CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, discussion of the different catalyst systems and the effect order of catalyst injection on the productivity and activity is presented. The catalyst systems studied are Cp_2ZrCl_2/TMA, $Cp_2ZrCl_2/B(C_6F_5)_3$, and Cp_2ZrCl_2/TMA/$B(C_6F_5)_3$.

4.1 Ethylene Polymerization with TMA/$Cp_2ZrCl_2/B(C_6F_5)_3$ Catalyst Systems

4.1.1 Comparison of different cocatalyst systems

Polymerization of ethylene was carried out in 150 ml of toluene at 20 °C with an ethylene pressure and total pressure of 2 atm and duration of 1 hr. The different catalyst systems used are Cp_2ZrCl_2/TMA, $Cp_2ZrCl_2/B(C_6F_5)_3$, and $Cp_2ZrCl_2)$/TMA/$B(C_6F_5)_3$ where [Al]/[Zr] ratio = 50, [Cp_2ZrCl_2] = 10 μ mol and [$B(C_6F_5)_3$] = 10 μmol. The productivity of these polymerization systems is shown in Table 4.1. The results show that for the system which has only zirconocene dichloride and TMA or $B(C_6F_5)_3$, the productivity is negligible. In the system with both TMA and $B(C_6F_5)_3$, the productivity is high at 14.5 kgPE/mol-Zr.hr.atm. The results show that both TMA and B $(C_6F_5)_3$ are required to be present in this system. This is because zirconocene dichloride has to be first methylated by TMA to generate dimethyl zirconocene which is then reacted with $B(C_6F_5)_3$ to form the cationic species (Chien *et al.*, 1994) as shown in the following equations:

$$Cp_2ZrCl_2 + xAlMe_3 \longrightarrow Cp_2ZrMe_2 + yAlMeCl_2 \qquad (4.1)$$

$$Cp_2ZrMe_2 + B(C_6F_5)_3 \longrightarrow Cp_2Zr^{+}Me(CH_3)B^{-}(C_6F_5)_3 \qquad (4.2)$$

In this case, when ($B(C_6F_5)_3$) was injected into the reactor, there was a rapid increase in the activity as shown in Figure 4.1. The activity then gradually decreased as the catalysts were used up.

In the case when the order of catalyst injection was changed by starting with TMA followed by $B(C_6F_5)_3$ and zirconocene (Table 4.1-d), the productivity decreases to 9.5 kgPE/mol-Zr.hr.atm. This is because TMA may react with $B(C_6F_5)_3$ to form $Al(C_6F_5)_3$ as shown in Equation 4.3 (Hlatky, 1999). This is a reversible reaction that will slow down the formation of the

$$B(C_6F_5)_3 + AlMe_3 \rightleftharpoons Al(C_6F_5)_3 + BMe_3 \qquad (4.3)$$

cationic active species. As shown in Figure 4.1, the activity of this catalyst injection order gradually increases as the reaction proceeds which is in the reverse order to the other activity curves. For the system with only TMA or $B(C_6F_5)_3$ the activity is low throughout the reaction time.

Table 4.1 Ethylene polymerization with different cocatalyst systems.

	Order of injection	[Al]/[Zr]	Productivity (kgPE(mol-Zr.hr.atm)$^{-1}$)
a	TMA → Zr	50	trace
b	Zr → $B(C_6F_5)_3$	-	nil
c	TMA → Zr → $B(C_6F_5)_3$	50	14.5
d	TMA → $B(C_6F_5)_3$ → Zr	50	9.5

Conditions: Cp_2ZrCl_2 10 μmol; $B(C_6F_5)_3$ 10 μmol; toluene 150 ml; ethylene pressure 2 atm; temperature 20 °C; polymerization time 1 hr.

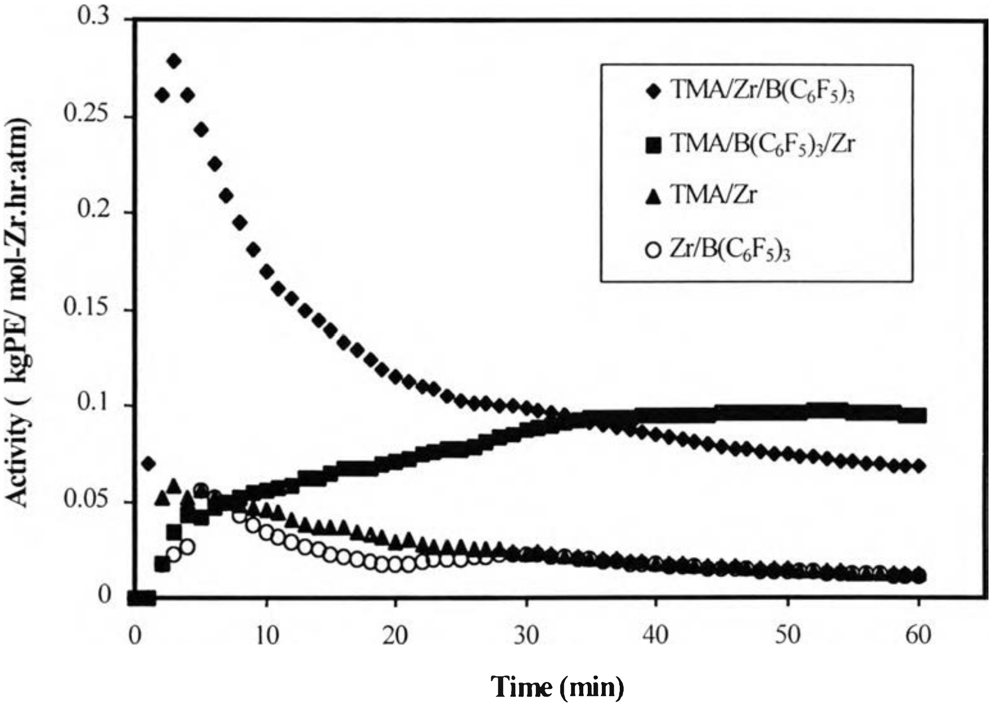

Figure 4.1 The dependence of activity on catalyst systems.

4.1.2 Effect of zirconocene concentration at constant [Al]/[Zr] ratio

The catalyst injection in the order of TMA followed by zirconocene dichloride and $B(C_6F_5)_3$ was used to study the effect of the amount of zirconocene catalyst on the productivity and activity. The productivity of ethylene polymerization with varying [Zr] increases with increase in [Zr] before it starts to drop at the amount of zirconocene equals 50 µmol. The results are shown in Table 4.2. Figure 4.2 shows the increase in activity as [Zr] increases. The increase in both productivity and activity with increase in [Zr] is due not only to the increase in the active sites, but also increase in amount of TMA as the Al/Zr ratio is kept constant.

Table 4.2 Ethylene polymerization with varying [Zr].

Order of injection	[Zr] μmol	Productivity (kgPE(molZr.hr.atm)$^{-1}$)
TMA → Zr → $B(C_6F_5)_3$	10	14.5
TMA → Zr → $B(C_6F_5)_3$	20	22.1
TMA → Zr → $B(C_6F_5)_3$	30	58.5
TMA → Zr → $B(C_6F_5)_3$	50	42.5

Conditions: Al/Zr = 50; $B(C_6F_5)_3$ 10 μmol; toluene 150 ml; ethylene pressure 2 atm; temperature 20 °C; polymerization time 1 hr.

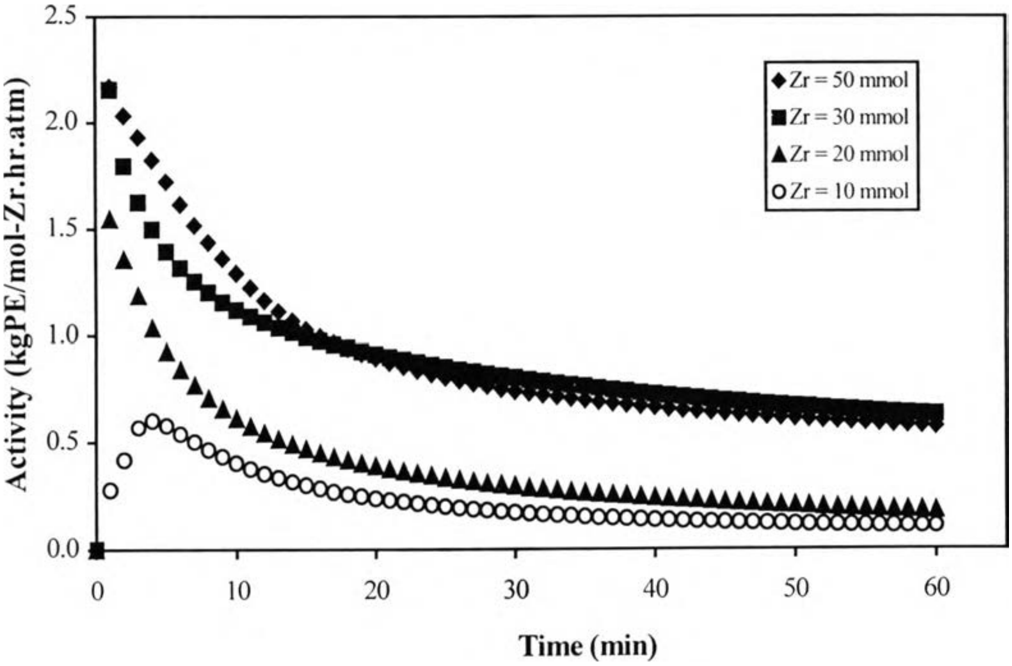

Figure 4.2 The dependence of activity of $Cp_2ZrCl_2/TMA/B(C_6F_5)_3$ system on [Zr].

4.1.3 Effect of varying [Al]/[Zr] ratio at constant [Zr]

The best order of catalyst injection, TMA → Zr → $B(C_6F_5)_3$ was used to study the effect of varying [Al]/[Zr] ratio on the productivity and activity. It was found that at constant amount of zirconocene dichloride and $B(C_6F_5)_3$ of 10 μmol, the productivity increases as the concentration of TMA increases as shown in Table 4.3. Figure 4.3 shows the corresponding activity curve at [Al]/[Zr] ratio. The increase in both productivity and activity is due to the stabilizing of the cationic active species by TMA.

Table 4.3 Ethylene polymerization with varying [Al]/[Zr] ratio.

Order of injection	[Al]/[Zr]	Productivity (kgPE(mol-Zr.hr.atm)$^{-1}$)
TMA → Zr → $B(C_6F_5)_3$	50	14.5
TMA → Zr → $B(C_6F_5)_3$	60	17.8
TMA → Zr → $B(C_6F_5)_3$	80	30.5
TMA → Zr → $B(C_6F_5)_3$	100	49.2

Conditions: Cp_2ZrCl_2 10 μmol; $B(C_6F_5)_3$ 10 μmol; toluene 150 ml; ethylene pressure 2 atm; temperature 20 °C; polymerization time 1 hr.

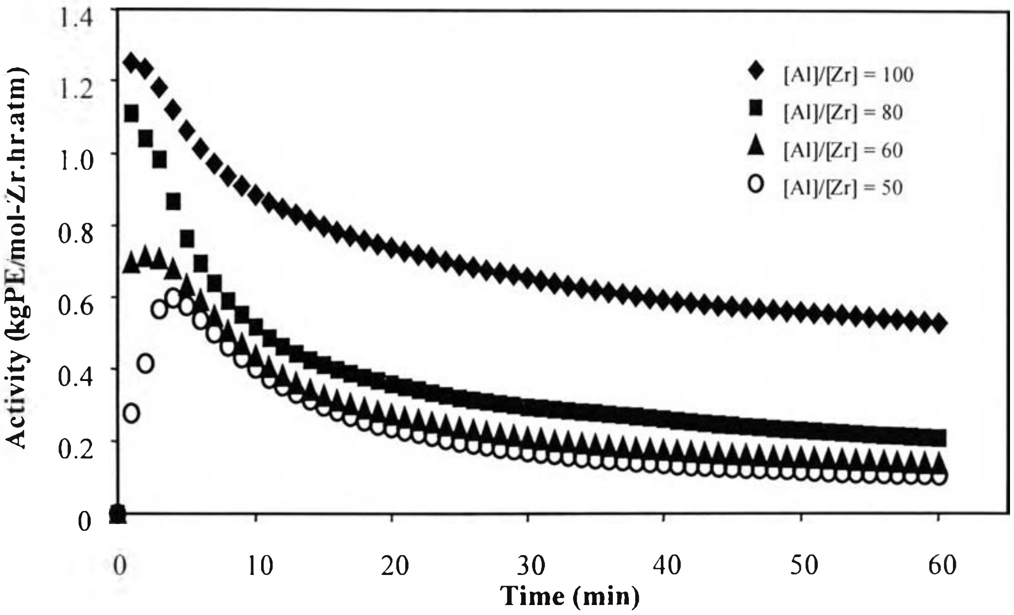

Figure 4.3 The dependence of activity of $Cp_2ZrCl_2/TMA/B(C_6F_5)_3$ system on [Al]/[Zr].

4.1.4 Effect of prealkylating the zirconocene catalyst with TMA

To improve the productivity and activity of the catalyst system with injection we tested the effect of prealkylating zirconocene. Zirconocene dichloride was first prealkylated with TMA before it was injected into the reactor. The results in Table 4.4 and Figure 4.4 show that the productivity and activity were found to decrease rapidly as the amount of TMA used in the prealkylating increases. This may be because the active species of prealkylated catalyst are destroyed by the TMA in the reactor as shown in the following Equation 4.4 (Liu *et al.*, 1997).

$$[Cp_2ZrR^+][^-ClB(C_6F_5)_3] \underset{-R_3Al}{\overset{+R_3Al}{\rightleftharpoons}} [Cp_2ZrR^+][^-ClAlR_3] + B(C_6F_5)_3 \quad (4.4)$$

Table 4.4 Ethylene polymerization with prealkylated zirconocene.

Order of injection	[Al]/[Zr]	Productivity (kgPE(mol-Zr.hr.atm)$^{-1}$)
500 μmol TMA → $B(C_6F_5)_3$ → Zr	50	9.5
500 μmol TMA → $B(C_6F_5)_3$ → (100 μmol TMA+Zr)	60	10.95
500 μmol TMA → $B(C_6F_5)_3$ → (200 μmol TMA+Zr)	70	3.55
500 μmol TMA → $B(C_6F_5)_3$ → (300 μmol TMA+Zr)	80	2.95

Conditions: Cp_2ZrCl_2 10 μmol; $B(C_6F_5)_3$ 10 μmol; toluene 150 ml; ethylene pressure 2 atm; temperature 20 °C; polymerization time 1 hr.

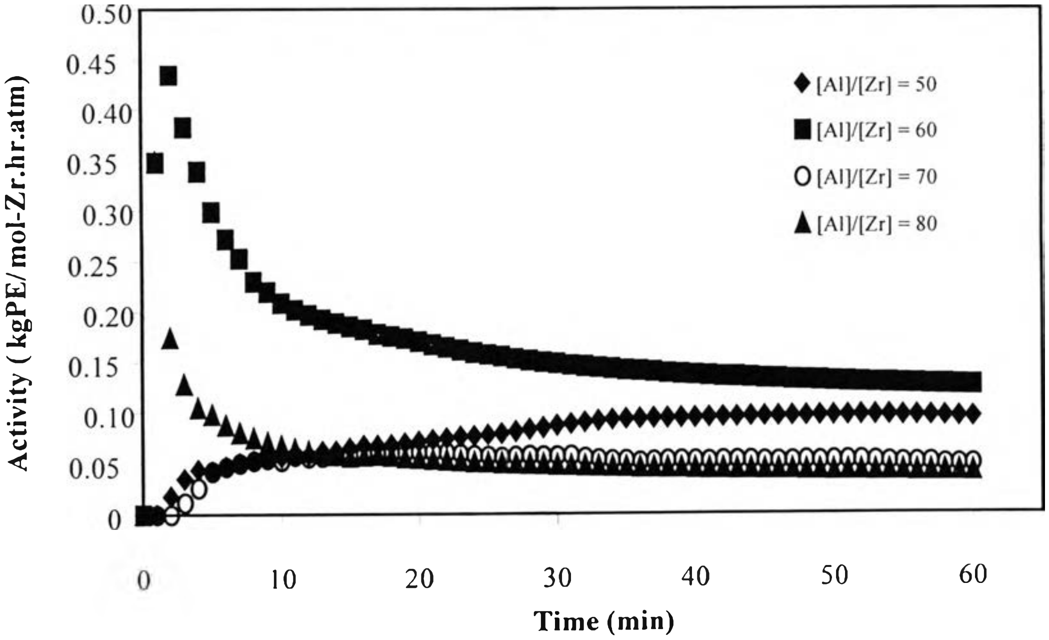

Figure 4.4 Comparison of rate curves with different [Al] in prealkylating of zirconocene dichloride.

4.1.5 Effect of preactivating the zirconocene catalyst at constant [Zr]

In this study, we compared the productivity of prealkylating and preactivating [The preactivating is carried out by adding both $B(C_6F_5)_3$ and TMA into zirconocene before injecting into the reactor] zirconocene catalyst at constant [Al]/[Zr] of 60 and constant $[Cp_2ZrCl_2]$ and $[B(C_6F_5)_3]$of 10 µmol. The productivity and activity of the preactivated system is found to be higher than in the case of prealkylation in as shown Table 4.5 and Figure 4.5. In the preactivated system, the reaction can take place immediately after catalyst injection leading to a higher activity at the beginning of the reaction, thus the productivity of the preactivated system is higher.

Table 4.5 Ethylene polymerization with preactivated zirconocene.

Order of injection	[Al]/[Zr]	Productivity (kgPE(mol-Zr.hr.atm)$^{-1}$)
500 µmol TMA → $B(C_6F_5)_3$ → (100 µmol TMA+Zr)	60	10.9
500 µmol TMA → ($B(C_6F_5)_3$ +100 µmol TMA+Zr)	60	15.9

Conditions: Cp_2ZrCl_2 10 µmol; $B(C_6F_5)_3$ 10 µmol; toluene 150 ml; ethylene pressure 2 atm; temperature 20 °C; polymerization time 1 hr.

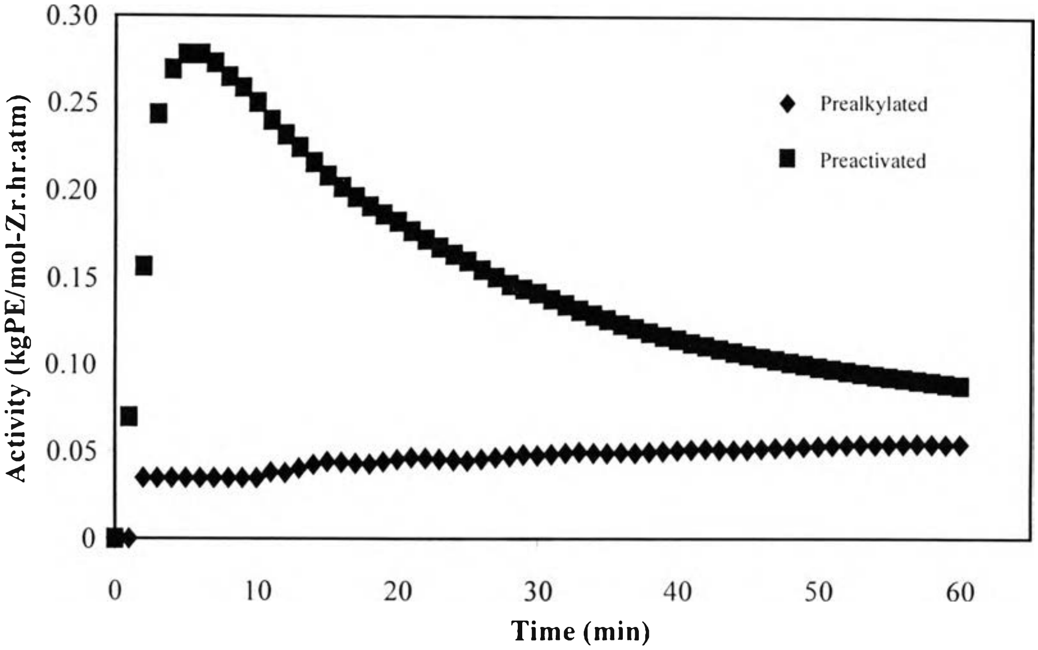

Figure 4.5 Comparison of rate curves between prealkylated and preactivated zirconocene dichloride.