

CHAPTER II

LITERATURE SURVEY

Catalyst activity is the most important characteristic for comparing different catalyst systems. The widely used unit of activity is [g PE/mol Zr.h. atm]. The unit can be used to compare reactions using different amounts of catalyst, polymerization time and monomer pressure. However, the unit does not take into account many other factors in polymerization conditions that may affect the polymer yield such as stirring rate and the capacity of reactor. Another problem of this unit is the unit of polymerization time which is in hours. Many reported polymerizations are carried out in a very short time (30-60 seconds). These data cover only the initial period which usually has high activity, in accordance with the typical kinetic profile of decreasing polymerization rate with polymerization time. Therefore the activities reported will be exaggerated if the above unit is used.

However it is still a very useful and the most acceptable unit at present. Britovsek et al. (1999) has defined the activity value from very low to very high as shown in Table 2.1. This unit will be used in this research work.

Table 2.1 Rating of the effectiveness of a catalyst based on its activity.

Rating	Activity [kg/mol Zr.atm.h]
very low	< 1
low	1-10
moderate	10-100
high	100-1,000
very high	> 1,000

2.1 From Early Time to Typical Metallocene-Methylaluminoxane Catalyst System

The reaction of bis(cyclopentadienyl) titanium dichloride [Cp_2TiCl_2] with diethylaluminum chloride [$(\text{C}_2\text{H}_5)_2\text{AlCl}$], common cocatalyst in Ziegler-Natta catalyst system, has been investigated by Breslow and Newburg (1959). This is one of the early studies of a soluble metallocene catalyst for ethylene polymerization. This polymerization took place in a solution of 5 mmol of Cp_2TiCl_2 with 10 mmol of $(\text{C}_2\text{H}_5)_2\text{AlCl}$ in 1 liter of toluene as solvent and 125 g of polyethylene was obtained in 90 minutes. The polyethylene product has higher melting temperature and degree of crystallinity than polyethylene produced by Ziegler catalyst. The polydispersity is only 3.6 lower than 7.0 of Ziegler's.

The reaction between alkylaluminum (AlR_3) and water has been studied by Sinn and Kaminsky (1980) to understand the high polymerization activity of metallocene in their presence. They found that an oligomeric aluminoxane was formed by the reaction of TMA and water (Scheme 2.1). This highly active methylaluminoxane with bis(cyclopentadienyl) dimethyl zirconium [$\text{Cp}_2\text{Zr}(\text{CH}_3)_2$] system gave high activity of 2,500-20,000 kg PE/mol Zr.atm.h.



Scheme 2.1 The reaction of trimethylaluminum and water.

Chien and Wang (1988, 1990) studied ethylene polymerization by Cp_2ZrCl_2 -methylaluminoxane (MAO) catalysts. The productivity was found to increase with Al/Zr ratio. It can be as high as 387,000 kgPE/([Zr].h. [ethylene]) at Al/Zr ratio of 93,400.

2.2 Tris (pentafluorophenyl) Borane [B(C₆F₅)₃] as Lewis Acid for Zirconocene in MAO-Free Olefin Polymerization

Tris (pentafluorophenyl) borane [B(C₆F₅)₃] as cocatalyst in metallocene catalyst system was first studied by Yang et al. (1991, 1994). It was used stoichiometrically with a variety of zirconocene dimethyl complexes [L₂Zr(CH₃)₂] (L=Ligand). They found that these catalyst systems were active for ethylene polymerization. At 25°C, [Zr] = 0.21-0.32 mM, 1 atm of ethylene, 3,200 – 6,800 kgPE/(molZr.atm.h) of polyethylene was obtained. The polymerization time used in this study was only 40-80 seconds, which covered the initial reaction period with the catalyst reaching the highest activity. Therefore the results may not be correctly comparable to other longer period polymerization systems.

The polyethylene produced by the above catalyst system is highly linear with relatively high molecular weight ($M_w = 124,000$, $M_n = 61,200$) and narrow MWD (~2). From NMR results show the coordinated complex structure between zirconocene and B(C₆F₅)₃ is formed via the methyl bridge (Fig. 2.1). The methyl ligand is only partly abstracted from zirconocene leading to a coordinated complex with a 'cation-like' catalytic species. They also suggested that (b) should be a more accurate structure than (a).

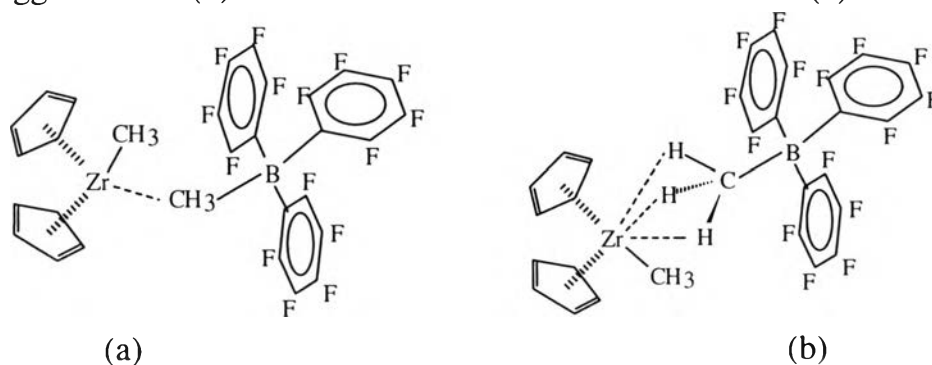


Figure 2.1 Proposed structure of $L_2Zr(CH_3)-CH_3-B(C_6F_5)_3$ from NMR.

Yang et al (1992) also showed that $\text{Cp}'_2\text{ZrH}_2$ ($\text{Cp}' = \text{C}_5\text{R}_5$; $\text{R} = \text{H}$ or alkyl group) with $\text{B}(\text{C}_6\text{F}_5)_3$ is a highly active catalyst system for ethylene polymerization. The polymerization proceeded rapidly at 25°C , 1 atm to yield a linear polyethylene ($M_w = 434,000$, $M_n = 154,200$) with 3,200 kgPE/(molZr.atm.h). The NMR results show the coordination is via the Zr-F bond (Fig. 2.2).

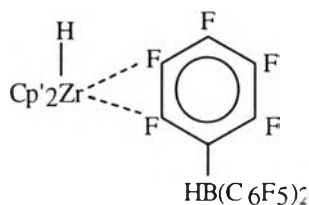
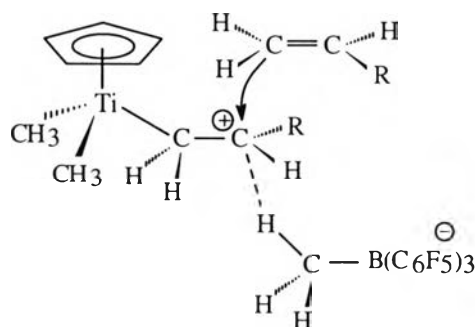


Figure 2.2 Proposed structure of $L_2\text{ZrH-HB}(\text{C}_6\text{F}_5)_3$ from NMR experiments.

The ternary systems of $\text{Et}(\text{Ind})_2\text{ZrCl}_2$, AlEt_3 , and cation forming agents $\text{B}(\text{C}_6\text{F}_5)_3$ were first demonstrated by Chien (1994) for propylene polymerization. In the ternary system which $\text{B}(\text{C}_6\text{F}_5)_3$ as the cation forming agent, very low yield was obtained (0.7-6.1 gPE/(molZr. [propylene].h) with Al/Zr ratio 60-90).

Liu et al. (1997) also studied the ternary system of zirconocene- $\text{B}(\text{C}_6\text{F}_5)_3$ catalysts with various aluminum compounds for ethylene polymerization. They found that for Cp_2ZrCl_2 , the activity decreased with the type of aluminum compounds as follows: $i\text{-Bu}_3\text{Al} > \text{Me}_3\text{Al} \gg \text{Et}_3\text{Al}$.

Quyoun et al. (1994) suggested that the reaction of $\text{Cp}'\text{Ti}(\text{CH}_3)_3$ with $\text{B}(\text{C}_6\text{F}_5)_3$ would give $[\text{Cp}'\text{Ti}(\text{CH}_3)_2][\text{BCH}_3(\text{C}_6\text{F}_5)_3]$ complex which should initiate the polymerization of electron-rich olefins as in Scheme 2.2. The second monomer will attack the carbocationic center of a metal ion-activated olefin followed by its insertion onto the growing chain.



Scheme 2.2 Proposed olefin polymerization mechanism by $[\text{Cp}^*\text{Ti}(\text{CH}_3)_2][\text{BCH}_3(\text{C}_6\text{F}_5)_3]$.

Chen et al. (1996) indicated that in $\text{Cp}_2\text{Zr}(\text{CH}_3)_2\text{-B}(\text{C}_{12}\text{F}_9)_3$ system, the activated metallocene catalysts would combine to each other to form dinuclear cation-anion pairs with nearly symmetrical $\mu\text{-CH}_3$ bridging in cation molecules (Fig. 2.3). While in the $\text{Cp}_2\text{Zr}(\text{CH}_3)_2\text{-B}(\text{C}_6\text{F}_5)_3$ system, only simple coordinated $[\text{Cp}_2\text{ZrCH}_3][\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]$ complex is found. In any case both systems are very active for ethylene polymerization with activity of 3,200-7,800 gPE/ molZr.atm.h. But this polymerization reaction takes place only within 40-60 seconds which is too short a period as described above.

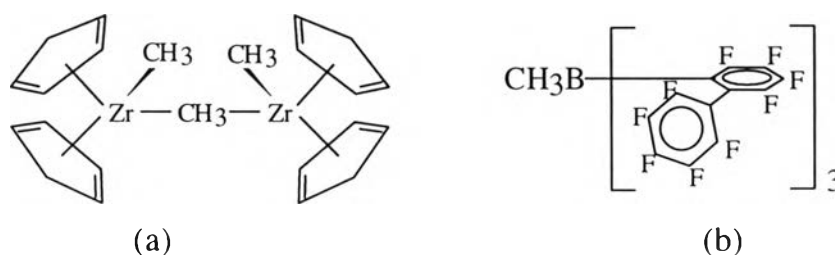
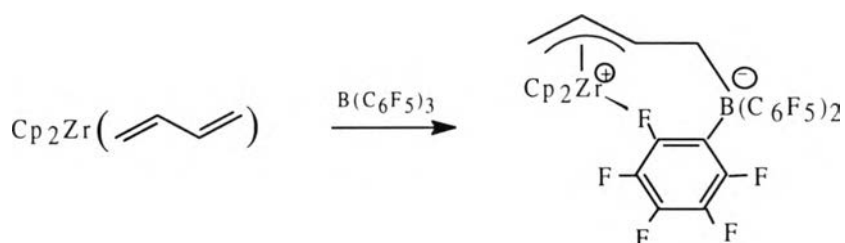


Figure 2.3 The structure proposed from NMR of dinuclear cationic (a) and anionic (b) pair, $[(\text{Cp}_2\text{ZrCH}_3)_2(\mu\text{-CH}_3)]^+[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$.

Both dinuclear $[(\text{Cp}_2\text{ZrCH}_3)_2(\mu\text{-CH}_3)]^+[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ and mononuclear $[\text{Cp}_2\text{ZrCH}_3]^+[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$ ion pairs are formed in different amounts depending on the B/Zr mole ratio as mentioned by Tritto et al.

(1999) from ^{13}C -NMR. At $\text{B}:\text{Zr} = 1:2$ only dinuclear ion pair was observed. While both of them were found at $\text{B}:\text{Zr} = 1:1$, and only mononuclear ion pair at $\text{B}:\text{Zr} = 2:1$.

Recently the new generation of a catalytic active species has been introduced by Temme et al. (1995) and Karl et al. (1997). The reaction of $[\text{Cp}_2\text{Zr}(\text{butadiene})]$ with $\text{B}(\text{C}_6\text{F}_5)_3$ results in a complex which consists of both cationic and anionic parts in one molecule called 'zwitterionic metallocene' (Scheme 2.3). The C_6F_5 bridge is easily opened allowing olefin polymerization to occur. This complex can produce polyethylene with activity about 135 kg PE/mol Zr.h and polypropylene with 2,200 kg PE/mol Zr.h.



Scheme 2.3 The zwitterionic metallocene, $\text{Cp}_2\text{Zr}(\mu\text{-C}_4\text{H}_6)\text{B}(\text{C}_6\text{F}_5)_3$.

2.3 Objectives

- 1) To study the polyethylene properties produced by Ziegler-Natta and metallocene catalyst system.
- 2) To study the effects of temperature and alkylaluminum concentration in Ziegler-Natta and metallocene catalyst system.
- 3) To study the influences of tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) on productivity and ethylene properties in metallocene catalyst system.