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สำหรับซินติโอแทคติกพอลิเมอโรเลฟินของสไตรีน



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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

TITANOCENE CATALYSTS WITH BORON COCATALYST FOR  
SYNDIOTACTIC POLYMERIZATION OF STYRENE



Miss Pinrat Pinweha

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ชัน อัตราส่วน Al/Ti ผลการทดลองแสดงว่า ภาวะที่เหมาะสมคือ อุณหภูมิ 65°C เวลาพอลิเมอไรเซชัน 20 ชั่วโมง อัตรา  
ส่วน Al/Ti เป็น 300 การเปรียบเทียบระหว่างตัวเร่งปฏิกิริยาสองชนิด คือ ไซโคลเพนทาไดอีนิลไททานเนียมไตรคลอไรด์  
และ เพนทาเมทิลไซโคลเพนทาไดอีนิลไททานเนียมไตรคลอไรด์ แสดงให้เห็นว่า หมู่ให้อิเล็กตรอนบนลิแกนด์เพิ่มแอกติวิตี  
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การหาค่า %ซินดิโอแทคติกซิตี นอกจากนี้ยังพบว่าการกระจายตัวของน้ำหนักโมเลกุลของพอลิเมอร์อยู่ในช่วงแคบ (1.8)  
ซึ่งเป็นข้อดีของตัวเร่งปฏิกิริยาประเภทนี้



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PINRAT PINWEHA: TITANOCENE CATALYSTS WITH BORON COCATALYST FOR SYNDIOTACTIC POLYMERIZATION OF STYRENE. THESIS ADVISOR: ASSOC. PROF. WIMONRAT TRAKARNPRUK, Ph.D. 86 pp., ISBN 974-13-0240-1

Half-titanocene catalysts (cyclopentadienyltitanium trichloride and pentamethylcyclopentadienyltitanium trichloride) were used to catalyze the polymerization of styrene. The cocatalysts used are based on boron compounds; tris(pentafluorophenyl)boron and triphenylcarbenium tetrakis(pentafluorophenylborate) with aluminium compounds (trimethylaluminium or triisobutylaluminium) as an alkylating agent. The factors affecting polymerization were studied: types of catalyst and cocatalyst, polymerization temperatures and time, Al/Ti ratio. The experimental results reveal that the optimum conditions are: temperature of 65°C, polymerization time of 20 hours, Al/Ti ratio of 300. Comparison between the two catalysts: cyclopentadienyltitanium trichloride and pentamethylcyclopentadienyltitanium trichloride showed that electron releasing group on the ligand increases the catalytic activity. Among the various catalytic systems tested, the pentamethylcyclopentadienyltitanium trichloride with triisobutylaluminium was found the best system for producing polystyrene with 73% syndiotacticity, This single-site catalyst allows the control of polymer structure, which was revealed from the FT-IR spectrum, and % syndiotacticity determination. In addition, the molecular weight distribution of the polymer is narrow (1.8) which is the advantage of this type of catalyst.



Program of ....Petrochemistry.and.Polymer.Science... Student's signature.....

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## LIST OF ABBREVIATIONS

PS	Polystyrene
APS	Atactic polystyrene
IPS	Isotactic polystyrene
SPS	Syndiotactic polystyrene
MAO	Methylaluminoxane
TMA	Trimethylaluminium
TEA	Triethylaluminium
TIBA	Triisobutylaluminium
THF	Tetrahydrofuran
MEK	Methyl ethyl ketone
L	Ligand
M	Metal
Ph	Phenyl
Me	Methyl
X	Halogen
R	Substituent R group
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Ind	Indenyl
DSC	Differential scanning calorimetry
MWD	Molecular weight distribution
GPC	Gel permeation chromatography
Cpd	Compound

# CHAPTER I

## INTRODUCTION

The petrochemical and polymer industries have driven Thailand toward a new era of economic growth. Polyolefins are among the most important polymers in term of production. The amount of polyolefins produced is about 47 million metric tons per year over the world [1]. In view of their commercial importance, they have attractive significant interest from both industrial and academic laboratories towards development of newer combinations of catalysts. Major objectives in developing such catalysts are high catalyst efficiency and high stereospecificity.

Polystyrene (PS), is a typical rigid plastic, has been known since the last century; it was commercialised in 1925 by IG Farben and it is now one of the most widespread polymeric materials, appreciated for its excellent stiffness, transparency and its good processability. It is an amorphous polymer with a softening temperature of about 100°C. Brittleness and poor thermal and chemical resistances are its main faults from an applicative point of view. The polymerization of styrene with radical, initiators either in bulk, in solution, in suspension or in emulsion affords atactic polystyrene (APS). In 1955, Natta et al. obtained isotatic polystyrene (IPS) by using Ziegler-Natta catalytic system  $\text{TiCl}_4/\text{Al}(\text{CH}_2\text{CH}_3)_3$  [2]. IPS is highly crystalline, with a melting temperature of 240°C. However, its crystallization rate is too slow to make any commercial applications of this material viable. More recently, Ishihara et al. were able to obtain syndiotactic polystyrene (SPS) by using homogeneous organometallic catalytic systems based on titanium compounds (titanocene) and methylaluminumoxane (MAO). SPS is also highly crystalline polymer, with a melting temperature of about 270°C and a glass transition temperature similar to APS.

The relatively fast crystallization rate, low specific gravity, low dielectric constant, high modulus of elasticity and excellent resistance to chemicals make SPS a promising material for a large number of applications in the automotive, electronic and packaging industries.

One of the most fascinating developments in the field of transition metal polymerization during recent years has been the discovery by Sinn and Kaminsky [3] of homogeneous metallocene based coordination polymerization catalysts. Group IVA metallocene catalysts are the most common for olefin polymerization [4]. Since Wilkinson and Fisher explained the discovery of ferrocene structure in 1954 as an iron atom sandwiched between parallel planar cyclopentadienyl groups. The name "metallocene" is now applied generally to similar structures, including those having substituted cyclopentadienyl (Cp) groups such as indene and fluorene, and those with only one Cp group. In contrast with the traditional Ziegler-Natta catalysts, the metallocene ligands allow monomer insertions in a very homogeneous manner with a single active site. Controlling the molecular architecture of polymers is of practical importance both in the development of new polymer or tailor-made polymers and in the control of polymer properties.

Metallocene catalytic systems have been used to polymerize more bulky monomer such as styrene, used with MAO cocatalyst made by the hydrolysis of trimethylaluminium (TMA), form extremely active polymerization catalysts [5]. This activity is higher than activity of conventional Ziegler-Natta catalysts.

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 study involved in the styrene polymerization in the presence of titanocene/ tris(pentafluorophenyl)boron as catalytic system. The various reaction parameters, which may influence the catalytic efficiency of metallocene for olefin polymerization have been investigated. The polystyrene produced were determined the percentage of syndiotacticity. The results of this study will increase our knowledge of the metallocene catalytic polymerization of syndiotactic polystyrene.

## 1.1 The objective of the thesis

To study the influences of titanocene catalysts and boron cocatalyst on catalytic activity and on percentage of syndiotactic polystyrene produced. The variations include types of catalyst and cocatalyst, aluminium / titanium, polymerization temperatures and polymerization time.

## 1.2 The scope of the thesis

- 1.2.1. Performing styrene polymerization using titanocene catalysts and boron compound as a cocatalyst.
- 1.2.2. Examining the effect on polymerization activity.
  - Types of titanocene catalyst and cocatalyst
  - Aluminium/titanium
  - Polymerization temperature
  - Polymerization time
- 1.2.3. Characterizing polystyrene products by using infrared spectroscopy (IR) and differential scanning calorimetry (DSC) and determining the percentage of syndiotacticity.

## CHAPTER II

### THEORY

#### 2.1 Syndiotactic polystyrene

Syndiotactic polystyrene represents an enlightening example of the technological and scientific innovative potential of the homogeneous Ziegler-Natta catalysts following the study of Kaminsky, Brintzinger, and Ewen [6]. In fact, syndiotactic polystyrene (SPS) was unknown until the mid 80's, since it is not achievable by the classical (mainly heterogeneous) catalysts, originally developed by Ziegler and Natta in 1950's. The reason for the commercial interest in this new polymer is that atactic polystyrene has low softening point. On the other hand, high-melting, crystalline isotactic polystyrene, discovered by Natta [7] has too slow crystallization rate, as shown in Figure 2.1. The latter limitation, however, does not pertain to SPS, highly stereoregular polymer with a melting point as high as 270°C.

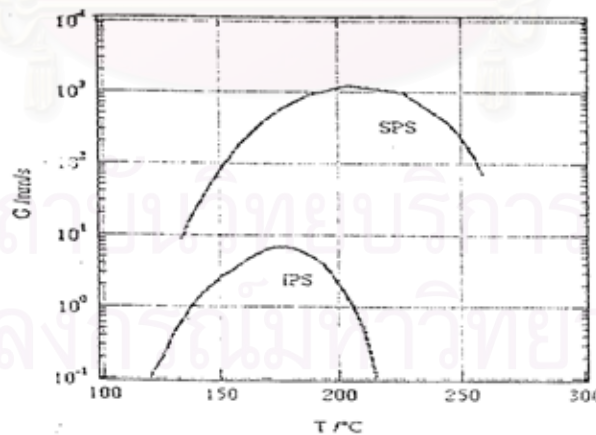


Figure 2.1 Crystallization rate of syndiotactic and isotactic polystyrenes

## 2.2 Polymer tacticity

Stereoregularity arises because of order in the spatial structure of polymer chains. If the backbone of a polymer chain is drawn in a flat zigzag form in the plane of the paper, the patterns shown in Figure 2.2 can be easily envisaged in the case of monosubstituted vinyl units. It should be noted that in (a) all the substituent R groups lie uniformly on the same side of the zigzag plane. Natta called this structure isotactic. In (b) the substituent R groups occupy positions alternatively above and below the backbone plane. Such a structure is termed syndiotactic. In (c) there is no regular arrangement of the substituent R groups and this structure is called atactic.

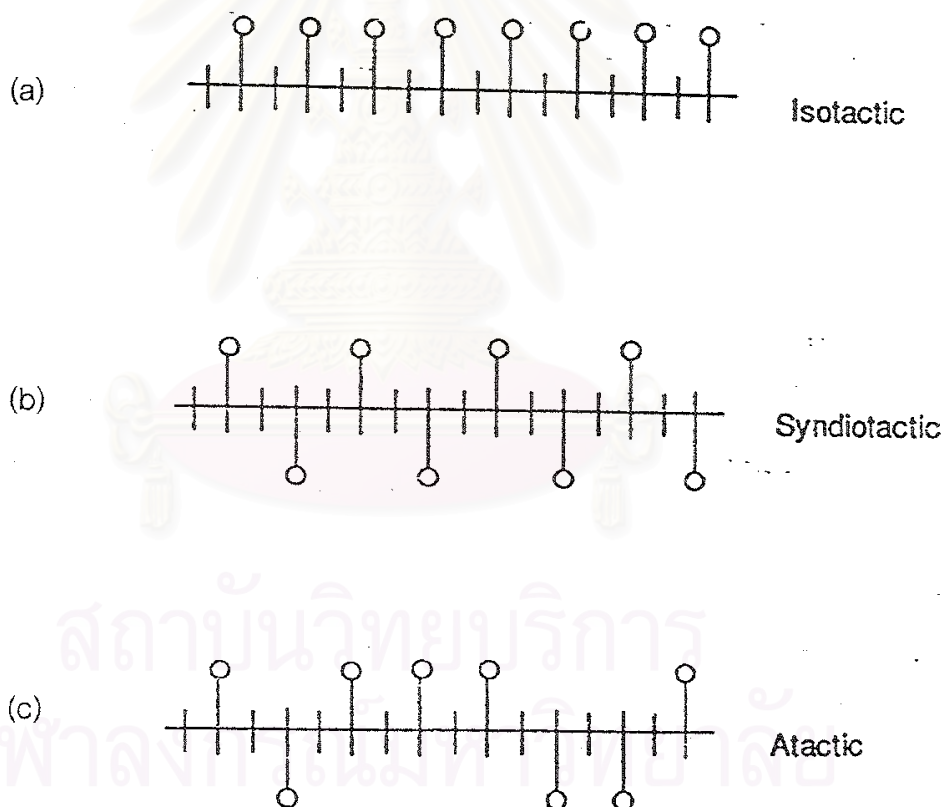


Figure 2.2 Types of olefin polymer tacticity

(○ means positions of the substituent of the R groups)

The regularity or lack of regularity in polymers affects their properties by way of large differences in their abilities to crystallize. Atactic polymers are amorphous (noncrystalline), soft (tacky) material with little or no physical strength. The corresponding isotactic and syndiotactic polymers are usually obtained as highly crystalline materials. The ordered structures are capable of packing into a crystal lattice, while the unordered structures are not. Crystallinity leads to high physical strength and increased solvent and chemical resistance as well as differences in other properties that depend on crystallinity. For example, isotactic polypropylene is a high-melting, strong, crystalline polymer, which finds large-scale uses as both a plastic and fiber. Atactic polypropylene is an amorphous material that finds some use in asphalt blends and formulations for sealants and adhesives but the volumes are very much lower than those for isotactic polypropylene.

## 2.3 Catalytic system

### 2.3.1 Catalyst compounds

Metallocenes are a class of compounds in which cyclopentadienyl or substituted cyclopentadienyl ligands are  $\pi$ -bonded to the metal atom. Examples of metallocene compounds are shown in Figure 2.3.

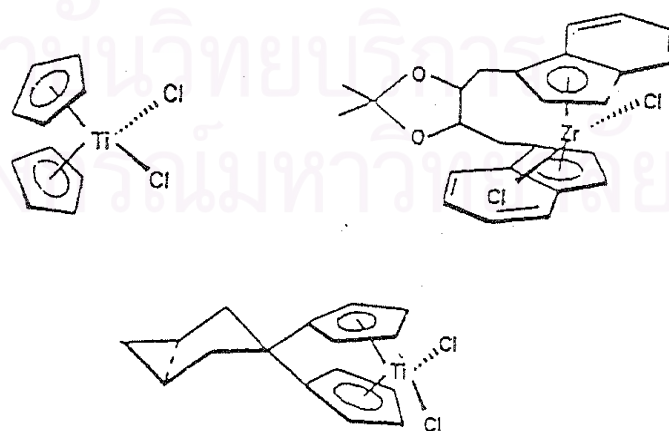


Figure 2.3 Metallocene Compounds

These compounds are becoming an important class of catalyst for the synthesis of organic molecules and polymers. These compounds also have good potential to act as catalysts or catalyst precursors for a number of organic reactions. The discovery of Group 4 metallocene-aluminoxane systems as catalyst for polymerization reactions has opened up a new frontier in the area of organometallic chemistry and polymer synthesis.

Metallocene system is comprised of:

- bicomponent consisting of a metallocene and an aluminoxane, or
- a single component such as  $[\text{Cp}_2\text{MR}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ .

The polymerization of monoolefins by metallocenes in comparison to conventional Ziegler-Natta systems offers a versatile possibility to polymer synthesis. The broader flexibility of electronic and steric variations in the cyclopentadienyl (Cp) type ligands allows the design of catalyst system. Such modifications govern the polyinsertion reaction leading to regio- and stereoregular polyolefins.

Homogeneous catalysts consisting of cyclopentadienyls of titanium with aluminium alkyls were found active for olefin polymerization. A general feature of these homogeneous catalysts is their relatively low activity ( $1 \times 10^3$  to  $4.2 \times 10^3$  gPE / gTi. h. atm). However, the addition of small amount of water was found to increase the activity of these catalyst systems significantly.

Metallocene catalyst systems require a large amount of methylaluminoxane (MAO) for achieving higher productivity. The high cost of the cocatalyst stimulated the search for new families of metallocene, which can perform in the absence of aluminoxane. Representative examples of each category of metallocenes are shown in Table 2.1.

Table 2.1 Representative Examples of Metallocenes

[A] Nonstereorigid metallocenes:

- 1)  $\text{Cp}_2\text{ZrCl}_2$  (M = Ti, Zr, Hf)
- 2)  $\text{Cp}_2\text{ZrR}_2$  (R = Me, Ph,  $\text{CH}_2\text{Ph}$ ,  $\text{CH}_2\text{SiMe}_3$ )
- 3)  $(\text{Ind})_2\text{ZrMe}_2$

[B] Nonstereorigid ring-substituted metallocenes:

- 1)  $(\text{Me}_5\text{C}_5)_2\text{MCl}_2$  (M = Ti, Zr, Hf)
- 2)  $(\text{Me}_5\text{SiCp}_5)_2\text{ZrCl}_2$

[C] Stereorigid metallocenes:

- 1)  $\text{Et}(\text{Ind})_2\text{Zr Cl}_2$
- 2)  $\text{Et}(\text{Ind})_2\text{Zr Me}_2$
- 3)  $\text{Et}[\text{IndH}_4]_2\text{Zr Cl}_2$

[D] Cationic metallocenes:

- 1)  $\text{Cp}_2\text{MR(L)}^+[\text{BPh}_4]^-$  (M = Ti, Zr)
- 2)  $[\text{Et}(\text{Ind})_2\text{ZrMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$
- 3)  $[\text{Cp}_2\text{ZrMe}]^+[(\text{C}_6\text{B}_9\text{H}_{11})_2\text{M}]^-$  (M = Co)

[E] Supported metallocenes:

- 1)  $\text{Al}_2\text{O}_3\text{-Et}[\text{IndH}_4]_2\text{Zr Cl}_2$
- 2)  $\text{MgCl}_2\text{-Cp}_2\text{ZrCl}_2$
- 3)  $\text{SiO}_2\text{-Et}(\text{Ind})_2\text{Zr Cl}_2$

Metallocenes having a single Cp group include bridged and unbridged compounds. Two Cp groups are not required to generate chiral complexes. Monocyclopentadienyl titanium derivatives combined with MAO, afford very efficient catalysts which promote polymerization of styrene to highly syndiotactic polymers. The structures of half-metallocene compounds are shown in Figure 2.4.

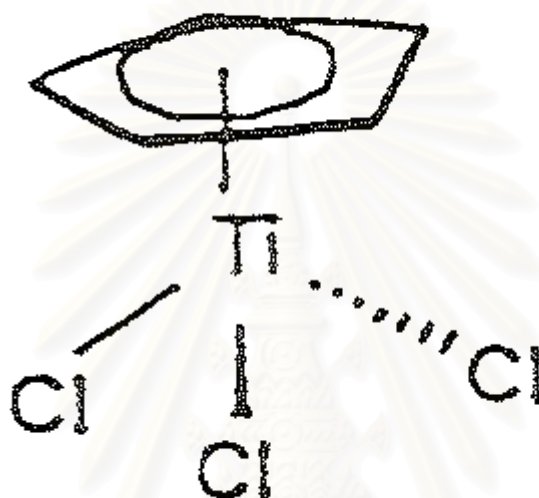


Figure 2.4 Half-metallocene Compounds

## 2.3.2 Cocatalysts

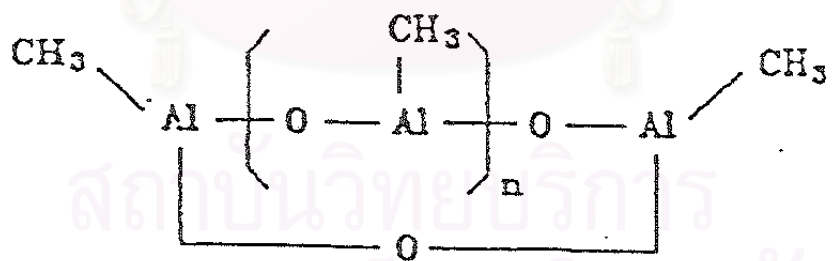
### 2.3.2.1 Aluminoxane (MAO)

Aluminoxanes (MAO) are synthesized by controlled hydrolysis of aluminium alkyls [8], [9]. Simple synthetic routes to methylaluminoxane are not available due to the high reactivity of trimethylaluminium (TMA) with water. Many inorganic hydrated compounds are used as a source of water for preparing aluminoxane from alkyl aluminium [10]. Hydrating compounds such as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$  are employed.

Various physicochemical data, such as compositional analysis, molecular weight determination, mass spectral technique, X-ray powder diffraction, infrared, and NMR spectroscopies, are used for the characterization of aluminoxane [11]. In spite of these measurements, the structures of the alkyl aluminoxane are not unambiguously known. Methylaluminoxane (MAO) is considered to be the oligomeric (cyclic or linear) mixture of  $-\text{AlMeO}-$  units [11] containing possibly clusterlike or supramolecular aggregates. (Figure 2.5)



Linear



Cyclic

$n=4-20$

Figure 2.5 Plausible structures of methylaluminoxane



The structure of MAO as shown in Figure 2.6, contains an unreacted TMA inside the ball.

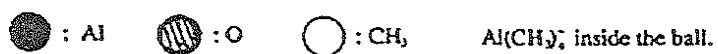
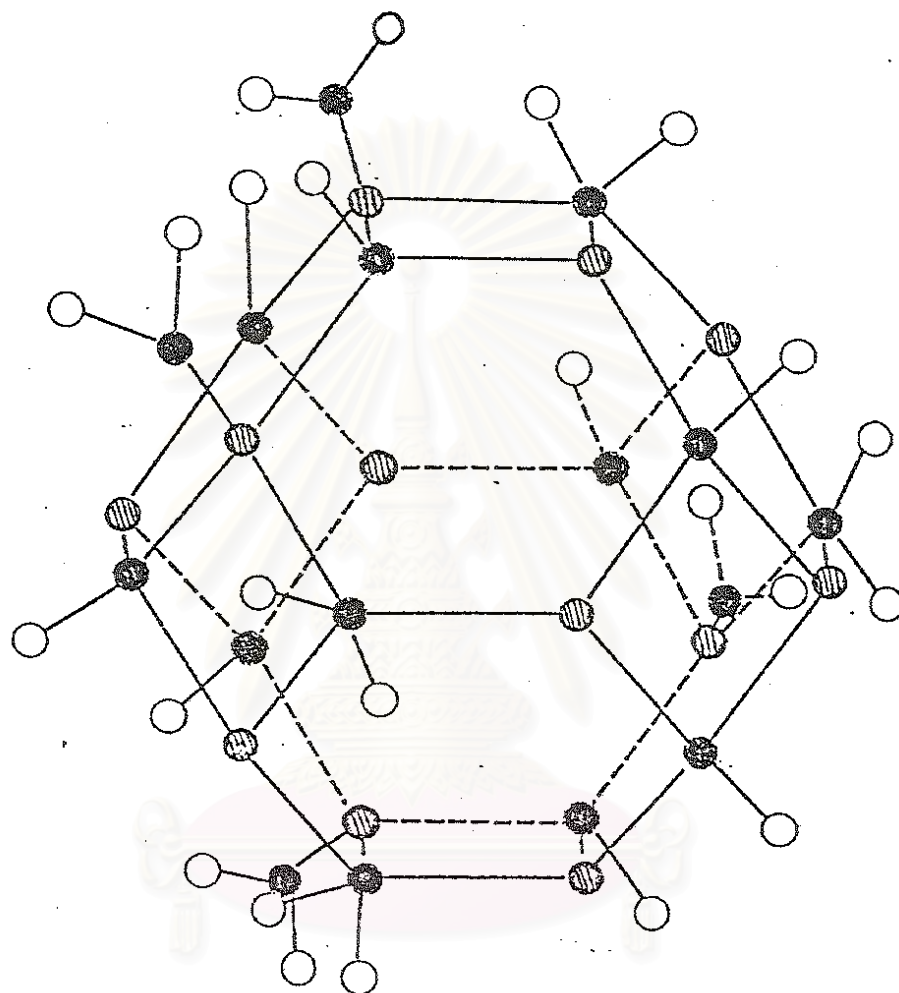


Figure 2.6 Crystalline structure of MAO containing TMA

### 2.3.2.2 Roles of MAO

In metallocene-based catalytic systems, MAO appears to have a combination of the following functions:

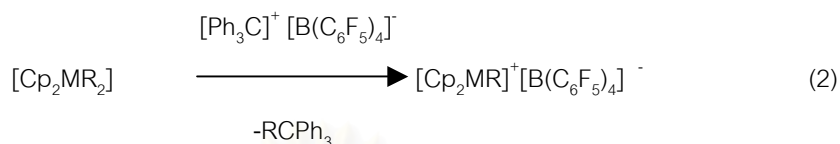
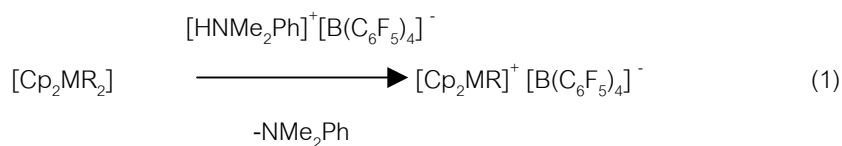
1. MAO alkylates the metallocene and scavenges the impurities.
2. MAO interacts with metallocene to generate cationic metallocene alkyl species.

MAO not only produces the cations but also stabilizes them. Thus, MAO must be a non-coordinating counteranion in order not to compete with an olefin monomer for coordinating to the active transition metal cation and also be chemically stable in order not to react with the very active metallocene catalyst.

### 2.3.2.3 MAO-free cocatalysts

Recently, success has been achieved in isolation and characterization of aluminium-free cationic metallocene compounds. This is due to the new class of activators or co-catalysts based on boranes, which demonstrates polymerization activity when used in combination with metallocene. Pentafluorophenyl borate derivatives have also been used as cocatalysts in SPS polymerization.

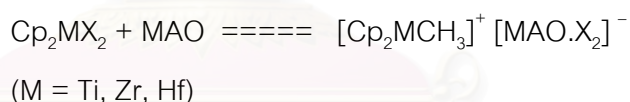
When  $B(C_6F_5)_3$  or its derivatives are used as cocatalyst, the active species can be formed only using an alkyl titanium compound, since no alkylating agents are present in the catalyst formulation. Furthermore Ti(IV) cannot be reduced to titanium (III) or (II). The proposed reactions leading to the formation of active species are the following:



## 2.4 Polymerization mechanisms

### A. Initiation step: active species

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



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  $[\text{Cp}_2\text{MCH}_3]^+$  cation can be advanced for styrene syndiospecific catalysts (Figure 2.7). Ti(IV) is reduced to Ti(III). Reduction is probably caused by the free trimethylaluminium (TMA) contained in MAO, since aluminium alkyls are better reducing agents than aluminoxanes. Methyl radicals formed as a consequence of  $\text{Al}(\text{CH}_3)_3$  oxidation could initiate the radical polymerization of styrene to an atactic polymer, although it is known that primary radicals have short life time and are poor initiators.

Coordination of  $[\text{Cp}_2\text{TiCH}_3]^+$  by a styrene molecule through the vinyl double bond and one aromatic double bond leads to a  $[\text{Cp}_2\text{MCH}_3(\text{styrene})]^+$  complex.

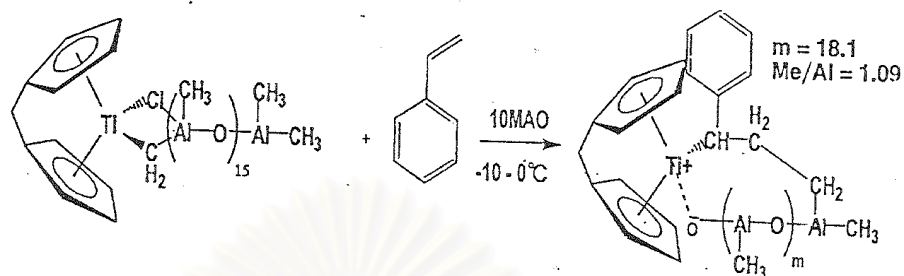


Figure 2.7 Formation of initiating species by  $[\text{Cp}_2\text{MCH}_3]^+/\text{MAO}$ .

Structure of active species formed by  $\text{CpTiX}_3/\text{MAO}$  and active sites on growing polymer chains are shown in Figures 2.8a and 2.8b, respectively.

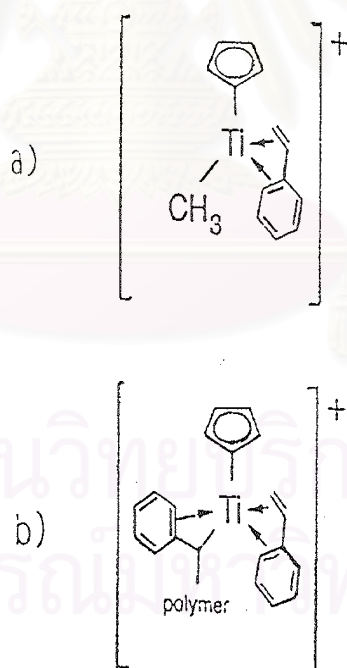


Figure 2.8 a) Structure of active species formed by  $\text{CpTiX}_3/\text{MAO}$

b) Structure of active sites on growing polymer chains

### B. Propagation step

Several experimental studies support the metal-coordinated mechanism. Experiments were carried out by analyzing end-groups, by using labeled isotopes, and by determining polymer configuration by NMR spectroscopy. 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.

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 ( $\text{CH}_3 > \text{H}(\text{styrene}) > \text{halogen}$ ).

By polymerizing deuterium labeled styrene (a mixture of perdeuterostyrene and *cis*-styrene- $\beta$ -d) and analyzing the  $^1\text{H}$  NMR spectrum, the exclusive presence of erythro-disyndiotactic conformer (Figure 2.9) has been detected [12], thus demonstrated that the insertion of styrene on M-C bond proceeds through *cis* opening of the double bond.

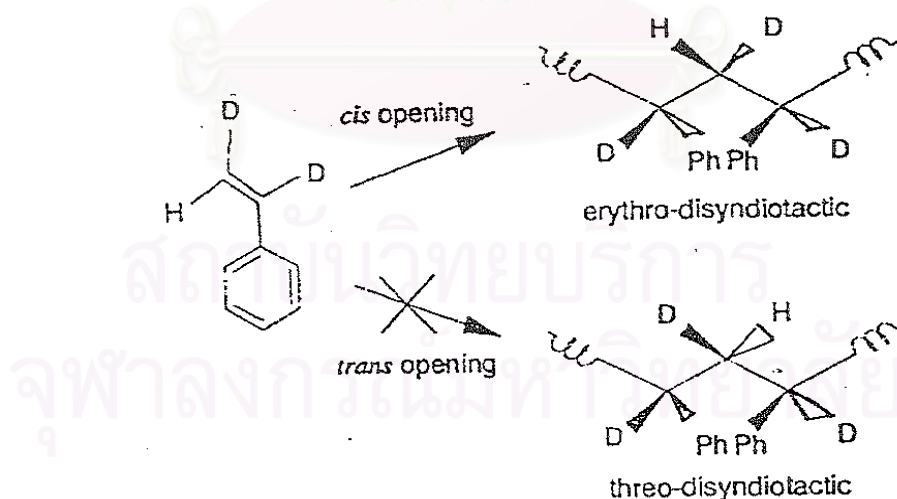
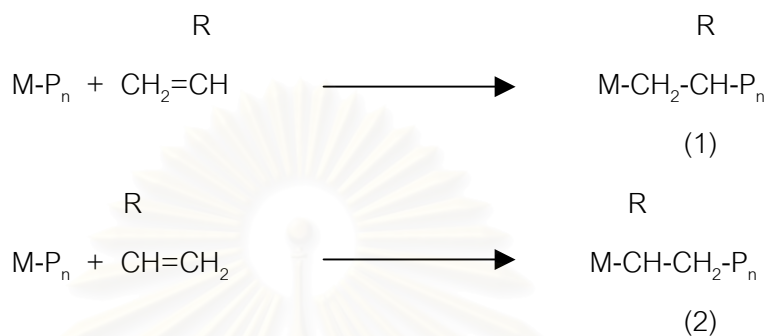


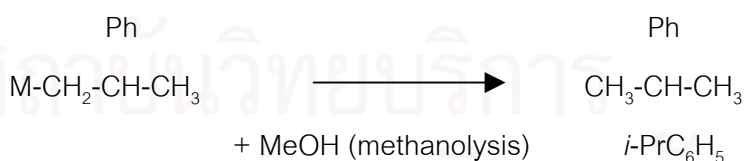
Figure 2.9 Stereochemistry of double bond opening of *cis*-styrene- $\beta$ -d by syndiospecific catalysts for styrene polymerization

The regiochemistry of the insertion can in principle proceed in two ways, either primary (formula 1) or secondary (formula 2).

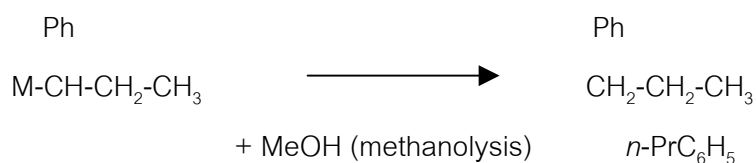


The possible insertion process for styrene into a metal-CH<sub>2</sub> bond, which is presumed to arise from methylation of the titanium by MAO in syndiospecific catalyst systems, may be formulated as primary insertion or secondary insertion shown in Scheme 2.1. *n*-Propylbenzene (*n*-PrC<sub>6</sub>H<sub>5</sub>) was the product after methanolysis of the syndiospecific polymerization reaction mixture. Therefore, it was concluded that the insertion of styrene into the Ti-CH<sub>3</sub> bond proceeds by a secondary (2,1 addition) process.

primary insertion:

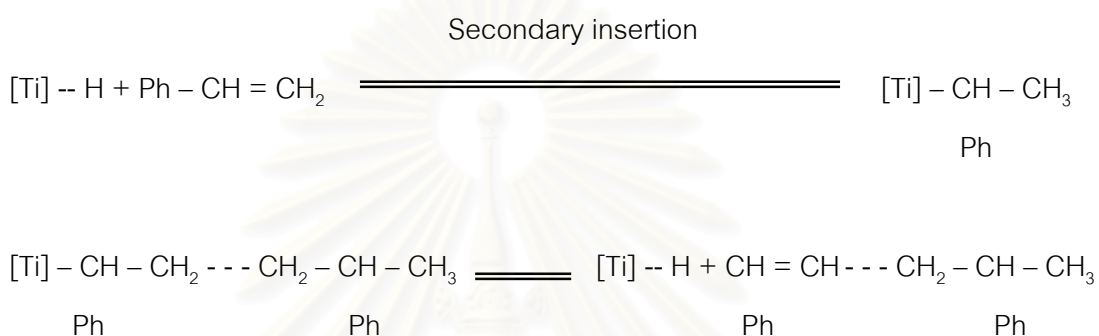


secondary insertion:



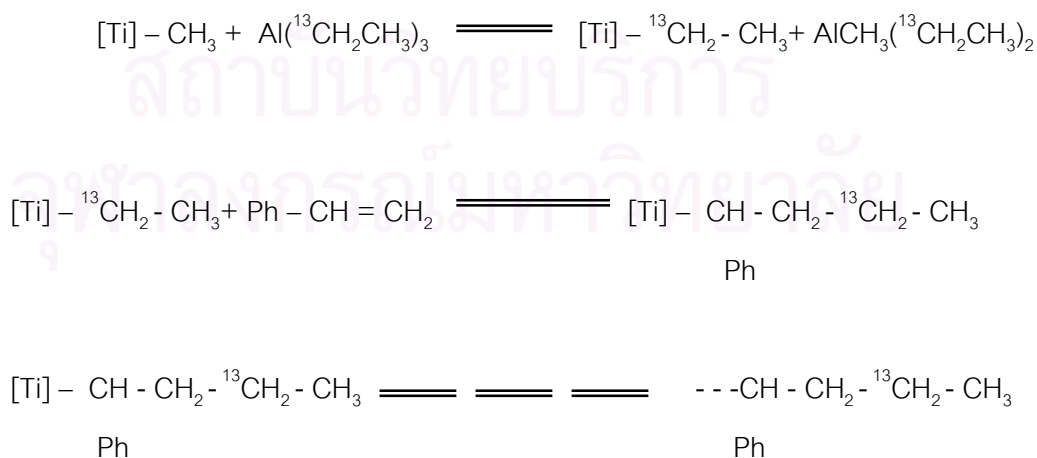
Scheme 2.1 Possible addition modes of a styrene molecule to a metal-CH<sub>2</sub> bonds.

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  $\beta$ -hydrido elimination of growing chain initiated by styrene insertion on a Ti-H bond.



Remarkably,  $^{13}\text{C}$  NMR analysis reveals that SPS bears  $-\text{CH}_2\text{-CHPh-CH}_3$ - and Ph-CH=CH- end groups in equal amounts [13].

Incidentally, SPS containing  $-\text{CH}_2\text{-CHPh-CH}_2\text{-}^{13}\text{CH}_2\text{-CH}_3$  end groups is obtained by adding small amounts of  $^{13}\text{C}$ -enriched triethylaluminium to the system, thus confirming the secondary insertion and the nature of initiating species:



A completely different polymerization mechanism has been put forward. Baird and co-workers [14] focused their consideration on the  $\text{Cp}^*\text{Ti}(\text{CH}_3)_3/\text{B}(\text{C}_6\text{F}_5)_3$  system. They found that the bulky styrene molecule can polymerise as fast as ethylene or propylene, and they advanced the hypothesis that the initiating species  $[\text{Cp}^*\text{Ti}(\text{CH}_3)_2]^+$  behaves also as a carbocationic initiating center. Thus they proposed the carbocationic mechanism depicted in Figure 2.10. 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  $[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$  counterion with the cationic center.

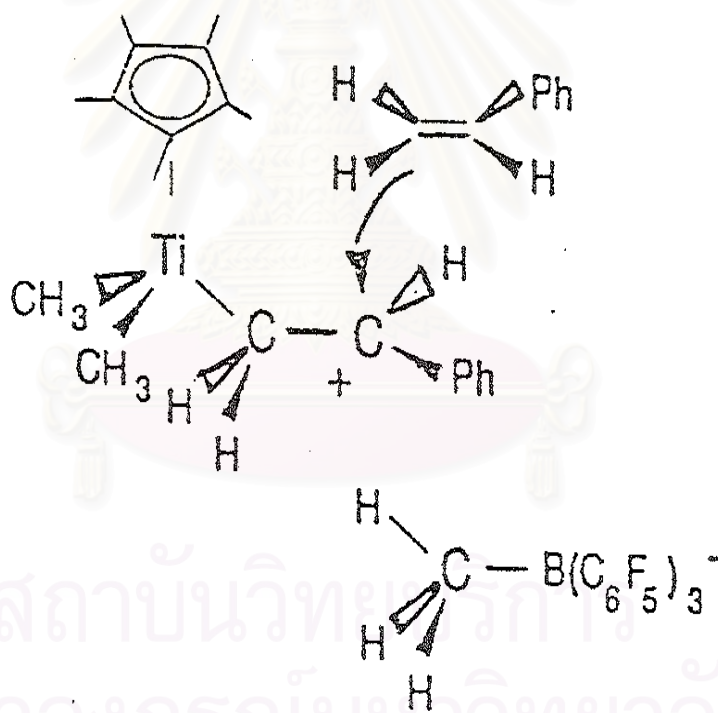


Figure 2.10 Carbocationic mechanism of syndiospecific polymerization of styrene by  $[\text{Cp}^*\text{Ti}(\text{CH}_3)_2][\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]$



### C. 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, while with other initiating systems the molecular weight continues to increase during the entire reaction.

Three factors may contribute to MWD broadening:

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

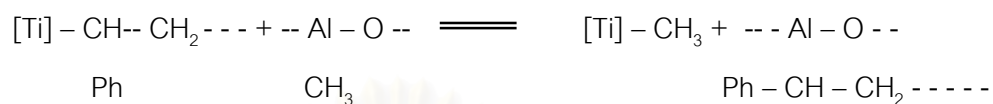
The living growing chain must be “killed” at the end of reaction by adding a proton donor (protonic acids, water, alcohols).

As previously mentioned, strong experimental evidence for  $\beta$ -hydride abstraction exists:

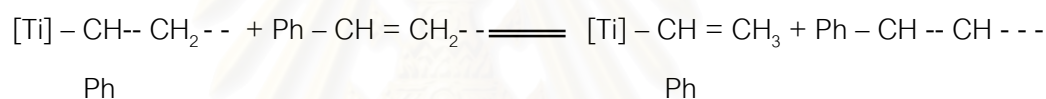


The so formed hydridotitanium species is able to reinitiate a new polymer chain.

In analogy with  $\alpha$ -olefin polymerization with  $\text{Cp}_2\text{MCl}_2/\text{MAO}$  ( $\text{M} = \text{Zr}, \text{Hf}$ ) catalysts, transfer to aluminium would lead to the formation of aluminium-polymer bonds:



Chain transfer with monomer could follow the following paths:



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## CHAPTER III

### LITERATURE REVIEW

Since the discovery of the Ziegler-Natta catalyst systems in the early 1950's, extensive studies concerning the stereospecific polymerization of olefins have been carried out.

#### 3.1 Catalysts for syndiotactic polystyrene

##### 3.1.1 Transition metal compounds

The syndiotacticity of SPS results from the homogeneous coordinative polymerization mechanism. Typically, Group 4 transition metal complexes are utilized with co-catalysts such as methylaluminoxane (MAO) or pentafluorophenyl borate derivatives. Initial evaluation of various titanium compounds with MAO have been published [15] – [18].

The results shown in Table 3.1. indicate that titanium halide compounds (e.g.  $\text{TiCl}_4$ ,  $\text{TiBr}_4$ ,  $\text{CpTiCl}_3$ ,  $\text{Cp}^*\text{TiCl}_3$ ), and even titanium compounds lacking halogen atoms (e.g.  $\text{Ti}(\text{OEt})_4$ ,  $\text{Ti}(\text{OBu})_4$ ,  $\text{Ti}(\text{NET}_2)_4$ ,  $\text{Ti}(\eta^5\text{-C}_6\text{H}_6)_2$  and  $\text{CpTi}(\eta^5\text{-CH}_3\text{C}_6\text{H}_5)_2$ ) can produce SPS. Not only Ti(IV) but also Ti(III) compounds, such as  $\text{CpTi}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2$ , give syndiotactic polystyrene.

Zambelli et al. [18] reported that Ti(II) (e.g.  $\text{Ti}(\eta^5\text{-C}_6\text{H}_6)_2$ ) also could produce SPS, but  $\text{Ti}(\text{bipy})_3$ , formally Ti(0), gave atactic PS. However, Ti(0) arene compounds can produce syndiotactic polystyrene.

Table 3.1 Polymerization of styrene using various metal compounds with MAO

Catalyst	[Al] mol	Conversion (wt%)	Stereospecificity
TiCl <sub>4</sub>	0.04	4.1	syndiotactic
TiBr <sub>4</sub>	0.04	2.1	syndiotactic
Ti(OCH <sub>3</sub> ) <sub>4</sub>	0.04	3.8	syndiotactic
Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	0.04	9.5	syndiotactic
Ti( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Cl <sub>3</sub>	0.015	68.2	syndiotactic
Ti( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Cl <sub>3</sub>	0.03	99.2	syndiotactic
Ti( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub>	0.03	1.0	syndiotactic
Ti[( $\eta^5$ -C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub>	0.03	2.0	syndiotactic
Ti[( $\eta^5$ -C <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> )ClH	0.03	8.8	syndiotactic
Ti( $\eta^5$ -C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	0.025	5.4	syndiotactic
Ti( $\eta^5$ -CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	0.025	5.9	syndiotactic
Ti( $\eta^5$ -(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub>	0.025	5.7	syndiotactic
Ti( $\eta^5$ -(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub>	0.025	6.0	syndiotactic
Ti(acac) <sub>2</sub> Cl <sub>2</sub>	0.04	0.4	syndiotactic
Ti(NEt <sub>2</sub> ) <sub>4</sub>	0.04	0.4	syndiotactic
ZrCl <sub>4</sub>	0.04	0.4	atactic
CpZrCl <sub>3</sub>	0.04	1.3	syndiotactic
Cp <sub>2</sub> ZrCl <sub>2</sub>	0.04	1.3	atactic
Cp <sub>2</sub> HfCl <sub>2</sub>	0.04	0.7	atactic
Cp <sub>2</sub> VCl <sub>2</sub>	0.04	0.7	atactic
Nb(OEt) <sub>5</sub>	0.04	0.2	atactic
Ta(OEt) <sub>5</sub>	0.04	0.1	atactic
Cr(acac) <sub>3</sub>	0.01	1.8 <sup>a</sup>	atactic
Co(acac) <sub>3</sub>	0.01	1.8 <sup>a</sup>	atactic
Ni(acac) <sub>2</sub>	0.01	80.8 <sup>a</sup>	atactic

Polymerization conditions [18]; metal compounds  $5 \times 10^{-5}$  mol, styrene 23 cm<sup>3</sup>, toluene 100 cm<sup>3</sup>, at 50°C for 2 h.

<sup>a</sup> As above condition, except metal compounds  $2.5 \times 10^{-5}$  mol, styrene 50 cm<sup>3</sup>.

### 3.1.2 Half-titanocene compounds

The catalytic activity was found to vary according to ligands on the titanium. Among the SPS producing catalysts, titanocenes with one cyclopentadienyl ligand yield the highest activity for SPS. The polymerization activities of half-titanocene compounds containing trimethoxide have been reported as shown in Table 3.2.

**Table 3.2** Catalyst activities of half-titanocenes containing trimethoxide

Compound	Activity (kg.SPS / gTi)
$\text{CpTi}(\text{OMe})_3$	10
$(\text{Me}_3\text{Si})_2\text{CpTi}(\text{OMe})_3$	25
$\text{Me}_4\text{CpTi}(\text{OMe})_3$	130
$(\text{Me}_3\text{Si})\text{Me}_4\text{CpTi}(\text{OMe})_3$	135
$\text{Cp}^*\text{Ti}(\text{OMe})_3$	200
$\text{EtMe}_4\text{CpTi}(\text{OMe})_3$	210

The data indicate that substituents on the cyclopentadienyl ligands which are electron releasing generally yield higher polymerization activities. This result suggests stabilization of the active site by electron releasing substituents. The polymerization activity in the presence of  $\text{Cp}^*\text{TiR}_3$  compounds (R is alkoxide or chloride ligand) is as follows, in order of decreasing catalytic activity:  $\text{Cp}^*\text{Ti}(\text{O}^i\text{Pr})_3$  and  $\text{Cp}^*\text{Ti}(\text{OMe})_3 > \text{Cp}^*\text{Ti}(\text{OPh})_3 > \text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{CH}_3)_3 > \text{Cp}^*\text{TiCl}_3 > \text{Cp}^*\text{Ti}(\text{O}^t\text{Bu})_3 > \text{Cp}^*\text{Ti}(\text{OC}_3\text{H}_4\text{F}_6)_3$ . 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*-methylphenoxide are all similar in terms of conversion. Recently, Kaminsky showed that the catalytic activity of  $\text{CpTiF}_3$  is better than  $\text{CpTiCl}_3$  [19].








Ready et al. [20] observed that indenyltitanium trichloride,  $\text{IndTiCl}_3$ , is a significantly more active catalyst than  $\text{CpTiCl}_3$ . However, Tomotsu et al. compared the two catalysts and found the catalytic activity of  $\text{IndTiCl}_3$  to be lower than that of  $\text{CpTiCl}_3$  [21]. Difference in polymerization condition may account for the observed differences in catalytic performance. Furthermore, Chien et al. [22] 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.

### 3.1.3 Ansa-titanocene compounds

The polymerization activities for several ansa-titanocene complexes have been reported by Tomotsu et al. [23]. 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. Catalytic activity decreased in the following order:  $\text{CH}_2\text{Cp}_2\text{TiCl}_2 > \text{SiMe}_2\text{Cp}_2\text{TiCl}_2 > \text{Me}_2\text{SiCp}_2\text{TiCl}_2 > (\text{Cp}^*)_2\text{TiCl}_2 > \text{Cp}_2\text{TiCl}_2$  (Table 3.3). The activities of ansa-titanocene complexes are less than those of monocyclopentadienyl complexes.

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Table 3.3 The effect of bite angle of Cp ligand on the catalyst performance

Complex	Bite Angle ( $^{\circ}$ )	Activity (g.SPS/gTi.h)	%SPS	Tacticity (rrr%)
$\text{Cp}_2\text{TiCl}_2$ 	131	21	11	94
$(\text{Cp}^*)_2\text{TiCl}_2$ 	137	57	73	94
$(\text{CH}_2)\text{Cp}_2\text{TiCl}_2$ 	121	573	96	99
$\text{CH}_2\text{Cp}_2\text{TiMe}_2$ 	121	1037	98	99
$\text{Me}_2\text{SiCp}_2\text{TiCl}_2$ 	128	669	98	99
$\text{Me}_2\text{SiCp}_2\text{TiMe}_2$ 	128	957	98	99
$\text{C}_2\text{H}_2(\text{Cp}^*)_2\text{TiCl}_2$ 	131	38	11	95

Condition:  $[\text{Al}]/[\text{Ti}] = 40$ ,  $[\text{Ti}] = 10 \text{ mM}$ , at  $15^{\circ}\text{C}$

### 3.1.4 Zirconocene and ansa-zirconocene catalysts

Zirconocenes produce isotactic polypropylene and atactic polystyrene while titanocenes produce atactic polypropylene and syndiotactic polystyrene.

The ansa-zirconocenes compounds show lower activity and lower stereospecificity than the corresponding ansa-titanocenes. These results are consistent with the suggestion that the catalyst center and the mechanism of syndiospecific polymerization of styrene may be different from those of olefin polymerization in the formation of an active catalyst by the reaction with MAO. In comparison with the Ti compounds, the Zr compounds show lower activity and lower stereospecificity, which could arise from less electrophilic and larger ionic radius of zirconium in comparison with titanium.

### 3.1.5 Other metal complexes

Yang et al. [24] examined rare earth coordination catalysts.  $\text{Nd}(\text{naph})_3/\text{Al}(i\text{-Bu})_3$  catalyst system was found to produce syndiotactic-rich polystyrene. They proposed that the catalytically active species might be an ionic complex, because the addition of  $\text{CCl}_4$  increased the catalytic activity.

On the other hand, there are an increasing number of investigations on heterogeneous supported metallocene catalysts. These catalyst systems can also reduce amount of MAO used.



### 3.1.6 Supported and heterogeneous catalyst

Mixtures of highly isotactic and highly syndiotactic polystyrene were mainly obtained using heterogeneous titanium compounds such as  $\text{TiCl}_3$ ,  $\text{TiCl}_4$  supported on Mg compounds [25]. There would be two types of polymer arising from two different active sites. The syndiotactic polystyrene fraction increases with increasing the molar ratio of Al to Ti. The supported catalyst was washed by toluene and the catalyst performance was examined. The toluene soluble portion of the catalyst was found to produce SPS and the insoluble portion of the catalyst was found to produce IPS.

$\text{Al}_2\text{O}_3$  supported  $\text{CpTiCl}_3$  or  $\text{Cp}^*\text{TiCl}_3$  with TIBA affords mixtures of IPS and SPS. Two possible initiating sites are thought to be present on the catalyst surface. The first one is formed by the reaction of  $\text{CpTiCl}_3$  with surface hydroxyl group of  $\text{Al}_2\text{O}_3$  and is responsible for isospecific polymerization. The second one is formed by the reaction of  $\text{CpTiCl}_3$  with Lewis acid sites and is responsible for syndiospecific polymerization.

## 3.2 Cocatalysts for syndiotactic polystyrene

### 3.2.1 Aluminoxane (MAO)

MAO is an important cocatalyst which activates the Group 4 metallocenes in homogeneous Ziegler-Natta polymerization (Table 3.4). Before the discovery of MAO, the homogeneous Ziegler-Natta catalyst  $\text{Cp}_2\text{TiCl}_2$ , activated with alkylaluminium, yielded atactic polystyrene with low catalytic activity. The use of MAO instead of alkylaluminium raised the catalyst activity by several orders of magnitude. MAO is routinely used for the synthesis of syndiotactic polystyrene [23].

Many researchers are trying to clarify the structure and roles of MAO. The role of MAO for syndiotactic polymerization of styrene was also examined by Miyashita [26]. MAO of different molecular weights were made by the distillation of normal MAO and the effects of molecular weight of MAO on the catalytic activity are examined. They found that  $\text{Me}(\text{Al}(\text{Me})\text{O})_{15}\text{AlMe}_2$  showed the highest activity and a large amount of MAO was required. They also examined the molar electric conductivity of the reacted compound between titanocene and MAO. It was  $0.006 \text{ S cm}^2/\text{mol}$  in toluene and it was concluded that the active site for polymerization must have the structure of zwitterionic Ti cation center.

MAO is known to contain trimethylaluminium (TMA) both in a form coordinated to MAO and as free TMA. Tomotsu et al. [23] examined the effects of TMA in MAO. They found it decreases the catalytic activity for SPS production.



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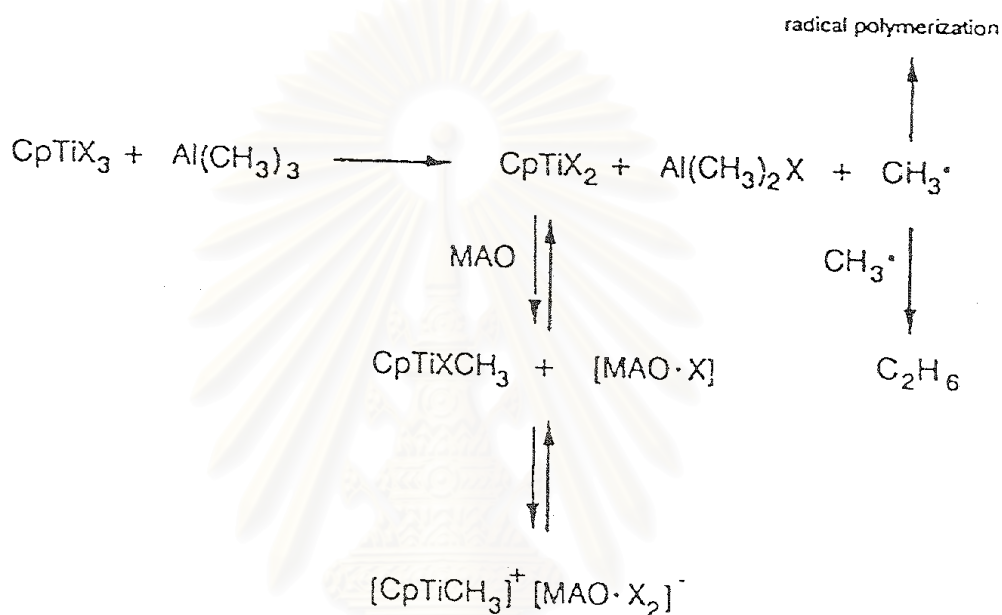
**Table 3.4** Polymerization of styrene using  $\text{CpTiCl}_3$  with various organoaluminium compounds [22].

Organoaluminium Al ( $\text{mol dm}^{-3}$ )	Yield (g)	Conversion (wt%)	Stereospecificity
-	0.8	0.5	atactic
TMA (0.05)	0.1	0.1	atactic
TEA (0.05)	0.2	0.1	atactic
TIBA (0.05)	0.1	0.1	atactic
TMA (0.4) + $\text{H}_2\text{O}$ (0.4)	17.6	10.8	syndiotactic
TEA (0.4) + $\text{H}_2\text{O}$ (0.4)	0.8	0.5	syndiotactic
MAO (0.4)	14.9	9.2	syndiotactic
MAO (0.2) + TMA (0.2)	7.1	4.4	syndiotactic
MAO (0.2) + TEA (0.2)	0.3	0.2	syndiotactic
MAO (0.2) + TIBA (0.2)	15.5	9.5	syndiotactic
CIAO (0.4)	94.7	100	atactic
MAO ( $M_w < 500$ ) (0.4)	Trace	-	syndiotactic
MAO ( $M_w > 500$ ) (0.4)	14.9	9.2	syndiotactic

$\text{CpTiCl}_3$   $5 \times 10^{-4}$   $\text{mol dm}^{-3}$ , toluene  $100 \text{ cm}^3$ , styrene 8.7 M,  $50^\circ\text{C}$ , 2h

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Cam and Giannini et al. [27] concluded that  $\text{Cp}_2\text{ZrCl}_2$  is monoalkylated to give  $\text{Cp}_2\text{Zr}(\text{Me})\text{Cl}$  by TMA contained in MAO and that the Cl of the resulting  $\text{Cp}_2\text{Zr}(\text{Me})\text{Cl}$  is removed by MAO to form active cation,  $\text{Cp}_2\text{Zr}(\text{Me})^+$ . The results described above might give a mechanism as shown in Scheme 3.1 for the formation of active cation species.

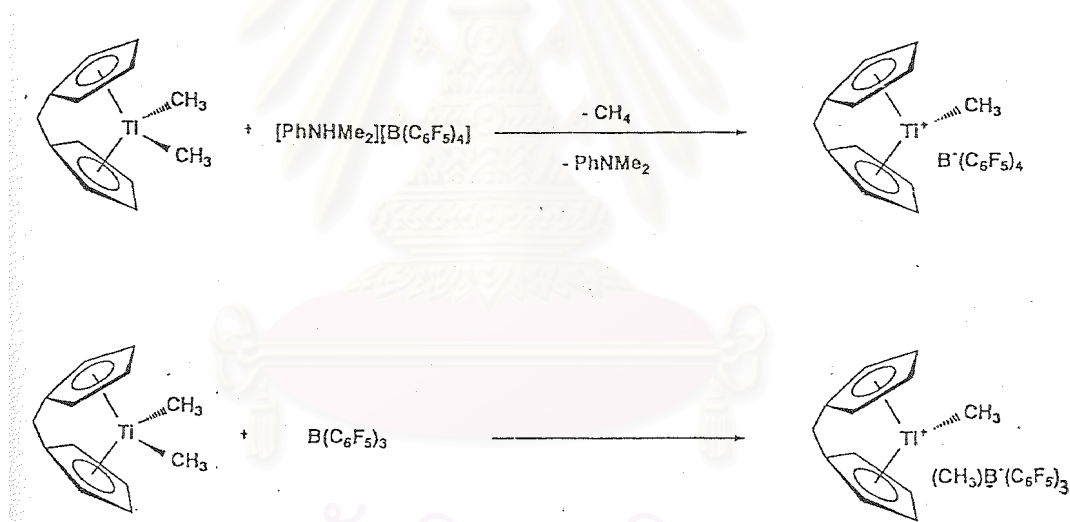


Scheme 3.1 Formation of cationic species by MAO

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### 3.2.2 Boron compounds (MAO-Free cocatalysts)

The reaction of  $\text{CH}_2(\text{Cp})_2\text{Ti}(\text{Me})_2$  in equimolar mixture with  $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (dimethylanilinium tetrakis(pentafluorophenyl)borate) or  $\text{B}(\text{C}_6\text{F}_5)_3$  (tris(pentafluorophenyl)borane) has been examined by Miyashita [28]. They isolated two types of methylene bis(cyclopentadienyl)titanium ion complexes, which are  $[\text{CH}_2(\text{Cp})_2\text{TiMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  and  $[\text{CH}_2(\text{Cp})_2\text{TiMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  respectively. These complexes were active in the polymerization of styrene but only atactic polystyrene was formed.



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Scheme 3.2 Reactions between Ti compounds and boron compounds

Treatment of  $\text{Cp}^*\text{TiMe}_3$  with the highly electrophilic borane  $\text{B}(\text{C}_6\text{F}_5)_3$  results in the formation of the methyl-bridge complex  $\text{Cp}^*\text{TiMe}_2(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  [29], which is a good source in solution of the cationic species  $[\text{Cp}^*\text{TiMe}_2]^+$ . The latter is a very effective carbocationic initiator for polymerization of styrene to atactic polystyrene and, in aromatic media at temperature  $\geq 0^\circ\text{C}$ , of styrene to syndiotactic polystyrene.

Pellecchia and co workers [30] observed the catalytic activity of  $\text{Cp}^*\text{TiMe}_3$  with  $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  was lower than that with  $\text{B}(\text{C}_6\text{F}_5)_3$ . They proposed that, free amine coordinates to the active site and interferes with the polymerization reaction.

The reaction of  $\text{Cp}^*\text{Ti}(\text{CH}_2\text{SiMe}_3)_3$  with 1 equivalent of  $\text{B}(\text{C}_6\text{F}_5)_3$  [31] was almost quantitative to give the cationic compound  $[\text{B}(\text{CH}_2\text{SiMe}_3)(\text{C}_6\text{F}_5)_3]^+$ , which was readily identified spectroscopically. This complex has also been found to be active for the syndiospecific polymerization of styrene, producing over 95% syndiotactic PS at an activity of  $0.86 \times 10^7$  g of PS / (mol of Ti. mol of styrene. h). Both activity and syndiospecificity significantly increase when triisobutylaluminium (TIBA) was used to scavenge the polymerization system. The electron-withdrawing substituents on the aromatic solvent ring could increase the activity and syndiotactic polystyrene yields, although toluene is the polymerization medium of best choice in the styrene polymerization.

The cationic compound  $[(\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{Ph})\text{TiMe}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  prepared in situ by reacting  $(\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{Ph})\text{TiMe}_3$  with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  [32], has also been active for the syndiospecific polymerization of styrene. Using the pentafluorophenyl borate with a small amount of TIBA as a cocatalyst for polymerization of styrene to SPS was examined. TIBA was found to be the scavenger of impurities in styrene and to increase the syndiotacticity of polymer.

### 3.2.3 Molar ratio of Al/Ti

Newman and Malanga [23] have synthesized  $\text{Cp}^*\text{Ti}(\text{OMe})_2$ , the titanium(III) metallocene, via reduction of  $\text{Cp}^*\text{Ti}(\text{OMe})_3$  with *t*-butyllithium and characterized the complex via X-ray crystallography. Table 3.5 shows a comparison of the percent conversion for  $\text{Cp}^*\text{Ti}(\text{OMe})_2$  and  $\text{Cp}^*\text{Ti}(\text{OMe})_3$  with various MAO ratios in the MAO activated system. At very low MAO ratio, both catalysts yield very little SPS. However,  $\text{Cp}^*\text{Ti}(\text{OMe})_2$  gives a higher conversion than  $\text{Cp}^*\text{Ti}(\text{OMe})_3$ .

**Table 3.5** Percent conversion to SPS with various MAO contents.

MAO/Ti	% Conversion	
	$\text{Cp}^*\text{Ti}(\text{OMe})_2$	$\text{Cp}^*\text{Ti}(\text{OMe})_3$
25	10	2
50	32	22
100	55	33
200	63	41

A comparison of percent conversion for  $\text{Cp}^*\text{Ti}(\text{OMe})_2$  and  $\text{Cp}^*\text{Ti}(\text{OMe})_3$  with the addition of TIBA in the MAO activated system is shown in Table 3.6. The trend of increasing conversion with TIBA content is observed for  $\text{Cp}^*\text{Ti}(\text{OMe})_3$  and relatively low conversion is observed without TIBA. However, for  $\text{Cp}^*\text{Ti}(\text{OMe})_2$ , high conversion is obtained even without TIBA and the conversion is higher than for  $\text{Cp}^*\text{Ti}(\text{OMe})_3$ . This suggests the function of aluminium alkyl is reduction of 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.

The effect of the molar ratio of MAO to Ti on the catalytic activity in the case of  $\text{CpTiCl}_3$  with a MAO cocatalyst system was investigated [23]. The activity increases with an increasing molar ratio of MAO to Ti.



Table 3.6 Percent conversion to SPS with various TIBA contents.

TIBA / Ti	% Conversion	
	Cp*Ti(OMe) <sub>2</sub>	Cp*Ti(OMe) <sub>3</sub>
0	58	30
6	62	47
10	64	53
50	66	62

### 3.2.4 Active species

The nature and formation of the true active catalytic species are not yet fully elucidated. In  $\alpha$ -olefins polymerization, it is generally accepted that homogeneous catalysts based on Group IV metallocene with MAO consist of cationic complexes.

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. Some evidence reported in the literature suggests that the active species promoting syndiotactic polymerization of styrene is a cationic Ti(III) complex bearing a  $\eta^5$  anionic ligand (Cp or Cp\*) and the growing polymer chain [30].

Chien et al. [33] reported that the titanium oxidation state for active catalytic species was Ti(III) both in CpTiX<sub>3</sub>/MAO and TiX<sub>4</sub>/MAO. They found that in Ti(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>/MAO system, titanium had a distribution of oxidation states, with Ti(IV):Ti(III):Ti(II) about 53 : 27 : 20. The addition of styrene caused a change in this ratio to 36 : 48 : 16. The ESR spectra are also consistent with the almost quantitative formation of such hydrotitanium (III) complexes.



Zucchini et al. [34] also found that the titanium had oxidation state +3. ESR measurements revealed the formation of an unidentified new Ti(III) species, possibly containing a Ti-H bond, suggesting a certain degree of  $\beta$ -hydrogen abstraction of the bonded polymer.

Titanium compounds are most likely reduced before the active site formation. Alkylaluminium compounds are both alkylating and reducing reagents for titanium. The effects of reductants on the catalytic activity were evaluated and the data are summarized in Table 3.7 [21]. Very strong reducing reagents like  $\text{Al}(\text{CH}_3)_3$ ,  $\text{Al}(\text{C}_3\text{H}_5)_3$  reduce the catalytic activity. In this case, the titanium compound may be reduced to Ti(II) or Ti(I). The catalytic activity is increased by the addition of TIBA, which reduces the molecular weight of the polymer. TIBA most likely reacts with the titanium compound to reduce it from Ti(IV) to Ti(III). Moreover, TIBA reacts with metal-alkyl bonds and, therefore, acts as a chain transfer reagent during polymerization.

**Table 3.7** Effect of reductants on styrene polymerization

Reagent	Relative activity	$M_w$
None	100	750,000
$\text{Al}(\text{CH}_3)_3$	13	64,000
$\text{Al}(\text{C}_3\text{H}_5)_3$	23	84,000
$\text{Al}(n\text{-C}_4\text{H}_9)_3$	76	570,000
$\text{Al}(i\text{-C}_4\text{H}_9)_3$	560	580,000
$\text{Al}(n\text{-C}_8\text{H}_{17})_3$	100	670,000
$\text{Al}(\text{C}_2\text{H}_5)_2(\text{OC}_2\text{H}_5)$	140	870,000
$\text{Zn}(\text{C}_2\text{H}_5)_2$	48	130,000

## CHAPTER IV

### EXPERIMENT

In the present study of the styrene polymerization on half-titanocenes and boron catalytic system, the experiments were divided into three parts:

1. Catalyst and cocatalyst preparation
2. Styrene polymerization with the prepared catalysts
3. Characterization of polystyrene products

The details of the experiments are explained in the following sections.

#### 4.1 Chemicals

The chemicals used in this experiment were from different suppliers as follows:

Chemicals	Suppliers
Trimethylaluminium, TMA 2M in toluene	Nippon Aluminium Alkyls Ltd., Japan
Triisobutylaluminium, TiBA	Donated from Thai Polyethylene Ltd., Thailand
Extra pure toluene	Merck, Germany
Cyclopentadienyltitanium trichloride, CpTiCl <sub>3</sub>	Fluka Chemie A.G., Switzerland
Pentamethyl(cyclopentadienyltitanium) trichloride, Cp*TiCl <sub>3</sub>	Donated from Japan Advanced Institute of Science and Technology, Japan
Tris(pentafluorophenyl)boron, B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Fluka Chemie A.G., Switzerland
Triphenylcarbenium tetrapentafluorophenylborate, [Ph <sub>3</sub> C][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	Donated from Japan Advanced Institute of Science and Technology, Japan
Monomer grade styrene	Fluka Chemie A.G., Switzerland
High purity nitrogen gas	Thai Industrial Gas Co., Ltd., Thailand
Methyl ethyl ketone, MEK	Fluka Chemie A.G., Switzerland

Many of the reagents encountered in synthetic inorganic and metalorganic chemistry in this work react sufficiently violently with water and ignite spontaneously in air (by reaction with oxygen and/or moisture), these chemicals can be handled safely using inert-atmosphere techniques such as Schlenk and glove bag techniques. Also, the chemicals and solvents were dried before use as following methods:

1. High purity nitrogen gas was dried by passing through three columns packed with molecular sieve, NaOH and  $P_2O_5$ , respectively.
2. Styrene monomer was treated over  $CaH_2$  and distilled under reduced pressure. The distillation still is shown in Figure 4.1.

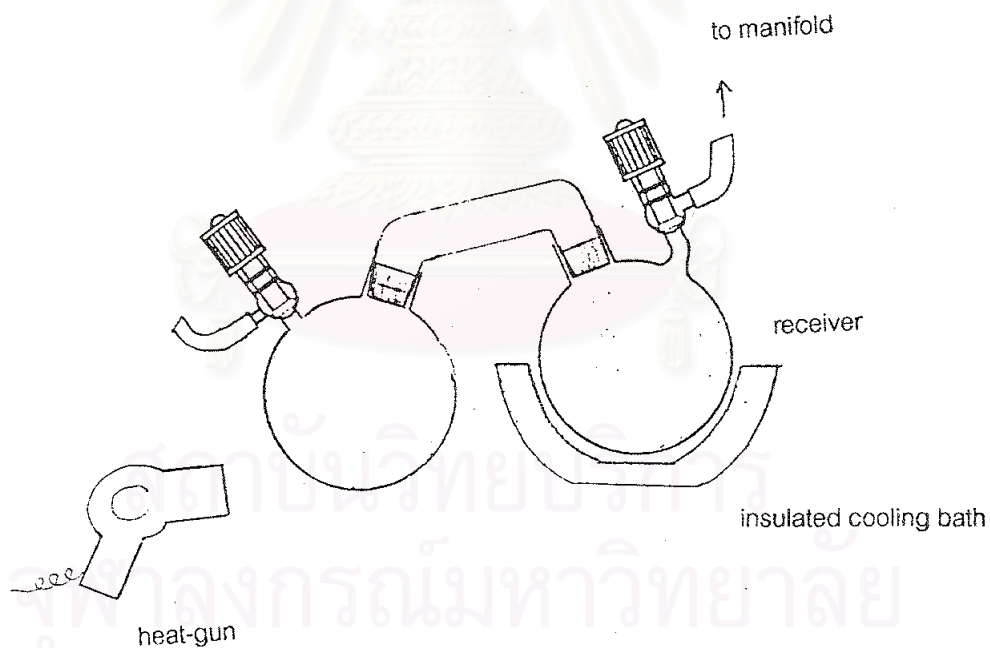
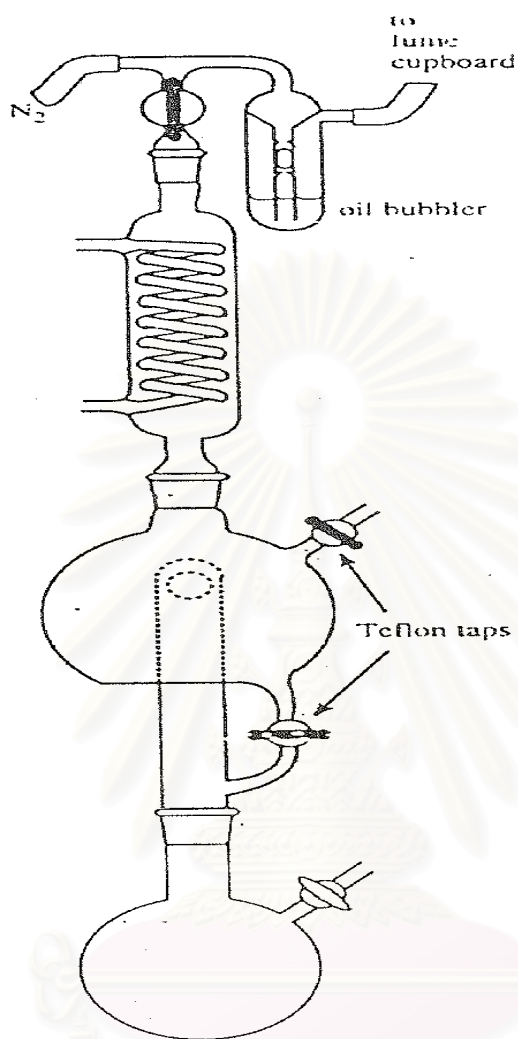


Figure 4.1 Reduced pressure distillation

3. Toluene was refluxed over sodium and benzophenone, and distilled before use by setting the still as shown in Figure 4.2.



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Figure 4.2 Solvent distillation

## 4.2 Equipment

### 1. Schlenk line

Schlenk line consists of nitrogen and vacuum manifold is equipped with the solvent trap and pump, respectively. The nitrogen line is connected to the trap and the oil bubbler that contain enough oil to provide a seal from the atmosphere when nitrogen line is evacuated. The Schlenk line is shown in Figure 4.3.

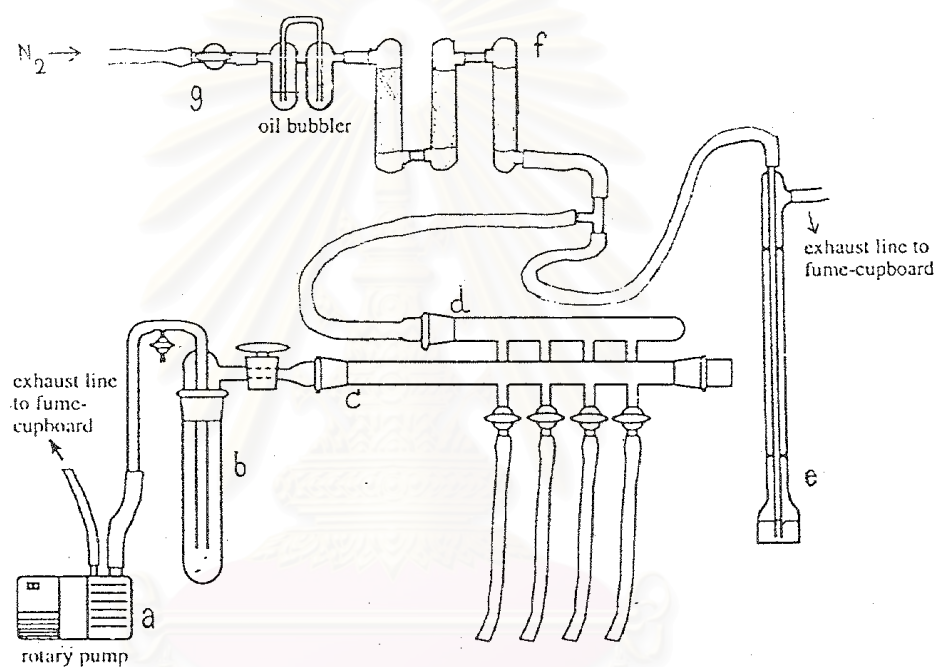


Figure 4.3 Schlenk line

- a. Vacuum pump
- b. Cold trap
- c. Vacuum manifold
- d. Nitrogen gas manifold
- e. Oil bubbler
- f. Drying columns
- g. Needle valve

## 2. Schlenk flask

A flask with a side-arm for use with inert gas was described by Walter Schlenk in 1913. 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 4.4.

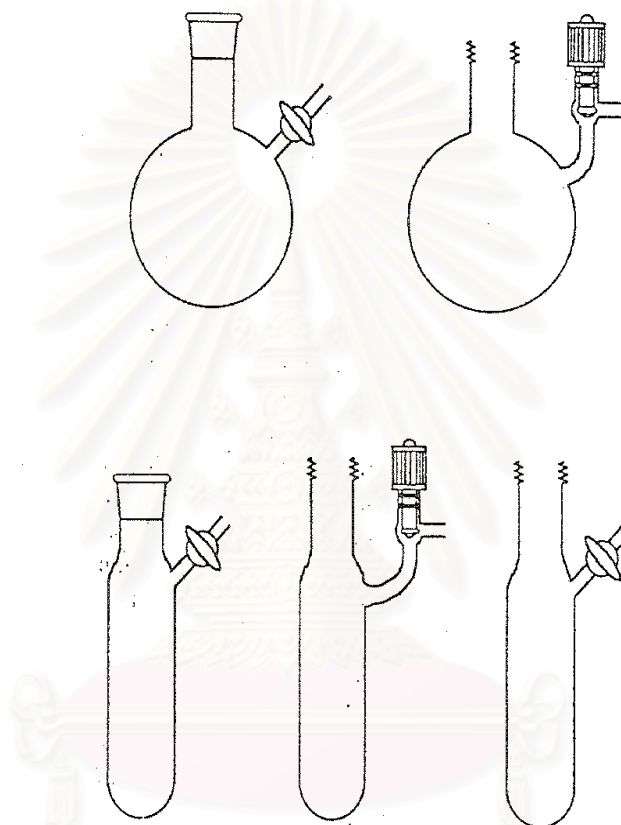


Figure 4.4 Round-bottomed and tube designs for Schlenk flasks incorporating ground-glass or screw joints and greased or greaseless taps.

3. Vacuum pump

A vacuum pump with approximate  $10^{-3}$  mmHg was used.

4. Inert gas supply

Nitrogen gas was used. It is dried by passing through drying columns packed with molecular sieves, NaOH and  $P_2O_5$ , respectively.

5. Glove bag

Glove bag is a moderate-volume gas-tight container from which air and/or moisture are excluded. The glove bag has a way to connect with Schlenk line, which can be evacuated and then filled with nitrogen. The glove bag is shown in Figure 4.5.

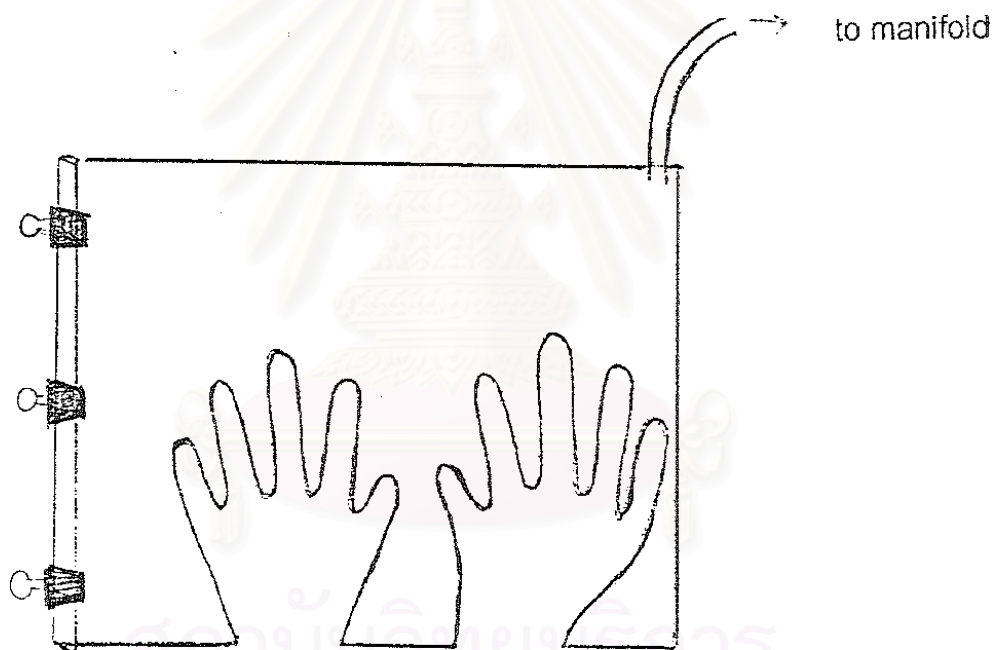


Figure 4.5 Glove bag

## 6. Soxhlet extractor

Soxhlet extractor was used for syndiotactic content determination (Figure 4.6). The obtained polystyrene was extracted with boiling 2-butanone or methyl ethyl ketone (MEK) to give syndiotactic (insoluble) and atactic (soluble) polystyrenes [35].

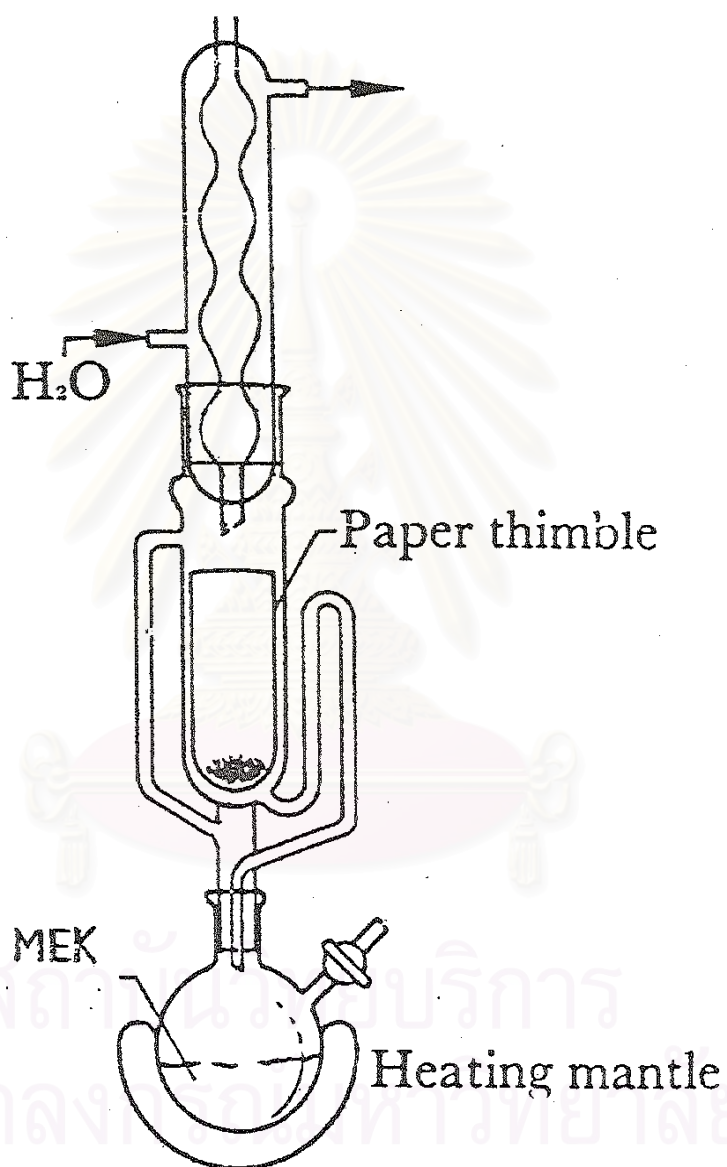


Figure 4.6 Soxhlet-type extractor



#### 7. Heating bath

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

#### 8. Syringes and needles

The syringes used in the experiment had a volume of 50, 10, 5, 3, 2, 1 cm<sup>3</sup>. The needles were No. 15, 20 and 22.

### 4.3 Characterization instruments

The instruments used to characterize the catalyst and polystyrene products were specified in the following:

#### 1. Fourier Transformed Infrared Spectroscopy (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 2000 cm<sup>-1</sup>. The pallet samples were prepared by pressing polystyrene powder with KBr.

#### 2. Differential Scanning Calorimetry (DSC)

The melting temperature ( $T_m$ ) of the polystyrene products 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°C/min. in the temperature range of 25-300°C. The heating cycle was run twice. The first scan, samples were heated and then cooled down to room temperature. 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.

### 3. Gel permeation chromatography (GPC)

Molecular weight determination of the produced polystyrene was made at 30°C using tetrahydrofuran as solvent at the flow rate of 1.0 ml/min by a Waters 150-CV GPC with PLgel 10  $\mu\text{m}$  mixed B 2 columns at National Metal and Materials Technology Center (MTEC), National Science and Technology Department Agency.

## 4.4 Procedures

All operations were performed under nitrogen atmosphere by using Schlenk line and glove bag.

### 4.4.1 Catalyst and cocatalyst preparation

1.  $\text{CpTiCl}_3$  or  $\text{Cp}^*\text{TiCl}_3$  approximately 70 mg. was stirred in 25  $\text{cm}^3$  of toluene under nitrogen atmosphere until dissolved.

2.  $\text{B}(\text{C}_6\text{F}_5)_3$  0.32  $\text{cm}^3$  was measured by a syringe, stirred in 100  $\text{cm}^3$  of toluene under nitrogen atmosphere until dissolved.

3.  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  approximately 40 mg., was stirred in 20  $\text{cm}^3$  of toluene under nitrogen atmosphere until dissolved.

4. A predetermined amount of TiBA was dissolved in toluene under nitrogen atmosphere to get 2 M concentration.

#### 4.4.2 Polymerization of styrene

The polymerizations were performed under nitrogen atmosphere by using Schlenk line. A 100-cm<sup>3</sup> Schlenk flask equipped with a magnetic stirring bar was charged with a measured amount of toluene by calculating the total volume of reaction mixture to be 25 cm<sup>3</sup>. A prescribed amount of catalyst (CpTiCl<sub>3</sub> or Cp\*TiCl<sub>3</sub>), 1 equivalent of boron compound (B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]) and aluminium compound (TMA or TiBA), were next measured by a syringe and were added into the flask, respectively. The catalyst mixture was preactivated with stirring for 15 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 cm<sup>3</sup> was then introduced by a syringe with rapid stirring under a nitrogen atmosphere, and the reaction mixture was stirred and polymerization started at the desired temperature. After a measured time interval, the polymerization was terminated by the addition of 20 cm<sup>3</sup> of 10% HCl in methanol. The polymer was collected by suction filtration and washed 3 times with methanol, dried at 100°C in the oven to remove solvent and monomer entrapped in crude materials. Each polymerization was repeated twice to ensure the reproducibility.

The term of catalytic activity in this work is expressed in unit of grams of polystyrene produced by 1 mole of titanium catalyst and styrene during 1 hour of polymerization time (g PS/Ti.S.h).

The various effects on the styrene polymerization with CpTiCl<sub>3</sub> catalyst and optimized conditions were investigated. After obtaining optimum conditions, the productions of polystyrene from Cp\*TiCl<sub>3</sub> catalyst with different boron and aluminium compounds were investigated.

#### 4.4.2.1. The effect of polymerization temperatures

The styrene polymerization with 0.35 mM of  $\text{CpTiCl}_3$  was investigated by varying polymerization temperatures from 35 to 80°C. The reaction time was 5 hours and the molar ratio of Al/Ti was set at 500.

#### 4.4.2.2. The effect of reaction time

Styrene polymerization was performed by varying reaction time from 2 to 20 hours and at the optimum temperature obtained from Section 4.4.2.1.

#### 4.4.2.3. The effect of Al/Ti molar ratio

The styrene polymerization was performed by varying molar ratio of Al/Ti from 125 to 1000, using the optimum reaction temperature from Section 4.4.2.1.

#### 4.4.2.4. The effect of non-preactivation of catalyst

To investigate the non-preactivated catalyst, the polymerization was performed without the preactivation step.

#### 4.4.2.5. The performance of $\text{Cp}^*\text{TiCl}_3$

The styrene polymerization was performed using  $\text{Cp}^*\text{TiCl}_3$  in place of  $\text{CpTiCl}_3$ .

#### 4.4.2.6. The effect of boron and aluminium compounds

The styrene polymerization with  $\text{Cp}^*\text{TiCl}_3$  was investigated by changing types of boron ( $\text{B}(\text{C}_6\text{F}_5)_3$  or  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ) and aluminium compounds (TMA or TiBA).

### 4.4.3 Polystyrene characterization

#### 4.4.3.1. Fourier Transformed Infrared Spectroscopy (FT-IR)

The FT-IR technique was used to characterize polymer structure. Comparison of 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.

#### 4.4.3.2. Differential Scanning Calorimeter (DSC)

Differential Scanning Calorimeter (DSC) was used to measure the thermal properties especially melting temperature ( $T_m$ ).

#### 4.4.3.3. Syndiotacticity

The syndiotacticity content of polystyrene can be determined by extraction of insoluble polystyrene in 2-butanone. About 1 gram of polystyrene was weighed in a cellulose thimble and extracted for 5 hours. The residual polystyrene was dried at 100°C until weight constant. The insoluble fraction multiplied by 100 was taken as %SPS.

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

From the best performance catalytic systems obtained from the previous sections, %syndiotacticity of polystyrene was determined, by varying the Al/Ti molar ratio: 50, 100 and 300.

#### 4.4.3.4. Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC), which employed the principle of size exclusion chromatography (SEC) was used to determine molecular weight (Mw) and molecular weight distribution (MWD). Toluene was used as a solvent for atactic polystyrene at 30°C while 1,2,4-trichlorobenzene was used for syndiotactic polystyrene at 135°C [53].



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## CHAPTER V

### RESULTS AND DISCUSSION

#### 5.1 Styrene polymerization

##### 5.1.1 The effect of polymerization temperature on CpTiCl<sub>3</sub> catalyst

The effect of the polymerization temperature was investigated; 35, 65 and 80°C by using 0.35 mM of CpTiCl<sub>3</sub> catalyst with one equivalent of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. The results were shown in Table 5.1 and Figure 5.1.

**Table 5.1** Styrene polymerization catalyzed by CpTiCl<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TMA at various temperatures

Temperatur e (°C)	Yield(g)		Average yield (g)	Activity (gPS/Ti.S.h)	%conversion
	#1	#2			
35	0.1530	0.1553	0.1542	40,566	1.70
65	0.6676	0.5228	0.5952	156,632	6.57
80	0.4123	0.4977	0.4550	119,404	5.02

Polymerization conditions: t, 5h; Al /Ti, 500; total volume, 25 cm<sup>3</sup>; [Ti], 0.35 mM

Activity in unit of grams of polymer / (mole of Ti. mole of styrene. hour)



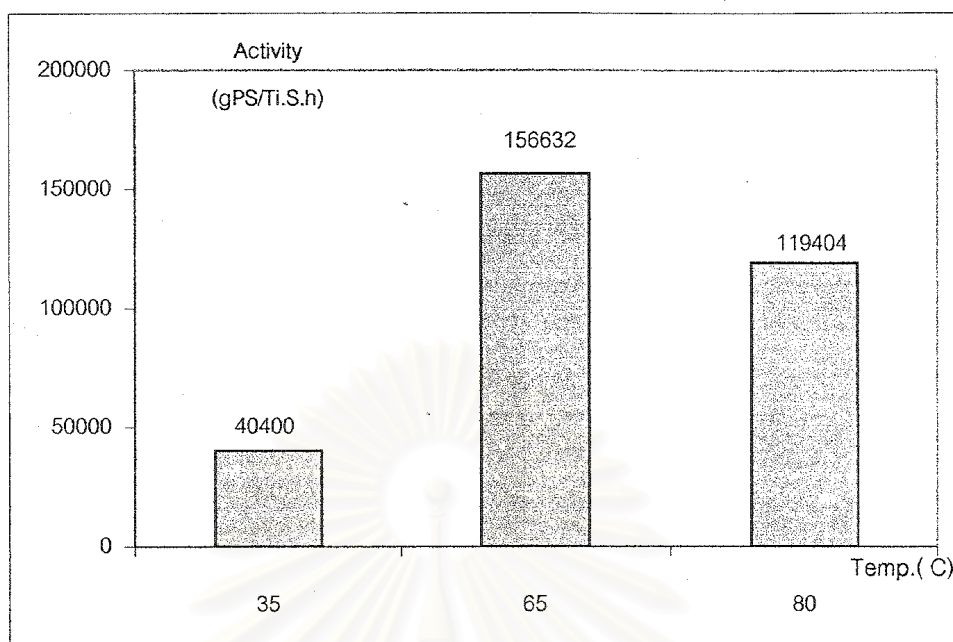


Figure 5.1 Activity of polystyrene produced on different polymerization temperatures

The results in Figure 5.1 indicate that the activity is enhanced with increasing temperature, and reached maximum at 65°C and then decreases with a further increase of temperature. This could be explained that at below and above 65°C, the catalytic system is either scarcely active or is deactivated by thermal decomposition of the catalyst.

At optimum temperature (65°C), the catalyst shows relatively high rates of propagation and relatively low rates of deactivation, so that the high activity is observed. At high temperature, rates of propagation as well as deactivation presumably increase, whereas at low temperature, both rates decrease. As a result, in both cases low activities were observed.



The above explanation is based on the widely accepted mechanism of propagation step in polymerization using Ziegler-Natta as well as metallocene catalysts, which involves the initial formation of  $\pi$ -complex of olefin with the metal center, followed by chain migratory insertion. In the high polymerization temperature, which resulted in lower activity, the  $\pi$ -complex of olefin dissociates, causing the lower propagation rate. In other words, reduced activity may be attributed to the deactivation of the catalytic species.

### 5.1.2 The effect of reaction time on CpTiCl<sub>3</sub> catalyst

Various reaction time were investigated; 2, 3, 5, 10 and 20 hours. The polymerization temperature chosen was 65°C from the results of Section 5.1.1. The experimental results were shown in Table 5.2 and Figure 5.2.

**Table 5.2** Styrene polymerization catalyzed by CpTiCl<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TMA on different reaction time at 65°C

Time (h)	Yield(g)		Average yield (g)	Activity (gPS/Ti.S.h)	% conversion
	#1	#2			
2	0.1231	0.1612	0.1422	93,399	1.57
3	0.2105	0.2753	0.2429	106,360	2.68
5	0.6676	0.5228	0.5952	156,632	6.57
10	1.8998	2.0094	1.9546	256,762	21.57
20	6.8087	7.0120	6.9104	453,888	76.27

Polymerization conditions: T<sub>p</sub>, 65°C; Al /Ti, 500; total volume, 25 cm<sup>3</sup>; [Ti], 0.35 mM

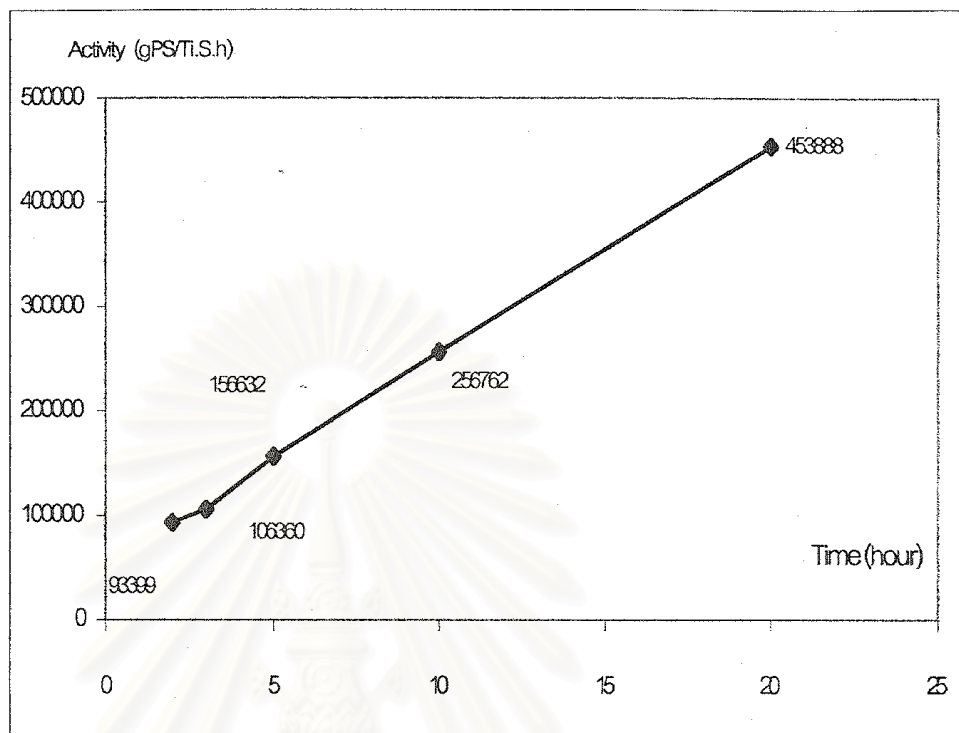


Figure 5.2 Activity of polystyrene produced on different reaction time

The result in Figure 5.2 shows that the catalytic activity increases with polymerization time, in the range tested (up to 20 hours). For the following experiments, 5 hours period of time was chosen unless for not so very active catalyst, in order to get enough yield for the further characterization of polystyrene, 20 hours period of time was chosen instead.

### 5.1.3 The effect of Al/Ti molar ratio on CpTiCl<sub>3</sub> catalyst

Various Al/Ti molar ratios were investigated; 125, 300, 500, 800 and 1000. The reaction temperature was 65°C and the polymerization time was 5 hours. The experimental results were shown in Table 5.3 and Figure 5.3.

**Table 5.3** Styrene polymerization catalyzed by CpTiCl<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TMA at different Al/Ti

[TMA] (mM)	Al / Ti	Yield (g)		Average yield (g)	Activity (gPS/Ti.S.h)	% conversion
		#1	#2			
43.75	125	0.1877	0.1951	0.1914	50,368	2.11
105.00	300	0.8211	1.1488	0.9850	259,211	10.87
175.00	500	0.6676	0.5228	0.5952	156,632	6.57
280.00	800	0.6187	0.5012	0.5560	146,316	6.14
350.00	1000	0.1238	0.1478	0.1358	35,737	1.50

Polymerization conditions: T<sub>p</sub>, 65°C; t<sub>p</sub>, 5 h; total volume, 25 ml; [Ti], 0.35 mM

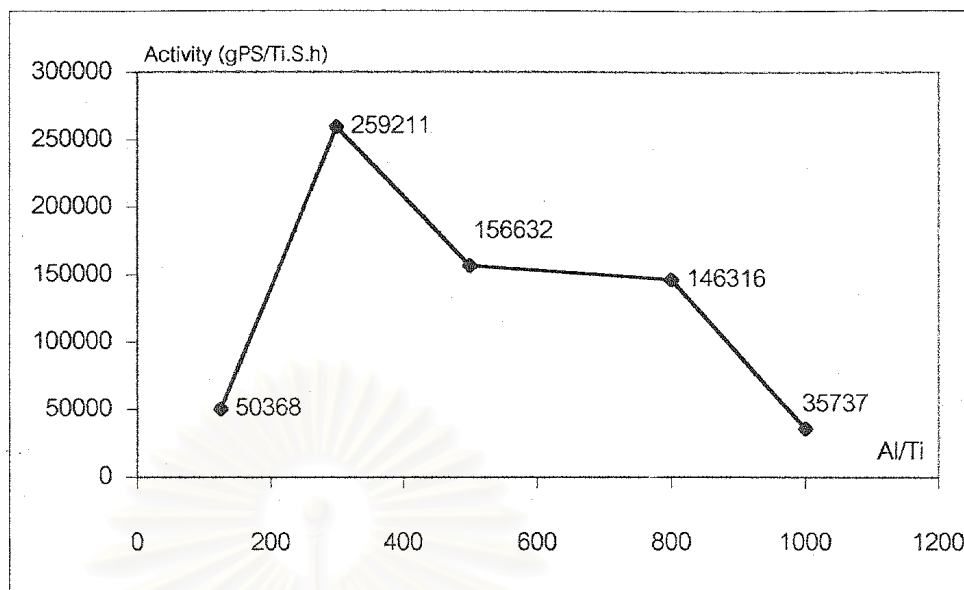


Figure 5.3 Activity of polystyrene produced at different Al/Ti

From Figure 5.3, the result shows that the activity tends to increase with increasing Al/Ti mole ratio. The maximum activity is achieved at Al/Ti = 300, and then the activity gradually decreases at higher mole ratios. It is noted that TMA which is an activator, acting as alkylating agent as well as reducing agent. For half titanocene catalyst, it was suggested that the active species are  $Ti(III)^+$  cations ( $d^1$ ) bearing the  $\eta^5$  ligand. So when using high amount of TMA (trimethyl aluminium) which is a good reducing agent, excessive alkylation of the  $CpTiCl_3$  occurred, Ti(IV) is reduced excessively to Ti (II) or (I), resulting in the reduced activity observed. On the contrary, if the amount of Al was insufficient, it resulted in a decreasing activity.

### 5.1.4 The performance of various catalysts on styrene polymerization

The optimum polymerization conditions were chosen to compare  $\text{CpTiCl}_3$  and  $\text{Cp}^*\text{TiCl}_3$  catalysts. The polymerization time was set at 20 h for the reason of high yield. The experimental results were shown in Table 5.4.

**Table 5.4** The performance of various catalysts on styrene polymerization

Catalyst	Cocatalyst		Average yield (g)	% conversion	Activity (gPS/Ti.S.h)	% SPS
	Boron Cpd.	Al Cpd.				
<sup>a</sup> $\text{CpTiCl}_3$	$\text{B}(\text{C}_6\text{F}_5)_3$	TMA	trace	-	-	-
$\text{CpTiCl}_3$	$\text{B}(\text{C}_6\text{F}_5)_3$	TMA	1.9683	21.73	129,133	16.30
$\text{Cp}^*\text{TiCl}_3$	$\text{B}(\text{C}_6\text{F}_5)_3$	TMA	3.5815	39.53	234,970	36.04

Polymerization conditions: temp,  $65^\circ\text{C}$ ; total volume,  $25\text{ cm}^3$ ;  $[\text{Ti}]$ , 0.35 mM;  $\text{Al/Ti}$ , 300.

<sup>a</sup>Polymerization without preactivation of catalytic system.

The result indicated that preactivation step of catalytic system has an effect on the yield of polymer produced.

Methyl substituents on the cyclopentadienyl ligand which are electron releasing groups yield higher polymerization activities. This result suggests stabilization of the active site by electron releasing substituents.

Therefore, the influence of other cocatalytic systems was investigated by using methyl substituted cyclopentadienyltitanium trichloride,  $\text{Cp}^*\text{TiCl}_3$  as a catalyst. The polymerization time was set at 20 h for the reason of higher yield except for those  $\text{Cp}^*\text{TiCl}_3 / [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] / \text{TiBA}$  catalytic system of which polymerization time was set at 1h because of immediate formation of solid blocks of predominant SPS. The results were shown in Table 5.5.

Table 5.5 The performance of various cocatalysts on styrene polymerization

Catalytic system	Time (h)	Average yield (g)	% conversion	Activity (gPS/Ti.S.h)	% SPS
Cp*TiCl <sub>3</sub> / B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> / TMA	20	3.5815	39.53	234,970	36.04
Cp*TiCl <sub>3</sub> / [Ph <sub>3</sub> C][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] / TMA	20	0.8536	9.42	56,001	N.D.
Cp*TiCl <sub>3</sub> / [Ph <sub>3</sub> C][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] / TiBA	1	3.6301	40.07	4,763,153	70.27

Polymerization conditions: temp, 65 °C; total volume, 25 cm<sup>3</sup>; [Ti], 0.35 mM; Al/Ti, 300.

N.D. = non-determined

From comparisons between the syndiotacticity of the different catalytic system, the polystyrene obtained from Cp\*TiCl<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] /TiBA catalytic system showed higher % syndiotacticity. The CpTiCl<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> / TMA catalytic system produced mainly amorphous polystyrene (containing 16.30% syndiotactic polystyrene), while the Cp\*TiCl<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TMA resulted in a higher stereoregular polystyrene. This finding suggests that the active species capable of inducing stereoregular polymerization are very much influenced by the interaction in their catalytic systems.

The result of using Cp\*TiCl<sub>3</sub> / B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/ TMA catalytic system shows low activity and low % syndiotacticity that could be due to the formation of the methyl bridged complex, Cp\*TiR<sub>2</sub>(μ-R)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, which is a good source in solution of cationic species [Cp\*TiR<sub>2</sub>]<sup>+</sup>. The latter is a very effective carbocationic initiator for polymerization of atactic polystyrene [29]. It is likely that polymerization would be initiated as suggested in Figure 5.4, where the carbocationic center of a metal ion-activated olefin is being attacked by a second monomer in the manner normally proposed for carbocationic polymerization processes.

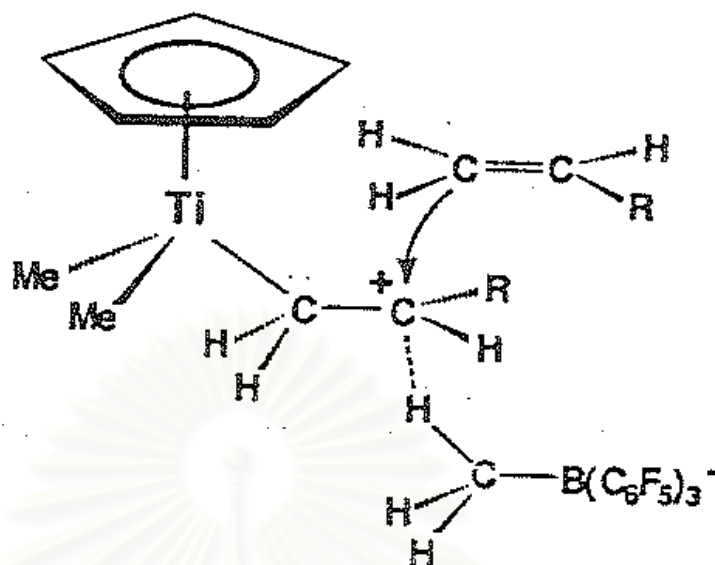


Figure 5.4 The carbocationic center of a metal ion-activated olefin

According to the same cation of the above catalytic systems but dissimilar counterion, there is a marked anion influence on both stereospecific and catalytic activity. The nature of counterions should be largely responsible in the polymerization. The activity and syndiotacticity of  $\text{Cp}^*\text{TiCl}_3 / [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] / \text{TiBA}$  catalytic system are related to the fact that the catalytic system produces the non-coordinating  $\text{B}(\text{C}_6\text{F}_5)_4^-$  counterion. That is to say this difference can be explained by the better accessibility or coordination and insertion of styrene into the Ti-C bond cationic center when the counterion is noncoordinated.

#### 5.1.5 The effect of Al/Ti molar ratio on $\text{Cp}^*\text{TiCl}_3$ catalyst

Various Al/Ti molar ratios were investigated; 50, 100 and 300. The reaction temperature was  $65^\circ\text{C}$  and the polymerization time was 1 h. The experimental results were shown in Table 5.6 and Figure 5.5.



Table 5.6 Styrene polymerization catalyzed by  $\text{Cp}^* \text{TiCl}_3 / [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] / \text{TiBA}$  at different Al/Ti at  $65^\circ\text{C}$  for 1h.

[TMA] (mM)	Al / Ti	Average yield (g)	% conversion	Activity (gPS/Ti.S.h)	% SPS
17.50	50	3.6301	40.07	4,763,153	70.27
35.00	100	6.3929	70.56	8,388,298	73.85
105.00	300	7.0970	78.33	9,312,167	72.69

Polymerization conditions:  $T_p$ ,  $65^\circ\text{C}$ ;  $t_p$ , 1 h; total volume,  $25\text{ cm}^3$ ; [Ti], 0.35 mM

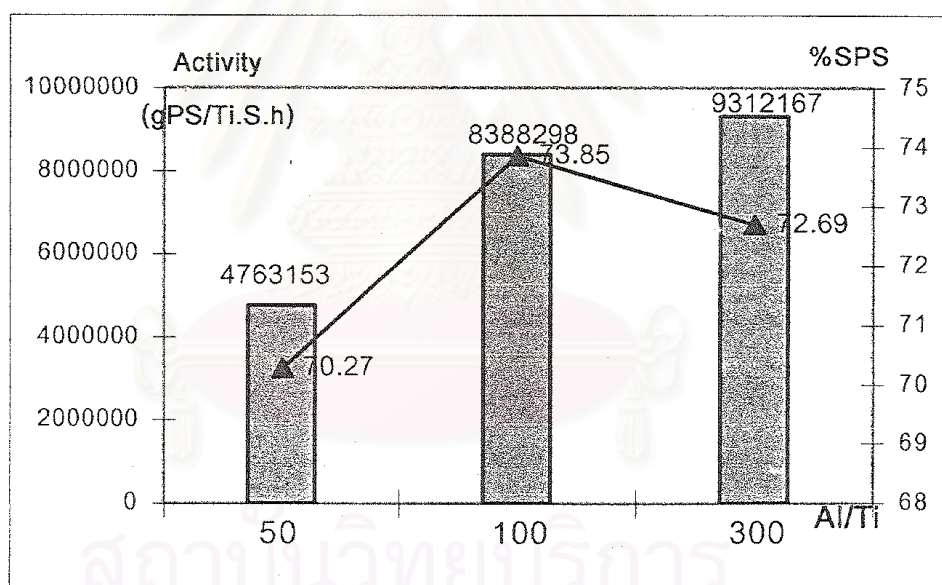


Figure 5.5 Activity and % syndiotacticity of polystyrene produced from

$\text{Cp}^* \text{TiCl}_3 / [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] / \text{TiBA}$  at different Al/Ti



According to the results from  $\text{Cp}^*\text{TiCl}_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{TiBA}$  catalytic system, all polystyrene products with various contents of aluminium do not show the great difference in syndiotacticity. This indicated that the aluminium content has no effect on % syndiotacticity as found in previously experimental study [36].

## 5.2 Polystyrene characterization

### 5.2.1. Microstructure determination

The polystyrene samples have been determined after Soxhlet extraction by IR spectroscopy. The identification of the spectrum is summarized in Table 5.7.

**Table 5.7** IR spectral data of the polystyrene produced

Wave number ( $\text{cm}^{-1}$ )	Assignment
1600, 1500	C=C aromatics
1470-1350	$-\text{CH}_2-$ , $-\text{CH}_3$ bending
1050-970	$\text{CH}=\text{CH}_2$ vinylidene
860-670	=C-H bending (aromatic rings)

An aromatic ring shows C=C stretching at 1500 and 1600  $\text{cm}^{-1}$  and C-H out-of-plane bending in the 860-670  $\text{cm}^{-1}$  region.  $\text{CH}_2-$  and  $-\text{CH}_3$  bendings appear at 1350-1470  $\text{cm}^{-1}$  region. The peaks between 970 and 1050  $\text{cm}^{-1}$  are the vinylidene chain end of polystyrene. Using  $\text{CpTiCl}_3 / \text{B}(\text{C}_6\text{F}_5)_3 / \text{TMA}$ ,  $\text{Cp}^*\text{TiCl}_3 / \text{B}(\text{C}_6\text{F}_5)_3 / \text{TMA}$  and  $\text{Cp}^*\text{TiCl}_3 / [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] / \text{TiBA}$  catalytic systems, IR spectra in Figure 5.6 (a), (b) and (c) match with those of referenced polystyrene as shown in Figure 5.7 (c) which is SPS (syndiotactic polystyrene).

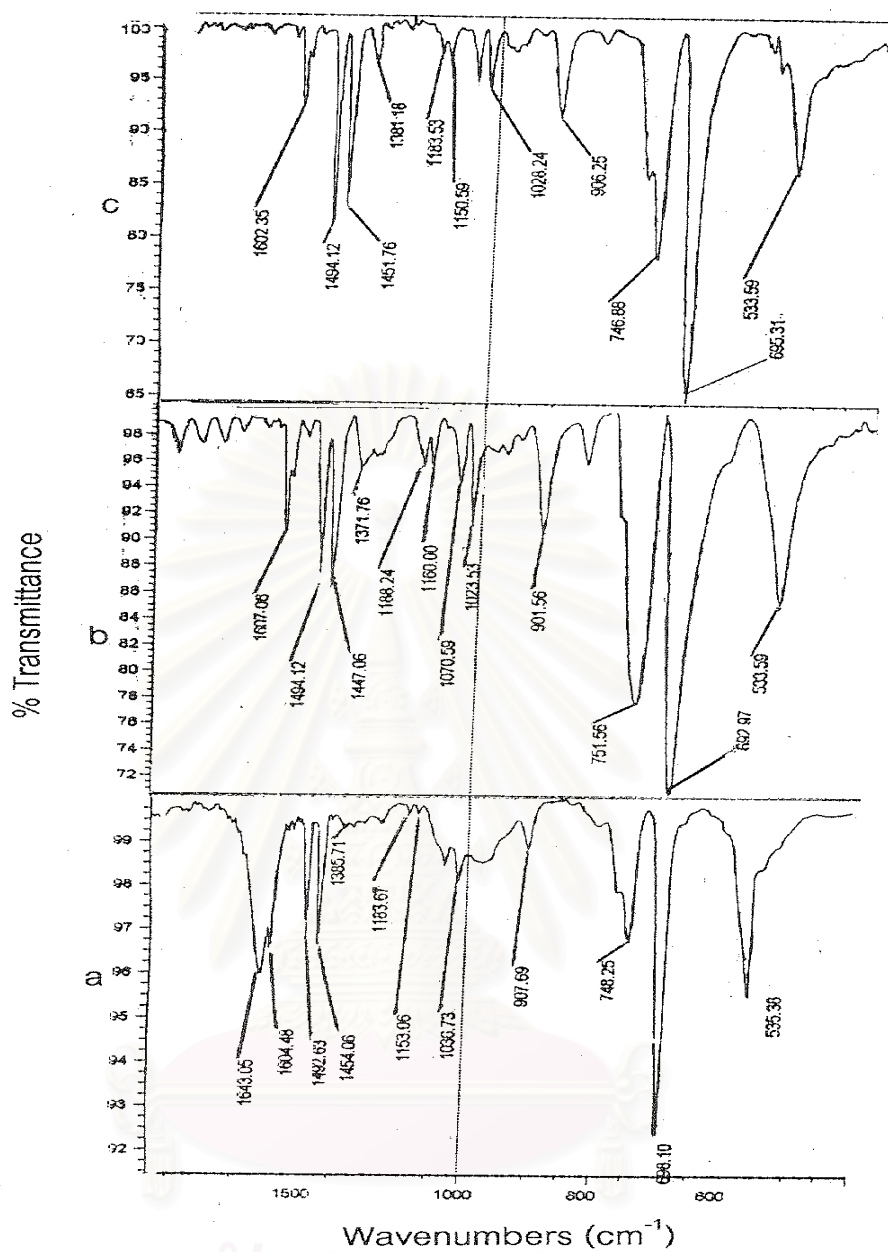


Figure 5.6 IR spectral data of polystyrenes from different catalysts:

- $\text{CpTiCl}_3/\text{B}(\text{C}_6\text{F}_5)_3/\text{TMA}$
- $\text{Cp}^*\text{TiCl}_3/\text{B}(\text{C}_6\text{F}_5)_3/\text{TMA}$
- $\text{Cp}^*\text{TiCl}_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{TiBA}$

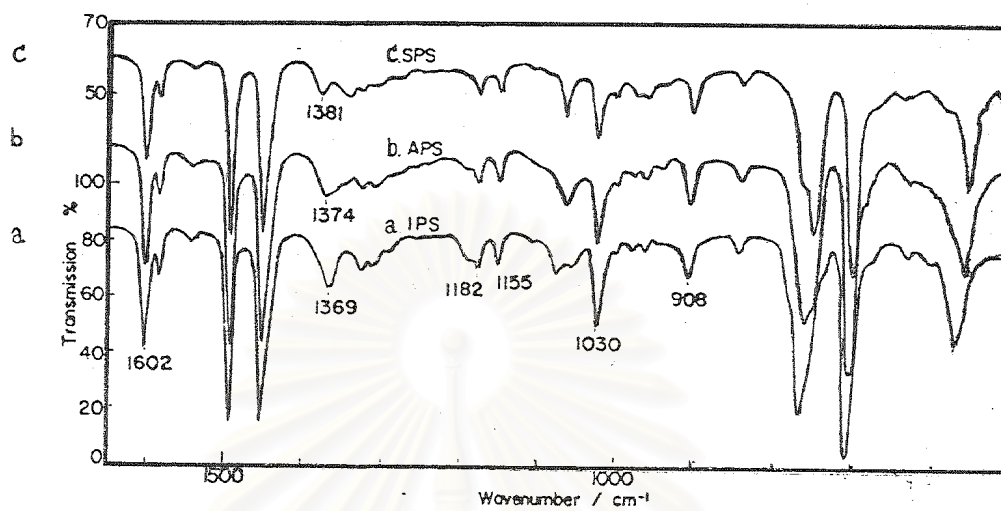


Figure 5.7 Referenced IR spectra of isotactic, atactic and syndiotactic polystyrenes[17]

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### 5.2.2. Melting Temperature (T<sub>m</sub>)

The melting temperature ( T<sub>m</sub> ) has been determined on different types of titanocene catalysts. The DSC melting temperatures ( T<sub>m</sub> ) of polystyrene produced are shown in Table 5.8 and Figure 5.8.

**Table 5.8** The effect of titanocene catalysts on the melting temperature ( T<sub>m</sub> )

Catalytic System	Temperature		Polymer
	( T <sub>g</sub> )	( T <sub>m</sub> )	
CpTiCl <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /TMA	102.0	-	Atactic
Cp*TiCl <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /TMA	118.8	-	Atactic
Cp*TiCl <sub>3</sub> /[Ph <sub>3</sub> C][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]/TiBA	-	268.3*	Syndiotactic

\* A minor peak at 257.7°C

The above table demonstrated the effect of different catalyst on the melting temperature of polystyrene obtained. T<sub>g</sub> of the polystyrene from CpTiCl<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TMA system and the Cp\*TiCl<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/TMA system revealed that the majority of polymer products was atactic (T<sub>g</sub> is about 102-118°C). This could also be seen from the result of Soxhlet extraction.

For Cp\*TiCl<sub>3</sub>/ [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] / TiBA system, T<sub>m</sub> is 268.3°C, which is close to T<sub>m</sub> of syndiotactic polystyrene, therefore, it can be confirmed that the polymer product is syndiotactic.

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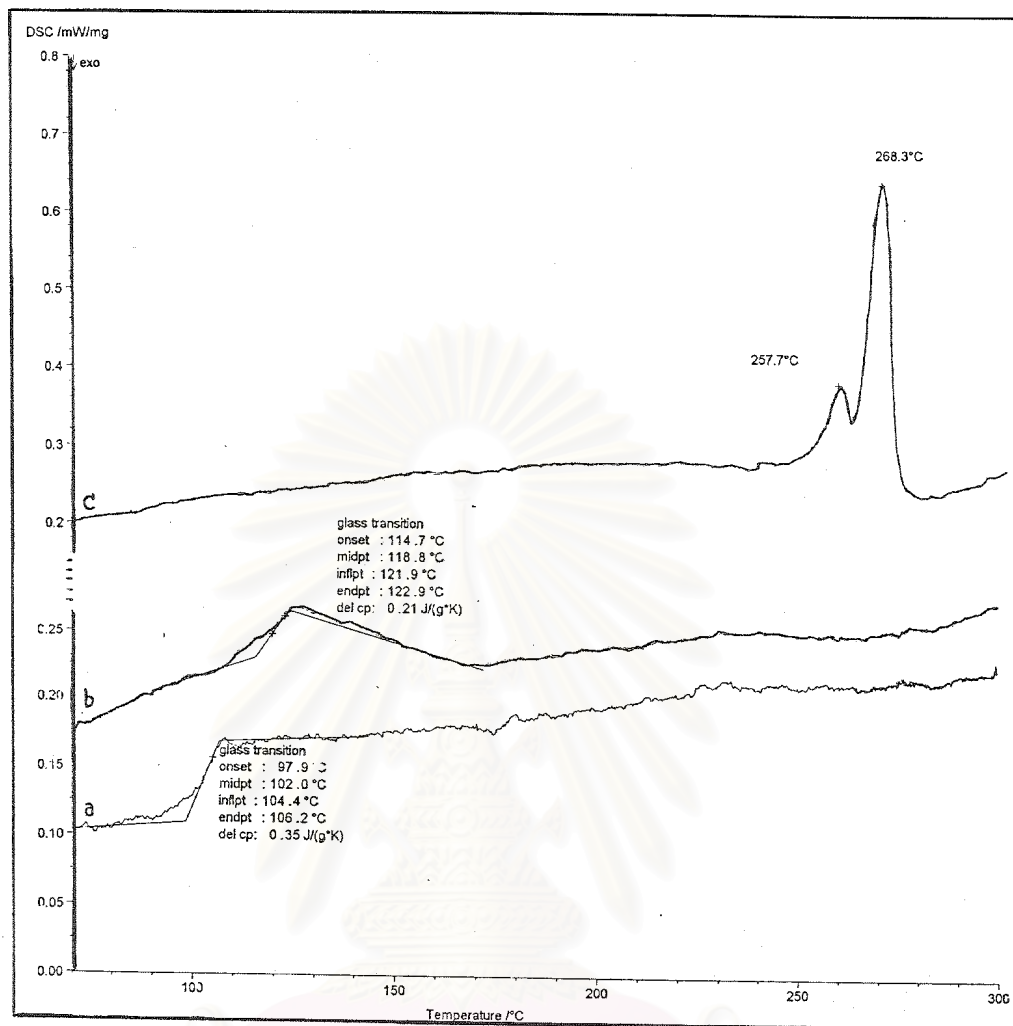


Figure 5.8 DSC thermograms of polystyrene from various catalytic systems

a)  $\text{CpTiCl}_3/\text{B}(\text{C}_6\text{F}_5)_3/\text{TMA}$ b)  $\text{Cp}^*\text{TiCl}_3/\text{B}(\text{C}_6\text{F}_5)_3/\text{TMA}$ c)  $\text{Cp}^*\text{TiCl}_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{TiBA}$

In Figure 5.8, The DSC thermogram of  $\text{Cp}^*\text{TiCl}_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{TiBA}$  catalytic system shows double peaks signal at  $257.7$  and  $268.3^\circ\text{C}$ . These appearance was also observed by other authors [37], [38] and is attributed to different ways of crystallizing of syndiotactic polystyrene. Syndiotactic polystyrene had at least two crystal forms, the  $\alpha$  form and  $\gamma$  form. The skeletal chain of  $\alpha$  form is the TT conformation. The skeletal chain of  $\gamma$  form is the TTGG conformation, as shown in Figure 5.9.

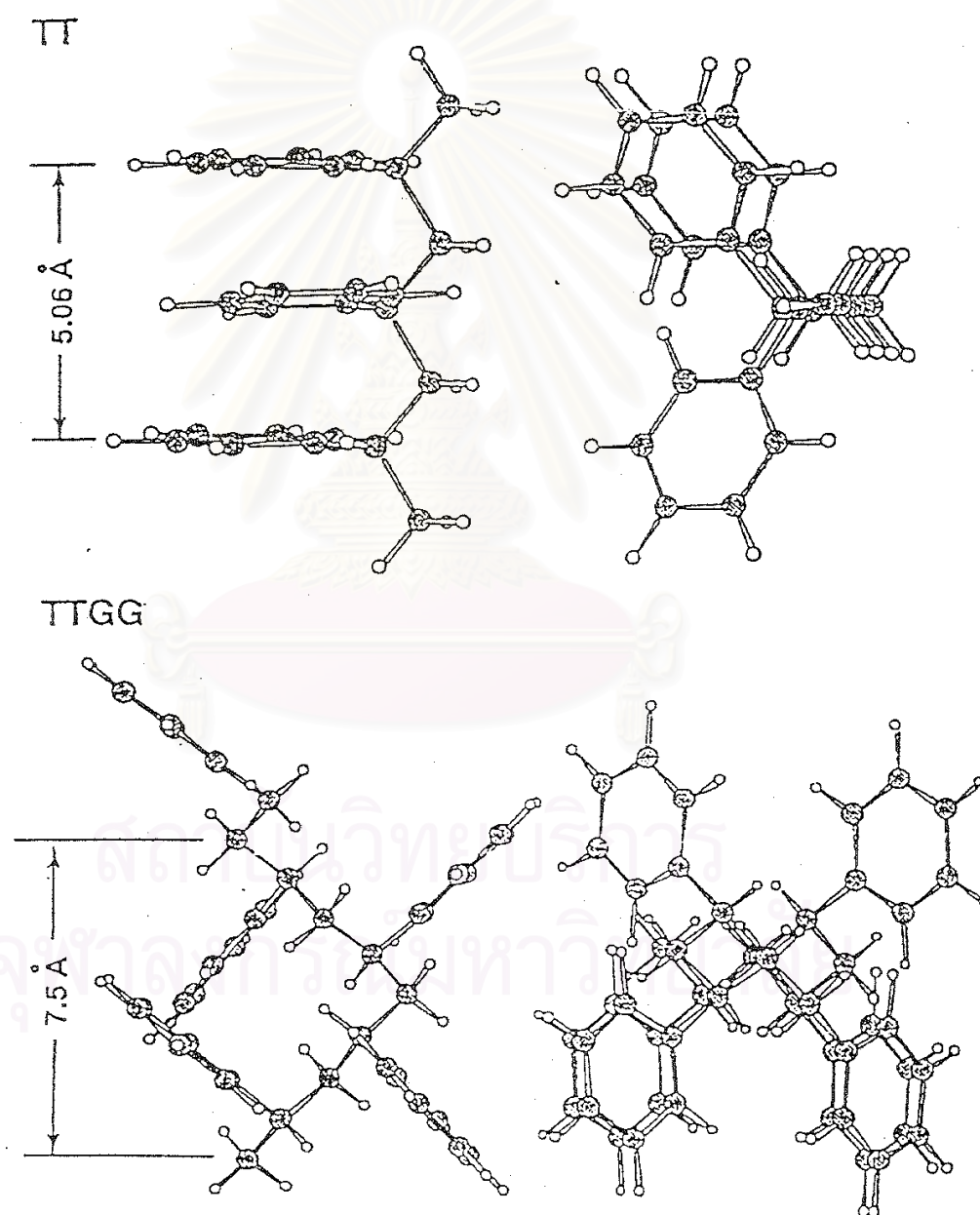


Figure 5.9 Schematic representation of two forms of SPS

### 5.2.3. Molecular weight (Mw) and molecular weight distribution (MWD)

Polymers produced from  $\text{CpTiCl}_3/\text{B}(\text{C}_6\text{F}_5)_3/\text{TMA}$  and  $\text{Cp}^*\text{TiCl}_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{TiBA}$  catalysts were determined for molecular weight (Mw) and molecular weight distribution (MWD) using GPC. Mw and MWD from  $\text{CpTiCl}_3/\text{B}(\text{C}_6\text{F}_5)_3/\text{TMA}$  are 122,813 and 1.93, respectively while those from  $\text{Cp}^*\text{TiCl}_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{TiBA}$  are 52,000 and 1.79, respectively. The chromatogram and molecular weight distribution curves are shown in Figure 5.10.

TiBA is not only a strong alkylating agent but also a good chain transfer agent. Therefore excess additional TiBA in polymerization system significantly results in the reduction of molecular weight of the polymer.

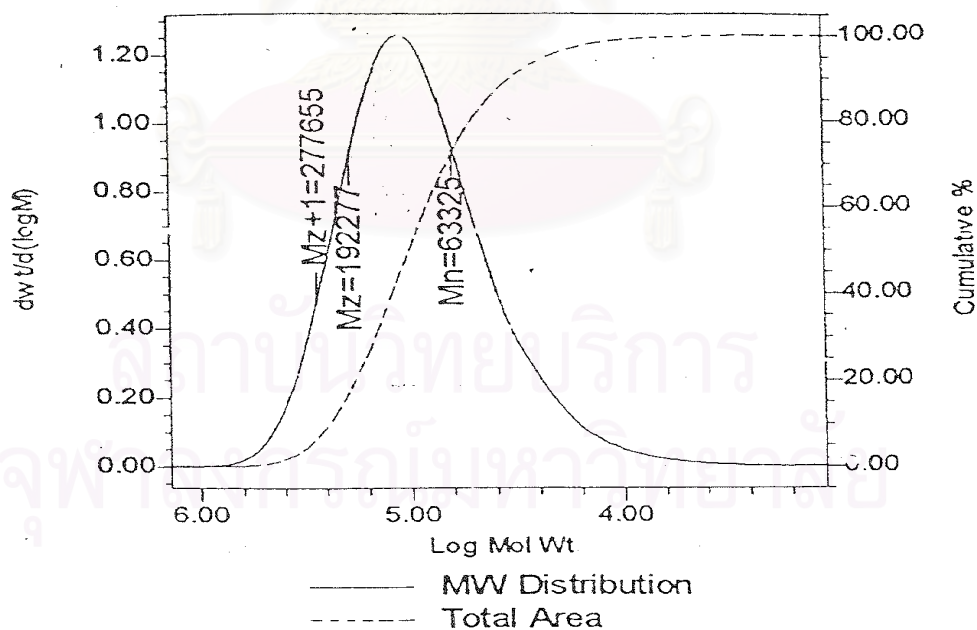


Figure 5.10 GPC curve of polystyrene from  $\text{CpTiCl}_3/\text{B}(\text{C}_6\text{F}_5)_3/\text{TMA}$



## CHAPTER VI

### CONCLUSIONS AND SUGGESTIONS

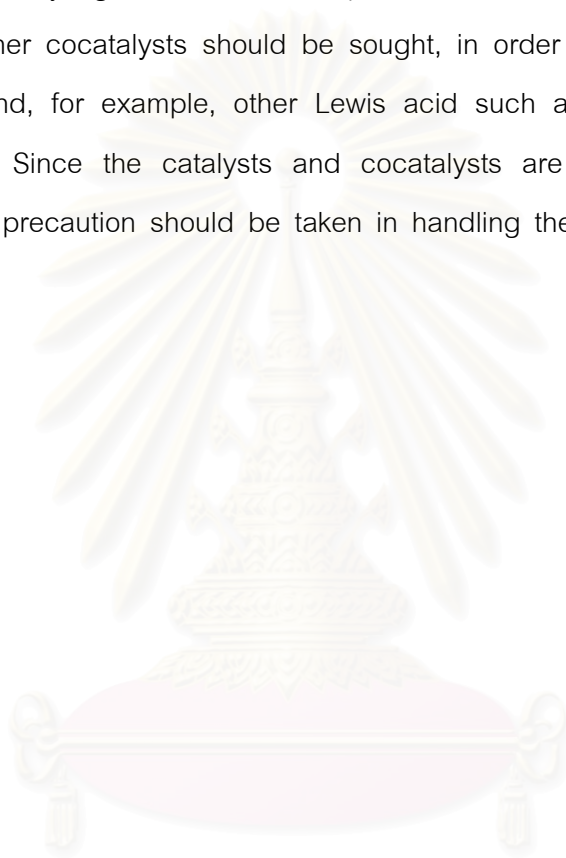
#### 6.1 Conclusions

Half-titanocene catalysts were used to catalyze the polymerization of styrene. The catalytic systems tested are  $\text{CpTiCl}_3 / \text{B}(\text{C}_6\text{F}_5)_3 / \text{TMA}$ ,  $\text{Cp}^* \text{TiCl}_3 / \text{B}(\text{C}_6\text{F}_5)_3 / \text{TMA}$  and  $\text{Cp}^* \text{TiCl}_3 / [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] / \text{TiBA}$ . The preactivation step is necessary to increase the activity by increasing the active species;  $[\text{CpTiR}_3]^+$  or  $[\text{Cp}^* \text{TiR}_3]^+$ . The reaction of catalyst and cocatalyst affords cation complex such as  $[\text{Cp}^* \text{TiR}_2]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ , which is active for the syndiotactic polystyrene. Ti(IV) is reduced to Ti(III), which is probably caused by aluminium alkyls acting as reducing agent of the reaction. The conditions for polymerization were examined and found that the suitable conditions of  $\text{CpTiCl}_3 / \text{B}(\text{C}_6\text{F}_5)_3 / \text{TMA}$  catalytic system used for styrene polymerization are: catalyst concentration of  $3.50 \times 10^{-4}$  mol/l, Al/Ti mole ratio of 300, polymerization temperature of  $65^\circ\text{C}$ . The activity order of catalysts is:  $\text{Cp}^* \text{TiCl}_3 / [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] / \text{TiBA} > \text{Cp}^* \text{TiCl}_3 / \text{B}(\text{C}_6\text{F}_5)_3 / \text{TMA} > \text{CpTiCl}_3 / \text{B}(\text{C}_6\text{F}_5)_3 / \text{TMA}$ . The order of syndiotacticity is:  $\text{Cp}^* \text{TiCl}_3 / [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] / \text{TiBA} > \text{Cp}^* \text{TiCl}_3 / \text{B}(\text{C}_6\text{F}_5)_3 / \text{TMA} > \text{CpTiCl}_3 / \text{B}(\text{C}_6\text{F}_5)_3 / \text{TMA}$ . The  $\text{Cp}^* \text{TiCl}_3 / [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] / \text{TiBA}$  gives 73.85% syndiotacticity. It is noteworthy that the activity and syndiotacticity of these catalytic system significantly increased when TiBA was used to scavenge monomer or solvent impurities. TiBA is not only a strong alkylating but also a good chain transfer agent. Therefore, additional TiBA in polymerization system significantly results in the reduction of molecular weight of polymer when comparing with TMA.



## 6.2 Suggestions

Some other half-titanocenes should be tested, for example, those with Si-substituted Cp or indenyl ligands. The active species should be investigated by using ESR technique. Other cocatalysts should be sought, in order to reduce the use of aluminium compound, for example, other Lewis acid such as  $[\text{HNEt}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  or  $[\text{Ph}_3\text{C}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ . Since the catalysts and cocatalysts are sensitive to air and moisture, a severe precaution should be taken in handling them, for example using standard glove box.



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