ผลของตัวเร่งปฏิกิริยาร่วมต่อสไตรีนพอลิเมอไรเซชัน

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EFFECTS OF COCATALYSTS ON STYRENE POLYMERIZATION

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ซินดิโอแทคทิคพอลิสไตรีนเป็นพลาสติกทางวิศวกรรมที่มีลักษณะกึ่งผลึก มีสมบัติต้านทานความร้อนและสารเคมี เพราะฉะนั้นซินดิโอแทคทิคพอลิสไตรีนจึงถูกนำมาใช้งานหลายอย่างเช่น อุตสาหกรรมอิเล็กโทรนิค ยานยนต์ และบรรจุภัณฑ์ จากงานวิจัยนี้ระบบซึ่งประกอบด้วย เพนทาเมทิลไซโคลเพนทาไดอีนิลไทเทเนียมไทรคลอไรด์(Cp^*TiCl_3)-ไทรไอโซบิวทิลอะลูมิเนียม(TIBA)/ไทรเฟนิลคาร์บีเนียมเททราคิส(เพนทาฟลูออโรเฟนิลบอเรต) ($[Ph_3C]^+[B(C_6F_5)_4]^-$) หรือ ไดเมทิลอะนิลิเนียมเททราคิส(เพนทาฟลูออโรเฟนิลบอเรต) ($[PhNMe_2H]^+[B(C_6F_5)_4]^-$) สามารถเหนี่ยวนำสไตรีนพอลิเมอไรเซชันแบบเลือกจำเพาะซินดิโอแทคทิค ทำพอลิเมอไรเซชันโดยแปรเปลี่ยนตัวแปรของปฏิกิริยา ผลการทดลองแสดงว่าภาวะที่ดีที่สุดสำหรับระบบ Cp^*TiCl_3-TIBA/$[Ph_3C]^+[B(C_6F_5)_4]^-$ คือ 0.087 โมลของสไตรีน อัตราส่วนโมลของ Al/Ti เท่ากับ 200 0.005 มิลลิโมลของตัวเร่งปฏิกิริยาที่อุณหภูมิของการเกิดพอลิเมอร์ 70 °ซ และ เวลาของการเกิดพอลิเมอร์ 60 นาที ภาวะที่เหมาะสมสำหรับระบบ Cp^*TiCl_3-TIBA/$[PhNMe_2H]^+[B(C_6F_5)_4]^-$ คือ 0.087 โมลของสไตรีน อัตราส่วนโมลของ Al/Ti เท่ากับ 200 0.001 มิลลิโมลของตัวเร่งปฏิกิริยาที่อุณหภูมิของการเกิดพอลิเมอร์ 70 °ซ และ เวลาของการเกิดพอลิเมอร์ 60 นาที ขั้นตอนพรีแอคติเวชันจำเป็นต่อการเพิ่มแอคติวิตีโดยการเพิ่มสปีชีส์ที่ว่องไวต่อการเกิดปฏิกิริยา นอกจากนี้การเติมเฟนิลไซเลนลงในระบบมีผลทำให้แอคติวิตีเพิ่มขึ้น พอลิเมอร์ทั้งหมดที่ได้จากระบบดังกล่าวมีจุดหลอมเหลวในช่วง 268-269 °ซ และ มีการกระจายของน้ำหนักโมเลกุลที่แคบ (1.54-1.78)

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต อุกฤษฏ์ วาณิชย์ก่อกุล

หลักสูตร ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา W. Trakarnpruk

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Syndiotactic polystyrene is a semi-crystalline engineering thermoplastic with heat and chemical resistant properties. Therefore, it has a potential for various applications, for example, electronics, automotive and packaging industries. From this research, the combined catalyst system $Cp^{*}TiCl_3$-TIBA/$[Ph_3C]^+[B(C_6F_5)_4]^-$ or /$[PhNMe_2H]^+[B(C_6F_5)_4]^-$ has proved to be able to induce syndiospecific styrene polymerization. The polymerizations were carried out by varying reaction parameters. The results indicated that the best condition for $Cp^{*}TiCl_3$-TIBA/$[Ph_3C]^+[B(C_6F_5)_4]^-$ system is: 0.087 mole of styrene, Al/Ti = 200, 0.005 mmol of catalyst at polymerization temperature of 70 ^{o}C and polymerization time for 60 minutes. The appropriate condition for $Cp^{*}TiCl_3$-TIBA/$[PhNMe_2H]^+[B(C_6F_5)_4]^-$ system is; 0.087 mole of styrene, Al/Ti = 200, 0.001 mmol of catalyst at polymerization temperature of 70 ^{o}C and polymerization time for 60 minutes. The preactivation step is necessary to increase the activity by increasing the active species. Moreover, the addition of phenylsilane in the system increases the activity. All polymers obtained with these catalyst systems have melting temperature in the range of 268-269 ^{o}C and narrow molecular weight distribution (1.54-1.78).

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Program Petrochemistry and polymer science Advisor's signature W. Trakarnpruk

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LIST OF ABBREVIATIONS

PS	Polystyrene
APS	Atactic polystyrene
IPS	Isotactic polystyrene
SPS	Syndiotactic polystyrene
MAO, MMAO	Methylaluminoxane
TMA	Trimethylaluminium
TEA	Triethylaluminium
TIBA, Al*i*Bu$_3$	Triisobutylaluminium
MEK	Methyl ethyl ketone
M	Metal
Ph	Phenyl
Me	Methyl
Et	Ethylene
R	Substituent R group
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Ind	Indenyl
BenzInd	Benzylindenyl
Flu	Fluorenyl
DSC	Differential scanning calorimetry
MWD	Molecular weight distribution
GPC	Gel permeation chromatography
ESR	Electron spin resonance

CHAPTER I

INTRODUCTION

One of the most important achievements in the fields of synthetic polymer chemistry during the past 50 years has been the discovery of polyethylene in 1953 by Ziegler. Ziegler's discovery, together with the ensuring work in the polymerization of propylene and other α-olefins by Natta, has given rise to the development of new classes both of catalysis and polymers. The commercial advantage is that polymer structure control could be achieved in the polymerization of such readily available and cheap monomers such as ethylene and propylene.

Controlling the molecular architecture of polymers (stereoregularity) is of practical importance both in the development of new polymers or tailor-made polymers and in the control of polymer properties. One of the most fascinating developments in the field of transition metal polymerization during recent years has been the discovery by Sinn and Kaminsky of homogeneous metallocene based coordination polymerization catalysts. In contrast with the traditional Ziegler-Natta catalysts, the metallocene ligands allow monomer insertions in a very homogeneous manner. The main difference between these metallocene catalysts and conventional Ziegler-Natta catalysts was in the distribution of active sites. The Ziegler-Natta catalysts were heterogeneous and have many active sites or called multi-site catalysts[1]. Only some of these sites were stereospecific and some were more accessible to monomers for coordination and subsequent polymerization than others. On the other hand, the metallocene catalysts were believed to be homogeneous. Each catalyst molecule has the same activity and each has essentially the same accessibility to the monomer. Therefore, these metallocene catalysts were referred to as single site catalysts and offered potential advantages over traditional multi-site Ziegler-Natta catalysts. Due to this structural control, metallocene catalysts can be easily modified to better control polymer stereoregularity, molecular weight and molecular weight distribution.

Atactic polystyrene (APS), which has long been used as a commodity plastic since being commercialized by I.G. Farben in 1925, is an indispensable material. Although polystyrene is endowed with excellent properties which are not found in other commodity plastics such as polyolefins, its amorphous nature limits the application areas because of its poor resistance to heat and solvents.

Since the discovery of the Ziegler-Natta catalyst systems in the early 1950s, extensive studies concerning the stereospecific polymerization of olefins have been carried out[2, 3]. In most cases, isotactic polymers are obtained and syndiotactic polymers are rare. Isotactic polystyrene (IPS), which was produced by Natta in 1995, is semi-crystalline polymer with a high melting point, 240 °C. Several companies have tried to commercialize this polymer, because IPS should be a plastic with high heat resistance. But the crystallization rate of IPS is too slow to be practical in injection molding.

Ishihara *et al.* have succeeded in the synthesis of syndiotactic polystyrene (SPS, XAREC®-IDEMITSU KOSAN CO., LTD.) in 1985. This is the first known case of syndiospecific polymerization for styrene. The melting point of SPS is 270 °C and its crystallization rate is much faster than that of IPS (Table 1). Furthermore, the low specific gravity, low dielectric constant, high modulus of elasticity and excellent resistance to water and chemicals make SPS a promising material for a large number of applications in many market areas.

Table 1.1 Properties of atactic, isotactic and syndiotactic polystyrenes

	Atactic PS (APS)	Isotactic PS (IPS) 1955 G.Natta	Syndiotactic PS (SPS) 1985 N. Ishihara (IDEMITSU KOSAN CO., LTD.)
Structure	Amorphous	Crystalline	Crystalline
Crystallization rate	-	Slow	Fast
Glass temperature(T_g)/ °C	100	99	100
Melting point(T_m)/ °C	-	240	270

For the most part, SPS as an engineering plastic is used in reinforced or filled compound to take advantage of the high melting point and high modulus of the base resin. SPS, when used alone, is not suitable for structural material because of the brittleness. Reinforcing the resin with fiber-glass, mineral fillers, or elastomers is one approach to offset this. In general these products are 30 and 40wt.% glass-filled products (GF-SPS) with the aspect ratio of the glass at 100-300 to 1 in final-part applications. In addition, elastomeric impact modifiers (i.e., hydrogenated block copolymers of styrene and butadiene and polyolefin elastomers) can be added to the SPS matrix to increase overall toughness of the engineering material. Table 1.2 compares the typical properties of neat SPS with fiberglass-reinforced SPS and other crystalline engineering resins.

Table 1.2 Summary of physical properties for SPS products[4]

Property	SPS			PET
	Neat resin	10% Glass filled	30% Glass filled	30% Glass filled
Specific gravity	1.0	1.1	1.3	1.6
Tensile strength (MPa)	35.3	71.6	118.0	152.0
Tensile elongation (%)	20.0	3.1	2.5	2.5
Flexural strength (MPa)	63.7	115.0	185.0	196.0
Flexural modulus (MPa)	2550.0	4000.0	9020.0	9810.0
Izod Impact (KJ/m^2)	10.0	8.8	10.8	8.0
Deflection temp. @ 1.82 MPa	95.0	130.0	251.0	245.0
Deflection temp. @ 1.82 MPa	110.0	262.0	269.0	250.0
Dielectric const. (1 MHz)	2.6	2.8	2.9	3.5
Dielectric loss tangent (1 MHz)	<0.001	<0.001	<0.001	<0.007

Source : Idemitsu

However, despite their numerous advantages, several problems still need to be solved before the metallocene catalysts can be used widely in industry. This can be observed two main problems: first, the difficulty in controlling polymer morphology with soluble homogeneous catalysts, their inability to be used in slurry and gas-phase processes, and reactor fouling; second, the very large amount of MAO as the cocatalyst for achieving maximum activity. The high levels of MAO were a problem commercially, due to relatively high cost of MAO. In addition, the very high level of MAO left a large amount of aluminium-containing ash in the polymer, which can affect the product properties.

Aluminoxane is the usual cocatalyst for the synthesis of SPS. Metallocene catalytic systems require a large amount of methylaluminoxane for achieving higher productivity. The high cost and explosion hazards of the cocatalyst stimulated the search for new families of metallocenes, which can perform in the absence of aluminoxane.

Other cocatalysts are based on tris(pentafluorophenyl)boron, ($B(C_6F_5)_3$) and its derivatives. Alkyl aluminium compounds are used to alkylate in place of MAO.

This thesis involved styrene polymerization in the presence of half-titanocene/triisobutylaluminium/boron compound as a catalytic system. The various reaction parameters, which may influence the catalytic efficiency of metallocene for olefin polymerization have been investigated.

1.1 The objective of the thesis

To study the influences of half-titanocene catalysts and boron compound cocatalysts on catalytic activity and percentage of syndiotactic polystyrene produced.

1.2 The scope of the thesis

1.2.1 Perform styrene polymerization using half-titanocene catalysts and boron compounds as a cocatalyst.

1.2.2 Investigate the optimum conditions in the polymerization of styrene:

   1.2.2.1 Examine the effect of mole of catalyst and cocatalyst on catalytic activity.

   1.2.2.2 Determine the effect of temperature, preactivation time and polymerization time on catalytic activity.

   1.2.2.3 Verify the effect of Al/Ti or phenylsilane/Ti on catalytic activity.

1.2.3 Characterize polystyrene products by using infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimetry (DSC) and gel permeation chromatography (GPC).

CHAPTER II

THEORY

The catalyst system always plays the key role in olefin oligomerization and polymerization processes. Metallocene compounds are becoming an important catalyst for the synthesis of organic molecules and polymers. Especially, group 4 metallocene catalyst are considered to be the most versatile transition metal catalyst for the polymerization. These catalyst systems show high performance for olefin polymerization and allow tailor making of polymers due to better control over the structure of metallocene and polymerization conditions. Further, there are other process advantages such as ease of handling of metallocene systems and the favorable conditions from a commercial viewpoint. Now, an enormous amount of industrial and academic works are significantly interested in developing these catalysts to be available with a suitable performance level in polyolefin manufactures.

2.1 Categories of metallocene catalyst systems

Metallocene catalyst systems can be classified into three categories. In the first category, an aluminoxane, an alkylaluminium or a combination of aluminoxanes and alkylaluminiums are used to activate the metallocene catalyst. In general these metallocenes have poor or no activity when used alone. In the second category, an ion exchange compound is combined with the metallocene catalyst, forming what is generally called a cationic metallocene catalyst. It is now generally accepted that the catalytic active species for metallocene/aluminoxane/alkylaluminium systems is also cationic. In the last category, the metallocene compounds are immobilized on inorganic supports such as silica, alumina or magnesium chloride to control the morphology of the polymer and prevent reaction fouling.

2.1.1 Metallocene catalyst systems containing aluminoxane compound

Breslow and Newburg were among the first researchers to apply metallocene catalysts for polymerization. They used soluble bis(cyclopentadienyl)titanium derivatives and alkylaluminiums for ethylene polymerization. Several other researches followed this original work, using the same catalytic system or modifications of that system, including Natta. However, these catalytic systems had low activities and stabilities for the polymerization of ethylene and produced only low molecular weight polymers. Additionally, they were not active for propylene polymerization. A breakthrough occurred when Kaminsky and his co-workers noticed that the addition of water to the trialkylaluminium in molar ratio 1:1 during ethylene polymerization significantly improved the catalyst activity.

It was already known that trialkylaluminium reacts with water to produce alkyl aluminoxane. Therefore, Kaminsky and his group decided to use alkyl aluminoxane oligomeric product as the cocatalyst with the metallocene catalyst. This combination made the breakthrough in the development of metallocene/aluminoxane catalyst systems for olefin polymerization. It produced a metallocene catalyst system whose activity is significantly higher than that of conventional Ziegler-Natta catalyst and is capable of producing stereoregular polyolefin with very narrow molecular weight distribution.

2.1.1.1 Metallocene

Metallocene catalysts are organometallic compounds in which one or two π-carbocyclic ligands such as cyclopentadienyl ring, substituted cyclopentadienyl ring, or derivative of cyclopentadienyl ring (such as fluorenyl, indenyl etc.) are bonded to a central transition metal atom. The cyclopentadienyl ring of metallocene which is singly bonded to the ring-metal bond is not centered on any one of the five carbon atoms in the ring but equally on all of them[5]. The typical chemical structure of a metallocene catalyst is represented by Figure 2.1 where M is the group 4B, 5B, or 6B transition metal, normally group 4B (Zr, Ti, Hf) ; A is an optional bridging atom usually Si or C atom; R is a σ-homoleptic hydrocarbyl such as H, alkyl, or other hydrocarbon groups; and X is chlorine or other halogens from group 7A or an alkyl group. The cyclopentadienyl ligands, halides, and σ-homoleptic hydrocarbyls represent the three classes of ligands of the metallocene catalysts. Variation of, and/or substitutions within, some of these ligands could result in variation of the catalytic activity, polymer stereoregularity, and average molecular mass. In case of metallocene catalyst, there is only one π-carbocyclic ligand with a heteroatom attached to the bridging atom[6-8].

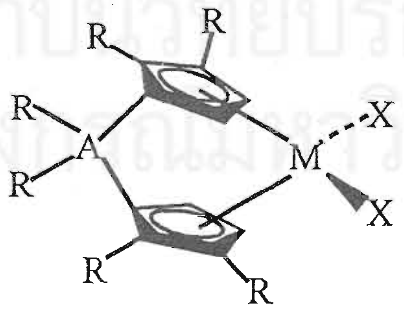
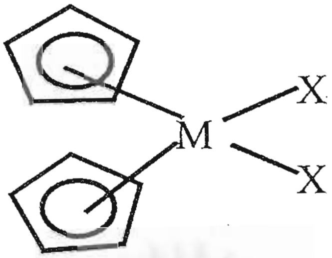


Figure 2.1 Typical chemical structure of a metallocene catalyst.

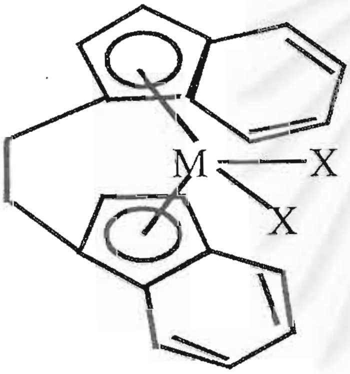
Compositions and types of metallocene have several varieties. When the two cyclopentadienyl (Cp) rings on either side of the transition metal are unbridged, the metallocene is nonstereorigid and it is characterized by C_{2v} symmetry. The Cp_2M (M= metal) fragment is bent back with the centroid-metal-centroid angle θ about 140^{o} due to an interaction with the other two σ bonding ligands. When the Cp rings are bridged (two Cp rings arranged in a chiral array and connected together with chemical bonds by a bridging group), the stereorigid metallocene, called ansa-metallocene, could be characterized by either a C_1, C_2 or C_s symmetry depending upon the substituents on two Cp rings and the structure of the bridging unit as schematically illustrated in Figure 2.2. A nonexhaustive list of the C_{2v}-, C_2-, and C_s-symmetric metallocenes is represented in Tables 2.1, 2.2 and 2.3, respectively. Two examples of C_1-symmetric metallocenes are as follows: i-Pr[(3-MeCp)(Flu)]$ZrCl_2$ and $Me_3C(3\text{-}MeCp)(Flu)ZrCl_2$[9].

Table 2.1 Selected list of C_{2v}-symmetric metallocenes [9]

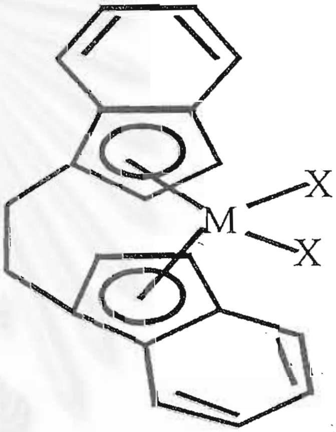
Metallocenes	Formula
Zirconocenes (with indenyl ligands)	Ind_2ZrCl_2, Ind_2ZrMe_2, Ind_2ZrBz_2
Zirconocenes (with cyclopentadienyl ligands)	Cp_2ZrCl_2, $CpZrCl_3$, Cp_2ZrMe_2, $(SiMe_3Cp)_2ZrMe_2$, $Me_2Si(Cp)_2ZrCl_2$
Titanocenes (with cyclopentadienyl ligands)	$Cp^{*}TiCl_3$, $CpTiCl_3$, Cp_2TiCl_2, Cp_2TiMe_2
Hafnocenes (with cyclopentadienyl ligands)	Cp_2HfCl_2, Cp_2HfMe_2



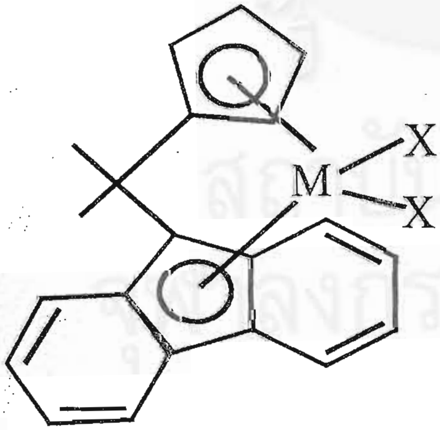
C_{2v}-symmetric



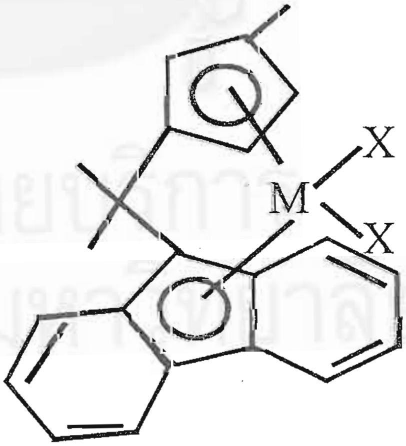
C_2-symmetric



C_s-symmetric



C_s-symmetric



C_1-symmetric

Figure 2.2 Schematic representations of metallocene symmetry[9]

Table 2.2 Selected list of C_2-symmetric metallocenes[9]

Metallocenes	Pentad (%)
Zirconocenes (with indenyl ligands)	mmmm%
$Et(Ind)_2ZrCl_2$	57-93
$Me_2Si(Ind)_2ZrCl_2$	82-95
$Me_2Si(2\text{-}MeBenzInd)_2ZrCl_2$	92
$Me_2Si(2\text{-}MeInd)_2ZrCl_2$	89-90
$Me_2Si(2\text{-}Me\text{-}4\text{-}Naph\text{-}Ind)_2ZrCl_2$	99
$i\text{-}Pr(Ind)_2ZrCl_2$	na
Zirconocenes (with cyclopentadienyl ligands)	
$Et(Cp)_2ZrMe_2$	na
$Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{-}Bu\text{-}Cp)_2ZrCl_2$	94-96
$Me_2Si(2,4\text{-}Me_2\text{-}Cp)_2ZrCl_2$	89
Zirconocenes (with fluorenyl ligands)	
$PhEt(1,2\text{-}Flu)_2ZrCl_2$	31-64
Hafnocenes (with indenyl ligands)	
$Et(Ind)_2HfCl_2$	68-94
$Me_2Si(Ind)_2HfCl_2$	83
Hafnocenes (with cyclopentadienyl ligands)	
$Me_2Si(2,4\text{-}Me_2Cp)_2HfCl_2$	97
Titanocenes (with indenyl ligands)	
$Et(4,5,6,7\text{-}IndH_4)_2TiCl_2$	na
$rac\text{-}(C_5H_4MePh)_2ZrCl_2$	na

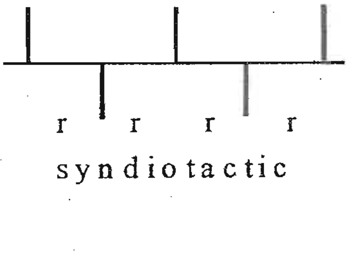
na = not available

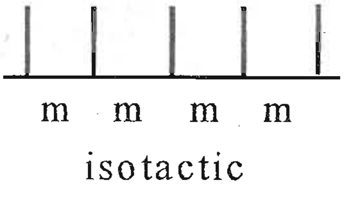
Table 2.3 Selected list of C_s-symmetric metallocenes[9]

Metallocenes	Pentad (%)
Zirconocenes	rrrr%
[1-(9-Flu)-2-(1-Ind)Et]$ZrCl_2$	na
[1-(9-Flu)-1(R)-Ph-2-(1(R)-Ind)Et]$ZrCl_2$	na
[1-(9-Flu)-1(R)-Ph-2-(1(S)-Ind)Et]$ZrCl_2$	na
i-Pr[(MeCp)(Ind)]$ZrCl_2$	mmmm, 54%
i-Pr[(3-t-BuCp)(Flu)]$ZrCl_2$	mmmm, na
Me_2Si(3-t-BuCp)(Flu)$ZrCl_2$	mmmm, na
Me_2C(MeCp)(Ind)$ZrCl_2$	mmmm, na
Me_2C(Cp)(2,7-t-Bu_2-Flu)$ZrCl_2$	mmmm, na
t-BuCH(3-t-Bu-Cp)(Flu)$ZrCl_2$	mmmm, na
Et(4,5,6,7-$IndH_4$)$_2ZrCl_2$	atactic

na = not available

Tacticity in NMR is represented by the relative configuraton of pair wise units. A typical ^{13}C-NMR spectrum of an atactic vinyl polymer in solution consists of numerous relatively sharp lines, that are assigned to the various sequences of meso (m) and racemic (r) dyads. These new lines are a result of configurational splitting. Meso (m) or isotactic dyads have the same optical configurations (dd or ll). Racemic (r) or syndiotactic dyads are pairs of adjacent asymmetric centers that have opposite optical configuration (dl). Triads, tetrads, pentads, etc., are denoted by a succession of dyads.





2.1.1.2 Methylaluminoxane

Ethylene was the first olefin to be polymerized using metallocene/aluminoxane catalysts. The activity of dicyclopentadienyl and tricyclopentadienyl zirconium derivatives could be greatly enhanced by the addition of small amount of water. This increased activity is related to the formation of aluminoxanes in the reaction between alkylaluminium and water.

The type of aluminoxane has a marked influence on the efficiency of the metallocene/aluminoxane catalytic system. Methylaluminoxane(MAO) seems to be more effective as a cacatalyst than other aluminoxane such as ethyaluminoxane (EAO) and isobutylaluminoxane (IBAO). More remarkably, the catalytic activity of the metallocene complex is directly proportional to the degree of oligomerization of the aluminoxane, For most homogeneous metallocene catalysts, a large excess of aluminoxane is required for the polymerization to reach its optimum value. Aluminium/transition metal ratios varying from 1,000 to 50,000 are commonly reported in the literature.

Despite its marked influence in catalytic performance, the exact role of the aluminoxane is not known precisely. Experimental evidence seems to indicate that besides acting as an alkylating angent and impurity scavenger, aluminoxane is involved in the formation of active sites and the prevention of their deactivation by bimolecular processes. Chien and Wang unequivocally demonstrated that the functions of the aluminoxane component go beyond alkylation of the metallocene. When 99% of MAO is substituted by trimethylaluminium (TMA), which also acts as an effective alkylation agent, polymerization rates are reduced by one third to one fourth of the value obtained when pure MAO is used. The molecular weight of the polymer is also lowered by 40% when the TMA/MAO ratio equals 10, but remains unaffected when the TMA/MAO ratio equals 2.

Aluminoxanes are obtained by the reaction of an alkylaluminium with water. Water should be present in a dilute or a less accessible form such as in wet solvents or hydrated salts, since the reaction between water and alkylaluminiums is extremely fast and highly exothermic. Several methods for synthesizing aluminoxane have been published in the literature[10]. Reddy and Sivaram recently published an extensive review of techniques for the synthesis of aluminoxanes[11].

The exact structure of aluminoxanes is still a matter of controversy. They supposedly exist as a mixture of different cyclic or linear oligomers with degrees of oligomerization commonly varying from 6 to 20. MAO, the most commonly used aluminoxane, may have the structures shown in Figure 2.3. Some recent experimental studies have suggested that MAO can also have a three-dimensional open cage structure.

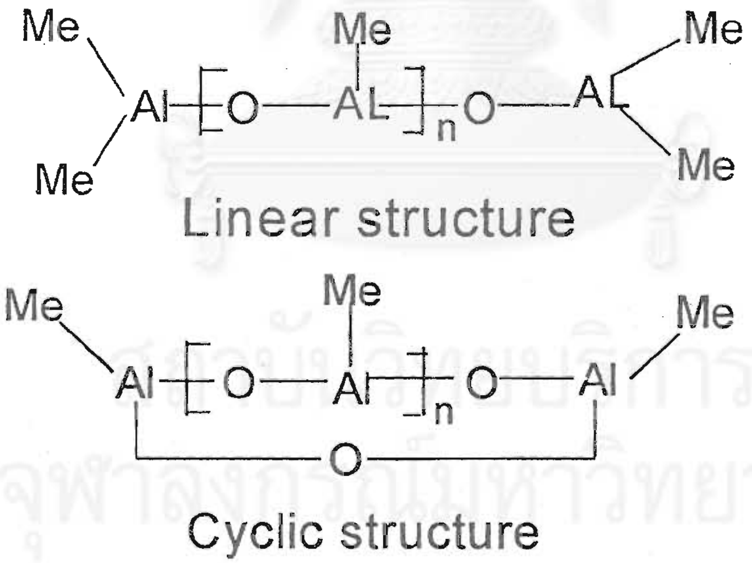


Figure 2.3 Linear and cyclic structures for methylaluminoxane[10]

The synthesis of aluminoxanes is associated with several serious limitations such as long reaction time to obtain a controlled exotherm, low yields, the risk of explosion and the formation of solid by-products. Recently some alternate methods have been applied to produce aluminoxanes[12-15].

New forms of aluminoxanes for use as cocatalysts have also been proposed. Resconi suggested the use of an aluminoxane obtained by the reaction of alkylaluminium and water vapor at the low temperature (0°C)[16]. Crapo and Malpass synthesized a modified form of methylaluminoxane (MMAO) by reacting TMA, a polyalkyldialuminoxane containing alkyl groups (ethyl or higher), and water[17]. MMAO contains alkyl substituents unlike conventional MAO. According to Crapo and Malpass, this process does not have the drawbacks of the conventional MAO synthesis. MMAO/metallocene and MAO/metallocene systems have comparable polymerization rates.

2.1.2 Cationic metallocene catalyst systems

Active homogeneous catalyst can be obtained, in the absence of MAO, by using cationic-metallocene-based single component catalysts. Cationic metallocene are a catalyst in which the transition metal atom is positively charged. The metallocene complex is therefore a cation associated with a stable anion. Currently, there is enough experimental evidence to support the hypothesis that all active center types operative with metallocene are cationic.

Cationic metallocene is prepared by combining at least two components. The first is a metallocene and the second is an ion exchange compound comprising a cation and a non-coordinating anion. The latter component is the new class of non-aluminium activators or cocatalysts based on boranes. The cation reacts irreversibly with at least one of the first component's ligands. The anion must be capable of stabilizing the transition metal cation complex and must be labile enough to be displaced by the polymerization monomer.

Non-aluminium activators such as $B(C_6F_5)_3$ or $[Ct]^+[B(C_6F_5)_4]^-$ (Ct =alkyl- or hydride-abstracting cation) may obviate many of the disadvantages of MAO as an activator for metallocene catalysts. Many cations have been developed for the $[B(C_6F_5)_4]^-$ anion, most recently silylium salts[18], prepared by metathesis of $Li[B(C_6F_5)_4]$ with R_3SiCl. Besides, tris(pentafluorophenyl)boron is a widely used activator for converting metallocene dihydrides and dialkyls to cationic catalysts. It has been prepared by reaction of C_6F_5MgBr (from C_6H_5Br and alkylmagnesium halides) with BF_3 etherate[19].

These cationic metallocene catalysts exhibits the same activity as MAO-activated catalysts. Unfortunately, the metallocene catalysts activated with the boron compounds are very sensitive to impurities during the polymerization process. A careful consideration is therefore needed before applying to industrial scale production[20].

2.1.3 Supported metallocene catalyst

Although original homogeneous metallocene catalysts exhibit several advantages for olefin polymerization as previously mentioned, control of the size and shape of produced polymer is very difficult. Additionally, due to the high cost of MAO as well as the disadvantage for slurry and gas phase processes, further practical application of homogeneous metallocene catalyst seems to be limited. Attempts to overcome those unsolved problems have led to a rapid development of heterogeneous metallocene catalysts during the last ten years. The special features of supported metallocene catalysts can be summarized as follows[21].

1. The morphology of polymers can be precisely controlled through replica process.
2. Most metallocene catalyst in solution produces polyolefins of a very low molecular weight (MW) especially at high polymerization temperature (Tp). The supported catalyst should produce higher MW polymers at high Tp.
3. Metallocene catalyst in solution gives polymers with narrow molecular weight distribution (MWD), and consequently with a poor processibility-physicomechanical property balance. The supported metallocene should have the capability of producing polymers having a desired broad or bimodal MWD for good rheological and physical properties.
4. The active species in case of supported metallocene catalyst are much more stabilized. Consequently, their thermal stability and longevity are markedly enhanced.
5. The steric control of metallocene catalysts is determined by molecular structure. It would be advantageous if this can be controlled or even altered by the support.

To apply the metallocene catalyst to slurry or gas phase processes, single site catalysts need to be supported on appropriate carriers. Silica is one of the most widely used inorganic carriers for polyolefin, especially ethylene polymerization since it leads to good morphological features for polymer particles[20, 22]. In addition, other materials such as alumina (Al_2O_3) or magnesium chloride ($MgCl_2$) are also main supports used. Some other materials have been investigated such as zeolites, MgO, MgF_2, CaF_2, AlF_3, etc; but they are not yet of commercial consequence[22].

The main preparative method for supported metallocene can be classified as follows:

Method 1 involves direct impregnation of metallocene on the support (modified with heating or chemical reagent by previous treatment or not). This can be done either (a) with mild impregnation conditions or (b) at high temperatures and long impregnation time. This method involved physical mixing of metallocene and support, and it was one of first method used. The dry support is reacted first with the metallocene compound in a solvent such as toluene. The solid part is then recovered by filtration and washed with hydrocarbon. The mixing temperature and the contact time are important parameters since they influence both the catalytic performances and final properties of the polymer[22].

Method 2 involves immobilization of MAO on the supported followed by reaction with the metallocene compound. A modified version of this method involves the replacement of MAO by an aluminium alkyl.

Method 3 involves precontacting metallocene and MAO complex and added to support[23].

Method 4 involves direct synthesis of metallocene on support (mainly modified SiO_2) by immobilization of aryl ligand on the support followed by addition of metal salt such as zirconium halide, recently, titanium and neodynium halides to form the attached metallocene[22, 24].

Among them, the most investigated method is based on the direct adsorption of metallocene on the support materials (method 1) or the initial adsorption of MAO on the support (method 2) [25, 26]. The methods 3 and 4 have been less employed[27-30].

All procedures afford different catalysts and these in turn produce polyolefins with different properties.

2.2 The mechanisms for stereochemical control in syndiotactic polymerization of styrene

2.2.1 Interaction of metallocene with aluminoxanes and nature of active species

The interaction of metallocene with aluminoxane has been studied in detail. Metallocene dichloride reacts with methylaluminoxane to yield a methylated compound (Figure 2.4). It undergoes either methyl or chloride abstraction to generate metallocene methyl cations. The research work reported by Marks, Bochmann, Jordan, and others gave synthetic and spectroscopic evidence that cationic metallocenes $\left[(Cp_2MR)\right]^+$ are the active species. The interaction of dichlorozirconocene, methylchlorozirconocene, and dimethylzirconocene with MAO has been studied by X-ray photoelectron spectroscopy. The formation of cationic species was also reported by Marks who studied the reaction of $Cp_2Zr(^{13}CH_3)_2$ with MAO. 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 Al:Zr ratio required to form this cation is considerably lower than that employed in a typical catalyst reaction. Siedle et al. employed solution ^{13}C-NMR spectroscopy to demonstrate that dimethyl metallocenes such as $Cp_2Zr(^{13}CH_3)_2$, $(Me_5Cp)_2Zr(^{13}CH_3)_2$, $(Indenyl)_2Zr(^{13}CH_3)_2$, $Me_2Si(C_5H_4)_2Zr(^{13}CH_3)_2$, and $Cp_2Hf(^{13}CH_3)_2$ undergo methyl exchange with methyl acceptor compounds such as Al_2Me_6 and $(MeAlO)_x$ (equation 2.1). The kinetics of 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.

$$Cp_2Zr(^{13}CH_3)_2 + Me_3Al \rightarrow Cp_2ZrCH_3^{+}\ AlMe_4^{-} \qquad (2.1)$$

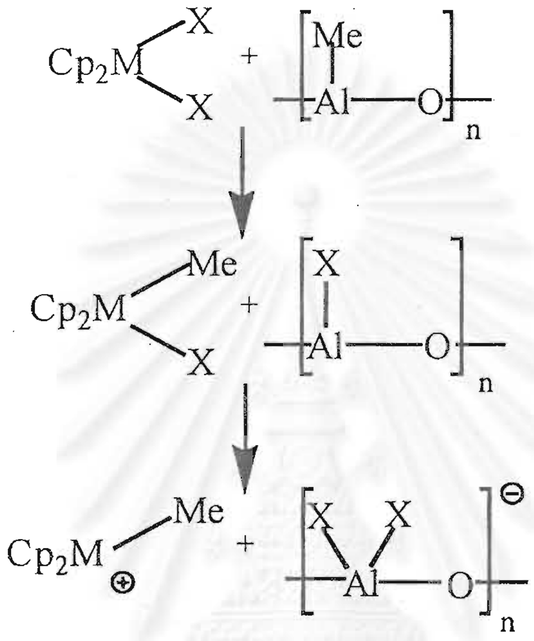


Figure 2.4 Postulated mechanism of formation of the active species in the reaction between metallocene and methylaluminoxane

2.2.2 Polymerization mechanisms

2.2.2.1 Initiation step : active species

According to Zambelli' s classification, two classes of group IV metal compounds show high activities in syndiospecific styrene polymerization:

1. $CpTiX_n$ or Cp^*TiX_n compounds (n= 2, 3; X = halide, alkoxide);
2. TiX_n compounds (n = 2-4; X= alkyl, alkoxide, halide).

Zirconium derivatives were also reported, but their activity is much lower than that of titanium homologues. Cyclopentadienyl anion is regarded as a "fixed" ligand, while X are "mobile" ligands. A cocatalyst must be added to the polymerization mixture to generate active species.

The nature and the formation of the true active catalytic species are not yet fully elucidated. For α-olefin polymerization it is generally accepted that homogeneous catalysts based on group IVA metallocene/MAO consist of cationic complexes formed by reaction of a metallocene with methylaluminoxane, according to the following equilibrium

$$Cp_2MX_2 + MAO \leftrightarrow [Cp_2MCH_3]^+[MAO \bullet X_2]^- \quad M = Ti, Zr, Hf \qquad (2.2)$$

Methylation and ligand abstraction by MAO are possible due to its pronounced Lewis acidity. Due to the low value of the equilibrium constant, the use of a large excess of MAO is often required.

A similar mechanism which leads to a $[CpTiCH_3]^+$ cation can be advanced for styrene syndiospecific catalyst (Figure 2.5). Ti(IV) is reduced to Ti(III). Reduction is probably caused by the free trimethylaluminium contained in MAO, since aluminium alkyls are better reducing agents than aluminoxanes. Methyl radicals formed as a consequence of $Al(CH_3)_3$ oxidation could initiate the radical polymerization of styrene to an atactic polymer, although it is known that primary radicals have short life times and are poor initiators.

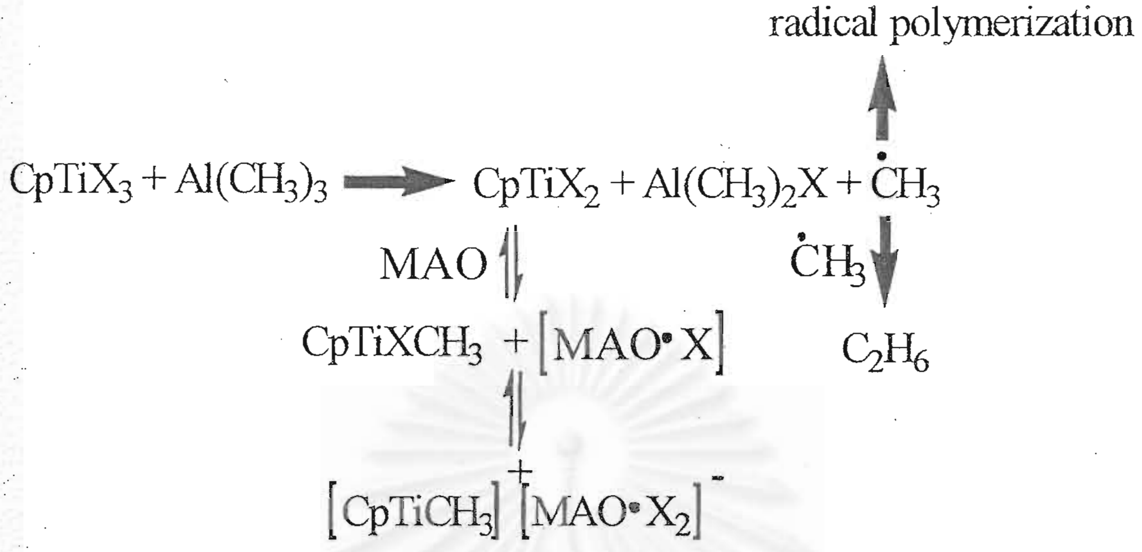


Figure 2.5 Formation of initiating species by CpTiX$_3$/MAO catalytic system[31].

Coordination of $[\mathrm{CpTiCH_3}]^+$ by styrene molecule through the vinyl double bond and one aromatic double bond (η^4-coordination) leads to a $[\mathrm{CpTiCH_3(styrene)}]^+$ complex (Figure 2.6a); for the polymer chain a η^3-coordination is assumed (Figure 2.6b). Toluene could compete with styrene in the co-ordination.

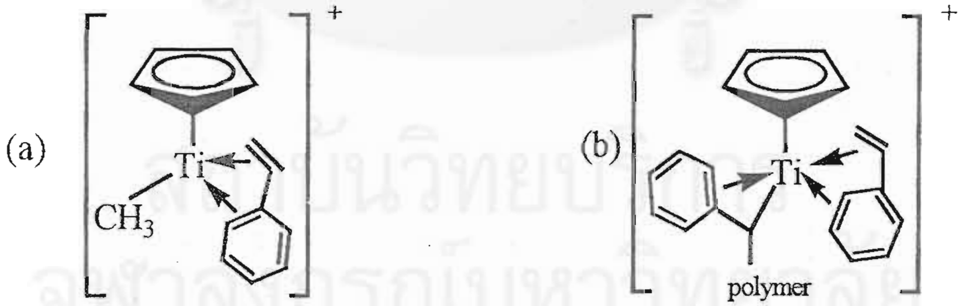


Figure 2.6 a) Structure of active species formed by CpTiX$_3$/MAO catalytic system.

b) Structure of active sites on growing polymer chains[31].

For TiX_n/MAO system the situation is much more ambiguous. Zambelli and co-workers suggested that titanium is probably reduced to Ti(II) and that all the "mobile" ligands are likely to be removed by MAO. Thus the proposed catalytic complex structure is $[(arene)TiCH_3(styrene)]^+$.

Chien et al. asserted that the titanium oxidation state in the active catalytic species is (III) both in $CpTiX_3$/MAO system and in TiX_4 one. They focused their atttention on Ti $(CH_2C_6H_5)_4$/MAO and $CpTi(OC_4H_9)_3$/MAO systems and carried out redox titrations to establish the metal oxidation state . They found that for $Ti(CH_2C_6H_5)_4$/MAO in toluene (Al/Ti molar ratio = 100), titanium has a distribution of oxidation states, with Ti(IV):Ti (III):Ti(II) about 53:27:20. The addition of styrene caused a change in these ratios to 36:48:16. ESR (Electron Paramagnetic Resonance) spectra are in agreement with titration determinations. ESR spectra are also consistent with the formation of $CpTi(OC_4H_9)H$ species when the $CpTi(OC_4H_9)_3$/MAO system is used; the formation of such hydridotitanium (III) complexes is almost quantitative. In this case, Ti(IV):Ti(III):Ti(II) ratios depend strongly on the titanium concentration. Experiments carried out in toluene using an electrodialysis polymerization apparatus did not afford syndiotactic polymer, suggesting that the catalytic species has little or no ionic mobility.

Analogous studies were carried out by Zucchini et al. [32] on the systems $Ti(OCH_2CH_3)_4$/MAO, $Ti(OCH_2CH_3)_3Cl$/MAO and $[Ti_2(OCH_2CH_3)_8Cl]Mg_2(\mu\text{-}Cl)_2$/MAO in toluene (Al/Ti =500). They found that in the absence of styrene, titanium has mainly a (III) oxidation state and the percentage of (II) oxidation state is around 10%. ESR measurements reveal the formation of an unidentified new Ti (III) species, possibly containing a Ti-H bond, suggesting a certain degree of β-hydrogen abstraction of bonded polymer. Ti(II) amounts remain unchanged. The authors remarked that an obvious correlation cannot be established between catalytic activity and Ti(III) concentration, since Ti(III) complexes could be only the results of an intermediate step in the true reaction mechanism.

A different situation occurs when $B(C_6F_5)_3$ derivatives are used as cocatalyst. In this case, the active species can be formed only using an alkyl titanium compound, since no alkylating agents (e.g. alkylaluminium or MAO) are present in the catalyst formulation. Furthermore Ti(IV) cannot be reduced to titanium(III) or (II) for the same reason. The proposed reactions leading to the formation of active species are the following[33]:

$$CpTi(CH_3)_3 + B(C_6F_5)_3 \Rightarrow \left[CpTi(CH_3)_2\right]^+\left[B(C_6F_5)_4CH_3\right]^- \qquad (2.3)$$

$$Ti(CH_2C_6H_5)_4 + B(C_6F_5)_3 \Rightarrow \left[Ti(CH_2C_6H_5)_3\right]^+\left[B(C_6F_5)_3CH_2C_6H_5\right]^- \qquad (2.4)$$

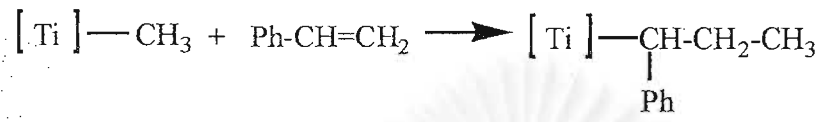
Ammonium salts of tris(pentafluorophenyl)boron are also able to generate cationic complexes:

$$CpTi(CH_3)_3 + \left[(CH_3)_2N(C_6H_5)H\right]^+\left[B(C_6F_5)_4\right]^- \Rightarrow \left[CpTi(CH_3)_2\right]^+\left[B(C_6F_5)_4\right]^- + CH_4 + (CH_3)_2N(C_6H_5) \qquad (2.5)$$

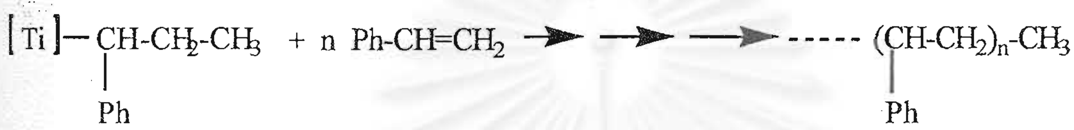
However, the polymerization affords atactic polymer. The aspecificity of polymerization is attributed to the poisoning of catalytic system by the formed amine.

2.2.2.2 Propagation step

Baird et al. proposed an interpretation of the polymerization mechanism for $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$ systems. Several experimental studies support the metal-coordinated mechanism. Experiments were carried out by analyzing end-groups, by using labelled isotopes, and by determining polymer configuration by NMR. The rate-determining step is probably the electrophilic attack of the electron-poor metal to styrene double bonds and the kinetics is first order with respect to styrene concentration:



$$[\text{Ti}]\text{—CH}_3 + \text{Ph-CH=CH}_2 \longrightarrow [\text{Ti}]\text{—}\underset{\text{Ph}}{\underset{|}{\text{CH}}}\text{-CH}_2\text{-CH}_3 \qquad (2.6)$$



$$[\text{Ti}]\text{—}\underset{\text{Ph}}{\underset{|}{\text{CH}}}\text{-CH}_2\text{-CH}_3 + n\ \text{Ph-CH=CH}_2 \longrightarrow \longrightarrow \longrightarrow \text{-----}\ (\underset{\text{Ph}}{\underset{|}{\text{CH}}}\text{-CH}_2)_n\text{-CH}_3 \qquad (2.7)$$

Indeed the reactivity of the initiating system increases with increasing the electron donating character of substituents located in the para position of the phenylene ring (CH_3 > H(styrene) > halogen).

By polymerizing deuterium labelled styrene and analyzing ^1H NMR spectra, Longo *et al.* detected the exclusive presence of erythro-disyndiotactic conformer (Figure. 2.7). This demonstrated that the insertion of styrene on Ti-C (or Zr-C) bond proceeds through cis opening of the double bond.

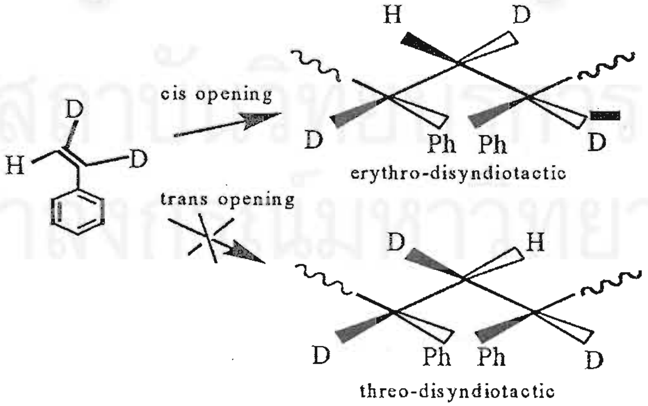


Figure 2.7 Stereochemistry of double bond opening of cis-styrene-β-d by syndiospecific catalysts for styrene polymerization[31].

Monomer concentration is head-to-tail and insertion is secondary, i.e. benzylic carbon is directly bonded to the metal atom (Figure 2.8). The prevailing steric sequence distribution was found to be ...*rrrrrrrmrrrr*... (*r* = racemic diad, *m* = meso diad), with a very low degree of steric defects. Pentad distribution is consistent with that calculated assuming a Bernoullian symmetric statistical model. When highly stereospecific catalysts are used, meso diads are essentially isolated: the probability of finding two contiguous meso diads is negligible. Therefore the stereochemistry of styrene monomer insertion is controlled in each step by the configuration of the benzylic carbon of the last inserted monomer unit (1, 3-asymmetric induction). In other words, the syndiotactic configuration would arise from phenyl-phenyl repulsive interaction between the last inserted unit of growing chain and incoming monomer (Figure 2.8 ; the circle represents the ligand co-ordination sphere).

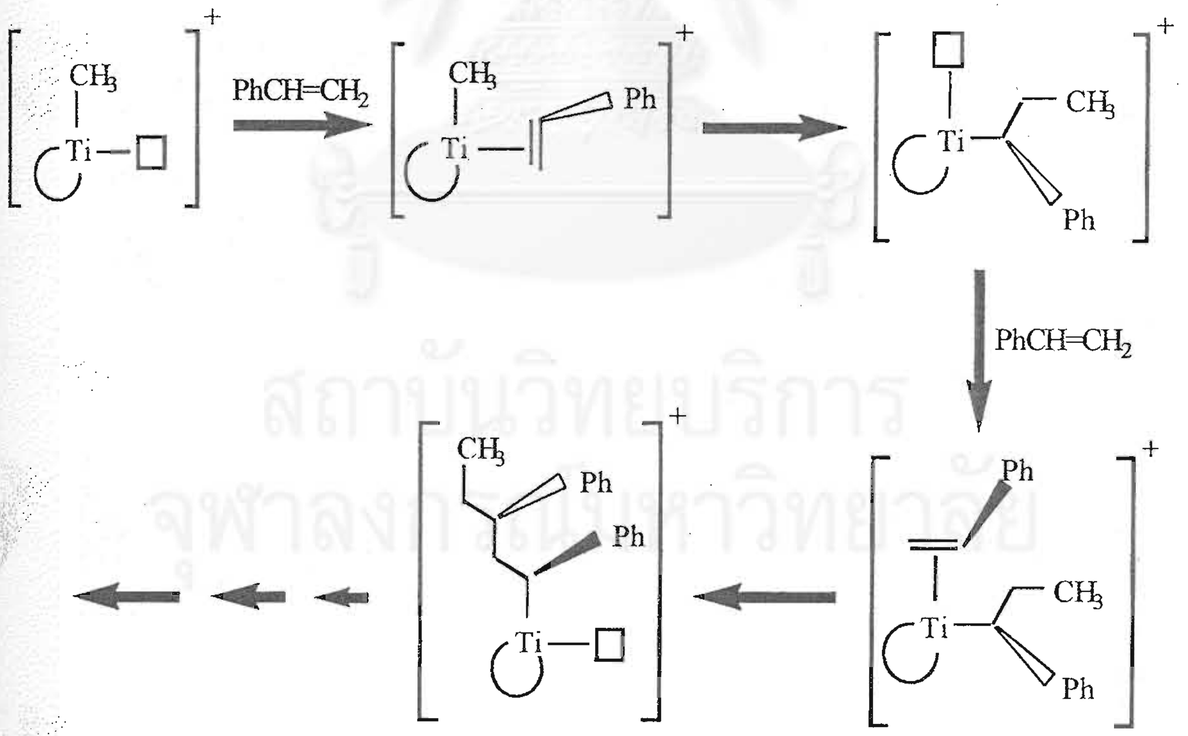
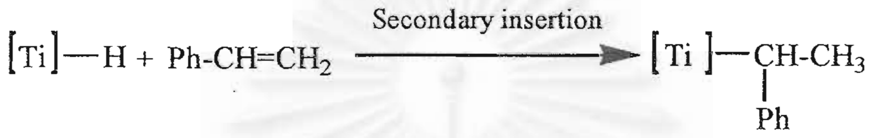
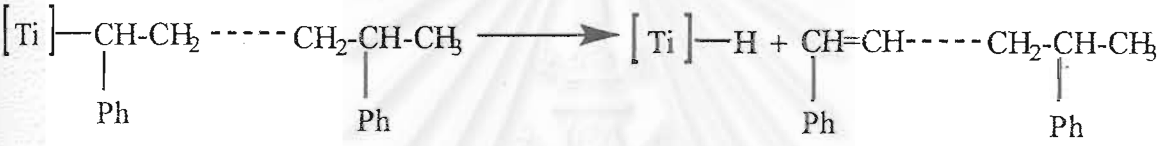


Figure 2.8 Steric control in propagation of syndiospecific polymerization of styrene[31].

End-group analysis gives further support to the secondary insertion mechanism and some hints on chain transfer phenomena. Indeed Ph-CH=CH- terminal groups are detected, which would arise from β-hydrido elimination of a growing chain initiated by styrene insertion on a Ti-H bond.


$$[Ti]\text{—}H + Ph\text{-}CH{=}CH_2 \xrightarrow{\text{Secondary insertion}} [Ti]\text{—}\underset{\displaystyle Ph}{CH}\text{-}CH_3$$

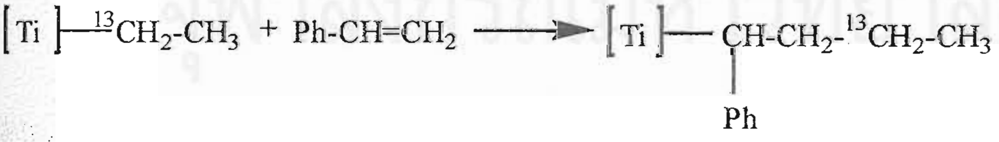
(2.8)


$$[Ti]\text{—}\underset{\displaystyle Ph}{CH}\text{-}CH_2\text{-----}CH_2\text{-}\underset{\displaystyle Ph}{CH}\text{-}CH_3 \longrightarrow [Ti]\text{—}H + \underset{\displaystyle Ph}{CH}{=}CH\text{-----}CH_2\text{-}\underset{\displaystyle Ph}{CH}\text{-}CH_3$$

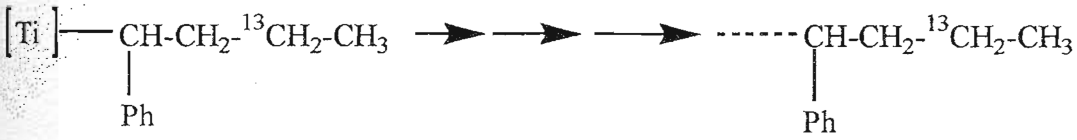
(2.9)

Remarkably, ^{13}C NMR analysis reveals that SPS bears $-CH_2\text{-}CHPh\text{-}CH_3$ and Ph-CH=CH- end groups in equal amounts. Incidentally, SPS containing $-CH_2\text{-}CHPh\text{-}CH_2\text{-}{}^{13}CH_2\text{-}CH_3$ end groups is obtained by adding small amounts of ^{13}C-enriched trimethylaluminum to the $Ti(CH_2C_6H_5)_4$/MAO system, thus confirming the secondary insertion and the nature of initiating species:

$$[Ti]\text{—}CH_3 + Al({}^{13}CH_2CH_3)_3 \longrightarrow [Ti]\text{—}{}^{13}CH_2\text{-}CH_3 + AlCH_3({}^{13}CH_2CH_3)_2 \quad (2.10)$$


$$[Ti]\text{—}{}^{13}CH_2\text{-}CH_3 + Ph\text{-}CH{=}CH_2 \longrightarrow [Ti]\text{—}\underset{\displaystyle Ph}{CH}\text{-}CH_2\text{-}{}^{13}CH_2\text{-}CH_3$$

(2.11)


$$[Ti]\text{—}\underset{\displaystyle Ph}{CH}\text{-}CH_2\text{-}{}^{13}CH_2\text{-}CH_3 \longrightarrow\longrightarrow\longrightarrow \text{------}\underset{\displaystyle Ph}{CH}\text{-}CH_2\text{-}{}^{13}CH_2\text{-}CH_3$$

(2.12)

In another study, a completely different polymerization mechanism has been put forward. Baird and co-workers focused their consideration on the $Cp^{*}Ti(CH_3)_3/B(C_6F_5)_3$ system. They found that the bulky styrene molecule can polymerise as fast as ethylene or propylene, and they advanced the hypothesis that the initiaing species $[Cp^{*}Ti(CH_3)_2]^{+}$ behaves also as a carbocationic initiating centre. Indeed vinyl ethers and N-vinylcarbazole, which are unable to polymerize following a metal-coordinated mechanism, afford the respective polymer in good yields in the presence of $Cp^{*}Ti(CH_3)_3/B(C_6F_5)_3$. Thus they proposed the carbocationic mechanism depicted in Figure 2.9, where styrene and metal interact through a η^1 rather than the traditional η^4 co-ordination mode.

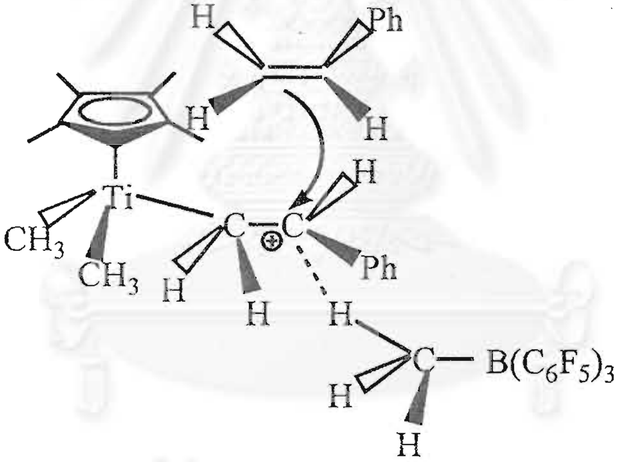


Figure 2.9 Carbocationic mechanism of syndiospecific polymerization of styrene by $[Cp^{*}Ti(CH_3)_2][CH_3B(C_6F_5)_3]$[31].

By quenching the reaction with tert-butylalcohol, a tert-butoxy terminated polystyrene is obtained, whose formation cannot be explained by a metal-coordinated mechanism. The steric control is attributed to ion pairing of the $CH_3B(C_6F_5)_3^{-}$ counterion with the cationic centre. It was concluded that the two mechanisms are probably concurrent and dependent on the particular catalytic system, and they attribute the formation of some fraction of low molecular weight SPS to the metal-coordinate path.

2.2.2.3 Chain transfer and termination steps

If the polymerization mechanism was a true living process, molecular weight distribution (MWD) value of 1 and an increase in molecular weight with reaction time would be observed.

Actually, a limiting molecular weight is reached with some initiating systems, depending on reaction conditions (temperature, diluent), while with other initiating systems the molecular weight continues to increase during the entire reaction.

Three factors mainly may contribute to MWD broadening:

1. existence of different catalytic centres;
2. existence of chain-transfer or termination reactions;
3. formation of some atactic PS due to spurious radical or ionic initiation.

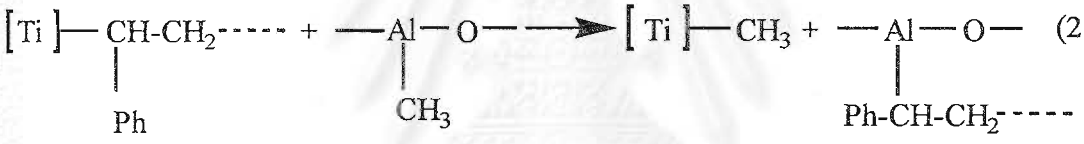
Point 3) can be regarded as a particular case of point 1). Termination reactions are generally considered absent. The living growing chain must be "killed" at the end of reaction by adding a proton donor (protonic acids, water, alcohols).

As far as atactic impurities are concerned, after atactic PS extraction, a narrowing of MWD is also observed. MWD values of 1.7-2.4 are obtained in most cases, suggesting that chain transfer is present.

As previously mentioned, strong experimental evidence for β-hydrido abstraction exists (transfer rate constant = k_β). The so formed hydridotitanium species is able to re-initiate a new polymer chain. :

$$[\mathrm{Ti}]-\underset{\mathrm{Ph}}{\mathrm{CH}}\text{-CH}_2\text{-----}\longrightarrow[\mathrm{Ti}]-\mathrm{H}+\text{Ph-CH=CH----}\qquad(2.13)$$

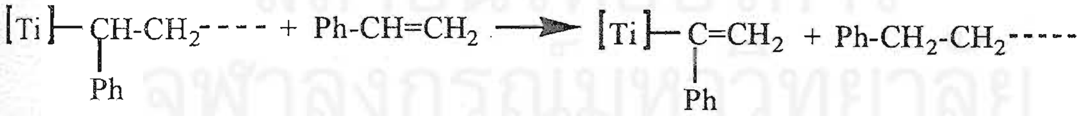
In analogy with α-olefin polymerization with Cp_2MCl_2/MAO (M =Zr, Hf) catalysts, transfer to aluminium would lead to the formation of aluminium- polymer bonds (transfer rate constant = k_m):



$$[\mathrm{Ti}]-\underset{\mathrm{Ph}}{\mathrm{CH}}\text{-CH}_2\text{-----}+-\underset{\mathrm{CH_3}}{\mathrm{Al}}-\mathrm{O}-\longrightarrow[\mathrm{Ti}]-\mathrm{CH_3}+-\underset{\text{Ph-CH-CH}_2\text{-----}}{\mathrm{Al}}-\mathrm{O}-\qquad(2.14)$$

Chain transfer with monomer could follow the following paths

$$[\mathrm{Ti}]-\underset{\mathrm{Ph}}{\mathrm{CH}}\text{-CH}_2\text{----}+\text{Ph-CH=CH}_2\longrightarrow[\mathrm{Ti}]-\underset{\mathrm{Ph}}{\mathrm{CH}}\text{-CH}_3+\text{Ph-CH=CH----}\qquad(2.15)$$



$$[\mathrm{Ti}]-\underset{\mathrm{Ph}}{\mathrm{CH}}\text{-CH}_2\text{----}+\text{Ph-CH=CH}_2\longrightarrow[\mathrm{Ti}]-\underset{\mathrm{Ph}}{\mathrm{C}}\text{=CH}_2+\text{Ph-CH}_2\text{-CH}_2\text{-----}\qquad(2.16)$$

2.3 Copolymer and applications

Metallocenes are highly useful for the copolymerization of ethylene with other olefins. Propene, 1-butene, 1-pentene, 1-hexene and 1-octene have been studied in their use as comonomers, forming linear low density polyethylene (LLDPE). These copolymers have a great industrial potential and show a higher growth rate than the homopolymer. Due to the short branching from the incorporated α-olefin, the copolymers show lower melting points, lower crystallinities, and lower densities, making films formed from these materials more flexible and better processible. Applications of the copolymers can be found in packaging, in shrink films with a low steam permeation, in elastic films, which incorporate a high comonomer concentration, in cable coating in the medical field because of the low part of extractables, and in foams, elastic fibers, adhesives, etc. The main part of the comonomers is randomly distributed over the polymer chain. The amount of extractables is much lower than in polymers synthesized with Ziegler catalysts.

The copolymerization parameter r_1, which says how much faster an ethylene unit is incorporated into the growing polymer chain than an α-olefin, if the last inserted monomer was an ethylene unit, lies between 1 and 60 depending on the kind of comonomer and catalyst. The copolymerization parameter r_2 is the analogous ratio for the α-olefin. The product $r_1 \bullet r_2$ is important for the distribution of the comonomer and is close to one when using C_2-symmetric metallocenes, indicating a randomly distributed comonomer. It is less than one with a more alternating structure when using C_s-symmetric catalysts.

Under the same conditions, syndiospecific (C_s-symmetric) metallocenes are more effective in inserting α-olefin into an ethylene copolymer than isospecific working (C_2-symmetric) metallocenes or unbridged metallocenes. In this particular case, hafnocenes are more effective than zirconocenes, too.

An interesting effect is observed for the polymerization with ethylene(bisindenyl) zirconium dichloride and some other metallocenes. Although the activity of the homopolymerization of ethylene is very high, it increases when copolymerizing with propene.

The copolymerization of ethylene with other olefins is effected by the variation of the Al/Zr ratio, temperature and catalyst concentration. These variations change the molecular weight and the ethylene content. Higher temperatures increase the ethylene content and lower the molecular weight.

2.4 Processes and reactors

Bulk polymerization has been frequently reported, reaction apparatuses are small and the polymer recovery is reasonably simple. However in these conditions, the reaction mixture becomes solid at around 20% conversion. The polymerization proceeds further in the solid phase and the conversion increases, but it is important to maintain the mixture under agitation to avoid local overheating and reactor fouling; overheating may cause polymer fusion and further fouling risk. Particularly harmful is the deposition of polymer macroparticles onto the thermometric probe and around the stirrer. The greater the catalyst activity and thus the polymerization rate, the more critical is the control of macroparticle formation. The use of an organic solvent like toluene as a dispersant only shifts the critical threshold conversion, but does not bypass the problem, because SPS forms gels with many substances (among them aromatic solvents).

Several solutions are proposed in the patent literature to circumvent these problems, which exist both for continuous and discontinuous processes.

If the catalyst and cocatalyst are added in two or more separate portions it is easier to control the initial rate of polymerization and thus to obtain fine polymer particles. In a reported example[34], half of the amount of the catalyst ($Cp^{*}Ti(OMe)_3/MAO/Al(^{i}C_4H_9)_3$) is added after 2 hours of reaction, when the conversion is about 30%. After 3 additional hours, a 70% conversion is reached. When all the catalyst is added simultaneously the reaction must be stopped after 30 minutes because stirring becomes impossible.

Continuous polymerization of styrene with periodic charge of monomer and catalyst and discharge of polymer is described by Imbayashi et al.[35] The reaction is carried out in a stirred-tank reactor, which is preconditioned in vacuo at 90 °C before the start-up. The reaction proceeds for several hours without fouling problems. Conversion is about 30-50%, SPS, M_w is about 700,000, and syndiotacticity is 96-98%. In an improved process, styrene is purified by nitrogen bubbling (elimination of oxygen), passage on activated alumina (dehydration) and partial hydrogenation on Pd catalyst (elimination of phenylacetylene). Powdered SPS is added at the start reaction. Temperature control (±2 °C) is achieved by dissipating the heat through a partial evaporation of the monomer. The reaction proceeds for more than 200 hours without any inconvenience. Catalyst activity is dramaticaly reduced if monomer impurities are not properly scavenged. In this respect, activated alumina is reported to be much more effective than molecular sieves or zeolites[36].

When polymerizations are carried out in the presence of hydrogen, there is no observed fouling formation on reactor walls[37]. Reactions were performed by using $Ti(OC_2H_5)_4/MAO$ or $CpTiCl_3/MAO$ systems. Molecular weights are rather low: 16,000-110,000, due to transfer reactions and metal-polymer complex hydrogenolysis. Syndiotacticity is not adversely affected by the presence of hydrogen (98%), but yields are only 7-13%.

A totally different kind of reactor (surface wiped reactor, Figure 2.10) was claimed in three other patents[38-40].. It comprises one or more rotating shafts bearing suitably shaped kneading members arranged in such a way that there is a close contact between the members, and between the members and the inner wall of the reactor. In this way no dead zone is present in the reactor and no fouling can occur. Styrene/MAO/triisobutylaluminum/(cyclopentadienyl) titanium trisphenoxide in mole ratios 50,000:100:100:1 were polymerized for 210 min at 70 °C to afford 4 kg of polymer[38]. without reactor plugging, stalling, leaking or overheating.

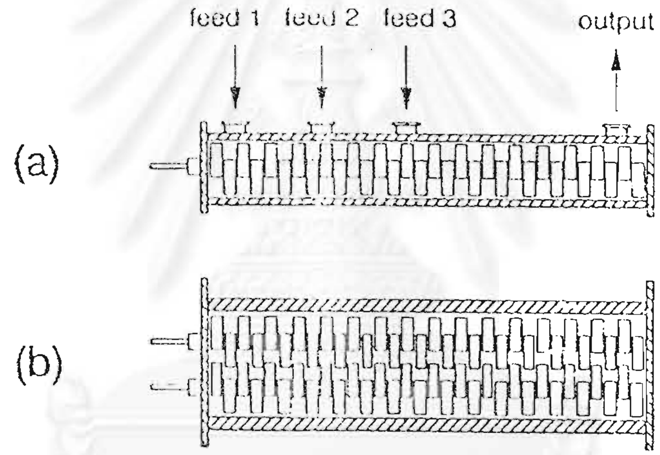


Figure 2.10 Schematic representation of a twin screw surface wiped reactor with three feeding zones for SPS manufacture. a) Longitudinal view. b) Upper view[38-40].

A stirred tank reactor can be used as a secondary reactor to prolong polymerization time[39]. Better temperature control is achieved by distributing the catalyst and/or the monomer in two or more portions and by controlling feeding rates[40].

Interestingly, Reaction Injection Molding (RIM) techniques have been applied for the manufacture of molded articles of SPS[41]. The $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$ system serves as the catalyst. Reaction time can be as short as 20 sec., with about 70-85% conversion. Longer reaction times are obtained by decreasing styrene concentration in toluene.

Malanga et al[42]. reported a suspension polymerization process. Styrene was polymerized in fluorinated solvents (perfluorocyclohexane, perfluorooctane) where both the monomer and the polymer are insoluble. Beads of SPS having 95% syndiotacticity are recovered with good yields (≈45%).

CHAPTER III

LITERATURE REVIEW

The first homogeneous metallocene catalysts were discovered in 1957 by Natta and Breslow, who used bis(cyclopentadienyl)titanium-(IV) compounds together with aluminium alkyls for ethylene polymerization. These catalyst systems replacing the chloride ligand of the Ziegler-Natta transition metal catalyst system by cyclopentadienyl(Cp) derivative compounds, were mainly used in mechanistic studies. Subsequently, Kaminsky and his co-workers found that the addition of water to the trialkyl aluminium in a molar ratio of 1:1 during ethylene polymerization significantly increased the catalytic activity. The reaction of trialkyl aluminium with water was shown to produce alkyl aluminoxane. In 1980 Kaminsky and coworkers used oligomeric methyl aluminoxane(MAO) with group 4B metallocene compounds to obtain ethylene polymerization catalysts having extremely high activities. For instance Cp_2TiCl_2/MAO has polyethylene productivity of 9.3×10^6 gPE/(mol Ti•hr•atm) at 20 °C; the productivity is 9×10^7 gPE/(mol Zr•hr•atm) at 70 °C with Cp_2ZrCl_2/MAO. However, these catalysts are non-stereospecific producing only atactic polypropylene, because of the symmetric feature of their active centers.

Homogeneous metallocene based catalysts are of theoretical significance in studies of Ziegler-Natta polymerization. Compared with conventional heterogeneous systems, in which a variety of active centers with different structures and activities usually coexist, homogeneous catalysts give very uniform catalytically active sites, which possess controlled, well-defined ligand environments[43, 44]. Therefore, the polymerization processes in homogeneous systems are often more simple, and kinetic and mechanistic analyses for these systems are greatly simplified. The recently developed base-free cationic metallocene is referred to as a “single-site” catalyst. The cationic metallocene catalyst affords a very simple and scientifically attractive system to investigate the details of stereoselective polymerization mechanisms.

3.1 Transition metal compounds

The syndiotactic of SPS results from the homogeneous coordinative polymerization mechanism. Typically, group IV transition metal complexes are utilized with co-catalysts such as methylaluminoxane (MAO) or pentafluorophenyl borate derivatives. Titanium halide compounds (e.g., $TiCl_4$, $TiBr_4$, $CpTiCl_3$, Cp^*TiCl_3), and even titanium compounds lacking halogen atoms (e.g., $Ti(OC_2H_5)_4$, $Ti(OC_4H_9)_4$, $Ti(N(C_2H_5)_2)_4$, $Ti(\eta^6\text{-}C_6H_6)_2$ and $CpTi(\eta^6\text{-}CH_3C_6H_5)_2$ can produce SPS. Not only Ti(IV) but also Ti(III) compounds, such as $CpTi^{III}Cl_2$, give SPS. Zambelli *et al.* reported that Ti(II) (e.g., $Ti(Ph)_2$) also could produce SPS, but $Ti(bipy)_3$, formally Ti(0), gave atactic PS.

The catalytic activity was found to vary according to the ligands on the titanium. Among the SPS producing catalysts, titanocene complexes with one cyclopentadienyl ligand yield the highest activity for SPS. The polymerization activities for several substituted $CpTi(OMe)_3$ complexes have been reported as follows[45], in order of decreasing catalytic activity: $EtMe_4CpTi(OMe)_3 > Cp^*Ti(OMe)_3 > Me_3SiMe_4CpTi(OMe)_3 > Me_4CpTi(OMe)_3 > (Me_3Si)_2CpTi(OMe)_3 > CpTi(OMe)_3$(Table 3.1). The data indicate that substituents on the cyclopentadienyl ligand which are electron releasing generally yield higher polymerization activities.

This result suggests stabilization of the active site by electron releasing substituents.

The polymerization activities in the presence of $Cp^{*}TiR_3$ compounds in which R is alkoxide and chloride ligands are as follows[45], in order of decreasing catalytic activity: $Cp^{*}Ti(Oi\text{-}Pr)_3$ and $Cp^{*}Ti(OMe)_3$ > $Cp^{*}Ti(OPh)_3$ > $Cp^{*}Ti(OC_6H_4CH_3)$ > $Cp^{*}TiCl_3$ > $Cp^{*}Ti(Ot\text{-}Bu)_3$ > $Cp^{*}Ti(Oi\text{-}C_3HF_6)_3$. The chloride ligand and the electron withdrawing alkoxide decrease the conversion as does the bulky *tert*-butoxide ligand. The methoxide, *iso*-propoxide, phenoxide and *p*-methyl-phenoxide are all similar in terms of conversion.

Table 3.1 Catalyst activities of substituted cyclopentadienyltitanium trimethoxide

Complex	Activity(kg-SPS/g-Ti)
$CpTi(OMe)_3$	10
$(Me_3Si)_2CpTi(OMe)_3$	25
$Me_4CpTi(OMe)_3$	130
$(Me_3Si)Me_4CpTi(OMe)_3$	135
$Cp^{*}Ti(OMe)_3$	200
$EtMe_4CpTi(OMe)_3$	210

Qing Wu *et al.*[46] investigated syndiotactic polymerization of styrene with cyclopentadienyltribenzyloxy titanium/methylaluminoxane(MAO) catalyst. The reaction conditions,e.g., the concentration of Ti, MAO, styrene, temperature and the content of retained trimethylaluminium(TMA) in MAO effected on the catalytic activity, syndiotacticity and molecular weight of the polymer. With the concentration of MAO = 0.17 mol/l, the catalyst exhibits higher activities. The catalytic activity increased with increase of the concentration of MAO, and reaches a maximum value at the concentration of MAO of 0.5 mol/l. The molecular weight of the polymer decreased and the molecular weight distribution became narrow with increasing the concentration of MAO. The concentration of MAO was necessary for activating the titanocene molecules and scavenging of impurities. Additionally, the MAO acted as a chain transfer agent, so that the higher the concentration of MAO used, the lower is the molecular weight of the polystyrene produced. The catalytic activity was directly proportional to the monomer concentration.

Cyclopentadienyl titanium complexes containing at least one alkoxide group appear to have superior catalytic performance to $Cp'TiCl_3$ [47]. Thus $CpTiCl_2(OR)$-MAO catalysts have activities double or more that of $CpTiCl_3$ with greater syndiotacticity (90-96 vs. 86.5%). Alkoxide-containing catalysts can be generated *in situ* by reacting $C_5Me_4HSiMe_3$ with $Ti(OR)_3X$ (X= Cl, OR) and contacting with MAO or TIBA-$[HNMe_2Ph][B(C_6F_5)_4]$.

Chien and Rausch have investigated a number of indenyl derivatives of the formula $LTiCl_3$ in combination with MAO for their behavior in styrene polymerization (Table 3.2) [48a,b]. Methyl substitution improves the activity of indenyl and benz[*e*]indenyltitanium trichloride, but ethyl and larger substituents depress catalytic activity. The methylthio derivative is virtually inactive, possibly from complexation of the lone pairs of electrons on the sulfur atom with MAO reversing the polarity of this substituent.

Ready et al.[49] observed that indenyltitanium trichloride, $IndTiCl_3$, is a significantly more active catalyst than $CpTiCl_3$. But Tomotsu *et al*. compared the two catalysts and found the catalytic activity of $IndTiCl_3$ to be lower than that of $CpTiCl_3$. Difference in polymerization conditions may account for the observed differences in catalyst performance. Furthermore, Chien *et al.* investigated the influence of aromatic substituents on indenyl ligands. The results suggested that benzindene stabilized the active catalytic species more compared to the phenyl substitution on the C_5 ring for the indenyl ligand.

Table 3.2 Polymerization of styrene by $LTiCl_3$ catalysts

L	Activity ($\times 10^{-7}$)	SPS (%)	T_m (°C)	M_w ($\times 10^{-3}$)	Ref.
Cyclopentadienyl	1.4	67.4	259.7	435	69(b)
Indenyl	3.7	98.2	270.8	720	69(b)
Tetrahydroindenyl	2.7	89.1	270.9	620	69(b)
1-Methylindenyl	5.1	89.5	271.9	650	69(b)
2-Mehtylindenyl	16.6	90.2	272.2	660	69(b)
1-Ethylindenyl	2.6	82.0	272.3	430	69(b)
1-t-Butylindenyl	0.2	64.8	271.2	95	69(b)
1-Trimethylsilylindenyl	0.7	86.4	268.0	125	69(b)

1-Methylthioindenyl	0.2	80.5	268.1	14	69(b)
1-Phenylindenyl	7.7	90.0	260.7	424	69(a)
2-Phenylindenyl	5.2	91.3	262.5	323	69(a)
1,3-Diphenylindenyl	3.6	94.8	262.0	496	69(a)
1-Benzylindenyl	0.2	87.2	268.3	323	69(a)
3-(2-Phenylethyl)indene	1.1	88.2	267.8	401	69(a)
Benz[e]indenyl	17	92.5	270.4	545	69(a)
2-Methylbenz[e]indenyl	18	92.8	275.2	424	69(a)
1,2,3-Trimethylbenz[e]indenyl	2.0	96.0	276.0	323	69(a)

Activity = (grams of bulk polymer) / (mole of Ti•mole of styrene•hr)

Kim et al. [50] synthesized and characterized five substituted indenyltrichlorotitanium compounds with spectroscopic methods. The catalytic behavior for the polymerization of styrene was studied in the presence of methylaluminoxane(MAO) as a cocatalyst. Substituted indenyl ligands include 1,3-dimethyl, 1-methyl, 1-ethyl, 1-isopropyl and 1-(trimethylsilyl)indenyl groups. All five compounds gave extremely pure syndiotactic polystyrene and conversion rates of at least 95%. The UV-visible and Ti NMR spectra provided a consistent measure of the electron densities at the metal centers of five substituted indenyltrichloro titanium compounds. The catalytic activity was enhanced by less bulky and better electron-releasing substituents of the indenyl ligand.

(η^5-trimethylsiloxytetramethylcyclopentadienyl) and (η^5-2-trimethylsiloxyindenyl) trichlorotitanium have been synthesized and characterized by Tian *et al.* Their catalytic behavior for the polymerization of styrene was studied in the presence of methylaluminoxane (MAO) as a cocatalyst. The cocatalyst MAO, as a Lewis-acid, might coordinate with oxygen atom of siloxy group. The coordination suppressed the resonance effect and enhanced the inductive effect of the siloxy group. As a result, the compounds showed only low activity for styrene polymerization.

Brintzinger *et al.* prepared and tested the 2-substituted cyclopenta[*l*]phenanthrene titanium trichloride complexes in styrene polymerizations[51], Figure 3.1.

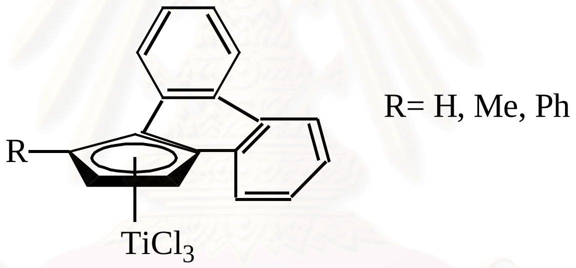


Figure 3.1 2-substituted cyclopenta[*l*]phenanthrene titanium trichloride complexes[51]

The 2-phenyl derivative exhibits higher activities and polymer molecular weights than do the unsubstituted or methyl-substituted complexes and the catalyst syndiospecificity remains almost unchanged between 50 and 100 °C.

Kaminsky and co-workers have found that fluorinated half-metallocene complexes such as $CpTiF_3$ and Cp^*TiF_3 exhibit higher catalytic activities at higher temperatures than their trichloride analogues[52]. Polymer molecular weights are significantly greater as well. Cp^*TiF_3 affords syndiotactic polystyrene (SPS) with a molecular weight of 660,000 at 50 °C versus 169,000 for $Cp^{*}TiCl_3$ under similar conditions.

The molecular weight of SPS can be controlled primarily by polymerization temperature, which sharply affects the rate of chain transfer via β-hydride elimination. As the polymerization temperature is increased, the SPS molecular weight decreases significantly. However, substituents on the cyclopentadienyl ring of the monometallocene titanium complexes can also affect the SPS molecular weight. A dramatic decrease in the molecular weight of the SPS produced with $CpTiCl_3$ is observed relative to that with $Cp^{*}TiCl_3$. This would indicate that β-hydride elimination occurs more readily for $CpTiCl_3$. The Cp^{*} ligand apparently stabilizes the active center and retards β-hydride elimination.

Octahydrofluorenyltitanium trichloride functions at least as effectively as $Cp^{*}TiCl_3$ in syndiotactic styrene polymerization[53] and $CpTiCl_2(O^{I}Pr)$ has been claimed to be a more active and more stereospecific catalyst than $CpTiCl_3$[54]. Bis(cyclopentadienyl)titanium and –zirconium derivatives activated by Ph_2Zn and MAO were also used to polymerize styrene[55]; however, conversions were low (1-9% of initial styrene) as were the butanone-insoluble fractions. Cp_2TiCl_2-Ph_2Zn-MAO produced the most syndiospecific catalyst, with 68% of the polymer formed insoluble in 2-butanone.

The polymerization activities for several ansa-titanocene complexes have been reported by Miyashita et al.[56] in order of decreasing catalytic activity: $CH_2(Cp)_2TiCl_2 > SiMe_2(Cp)_2TiCl_2 > Me_2Si(Cp)_2TiCl_2 > C_2H_2(Cp^{*})_2TiCl_2 > (Cp^{*})_2TiCl_2 > Cp_2TiCl_2$. The data indicate that the polymerization activity as well as syndiospecificity increase by decreasing the bite-angle, (the angle of the Cp centroid-Ti-Cp centroid), in these ansa-titanocene compounds. The activities of ansa- titanocene complexes are less than those of monocyclopentadienyl complexes.

Syndiotactic polystyrene with a broad MWD is formed from mixtures of half-titanocenes (e.g. Cp^*TiMe_3 and $Cp^*Ti(OMe)_3$) activated by MAO. $CpTiCl_3$-MAO catalysts also copolymerize styrene and vinyltoluenes to form syndiotactic terpolymers with melting points in the range 210-240 °C, lower than those of the homopolymer[57]. The molecular weight of SPS can be controlled by using judicious amounts of alkylaluminum or alkylzinc compounds as chain-transfer agents[58].

Ishihara *et al.* found that a mixture of titanium compounds [$TiCl_4$, $Ti(OEt)_4$, or $(\eta^5\text{-}C_5H_5)TiCl_3$] with methylaluminoxane catalyzed the polymerization of styrene, even above room temperature, to the pure syndiotactic polystyrene, which had a narrow molecular weight distribution($M_w/M_n = 2$). Pure syndiotactic polymers were also obtained with ring-substituted styrenes. Monomer reactivity was enhanced by electron-releasing substituents on the aromatic ring.

It was first thought that only titanium compounds when combined with MAO gave pure SPS and much attention has been paid to developing more efficient catalysts. Later, Zr compounds (e.g., $Zr(CH_2C_6H_5)_4$, $Zr(\eta\text{-}C_7H_8)_2$, $(Me_3CCOCHCOCMe_3)_2ZrCl_2$) were also found to catalyze syndiospecific styrene polymerization[59]. In comparison with the Ti compounds, the Zr compounds show lower activity and lower stereospecificity, which could arise from the less electrophilic and larger ionic radius of zirconium in comparison with titanium.

Syndiotactic polystyrene can be produced in a continuous process without fouling by injection of monomer and TIBA and MAO with $Cp^{*}Ti(OMe)_3$) into a continuously agitated and pulverized bed of SPS[60]. Styrene has been prepared in a reaction injection molding (RIM) process using a $Cp^{*}TiMe_3$-$B(C_6F_5)_3$ catalyst[61]; however the relatively low conversion of monomer (60-80%) under the conditions used is a limitation.

Seppala *et al*. [62] studied the copolymerization of ethylene and styrene using the catalytic system $CpTiCl_3$-methylaluminoxane. The polymerization product was composed of polyethylene and syndiotactic polystyrene. No ethylene-styrene copolymer was detected. The composition of the product was dependent on the polymerization conditions. The catalytic activity was highest at polymerization temperature of 30 °C and Al/Ti ratio of 1500. Styrene content of the product was highest at polymerization temperature of 50 °C and Al/Ti ratio of 1500. The formation of separate polymer fractions might indicate a different polymerization mechanism for the two monomers, of the presence of more than one active species in the catalyst, one producing polyethylene and the other syndiotactic polystyrene.

Pappalardo *et al.* [63] investigated the copolymerization of ethylene and styrene using the catalytic system η^5-$C_5Me_5Ti(CH_2Ph)_3$-$B(C_6F_5)_3$. Alternating ethylene-styrene copolymers was obtained, together with some polyethylene and syndiotactic polystyrene, from which the former could be seperated by solvent extraction. NMR analysis of suitably C^{13}-enriched end groups shows that the regiospecificity of styrene insertion in the initiation step is largely secondary.

Pinweha[64] studied the various of catalyst systems for styrene polymerization. The results indicate that the catalytic activity order of catalyst systems is : $Cp^{*}TiCl_3$-TIBA/ $[Ph_3C]^{+}[B(C_6F_5)_4]^{-} >$ $Cp^{*}TiCl_3$-TMA/$B(C_6F_5)_3 >$ $CpTiCl_3$-TMA/$B(C_6F_5)_3$, The same order of syndiotacticity. The $Cp^{*}TiCl_3$-TIBA/$[Ph_3C]^{+}[B(C_6F_5)_4]^{-}$ gives 74% syndiotacticity.

3.2 Cocatalysts

3.2.1 Methylaluminoxane (MAO)

Methylalumoxane (MAO), the product of the controlled reaction of trimethylaluminium and water, remains the most frequently used cocatalyst in metallocene polymerizations. It is by far a superior cocatalyst to other hydrolyzed aluminium alkyls. For example, ethylene polymerization activities by Cp_2ZrCl_2 were found to be 100 times lower when tetraisobutyldialumoxane was used as the cocatalyst rather than MAO[65]. Attempts to find substitutes continue, however: investigators at Montell have disclosed that more branched trialkylaluminiums and dialkylaluminium hydrides such as tris(2,4,4-trimethylpenyl)aluminium or 2-phenylpropyl modified diisobutylaluminium hydride, when contacted with water, are far more effective cocatalysts for metallocene complexes than is tetraisobutyldialuminoxane.

Further modifications of MAO are claimed to improve the performance of the cocatalyst. An increase in catalyst activity was observed when siloxanes are added to the MAO. The addition of methoxyboroxine to MAO affords a granular alumoxane product well suited to use in slurry polymerizations[66-67].

Alumoxanes can be generated from oxygen-containing compounds other than water. CO_2, benzophenone, and benzoic acid react with $AlMe_3$ to produce precursors which are converted to alumoxanes on heating. Other protolytic agents used with trialkylaluminiums to generate cocatalysts for polymerization by metallocene complexes include triphenylmethanol, tetrafluoroterephthalic acid, *t*-butyl-substituted phenols, bisphenols, and *t*-butylcatechol.

3.2.2 Boron compounds

The first MAO free systems for SPS formation were reported in 1992 and involved $Cp^{*}TiMe_3$ and the benzyl analogue $Cp^{*}Ti(CH_2Ph)_3$. It was found that activation of both compounds with $B(C_6F_5)_3$ resulted in highly active compounds for polymerization of styrene to SPS, but that activation with $[HNPhMe_2]^{+}[B(C_6F_5)_4]^{-}$, as in equation 3.1, gave only low yields of atactic PS.

$$Cp^{*}TiMe_3 + [HNPhMe_2]^{+}[B(C_6F_5)_4]^{-} \rightarrow [Cp^{*}TiMe_2]^{+} + NPhMe_2 + [B(C_6F_5)_4]^{-}$$

(3.1)

The likely reason for the low activities when using the ammonium salt as cocatalyst is that the amine which is produced coordinates to the site and hinders monomer coordination. A subsequent investigation of the $Cp^{*}TiMe_3/B(C_6F_5)_3$

system showed that styrene is converted predominantly to SPS above about -15°C in toluene or in the absence of solvent, but to atactic PS in methylene chloride or in toluene below about -15 °C.

The boron activators abstract an alkyl group from the metallocene dialkyl. The active catalyst can be generated by reacting the metallocene dichloride with an aluminium alkyl, followed by the boron activator. A study indicates that MAO and branched aluminium alkyls such as triisobutylaluminium are preferable alkylating agents to triethylaluminium[68].

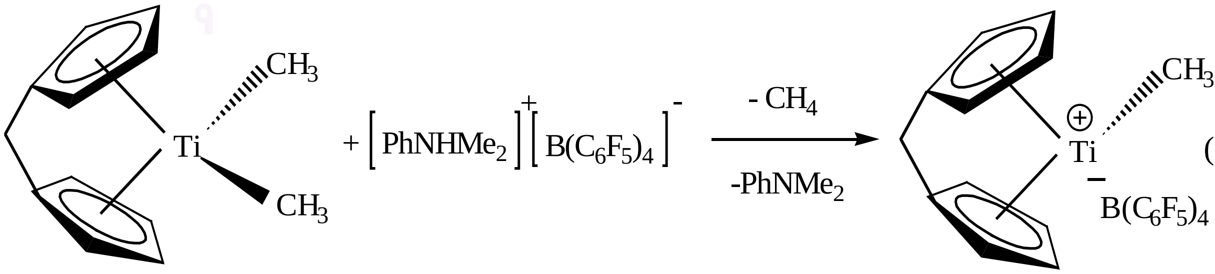
Tris(pentafluorophenyl)boron is a widely used activator for coverting metallocene dihydrides and dialkyls to cationic catalysts. It has been prepared by reaction of C_6F_5MgBr (from C_6F_5Br and alkylmagnesium halides) with BF_3•etherate. Use of the less expensive C_6F_5Cl and *i*-PrMgBr has been found to work equally well[69]. After reaction of the Grignard reagent with BF_3•etherate, the magnesium salts can be precipitated with 1,4-dioxane or 1,3-dioxolane to give $(C_6F_5)_3B$•etherate, which can be extracted into aromatic or aliphatic solvents to give an ether-free solution[70].

Both tetrakis(pentafluorophenyl)borate salts and tris(pentafluorophenyl)borane are commercially available reagents and research into new and more economical routes to these complexes is ongoing. The need to cool the reaction of an ethereal solution of C_6F_5MgX with BCl_3 is avoided when at least of the reaction solvent has a higher boiling point[71]. $B(C_6F_5)_3$ has been prepared by extrusion of CO_2 from zinc pentafluorophenylbenzoate, followed by reaction of the organozinc product with BCl_3 as in equation 3.2[72].

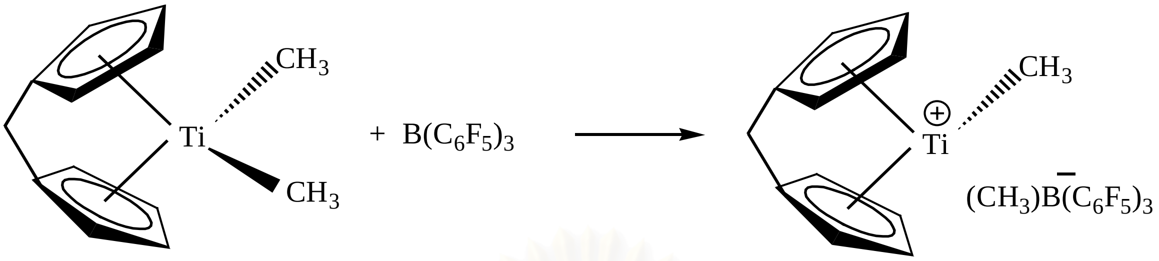
$$(C_6F_5CO_2)_2Zn \rightarrow (C_6F_5)_2Zn + BCl_3 \rightarrow B(C_6F_5)_3$$
(3.2)

Marks et al. have found that reaction of $Cp'MMe_2$ (Cp' =Cp, 1,2-Me_2Cp, or Cp^*) or $Me_2Si(C_5Me_4)(N\text{-}t\text{-}Bu)MMe_2$ with tris(2,2′,2″-perfluorobiphenyl)boron[73] affords catalysts with greater activity than with $B(C_6F_5)_3$[74]. This has been ascribed to the lower coordinating strength of the $[MeB(C_{12}F_9)_3]^-$ anion with respect to the $[MeB(C_6F_5)_3]^-$ anion. Whereas Cp'_2MMe_2 complexes and $B(C_6F_5)_3$ afford $[Cp'_2MMe][MeB(C_6F_5)_3]$ ion pairs, reaction of bis(cyclopentadienyl)metal dimethyl complexes with $B(C_{12}F_9)_3$ forms exclusively the methyl bridged dimers $[(Cp'_2MMe)_2(\mu\text{-Me})][MeB(C_{12}F_9)_3]$ even in the presence of excess boron reagent.

Perfluorophenyl borate derivatives have also been used as cocatalysts in SPS polymerizations. The reaction of $CH_2(Cp)_2TiMe_2$ in equimolar mixture with dimethylaniliniumtetrakis(pentafluorophenyl)borate or tris(pentafluorophenyl)borane has been examined by Miyashita[75]. They isolated two types of methylene bis(cyclopentadienyl)titanium ion complexes as in equations 3.3-3.4. These complexes were active in the polymerization of styrene but only atactic polystyrene was formed.



(3.3)



(3.4)

Baird et al. examined the catalytic activity of $Cp^{*}TiMe_3$ with similar boranes. The polymer produced was a mixture of atactic and syndiotactic polystyrenes. They examined the effect of polarity of solvent for polymerization by using CH_2Cl_2 and 1,2-$C_2H_4Cl_2$ and found that polar solvents increased the yield of atactic polystyrene.

Pellecchia also examined the catalytic activity of several organometallic derivatives with similar boranes. They observed the catalytic activity of $Cp^{*}TiMe_3$ with dimethylaniliniumtetrakis(pentafluorophenyl) borate was lower than that with trispentafluorophenyl borane. They proposed free amine coordinates to the active site and interferes with the polymerization reaction.

Using the pentafluorophenyl borate with a small amount of TIBA as cocatalyst for polymerization of styrene to SPS was examined by Campell *et al.* [76], and Kucht *et al.* [77]. TIBA was found to be the scavenger of impurities in styrene and to increase the syndiotacticity of the polymer.

Preparation of an alternative neutral activator $Al(C_6F_5)_3$ by reaction of $AlCl_3$ with ethereal $[Li][C_6F_5]$ was done with caution due to the explosive nature of the $Al(C_6F_5)_3$•etherate product. An apparently safer preparation involves methathesis of

$B(C_6F_5)_3$ and $AlMe_3$, $AlEt_3$, $Al(i\text{-}Bu)_3$, or $HAl(i\text{-}Bu)_2$ in aromatic or aliphatic solvents , as in equation 3.5. Yields of 70-90% of the unsolvated $Al(C_6F_5)_3$ have been obtained[78].

$$B(C_6F_5)_3 + AlMe_3 \rightarrow Al(C_6F_5)_3 + BMe_3 \qquad (3.5)$$

A number of adjuvants have been suggested to improve catalyst performance. The use of tetraisobutylalumoxane (500 equivalents) to a $Cp^*Ti(OMe)_3$-TIBA-$[HNMe_2Ph]^+$ $[B(C_6F_5)_4]^-$ catalyst is claimed to almost double catalyst activity[79]. Adding $SnMe_4$ or $SnPh_4$ to a Cp^*TiCl_3-MAO catalyst system leads to a greater percentage of styrene converted to SPS[80]. Phenylsilane has a similar beneficial effect on monomer conversion. It acts as a chain transfer agent; like hydrogen, it tends to increase catalyst activity. Treatment of the styrene monomer with dibutylmagnesium removes phenylacetylene and indene impurities, leading to better catalyst performance.

An analysis of styrene polymerization by Cp^*TiR_3 (R= CH_2Ph, Me) cocatalyzed by MAO, $B(C_6F_5)_3$, or $[Ph_3C]^+[B(C_6F_5)_4]^-$ indicates that polymerization is first order in monomer, at least at low conversions with chain termination predominantly by β-H elimination[81]. Catalysts with the $[B(C_6F_5)_4]^-$ counterion produce polymers with the highest molecular weight, attributed to the relative coordinating ability of the two anions.

In the process for polymerizing styrene by single-site catalysts, it has been found that raising the pressure and temperature in the reactor system improves the activity of a $CpTiCl_3$-MAO catalyst.[82]. Styrene is smoothly homopolymerized or copolymerized with divinylbenzene by a Cp^*TiMe_3-MAO-Al(*i*-Bu)$_3$ in a corotating twin-screw extruder, the product from which can be fabricated directly from the exit die into a mold or a fiber or film line.

3.3 Active species

Nature and formation of the true active catalytic species are not yet fully elucidated. In polymerization of α-olefins, it is generally accepted that homogeneous catalysts based on group IV metallocenes with MAO consist of cationic complexes.

A series of experiments by Baird et al. examined the behavior of Cp^*TiMe_3 and $B(C_6F_5)_3$ in styrene polymerization[83]. A temperatures below $0^{\circ}C$, species $[Cp^*TiMe_2]$ $[MeB(C_6F_5)_3]$ is formed[84]; this polymerizes ethylene at low temperatures, but forms only atactic polystyrene, indicating that it functions as a Ziegler-Natta catalyst towards ethylene but as a carbocationic initiator towards styrene. Above $0^{\circ}C$, the catalyst produces syndiotactic PS; this is accompanied by a weakening and broadening of the NMR signals of the catalyst solution. At room temperature, a Ti(III) species, detected by ESR, is formed from Cp^*TiMe_3 and $B(C_6F_5)_3$[85]; the formation of this complex is accelerated by addition of styrene to the mixture.

Table 3.3 shows a comparison of percent conversion for Cp^*TiOMe_2 and Cp^*TiOMe_3 with the addition of tri-isobutylaluminium(TIBA) in the MAO cocatalyst system. The trend of increasing conversion with TIBA content is observed for Cp^*TiOMe_3 and relatively low conversion is observed without TIBA. However, for Cp^*TiOMe_2, high conversion is obtained even without TIBA and the conversion is higher than for Cp^*TiOMe_3. This suggests the function of the aluminium alkyl is reduction of the Ti IV species while the MAO cocatalyst generates the active Ti III cationic site. Thus, the Ti III complex requires less aluminium alkyl overall, i.e., less MAO and no TIBA.

Table 3.3 Percent conversion to SPS with TIBA content.
Mole ratios styrene:MAO:TIBA:Ti (233,333:200:TIBA:1)
70°C for 1 hr.[87]

Catalyst	TIBA:Ti	%Conversion
Cp^*TiOMe_2	0	58
	6	62
	10	64
	50	66
Cp^*TiOMe_3	0	30
	6	47
	10	53
	50	62

The effect of the molar ratio of MAO to Ti on the catalytic activtiy in the case of $CpTiCl_3$ with a MAO catalyst system was investigated. The activity increases with an increasing molar ratio of MAO to Ti. The amount of cationic Ti III species measured by ESR increases with increasing ratio of MAO to Ti as well. This suggests that MAO acts as a reducing agent for Ti IV to Ti III. Cationic Ti III might be an active species for synthesis of SPS.

It is generally agreed that the mechanism of syndiospecific polymerization of styrene is metal-coordinated. The possible insertion process for styrene into a metal-methyl bond, which is presumed to arise from methylation of the titanium by MAO in syndiospecific catalyst systems, may be formulated as primary insertion(I) or secondary insertion(II) shown in Figure 3.2. n-Propylbenzene(n-PrC_6H_5) was the product after methanolysis of the syndiospecific polymerization reaction mixture. Therefore, it was concluded that the insert of styrene into the Ti-CH_3 bond proceeds by a secondary(2,1- addition) process.

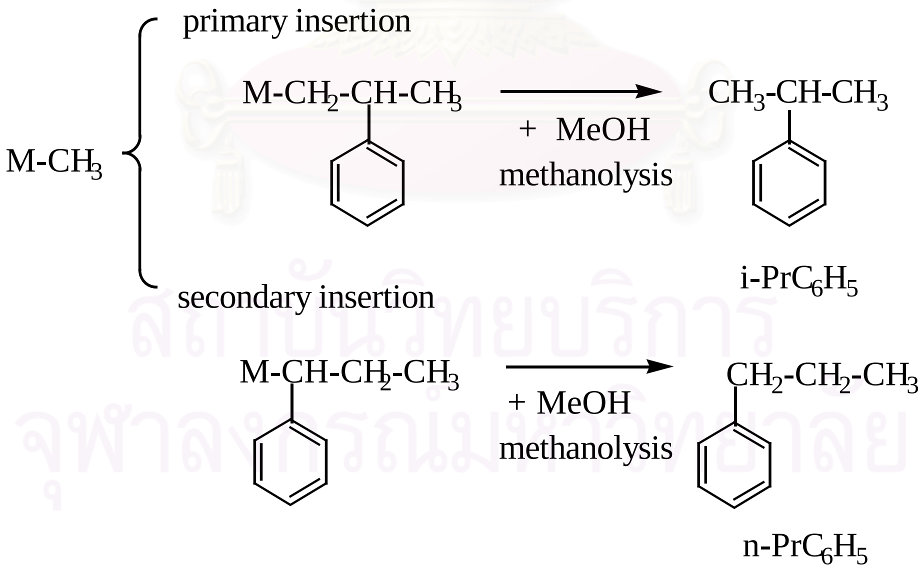


Figure 3.2 Possible addition modes of a styrene molecule to a metal-CH_2 bond[86]

The results also show, in addition, that ethylbenzene(EtC_6H_5) was formed after methanolysis of the catalytic reaction. The ethylbenzene arises via secondary insertion into a titanium hydride formed from β-hydride elimination of the growing polymer chain, according to Figure 3.3.

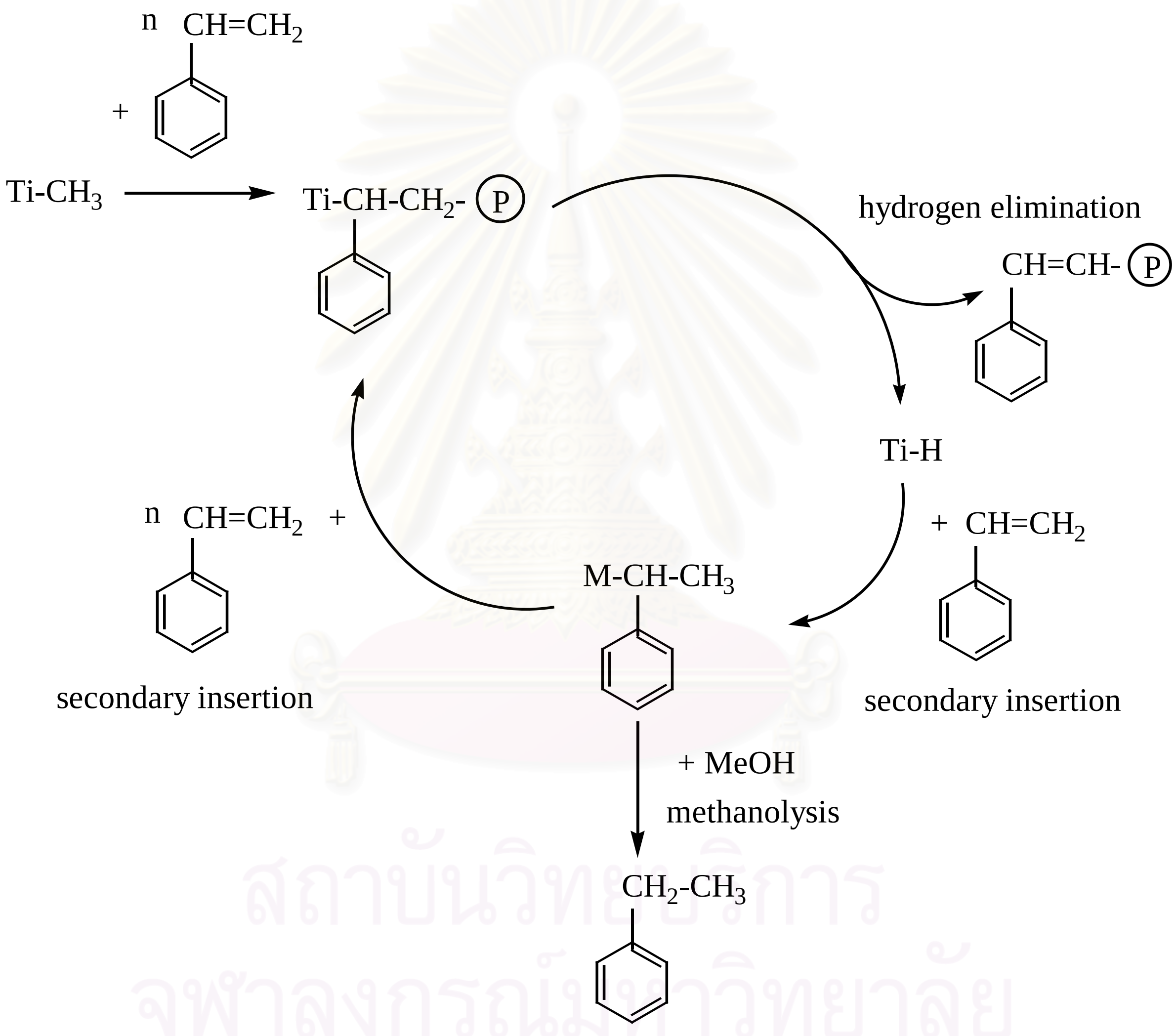


Figure 3.3 The formation of ethylbenzene arising from β-hydrogen elimination[86].

It was proposed that these groups arise from reinitiation via secondary insertion on the M-H bonds which would give the observed 1-phenylethyl end groups. These end groups could arise also from primary insertion into M-CH_3 bonds, but this possibility can be disregarded, since a secondary insertion has been observed by gas chromatography, and there is no evidence (NMR) for head-head arranged monomer units. Furthermore, it is observed that the amount of ethylbenzene is larger than that of n-PrC_6H_5. This fact suggests polymer chains are mainly initiated via M-H bonds and terminated by β-hydride elimination.

The addition of hydrogen may increase the amount of Ti-H which is the initial structure of active site. The effects of hydrogen on catalytic activity was examined by Tomotsu *et al.*[87]. The data are shown in Table 3.4. The addition of hydrogen increases catalytic activity and these results support the hypothesis that polymerization proceeds via a Ti-H complex.

Table 3.4 Effects of hydrogen on polymerization

Hydrogen pressure (bar)	Relative activity
None	100
0.1	160
0.5	210
1.0	220

3.4 Supported metallocene catalyst

In order to reduce the amount of MAO used in the polymerization $CpTiCl_3$ has been supported on silica and used to polymerize styrene[88]. Highest activities result when the metallocene is supported, then activated with MAO rather than supporting the MAO and combining with the metallocene. Cp^*TiMe_3 has also been supported on silica and activated with $B(C_6F_5)_3$ in the presence of TIBA to form an active styrene polymerization catalyst.

Solution polymerization processes are suitable for the preparation of low-crystallinity polyolefins such as elastomers, very low density ethylene copolymers, and amorphous poly-α-olefins. In these cases, the polymer product is soluble in the reaction medium and a solution-soluble catalyst system can be used.

Higher-crystallinity resins such as isotactic polypropylene or higher-density polyethylene are usually prepared in continuous slurry, fluidized-bed gas phase, or bulk monomer processes. Here, the polymer is insoluble in the reaction medium. A morphologically uniform polymer particle is needed to avoid reactor fouling and facilitate smooth operations. Indeed, with proper control of catalyst and polymerizing conditions, polymer particle can be produced which can be used in fabrication processes like rotational molding without recourse to grinding or pelletizing.

Silica has been the most widely used support for metallocene catalysts, but other materials and methods for immobilizing the catalysts have been explored recently. Polypropylene produced by a $Et(Ind)_2ZrCl_2$-MAO catalyst confined within the pores of the zeolites MCM-41 and VPI-5 was found to be more stereoregular and of a higher molecular weight than that produced from the homogeneous catalyst[89]. Treatment of silica or alumina with 10-30 wt% boric acid has been claimed to lead to improvements in catalyst activity[90].

Metallocene catalysts have been assembled on the support material by impregnating silica with group 4 tetrahalides and reacting with Cp'-$SiMe_3$, $Cp'Li$, or $Cp'Mg$ to afford a supported metallocene complex which can be activated by MAO or boron activators[91]. Conversely, CpLi has been reacted with chlorinated silica giving silica with cyclopentadienyl groups attached. This material is then allowed to react with $M(NMe_2)_4$ (M= Ti, Zr) to form (silica)-$C_5H_4M(NMe_2)_3$ (Figure 3.4).

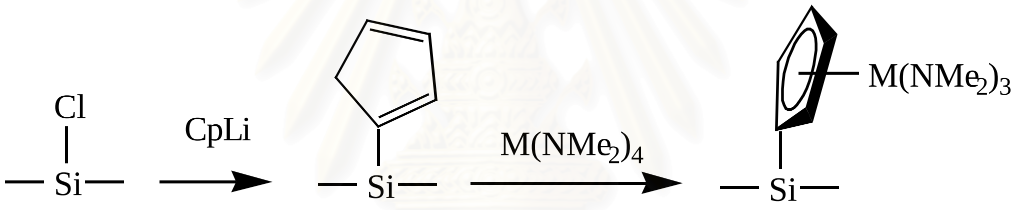


Figure 3.4 Preparation of silica-supported cyclopentadienes.

In a similar preparation, NaCp is allowed to react with ethylene-methyl acrylate copolymer to form what is presumed to be a keto-Cp intermediate. (Figure 3.5) Reaction of this species with $ZrCl_4(THF)_2$ or $CpZrCl_3$ forms a polymer-bound metallocene[92].

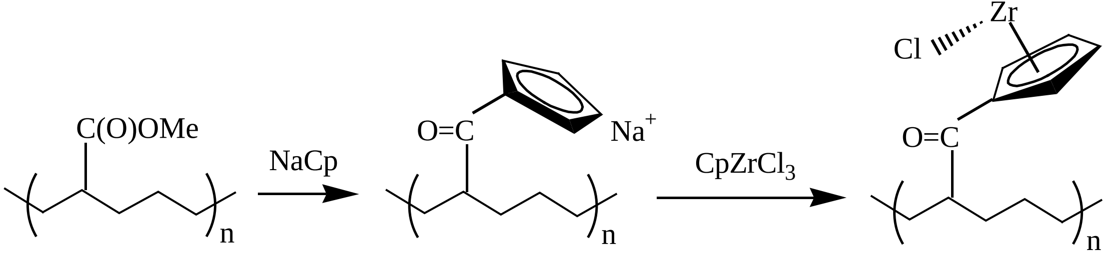


Figure 3.5 Preparation of polymer-bound zirconocene.

Supporting a $CpTiCl_3$-MAO catalyst on silica results in a drop both in a activity and syndiospecificity, possibly because the support material has a steric influence on the active catalyst site[93].

CHAPTER IV

EXPERIMENT

In the present study of the styrene polymerization with half-titanocene catalyst, the experiments were divided into

1. Synthesis and characterization of catalyst
2. Catalyst and cocatalysts solution preparation
3. Styrene polymerization with the prepared catalyst
4. Characterization of polystyrene products

The details of the experiments were explained in the following.

4.1 Chemicals

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

Chemicals	Suppliers
Ultra high purity nitrogen gas (99.999%)	Thai Industry Gas Co., Ltd., Thailand
Toluene and pentane	Lab scans Co., Ltd. Ireland
Titanium tetrachloride	Carlo Erba, Italy
Pentamethylcyclopentadiene and *n*-butyllithium	Fluka Chemie A.G., Switzerland

Triphenylcarbenium tetrapentafluorophenylborate, $[Ph_3C]^+[B(C_6F_5)_4]^-$ and triisobutylaluminium(TIBA)	Donated from Japan Advanced Institute of Science and Technology (JAIST), Japan

Chemicals	Suppliers
Dimethylanilinium tetrakis(pentafluorophenyl)borate, $[PhNMe_2H]^+[B(C_6F_5)_4]^-$	Donated from Dow Chemical, USA
Trimethylaluminum (TMA)	Nippon Aluminum Alkyls Ltd., Japan, donated from Chemical Engineering,Chulalongkorn University
Tris(pentafluorophenyl)boron, $B(C_6F_5)_3$	Fluka Chemie A.G., Switzerland
Styrene monomer	Fluka Chemie A.G., Switzerland
Methyl ethyl ketone (MEK)	Carlo Erba, Italy

Many of the reagents encountered in this work react violently with water and ignite spontaneously in air (by reaction with oxygen and/or moisture). These chemicals were handled safely under inert-atmosphere by Schlenk and glove bag techniques. All chemicals and solvents were dried before use as following methods:

1. Ultra high purity nitrogen gas was purified by passing through three columns packed with molecular sieve 4 Å, NaOH and P_2O_5, respectively.

2. Toluene and pentane were purified by refluxing over sodium/benzophenone and distilled under nitrogen atmosphere before use.
3. Styrene monomer is colourless liquid containing inhibitor, which was removed by washing twice with 10% aqueous sodium hydroxide and subsequently demineralised water until the pH of aqueous phase was neutral. After being dried over anhydrous magnesium sulfate, 0.5 g CaH_2 was added to inhibitor-free styrene monomer. Then it was distilled under reduced pressure. The styrene monomer was collected and dissolved oxygen was removed by purging nitrogen gas through.

4.2 Equipment

All equipments, used in the catalyst preparation and polymerization, were listed as follows:

4.2.1 Schlenk line

Schlenk line consists of nitrogen and vacuum line. The vacuum line was equipped with the solvent trap and pump, respectively. The nitrogen line was connected to the moisture trap and the oil bubbler that was a manometer tube and contain enough oil to provide a seal from the atmosphere when nitrogen line was evacuated. The Schlenk line was shown in Figure 4.1.

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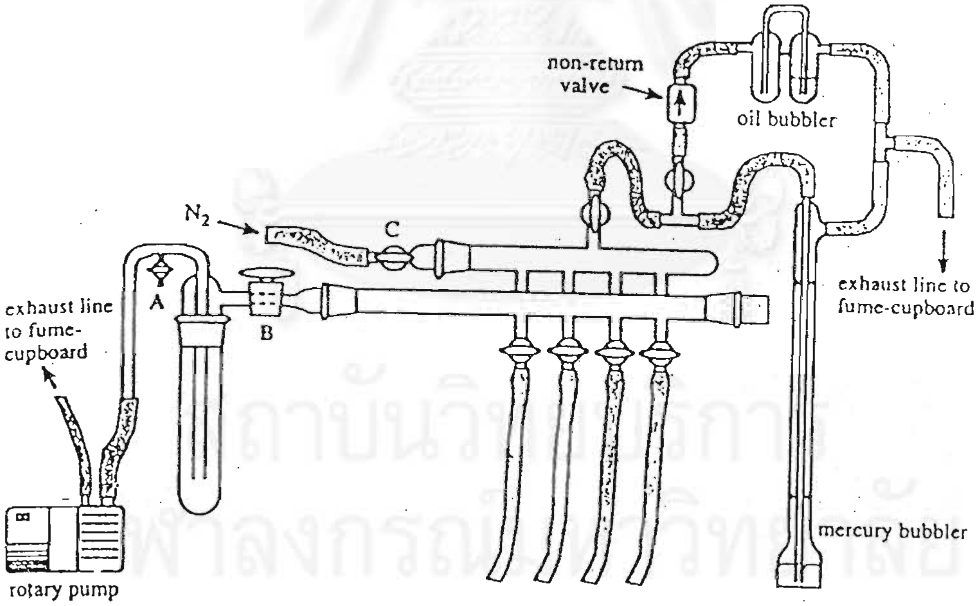

Figure 4.1 Schlenk line

4.2.2 Schlenk flask

A flask with a side-arm for use with inert gas. The standard requirements of a joint to connect to other items of glassware and provide access to the contents, and a tab for connection to the manifold and some typical examples are shown in Figure 4.2

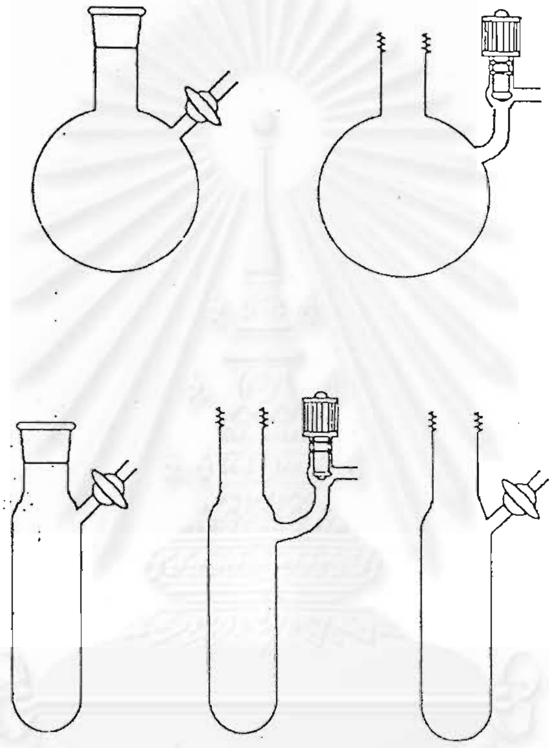

Figure 4.2 Round-bottomed and tube designs for Schlenk flasks incorporating ground-glass or screw joints and greased or greaseless taps.

4.2.3 Heating bath

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

4.2.4 Vacuum pump

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

4.2.5 Inert gas supply

The inert nitrogen gas was passed through drying column with 4A molecular sieves. The inert gas was used to feed in the nitrogen line of Schlenk line and polymerization reactor.

4.2.6 Syringe and needle

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

4.2.7 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.

4.2.8 Soxhlet extractor

Soxhlet extractor was used for determining syndiotactic content(Figure 4.3). Polystyrene product was weighed in cellulose thimble, and then was extracted with methyl ethyl ketone for 5 hours. The residual polymer was dried at 80 °C until constant weight. The fraction of the whole polymer unextracted and multiply by 100 was taken as a percent of syndiotactic polystyrene (%SPS) according to the equation.

$$\%SPS = \frac{Insoluble\ weight\ of\ polystyrene}{Total\ weight\ of\ polystyrene} \times 100$$

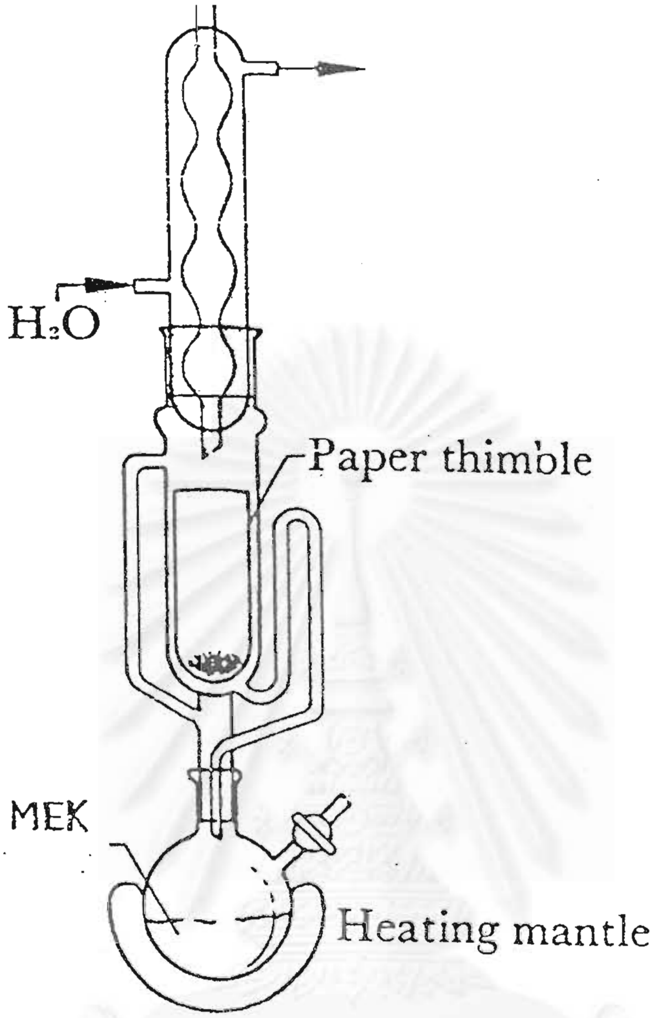

Figure 4.3 Soxhlet-type extractor

4.3 Characterization instruments

The instruments used to characterize catalysts and polystyrene were specified in the following.

4.3.1 Fourier transform infrared spectrometer (FT-IR)

Nicolet FT-IR Impact 410 Spectrophotometer at Chemistry Department, Chulalongkorn University , was employed to characterize polystyrene products. Infrared spectra were recorded between 400 and 4000 cm^{-1}. Pellet samples were prepared by pressing polystyrene powder with KBr.

Figure 4.3 Soxhlet-type extractor

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4.3.2 Differential scanning calorimetry (DSC)

The melting temperature (T_m) of the polystyrene was 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 $^{\circ}$C/min. in the temperature range of 25-300 $^{\circ}$C. The heating cycle was run twice. In the first scan, samples were heated and then cooled down to room temperature. In the second scan, samples were reheated at the same rate, only the second scan was recorded because the first scan was influenced by the mechanical and thermal history of samples.

4.3.3 Gel permeation chromatography (GPC)

Molecular weight and molecular weight distribution of the produced polystyrene were measured at 135 °C using 1,2,4-trichlorobenzene as solvent at 1.0 ml/min by a Water 150-C column. GPC curves of polystyrene were determined at Chemical Resources Laboratory, Tokyo Institute of Technology, Japan.

4.3.4 Nuclear magnetic resonance spectroscopy (NMR)

^{1}H- and ^{13}C-NMR spectra were recorded on JEOL JNM-A500 at Chemical Resources Laboratory, Tokyo Institute of Technology, Japan.

4.4 Synthesis of catalyst

All operations were performed under nitrogen atmosphere by using Schlenk techniques.

Pentamethylcyclopentadienyltitanium trichloride ($Cp^{*}TiCl_3$)

Degassed pentamethylcyclopentadiene (5.9 ml/0.05mole) was added to a N_2-flushed, 250 ml, 3-necked, round-bottomed flask containing pentane (60 ml) and a magnetic stir bar. Using a pressure-equalizing dropping funnel, *n*-butyllithium (31.3 ml of 1.6 M solution, 0.05 mole) was slowly added at *ca*. 1 drop sec^{-1} while stirring at room temperature with a mineral oil bubbler to vent the butane that evolves.

The solution was stirred for 12 hr. and, as the reaction occured, a white precipitate of lithium pentamethylcyclopentadienide formed. It was filtered through filter paper and washed with pentane. A solution of lithium pentamethylcyclopentadienide (0.3 mole) in dichloromethane (10 ml) was added to a solution of $TiCl_4$ (0.35 mole) in dichloromethane (35 ml). The reaction solution immediately turned dark red. The reaction mixture was then stirred at room temperature for 12 hr. and filtered through filter paper. The filtered solution was cooled overnight at -20 °C to give dark red crystals of $Cp^{*}TiCl_3$.

4.5 Procedures

4.5.1 Catalyst and cocatalyst solution preparation

1.$Cp^{*}TiCl_3$ approximately 30 mg was stirred in 30 ml of toluene under nitrogen atmosphere until dissolved. The solution was used as a catalyst for styrene polymerization.

2. $B(C_6F_5)_3$ 0.32 ml was measured by a syringe, dissolved in 100 ml of toluene.

3. $[Ph_3C]^+[B(C_6F_5)_4]^-$, $[PhNMe_2H]^+[B(C_6F_5)_4]^-$ approximately 40 mg was dissolved in 30 ml of toluene.

4. TIBA 12.6 ml was dissolved in 87.4 ml of hexane under nitrogen atmosphere to get 0.5 M concentration.

4.5.2 Styrene polymerization procedure

The polymerizations were performed under nitrogen atmosphere by using Schlenk line. A 100 ml Schlenk flask equipped with a magnetic stirring bar were charged with a prescribed amount of catalyst ($Cp^{*}TiCl_3$), 1 equivalent of boron compound $\{B(C_6F_5)_3$ or $[Ph_3C]^+[B(C_6F_5)_4]^-$ or $[PhNMe_2H]^+[B(C_6F_5)_4]^-\}$ and aluminium compound (TIBA), respectively. The catalyst mixture was preactivated for 10 min. at room temperature. The pale yellow to dark green solution was then equilibrated at the desired reaction temperature using a heating bath. Styrene 10 ml (0.087 mol) was then introduced by syringe with rapid stirring under a nitrogen atmosphere, and the reaction mixture was stirred and polymerization started at the desired temperature. After a given time interval , the polymerization was terminated by the addition of 10% HCl in methanol. The polymer was collected by filtration and washed several times with methanol, dried at 80 °C until constant weight. Each polymerization was repeated twice to ensure reproducibility.

The term of catalytic activity in this work is expressed as unit of grams of polystyrene produced, divided by mole of titanium catalyst and styrene during 1 hour of polymerization time.

The various effects on the styrene polymerization with Cp^*TiCl_3 catalyst and optimized conditions were investigated.

4.5.2.1 The effect of polymerization temperature

The polymerization of styrene using Cp^*TiCl_3-Al*i*Bu_3/$[PhNMe_2H]^+[B(C_6F_5)_4]^-$ system was investigsted by varying polymerization temperature from 30 to 90 °C. The other parameters such as Al/Ti mole ratio, millimole of Cp^*TiCl_3 catalyst and polymerization time were fixed at 200, 0.005 mmol and 60 minutes, respectively.

4.5.2.2 The effect of Al/Ti mole ratio

The Al/Ti mole ratios were varied from 100 to 400. The polymerizations were carried out at 70 °C, Ti 0.005 mmol and polymerization time as 60 minutes.

4.5.2.3 The effect of aging time

Styrene polymerization was performed by varying aging time at 10 and 60 minutes, using the optimum condition from section 4.5.2.2.

4.5.2.4 The effect of polymerization time

The Al/Ti mole ratio, polymerization temperature and aging time were chosen from as the best result of sections 4.5.2.1-3. The polymerization times were varied between 20 to 90 minutes.

4.5.2.5 The effect of mole of Cp^*TiCl_3 catalyst

The polymerization of styrene using Cp^*TiCl_3-Al*i*Bu_3/boron compound system was investigated by varying millimole of catalyst from 0.0005 to 0.05. The styrene polymerization was controlled at 70 °C for one hour while the mole ratio Al/Ti was 200.

4.5.2.6 The effect of boron compounds and alkylating agents

The styrene polymerization with Cp^*TiCl_3 was investigated by changing types of boron: ($B(C_6F_5)_3$, $[Ph_3C]^+[B(C_6F_5)_4]^-$ and $[PhNMe_2H]^+[B(C_6F_5)_4]^-$) and alkylating agents (TMA, TIBA, MeMgBr and $PhCH_2MgBr$).

4.5.2.7 The effect of phenylsilane

Phenylsilane/Ti mole ratios were investigated; 10, 50 and 100. Polymerization was carried out at 70 °C, Al/Ti mole ratio of 200, Ti 0.005 mmol and polymerization time 60 minutes.

4.6 Catalyst characterization

Nuclear Magnetic Resonance Spectroscopy (NMR) was used to investigate the chemical structure of catalyst. ^{1}H-NMR spectra indicated the ratio of protons in the catalyst and showed the electronic environment of each kind of proton. ^{13}C-NMR spectra illustrated carbon nucleus that each had its own electronic environment and showed the different chemical shift. The chemical shift reflected the electronic environment of each hydrogen and carbon. The coupling constant, J, was defined to the distance between peaks in a multiplet, a measure of the effectiveness of spin-spin coupling.

4.7 Characterization of the polystyrene

Polystyrene has remarkable chemical inertness to most chemicals including acids and alkalines, particularly at ordinary temperature. For this reason, there were few of chemical analysis procedures available for characterization of polystyrene. Therefore, quantitative measurements of physical properties and determinations of the involved chemicals and physical structure have become increasingly important. In this work, the polystyrene products were characterized by the following methods.

1. Fourier transform infrared spectrometer (FT-IR)

The FT-IR technique was used to characterize a polymer structure. Comparison the position of absorption in the IR spectrum of polymer sample with the characteristic absorption led to identification of the bands and functional groups in the polymer.

2. Differential scanning calorimeter (DSC)

Differential scanning calorimeter (DSC) was used to measure the thermal properties especially melting temperature (T_m).

3. Syndiotacticity

The syndiotacticity content of polystyrene can be determined in a number of ways. The most widely used method involved extracting the polymer in a Soxhlet extractor with a methyl ethyl ketone or 2-butanone. The fraction of the polystyrene unextracted multiply by 100 was a percent of syndiotacticity.

4. Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC), which employed the principle of size exclusion chromatography (SEC) was used to determine molecular weight (M_w) and molecular weight distribution (MWD). Molecular weight and molecular weight distribution of the produced polystyrene were measured at 135 $^{\circ}$C using 1,2,4- trichlorobenzene as solvent at 1.0 ml/min by a Water 150-C column.

5. Nuclear magnetic resonance spectroscopy (NMR)

^{1}H- and ^{13}C-NMR spectra were recorded in 1, 2, 4-trichlorobenzene at 130 °C with JEOL JNM-A500 spectrometer.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Synthesis and characterization of catalyst

5.1.1 Pentamethylcyclopentadienyltitanium trichloride

The synthesis of $Cp^{*}TiCl_3$ is modified from that of $IndTiCl_3$ catalyst. The procedure of $Cp^{*}TiCl_3$ synthesis is presented as in equations 5.1-5.2.

$$C_5(CH_3)_5H + BuLi \rightarrow Cp^{*}Li \qquad (5.1)$$

$$Cp^{*}Li + TiCl_4 \rightarrow Cp^{*}TiCl_3 \qquad (5.2)$$

The structure of $Cp^{*}TiCl_3$ catalyst (Figure 5.1) was confirmed by ^{1}H-NMR spectroscopy, the spectrum was shown in Figure 5.2. The chemical shift at 2.36 ppm is assigned to CH_3 protons of $Cp^{*}TiCl_3$.

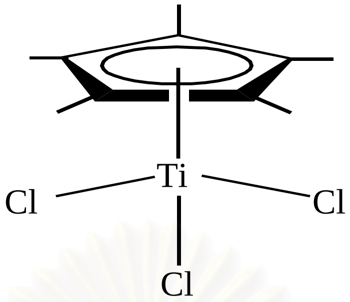


Figure 5.1 Chemical structure of $Cp^{*}TiCl_3$

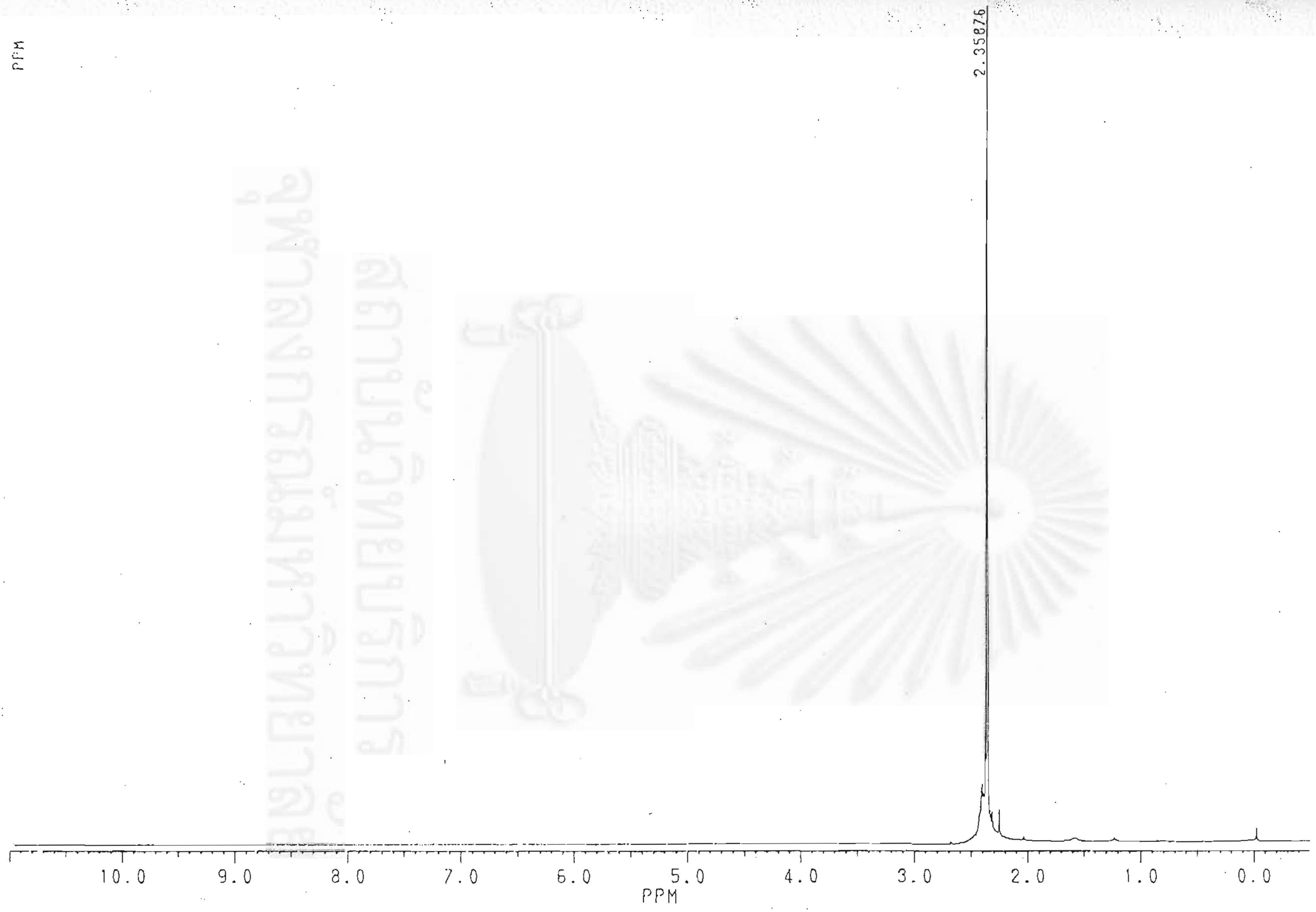


Figure 5.2 ^{1}H-NMR spectrum of (pentamethylcyclopentadienyl)titanium trichloride catalyst

5.2 Polymerization of styrene with Cp^*TiCl_3 catalyst

5.2.1 The effect of polymerization temperature

The influence of the polymerization temperature (T_p) was investigated with different temperatures viz., 30, 50, 70 and 90 $^{\circ}$C. The other parameters such as Al/Ti mole ratio, mole of Cp^*TiCl_3 catalyst and polymerization time were fixed at 200, 0.005 mmol and 60 minutes, respectively with one equivalent of $[PhNMe_2H]^+[B(C_6F_5)_4]^-$. Table 5.1 and Figure 5.3 illustrate the results for the influence of temperature on catalytic activity.

Table 5.1 Polymerization of styrene catalyzed by Cp^*TiCl_3-Al*i*Bu_3/$[PhNMe_2H]^+[B(C_6F_5)_4]^-$ system at various temperatures

Temp ($^{\circ}$C)	Yield PS (g)	Activity	%SPS	%Conversion
30	na	-	-	-
50	4.49	1.03×10^7	90.2	49.6
70	6.35	1.46×10^7	92.1	70.1
90	5.53	1.27×10^7	89.3	61.0

Activity = (grams of bulk polymer) / (mole of Ti•mole of styrene•hr)

(The data shown are the average values of two repeating experiment.)

The results reported in Figure 5.3 indicated that the catalytic activity is enhanced with increasing temperature. Maximum catalytic activity is reached at 70 $^{\circ}$C and slowly decreases with a further increase of temperature.

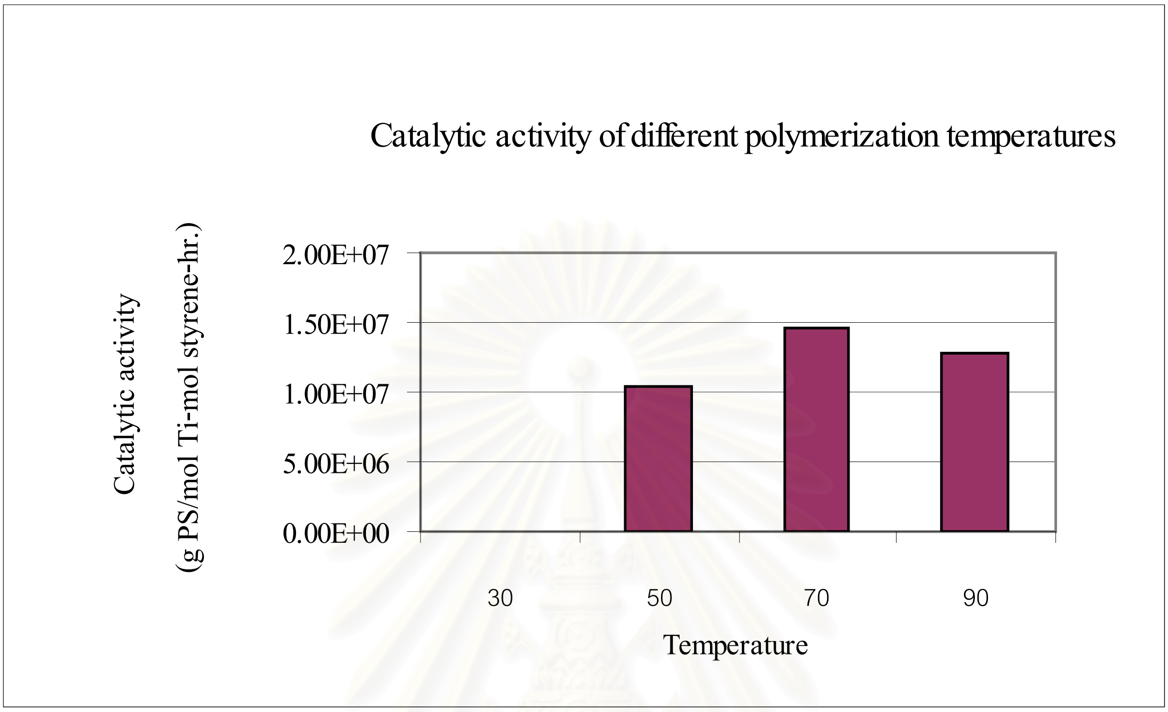
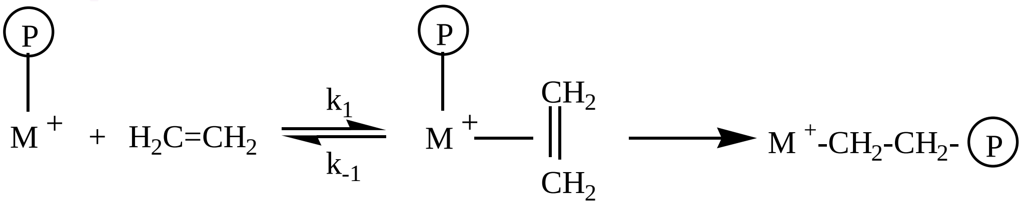


Figure 5.3 Catalytic activity of different polymerization temperatures

The above results can be explained by a widely accepted mechanism of propagation in Ziegler-Natta catalysis which involves the initial formation of a π-complex of an olefin with the catalyst metal, followed by chain migratory insertion.

Using the same mechanism, the propagation process in metallocene system for olefin polymerization can be written as,



At the low polymerization temperature range, the π-olefin complex is more stable which is associated to the process of activated insertion. This affects to the increase of activity with the increasing polymerization temperature (T_p). On the other hand, the decline in activity with further rising temperature probably involves the readily dissociation of the complex causing low propagation rate. In other words, reduced catalytic activity may be attributed to the deactivation of the catalytic species.

5.2.2 The effect of aluminium/titanium (Al/Ti) mole ratio

The effect of Al/Ti mole ratio was studied with $Cp^{*}TiCl_3\text{-}Al\mathit{i}Bu_3/[Ph_3C]^{+}[B(C_6F_5)_4]^{-}$ system. The mole ratios of Al/Ti were varied in the range of 100 to 400. The polymerization were carried out at 70 °C, Ti 0.005 mmol and polymerization time as 60 minutes. The results were summarized in Table 5.2. The catalytic activity versus Al/Ti mole ratio was shown in Figure 5.4.

Table 5.2 Polymerization of styrene catalyzed by $Cp^{*}TiCl_3\text{-}Al\mathit{i}Bu_3/[Ph_3C]^{+}[B(C_6F_5)_4]^{-}$ system at various Al/Ti mole ratios

Al/Ti	Yield PS (g)	Activity	%SPS	%Conversion
100	5.69	1.31×10^{7}	95.1	62.8
200	8.15	1.87×10^{7}	97.8	90.0
400	6.54	1.50×10^{7}	96.3	72.2

Activity = (grams of bulk polymer) / (mole of Ti•mole of styrene•hr)

(The data shown are the average values of two repeating experiment.)

From Figure 5.4, it can be noted that the amount of Al*i*Bu$_3$ in catalytic system affects the activity in styrene polymerization. The activity shows a tendency to increase with increasing Al/Ti mole ratio. The maximum activity is achieved at Al/Ti as 200 and then the activity decreases at higher mole ratio.

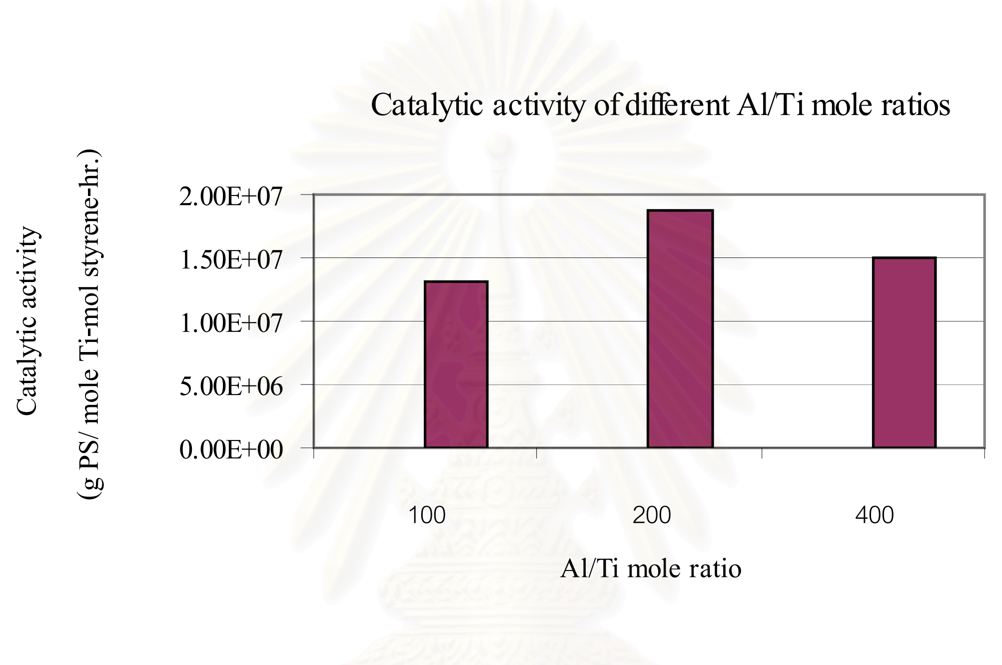


Figure 5.4 Catalytic activity of different Al/Ti mole ratios

It is interesting to attribute that Al*i*Bu$_3$ is an activator, which alkylates half-titanocene catalyst and improves the catalytic activity in styrene polymerization. The decreasing activity at higher Al/Ti mole ratios may be concerned with the appropriate oxidation state of catalytic species for the polymerization. It has been suggested that the active species for styrene polymerization is Ti^{3+}. Based on this consideration, a higher mole of Al*i*Bu$_3$, which is a strong reducing agent in catalytic system, favors the reduction of Ti^{3+} to inactive Ti^{2+} species.

Schellenberg *et al.*[94] have stated that an excess of Al*i*Bu$_3$ might coordinate to the active titanium species, decomposing the active Ti-MAO site or the MAO structure, resulting in an continuous decrease of the catalytic activity with an increase of the aluminium alkyl concentration.

5.2.3 The effect of aging time

Various preactivation times were investigated; 0, 10 and 60 minutes. Polymerization conditions were carried out at Al/Ti mole ratio of 200, Ti 0.005 mmol, polymerization time 60 minutes and polymerization temperature of 70 °C. The results are shown in Table 5.3 and Figure 5.5.

Table 5.3 Polymerization of styrene catalyzed by $Cp^{*}TiCl_3$-Al*i*Bu$_3$/$[Ph_3C]^{+}[B(C_6F_5)_4]^{-}$ system at various aging times

Al/Ti	Aging Time (min)	Yield PS (g)	Activity	%SPS	%Conversion
200	0	3.87	8.90×10^{6}	95.3	42.7
200	10	8.15	1.87×10^{7}	97.8	90.0
200	60	6.35	1.46×10^{7}	94.2	70.1

Activity = (grams of bulk polymer) / (mole of Ti•mole of styrene•hr)

(The data shown are the average values of two repeating experiment.)

From the above experimental results, an immediate polymerization without a premixing of catalyst, cocatalyst and Al*i*Bu$_3$, led to a lower polymerization activity, probably because of an insufficient formation of active centers. However, activity was decreased when a longer preactivation time was used.

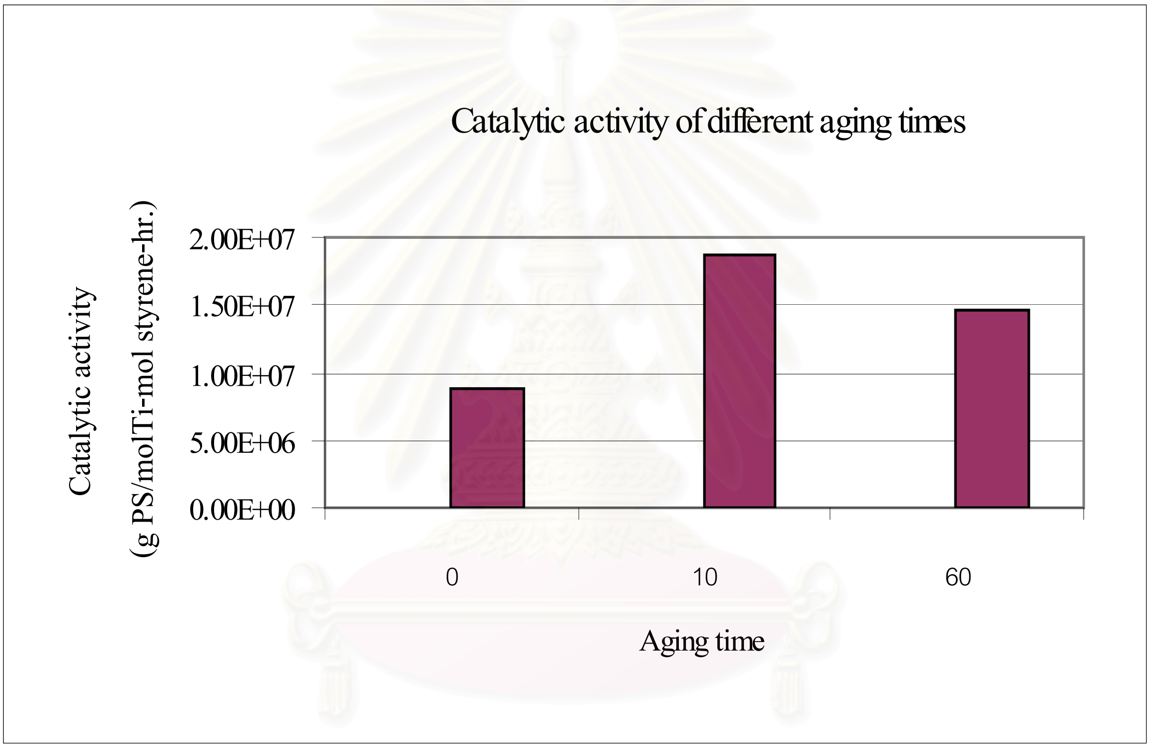


Figure 5.5 Catalytic activity of different aging times

5.2.4 The effect of polymerization time

The effect of various polymerization times on styrene polymerization was investigated. The polymerizations were conducted at 70 °C, Al/Ti mole ratio of 200 and Ti 0.005 mmol with four different polymerization times viz., 20, 40, 60 and 90 minutes. The experimental results and relationship between catalytic activity versus polymerization time are shown in Table 5.4 and Figure 5.6.

Table 5.4 Polymerization of styrene catalyzed by $Cp^{*}TiCl_3\text{-}Al\textit{i}Bu_3/[Ph_3C]^{+}[B(C_6F_5)_4]^{-}$ system at various times

Time (min.)	Yield PS (g)	Activity	%SPS	% Conversion
20	0.65	4.53×10^{6}	94.1	7.2
40	3.37	11.73×10^{6}	95.4	37.2
60	8.15	18.70×10^{6}	97.8	90.0
90	8.21	12.60×10^{6}	95.7	90.6

Activity = (grams of bulk polymer) / (mole of Ti•mole of styrene•hr)

(The data shown are the average values of two repeating experiment.)

As shown in Figure 5.6, the catalytic activity increases with increasing polymerization time and then % conversion of polystyrene begins to be constant after 60 min. Hence, the polymerization time about 60 min. is sufficient for the styrene polymerization and was used in further experiments.

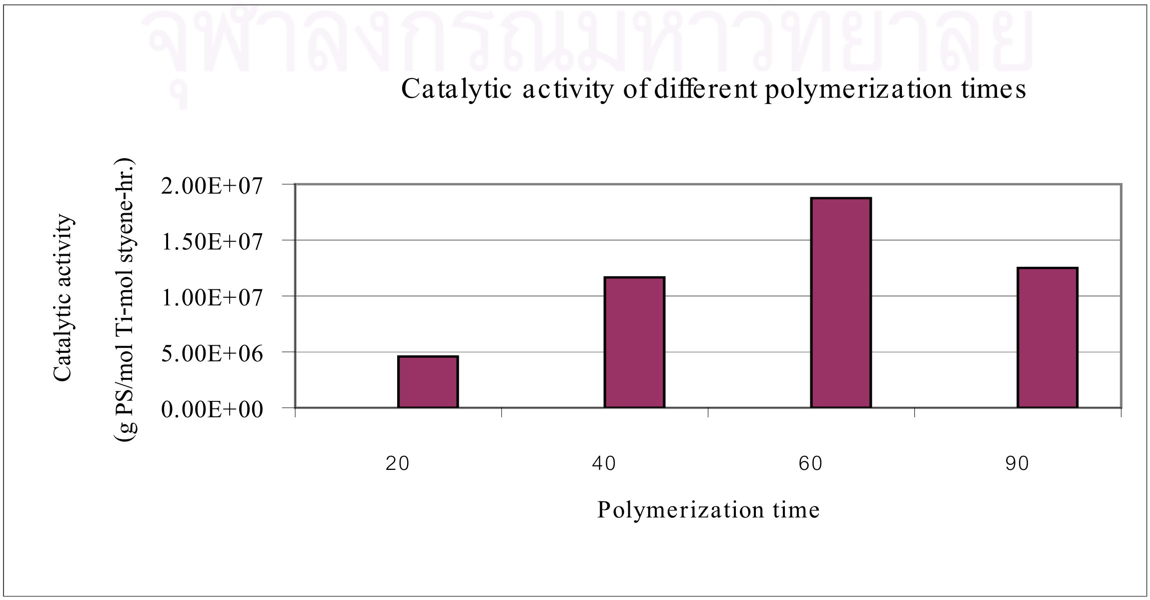


Figure 5.6 Catalytic activity of different polymerization times

5.2.5 The effect of mole of catalyst

The effect of amount of catalyst on styrene polymerization was investigated with $Cp^{*}TiCl_3$-TIBA/boron compound systems. In the case of $Cp^{*}TiCl_3$-$AliBu_3/[Ph_3C]^{+}$ $[B(C_6F_5)_4]^{-}$ system, the mole of catalyst was tested in the range of 0.0005 to 0.05 mmol. While that of $Cp^{*}TiCl_3$-$AliBu_3/[PhNMe_2H]^{+}[B(C_6F_5)_4]^{-}$ system was tested in the range of 0.0005 to 0.025 mmol. The polymerization of both systems were performed at 70 °C for 60 minutes with Al/Ti mole ratio of 200. The results are shown in Tables 5.5-5.6 and Figures 5.7-5.8.

Table 5.5 Polymerization of styrene catalyzed by $Cp^{*}TiCl_3$-$AliBu_3/[Ph_3C]^{+}$ $[B(C_6F_5)_4]^{-}$ system at various moles of catalyst

$Cp^{*}TiCl_3$ (mmol)	Yield PS (g)	Activity	%SPS	%Conversion
0.0005	0.57	1.31×10^{7}	0	6.3
0.001	2.96	3.40×10^{7}	57.9	32.7
0.005	8.15	1.87×10^{7}	97.8	90.0
0.025	0.44	2.00×10^{5}	81.7	4.9
0.05	0.42	9.60×10^{4}	65.7	4.6

Activity = (grams of bulk polymer) / (mole of Ti•mole of styrene•hr)

(The data shown are the average values of two repeating experiment.)

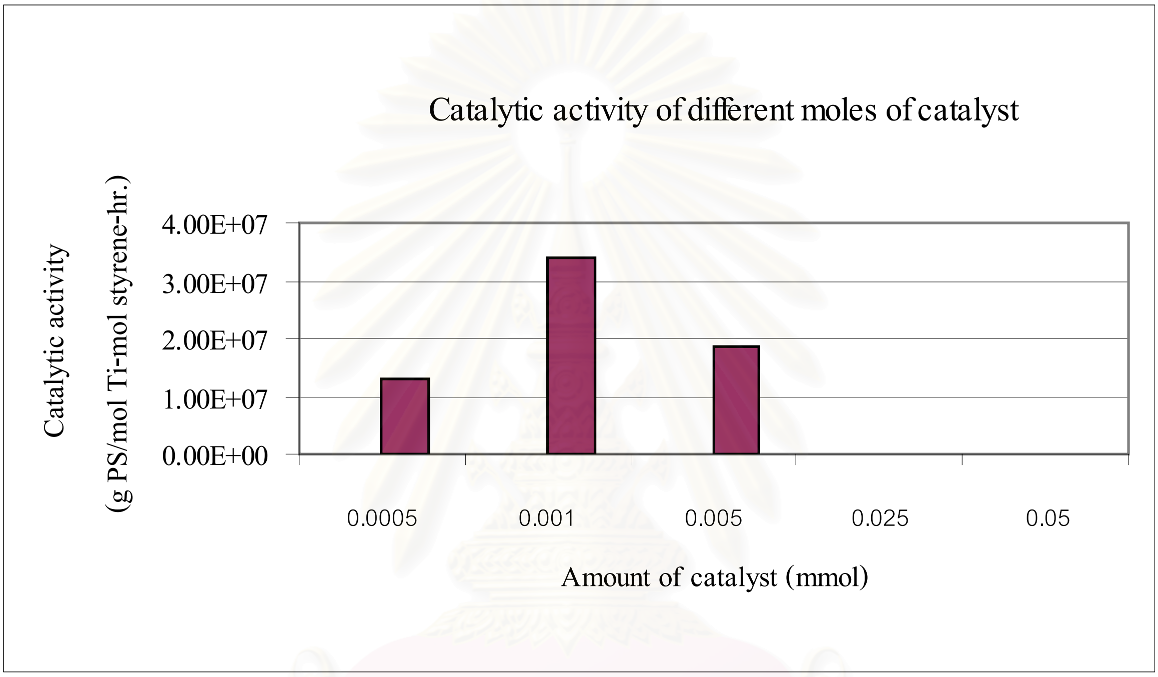


Figure 5.7 Catalytic activity of different moles of catalyst

From the results in Table 5.5 and Figure 5.7, the catalytic activity is strongly affected by the mole of catalyst. The catalytic activity and % syndiotacticity increase markedly with an increase in the amount of catalyst. The best condition is 0.005 mmol of catalyst. When the amount of catalyst is more than 0.005 mmol, activity apparently decreases. The increasing of activity at the low amount of catalyst could be attributed to the increasing of active species. The decreasing of activity with higher amount of catalyst might be caused by the decline of active species due to dimerization of active species into inactive species[95].

Table 5.6 Polymerization of styrene catalyzed by Cp*TiCl$_3$-Al*i*Bu$_3$/$[\mathrm{PhNMe_2H}]^{+}$ $[\mathrm{B(C_6F_5)_4}]^{-}$ system at various moles of catalyst

Cp*TiCl$_3$(mmol)	Yield PS (g)	Activity	%SPS	%Conversion
0.0005	0.55	1.26×10^{7}	85.4	6.1
0.001	3.17	3.63×10^{7}	96.0	35.0
0.005	6.35	1.46×10^{7}	92.1	70.1
0.025	0.14	0.63×10^{5}	75.4	1.6

Activity = (grams of bulk polymer) / (mole of Ti•mole of styrene•hr)

(The data shown are the average values of two repeating experiment.)

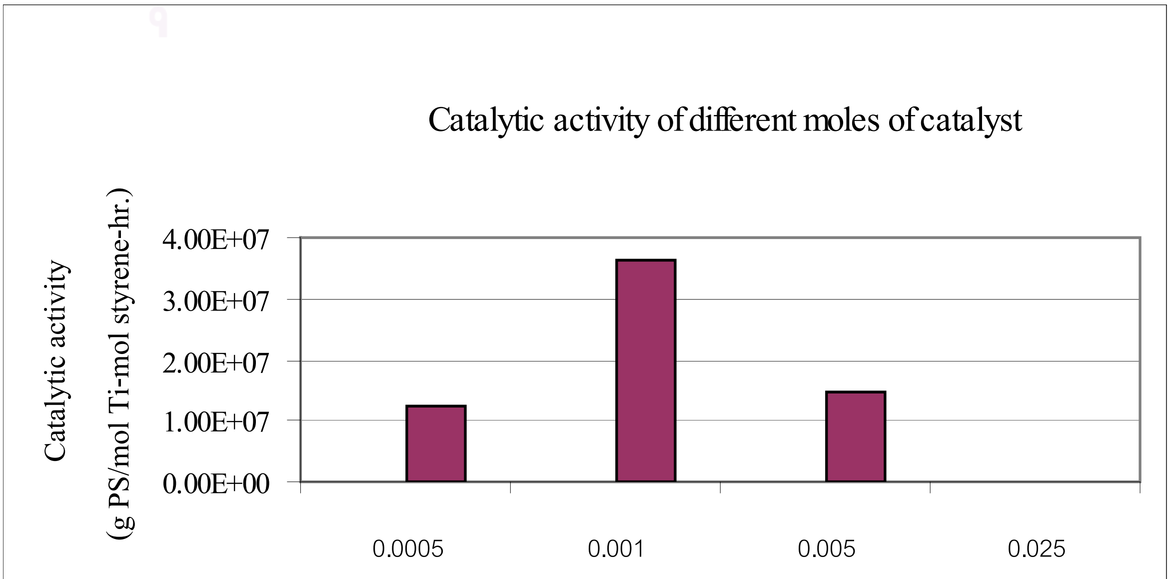


Figure 5.8 Catalytic activity of different moles of catalyst

It is found that the results shown in Table 5.6 have similar tendency to those in Table 5.5. The maximum activity appears at 0.001 mmol of catalyst and then the catalytic activity decreases at higher amount of catalyst. This can be concluded with the same reasons as.

5.2.7 The effect of boron cocatalyst

Three types of boron compounds were investigated; $B(C_6F_5)_3$, $[Ph_3C]^+[B(C_6F_5)_4]^-$, $[PhNMe_2H]^+[B(C_6F_5)_4]^-$. Styrene polymerization was conducted at polymerization temperature of 70 °C, Al/Ti mole ratio of 200, 0.005 mmol Ti and polymerization time of 1 hour. The results are summarized in Table 5.7.

Table 5.7 Polymerization of styrene catalyzed by various boron compounds with Cp^*TiCl_3-Al*i*Bu_3.

Boron cocatalysts	Yield PS (g)	Activity	%SPS	T_m(°C)
$B(C_6F_5)_3$	na	-	-	-
$[Ph_3C]^+[B(C_6F_5)_4]^-$	8.15	1.87×10^7	97.8	268.6
$[PhNMe_2H]^+[B(C_6F_5)_4]$	6.35	1.46×10^7	92.1	268.8

-				

Activity = (grams of bulk polymer) / (mole of Ti•mole of styrene•hr)

(The data shown are the average values of two repeating experiment.)

As shown in Table 5.7, both borate cocatalysts; $\left[Ph_3C\right]^+\left[B(C_6F_5)_4\right]^-$ and $\left[PhNMe_2H\right]^+\left[B(C_6F_5)_4\right]^-$ have efficiency in styrene polymerization with Cp^*TiCl_3- Al*i*Bu_3/boron compound systems. However, at 0.005 mmol of catalyst, $\left[Ph_3C\right]^+\left[B(C_6F_5)_4\right]^-$ cocatalyst exhibits a higher catalytic activity than the other. In addition, $B(C_6F_5)_3$ is unable to be used as a cocatalyst for Cp^*TiCl_3-Al*i*Bu_3/boron compound system.

5.2.8 The effect of alkylating agent

Different alkylating agents were examined; TMA, TIBA, MeMgBr, $PhCH_2MgBr$. The polymerizations were performed at 70 °C, Al/Ti mole ratio of 200, polymerization time 60 minutes and 0.015 mmol of alkylating agent. The results of styrene polymerization are shown in Table 5.8.

Table 5.8 Polymerization of styrene catalyzed by various alkylating agents with Cp^*TiCl_3-alkylating agent/$\left[Ph_3C\right]^+\left[B(C_6F_5)_4\right]^-$ systems.

Alkylating agent	Yield PS (g)	Activity
$Al(CH_3)_3$	na	-
Al*i*Bu_3	8.15	1.87×10^7
CH_3MgBr	na	-
$PhCH_2MgBr$	na	-

Activity = (grams of bulk polymer) / (mole of Ti•mole of styrene•hr)

(The data shown are the average values of two repeating experiment.)

It is clearly shown that only TIBA is efficient to alkylate the half-titanocene catalyst for $Cp^{*}TiCl_3$-alkylating agent/$[Ph_3C]^+[B(C_6F_5)_4]^-$ system, due to the fact that TIBA acts as a good nucleophile.

5.2.9 The effect of phenylsilane

Phenylsilane/Ti mole ratios were investigated; 10, 50 and 100. Polymerizations were carried out at 70 °C, Al/Ti mole ratio of 200, Ti 0.005 mmol and polymerization time 60 minutes. The experimental results are shown in Table 5.9.

Table 5.9 Polymerization of styrene catalyzed by $Cp^{*}TiCl_3$-Al*i*Bu_3/$[Ph_3C]^+[B(C_6F_5)_4]^-$-$PhSiH_3$ system at various phenylsilane/Ti ratios.

Phenyl/Ti	Yield PS (g)	Activity	%SPS	%Conversion
10	2.65	1.22×10^7	70.3	58.5
50	4.33	1.99×10^7	76.2	95.6
100	3.84	1.76×10^7	72.5	84.8

Activity = (grams of bulk polymer) / (mole of Ti•mole of styrene•hr)

(The data shown are the average values of two repeating experiment.)

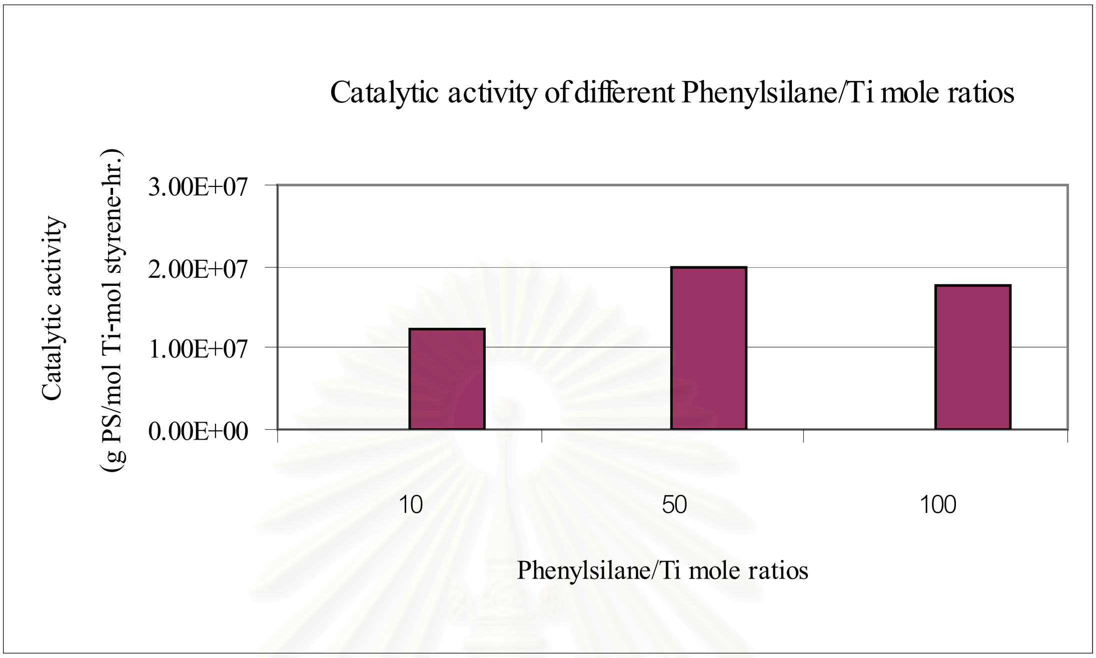


Figure 5.9 Catalytic activity of different phenylsilane/Ti mole ratios

The results indicated that the catalytic activity is enhanced with increasing phenylsilane/Ti mole ratios. Maximum catalytic activity is achieved at phenylsilane/Ti as 50 and then the activity decreases at higher mole ratio.

It is evident that the polymerization activity of the system is increased by the addition of phenylsilane. The reason for the observed acceleration by phenylsilane might be an increase in amount of active Ti-H sites by a chain-transfer reaction or the activation of dormant states of the active titanium species[94] as in equation 5.3.

$$\text{Ti-P} + C_6H_5SiH_3 \longrightarrow \text{Ti-H} + C_6H_5SiH_2\text{-P} \qquad (5.3)$$

From the experimental results, SPS can be obtained using half-titanocene compound-alkylating agent/ tetra(pentafluorophenyl)borate salts as homogeneous catalytic systems. This catalytic system affords cationic complex $[\mathrm{Cp^*TiR_2}]^+[\mathrm{B(C_6F_5)_4}]^-$ which is decomposed to active species $[\mathrm{Cp^*TiR}]^+$. The formation of $[\mathrm{Cp^*TiR_2}]^+[\mathrm{B(C_6F_5)_4}]^-$ was shown in equation 5.4. The syndiotactic configuration arises from phenyl-phenyl repulsive interactions between the last inserted unit of the growing chain and incoming monomer (1,3-asymmetric induction). Mechanism of syndiospecific styrene polymerization was proposed in Figure 5.10.

$$\mathrm{Cp^*TiCl_3 + TIBA \longrightarrow Cp^*Ti(\mathit{i}\text{-}Bu)_3 \xrightarrow{[Ph_3C]^+[B(C_6F_5)_4]^-} \left[Cp^*Ti(\mathit{i}\text{-}Bu)_2\right]^+\left[B(C_6F_5)_4\right]^-} \quad (5.4)$$

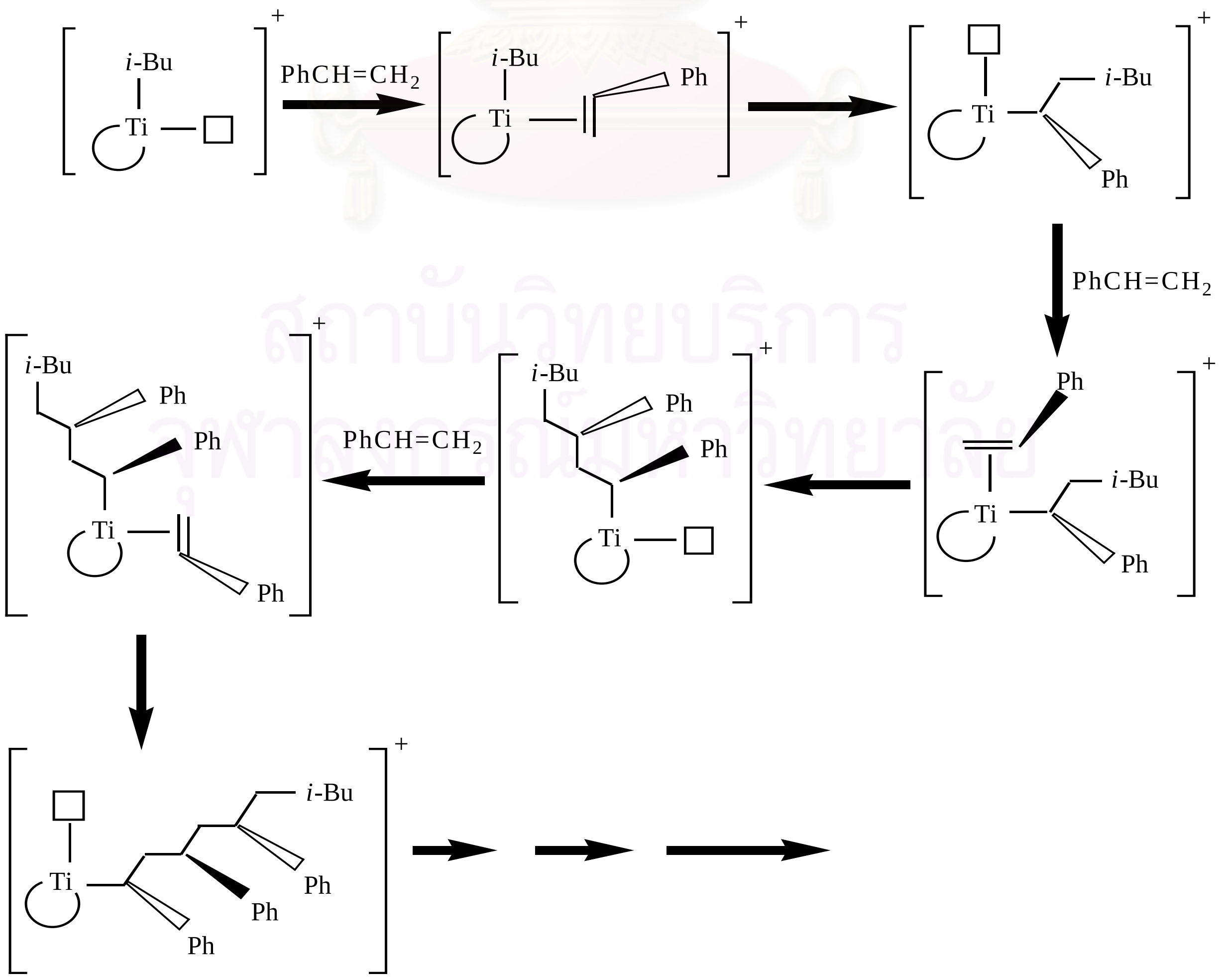


Figure 5.10 Proposed mechanism in propagation of syndiospecific styrene polymerization

5.3 Characterization of polystyrene

5.3.1 Chemical structure determination

5.3.1.1 Infrared spectroscopy (IR)

The infrared spectroscopy is an effective method to determine the microstructure of polymer. It is sufficient to characterize the functional groups of polystyrene in the wave number of 400-4000 cm^{-1}. The identification of the spectrum is summarized in Table 5.10

Table 5.10 IR spectral data of the polystyrene

Wave number range, cm^{-1}	Assignment
670-860	=C-H bending aromatic
970-1050	$CH=CH_2$ vinylidine bending
1350-1470	$-CH_2-$, $-CH_3$ bending
1500, 1600	C=C aromatic
2850-2960	C-H stretching aliphatic
3000-3100	=C-H stretching aromatic

The band in the range of 3000-3100 cm^{-1} results from =C-H stretching vibrations, and aliphatic C-H stretching vibrations absorb around 2800-3000 cm^{-1}. The absorptions at 1500 and 1600 cm^{-1} result from C=C ring stretching. The bending vibrations generally appear in the 600 to 1400 cm^{-1} region of the spectrum.

It is found that all polystyrene produced in this study exhibited similar IR patterns. The infrared spectra of the produced polystyrenes compared with the reference polystyrene spectrum are shown in Figure 5.11. It is confirmed that all the products obtained are polystyrene.

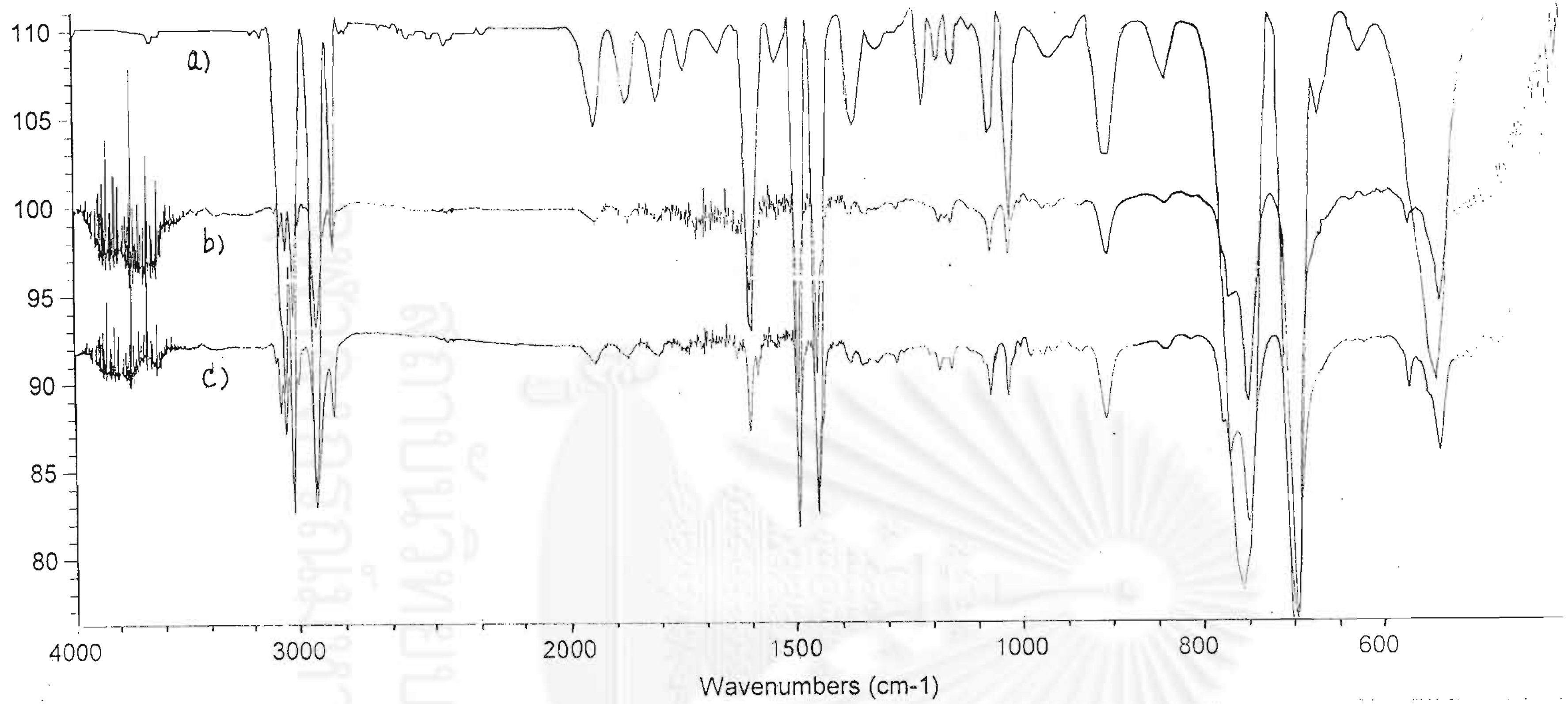


Figure 5.11 IR spectra of polystyrene : a) Standard polystyrene b) from Cp^*TiCl_3-Al*i*Bu_3/$[Ph_3C]^+[B(C_6F_5)_4]^-$ system

c) from Cp^*TiCl_3-Al*i*Bu_3/$[PhNMe_2H]^+[B(C_6F_5)_4]^-$ system

5.3.1.2 Nuclear magnetic resonance spectroscopy (NMR)

The tacticity of polymer is determined by high-resolution ^{1}H- and ^{13}C-NMR spectroscopy. ^{13}C and ^{1}H spectra of the prepared polystyrene by Cp*TiCl$_3$-TIBA/$[Ph_3C]^+$ $[B(C_6F_5)_4]^-$ system are presented in Figures 5.13 and 5.14.

The ^{13}C-NMR spectrum of obtained polystyrene is presented in Figure 5.13. The aromatic C$_1$ carbons resonate at 145 ppm, while the remaining aromatic carbons resonances appear at 128 and 125 ppm. The methine carbons are observed to resonate at 44 ppm. The methylene carbons exhibit sharp singlet at 41 ppm. Figure 5.12 shows ^{13}C-NMR spectrum of the phenyl C$_1$ carbon of the three types of polystyrene, the spectrum of atactic polystyrene (Figure 5.12-(1)) shows five peaks in the range 145-146 ppm, corresponding to its various configurational sequences. The spectrum of isotactic polystyrene (Figure 5.12-(2)) shows the phenyl C$_1$ carbon as a single sharp peak at lower magnetic field (δ = 146) corresponding to the mmmm pentad configuration. In contrast, a peak in syndiotactic polystyrene (Figure 5.12-(3)) was observed at higher magnetic field (δ = 145). The obtained ^{13}C-NMR spectrum corresponds with the result reported for SPS[96]. Therefore, it is concluded that the produced polymer is syndiotactic polystyrene.

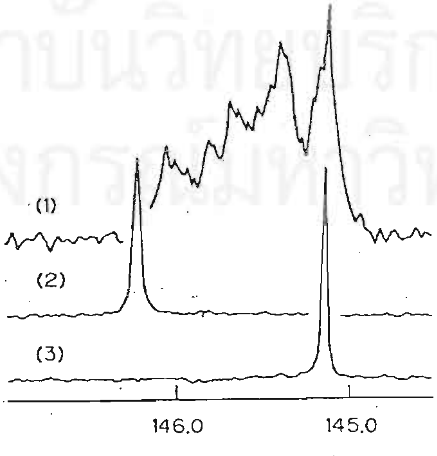


Figure 5.12 ^{13}C-NMR spectra of polystyrene: (1) atactic; (2) isotactic; (3) syndiotactic

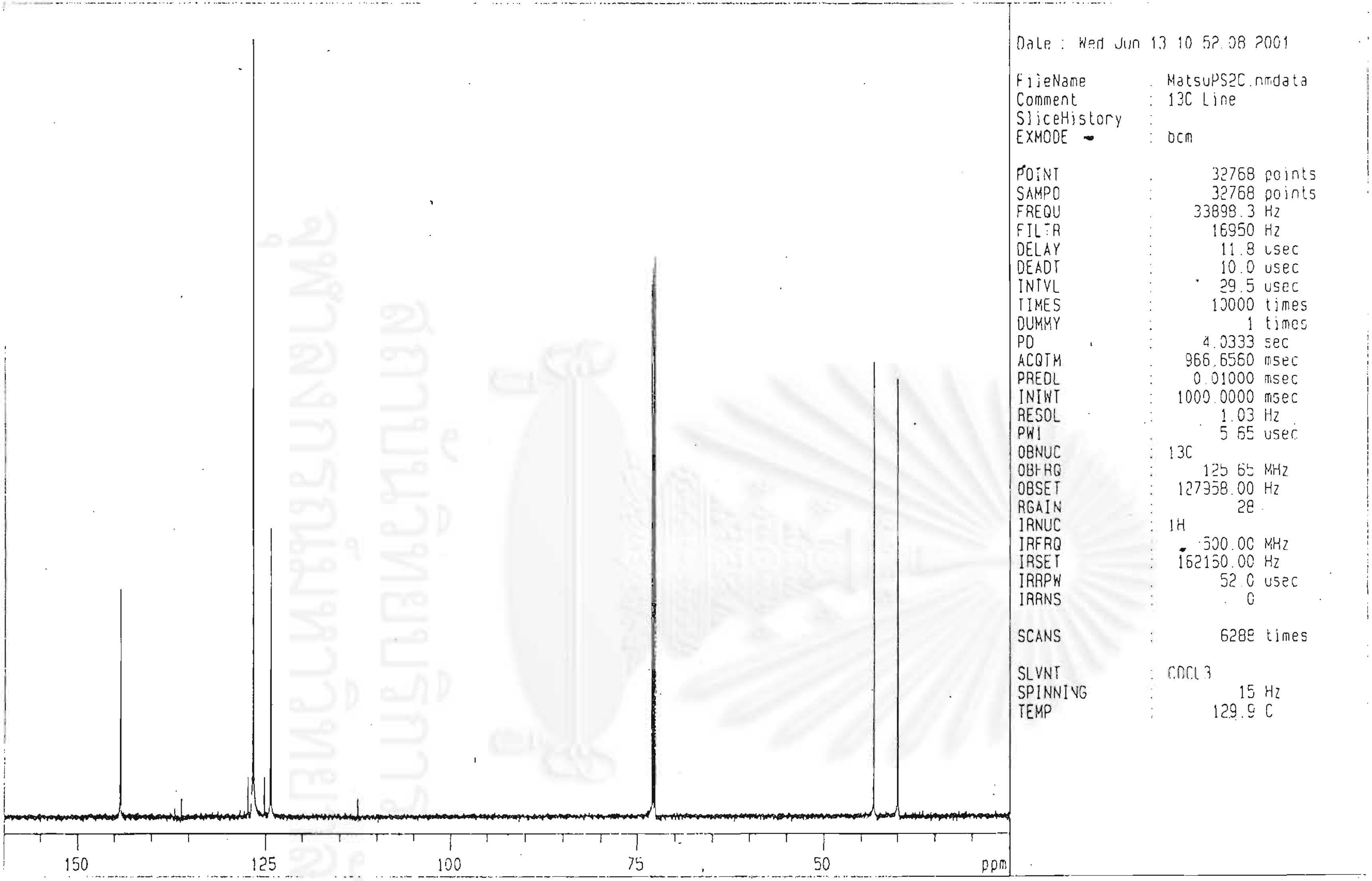


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Figure 5.13 ^{13}C-NMR spectrum of polystyrene obtained with Cp*TiCl$_3$-TIBA/$[Ph_3C]^{+}[B(C_6F_5)_4]^{-}$ system

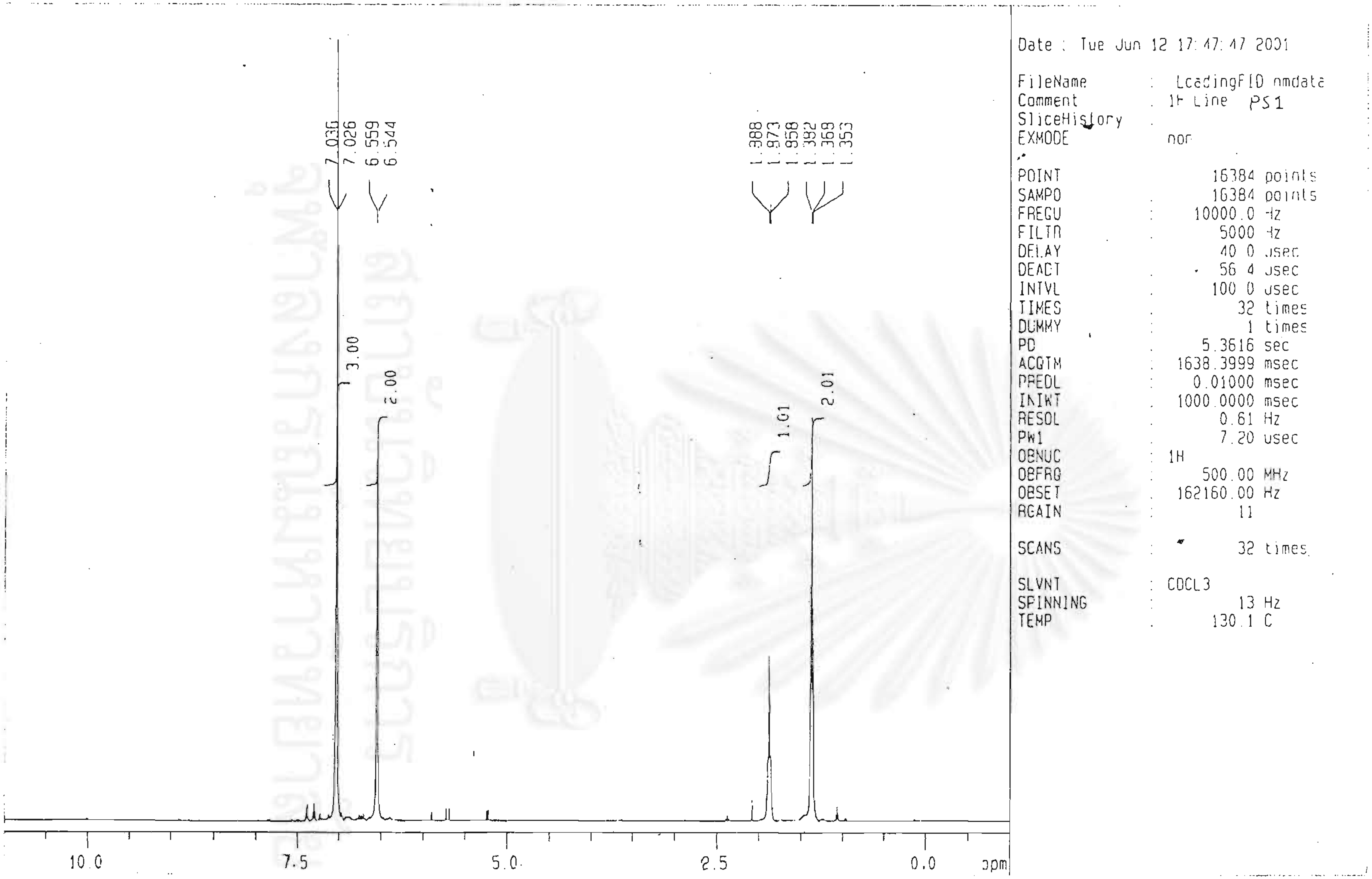

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Figure 5.14 ^{1}H-NMR spectrum of polystyrene obtain Cp*TiCl$_3$-TIBA/$[Ph_3C]^{+}[B(C_6F_5)_4]^{-}$ system

In the ^{1}H-NMR spectrum, the resonance of aliphatic protons appears as two peaks at 1.3 (methylene) and 1.8 ppm (methine). The methylene proton resonance appears as a triplet, this suggests that the two methylene protons are equivalent and that the structure of obtained polystyrene is syndiotactic.

5.3.2 Melting temperature (T_m)

The melting temperatures of polystyrene obtained with Cp^*TiCl_3-Al*i*Bu_3/boron compound systems were measured by differential scanning calorimetry, shown in Table 5.11 and Figures 5.15-5.16.

Table 5.11 Melting temperature of polystyrene with Cp^*TiCl_3-Al*i*Bu_3/boron compound systems

Catalytic system	**Melting temperature (^{o}C)**
Cp^*TiCl_3-Al*i*Bu_3/$[Ph_3C]^+[B(C_6F_5)_4]^-$	268.6
Cp^*TiCl_3-Al*i*Bu_3/$[PhNMe_2H]^+[B(C_6F_5)_4]^-$	268.8

For Cp^*TiCl_3-Al*i*Bu_3/$[Ph_3C]^+[B(C_6F_5)_4]^-$ or /$[PhNMe_2H]^+[B(C_6F_5)_4]^-$ systems, the melting temperatures are observed in the range of 268-269 ^{o}C, which is close to T_m of syndiotactic polystyrene (270 ^{o}C). Therefore, it can be confirmed that the polystyrene product is syndiotactic.

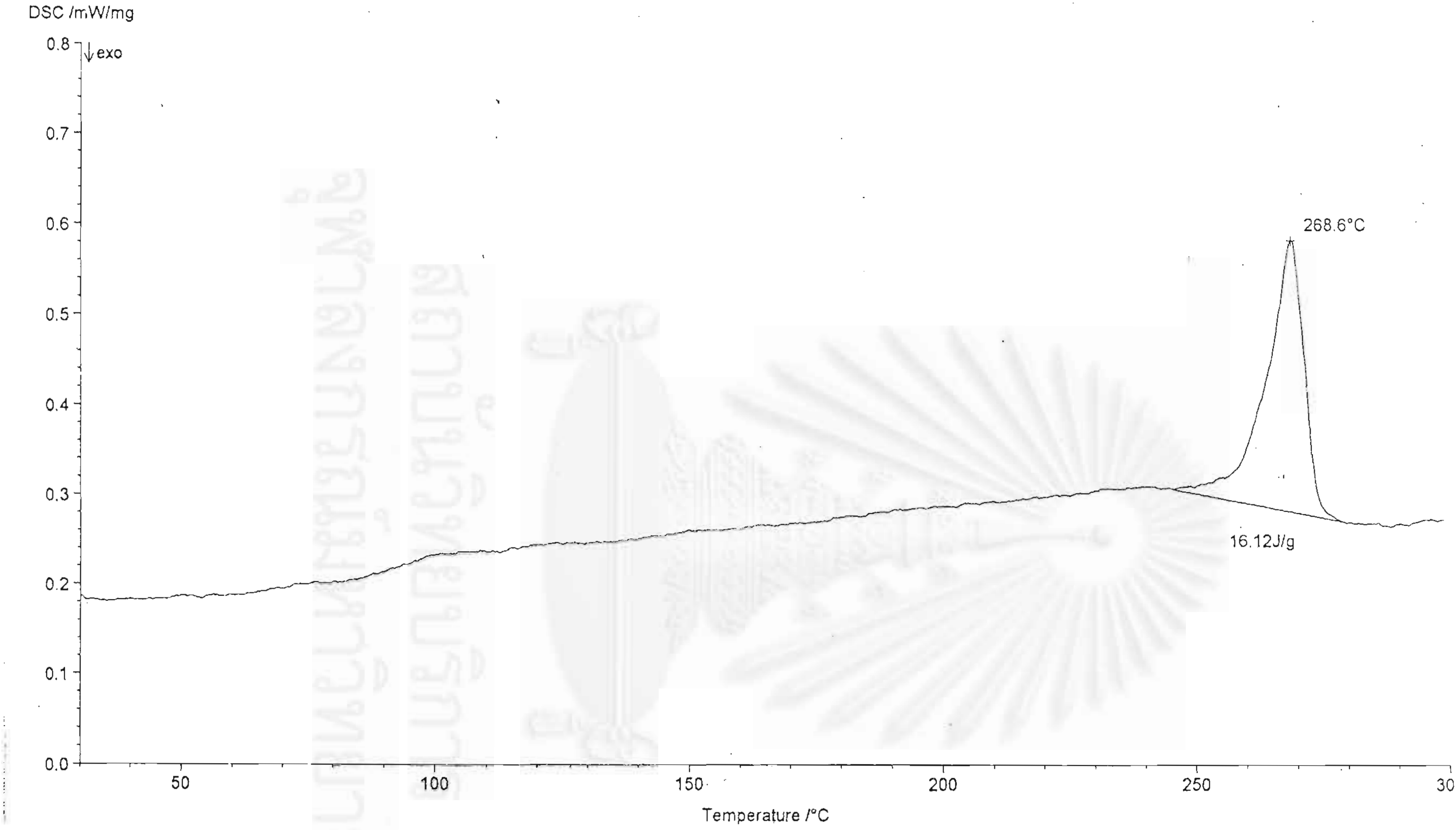


Figure 5.15 DSC curve of polystyrene produced with $Cp^{*}TiCl_3$-Al*i*Bu_3/$[Ph_3C]^{+}[B(C_6F_5)_4]^{-}$ system

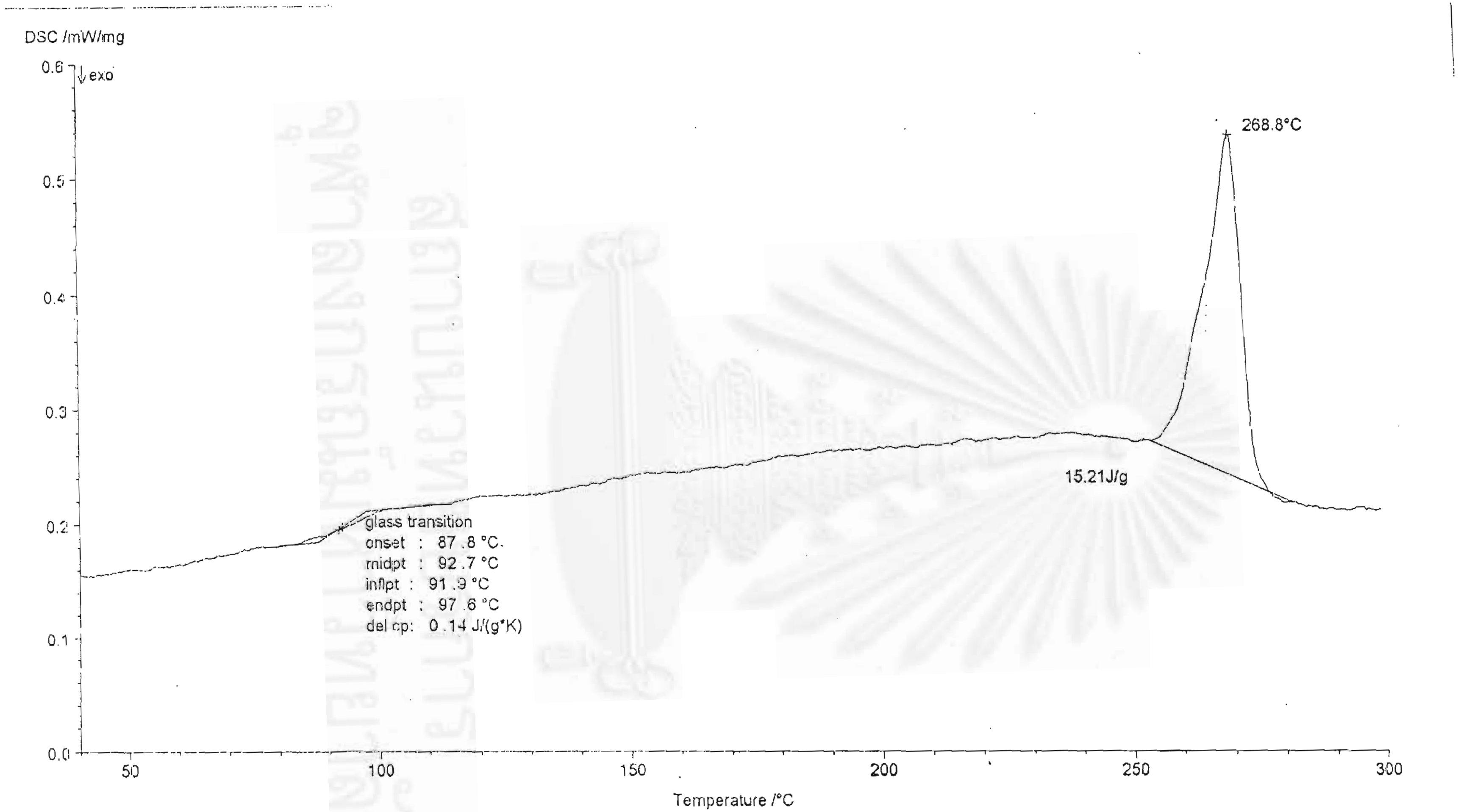


Figure 5.16 DSC curve of polystyrene produced with $Cp^{*}TiCl_3$-Al*i*Bu_3/$[PhNMe_2H]^{+}[B(C_6F_5)_4]^{-}$ system

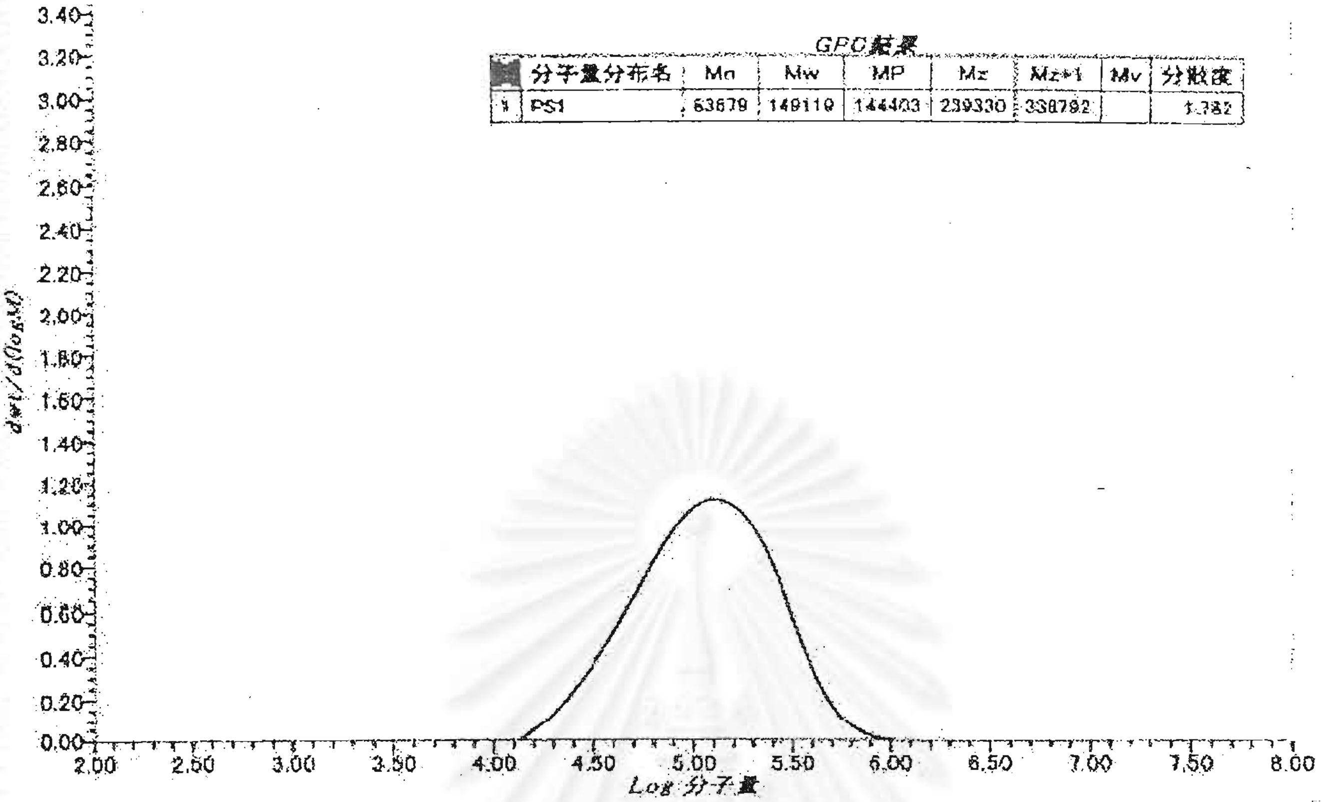
5.3.3 Molecular weight (M_w) and molecular weight distribution (MWD)

The molecular weight and molecular weight distribution of polystyrene produced by Cp^*TiCl_3-Al*i*Bu_3/$[Ph_3C]^+[B(C_6F_5)_4]^-$ and Cp^*TiCl_3-Al*i*Bu_3/$[PhNMe_2H]^+[B(C_6F_5)_4]^-$ systems are presented in Table 5.12. The GPC curves are shown in Figures 5.17-5.18.

Table 5.12 M_w and MWD of the obtained polystyrene by Cp^*TiCl_3-Al*i*Bu_3/boron compound systems

Catalyst system	M_w	M_n	M_w/M_n
Cp^*TiCl_3-Al*i*Bu_3/$[Ph_3C]^+[B(C_6F_5)_4]^-$	149,119	63,679	1.782
Cp^*TiCl_3-Al*i*Bu_3/$[PhNMe_2H]^+[B(C_6F_5)_4]^-$	182,493	118,562	1.539

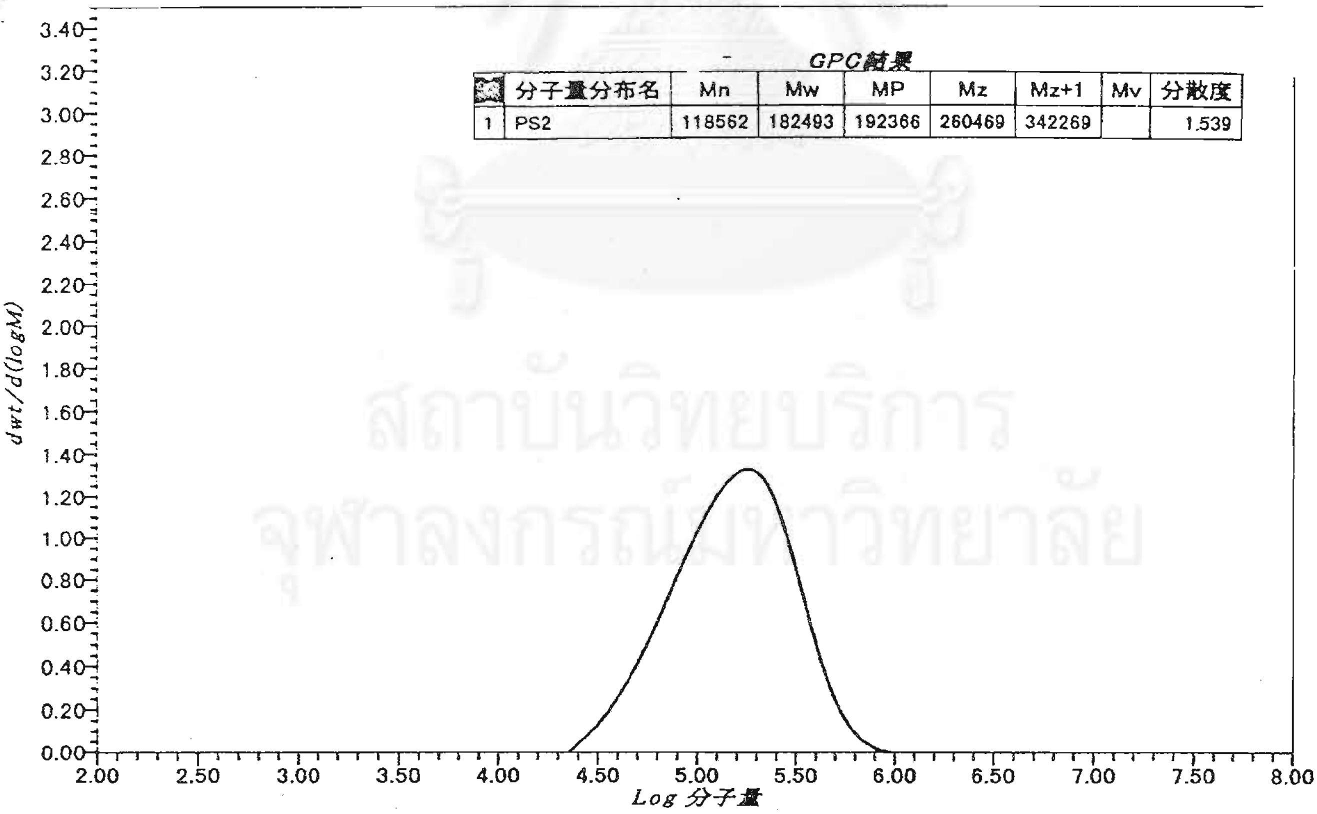
According to the data in Table 5.12, the polystyrene produced with Cp^*TiCl_3-Al*i*Bu_3/$[PhNMe_2H]^+[B(C_6F_5)_4]^-$ system gives higher molecular weight as compared with Cp^*TiCl_3-Al*i*Bu_3/$[Ph_3C]^+[B(C_6F_5)_4]^-$ system. Moreover the molecular weight distribution or polydispersity (M_w/M_n) values of both systems are narrow.



GPC結果

	分子量分布名	Mn	Mw	MP	Mz	Mz+1	Mv	分散度
1	PS1	83679	149119	144403	239330	338782		1.782

Figure 5.17 GPC curve of polystyrene produced with $Cp^{*}TiCl_3$-Al*i*Bu_3/$[Ph_3C]^{+}[B(C_6F_5)_4]^{-}$



GPC結果

	分子量分布名	Mn	Mw	MP	Mz	Mz+1	Mv	分散度
1	PS2	118562	182493	192366	260469	342269		1.539

Figure 5.18 GPC curve of polystyrene produced with $Cp^{*}TiCl_3$-Al*i*Bu_3/$[PhNMe_2H]^{+}$ $[B(C_6F_5)_4]^{-}$

CHAPTER VI

CONCLUSION AND SUGGESTIONS

6.1 Conclusion

In this research, Cp^*TiCl_3 catalyst has been synthesized and used for styrene polymerization with TIBA and boron cocatalysts. The reaction of Cp^*TiCl_3-TIBA/boron compound affords cationic complex $[Cp^*TiR_2]^+[B(C_6F_5)_4]^-$, which is active for the syndiospecific polymerization of styrene. The best condition for Cp^*TiCl_3-TIBA/$[Ph_3C]^+[B(C_6F_5)_4]^-$ system is : 0.087 mole of styrene, Al/Ti mole ratio of 200, 0.005 mmol of catalyst, polymerization temperature at 70 °C and polymerization time of 60 minutes. The appropriate condition for Cp^*TiCl_3-TIBA/ $[PhNMe_2H]^+$ $[B(C_6F_5)_4]^-$ system is : 0.087 mole of styrene, Al/Ti mole ratio of 200, 0.001 mmol of catalyst, polymerization temperature at 70 °C and polymerization time of 60 minutes. The preactivation step is necessary to increase the activity by increasing the active species. $B(C_6F_5)_3$ is not an appropriate cocatalyst for the above systems. For Cp^*TiCl_3-alkylating agent/$[Ph_3C]^+[B(C_6F_5)_4]^-$ system, it is found that only TIBA is a good alkylating agent for half-titanocene catalyst. Triisobutylaluminium (TIBA) not only alkylates the catalyst but also scavenges impurities in the system. Moreover, the addition of phenylsilane as a chain-transfer agent in the system increases the activity by increasing active species. The melting temperature of the obtained polystyrene is in the range of 268-269 °C which confirms the syndiotactic character. The narrow molecular weight distribution (1.54-1.78) is demonstrated the advantage of this type of catalyst.

6.2 Suggestion for the future work

1. Search for new cocatalyst that has more efficiency than MAO, which is inexpensive and nontoxic.
2. Develop supported metallocene catalyst which can control morphology of the obtained polymer.
3. Isolate the alkylated species of the catalyst and study its mechanism on polymerization of styrene.

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