



CHAPTER I INTRODUCTION

The discovery of metallocene catalysts is considered to be one of the milestones in the polymer and catalyst fields in the past decade (Farina, 1994; Horton, 1994; Brintzinger et al., 1995; Huang and Rempel, 1995; Hamielec and Soares, 1996; Bochmann, 1996). Metallocenes which generally contain a single kind of active sites, in comparison to conventional Ziegler-Natta systems, offer good control over the uniformity of chain length, degree of branching, and/or stereospecificity in polymer products. The catalyst structure is an important parameter in determining polymer properties and the flexibility of ligand types on the cyclopentadienyl rings allows a wide range of catalyst design leading to great versatility in polymer synthesis.

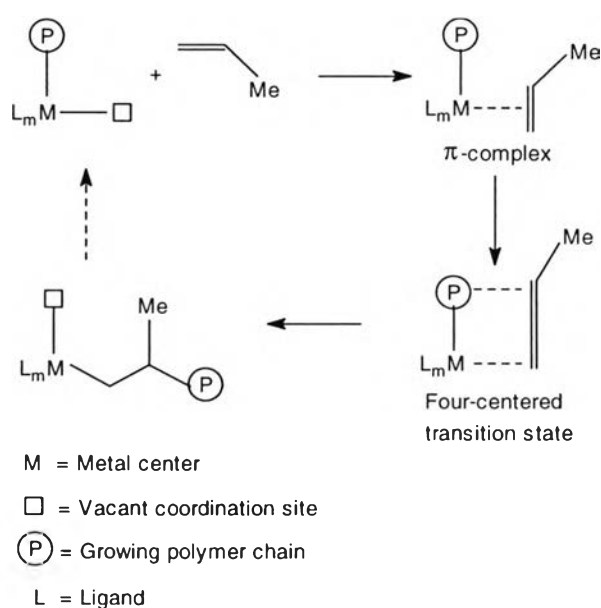
1.1 Ziegler-Natta Catalyst System

Since Ziegler's breakthrough discovery of transition metal catalysis for the low-pressure olefin polymerization over 40 years ago (Ziegler, 1955) followed shortly by Natta's successful polymerization of propene with stereoselectivity (Natta, 1956), heterogeneous Ziegler catalysts have become highly successful industrial catalysts for polyolefins with continuous developments.

In the past ten years, highly active heterogeneous catalysts based on TiCl_4 supported on MgCl_2 with alkylaluminum have played a key role in both research and industrial production.

Scheme 1.1 shows the monomer insertion mechanism proposed by Cossee (1961). A vacant site is generated at the metal center and is attacked by the incoming monomer forming a π -complex. The orientation of the

reacted olefin depends on the structure of the monomer, the growing chain, and the nature of the catalyst. In the next step, the olefin is partially inserted into the metal-C bond of the growing polymer chain. The migration of the polymer chain, P, and the formation of the metal-carbon bond occur in concert through a four-center transition state. In the final step, the olefin is fully inserted, recreating the vacant coordination site at the site originally occupied by the polymer chain. This process involving shifting of growing chain to the position previously occupied by a coordinated monomer continues until termination of the polymer chain.



Scheme 1.1 Cossee-Arlmann mechanism of propylene polymerization.

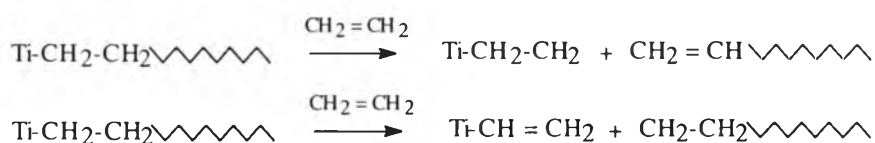
Different termination reactions have been observed and studied. The most common chain termination reactions are listed in Scheme 1.2. All four reported termination reactions give a new metal-hydrogen or metal-alkyl compound with an unsaturated (a and b) or a saturated (c and d) polymer.

Although high productivity, good specificity, and low cost are the main advantages in the industrial application of these catalysts, they still suffer some drawbacks. The polymerization on these brown slurry catalysts takes place on dislocations and edges of TiCl_3 crystals with relatively low number of active centers. Consequently, there are many different types of active sites, so called *multi-site* catalysts, and the resulting polymer has a typical broad molecular weight distribution. The diversity of active sites in heterogeneous catalysts also leads to an uneven degree of comonomer incorporation, a drawback where metallocenes offer particular promise.

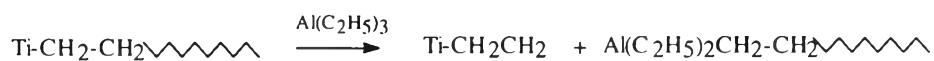
(a) β -elimination



(b) Chain transfer to monomer



(c) Chain transfer to alkylaluminum



(d) Chain transfer to hydrogen



Scheme 1.2 Chain termination reactions.

1.2 Metallocene Catalyst System

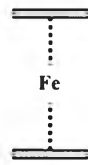
Bis(cyclopentadienyl) titanium(IV) chloride (Cp_2TiCl_2) was first used in the presence of alkylaluminum under the same conditions as Ziegler's catalysts (Breslow and Newburg, 1957, Natta, 1957). This homogeneous clear catalyst solution gives narrow molecular weight distribution polyolefin and low to medium activities with rapid deactivation of active species, and so it found no commercial interest.

An important development began with the unexpected observation that although Ziegler catalysts are very sensitive to hydrolysis, traces of water actually increased the rate of polymerization in $\text{Cp}_2\text{TiCl}_2/\text{AlEtCl}_2$ catalyst system (Reichert and Meyer, 1973), and the formation of aluminoxanes by partial hydrolysis of the aluminium alkyl component was suggested. Sinn and Kaminsky later introduced methylaluminoxane (MAO) as a new potential class of coactivator in metallocene catalyst system (Andersen et al., 1976; Kaminsky et al., 1976)

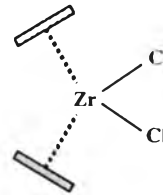
1.2.1 The Composition of Metallocene Catalyst System

1.2.1.1 Metallocene

Simple metallocene molecules contain a single group IV transition metal atom, usually titanium (Ti) or zirconium (Zr) coordinated with cyclopentadienyl (Cp) or substituted cyclopentadienyl ligands (Cp'), and to two other groups, often halide atoms or methyl groups. The rings partly enclose the metal atom like a half-open clamshell (Fig. 1.1).



FERROCENE



ZIRCONOCENE

Figure 1.1 Structure of sandwiched *ferrocene* and clam-shell *zirconocene*.

The six electrons left on the ring make cyclopentadienyl ligand *aromatic* which is very stable (Fig. 1.2). These electrons exert influence on the transition metal center which then tends to attack carbon-carbon double bonds.

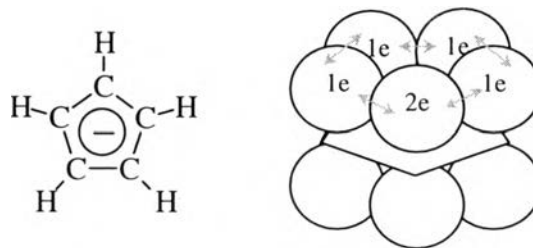


Figure 1.2 Delocalization of 6 electrons in p-orbital of cyclopentadienyl anion.

It is believed that steric interaction between the Cp ligands and the incoming monomer plays a key role in the stereoselectivity of the polymerization. Changing the ligand structure leads to changes in polymer structure.

1.2.1.2 Methyl Aluminoxane (MAO)

The increased activity in polymerization when a small amount of water is added to the metallocene-alkylaluminum catalyst system is related to the formation of aluminoxanes by the reaction of alkylaluminum and water.

This effect has been confirmed by using MAO directly with metallocene catalysts.

Direct reaction of water with alkylaluminum in the absence of solvent is highly exothermic with flame and aluminum oxide is obtained. So the controlled hydrolysis of alkylaluminum is recommended for safety. Hydrating compounds such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ are employed as a source of water for preparing aluminoxane.

Methylaluminoxane (MAO) is an oligomer having $-\text{[Al}(\text{CH}_3)\text{-O-}]_n-$ as the repeating unit with a degree of oligomerization between 5 to 28. The oligomers consist of linear, cyclic, and cross-linked compounds (Fig.1.3). The compound dissolves readily in hydrocarbons such as toluene where, due to the facile ligand exchange in aluminium complex, it establishes complex solution equilibrium.

The aluminoxanes appear to have a combination of the following functions depending on the nature of the catalyst and the polymerization conditions:

- ◆ An alkylating agent for the generation of transition metal-alkyl adducts.
- ◆ A Lewis acid for anion abstraction from the complex generating cationic metallocene alkyl species.
- ◆ A scavenger for removal of impurities, particularly water in the olefin and solvent.

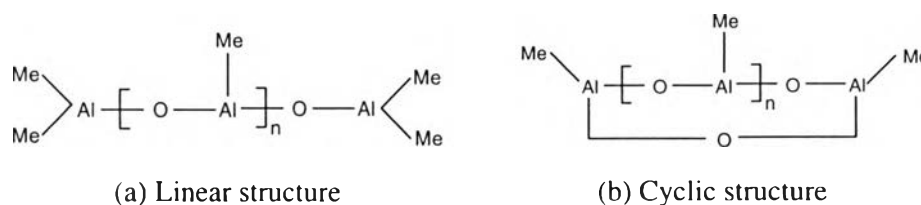


Figure 1.3 Proposed structures of methyl aluminoxane.

In order to achieve high activity, metallocene catalyst systems require a large amount of MAO, usually at Al:Zr ratios of 10^3 - 10^4 :1. So in such

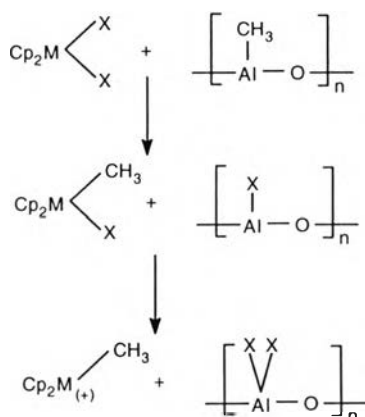
catalyst systems, the high cost comes from the high proportion of MAO over the zirconium complex. In spite of this drawback MAO has become the most widely used activator for metallocene-based catalyst systems, including large-scale industrial processes. These catalyst systems are currently the most interesting and important class of catalysts for polyolefin synthesis.

1.2.2 Polymerization Mechanisms

1.2.2.1 The Formation of Active Center

In 1986 Jordan and coworkers isolated the tetraphenylborate salts of cations such as $[\text{Cp}_2\text{ZrCH}_3\cdot\text{THF}]^+$ and $[\text{Cp}_2\text{ZrCH}_2\text{Ph}\cdot\text{THF}]^+$ and demonstrated their capability to polymerize ethylene without addition of any activator (Jordan, 1986-7). These and related findings (Hlatky et al., 1989; Bochmann et al., 1990) lead to the proposal that (alkyl)metallocene cations, i.e. cationic d^0 14-electron complexes of $[\text{Cp}_2\text{M}(\text{R})]^+$ ($M = \text{Ti}, \text{Zr}, \text{Hf}$), are crucial intermediates in homogeneous polymerization catalysis.

The initial step of polymerization reaction is the formation of an alkylated cation of the transition metal via either methyl or chloride abstraction. MAO acts as the counterion of the cationic active species $[(\text{Cp}_2\text{MR})]^+$.

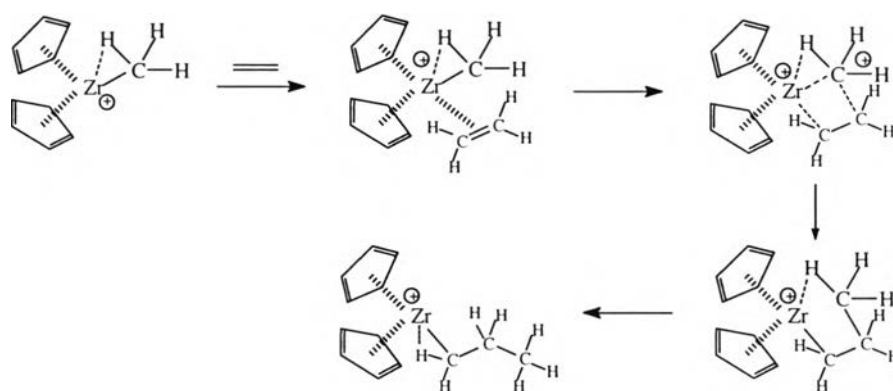


Scheme 1.3 Formation of the active species in the reaction between metallocene and methyl aluminoxane.

1.2.2.2 Mechanism of Polymerization

Up to now there is still no definite polymerization mechanism for Ziegler-Natta catalysts and metallocene catalysts. The most widely accepted model was proposed by Cossee and is shown in Scheme 1.1.

Another mechanism was proposed by Brookhart and Green (1983). The major differences of this model from Cossee-Arlman mechanism are the binding of the monomer and the transition state during insertion which are based on the α -agostic association (Scheme 1.4), the stable form of positively charged zirconium because the electrons from the carbon-hydrogen bond are shared with the zirconium.



Scheme 1.4 Brookhart-Green mechanism.

1.2.2.3 Chain Transfer Mechanism

The termination of growing polymer chain mostly occurs via chain transfer reactions involving β -H elimination and β -Me elimination as revealed by the study of the endgroups of low M_w oligomers. The termination is also caused by chain transfer to aluminum, monomer, or hydrogen as in Ziegler-Natta system.

1.2.3 Advantages and Disadvantages of Typical Metallocene-MAO Catalyst System

Advantages :

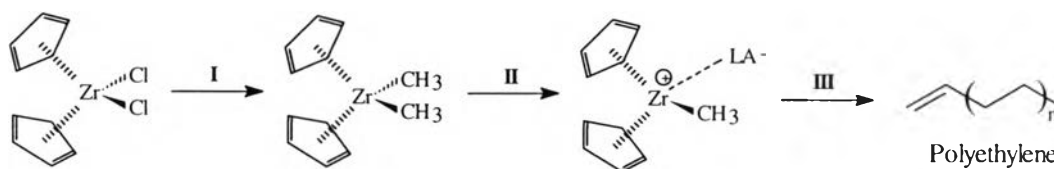
- ◆ High catalyst activity
- ◆ Small amount of catalyst requirements
- ◆ Versatile possibility in polymerization by suitably turning the ligands around the transition metal
- ◆ Narrow molecular weight distribution ~ 2.0
- ◆ Sharp melting transition (T_m) and uniform solubility characteristics
- ◆ Ability to polymerize various monomers with almost any desired stereospecificity

Disadvantages :

- ◆ High Al:Zr ratio required for obtaining high catalyst activity
- ◆ High cost of MAO
- ◆ Inability to operate in slurry or gas phase processes
- ◆ Poor control over polymer morphology

1.3 MAO-FREE METALLOCENE CATALYST SYSTEM

It is generally accepted that *neutral* metallocene dichloride or dimethyl combines with a strong Lewis acid cocatalyst to give an active *cationic* alkyl species for ethylene polymerization in the presence of monomer (Scheme 1.5).



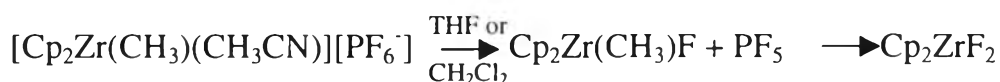
Scheme 1.5 Ethylene polymerization by metallocene.

I. Alkylating agent, e.g. CH₃Li, AlR₃ or MAO;

II. Strong Lewis acid, e.g. MAO, B(C₆F₅)₃ or [Ph₃C][B(C₆F₅)₄];

III. Excess C₂H₄.

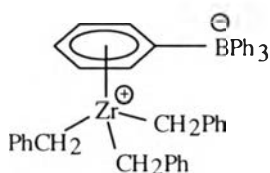
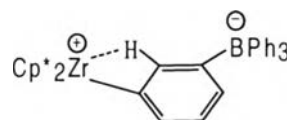
As discussed above, there are many disadvantages of metallocene-MAO catalyst system especially the high Al/M ($M = \text{Ti, Zr}$) required resulting in high cost. Other Lewis acids have been used instead of MAO. The complex anion such as BF₄⁻, PF₆⁻ and ClO₄⁻ were first considered. Jordan (1986) showed that with strongly electrophilic cationic complexes (Cp₂M(CH₃)⁺), these anions irreversibly transfer F⁻ or Cl⁻ to the metal center affording inactive metallocene halides (Scheme 1.6).



Scheme 1.6 Fluoride abstraction to cationic species.

Therefore the more stable and weaker basic compound such as BPh₄⁻ was used. It exhibits only modest catalytic activity for many reasons. One of

them is the π back-donation (Bochmann, 1990). If π -orbitals of phenyl ring get close enough to share electrons with d-orbitals of Zr^+ , the complex will be stable and will not react further with alkene monomers (Fig. 1.4 (a)). Metalation of phenyl ring can also occur (Hlatky, 1989). The C-H bond ortho to boron acts as a ligand to the zirconium atom through an agostic interaction which will stabilise the complex (Fig. 1.4 (b)).

(a) π back-donation

(b) metalation

Figure 1.4 π back-donation and metalation process of inactive metallocene- BPh_4^- catalyst system.

If the cocatalyst is a very strong anionic species, such as BF_4^- or PF_6^- , fluoride abstraction to metal atom can occur. The catalyst/cocatalyst will become isolated salt. For weakly coordinating anion, BPh_4^- , fairly strong interactions have been observed with cationic alkyl (zirconocene) species. But this cation-anion interactions are strong enough (the bond is shorter than ionic bond) to stabilize the complex.

Introducing fluoro substituents on the phenyl ring is a way to reduce anionic property of the cocatalyst that is expected to give a significantly higher catalytic activity. In this experiment, the relatively strong Lewis acid tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) was used with bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2) and alkylaluminum as alkylating agent.