CHAPTER IV
RESULTS AND DISCUSSION

In this research work the ethylene consumption rate and productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system in the polymerization of ethylene were investigated. The resulting polyethylene products were also characterized by DSC, WAXD, SEM, GPC and FT-IR.

4.1 Factors Affecting Ethylene Polymerization with Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA Catalyst System

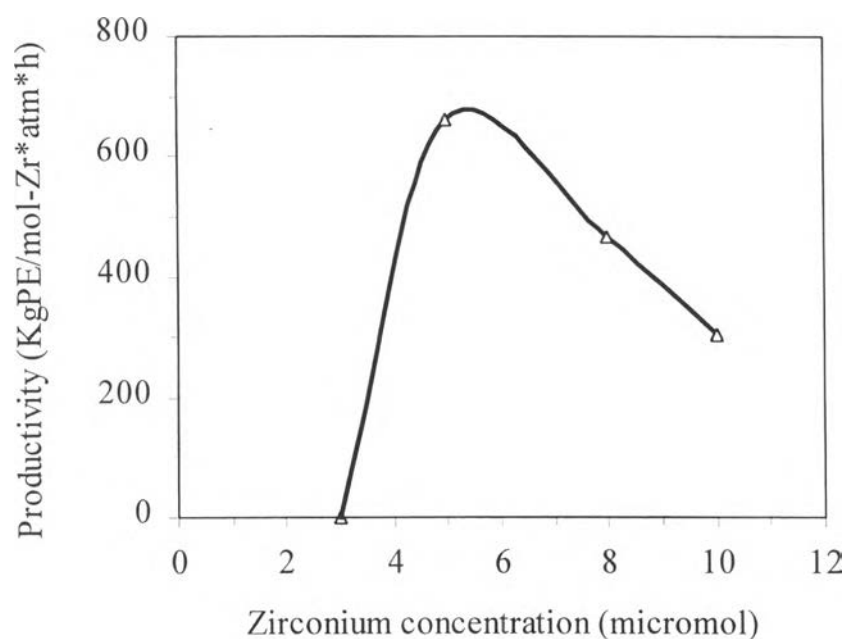### 4.1.1 Effect of Zirconocene Concentration at Constant Al/Zr Ratio

The first set of polymerization runs was performed in order to determine the effect of zirconocene concentration on productivity and to choose an optimum catalyst concentration for the remaining runs.

Polymerization of ethylene was carried out at a constant Al/Zr ratio of 100. The productivity critically depends on the zirconocene concentration, as shown in Table 4.1 and Figure 4.1. There was no productivity at the low Al/Zr ratio of 3 µmol. Above the catalyst concentration of 5 µmol, there was a decrease in productivity with increase in zirconocene concentration. The decrease in productivity with increasing concentration is thought to be due to precipitation of the resulting polymer which, at high concentration, led to a diffusion-controlled rate limit.

Table 4.1 Dependence of productivity using Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA system on zirconocene concentrations at constant Al/Zr =100.

(B/Zr = 1, P_{ET} = 2 bar, T = 20°C, total volume = 150 ml in toluene, reaction time = 1h)

[Zr] μmol	[Al] μmol	Al/Zr	Yield (g)	Productivity (kgPE/molZr*atm*h)
3	300	100	-	-
5	500	100	6.03	603
8	800	100	7.46	466
10	1000	100	7.66	383

Figure 4.1 The productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA system at varying zirconocene concentration at constant Al/Zr ratio of 100 at 20°C.

(B/Zr = 1, P_{ET} = 2 bar, T = 20°C, total volume = 150 ml in toluene, reaction time = 1h)

Figure 4.2 shows the ethylene consumption rate of the system at varying zirconocene concentration. In all cases, the ethylene consumption rate reaches a maximum within the first few minutes followed by a steady decline down to almost zero within 20 minutes. This kind of polymerization behavior was also observed by Kim and Choi (1999). Generally a slow activation was observed with metallocene/MAO catalyst system. The deactivation is attributed to the formation of inactive species with Metal-CH_2-Al structure. Since these inactive species can be regenerated by MAO, the polymerization decays slowly. In the present work, the rapid deactivation could be explained by a reversible deactivation at the initial stage followed by an irreversible deactivation of the catalytically active center (Rieger and Janiak, 1994). As the polymerization proceeds, the polymer precipitation forms rapidly and results in the change from a truly homogeneous system at the beginning to a heterogeneous system. The reaction is then controlled by diffusion-controlled processes of the ethylene monomer through the polymer matrix to the enclosed active center. Such a reversible/irreversible decay is believed to play a role for the decrease in activation in the present system.
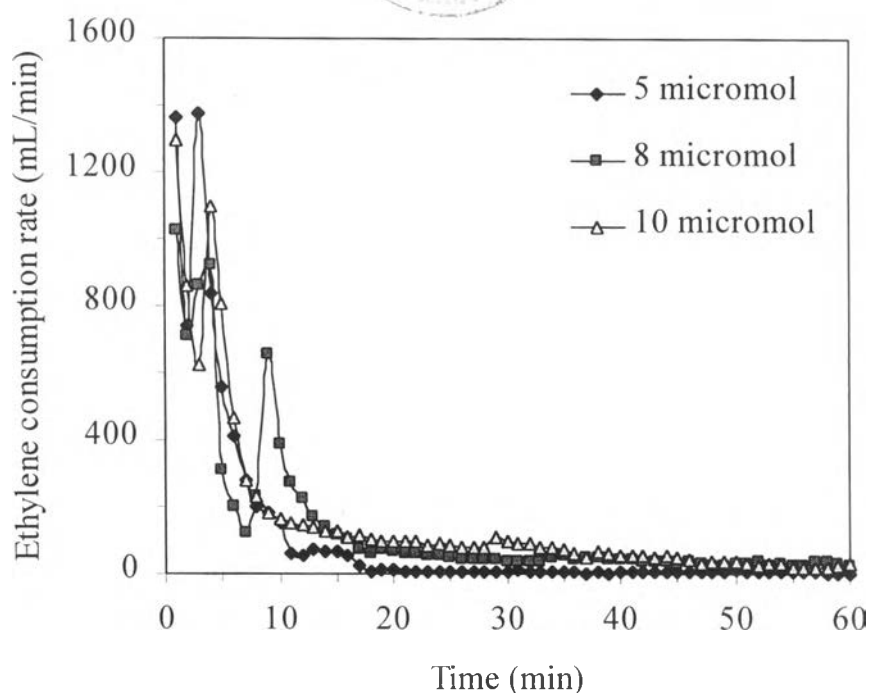
Figure 4.2 The ethylene consumption rate of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system at varying zirconocene concentrations at constant Al/Zr ratio of 100.

(B/Zr = 1, P_{ET} = 2 bar, T = 20°C, total volume = 150 ml in toluene, reaction time = 1h)

There is a limit for lowering the zirconocene concentration and increasing the productivity at constant Al/Zr ratio. At zirconocene concentration at 3 μmol, the productivity was zero. This is probably due to the presence of remaining impurities in the system. To retain a comparable productivity for the smaller zirconocene concentration, the Al/Zr ratio had to be raised from 230-400, as shown in Table 4.2. The necessity to increase in TEA content is to scavenge the impurities in the reaction medium and form the complex equilibrium. As consequence, employing a moderate zirconocene concentration can drastically reduce the necessary amount of TEA for the scavenging and alkylation process. Taking into account the cost factor and the

residual of TEA remaining in the resulting polymer, polymer productivity can well be optimized with a moderate zirconocene concentration of 5 μmol and Al/Zr ratio range of 200-300.

Table 4.2 Productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system at low zirconocene concentration at varying Al/Zr ratios.

([Zr] = 3 μmol, B/Zr = 1, P_{ET} = 1 bar, T = 30°C, total volume = 150 ml in toluene, reaction time = 1 h)

[Al] (μmol)	Al/Zr	Yield (g)	Productivity (KgPE/mol-Zr*atm*h)
300	100	-	-
600	200	-	-
690	230	5.1	1700
780	260	6.9	2300
900	300	9.4	3133
1200	400	5.9	1966
1500	500	-	-
1800	600	-	-

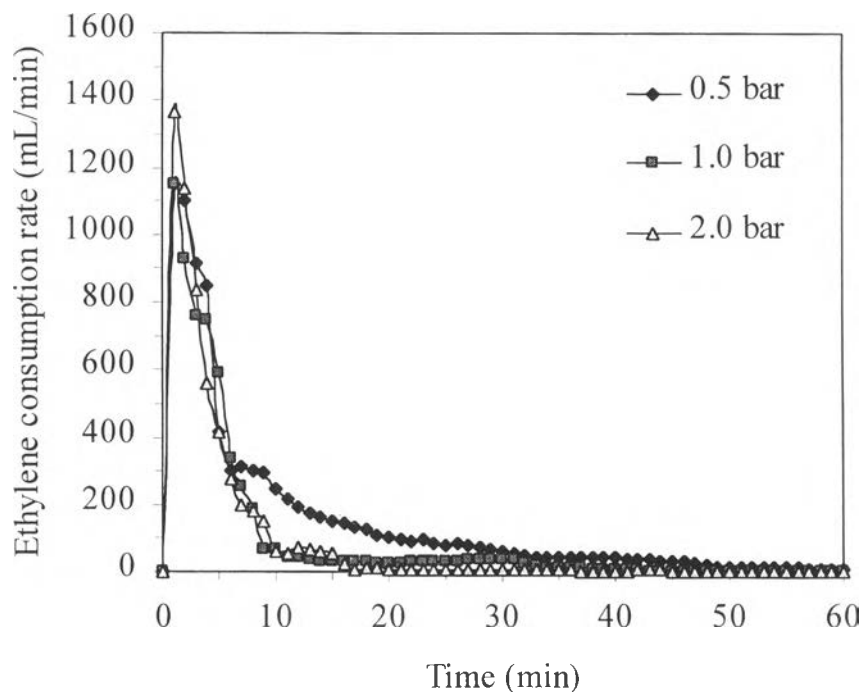### 4.1.2 Effect of Ethylene Pressure on Ethylene Consumption Rate

In an attempt to obtain the optimum ethylene consumption rate, three different ethylene pressures were employed. The activity over 1 h behaves very differently with respect to ethylene pressure. The catalytic activity was found to increase with increasing monomer pressure during the beginning of the polymerization and drastically drop down to zero consumption rate very fast when compared to the lower pressure, as seen in Figure 4.3. This can be explained that, at higher ethylene pressure, the polymerization is truly homogeneous only at the very beginning. As the

reaction proceeds, polymer precipitation forms rapidly, a the reaction is then controlled by a diffusion process. The effect of ethylene pressure is tabulated in Table 4.3 and Figure 4.3. As the ethylene pressure is decreased from 2 to 0.5 bar, the productivity increases from 603 to 3000 kgPE/mol-Zr*atm*h. This indicates that the ethylene consumption rate is limited by diffusion in the polymer matrix at high ethylene pressure. To avoid this problem, lower ethylene pressure at 1.0 bar was used to study the effects of other parameters of ethylene polymerization.

Table 4.3 Productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system at varying ethylene pressures.

([Zr] = 5 μmol, B/Zr = 1, Al/Zr = 200, T = 30°C, total volume = 150 ml in toluene, reaction time = 1 h)

Ethylene Pressure (bar)	Yield (g)	Productivity (kgPE/mol-Zr*atm*h)
2.0	12.92	1292
1.0	9.50	1900
0.5	7.50	3000

Figure 4.3 The ethylene consumption rate of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system at varying ethylene pressures.

([Zr] = 5 μmol, Al/Zr = 200, T = 30°C, total volume = 150 ml in toluene, reaction time = 1 h)

4.1.3 Effect of Al/Zr Ratio on Ethylene Consumption Rate and Productivity

Figure 4.4 shows ethylene consumption rate as a function of Al/Zr ratio using Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system. The ratio was changed by maintaining a constant catalyst concentration and varying the concentration of TEA in the reactor.

At zero or low TEA concentration, no catalyst activity was observed due to the incomplete TEA alkylation of Cp_2ZrCl_2. Polymerization activity increased with increase in Al/Zr ratio up to 220.
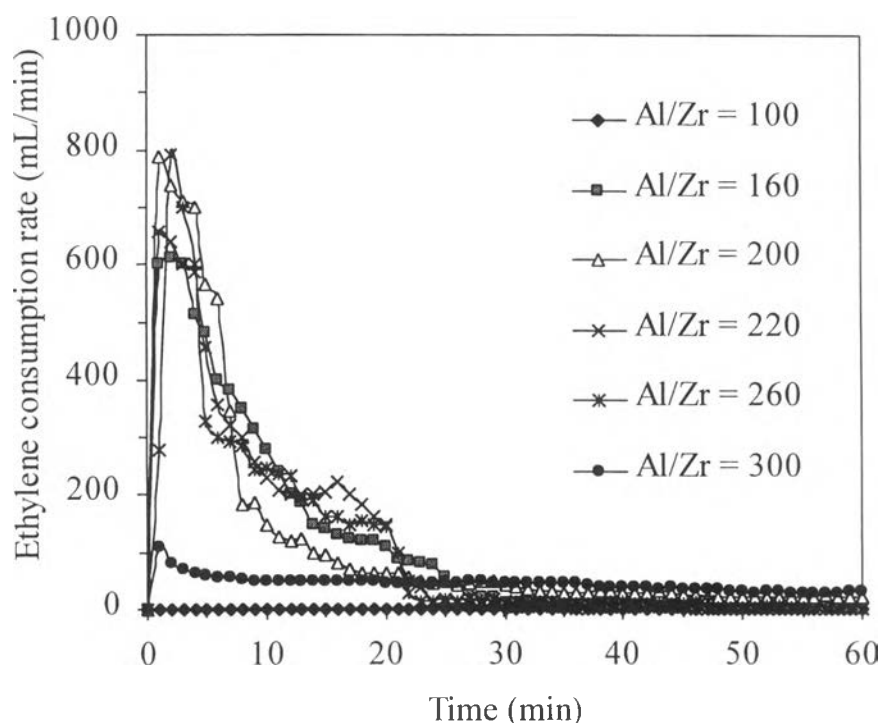
Figure 4.4 Ethylene consumption rate of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system at varying Al/Zr ratios.

([Zr] = 5 μmol, B/Zr = 1, P_{ET} = 0.5 bar, T = 30°C, total volume = 150 ml in toluene, reaction time = 1 h)

A considerable amount of TEA is expected to be utilized to scavenge impurities existed in the reaction medium. The polymerization showed activities within a narrow range of Al/Zr ratio. All polymerization reactions reached the maximum rates quickly and decayed very fast within 20 minutes to zero rate after reaching maximum. These results demonstrate that both the formation of catalytically active sites and deactivation of the active sites are very rapid processes. Generally a slow deactivation was observed in almost all polymerizations with metallocene catalyst systems (Kim and Choi, 1999).

At high Al/Zr ratio the surplus of TEA may lead to the formation of species like $[Cp_2ZrR^+][^-Cl_2AlR_2]$ which may prevent further reaction between the alkylated Cp_2ZrCl_2 and $B(C_6F_5)_3$, as the species $[Cp_2ZrR^+][^-Cl\ B(C_6F_5)_3]$ is highly active whereas the species like $[Cp_2ZrR^+][^-Cl_2AlR_2]$ is much less active, and this probably explains the lowering in activity when TEA exceeds a certain amount (Liu *et al.*, 1997).

Productivity was also found to increase with Al/Zr ratio up to 200 with the maximum productivity of 3,000 kgPE/(mol-Zr*atm*h), as shown in Table 4.4.

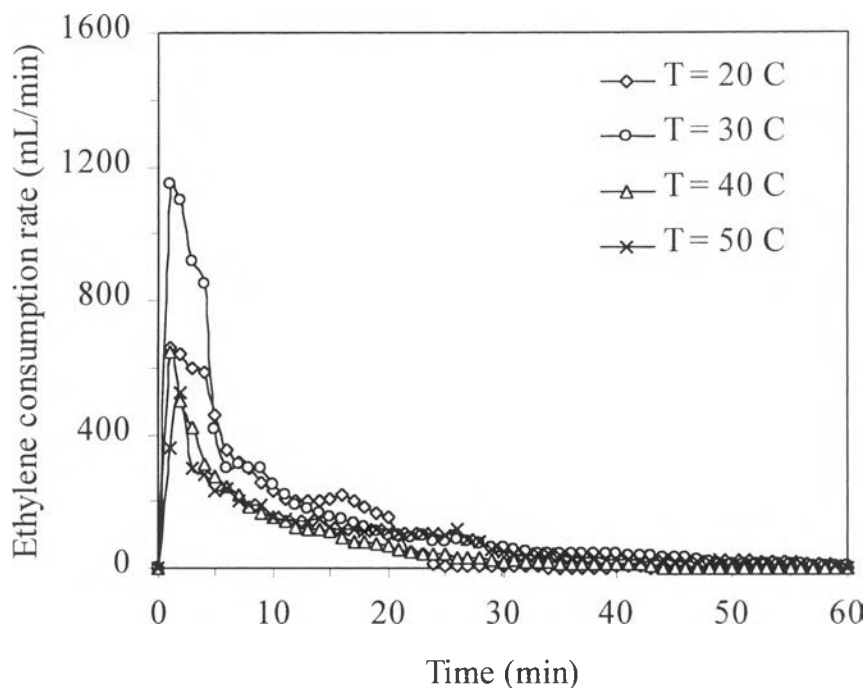**Table 4.4** Productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system at varying Al/Zr ratios.

($[Zr]$ = 5 μmol, B/Zr = 1, P_{ET} = 0.5 bar, T = 30°C, total volume = 150 ml in toluene, reaction time = 1 h)

[Al] (μmol)	Al/Zr	Yield (g)	Productivity (kgPE/mol-Zr*atm*h)
500	100	0	0
800	160	4.10	1640
1000	200	7.50	3000
1100	220	5.30	2120
1200	240	4.50	1800
1300	260	2.80	1120
1500	300	0	0

4.1.4 Effect of Polymerization Temperature on Ethylene Consumption Rate

The dependence of ethylene consumption rate on polymerization temperature is shown in Figure 4.5. The catalyst activity increased dramatically between 20° and 30°C and steadily declined when temperature was above 30°C. The Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system gave maximum activity at 30°C.

These results maybe attributed to the better solubility of polyethylene in toluene at elevated temperature. At low temperatures the active center is encapsulated in high-density polyethylene and the diffusion of the monomer molecule becomes hindered. At higher temperatures the polyethylene chains are dissolved and the diffusion rate of ethylene is significantly improved. The other reason for increased activity would appear to be the increase in both the rates of propagation and deactivation with increase in temperature. At optimum temperature, the catalyst shows relatively high rates of propagation and relatively low rates of deactivation, so a high activity is monitored. Above the optimum temperature, rates of deactivation strongly increases and overcomes the rates of propagation thus low activities will be observed (Eskelinen and Seppala, 1995).

Figure 4.5 Effect of temperature on Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system. ([Zr] = 5 μmol, B/Zr = 1, P_{ET} = 0.5 bar, total volume = 150 ml in toluene, reaction time = 1 h)

### 4.1.5 Effect of Polymerization Temperature on Productivity

Table 4.5 and Figure 4.6 indicated that the maximum productivity was achieved at a lower Al/Zr ratio for higher reaction temperature. Thus it can be seen that at 20°C, the maximum productivity of 2760 kgPE/(mol-Zr*atm*h) was obtained at Al/Zr ratio = 220. Above that temperature, the optimum Al/Zr ratio was constant at the ratio of 200. The maximum productivity of 3000 kgPE/(mol-Zr*atm*h) was observed at 30°C and Al/Zr = 200.

Table 4.5 Effect of polymerization temperature on the productivity of
Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA system.

([Zr] = 5 µmol, B/Zr = 1, P_{ET} = 0.5 bar, total volume = 150 ml in toluene,
reaction time = 1 h)

Al/Zr	Productivity (kg PE / mol-Zr*atm*h)			
	20°C	30°C	40°C	50°C
100	-	-	-	-
160	1100	1640	800	280
200	1840	3000	2400	2080
220	2760	2120	1922	1900
240	1840	1800	1400	1760
260	1200	1120	520	1240
300	380	-	-	-

* Ethylene pressure = 1.0 bar
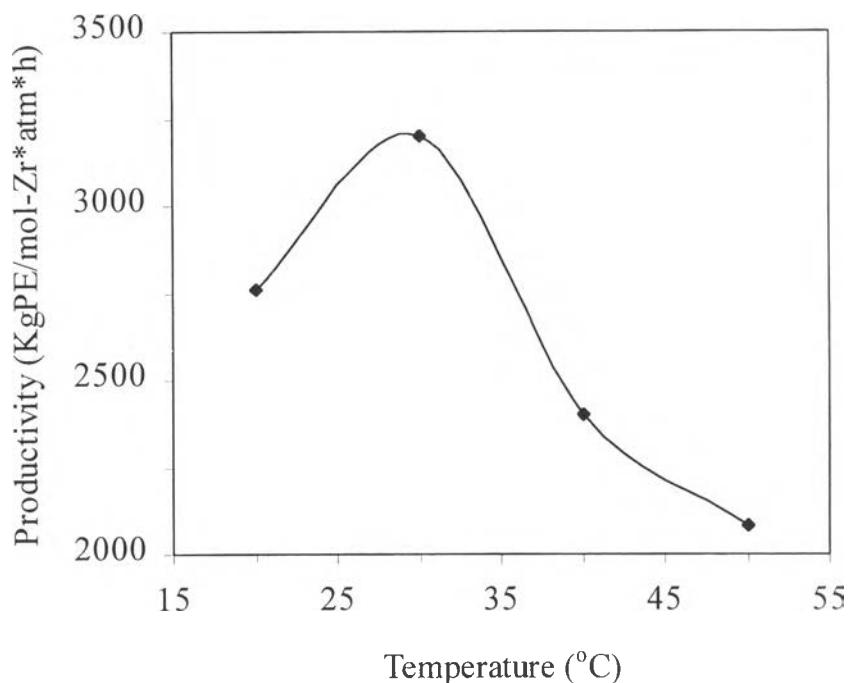
Figure 4.6 Effect of temperature on the productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system.

([Zr] = 5 μmol, B/Zr = 1, P_{ET} = 0.5 bar, total volume = 150 ml in toluene, reaction time = 1 h)

4.1.6 The Role of Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$

To clarify the role of $B(C_6F_5)_3$, ethylene polymerization using free $B(C_6F_5)_3$ was conducted at different Al/Zr ratios from 100-1000. Figure 4.7 shows that Cp_2ZrCl_2-TEA catalyst system was not active in the absence of $B(C_6F_5)_3$ at all Al/Zr ratios studied. The addition of $B(C_6F_5)_3$ after 10 min of polymerization activated Cp_2ZrCl_2-TEA, but the catalytic activity was lower than when $B(C_6F_5)_3$ was present from the beginning of the polymerization.

This results confirm that $B(C_6F_5)_3$ acted as a strong Lewis acid to ionize the neutral metallocene to form cationic species and TEA is not a strong Lewis acid when compared to MAO. The introduction of $B(C_6F_5)_3$ is

necessary for the Cp_2ZrCl_2-TEA catalyst system to initiate ethylene polymerization.
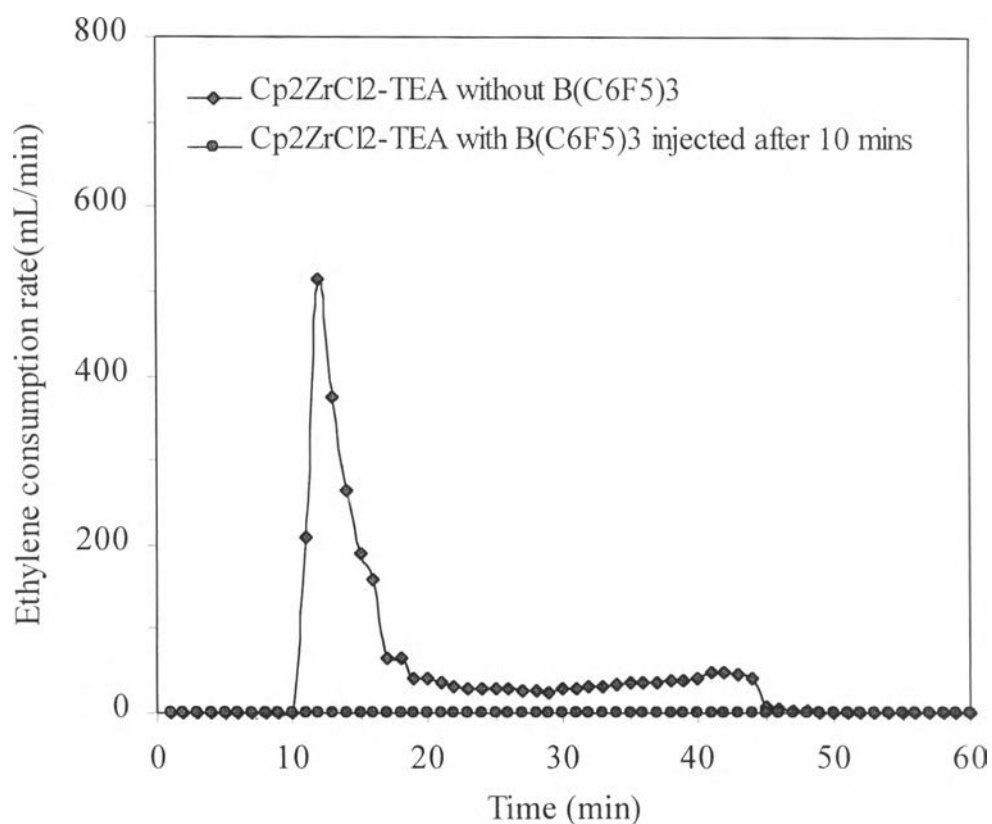
**Figure 4.7** Effect of $B(C_6F_5)_3$ on Cp_2ZrCl_2-TEA catalyst system.

([Zr] = 5 μmol, B/Zr = 1, P_{ET} = 0.5 bar, T = 30°C, Al/Zr = 200, total volume = 150 ml in toluene, reaction time = 1 h)

## 4.2 Characteristics of the Polyethylene Products

4.2.1 Crystallinity from DSC

DSC characterization was operated from 50 to 180°C with a heating rate of 10°C/min. The sample was held at 180°C for a minute and then cooled down at the same rate before it was heated up again. The values of melting point and crystallinity were collected from the first and second scans.

The DSC thermogram of the first scan is shown in Figure 4.8 and Figure 4.9 for the second scan, where the melting point and area under the melting peak were used to calculate the heat of fusion and degree of crystallinity
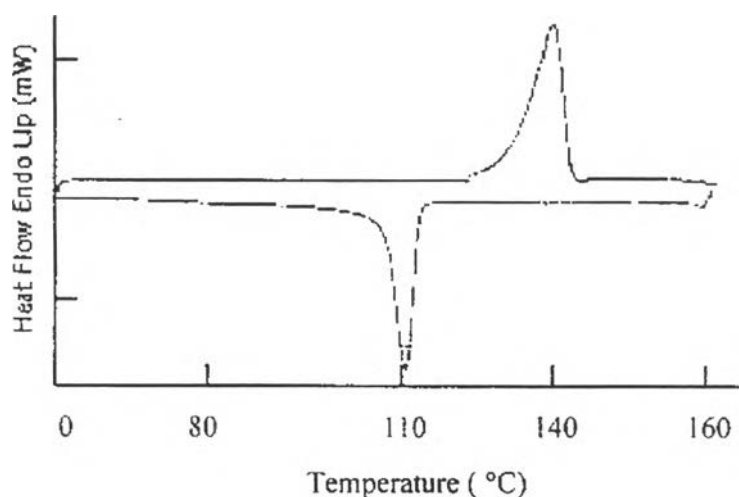
**Figure 4.8** The DSC thermogram of the first scan.
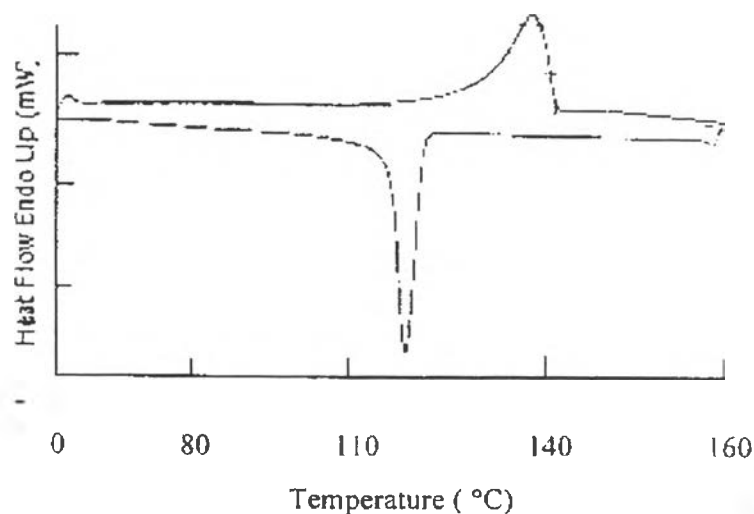
Figure 4.9 The DSC thermogram of the second scan.

The melting point and crystallinity from the first scan were higher than the second scan indicating that the original sample had a more order polymer morphology than after recrystallization. The experimental conditions that gave the highest productivity were also found to produce polymer with the highest crystallinity. The crystallinity was also found to decrease at the reaction temperature above 30°C.

4.2.2 Crystallinity from XRD

The XRD pattern used to calculate the degree of crystallinity of polyethylene product from Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst systems is shown in Figure 4.10.
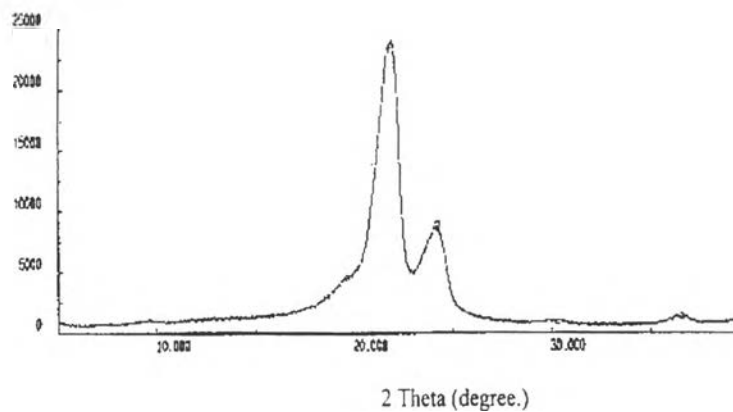
Figure 4.10 The XRD pattern of the polyethylene product.

The degree of crystallinity obtained from XRD is shown in Table 4.6, it can be seen that the values are slightly lower than those obtained from DSC but the trend is still the same.

Table 4.6 Polyethylene properties at different reaction temperatures and Al/Zr ratios.

([Zr] = 5 μmol, B/Zr = 1, P_{ET} = 0.5 bar, total volume = 150 ml in toluene, reaction time = 1 h)

Al/Zr ratio	Ethylene						
	Prod.[#]	T_c	$T_m^{[1]}$	$T_m^{[2]}$	$X_c^{[1]}$	$X_c^{[2]}$	%C
T = 20°C							
220[*]	2760	112	137	135	76.01	49.88	61.68
T = 30°C							
160	1640	112	138	136	75.43	46.38	62.50
200	3200	112	137	136	76.17	54.59	62.62
220	2120	112	137	135	76.01	49.88	63.94
240	1800	112	137	135	74.89	46.07	60.29
260	1120	112	135	135	67.73	44.07	61.39
T = 40°C							
200	2400	112	137	136	74.55	46.35	54.40
T = 50°C							
200	2080	112	135	134	72.17	45.56	53.29

[*] Ethylene pressure = 1 bar

(#) = Productivity (kgPE/mol-Zr*atm*h)

[1] = T_m and X_c from the first scan

[2] = T_m and X_c from the second scan

%C = degree of crystallinity from XRD

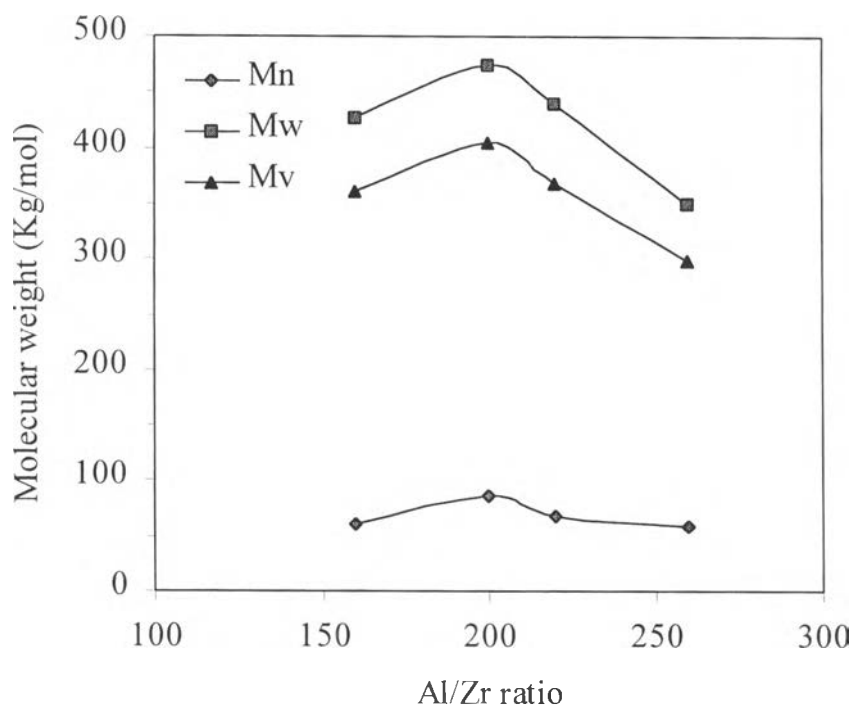### 4.2.3 Mw and MWD by Gel Permeation Chromatography (GPC)

4.2.3.1 Effect of Al/Zr Ratio on Molecular Weight and Molecular Weight Distribution

The molecular weight of the polyethylene products increased from Al/Zr ratio 160 to 200 and slowly decreased with increasing Al/Zr ratio from 220 to 260 and the molecular weight distribution (MWD) of the obtained polymers ranged from 5.25-6.99 as tabulated in Table 4.7. Figure 4.11 shows the curves of M_n, M_v and M_w. It can be seen that the molecular weights are sensitive to Al/Zr ratio. As Al/Zr ratio increased, the molecular weight decreased due to the action of TEA as a chain transfer agent.

Table 4.7 Molecular weight and molecular weight distribution (MWD) of polyethylene products at varying Al/Zr ratios.

([Zr] = 5 µmol, B/Zr = 1, P_{ET} = 0.5 bar, T = 30°C, total volume = 150 ml in toluene, reaction time = 1 h)

Al/Zr ratio	$\overline{M}_n$ (kg/mol)	$\overline{M}_v$ (kg/mol)	$\overline{M}_w$ (kg/mol)	MWD
160	61.07	360.29	426.58	6.99
200	85.50	403.94	473.50	5.54
220	67.75	368.24	439.33	6.56
260	58.34	298.79	350.72	6.01

Figure 4.11 Effect of Al/Zr ratio on the Mn, Mw and Mv of the polyethylene product.

([Zr] = 5 µmol, B/Zr = 1, P_{ET} = 0.5 bar, T = 30°C, total volume = 150 ml in toluene, reaction time = 1 h)

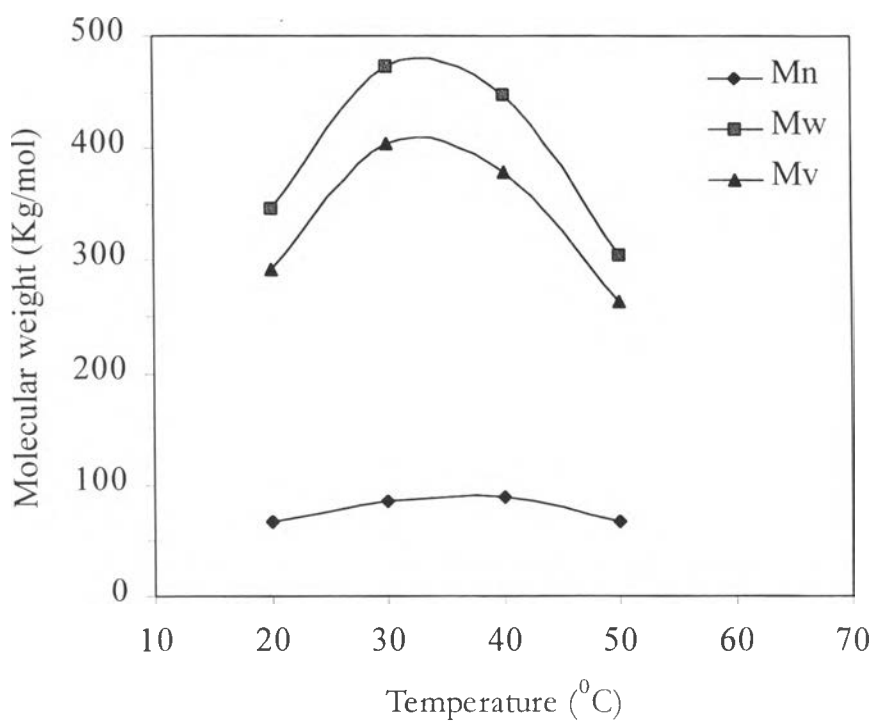*4.3.2.2 Effect of Polymerization Temperature on Molecular Weight and Molecular Weight Distribution*

Figure 4.12 shows the curves of M_n, M_v and M_w of the resulting polyethylene from different polymerization temperatures ranging from 20°, 30°, 40° and 50°C. The molecular weight of polyethylene at polymerization temperature of 30°C shows the highest molecular weight. At about 30°C the rate of the chain transfer reactions began to accelerate and the molecular weights began to decrease. The molecular weight distributions (MWD) of the obtained polyethylene ranged from 4.50-5.53, as shown in Table 4.8.

Table 4.8 Effect of polymerization temperature on molecular weight and molecular weight distribution (MWD) of polyethylene product. ([Zr] = 5 μmol, B/Zr = 1, P_{ET} = 0.5 bar, Al/Zr = 200 total volume = 150 ml in toluene, reaction time = 1 h)

| Temperature (°C)	$\overline{M}_n$ (kg/mol)	$\overline{M}_v$ (kg/mol)	$\overline{M}_w$ (kg/mol)	MWD
20*	67.73	292.50	346.58	5.12
30	85.50	403.94	473.50	5.53
40	88.32	378.64	447.92	5.07
50	67.67	263.43	303.66	4.50

*Al/Zr = 220

Figure 4.12 Effect of polymerization temperature on the Mn, Mw and Mv of the polyethylene product.

4.2.4 Comparison of the FT-IR Spectra of LDPE, HDPE and Metallocene Polyethylene

Figure 4.13 shows IR spectra in the range 1000-1800 cm^{-1} which cover the absorption due to the methyl branches at 1378 cm^{-1}. Compared to LDPE, the polyethylene produced by metallocene catalyst and HDPE shows no peak at 1378 cm^{-1}, while LDPE shows distinct C-H symmetric bending of -CH$_3$. This indicates that HDPE and metallocene polyethylene are relatively linear with only small amount of branches.
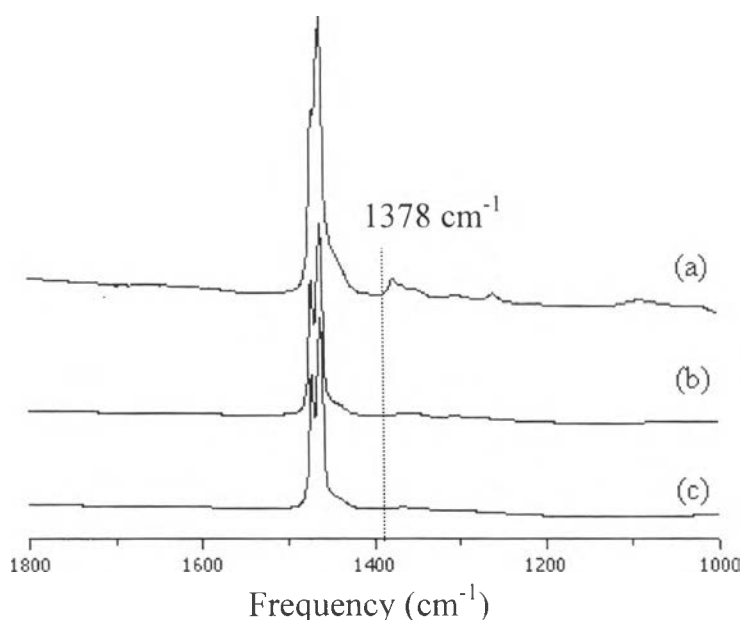

Figure 4.13 FT-IR spectra of (a) commercial LDPE (b) commercial HDPE and (c) metallocene polyethylene.

4.2.5 Morphology Study by SEM

Scanning electron microscopy study of polymer particles obtained at any Al/Zr ratio shows that the polymer is formed in spherical shape with approximately 700 μm in diameter. In ethylene polymerization by using this Cp$_2$ZrCl$_2$-B(C$_6$F$_5$)$_3$-TEA catalyst system, metallocene catalyst will generate

the homogeneously disperse active sites throughout the solution. When polymerization occurs, each polymer chain will grow individually thus the spherical particles are obtained. (Figure 4.14)
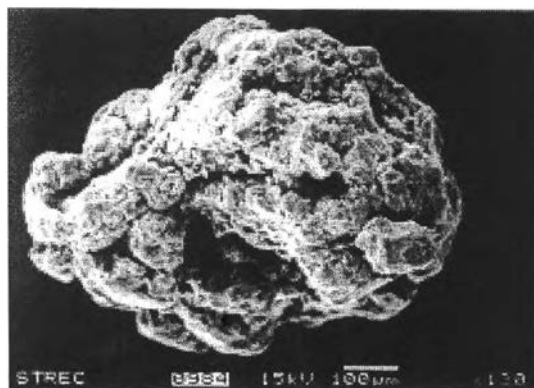
(a)
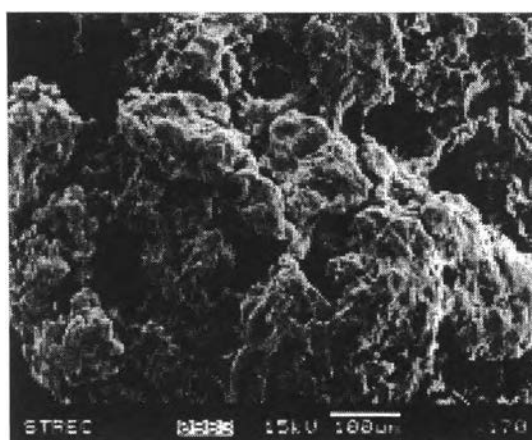
(b)

Figure 4.14 SEM pictures of metallocene polyethylene particle (a) x 130 (b) x 170.