CHAPTER II

LITERATURE SURVEY

In olefin polymerization new catalyst types offer opportunity for the broadening of product variety. Metallocene is one of the new catalyst systems which entered into this technology race. This catalyst can be used in all existing industrial plants for polyolefin manufacture and has the potential to revolutionize the technology for the production of these polymers. The older Ziegler-Natta ethylene polymers consist of a broad array of molecular weights and copolymer compositions. The wide distribution shows that more than one reaction is occurring during polymerization. In contrast, metallocenes offer single site activity with narrow molecular weight distribution and better stereochemical control for ethylene-based polymers.

2.1 Homogeneous Metallocene Catalysts

Hamielec *et al.* (1996) studied the activity of metallocene catalysts. These organometallic coordination compounds in which one or two cyclopentadienyl rings or substituted cyclopentadienyl rings are bonded to a central transition metal atom (Figure 2.1).
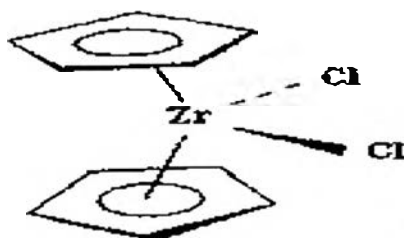

Figure 2.1 The chemical structure of Cp_2ZrCl_2.

The cyclopentadienyl ring of a metallocene is singly bonded to the central metal atom by a π-bond. Consequently, the formal valence of the ring metal bond is not centered on any one of the five carbon atoms in the ring but equally on all of them. The nature and number of the rings and substituents, the type of transition metal and its substituents, the type of the bridge, if present, determine the catalytic behavior of these organometallic compounds towards the polymerization of linear and cyclic olefins. The transition metal is usually zirconium, but other group iv metals are sometimes used. In fact, metallocene compounds are not active in polymerizing polyethylene but then aluminoxane compounds were found to act as powerful activators (Hamielec *et al.*, 1993).

2.2 The Role of Aluminoxane Cocatalyst

The type of aluminoxane has a marked influence on the efficiency of the metallocene/aluminoxane catalytic system (Soares et al., 1996). 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. An alkylating agent for the generation of transition metal-alkyl adduct.

2. A Lewis acid for anion abstraction from the complex generatingcationic metallocene alkyl species.

3. A scavenger for removal of impurities, particularly water, in the olefin and solvent.

Aluminoxanes are prepared by controlled hydrolysis of alkylaluminums. Water should be present in a dilute or a less accessible form such as in wet solvents or hydrated salts, since the reaction between water and

alkylaluminums are extremely fast and highly exothermic.The typical structural element of aluminoxane is an oxygen atom joining two aluminum atoms bearing alkyl groups.

The synthesis of aluminoxanes is associated with several serious limitations such as long reaction time to obtain a controlled exotherm, low yields, and the risk of explosion. Methylaluminoxane (MAO) is by for the most effective cocatalyst when compared to other aluminoxanes such as ethylaluminoxane (EAO) and isobutylaluminoxane (IBAO) due to its high catalytic activity (Kaminsky *et al.*, 1988).

2.3 Methylaluminoxane (MAO)

MAO is the most important cocatalyst which activates metal on the metallocene catalyst. It is an oligomer with a degree of oligomerization between 4-20. The repeating unit is -[Al(CH$_3$)$_3$-O]- (Sivaram *et al.*, 1995).

Reaction between water and alkylaluminums in the absence of solvent is highly exothermic, accompanied by flames. It yields aluminum oxide and the reaction is performed in an inert solvent. The preferred solvents are aromatic solvents and the most preferred one is toluene. Several methods have been developed by controlling and using only partial hydrolysis of alkylaluminums. The methods developed are different in the carrier used to dilute the water to slow down the reaction rate (Reddy *et al.*, 1995).

MAO is synthesized by controlled hydrolysis of trimethlyaluminum (TMA) as shown in Figure 2.2.

$$nAl(CH_3)_3 + nH_2O \longrightarrow -[Al\text{-}O]_n\text{-} + 2nCH_4$$
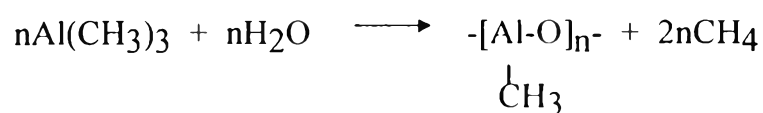$$\overset{|}{C}H_3$$
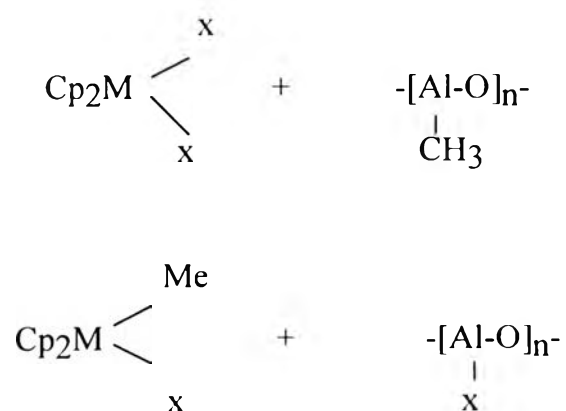
Figure 2.2 Hydrolysis of MAO using TMA.

High reactivity occurs in synthesizing MAO using TMA with water. Many hydrated inorganic compounds have been used as a source of water in preparing MAO from TMA. Hydrating compounds such as $CuSO_4.5H_2O$ and $Al_2(SO_4)_3.6H_2O$ have been employed (Kaminsky *et al.*, 1982).

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 this kind of catalyst systems, the high proportion of MAO over the zirconium complex leads to high cost but still this catalyst system has now been employed in large scale industrial processes and is currently one of the important classes of catalysts for polyolefin synthesis.

2.4 Polymerization Mechanism

2.4.1 The formation of active center

In Cp_2ZrCl_2-MAO catalyst system, MAO acts as an alkylating agent to generate a metal-alkyl ligand, primarily $Cp_2ZrMeCl$. It will next abstract the remaining halide to produce a positive charge on the metal as shown in Figure 2.3.
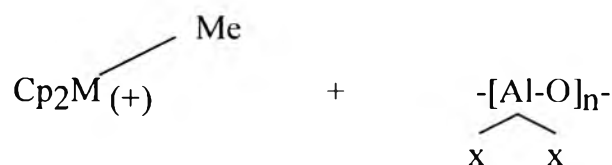
$$Cp_2M \begin{matrix} \diagup X \\ \diagdown X \end{matrix} \quad + \quad \begin{matrix} -[Al\text{-}O]_n\text{-} \\ | \\ CH_3 \end{matrix}$$

$$Cp_2M \begin{matrix} \diagup Me \\ \diagdown X \end{matrix} \quad + \quad \begin{matrix} -[Al\text{-}O]_n\text{-} \\ | \\ X \end{matrix}$$

$$\text{Cp}_2\text{M}_{(+)}\overset{\displaystyle \text{Me}}{\diagup} \qquad + \qquad \text{-[Al-O]}_n\text{-}$$
$$\overset{\displaystyle \diagup \diagdown}{x \quad x}$$

Figure 2.3 Formation of active center on metallocene with excess MAO.

This catalytic system only becomes active if Al/Zr ratio used is about 200:1 or even greater (Reddy *et al.*, 1995). The active site is loosely associated with the MAO anion.

2.4.2 The polymerization mechanism

There is still no definite polymerization mechanism for metallocene catalysts. The widely accepted model today is that proposed by Cossee *et al.* (1995) and is shown in Figure 2.4.
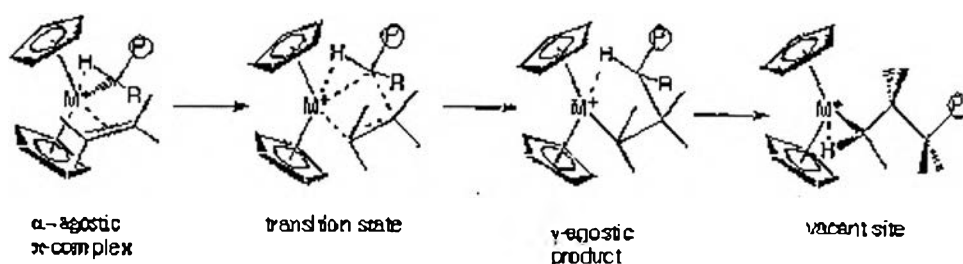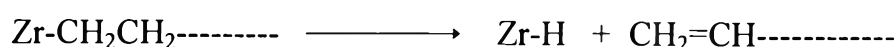

α-agostic   transition state   γ-agostic   vacant site
π-complex   product

Figure 2.4 The ethylene polymerization mechanism.

In this mechanism, the double bond of olefin monomer will first form a complex with the active site on the metal as a transition state. The olefin monomer will then insert itself into the metal-carbon bond giving back the positive charge on the metal-carbon.
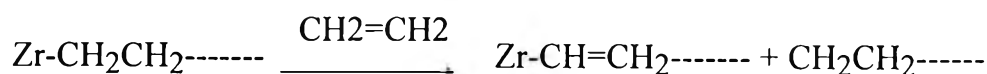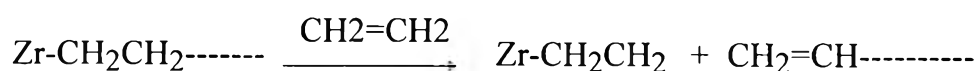
2.4.3 Chain transfer mechanism

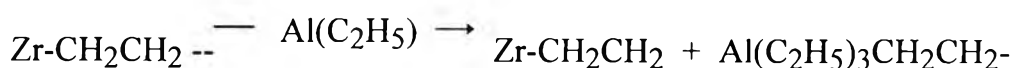Several types of transfer reactions which may occur in the metallocene catalyst system are listed in Scheme 2.1.
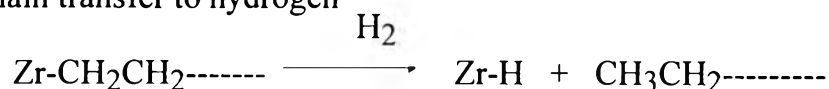
(a) β-elimination

$$Zr\text{-}CH_2CH_2\text{--------} \longrightarrow Zr\text{-}H + CH_2\text{=}CH\text{------------}$$

(b) Chain tranfer to monomer

$$Zr\text{-}CH_2CH_2\text{-------} \xrightarrow{CH2=CH2} Zr\text{-}CH_2CH_2 + CH_2\text{=}CH\text{----------}$$

$$Zr\text{-}CH_2CH_2\text{-------} \xrightarrow{CH2=CH2} Zr\text{-}CH\text{=}CH_2\text{-------} + CH_2CH_2\text{------}$$

(c) Chain tranfer to alkylaluminum

$$Zr\text{-}CH_2CH_2 \text{--} \overline{\quad Al(C_2H_5)\quad} \rightarrow Zr\text{-}CH_2CH_2 + Al(C_2H_5)_3CH_2CH_2\text{-}$$

(d) Chain transfer to hydrogen

$$Zr\text{-}CH_2CH_2\text{-------} \xrightarrow{H_2} Zr\text{-}H + CH_3CH_2\text{---------}$$

Scheme 2.1 Chain termination reactions.

2.5 Metallocene catalyst system containing nonaluminoxane compounds

2.5.1 Effect of replacing MAO with TMA

Hamielec et al. (1997) found that by increasing the MAO concentration, which also increased the Al/Zr ratio, the polymerization activity was increased up to a 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 Al/Zr ratio. Reddy *et al.* (1995) also gave the same results but only at Al/Zr ratio = 100. Recently they also demonstrated that, with the addition of TMA to a Cp_2ZrCl_2-MAO catalyst system, the kinetic profile changed from a decay type to a build-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., 1988). Polymerization using 0.1 MAO + 0.9TMA cocatalyst results in savings in TMA starting material and in time for MAO synthesis.

2.5.2 Organo-Lewis acid, 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 "cation-like" active centers such as Cp_2MR^+, but the exact structural nature of the catalyst-cocatalyst interaction 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 follows (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. Good solubility in non-polar, noncoordinating solvents.

3. The boron center is surrounded by highly electronegative, chemically robust functional groups having only nonpolar, minimally coordinating fluoro substituents.

$B(C_6F_5)_3$ is prepared by treating pentafluorophenyllithium with BCl_3 at -78 °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 shown in Figure 2.5.
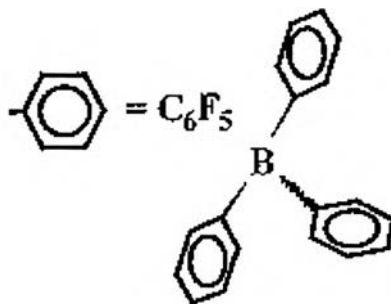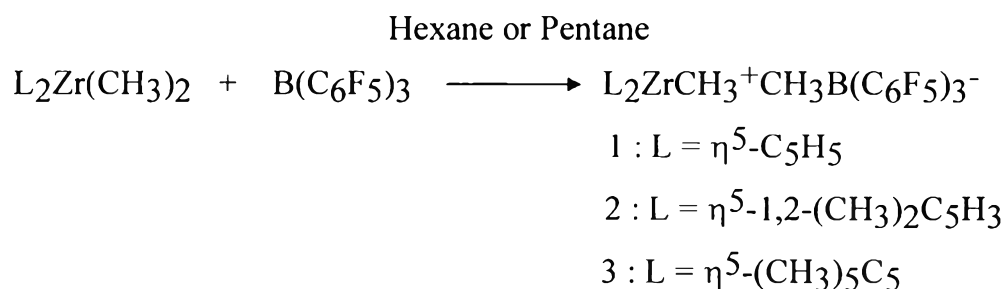
Figure 2.5 The chemical structure of $B(C_6F_5)_3$.

2.5.3 The reaction of $B(C_6F_5)_3$ with ziconocene

The complexation of $B(C_6F_5)_3$ with Cp_2ZrCl_2 proceeds rapidly and quantitavely as shown in Scheme 2.2 (Yang *et al.*, 1990). In dichlorozirconocene, it needs to be alkylated first by an aluminum compound, followed by extraction of the anionic ligand to produce active sites.

$$L_2Zr(CH_3)_2 \ + \ B(C_6F_5)_3 \ \xrightarrow{\text{Hexane or Pentane}} \ L_2ZrCH_3{}^+CH_3B(C_6F_5)_3{}^-$$

$$1 : L = \eta^5\text{-}C_5H_5$$

$$2 : L = \eta^5\text{-}1,2\text{-}(CH_3)_2C_5H_3$$

$$3 : L = \eta^5\text{-}(CH_3)_5C_5$$

Scheme 2.2 The reaction of $B(C_6F_5)_3$ with Cp_2ZrCl_2.

The coordinated complex structure between Cp_2ZrCl_2 and $B(C_6F_5)_3$ is formed via the methyl bridge (Fig 2.6). The methyl ligand is only partly abstracted from zirconocene leading to a coordinated complex with a "cation-like" catalytic species.

Liu *et al.* (1997) also studied the ethylene polymerization using zirconocene- $B(C_6F_5)_3$ catalytic system with various aluminum compounds. It was found that the catalytic activity depended on zirconocenes used, and especially on the type of aluminum compounds. For $Et(H_4Ind)_2ZrCl_2$ (H_4Ind : tetrahydroindenyl), the activity decreased in the following order TMA > TBA >TEA > Et_2AlCl. The much lower activity achieved by Et_2AlCl was attributed to the fact that Et_2AlCl cannot effectively alkylate dichlorozirconocene due to its relatively low alkyl content. While for Cp_2ZrCl_2, it varied as follows : TBA > TMA > TEA.

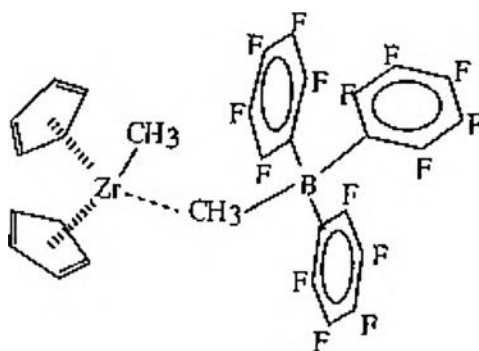**Figure 2.6** The chemical structure of the complex between Cp_2ZrCl_2 and $B(C_6F_5)_3$.