สารเร่งปฏิกิริยาเซอร์โคโนซีนกับสารเร่งปฏิกิริยาร่วมโบรอนสำหรับพอลิเมอไรเซชันของเมทิลเมทาคริเลต

นายพีรวัฒน์ ขจรกีรติกุล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2544

ISBN 974-03-0729-9

ZIRCONOCENE CATALYST WITH BORON COCATALYST FOR METHYL METHACRYLATE POLYMERIZATION

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Chemistry

Department of Chemistry
Faculty of Science
Chulalongkorn University

Academic Year 2001
ISBN 974-03-0729-9

Thesis Title	Zirconocene Catalyst with Boron Cocatalyst for Methyl Methacrylate Polymerization
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Field of Study	Chemistry
Thesis Advisor	Associate Professor Wimonrat Trakarnpruk, Ph.D.

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ได้ทำการแอลคิเลทตัวเร่งปฏิกิริยาเซอร์โคโนซีน *rac*-Et(Ind)$_2$ZrCl$_2$ ด้วยสารกริยานด์ หลังจากนั้น รวมกับตัวเร่งปฏิกิริยาร่วมโบรอน: $B(C_6F_5)_3$, Ph_3C^+ $B(C_6F_5)_4^-$ หรือ $PhNMe_2H^+$ $B(C_6F_5)_4^-$ ในการพอลิเมอไรเซชันของเมทิลเมทาคริเลทโมโนเมอร์ ได้ใช้ $Zn(C_2H_5)_2$ ซึ่งเป็นกรดเลวิส เพื่อให้เกิดสารเชิงซ้อนกับเมทิลเมทาคริเลตก่อนเติมตัวเร่งปฏิกิริยาลงไปในปฏิกิริยา เพื่อป้องกันตัวเร่งปฏิกิริยาเซอร์โคโนซีนจากการเสื่อมสภาพจากหมู่ฟังก์ชันที่มีขั้วของโมโนเมอร์ บทบาทของกรดเลวิสคาดว่าเกี่ยวข้องในขั้นการริเริ่มของพอลิเมอไรเซชัน สามารถทำปฏิกิริยาในช่วงอุณหภูมิพอลิเมอไรเซชัน จาก –78°ซ ถึง 30°ซ พอลิเมอร์ที่ได้เป็นไอโซแทกทิกพอลิ(เมทิลเมทาคริเลต) (PMMA) ที่มีน้ำหนักโมเลกุลที่สูง ซึ่งพิสูจน์ได้จากสเปกตรัม NMR และการวัด GPC นอกจากนี้ อุณหภูมิสภาพแก้วของพอลิเมอร์จากการวัด DSC พบว่าประมาณ 50°ซ ประสิทธิภาพการเร่งปฏิกิริยาเพิ่มขึ้นตามความเข้มข้นของตัวเร่งปฏิกิริยา ผลได้ของพอลิเมอร์เพิ่มขึ้นตามเวลาที่ทำพอลิเมอไรเซชัน ซึ่งแสดงว่า อัตราเร็วในการเกิดพอลิเมอร์ ไม่ขึ้นกับความเข้มข้นของโมโนเมอร์ อัตราส่วนโดยโมลที่เหมาะสมของ MMA/Zn คือ 4 ในการศึกษานี้ยังแสดงให้เห็นการกระจายน้ำหนักโมเลกุลของพอลิเมอร์ที่แคบ ซึ่งเป็นลักษณะเฉพาะสำหรับตัวเร่งปฏิกิริยาเมทัลโลซีน (Mw/Mn < 2.5).

ภาควิชา.....เคมี..... ลายมือชื่อนิสิต.....Peerawat K.....

สาขาวิชา..... เคมี..... ลายมือชื่ออาจารย์ที่ปรึกษา.....W. Prukkasaporn.....

ปีการศึกษา..... 2544.....

4272355023 : MAJOR CHEMISTRY

KEY WORD: POLYMETHYL METHACRYLATE / ZIRCONOCENE / BORON COMPOUND / ORGANOZINC

PEERAWAT KAJORNKIRATIKUL: ZIRCONOCENE CATALYST WITH BORON COCATALYST FOR METHYL METHACRYLATE POLYMERIZATION. THESIS ADVISOR : ASSOC.PROF. WIMONRAT TRAKARNPRUK, Ph.D., 73 pp. ISBN 974-03-0729-9.

Zirconocene catalyst, *rac*-Et(Ind)$_2$ZrCl$_2$ was alkylated with Grignard reagent, then combined with a boron cocatalyst: $B(C_6F_5)_3$, Ph_3C^+ $B(C_6F_5)_4^-$ or $PhNMe_2H^+$ $B(C_6F_5)_4^-$. To perform the polymerization of methyl methacrylate monomer, $Zn(C_2H_5)_2$ which is a Lewis acid, was used to complex with methyl methacrylate before adding the catalyst to the reaction in order to protect the zirconocene catalyst from being poisoned with a polar functional group of the monomer. The role of Lewis acid presumably involved in the initiation step of polymerization. The reaction can be carried out over a range of polymerization temperature from –78 °C to 30 °C. The polymer obtained was isotactic poly(methyl methacrylate) (PMMA) with high molecular weight, revealed from NMR spectrum and GPC measurement. In addition, the glass transition temperature of the polymer from DSC measurement was around 50°C. The catalytic activity increases with an increase of catalyst concentration. The polymer yield increases with polymerization time, which indicates that the propagation rate is independent on monomer concentration. The optimum mole ratio of MMA/Zn is 4. In this study, the narrow molecular weight distribution, a characteristic demonstrated by metallocene catalyst is also shown (Mw/Mn < 2.5).

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Field of study.....Chemistry..... Advisor's signature.....W. Trakarnpruk.....

Academic year .....2001.....

ACKNOWLEDGEMENT

The author would like to express his sincere thanks to his thesis advisor, Associate Professor Dr. Wimonrat Trakarnpruk, for her advice, suggestion, assistance and generous encouragement throughout the course of graduate study. Furthermore, he would like to thank Associate Professor Dr. Siri Varothai, Associate Professor Dr. Sirirat Kokpol and Dr. Soamwadee Suwanakijboriharn for their valuable suggestion as thesis committee members.

Moreover, he would like to thank Dr. Uozumi (JAIST) and Dr. Wilson (Dow Chemical Company) for donation of chemicals, the Technological Research Equipment Center of Chulalongkorn University for DSC results, the National Metal and Material Technology Center (MTEC) for GPC analysis and the Department of Chemistry for research facilities. The financial support from the Graduate School is gratefully acknowledged.

This thesis could not have been complete without generous help of the staff members of the Organometallics Group, the Zeolite Group and the Supramolecular Group.

Finally, he would like to express his appreciation to his parents and family members for their understanding, kindness, encouragement and generous supports throughout the course of his education.

CONTENTS

CONTENTS (Cont.)

CONTENTS (Cont.)

LIST OF TABLES

LIST OF TABLES (Cont.)

LIST OF FIGURES

LIST OF FIGURES (Cont.)

LIST OF ABBREVIATIONS

Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
DSC	Differential scanning calorimetry
Et	Ethylene
Flu	Fluorenyl
FT-IR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
Ind	Indenyl
i-Pr	Isopropyl
M	Metal
Me	Methyl
MAO	Methylaluminoxane
MMA	Methyl methacrylate monomer
MW	Molecular weight
MWD	Molecular weight distribution
NMR	Nuclear magnetic resonance spectroscopy
Ph	Phenyl
PMMA	Polymethyl methacrylate
a-PMMA	Atactic polymethyl methacrylate
i-PMMA	Isotactic polymethyl methacrylate
s-PMMA	Syndiotactic polymethyl methacrylate
Pr	Propyl
R	Substituent group
rac	Racemic
T_g	Glass transition temperature
T_m	Melting temperature
TIBA	Triisobutylaluminum

CHAPTER I

INTRODUTION

Polymer are materials used in all fields of life. These materials have been discovered and now produced all over the world. Polymer-based materials such as plastics, fibers, elastomers were consumed. In the portion of markets, polyolefins is majority. The production and consumption of polyolefins will proportionally increase with the increasing population member. The key success factors for polyolefins manufacturing are the following ones[1]:

1. The raw materials (monomers) are easily accessible from oil or natural gas.
2. The production costs are low due to modern, energy saving and non-polluting large volume processes.
3. The products are environmentally harmless thus contributing to the principle of sustainable development.
4. These polymers can be burnt giving off combustion energies like oil.
5. A broad product portfolio of polyolefins is obtainable by catalytic polymerization process ranging from very low up to ultrahigh molecular mass compound and covering a broad range of densities.
6. Polymer products can be tailored to reach excellent product quality in respect to processing and final product performance.

One of the interesting polyolefins is polymethyl methacrylate (PMMA) which is the first acrylic polymer to be produced commercially. The production was begun in 1927 by Rohm and Haas AG in Germany [2].

In 1932 Rohm and the collaborators were the first to polymerize methyl methacrylate into transparent sheet. A few years later the first thermoplastically processible molding compounds based on PMMA were available [3].

After that, the cast sheet polymethyl methacrylate have been developed. These include display signs, lighting fittings and bathroom fittings. PMMA is more transparent than glass. Thus, it can be made as very thick windows and it is still perfectly transparent, for example, in large aquariums. PMMA is found in paint. Acrylic latex paints often contain PMMA suspended in water. Lubricating oil and hydraulic fluids tend to get really viscous and even gummy when they get really cold.

The properties that make PMMA a high-prized plastic are good mechanical strength, outstanding optical properties (clarity, brilliance, transparency) and extremely good weather resistance. This favorable profile can be supplemented by the surface modification of semifinished products (scratch-resistant or antistatic coating), coloring or pigmenting and treated with flame retardants to open up a wide variety of potential uses for this polymer.

Pure PMMA is an amorphous plastic with a high surface gloss, high brilliance and crystal-clear transparency. It is classified as a hard, rigid but brittle material. The tensile, compressive and flexural strengths are considered satisfactory. Scratch resistance is also good and can be improved further by special coatings. Incorporation of acrylate allows the rheological properties of the thermoplastics to be varied within a wide range to satisfy the processing requirements during injection molding and extrusion [3].

PMMA are high-tech polymers or engineering plastics. The stereoregularity of which was known by the end of the 1950s to vary with the catalysts, solvents and temperatures used in the preparation.

The stereoregularity of PMMA can be varied from highly isotactic to highly syndiotactic configurations by controlling polymerization conditions. The isotactic polymers are synthesized with anionic catalyst such as Grignard reagents or alkyllithium in nonpolar solvents such as toluene. However, the side reactions are often present. A number of propagating species are formed, resulting in broad molecular weight distribution and lowering of isotacticity. Syndiotactic polymers are usually obtained from radical polymerization at low temperature or with Ziegler-Natta catalysis such as $TiCl_4$-$Al(C_2H_5)_3$ at very low temperature.

Kitayama et al. found that polymerization with tert-C_4H_9Li combined with trialkylaluminum compounds at low temperatures gave highly syndiotactic PMMA with narrow molecular weight distribution. Ferguson et al. prepared atactic structure PMMA by bulk polymerization of the monomer with sodium borohydride as catalyst [4-5].

Since the beginning of the 1980s, the chemistry of cationic group IVB metallocene complexes has attracted much more attention for their high activity and high stereospecificity in organic synthesis. These complexes function as useful models for the catalytic intermediates involved in hydrogenetion and Ziegler-Natta (Z-N) polymerization of α-olefins when methylaluminoxane (MAO) and boron compounds such as $B(C_6F_5)_3$, $Ph_3C^+BC_6F_5)_4^-$ and $PhNMe_2H^+B(C_6F_5)_4^-$ are used as cocatalyst. The propagation species were confirmed as cationic complexes, for example, iPr[Cp(Flu)] $ZrMe^+$ and Cp_2ZrMe^+. However, it is difficult for these kinds of catalysts to polymerize common polar vinyl monomer e.g., methyl methacrylate monomer (MMA).

Polymers prepared with metallocene catalysts have narrow molecular weight distribution than those prepared with heterogeneous catalysts and consequently better mechanical properties. Mw/Mn range 1 – 2.5 for the former, compared with 5 – 6 for the latter. This is a consequence of the single site feature of the metallocenes.

Activities of metallocene catalysts are from 10 – 100 times higher than those of conventional Ziegler-Natta catalysts. While it is often difficult to correlate structural variables with activity, the following generalizations can be made [6]:

1. For the group IVB metals, the order of activity is Zr > Ti > Hf .
2. Alkyl group on the cyclopentadienyl rings increase catalyst activity if they are not too bulky. Large, bulky alkyl groups and electron withdrawing groups decrease the activity.
3. Increasing the size of the groups attach to the atom bridging the cyclopentadienyl rings (C or Si) reduces the activity.
4. MAO affords much higher catalyst activities than other alkyl aluminum cocatalysts.

Therefore, in this work, zirconocene is chosen to be used as a catalyst. Since many reports found that several zirconocene are appropriate catalysts for α-olefins polymerization.

Many researches reveal that the bridging C_2-symmetric zirconocene compound such as *rac*-Et(ind)$_2$ZrMe$_2$ is a good catalyst for α-olefins polymerization [7-11]. For example, Soga et. al. polymerized propylene with *rac*-Et(ind)$_2$ZrMe$_2$ combined with excess MAO or alkyl aluminum as cocatalyst, the catalytic system gave isotactic polypropylene with high molecular weight and narrow molecular weight distribution.

MAO is required in a large excess (1,000 – 5,000 times of catalyst). Lewis acids such as boron compounds were examined to replace the MAO without significant loss in polymerization activity. The boron compound that can be used as is $B(C_6H_5)_4^-$ but the polymerization activity is low. The boron compounds which show higher activity are perfluorinated arylboranes and borate anion; $B(C_6F_5)_3$, $PhNMe_2H^+B(C_6F_5)_4^-$ and Ph_3C^+ $B(C_6F_5)_4^-$.

The metallocene/boron compound catalytic system can polymerize general α-olefins monomer, except the functional or polar monomers such as methyl methacrylate and other acrylate monomers. It was believed that functional group (alkoxy carbonyl) on monomer which is Lewis basic, will destroy the catalyst and cocatalyst. Thus, the binary catalytic system was found to be inactive towards the polymerization of MMA without the addition of a third component, Lewis acid such as alkyl aluminum compounds or organozinc [12].

In this research, zirconocene catalyst *rac*-Et(ind)$_2$ZrMe$_2$ will be used combined with different type of boron cocatalyst such as $B(C_6F_5)_3$, $PhNMe_2H^+B(C_6F_5)_4^-$ or $Ph_3C^+B(C_6F_5)_4^-$ together with $Zn(C_2H_5)_2$ for methyl methacrylate polymerization. The catalytic activity will be tested. The resulting polymer will be characterized.

1.1 The objective of the thesis

1.1.1 To study the influence of the ansa-zirconocene catalysts with boron cocatalysts on catalytic yields and activity.

1.1.2 To investigate the produced polymer structure and determine the optimum conditions for methyl methacrylate polymerization.

1.2 The scope of the thesis

1.2.1 Polymerize methyl methacrylate monomer using ansa-zirconocene catalysts and boron compounds as a cocatalyst.

1.2.2 Investigate the corresponding parameters affecting the methyl methacrylate polymerization :

- 1.2.2.1 Types of solvent and types of boron cocatalyst
- 1.2.2.2 Zn / monomer mole ratio
- 1.2.2.3 Polymerization temperature and polymerization time
- 1.2.2.4 Types of alkylating agents

1.2.3 Characterize produced polymethyl methacrylate

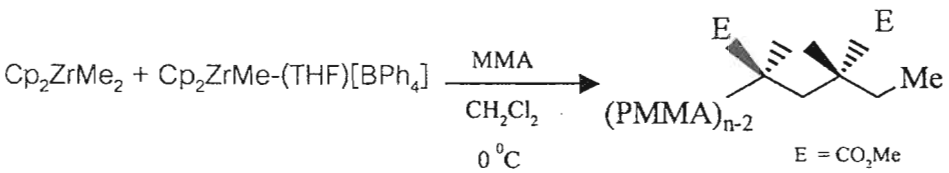
- 1.2.3.1 Fourier transform infrared spectroscopy (FT-IR)
- 1.2.3.2 Nuclear magnetic resonance spectroscopy (NMR)
- 1.2.3.3 Differential scanning calorimetry (DSC)
- 1.2.3.4 Gel permeation chromatography (GPC)

CHAPTER II
THEORY

The catalyst systems can play the key rule in olefin polymerization. Metallocene compounds becomes important catalysts for the systhesis of polymers. Especially, group IVB metallocene complexes are currently introduced in industry as a new generation of Ziegler-Natta catalysts for olefin polymerization. Ziegler-Natta catalysis is the rapid polymerization of ethylene and α-olefins with the aid and in the coordination sphere of a metal catalyst, operating at low pressure and low temperature. The group IVB metallocenes include titanocene, zirconocene and hafnocene, The zirconocene complexes are the most interesting both academically and industrially. Their development as practical polymerization catalysts is the first large scale industrial application for the long known and well developed class of metallocene complexes. About all the fascinating organometallic chemical aspect in metallocene catalysis, the key aspect which earned them their enormous industrial research input is that group IVB metallocene catalysts make polymers which cannot be produced by conventional Ziegler-Natta catalysts.

2.1 Polar monomer

Polar group such as esters are beiieved to act as a catalytic poison in Ziegler-Natta polymerizations. Thus, it is usually difficult to polymerize polar vinyl monomers with Ziegler-Natta catalysts. Nevertheless, polymerizations of vinyl monomers containing polar groups have been studied from the point of the synthesis of stereoregular polymers. Group IVB metallocene complexes are used as initiating systems for synthesis of polar or functional monomers. Methyl methacrylate monomers (MMA) can be efficiently polymerized stereoselective using a two-component catalytic system. Collins and Ward polymerized MMA using a mixture of a Cp_2ZrMe_2 and Cp_2ZrMe-(THF) [BPh_4], the reaction is shown in equation 2.1



(2.1)

The mechanism probably involved enolate complexes in a group transfer polymerization. The sensitivity of this two-component initiator system to impurities in monomer and solvent suggested that development of a scrubbing agent that could be used, in situ, to purify them would be attractive. In contrast, Cp_2ZrCl_2 / MAO [13], rac-$Et(ind)_2ZrCl_2$ / $Ph_3C^+B(C_6F_5)_4^-$, rac-$Et(indH_4)_2ZrCl_2$ / Ph_3C^+ $B(C_6F_5)_4^-$ and rac-$Me_2Si(ind)_2ZrCl_2$ / $Ph_3C^+B(C_6F_5)_4^-$ were found to be inactive towards the polymerization of MMA without the third component, Lewis acids such as dialkylzinc and alkylaluminum compounds.

2.2 Catalytic system

2.2.1 Metallocene

Metallocene catalysts are organometallic compounds in which one or two carbocyclic ligands or substituted carbocyclic ligands such as cyclopentadienyl ring, substituted cyclopentadienyl ring or derivatives of cyclopentadienyl ring (for example, fluorenyl, indenyl, etc.) are π-bonded to the metal center atom.

The typical chemical structure of metallocene catalyst is shown by Figure 2.1 where M is the group IVB, VB or VIB transition metals, generally in group IVB (Ti, Zr and Hf). A, a bridging atom (usually C, Si atom) or bridging molecule e.g. ethylene, R, is a σ-homoleptic hydrocarbyl such as H, alkyl, or hydrocarbon groups and X represents chlorine or other halogens or an alkyl group.

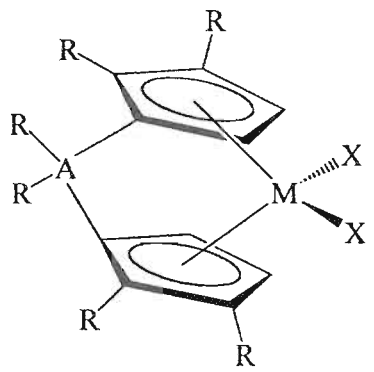


Figure 2.1 Typical chemical structure of a metallocene catalyst

The central transition metal atom, cyclopentadienyl (or cyclopentadienyl derivatives) ligands, bridging atom and halides modified by variation and / or substitutions some of these parts can result in variation of the catalytic activity, polymer structure, molecular weight and molecular weight distribution.

A major difference between metallocene and conventional heterogeneous Ziegler-Natta catalyst is that the former has well-defined molecular structure and polymerization occurs at one position in the molecule, the transition metal atom. Metallocene is called single-site catalyst, in contrast to multiple active sites characteristic of the more traditional Ziegler-Natta catalysts.

The structures or compositions of metallocene catalysts have many varieties. Type of catalysts are divided by different structures or compositions. When the two cyclopentadienyl (Cp) rings on either side of the transition metal are unbridged, (Figure 2.2), this metallocene is nonstereorigid, it is C_{2v} symmetry.

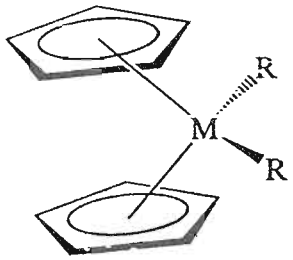


Figure 2.2 Non-bridging C_{2v} symmetric metallocene catalyst.

When the two cyclopentadienyl ligands which are bonded to the metal atom, are connected by bridging atom or bridging molecule (Figure 2.3), the metallocene is stereorigid compound, called 'ansa' metallocene (ansa means handle).

The rotation of Cp ligands can be prevented by bridging which connect them together, to give a rigid and stereoselective ligands framework. It shows C_1, C_2 or C_s symmetry, depending on the substituents on two Cp rings and the structure of the bridging unit.

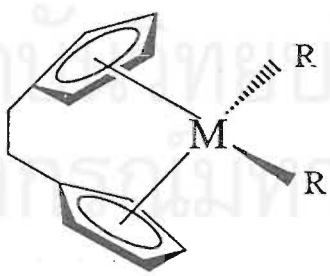


Figure 2.3 Ethylene bridged cyclopentadienyl metallocene catalyst.

The lists of the C_{2v}, C_2 and C_s symmetric metallocenes are demonstrated in Tables 2.1, 2.2 and 2.3, respectively.

Table 2.1 C_{2v}- symmetric metallocenes

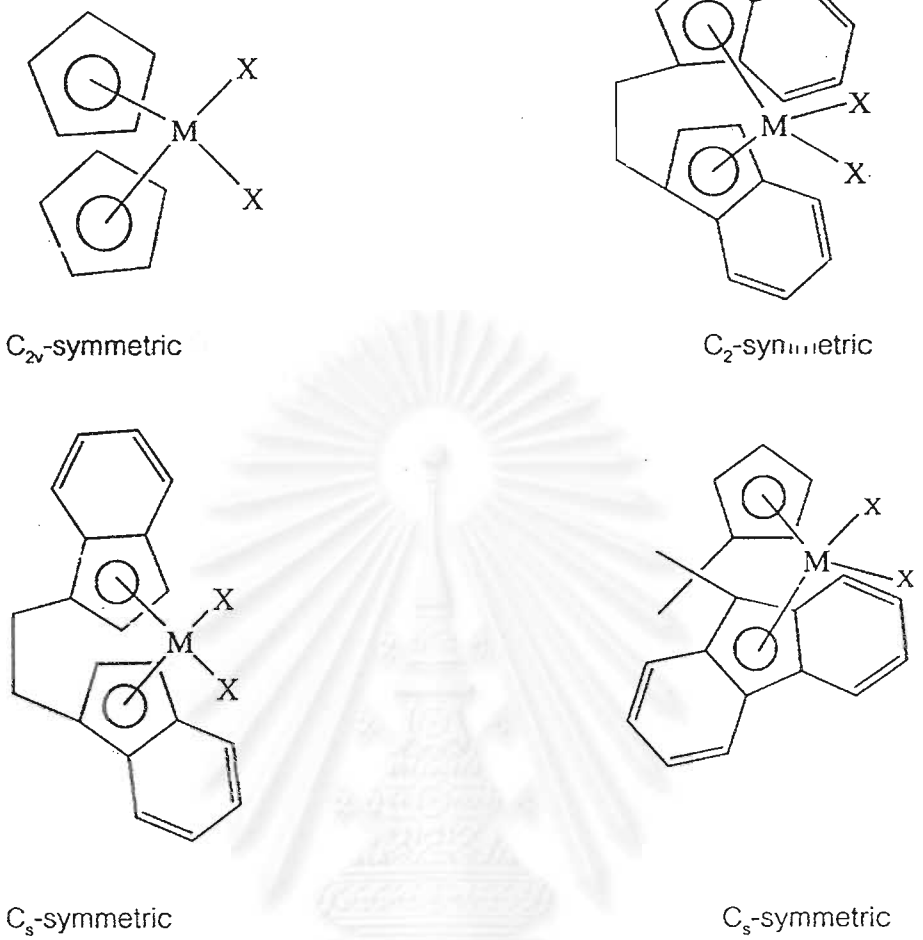
Metallocenes	Examples
Titanocene	Cp_2TiCl_2, $CpTiCl_3$, Cp_2TiMe_2
Zirconocene	Ind_2ZrCl_2, Ind_2ZrMe_2
Hafnocene	Cp_2HfCl_2, Cp_2HfMe_2

Table 2.2 C_2-symmetric metallocenes

Metallocenes	Examples
Titanocene	$(C_5H_4Me)PhTiCl_2$
Zirconocene	$Et(ind)_2ZrCl_2$, $Me_2Si(Ind)_2ZrCl_2$, $Me_2Si(2\text{-}MeInd)_2ZrCl_2$, $Me_2Si(2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind)_2ZrCl_2$
Hafnocene	$Et(ind)_2HfCl_2$, $Me_2Si(Ind)_2HfCl_2$

Table 2.3 C_s-symmetric metallocenes

Bridging zirconocenes	Examples
tert-butyl bridge	t-BuCH(3-t-Bu-Cp)(Flu)$ZrCl_2$
isopropyl bridge	i-Pr[(MeCp)(Ind)]$ZrCl_2$
isopropylidene bridge	Me_2C(MeCp)(Ind)$ZrCl_2$
dimethylsilyl bridge	Me_2Si(3-t-Bu-Cp)(Flu)$ZrCl_2$



C_{2v}-symmetric C_2-symmetric

C_s-symmetric C_s-symmetric

Figure 2.4 Structures of the metallocenes showing various symmetries

2.2.2 Cocatalysts

Methylaluminoxane (MAO)

MAO is an oligomeric product of incomplete hydrolysis of trimethylaluminum and consists of monomer [-Al(CH_3)O-] units. Many inorganic hydrated compounds are used as a source of water for preparing MAO from alkylaluminum such as $CuSO_4.5H_2O$, $Al_2(SO_4)_3.6H_2O$, $MgCl_2.6H_2O$, etc.

The structure of MAO can only be postulated as being a mixture of linear or cyclic oligomers of MeAlO units (shown in Figure 2.5) with degree of oligomerization commonly varying from 6 – 20 MAO [1]. The systhesis of MAO is associated with several serious limitations due to reaction time to obtain a controlled exotherm, the risk of explosion, low yields and the formation of solid by products. The agreements appear to be that MAO oligomers are fluxional molecules with a dynamic equilibrium among them, which change their size and structure. The average molecular weight depends on the preparative conditions. In Figure 2.6 shown the activation of zirconocene dichloride by MAO [14].

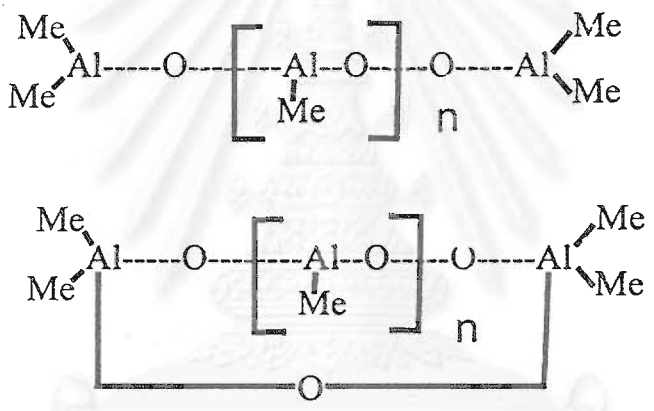


Figure 2.5 Linear and cyclic oligomers of MAO

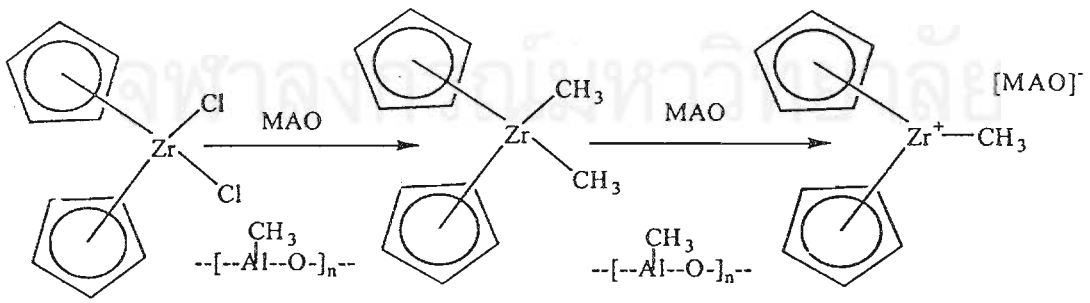


Figure 2.6 Activation of zirconocene dichloride precursor by MAO

In polymerization, it has been found that very high ratios of MAO to metallocene are required to achieve a good polymerization activity. MAO appears to have a combination of the following functions:

1. MAO alkylates the metallocene.
2. MAO abstracts alkyl group from metallocene to generate cationic metallocenium active species.
3. MAO stabilizes metallocenium active species.
4. MAO can scavenge the impurities in polymerization system.

Metallocene catalytic systems require a large amount of MAO for high activity in polymerization. The high cost of aluminum cocatalyst stimulates the search for new kind of cocatalysts, which can perform in the absence of MAO.

2.2.3 Boron compounds

Non-aluminum cocatalyst such as $B(C_6F_5)_3$, $PhNMe_2H^+B(C_6F_5)_4^-$ and $Ph_3C^+B(C_6F_5)_4^-$ was discovered as an activator for metallocene catalyst. These boron compounds can give high activity when combine with metallocene. In the polymerization of MMA, boron compounds were used as cocatalyst in an equimolar with metallocene catalysts. However, no polymers were produced until the third component, Lewis acid as $Zn(C_2H_5)_2$ was added. Soga et al.[15-16] reported that cationic zirconocene complexes formed from dimethylzirconocene and $B(C_6F_5)_3$ or $Ph_3C^+B(C_6F_5)_4^-$ polymerize MMA when activated with alkylzinc or alkylaluminum compounds.

To generate active species catalyst, zirconocene dichloride precatalyst was alkylated by alkylating agents such as alkyl aluminum or Grignard reagent. Chloride atoms were replaced with alkyl group to form C-C bond with zirconium. The boron compounds abstract alkyl group from dialkyl zirconocene. Zirconium cation, active site was formed and stabilized by boron compounds throughout the polymerization reaction.

Figure 2.7 shown the dimethyl zirconocene has been abstracted methyl group to generate active species by boron compounds [17].

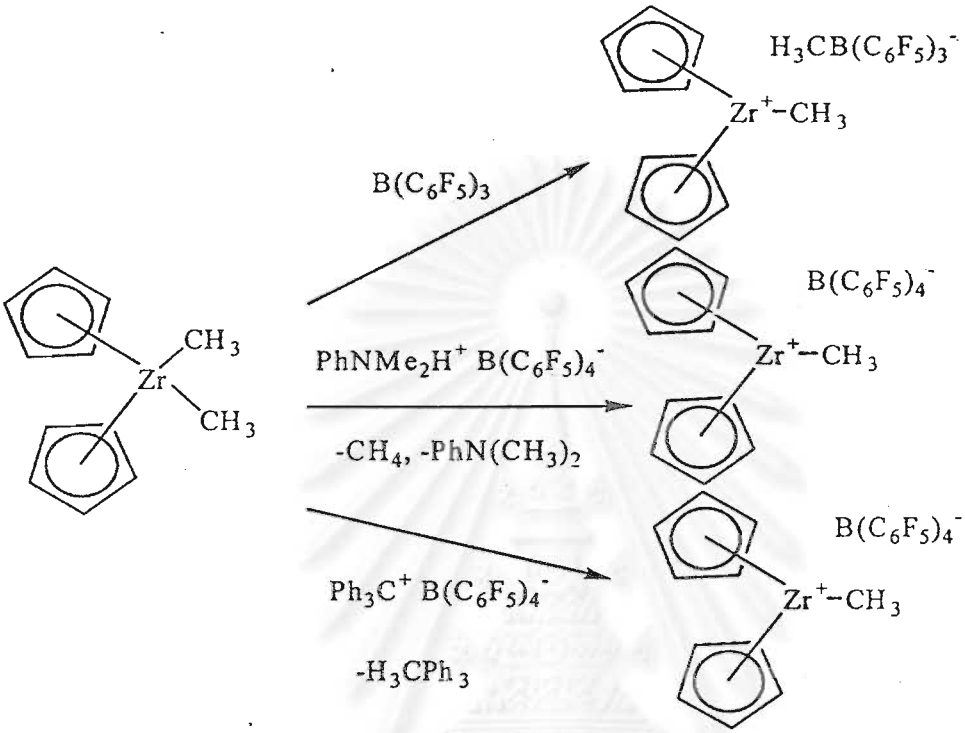


Figure 2.7 Methyl group abstraction by boron compounds

2.2.4 Organozinc

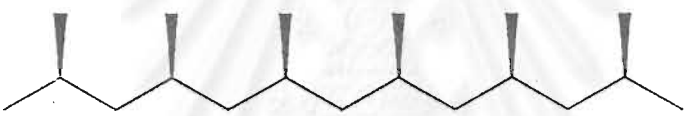
Organozinc such as $Zn(C_2H_5)_2$ is Lewis acid, complexed with monomer. When no Lewis acid was used, no product was obtained.

In polymerization, MMA was at first mixed with $Zn(C_2H_5)_2$ in toluene solvent and aged for 1 hour before subsequent addition of $B(C_6F_5)_3$ and Cp_2ZrMe_2. However, polymerizations were initiated to give PMMA with high molecular weight and narrow molecular weight distribution in good yields.

2.3 Polymer tacticity

Stereoregularity arises because of order in the spacial structure of polymer chains. If the backbone of a polymer chain is drawn in a flat zigzag form in the plane of the paper, in (a) all the substituent R groups lie uniformly on the same side of the zigzag plane, the structure is called isotactic, (b) the substituent R groups occupy positions alternatively above and below the backbone plane, the structure is called syndiotactic, (c) there is no regular arrangement of the substituent R groups, the structure is called atactic. Figure 2.8 illustrates olefin tacticity, for PMMA, R group is CO_2Me.

(a) Isotactic



(b) Syndiotactic

(c) Atactic

Figure 2.8 Schematic illustration of olefin tacticity

2.4 The mechanisms for stereochemical control in olefin polymerization

The polymerization of α-olefin such as polypropylene with a catalyst would lead to a polymer with randomly oriented alkyl side-chain. However, since cyclopentadienyl ligands are easily modified by substituents and can be tailored to suit particular requirements, appropriate ligand design has been used to control the orientation of the coordinated monomer in such a way that either isotactic or syndiotactic polymer must result. Such stereoregular polymers have quite different physical properties, for example, crystallinity, glass transition temperature, etc,.

For bis-(ind)zirconocene complexes, the rotation of the ligands can be prevented by connecting them via a $-CH_2-CH_2-$ bridge to give a rigid and stereoselective ligand framework. The general mechanism for controlling polymer tacticity of α-olefin by C_2-symmetric zirconocene catalyst is shown in Figure 2.9 [18].

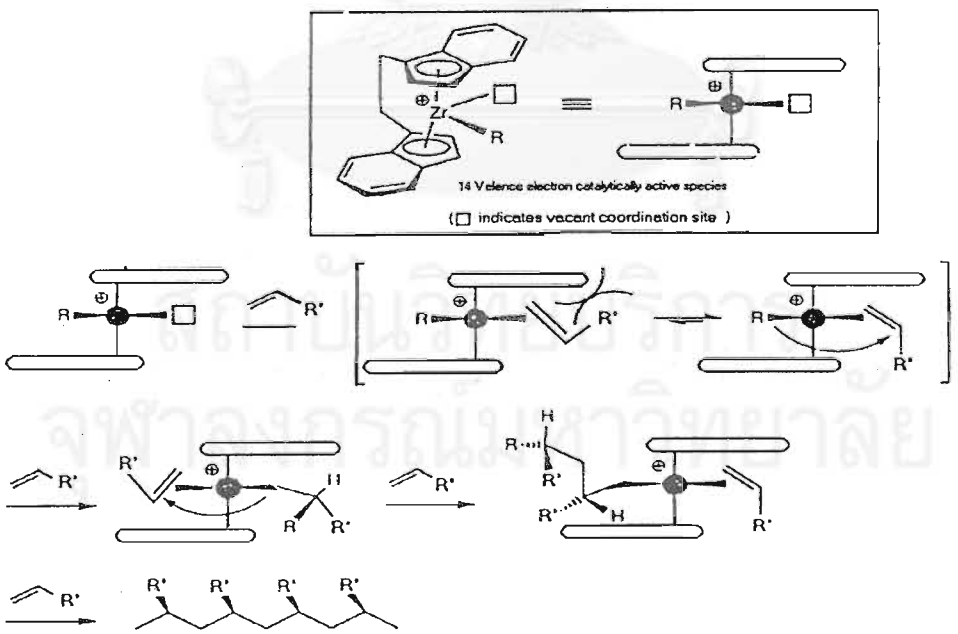


Figure 2.9 Mechanism of α-olefin polymerization using C_2- symmetric zirconocene

2.5 Active species

It is generally agreed that the catalytically active species in olefin is a coordinatively unsaturated cationic alkyl complex $[L_nMR]^+$ that is stabilized by several ligands (L). To generate such species several methods can be employed. Three different routes (A, B and C) are shown in Figure 2.10 [19].

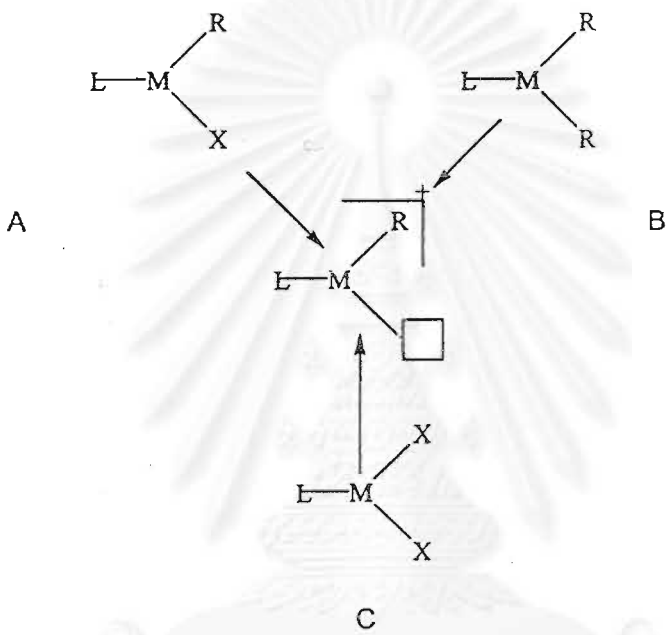


Figure 2.10 Three routes for generating active species

Route A involves the abstraction of an anionic ligand (e.g. a halide) and its substitution for a "noncoordinating" anion by a salt elimination. Common reagents are $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ or silver salt such as $AgBF_4$ or $AgOSO_2CF_3$ (AgOTf) for the later transition metals.

Route B involves the abstraction of an alkyl ligand or, more strictly, an alkyl anion. Reagents used for these ligands are, for example, $Ph_3C^+B(C_6F_5)_4^-$, $PhNMe_2H^+$ $B(C_6F_5)_4^-$, $H(OEt_2)_2$ $B\{3,5\text{-}(CF_3)_2C_6H_3\}_4$ or $B(C_6F_5)_3$, whareas the trityl reagents as an abstracting agent, the aluminum salt and the acid remove the alkyl ligand by protonation. In the case of $B(C_6F_5)_3$ the alkyl ligand is only partly abstracted leading to cation-like catalytic species.

Route C is a combined alkylation and abstraction process, which can be achieved by treating a dihalide precatalyst firstly with an alkylating species and then with one of the aforementioned alkyl-abstracting agents, for example a trialkylaluminum compound followed by $B(C_6F_5)_3$. Some reagents can perform both processes, for example, alkylaluminum halides and especially aluminoxane such as methylaluminoxane (MAO)[20].

In MMA polymerization, the precatalyst was alkylated by alkylating agent to replace chloride ligands. Boron cocatalyst abstracts one alkyl group to generate Et-bis(ind)$_2$ZrMe$^+$ with one vacant site which was believed as active species. Two indenyl ligands and bridging ethylene on zirconocene catalyst can control the direction and insertion of monomer by steric effect. Thus, C_2 symmetric catalyst type produces isotactic polymer.

2.6 Polymerization mechanisms

2.6.1 Initiating step

The nature and the information of the true active catalytic species are not yet fully elucidated. But, for group IVB metallocene polymerization catalysts are generally accepted that metallocene catalysts combined with MAO consist of cationic complexes formed by reaction of a metallocene with MAO.

$$Cp_2MX_2 + MAO \rightleftharpoons [Cp_2MCH_3]^+[MAO\text{-}X_2]^- \qquad (2.2)$$

M = Ti, Zr and Hf

MAO methylated and abstracted ligands on metallocene catalyst to pronounce Lewis acidity. The use of a large excess of MAO is necessary because of the low value of the equilibrium constant.

Economically, such the high excess amount of the expensive MAO are very unfavorable. The investigation were carried out to reduce the amount of MAO. The boron compounds were used as cocatalyst to replace MAO or aluminum compounds.

When boron compounds were used as cocatalyst, the metallocenium active species can be generated by boron abstraction. Thus, the catalyst precursor such as Cp_2ZrCl_2 must be alkylated by alkylating agent (e.g. MAO, alkyl aluminum or Grignard reagent). The formation of active species are proposed following these equations.

$$Cp_2ZrMe_2 + B(C_6F_5)_3 \longrightarrow Cp_2ZrMe^+MeB(C_6F_5)_4^- \quad (2.3)$$

$$2\,Cp_2ZrMe_2 + 2\,Ph_3C^+B(C_6F_5)_4^- \longrightarrow 2Cp_2ZrMe^+MeB(C_6F_5)_4^- + 2\,Ph_3CMe \quad (2.4)$$

2.6.2 Propagation step

The mechanism of homogeneous group IV metallocene polymerization catalysts was proposed by many researchers. There are three basic mechanism suggested for the insertion of olefin into a transition metal alkyl bond in metallocene catalyst [21], shown in Figure 2.11 – 2.13. These mechanism are:

1. The direct insertion mechanism proposed by Cossee and Arlman.
2. The metathesis mechanism proposed by Green and Rooney.
3. The modified Green-Rooney mechanism proposed by Brookhart and Green.

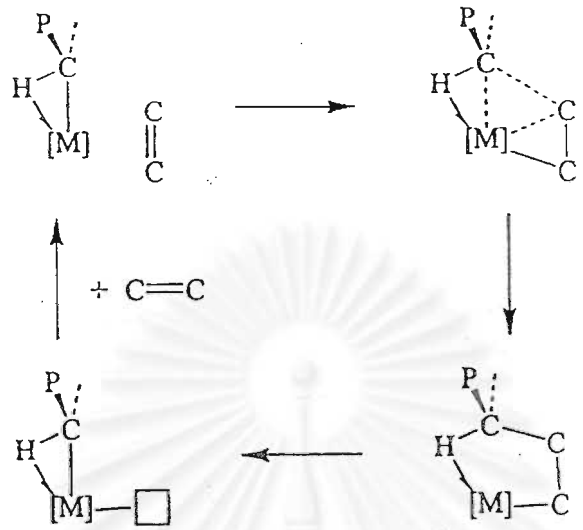


Figure 2.11 Direct insertion mechanism (□vacant coordination site)

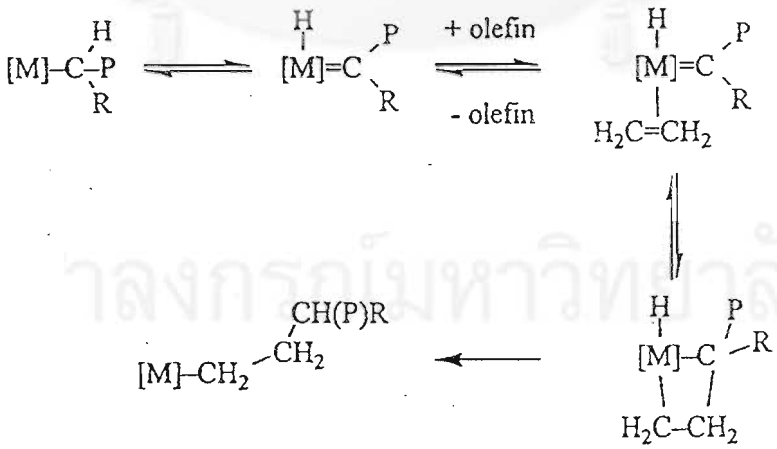


Figure 2.12 Metathesis mechanism

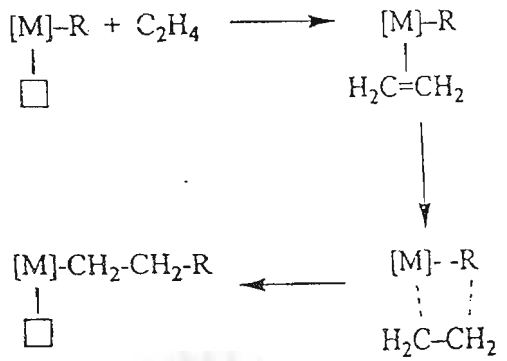


Figure 2.13 Modified Green-Rooney mechanism

Figure 2.14 illustrates the model of active complex of isospecific, C_2 symmetrical zirconocene with the two possible positions of 1,2 coordinated α-olefins molecule: (a) (a) to (c) pathway, this pathway is the energetically favored one, the steric demand of the indenyl ligands force the growing chain and the R group on molecule into an orientation in the fourth and second quadrant, respectively, give isotactic polymer. (b) (b) to (e) pathway, the disfavored insertion from position (b) then lead to the stereoerror a racemic stereosequence (d), because of the enantiomorphic site control of the catalyst this error can be corrected upon the next insertion (d) to (e) [21].

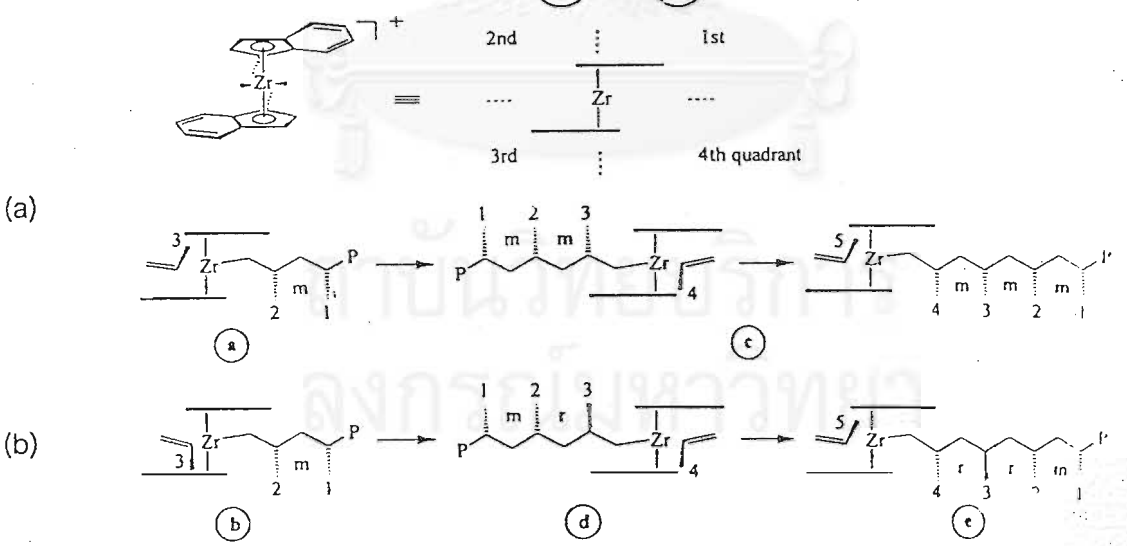


Figure 2.14 Model of active complex of isospecific, C_2 symmetrical zirconocene with the two possible positions (a) energetically favor (b) enegetically unfavor

2.6.3 Chain transfer and termination step

General mechanism of chain transfer reaction can be divided by four types:

1. Reaction to aluminum

In α-olefin polymerization with metallocene catalyst / MAO or alkyl Aluminum, chain-end takes place by transfer to aluminum which lead to the formation of aluminum-polymer bonds:

$$[M^+]-(CH_2CH_2)_n-R + AlR_3 \longrightarrow [M]^+-R + R_2Al-(CH_2CH_2)_n-R \quad (2.5)$$

2. β-hydrogen transfer to metal.

$$[M]^+-(CH_2CH_2)_n-R \longrightarrow [M]^+-H + (CH_2CH_2)-(CH_2CH_2)_{n-1}-R \quad (2.6)$$

3. β-hydrogen transfer to monomer.

$$[M]^+-(CH_2CH_2)_n-R + \parallel \longrightarrow [M]^+-CH_2CH_3 + (CH_2CH)-(CH_2CH_2)_{n-1}-R \quad (2.7)$$

4. Hydrogenolysis.

$$[M]^+-(CH_2CH_2)_n-R \xrightarrow{H_2} [M]^+-H + (CH_3CH_2)-(CH_2CH_2)_{n-1}-R \quad (2.8)$$

$[M]^+-H$ and $[M]^+-R$ species formed from chain transfer are able to reinitiate a new polymerization process again. For living growing chain polymer, the catalyst must be killed at the end of reaction by adding a proton donor such as methanol, acids and water.

CHAPTER III

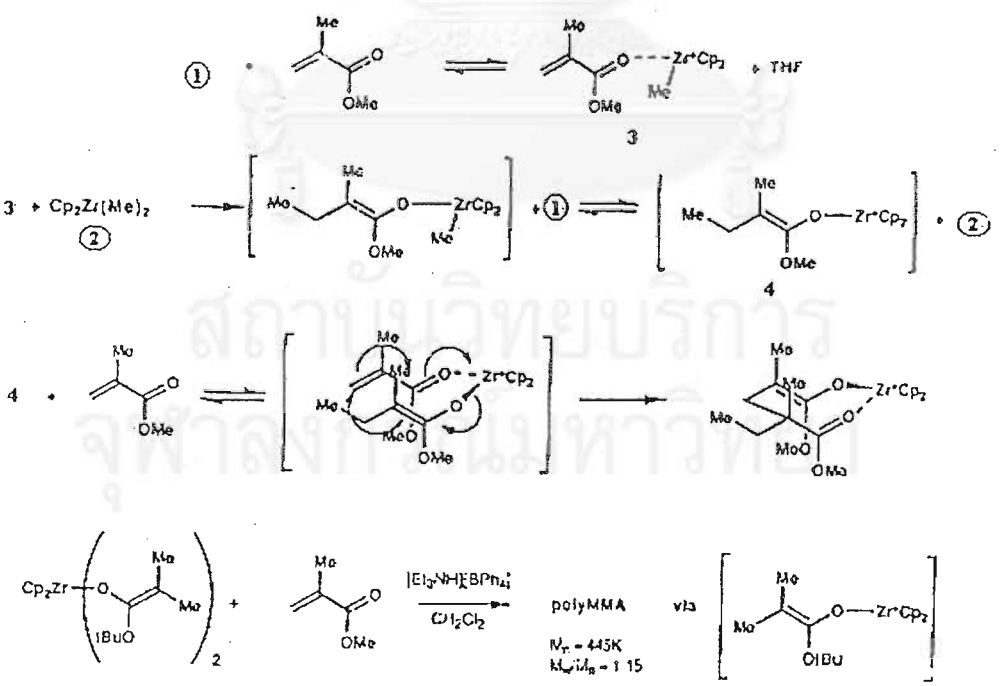
LITERATURE REVIEWS

3.1 Catalysts

3.1.1 Metallocene catalysts

3.1.1.1 Group IVB metallocene catalysts

A neutral metallocene Cp_2ZrMe_2 (2) combined with the second component, $Cp_2ZrMe(THF)^+$ (1) was found to polymerize methyl methacrylate [22]. The catalytic system can produce in this polymerization is predominantly syndiotactic at 0 ^{0}C. The polymers posses narrow molecular weight distributions and molecular weight increases with decreasing temperature of polymerization. Donor solvents decrease the rate of polymerization and the higher molecular weight is produced with a broader molecular weight distribution. A proposed mechanism is shown in Figure 3.1.



(3.1)

(3.2)

(3.3)

(3.4)

Figure 3.1 The polymerization mechanism of MMA using Cp_2ZrMe_2 / $Cp_2ZrMe(THF)^+$ system

Collins et al. [23] polymerized methyl methacrylate by using chiral metallocene [Et(IndH$_4$)ZrMe$_2$] catalyst with tetraphenyl borate $nBu_3NH^+BPh_4^-$ as cocatalyst. This system gave isotactic polymer and narrow molecular weight distribution. The polymerization showed a living polymer via intramolecular Michael addition of neutral enolates with monomer process, the mechanism was shown in Figure 3.2.

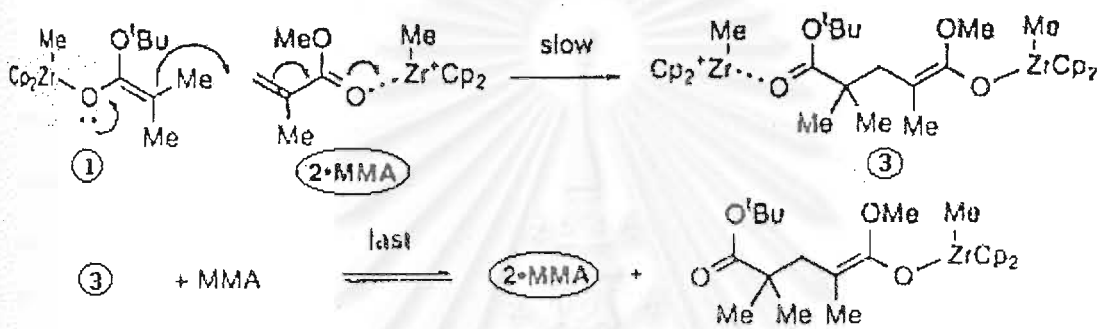


Figure 3.2 Intramolecular Michael addition of neutral enolates with monomer

Li et al. [24] reported that the polymerization of polymethyl methacrylate, initiated by zirconocene complexes Cp_2ZrMe and $Cp_2ZrMe(THF)^+$ provides partially syndiotactic PMMA in high yield with narrow molecular weight distribution. The kinetics of this process were studied and revealed that in this system the rate of initiation is much slower than that of propagation. The process is not living and at high temperature, the growing chain are deactivated by this process and also by competitive α- hydrogen transfer.

Deng et al. [25] used chiral ansa-zirconocene dimethyl / $Ph_3C^+B(C_6F_5)_4^-$ catalyst combined with suitable Lewis acids such as alkyl aluminum or organozinc to generate highly isotactic PMMA. The polymerization was found to proceed by an enantiomorphic site-controlled mechanism. Using achiral zirconocene catalyst in the same condition gave syndiotactic-rich PMMA. Both systems could produce high molecular weight and narrow molecular weight distribution PMMA.

Hocker et al. [26] reported that the cationic complexes $Me_2C(Cp)(Ind)ZrMe(THF)^+BPh_4^-$ (1) and $Me_2C(Cp)_2ZrMe(THF)^+BPh_4^-$(2) are highly active for the polymerization of MMA without the addition of the corresponding ester enolate complex. Complexes 1 can produce highly isotactic PMMA whereas complexes 2 gives syndiotactic PMMA at low temperature. This is the first example for a rational control of PMMA microstructure via catalyst symmetry.

Stuhldreier et al. [27] synthesized bridged cationic zirconocene complex (iPr-Cp)(Ind)Zr(Me)(THF)/[BPh_4] for polymerization of PMMA. The result showed that this complex is an efficient catalyst for the stereospecific polymerization of MMA. It was concluded that the polymerization is living. The isotactic PMMA is formed by enantiomorphic site mechanism. It should be mentioned that during polymerization, no enolate complex is formed and the mechanism of polymerization differed from the mechanism proposed by Collins.

Collins et al. [28] synthesized the linked Cp-amido complexes of zirconocene, $MeSi(Cp^*)(BuN)ZrCl_2$ and used for polymerization of MMA. The isotactic PMMA were produced. At higher temperature, molecular weight distribution is broad and the polymer was less isotactic.

Karanikolopoulos et al. [29] polymerized PMMA using catalytic system $Cp_2ZrMe_2/B(C_6F_5)_3/Zn(C_2H_5)_2$ in toluene, under thoroughly purified conditions, it was found to produce high syndiotactic PMMA with narrow molecular weight distribution and almost quantitative yields.

3.1.1.2 Group IIIB metallocene catalysts

Jiang et al. [13] used yttrocene, $Cp_2YCl(THF)$ as a catalyst combined with methyl aluminoxane (MAO) and diethyl zinc. Living polymerization took place when conducted at 0 ^{0}C in toluene. The reaction temperature reached –60^{0}C, PMMA was highly syndiotactic and molecular weight. This catalyst system could not synthesize PMMA when the reaction temperature exceeded room temperature.

Mao et al. [30] found that (diisopropylamido)bis(methylcyclopentadienyl) lanthanides $(MeC_5H_4)_2LnN(i\text{-}Pr)_2(THF)$ (Ln =Yb, Er and Y) exhibit extremely high catalytic activity in the polymerization of methyl methacrylate. The reaction can be carried out over a quite broad range of polymerization temperature from –78 to 40 ^{0}C. The catalytic activity of the complexes increased with an increase of ionic radii of metal elements, i.e. Y > Er > Yb . High molecular weight polymer obtained exceeded 100,000 and molecular weight distribution became broad with the increase of temperature. Highly syndiotactic of PMMA were obtained by lowering the reaction temperature.

Marks et al. [31] used an achiral organolanthanide $[Cp^*SmH_2]$ to efficiently catalyze the living, highly syndiospecific polymerization of methyl methacrylate. The result confirmed that achiral hydride precatalysts yield syndiotactic PMMA with narrow molecular weight distribution. Assuming that the mechanism involves initial 1,4 addition of the Ln-R functionality to MMA to generate an enolate which then undergoes rapid, subsequent conjugate addition sequences. In Figure 3.3 the mechanism was proposed for the stereoregular polymerization of MMA mediated by C_1-symmetric organolanthanide complexes.

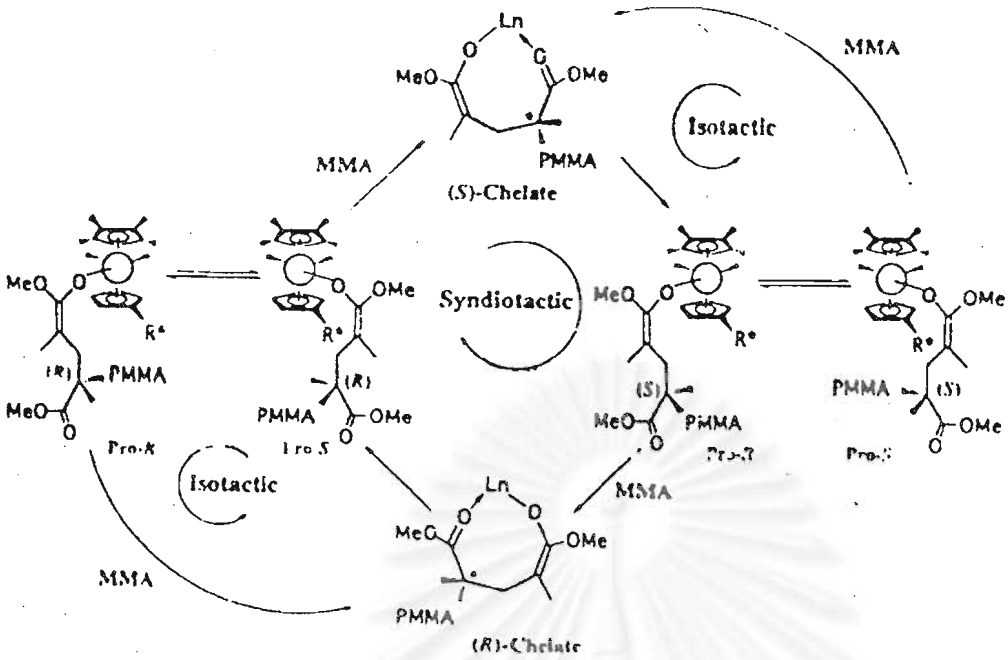


Figure 3.3 The mechanism of MMA polymerization by C_1-symmetric organolanthanide complexes

Do et al. [32] synthesized rac-$Zr(CpCMe_2CB_{10}H_{10}C)_2$ from the reaction of $CpHCMe_2CB_{10}H_{10}CH$ with $ZrCl_4$, this catalyst catalyzed the formation of the syndiotactic PMMA in THF, in the absence of any alkylating agent or cationic center generator. The PMMA produced with these catalytic systems have a narrow molecular weight distribution. The syndiotacticity decreased with the increase of polymerization temperature.

3.1.2 Non- metallocene catalysts

Miyamoto et al. [33] polymerized PMMA with a series of enamines ((1-pyrolidinyl)(cyclohexene), act as an initiator in the presence of methylaluminum bis (2,6-di-tert-butylphenoxide) which acts as an activator. MMA polymerization proceeded smoothly in toluene at or below room temperature, went to completion within 1 hr, and afforded syndiotactic-rich PMMA with narrow molecular weight distribution (1.1-1.4).

Endo et al. [34] polymerized methyl methacrylate with metal acetylacetonates, especially vanadium(III) acetylacetonate in combination with $Al(C_2H_5)_3$. This catalyst could initiate the polymerization of MMA, proceeded through a coordination mechanism . The resulting polymers were found to form stereocomplex in acetone. The structure was estimated to be stereocomplex from an analysis of NMR spectroscopy. It was concluded that multiactive sites bearing different stereospecificites, including iso-specific and syndio-specific, were produced in the polymerization of this system.

Polymerization mechanisms of vinyl monomers with metal acetylacetonates ($M(acac)_x$) were reported to depend on both monomers and catalysts used, for example, when methyl methacrylate, styrene and vinyl acetate were used as monomers, radical polymerizations were induced. Among the $M(acac)_x$ examined, $M(acac)_3$ show the highest catalytic activity for the polymerization of MMA. The assertion is that the polymerizations initiate with a monomer radical generated through complexes formed between a central metal and monomer, and the following initiation mechanism was proposed (equation 3.5).

$$M(acac)_x + \text{Monomer} \rightleftharpoons [\text{Monomer-}M(acac)_3] \longrightarrow (acac)\text{-Monomer}^{\bullet} + M(acac)_{x-1} \qquad (3.5)$$

Polar group such as esters are believed to act as a catalytic poison in Ziegler-Natta polymerizations. Thus, it is usually difficult to polymerize polar vinyl monomers with Ziegler-Natta catalysts. Nevertheless, polymerizations of vinyl monomers containing polar groups have been studied from the point of the synthesis of stereoregular polymers. Concerning MMA, the polymerization with $TiCl_4$- $Al(C_2H_5)_3$ catalyst was reported to give predominantly syndiotactic polymers at low temperatures such as –78 ^{0}C. Stereoblock polymers were also synthesized with $VOCl_3$- $Al(C_2H_5)_3$ and VCl_4- $Al(C_2H_5)_3$ catalysts at 40 ^{0}C.

Cameron et al. [35] described a remarkably active and robust aluminum initiator system based upon the tetradentate N, N'-ethylene bis(salicylideneimine) Schiff base ligand and a novel nickel-catalyzed approach to generating the active aluminum enolate centers. However, the system was not good for MMA polymerization, until three equivalents of the third component, bis(2,6-di-tert-butyl-4-methyl-phenoxide) aluminummethyl was added to the system. The structure of polymer product was atactic, molecular weight and narrow molecular weight distribution were high.

3.2 Organozinc

Although an interaction between $Zn(C_2H_5)_2$ and MMA can be observed in the ^{13}C NMR spectrum, the role of $Zn(C_2H_5)_2$ in the polymerization remains unknown. Deng et al. [25] investigated the effect of $Zn(C_2H_5)_2$ under the conditions of [MMA] = 0.85 M. $[Cp_2ZrMe_2] = Ph_3C^+B(C_6F_5)_4^-$ = 0.45 mM. Increasing of the concentration of $Zn(C_2H_5)_2$ from 23 to 364 mM. caused a sharp increase in polymer yield. Then, the polymer yield gradually reached a constant value with increasing concentration of $Zn(C_2H_5)_2$ to as far as 727 mM.

Jiang et al. [13] polymerized methyl methacrylate with $Cp_2YCl(THF)$ catalyst in the presence of Lewis acid like $Zn(C_2H_5)_2$ which was complexed with the MMA monomer in this experiment. The $Zn(C_2H_5)_2$ concentration used in this study was limited to 0, 5, 7.5 and 10 mmol. When no Lewis acid was used in this polymerization, no product was obtained because the metallocene catalyst activity was poisoned by the monomer. Stronger activity is obtained with a concentration of $Zn(C_2H_5)_2$ of 7.5 mmol. The percent of isotacticity was decreased with increasing of zinc concentration. Therefore, the glass transition temperature (T_g) could reach 112 ^0C with a high amount of $Zn(C_2H_5)_2$.

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CHAPTER IV
EXPERIMENT

In the present study of the methyl methacrylate polymerization with ansa-zirconocene catalyst, the experiment was divided into three steps.

1. Catalyst and cocatalysts solution preparation.
2. Methyl methacrylate polymerization with the prepared catalyst.
3. Characterization of polymethyl methacrylate products.

The details of the experiments were explained in the following clauses.

4.1 Operation and equipments

The experiments were done in inert atmosphere, prepurified nitrogen, using standard Schlenk technique. All equipments used in the catalyst preparation and polymerization, are listed as follows :

4.1.1 Schlenk line

Schlenk line consists of nitrogen and vacuum lines. The vacuum line was equipped with the solvent trap and pump, respectively. The nitrogen line was connected to the moisture trap (purified nitrogen gas by passing molecular sieve, NaOH and P_2O_5, respectively.) and the oil bubbler that contained enough oil to provide a seal from the atmosphere. The Schlenk line was shown in Figure 4.1.

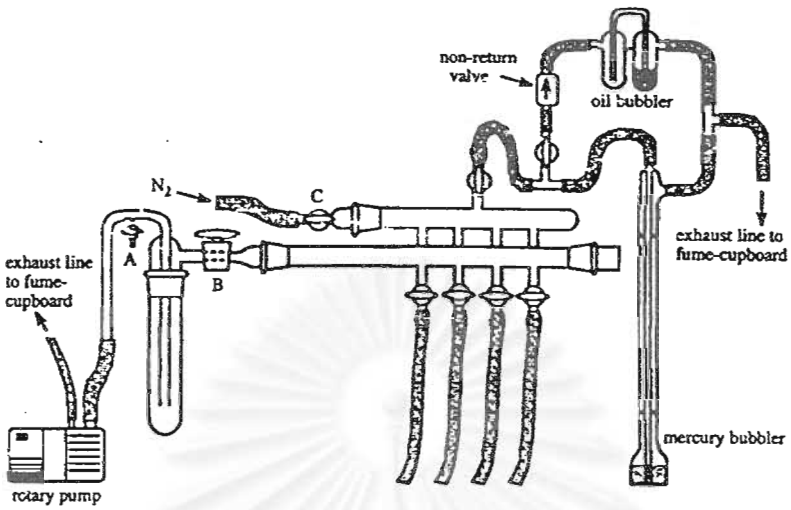

Figure 4.1 Schlenk line.

4.1.2 Schlenk flask

A flask with a side-arm for use with inert gas. It has a side-arm to connect to the Schlenk line manifold. Some typical models are shown in Figure 4.2

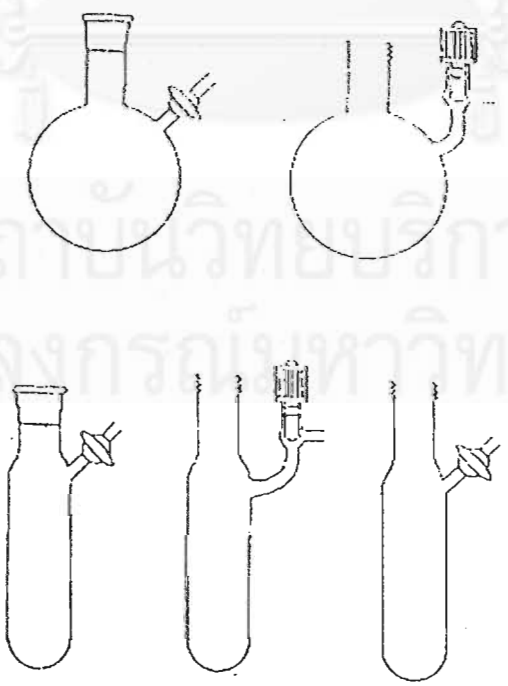

Figure 4.2 Round-bottomed and tube designed for Schlenk flasks.

4.1.3 Vacuum pump

A pressure of $10^{-3} - 10^{-1}$ mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

4.1.4 Heating bath

The heating bath with thermometer was used to hold the temperature of polymerization reaction.

4.1.5 Dewar flask

The semi-spherical lower Dewar flask was used to hold the very low temperature for reaction.

4.1.6 Inert gas supply

The ultra high purity nitrogen inert gas was passed through drying columns. The inert gas was used to feed in the nitrogen line of Schlenk line and polymerization reactor.

4.1.7 Syringe and needle

The syringes with volume of 50, 10, 5, 2, 1 and 0.5 ml. needles No. 19, 20, and 22 were used.

4.1.8 Glove bag

Glove bag is a moderate-volume gas-tight container from which air or moisture are excluded. The glove bag has a way to connect with Schlenk line, which can be evacuated and then filled with nitrogen gas.

4.2 Chemicals

The chemicals used in this experiment were analytical grade, except critical materials are specified as follows:

Table 4.1 Chemical reagents and suppliers

Chemicals	Suppliers
Ultra high purity nitrogen gas (99.999%)	Thai Industry Gas Co.,Ltd.,Thailand
Toluene	Lab Scans Co., Ltd., Ireland
Methyl methacrylate monomer	Hopkin & Williams Ltd., England
Diethyl zinc solution 1.0 M in toluene	Fluka Chemie A.G., Switzerland
Ethylene bis (indenyl)zirconium dichloride	Aldrich Chemical Company, Inc., USA.
Dimethylanilinium tetrakis(pentafluorophenyl) borate $[PhNMe_2H]^+[B(C_6F_5)_4]^-$	Donated from DOW Chemical Company, USA.
Tris(pentafluorophenyl)boron $B(C_6F_5)_3$	Fluka Chemie A.G., Switzerland
Triphenylcarbenium tetrapentafluorophenylborate $[Ph_3C]^+[B(C_6F_5)_4]^-$	Donated from Japan Advanced Institute of Science and Technology (JAIST), Japan
Methyl magnesium bromide (MeMgBr) 1.0 M in diethyl ether	Aldrich Chemical Company, Inc., USA.
Tri-isobutylaluminium (TIBA)	Donated from Japan Advanced Institute of Science and Technology (JAIST), Japan

In this work, several reagents react violently with water and ignite spontaneously in air (by reaction with oxygen and/or moisture). So they were handled safely using inert-atmosphere techniques (Schlenk and glove bag techniques). Also, the chemicals and solvents were dried before using with following methods:

1. Ultra high purity nitrogen gas was purified by passing through three columns packed with molecular sieve 4°A, NaOH and P_2O_5, respectively.
2. Non-halogenated solvents were purified by refluxing over sodium/benzophenone and distilled under nitrogen atmosphere. Dichloromethane was purified by refluxing with P_2O_5 before use.
3. Methyl methacrylate monomer, a colorless liquid, hydroquinone inhibitor was removed by washing twice with 5 % NaOH and twice with demineralised water until the pH of aqueous phase was neutral. After being dried over anhydrous $MgSO_4$, it was distilled under reduced pressure. The distilled methyl methacrylate monomer was collected and dissolved oxygen was removed by purging nitrogen gas. The distillate was stored in Schlenk flask at low temperature.

In many low temperature reactions, the mixture of dry ice and acetone (1 :1) was used for temperature of –78 ^{0}C .

4.3 Characterization instruments

The instruments used to characterize catalysts and polymer products are specified in the following:

4.3.1 Fourier transform infrared spectrometer (FT-IR)

Fourier transform infrared spectra were recorded on Nicolet FT-IR Impact 410 Spectrophotometer at Department of Chemistry, Chulalongkorn University, for polymethyl methacrylate products. The samples were made into KBr pellets. Infrared spectra were recorded between 400 cm^{-1} to 4,000 cm^{-1} in transmittance mode.

4.3.2 Nuclear magnetic resonance spectrometer (NMR)

^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker ACF 200 MHz at Department of Chemistry, Chulalongkorn University. The NMR spectra were measured in chloroform-d at room temperature. Broad-band decoupling was used to remove the ^{13}C - ^{1}H coupling. The center peak of chloroform-d was used as the internal reference (77.0 ppm).

4.3.3 Differential scanning calorimeter (DSC)

The melting temperature (T_m) and the glass transition temperature (T_g) of the polymethyl methacrylate were determined by a NETZSCH DSC 200 at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. The analyses were performed at the heating rate of 10 ^{0}C/min. in the temperature range of 25 – 300 ^{0}C. The heating cycle was run twice. In the first scan, polymer products were heated and then cooled down to room temperature. In the second scan, samples were reheated at the same rate, only the last scan was recorded because the first scan was influenced by the mechanical and thermal history of samples.

4.3.4 Gel permeation chromatograph (GPC)

GPC curves of polymethyl methacrylate were determined on a Water 150-CV GPC at the National Metal and Materials Technology Center (MTEC), the National Science and Technology Development Agency (NSTDA). The molecular weight and molecular weight distribution of the polymethyl methacrylate were measured at room temperature using chloroform as a solvent at flow rate of 1 ml/min and calibrated with standard polystyrene samples.

4.4 Procedures

4.4.1 Catalyst and cocatalysts solution preparation

1. *rac*-Et bis(ind)$_2$ZrCl$_2$ catalyst stock solution.

rac-Et bis(ind)$_2$ZrCl$_2$, yellow-brownish solid catalyst, 0.0836 g. (0.0002 mole) was dissolved in 60 ml distilled toluene in a Schlenk flask with a magnetic bar. The solution was stirred under nitrogen atmosphere until all of the solid catalyst dissolved.

2. $B(C_6F_5)_3$ cocatalyst stock solution.

$B(C_6F_5)_3$ solution was drawn via syringe 0.35 ml. (0.0005 mole) and mixed in 50 ml. distilled toluene in a Schlenk flask.

3. $[Ph_3C]^+[B(C_6F_5)_4]^-$ cocatalyst stock solution.

$[Ph_3C]^+[B(C_6F_5)_4]^-$ white solid cocatalyst 0.2305 g. (0.00025 mole) was dissolved in 50 ml. distilled toluene in a Schlenk flask.

4. $[PhNMe_2H]^+[B(C_6F_5)_4]^-$ cocatalyst stock solution.

$[PhNMe_2H]^+[B(C_6F_5)_4]^-$, white solid cocatalyst, 0.2 g. (0.00025 mole) was dissolved in 50 ml. distilled toluene in a Schlenk flask.

5. TIBA stock solution.

Mixed 1.25 ml. TIBA solution (2M) in 98.75 ml of distilled hexane under nitrogen atmosphere to get 0.05 M. 100 ml.

4.4.2 Polymerization procedure

Polymerization of methyl methacrylate monomer (MMA) was carried out under dry nitrogen atmosphere in a 100 ml round-bottomed Schlenk flask with a magnetic bar. A typical polymerization step was as follows: add toluene as solvent, methyl methacrylate monomer and toluene solution of $Zn(C_2H_5)_2$ were injected into the flask, and the mixture was stirred for 1 hr. After the addition of boron cocatalyst solution, catalyst solution was immediately injected to start the polymerization. After a given time interval, the polymerization was terminated by the addition of 10 % HCl in methanol. Next, methanol was added to precipitate the product. The polymer was collected by filtration and washed several times with methanol, after that dried in vacuum oven at 60 °C for 6 hr.

Yields and activity

Percent yields and activity in this experiment can be calculated by equations 4.1 and 4.2

% Yields = (weight of polymer obtained / weight of monomer) x 100 (4.1)

Activity = (grams of polymer) / (mole of catalyst x mole of MMA monomer x hr) (4.2)

4.4.3 Various effects on the methyl methacrylate polymerization

4.4.3.1 Effect of solvent

The polymerization of methyl methacrylate using *rac*-Et(ind)$_2$ZrCl$_2$ catalyst /B(C_6F_5)$_3$ cocatalyst system was investigated by varying solvent: hexane, toluene and dichloromethane. The other parameters were fixed: 5 x 10^{-6} mole catalyst, MMA/Zn(C_2H_5)$_2$ = 10 mole ratio, room temperature and reaction time 4 hrs.

4.4.3.2 Effect of MMA/Zn(C_2H_5)$_2$ mole ratio

The MMA/ Zn(C_2H_5)$_2$ mole ratios were varied from 2 – 16.The polymerization condition was set at room temperature, 1 x 10^{-5} mole catalyst, one equivalent of PhNMe$_2$H$^+$ B(C_6F_5)$_4^-$ cocatalyst and 8 hrs.

4.4.3.3 Effect of concentration of catalyst

The effect of concentration of catalyst was investigated by varying catalyst concentration from 1 x 10^{-6} mole to 5 x 10^{-5} mole. The polymerization condition was set at MMA/ Zn(C_2H_5)$_2$ = 4 mole ratio, room temperature and reaction time 24 hrs. with one equivalent of PhNMe$_2$H$^+$B(C_6F_5)$_4^-$ cocatalyst.

4.4.3.4 Effect of type of boron cocatalyst

The effect of types of boron cocatalyst were examined. Boron complexes used are B(C_6F_5)$_3$, Ph$_3$C$^+$B(C_6F_5)$_4^-$ and PhNMe$_2$H$^+$B(C_6F_5)$_4^-$. The condition was set at room temperature, 1 x 10^{-5} mole catalyst, MMA/ Zn(C_2H_5)$_2$ = 4 mole ratio and reaction time 12 hrs.

4.4.3.5 Effect of temperature

The effect of temperature was studied by varying the polymerization temperature; room temperature, 0 ^{0}C and –78 ^{0}C., 1 x 10^{-5} mole catalyst with one equivalent of Ph$_3$C$^+$B(C_6F_5)$_4^-$ cocatalyst., MMA/Zn(C_2H_5)$_2$ = 4 mole ratio and reaction time 8 hrs.

4.4.3.6 Effect of time

The effect of polymerization time was investigated by varying reaction time from 2 – 24 hrs. using the same condition as Section 4.4.3.5.

4.4.3.7 Effect of type of alkylating agents

MeMgBr and TIBA were used. The reaction condition was the same as in Section 4.4.3.4.

4.5 Characterization of polymethyl methacrylate

In this work, polymethyl methacrylate products were characterized by the following methods.

1. Fourier transform infrared spectrometry (FT-IR)

The FT-IR technique was used to characterize a polymer structure and was compared with the reference polymethyl methacrylate.

2. Nuclear magnetic resonance spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy was used to record ^{1}H-NMR and ^{13}C-NMR spectra. The samples were dissolved in chloroform-d, run at room temperature. The carbonyl resonances in ^{13}C-NMR spectra determined the tacticity of the polymethyl methacrylate.

3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was used to determine the thermal properties of polymethyl methacrylate products such as melting temperature (T_m) and glass transition temperature (T_g).

4. Gel permeation chromatography (GPC)

Gel permeation chromatography was used to determine molecular weight (Mw), number average molecular weight (Mn) and molecular weight distribution (MWD) by principle of size exclusion chromatography (SEC). Molecular weight and molecular weight distribution of the produced polymethyl methacrylate were measured at room temperature using chloroform as solvent at 1.0 ml/min by a Water 150-C column.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Polymerization of methyl methacrylate with rac-Et(ind)$_2$ZrCl$_2$ catalyst.

5.1.1 The effect of solvent on methyl methacrylate polymerization

The influence of the solvent was investigated with three types of solvent :hexane, toluene and dichloromethane using 5 x 10^{-6} mole catalyst with one equivalent of $B(C_6F_5)_3$ cocatalyst, MMA/Zn mole ratio = 10 and polymerization time 4 hrs. Table 5.1 and Figure 5.1 showed the results for the effect of solvent on catalyst activity.

Table 5.1 Polymerization of methyl methacrylate catalyzed by rac- Et(ind)$_2$ZrCl$_2$ – MeMgBr / $B(C_6F_5)_3$ system using various solvents.

Solvents	Yields		Activity
	(g)	(%)	
n-hexane	0.2315	4.85	205,230
toluene	0.2444	5.12	216,666
dichloromethane	0.2261	4.74	200,443

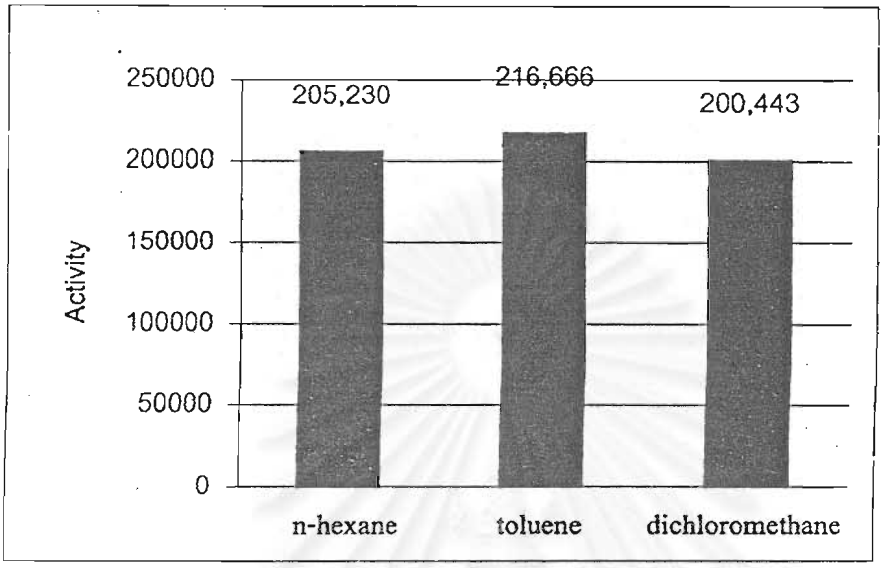

Figure 5.1 Catalytic activity using different solvent

The results in Figure 5.1 showed that using toluene as solvent in polymerization gave a little better activity than using n-hexane and dichloromethane. Thus, toluene was chosen for next reactions.

5.1.2 The effect of MMA /$Zn(C_2H_5)_2$ mole ratio on methyl methacrylate polymerization.

The effect of the MMA/Zn mole ratio was investigated using catalyst 1 x 10^{-5} mole and one equivalent of $PhNMe_2H^+$ $B(C_6F_5)_4^-$ cocatalyst at room temperature and polymerization time 8 hrs. The experimental results were shown in Table 5.2 and Figure 5.2.

Table 5.2 Polymerization of methyl methacrylate catalyzed by rac-Et(indenyl)$_2$ZrCl$_2$-MeMgBr / PhNMe$_2$H$^+$ B(C$_6$F$_5$)$_4^-$ system using various MMA/Zn mole ratios.

MMA /Zn mole ratios	Yields		Activity
	(g)	(%)	
3	0.3962	14.05	175,620
4	0.4108	14.26	178,300
6	0.3523	12.49	156,160
8	0.3387	11.76	150,132
16	trace	-	-
Without Zn	0	0	0

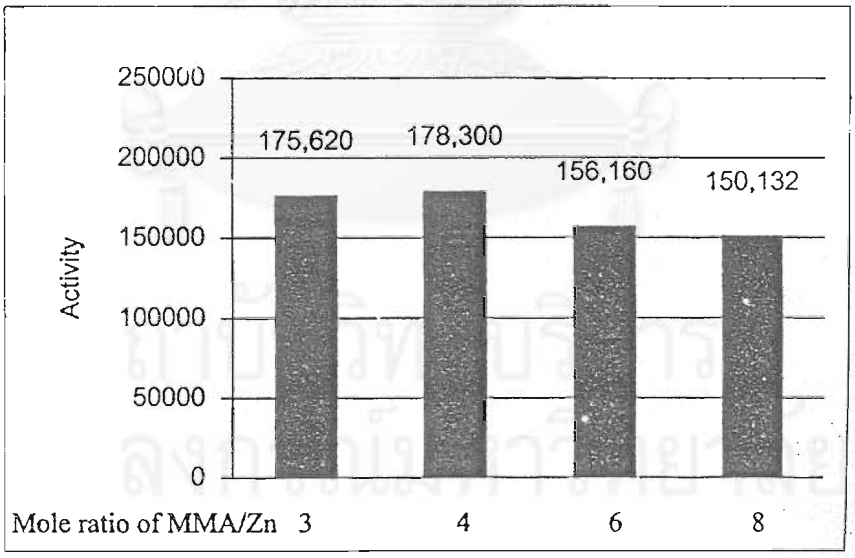

Figure 5.2 Catalytic activity using different MMA/Zn mole ratio

The results in Table 5.2 and Figure 5.2 show that no polymer was obtained without using $Zn(C_2H_5)_2$. This compound is a Lewis acid, it was believed that it can coordinate with methoxy carbonyl which is a nucleophilic group on MMA. Some complexes were formed between MMA and zinc compound which were indicated by a downfield shift of carbonyl of MMA from 167.7 to 169.9 ppm and an upfield shift of methylene protons of $Zn(C_2H_5)_2$ from 7.2 to 7.0 ppm observed in ^{13}C NMR spectrum [15]. Polar monomer will destroy metallocene catalyt and boron cocatalyst [34].

The optimum ratio of MMA/Zn was found from the experiment results to be around 4. This obtained figure is in the agreement with the previously report [15]. So, MMA/Zn mole ratio = 4 will be used in the other polymerization reactions. For MMA/Zn mole ratio higher than 4, the catalytic activity decreased. This can be explained by an inedequate amount of Zn, therefore there is a chance that metallocene catalyst was destroyed when bound to the polar end of MMA. In the cases of lower MMA/Zn mole ratios, the activities were also decreased, this is presumably due to the large excess of Zn which caused too crowded environment around the metallocene catalyst, preventing the approach of cocatalyst.

5.1.3 The effect of concentration of catalyst on methyl methacrylate polymerization

The effect of concentration of catalyst was investigated by varying catalyst concentration from 1×10^{-6} mole to 5×10^{-5} mole. The polymerizations were performed using MMA/Zn mole ratio of 4, at room temperature for 24 hrs. with one equivalent of $PhNMe_2H^+ B(C_6F_5)_4^-$ cocatalyst. The results were shown in Table 5.3 and Figure 5.3.

Table 5.3 Polymerization of methyl methacrylate catalyzed by rac- $Et(ind)_2ZrCl_2$ MeMgBr / $PhN(Me)_2H^+B(C_6F_5)_4^-$ system using various concentration of catalysts.

Mole of catalyst (x 10^{-5}mole)	Yields		Activity
	(g)	(%)	
0.1	trace	-	-
0.5	0.2787	9.67	82,358
1.0	0.9808	34.78	144,917
2.0	1.5485	54.91	114,398
5.0	2.4211	85.85	71,545

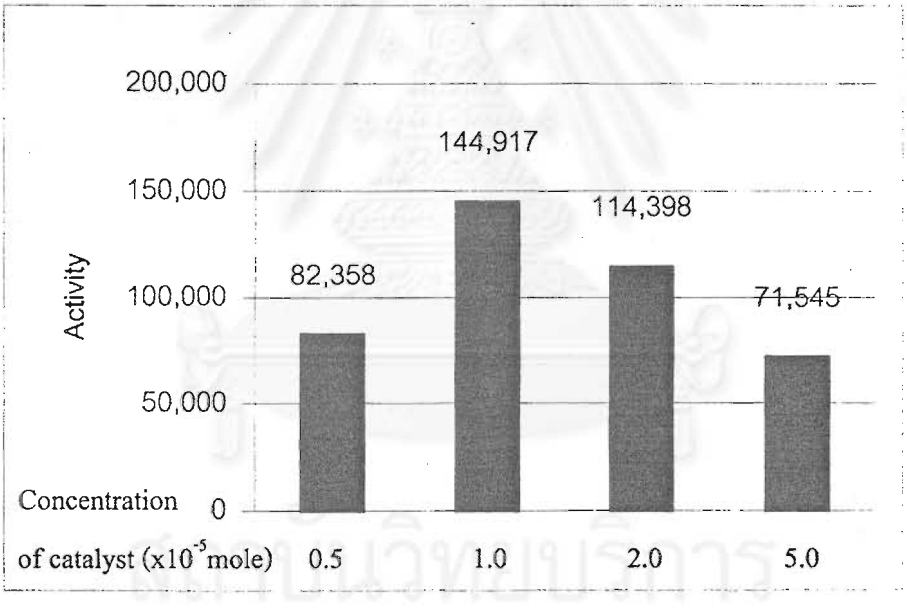

Figure 5.3 Catalytic activity of different mole of catalysts

The results in Table 5.3 and Figure 5.3 showed that the catalytic activity is strongly affected by mole of catalyst. The catalyst activity increases with an increase in the amount of catalyst. The highest catalytic activity was obtained at 1.0 x 10^{-5} mole catalyst. Increasing the mole of catalyst caused the decreasing in the activity. This might be caused by the decreasing of active species due to the dimerization of metallocene forming inactive species [36].

5.1.4 The effect of boron cocatalyst on methyl methacrylate polymerization

The effect of types of boron cocatalyst was examined. Three types used are $B(C_6F_5)_3$, $[Ph_3C]^+[B(C_6F_5)_4]^-$ and $[PhNMe_2H]^+[B(C_6F_5)_4]^-$. The polymerization condition was set at room temperature, 1 x 10^{-5} mole catalyst, MMA/Zn mole ratio of 4 and polymerization time 12 hrs. with one equivalent of boron compounds. Table 5.4 and Figure 5.4 showed the experimental results.

Table 5.4 Polymerization of methyl methacrylate catalyzed by rac- $Et(ind)_2ZrCl_2$–MeMgBr system using various boron compounds.

Boron compounds	Yields		Activity
	(g)	(%)	
$B(C_6F_5)_3$	0.4503	15.96	133,067
$Ph_3C^+B(C_6F_5)_4^-$	1.3792	48.91	407,565
$PhNMe_2H^+B(C_6F_5)_4^-$	1.3533	47.99	399,911

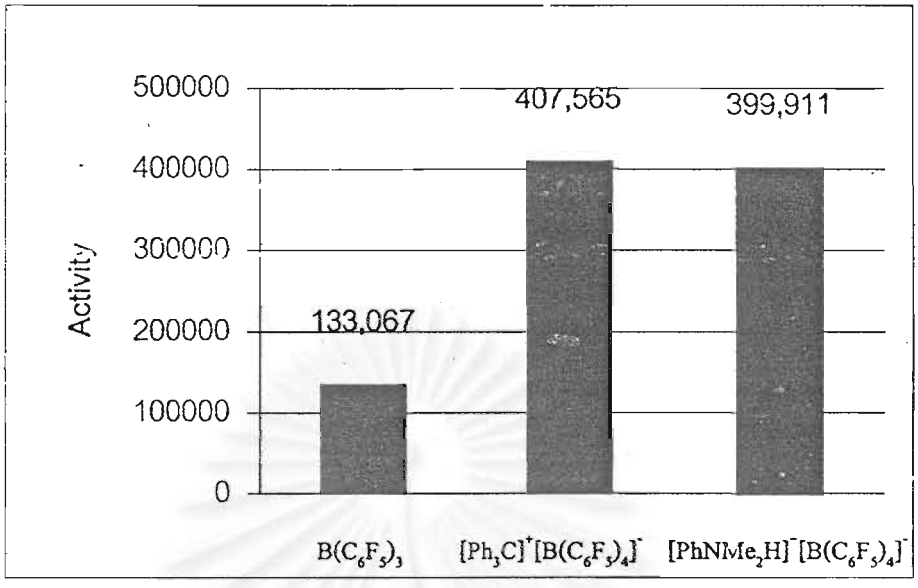

Figure 5.4 Catalytic activity of different boron cocatalysts.

From the experimental results, it revealed that both $[Ph_3C]^+[B(C_6F_5)_4]^-$ and $[PhNMe_2H]^+[B(C_6F_5)_4]^-$ have efficiency to activate the polymerization of methyl methacrylate. However, the trityl compound seems to be a little better than the anilinium one. Meanwhile, the neutral boron, $B(C_6F_5)_3$ was found to be inferior to the other two borate compounds.

5.1.5 The effect of temperature on methyl methacrylate polymerization

The effect of temperature on methyl methacrylate polymerization was performed by varying the polymerization temperatures; –78 ^{0}C, 0 ^{0}C and room temperature using 1 x 10^{-5} mole catalyst with one equivalent of $Ph_3C^+B(C_6F_5)_4^-$ cocatalyst, MMA/Zn mole ratio of 4 and polymerization time 8 hrs. The experimental results were shown in Table 5.5 and Figure 5.5.

Table 5.5 Polymerization of methyl methacrylate catalyzed by rac- $Et(ind)_2ZrCl_2$ MeMgBr / $Ph_3C^+B(C_6F_5)_4$ system using various polymerization temperature.

Polymerization temperature (^{0}C)	Yields		Activity
	(g)	(%)	
-78	1.0605	37.60	470,079
0	0.9441	33.47	418,484
30	0.8921	31.63	395,434

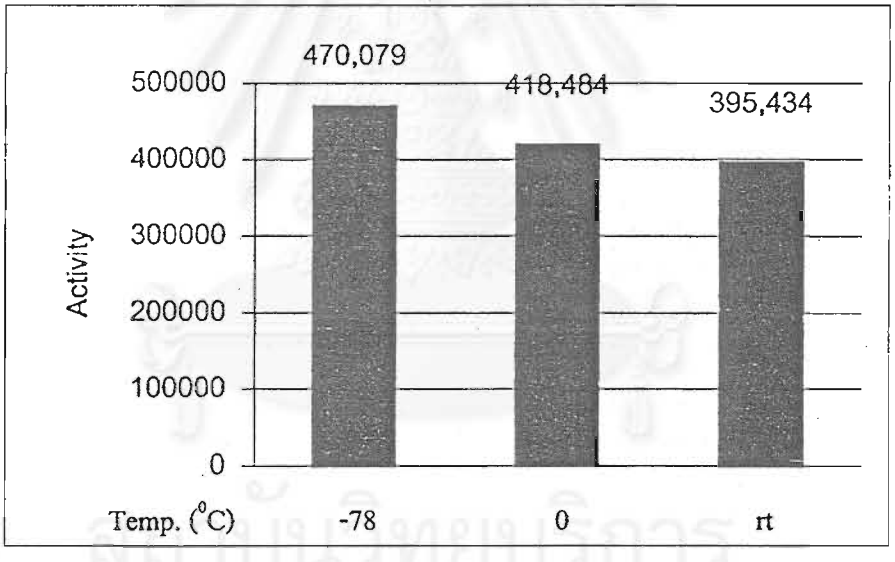

Figure 5.5 Catalytic activity at different temperature

The results of the effect of temperature on the catalytic activity showed that the polymerization can be performed at different temperature, from very low temperature to even a temperature as high as 30 ^{0}C or room temperature. This indicates that the propagation site is quite stable.

5.1.6 The effect of time on methyl methacrylate polymerization

The effect of polymerization time was investigated; 2, 4, 8, 12 and 24 hrs. The polymerization condition was set at room temperature, 1 x 10^{-5} mole catalyst, MMA/Zn mole ratio of 4 and with one equivalent of $PhNMe_2H^+ B(C_6F_5)_4^-$ cocatalyst. Table 5.6 and Figure 5.6 showed the results and relationship between activity and polymerization time. In addition, the relationship between yield and polymerization time was shown in Figure 5.7.

Table 5.6 Polymerization of methyl methacrylate catalyzed by rac- $Et(ind)_2ZrCl_2$ – MeMgBr / $PhNMe_2H^+ B(C_6F_5)_4^-$ system using various polymerization time.

Polymerization time (hr)	Yields		Activity
	(g)	(%)	
2	trace	-	-
4	0.2420	8.58	214,539
8	0.4877	17.29	216,179
12	0.8707	30.23	257,299
24	1.3515	46.93	199,689

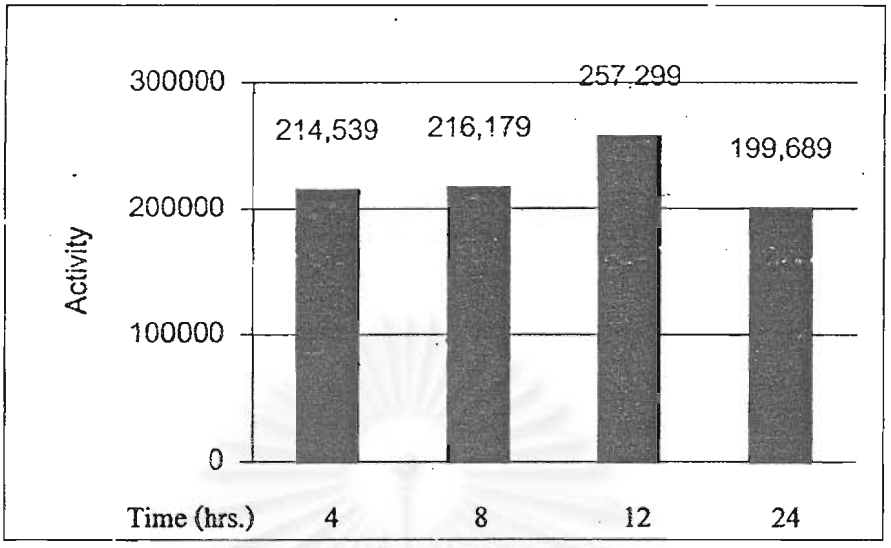

Figure 5.6 Catalytic activity of different polymerization time.

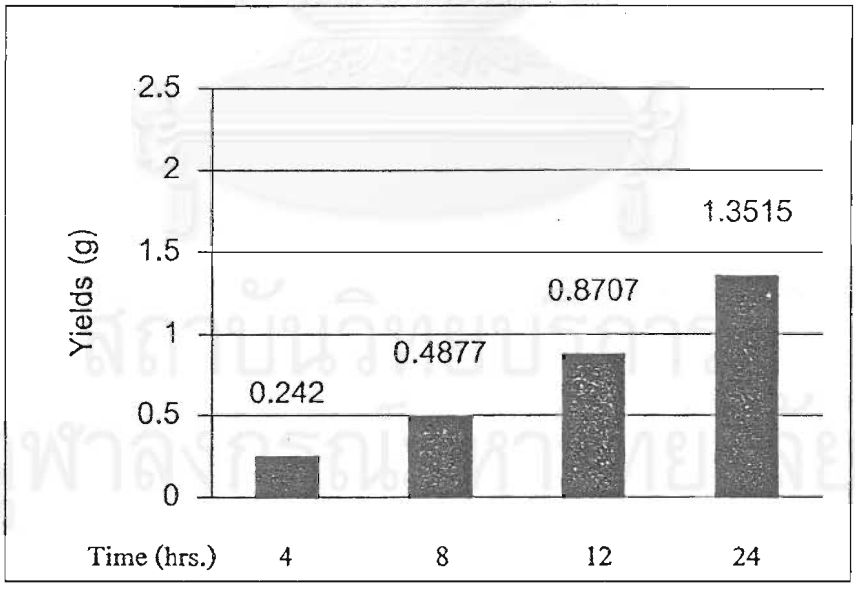

Figure 5.7 Relationship between yield and polymerization time.

The results from Figure 5.6 indicated that the catalyst activity increases with increasing polymerization time, in the range of 0 to 12 hrs., after that, the activity decreases. Figure 5.7 showed the relationship between polymer yield *versus* polymerization time, the polymer yield increases linearly with polymerization time. 8 hrs. polymerization time can get enough yield for the further characterization of polymethyl methacrylate.

5.1.7 The effect of alkylating agents

The two alkylating agents: MeMgBr and TIBA were compared for alkylating rac- $Et(ind)_2ZrCl_2$ catalyst. The optimum condition used is 1×10^{-5} mole catalyst, MMA/Zn mole ratio of 4 and polymerization time 12 hrs. with one equivalent of each of boron compounds. The results were shown in Table 5.7.

Table 5.7 Polymerization of methyl methacrylate catalyzed by rac- $Et(ind)_2ZrCl_2$/ $[Ph_3C]^+[B(C_6F_5)_4]^-$ system using various alkylating agents.

Alkylating agents	Yields		Activity
	(g)	(%)	
MeMgBr	1.3792	48.91	407,565
TIBA	0	-	-

The triisobutyl aluminium compound (TIBA) was attempted as an alkylating agent, the result showed that no polymerization was occurred. TIBA might be a too strong reducing agent. It should be noted that using TIBA instead of $Zn(C_2H_5)_2$ produced no polymer.

5.2 Characterization of polymethyl methacrylate

5.2.1 Chemical structure determination

5.2.1.1 Fourier transform infrared spectroscopy (FT-IR).

The polymer samples were characterized the microstructure of polymer by using Fourier transform infrared spectroscopy (FT-IR) in wave number of 800 cm^{-1} – 4000 cm^{-1}. The identification of the spectrum is summarized in Table 5.8.

Table 5.8 IR spectral data of the polymethyl methacrylate.

Wave number range (cm^{-1})	Assignment
2,850 – 3,000	C-H stretching aliphatic
1,730	C=O
1,350-1,470	$-CH_2$,$-CH_3$ bending
1,150	C-O

IR spectrum of PMMA using *rac*-Et(ind)$_2$$ZrCl_2$-MeMgBr/boron compound, shows the C=O peak at 1,730 cm^{-1}. CH_2- and CH_3- bendings appear at 1,350-1,470 cm^{-1} region. The absorptions at 1,150 cm^{-1} results from C-O. and aliphatic C-H stretching absorbs around 2,850 – 3,000 cm^{-1}.

All polymer in this work showed the characteristic peaks of PMMA (Figure 5.8b) which match those of the reference PMMA (Figure 5.8a), thus, it can be confirmed that the produced polymer are polymethyl methacrylate.

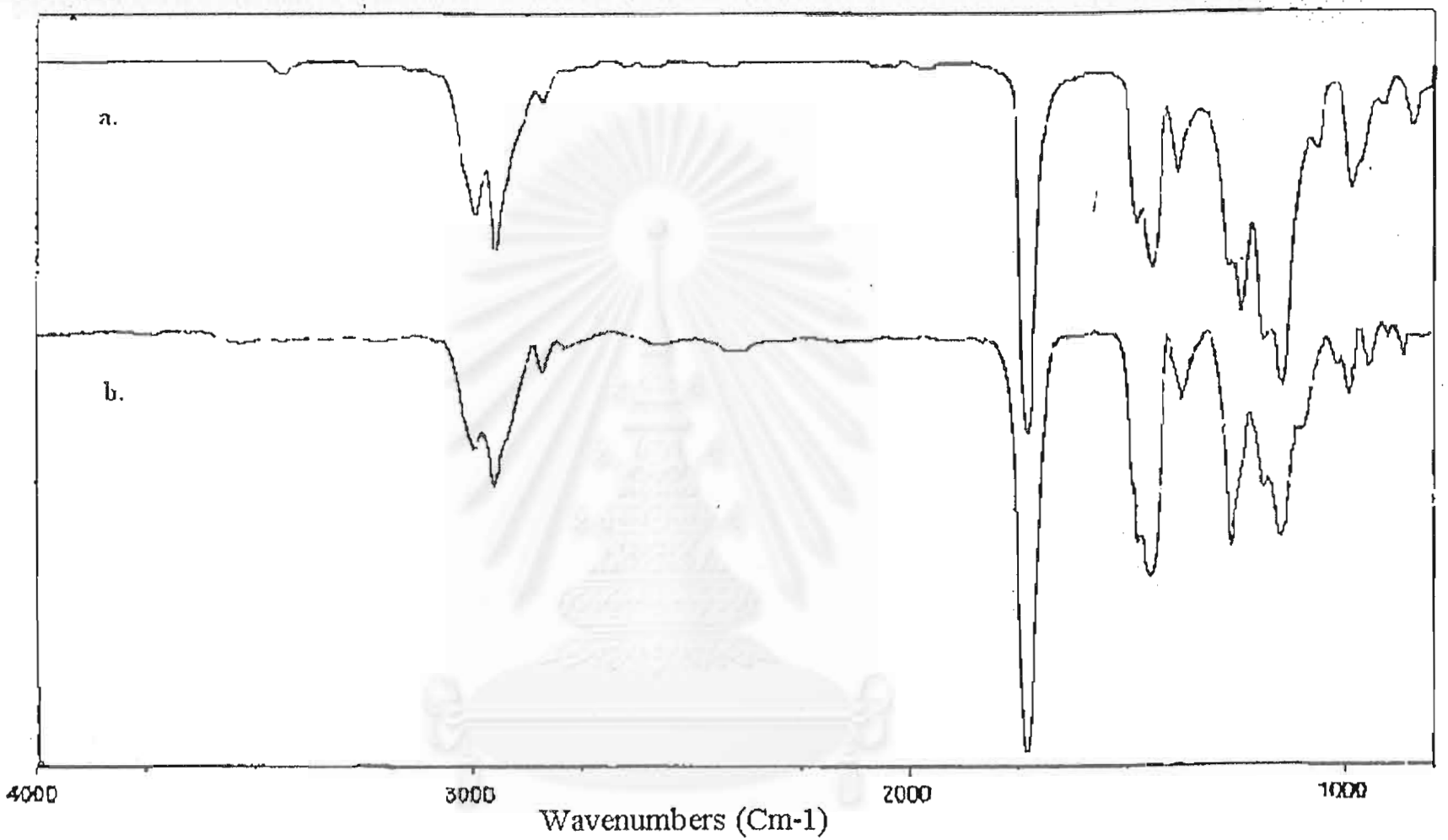

Figure 5.8 FT-IR spectra of polymethyl methacrylate.

a. FT-IR spectrum of reference PMMA .

b. FT-IR spectrum of PMMA obtained with $Et(Ind)_2ZrCl_2$-MeMgBr/ $Ph_3C^+B(C_6F_5)_4^-$.

5.2.1.2 Nuclear magnetic resonance spectroscopy (NMR)

The tacticity of polymethyl methacrylate was determined by high-resolution ^{13}C NMR spectroscopy. ^{13}C-NMR spectrum of the produced polymethyl methacrylate by $Et(Ind)_2ZrCl_2$-MeMgBr/ $Ph_3C^+B(C_6F_5)_4^-$ system is presented in Figure 5.9 and the spectra for other catalytic systems are similar. The methyl group is shown at 22 ppm. and the carbonyl group of PMMA is at 176-177 ppm. The stereospecificity of PMMA can be defined at 16-24 ppm. for methyl group region and 176-180 ppm. for carbonyl group region. (The expanded peaks for methyl and carbonyl are shown in Figures 5.10 - 5.11) ^{13}C-NMR spectra for isotactic, syndiotactic and atactic structures show methyl resonances at 22 ppm.,18.5 ppm. and 16.3 ppm., respectively [13, 25]. For carbonyl resonance, peaks appear at 176.5 ppm., 177.0 ppm. and 177.6 ppm., respectively. Figure 5.12 shows ^{13}C-NMR spectrum of atactic PMMA reference [25], the expanded peaks for methyl and carbonyl are shown in Figures 5.13 - 5.14.

Therefore, the ^{13}C-NMR spectra of all produced polymers showed that the obtained polymers from the experiments are isotactic.

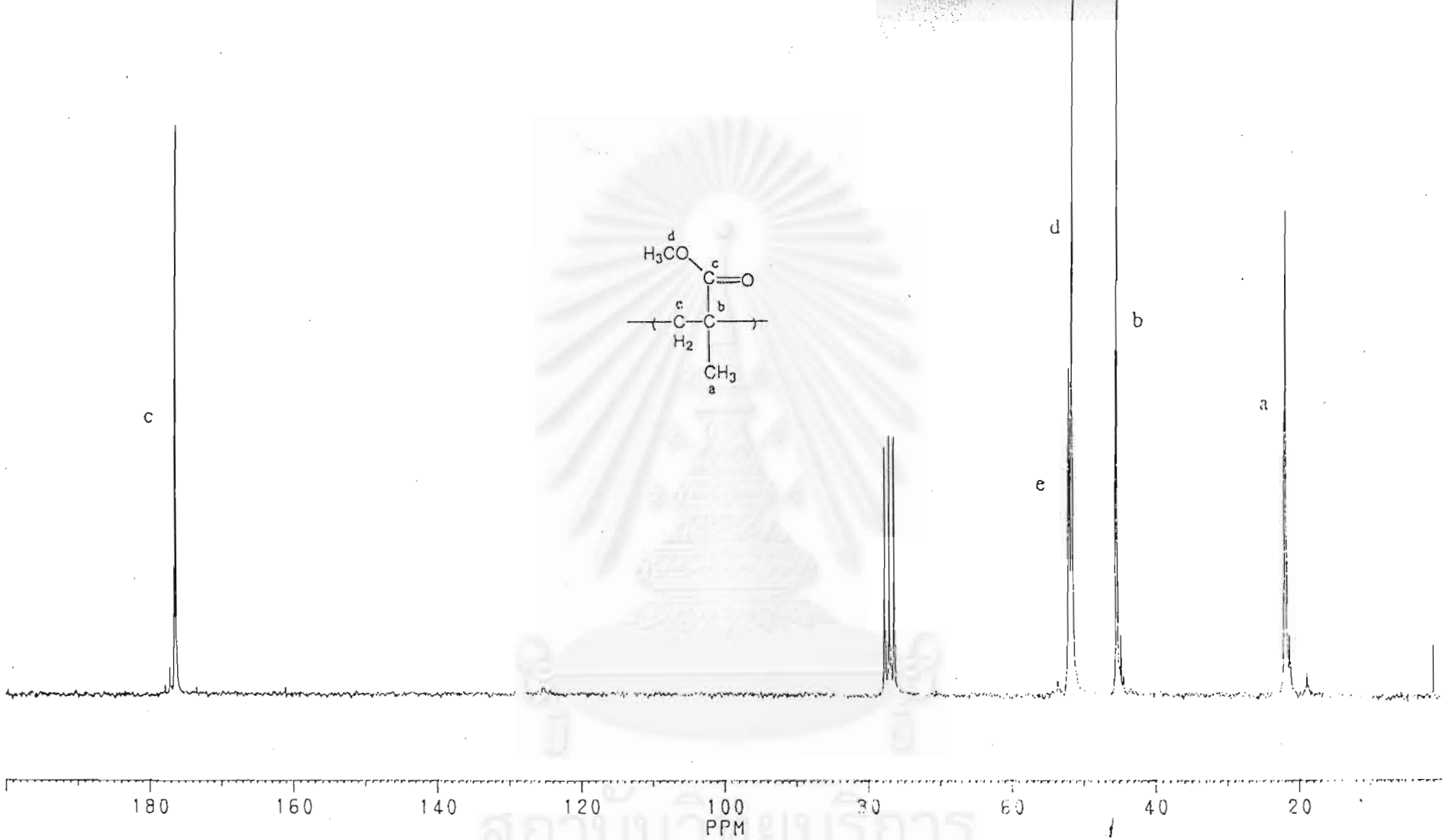

Figure 5.9 ^{13}C NMR spectrum of isotactic polymethyl methacrylate obtained with $Et(Ind)_2ZrCl_2$-MeMgBr/ $Ph_3C^+B(C_6F_5)_4^-$ 1 x 10^{-5} mole catalyst, MMA/Zn mole ratio of 4, polymerization temperature of -78^0C and 12 hrs polymerization time.

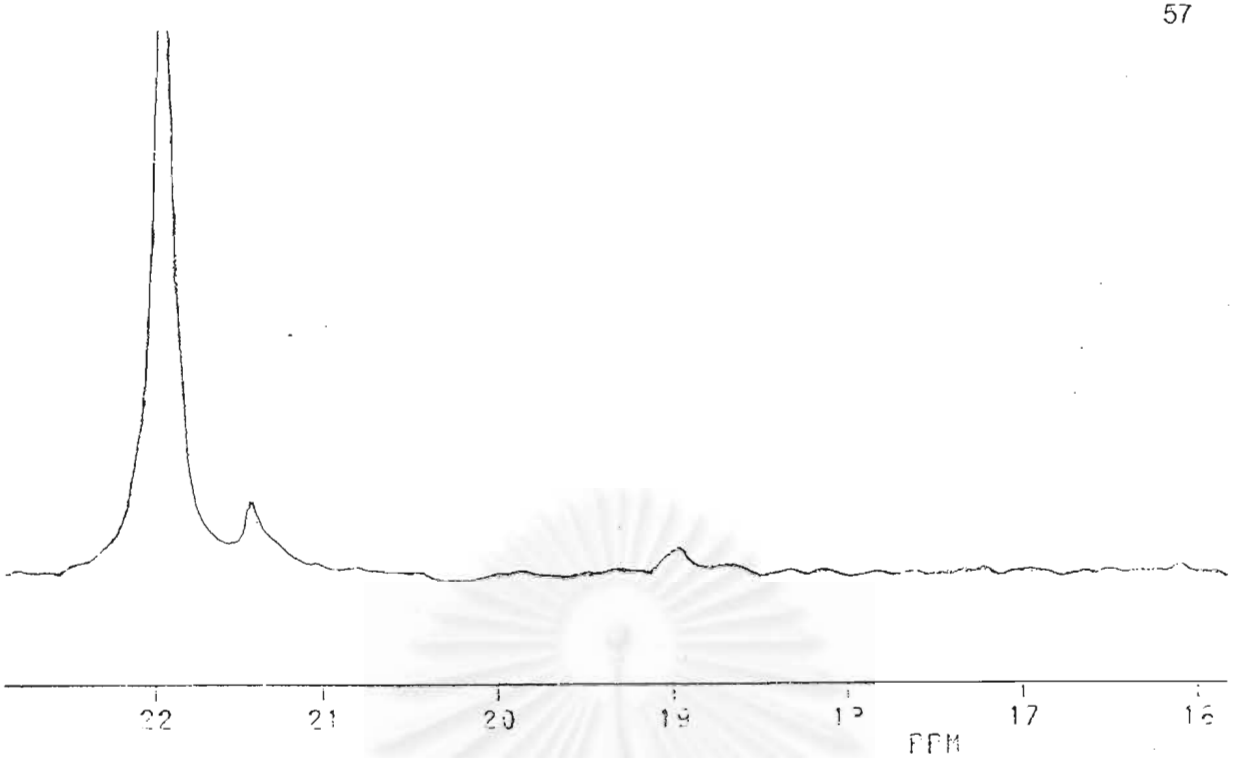

Figure 5.10 ^{13}C NMR methyl region spectrum of produced polymethyl methacrylate expanded from Figure 5.9

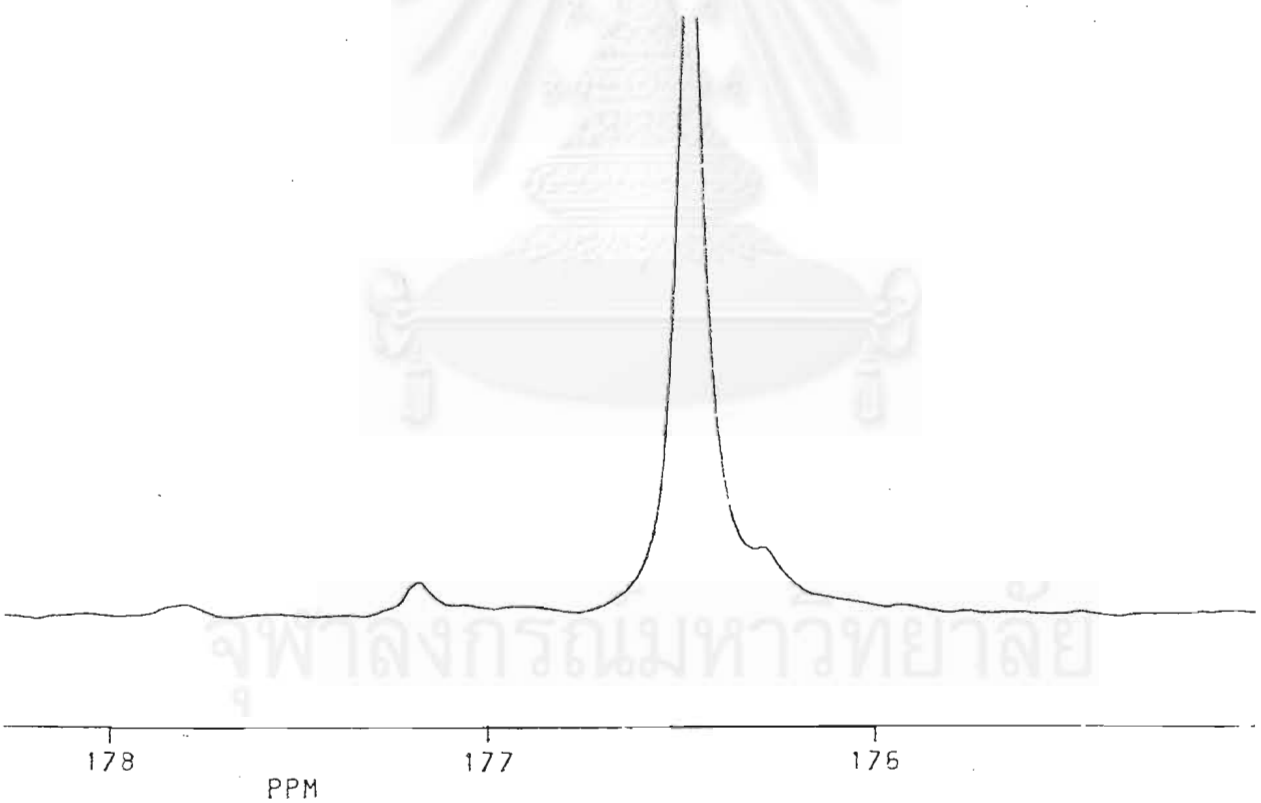

Figure 5.11 ^{13}C NMR carbonyl region spectrum of produced polymethyl methacrylate expanded from Figure 5.9

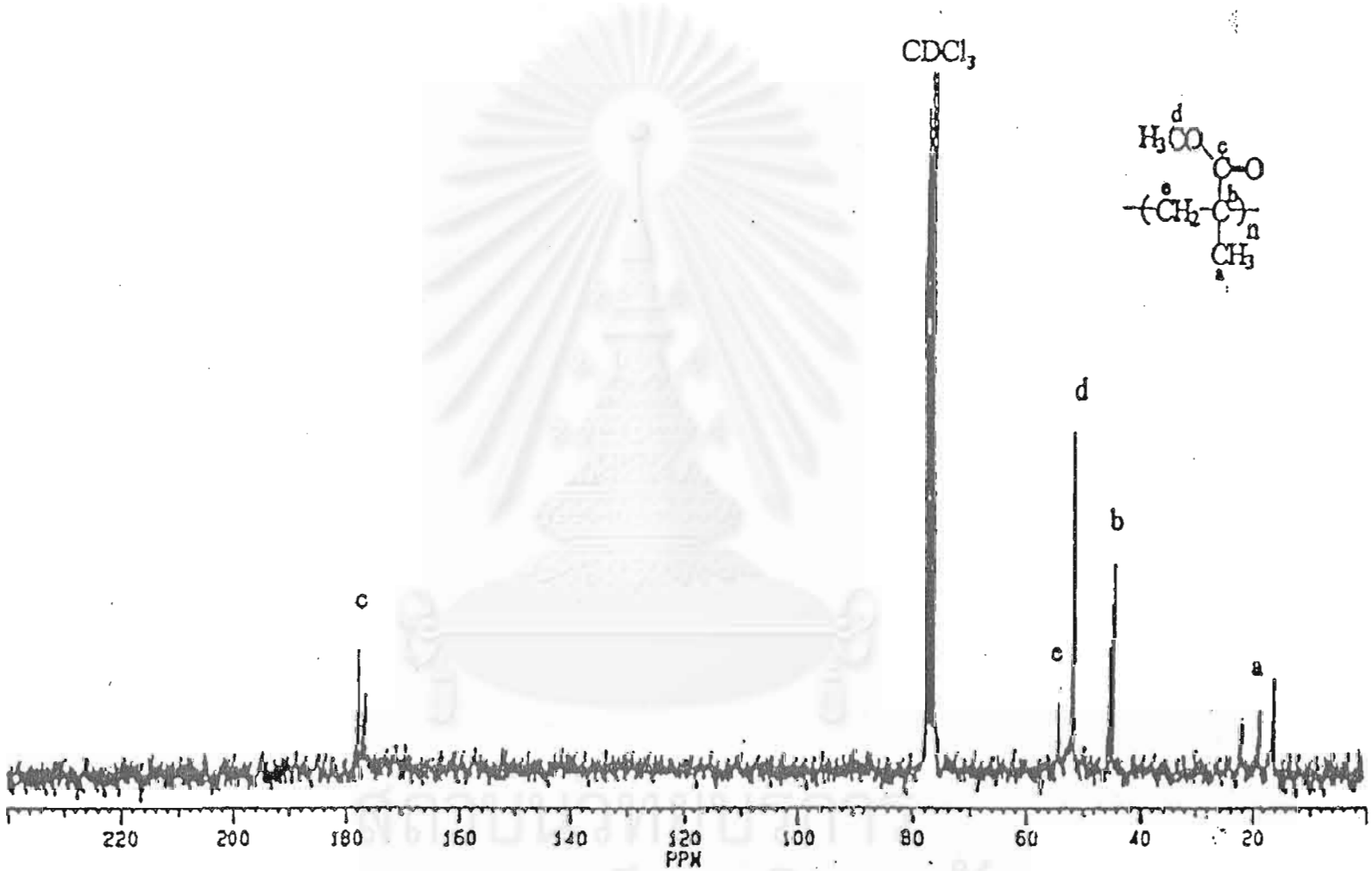

Figure 5.12 ^{13}C NMR spectrum of atactic polymethyl methacrylate reference [25].

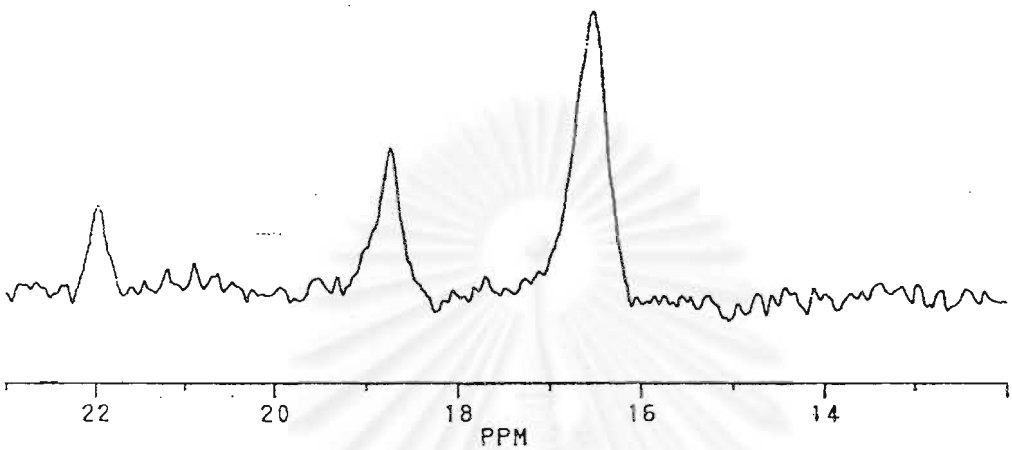

Figure 5.13 ^{13}C NMR methyl region spectrum of atactic polymethyl methacrylate referenece expanded from Figure 5.12.

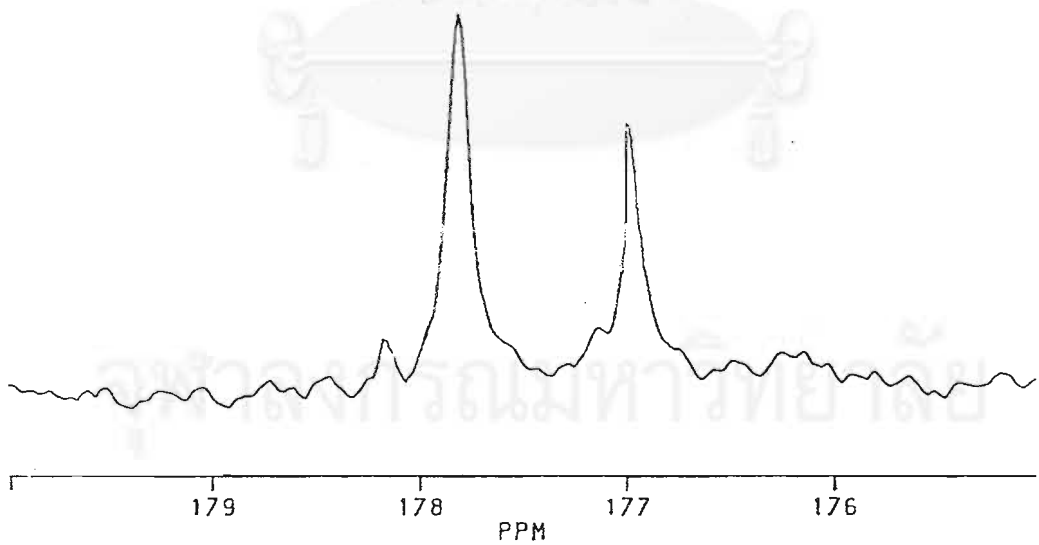

Figure 5.14 ^{13}C NMR carbonyl region spectrum of atactic polymethyl methacrylate reference expanded from Figure 5.12.

5.2.2 Glass transition temperature (T_g)

5.2.2.1 The effect of boron cocatalyst

The glass transition temperature (T_g) of polymethyl methacrylate has been determined on different types of boron cocatalysts. $B(C_6F_5)_3$, $[Ph_3C]^+[B(C_6F_5)_4]^-$ and $[PhNMe_2H]^+[B(C_6F_5)_4]^-$. The polymerization condition was set at –78 ^{0}C , 1 x 10^{-5} mole catalyst, MMA/Zn mole ratio of 4. with one equivalent of boron compound. The results are shown in Table 5.9 and DSC curves shown in Figure 5.15.

Table 5.9 Glass transition temperature of polymers using various boron compounds.

Boron compounds	T_g (^{0}C)	Polymer structure
$B(C_6F_5)_3$	58.4	Isotactic
$Ph_3C^+B(C_6F_5)_4^-$	53.5	Isotactic
$PhNMe_2H^+B(C_6F_5)_4^-$	57.2	Isotactic

Table 5.9 shows that all boron compounds which used as cocatalyst, produce polymethyl methacrylate with the glass transition temperatures observed at approximately 50 ^{0}C which is close to T_g of isotactic polymethyl methacrylate (50 ^{0}C). Therefore the produced polymers are isotactic.

5.2.2.2 The effect of temperature

The glass transition temperature of polymethyl methacrylate has been determined on polymers which were polymerized at different temperature. The condition used is: 1 x 10^{-5} mole catalyst with one equivalent of $Ph_3C^+B(C_6F_5)_4^-$ cocatalyst, MMA/Zn mole ratio of 4. The results are shown in Table 5.10. and DSC curves shown in Figure 5.16.

Table 5.10 Glass transition temperature of polymers using various polymerization temperature.

Temperature (^{0}C)	T_g (^{0}C)	Polymer structure
-78	53.5	Isotactic
0	58.6	Isotactic
30	61.7	Isotactic

The above table illustrates the effect of different polymerization temperature on the glass transition temperature of polymethyl methacrylate obtained. Tg of the polymers show that the majority of all polymer products is isotactic (T_g is about 50 ^{0}C). Tg increases with the increasing temperature, this reveals that the percent of isotacticity decreases with the increasing temperature. Figure 5.16 shows DSC curves at 0 ^{0}C (Figure 5.16a) and 30^{0}C (Figure 5.16b) while Figure 5.16c shows DSC curve of reference syndiotactic PMMA [28].

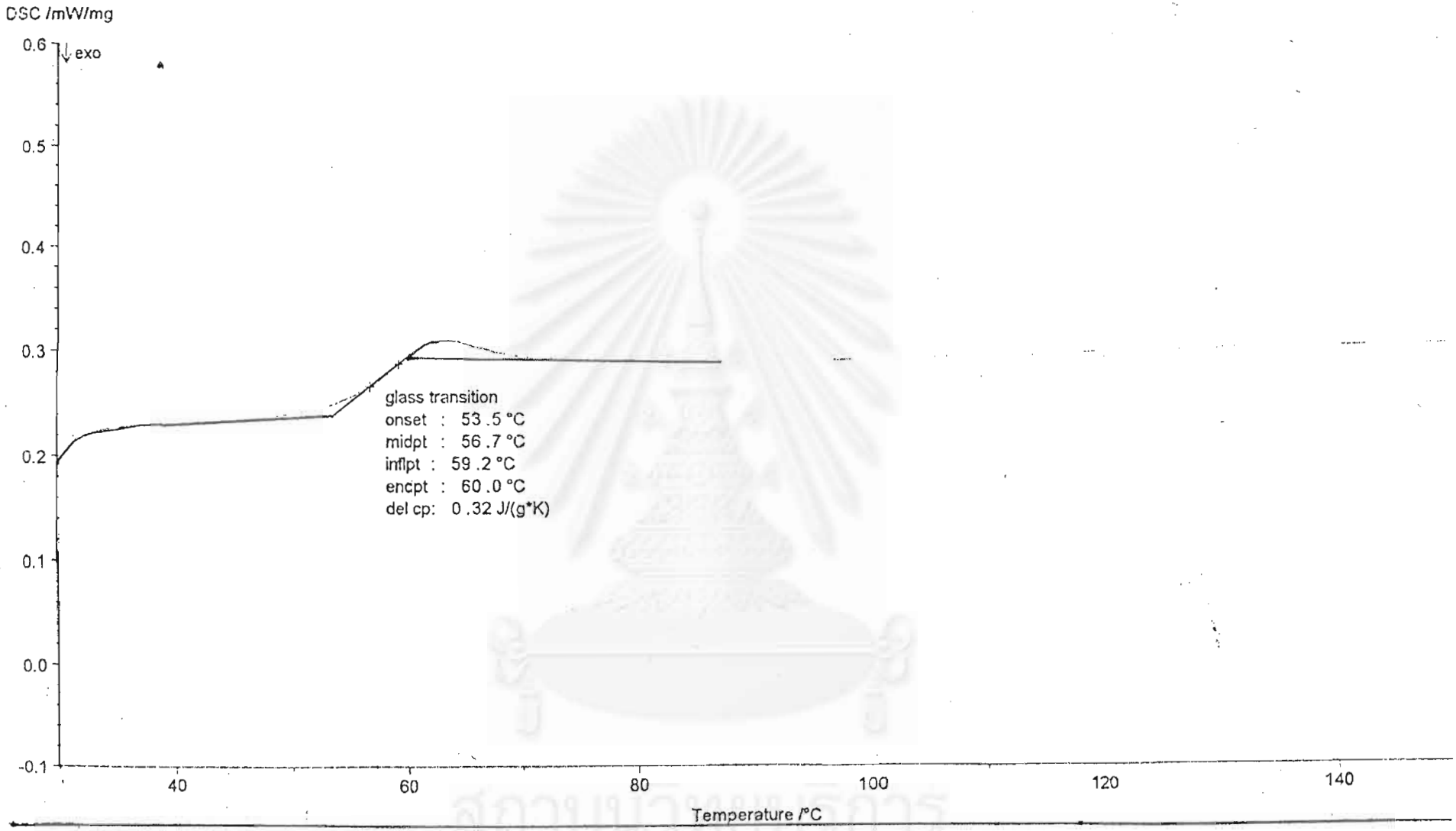

Figure 5.15 DSC curve of polymethyl methacrylate obtained with $Et(Ind)_2ZrCl_2$-MeMgBr/ $Ph_3C^+B(C_6F_5)_4^-$ 1 x 10^{-5} mole catalyst, MMA/Zn mole ratio of 4, polymerization temperature of –78^{0}C.

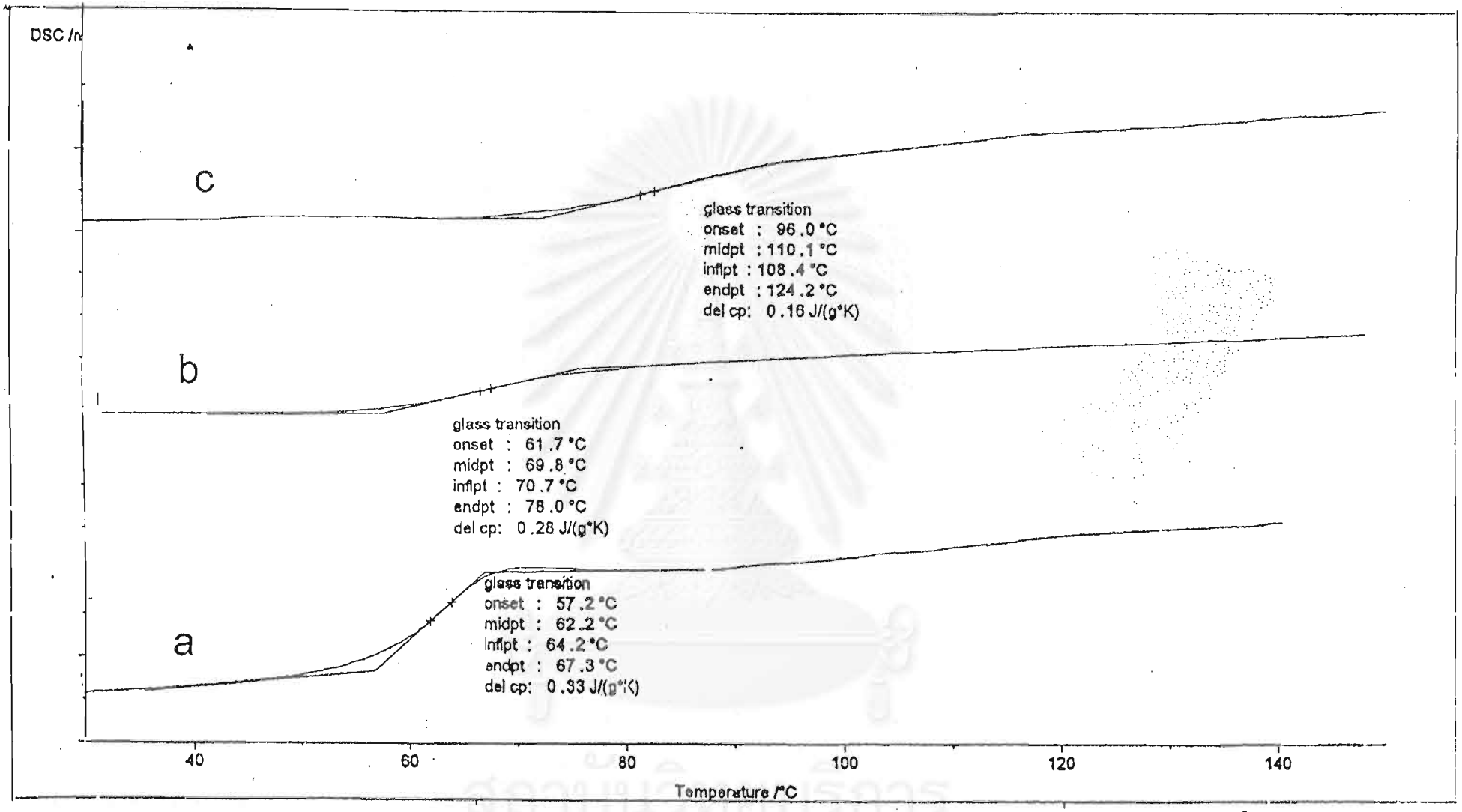

Figure 5.16 DSC curves of polymethyl methacrylate obtained with $Et(Ind)_2ZrCl_2$-MeMgBr/ $Ph_3C^+B(C_6F_5)_4^-$ 1 x 10^{-5} mole catalyst, MMA/Zn mole ratio of 4, using different polymerization temperature.

a. 0 °C b. 30 °C

c. DSC curve of reference syndiotactic PMMA [28]

5.2.3 Molecular weight (Mw) and Molecular weight distribution (MWD)

The molecular weight and molecular weight distribution of polymethyl methacrylate produced with different type of boron compounds; $B(C_6F_5)_3$ and $[Ph_3C]^+[B(C_6F_5)_4]^-$ were investigated. The polymerization condition was set at –78 ^{0}C , 1 x 10^{-5} mole catalyst, MMA/Zn mole ratio of 4. with one equivalent of boron compounds. The results are shown in Table 5.11.

Table 5.11 Mw and MWD of the obtained polymethyl methacrylate by *rac*- $Et(ind)_2ZrCl_2$–MeMgBr system using various boron compounds

Boron compounds	Mw	Mn	MWD
$B(C_6F_5)_3$	191,682	100,462	1.908
$[Ph_3C]^+[B(C_6F_5)_4]^-$	1,345,892	875,660	1.537

The data in Table 5.11 shows that the catalytic system with $[Ph_3C]^+[B(C_6F_5)_4]^-$ as cocatalyst, produces polymethyl methacrylate with high molecular weight. In contrast, $B(C_6F_5)_3$ produces lower molecular weight polymer. However, both can produce the polymer with narrow MWD. The GPC curves are shown in Figure 5.17.

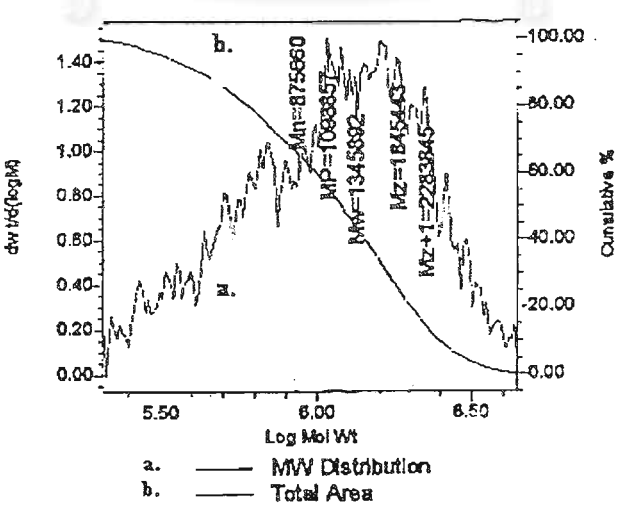

Figure 5.17 GPC curves of polymethyl methacrylate obtained from *rac*- $Et(ind)_2ZrCl_2$–MeMgBr/$[Ph_3C]^+[B(C_6F_5)_4]^-$

CHAPTER VI
CONCLUSION AND SUGGESTION

6.1 Conclusion

A chiral C_2-symmetric catalyst, $Et(Ind)_2ZrCl_2$ has been used as a precatalyst in methyl methacrylate polymerization with Grignard reagent (MeMgBr) as an alkylating agent and boron compound as a cocatalyst. Premixing of methyl methacrylate monomer, which is a polar monomer with suitable Lewis acids such as diethylzinc for at least 1 hr. before polymerization is found to be a very necessary step. Without addition of diethylzinc to monomer, there is no polymer produced. The catalytic system is $Et(Ind)_2ZrCl_2$-MeMgBr/ $Ph_3C^+B(C_6F_5)_4^-$ (or $PhN(Me)_2H^+B(C_6F_5)_4^-$)/$Zn(C_2H_5)_2$, which is active for the isospecific polymerization of methyl methacrylate. The conditions for polymerization were examined and found as follows: 1×10^{-5} mole catalyst and an equimolar of boron cocatalyst, 2.82×10^{-2} mole MMA, 7.1×10^{-3} mole $Zn(C_2H_5)_2$, MMA/Zn mole ratio of 4, polymerization temperature of -78^0C and 12 hours polymerization time which give the highest activity. The polymer yield increases linearly with polymerization time. There is no significant difference from varying solvent; toluene, hexane and dichloromethane. In this experiment, $B(C_6F_5)_3$ can be used as a cocatalyst for the above system but gives a lower yield and activity than $Ph_3C^+B(C_6F_5)_4^-$ or $PhNMe_2H^+$ $B(C_6F_5)_4^-$. Comparison of the alkylating agents between MeMgBr and TIBA, it was found that only MeMgBr is efficient to alkylate the catalyst. The glass transition temperature (T_g) of the obtained polymer is approximately 50 ^{0}C which confirmed that the produced polymethyl methacrylate is isotactic. The molecular weight distribution of the obtained polymer is narrow (< 2.5). This characteristic is belonged to the metallocene catalysts.

The results show that this studied catalytic system give higher isotacticity than the catalytic system reported by Soga, $Cp_2ZrMe_2/B(C_6F_5)_3$ and $Et(Ind)_2ZrMe_2/Ph_3C$ $B(C_6F_5)_4$ [15,16,25].

6.2 Suggestion

For the future work, the catalyst might be developed by changing metals and/or ligand environment. Search for new cocatalyst that is more efficient, safer and has lower price would be worth done.

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