ScienceAsia 28 (2002) : **377-383**

Ethylene Polymerization by Cp_2ZrCl_2-$B(C_6F_5)_3$-Tea Catalyst System Using Low Al/Zr Ratio

Nattaya Punrattanasin[a], Nantaya Yanumet[a, *], Pramote Chaiyavech[b] and Erdogan Gulari[c]

[a] The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, THAILAND.
[b] National Petrochemical Public Company Limited, Bangkok, THAILAND.
[c] Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136, USA.
Corresponding author, E-mail: ynantaya@chula.ac.th

Received 18 Jan 2002
Accepted 21 May 2002

ABSTRACT Ethylene polymerization by Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system using low Al/Zr ratio has been studied with varying ethylene pressure, catalyst concentration, Al/Zr ratio, and reaction temperature. The study showed that there was an optimum condition for each variable at which maximum productivity was obtained. It was proposed that there were two competing reactions, the catalyst activation and deactivation, taking place simultaneously. The maximum productivity of 3133 kgPE/mole-Zr.atm.h was obtained using 3 mmol each of zirconocene and borane, and a Al/Zr ratio of 300 at 30 °C. The crystallinity of the product was obtained using DSC and its morphology was studied by SEM.

KEYWORDS: Ethylene polymerization, zirconocene, triethylaluminum, borane.

INTRODUCTION

Metallocenes are a class of compounds in which cyclopentadienyl or substituted cyclopentadienyl ligands are p-bonded to a transition metal (Ti, Zr, or Hf) from group 4. The possibility of polymerizing ethylene by using a metallocene catalyst was first shown with bis-cyclopentadienyl titanium dichloride and dialkyl aluminum chloride, but the activity was low.[1] Later, Kaminsky and co-workers obtained an extremely high activity by substituting Zr for Ti and using methylaluminoxane (MAO) as co-catalyst.[2] Since then there has been a great interest in olefin polymerization using metallocene/MAO catalyst system. Several reviews on the subject have been published in recent years.[2-6] It is well established that the 14-e^- cationic metallocene, $[Cp_2MR]^+$, is the active species.[5, 7-8] The most widely accepted model of polymerization mechanism is that proposed by Cosee-Arlman.[9] In this mechanism, the double bond of olefin first forms a complex with the positive charge at the metal center. The process is followed by insertion of the monomer between the metal atom and the growing polymer chain. Termination of the polymer chain occurs through a chain transfer involving b-H and b-Me elimination. Chain transfer to aluminum, monomer, and hydrogen may also occur.[5, 7] However in order to achieve a high catalyst activity, extremely high aluminum to metal ratios of between 1000-15000:1 is required. Such ratios are unacceptable in terms of cost and the amount of residues in the resulting polymer. This has led to many studies to reduce or replace MAO.[10-13]

One alternative is to use a boron-based co-catalyst. The role of boron-based co-catalyst is to promote the formation of complex structure between cationic active center and boron via the methyl bridge. The methyl ligand is only partly abstracted from catalyst leading to a coordinated complex with a cation-like catalytic species.[14-15] Boron-based co-catalysts are required only in a stoichiometric amount to achieve maximum catalytic activity. However, they cannot scavenge impurities present in the system. Therefore, to overcome this problem, trialkylaluminum compounds are usually introduced to accomplish the task.

Liu et al[11] investigated ethylene polymerization by zirconocene-$B(C_6F_5)_3$ catalyst with various aluminum compounds. They found that the catalytic activity depended on zirconocene used as well as the type of aluminum compound. Activity and rate-time profiles of ethylene polymerization with zirconocene combined with three different trialkyl-aluminums and two different boranes were studied by Naga et al.[15] It was found that both the types of trialkylaluminum and borane affected the induction time and activity of ethylene polymerization.

Although previous studies have been carried out on the effects of trialkylaluminum and borane compound on the activity of olefin polymerization with metallocene catalysts, there have been no reports on polymerization of ethylene with Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA system which yields high activity with low Al/Zr ratio less than 500.

This paper reports the results of ethylene polymerization by Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA system at low Al/Zr ratio below 500. The use of low Al/Zr ratio is desirable as, apart from the cost factor, it helps to reduce the amount of aluminum left in the final product. We examined productivity at low Al/Zr ratio and the properties of the products obtained.

EXPERIMENTAL

Materials

Ethylene, polymerization-grade, was donated by National Petrochemical Public Company (NPC) and nitrogen was commercially obtained from Thai Industrial Gas. Both were used after passing through Matheson gas purifiers which decreased the oxygen and water vapor impurities to below 20 ppb level. Toluene was commercially obtained from JT Baker and was used after distilling over metallic sodium using benzophenone as indicator. Bis(cyclopentadienyl)zircononium dichloride (Cp_2ZrCl_2) and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) were purchased from Fluka and Albemarle, respectively, and used without further purification. Triethylaluminum (TEA) was donated from Thai Polyethylene Co Ltd and was used as received.

Polymerization

Polymerization of ethylene was carried out with stirring in a 300 mL Parr reactor. After evacuating the reactor, it was purged with nitrogen several times. Toluene solutions of TEA and the Cp_2ZrCl_2 catalyst were then injected respectively, and the solution was then saturated with ethylene pressure at the desired pressure. In the present work, three ethylene pressures, 0.5, 1.0, and 2.0 bar, were used. Polymerization was started by introducing the co-catalyst solution of $B(C_6F_5)_3$ in toluene. Consumption of ethylene in mL/min was read off the mass flowmeter inserted in the ethylene line at one minute interval up to 1 h. After 1 h of polymerization, polymerization was terminated by adding dilute hydrochloric acid solution in methanol. Polyethylene obtained was washed several times with methanol and dried at 40 °C for 24 h and weighed. The weight obtained was taken as the yield of the reaction. The productivity of the reaction was calculated by the following equation.

$$\text{Productivity (KgPE/mol-Zr.atm.h)} = \frac{[\text{Polyethylene product (kg)}]}{[\text{Amount of catalyst (mol-Zr)}][\text{Ethylene pressure (atm)}][\text{Time (h)}]}$$

Characterization

The number average and weight average molecular weight (Mn, Mw), and molecular weight distribution (MWD) of the resulting polymer were measured at 140 °C by means of a high-temperature gel-permeation chromatography (GPC, Waters 150CV) using *o*-dichlorobenzene as a solvent and calibrated with standard polystyrene sample. Differential scanning calorimetry (DSC) measurements were made with a Perkin-Elmer DSC 7 system. Each sample was heated from 50 to 180 °C at a heating rate of 20 °C/min, cooled down to 50 °C and reheated at the same rate. The values of melting point (T_m) of the first scan and the second scan were obtained. Crystallinity of the polymer was calculated from the equation.

$$X\ (\%) = (\Delta H_f / \Delta H_f^{\,*}) \times 100$$

Where ΔH_f is the heat of fusion of the sample as determined from DSC curves and ΔH_f^{*} is the heat of fusion of perfectly crystalline polyethylene, taken as 286 J/g.[11]

RESULTS AND DISCUSSION

Effects of Important Reaction Parameters on Productivity

i) *The amount of zirconocene*

In this experiment the amount of zirconocene was varied from 5 to 10 µmol. A low Al/Zr ratio of 100 was used and the reaction temperature was 20 °C. The results in Table 1 show that, as the amount of zirconocene increased, the yield increased slightly from 6.03 to 7.66 g, while the productivity was reduced by almost half from 603 to 383 kgPE/mol-Zr atm h. The decrease in the activity with increase in catalyst concentration has been found by other workers in propylene polymerization with zirconocene.[16] The decrease was attributed to the dimerization of the active centers leading to a lower activity. Since the productivity obtained in this experiment is generally low, in the next experiment, the Al/Zr ratio was increased to 200 and a reaction temperature of 30 °C was used for better control of the temperature.

ii) Ethylene pressure

Table 2 shows the yields and productivity at three different ethylene pressures of 0.5, 1.0 and 2.0 bar. The reaction was carried out using 5 μmol of zirconocene, a B/Zr ratio of 1, an Al/Zr ratio of 200, the temperature was 30 °C, and the reaction time was 1 h. The yield was found to increase from 7.50 g to 12.92 g as the pressure increased from 0.5 to 2.0 bar. However, at the same time, the productivity decreased from 3000 to 1292 kgPE/mol-Zr atm h. The results show that the yield did not increase in the same proportion as the increase in ethylene pressure. It was possible that, as reaction proceeded, polymer precipitates formed in the solution may have obstructed the diffusion of the monomer to the active sites. Hence, productivity was decreased at high monomer concentration, at which a large amount of polymer was formed.

iii) Al/Zr ratio

Table 3 shows the change in the productivity with Al/Zr ratios at two different amounts of zirconocene of 3 and 5 μmol. In both cases, the catalyst was found to be active only over a narrow range of Al/Zr ratio of 230-400 and 160-260, at 3 and 5 μmol zirconocene, respectively. At low Al/Zr ratio, the amount of aluminum was not sufficient to scavenge the impurities and alkylate the zirconocene, hence, no activity was observed. At high Al/Zr ratio, the excess amount of aluminum may have acted as a deactivating agent leading to zero activity. Both systems gave almost the same maximum productivity of 3133 and 3000 kgPE/mol-Zr atm h at 3 and 5 μmol zirconocene, respectively. The results also indicated that there was a different optimum range of Al/Zr ratio for different amounts of zirconocene. The optimum range moved to a lower value at higher

Table 1. Yield and productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system at varying amounts of zirconocene. (B/Zr = 1, P_{ET} = 2 bar, Al/Zr =100, T = 20 °C, total volume = 150 ml in toluene, reaction time = 1 h).

(Zr) μmol	Yield (g)	Productivity (kgPE/mol-Zr atm h)
5	6.03	603
8	7.46	466
10	7.66	383

Table 2. Yield and productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system at varying ethylene pressure. ((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)
0.5	7.50	3000
1.0	9.50	1900
2.0	12.92	1292

Table 3. Yield and productivity of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system at varying Al/Zr ratio. (B/Zr = 1, T = 30 °C, total volume = 150 ml in toluene, reaction time = 1 h)

Al/Zr Ratio	(Zr) = 3 μmol (P_{ET}= 1 bar)		(Zr) = 5 μmol (P_{ET}= 0.5 bar)	
	Yield (g)	Productivity (kgPE/mol-Zr atm h)	Yield (g)	Productivity (kgPE/molZr atm h)
100	0	0	0	0
160	-	-	4.10	1640
200	0	0	7.50	3000
220	-	-	5.30	2120
240	5.1*	1700*	4.50	1800
260	6.9	2300	2.80	1120
300	9.4	3133	0	0
400	5.9	1966	-	-
500	0	0	-	-

* Al/Zr ratio = 230

zirconocene concentration. Kim and Choi[17] studied the effect of AlR_3 on propylene polymerization with zirconocene and borane catalyst. They also found the catalyst to be active within a narrow range of Al/Zr ratio.

iv) <u>Reaction temperature</u>

Table 4 shows the productivity of the catalyst at varying reaction temperature and Al/Zr ratios. The productivity generally decreased with an increase in temperature. The results were taken to indicate that there were two competing reactions in the system: the activation and deactivation processes. At high temperature, the deactivation process proceeded faster and hence the reduction in productivity. The catalyst was shown to be active over only a narrow range of Al/Zr ratio. In this case the maximum productivity was obtained over an Al/Zr ratio of 200-220 at all temperatures. There was also an optimum temperature for a specific Al/Zr ratio.

The present study showed that Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system can be used to produce polyethylene with high productivity. However, the system is active only over a very narrow range of Al/Zr ratio. This explains why other workers[11, 15] failed to obtain polymer product from the system. With such a high productivity, this catalyst system has the potential of becoming commercial viable as zirconocene dichloride is the cheapest of all metallocenes and the high productivity can be obtained at room temperature (20-30 °C).

Reaction Profiles

Fig 1-3 show the ethylene consumption rate over a reaction time of 1 h for reactions carried out with varying ethylene pressures, Al/Zr ratios, and reaction temperatures respectively. In all cases the reaction curves were typified by a very fast reaction reaching a maximum within the first few minutes, followed by a rapid decay to almost zero within 20 minutes. Kim and Choi[17] obtained similar rate curves in their polymerization of propylene with metallocene and a range of alkyl aluminum compounds. The rapid decay was taken to indicate that both the formation of active sites and the deactivation of the active sites were very rapid processes. The deactivation was attributed to chain transfer to the alkyl aluminum.

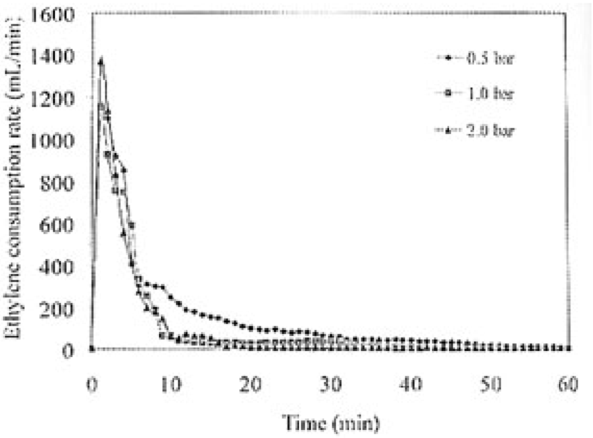

Fig 1. The ethylene consumption rate of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system at varying ethylene pressure. ([Zr] = 5 µmol, Al/Zr = 200, T = 30 °C, total volume = 150 ml in toluene, reaction time = 1 h).

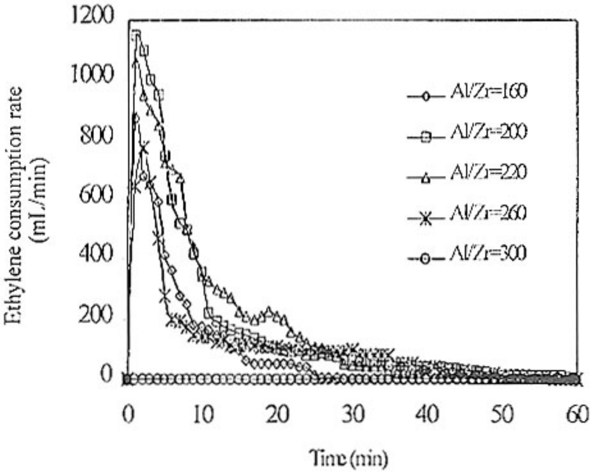

Fig 2. Ethylene consumption rate of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system at varying Al/Zr ratio at 30 °C. ([Zr] = 5 µmol, B/Zr = 1, P_{ET} = 0.5 bar, T = 30 °C, total volume = 150 ml in toluene, reaction time = 1 h).

Table 4. Effect of polymerization 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).

Al/Zr Ratio	Productivity (kg PE / mol-Zr atm h)			
	20 °C*	30 °C	40 °C	50 °C
160	1,100	1,640	800	280
200	1,840	3,000	2,400	2,080
220	2,760	2,120	1,922	1,900
240	1,840	1,800	1,400	-

* Ethylene pressure = 1.0 bar

The Role of $B(C_6F_5)_3$

To verify the role of $B(C_6F_5)_3$ and to find out whether TEA can act as a co-catalyst on its own, reactions were carried out with only TEA over an Al/Zr ratio range of 100-1000. No activity was found over a reaction time of 1 h. The addition of $B(C_6F_5)_3$ after 10 min activated the system, but the catalytic activity was lower than when $B(C_6F_5)_3$ was present from the beginning (Fig 4). This experiment confirmed that $B(C_6F_5)_3$ acted as a strong Lewis acid to ionize the neutral metallocene to form the active cationic species. TEA alone could not initiate the metalllocene catalyst.

Polymer Properties

The properties of polyethylene products are tabulated in Table 5. The degree of crystallinity from the first scan was in the range of 67-76 % which is relatively high and it was much higher than the values from the second scan which was in the range of 44-54%. This showed that the as-synthesized products had a highly ordered structure as confirmed by the FTIR spectra taken over the range 1000-1800 cm^{-1}, which covered the absorption due to the methyl branches at 1378 cm^{-1} (Fig 5). Compare to low-density polyethylene (LDPE), the polyethylene produced by metallocene catalyst and high-density polyethylene (HDPE) showed no peak at 1378 cm^{-1},

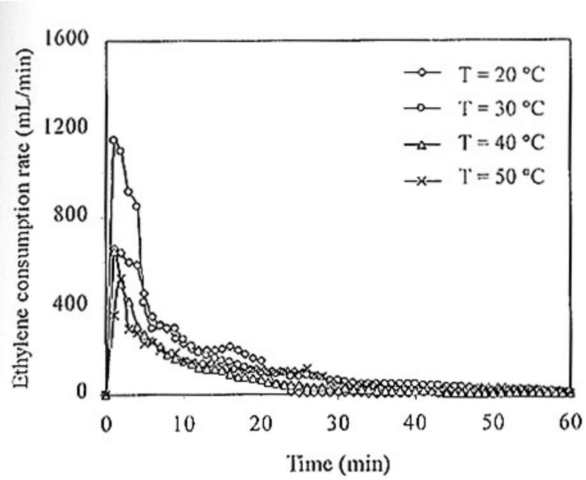

Fig 3. Effect of temperature on ethylene consumption rate of Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system. ([Zr] = 5 µmol, B/Zr = 1, P_{ET} = 0.5 bar, Al/Zr = 200, total volume = 150 ml in toluene, reaction time = 1 h).

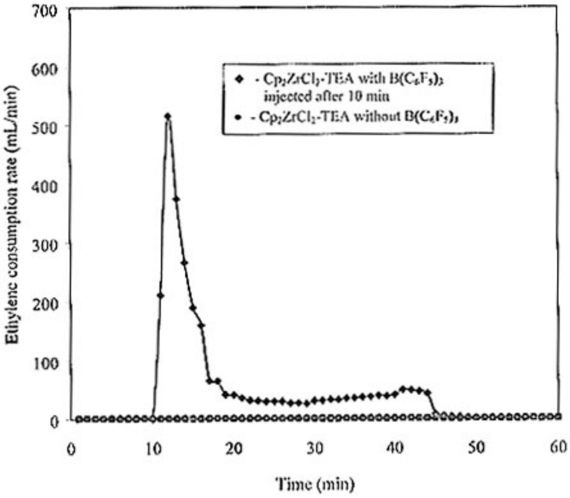

Fig 4. Effect of $B(C_6F_5)_3$ on Cp_2ZrCl_2-TEA catalyst system. ([Zr] = 5 µmol, B/Zr = 1, P_{ET} = 0.5 bar, T = 30 °C, Al/Zr = 200, total volume = 150 ml in toluene, reaction time = 1 h).

Table 5. Polyethylene properties at different reaction temperatures. (Zr) = 5 µmol, B/Zr = 1, P_{ET} = 0.5 bar, total volume = 150 ml in toluene, reaction time = 1 h.

Al/Zr Ratio	**Properties of polyethylene product**							
	Productivity (KgPE/mol-Zr*atm*h)	**Tm[1] (°C)**	**Tm[2] (°C)**	**Crystallinity[1] (%)**	**Crystallinity[2] (%)**	**Mn (kg/mol)**	**Mw (kg/mol)**	**MWD**
T = 20 °C								
220	2760	137	135	76.01	49.88	67.73	346.58	5.1
T = 30 °C								
160	1640	138	136	75.43	46.38	61.07	426.58	6.9
200	3000	137	136	76.17	54.59	85.50	473.50	5.5
220	2120	137	135	76.01	49.88	67.75	439.33	6.5
260	1120	135	135	67.73	44.07	58.34	350.72	6.0
T = 40 °C								
200	2400	137	136	74.55	46.35	88.32	447.92	5.0
T = 50 °C								
200	2080	135	134	72.17	45.56	67.67	303.66	4.5

[1] From the first scan, [2] From the second scan

while LDPE showed distinct C-H symmetric bending of $-CH_3$ at this wavenumber. This indicated that HDPE and metallocene polyethylene is relatively linear with little or no branching. Also, the degree of crystallinity showed the same trend as the productivity. As the productivity decreased, the degree of crystallinity also decreased.

The Mn and Mw were found to be in the range of 58-88 and 303-473 kg/mol respectively. Mw also followed the same trend as the productivity, ie it decreased at high Al/Zr ratio and high reaction temperature above 30 °C. Several workers[10,17] found molecular weight to decrease monotonically with increasing temperature. Chain transfer to the excess aluminum was thought to be responsible for the reduction in molecular weight at high Al/Zr ratio. The MWD was found to be in the range 4.5-6.9. Above 30 °C, the MWD at Al/Zr ratio of 200 was found to decrease from 5.5 at 30 °C to 4.5 at 50 °C indicating that the products are more uniform at higher polymerization temperature.

Scanning electron microscopy study on polymer particles obtained at all Al/Zr ratios showed the particles to be in spherical shape. In ethylene polymerization using Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system, homogeneously dispersed active sites are generated throughout the solution. When polymerization occurs, each active site grows individually thus spherical particles are obtained. In the present work, spherical particles of approximately 700 μm in diameter were obtained (Fig 6).

CONCLUSIONS

The Cp_2ZrCl_2-$B(C_6F_5)_3$-TEA catalyst system can be used to activate ethylene polymerization with high productivity at low Al/Zr ratio. The catalyst was active only over a narrow range of Al/Zr ratio. The optimum Al/Zr ratio was found to be in the range of 200-220 over the temperature range of 20-50 °C for a zirconocene amount of 5 mmole. The productivity was found to decrease with increasing amount of zirconocene, ethylene pressure, and reaction temperature. Reaction profiles showed that the reaction was completed within the first 20 min. TEA alone could not activate the Cp_2ZrCl_2 catalyst. The polyethylene product formed was highly crystallized with little or no branching.

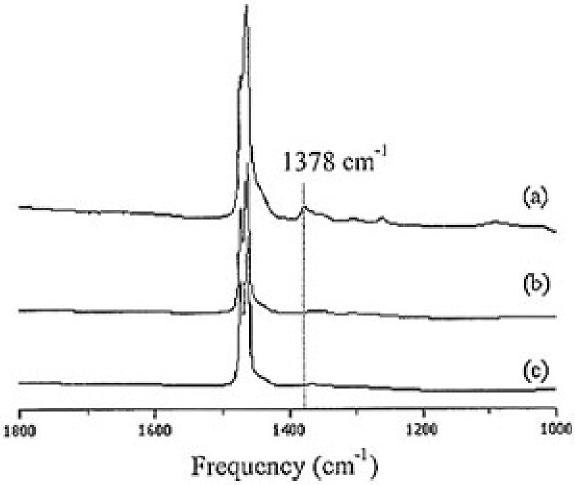

Fig 5. FT-IR spectra of (a) commercial LDPE (b) commercial HDPE and (c) metallocene polyethylene.

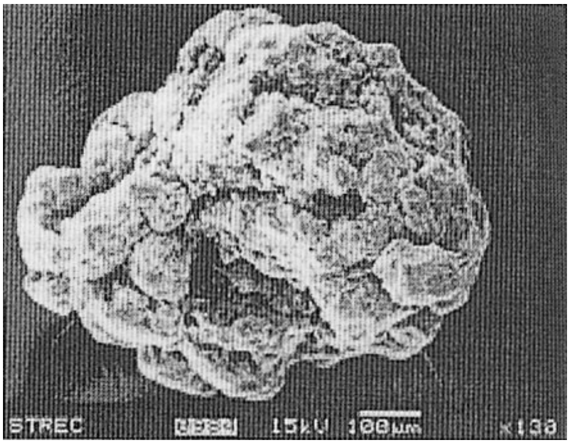

Fig 6. SEM micrograph of metallocene polyethylene particle (X 130).

ACKNOWLEDGEMENTS

The authors are deeply grateful to National Petrochemical Public Company for the financial support of this work and for providing ethylene gas. We would also like to thank Thai Polyethylene Co Ltd for donating triethylaluminum (TEA).

REFERENCES

1. Breslow DS and Newburg NR (1959) Bis-(cyclopentadienyl)-titanium dichloride-alkylaluminum complexes as soluble catalysts for the polymerization of ethylene, *J Am Chem Soc* **81**, 81-7.
2. Kaminsky W (1994) Zirconocene catalysts for olefin polymerization, *Catalysis Today* **20**, 257-71.
3. Horton AD (1994) Metallocene catalysis: Polymers by design?, *TRIP* **2**, 158-66.
4. Ciardelli F, Altomare A and Michelotti M (1998) From homogeneous to supported metallocene catalysts, *Catalysis Today* **41**, 149-57.
5. Gupta VK, Satish S and Bhardwaj IS (1994) Metallocene complexes of group 4 elements in the polymerization of monoolefins. *Rev Macromol Chem Phys* **C34(3)**, 439-514.
6. Gladysz JA (2000) Frontiers in metal-catalyzed polymerization: Designer metallocene, designs on new monomer, demystifying MAO. *Chem Rev* **100**, 1167-8.

7. Siedle AR, Lamanna WM, Newmark RA and Schroepfer JN (1998) Mechanism of olefin polymerization by a soluble zirconium catalyst. *J of Molecular Catalysis A: Chemical* **128**, 257-71.
8. Alt HG and Koppl A (2000) Effect of the nature of metallocene complexes of Group IV metals on their performance in catalytic ethylene and propylene polymerization. *Chem Rev* **100**, 1205-22.
9. Petitjean L, Pattou D and Ruiz-Lopez MF (1991) Theoretical study of the mechanisms of ethylene polymerization with metallocene-type catalysts. *J Phys Chem B* **103**, 27-32.
10. Srinivasa R, Shashidhar G and Sivaram S (1992) Role of trimethylaluminum on the zirconocene-methylaluminoxane-catalyzed polymerization of ethylene. *Macromolecules* **26**, 1180-2.
11. Liu S, Yu G and Huang B (1997) Polymerization of ethylene by zirconocene-$B(C_6F_5)_3$ catalysts with aluminum compounds, *J of Appl Polym Sci* **66**, 1715-20.
12. Belov GP, Gyulumyan HR, Khrapuva IM, Maryin VP and Korneev NN (1997) Kinetics of olefin polymerization catalyzed by various zirconocene/aluminoxane systems at low Al/Zr ratios. *J of Molecular Catalysis A: Chemical* **115**, 155-61.
13. Yang X, Stern CL and Mark JJ (1991) Cation-like homogeneous olefin polymerization catalysts based upon zirconocene alkyls and tris(pentafluorophenyl)borane. *J Am Chem Soc* **113**, 3629-25.
14. Yang X, Stern CL and Mark JJ (1994) Cationic zirconocene olefin polymerization catalyst based on the organo-Lewis acid tris(pentsfluorophenyl)borane A. Synthetic, structural, solution, dynamic, and polymerization catalytic study. *J Am Chem Soc* **116**, 10015-31.
15. Naga N, Shiono T and Ikeda T (1999) Profiles of ethylene polymerization with zirconocene-trialkylaluminium/borane compound. *J of Molecular Catalysis A: Chemical* **150**, 155-62.
16. Huang AJ and Rempel GL (1997) Kinetic study of propylene polymerization using Et9H4Ind)2ZrCl2/methylaluminoxane catalyst. *Ind Eng Chem Res* **36**, 1151-7.
17. Kim I and Choi C (1999) The effect of AlR3 on propylene polymerization by rac-(EBI)$Zr(NMe_2)_2/AlR_3/[CPh_3][B(C_6F_5)_4]$ catalyst. *J Polym Sci Part A: Polym Chem* **37**, 1523-39.