CHAPTER V

RESULTS AND DISCUSSIONS

5.1 THE EFFECT OF CATALYST RATIO

Ethylene polymerization were conducted in toluene using bis(cyclopentadienyl) zirconium dichloride catalyst (Cp_2ZrCl_2) and methylaluminoxane (MAO) cocatalyst at different Al/Zr mole ratio. In a typical polymerization experiment an appropriate amount of cocatalyst was injected into a constant and known volume of ethylene saturated in 200 ml. of toluene followed by catalyst injection. Polymerization were carried out at 300 K, ethylene partial pressure at 40 psi., [Zr] = $8.00*10^{-7}$ mole/l, polymerization time = 90 min. with six different ratios of Al/Zr mole ratio viz., 500, 1000, 2000, 4000, 6000, and 8000. The results are summarized in Table 5.1. The graphical plot of ethylene consumption versus polymerization time is shown in Figure 5.1 and the catalytic activity versus Al/Zr mole ratio is shown in Figure 5.2. The polymerization rate is referred to the rate of ethylene consumption during polymerization and the catalytic activity is referred to gram of polyethylene produced per gram of zirconium per unit partial pressure of ethylene during unit hour of polymerization time [gPE/(gZr*atm*hr)].

Table 5.1 Effect of Al/Zr mole ratio on polymerization activity[a]

[Al]/[Zr]	Catalytic Activity gPE/(gZr*atm*hr)
500	18032
1000	31506
2000	40870
4000	48177
6000	98090
8000	67176

[a] Toluene = 200 ml., catalyst = Cp_2ZrCl_2; cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;
Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;
Used $Al_2(SO_4)_3{\cdot}18H_2O$ for preparing MAO

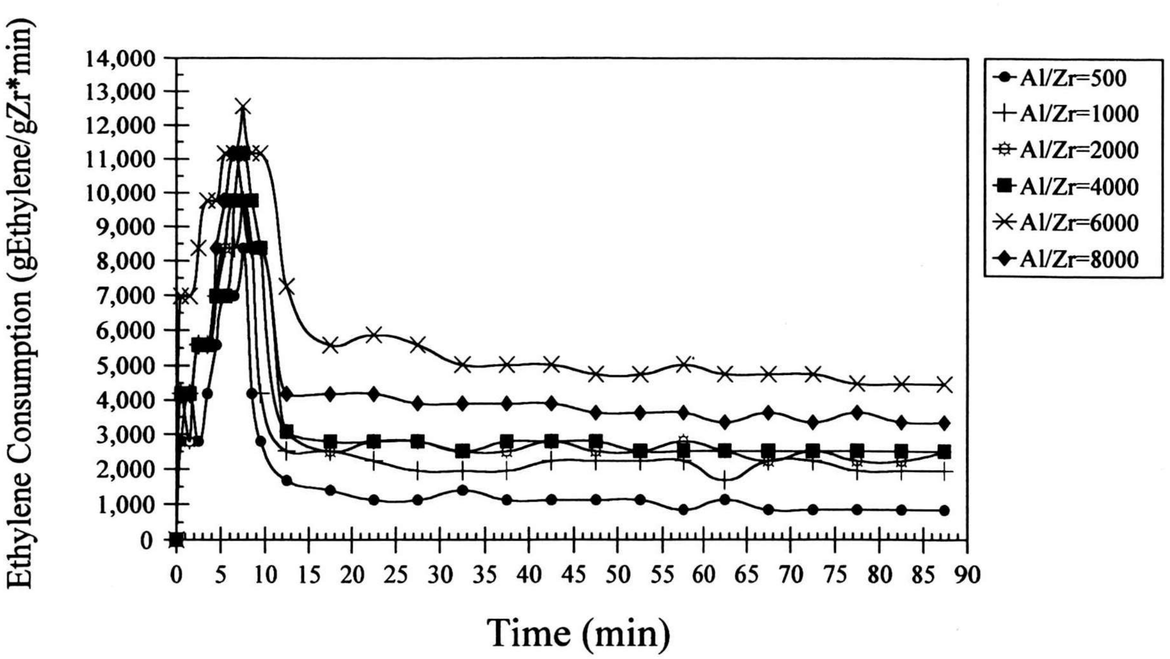


Figure 5.1 Ethylene consumption versus Polymerization time curve at various Al/Zr mole ratio.

Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Polymerization time = 90 min.; Used $Al_2(SO_4)_3 \cdot 18H_2O$ for preparing MAO

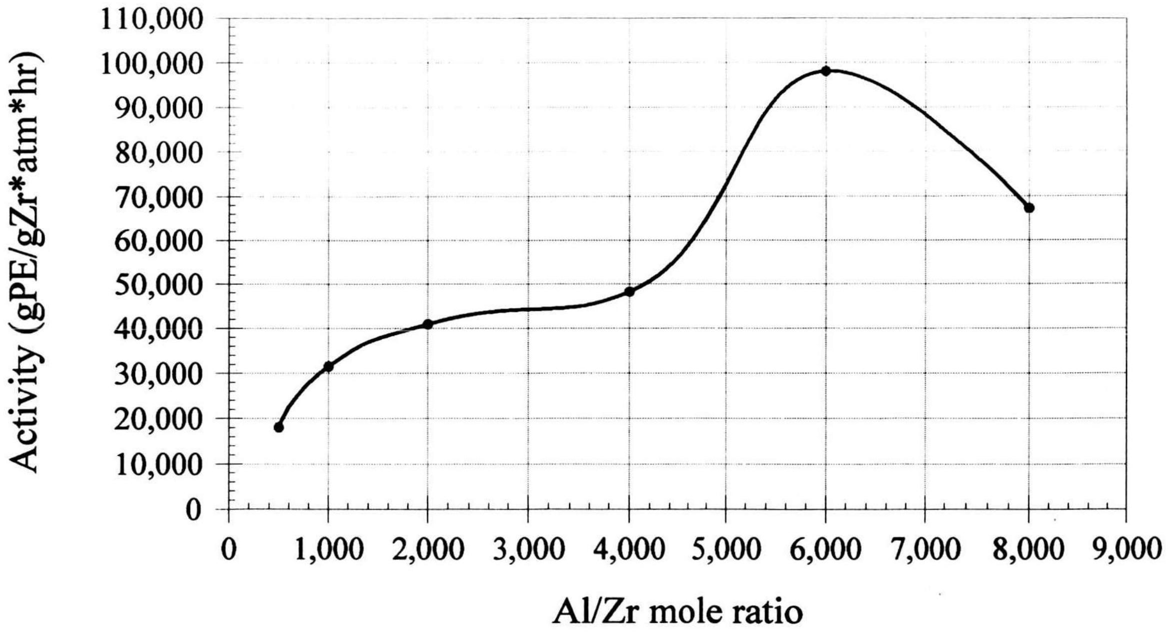


Figure 5.2 Activity versus Al/Zr mole ratio.

Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

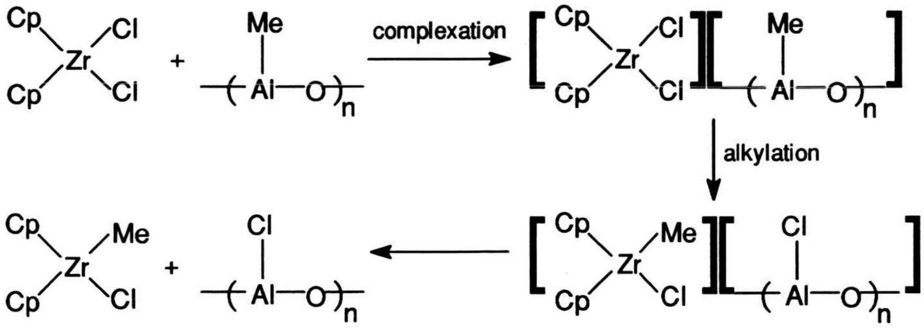
Polymerization time = 90 min.; Used $Al_2(SO_4)_3 \cdot 18H_2O$ for preparing MAO

Figure 5.1 shows the rate of ethylene consumption (r_p) versus polymerization time for Cp_2ZrCl_2/MAO catalyzed ethylene polymerization. The maximum rate of ethylene consumption ($r_{p,m}$) was attained within 10 minutes of Cp_2ZrCl_2 addition. Its was found that the $r_{p,m}$ was attained less than 10 minutes with increase Al/Zr mole ratio because more MAO rapidly react with Cp_2ZrCl_2 to form active site *[127]*. For polymerizations employing more MAO, there is only a simple rapid rise to a $r_{p,m}$ followed by a moderate decay to a stationary rate of polymerization. This simple kinetic behavior is like those found for other metallocene/MAO catalyzed ethylene polymerizations *[128]*. This decay type kinetics is due to the formation of inactive species by deactivation of active Zr(IV) species *[8,129]*.

Figure 5.2 was a plot of catalytic activity versus Al/Zr mole ratio for Cp_2ZrCl_2/MAO catalyzed ethylene polymerization. The maximum of catalytic activity was observed at the Al/Zr mole ratio 6000. At the mole ratio more than 6000, catalytic activity decreased.

The effect of Al/Zr mole ratio on Cp_2ZrCl_2/MAO catalyzed ethylene polymerization had been studied in several laboratories. Kaminsky et al. *[129]* presented a very detailed picture for the formation of active centers in metallocene/MAO system (see Figure 5.3). Four types of metallocenes with different σ-bonding ligands, Cp_2ZrCl_2, $Cp_2Zr(CH_3)Cl$, $Cp_2Zr(CH_3)_2$ and $(Cp_2ZrCl)_2O$, are included. According to Kaminsky et al. *[129]* the reaction of cocatalyst on catalyst for ethylene polymerization can be divided into three steps:

1) Starting from Cp_2ZrCl_2, the first step of the reactions after mixing the metallocene with MAO is the complexation and alkylation of Cp_2ZrCl_2 with MAO:



Eq.5.1

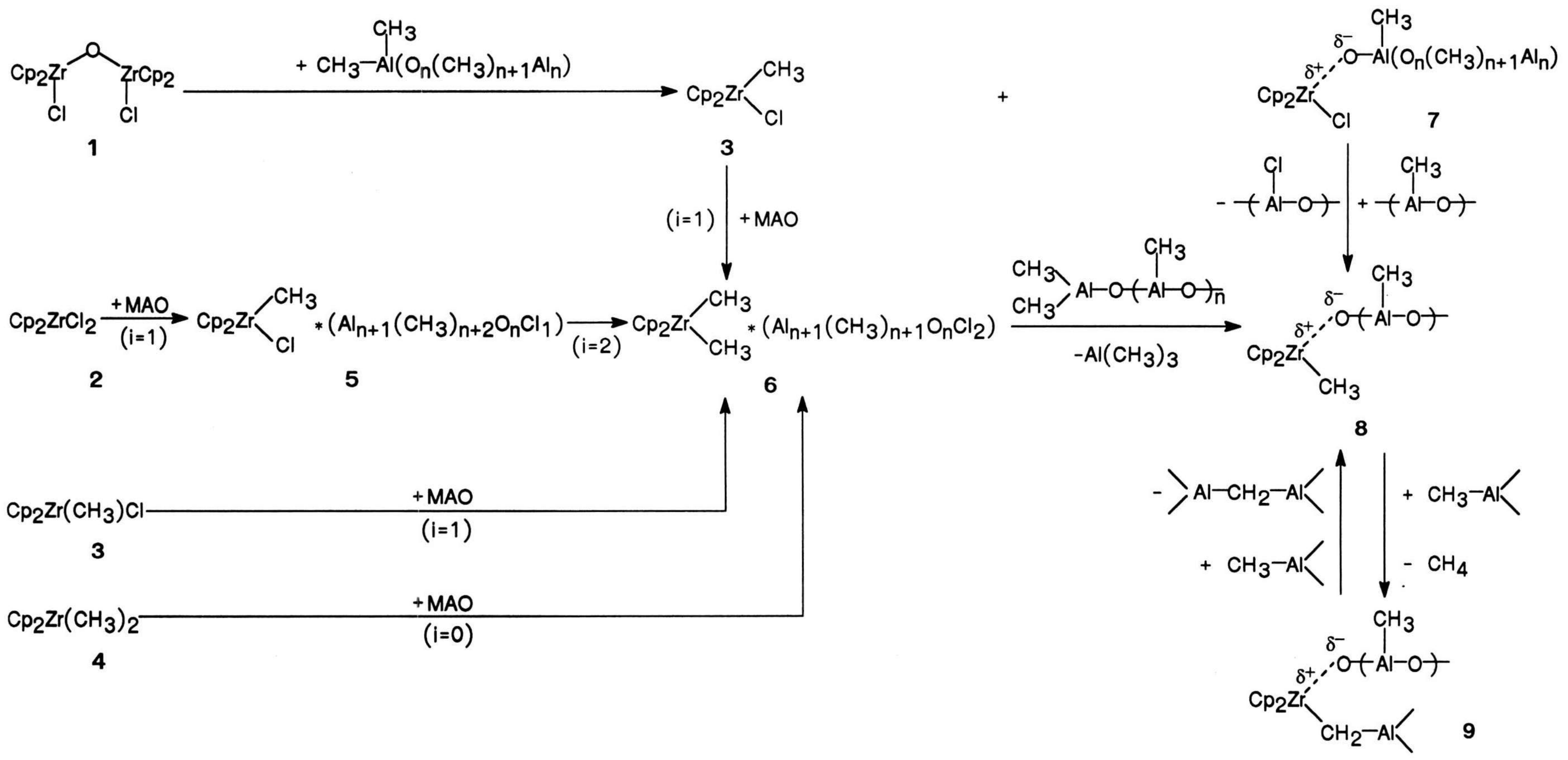
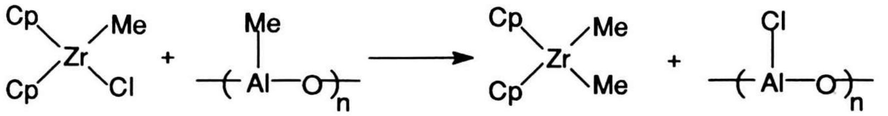


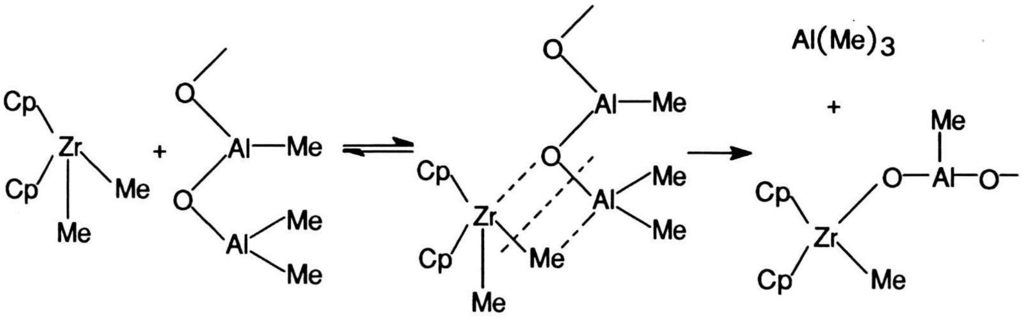
Figure 5.3 Scheme of the reaction of different zirconocene with MAO *[129]*; i = number of chloride ligands exchange into MAO structure; n = oligomerization grade of MAO *[82]*.

In a subsequent alkylation, $Cp_2Zr(CH_3)_2$ is formed (according to eq. 5.2):



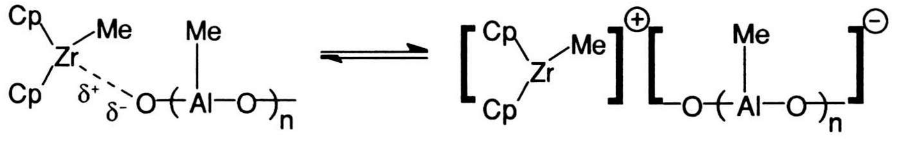
Eq. 5.2

$Cp_2Zr(CH_3)_2$ further reacts with MAO, forming compound (**8**) (see Figure 5.3). Compound (**8**) contains the structural element Zr-O-Al (see eq. 5.3).



Eq. 5.3

The Zr-O bond has a polar character and could be of ionic nature. Compound **8** is believed to be the active species in the metallocene/MAO systems. Possibly, compound **8** exists in two different states that are in equilibrium (as shown in eq. 5.4):



Eq. 5.4

The metallocene alkyl cation (at one side of the equilibrium) might be the true active center.

2) The insertion leads to a new alkyl complex that can then coordinate with ethylene which would also insert, and so forth, leading eventually to a polymer (see Figure 5.4).

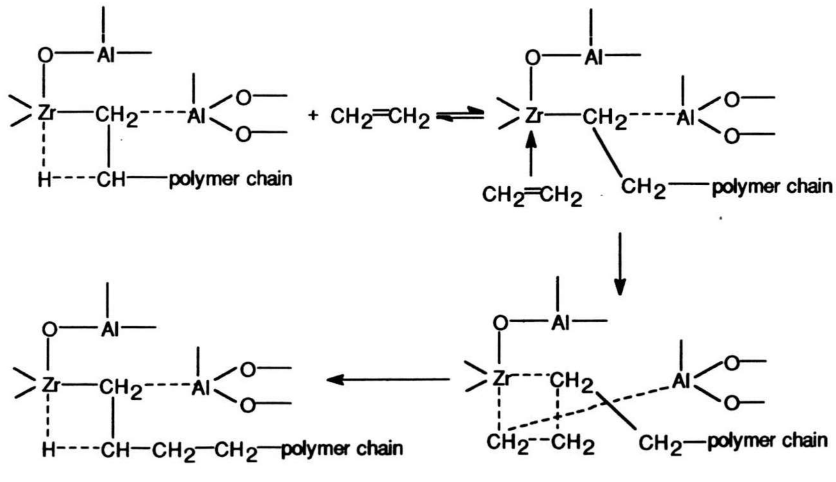
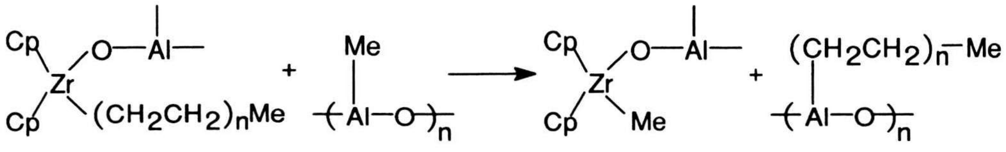


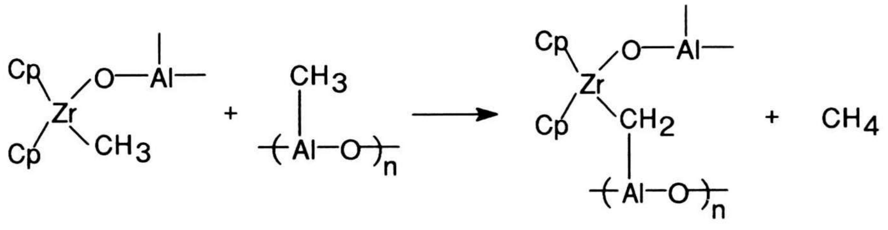
Figure 5.4 Possible mechanism for ethylene polymerization (Kaminsky's model) *[130]*.

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



Eq.5.5

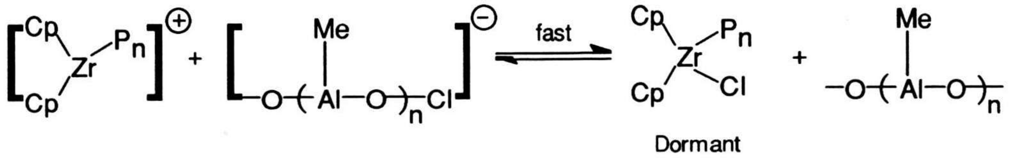
At high Al/Zr mole ratio, evolution of methane was observed after metallocene was mixed with MAO. Methane is the product of a side reaction which is relatively fast under polymerization conditions. More than 50 moles of methane were eliminated per mole of zirconium in 2 hr *[129]*. The resulting Zr-CH_2-Al structures (compound **9** in Fig.5.3) seem to be inactive for polymerization. The MAO present in the system could reactivate this structure to the active Zr-CH_3 structure (see eq. 5.6):



Eq.5.6

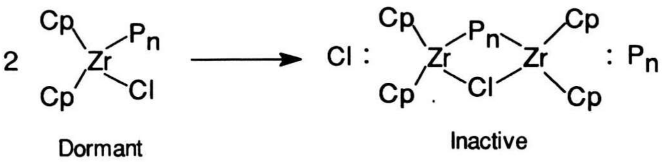
A slow catalyst deactivation was observed in almost all polymerizations with metallocene/MAO catalysts. The deactivation might be attributed to the formation of inactive species with a Zr-CH_2-Al structure *[129]*. Although these inactive species can be reactivated by reaction with MAO at high [MAO] - as MAO is consumed during the polymerization by side reactions, by impurities, by chain transfer and by recreating the active sites. Thus a polymerization rate decay occurs.

On the other hand, Mulhaupt et al. *[8]* found that there is another type of deactivation, which is fast and second-order relative to the active site concentration, in the Cp_2ZrCl_2/MAO system. The catalyst activation is completed within a few seconds after contacting zirconocene with MAO. After the maximum rate is reached, the second-order decay starts. It is fast in comparison to the very slow subsequent decay. Mulhaupt et al. *[8]* proposed a kinetic scheme as shown below:

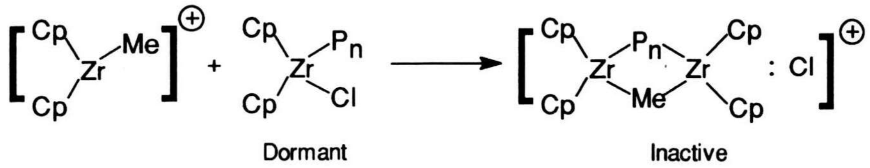


Eq.5.7

The reversible conversion of active cationic zirconium sites into dormant neutral zirconium sites is shown in Eq.5.7. Most likely, the second-order deactivation results from zirconocene dimerization as illustrated in Eq.5.8 and 5.9.



Eq.5.8



Eq.5.9

From this result, a standard condition of mole ratio Al/Zr of 6000 was used in further experiment because it shows the highest catalytic activity.

5.2 THE EFFECT OF ETHYLENE PARTIAL PRESSURE ON ETHYLENE POLYMERIZATION

Ethylene polymerization was conducted in toluene using bis(cyclopentadienyl) zirconium dichloride catalyst (Cp_2ZrCl_2) and methylaluminoxane (MAO) cocatalyst at different ethylene partial pressure. Polymerization was carried out at 300 K, Al/Zr mole ratio = 6000, [Zr] = $8.00*10^{-7}$ mole/l, polymerization time = 90 min. with seven different ethylene partial pressure viz., 10, 20, 30, 40, 50, 60 and 70 psi. The results are summarized in Table 5.2. The graphical plot of ethylene consumption versus polymerization time at different partial pressure are shown in Figure 5.5 and the catalytic activity versus ethylene partial pressure is shown in Figure 5.6. The polymerization rate is referred to the rate of ethylene consumption during polymerization and the catalytic activity is referred to gram of polyethylene produced per gram of zirconium per unit partial pressure of ethylene during unit hour of polymerization time [gPE/(gZr*atm*hr)].

Table 5.2 Effect Ethylene partial pressure on polymerization activity[a]

Ethylene partial pressure (psi.)	Catalytic Activity gPE/(gZr*atm*hr)
10	26974
20	33448
30	46026
40	67303
50	79116
60	84920
70	88823

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l; Polymerization Temperature = 300 K; Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Used $Al_2(SO_4)_3{\cdot}18H_2O$ for preparing MAO

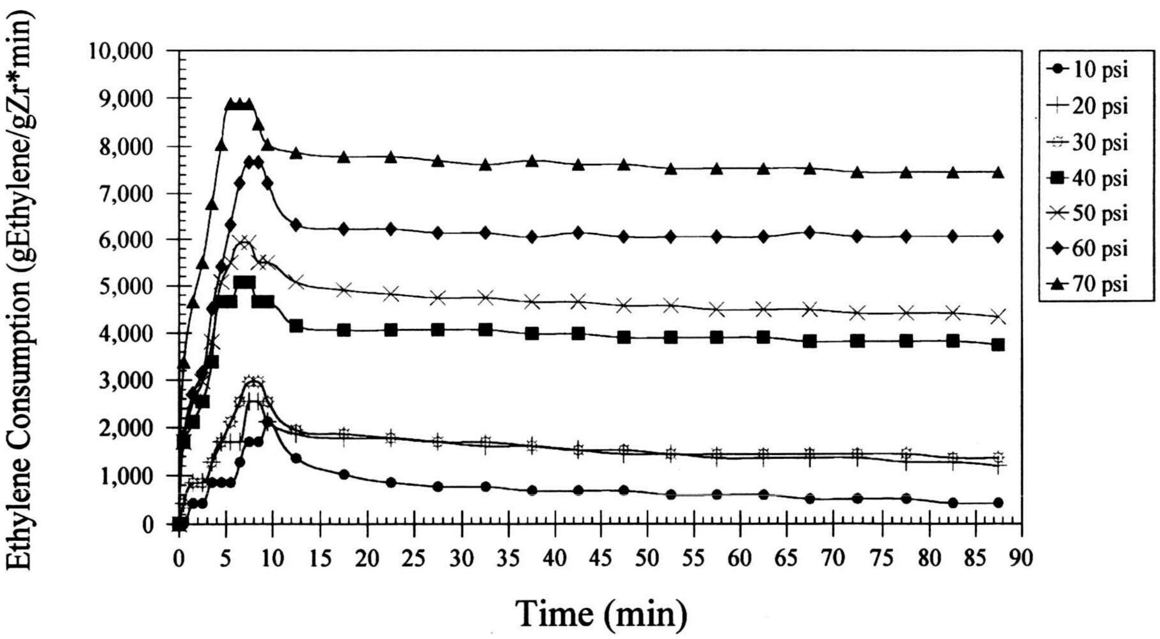


Figure 5.5 Ethylene consumption versus Polymerization time curve at various Partial pressure of Ethylene.

Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l; Polymerization Temperature = 300 K; Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Used $Al_2(SO_4)_3{\cdot}18H_2O$ for preparing MAO

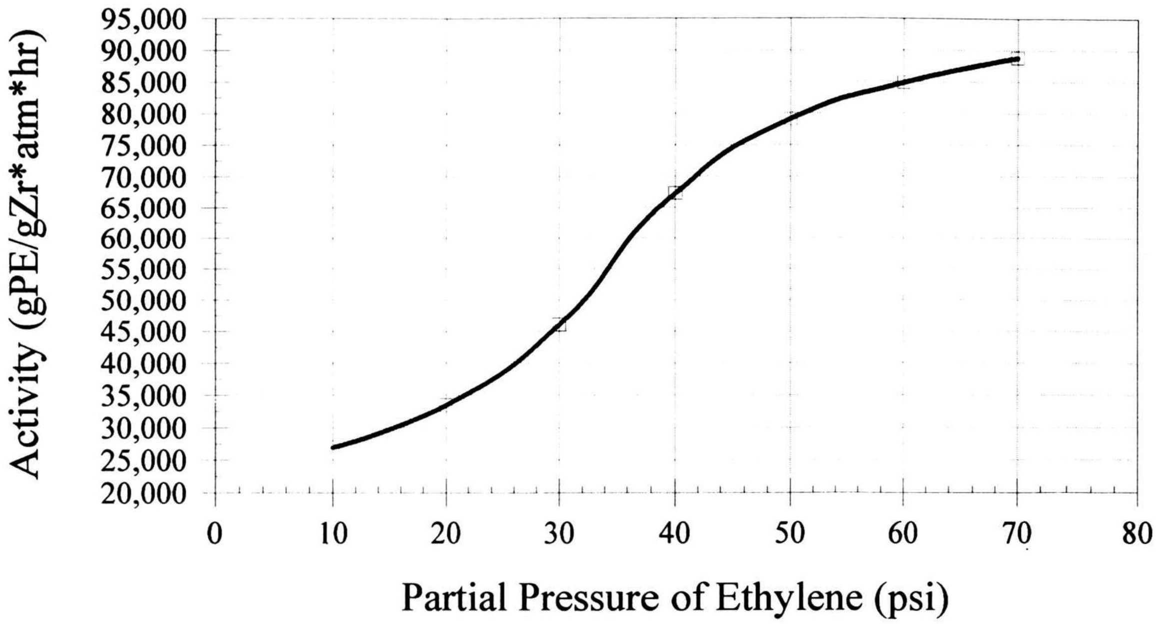


Figure 5.6 Activity versus Partial pressure of Ethylene.

Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Al/Zr mole ratio = 6000;

Polymerization time = 90 min.; Used $Al_2(SO_4)_3 \cdot 18H_2O$ for preparing MAO

Figure 5.5 shows the polymerization profiles for ethylene polymerization with Cp_2ZrCl_2 catalyst with MAO cocatalyst ([Al]/[Zr] = 6000) at seven different ethylene partial pressure. The shapes of the polymerization profile obtained in the ethylene partial pressure range of 10-70 psi (the decay type kinetic curve) are similar. The polymerization rate reaches a maximum ($r_{p,m}$) within a very short time about 3-10 min. and then gradually decreases. However, the kinetic profile at lower ethylene partial pressure (between 10-30 psi) shows an induction period of 5-10 min., while only a short induction period (ca. 3-6 min.) is observed in the polymerizations at higher ethylene partial pressure (between 40-70 psi). The longer induction period indicates that it takes longer to form the active centers with lower ethylene partial pressure than with higher ethylene partial pressure.

In slurry polymerization, increasing reactor pressure increases reaction rate because of the increased monomer concentration. According to the equation ($R_p = k_p[C_i^*][M]$), it is reasonable that the productivity depends on the monomer concentration. Chien *[18]* found that increasing the ethylene partial pressure increased the concentration of ethylene diffused in to the media, subsequently, it caused the rise of the catalytic activity. Thus catalytic activity increased as the ethylene partial pressure increased.

5.3 THE EFFECT OF POLYMERIZATION TEMPERATURE

Ethylene polymerization was conducted in 200 ml. toluene using bis(cyclopentadienyl)zirconium dichloride catalyst (Cp_2ZrCl_2) and methylaluminoxane (MAO) cocatalyst at different polymerization temperature. Polymerization was carried out at Al/Zr mole ratio = 6000, ethylene partial pressure = 20 psi., [Zr] = $8.00*10^{-7}$ mole/l, polymerization time = 90 min. with five different polymerization temperature viz., 300, 318, 333, 348, and 363 K. The results were summarized in Table 5.3. The graphical plot of ethylene consumption versus polymerization time was shown in Figure 5.7 and the catalytic activity versus polymerization temperature was shown in Figure 5.8.

Table 5.3 Effect of Polymerization Temperature (T_p) on polymerization activity[a]

T_p (K)	Catalytic Activity gPE/(gZr*atm*hr)
300	33448
313	64050
333	126352
348	197213
363	190322

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;
Al/Zr mole ratio = 6000; Ethylene Partial Pressure = 20 psi.;
Polymerization time = 90 min.; Used $Al_2(SO_4)_3{\cdot}18H_2O$ for preparing MAO.

Figure 5.7 shows ethylene polymerization rate profiles at 300, 313, 333, 348, and 363 K catalyzed by the Cp_2ZrCl_2. It takes about 10 min. to reach the maximum rate ($r_{p,m}$) at 300 K, while only a short induction period (ca. 1-2 min.) is observed in the polymerizations at higher temperatures (348-363 K). The longer induction period of ethylene polymerization indicates that it takes longer to form the active centers at lower polymerization temperature than at higher polymerization temperature. At higher polymerization temperature (348-363 K) catalyst activity increases steeply within the first minutes of the polymerization, followed by a fast deactivation to 50% in 5 min. after the maximum was reached, while at lower polymerization temperature catalyst deactivates much slower. After 10 min. of polymerization the rate of ethylene consumption (r_p) became constant.

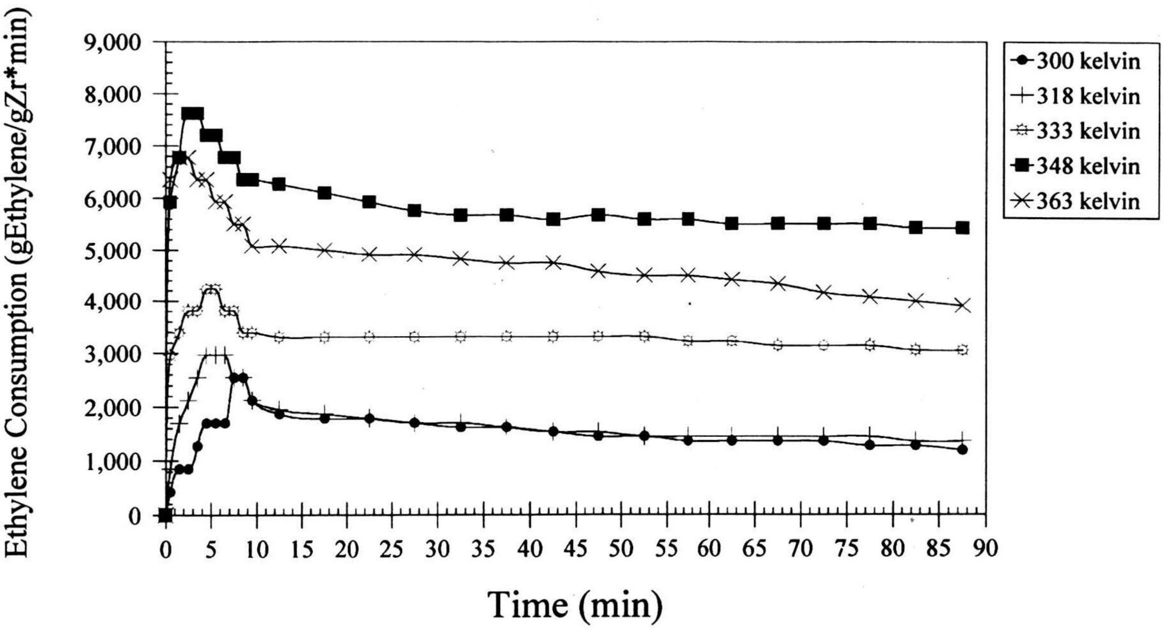


Figure 5.7 Ethylene consumption versus Polymerization time curve at various Polymerization Temperature.

Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Al/Zr mole ratio = 6000; Ethylene Partial Pressure = 20 psi.;

Polymerization time = 90 min.; Used $Al_2(SO_4)_3{\cdot}18H_2O$ for preparing MAO

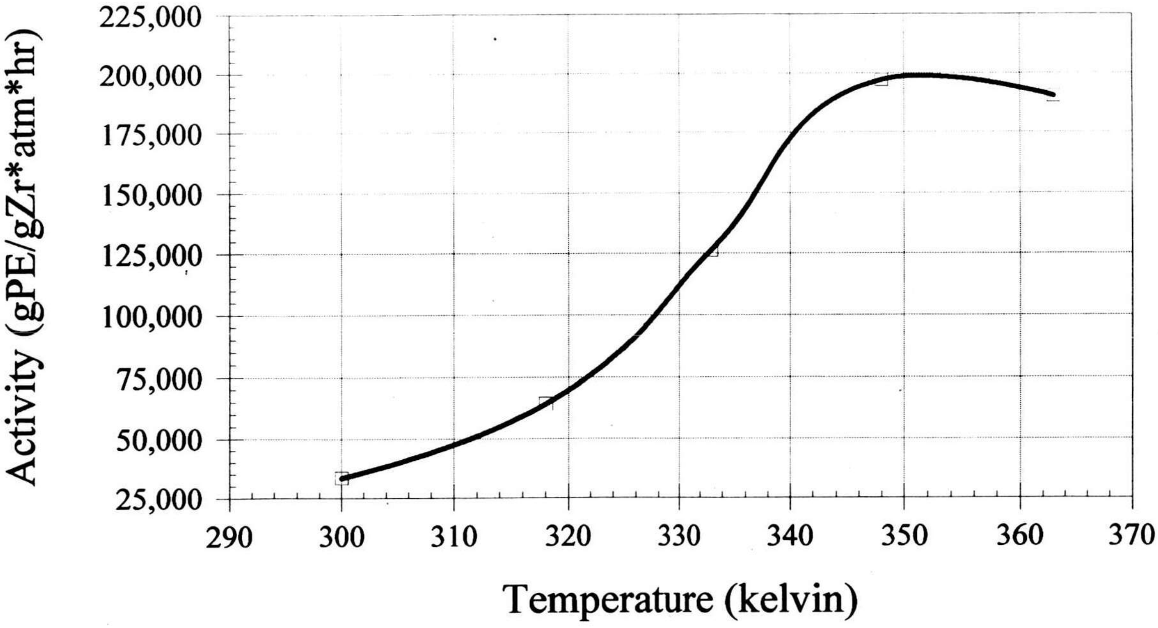


Figure 5.8 Activity versus Polymerization Temperature.

Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Al/Zr mole ratio = 6000; Ethylene Partial Pressure = 20 psi.;

Polymerization time = 90 min.; Used $Al_2(SO_4)_3{\cdot}18H_2O$ for preparing MAO

Figure 5.7 is the plot of catalytic activity versus polymerization temperature time for Cp_2ZrCl_2/MAO catalyzed ethylene polymerization. The catalytic activity increases as polymerization temperature increases until maximum catalytic activity is reach at ca. 350 K and slowly decreases later. This was a common characteristic of metallocene catalyst that there was an optimum temperature range for maximum activity. At temperature either above or below this optimum temperature, the catalyst activity decreases.

Polymerization temperature (T_p) is one of the most important operational factors for polymerization. A detailed study of the T_p effect on catalyst activity was reported by Chien et al. *[18,131]*. They proposed a kinetic model for the systems in which more than one active species was present, and applied the model in the study of ethylene polymerization with Cp_2ZrCl_2/MAO catalyst and propylene polymerization with $Et(Ind)_2ZrCl_2$/MAO and $Et(H_4Ind)_2ZrCl_2$/MAO catalysts. The model assumes the presence of multiple active center types, chain transfer to MAO, chain transfer by β-H elimination and first order deactivation reactions of active centers. For the system existing i types of active centers, the polymerization rate of the i^{th} species is:

$$R_{p,i} = k_{p,i} [C_i^*] [M] \qquad \text{Eq.5.10}$$

where $k_{p,i}$ and $[C_i^*]$ are the propagation rate constant and the concentration of the i^{th} active species, respectively. The overall rate of polymerization is the sum of $R_{p,i}$ which is:

$$R_p = \sum_i k_{p,i} [C_i^*] [M] \qquad \text{Eq.5.11}$$

or, if $k_{p,i}$ cannot be determined,

$$R_p = k_{p,avg} [C_i^*] [M] \qquad \text{Eq.5.12}$$

The productivity of i^{th} species is:

$$P_i = [M]\, k_{p,i} \int [C_i^*]\, dt \qquad \text{Eq.5.13}$$

The total productivity (P) can be written as:

$$P = [M] \sum_i k_{p,i} \int [C_i^*]\, dt \qquad \text{Eq.5.14}$$

Assuming that the catalytic species deactivate according to first order kinetic:

$$P\,(t) = [M] \sum_i k_{p,i} [C_i^*]_0 \,(1-\exp(-k_{d,i}t)) \qquad \text{Eq.5.15}$$

Figure 5.8 shows that the catalytic activity increases by 3 folds with 10% increase in temperature. It showed the maximum catalytic activity at polymerization temperature ca. 350 K. The strong dependence of the catalytic activity of zirconocene/MAO system on T_p was initially thought to be just the activation energy required for polymerization *[132]*. When it was recognized that the active species is the zirconocenium ion, then one explanation for the T_p dependence could be the activation energy needed to produce the ionic species because the zirconocene cation itself has a very low energy of activation for propagation. The actual effect of T_p is probably to shift the equilibrium between free active species and inactive species (see Eq.5.7-5.9). The higher polymerization temperature caused deactivation rate constant (k_d) to increase, and hence, productivity (P) decrease (see Eq.5.15).

From the practical view point, a standard condition of polymerization temperature, 350 K, was used in further experiments because it shows the highest catalytic activity.

5.4 THE EFFECT OF CATALYST CONCENTRATION

Ethylene polymerization was conducted in 200 ml. toluene using bis(cyclopentadienyl)zirconium dichloride catalyst (Cp_2ZrCl_2) and methylaluminoxane (MAO) cocatalyst at different catalyst concentration. Polymerization were carried out at 300 K, Al/Zr mole ratio = 6000, ethylene partial pressure is 40 psi (2.72 atm.), polymerization time = 90 min. with six different catalyst concentration viz., $2.35*10^{-7}$, $4.49*10^{-7}$, $6.50*10^{-7}$, $8.00*10^{-7}$, $9.99*10^{-7}$, and $1.20*10^{-6}$ mole/l. The results are summarized in Table 5.4. The graphical plot of ethylene consumption versus polymerization time was shown in Figure 5.9 and the catalytic activity versus catalyst concentration was shown in Figure 5.10.

Figure 5.9 shows ethylene polymerization rate profiles at several catalyst concentration. It takes about 8-10 min. to reach the maximum rate ($r_{p,m}$) at 300 K, while only a short induction period (ca. 6-7 min.) is observed in the polymerizations at lower catalyst concentration ($2.35*10^{-7}$ moleZr/l). The longer induction period of ethylene polymerization indicates that it takes longer to form the active centers at lower catalyst concentration than at higher catalyst concentration. At lower catalyst concentration, catalyst activity increases steeply within the five minutes of the polymerization, followed by a fast deactivation to 40% in 5 min. after the maximum was reached, while at higher catalyst concentration, the catalyst deactivates much slower. After that about 5 min. of maximum rate of polymerization ($r_{p,m}$) the rate of ethylene consumption (r_p) became constant along the polymerization time.

Table 5.4 Effect of Catalyst Concentration ([Zr]) on polymerization activity[a]

Catalyst concentration (moleZr/l)	Catalytic Activity gPE/(gZr*atm*hr)
$2.35*10^{-7}$	167734
$4.49*10^{-7}$	101079
$6.50*10^{-7}$	79517
$8.00*10^{-7}$	67303
$9.99*10^{-7}$	64277
$1.20*10^{-6}$	53058

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; Al/Zr mole ratio = 6000; Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.; Polymerization time = 90 min.; Used $Al_2(SO_4)_3{\cdot}18H_2O$ for preparing MAO

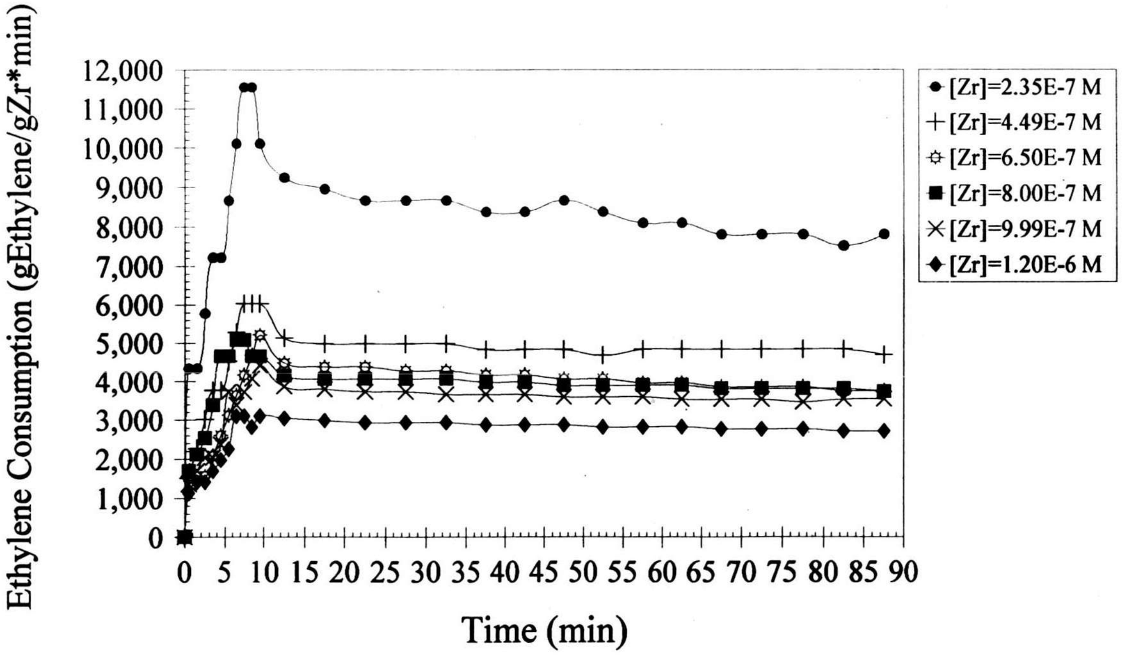


Figure 5.9 Ethylene consumption versus Polymerization time curve at various Concentration of catalyst.

Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; Al/Zr mole ratio = 6000; Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.; Polymerization time = 90 min.; Used $Al_2(SO_4)_3{\cdot}18H_2O$ for preparing MAO

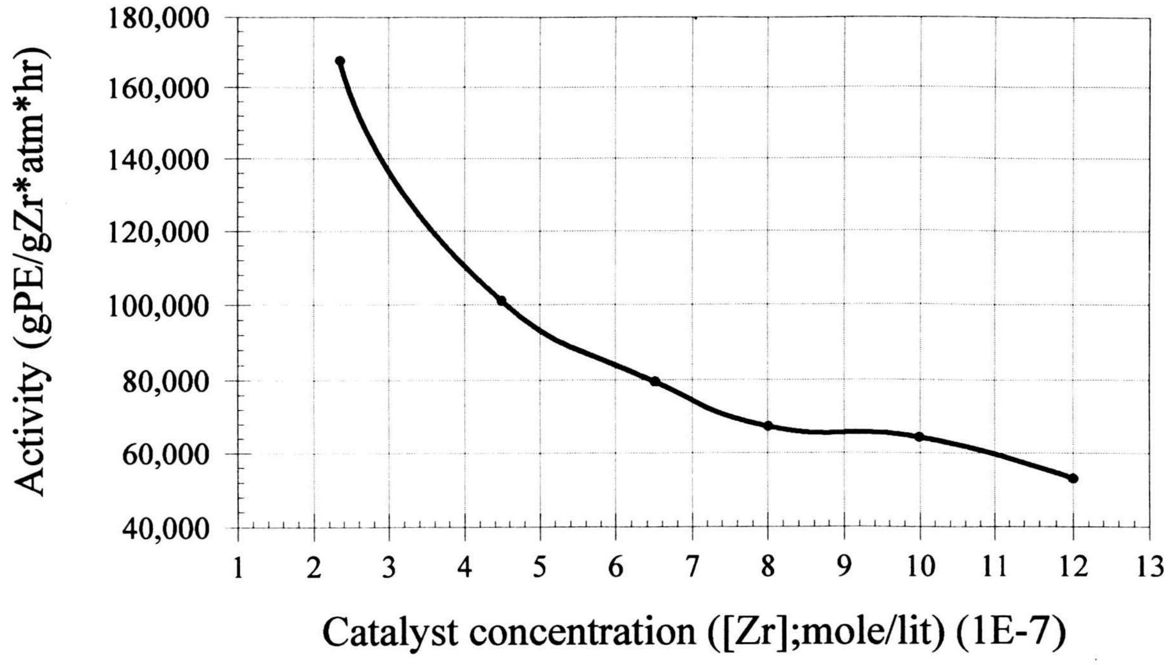


Figure 5.10 Activity versus Concentration of catalyst.

Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; Al/Zr mole ratio = 6000;
Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;
Polymerization time = 90 min.; Used $Al_2(SO_4)_3 \cdot 18H_2O$ for preparing MAO

Figure 5.10 shows that catalytic activity was very strongly affected by catalyst concentration. The catalyst activity decreases significantly with increasing catalyst concentration. For this result, it could be showed that there were more percent active site at lower catalyst concentration than at higher catalyst concentration. Chien *[18]* reported that for polymerization of ethylene with Cp_2ZrCl_2 catalyst with MAO as cocatalyst, polymerization productivity is proportional to $[Zr]^{-0.77}$. Mulhaupt et al. *[8]* found a similar situation for propylene polymerization with the Cp_2ZrCl_2/MAO catalyst system and proposed a mechanism for fast deactivation which is second-order relative to [Zr].

The determination of $[C^*]_0$ by CH_3O^3H radiolabeling by Chien et al. *[18]* has given reliable and reproducible results. The technique finds all the transition metal ion to be catalytically active in ethylene polymerization for the Cp_2ZrCl_2/MAO, and $CpZrCl_3$/MAO catalyst system. The results are summarized in Table 5.5. At polymerization temperature of 70 °C and Cp_2ZrCl_2/MAO catalyst system, the initial active site ($[C^*]_0$) decreasing from 100% of active site at [Zr] = 3.8 μM to 84% of active site at 48 μM. For this result, it could be showed that at lower catalyst concentration there are higher percentage of active site than at higher catalyst concentration.

Table 5.5 Active Site Concentrations of Zirconocene/MAO Catalysts Determined by CH_3O^3H *[18]*

Catalyst	[Zr] (μM)	[Al]/[Zr]	Temperature (°C)	$[C^*]_0$ (mole % of Zr)
Cp_2ZrCl_2/MAO	3.8	$1.1*10^4$	70	100
Cp_2ZrCl_2/MAO	48.0	$1.1*10^4$	70	84
$CpZrCl_3$/MAO	3.8	$1.1*10^4$	70	95
$CpZrCl_3$/MAO	48.0	$1.1*10^3$	70	75
$CpZrCl_3$/MAO	48.0	$5.5*10^3$	70	74
$CpZrCl_3$/MAO	48.0	$5.5*10^3$	50	21

5.5 THE EFFECT OF HYDRATED SALT FOR PREPARING COCATALYST

Ethylene polymerization was conducted in 200 ml. toluene using bis(cyclopentadienyl)zirconium dichloride catalyst (Cp_2ZrCl_2) and methylaluminoxane (MAO) cocatalyst at different type of hydrated salts. Polymerization was carried out at 300 K, [Zr] = $8.00*10^{-7}$ mole/l, Al/Zr mole ratio = 6000, ethylene partial pressure is 40 psi., polymerization time = 90 min. with five different hydrated salts for preparing cocatalyst viz. aluminum sulfate octahexahydrate [$Al_2(SO_4)_3 \cdot 18H_2O$], aluminum sulfate hexadecahydrate [$Al_2(SO_4)_3 \cdot 16H_2O$], copper(II)sulphate pentahydrate [$CuSO_4 \cdot 5H_2O$], aluminum chloride hexahydrate [$AlCl_3 \cdot 6H_2O$] and natriumthiosulfate pentahydrate [$Na_2S_2O_3 \cdot 5H_2O$] and time for preparing methylaluminoxanes cocatalyst is 40 hours. The results are summarized in Table 5.6. The graphical plot of ethylene consumption versus polymerization time is shown in Figure 5.11 and the catalytic activity versus type of hydrated salts is shown in Figure 5.12.

Table 5.6 Effect of Hydrated Salt for Preparing Cocatalyst on polymerization activity[a]

Type of Hydrated Salt for Preparing methylaluminoxane	Catalytic Activity gPE/(gZr*atm*hr)
$Al_2(SO_4)_3 \cdot 18H_2O$	67303
$Al_2(SO_4)_3 \cdot 16H_2O$	50312
$CuSO_4 \cdot 5H_2O$	38968
$AlCl_3 \cdot 6H_2O$	27830
$Na_2S_2O_3 \cdot 5H_2O$	32366

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l; Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.; Al/Zr mole ratio = 6000; Polymerization time = 90 min., Time for preparing MAO = 40 hours.

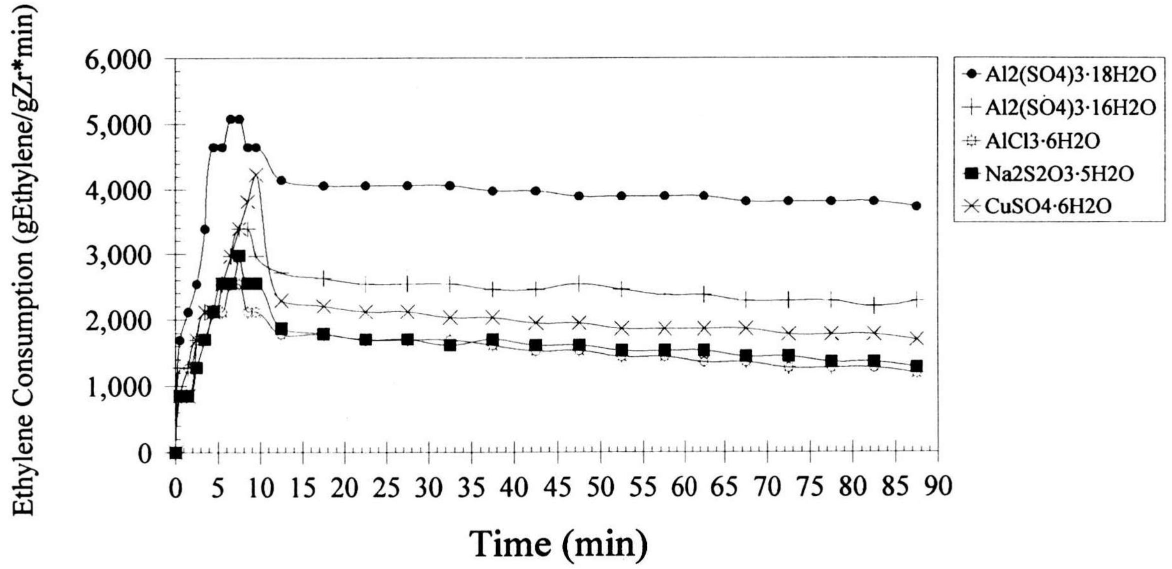


Figure 5.11 Ethylene consumption versus Polymerization time curve at various Hydrated Salt for Preparing Cocatalyst.

Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l; Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.; Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours.

Figure 5.11 shows ethylene polymerization rate profiles at several hydrated salt which are used to supply water for preparing methylaluminoxane (MAO). All profile shows the maximum rate ($r_{p,m}$) at about 5-12 min., its showed that the short induction period is in the following order: $AlCl_3 \cdot 6H_2O$ > $Al_2(SO_4)_3 \cdot 18H_2O$ > $Na_2S_2O_3 \cdot 5H_2O$ = $Al_2(SO_4)_3 \cdot 16H_2O$ > $CuSO_4 \cdot 5H_2O$. These results indicate that type of hydrate salt for preparing MAO had effect on the formation of the active centers. Generally, there was a drop of ethylene consumption (r_p) by about 50% after shows the maximum rate of polymerization ($r_{p,m}$). After that about 5 min. of maximum rate of polymerization ($r_{p,m}$) the rate of ethylene consumption (r_p) slowly decrease along the polymerization time.

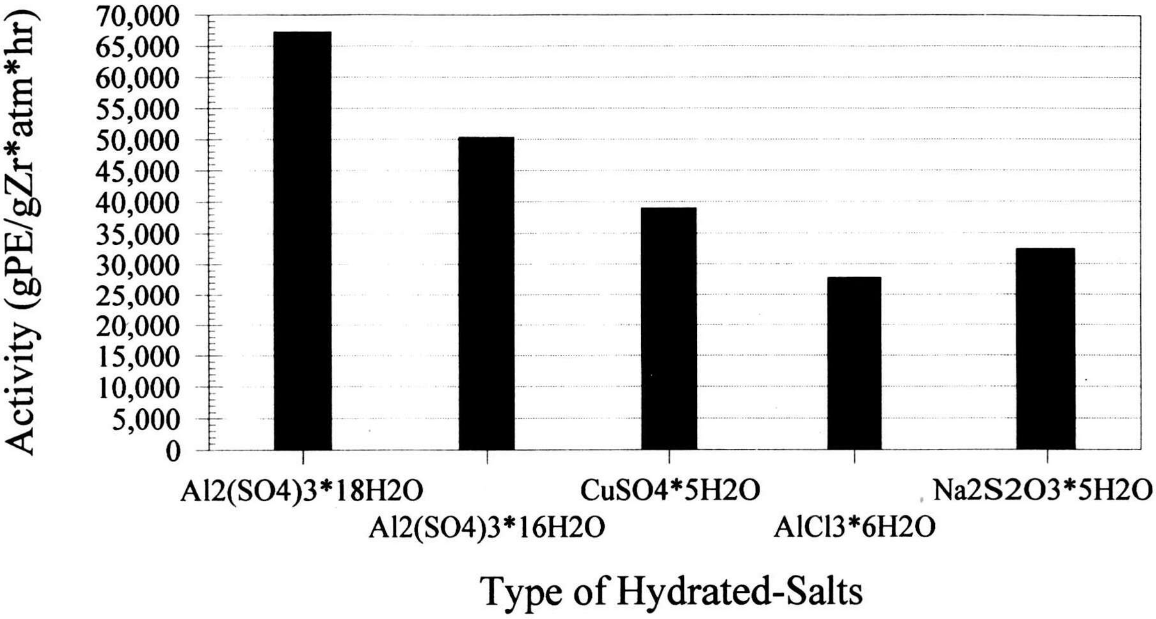


Figure 5.12 Activity versus Type of Hydrated-salt for Preparing Cocatalyst.

Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours.

Figure 5.12 shows that catalytic activity was depended on hydrated salt use in the preparation of methylaluminoxane. For this result, it could be showed that type of hydrated salt had effect on catalytic activity. The measurements of the capability to give water of hydrated salt by Thermal Gravimetry Analysis (TGA) at constant heating rate of 10 °C/min were shown in Figure 5.13-5.17. It also showed the rate of water release from hydrated-salt samples. It showed that the water releasing rate from hydrated-salt was in the following order: $AlCl_3 \cdot 6H_2O$ > $Al_2(SO_4)_3 \cdot 18H_2O$ > $Na_2S_2O_3 \cdot 5H_2O$ = $Al_2(SO_4)_3 \cdot 16H_2O$ > $CuSO_4 \cdot 5H_2O$ and are summarized in Table 5.7.

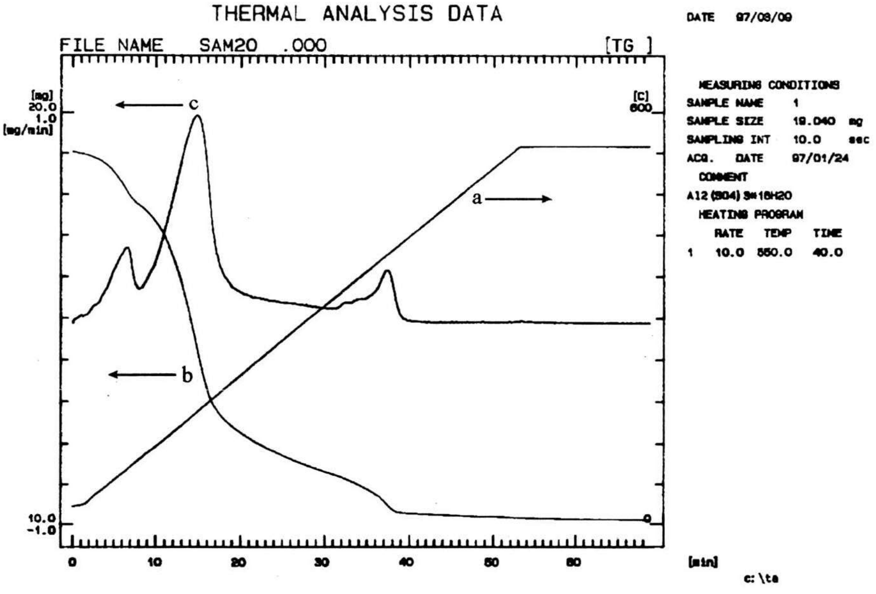
Figure 5.18 is the plot of catalytic activity versus the water releasing rate from hydrated-salt for Cp_2ZrCl_2/MAO catalyzed ethylene polymerization. The catalytic activity was found to increase with increasing water releasing rate, then reached a maximum around ca. 0.465 mgH_2O/min, and decreased afterward

Table 5.7 Effect of the water releasing rate[a] from hydrated-salt on polymerization activity[b]

Type of Hydrated Salt for Preparing	Catalytic Activity	Rate of spit out water
$Al_2(SO_4)_3 \cdot 18H_2O$	67303	0.4656
$Al_2(SO_4)_3 \cdot 16H_2O$	50312	0.4848
$AlCl_3 \cdot 6H_2O$	27830	0.4128
$CuSO_4 \cdot 5H_2O$	38968	0.5969
$Na_2S_2O_3 \cdot 5H_2O$	32366	0.4321

[a] TGA operating by heated from room temperature to 550 °C with a constant heating rate of 10 °C/min with N_2 gas flowing at 50 ml/min. The temperature was kept at 550 °C for 25 min until hydrated-salts weight constant.

[b] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l; Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.; Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours.



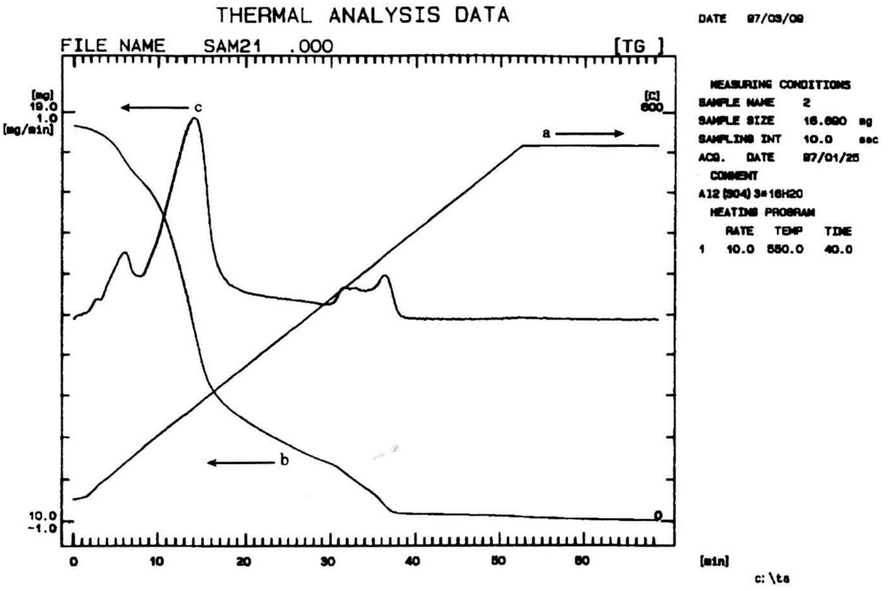
DATE 97/08/09

MEASURING CONDITIONS
SAMPLE NAME 1
SAMPLE SIZE 19.040 mg
SAMPLING INT 10.0 sec
ACQ. DATE 97/01/24
COMMENT
A12(SO4)3*18H2O
HEATING PROGRAM
RATE TEMP TIME
1 10.0 550.0 40.0

Figure 5.13 Thermogravimetric analysis of $Al_2(SO_4)_3 \cdot 18H_2O$ [a]

[a] Measuring condition: N_2 flow 50 ml/min.; heating rate 10 °C/min.; temperature range 25-550 °C; hold time 25 min.

note: a = temperature (°C) b = weight (mg) c = differentiated weight (mg/min.)



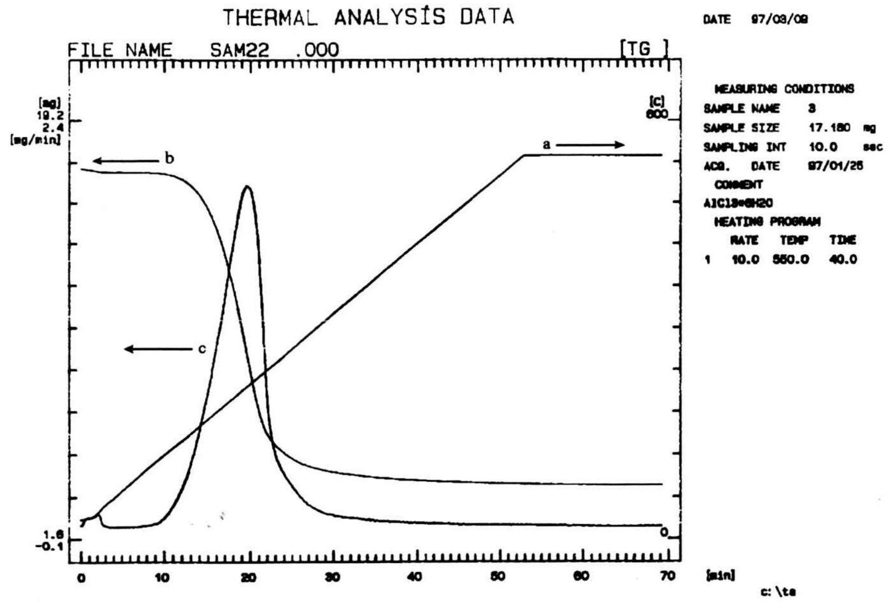
```
DATE   97/03/09

  MEASURING CONDITIONS
SAMPLE NAME     2
SAMPLE SIZE     16.690  mg
SAMPLING INT    10.0    sec
ACQ.   DATE     97/01/25
  COMMENT
A12(SO4)3*16H2O
  HEATING PROGRAM
     RATE   TEMP    TIME
1    10.0   550.0   40.0
```

Figure 5.14 Thermogravimetric analysis of $Al_2(SO_4)_3{\cdot}16H_2O$ [a]

[a] Measuring condition: N_2 flow 50 ml/min.; heating rate 10 °C/min.; temperature range 25-550 °C; hold time 25 min.

note: a = temperature (°C) b = weight (mg) c = differentiated weight (mg/min.)



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DATE   97/03/09

  MEASURING CONDITIONS
SAMPLE NAME     3
SAMPLE SIZE     17.180  mg
SAMPLING INT    10.0    sec
ACQ.   DATE     97/01/25
  COMMENT
AlCl3*6H2O
  HEATING PROGRAM
     RATE   TEMP    TIME
1    10.0   550.0   40.0
```

Figure 5.15 Thermogravimetric analysis of $AlCl_3{\cdot}6H_2O$ [a]

[a] Measuring condition: N_2 flow 50 ml/min.; heating rate 10 °C/min.; temperature range 25-550 °C; hold time 25 min.

note: a = temperature (°C) b = weight (mg) c = differentiated weight (mg/min.)

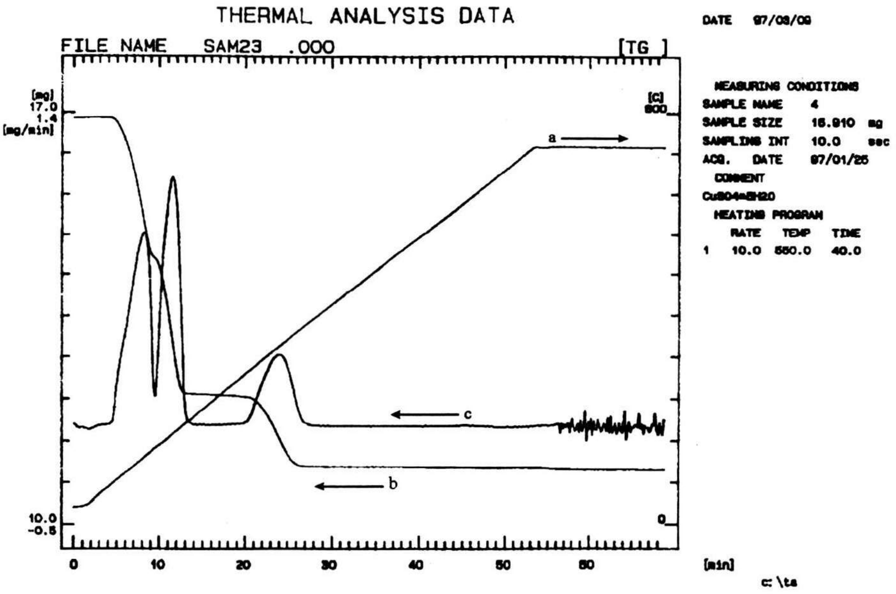


Figure 5.16 Thermogravimetric analysis of $CuSO_4{\cdot}5H_2O$ [a]

[a] Measuring condition: N_2 flow 50 ml/min.; heating rate 10 °C/min.; temperature range 25-550 °C; hold time 25 min.

note: a = temperature (°C) b = weight (mg) c = differentiated weight (mg/min.)

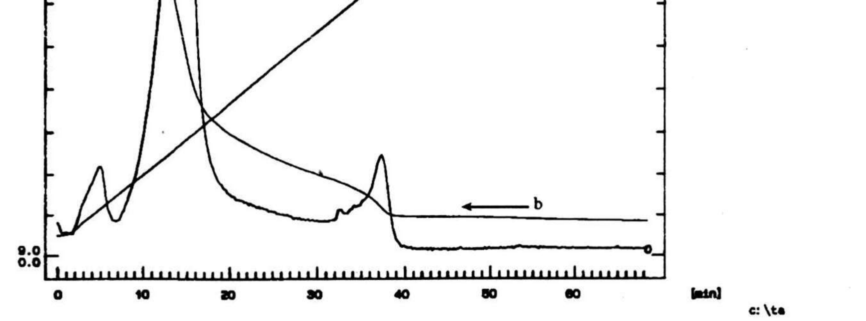


Figure 5.17 Thermogravimetric analysis of $Na_2S_2O_3{\cdot}5H_2O$ [a]

[a] Measuring condition: N_2 flow 50 ml/min.; heating rate 10 °C/min.; temperature range 25-550 °C; hold time 25 min.

note: a = temperature (°C) b = weight (mg) c = differentiated weight (mg/min.)

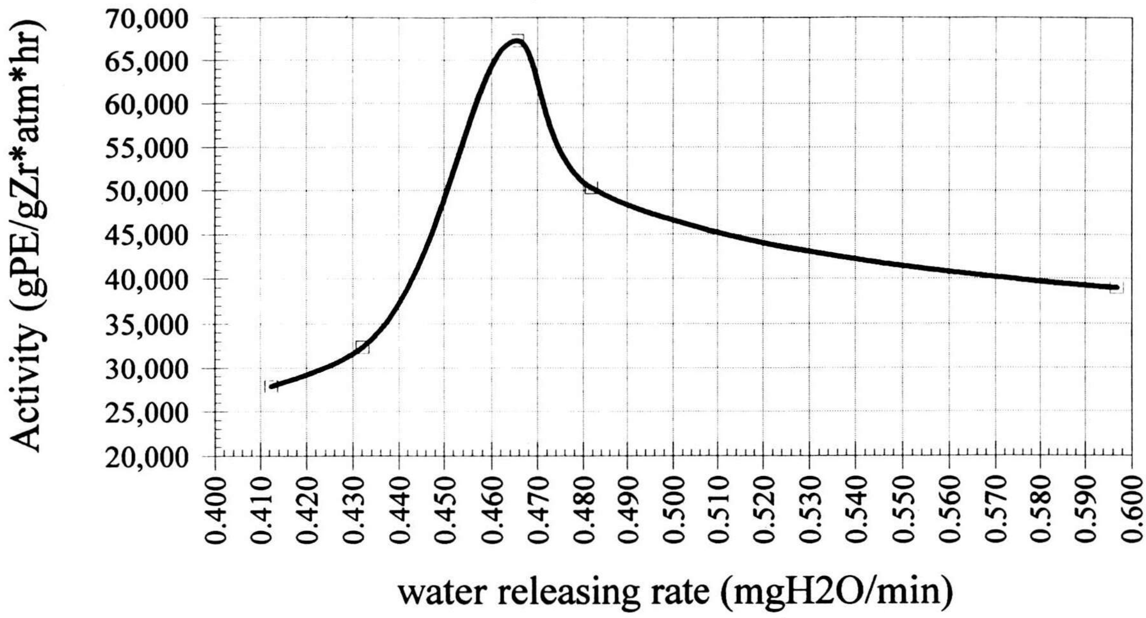


Figure 5.18 Activity versus water releasing rate from Hydrated-salt.

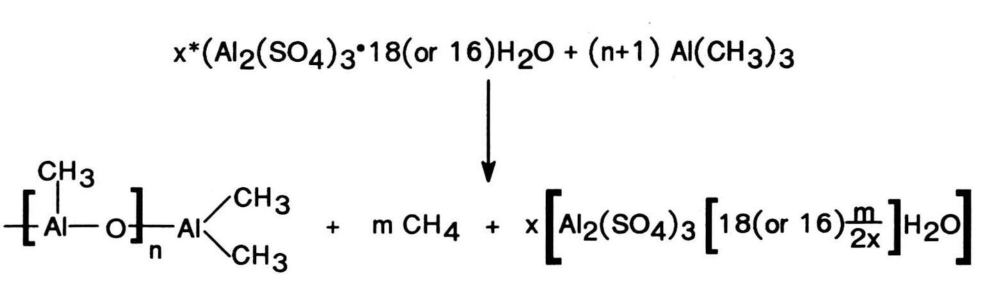
Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Al/Zr mole ratio = 6000; Polymerization time = 90 min., Time for preparing MAO = 40 hours.

The invention of Kaminsky et al. *[11]* relates to a process for the preparation of oligomeric alkylaluminoxanes by reacting aluminum salts containing water of crystallization, preferably aluminum sulfate containing water of crystallization, with an trialkylaluminum, preferably aluminum trimethyl. Aluminoxanes of this type can be used as a catalyst component in the preparation of high-activity, homogeneous Ziegler catalysts.

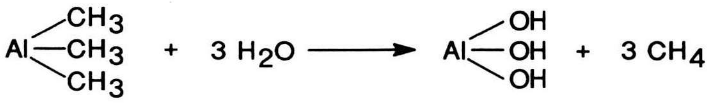
Trimethylaluminum which has been diluted with an inert solvent, for example haptane or toluene, reacts with $Al_2(SO_4)_3{\cdot}18H_2O$ or $Al_2(SO_4)_3{\cdot}16H_2O$ which are used particularly preferentially in accordance with the Eq.5.16:



$$x*(Al_2(SO_4)_3{\cdot}18(\text{or } 16)H_2O + (n+1)\ Al(CH_3)_3 \longrightarrow \left[\overset{\overset{\displaystyle CH_3}{|}}{Al}-O\right]_n-Al(CH_3)_2 + m\ CH_4 + x\left[Al_2(SO_4)_3\left[18(\text{or } 16)-\frac{m}{2x}\right]H_2O\right]$$

Eq.5.16

in which n = 2 to 40, preferably 10-20, m = 2n for linear aluminoxanes or 2n+2 for cyclic aluminoxanes and x = 0.006n to 0.15n, preferably 0.11n. On the other hand, higher water releasing rate from hydrated-salt had the effect on this reaction in accordance with Eq. 5.17 *[133]*.



$$\mathrm{Al(CH_3)_3} + 3\,\mathrm{H_2O} \longrightarrow \mathrm{Al(OH)_3} + 3\,\mathrm{CH_4} \qquad \text{Eq.5.17}$$

In these cases, a methane is formed, and the aluminum appears as aluminum hydroxide. These products do not react with metallocene catalysts to form active site. This indicates that the higher water releasing rate the lower catalytic activity. On the other end, the lower water releasing rate the lower catalytic activity. Hence a suitable water releasing rate is required, i.e. between 0.46 to 0.47 mgH_2O/min, for the reaction of trimethylaluminum to form methylaluminoxane. This methylaluminoxane when used in combination with bis(cyclopentadienyl)zirconium dichloride will yield the maximum catalytic activity.

5.6 THE EFFECT OF TIME FOR PREPARING COCATALYST

Ethylene polymerization were conducted in 200 ml. toluene using bis(cyclopentadienyl)zirconium dichloride catalyst (Cp_2ZrCl_2) and methylaluminoxane (MAO) cocatalyst at different time for preparing methylaluminoxane. Polymerization were carried out at 300 K, [Zr] = $8.00*10^{-7}$ mole/l, Al/Zr mole ratio = 6000, ethylene partial pressure is 40 psi., polymerization time = 90 min., methylaluminoxane used $Al_2(SO_4)_3 \cdot 18H_2O$ to supply water with seven different time for preparing methylaluminoxane viz. 20, 30, 40, 50, 60, 70, and 80 hours. The results are summarized in Table 5.8. The graphical plot of ethylene consumption versus polymerization time are shown in Figure 5.19 and the catalytic activity versus time for preparing cocatalyst are shown in Figure 5.20.

Figure 5.19 shows ethylene polymerization rate profiles at several time for preparing methylaluminoxane (MAO). All profile shows the maximum rate ($r_{p,m}$) at the same time about 8 min. This results indicate time for preparing MAO has no effect to form the active centers. There was a drop of ethylene consumption (r_p) about 30% after shows the maximum rate of polymerization ($r_{p,m}$). After about 5 min. of the time of the maximum rate of polymerization ($r_{p,m}$) the rate of ethylene consumption (r_p) slowly decreased along the polymerization time.

Table 5.8 Effect of Time for Preparing Cocatalyst on polymerization activity[a]

Time for Preparing methylaluminoxane (hour)	Catalytic Activity gPE/(gZr*atm*hr)
20	32178
30	44987
40	67303
50	81676
60	82493
70	83264
80	82550

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Al/Zr mole ratio = 6000; Polymerization time = 90 min.;

Used $Al_2(SO_4)_3 \cdot 18H_2O$ for preparing MAO

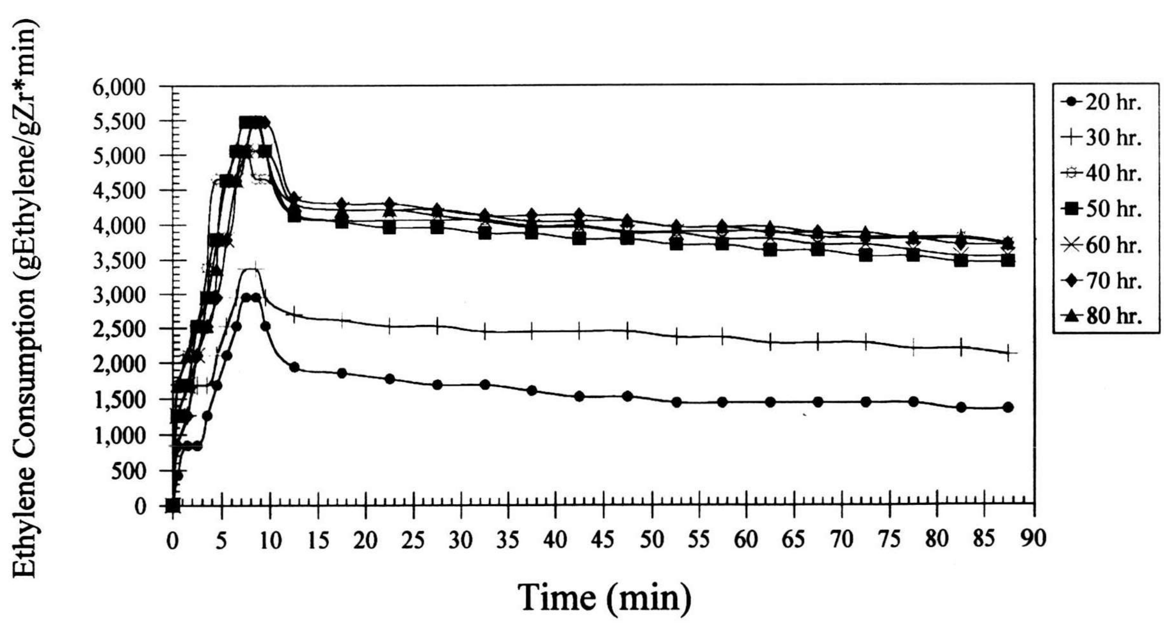


Figure 5.19 Ethylene consumption versus Polymerization time curve at various Time for Preparing Cocatalyst.

Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Al/Zr mole ratio = 6000; Polymerization time = 90 min.;

Used $Al_2(SO_4)_3 \cdot 18H_2O$ for preparing MAO

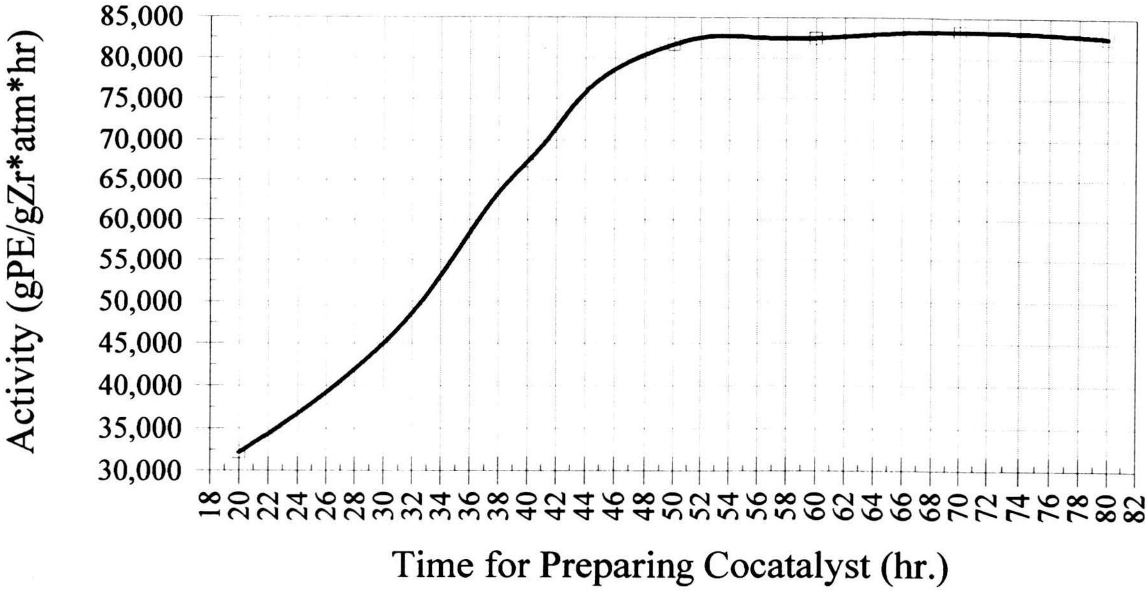


Figure 5.20 Activity versus Time for Preparing Cocatalyst.

Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Al/Zr mole ratio = 6000; Polymerization time = 90 min.;

Used $Al_2(SO_4)_3{\cdot}18H_2O$ for preparing MAO

Figure 5.20 shows that catalytic activity depends on the time used for preparing methylaluminoxane. For this result, it could be showed that the time for preparing methylaluminoxane had an effect on catalytic activity. When the time for preparing methylaluminoxane was increased, the activity was greatly enhanced, attaining a maximum value at time of about 50 hours. The time for preparing methylaluminoxane had an effect on quantity of methylaluminoxane, namely, the increased time will increase quantity of methylaluminoxane or decrease quantity of trimethylaluminoxane (see reaction from Eq.5.16). This result found a constant value after having reached the maximum catalytic activity because of no trimethylaluminoxane remain to react with water that supply from hydrated salt. Therefore, the time about 50 hours is suitable for preparing methylaluminoxane by used $Al_2(SO_4)_3{\cdot}18H_2O$ as water supply source.

5.7 CHARACTERIZATION OF POLYETHYLENE

5.7.1 *Melting Temperature (T_m)*

Differential scanning calorimetry or DSC is a thermal analysis instrument that can be used to test many polymer. The DSC has been used to determine the transition temperature and the heat flow associated with material transition as a function of time and temperature. It also provides quantitative and qualitative data on the endothermic (heat absorption) and the exothermic (heat evolution) processes of materials during physical transitions. This information helps in identifying the processing and end-use performance of the tested polymers *[134]*.

One important transition property of polymer which can be tested with the DSC is the melting temperature (T_m). Figure 5.21 shows the melting temperature for polyethylene produced from Cp_2ZrCl_2/MAO catalyst system that MAO preparing from various hydrated salt viz. $Al_2(SO_4)_3{\cdot}18H_2O$, $Al_2(SO_4)_3{\cdot}16H_2O$, $AlCl_3{\cdot}6H_2O$, $CuSO_4{\cdot}5H_2O$, and $Na_2S_2O_3{\cdot}5H_2O$ to supply the water for reaction with trimethylaluminum to methylaluminoxane. The results of hydrated salt on the melting temperature of polyethylene produced are summarized in Table 5.9. The melting temperature relates to molecular weight of polyethylene that the higher melting temperature the higher molecular weight. Kaminsky *[130]*, Srinivasa Reddy *[135]* and in several laboratories have studied the effect of zirconocene/methylaluminoxane on catalytic activity and properties of polymer products. The results showed that the effect of catalytic activity on molecular weight of polymer is that higher molecular weight were obtained at lower catalytic activity. This is due to the reduced chain transfer at lower catalytic activity. From results that indicate that the melting temperature decreased with an increase in the catalytic activity, and MAO (in case of used $Al_2(SO_4)_3{\cdot}18H_2O$ to supply the water) is acting as better chain transfer agent when compared to MAO (in case of used $AlCl_3{\cdot}6H_2O$ to supply the water).

Table 5.9 Effect of hydrated salt on melting temperature of PE[a]

Type of Hydrated Salt for Preparing methylaluminoxane	Catalytic Activity gPE/(gZr*atm*hr)	Melting Temperature (T_m) (°C)
$Al_2(SO_4)_3 \cdot 18H_2O$	67303	130.33
$Al_2(SO_4)_3 \cdot 16H_2O$	50312	131.59
$AlCl_3 \cdot 6H_2O$	27830	138.65
$CuSO_4 \cdot 5H_2O$	38968	133.01
$Na_2S_2O_3 \cdot 5H_2O$	32366	133.62

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;
Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;
Al/Zr mole ratio = 6000; Polymerization time = 90 min., Time for preparing MAO = 40 hours.

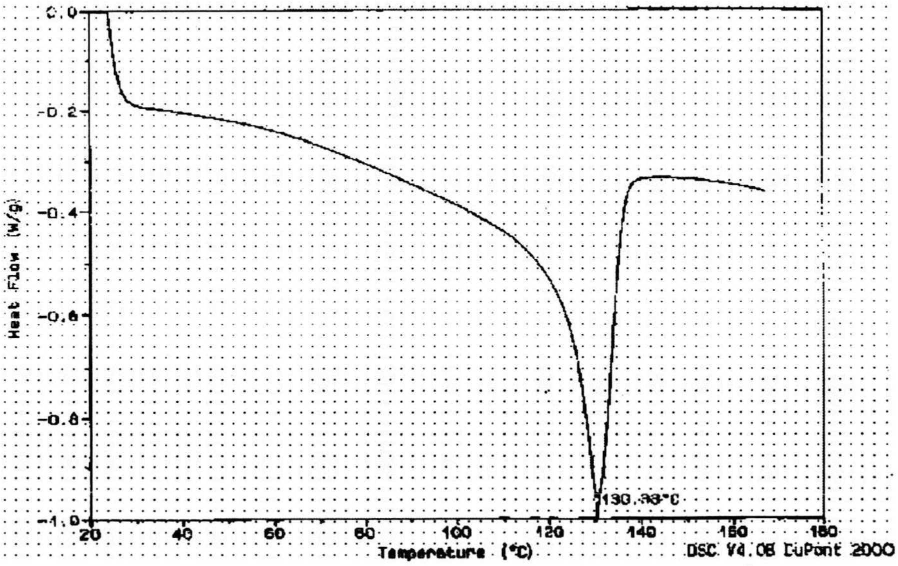


Figure 5.21(a) DSC curve of Polyethylene produced by Cp_2ZrCl_2/MAO[a].

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;
Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;
Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours.
Used $Al_2(SO_4)_3 \cdot 18H_2O$ to supply the water for preparing MAO

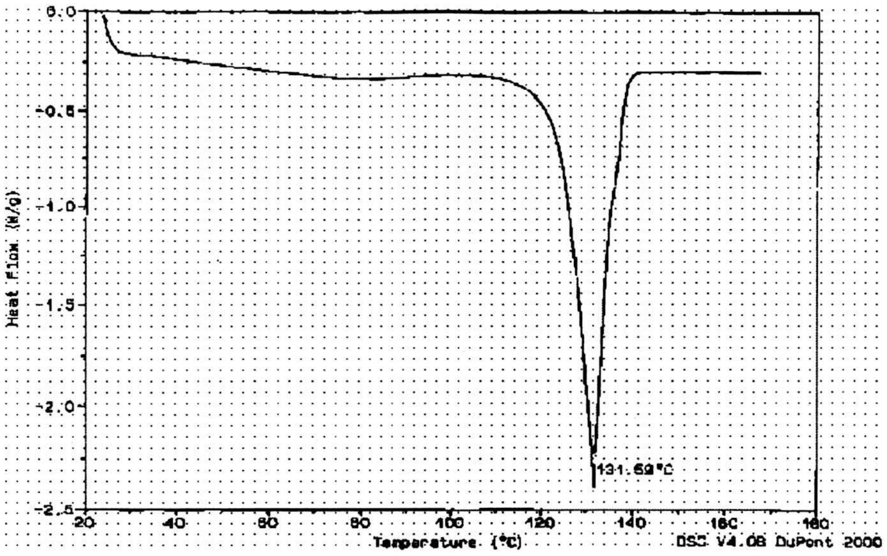


Figure 5.21(b) DSC curve of Polyethylene produced by Cp_2ZrCl_2/MAO^a.

^{a} Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours.

Used $Al_2(SO_4)_3 \cdot 16H_2O$ to supply the water for preparing MAO

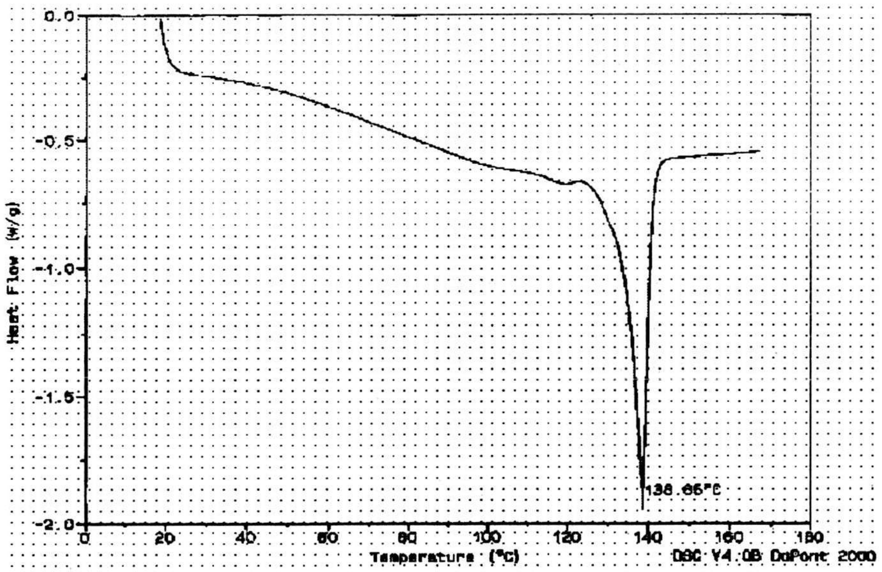


Figure 5.21(c) DSC curve of Polyethylene produced by Cp_2ZrCl_2/MAO^a.

^{a} Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours.

Used $AlCl_3 \cdot 6H_2O$ to supply the water for preparing MAO

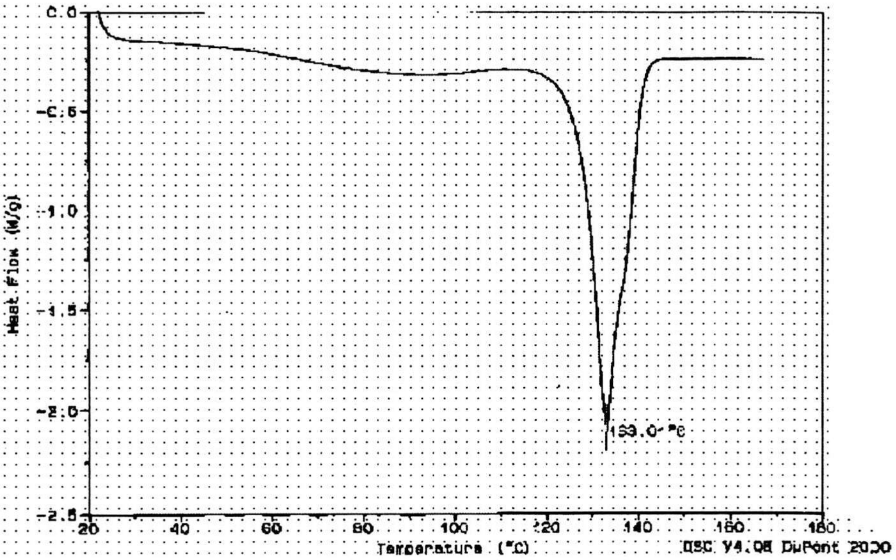


Figure 5.21(d) DSC curve of Polyethylene produced by Cp_2ZrCl_2/MAO^a.

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours.

Used $CuSO_4{\cdot}5H_2O$ to supply the water for preparing MAO

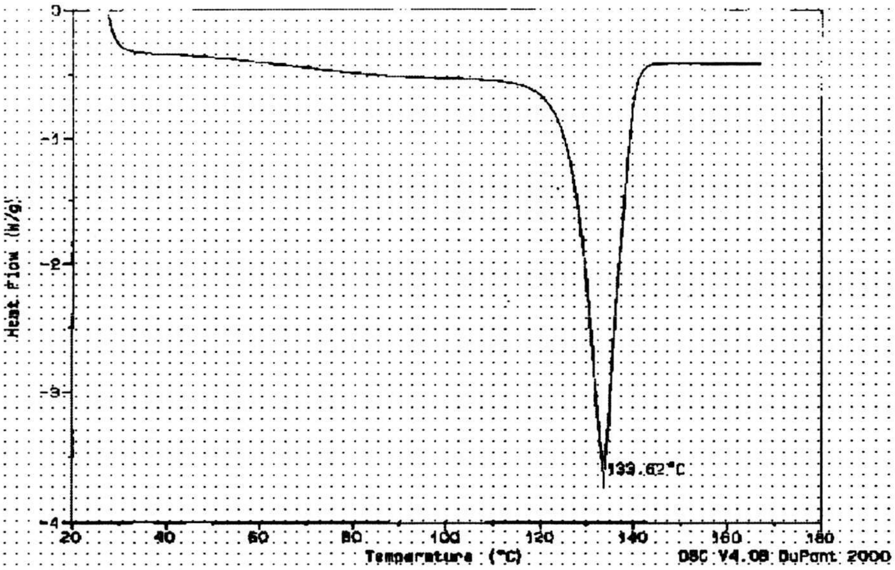


Figure 5.21(e) DSC curve of Polyethylene produced by Cp_2ZrCl_2/MAO^a.

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours.

Used $Na_2S_2O_3{\cdot}5H_2O$ to supply the water for preparing MAO

5.7.2 *Morphology of Polyethylene*

The methylaluminoxane as cocatalyst preparing from various hydrated salt viz. $Al_2(SO_4)_3{\cdot}18H_2O$, $Al_2(SO_4)_3{\cdot}16H_2O$, $AlCl_3{\cdot}6H_2O$, $CuSO_4{\cdot}5H_2O$, and $Na_2S_2O_3{\cdot}5H_2O$ to supply the water for reaction with trimethylaluminum to methylaluminoxane in combination with bis(cyclopentadienyl)zirconium dichloride used as catalyst for ethylene polymerization. The amorphous solids of the polyethylene products obtained from this catalyst system has been studied by Scanning Electron Microscopy (SEM) and are shown in Figure 5.22.

Morphology of polyethylene obtained from Cp_2ZrCl_2/MAO (used $Al_2(SO_4)_3{\cdot}18H_2O$ to supply the water) and Cp_2ZrCl_2/MAO (used $Al_2(SO_4)_3{\cdot}16H_2O$ to supply the water) are similar (see Figures 5.22(a) and 5.22(b)). Both have smooth surface. In other hand, morphology of polyethylene obtained from Cp_2ZrCl_2/MAO (used $CuSO_4{\cdot}5H_2O$) and Cp_2ZrCl_2/MAO (used $Na_2S_2O_3{\cdot}5H_2O$) (see Figures 5.22(d) and 5.22(e)) has a porous surface. Morphology of polyethylene obtained from Cp_2ZrCl_2/MAO (used $AlCl_3{\cdot}6H_2O$) shows a fibrous surface (Figure 5.22(c)).

From the result discussed in section 5.7.1, it can be shown that the polymer which have porous or fibrous surface are obtained from lower catalytic activity catalyst. While the polymer which have smooth surface are obtained from higher catalytic activity catalyst. Therefore, the morphology can refer to molecular weight of polyethylene products for Cp_2ZrCl_2/MAO catalyst system.

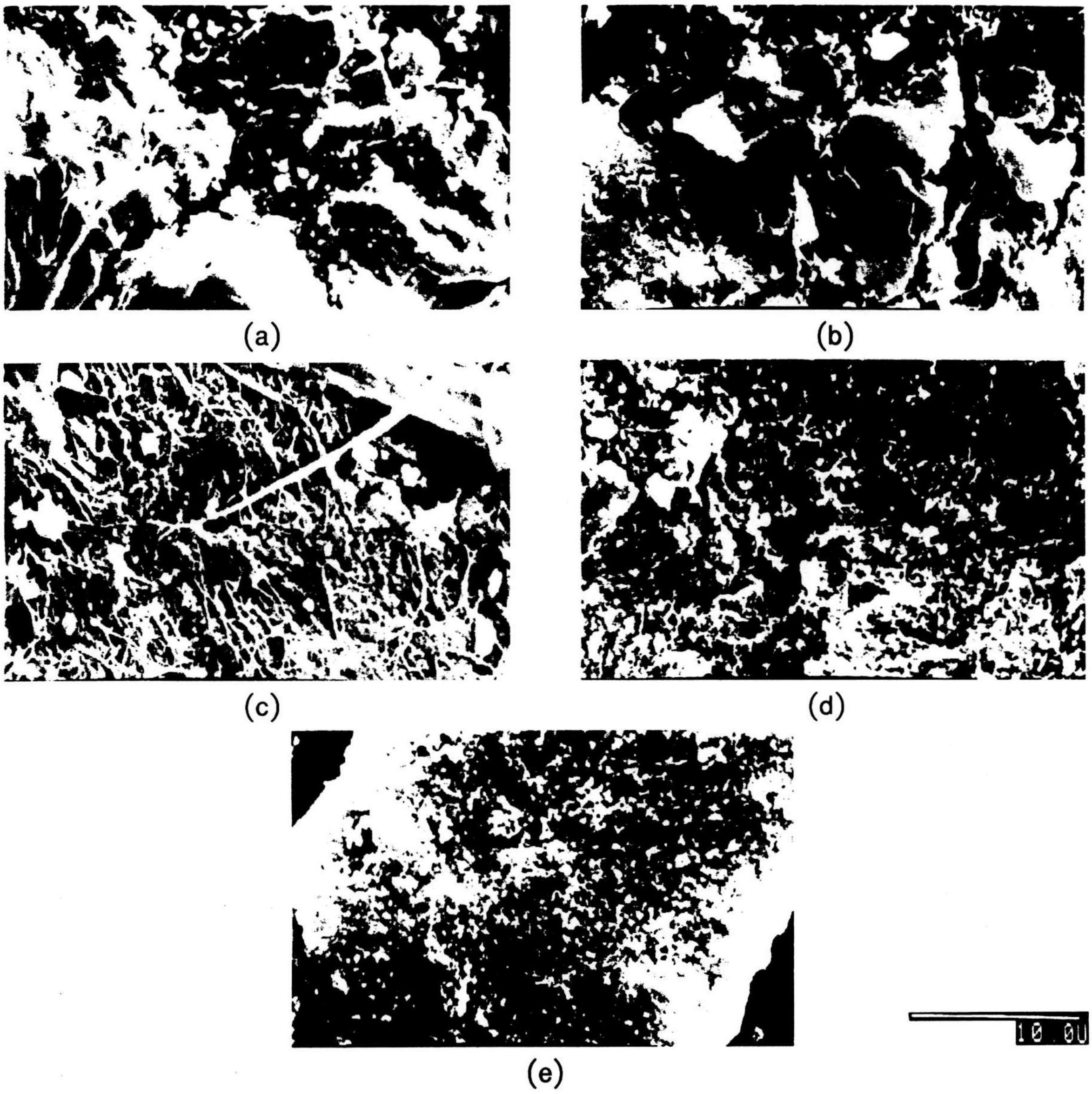


Figure 5.22 Scanning Electron Micrograph[a] of Polyethylene produced by Cp_2ZrCl_2/MAO[b]

(a) Used $Al_2(SO_4)_3 \cdot 18H_2O$ to supply the water for preparing MAO

(b) Used $Al_2(SO_4)_3 \cdot 16H_2O$ to supply the water for preparing MAO

(c) Used $AlCl_3 \cdot 6H_2O$ to supply the water for preparing MAO

(d) Used $CuSO_4 \cdot 5H_2O$ to supply the water for preparing MAO

(e) Used $Na_2S_2O_3 \cdot 5H_2O$ to supply the water for preparing MAO

[a] Operated at 20 KV and enlargement of 3600 times.

[b] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00 * 10^{-7}$ mole/l; Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.; Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours.

5.7.3 *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 *[125]*. The infrared spectra of polyethylene produced from Cp_2ZrCl_2/MAO catalyst system that MAO preparing from various hydrated salt viz. $Al_2(SO_4)_3 \cdot 18H_2O$, $Al_2(SO_4)_3 \cdot 16H_2O$, $AlCl_3 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, and $Na_2S_2O_3 \cdot 5H_2O$ are shown in Figure 5.23. The infrared identification for each peak had been assigned to the organic groups as summarized in Table 5.10.

Table 5.10 Identification of Infrared spectrum of PE

Wave No. (cm^{-1})	Assignment
720/730	Long Chain $-(CH_2)-$
910	Vinylidene chain end
1378	Chain Branching
1460	$-(CH_2)-$ Bending
2850/2920	$-(CH_2)-$, $-(CH_3)-$ Stretching
3448	Hydroxyl group (-OH)

The wave number of 1378 cm^{-1} was the fingerprint of unsaturated group of chain branching. It was used to identify that low density polyethylene (LDPE) prepared at high pressure process, the polyethylene had branch chain. The wave number of 1479 cm^{-1} was the bending mode of $-CH_2-/-CH_3-$. In addition, the wave number of 2850 and 2920 were the stretching mode of $-CH_2-/-CH_3-$. From this experiment, the infrared spectrum of polyethylene produced by Cp_2ZrCl_2/MAO were shown in Figure 5.23(a) to 5.23(e). All the figures show the small peak at wave number of 1378 cm^{-1} which identified about branch chain in polyethylene products. While the peak at wave number of 910 cm^{-1} was the fingerprint of vinylidene chain end which identified the amount of chain in polyethylene products or molecular weight of polyethylene. The higher molecular weight polyethylene has lower number of chain. From the infrared spectrum of polyethylene produced in this experiment, it is found that it can not identified the peak between wave number 800 to 1000 cm^{-1} because of another bands are overlap on this sections, so the infrared spectrum of this polyethylene could not identify the number of chain. But from section 5.7.1 (melting temperature), it can be said that the polyethylene product had the high molecular weight or had low the number of chain.

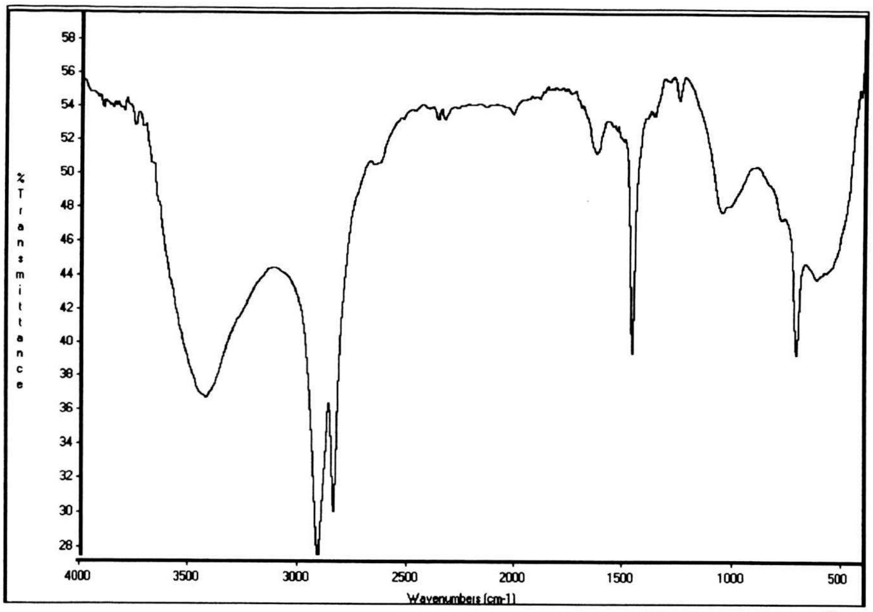


Figure 5.23(a) Infrared spectrum of Polyethylene produced by Cp_2ZrCl_2/MAO[a].

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours.

Used $Al_2(SO_4)_3{\cdot}18H_2O$ to supply the water for preparing MAO

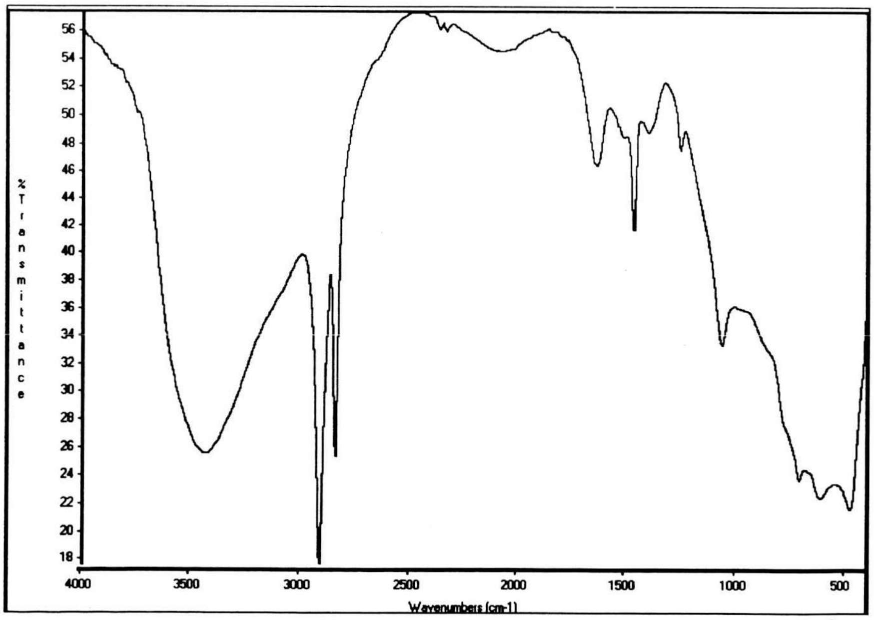


Figure 5.23(b) Infrared spectrum of Polyethylene produced by Cp_2ZrCl_2/MAO[a].

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours.

Used $Al_2(SO_4)_3{\cdot}16H_2O$ to supply the water for preparing MAO

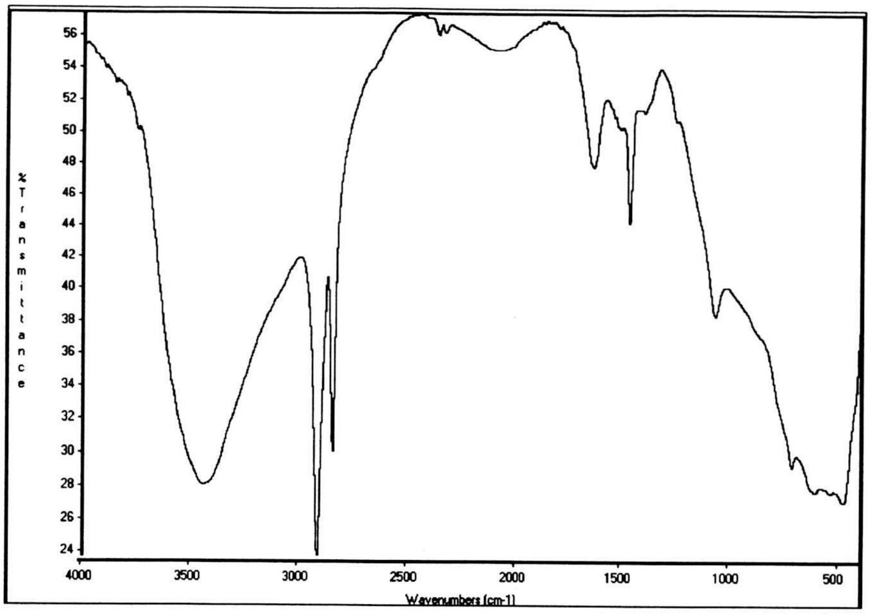


Figure 5.23(c) Infrared spectrum of Polyethylene produced by Cp_2ZrCl_2/MAO[a].

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l; Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.; Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours. Used $AlCl_3{\cdot}6H_2O$ to supply the water for preparing MAO

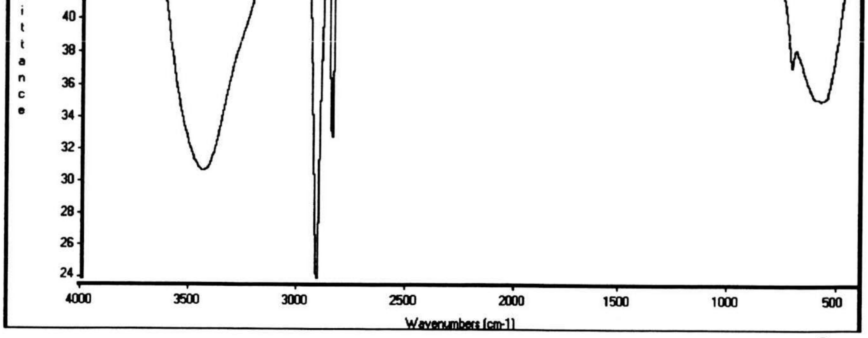


Figure 5.23(d) Infrared spectrum of Polyethylene produced by Cp_2ZrCl_2/MAO[a].

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l; Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.; Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours. Used $CuSO_4{\cdot}5H_2O$ to supply the water for preparing MAO

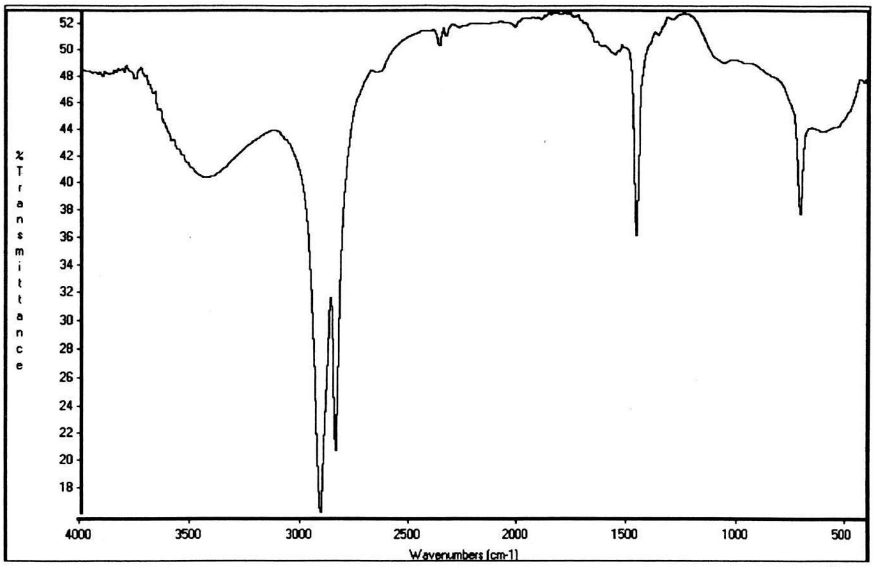


Figure 5.23(e) Infrared spectrum of Polyethylene produced by Cp_2ZrCl_2/MAO[a].

[a] Toluene = 200 ml.; Catalyst = Cp_2ZrCl_2; Cocatalyst = MAO; [Zr] = $8.00*10^{-7}$ mole/l;

Polymerization Temperature = 300 K; Ethylene Partial Pressure = 40 psi.;

Al/Zr mole ratio = 6000; Polymerization time = 90 min.; Time for preparing MAO = 40 hours.

Used $Na_2S_2O_3 \cdot 5H_2O$ to supply the water for preparing MAO