CHAPTER IV

RESULTS AND DISCUSSION

In this work the activity and productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$ catalyst system with different aluminum compounds were studied. The resulting polyethylene products were also characterized by DSC, WAXD, and SEM.

4.1 Metallocene Catalyst System with TEA

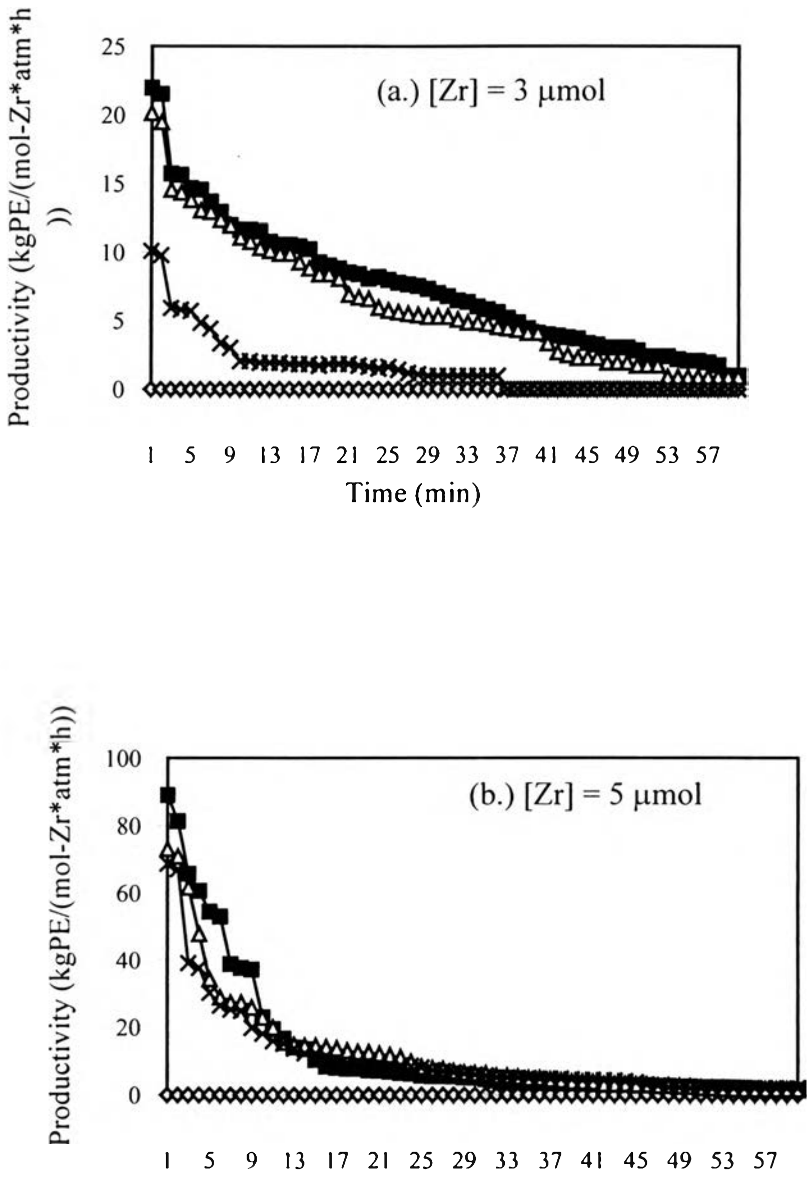
4.1.1 Effect of Al/Zr ratio

Polymerization of ethylene was carried out at varying Al/Zr ratio from 30, 50, 80 to 100 using 4 different Zr concentrations of 3, 5, 8 and 10 μ mol respectively. The activity of the reactions is shown in Figure 4.1.

In all cases, it can be seen that the activity was high in the beginning but decreased rapidly down to almost zero within 30 minutes. The results show that the metallocene catalyst system with TEA has relatively short life.

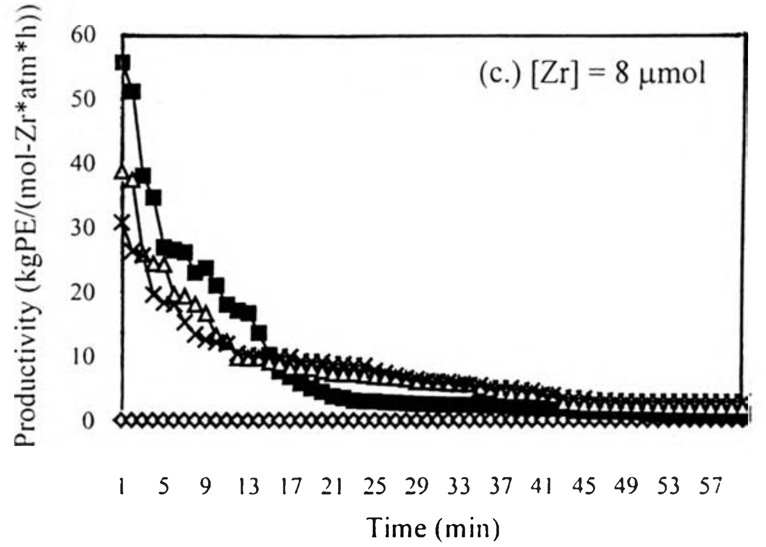
At Al/Zr of 30, no activity was observed in all cases. The maximum was observed at Al/Zr = 50, but the activity started to decline as Al/Zr was increased further until it reached zero at Al/Zr ratio above 100. The results show that for system with TEA, the optimum Al/Zr ratio is in the range 50-100.

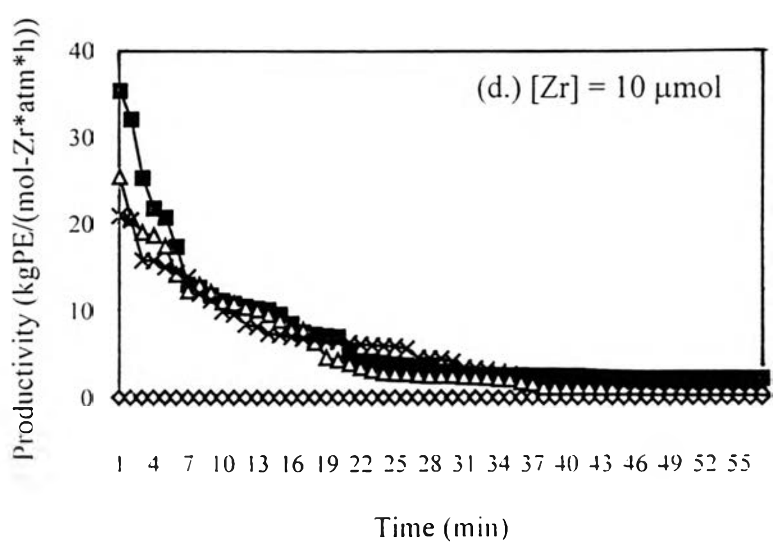
When comparing the activity at different [Zr], it can be seen that maximum activity of 90 kgPE/(mol-Zr*atm) was obtained with [Zr] = 5μmol at Al/Zr = 50. The results shows that an optimum Zr concentration is required for maximum activity.



♦Al/Zr = 30 □Al/Zr = 50 Δ Al/Zr = 80 × Al/Zr = 100

Figure 4.1 The activity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA system at varying Al/Zr ratio.





♦ Al/Zr = 30 □Al/Zr = 50 Δ Al/Zr = 80 × Al/Zr = 100

Figure 4.1 (contid)The activity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA system at varying Al/Zr ratio

Table 4.1 shows the productivity of the metallocene catalyst system with TEA at different [Zr] and Al/Zr ratios. Similar trends were observed as in the case of activity. Maximum productivity of 868 kgPE/mol-Zr*atm*h was obtained at [Zr] = 5 μmol and a Al/Zr ratio = 50. The results shows that optimum condition for the production of polyethylene with Cp_2ZrCl_2-B $(C_6F_5)_3$ catalyst system with TEA at 20 °C was with [Zr] 5 μmol and an Al/Zr ratio 50.

4.2 Metallocene Catalyst System with TBA

4. 2. 1 Effect of Al/Zr ratio on the activity and productivity

Figure 4.2 shows the activity of the system with TBA. It can be seen that the maximum activity increased from 14 to 18 kgPE/(mol-Zr*h) as the Al/Zr increased from 600 to 1400 before it started to decrease rapidly on further increase in TBA. Productivity was also found to increase with Al/Zr ratio up to 1400 with a maximum productivity of 1220 kgPE/(mol-Zr*atm*h) as shown in Table 4.2.

At high Al/Zr ratio the surplus [Al] from TBA may lead to the formation of species like $[Cp_2ZrR^+][^-Cl_2AlR_2]$ which may prevent further reaction between the alkylated zirconocene and $B(C_6F_5)_3$, as the species $[Cp_2ZrR^+][^-ClB(C_6F_5)_3]$ 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 TBA exceeds a certain amount.

Table 4.1 Productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA system at varying [Zr] and Al/Zr ratios.

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

[Zr] μmol	**[Al] (μmol)**	**Al/Zr**	**yield (g)**	**Productivity (kgPE/molZr*atm*h)**
3	90	30	0	0
3	150	50	2.69	448
3	240	80	1.29	216
3	300	100	0.03	5
5	150	30	0	o
5	250	50	8.68	868
5	400	80	7.87	787
5	500	100	7.54	754
8	240	30	0	0
8	400	50	9.73	608
8	640	80	8.99	562
8	800	100	8.96	560
10	300	30	0	0
10	500	50	12.15	608
10	800	80	10.98	549
10	1000	100	10.44	522

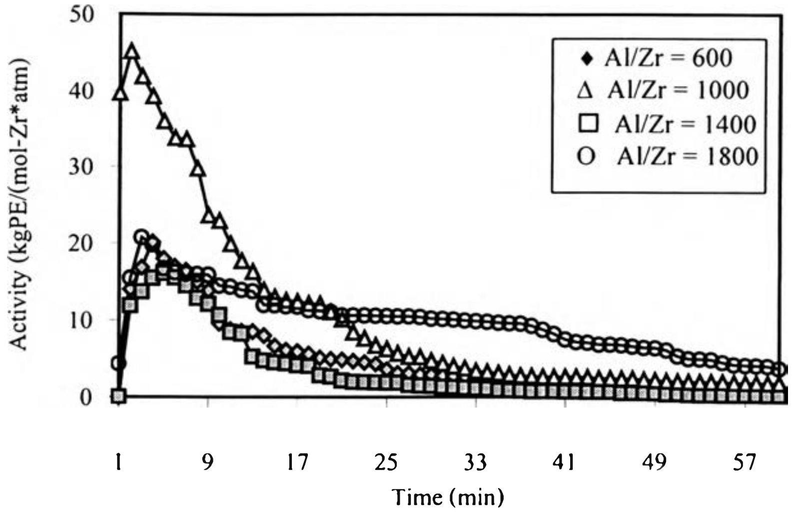


Figure 4.2 The activity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TBA system using [Zr] = 10 μmol at varying Al/Zr ratio.

Table 4.2 Productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TBA system at varying Al/Zr ratio.

[Zr] = 10 μmol, B/Zr = 1, P_{ET} = 1 bar, T = 20 °C, total volume = 150 ml in toluene, reaction time = 1 h.

[Al] (μmol)	Al/Zr ratio	yield (g)	Productivity (kgPE/(mol-Zr*atm*h)
6000	600	6.27	627
10000	1000	11.09	1109
14000	1400	12.20	1220
18000	1800	5.53	553

4. 2. 2 Effect of the temperature on the activity

Temperature influences the polymerization activity. It is known that there is an optimum temperature range for maximum activity, below or above which catalyst activity decreases as shown in Figure 4.3. The Cp_2ZrCl_2-$B(C_6F_5)_3$-TBA system gave maximum activity at 30 °C.

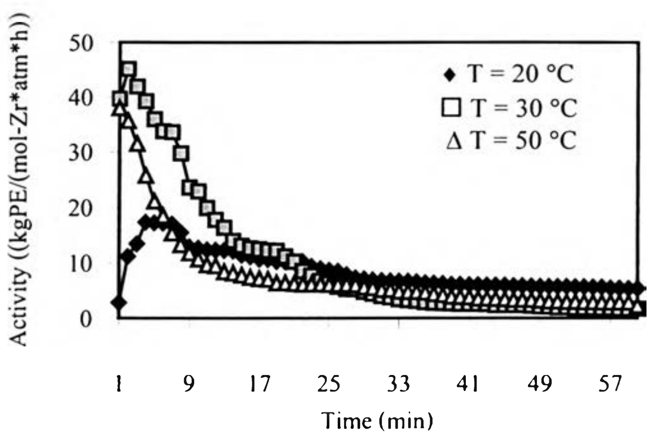


Figure 4.3 Effect of temperature on Cp_2ZrCl_2-$B(C_6F_5)_3$-TBA catalyst system using [Zr] = 10 μmol and Al/Zr ratio = 1000.

These results may be attributed to the increase in the rates of both propagation and deactivation with increase in temperature. At optimum temperature, the catalyst show relatively high rates of propagation and relatively low rates of deactivation, so a high activity is observed. Above the optimum temperature, rates of propagation as well as deactivation increase and below the optimum temperature rates of propagation as well as deactivation decrease and as a result, low activities will be observed in both cases. In addition, at low temperature, the chain transfer rate is also low.

4. 2. 3 Effect of temperature on the productivity

The results in Figure 4.3 shows that maximum productivity was achieved at a higher Al/Zr ratio for lower reaction temperature. Thus it can be seen that at 20 °C, the maximum productivity of 1220 kgPE/(mol-Zr*atm*h) was obtained at Al/Zr ratio = 1400. At 30 °C, maximum productivity of 1375 kgPE/(mol-Zr*atm*h) was obtained at Al/Zr ratio = 800 and at 50 °C, maximum productivity of 1085 kgPE/(mol-Zr*atm*h) was obtained at Al/Zr ratio = 600. It can therefore be concluded that, at high temperature, a lower Al/Zr ratio can be used. It can also be observed that maximum productivity was obtained at 30 °C at Al/Zr = 800.

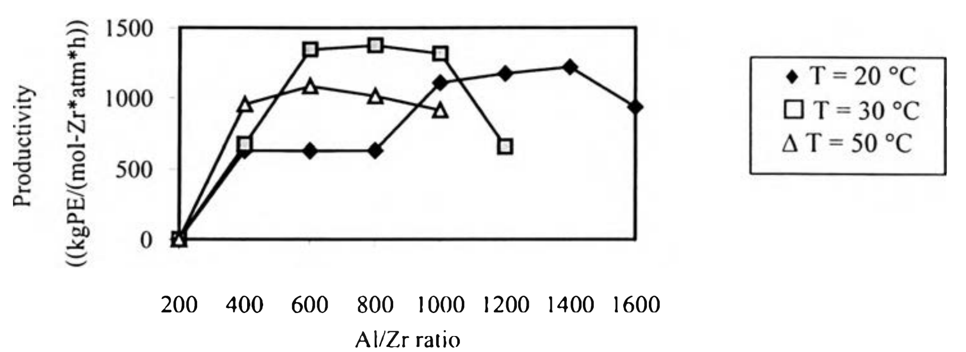


Figure 4.4 The effect of temperature on the productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TBA system at varying Al/Zr ratio.

4.3 Comparison of the TEA and TBA Catalyst Systems

Figure 4.5 compares the activity of TEA system at Al/Zr = 50 and TBA system at Al/Zr = 550 which are the conditions at which both achieve a maximum activity. It can be seen that the activity in the early stage of the reaction of the TEA system was much higher than TBA system. In case of TBA, the activity gradually increased to a maximum in about 5 minutes before it started to decline.

TBA catalyst system also had a longer life time than TEA system. This may be because TBA plays a more important role in stabilizing the active centers and thus extending the catalyst lifetime, probably by suppressing the side reactions. In the case of TEA, it is a stronger alkylating agent, therefore it has higher activity and can generate faster chain transfer reactions.

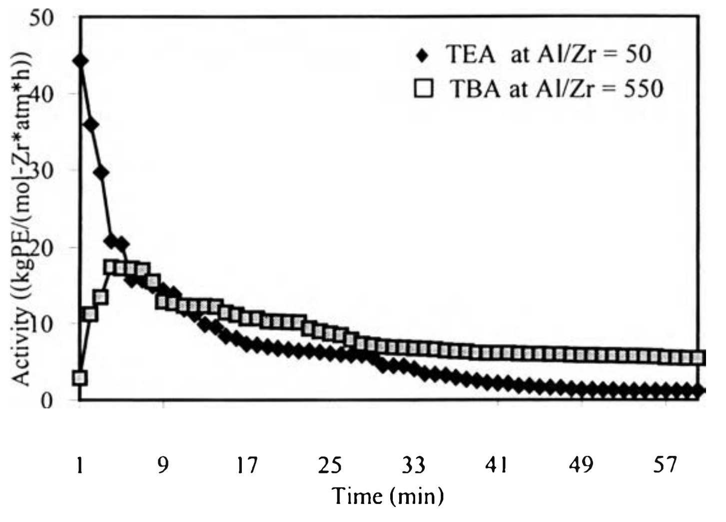


Figure 4.5 Comparison of the activity in TEA and TBA catalyst systems using [Zr] = 10 μmol at 20 °C.

Table 4.3 compares the productivity of TEA system with TBA system. It can be seen that TEA system worked at a lower Al/Zr ratio range of 50-100 while TBA system worked at a much higher range of 250 to over 600. TBA system also gave a higher maximum productivity of 1220 kgPE/(mol-Zr*atm*h) compared with the value of 868 kgPE/(mol-Zr*atm*h) for TEA system at the same temperature.

Table 4.3 Effect of Al/Zr ratio on productivity using TEA and TBA.

[Zr] = 10 μmol, B/Zr = 1, P_{ET} = 2 bar, T = 20 °C, reaction time = 1 hr, total volume = 150 ml in toluene.

Al/Zr ratio	**Productivity ((kgPE/mol-Zr*atm*h))**	
30	Trace	-
50	608	-
80	549	-
100	522	-
200	0	0
250	-	210
350	-	505
450	-	650
550	-	876
600	-	738

4.4 Characterization of the Polyethylene Products

4. 4. 1 Crystallinity from DSC

DSC characterization was operated from 50 to 160 °C with heating rate of 10 °C/min. The samples were hold at 160 °C for a minute and then cooled down at the same rate before they were heated up again. The values of melting point and crystallinity were collected from the second scan to eliminate the polymerization history.

The DSC thermogram of the first scan is shown in Figure 4.6 and Figure 4.7 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.

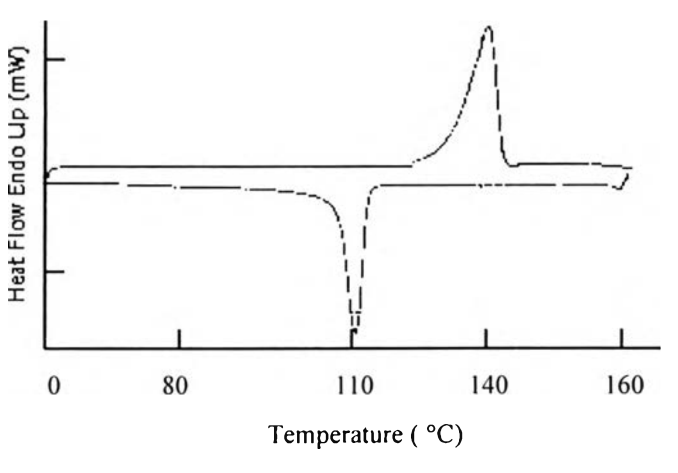


Figure 4.6 The DSC thermogram of the first scan.

The melting point of the polyethylene product from the DSC thermogram of the first scan gave the value of 141 °C whereas in the second scan the value was 136 °C. The same results were obtained for both TEA and TBA catalyst systems as shown in Table 4.4.

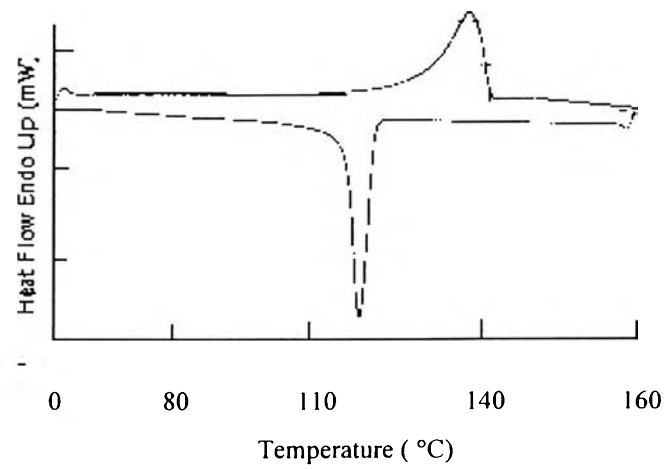


Figure 4.7 The DSC thermogram of the second scan.

Table 4.4 The melting temperature and degree of crystallinity of first and second scan of TEA and TBA catalyst systems by DSC.

[Zr] = 10 μmol, P_{ET} = 2 bar, T = 20 °C, reaction time = 1 h.

Al/Zr ratio	Ethylene					
	Prod[#]	T_c	$T_m^{[1]}$	$T_m^{[2]}$	$X_c^{[1]}$	$X_c^{[2]}$
TEA						
50	608	113	141	136	68.04	46.17
80	549	113	140	136	69.99	47.26
100	522	113	140	135	67.68	46.53
TBA						
300	609	114	143	138	64.46	48.28
400	528	114	142	136	67.64	45.96
550	876	114	141	136	66.62	44.39
600	738	114	141	136	71.43	49.11

(#) = 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

The melting point and crystallinity from the first scan were higher than the second scan indicating that the original sample had a better polymer morphology than after recrystallization.

4. 4. 2 Crystallinity from XRD

The XRD patterns used to calculate the degree of crystallinity by polyethylene produced from TEA and TBA catalyst systems are shown in Figure 4.8 and Figure 4.9.

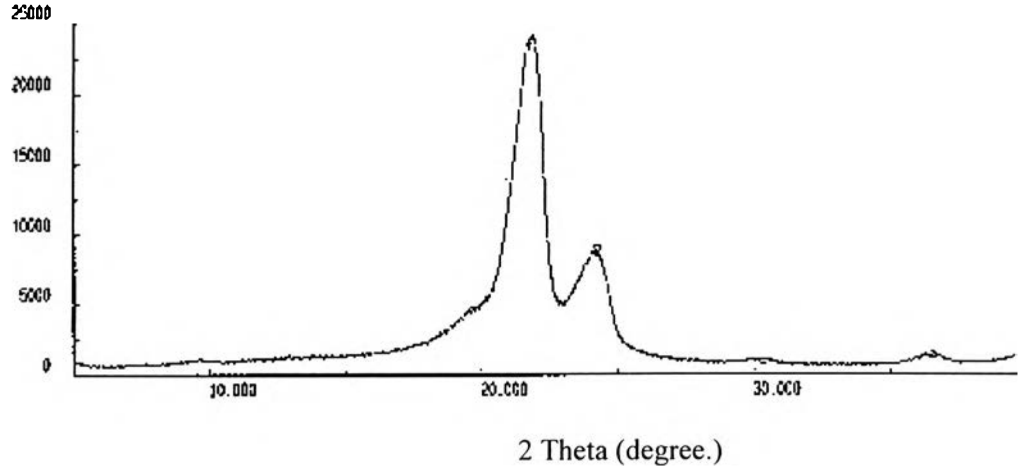


Figure 4.8 The XRD pattern of TEA system.

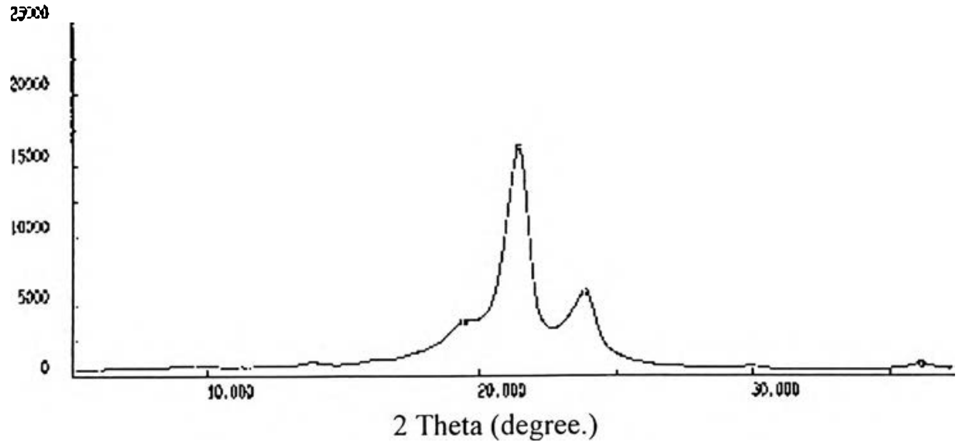


Figure 4.9 The XRD pattern of TBA catalyst system.

The degree of crystallinity obtained from XRD is shown in Table 4.5 it and can be seen that the crystallinity of polyethylene did not vary much with change in Al/Zr ratio.

Table 4.5 The degree of crystallinity from XRD

[Zr] =10 μmol, P_{ET} = 2 bar, T = 20 °C, reaction time = 1 h.

Al/Zr ratio	**Polyethylene %C**
TEA	
50	59.24
80	54.27
100	59.99
TBA	
300	54.52
400	56.31
550	58.36
600	54.80

4. 4. 3 Properties of polyethylene obtained at different temperatures

The melting point of polyethylene from 2 different reaction temperatures did not differ much but the crystallinity obtained from XRD at reaction temperation of 50 °C was slightly higher than that at 20 and 30 °C as is shown in Table 4.6.

Table 4.6 Polyethylene properties at different reaction temperatures

[Zr] = 10 μmol, P_{ET} = 1 bar, reaction time = 1 h.

TBA properties	**Al/Zr ratio**			
	400	**600**	**800**	**1000**
T = 20 °C				
Prod.[#]	603	627	629	1109
T_m[1]	142	141	141	142
T_m[2]	136	136	137	137
X_c	46.87	45.22	42.97	42.97
%C	54.52	56.31	57.18	57.18
T = 30 °C				
Prod.[#]	672	1345	1375	1316
T_m[1]	140	141	141	141
T_m[2]	136	136	136	136
X_c	47.73	47.30	49.82	47.39
%C	60.00	58.17	55.55	46.26
T = 50 °C				
Prod.[#]	955	1086	1015	915
T_m[1]	138	136	137	138
T_m[2]	137	134	135	135
X_c	54.06	54.25	52.16	54.75
%C	59.4	51.6	54.7	52.5

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

[1] : first scan

[2] : second scan