer		Ethylene (Kg)	Kg ethylene/ g cat.min	Propylene (Kg)	Kg propylene/ g cat.min
	E	P		E	P	E	P	E	P				
0	75.64	24.36	250	189.09	60.91	0	0	0	0	0	0	0	0
5	76.64	23.36	160	122.63	37.37	66.46	23.54	1.76E-02	6.23E-03	4.93E-04	2.64E-01	2.62E-04	1.40E-01
10	75.16	24.84	150	112.74	37.26	76.35	23.65	2.02E-02	6.26E-03	5.66E-04	1.52E-01	2.63E-04	7.05E-02
20	74.59	25.41	125	93.24	31.76	95.85	29.15	2.54E-02	7.72E-03	7.11E-04	9.53E-02	3.24E-04	4.35E-02
35	75.93	24.07	100	75.93	24.07	113.16	36.84	3.00E-02	9.76E-03	8.39E-04	6.43E-02	4.10E-04	3.14E-02
45	75.12	24.88	95	71.36	23.64	117.73	37.27	3.12E-02	9.87E-03	8.73E-04	5.20E-02	4.15E-04	2.47E-02
60	75.56	24.44	90	68.00	22.00	121.09	38.91	3.21E-02	1.03E-02	8.98E-04	4.01E-02	4.33E-04	1.93E-02

Table B-4. Calculation of Ethylene (E) and Propylene (P) rate consumption for EP copolymerization [EP (3)] at initial ethylene/propylene molar ratio 3 (batch system).

Time (min)	% Mole		Total pressure (psi)	Partial pressure (psi)		Consumption (psi)		Mole monomer		Ethylene (Kg)	Kg ethylene/ g cat.min	Propylene (Kg)	Kg propylene/ g cat.min
	E	P		E	P	E	P	E	P				
0	77.09	22.91	170	131.06	38.94	0	0	0	0	0	0	0	0
5	77.24	22.76	123	95.00	28.00	36.06	10.94	9.55E-03	2.90E-03	2.67E-04	0.1434	1.22E-04	0.0653
10	77.34	22.66	115	88.94	26.06	42.12	12.88	1.12E-02	3.41E-03	3.12E-04	0.0838	1.43E-04	0.0384
20	78.51	21.49	85	66.73	18.27	64.33	20.67	1.70E-02	5.48E-03	4.77E-04	0.0639	2.30E-04	0.0308
30	77.70	22.30	80	62.16	17.84	68.90	21.10	1.82E-02	5.59E-03	5.11E-04	0.0457	2.35E-04	0.0210
40	74.55	25.45	75	55.91	19.09	75.15	19.85	1.99E-02	5.26E-03	5.57E-04	0.0374	2.21E-04	0.0148
50	73.45	26.55	70	51.42	18.58	79.64	20.36	2.11E-02	5.39E-03	5.91E-04	0.0317	2.27E-04	0.0121
60	73.21	26.79	65	47.59	17.41	83.47	21.53	2.21E-02	5.70E-03	6.19E-04	0.0277	2.40E-04	0.0107

APPENDIX C

NUCLEAR MAGNETIC RESONANCE

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

Table C.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) = $(1/2)\ (T_{DEF} + T_A + T_C + 3\ T_G - T_B - 2\ T_H)$

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

k(PEP) = T_G

k(EPE) = T_C

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

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

Incorporation of ethylene (% mole) = k(EEE) + k(PEE+EEP) + k(PEP)

Incorporation of propylene (% mole) = k(EPE) + k(EPP+PPE) + k(PPP)

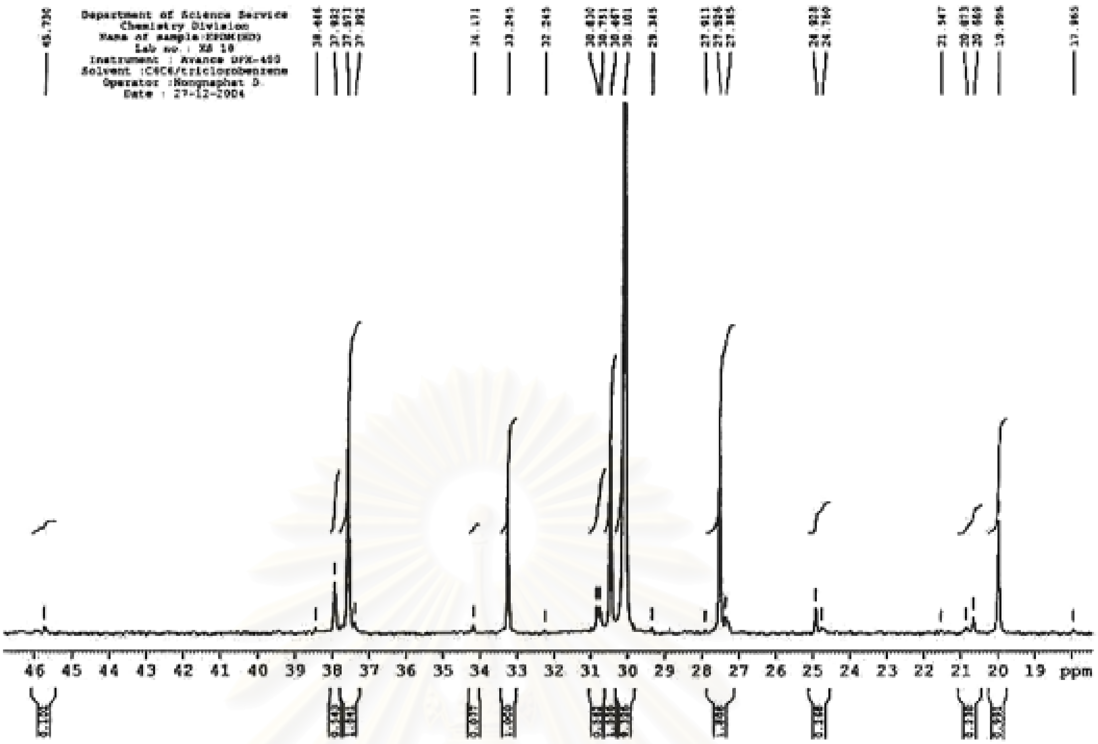


Figure C-1. ^{13}C-NMR spectrum of EP copolymer with 1,4HD [EP (0)] at initial ethylene/propylene molar ratio of 3 (batch system)

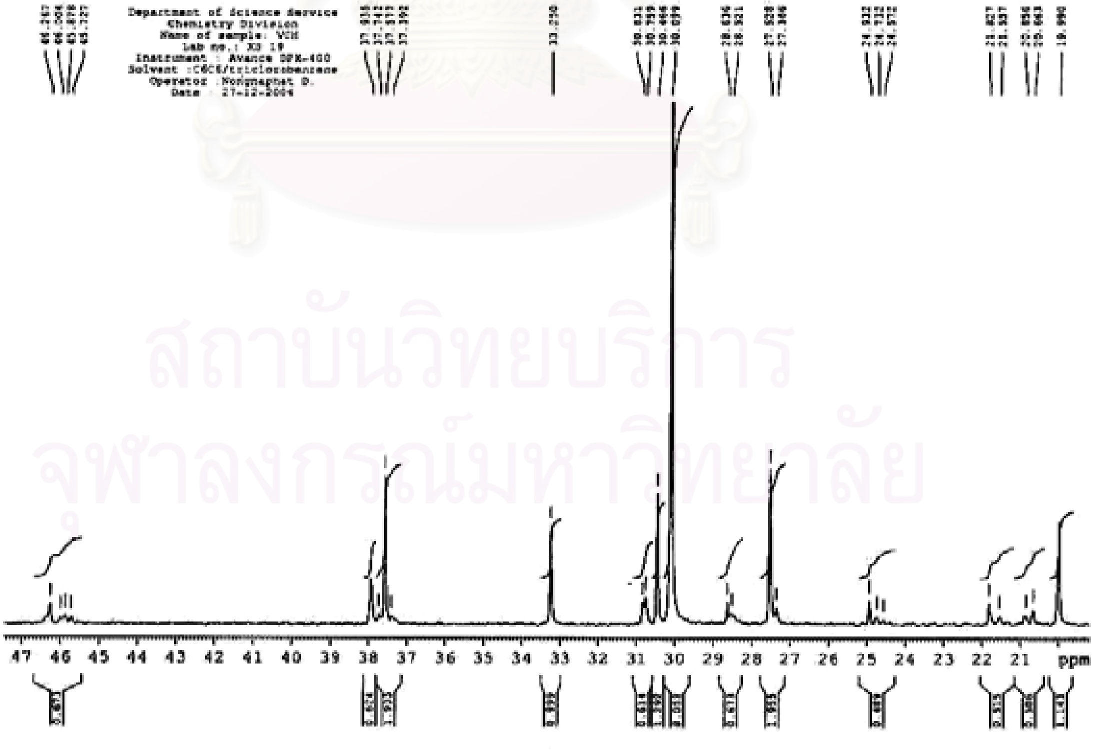


Figure C-2. ^{13}C-NMR spectrum of EP copolymer with VCH [EP (1)] at initial ethylene/propylene molar ratio of 3 (batch system)

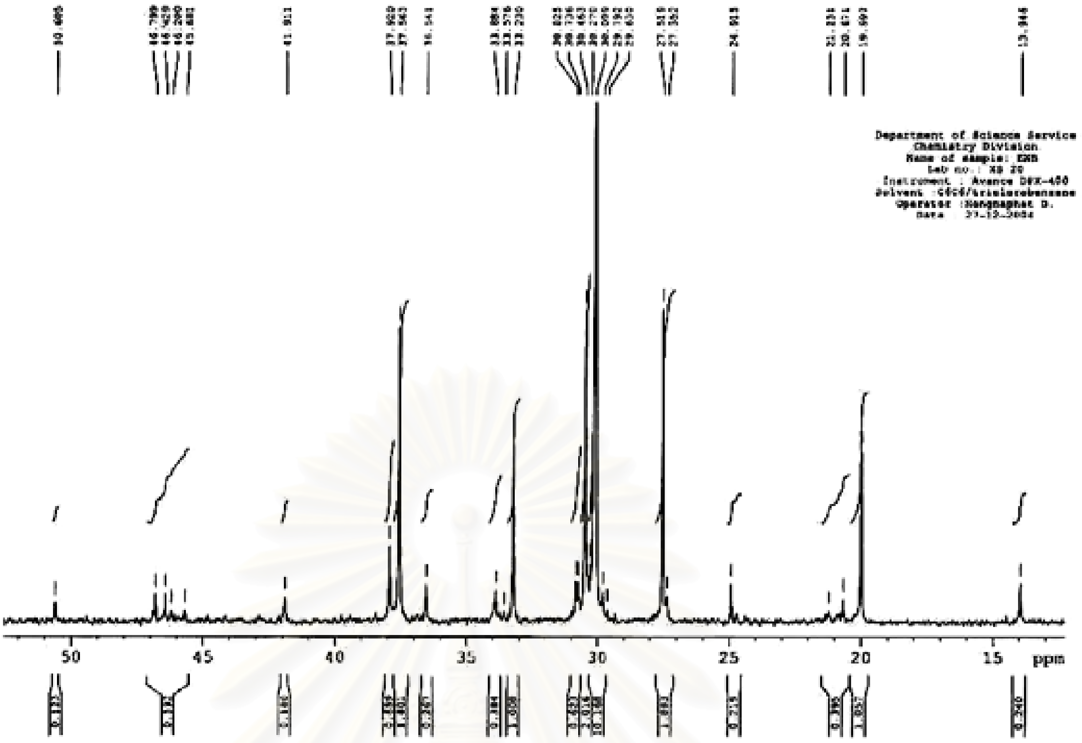


Figure C-3. ^{13}C-NMR spectrum of EP copolymer with ENB [EP (2)] at initial ethylene/propylene molar ratio of 3 (batch system)

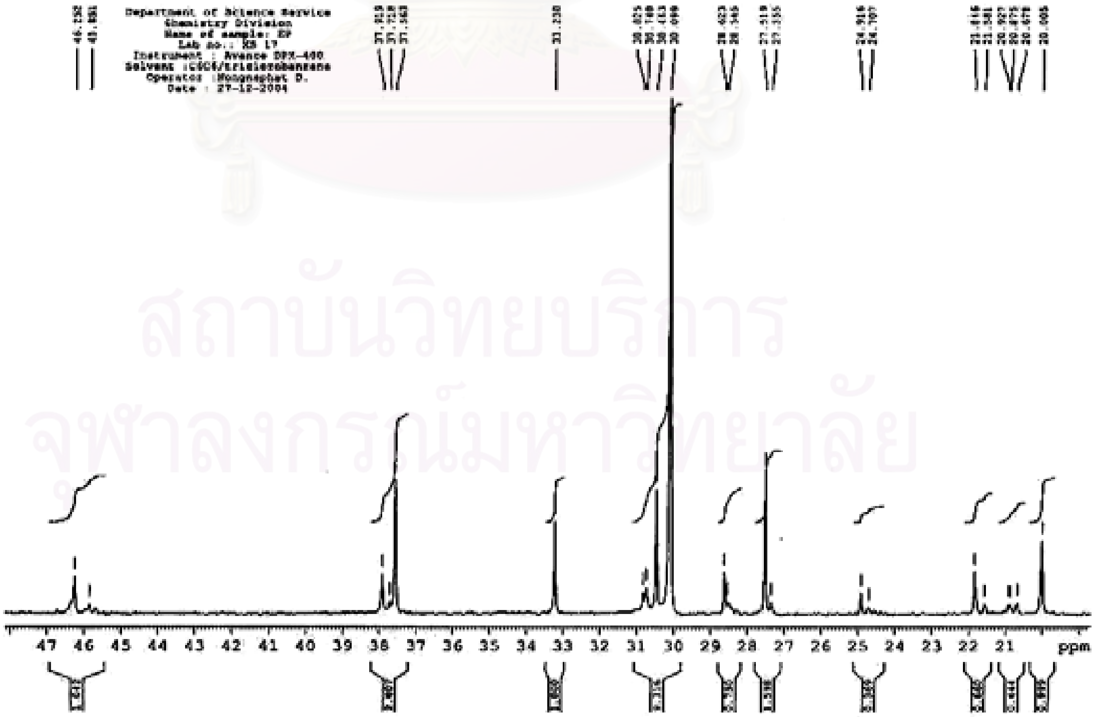


Figure C-4. ^{13}C-NMR spectrum of EP copolymer [EP (3)] at initial ethylene/ propylene molar ratio of 3 (batch system)

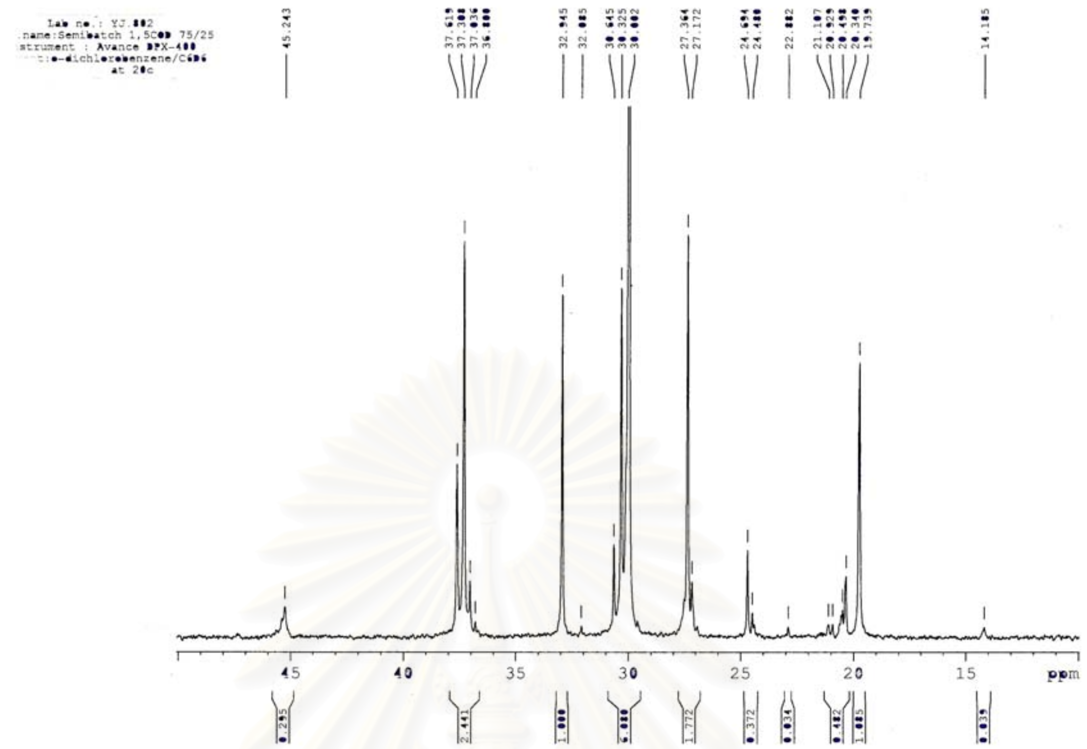


Figure C-5. ^{13}C-NMR spectrum of EP copolymer with COD [EP (0)] at initial ethylene/propylene molar ratio of 3 (semibatch system)

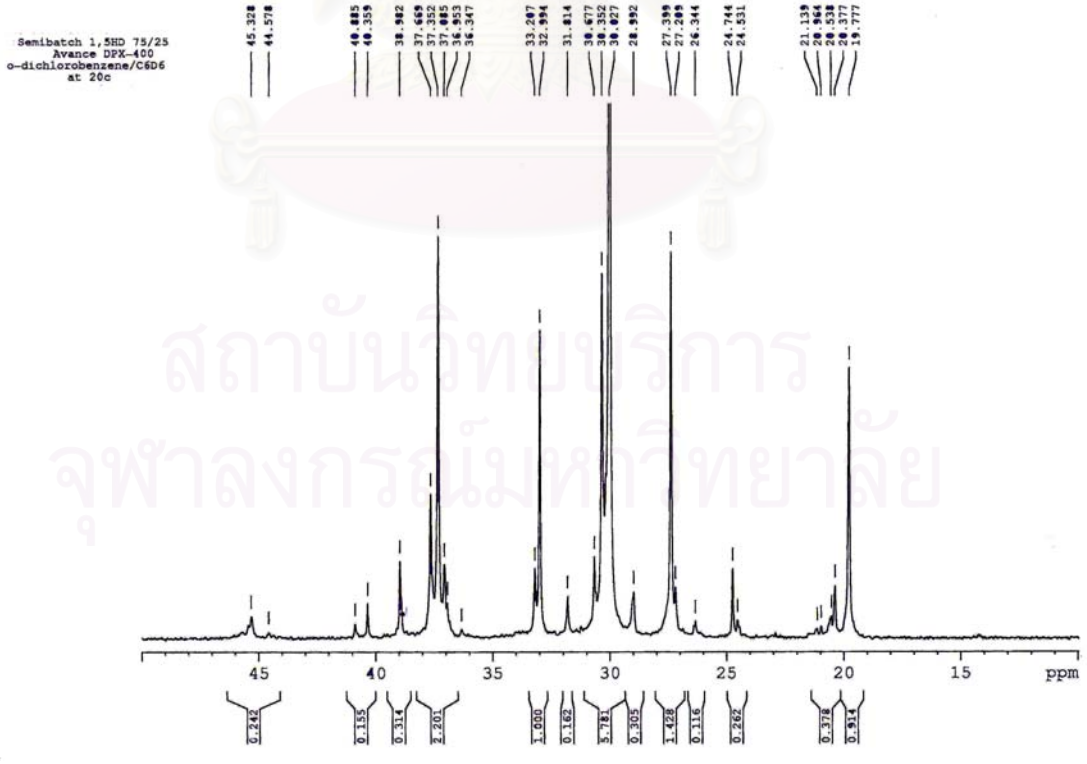


Figure C-6. ^{13}C-NMR spectrum of EP copolymer with 1,5 HD [EP (1)] at initial ethylene/propylene molar ratio of 3 (semibatch system)

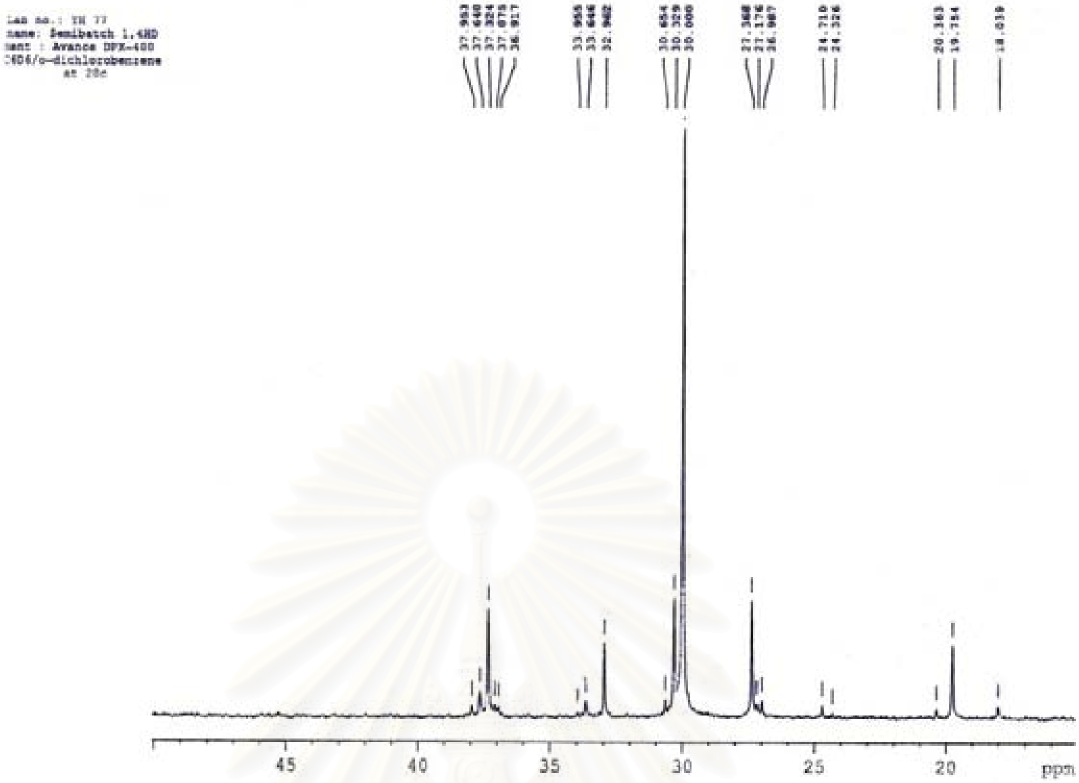


Figure C-7. ^{13}C-NMR spectrum of EP copolymer with 1,4 HD [EP (2)] at initial ethylene/propylene molar ratio of 3 (semibatch system)

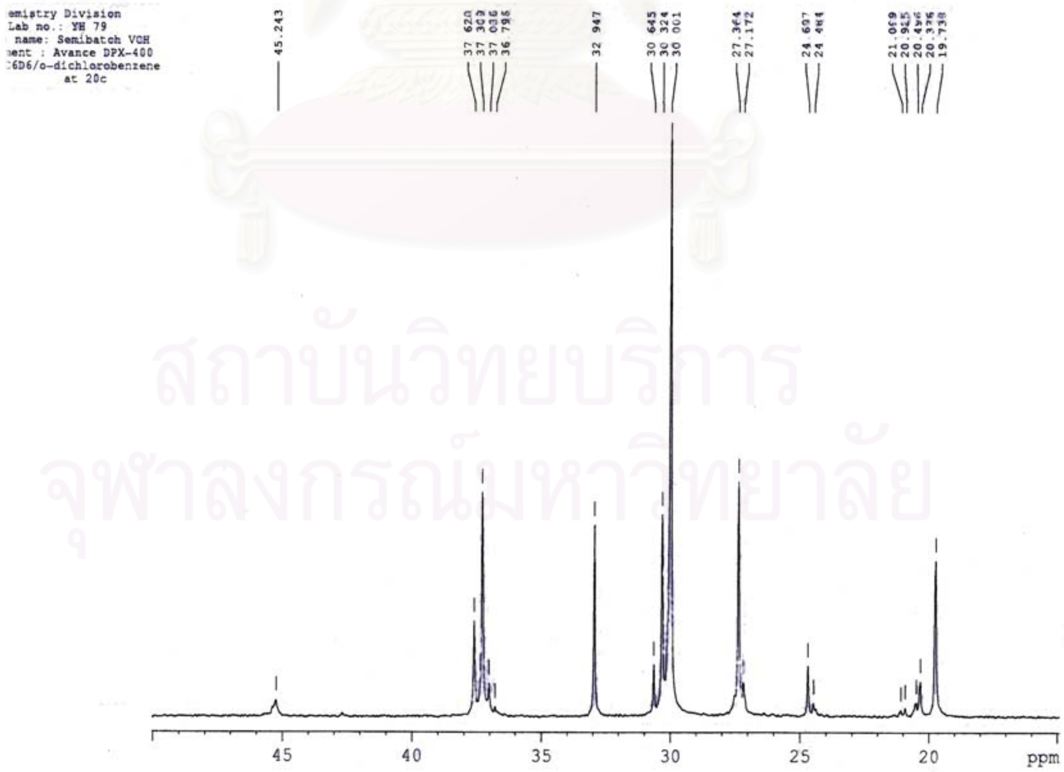


Figure C-8. ^{13}C-NMR spectrum of EP copolymer with VCH [EP (3)] at initial ethylene/propylene molar ratio of 3 (semibatch system)

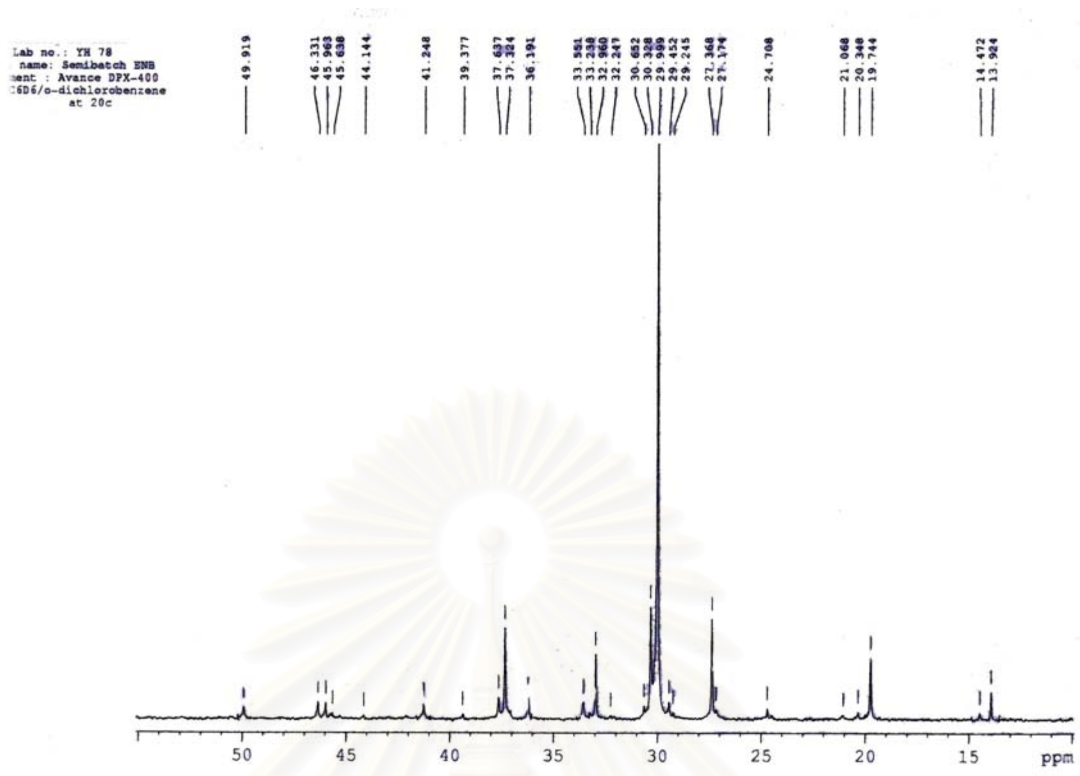


Figure C-9. ^{13}C-NMR spectrum of EP copolymer with ENB [EP (4)] at initial ethylene/propylene molar ratio of 3 (semibatch system)

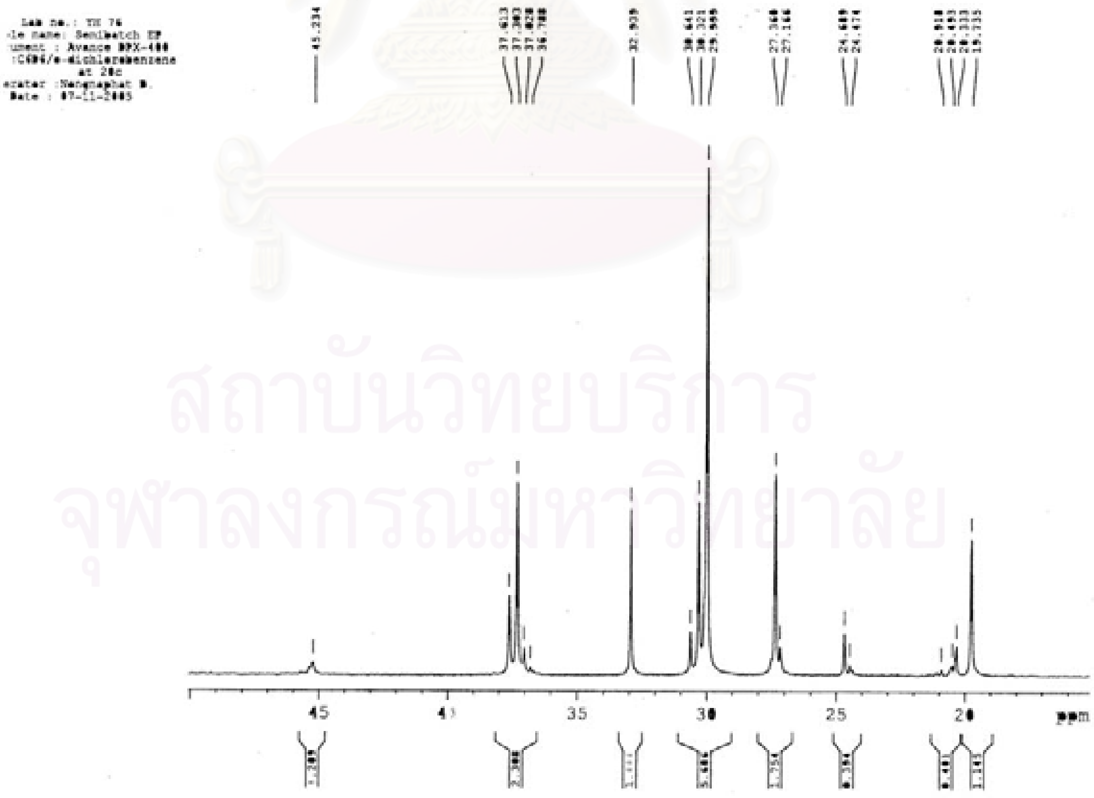


Figure C-10. ^{13}C-NMR spectrum of EP copolymer without diene [EP (5)] at initial ethylene/propylene molar ratio of 3 (semibatch system)

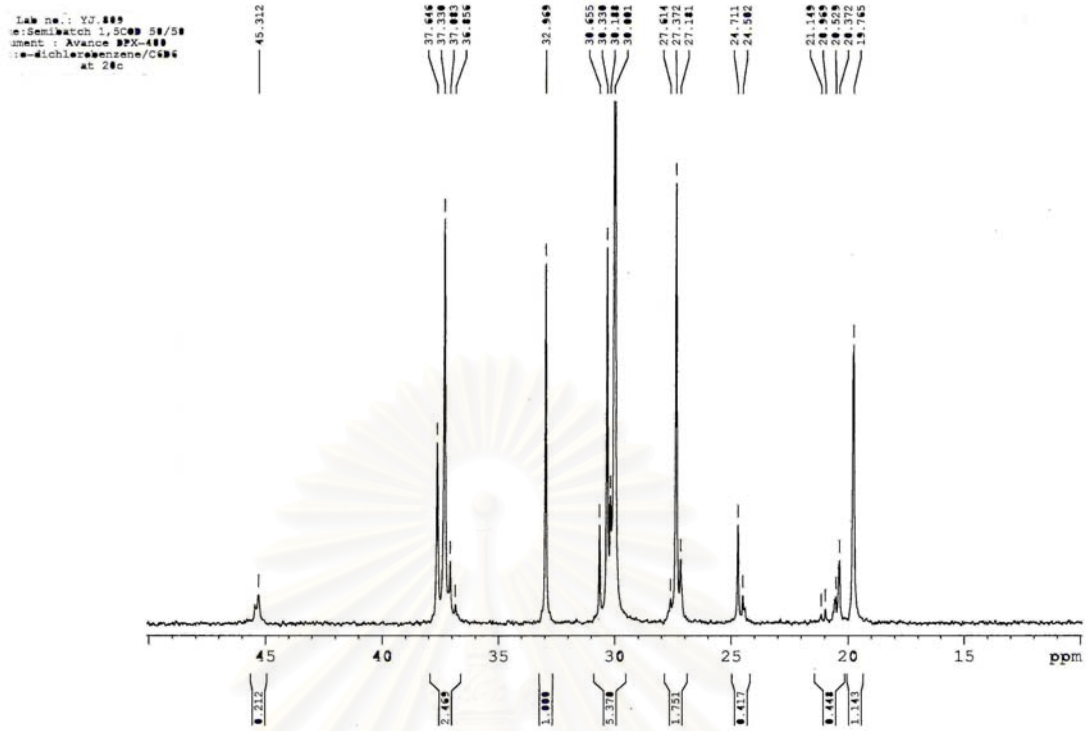


Figure C-11. ^{13}C-NMR spectrum of EP copolymer with COD [EP (6)] at initial ethylene/propylene molar ratio of 1 (semibatch system)

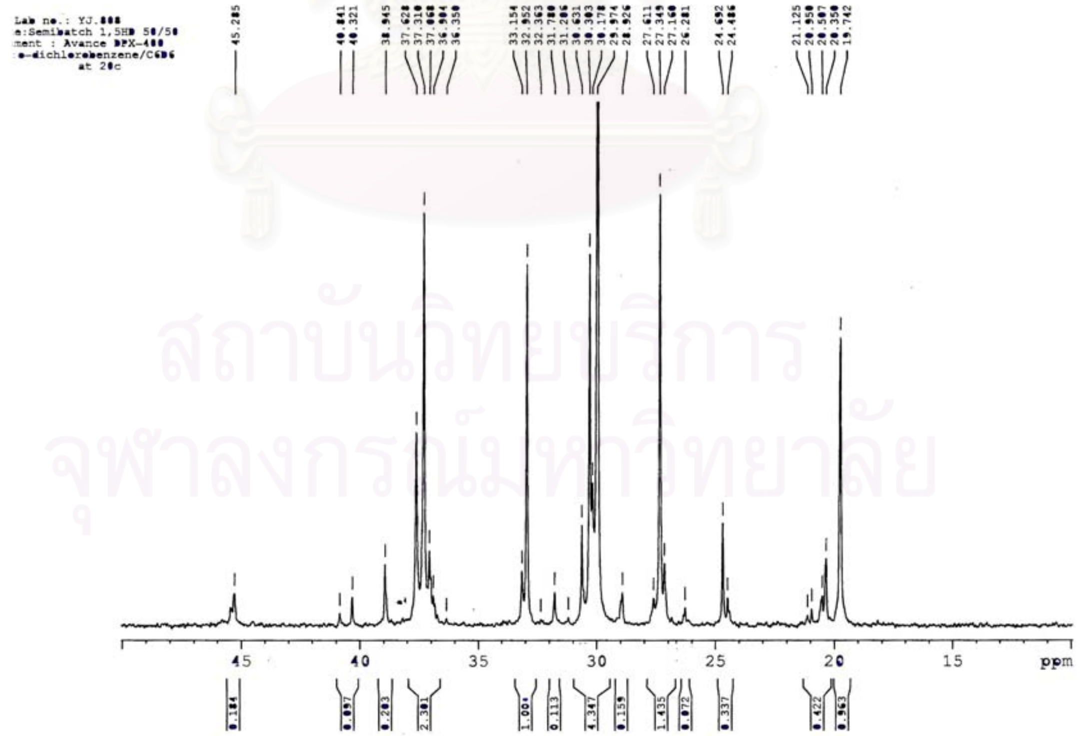


Figure C-12. ^{13}C-NMR spectrum of EP copolymer with 1,5HD [EP (7)] at initial ethylene/propylene molar ratio of 1 (semibatch system)

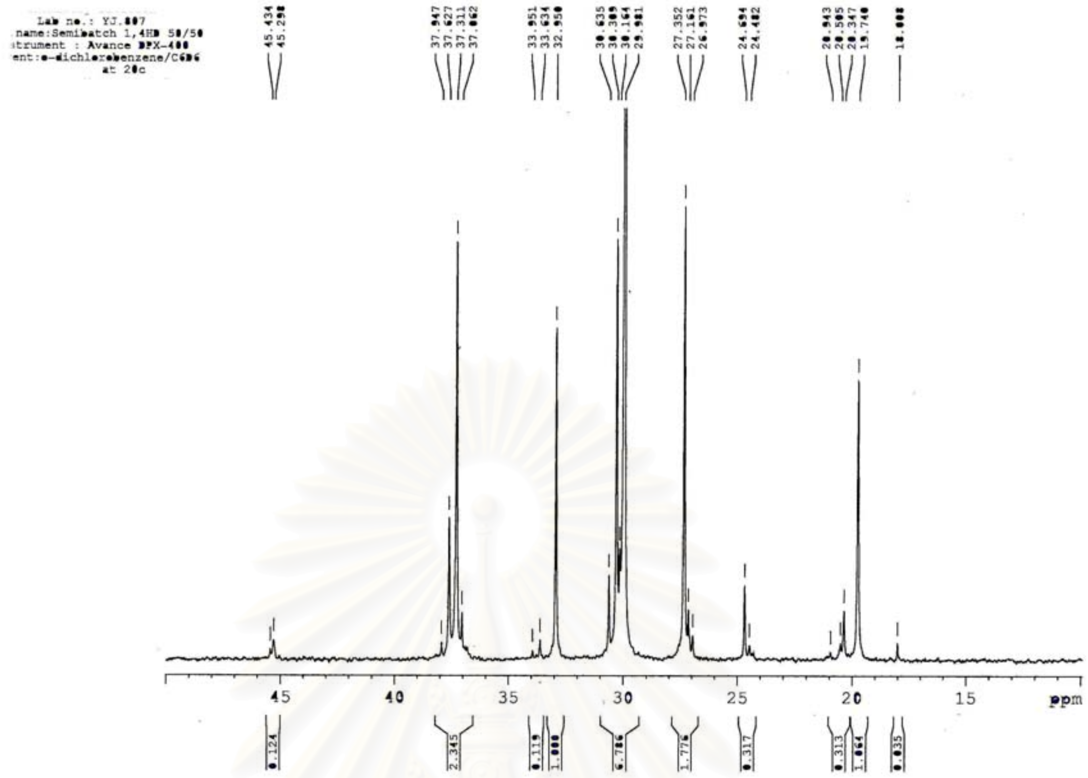


Figure C-13. ^{13}C-NMR spectrum of EP copolymer with 1,4HD [EP (8)] at initial ethylene/propylene molar ratio of 1 (semibatch system)

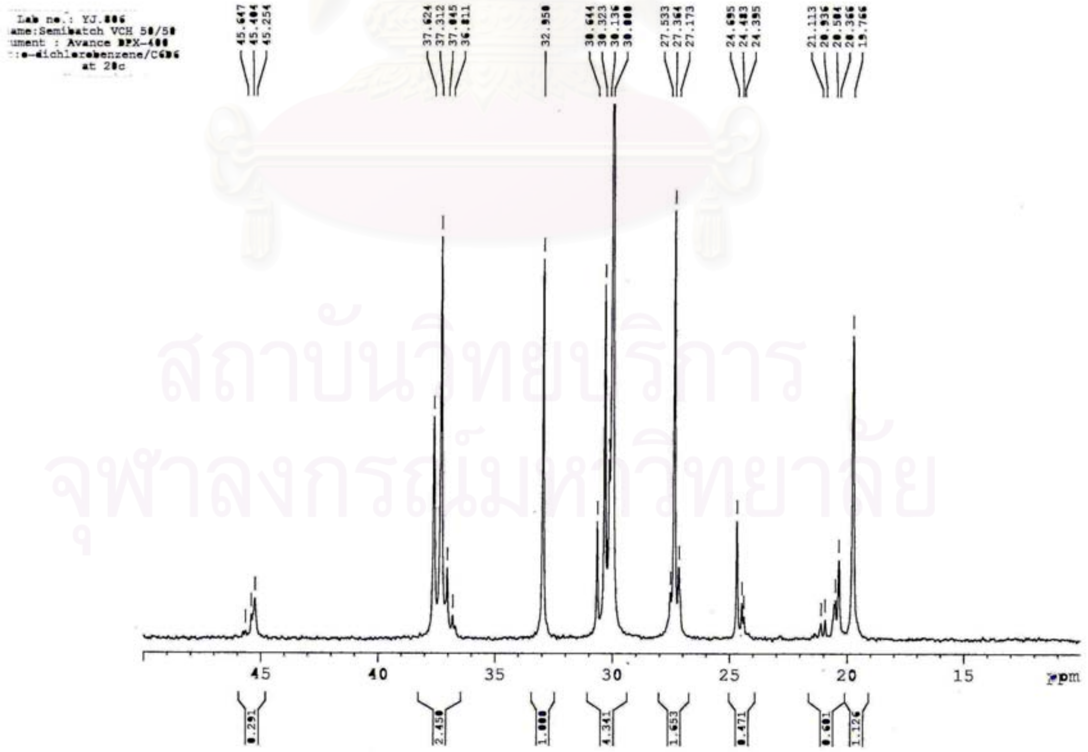


Figure C-14. ^{13}C-NMR spectrum of EP copolymer with VCH [EP (9)] at initial ethylene/propylene molar ratio of 1 (semibatch system)

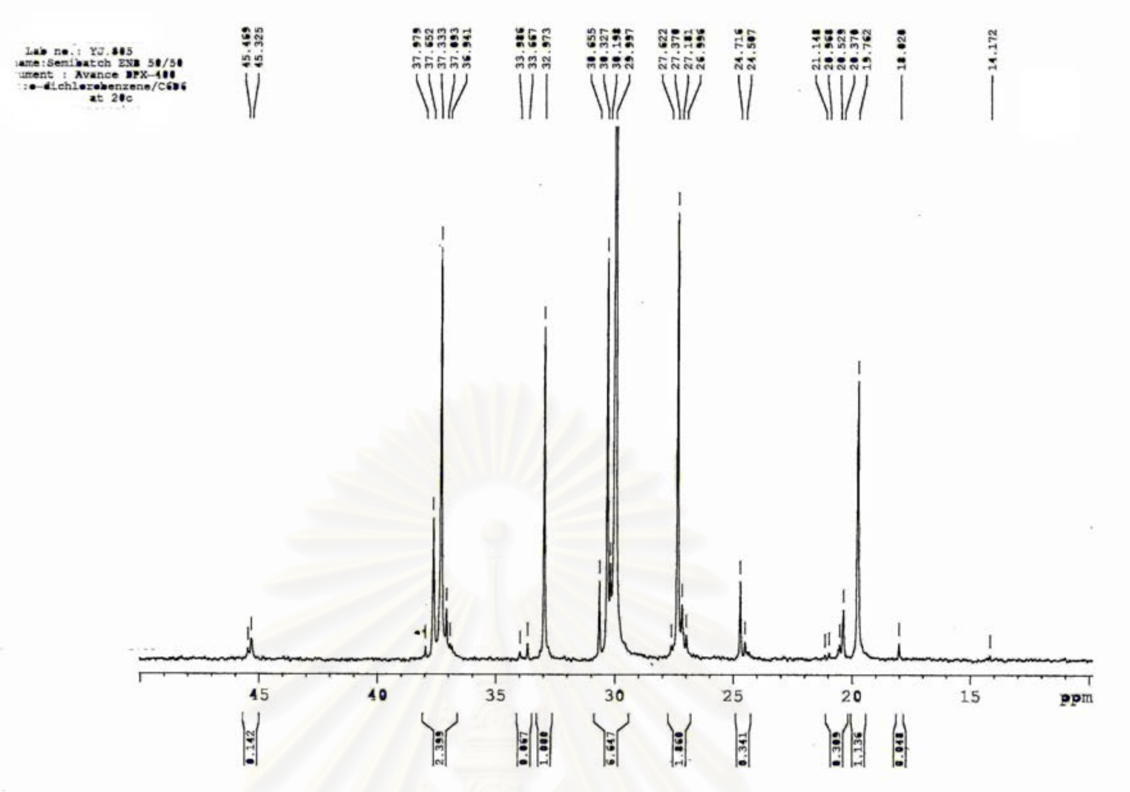


Figure C-15. ^{13}C-NMR spectrum of EP copolymer with ENB [EP (10)] at initial ethylene/propylene molar ratio of 1 (semibatch system)

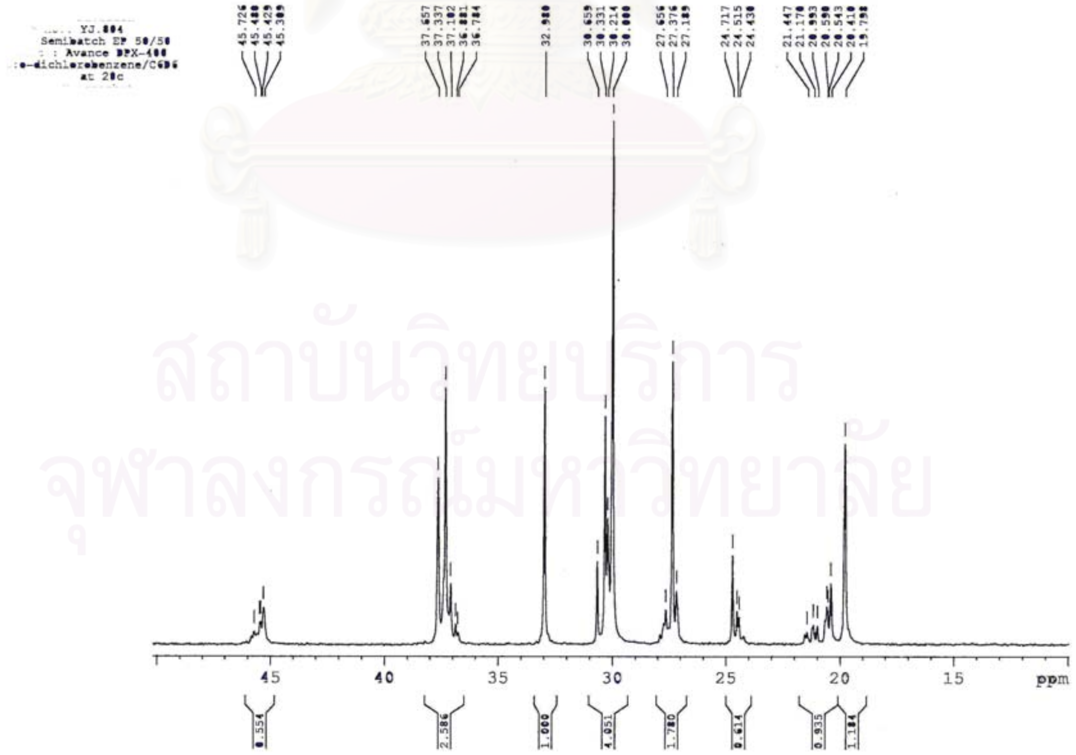


Figure C-16. ^{13}C-NMR spectrum of EP copolymer [EP (11)] at initial ethylene/propylene molar ratio of 1 (semibatch system)

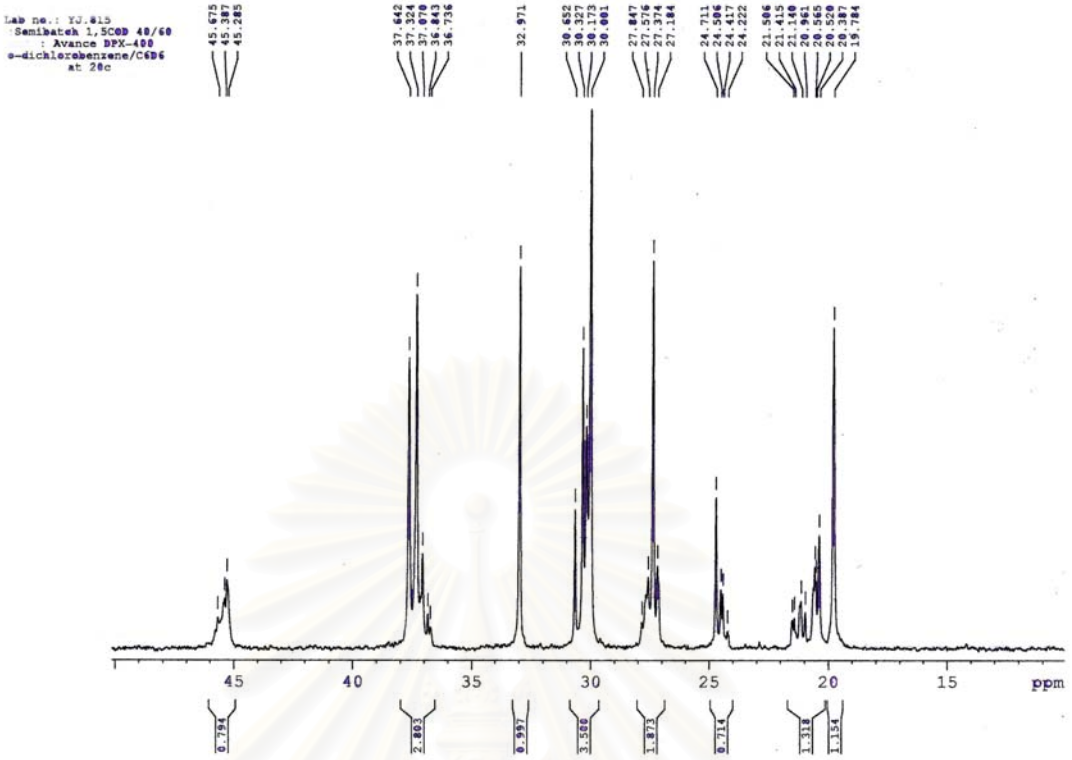


Figure C-17. ^{13}C-NMR spectrum of EP copolymer with COD [EP (12)] at initial ethylene/propylene molar ratio of 0.667 (semibatch system)

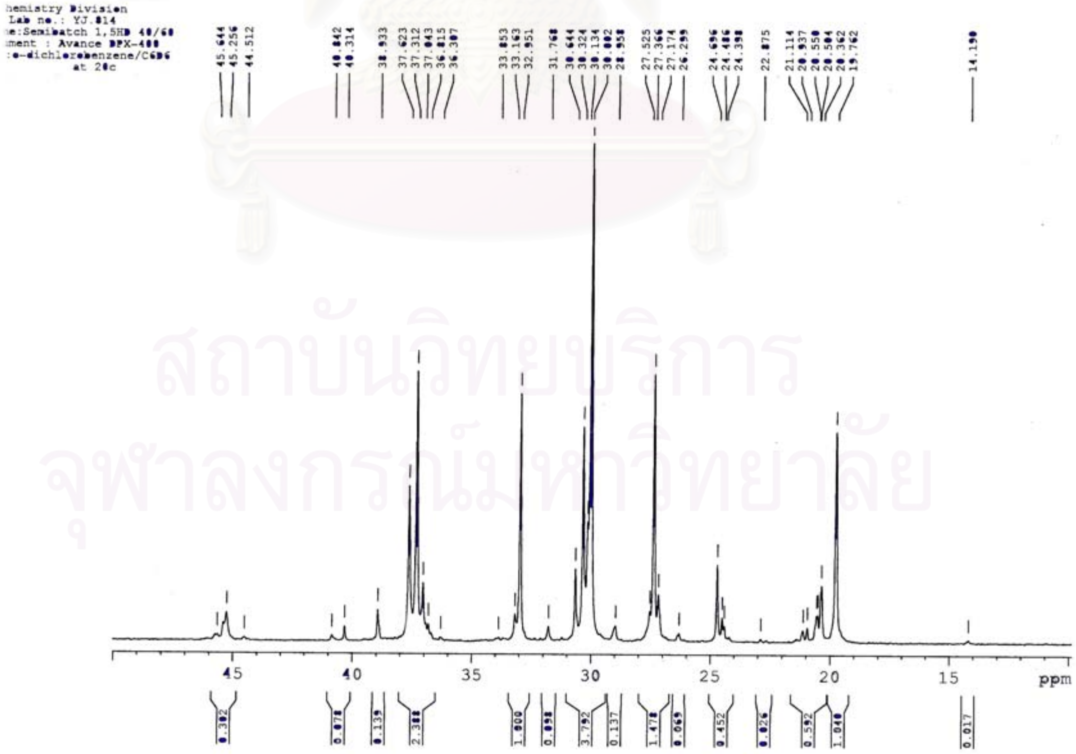


Figure C-18. ^{13}C-NMR spectrum of EP copolymer with 1,5HD [EP (13)] at initial ethylene/propylene molar ratio of 0.667 (semibatch system)

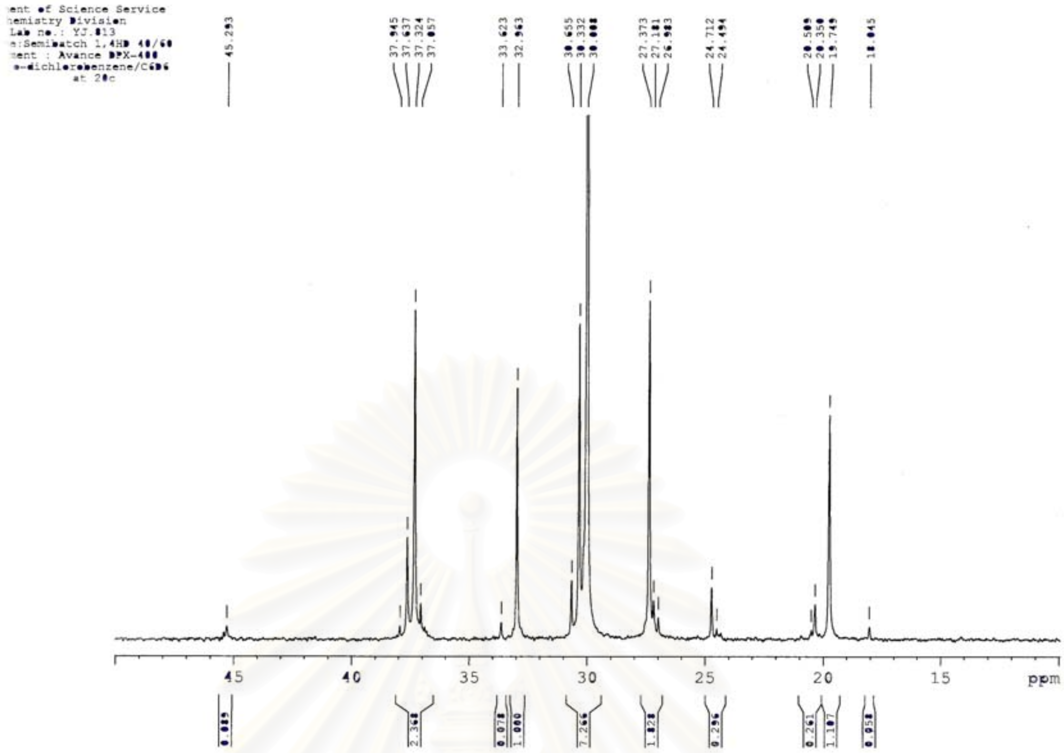


Figure C-19. ^{13}C-NMR spectrum of EP copolymer with 1,4HD [EP (14)] at initial ethylene/propylene molar ratio of 0.667 (semibatch system)

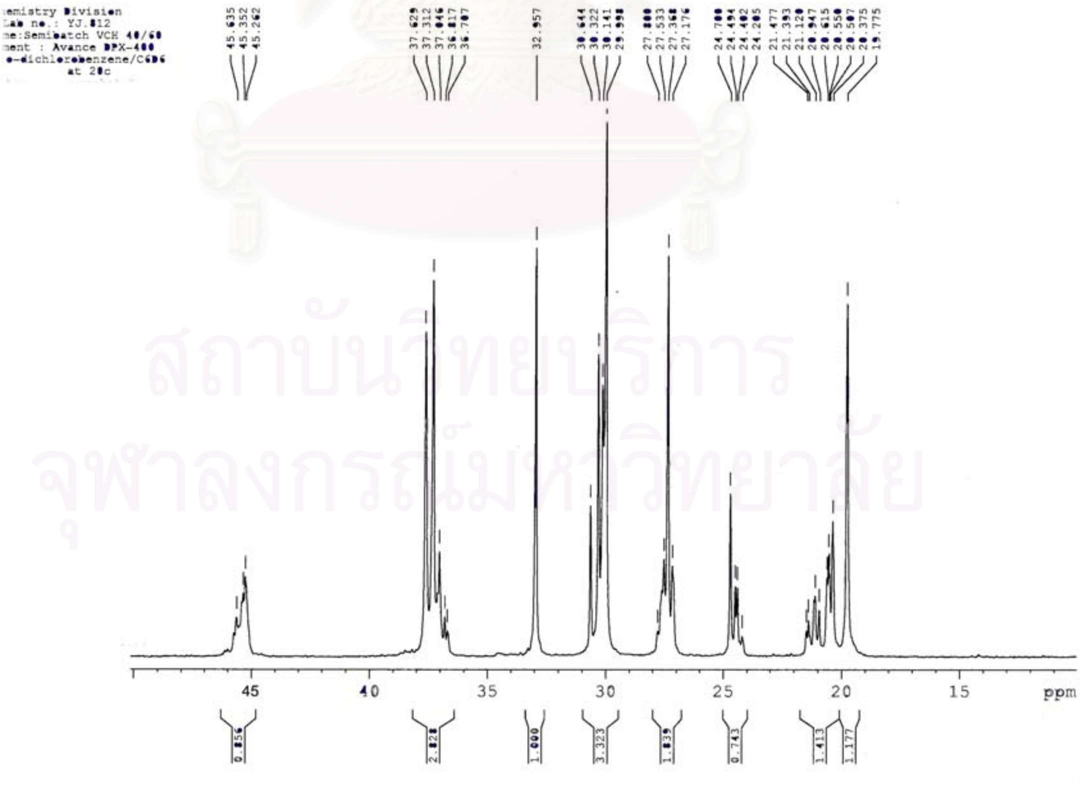


Figure C-20. ^{13}C-NMR spectrum of EP copolymer with VCH [EP (15)] at initial ethylene/propylene molar ratio of 0.667 (semibatch system)

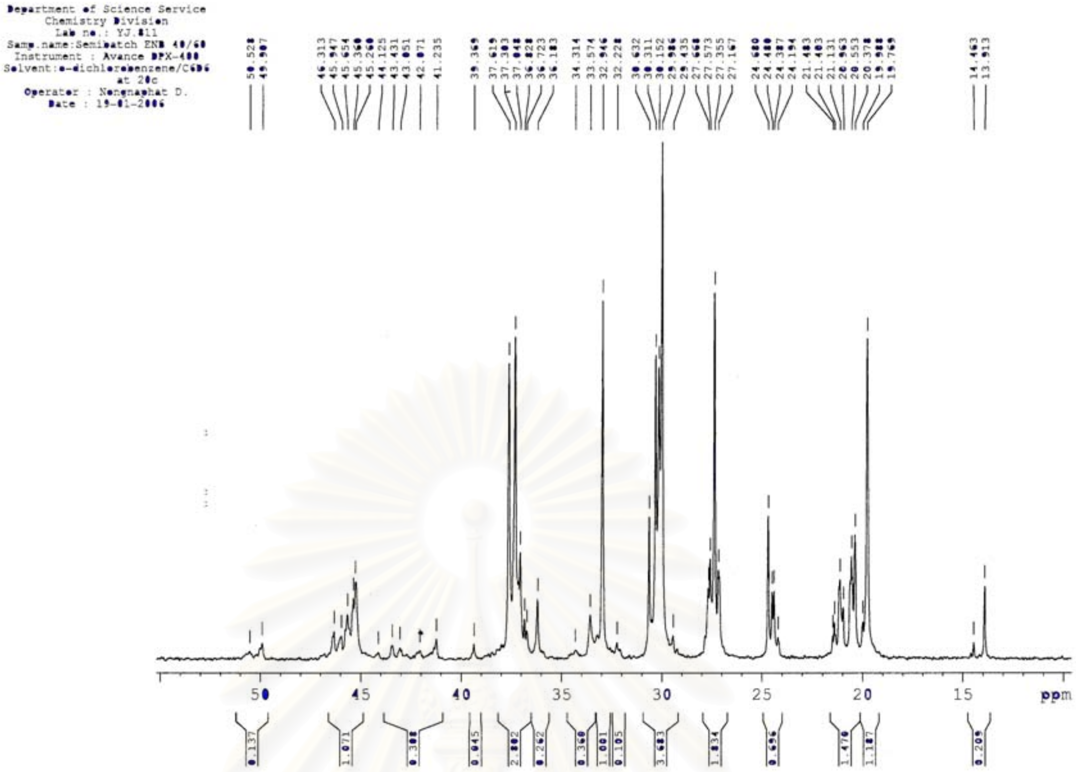


Figure C-21. ^{13}C-NMR spectrum of EP copolymer with ENB [EP (16)] at initial ethylene/propylene molar ratio of 0.667 (semibatch system)

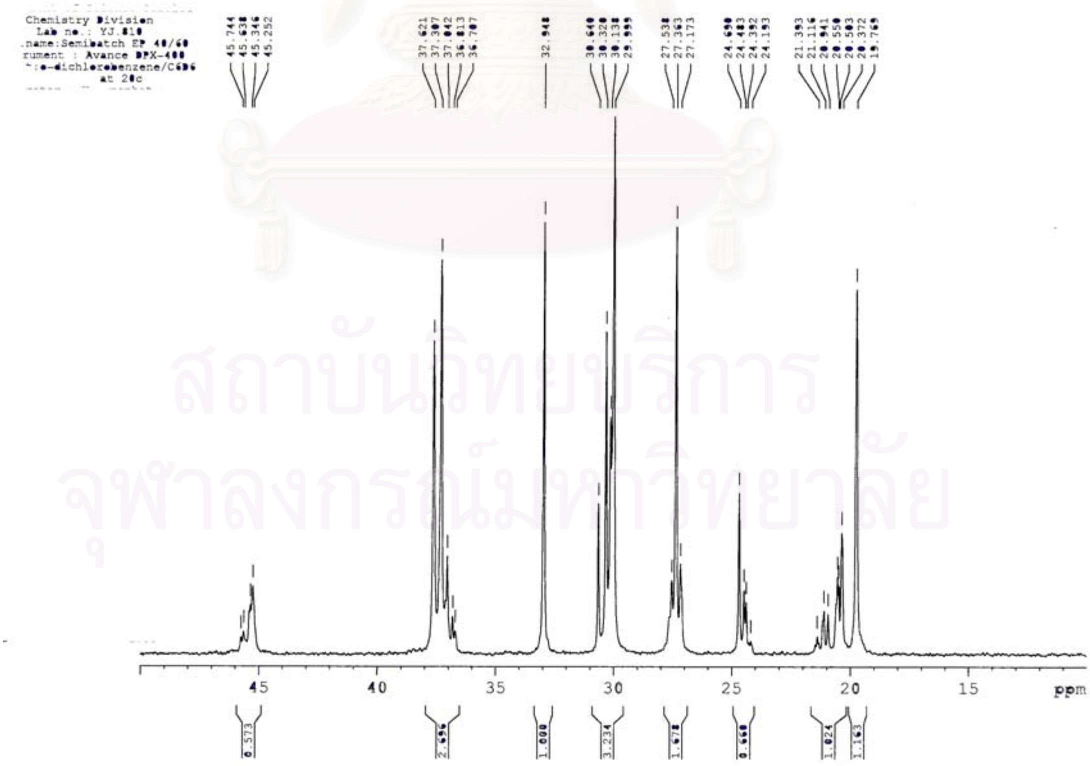


Figure C-22. ^{13}C-NMR spectrum of EP copolymer [EP (17)] at initial ethylene/propylene molar ratio of 0.667 (semibatch system)

APPENDIX D

DIFFERENTIAL SCANNING CALORIMETRY

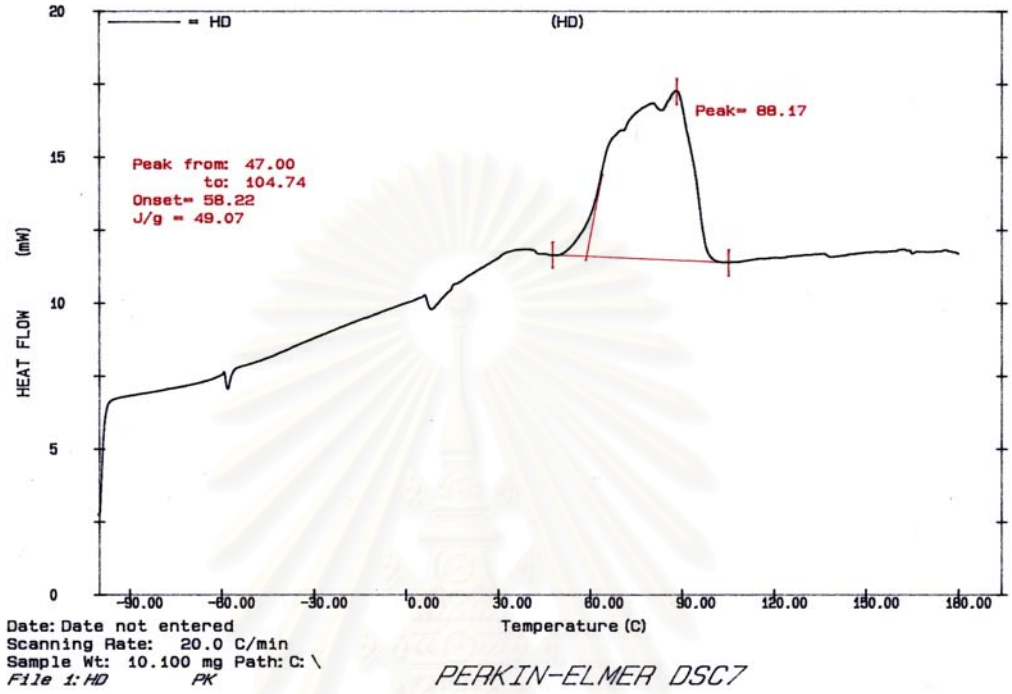


Figure D-1. DSC curve of EP copolymer with 1,4HD [EP (0)] at initial ethylene/propylene molar ratio of 3 (batch system)

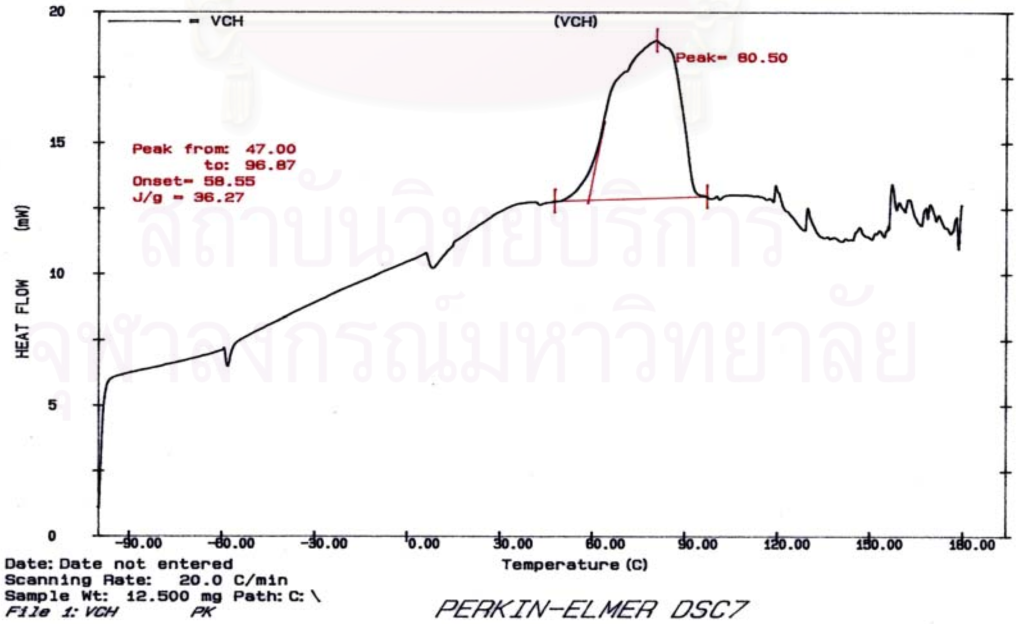


Figure D-2. DSC curve of EP copolymer with VCH [EP (1)] at initial ethylene/propylene molar ratio of 3 (batch system)

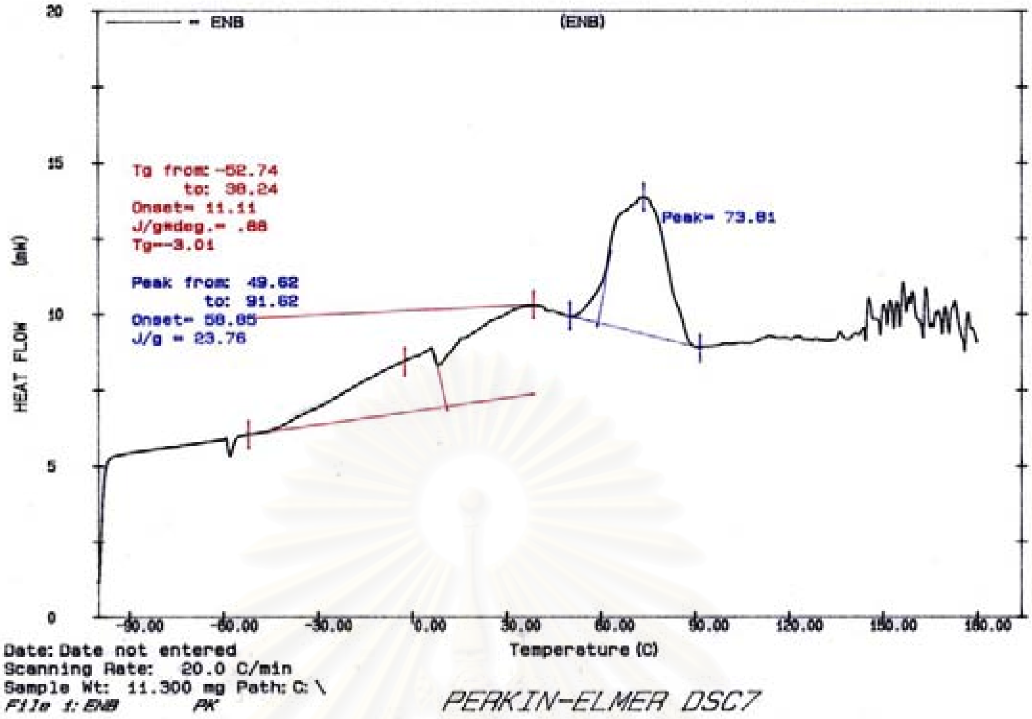


Figure D-3. DSC curve of EP copolymer with ENB [EP (2)] at initial ethylene/propylene molar ratio of 3 (batch system)

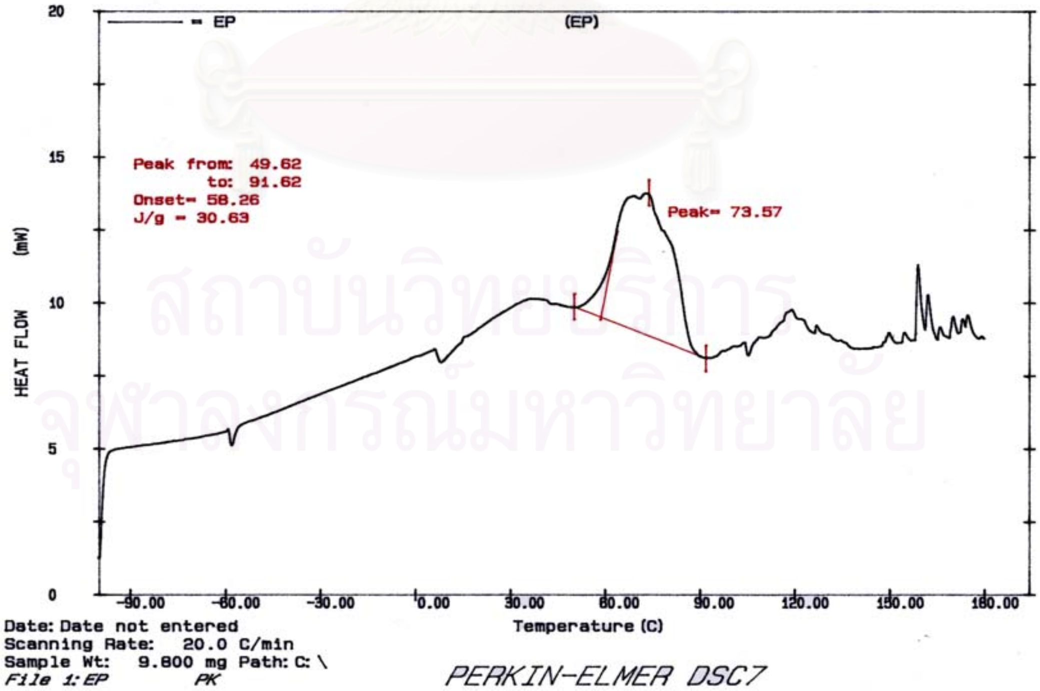


Figure D-4. DSC curve of EP copolymer [EP (3)] at initial ethylene/propylene molar ratio of 3 (batch system)

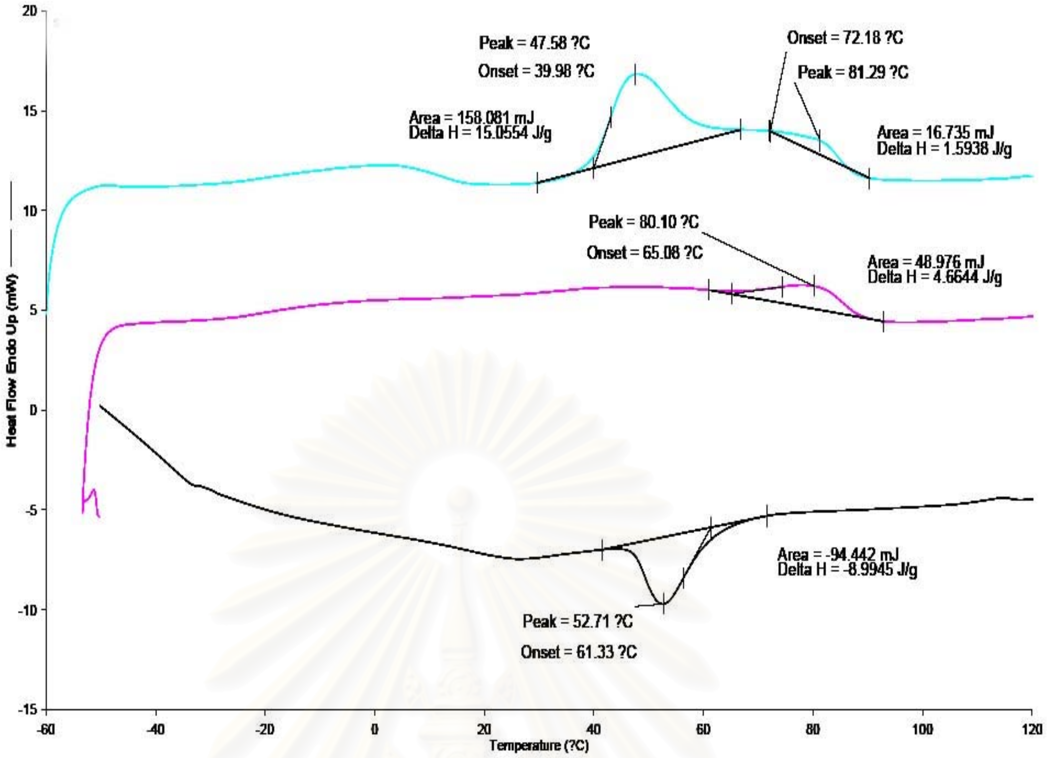


Figure D-5. DSC curve of EP copolymer with COD [EP (0)] at initial ethylene/propylene molar ratio of 3 (semibatch system)

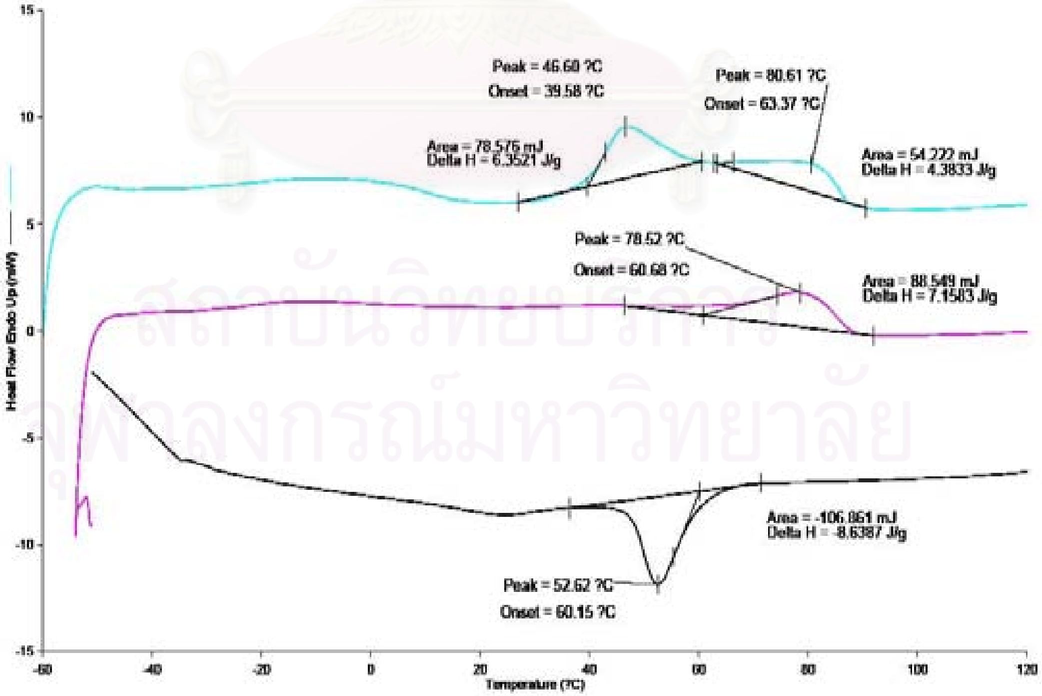


Figure D-6. DSC curve of EP copolymer with 1,5HD [EP (1)] at initial ethylene/propylene molar ratio of 3 (semibatch system)

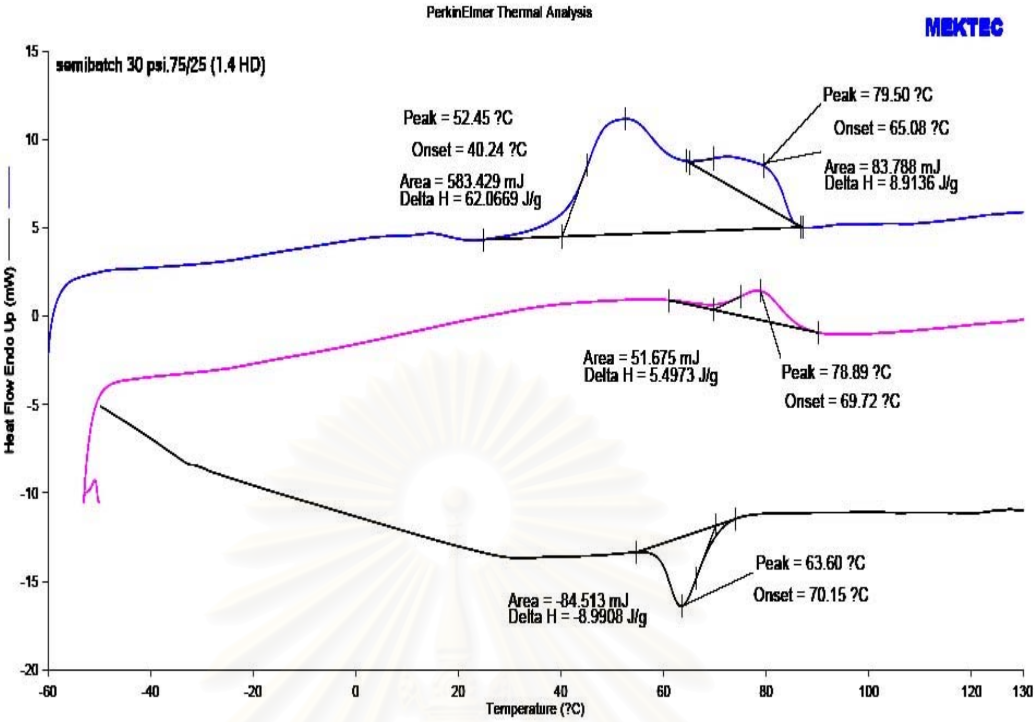


Figure D-7. DSC curve of EP copolymer with 1,4HD [EP (2)] at initial ethylene/propylene molar ratio of 3 (semibatch system)

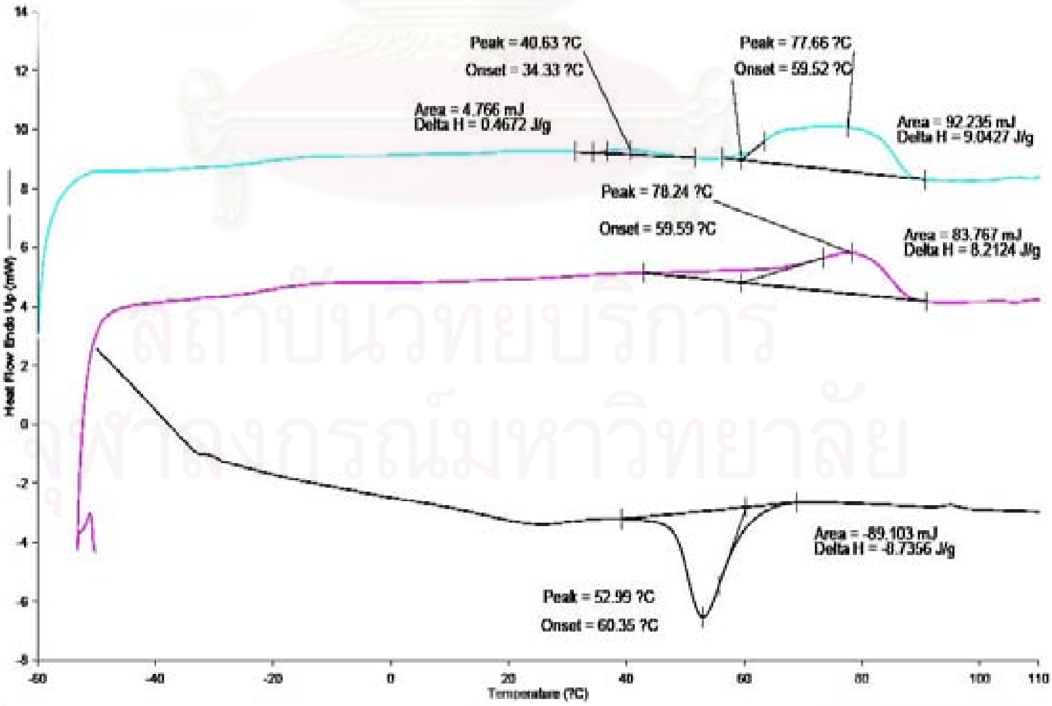


Figure D-8. DSC curve of EP copolymer with VCH [EP (3)] at initial ethylene/propylene molar ratio of 3 (semibatch system)

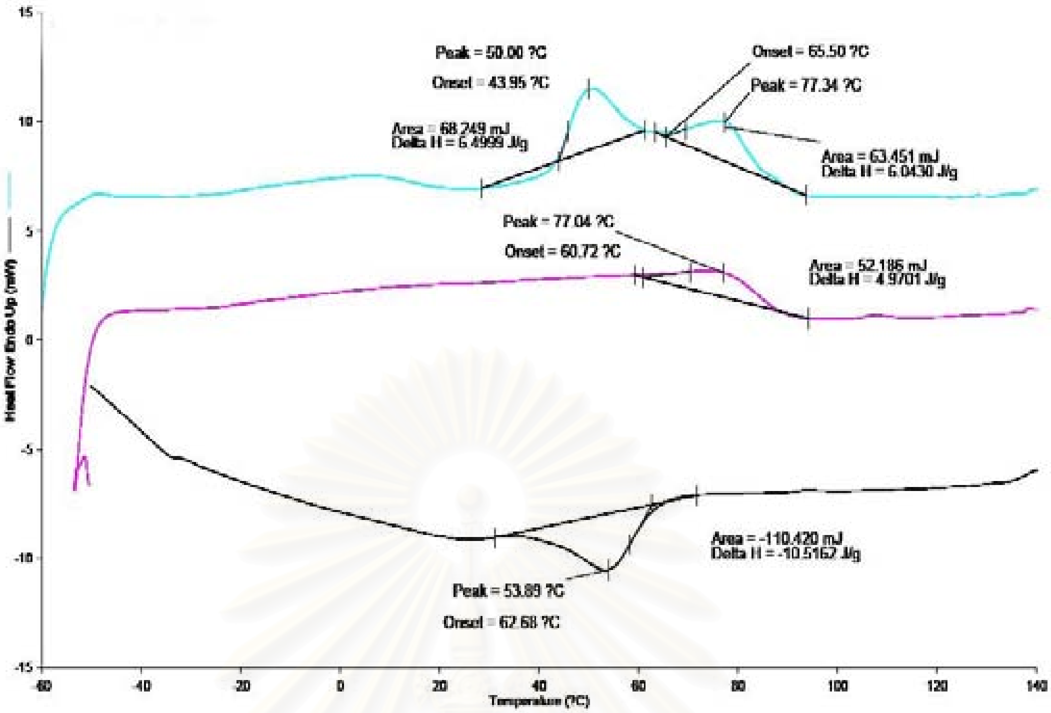


Figure D-9. DSC curve of EP copolymer with ENB [EP (4)] at initial ethylene/propylene molar ratio of 3 (semibatch system)

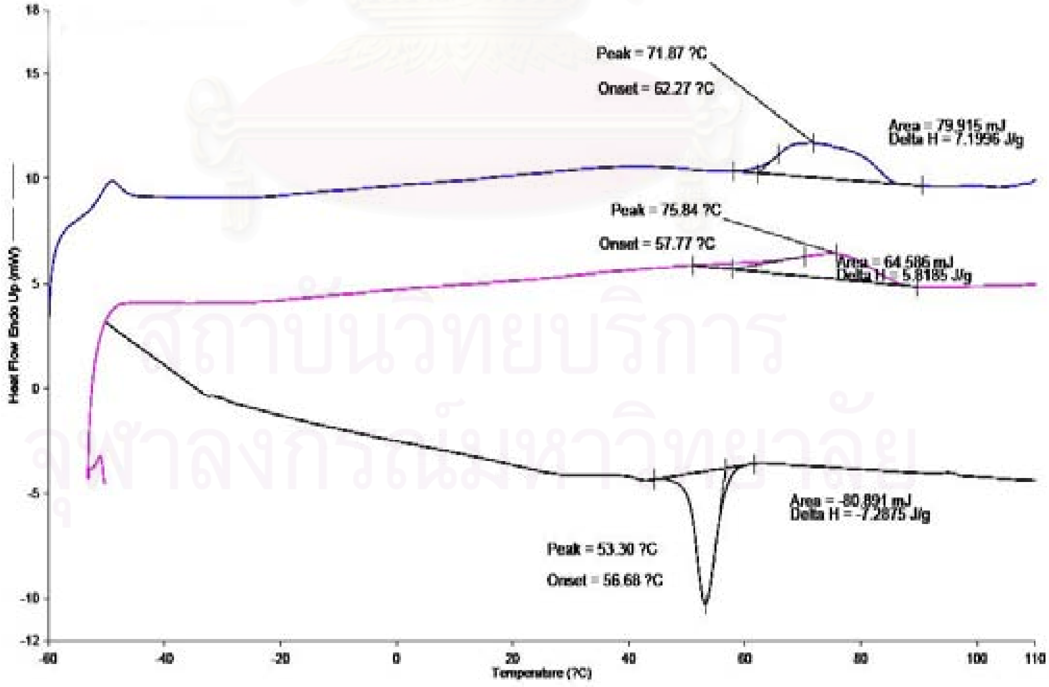


Figure D-10 DSC curve of EP copolymer [EP (5)] at initial ethylene/ propylene molar ratio of 3 (semibatch system)

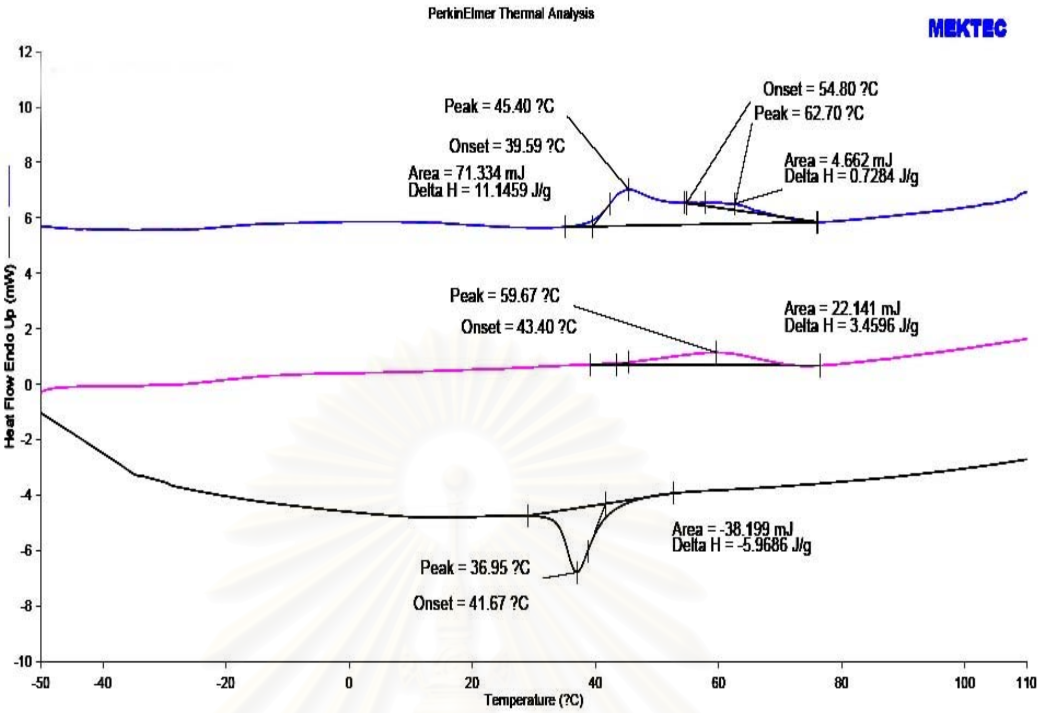


Figure D-11. DSC curve of EP copolymer with COD [EP (6)] at initial ethylene/propylene molar ratio of 1 (semibatch system)

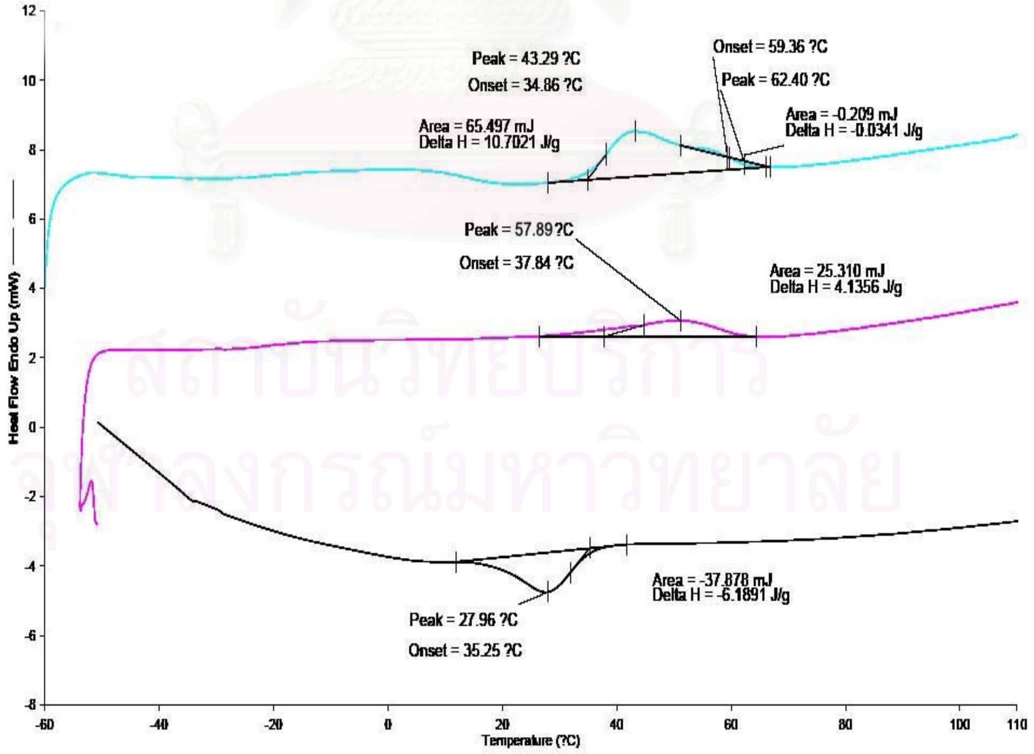


Figure D-12. DSC curve of EP copolymer with 1,5HD [EP (7)] at initial ethylene/propylene molar ratio of 1 (semibatch system)

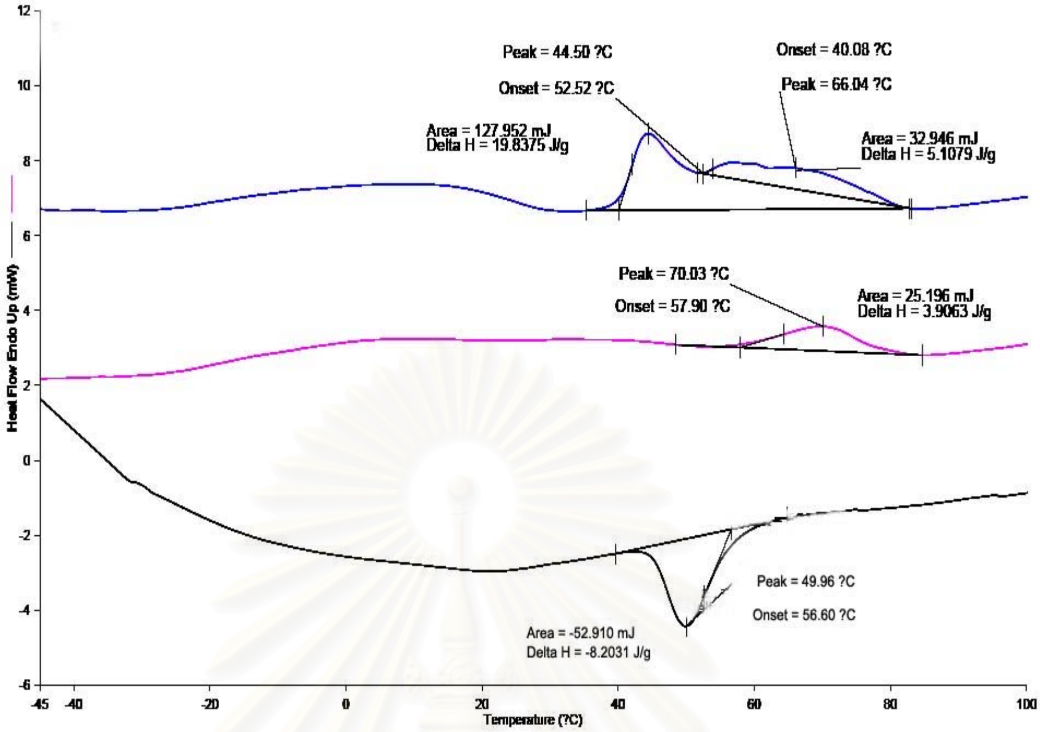


Figure D-13. DSC curve of EP copolymer with 1,4HD [EP (8)] at initial ethylene/propylene molar ratio of 1 (semibatch system)

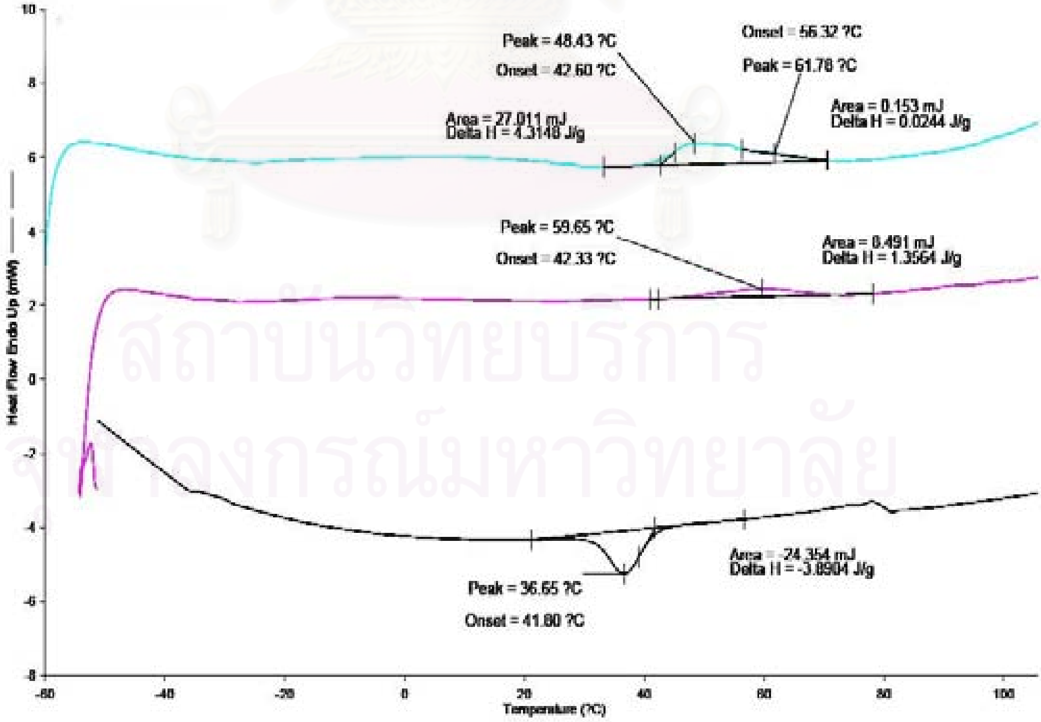


Figure D-14. DSC curve of EP copolymer with VCH [EP (9)] at initial ethylene/propylene molar ratio of 1 (semibatch system)

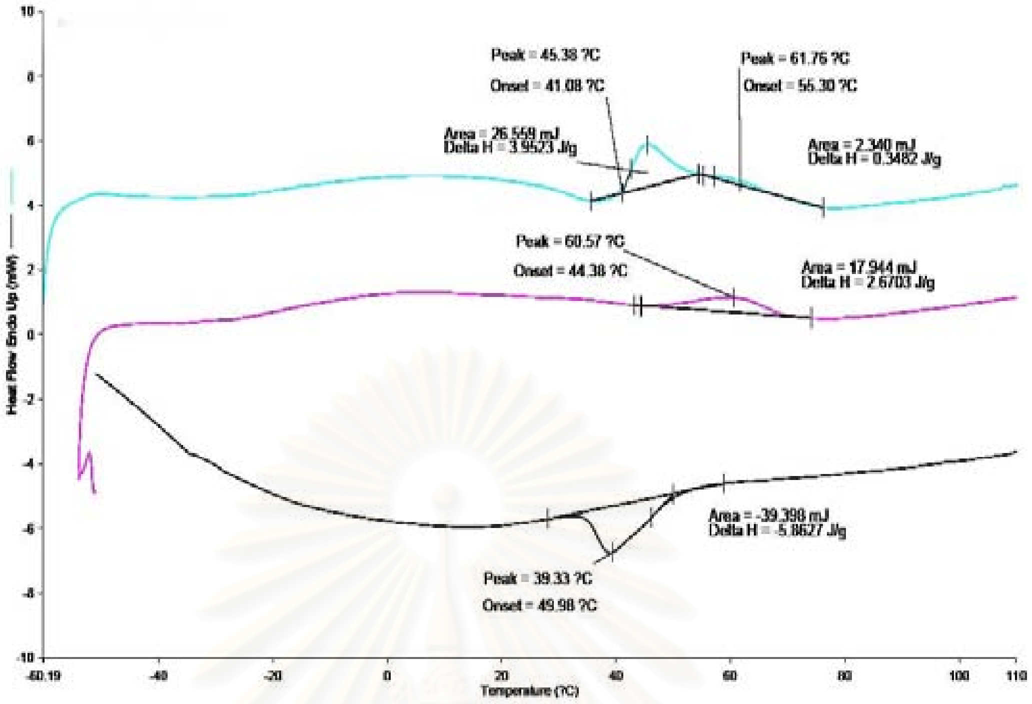


Figure D-15. DSC curve of EP copolymer with ENB [EP (10)] at initial ethylene/propylene molar ratio of 1 (semibatch system)

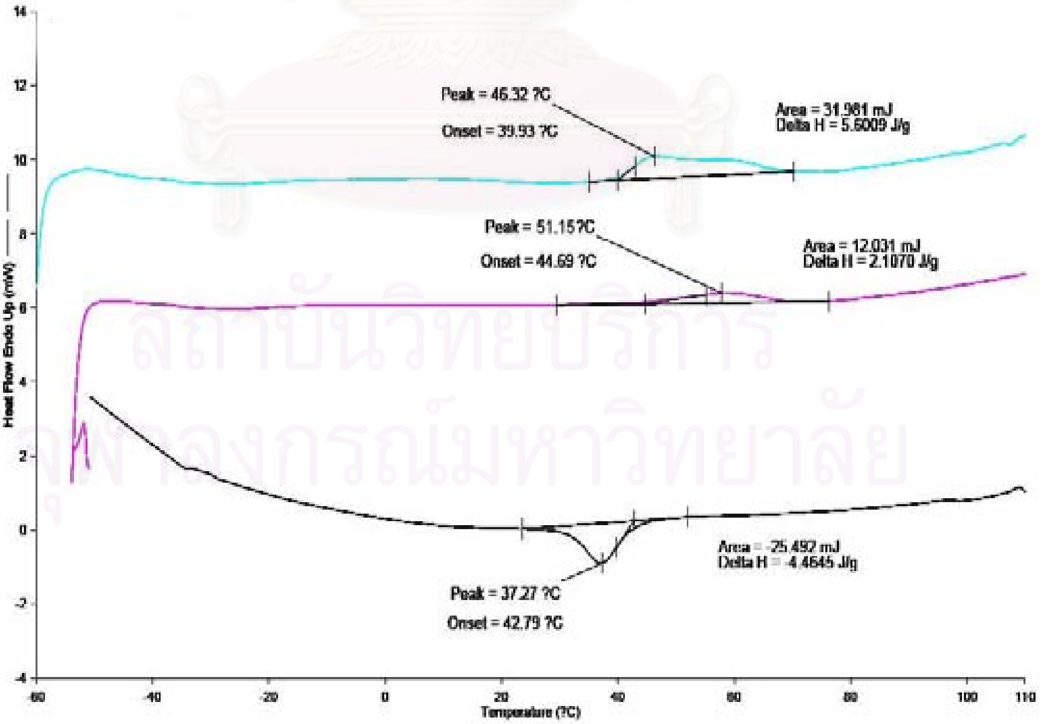


Figure D-16. DSC curve of EP copolymer [EP (11)] at initial ethylene/propylene molar ratio of 1 (semibatch system)

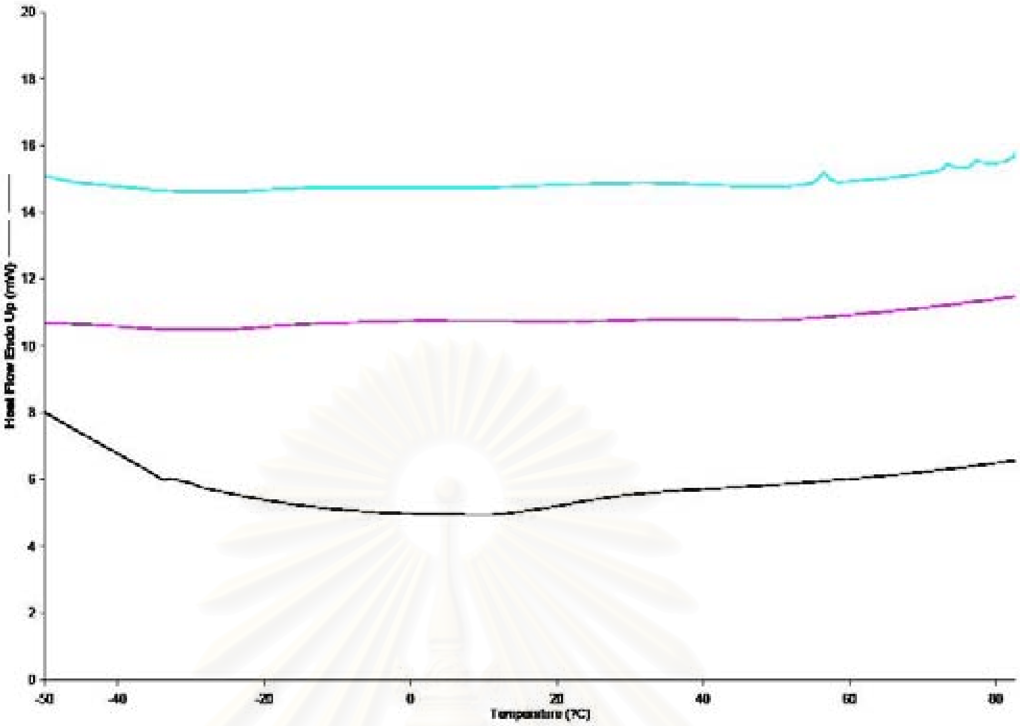


Figure D-17. DSC curve of EP copolymer with COD [EP (12)] at initial ethylene/propylene molar ratio of 0.667 (semibatch system)

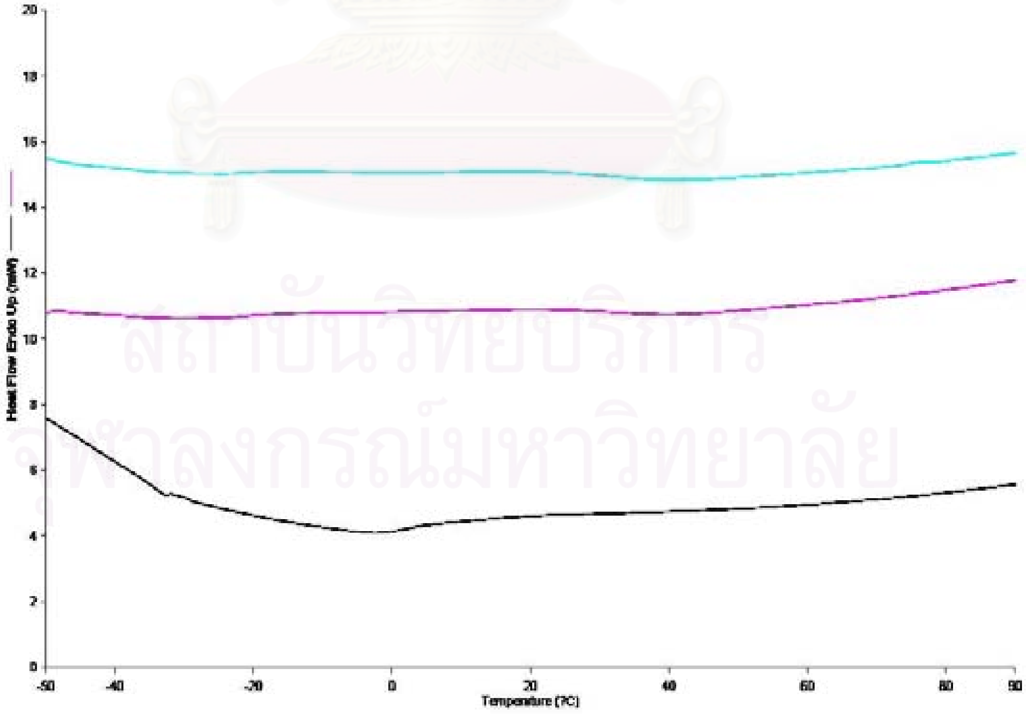


Figure D-18. DSC curve of EP copolymer with 1,5HD [EP (13)] at initial ethylene/propylene molar ratio of 0.667 (semibatch system)

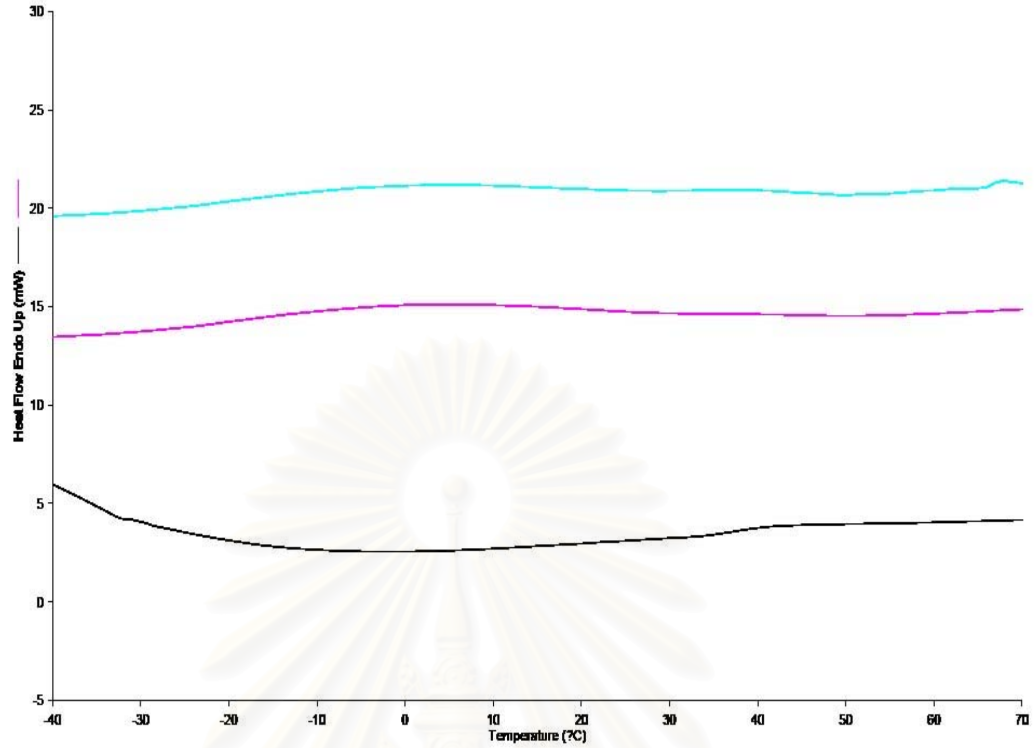


Figure D-19. DSC curve of EP copolymer with 1,4HD [EP (14)] at initial ethylene/propylene molar ratio of 0.667 (semibatch system)

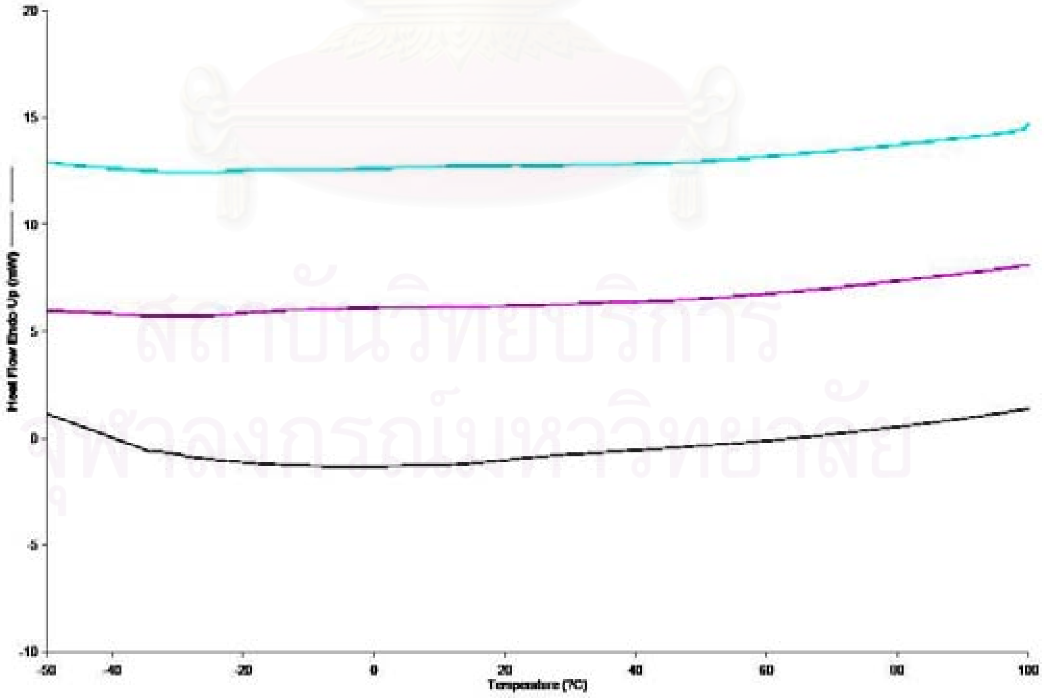


Figure D-20. DSC curve of EP copolymer with VCH [EP (15)] at initial ethylene/propylene molar ratio of 0.667 (semibatch system)

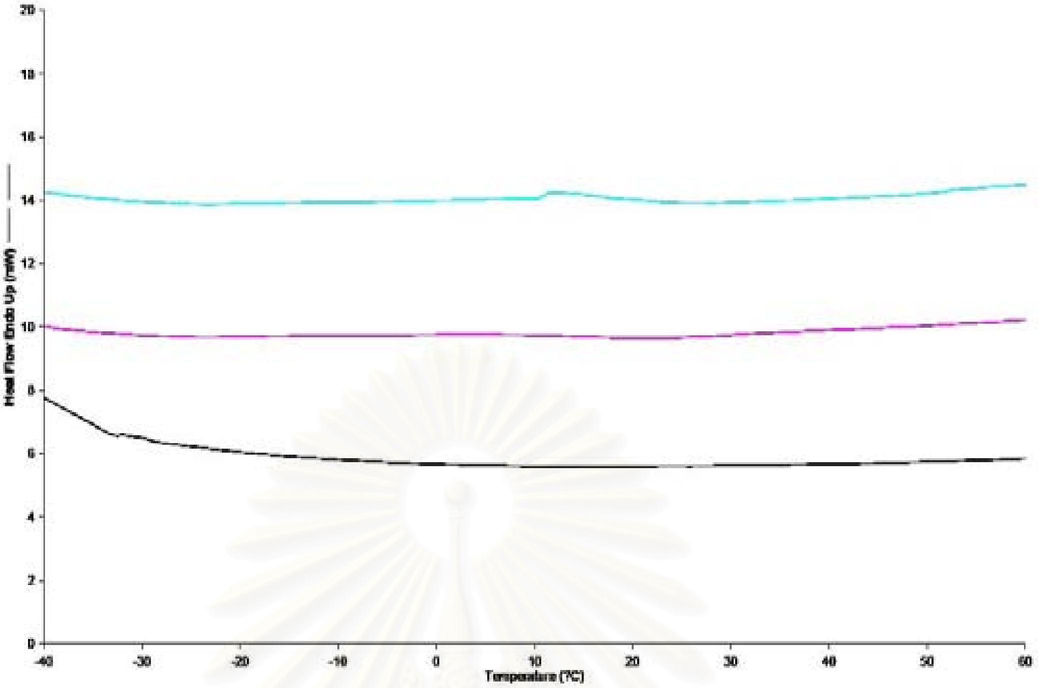


Figure D-21. DSC curve of EP copolymer with ENB [EP (16)] at initial ethylene/propylene molar ratio of 0.667 (semibatch system)

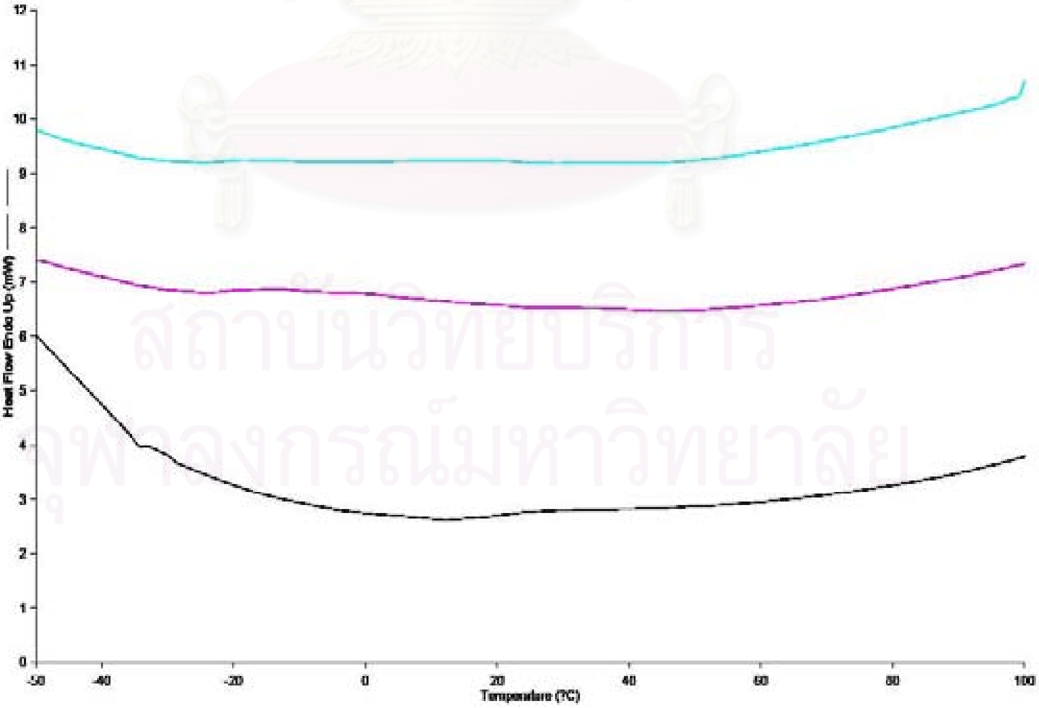


Figure D-22. DSC curve of EP copolymer [EP (17)] at initial ethylene/propylene molar ratio of 0.667 (semibatch system)

APPENDIX E

PROPYLENE INCORPORATION IN POLYMER / PROPYLENE IN FEED (%)

The calculation of propylene incorporation in polymer (% mole)/propylene in feed (% mole) in Table 4.17 are summarized in Table E-1.

Table E-1. Propylene incorporation in polymer/propylene in feed (%) at various molar ratios of ethylene/propylene.

Sample	E/P	Types of diene[a]	P incorporation in polymer[b] (% mole)	P in feed (% mole)	P incorporation in polymer / P in feed (%)
EP (0)	3	COD	25.7	25	100.0
EP (1)	3	1,5 HD	24.1	25	96.4
EP (2)	3	1,4 HD	16.3	25	65.2
EP (3)	3	VCH	27.2	25	100.0
EP (4)	3	ENB	22.8	25	91.2
EP (5)	3	None added	25.7	25	100.0
EP (6)	1	COD	27.9	50	55.8
EP (7)	1	1,5 HD	29.1	50	58.2
EP (8)	1	1,4 HD	22.6	50	45.2
EP (9)	1	VCH	31.7	50	63.4
EP (10)	1	ENB	23.6	50	47.2
EP (11)	1	None added	36.5	50	73.0
EP (12)	0.667	COD	42.6	60	71.0
EP (13)	0.667	1,5 HD	32.8	60	54.7
EP (14)	0.667	1,4 HD	22.1	60	36.8
EP (15)	0.667	VCH	44.6	60	74.3
EP (16)	0.667	ENB	46.2	60	77.0
EP (17)	0.667	None added	40.6	60	67.7

[a] COD (Cyclooctadiene), 1,5 HD (1,5-Hexadiene), 1,4 HD (1,4-Hexadiene), VCH (4-Vinyl-1-cyclohexene) and ENB (5-Ethylidene-2-norbornene)

[b] Propylene incorporation in polymer (% mole) calculated from ^{13}C NMR measurement.

APPENDIX F

GEL PERMEATION CHROMATOGRAPHY

Sample were prepared approximate concentration at 1.0-2.0 mg/ml in the trichlorobenzene (mobile phase) and dissolved by using the sample preparation unit (PL-SP 260) at temperature at 150°C.

Table F-1 Results of molecular weight analysis of rubber samples.

Sample	GPC analysis		
	M_n	M_w	MWD
EP-1,4HD	30100	73400	2.6
EP-VCH	60800	84700	2.8
EP-ENB	61600	113900	1.9
EP	33700	79900	2.4

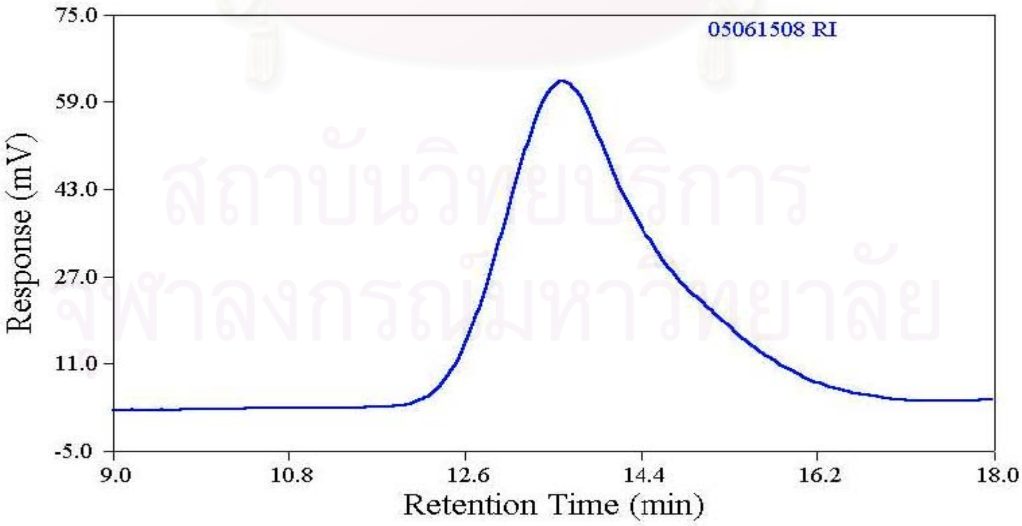


Figure F-1. GPC chromatogram of EP copolymer with 1,4 HD [EP (0)] (batch system).

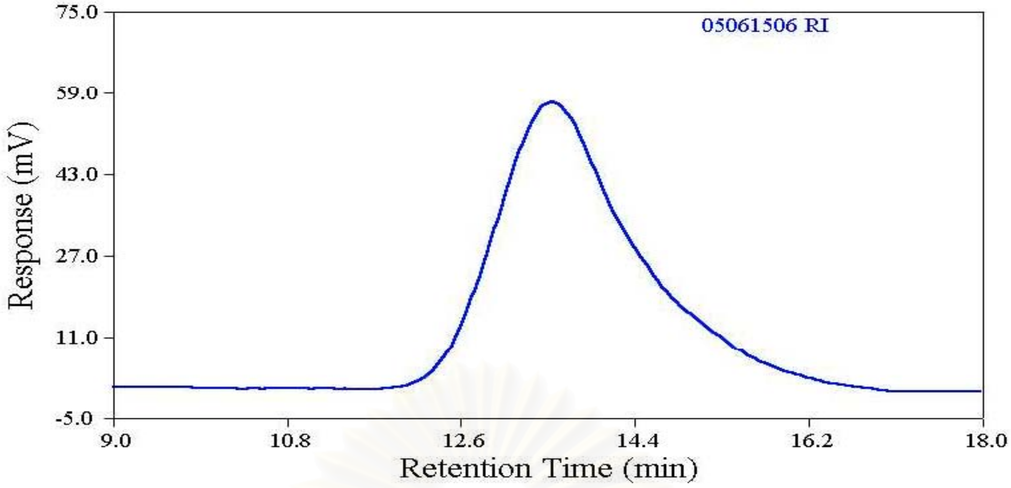


Figure F-2. GPC chromatogram of EP copolymer with VCH [EP (1)] (batch system).

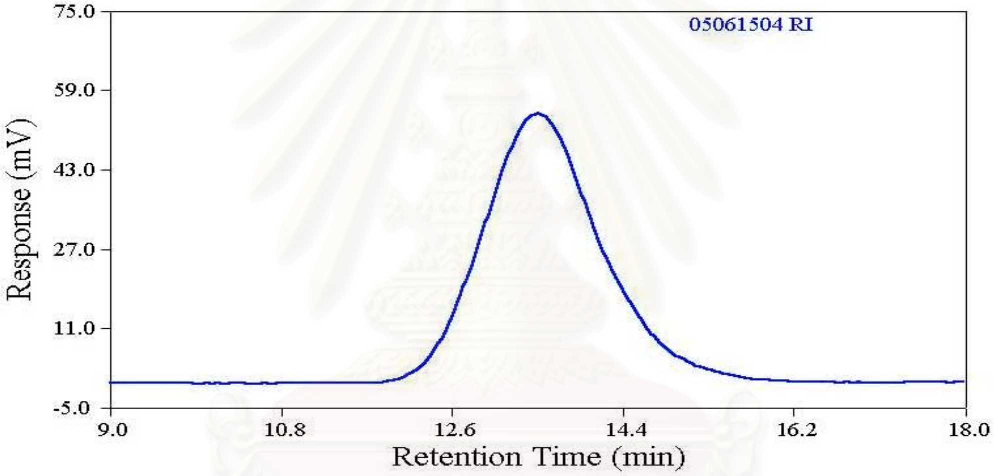


Figure F-3. GPC chromatogram of EP copolymer with ENB [EP (2)] (batch system).

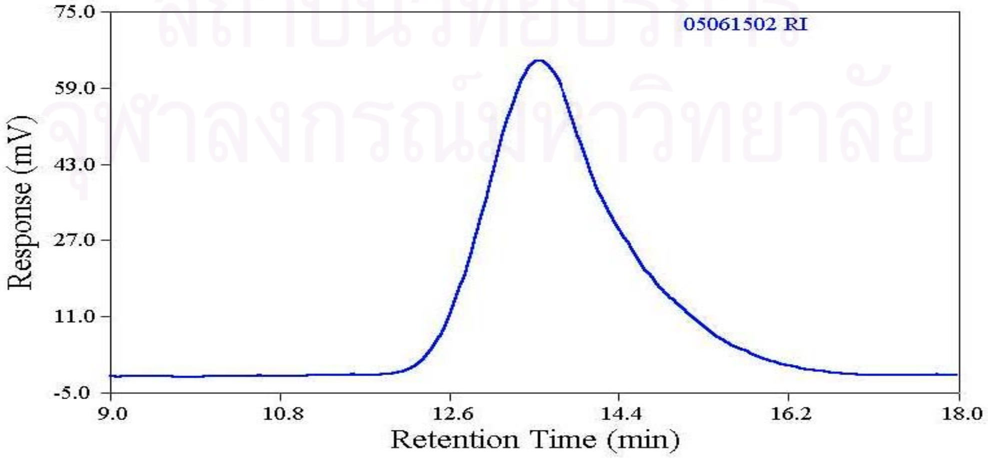


Figure F-4. GPC chromatogram of EP copolymer [EP (3)] (batch system).

APPENDIX G

LIST OF PUBLICATION

1. Sireethorn Phoowakeereewiwat, Bunjerd Jongsomjit, and Piyasan Praserthdam, "A Comparative Study of Diene on EPDM Terpolymerization using MAO/ Zirconocene Catalyst", Proceedings of the Thai Institute of Chemical Engineering and Applied Chemical Conference 14th, Bangkok, Thailand, Dec., 1-3, 2004, Ref. No. NS-240.

2. Bunjerd Jongsomjit, Sireethorn Phoowakeereewiwat, Supakanok Thongyai, Takeshi Shiono, and Piyasan Praserthdam, "Impact of diene addition on properties for ethylene–propylene copolymerization with *rac*-Et[Ind]$_2$ZrCl$_2$/MAO catalyst", Materials Letters 59 (2005): 3771-3774.

3. Sireethorn Phoowakeereewiwat, Bunjerd Jongsomjit, and Piyasan Praserthdam "Investigation of diene addition on ethylene-propylene (EP) copolymerization with a zirconocene catalyst: effects of diene types and E/P ratios". Submitted to Materials Letters, Apr., 2006

A COMPARATIVE STUDY OF DIENE EFFECT ON EPDM TERPOLYMERIZATION USING MAO/ZIRCONOCENE CATALYST

Sireethorn Phoowakeereewiwat, Bunjerd Jongsomjit and Piyasan Praserthdam*[*]

Center of Excellence on Catalysis and Catalytic Reaction Engineering
Department of Chemical Engineering Faculty of engineering
Chulalongkorn University, Bangkok 10330, Thailand
E-mail: piyasan.p@chula.ac.th

ABSTRACT

Various dienes were investigated as termonomers in EPDM synthesis by using methylaluminoxane (MAO)/zirconocene catalyst. Terpolymerization of dienes such as 5-Ethylidene-2-norbonene (ENB), 1,4-Hexadiene (HD) and 4-Vinylcyclohexene (VCH) was compared. It was appeared that types of diene did not exhibit any differences in terms of catalytic activity. In addition the presence of dienes resulted in a slight decrease in polymerization activities. Rate of ethylene and propylene consumption for EP copolymerization exhibited a similar trend as seen for the EPDM terpolymerization where different types of diene were applied. Thus, dienes did not appreciably affect the rate of consumption.

Keywords: ethylene-propylene-diene (EPDM), metallocene catalysts, methylaluminoxane, terpolymerization

1. INTRODUCTION

Ethylene / Propylene copolymers and terpolymers with diene, referred to as EPDM, is currently produced with vanadium catalysts, which are low in activities and have toxicity concerns. The reduction of vanadium in the presence of linear and cyclic dienes was reported to be the cause of low terpolymerization activity [1,2]. Recently homogeneous metallocene catalyst systems have been developed for olefin polymerization with exceedingly high activities and their abilities to effect random distributions of monomers and to provide good control over molecular weight distribution [3-8].

In this present study, ethylene-propylene-diene terpolymers were synthesized using a batch reactor system. The effect of dienes [5-Ethylidene-2-norbonene (ENB), 1,4-Hexadiene (HD) and 4-Vinylcyclohexene (VCH)] with a zirconocene catalyst on EPDM terpolymerization was investigated.

2. EXPERIMENTAL

All chemicals (toluene, rac-ethylenebis(indenyl)zirconium dichloride, MAO, 5-Ethylidene-2-norbonene (ENB), 1,4-Hexadiene (HD) and 4-Vinylcyclohexene (VCH)) were manipulated under purified argon using a vacuum atmosphere glove boxes and/or Schlenk techniques. Polymerization was carried out in 100 mL stainless steel reactor with magnetic stirrer in the following manner. Using Schlenk technique, solvent was first added to the reactor in the amount to make the total volume of 30 mL. Cocatalyst solution is then added according to the specified ratio to the catalyst concentration followed by a diene. Then, the metallocene catalyst was injected and immediately put the reactor in liquid nitrogen to stop reaction between the catalyst and cocatalyst. After the solution was frozen for 15 minutes, the reactor was evacuated for 3 minutes to remove argon then filled with gaseous monomer (ethylene/propylene feed ratio of 75/25 by mole) 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.

Reactor was taken out of liquid nitrogen and heated up to polymerization temperature ($40^{o}C$) to start the polymerization reaction. Polymerizations were run 1 hr. To stop reaction, the gaseous monomer was released and the solution was washed with 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.

Characterization of terpolymers was performed using SEM (JSM-5800 LV) in order to reveal the morphologies of polymers.

3. RESULTS AND DISCUSSION

Activities and yields of the EP and EPDM produced with various dienes is shown **Table 1.** It indicated that types of diene did not exhibit any significant differences in the catalytic activity. In addition the presence of diene only resulted in a slight decrease in polymerization activity. The similar trend was found by the other groups [9a] using different catalyst system. However, it was reported that when various types of diene were added to the systems, the activities dramatically decreased compared to the conventional EP copolymerization. Yu *et al*. [9b] also studied terpolymerization of E/ P/ ENB using Et[Flu]$_2$ZrCl$_2$/MAO at E/P = 4. They reported that the presence of ENB significantly reduced the polymerization activity by 10-20 fold from E/P copolymerization. The results of terpolymerization with VCH were similar but the reduction of polymerization activity by VCH was smaller. The polymerization activities in the presence of HD lied in between those of ENB and VCH. The activities for terpolymerization with HD were comparable to the results for ENB as the termonomer. They proposed that both double bonds in HD can chelate to the metal center. Chelation is unlikely for VCH because of low steric flexibility of the double bond in the cyclohexene ring.

Rate of ethylene and propylene consumption for EP copolymer (**Figure 1**), EPDM terpolymers by the various dienes; ENB (**Figure 2**), HD (**Figure 3**) and VCH (**Figure 4**) are also presented. It was observed that Diene types did not appreciably affect the rate of consumption for ethylene and propylene at all indicating similar consumption profiles. Rate of ethylene and propylene consumption for EP as shown in **Figure 2** also had similar trends as seen from those for EPDM. It was also found that the rate enhancement of ethylene monomer was higher than the propylene monomer due to higher amounts of ethylene fed. The morphologies of the polymers produced are also shown in **Figure 5**. It can be observed that there were some significant differences in morphologies of polymers produced. Apparently, the EPDM produced from ENB and HD were larger compared to any other samples.

4. SUMMARY

The present study revealed effect of various dienes for EPDM terpolymerization with MAO/zirconocene on characteristics and catalytic properties of polymers produced. It was observed that there was no significant change on catalytic activities upon various dienes such as ENB, HD, and VCH. It was observed that the presence of dienes only resulted in a slight decrease in activities of catalyst during EPDM terpolymerization. In addition, diene types did not appreciably affect the rate of consumption for ethylene and propylene as well. Rate of ethylene and propylene consumption for EP had a similar trend as seen from that with EPDM. However, morphologies seemed to be altered with various dienes as well.

ACKNOWLEDGEMENTS

The authors would like to thank the Thailand Research Fund (TRF), the Nation Research Council of Thailand (NRCT) and Thailand-Japan Transfer Technology Project (TJTTP-JBIC) for the financial support of this work. We would like to extend our thankful to Professor Takeshi Shiono at Hiroshima University, Japan for his advice of this project.

REFERENCES

[1] A. Malmberg, B.Lofgren, J. Appl. Polym. Sci. 66 (1997) 35.
[2] A. Deffieux, M.Dolakthani, H. Cramail, Macromol. Chem Phys., 197 (1996) 289.
[3]] J.A.Ewen, T. Keii, K. Soga, Catalytic Polymerization of olefins. (1986) 271.
[4 J.C.W. Chien, D. He, J. Polym. Sci. Part A: Polym. Chem. 29 (1991) 1609.
[5] W. Kaminsky, M. Miri, J. Polym. Sci., Polym. Chem. 23 (1985) 2151.
[6] W. Kaminsky, A. Laban, Appl. Catal. A : General. 222 (2001) 47.
[7] M.C. Haag, J. H. Z. Dos Santos, F.C. Stedile, J. Dupont, J. Appl. Polym. Sci. 74 (1999) 1997.
[8] M. Marques, Z. Yu, M.D. Rausch, J.C.W. Chien, J. Polym. Sci. Part A: Polym. Chem. 33 (1995) 2787.
[9] Z. Yu, M. Marques, M.D. Rausch, J.C.W. Chien, J. Polym. Sci. Part A: Polym. Chem. 33 (1995) [9a] 979, [9b] 2795.

Table 1: Activity of EP and EPDM produced with various dienes using Et[Ind]$_2$ZrCl$_2$/MAO; [Zr] 30 μM, [Diene] 0.1 M, [Al]/[Zr] 2000, ethylene/propylene molar ratio 75/25, 40°C, 1 hr.

Run no.	**Diene type**[a]	**Polymer Yield (g)**	**Activity (kg polymer/mol Zr.hr)**
EP 1	–	2.8778	3198
EPDM 1	ENB	2.4043	2671
EPDM 2	HD	2.5417	2824
EPDM 3	VCH	2.5985	2887

[a] ENB (5-Ethylidene-2-norbornene), HD (1,4-Hexadiene) and VCH (4-Vinyl-1-cyclohexene)

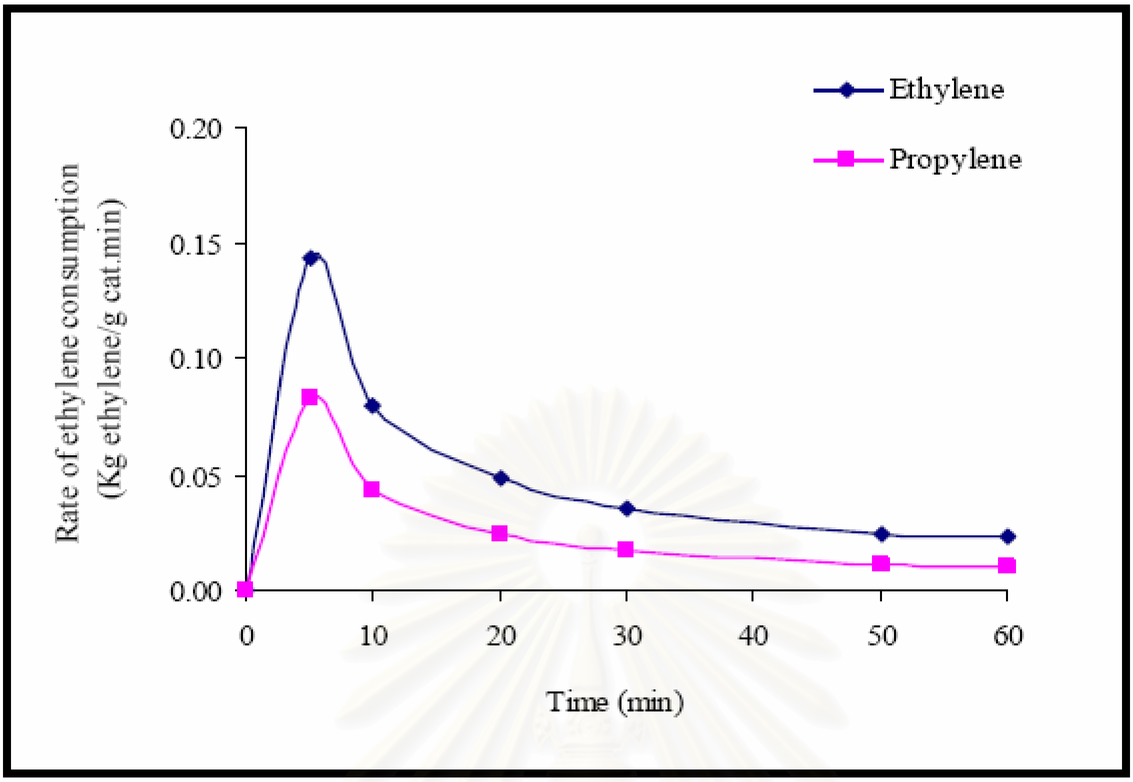


Figure 1: Activity profiles for ethylene-propylene copolymerization at ethylene/propylene molar ratio 75/25; Et[Ind]$_2$ZrCl$_2$, [Zr] = 30 µM, [Al]/[Zr] = 2000, T = 40°C

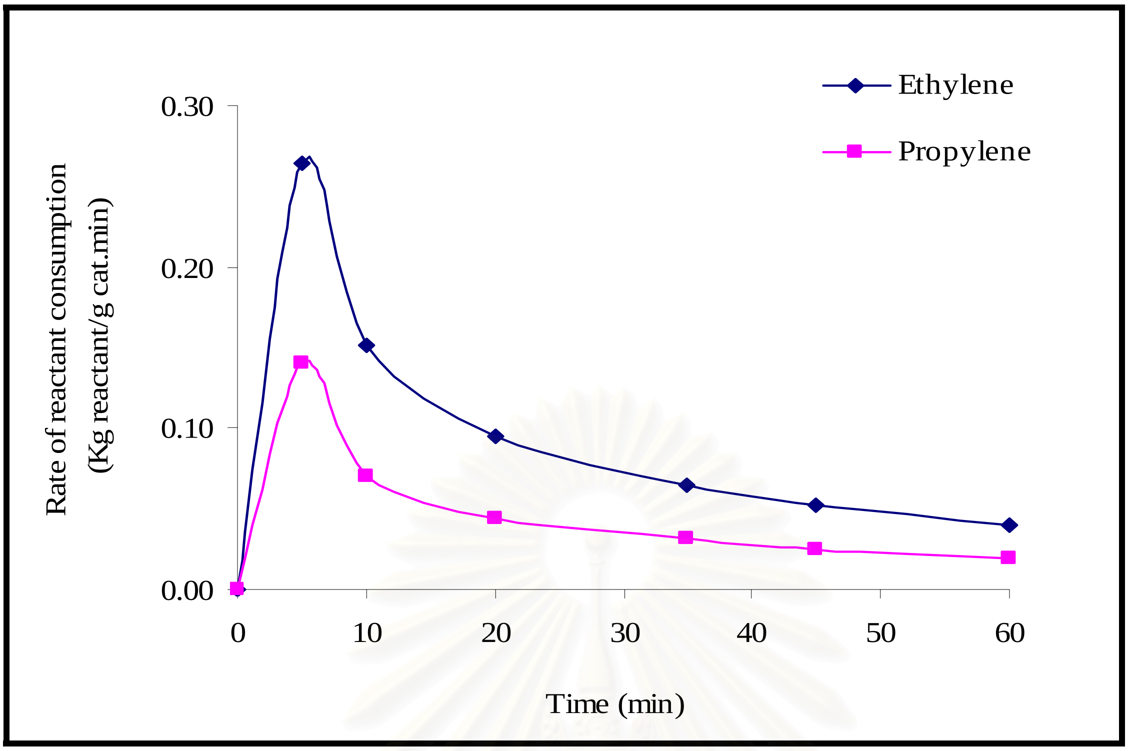


Figure 2: Activity profiles for ethylene-propylene diene terpolymerization at ethylene/propylene molar ratio 75/25; Et[Ind]$_2$ZrCl$_2$, [Zr] = 30 µM, [Al]/[Zr] = 2000, T = 40^{o}C , Diene (ENB) 0.1 M

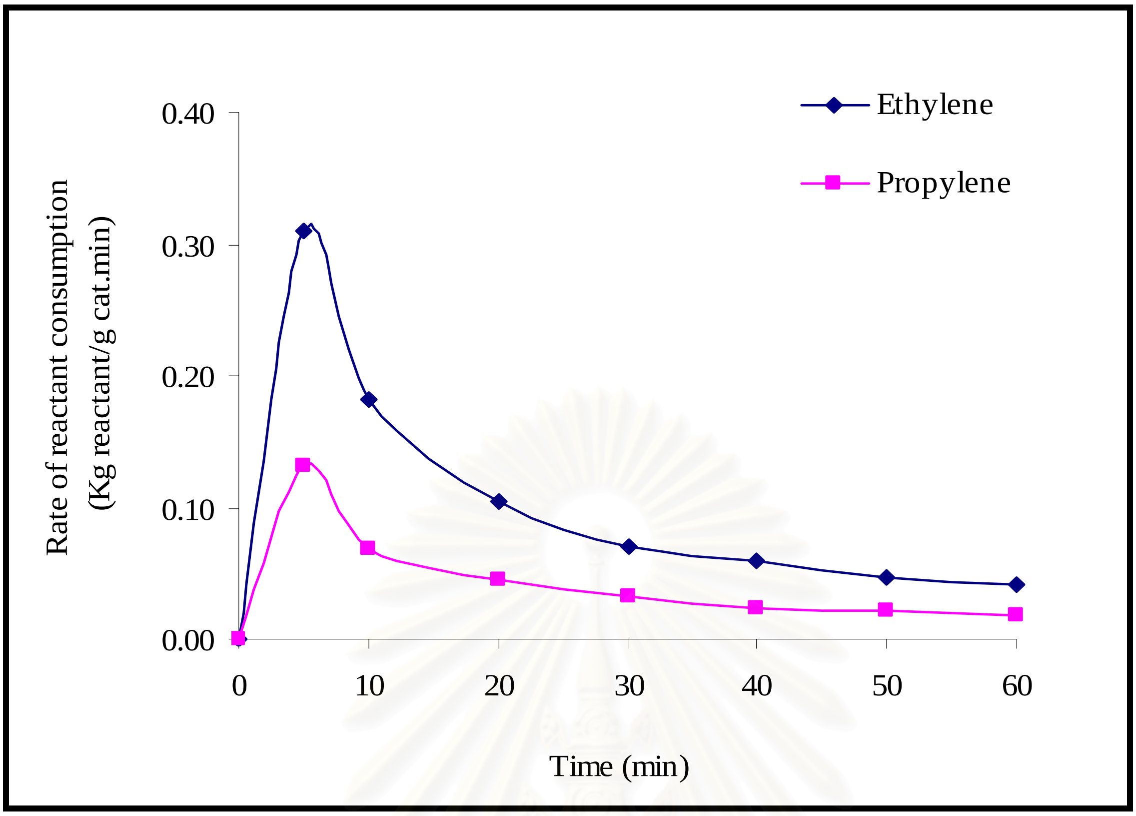


Figure 3: Activity profiles for ethylene-propylene diene terpolymerization at ethylene/propylene molar ratio 75/25; Et[Ind]$_2$ZrCl$_2$, [Zr] = 30 µM, [Al]/[Zr] = 2000, T = 40°C , Diene (VCH) 0.1 M

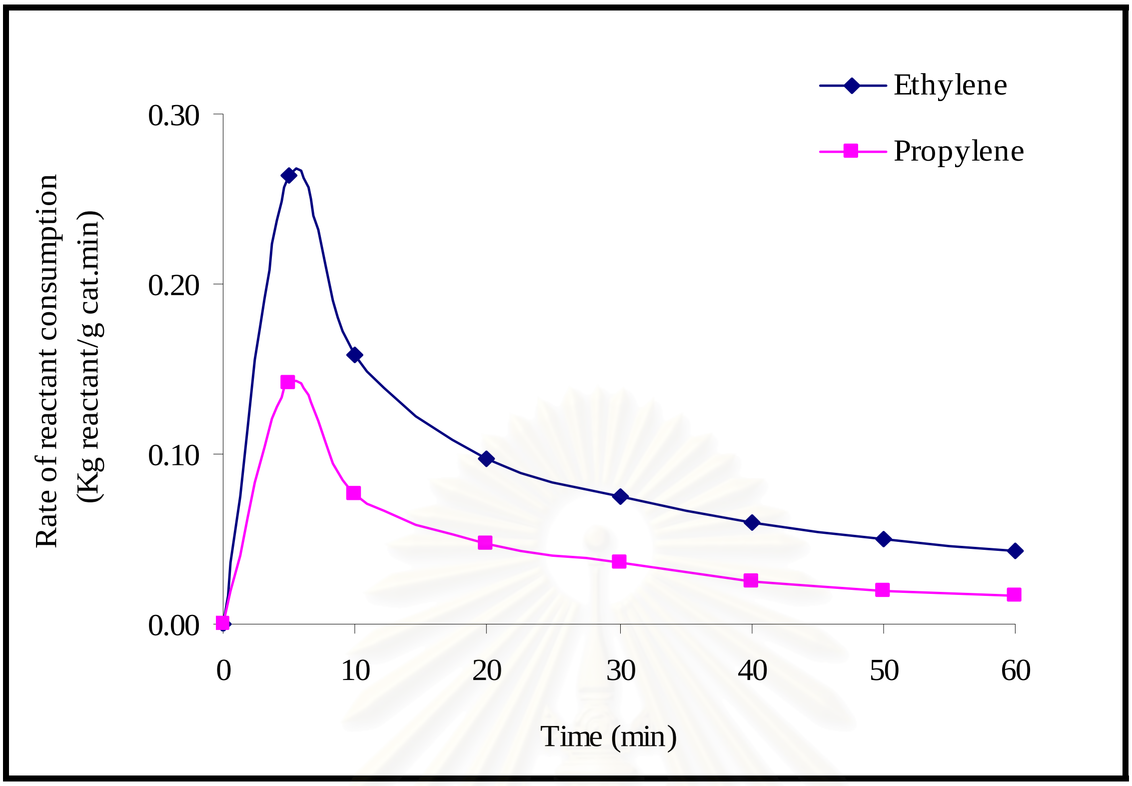


Figure 4: Activity profiles for ethylene-propylene diene terpolymerization at ethylene/propylene molar ratio 75/25; Et[Ind]$_2$ZrCl$_2$, [Zr] = 30 µM, [Al]/[Zr] = 2000, T = 40^{o}C , Diene (1,4HD) 0.1 M

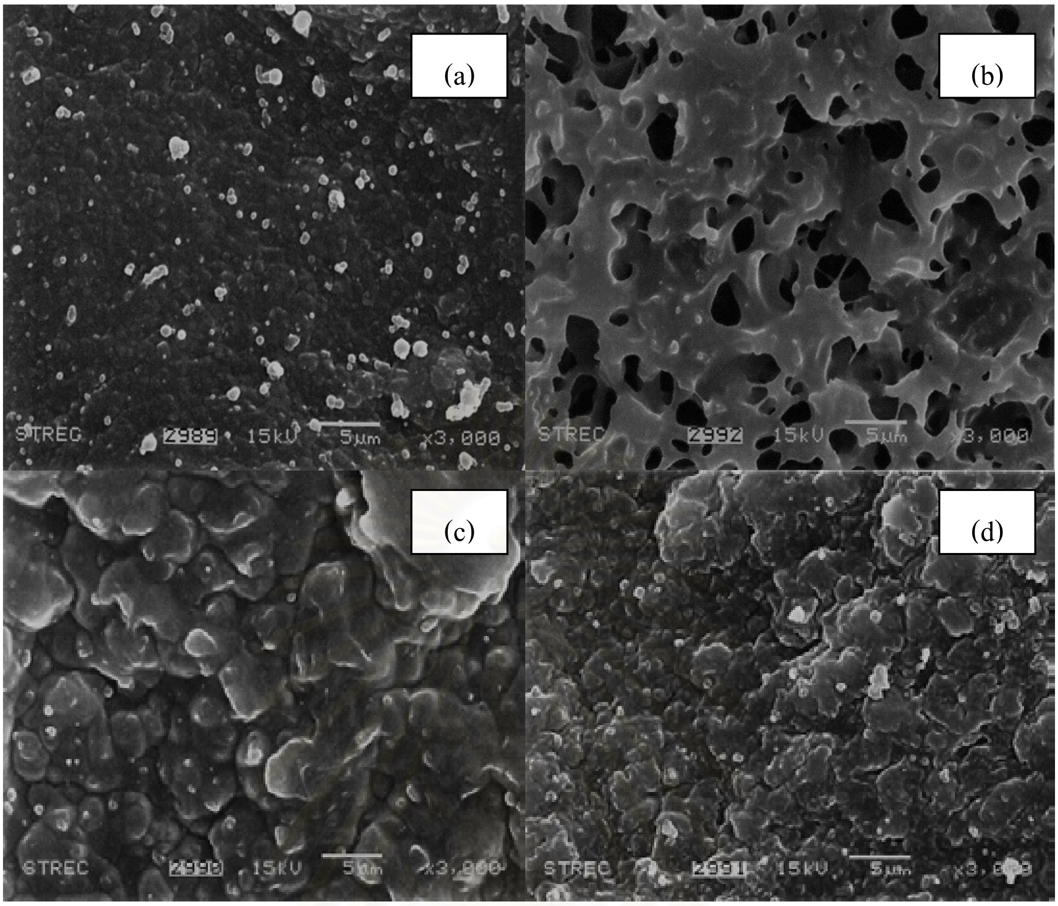


Figure 5: SEM micrographs of polymer produced: (a) EP, (b) EPDM (ENB), (c) EPDM (VCH), (d) EPDM (1,4HD).

Available online at www.sciencedirect.com
SCIENCE DIRECT®
Materials Letters 59 (2005) 3771 – 3774
materials letters
www.elsevier.com/locate/matlet

Impact of diene addition on properties for ethylene–propylene copolymerization with *rac*-Et[Ind]$_2$ZrCl$_2$/MAO catalyst

Bunjerd Jongsomjit [a,*], Sireethorn Phoowakeereewiwat [a], Supakanok Thongyai [a], Takeshi Shiono [b], Piyasan Praserthdam [a]

[a] *Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand*
[b] *Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan*

Received 20 May 2005; accepted 7 July 2005
Available online 28 July 2005

Abstract

In the present study, the impact of diene addition during copolymerization of ethylene and propylene using a metallocene/MAO catalyst was investigated. It showed that with a small amount of diene added, the dienes (except for ENB) did not incorporate in the polymer backbone pronouncedly. However, the addition of dienes can alter the incorporation of ethylene and propylene in the polymer backbone according to different types of dienes used. The catalytic behaviors and yields were not significant changes with the addition of dienes. The characteristics of polymer obtained using ^{13}C NMR, SEM, and DSC were also further discussed in more detail.

Keywords: Polymerization; Metallocene; Catalyst; Elastomers; Methylaluminoxane

---

1. Introduction

It is known that the copolymerization of ethylene (E) and propylene (P) can result in a production of rubbery materials called EP elastomers [1–3]. Because there are no double bonds in the backbone of polymer chain, they are usually insensitive to oxygen, ozone, acids, and alkaline. It was found that addition of the third monomer such as dienes could be applied in order to escalate the properties of EP elastomers, the so-called EPDM elastomers. As known, EPDM can be widely used in many applications so far [4–6]. Currently, EPDM is synthesized using vanadium-based catalysts. With the presence of dienes, it was found that the vanadium-based catalysts exhibited low activities along with toxicity concerns due to the residual vanadium remains in the polymer [7]. Thus, in order to overcome those problems, an alternative way of using the homogeneous metallocene catalysts has been substantially investigated by many authors [8–10]. Nevertheless, the production of EPDM is considered to be an important matter, the approach of our present study was apparently different from the

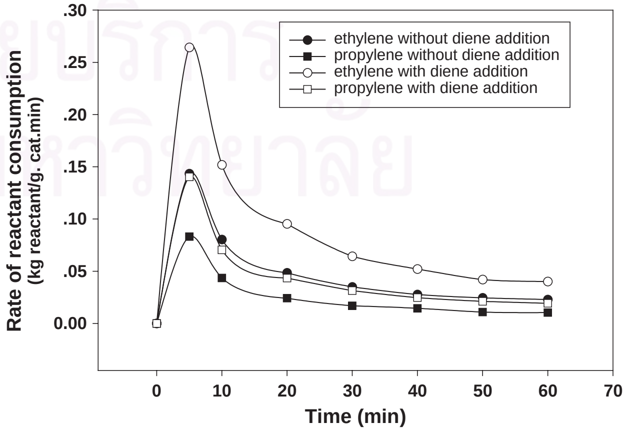


Fig. 1. Activity profiles based on ethylene (E) and propylene (P) consumption with and without diene addition.

---

[*] Corresponding author. Tel.: +66 662 2186869; fax: +66 662 2186877.
E-mail address: bunjerd.j@chula.ac.th (B. Jongsomjit).

0167-577X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.07.014

Table 1
Yields and activities of EP elastomers produced from *rac*-Et[Ind]$_2$ZrCl$_2$/MAO catalyst; [Zr]=30 μM in toluene, [Al]/[Zr]=2000, [diene]=0.1 M, E/P molar ratio=75/25, polymerization temperature=40 °C, and polymerization time=1 h

Sample	Types of diene	Polymer yield (g)	Activity (kg polymer/mol Zr h)
EP (0)	None added	2.88	3198
EP(1)	ENB	2.40	2671
EP(2)	VCH	2.60	2887
EP(3)	HD	2.54	2824

Table 2
Triad distribution obtained by ^{13}C NMR measurement of ethylene (E) and propylene (P) in polymers produced

Sample	Types of diene	EEE	PEE+EEP	PEP	EPE	EPP+PPE	PPP
EP (0)	None added	0.502	0.187	0.045	0.122	0.032	0.112
EP (1)	ENB	0.604	0.191	0.023	0.107	0.024	0.051
EP (2)	VCH	0.505	0.205	0.056	0.114	0.088	0.032
EP (3)	HD	0.609	0.210	0.032	0.118	0.031	–

others. Hereby, only a small amount of various dienes was introduced into the system during EP copolymerization, not for the purpose of synthesizing the EPDM as in general, but specifically for altering the behaviors of EP copolymerization. Thus, in our present study, the small amount of various dienes added did not incorporate into the polymer backbone, which can be determined using ^{13}C NMR measurement.

2. Experimental

In this study, EP copolymerization was performed using *rac*-Et[Ind]$_2$ZrCl$_2$ catalyst. All chemicals were manipulated under purified argon using a vacuum atmosphere glove boxes and/or Schlenk techniques. Polymerization was carried out in 100-ml stainless steel reactor with magnetic stirrer. First, 30 ml of toluene used as a solvent was added to the reactor. Then, methylaluminoxane (MAO) solution was added according to the specified ratio to the catalyst concentration ([Al]/[Zr]=2000) followed by the addition of 0.1 M of a selected diene [dienes used were 5-ethylidene-2-norbonene (ENB);(1), 4-vinylcyclohexene (VCH);(2), and 1,4-hexadiene (HD);(3)]. Then, the catalyst was injected into the system. The reactor was immediately put into liquid nitrogen to stop the reaction between the catalyst and cocatalyst (MAO). After the reaction mixture was frozen for 15 min, the reactor was evacuated for 3 min to remove argon then filled with the gaseous monomers (ethylene/propylene with a molar ratio of 75/25) while the reactor was still frozen in liquid nitrogen. Then, the reactor was taken out of liquid nitrogen and heated up to polymerization temperature (40 °C) to start the polymerization reaction. The polymerization time was kept for 1 h. In order to stop the reaction, the gaseous monomers were released and the reaction mixture was washed with acidic methanol. The polymer (white rubbery powder) obtained was filtered and dried overnight at ambient condition. Technically, for each diene, the polymerization was run at least three times to ensure the results obtained. The average values were reported. Characterization of the polymer obtained was performed using the ^{13}carbon nuclear magnetic resonance, ^{13}C NMR (JEOL JMR-A500 operating at 125 MHz), differential scanning calorimetry, DSC (Perkin-Elmer DSC 7), and scanning electron microscopy, SEM (JSM-5800 LV).

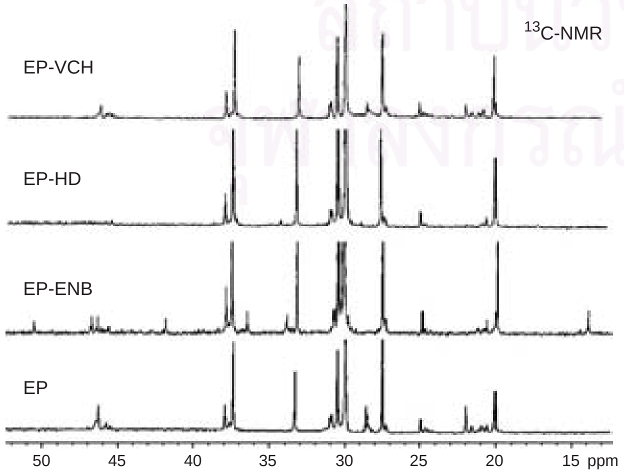


Fig. 2. ^{13}C NMR spectra of various EP elastomers with and without diene addition.

3. Results and discussion

The present research indicated that a small amount of dienes (ENB, VCH, and HD) added could have impact on behaviors of ethylene–propylene (EP) copolymerization with a metallocene/MAO catalyst. In fact, a large amount of diene addition could result in a decreased activity of polymerization as reported by Malmberg et al. [5]. However, it should be noted that the large amounts (~10–16 mol%) of diene were technically required in order to produce the terpolymer of EPDM. In particular, only a small amount (~3.6 mol%) of each diene was added during EP copolymerization in this study in order to maintain high activity of polymerization at this specified condition.

The rates of consumption for E and P with and without the diene addition are shown in Fig. 1. It was found that the

Table 3
Incorporation of ethylene (E), propylene (P) and reactivity ratios of ethylene (r_E) and propylene (r_P) calculated from ^{13}C NMR measurement

Sample	Types of diene	Incorporation (%)		Reactivity ratios		
		E	P	r_E	r_P	r_Er_P
EP (0)	None added	73	27	5.3	1.9	10.1
EP (1)	ENB[a]	80	18	6.9	1.5	10.4
EP (2)	VCH	76	24	4.8	1.5	7.2
EP (3)	HD	85	15	6.2	1.1	6.8

[a] ENB incorporation ca. 2%.

Table 4
Thermal properties of polymers obtained from DSC measurement

Sample	Types of diene	T_c (°C)	T_m (°C)	ΔH_m (J/g)	% Crystallinity (% χ)
EP (0)	None added	59.3	73.6	30.6	10.6
EP (1)	ENB	57.2	73.8	23.8	8.2
EP (2)	VCH	65.2	80.5	36.3	12.5
EP (3)	HD	70.0	88.2	49.1	17.0

induction period of the catalyst was also observed at the beginning of polymerization. The consumption rate went to a maximum after 6–7 min, then decreased due to catalyst deactivation. With the diene addition, similar activity profiles can still be observed as also shown in Fig. 1. It was suggested that the addition of dienes would have no effect on the catalyst performance at all indicating the similar rate profiles. Yields and activities of various EP elastomers are shown in Table 1. It indicated that the addition of dienes could result in only slightly decreased activities regardless of the dienes used. The polymers obtained were then further characterized using ^{13}C NMR, SEM, and DSC as mentioned. As known, ^{13}C NMR is one of the most powerful techniques used to identify the microstructure of a polymer. The ^{13}C NMR spectra for all polymer samples are shown in Fig. 2. It can be observed that the ^{13}C NMR spectra of EP, EP-VCH, and EP-HD samples exhibited similar patterns corresponding with those as reported by Randall [11]. These revealed that there was no incorporation of HD and VCH in the polymer backbone. The ^{13}C NMR spectrum of EP-ENB sample is also shown in Fig. 2, which apparently exhibited the slightly different patterns compared with other samples as mentioned before. Besides the characteristic peaks of EP copolymer, the incorporation of ENB can be additionally observed at $\delta = 14$, 36.5 and 42 ppm. This indicated that only ENB was able to incorporate into the polymer backbone at this specified condition. The triad distribution, % incorporation, and the reactivity ratios of E and P can be also calculated based on the method described by Randall [11]. The triad distribution of E and P for all samples is shown in Table 2. It indicated that the similar triad distribution was observed, except no block PPP in EP (3) sample. However, % incorporation of E and P along with the reactivity ratios (r_E and r_P) are shown in Table 3. It revealed that upon the addition of a small amount of dienes during copolymerization of EP, the incorporation of ethylene in the polymer apparently increased, especially for the ENB and HD. Since the reactivity ratio of $r_E r_P > 1$, the blocky incorporation of comonomer was obtained, which was different from the behaviors for copolymerization of ethylene and higher 1-olefins such as 1-hexene, 1-octene, and 1-decene [9,10]. The thermal properties such as T_c and T_m obtained from DSC measurement along with % crystallinity [12] are also summarized in Table 4. It was found that T_m, T_c and % crystallinity of EP tended to increase with the addition of dienes. In addition, the various dienes gave different impacts on % crystallinity of EP. It showed that using HD would result in the largest number of T_m, T_c and % crystallinity. The SEM micrographs of various EP produced are shown in Fig. 3. It can be observed that there were some differences in morphologies of the various EP produced. Apparently, the EP produced with the addition of dienes appeared in a larger air gap in the texture compared to those without diene addition. It should be noted that the impact of diene on the different ratios of E/P would be interesting to

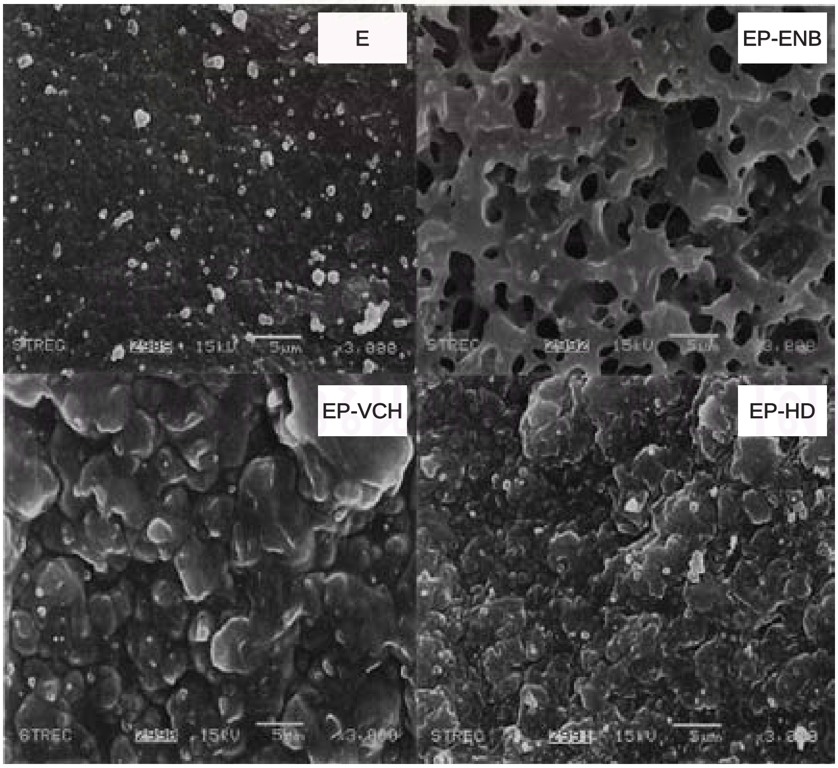


Fig. 3. SEM micrographs of various EP elastomers.

further investigate for our future work. In particular, the various ratios of E/P in the polymer backbone are considered to be the key role to obtain different properties for EP rubbers.

According to our experimental data, the mechanism of this copolymerization of ethylene and propylene could be drawn based on changes in the incorporation of ethylene and propylene upon the diene addition. As seen in Table 3, it can be observed that the insertion of propylene apparently decreased with the diene addition. Therefore, it can be proposed that the addition of diene probably inhibited the propylene insertion catalytic site and/or somehow promoted the catalytic site of ethylene insertion. Those phenomena resulted in a decreased propylene insertion. However, in order to provide a better understanding of the rigorous mechanism inside, we believe that a more powerful technique such as the steady-state isotopic transient kinetic analysis (SSITKA) [13–15], where the reaction intermediates can be identified would be helpful. This technique requires an additional instrument such as a mass spectrometer along with the isotopes (^{13}C) of the corresponding reactants.

4. Conclusions

In summary, our present study revealed, for the first time, that the addition of only a small amount of dienes under the specified condition could alter the copolymerization behaviors of ethylene and propylene instead of making the EPDM as in general. At the specified condition, dienes (except for ENB) did not incorporate into the polymer backbone as proved by ^{13}C NMR. Upon the various dienes used, % incorporation, T_m, T_c, and % crystallinity can be changed dramatically. However, in order to provide a better understanding, the roles of dienes should be further investigated in more detail, especially when the ratios of E/P are varied.

Acknowledgements

The authors thank the Thailand Research Fund (TRF), the National Research Council of Thailand (NRCT), the National Science and Technology Development Agency (NSTDA) and Thailand–Japan Technology Transfer Project (TJTTP-JBIC) for the financial support of this work.

References

[1] W. Kaminsky, M. Miri, J. Polym. Sci., Polym. Chem. 23 (1985) 2151.

[2] R.D. Allen, J. Elastomers Plast. 15 (1983) 19.

[3] E.L. Borg, in: M. Morton (Ed.), Rubber Technology, Krieger, Malabar, FL, 1981, p. 220.

[4] G.V. Strate, in: H.F. Mark, N.M. Bikales, C.G. Overberger, J.J Koschwitz (Eds.), Encyclopedia of Polymer Science and Engineering, J. Wiley & Sons, New York, 1973, p. 522.

[5] A. Malmberg, B. Lofgren, J. Appl. Polym. Sci. 66 (1997) 35.

[6] A. Deffieux, M. Dolakthani, H. Cramail, Macromol. Chem. Phys. 197 (1996) 289.

[7] K.L. Walton, M.M. Hughes, D.R. Parikh, Rubber Chem. Technol. 74 (2001) 688.

[8] W. Kaminsky, A. Laban, Appl. Catal., A Gen. 222 (2001) 47.

[9] B. Jongsomjit, P. Praserthdam, P. Kaewkrajang, Mater. Chem. Phys. 86 (2004) 243.

[10] B. Jongsomjit, P. Kaewkrajang, S.E. Wanke, P. Praserthdam, Catal. Lett. 94 (2004) 205.

[11] C. Randall, Macromol. Chem. Phys. 29 (1989) 201.

[12] S. Ottani, R.S. Porter, J. Polym. Sci., Part B, Polym. Phys. 29 (1991) 1179.

[13] A.R. Belambe, R. Oukaci, J.G. Goodwin Jr., J. Catal. 166 (1997) 8.

[14] S.L. Shannon, J.G. Goodwin Jr., Chem. Rev. 95 (1995) 677.

[15] B. Jongsomjit, J. Panpranot, J.G. Goodwin Jr., J. Catal. 215 (2003) 66.

Investigation of diene addition on ethylene-propylene (EP) copolymerization with a zirconocene catalyst: effects of diene types and E/P ratios

Sireethorn Phoowakeereewiwat, Bunjerd Jongsomjit [*], Piyasan Praserthdam

Center of Excellence on Catalysis and Catalytic Reaction Engineering
Department of Chemical Engineering, Faculty of Engineering
Chulalongkorn University, Bangkok 10330, Thailand

[*]Corresponding author: *Tel:* 662-2186869; *Fax:* 662-2186877, *e-mail:*
bunjerd.j@chula.ac.th
piyasan.p@chula.ac.th

Abstract

In the present study, the polymerization behaviors of EP copolymerization with a zirconocene/MAO catalyst upon the addition of a small amount of diene were investigated. It indicated that besides the addition of dienes, the polymerization behaviors were also dependent on the E/P ratios and types of diene. Apparently, diene addition resulted in decreased activity, especially at high E/P ratio (E/P = 3). In all cases, the addition of 1,4 HD rendered the lowest activities. It seemed that there was no significant change in the microstructure of EP elastomers upon different E/P ratios. The characteristics of polymer obtained by means of DSC and ^{13}C NMR were further discussed in more details.

Keywords: metallocene catalysts; elastomers; EP copolymer; NMR; DSC

1. Introduction

It is known that the copolymerization of ethylene (E) and propylene (P) can result in a production of rubbery materials called EP elastomers [1–3]. Because there are no double bonds in the backbone of polymer chain, they are usually insensitive to oxygen, ozone, acids, and alkaline. It was found that addition of the third monomer such as dienes could be applied in order to escalate the properties of EP elastomers, the so-called EPDM elastomers. As known, EPDM can be widely used in many applications so far [4–6]. Currently, EPDM is synthesized using vanadium-based catalysts. With the presence of dienes, it was found that the vanadium-based catalysts exhibited low activities along with toxicity concerns due to the residual vanadium remains in the polymer [7]. Thus, in order to overcome those problems, an alternative way of using the homogeneous metallocene catalysts has been substantially investigated by many authors [8–10]. Nevertheless, the production of EPDM is considered an important matter, the approach of our present study was apparently different from the others. Hereby, only a small amount of various dienes was introduced into the system during EP copolymerization, not for the purpose of synthesizing the EPDM as in general, but specifically for altering the behaviors of EP copolymerization.

In the previous work, we revealed that the addition of dienes can alter the incorporation of ethylene and propylene in the polymer backbone according to the different types of dienes employed [11]. In this present study, effects of diene types and E/P ratios were the focus of this study. Experimentally, types of dienes used and the ratios of E/P at 3, 1, and 0.667 were varied. The resulted activity and characteristics of polymer obtained were further discussed.

2. Experimental section

All chemicals (toluene, *rac*-ethylenebis(indenyl)zirconium dichloride, MAO, dienes [5-ethylidene-2-norbonene (ENB), 4-vinylcyclohexene (VCH), 1,4-hexadiene (1,4 HD), 1,4-hexadiene (1,5 HD) and 1,5 cyclooctadiene (1,5 COD)] were manipulated under an inert atmosphere using a vacuum atmosphere glove box and/or Schlenk techniques.

2.1 Materials

rac-ethylenebis(indenyl)zirconium dichloride ($Et[Ind]_2ZrCl_2$), 5-ethylidene-2-norbonene (ENB), 4-vinylcyclohexene (VCH), 1,4-hexadiene (1,4 HD), 1,5-hexadiene (1,5 HD) and cyclooctadiene (COD) were supplied from Aldrich. Ethylene and propylene were polymerization grade from National Petrochemical Co., Ltd., Thailand.

2.2. Polymerization

In this procedure, ethylene and propylene were premixed in a cylinder at the desired molar ratios (3, 1, and 0.667). Ethylene/propylene gas mixture is continuously fed into the reactor in order to keep the pressure to be constant at 30 psi. The polymerization was carried out in a 100 ml stainless steel autoclave reactor equipped with magnetic stirrer. Toluene was first added to the reactor in the amount to make the total volume of 30 ml. Cocatalyst solution is then added according to the specified ratio to the catalyst concentration followed by a diene (0.1 M). After that, the metallocene catalyst was injected into the reactor immediately. The reactor was frozen in liquid nitrogen to stop reaction between the catalyst and cocatalyst. After the solution was frozen for 15 minutes, the reactor was evacuated for 3 minutes to remove argon then heated up to polymerization temperature at 40°C. Feeding the gas mixture started the polymerization. The reaction of polymerization was terminated after 1 h by addition of acidic methanol. The precipitated polymer was washed with methanol and dried in room temperature. Characterization of the polymer obtained was performed using the ^{13}carbon nuclear magnetic resonance, ^{13}C NMR (JEOL JMR-A500 operating at 125 MHz) and differential scanning calorimetry, DSC (Perkin-Elmer DSC 7).

3. Results and discussion

The present research indicated that a small amount of various dienes added could have impact on behaviors of ethylene-propylene (EP) copolymerization with a zirconocene/MAO catalyst as also reported in our previous work [11]. In fact, a large amount of diene addition could result in a decreased activity of polymerization as reported by Malmberg et al. [5]. However, it should be noted that the large amounts (~10-16 mol%) of diene were technically required in order to produce the terpolymer of EPDM. In our particular study, only a small amount (~3.6 mol%) of each diene was added during EP copolymerization in order to maintain high activity at the specified conditions. The E/P ratios were varied at 0.667 (E < P), 1 (E = P), and 3 (E > P). The polymer yields, activities, and melting temperature (T_m) are given in **Table 1**. In order to focus on the impact of diene addition involving in polymerization activity, the activity profiles at various E/P ratios and various types of dienes were constructed as shown in **Figure 1**. It was found that diene addition resulted in slightly decreased activities of polymerization in regardless to E/P ratios. However, the decreased activities were more pronounced with increasing the E/P ratios. This was probably due to lower activity for ethylene polymerization with the presence of diene under the specified system. It should be mentioned that the activity for EP copolymerization was higher than both ethylene and propylene homopolymerization due to the comonomer effect [12]. Some explanations have been forwarded to explain this phenomenon, including the trigger mechanism [13] and improved rates of diffusion due to the solubilization of active centers by incorporation of comonomer [14]. However, based on the study, it was suggested that the addition of diene would inhibit the attachment of ethylene to the active center resulting in decreased activity with increasing the E/P ratios. The similar trend was found by the other groups [5, 15, 16] using different catalyst system. However, it was reported that when various types of diene were added to the system, the activities dramatically decreased compared to the conventional EP copolymerization.

Considering the types of diene employed, it can be observed that the addition of VCH gave the highest activity among the other dienes whereas the addition of 1,4 HD resulted in the lowest activity. Those results were similar to what we found in the previous work [11]. Yu *et al.* [17] also studied terpolymerization of E/P/ENB using Et[Flu]$_2$ZrCl$_2$/MAO at E/P = 4. They found that the presence of ENB significantly reduced the polymerization activity by 10-20 fold from EP copolymerization. The results of terpolymerization with VCH were similar, but somehow the reduction of polymerization activity by VCH was smaller. The polymerization activities in the presence of HD lied in between those of ENB and VCH. The activities for terpolymerization with HD were comparable to the results for ENB as the termonomer. They proposed that both double bonds in HD can chelate to the metal center. Chelation is unlikely for VCH because of low steric flexibility of the double bond in the cyclohexene ring. The EP elastomers obtained were then further characterized using DSC and ^{13}C NMR.

The thermal property such as T_m obtained from DSC measurement was also listed in **Table 1**. It can be observed that the T_m of EP elastomers tended to increase with the addition of dienes. It should be noted that Tm increased with increasing the E/P ratios due to the crystallinity of PE. However, with E/P < 1, the disappearance of T_m can be observed. Hence, the EP elastomers with the low content of E became absolutely amorphous materials. In addition, the thermal properties are also dependent on the fraction of E and P in the polymer backbone. Thus, it is necessary to determine the incorporation of E and P in the polymer sample.

As known, ^{13}C NMR is one of the most powerful techniques used to identify the microstructure of a polymer. The typical ^{13}C NMR spectra for all EP elastomers with various dienes at E/P = 3 are shown in **Figure 2**. It can be observed that the ^{13}C NMR spectra for other samples with various E/P ratios also exhibited the similar patterns. It revealed that VCH and COD did not incorporate in EP indicating the similar patterns for EP, EP-VCH, and EP-COD corresponding with those as reported by Randall [18]. The ^{13}C spectra of EP-ENB, EP-1,4 HD, and EP-1,5 HD are also shown in **Figure 2**, which apparently exhibited the slightly different patterns compared with other samples as mentioned before. Besides the characteristic peaks of EP copolymer, the incorporation of those dienes can be additionally observed at δ = 50, 46, 41, 36, 33.5, and 14 for ENB, at δ = 18 for 1,4 HD, and at δ = 39 for 1,5 HD. These indicated that only ENB, 1,4 HD, and 1,5 HD were able to slightly incorporate into the polymer backbone at the specified condition. The % incorporation and the reactivity ratios (r_E and r_P) of E and P can be also calculated based on the method described by Randall [18] as shown in **Table 2**. It revealed that upon the addition of a small amount of dienes during copolymerization of EP, the incorporation of ethylene in the polymer apparently increased, especially for 1,4 HD and 1,5 HD at various ratios of E/P. On the other hand, the addition of 1,4 and 1, 5 HD may inhibit the insertion of propylene. Since the reactivity ratios of $r_E.r_P > 1$ in all cases, the blocky incorporation of comonomer was obtained, which was different from the behaviors for copolymerization of ethylene and higher 1-olefins such as 1-hexene, 1-octene, and 1-decene [9, 10]. The triad distribution of E and P for all samples is shown in **Table 3**. It indicated that the similar triad distribution was observed, except for the observation of PPP block in some cases. However, it revealed that the block EEE was predominant even at E < P.

Based on our experimental data, the effects of E/P ratios along with the types of dienes could be drawn from the resulting polymerization activity and E/P incorporation. It was obvious that the addition of a small amount of dienes could alter the behaviors of EP copolymerization using a zirconocene/MAO catalyst. It can be observed that the effects of diene addition were apparently dependent on the E/P ratios and types of dienes. However, in order to develop a better understanding of the rigorous mechanism inside, we do believe that a more powerful technique such as the steady-state isotopic transient kinetic analysis (SSITKA) [19-21], where the reaction intermediates can be identified would be helpful. This technique requires an additional instrument such as a mass spectrometer along with the isotope (^{13}C) of the corresponding reactants. Hence, the further investigation beyond this study should be done by means of this extraordinary instrument and system.

4. Conclusions

In summary, the addition of a small amount of dienes could alter the behaviors of EP copolymerization with a zirconocene/MAO catalyst. In particular, changes in polymerization behaviors were dependent on E/P ratios and types of diene. It revealed that activities decreased with diene addition. However, the decrease in activity was more pronounced with increasing the E/P ratio (E/P = 3). In addition, for all cases, the addition of 1,4 HD resulted in the lowest activity among the other dienes added. At the specified condition, only ENB, 1,4 HD and 1,5 HD can incorporate in the polymer backbone based on ^{13}C NMR results. It also indicated that all EP elastomers exhibited only the block copolymer ($r_E.r_P > 1$).

Acknowledgements

The authors thank the Thailand Research Fund (TRF), the National Research Council of Thailand (NRCT) and Thailand-Japan Transfer Technology Project (TJTTP-JBIC) for the financial support of this work. We also extend our thankful to Professor Takeshi Shiono at Hiroshima University, Japan for his advice of this project.

References

[1] W. Kaminsky, M. Miri, J. Polym. Sci., Polym. Chem. 23 (1985) 2151.

[2] R.D. Allen, J. Elastomers Plast. 15 (1983) 19.

[3] E.L. Borg, in: M. Morton (Ed.), Rubber Technology, Krieger, Malabar, FL, 1981, p. 220.

[4] G.V. Strate, in: H.F. Mark, N.M. Bikales, C.G. Overberger, J.J Koschwitz (Eds.), Encyclopedia of Polymer Science and Engineering, J. Wiley & Sons, New York, 1973, p. 522.

[5] A. Malmberg, B. Lofgren, J. Appl. Polym. Sci. 66 (1997) 35-44.

[6] A. Deffieux, M. Dolakthani, H. Cramail, Macromol. Chem. Phys. 197 (1996) 289.

[7] K.L. Walton, M.M. Hughes, D.R. Parikh, Rubber Chem. Technol. 74 (2001) 688.

[8] W. Kaminsky, A. Laban, Appl. Catal., A Gen. 222 (2001) 47.

[9] B. Jongsomjit, P. Praserthdam, P. Kaewkrajang, Mater. Chem. Phys. 86 (2004) 243.

[10] B. Jongsomjit, P. Kaewkrajang, S.E. Wanke, P. Praserthdam, Catal. Lett. 94 (2004) 205.

[11] B. Jongsomjit, S. Phoowakeereewiwat, S. Thongyai, T. Shiono, P. Praserthdam, Materials Letters 59 (2005) 3771.

[12] R. Kravchenko, R. M. Waymouth, Macromolecules 31 (1998) 1.

[13] N. Naga, Y. Ohbayashi, K. Mizunuma, Macromol. Rapid Commun 18 (1997) 837.

[14] J. Koivumaki, J. V. Seppala,_Polym. Bull. 31 (1993) 441.

[15] Z. Yu, M. Marques, M.D. Rausch, J.C.W. Chien, J. Polym. Sci. Part A: Polym. Chem. 33 (1995) 979.

[16] M. Marques, Z. Yu, M. D. Rausch, J.C.W. Chien, J. Polym. Sci. Part A: Polym. Chem. 33 (1995) 2787-2793.

[17] Z. Yu, M. Marques, M.D. Rausch, J.C.W. Chien, J. Polym. Sci. Part A: Polym. Chem. 33 (1995) 2795.

[18] C. Randall, Macromol. Chem. Phys. 29 (1989) 201.

[19] A.R. Belambe, R. Oukaci, J.G. Goodwin Jr., J. Catal. 166 (1997) 8.

[20] S.L. Shannon, J.G. Goodwin Jr., Chem. Rev. 95 (1995) 677.

[21] B. Jongsomjit, J. Panpranot, J.G. Goodwin Jr., J. Catal. 215 (2003) 66.

Table 1

Yields and activities of EP elastomers produced with various E/P molar ratios from the *rac*-Et[Ind]$_2$ZrCl$_2$/MAO catalyst; [Zr]=30 μM in toluene, [Al]/[Zr]=2000, [diene]=0.1 M, polymerization temperature=40°C, and polymerization time=1 h. The melting temperature of polymers obtained from DSC measurement.

Sample	**E/P**	**Types of diene**	**Polymer Yield (g)**	**Activity (Kg Polymer/molZr.hr)**	**Tm (°C)**
EP (0)	3	None added	2.26	2505	76
EP (1)	3	ENB	1.77	1963	77
EP (2)	3	VCH	1.99	2210	78
EP (3)	3	1,4 HD	1.68	1862	79
EP (4)	3	1,5 HD	1.93	2145	79
EP (5)	3	COD	1.97	2192	80
EP (6)	1	None added	2.40	2665	51
EP (7)	1	ENB	1.83	2038	60
EP (8)	1	VCH	2.00	2226	60
EP (9)	1	1,4 HD	1.77	1962	70
EP (10)	1	1,5 HD	2.00	2214	58
EP (11)	1	COD	1.99	2209	60
EP (12)	0.667	None added	2.53	2811	n a
EP (13)	0.667	ENB	2.10	2330	n a
EP (14)	0.667	VCH	2.24	2492	n a
EP (15)	0.667	1,4 HD	1.98	2204	n a
EP (16)	0.667	1,5 HD	2.10	2332	n a
EP (17)	0.667	COD	2.11	2343	n a

n a = not appreciable

Table 2

Incorporation of ethylene (E), propylene (P) and the reactivity ratios of ethylene (r_E) and propylene (r_P) calculated from ^{13}C NMR measurement.

Sample	**E/P**	**Types of diene**	**Incorporation (%)**		**Reactivity ratios**		
			E	**P**	r_E	r_P	r_Er_P
EP (0)	3	No added	74.3	25.7	3.46	1.20	4.14
EP (1)	3	ENB	77.2	22.8	9.41	2.02	19.06
EP (2)	3	VCH	72.8	27.2	3.32	1.24	4.13
EP (3)	3	1,4HD	83.7	16.3	5.94	1.16	6.87
EP (4)	3	1,5 HD	75.9	24.1	1.21	4.62	5.59
EP (5)	3	COD	74.3	25.7	1.24	4.43	5.48
EP (6)	1	No added	63.5	36.5	2.41	1.39	3.35
EP (7)	1	ENB	76.4	23.6	4.78	1.30	6.23
EP (8)	1	VCH	68.3	31.7	3.47	1.41	4.90
EP (9)	1	1,4HD	77.4	22.6	4.82	1.25	6.03
EP (10)	1	1,5 HD	70.9	29.1	3.48	1.27	4.42
EP (11)	1	COD	72.1	27.9	4.07	1.38	5.60
EP (12)	0.667	No added	59.4	40.6	2.03	1.39	2.81
EP (13)	0.667	ENB	53.8	46.2	1.96	1.68	3.29
EP (14)	0.667	VCH	55.4	44.6	1.92	1.54	2.97
EP (15)	0.667	1,4HD	77.9	22.1	4.18	1.19	4.97
EP (16)	0.667	1,5 HD	67.2	32.8	2.53	1.23	3.12
EP (17)	0.667	COD	57.4	42.6	2.04	1.52	3.10

Table 3

Triad distribution obtained by ^{13}C NMR measurement of ethylene (E) and propylene (P) in polymers produced.

Sample	E/P	Types of diene	EEE	PEE+EEP	PEP	EPE	EPP+PPE	PPP
EP (0)	3	No added	0.382	0.293	0.068	0.172	0.085	0
EP (1)	3	ENB	0.634	0.112	0.026	0.112	0	0.115
EP (2)	3	VCH	0.357	0.304	0.067	0.166	0.106	0
EP (3)	3	1,4 HD	0.583	0.225	0.028	0.119	0.044	0
EP (4)	3	1,5 HD	0.407	0.307	0.045	0.172	0.053	0.015
EP (5)	3	COD	0.390	0.291	0.062	0.167	0.082	0.008
EP (6)	1	No added	0.221	0.300	0.113	0.184	0.158	0.023
EP (7)	1	ENB	0.423	0.286	0.054	0.157	0.079	0
EP (8)	1	VCH	0.266	0.328	0.090	0.191	0.126	0
EP (9)	1	1,4 HD	0.439	0.284	0.050	0.159	0.068	0
EP (10)	1	1,5 HD	0.286	0.356	0.067	0.200	0.091	0
EP (11)	1	COD	0.340	0.308	0.072	0.173	0.106	0
EP (12)	0.667	No added	0.138	0.325	0.131	0.198	0.190	0.018
EP (13)	0.667	ENB	0.110	0.306	0.122	0.175	0.199	0.088
EP (14)	0.667	VCH	0.114	0.305	0.136	0.183	0.210	0.052
EP (15)	0.667	1,4 HD	0.451	0.283	0.045	0.151	0.070	0
EP (16)	0.667	1,5 HD	0.233	0.346	0.093	0.205	0.122	0.001
EP (17)	0.667	COD	0.142	0.301	0.130	0.182	0.198	0.046

List of Figure

Figure 1 Activity profiles of EP copolymerization with various dienes addition and E/P ratios

Figure 2 Typical ^{13}C NMR spectra of EP elastomers consisting of various dienes at E/P ratios = 3.

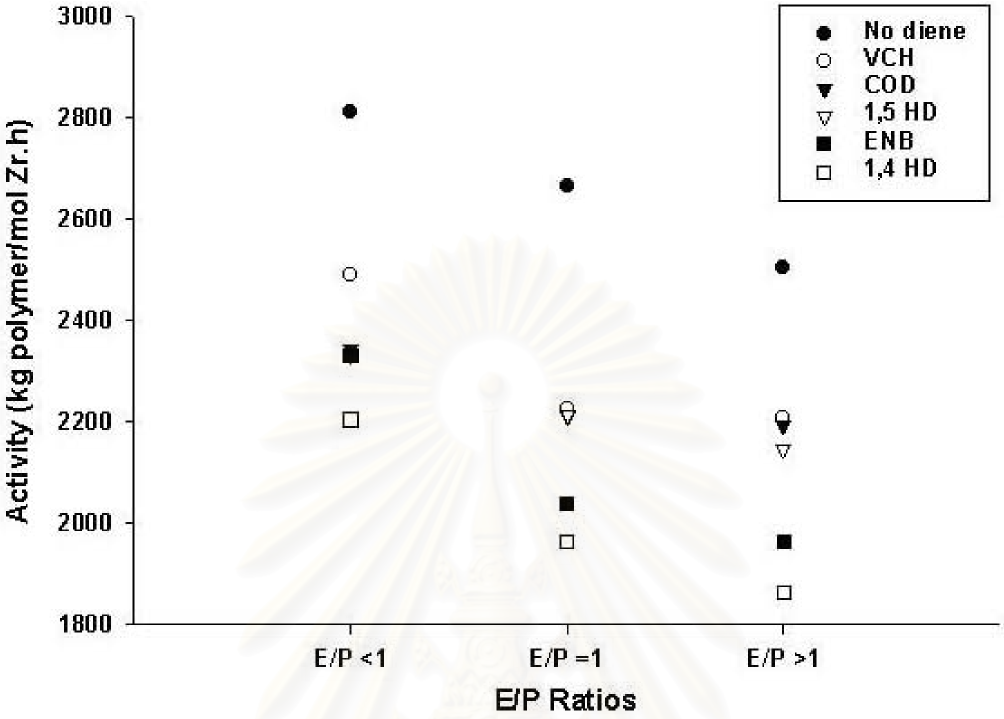

3000
2800
2600
2400
2200
2000
1800
Activity (kg polymer/mol Zr.h)
E/P <1
E/P =1
E/P >1
E/P Ratios
● No diene
○ VCH
▼ COD
▽ 1,5 HD
■ ENB
□ 1,4 HD

Figure 1

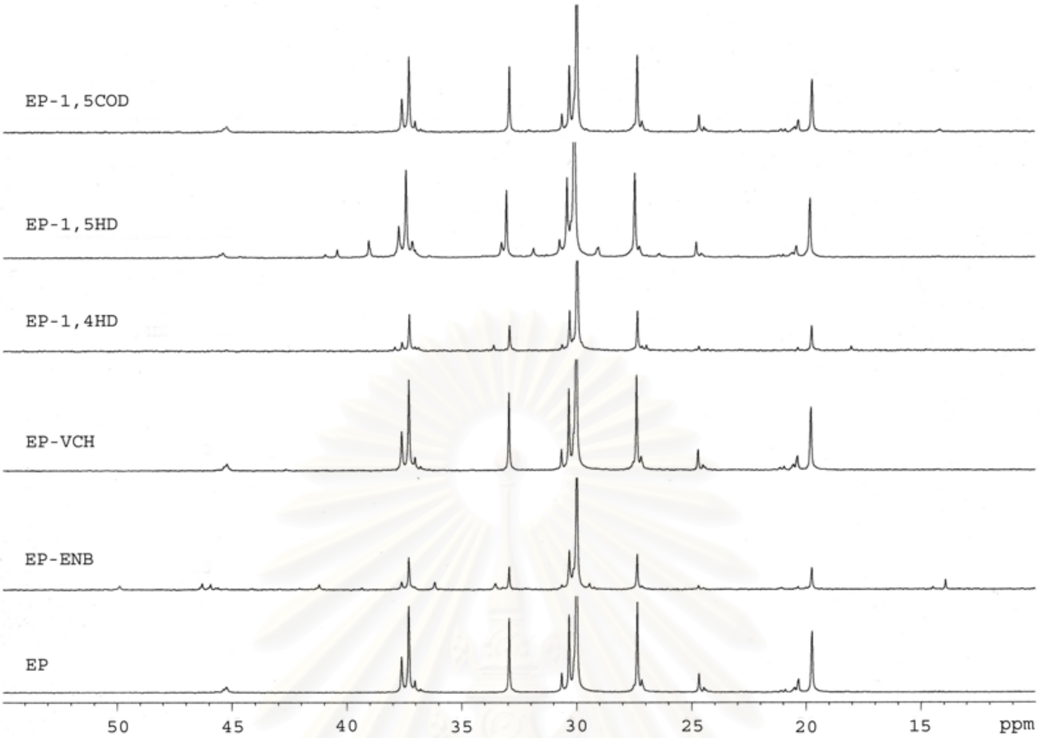

EP-1,5COD
EP-1,5HD
EP-1,4HD
EP-VCH
EP-ENB
EP
50
45
40
35
30
25
20
15
ppm

Figure 2

VITAE

Miss Sireethorn Phoowakeereewiwat was born on February 18, 1981 in Bangkok, Thailand. She received the degree of Bachelor of Science (Chemistry) from Mahidol University on March 2003. She continued in Master Degree of Engineering from the Department of Chemical Engineering, Chulalongkron University on June 2003.