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Polymerization characteristics of in situ supported pentamethylene bridged dinuclear zirconocene

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Abstract

An in situ supporting method was applied to newly synthesized $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst and other commercial catalysts, and its effects on the polymerization characteristics of these catalysts were examined through reaction experiments. The changes in the molecular weight distribution varied depending on the metallocene catalyst while the changes in the catalytic activity, average molecular weight and the melting point showed the same trend. The reason for the decrease in the molecular weight with in situ supporting was discussed in relation to the co-catalysts. The polymerization characteristics of each catalyst also varied according to the alkyl aluminum, and so it is important to select a proper co-catalyst or a combination of co-catalysts to obtain a desired polymer product from each metallocene catalyst supported by in situ method.

Keywords: In situ supporting; Dinuclear zirconocene catalyst; Ethylene polymerization; Co-catalyst; Molecular weight distribution

1. Introduction

Metallocene catalysts having single sites have received much attention since they can produce polymers with a narrow molecular weight distribution and uniform chemical composition, or polymers with a stereo-specificity. But metallocene catalysts need to be supported before their application to the existing industrial processes due to the difficulties in controlling the polymer morphology and the problem of reactor fouling [1].

Metallocene catalysts are usually supported on silica or modified silica but the activity of the supported catalyst is significantly reduced compared to that of the homogeneous catalyst. In addition, the weight percent of the metallocene catalyst mounted on the support is small and the mounted metallocene tends to be lost gradually by leaching during polymerization [2–4].

As an effort to overcome these problems, an in situ supporting method was developed by Chu et al. [5,6]. This method consists of introducing a metallocene catalyst into the reaction mixture containing MAO-treated silica (SMAO) and a co-catalyst. In situ supported catalysts showed high activities and produced polymers with a good morphology. But the work by Chu et al. [5] were limited to in situ supporting of the rac-Et(Ind)$_2$ZrCl$_2$ catalyst. Therefore, a more detailed work on this new supporting method with various metallocene catalysts is necessary to use this method more effectively.

In this work, the in situ supporting method was applied to several metallocene catalysts which

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include a new metallocene catalyst. Polymerization was also performed for each in situ supported metallocene varying the type of alkyl aluminums and the corresponding changes in the polymerization characteristics were studied. The new catalyst studied in this work was a pentamethylene bridged dinuclear zirconocene ($[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$), which was originally synthesized by Noh et al. [7,8] but its polymerization characteristics were not examined in depth. This work was done as a part of a governmental project to commercialize newly synthesized metallocene catalysts in Korea. In the process of catalyst scale-up, the in situ supporting method was tested as efficient method for supporting the $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst and the optimum conditions for in situ supporting of this catalyst were sought after.

2. Experimental

2.1. Materials

Nitrogen gas and ethylene gas were purified by passing through columns packed with molecular sieves 4A and ridox copper. Tetrahydrofuran (THF), hexane, toluene and diethylether (purchased from Junsei, Japan) were distilled from sodium/benzophenone ketyl prior to use. Silica (Grace Davison 948) was calcinated at 260 °C for 6 h. Indene, *n*-butyllithium (*n*-BuLi), tributyltinchloride (Bu_3SnCl), trimethyltinchloride (Me_3SnCl), sodium cyclopentadienid (CpNa) and 1,5-dibromophentane were used as-received.

The co-catalysts used for polymerization were modified methyl aluminoxane (MMAO, Type 4, Akzo Noble), trimethyl aluminum (TMA, Aldrich), triethyl aluminum (TEA, Aldrich) and triisobutyl aluminum (TiBA, Aldrich). MAO-treated silica (SMAO, Witco) which contains 23 wt.% aluminum was used for in situ supporting.

Commercial metallocene catalysts including bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2, Stream) and rac-ethylenebis(indenyl)zirconium dichloride (rac-$Et(Ind)_2ZrCl_2$, Aldrich)) were used as-purchased.

2.2. Synthesis of pentamethylene bridged dinuclear zirconocene catalyst

A pentamethylene bridged dinuclear zirconocene, pentamethylene bis(cyclopentadienylindenyl zirconium dichloride) ($[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$), was prepared in a larger scale for pilot reactions using the recipe developed by Noh et al. [8].

Preparation of metallocene catalysts were carried out under a dry, oxygen-free atmosphere using standard schlenk techniques. The $(Ind)ZrCl_3$ were obtained from the reaction between $ZrCl_4$ and $(Ind)SnBu_3$ which was synthesized from indene and Bu_3SnCl. The $[(CH_2)_5][(CpSnMe_3)]_2$ ligand was obtained from the reaction of two Me_3SnCl and $[(CH_2)_5(C_5H_4)_2]$ which was produced from CpNa and 1,5-dibromopentane. Then the resulting ligand was metallated with $(Ind)ZrCl_3$ at 60 °C. The catalyst, $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$, catalyst was finally obtained from recrystallization of the resultant mixture at −78 °C. The synthesized catalyst was characterized with FT NMR (VARIAN, MERCURY-300) spectrometer.

2.3. Catalyst supporting

Metallocene catalysts were supported using the conventional method and in situ method. For conventional, 13×10^{-5} mol Zr $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst were added to a suspension of calcinated silica or SMAO (1 g) in toluene (20 ml). The suspension was stirred at 75 °C for 20 h for supporting on silica or 2 h for supporting on SMAO. After the liquid was filtered out, the resulting solid was washed five times and dried in high vacuum.

For in situ supporting, SMAO powder was introduced into the reaction mixture containing a metallocene catalyst and co-catalyst to induce an in situ supporting during the polymerization process.

2.4. Polymerization

Reaction experiments were performed in a glass reactor (250 ml) as shown in Fig. 1. The reaction temperature was controlled by circulating a heating medium through the reactor jacket. The reaction mixture was stirred by either magnet or impeller. The consumption

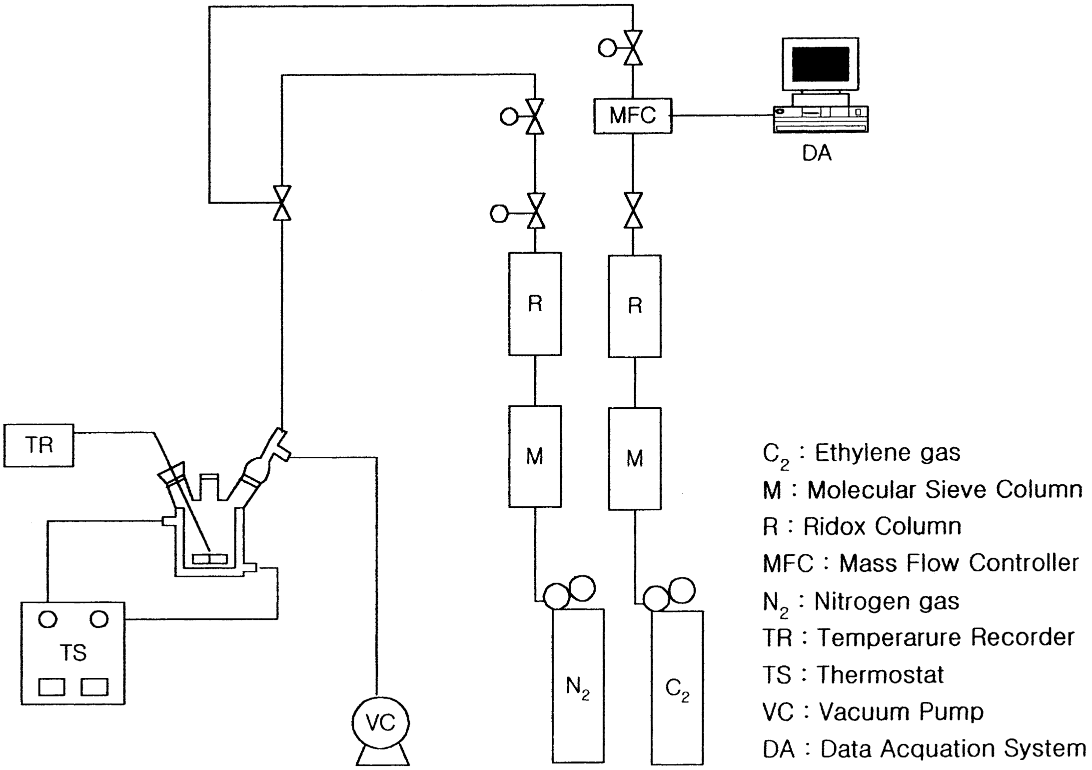

Fig. 1. Experimental apparatus for polymerization with metallocene catalysts.

rate of monomer gas during the reaction was monitored by a mass flow meter.

For polymerization, 150 ml of toluene (or 1500 ml in autoclave) was added into the reactor and the reaction mixture was saturated with ethylene under an atmospheric pressure. Then polymerization was initiated by injecting the co-catalyst and metallocene catalyst into the reactor. For reactions with in situ supported catalyst, SMAO was injected additionally. The polymerization time was varied from 30 min to 10 h while the polymerization temperature was set to 40 °C. After the reaction, the resulting polymer was precipitated in an excess amount of methanol, filtered and dried in a vacuum oven for 1 day.

2.5. Analysis of polymer product

The average molecular weight $\bar{M}_w$ and molecular weight distribution (MWD) of the polymer product were determined by gel permeation chromatography (GPC, PL-GPC 210), and the data were analyzed using polystyrene calibration curves. The polymer samples were prepared by dissolving in 1,2,4-trichlorobezene at 145 °C. The melting temperature (T_m) of polymer was measured using differential scanning calorimeter (DSC, TA 2010) at a scanning rate of 20 °C/min. The morphology of polymer particles was examined with scanning electron microscopy (SEM, Akashi WB-6).

3. Results and discussion

3.1. Catalyst preparation

The pentamethylene bridged dinuclear zirconocene $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ was obtained as brown powder and was found to have the correct ^1H NMR spectra for the given catalyst structure (Fig. 2).

^1H NMR ($CDCl_3$): δ 7.68 (m, 4H), δ 7.30 (m, 4H), δ 6.92 (t, 2H), δ 6.51 (d, 2H), δ 5.94 (t, C_5H_4), δ 5.84

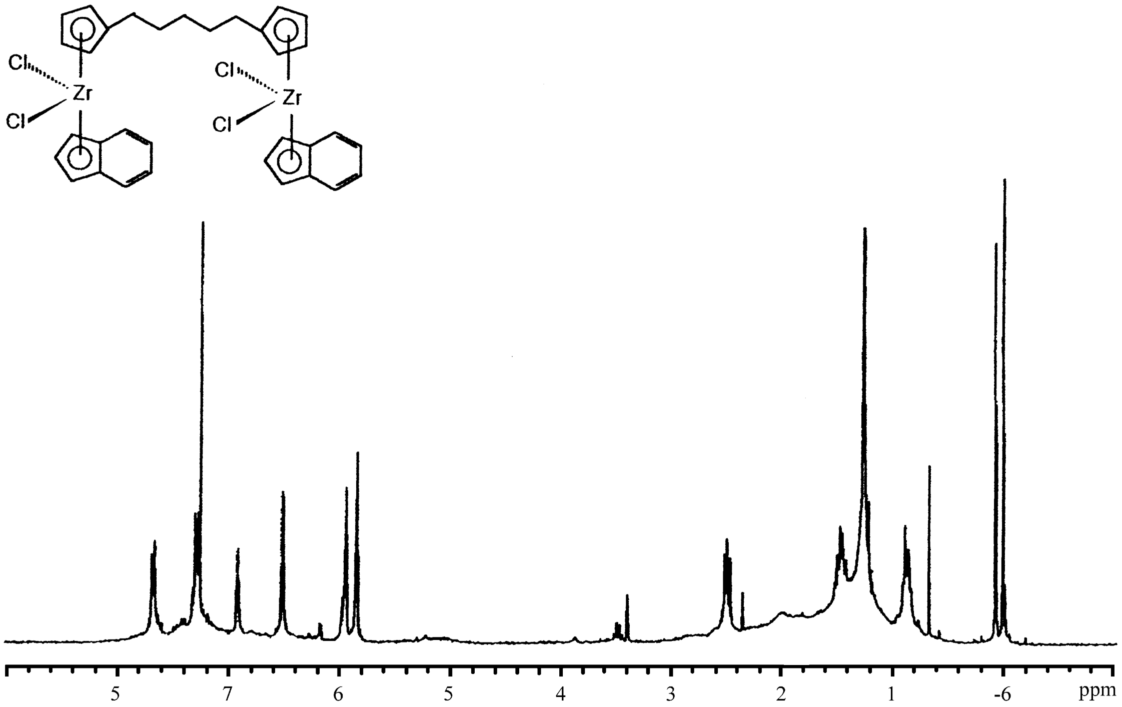

Fig. 2. Structure and ^{1}H NMR spectra for the $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst prepared in a large scale.

(t, C_5H_4), δ 2.49 (m, 2H), δ 1.47 (q, 4H), δ 1.25 (m, 2H) ppm.

3.2. Polymerization characteristics of the homogeneous dinuclear zirconocene catalyst

Ethylene polymerization experiments were carried out with the homogeneous dinuclear zirconocene catalyst to check its intrinsic catalytic activity and the results were compared with those of the commercial catalysts as shown in Table 1. The catalytic activity of the homogeneous $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst was 266 kg of PE/mol of Zr atm h, which was 1/10th of those from Cp_2ZrCl_2 and rac-Et(Ind)$_2$ZrCl$_2$ catalysts in the same reaction condition. When the Al/Zr ratio was increased to 1000, the activity reached a value (2496 kg of PE/mol of Zr atm h) which was similar to those obtained from the commercial catalysts. The polymer product from $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst had a higher

Table 1
Results of ethylene polymerization with different kinds of homogeneous catalysts[a]

Catalyst	Zr (μmol)	Al/Zr[b]	Yield (g)	T_m (°C)[c]	$\bar{M}_w$ ($\times 10^{-3}$)	MWD[d]	Activity[e]
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$	2.64	500	0.35	136	–	–	266
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$	2.64	1000	3.29	136	577.1	2.31	2496
Cp_2ZrCl_2	2.56	500	3.82	130	322.2	3.51	2988
rac-Et(Ind)$_2$ZrCl$_2$	2.41	500	3.56	134	450.9	3.26	2954

[a] Reaction conditions: co-catalyst MMAO; temperature 40 °C; pressure 1 atm; time 30 min.

[b] The mole ratio of Al in the co-catalyst to Zr in the metallocene.

[c] Melting temperature.

[d] Molecular weight distribution.

[e] [kg of PE/mol of Zr atm h].

Table 2
Results of ethylene polymerization with the $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalysts supported in different methods[a]

Catalyst[b]	Co-catalyst	Time (h)	Yield (g)	T_m (°C)[c]	$\bar{M}_w$ ($\times 10^{-3}$)	MWD[d]	Activity[e]
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$	MMAO	0.5	3.29	136	577.1	2.31	2496
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$/silica	MMAO	1	Trace[f]	–	–	–	–
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$/MAO/silica	MMAO	1	0.70	141	935.9	4.25	256
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$/MAO/silica	TiBA	1	0.34	139	779.2	5.32	129
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$/SMAO[g]	TMA	1	1.19	139	494.8	4.31	451

[a] Reaction conditions: Al/Zr = 1000 (mole ratio of Al in the co-catalyst to Zr in the metallocene); temperature 40 °C; pressure 1 atm.

[b] Zr amount in each catalyst: $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ 2.64 μmol; Cp_2ZrCl_2 2.56 μmol; rac-Et(Ind)$_2$ZrCl$_2$ 2.41 μmol.

[c] Melting temperature.

[d] Molecular weight distribution.

[e] [kg of PE/mol of Zr atm h].

[f] The yield of PE is too small to evaluate activity.

[g] In situ supported catalyst (the amount of SMAO used for in situ supporting is 1.4 mmol Al).

molecular weight with a narrower MWD when compared with the polyethylene from the commercial catalysts at the similar level of catalytic activity. It was reported [9] that this type of dinuclear zirconocene catalyst produced polymer with a higher molecular weight since its bulky structure suppressed β-H chain transfer reactions. The reason for the fact that a dinuclear zirconocene catalyst may need a larger amount of MMAO to get the same catalytic activity than a mononuclear catalyst is considered to be its limited mobility of Zr which is connected to other Zr through a rigid bridge.

A notable characteristic of the polyethylene prepared by $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst was that the polymer particles were rather separate and flowed freely even though there still remained problem of reactor fouling during reaction. This superiority of the morphology of the polymer prepared by $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst seems to be caused by the unique structure of the $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst. The two metal centers of the catalyst are separated by a definite distance so that polymer chains from the two centers may get entangled to form a rather bulky polymer particle with a definite shape.

3.3. Polymerization characteristics of the in situ supported dinuclear zirconocene catalyst

The new $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst was supported in three different methods to examine how the supporting method influences the performance of the catalyst in the polymerization. When it was supported on silica by a traditional method, the resulting catalyst showed a very little catalytic activity as in Table 2. When $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst was supported on SMAO, a silica pretreated with MAO, the catalytic activity became significant but still 1/10th of that of the homogeneous catalyst. When the same supported catalyst reacted with TiBA co-catalyst, the activity decreased further. The average molecular weight increased with supporting $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ on SMAO, which was different from the result of Sacchi [2] that supporting Cp_2ZrCl_2 catalysts on MAO-treated silica did not change the molecular weight of polymer product significantly.

When in situ supporting method was employed, the catalytic activity increased more than twice of that from the catalyst supported in other ways. The molecular weight of polymer product from the in situ supported $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst became slightly lower (494 800) than that of homogeneous catalyst (577 100). The MWD of the products from the in situ supported $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst became broader, indicating an increase in the processability of the resultant polymer. The melting temperature of the resultant polymer slightly increased with in situ supporting of the catalyst.

In addition to the advantage of giving the highest activity of the $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst among various supporting methods, other known effects of supporting were also achieved by

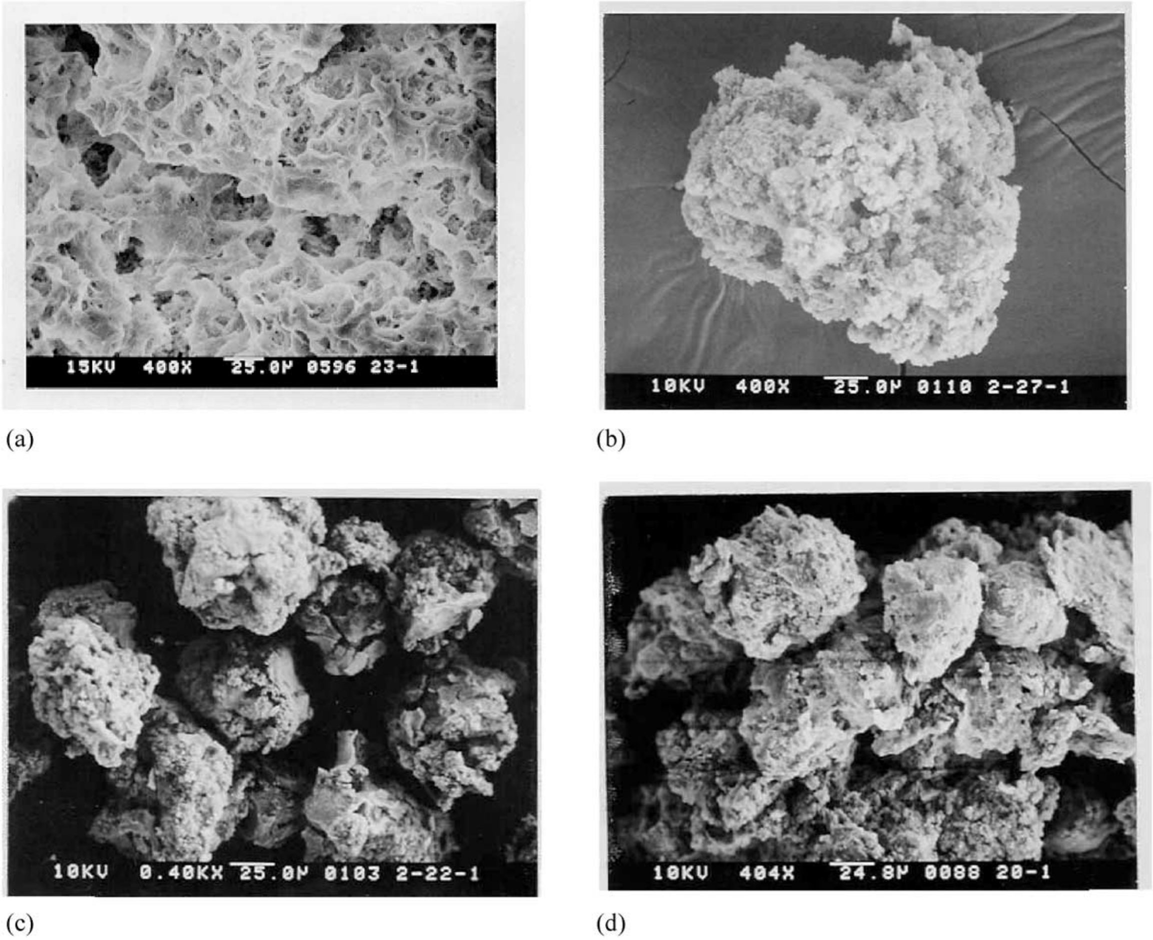

Fig. 3. SEM pictures of polyethylene particles obtained with PBDZ catalysts: (a) homogeneous $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$; (b) in situ supported $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$/TMA; (c) in situ supported $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$/TEA; (d) in situ supported $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$/TiBA.

the in situ method. Fig. 3 shows the spherical shape of the polymer particles obtained with the in situ supported $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst, which contrast to the amorphous polymer from the homogeneous $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst. Fig. 4 shows that the reaction rate over in situ supported catalyst was steady over a long time in contrast to the decaying-type rate profile for the homogeneous catalyst. The reaction results are summarized in Table 3. Due to its steady rate, the yield from the polymerization over in situ supported catalyst was higher than that from the reaction over the homogeneous catalyst. When the reaction was performed with the in situ supported catalyst at a higher pressure (6 atm) in an autoclave for 24 h, a large amount (260 g) of polymer with a very high molecular weight (1 708 000) could be obtained indicating that a large amount of polymer with a high molecular weight could be prepared for commercialization from the new $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst by changing the reaction conditions. No sign of fouling was observed in the reactor after the reaction with in situ supported catalyst.

In order to determine the optimum conditions for in situ supporting of catalyst, the effects of the amount of the co-catalyst and SMAO on the poly-

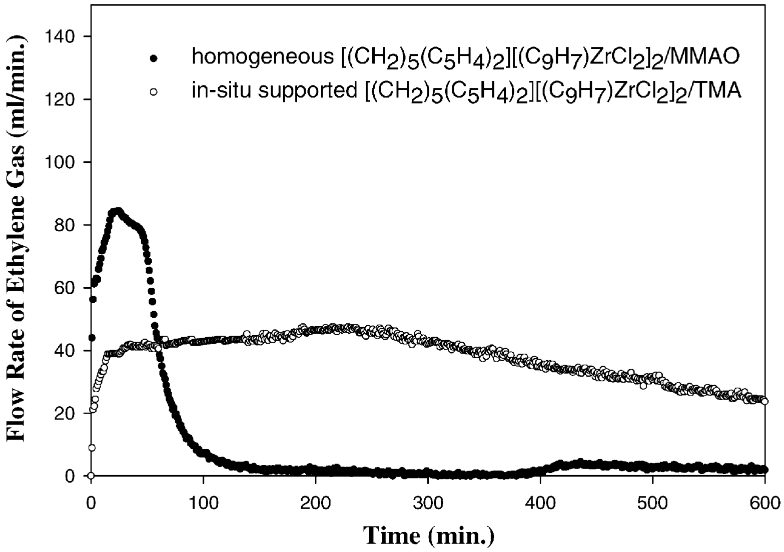

Fig. 4. Kinetic behavior of ethylene polymerization with $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalysts (Zr: 2.64 μmol; Al/Zr ratio: 1000; temperature: 40 °C; time: 10 h; pressure: 1 atm).

merization behavior of the in situ supported catalyst were investigated, respectively. As the amount of the TMA changed, the catalytic activity increased up to Al/Zr = 1000, and then decreased with further increase in the Al/Zr ratio (Fig. 5). The average molecular weight did not change much with the increase in the amount of TMA up to Al/Zr = 1000 but it decreased afterwards. TMA seemed to enhance the catalytic activity of $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst but TMA in an excess amount interfered the polymerization. The decrease in the catalytic activity and average molecular weight with use of an excess amount of TMA seemed to be caused by interaction of excess TMA molecules with the metallocene or growing polymer to result in catalyst deactivation [10] or chain transfer reaction.

When the amount of SMAO was increased in the polymerization over in situ supported $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst, the catalytic activity increased continuously while the average molecular weight did not change much (Fig. 6). The increase in the catalytic activity with increased amount of SMAO seems to be due to the increase in the number of active sites which are formed on MAO molecules adsorbed on silica particles.

Table 3
Results of ethylene polymerization over a long time with the $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalysts[a]

Catalyst	Zr (μmol)	Co-catalyst	Time (h)	Pressure (atm)	Yield (g)	$\bar{M}_w$ ($\times 10^{-3}$)	MWD[b]	Activity[c]
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$	2.64	MMAO	10	1	6.1	983.3	3.59	229
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$/SMAO[d]	2.64	TMA	10	1	7.6	623.7	3.10	289
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$/SMAO[e]	5.28	TMA	24	6	260	1708	4.11	342

[a] Reaction conditions: Al/Zr = 1000 (mole ratio of Al in the co-catalyst to Zr in the metallocene); temperature 40 °C.

[b] Molecular weight distribution.

[c] [kg of PE/mol of Zr atm h].

[d] In situ supported catalyst (the amount of SMAO used for in situ supporting is 1.4 mmol Al) in the glass reactor (250 ml volume).

[e] In situ supported catalyst (the amount of SMAO used for in situ supporting is 2.8 mmol Al) in the autoclave reactor (2000 ml volume).

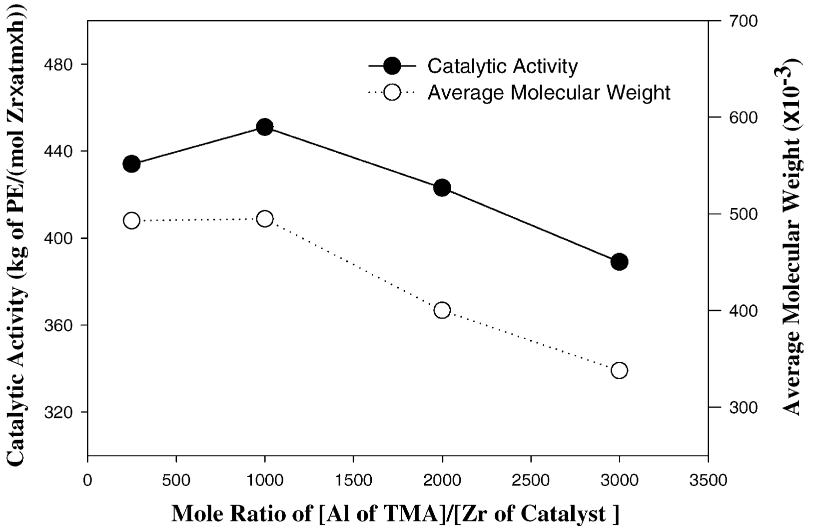

Fig. 5. Effect of TMA amount on the catalytic activity and the average molecular weight of the obtained polymer (Zr: 2.64 μmol; Al of SMAO: 1.4 mmol; temperature: 40 °C; time: 1 h; pressure: 1 atm).

From these experiments, it was found that the optimum amount of TMA is that corresponding to Al/Zr ratio of about 1000 for in situ supported $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst while larger amount of SMAO is desirable as long as the process economics permits.

3.4. *Effects of in situ supporting on the performance of other catalysts*

In situ supporting method was applied to other commercial catalysts, Cp_2ZrCl_2 and rac-Et(Ind)$_2$ZrCl$_2$, and its effects on the polymerization were compared

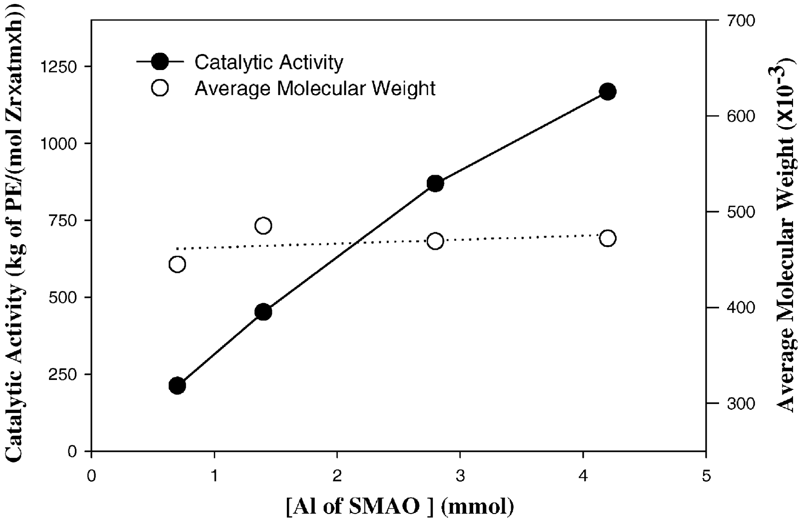

Fig. 6. Effect of SMAO amount on the catalytic activity and the average molecular weight of the obtained polymer (Zr: 2.64 μmol; Al/Zr: 1000; temperature: 40 °C; time: 1 h; pressure: 1 atm).

Table 4
Results of ethylene polymerization with different catalysts and co-catalysts[a]

Catalyst[b]	Co-catalyst	Al/Zr[c]	Time (h)	Yield (g)	T_m (°C)[d]	$\bar{M}_w$ ($\times 10^{-3}$)	MWD[e]	Activity[f]
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$	MMAO	1000	0.5	3.29	136	577.1	2.31	2496
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$/SMAO[g]	TMA	1000	1	1.19	139	494.8	4.31	451
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$/SMAO[g]	TEA	1000	1	0.64	135	121.5	4.35	243
$[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$/SMAO[g]	TiBA	1000	1	0.32	136	326.9	4.06	121
Cp_2ZrCl_2	MMAO	500	0.5	3.82	130	322.2	3.51	2988
Cp_2ZrCl_2/SMAO[g]	TMA	1000	1	2.55	139	240.5	4.12	994
Cp_2ZrCl_2/SMAO[g]	TEA	1000	1	1.33	134	232.8	4.64	519
Cp_2ZrCl_2/SMAO[g]	TiBA	1000	1	0.96	138	288.0	3.60	375
rac-Et(Ind)$_2$ZrCl$_2$	MMAO	500	0.5	3.56	134	450.9	3.26	2954
rac-Et(Ind)$_2$ZrCl$_2$/SMAO[g]	TMA	1000	1	2.15	137	371.5	2.90	890
rac-Et(Ind)$_2$ZrCl$_2$/SMAO[g]	TEA	1000	1	2.00	135	52.9	2.95	830
rac-Et(Ind)$_2$ZrCl$_2$/SMAO[g]	TiBA	1000	1	2.00	136	191.5	2.15	830

[a] Reaction conditions: temperature 40 °C; pressure 1 atm.

[b] Zr amount in each catalyst: $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ 2.64 μmol; Cp_2ZrCl_2 2.56 μmol; rac-Et(Ind)$_2$ZrCl$_2$ 2.41 μmol.

[c] The mole ratio of Al in the co-catalyst to Zr in the metallocene.

[d] Melting temperature.

[e] Molecular weight distribution.

[f] [kg of PE/ mol of Zr atm h].

[g] In situ supported catalyst (the amount of SMAO used for in situ supporting is 1.4 mmol Al).

with the case of $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst. With in situ supporting of Cp_2ZrCl_2 catalyst, the average molecular weight of the resulting polymer decreased, the MWD got broader and the melting temperature increased (Table 4). But in the case of the in situ supported rac-Et(Ind)$_2$ZrCl$_2$ catalyst, both the molecular weight and polydispersity decreased while the melting temperature increased. From these results, it was found that the common effects of in situ supporting among the metallocenes were the decrease in the molecular weight and catalytic activity while the changes in MWD were different according to the nature of the metallocene catalysts (Table 4).

It was a matter of concern that the average molecular weight decreased to some extent with in situ supporting of metallocenes. Especially, when TEA was used as the co-catalyst the molecular weights of polymers from in situ supported catalysts decreased more than 30% with supporting for all the metallocenes. Therefore, it is important to choose the proper type of co-catalyst for each in situ supported metallocene catalyst to prevent significant loss in the molecular weight of the polymer product.

The reasons for the decrease in the molecular weight with in situ supporting could be explained by the capability of alkyl aluminums in invoking chain transfer reactions which lead to a decreased molecular weight of the polymer product. The homogeneous metallocene catalyst was activated by MAO while activation of the in situ supported catalyst was performed by TMA. But these co-catalysts are believed to cause undesirable chain transfer reactions additionally during polymerization. TMA seemed to cause these side reactions more easily than MAO with a bulky structure, which leads to a decrease in the polymer molecular weight in the reaction over in situ supported catalyst. It was also reported [11] that the co-catalysts containing higher amount of alkyl aluminums produced polymer with a lower molecular weight than pure MAO in the polymerization with homogeneous metallocene catalysts.

In the polymerization with in situ supported catalyst alkyl aluminum is used as co-catalyst. The effects of the type of the alkyl aluminum on the reaction need to be examined for determination of the optimum reaction condition. Results from the reaction experiments performed with in situ supported metallocene catalysts showed different polymerization characteristics according to the type of the co-catalysts. Regarding the molecular weight of the polymer, TiBA produced polymer with highest

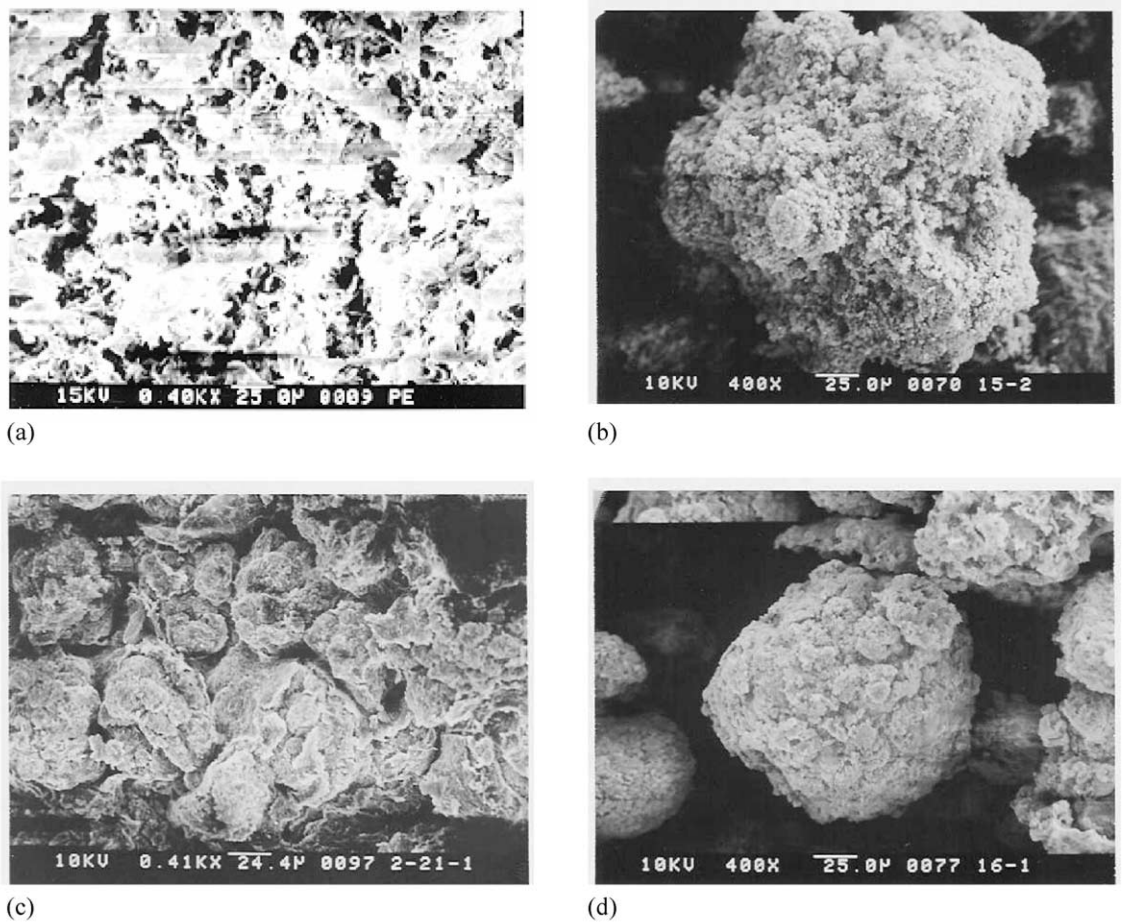

Fig. 7. SEM pictures of polyethylene particles obtained with Cp_2ZrCl_2 catalyst: (a) homogeneous Cp_2ZrCl_2; (b) in situ supported Cp_2ZrCl_2/TMA; (c) in situ supported Cp_2ZrCl_2/TEA; (d) in situ supported Cp_2ZrCl_2/TiBA.

molecular weight for Cp_2ZrCl_2 catalyst, while TMA produced polymer with highest molecular weight for $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ and rac-Et(Ind)$_2$ZrCl$_2$ catalysts. With respect to the MWD, both TEA and TMA produced polymers with higher polydispersities for $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ and rac-Et(Ind)$_2$ZrCl$_2$ catalysts while TEA gave broadest distribution for polymer from Cp_2ZrCl_2 catalyst. The order of co-catalysts for the melting points of the polymer products were the same for all three metallocenes supported by in situ method. The activity of all the in situ supported catalyst was dependant on the nature of the co-catalyst regardless of the metallocene catalysts used: its order was TMA > TEA > TiBA. The higher efficiency of the TEA and TiBA in invoking α-hydrogen transfer seemed to be responsible for the more significant decrease in the catalytic activity.

The effect of co-catalyst on the size of polymer particles also differed according to the nature of the supported metallocenes, even though spherical polymer particles were obtained in all cases (Figs. 3, 7 and 8). For in situ supported $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst, TMA gave much larger polymer particles than TEA and TiBA. With in situ supported Cp_2ZrCl_2 catalyst, the polymer particles were larger in the order of TMA > TiBA > TEA. In case of in situ supported rac-Et(Ind)$_2$ZrCl$_2$ catalyst, the particles produced from TMA and TiBA (280 μm) were of similar

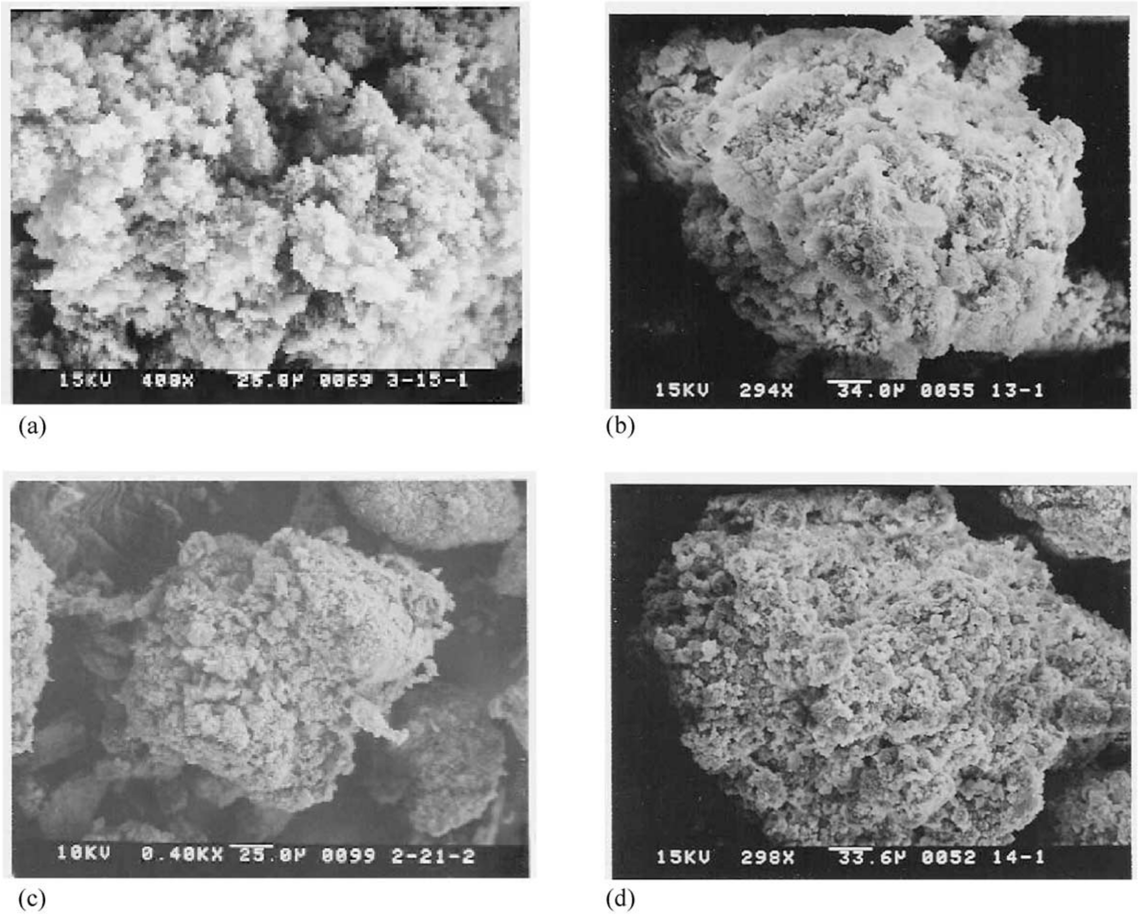

Fig. 8. SEM pictures of polyethylene particles obtained with rac-Et(Ind)$_2$ZrCl$_2$ catalyst: (a) homogeneous rac-Et(Ind)$_2$ZrCl$_2$; (b) in situ supported rac-Et(Ind)$_2$ZrCl$_2$/TMA; (c) in situ supported rac-Et(Ind)$_2$ZrCl$_2$/TEA; (d) in situ supported rac-Et(Ind)$_2$ZrCl$_2$/TiBA.

size but much larger than that from TEA (150 μm). It was also notable that the size of polymer particles obtained from in situ supported rac-Et(Ind)$_2$ZrCl$_2$ catalyst (280 μm) was much larger than those from other in situ supported catalysts.

These differences among the three in situ supported catalyst indicates that they form active sites on MAO-treated silica in different ways according to their own catalyst structure and electronic configurations to result in different characteristics of polymerization. In addition, it seems important to select a proper co-catalyst or a combination of co-catalysts for each metallocene to obtain a polymer product with desired properties.

4. Conclusions

1. Newly synthesized $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst with a bulky catalyst structure produced polyethylene with a higher molecular weight and better morphology than other commercial catalysts. In situ supporting of this catalyst decreased the activity and produced polymer with a slightly lower average molecular weight and broader MWD. Other supporting effects were also achieved including morphology improvement, steady reaction rate and removal of reactor fouling.
2. When the effects of in situ supporting on the polymerization characteristics were compared among

three zirconocenes, the decrease in the molecular weight and catalytic activities and the increase in the melting point were the same for all the catalysts. But the MWD became broader with $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ and Cp_2ZrCl_2 while it became narrower with rac-Et(Ind)$_2$ZrCl$_2$. The reason for the decrease in the molecular weight with in situ supporting was ascribed to the higher capabilities of TMA over MMAO in invoking chain transfer reactions.

3. The polymerization characteristics of each in situ supported catalyst changed according to the type of alkyl aluminum used as co-catalyst. The highest catalytic activity was obtained with use of TMA for all metallocenes. The highest molecular weight was obtained with TiBA for Cp_2ZrCl_2 while TMA gave the highest value for $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ and rac-Et(Ind)$_2$ZrCl$_2$. The MWD and particle size of the polymer product from each supported catalyst also changed with the co-catalyst. So it seems important to select a proper co-catalyst or combination of co-catalysts for each in situ supported metallocene to obtain a polymer product with desired properties.

Acknowledgements

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