

CHAPTER V

RESULTS AND DISCUSSIONS

5.1 THE EFFECT OF CATALYST RATIO

The general characteristic of Ziegler-Natta catalyst is activated by cocatalyst, alkyl aluminum. $\text{Cp}_2\text{TiCl}_2/\text{AlR}_2\text{Cl}$ (Cp = η^5 -cyclopentadienyl, R = alkyl) was the first homogeneous Ziegler-Natta catalyst found for ethylene polymerization[12]. The catalytic activity decayed rapidly due to reduction of titanium so catalyst have very poor activity. $\text{Cp}_2\text{TiCl}_2/\text{AlR}_2\text{Cl}$ was virtually inactive because of even faster reduction of titanium. many reaction was found to activate by alkyl aluminum.

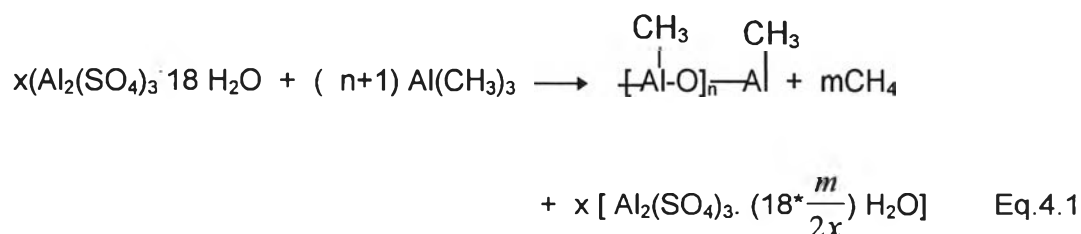
There is now a new family of catalyst, found by Kaminsky and coworker[99]. Homogeneous catalyst such as Cp_2ZrMe_2 or Cp_2ZrCl_2 in toluene solution activated with methylaluminoxane can polymerize ethylene with high activities

The ethylene consumption versus polymerization time was shown in Figure 5.1 and the catalytic activity versus Al/Zr mole ratio was shown in Figure 5.2. Figure 5.2 was shown a maximum activity at Al/Zr mole ratio of 4400. The term of rate of polymerization referred to the rate of ethylene consumption during polymerization. The term of activity referred to gram of polyethylene produced per gram of zirconium at 1 atmosphere partial pressure of ethylene during 1 hour of polymerization time. The concentration of Al in aluminoxane refer to amount of trialkylaluminum using in preparing

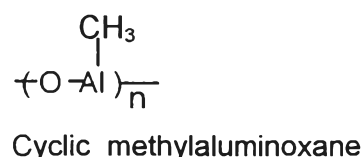
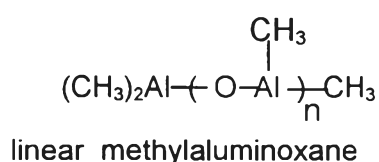
cocatalyst. A concentration of Cp_2ZrCl_2 , temperature polymerization and ethylene partial pressure in system were $34 \mu\text{M}$, 30°C and 20 psi , respectively.

Figure 5.1 was plotted of ethylene consumption versus polymerization time and shown activity higher as the mole ratio of Al/Zr increased from 700 to 1400. The highest was observed at the mole ratio 4400. At the Al/Zr mole ratio, 8800, was decreased of catalytic activity. In Figure 5.2 showed a maximum point at the ratio 4400.

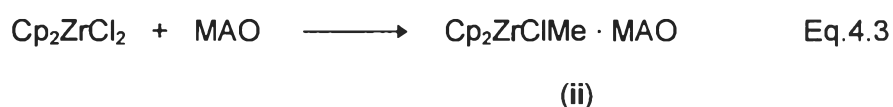
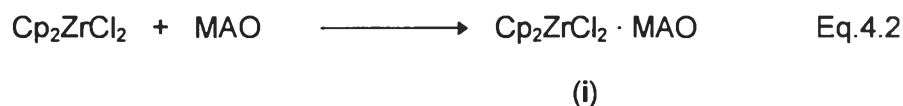
Aluminoxanes were synthesized by controlled hydrolysis of aluminum alkyl. Simple symmetric routes to methylaluminoxane were not available due to the high reactivity of trimethylaluminum with water. Many inorganic hydrated compound were use as a source of water for preparing aluminoxane from alkyl aluminum. The use of metallocene and aluminoxane as cocatalyst resulted in extremely high polymerization activity. The methylaluminoxane was prepared by careful treatment of trimethylaluminum with hydrated aluminum salts[100].



There are two different structures for methylaluminoxane:



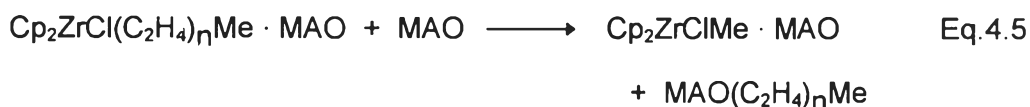
It is reasonable to assume that MAO acts in the following function. The first is to complex with and alkylated the metallocene.



This results in the catalytic active species and propagation follows.

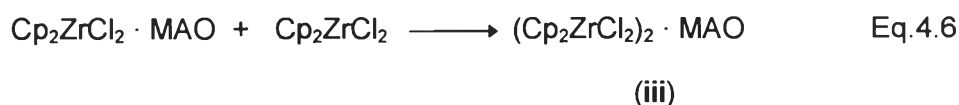
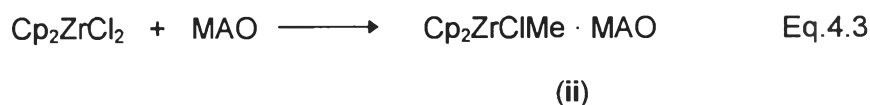
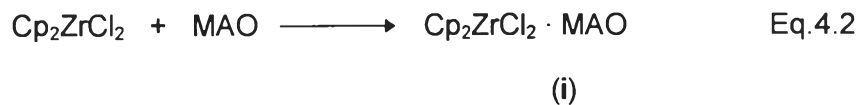


The second role of MAO is to act as chain transfer agent.



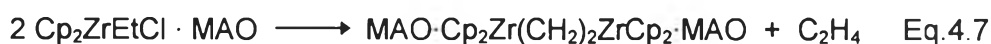
For the simple $\text{Cp}_2\text{TiCl}_2/\text{AlR}_2\text{Cl}$ systems [12], the catalytic activity is highest at Al/Ti ratio of approximate 2. For the MgCl_2 supported catalyst, the productivity is greatest at Al/Ti = 160 [101]. In contrast the activity of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ seem to increase with increase of Al/Zr mole ratio.

The polymerization profile of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ is in Figure 5.1. The initial rate of polymerization is large followed by decay to about half the rate. The metallocene/MAO catalyst have the characteristics which are contrast to other supported Ziegler-Natta catalyst systems. In the supported catalyst, Ti metal are thought to fix on the MgCl_2 supported. But the interaction of metallocene/MAO complex is weaker. there is the following complexation[17].



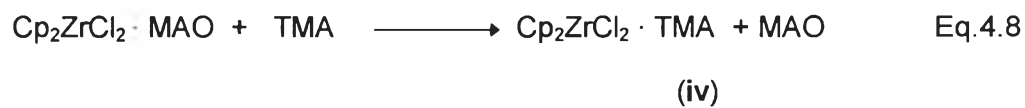
The methylaluminoxane was the oligomer of -(O-Al)_n , so the general structure $(\text{Cp}_2\text{ZrCl}_2)_a \cdot \text{MAO}$ (iii) where $2 \leq a \leq n$ and n lies between 6 - 20.

At high $[\text{MAO}]/[\text{Zr}]$, the dominant species present was (i). The methyl metallocene (ii) complexed to MAO was reasonable stable. However, monomer insertion the higher alkyl undergo ready bimolecular deactivation[102].



To avoid this process, species (ii) should be surrounded by MAO without complexed metallocene. This was explanation for the higher catalytic activity of ethylene polymerization increasing Al/Zr mole ratio. It was important that the ratio $[\text{MAO}]/[\text{Zr}] > n$ to avoid the formation of (iii) which would undergo reaction Eq.4.7 intramolecular causing of deactivation.

However, Al/Zr mole ratio of 8800 the catalytic activity was lower than Al/Zr mole ratio because trimethylaluminum (TMA) residue in prepared cocatalyst was more excess in system. Trimethylaluminum which exceed in the system can be reduced catalytic activity. It was reasonable to assume competitive equilibrium.



This specie (iv) can be deactivate according to Eq.4.7

From the practical view point, a standard condition of mole ratio Al/Zr of 4400 was investigated for further experiment because it show the highest of catalytic activity.

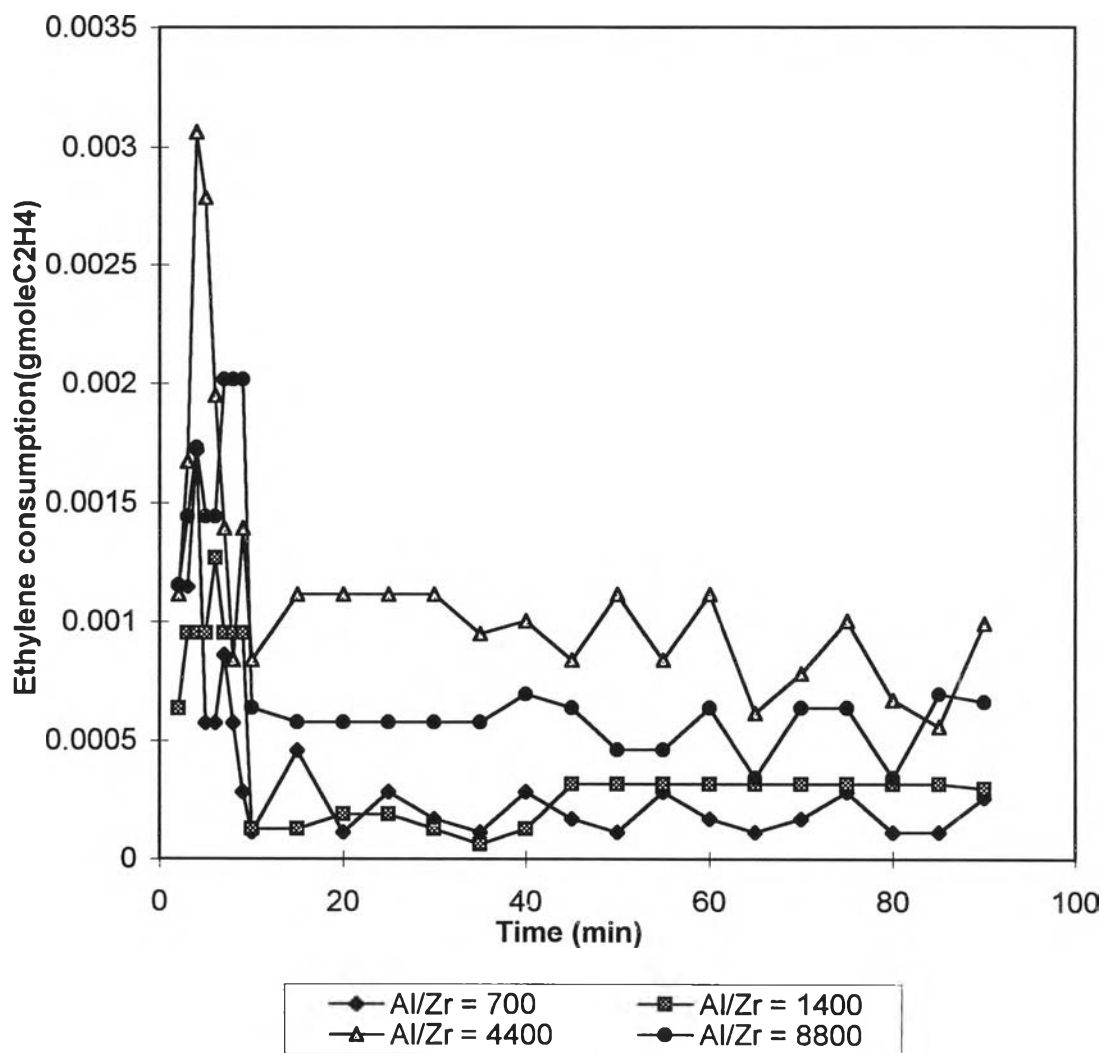


Figure 5.1 Ethylene Consumption versus Polymerization time curve at various Al/Zr mole ratios

Polymerization condition : $[Zr] = 34 \cdot 10^{-6}$ moleZr/l,

Temperature = 30 °C,

Ethylene partial pressure = 20 psi,

Al/Zr mole ratios of 700, 1400, 4400, 8800, respectively

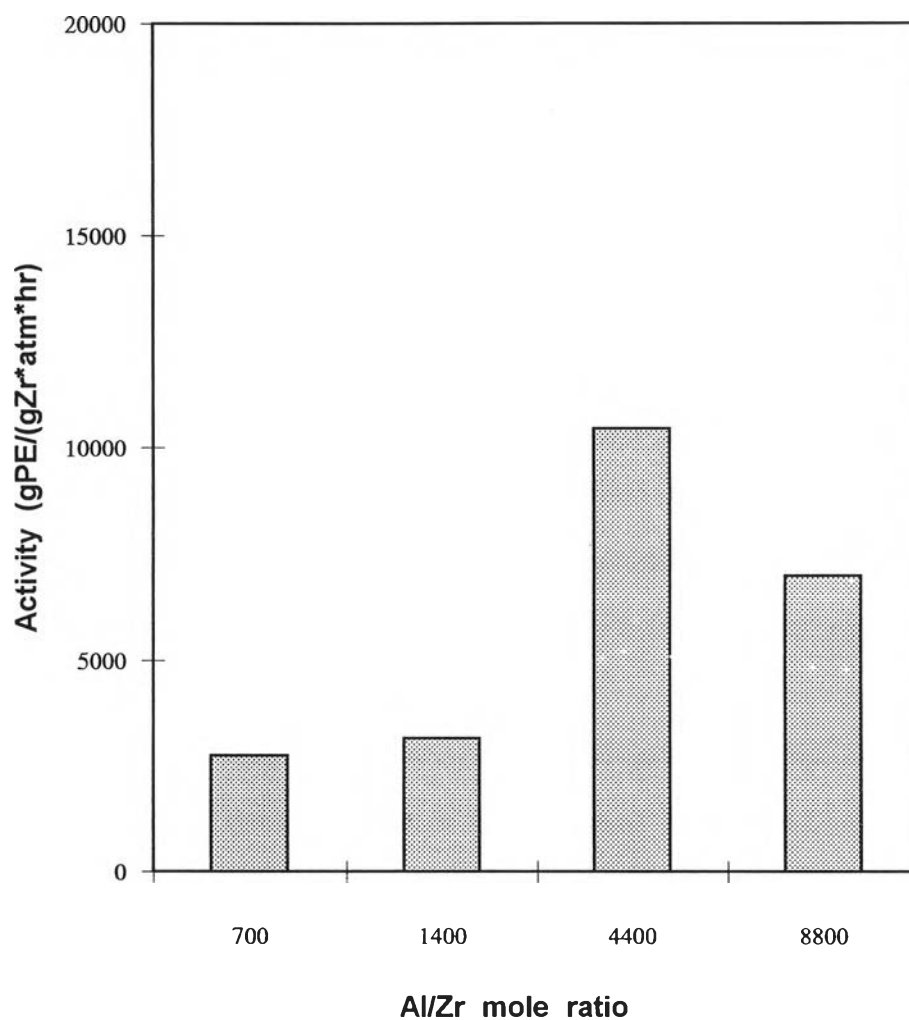


Figure 5.2 Activity versus Al/Zr mole ratio

Polymerization condition : $[Zr] = 34 \cdot 10^{-6}$ moleZr/l,

Temperature = 30 °C,

Ethylene partial pressure = 20 psi,

Al/Zr mole ratios of 700, 1400, 4400, 8800, respectively

5.2 THE EFFECT OF ETHYLENE PARTIAL PRESSURE

The characteristic curve of ethylene consumption versus time at various ethylene partial pressure was showed in a Figure 5.3. The polymerization rate of ethylene was increased as the partial pressure of ethylene was increased. At the partial pressure of ethylene of 30, 40 psi, the media in system of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ high viscous until could not stir, thus polymerization was stop at 30 min. The catalytic active versus the partial pressure of ethylene indicated that activity increased with increasing of partial pressure of ethylene as shown in a Figure 5.4.

Because ethylene monomer diffused into the media, toluene, it was polymerization at active site. The polymerization reaction was an exothermic reaction, the rapid increase in growth chain induces the high temperature so that heat transfer effect was careful.

According to the equation ($R_p = k_p[C_i^*][M]$), It is reasonable the productivity depend on the monomer concentration. When increasing the partial pressure of ethylene was induced to rise the concentration of ethylene diffused into the media, it caused to rise the catalytic activity thus catalytic activity increased as the partial of ethylene increased, corresponding to report by Jungling et al[103]. Chien and Wang[19] showed that rate of polymerization of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ was proportional to monomer concentration.

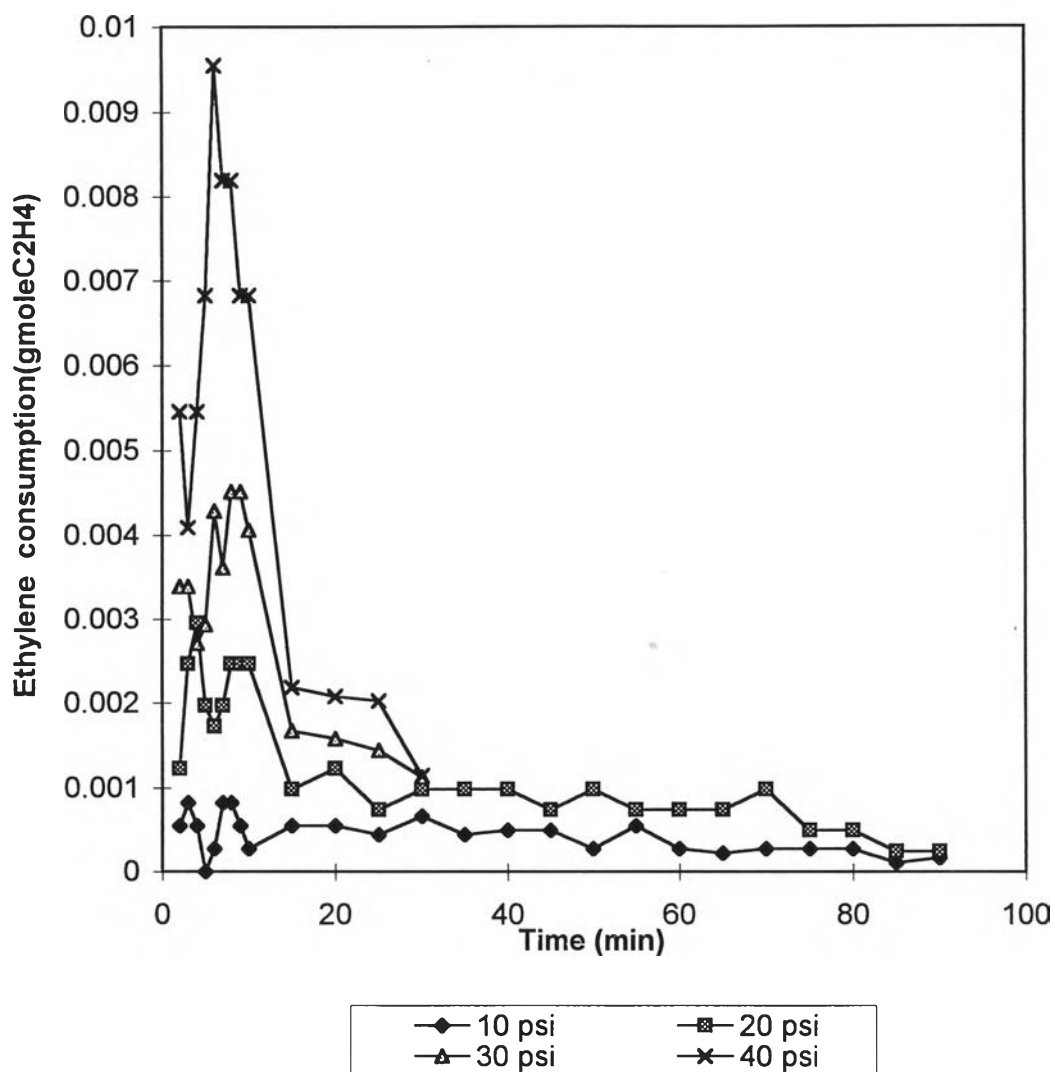


Figure 5.3 Ethylene Consumption versus Polymerization time curve

at various Partial pressure of ethylene

Polymerization condition : $[Zr] = 34 \cdot 10^{-6}$ moleZr/l,

Temperature = 30 °C,

Al/Zr mole ratio = 4400

Partial pressure of ethylene of 10, 20, 30, 40 psi, respectively

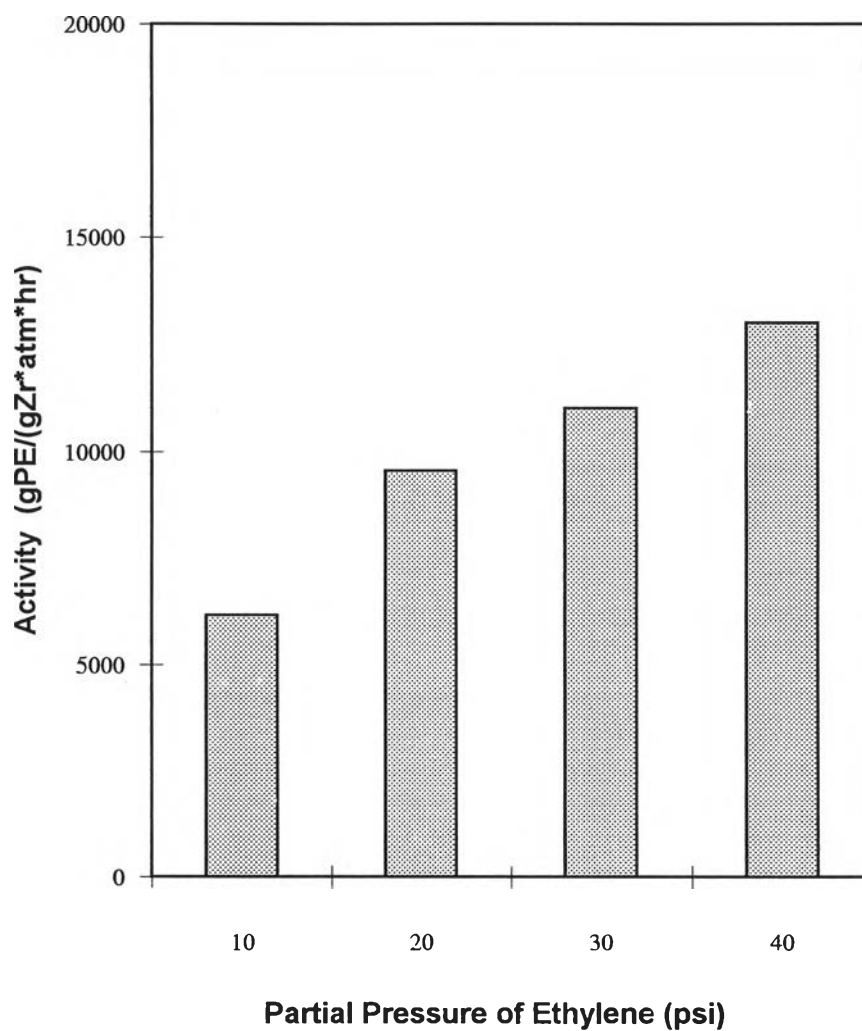


Figure 5.4 Activity versus Partial pressure of ethylene

Polymerization condition : $[Zr] = 34 \cdot 10^{-6}$ moleZr/l,

Temperature = 30 °C,

Al/Zr mole ratio = 4400

Partial pressure of ethylene of 10, 20, 30, 40 psi, respectively

5.3 THE EFFECT OF TEMPERATURE

This section was designed to study the effect of temperature. This study was performed at different condition. The temperature was varied from 0 - 80 °C and pressure was constant at 20 psi. The metallocene catalyst, Cp₂ZrCl₂, is a concentration at 34 μM and mole ratio Al/Zr of 4400.

The ethylene consumption profile versus polymerization time showed in Figure 5.5 and the catalytic activity versus polymerization temperature show in Figure 5.6. At low temperature, the polymerization rate increased as the temperature of polymerization increased. The fall off in rate reaction rate was observed at the high temperature of polymerization. Figure 5.6 showed the maximum catalytic activity at temperature of polymerization of 55 °C. The catalytic activity was found low activity at the low temperature and increasing the catalytic as temperature increase until maximum activity this temperature and decrease latter. It was a common a characteristic of Ziegler-Natta catalyst that was an optimum temperature range for maximum activity which decrease at temperature either above or below it.

The variation of polymerization rate, R_p, with time was from 0 to 80 °C. There was a short period of rate build up of a few minutes, the duration of which is shorter for high temperature. At 55 °C initiation was instantaneous. There was a drop of polymerization rate about 50% after the maximum was reach in the rate build up. After 10 min. of polymerization the polymerization rate, R_p, became constant along the polymerization time.

The polymerization rate of the *i*th species is

$$R_{p,i} = k_{p,i} [C_i^*] [M] \quad \text{Eq.4.9}$$

The overall polymerization rate is the sum of $R_{p,i}$

$$R_p = \sum_i k_{p,i} [C_i^*] [M] \quad \text{Eq.4.10}$$

The productivity of i^{th} species is

$$P_i = k_{p,i} [M] \int [C_i^*] dt \quad \text{Eq4.11}$$

and the total P can be written as

$$P = [M] \sum_i k_{p,i} \int [C_i^*] dt \quad \text{Eq4.12}$$

$[M]$ = monomer concentration

$[C_i^*]$ = active species concentration

k_p = propagation rate constant

Figure 5.6 showed that catalytic activity was very strongly affected by increasing temperature. The increase in the temperature caused an increase in k_p (propagation rate constant) and active site. Chien and Wang[104] investigated rate of polymerization and active site concentration. They found that at 70 °C, rate of polymerization maximum, $R_{p,m}$, of $7.2 \cdot 10^{-4} \text{ Ms}^{-1}$ and steady rate of polymerization, $R_{p,f}$, of $4.4 \cdot 10^{-4} \text{ Ms}^{-1}$ in the case of Al/Zr of $1.1 \cdot 10^{-4} \text{ Ms}^{-1}$ and the value $[C^*]$ was a 74% $[\text{CpZrCl}_3]$. At 50 °C, $R_{p,m}$ of $1.6 \cdot 10^{-4} \text{ Ms}^{-1}$ and $R_{p,f}$ of $1.1 \cdot 10^{-4} \text{ Ms}^{-1}$ in the case of Al/Zr of $1.1 \cdot 10^{-4} \text{ Ms}^{-1}$ and the value $[C^*]$ was 21% $[\text{CpZrCl}_3]$.

Investigate on the dependence of catalytic activity upon the polymerization temperature was corresponding to report Gannettic, Nicoletti, and Mazzocchi[15]. They showed the maximum productivity of $(\text{Ind})_2\text{Zr}(\text{CH}_3)_2$ and $\text{Cp}_2\text{Zr}(\text{C}_6\text{H}_5)_2$ at about 50 °C. On the other hand, the decrease catalytic activity was observed at 80 °C because complex of metallocene/MAO is unstable. It was caused to deactivated and low catalytic activity.

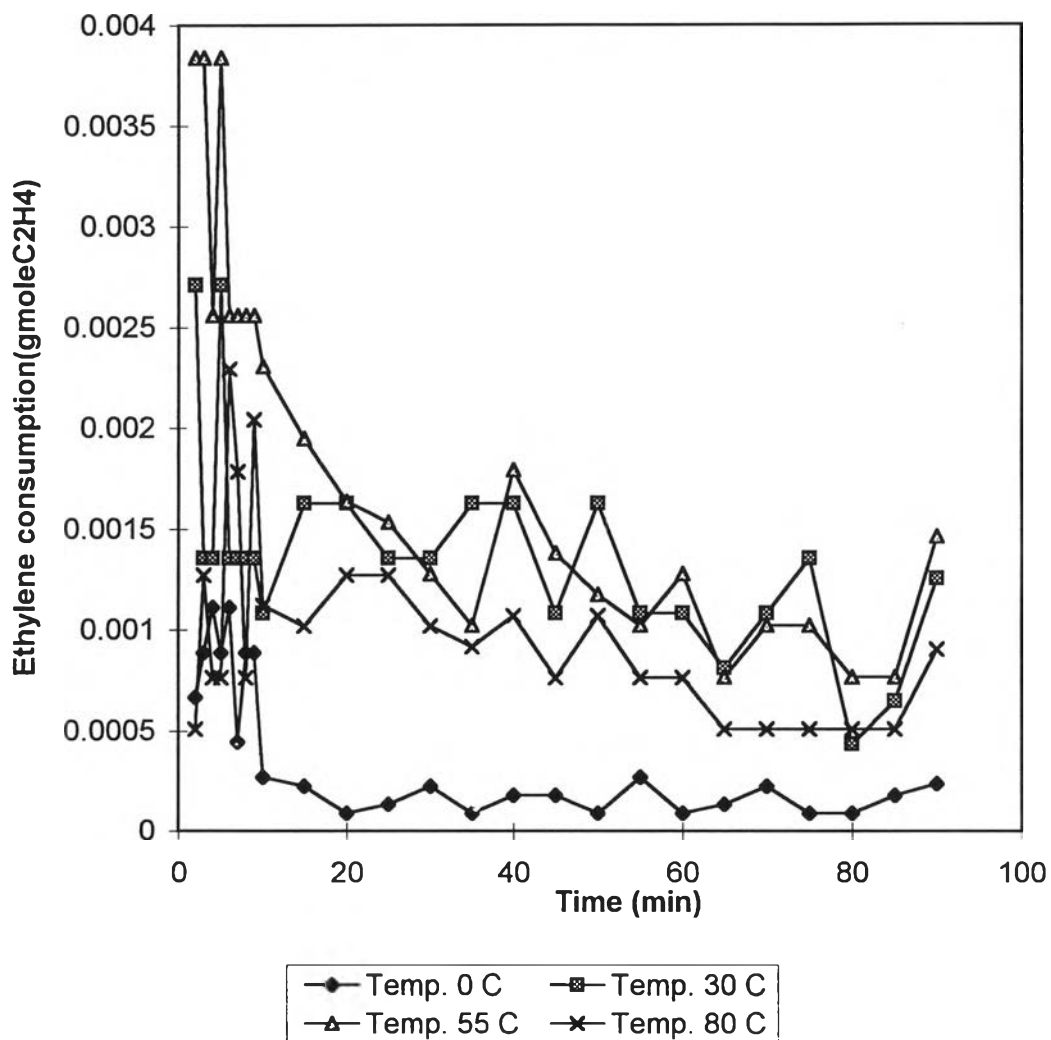


Figure 5.5 Ethylene Consumption versus Polymerization time curve at various Temperature

Polymerization condition : $[Zr] = 34 \cdot 10^{-6}$ moleZr/l,

Ethylene partial pressure = 20 psi,

Al/Zr mole ratio = 4400,

Temperature of 0, 30, 55, 80 °C, respectively

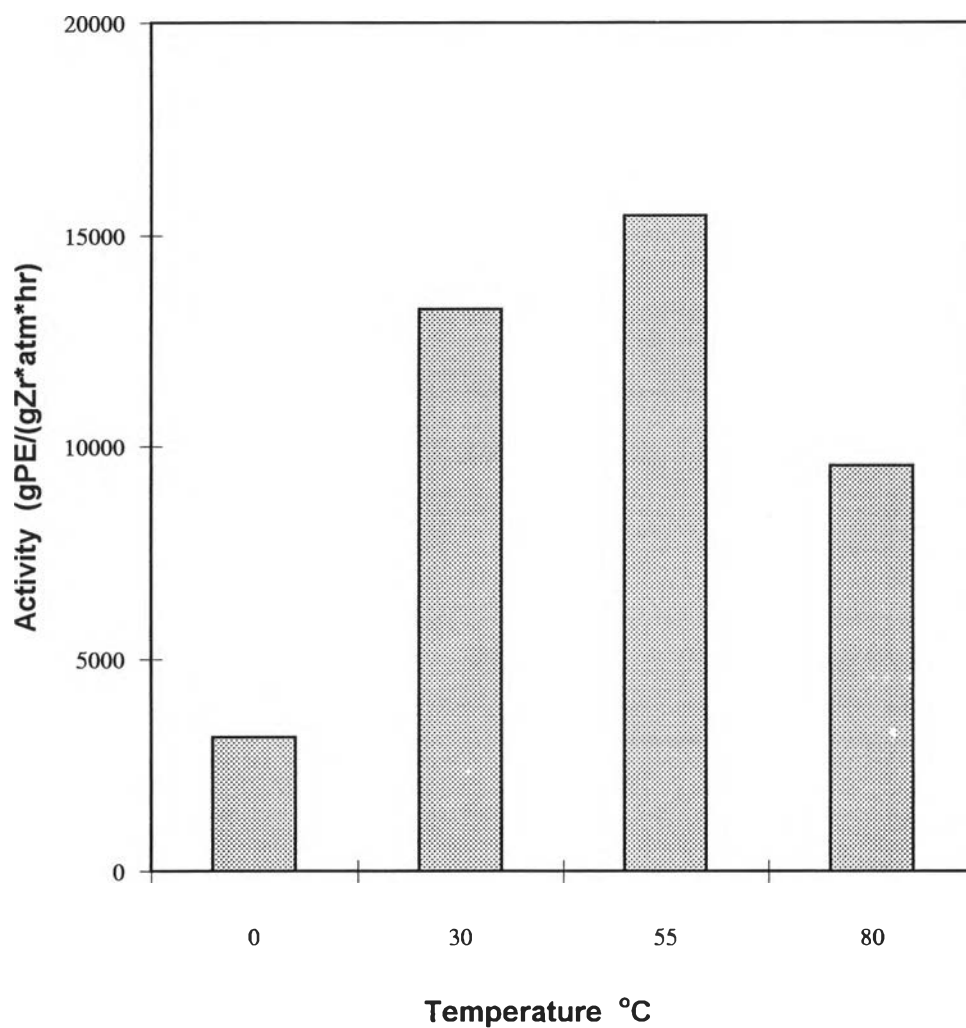


Figure 5.6 Activity versus Temperature

Polymerization condition : $[Zr] = 34 \cdot 10^{-6}$ moleZr/l,

Ethylene partial pressure = 20 psi,

Al/Zr mole ratio = 4400,

Temperature of 0, 30, 55, 80 °C, respectively

5.4 THE EFFECT OF COCATALYST

In metallocene-base catalyst systems, the aluminoxane appear to have combination of the following function :

1. Aluminoxane alkylates the metallocene compound and scavengers the impurities.
2. Aluminoxane interaction with metallocene to generate a cationic metallocene.

In this experiment, it carried out to investigated the effect of cocatalyst on the ethylene polymerization. The condition of ethylene polymerization was performed in the ethylene partial pressure of 20 psi, Al/Zr mole ratio of 4400 temperature 55 °C and Cp_2ZrCl_2 of 34 μM .

The characteristic curve of ratio of ethylene polymerization versus polymerization time is shown in a Figure 5.7 and the catalytic activity was plot with cocatalyst is shown in a Figure 5.8. It was found that Methylaluminoxane (MAO) cocatalyst was given the catalytic activity dramatic higher than ethylaluminoxane (EAO)

The aluminoxane not only produced the cation but also stabilized them[105]. The interaction of metallocene with aluminoxanes had been studied in detail[106]. It undergo either methyl or chloride abstraction to generate metallocene methyl cation. The interaction of dichlorozirconocene, methylchlorozirconocene, and dimethylzirconocene with MAO had been studied by x-ray photoelectron spectroscopy by Gassman and Callstrom[107]. The

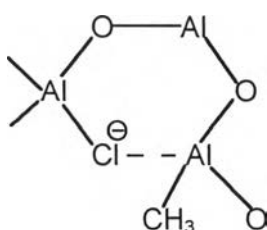
results indicated the formation of cationic metallocene with MAO as the counteranion.

The mechanism of monoolefins polymerization catalyzed by a high active metallocene-aluminoxane system had been the subject of many experimental and theoretical investigations. In the cation metallocene species, the metal atom is coordinated with the π -ligands and alkyl group. During polymerization, the monomer is coordinated with a highly electrophilic and coordinatively unsaturated cationic complex. It is followed by insertion of a monomer in the metal-carbon bond to produce a polymer chain. The migration of polymer chain, P, and the formation of the metal-carbon bond occur in concert throughout a four-center transition state. This results in the recreation of a vacant coordination site at the originally occupied by the polymer chain. This process involving shifting of the growing chain to the position previously occupied by a coordinate monomer continues until termination of the polymer.

According to the above reason, it was reasonable to postulated the reaction between Cp_2ZrCl_2 and MAO to produce the ion couple[108].



The halogenated MAO anion was stabilized by electron deficient bond shown as below. It can be prevent the reverse process of Eq.4.13.



Ethylaluminumoxane was found to be not as good the coactivator as MAO. It was reasonable to explain the low activity when using EAO as cocatalyst. Higher aluminumoxane alkyl results in lower Lewis acidity and weaker Al-Cl-Al bonds. The former causes smaller equilibrium of Eq.4.13 and the later should enhance destabilization.

Another set of experiment was investigated the effect of catalyst concentration. The concentration 34 μM of Cp_2ZrCl_2 was replaced of 17 μM of its. The activity was plotted with concentration as shown in Figure 5.9, it showed higher activity at lower concentration. Decreasing of the catalyst concentration could be increased activity. For this result, it could be showed that low concentration were more percent active site than high concentration. Chien and Wang[19] showed catalyst system of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ for metallocene of 48 μM having active site 84% $[\text{Zr}]_{\text{initial}}$ and at 3.8 μM having active site 100% $[\text{Zr}]_{\text{initial}}$.

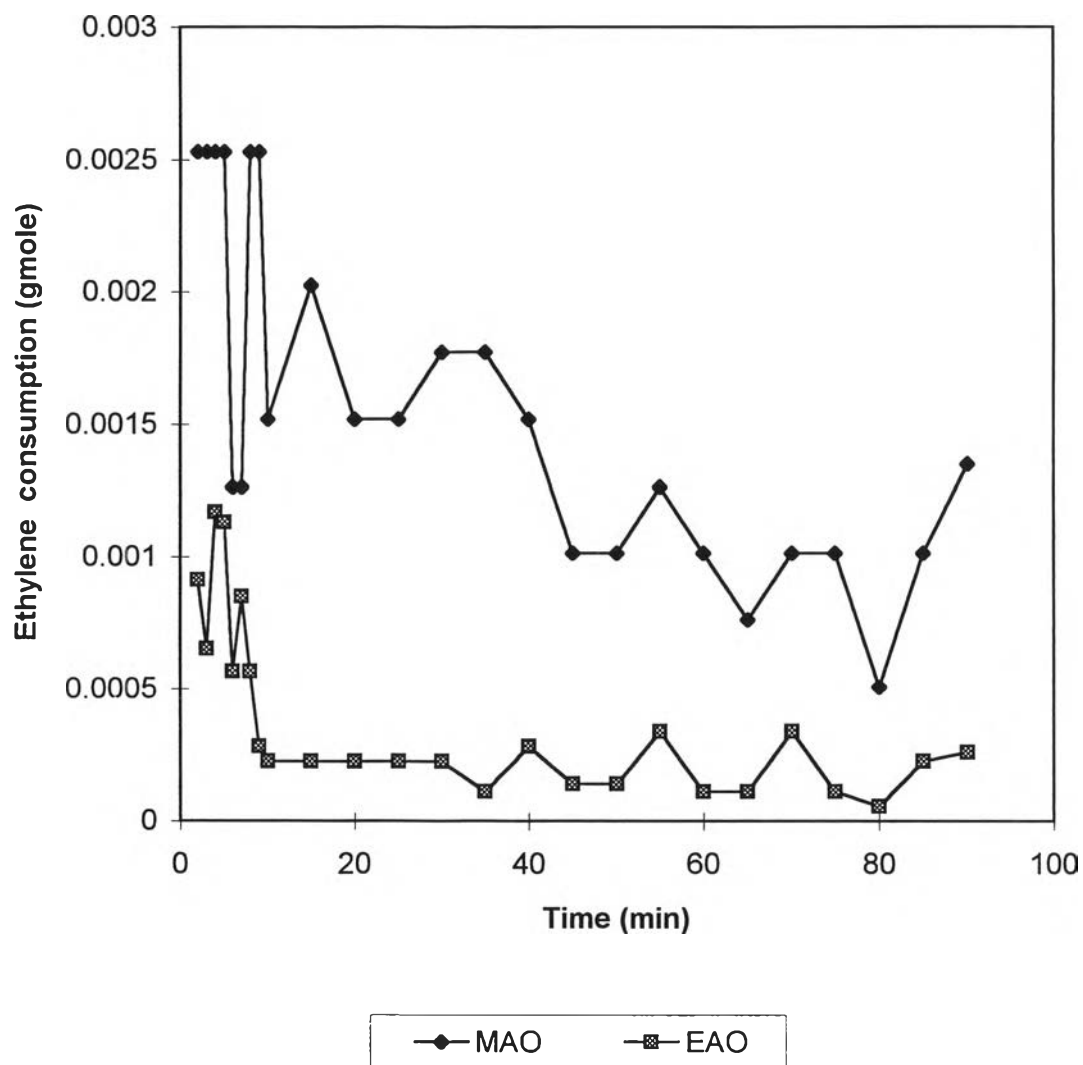


Figure 5.7 Ethylene Consumption versus Polymerization time curve at various Cocatalyst

Polymerization condition : $[Zr] = 34 \cdot 10^{-6}$ moleZr/l,

Temperature = 55 °C,

Ethylene partial pressure = 20 psi,

Al/Zr mole ratio = 4400

Cocatalyst of MAO, EAO

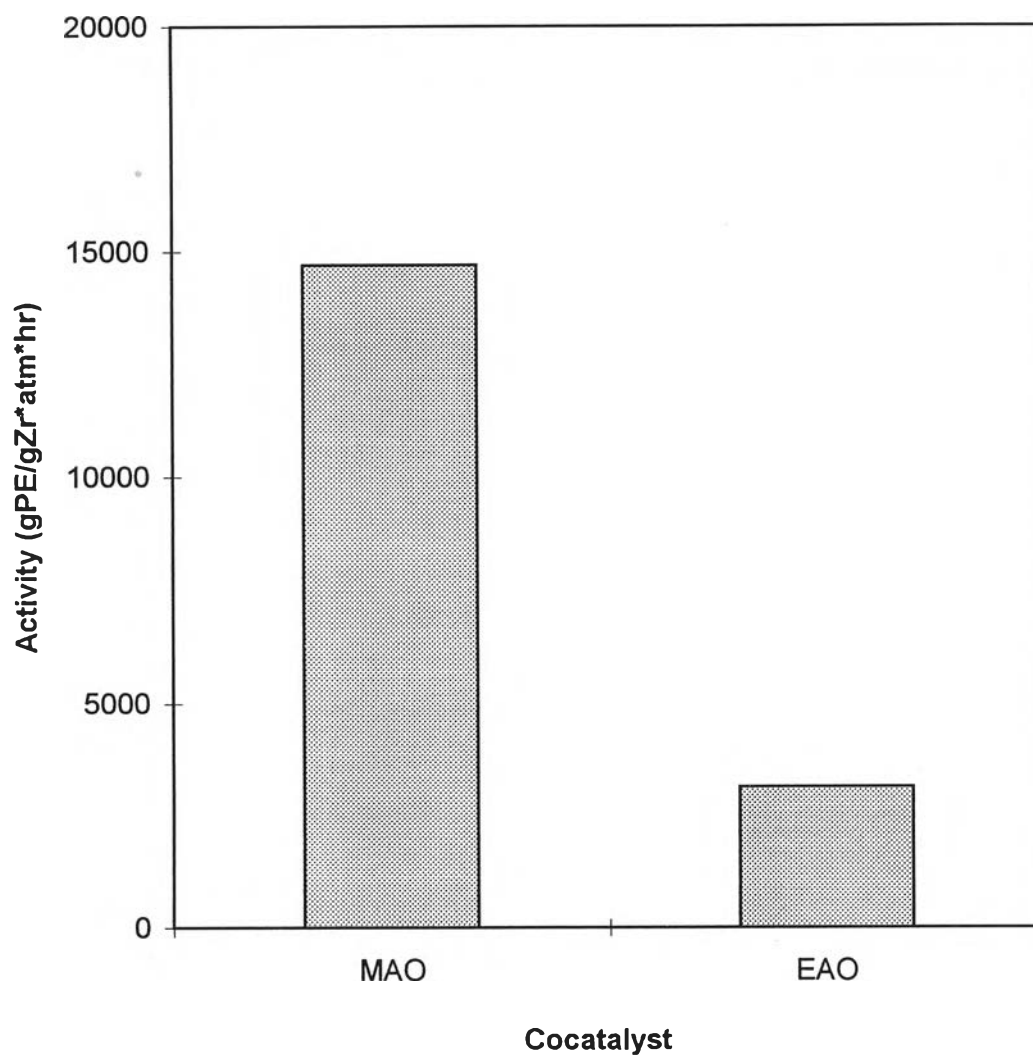


Figure 5.8 Activity versus Cocatalyst

Polymerization condition : $[Zr] = 34 \cdot 10^{-6}$ moleZr/l,

Temperature = 55 °C,

Ethylene partial pressure = 20 psi,

Al/Zr mole ratio = 4400

Cocatalyst of MAO, EAO

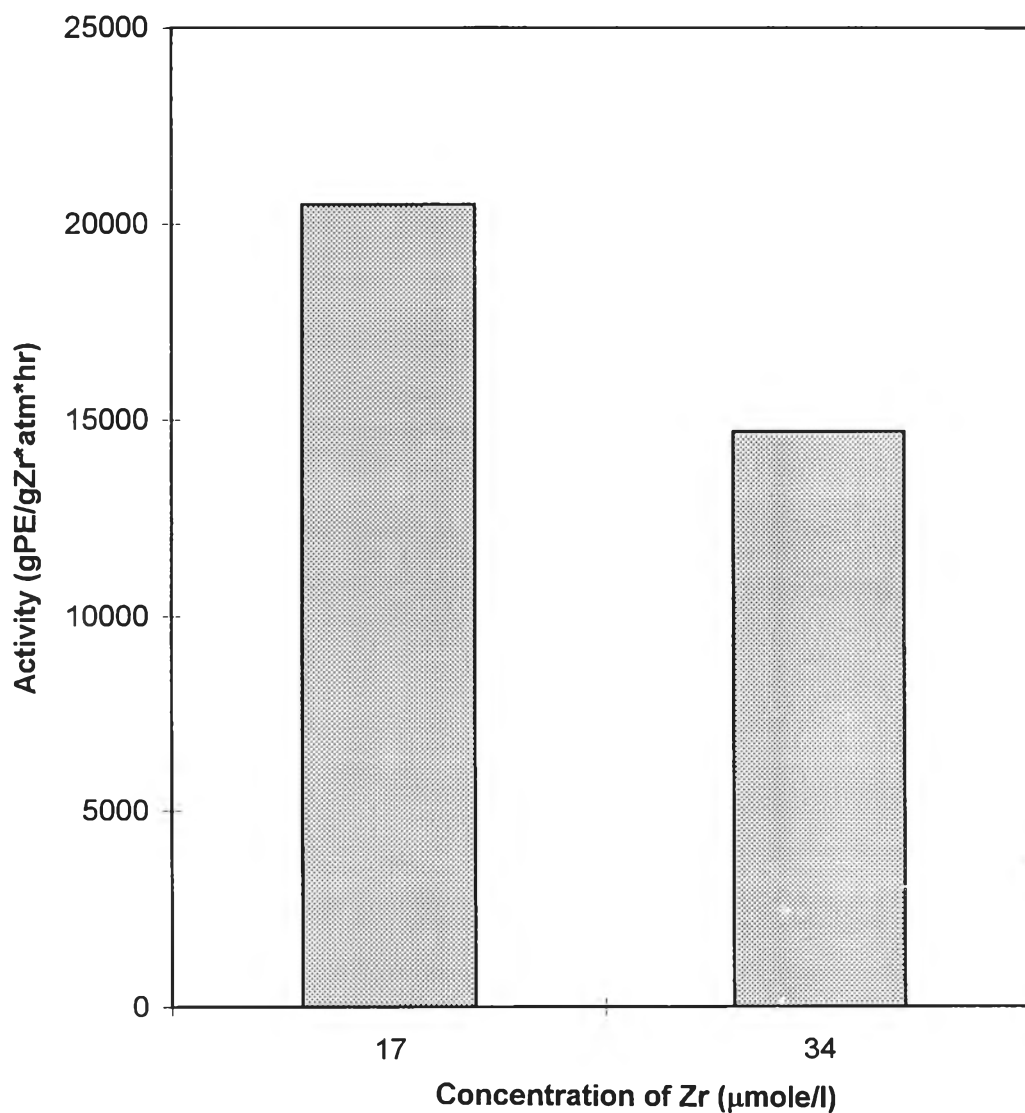


Figure 5.9 Activity versus Concentration of Cp_2ZrCl_2

Temperature = 55°C

Ethylene partial pressure = 20 psi,

Al/Zr mole ratio = 4400

[Zr] of $17\cdot 10^{-6}$ and $34\cdot 10^{-6}$, respectively

5.5 CHARACTERIZATION OF POLYETHYLENE

5.5.1 Morphology of polyethylene

After polymerization the polymer was precipitated from toluene solvent by adding methanol. Polyethylene powder were investigated a morphology with Scanning Electron Microscope. They were coated with gold by ion sputtering device. Then the sample were load in the sample of Scanning Electron Microscope. It was found that all particles comprising of small flasks bounded together as shown in Figure 5.10.

5.5.2 Microstructure Determination

The infrared spectroscopic technique is the effective method to determine the microstructure of polymer. It is sufficient to characterize the functional group of a sample especially for organic group[109]. The infrared spectra of polyethylene produced from MAO and EAO as cocatalyst show in Figure 5.11- 5.12, respectively. The infrared identification for each peak had been assigned the organic group and shown in Table 5.1-5.2

Table 5.1 Identification of IR spectrum PE (MAO as cocatalyst)

Wave no (cm ⁻¹)	assignment
719	Long chain -(CH ₂)-
1468	-(CH ₂)- bending
2850	-(CH ₂)-, -(CH ₃)- stretching
2920	
3448	-OH Hydroxy group

Table 5.2 Identification of IR spectrum PE (EAO as cocatalyst)

Wave no (cm ⁻¹)	assignment
719	Long chain -(CH ₂)-
1468	-(CH ₂)- bending
2850	-(CH ₂)-, -(CH ₃)- stretching
2919	
3449	-OH Hydroxy group

5.5.3 Molecular Weight[110]

Polyethylene from both of cocatalyst were dissolved in decahydronaphthalene (decalin). They were dissolve in temperature 140 °C. The concentration range 0.1% to 0.5% w/v. The molecular weight determination by viscometer is convenient and more practical than other method.

The viscosity-average molecular weight (\bar{M}_v) of MAO as cocatalyst was 6555 that from EAO cocatalyst was 29024. The \bar{M}_v of polyethylene from EAO was higher than MAO. It was suggest that EAO. was possible less chain transfer than MAO.

The \bar{M}_v of polyethylene depend on the temperature polymerization, as shown Table 5.3 that \bar{M}_v decrease with increasing temperature polymerization. It was suggest that high temperature rate chain transfer was rapid than low temperature then \bar{M}_v decreased.

Table 5.3 Effect of Temperature on \bar{M}_v

Temperature (°C)	\bar{M}_v
0	31742
30	25031
55	7601
80	5790

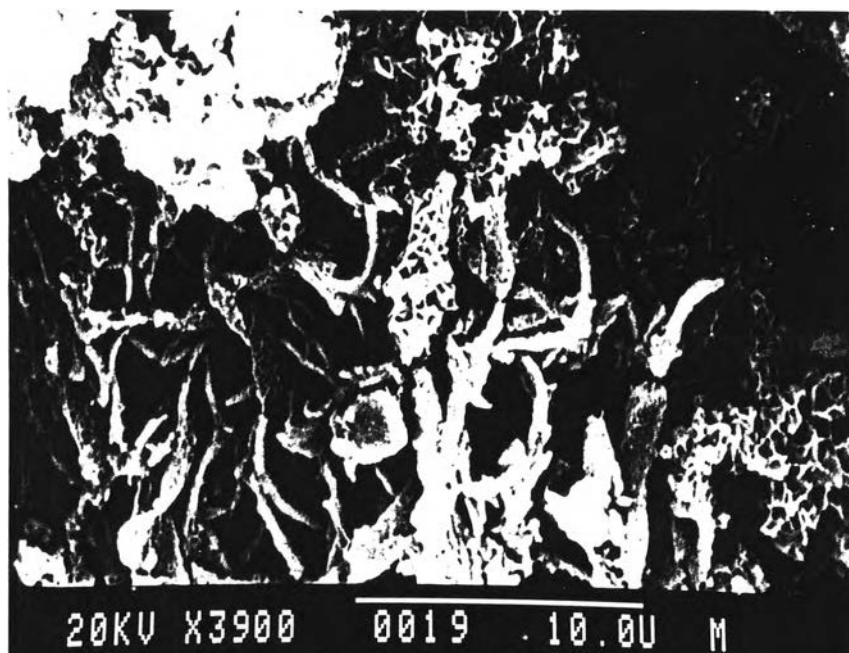


Figure 5.10(a) Scanning electron micrograph of polyethylene produced by MAO

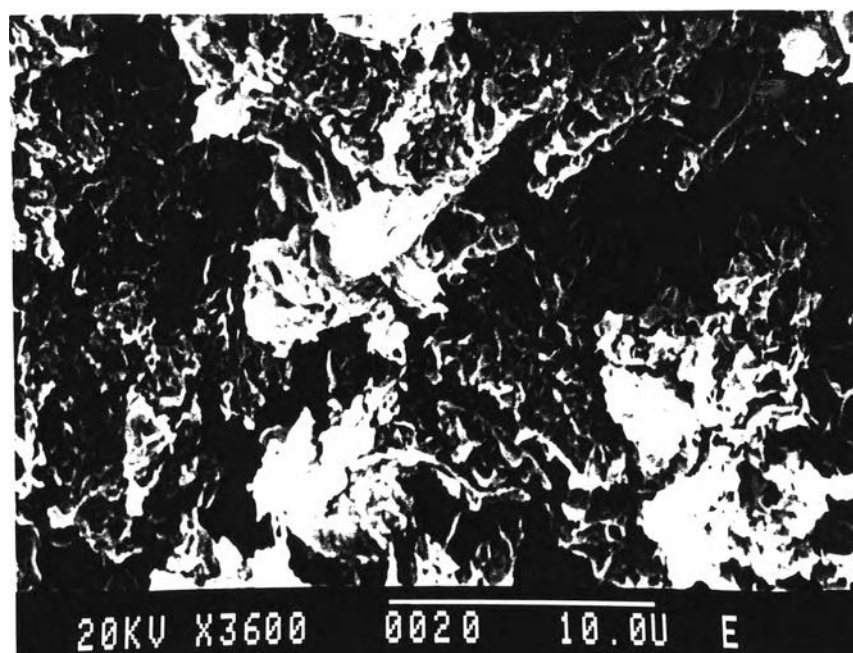


Figure 5.10(b) Scanning electron micrograph of polyethylene produced by EAO

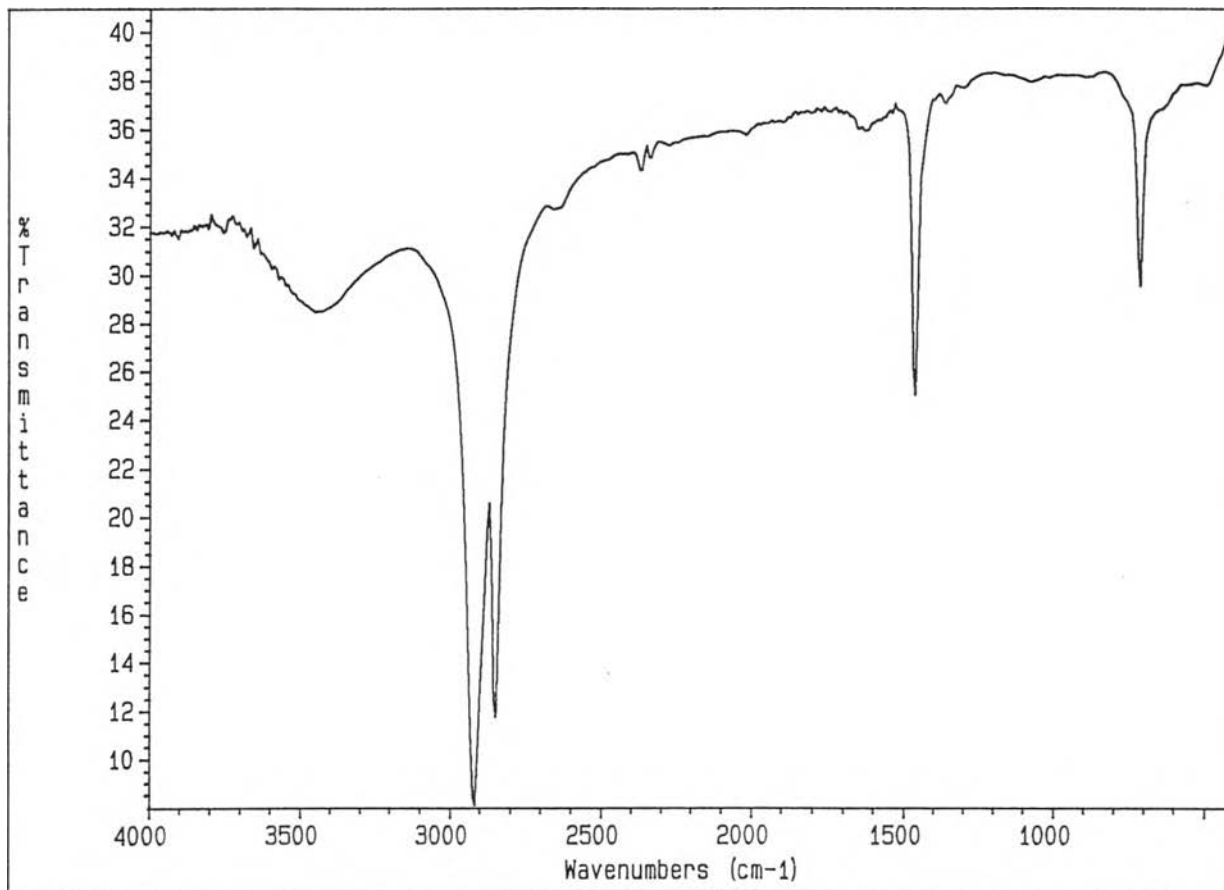


Figure 5.11 Infrared spectrum of polyethylene from MAO as cocatalyst

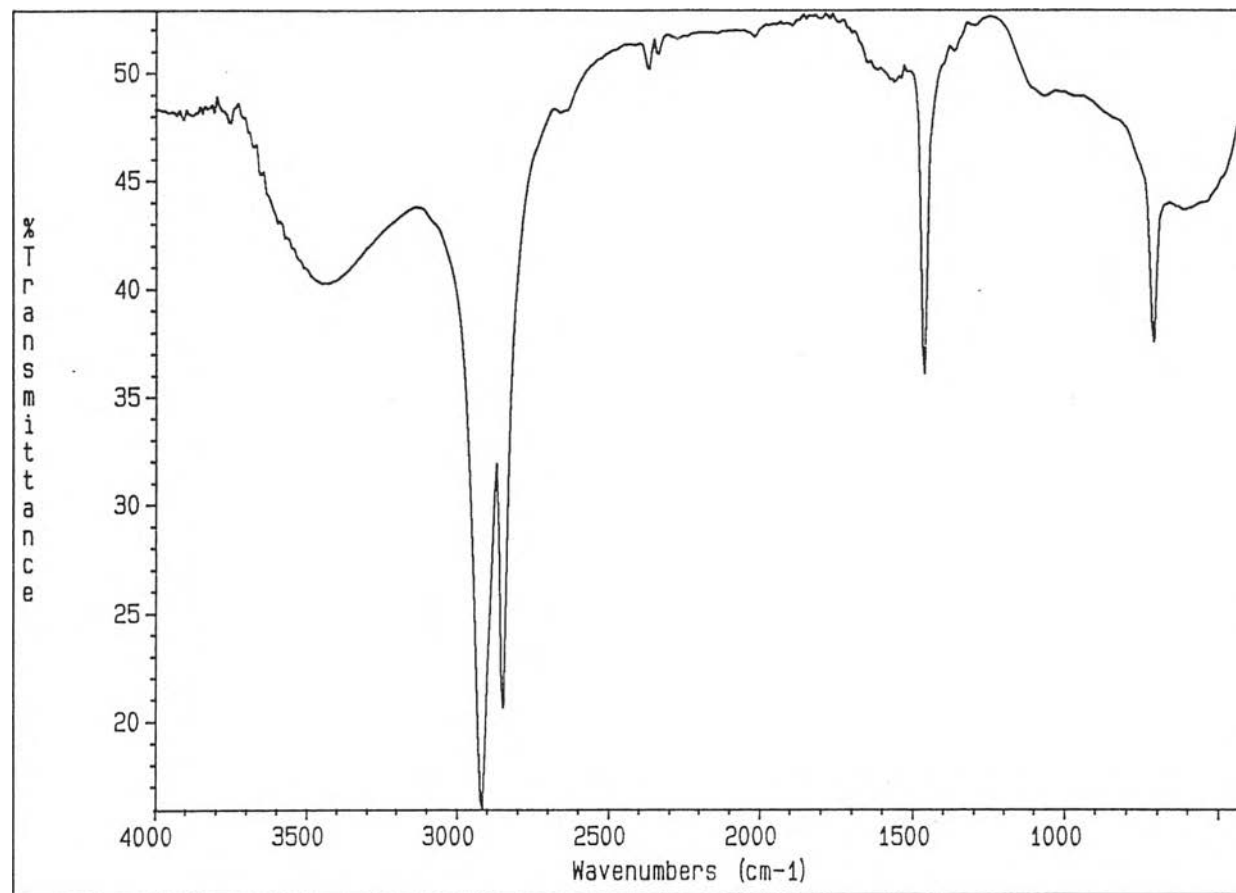


Figure 5.12 Infrared spectrum of polyethylene from EAO as cocatalyst