

CHAPTER II

LITERATURE SURVEY

The development of metallocene and single site catalyst technology has led during recently years to syntheses of metallocene polyolefins. The impact of metallocene catalysts extends beyond simple olefin polymerization. It has opened the doors to new classes of polyolefins inaccessible by classical Ziegler-Natta polymerization. It is interesting to explore the possible applications of metallocene catalysts in general and to search for other single-site catalysts in place of heterogeneous catalyst systems.

2.1 Homogeneous Metallocene Catalysts

Sinn and Kaminsky (1980) reported the synthesis from metallocene and methylaluminoxane of a soluble olefin polymerization catalyst. This high-activity catalyst is capable of producing polyethylene having narrow polydispersity.

Metallocene is the class of compound in which cyclopentadienyl or substituted cyclopentadienyl ligands are π -bonded to the transition metal from group 4b (Figure 2.1). The transition metal is usually zirconocene but other group 4b metals are sometimes used.

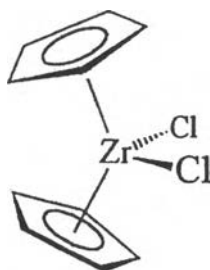


Figure 2.1 The structure of metallocene.

The main features that distinguish homogeneous metallocene catalysts from conventional Ziegler-Natta catalysts are

- (a) the ability to polymerize a wide variety of bulky monomers, such as higher α -olefins, styrenic compounds, dienes, cyclo-olefins and polar monomers (Starck *et al.*, 1999).
- (b) the ability to produce extremely uniform polymers and copolymers of narrow molecular weight distribution and narrow compositional distribution (Janimak and Stevens, 2000).
- (c) the ability to control vinyl unsaturation in polymer (Janimak and Stevens, 2000).
- (d) the ability to polymerize α -olefins with very high stereoregularity affording isotactic and syndiotactic polymers (Janimak and Stevens, 2000).

Metallocene catalysts can also produce tailor-made properties by varying

- (a) ligand type,
- (b) bridge joining ligands,
- (c) substituent on ligands and bridge to alter the steric and electronic surroundings of the active center,
- (d) transition metal type (Kolodka *et Al.*, 2000).

2.2 The Role of Aluminoxane Cocatalyst

Typically, metallocene catalysts are generated by activating metallocene halides with methylaluminoxane (MAO). The type of aluminoxane has marked influence on the efficiency of the metallocene/aluminoxane catalytic system (Soares *et al.*, 1997). The exact role of aluminoxane component is not known precisely, but from the experimental evidence, it appears that

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

1. to alkylate metallocene catalysts to form the cationic species,
2. to scavenge the impurities in the system,
3. to stabilize the cationic center in ion-pair interaction,
4. to prevent bimetallic deactivation process.

Many zirconocene/aluminoxane catalyst systems described in the literature required Al:Zr ratios in the order of 1000:1 to 10 000: 1 to achieve a reasonable activity. Such high excess ratios of expensive MAO are very unfavourable. The ratio can be reduced by supporting the metallocene on a solid surface (Chu *et al.*, 2000) or using MAO-free cocatalyst systems (Liu *et al.*, 1997).

2.3 Polymerization Mechanism

2.3.1 The Formation of Active Center

In metallocene catalyst system, it is generally accepted that the catalyst precursors, neutral metallocene dichloride Cp_2ZrCl_2 combined with MAO, can provide cationic active center to polymerize polyolefins. It is believed that firstly, MAO will act as an alkylating agent to generate a metal-alkyl ligand (Cp_2ZrMeCl). MAO will next abstract the remaining halide to produce a positive charge on the metal center, as shown in Figure 2.2.

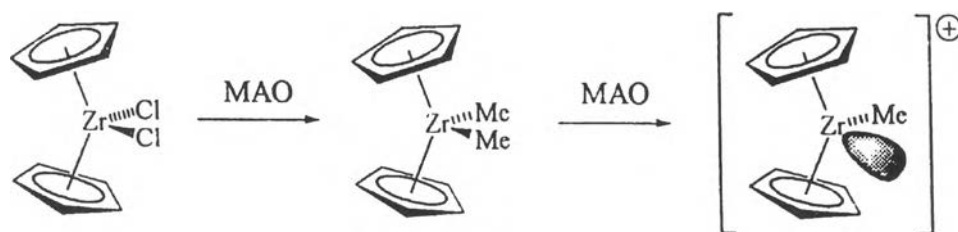


Figure 2.2 Formation of active center on metallocene catalyst with excess MAO.

2.3.2 The Polymerization Mechanism

Up to now there is still no definite polymerization mechanism for metallocene catalysts. The most widely accepted model was proposed by Cossee which is later called Cossee-Arlman mechanism (Petitjean *et al.*, 1999), as shown in Figure 2.3. It is the same mechanism followed by traditional Ziegler-Natta catalysts. The actual process involves several steps in which temporary bonds are formed to produce an electrical attraction between the polymer chain and the monomer.

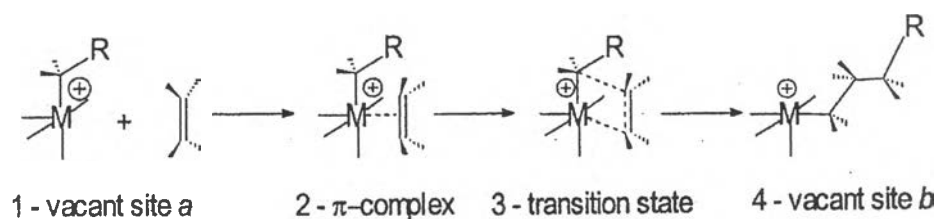


Figure 2.3 Cossee -Arlman mechanism.

In this mechanism, the double bond of olefin will first form a complex with the positive charge at the metal center. This charge is believed to allow the metal to attack the double bond of olefin monomer. After that they will rearrange themselves. Once this step is complete, the polymer chain

is longer by the length of one monomer unit and the procedure is repeated many times to form polymer of varying length.

Another mechanism was proposed by Brookhart and Green (Petitjean *et al.*, 1998). The main differences of this model from Cossee-Arlman mechanism are the binding of monomer and the transition state during insertion which are based on α -agostic association (Figure 2.4).

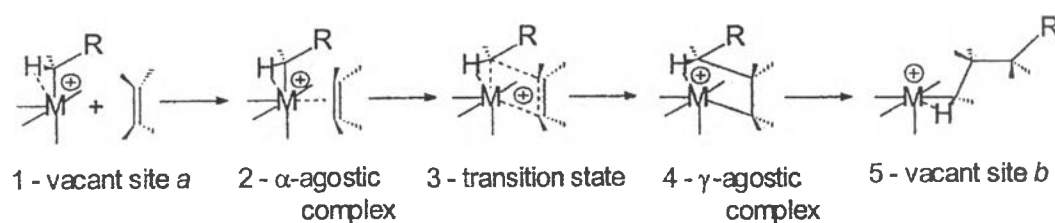


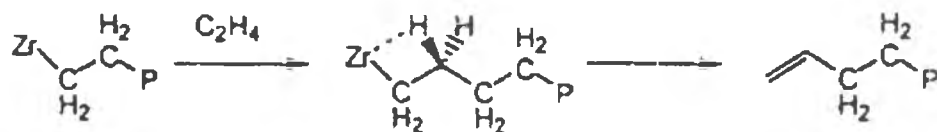
Figure 2.4 Brookhart-Green mechanism.

2.3.3 Chain Transfer Mechanism

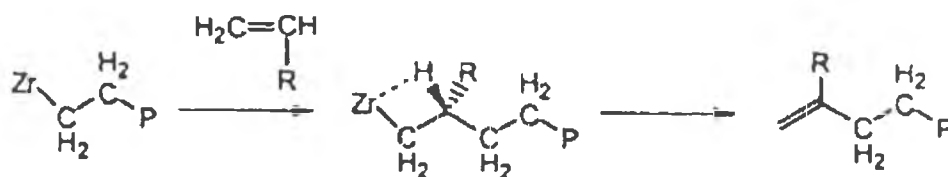
Possible chain transfer reactions of ethylene/ α -olefin polymerization with usual catalysts (Akimoto and Yano, 1999) are shown in Figure 2.5.

Vinyl and vinylidene end groups are formed by β -H transfer from propagating chain containing ethylene and primary inserted α -olefin as terminal units respectively. Trans vinylene end groups are formed by two mechanisms, one of which is β -H transfer from propagating chains containing secondary inserted α -olefin as terminal units, the other one is the β -H transfer from species that are formed by rearrangement after primary insertion of α -olefin.

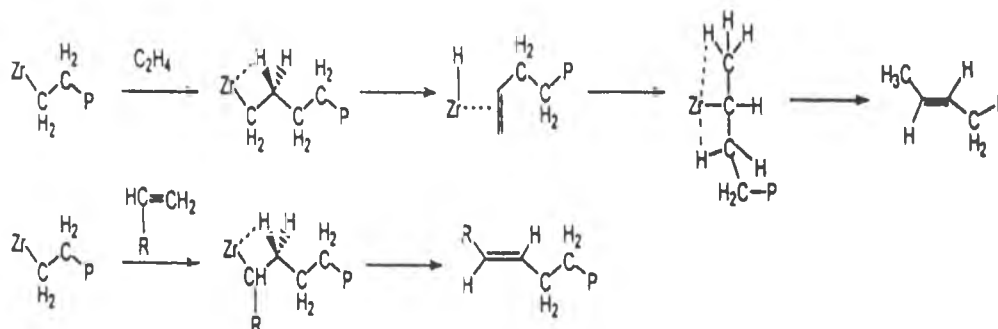
(a) Vinyl end group



(b) Vinylidene end group



(c) Trans vinylene end group



(d) Transubstituted end group

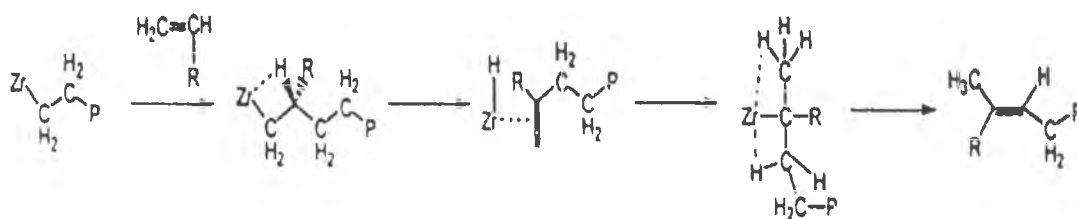


Figure 2.5 Possible chain transfer reactions in ethylene/ α -olefin copolymerization.

2.3.4 Deactivation

The activation of Cp_2ZrCl_2 by MAO involves a very fast reaction yielding the catalytically active sites. The catalyst activity decays depending on temperature and catalyst characteristics. For the well investigated system, $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2/\text{MAO}$, there is a very rapid initial activity decay above 40°C during the first few minutes followed by a second deactivation. At 0°C , the activity slowly decreases over several hours. It is suggested that the catalytically active complexes C^* are deactivated in a two-step deactivation process by a reversible followed by an irreversible process to form inactive species I_1 and I_2 (Figure 2.6).



Figure 2.6 Deactivation process.

2.4 Metallocene Catalyst with Free-Aluminoxane Systems

2.4.1 Effect of Replacing MAO with Other Cocatalysts

MAO activates the metallocene catalyst which is then able to promote polymerization of α -olefins. Other organometallic compounds of aluminum, such as trimethylaluminum (TEA) and dimethylaluminum alkyls halide are known not to promote polymerization themselves but a combination of TMA and dimethylaluminum fluoride has been shown to be effective as a cocatalyst in place of MAO. Such a combination is reported by Zambelli *et al.* (1989).

It has also been reported by Heddin *et al.* (1988) that metallocene catalyst with magnesium chloride forms a catalyst system with bis

(cyclopentadienyl)thorium dimethyl which is effective in ethylene polymerization.

Hamielec *et al.* (1997) found that by increasing the MAO concentration, which also increases the Al/Zr ratio, the polymerization activity increased up to the maximum at an Al/Zr ratio of 2400, at which further increase of Al/Zr ratio decreased the catalytic activity. Whereas the use of TMA, along with MAO, gave lower activity than the use of MAO alone for a given ratio. Reddy *et al.* (1995) also gave the same results but only at Al/Zr of 100. Recently they also demonstrated that, with the addition of TMA to a $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst system, the kinetic profile changed from a decay type to a built-up type curve for ethylene polymerization. This could be due to TMA which played the important role of stabilizing the active center and extending the catalyst life time. It was also found that the replacement of 90% MAO with TMA caused only a small loss of activity (Chien *et al.*, 1998). Polymerization using 0.1 MAO + 0.9 TMA cocatalyst results in savings in TMA starting material and in time for MAO synthesis.

2.4.2 Organo-Lewis Acid, Tris(pentafluorophenyl)borane, $\text{B}(\text{C}_6\text{F}_5)_3$ and Other MAO-Free Systems

Jordan *et al.* (1986) first opened the possibility to synthesize and isolate cationic metallocene complexes of group 4b $[\text{Cp}_2\text{ZrCH}_3(\text{THF})]^+[\text{BPh}_4]^-$ and showed the polymerization behavior in a polar solvent without any cocatalysts. After that, many researchers have been focused on the development of cationic metallocene complexes and cocatalyst for olefin polymerization.

Marks *et al.* (1991) studied the structure, solution dynamics and catalytic activity for olefin polymer obtained from tris(pentafluorophenyl) borane, $\text{B}(\text{C}_6\text{F}_5)_3$ and bis(cyclopentadienyl)zirconocene dimethyl, $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$.

The Lewis acid useful for α -olefin polymerization is any material, which can accept an electron pair and is of sufficient acidity to ionize a neutral metallocene catalyst to form a cationic species. In addition, the ligand of the Lewis acid must not be reactive with the metallocene cations. One such Lewis acid is tris(pentafluorophenyl)borane, $B(C_6F_5)_3$.

The role of the Lewis acid in metallocene catalyst system is to promote the formation of unsaturated cationic active center but the exact structural nature of catalyst-cocatalyst insertion has remained elusive (Yang *et al.*, 1990). Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, has been used as an alternative cocatalyst for metallocene in place of MAO for three reasons as follow (Yang *et al.*, 1994) :

1. It is a relatively strong molecular Lewis acid and has been shown to form a variety of characterizable Lewis base adducts.
2. It has good solubility in non-polar, noncoordinating solvent.
3. The boron center is surrounded by highly electronegative, chemically robust functional group having only nonpolar, minimally coordinating fluoro substituents.

$B(C_6F_5)_3$ is prepared by treating pentafluorophenyllithium with BCl_3 at $-78^\circ C$. Liu *et al.* (1997) also suggested that another significant advantage of $B(C_6F_5)_3$ is that only a stoichiometric amount of the cocatalyst is required to achieve the maximum catalytic activity of the system. Its chemical structure is known in Figure 2.7. A combination of aluminum alkyl and a Lewis acid was found to be necessary for reproducible, controllable, high efficiency polymerization.

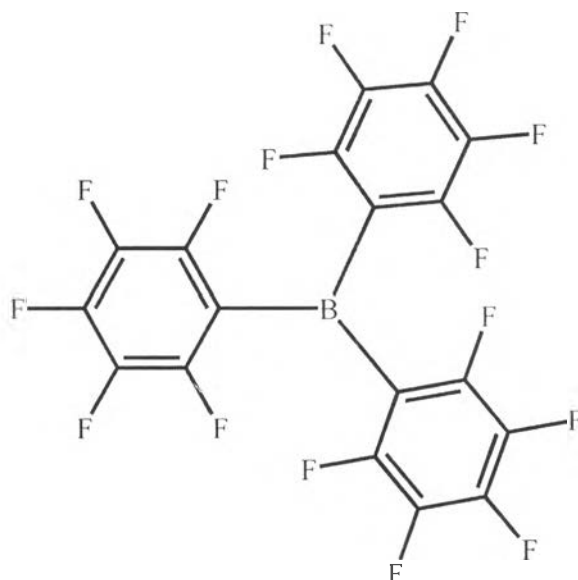
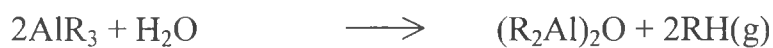


Figure 2.7 The structure of $B(C_6F_5)_3$.

The aluminum alkyl has general formula as AlR_3 where R is halogen, hydride, alkyl, alkoxy or aryl. Each R can be the same or different and at least one R is an alkyl. Preferably, the aluminum alkyl is trimethyl aluminum (TMA), triethyl aluminum (TEA) and triisobutyl aluminum (TIBA). The role of aluminum alkyl is to scavenge the impurities such as air and moisture left in the system as shown in the following equations:

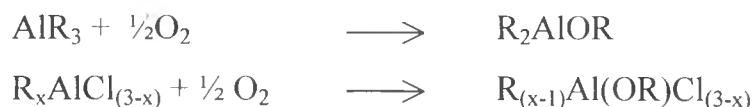
Limited water



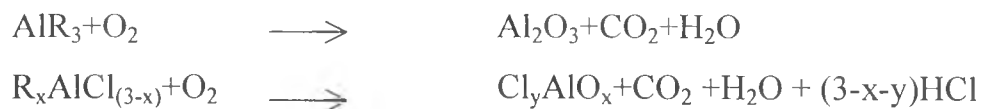
Excess water



Limited air



Excess air



2.4.3 The Reaction of B(C₆F₅)₃ with Zirconocene

The complexation of B(C₆F₅)₃ with Cp₂ZrCl₂ proceeds rapidly and quantitatively as shown, in Figure 2.8 (Yang *et al.*, 1990). In zirconocenedichloride, it needs to be alkylated first by an aluminum alkyl compound, followed by extracting of anionic ligand to produce cationic active center.

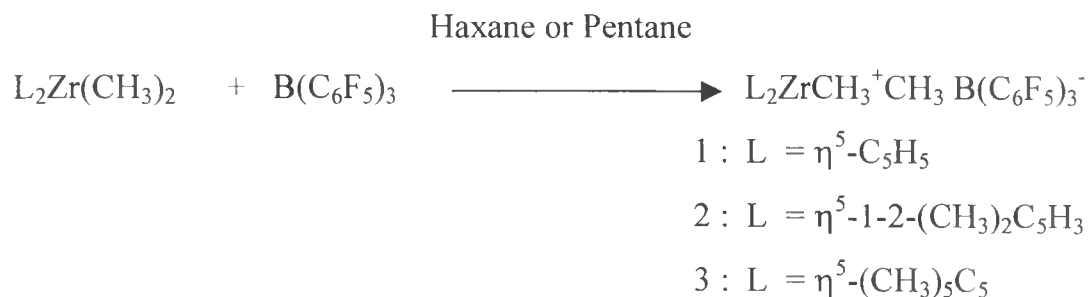


Figure 2.8 The reaction of B(C₆F₅)₃ with Cp₂ZrCl₂.

The coordinated complex structure between Cp₂ZrCl₂ and B(C₆F₅)₃ is formed via the methyl bridge (Figure 2.9). The methyl ligand is only partly abstracted from zirconocene leading to a coordinated complex with a cation-like catalytic species.

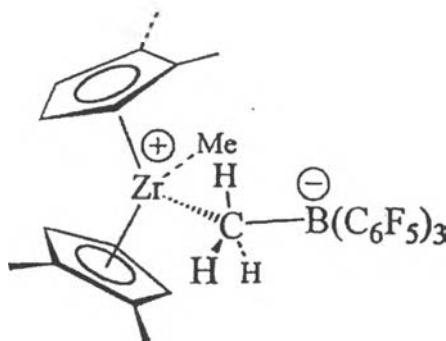


Figure 2.9 The chemical structure of the complex between Cp_2ZrCl_2 and $\text{B}(\text{C}_6\text{F}_5)_3$.

Ethylene polymerization by using two types of zirconocene combined with $\text{B}(\text{C}_6\text{F}_5)_3$ and various types of aluminum compounds has been conducted by Liu *et al.* (1997). In summary, not only the type of zirconocene but the aluminum compounds used as alkylating agents affected the activity. $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrCl}_2$ catalyst system was found to show higher activity than that of Cp_2ZrCl_2 and the catalytic activity decreased in the following order $\text{TMA} > \text{TIBA} > \text{TEA} > \text{Et}_2\text{AlCl}$. While for Cp_2ZrCl_2 , it varied as follows on: $\text{TIBA} > \text{TMA} > \text{TEA}$.

Activity, effect of cocatalyst and rate-time profiles of ethylene polymerization with zirconocene catalyst by using trialkyl aluminum (TMA, TEA, TIBA) and borane compound ($\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, $\text{B}(\text{C}_6\text{F}_5)_3$) were investigated by Naga *et al.* (1999). The results showed that not only the type of trialkyl aluminum but the borane compound used as the cation-forming reagent affected the induction time and activity of ethylene polymerization. Very low activity or no activity was observed with TMA independent of borane compound used. In the case of $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, high activity was observed with both TEA and TIBA. On the other hand, when $\text{B}(\text{C}_6\text{F}_5)_3$ was used, high activity was observed only with TIBA.