Ethylene Polymerization Initiated by Anchored CpIndZrCl$_2$ on Silica with Hexamethyltrisiloxane and Pentamethylene Spacers

DONG-HO LEE,[1] HUN-BONG LEE,[1] SEOK KYUN NOH,[2] BYUNG KYU SONG,[3] SAH MUN HONG[3]

[1] Department of Polymer Science, Kyungpook National University, Taegu, South Korea

[2] School of Chemical Engineering and Technology, Yeungnam University, Kyungsan, South Korea

[3] Dae-duk Research Center, Daelim Ind., Taejeon, South Korea

ABSTRACT: For ethylene polymerization, the supported metallocene catalyst was prepared by anchoring CpIndZrCl$_2$ on silica with an appropriate spacer. The three procedures were applied for CpIndZrCl$_2$ anchoring on silica with a hexamethyltrisiloxane or pentamethylene spacer. The anchoring procedures exerted a strong influence on the catalyst activity since the different anchoring methods gave the formation of different structures of active sites. With the new anchoring route, it was possible to prepare the "heterogeneous single-site" catalyst which was found to have only one catalyst structure on silica and exhibited a higher catalyst activity than that of the other supported catalysts. At a polymerization temperature of 70°C, the activity of the heterogeneous single-site catalyst was comparable to that of the unsupported homogeneous zirconocene. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1071–1080, 1999

Key words: ethylene polymerization; supported metallocene; anchored zirconocene on silica with spacer; heterogeneous single-site catalyst

INTRODUCTION

Since Kaminsky's discovery in 1980, the metallocene catalyst has become increasingly important as a potential new generation of Ziegler–Natta catalyst.[1,2] As an advantage over the conventional Ziegler–Natta catalyst, the metallocene/methylaluminoxane (MAO) catalyst system exhibits high activity with the possibility of tailoring the polymer properties such as molecular weight (MW) and molecular weight distribution as well as stereochemistry through an appropriate ligand design at the metal center.[3–5]

Because most of the existing polyolefin plants run in slurry and the gas phase with the heterogeneous Ziegler–Natta catalyst, the metallocene catalyst must be immobilized on a support not only to be applicable for the existing fluidized bed process but also to control the morphology of the resulting polyolefin. In general, the immobilization of soluble metallocene to various supports has been accomplished by three methods[6]: (1) direct impregnation of metallocene on support[7,8]; (2) treatment of silica with MAO or alkylaluminum followed by reaction with metallocene[9–11]; and (3) immobilization of aryl ligand on support followed by addition of metal salt.[12,13]

Among the polymerization features by the supported metallocene catalyst, some beneficial points over the homogeneous one have been observed: Two

typical examples are the enhancement of the MW of polymer and the smaller amount of MAO as well as alkylaluminum as a cocatalyst for the suitable activity. On the other hand, the heterogeneized metallocene leads, in general, to the reduction of catalytic activity compared with that of the corresponding soluble catalyst. In addition, the metal content of the immobilized metallocene is found to be very low (< 1.0 wt %).

As model compounds for a supported metallocene on silica, the various polysiloxane-bridged dinuclear zirconocenes were prepared and examined for ethylene polymerization.[14] It was found that the longer the length of the polysiloxane bridge, the higher activity and the lower MW resulted due to the variation of the electronic and steric influences.

On this basis, we have been interested in supported metallocene possessing a spacer between the silica surface and the metallocene moiety, and the CpIndZrCl$_2$ anchored on silica with a spacer was prepared by reacting tosylated silica with the monoanion species holding the metallocene fragment through a spacer.[15] The catalyst activity of spacer-anchored metallocene was much higher than that of an ordinarily supported one, but the synthesis of monoanion species was too delicate to use for practical purposes.

In this article, three different preparation methods were applied for the anchoring of metallocene on silica with a spacer. To discover any difference in the catalyst properties among the anchored metallocenes that arose from the various anchoring methods, the chemical composition of the prepared catalyst and catalyst precursor was examined and the polymerization of ethylene was carried out with modified MAO as a cocatalyst. On the basis of the experimental results, the plausible anchoring pathway of zirconocene on silica and the active site structure of anchored zirconocene were proposed. Most of the experiments discussed in the present work were performed with the anchored catalyst possessing a CpIndZrCl$_2$ fragment as a metallocene site and a hexamethyltrisiloxane or pentamethylene unit as a spacer.

EXPERIMENTAL

Materials

Ethylene (polymerization grade, 99.5% purity, Korea Petrochemical Ind. Co., Korea) was dried by passing through two columns of P$_2$O$_5$. 1,5-Dibromopentane (Aldrich Chemical Co.) and 1,5-dichlorohexamethyltrisiloxane (United Chemical Tech. Inc.) were distilled from calcium hydride just prior to use. CpNa (2.5M solution in THF), TlOEt, and n-BuLi were used as purchased from Aldrich Chemical Co. Methylaluminoxane (MAO) was a commercial grade of modified MAO (MMAO-4, 6.4 wt %, Akzo) and used as a cocatalyst without further purification. Silica (SiO$_2$, Davidson, grade #952) was adopted after calcination at 600°C for 10 h. Toluene and tetrahydrofuran (Duksan Chem., Korea) were distilled from a sodium–benzophenone complex.

Preparation of Anchored Catalyst

The supported catalysts on the basis of cyclopentadienylindenylzirconium dichloride (CpIndZrCl$_2$) anchored on silica with a hexamethyltrisiloxane spacer (ZATS) and a pentamethylene spacer (ZAPM) were prepared by three different procedures:

Route 1 (new approach): As a newly developed method,[15] anchoring, which is the only heterogeneous reaction, was simply achieved by the mixing of the monoanionic materials with the tosylated silica which was pretreated with tosyl chloride. The zirconocene having a hexamethyltrisiloxane substituent, Tl$^+$Cp$^-$—Si(CH$_3$)$_2$—O—Si(CH$_3$)$_2$—O—Si(CH$_3$)$_2$—Cp—ZrIndCl$_2$ (**1**), was prepared by reacting the dithallium salt (**2**) of 1,5-dicyclopentadienylhexamethyltrisiloxane (**3**) with 1 equivalent of indenylzirconium trichloride[16] in THF at room temperature for 2 h, and then **1** was reacted in toluene with tosylated SiO$_2$ (**7**) at 50°C for 15 h to prepare the anchored zirconocene, ZATS-1.

In addition, a zirconocene having a pentamethylene substituent, Li$^+$Cp$^-$—(CH$_2$)$_5$—Cp—ZrIndCl$_2$ (**6**), was obtained by replacing the dilithium salt (**5**) of 1,5-dicyclopentadienylpentamethylene (**4**) with **2** as shown in Scheme 1. Also, then, ZAPM-1 (**8**) was prepared by reacting **6** with **7.**

In an effort to examine the differences associated with the anchoring process of the metallocene, two other methods were applied to anchoring:

Route 2 (modified method): This method was composed of two reactions as shown in Scheme 2. At first, **5** was reacted with **7** to obtain the anions anchored on the silica surface (**9**). Then, the anchored metallocenes ZAPM-2 (**10**) would be formed by the metallation of **9** with IndZrCl$_3$. By using **2** instead of **5,** ZATS-2 was prepared.

Scheme 1

Route 3 (known method): This procedure as shown in Scheme 3 was basically analogous to those reported by others.[17–19] First, the lithiated silica (**11**) was obtained by treating silica with *n*-BuLi. The spacer-anchored silica (**12**) was prepared by the reaction of **11** with 1,5-dibromopentane followed by the incorporation of a Cp ligand (**13**) and formation of monoanion salt (**14**). Then, **14** was metallated with IndZrCl$_3$ to obtain ZAPM-3 (**15**). ZATS-3 was prepared by reaction of **11** and 1,5-dichlorohexamethyltrisiloxane in place of 1,5-dibromopentane.

Scheme 2

The silica-supported CpIndZrCl$_2$ (SiO$_2$/CpIndZrCl$_2$) was prepared by reacting zirconocene directly with a calcinated silica in toluene at 50°C for 15 h.[7,8]

Polymerization

To a 400-mL glass reactor, 100 mL of toluene and a necessary amount of the cocatalyst were added followed by the saturation of ethylene under atmospheric pressure. With a continuous flow of ethylene, the polymerization was initiated by injection of the catalyst. The produced polyethylene (PE) was precipitated in acidified methanol. The catalyst activity was estimated from the weight of the polymer produced per mole of zirconium in the catalyst for a unit time.

Measurements

The zirconium content of the prepared catalyst was measured by an inductively coupled plasma emmission spectrophotometer (ICP, JY38 Plus). The carbon analysis was carried out by an elemental analyzer (EA 1108, Carlo Erba) and the amount of the cyclopentadienyl ligand was measured by a UV spectrophotometer (UV-2000, Shimadzu).

The thermal properties of PE were measured by differential scanning calorimetry (DSC, DuPont TA 2000) at 20°C/min. The molecular weight and mo-

Scheme 3

lecular weight distribution were determined using gel-permeation chromatography (GPC, Waters 150C, Waters Associates) in 1,2,4-trichlorobenzene at 135°C, and the data were analyzed using a poly-styrene calibration curve.

RESULTS AND DISCUSSION

Chemical Composition of Anchored CpIndZrCl$_2$

The chemical compositions of the prepared cata-lysts and catalyst precursors were measured as shown in Table I. From the results, it should be noted that the zirconium content of the anchored

catalyst is strongly dependent upon the anchoring method employed (Route 1: 3.4–3.5 wt % > Route 2: 1.9–2.0 wt % > Route 3: 0.6–0.7 wt %) and increase remarkably (five to six times) with the new anchoring method (Route 1). It was also note-worthy that the anchoring method with more het-erogeneous reaction steps leads to the formation of the catalyst containing less zirconium content. Another feature to be noted was that 3.5 wt % of zirconium attached to the silica surface is the largest amount ever reported as far as we know. This result positively suggested that the charac-teristics of the heterogenized metallocene can be controlled with the newly employed method by

Table I   Chemical Composition of Prepared Catalyst and Catalyst Precursor

Catalyst	Catalyst Precursor	C (wt %)	Tosyl (mmol/g cat)	TS[a] or PM[b] (mmol/g cat)	Cp (mmol/g cat)	Zr (wt %)	Zr (mmol/g cat)
	SiO$_2$/tosyl	6.0	0.84				
ZATS-1						3.4	0.39
ZAPM-1						3.5	0.39
ZATS-2	SiO$_2$/tosyl/Cp–TS–Cp	13.5		0.62		1.9	0.20
ZAPM-2	SiO$_2$/tosyl/Cp–PM–Cp–Na	9.2		0.64		2.0	0.21
ZATS-3	SiO$_2$/TS/Cp	4.8			0.21	0.6	0.07
	SiO$_2$/TS	3.6		0.50			
ZAPM-3	SiO$_2$/PM/Cp	4.4			0.24	0.7	0.08
	SiO$_2$/PM	3.1		0.52			
SiO$_2$/CpIndZrCl$_2$						0.8	0.09

[a] TS, hexamethyltrisiloxane spacer.
[b] PM, pentamethylene spacer.

adopting a variety of types of ligand, metal, spacer, and silica.

In addition, it was observed that the anchored metallocenes made from the same procedure exhibited almost identical zirconium content regardless of the spacer structure. For example, ZATS-1 and ZAPM-1 resulted from the new Route 1 had the respective zirconium content of 3.4 and 3.5 wt %.

The chemical compositions of the prepared catalysts and catalyst precursors were found to be a very convenient parameter for distinguishing the features associated with the anchoring pathway as shown in Figure 1. From the carbon content of tosylated silica, it was found that 0.84 mmol of tosyl groups were placed on 1 g of silica. This indicated that ca. 85% of the —OH groups of the total —OH on the silica surface were substituted to tosyl groups.

With Route 1, ca. 46% of tosyl groups were reacted with monoanion species to form the active site **A**. The obtained catalyst had only one structure of the active site so that it could be noted as a real heterogeneous single-site catalyst.

The important feature to be noted was that there is no inefficient metallation step in the heterogeneous condition. The only heterogeneous reaction was the last step which is a anchoring step between the tosylated silica and the monoanion species connected with the metallocene fragment through a spacer.

The new method (Route 1) seemed to have many potential benefits over the other known heterogenation methods. First, by minimizing the heterogeneous and uncharacterizable reaction steps, the uncertainty of properties of the active sites could be minimized. Second, the presence of a spacer group between the metallocene unit and silica surface should provide the similarity of the active site generated by the anchored catalyst to that formed by the homogeneous catalyst. Third, a better control of heterogenation could be realized using this procedure. Various kinds of the anchored metallocene could be synthesized by combination of different types of ligands, metals, and spacers. Putting all these effects together will enhance the probability to achieve heterogenation without losing the characteristics of a single active site of the soluble catalyst system as well as the widening of industrial applicability which is absolutely the eventual purpose of the immobilization of metallocene.

For Route 2, the reaction between the tosylated silica and the dianion of the spacer compound was performed in ca. a 75% yield (ca. 63% based on total —OH) to give possibly two types of the surface-modified silica (**a** and **b**). The "dead or inert" site **b** could not be contributed to anchoring zirconocene but increased the carbon content of the catalyst. Only site **a** could form the active site **A** as well as site **B** by double anchoring. It was estimated that site **B** caused the decrease of the catalyst activity due to its low activity but increased the Zr content of the catalyst.

Recently, a very interesting route to prepare a modified silica surface which has cyclopentadiene units with a functionalized silane fragment by an alkylidene spacer group was reported,[17–19] although there has been no example to adopt this method for the preparation of immobilized metallocene as an olefin polymerization catalyst. One common feature of the reported process is that most of the reactions were conducted in a heterogeneous condition, which indicated that the real structure and chemistry involved in this procedure were hardly characterizable.

At Route 3 similar to the above-reported procedure, the treatment of silica with n-BuLi resulted in the formation of an —OLi site in 87% yield. The materials obtained by mixing the lithiated silica with the dihalides such as 1,5-dichlorohexamethyltrisiloxane and 1,5-dibromopentane contained 3.6 and 3.1 wt % of carbon, respectively, which represented that ca. 57% of the —OLi sites were transformed to sites **c** and **d** by the added dihalide (ca. 50% based on total —OH). Site **c** could not be reacted further as site **b,** and only site **d** reacted with CpLi to incorporate the Cp ligand in ca. a 46% conversion.

From the Cp ligand content of the product obtained by the reaction between the modified silica mentioned previously and CpLi or CpNa, it turned out that only ca. 23% of —OH sites based on the original silica surface have been replaced with the —O–spacer–Cp bonded to silica. The obtained silica was metallated with $IndZrCl_3$ to form the sites **A′** and **B′**. As with site **B** mentioned previously, site **B′** was less efficient in polymerization than was site **A′**. In addition, the low active sites such as **C, D,** and **E** could be formed by the reaction of $IndZrCl_3$ with the unconverted —OLi sites. These results illustrated clearly that the many reaction steps under the heterogeneous condition lead to a drastic drop of anchoring immobilization efficiency.

Although the reaction pathway of Figure 1 was plausible based on the chemical analysis, some important features could be pointed out: The key

Figure 1   Plausible pathway of anchoring zirconocene on silica with different routes and proposed structure of the active site.

Table II   Polymerization of Ethylene Initiated by Various Catalysts and MMAO at 40°C

Catalyst	Activity[a]	M_w ($\times 10^{-3}$)	M_w/M_n	T_m (°C)
CpIndZrCl$_2$	2343	223	3.0	135
SiO$_2$/CpIndZrCl$_2$	130	301	3.9	134
ZATS-1	557	254	4.8	134
ZAPM-1	658	221	3.9	135
ZATS-2	284	204	4.2	135
ZAPM-2	368	196	3.9	134
ZATS-3	236	256	3.3	134
ZAPM-3	298	204	3.4	135

Polymerization condition: [Zr] = 3.0–5.8 $\times$ 10^{-6} mol/L, [Al]/[Zr] = 5000, 40°C, 2 h.
[a] Activity: kg PE/mol Zr h^{-1} atm^{-1}.

aspect of the new anchoring process (Route 1) was the simplicity of the procedure. As a consequence, it was anticipated that the degree of flexibility of the process should be very limited. Furthermore, the reaction between the tosyl group on modified silica, which is an excellent leaving group, and the monoanionic species was expected to go on very effectively to end up with the formation of the designed anchored metallocene (site **A**). On the other hand, as for the other two routes, some degree of flexibility could be permitted. Both procedures included the reaction step between the modified silica and the difunctionalized reactants: the dianion species in Route 2 and the dihalide compounds in Route 3, respectively. These difunctionalized reactants were able to make a bond not only with one end to form a desired catalyst precursor for metallation but also with both reactive sites simultaneously on the silica surface to result in the creation of a "dead or inert" site for further reaction. However, these "dead or inert" sites had been counted as potential metallation sites based on carbon analysis of the catalyst precursor although these sites were clearly no longer reactive to provide the expected metallation.

Polymerization Behaviors of Anchored CpIndZrCl$_2$

To investigate the effect of the anchoring method on the catalytic property of the prepared catalysts, the ethylene polymerization was conducted with these catalysts and MMAO in comparison with the corresponding homogeneous CpIndZrCl$_2$ as well as the usual supported catalyst SiO$_2$/CpIndZrCl$_2$ obtained by a direct impregnation of CpIndZrCl$_2$ with SiO$_2$. The experiment was carried out at 40°C with a constant [Al]/[Zr] ratio and the results were given in Table II.

The CpIndZrCl$_2$ anchored on silica with a hexamethyltrisiloxane or pentamethylene spacer (ZATS or ZAPM) had less catalyst activity than that of the unsupported free CpIndZrCl$_2$. But the catalyst activity of ZATS and ZAPM was much higher than that of SiO$_2$/CpIndZrCl$_2$. In other words, the catalyst activity of the silica-supported catalyst could be enhanced by introducing an appropriate spacer between zirconocene and the silica surface.

ZAPM exhibited higher activity than that of ZATS. This result was interpreted to mean that the pentamethylene spacer acts as an alkyl substituent group of electron-donating ability and the catalyst activity increases by electron enrichment of the metal center.[20]

Among the anchored catalysts, ZATS-1 and ZAPM-1 generated by the new method of Route 1 exhibited two to three times larger activities than those of ZATS-2, 3 and ZAPM-2, 3 made by the other methods. This result could be understood with the fact that only one structure of site **A** is obtained by Route 1 while less active sites such as **B** for Route 2 as well as **B′, C, D,** and **E** for Route 3 can be formed. In summary, the catalyst activity of the ZATS and ZAPM series decreased in the following order: ZAPM-1 > ZATS-1 $\gg$ ZAPM-2 > ZATS-2 $\sim$ ZAPM-3 > ZATS-3.

The weight-average molecular weight (M_w) of PE obtained with the used catalysts decreased in the following order: SiO$_2$/CpIndZrCl$_2$ > ZATS $\geq$ ZAPM $\geq$ unsupported CpIndZrCl$_2$. The polydispersity index (M_w/M_n) of PE produced by ZATS and ZAPM was higher than that of PE by CpIndZrCl$_2$, which could be understood because the structure of the active site is various as shown in Figure 1 and the distribution of the active sites

Table III   Polymerization of Ethylene Initiated by Various Catalysts and MMAO at 70°C

Catalyst	Activity[a]	M_w $(\times 10^{-3})$	M_w/M_n	T_m (°C)
CpIndZrCl$_2$	1452	56	2.6	135
SiO$_2$/CpIndZrCl$_2$	162	102	3.4	135
ZATS-1	1026	104	3.4	134
ZAPM-1	1324	98	3.6	134
ZATS-2	621	99	3.5	135
ZAPM-2	864	101	3.4	134
ZATS-3	289	96	3.0	135
ZAPM-3	351	97	3.0	134

Polymerization condition: [Zr] = 3.0–5.8 × 10^{-6} mol/L, [Al]/[Zr] = 5000, 70°C, 2 h.
[a] Activity: kg PE/mol Zr h^{-1} atm^{-1}.

is random to cause the variation in the distance[14] between active sites. The melting point (T_m) of PE was almost independent of the types of catalyst, which indicated that the produced polymer is linear PE.

To examine the effect of the polymerization temperature on catalyst behaviors, the polymerization of ethylene was also conducted with various catalysts at 70°C and the experimental results are shown in Table III.

Comparison of the activities between in Tables II and III revealed an even more important point: The activity of homogeneous metallocene was sharply reduced by increasing the polymerization temperature from 40 to 70°C. On the other hand, the activity of the anchored catalysts in Table III was much larger than that in Table II. As a result, ZAPM-1 displayed an almost identical activity with the unsupported homogeneous CpIndZrCl$_2$ at 70°C polymerization. These results illustrated an increased tolerance of the supported catalyst toward high temperature and strongly suggested that the anchored catalyst was found to maintain its thermal stability for the polymerization conditions.

The higher-activity characteristics of the anchored catalyst prepared through Route 1 was likely to be more pronounced for the polymerization at 70°C. The observed superiority of the new supporting method to the other ones could be other supporting evidence of the presence of the considerable amount of low active metal sites on the conventionally supported catalyst as mentioned previously.

It is generally recognized that the M_w of a polymer is very sensitive to the polymerization temperature in the case of a soluble metallocene

system.[21] On this basis, it was not so surprising to observe a drastic decrease of M_w from 223,000 at 40°C to 56,000 at 70°C for the unsupported soluble CpIndZrCl$_2$. This tendency could be effectively suppressed by the immobilization of a homogeneous catalyst, that is, the M_w of PE from the polymerization by the anchored catalysts at 40°C was only twice larger than that of PE at 70°C. It should be noted that the anchoring methods employed do not give an appreciable influence on the M_w of the formed polymers.

The effects of the MMAO amount on the catalyst activity and the M_w of PE were examined at

Figure 2 Effects of MMAO amount on catalyst activity for ethylene polymerization with various supported catalysts. Polymerization condition: [Zr] = 3.0–5.8 × 10^{-6} mol/L, 70°C, 2 h.

Figure 3 Effects of MMAO amount on molecular weight of PE obtained with various supported catalysts. Polymerization condition: [Zr] = 3.0–5.8 × 10^{-6} mol/L, 70°C, 2 h.

70°C and the results are given in Figures 2 and 3, respectively.

As is well known, the catalyst activity increased with increasing MMAO amount. The increment of the catalyst activities of ZATS and ZAPM was more profound than that of SiO$_2$/CpIndZrCl$_2$. At [Al]/[Zr] = 5000, the catalyst activity of ZAPM-1 was eight times higher than that of SiO$_2$/CpIndZrCl$_2$.

As shown in Figure 3, the M_w of PE decreased with increasing MMAO amount due to the chain-transfer reaction of MMAO.[22] The decrement in the M_w of PE produced by ZATS and ZAPM was more profound than that of PE by SiO$_2$/CpIndZrCl$_2$.

The particle morphology of the catalyst and the obtained PE was observed by using SEM. The SEM photographs of (A) ZATS-1 and (B) PE produced with ZATS-1 and (C) PE obtained with unsupported CpIndZrCl$_2$ are given in Figure 4.

Both particles of A and B had a spherical shape with a smooth surface and their diameters were estimated to be ca. 50 and 1000 μm, respectively. However, the PE of C was an irregular-shaped and small-size particle.

CONCLUSIONS

To accomplish an efficient attachment of metallocene to silica, a new procedure (Route 1) was designed and two anchored catalysts (ZATS-1 and ZAPM-1) holding different types of spacers (hexamethyltrisiloxane and pentamethylene) were synthesized. In addition, four anchored catalysts were also made based on the other methods: Route-2 (ZATS-2 and ZAPM-2) and Route-3 (ZATS-3 and ZAPM-3).

With the experimental study which distinguished the anchored zirconocenes from their preparation routes, the following points were noted;

Figure 4 SEM photographs of (A) ZATS-1 and (B) PE produced with ZATS-1 and (C) PE obtained with unsupported CpIndZrCl$_2$.

1. The zirconium content of the anchored metallocene was strongly dependent upon the preparation methods employed (Route 1 > Route 2 > Route 3) and increased up to 3.5 wt % with the new Route 1, which had just one reaction step under the heterogeneous condition.

2. By Route 1, it was possible to prepare the heterogeneous single-site catalyst which might have only one type of active site.

3. The activity of anchored catalysts decreased in the following order: ZAPM-1 > ZATS-1 ≫ ZAPM-2 > ZATS-2 ~ ZAPM-3 > ZATS-3.

4. The activity of ZAPM was higher than that of ZATS due to the electron-donating ability of a pentamethylene spacer.

5. The higher-activity characteristics of the anchored catalyst through Route 1 was even more pronounced at high polymerization temperature.

6. The M_w of PE obtained with the catalysts used decreased in the following order: $SiO_2/CpIndZrCl_2$ > ZATS ≥ ZAPM ≥ unsupported $CpIndZrCl_2$, while the M_w/M_n of PE produced by ZATS and ZAPM was slightly higher than that of PE by $SiO_2/CpIndZrCl_2$.

7. By anchoring zirconocene on silica, the influence of the polymerization temperature on the M_w of PE could be diminished.

8. With increasing MMAO amount, ZATS and ZAPM became more active than did $SiO_2/CpIndZrCl_2$, while the decrement in the M_w of PE produced by ZATS and ZAPM was more profound than that of PE by $SiO_2/CpIndZrCl_2$.

9. The replication of the morphology between the catalyst particle and the polymer particle was also maintained for the anchored zirconocene.

With the above results, it is believed that the method employed in this work can be one of the good alternatives to allow the rapid practical application of the heterogeneous metallocene catalyst.

REFERENCES

1. Britzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. Angew Chem Int Ed Engl 1995, 34, 1143.

2. Thaylor, A. M. Chem Eng News 1995, 73, 15.

3. Johnson, L. K.; Mecking, S.; Brookhart, M. J Am Chem Soc 1996, 118, 267.

4. Leclerc, M. K.; Brintzinger, H. H. J Am Chem Soc 1996, 118, 9024.

5. Kravchenko, R.; Masood, A.; Waymouth, R. M. Organometallics 1997, 16, 3635.

6. Ribeiro, M. R.; Deffieux, A.; Portela, M. F. Ind Eng Chem Res 1997, 36, 1224.

7. Kaminsky, W.; Renner, F. Makromol Rapid Commun 1994, 14, 239.

8. Kaminaka, M.; Soga, K. Makromol Rapid Commun 1994, 15, 593.

9. Chien, J. C. W.; He, D. J Polym Sci Part A Polym Chem 1991, 29, 2603.

10. Lee, D. H.; Yoon, K. B.; Huh, W. S. Macromol Symp 1995, 97, 185.

11. Lee, D. H.; Shin, S. Y.; Lee, D. H. Macromol Symp 1995, 97, 195.

12. Soga, K.; Kim, H. J.; Shiono, T. Macromol Rapid Commun 1994, 15, 139.

13. Soga, K.; Kim, H. J.; Shiono, T. Macromol Chem Phys 1994, 195, 3347.

14. Noh, S. K.; Kim, S. C.; Kim, J. H.; Lee, D. H.; Yoon, K. B.; Lee, H. B.; Lee, S. W.; Huh, W. S. J Polym Sci Part A Polym Chem 1997, 35, 3717.

15. Lee, D. H.; Yoon, K. B.; Noh, S. K. Macromol Rapid Commun 1997, 18, 427.

16. Morris, R. J.; Huffman, J. C. J Organomet Chem 1985, 501, 211.

17. Jutzi, P.; Heidemann, T.; Neumann, B.; Stammler, H. G. J Organomet Chem 1994, 472, 27.

18. van den Ancker, T. R.; Raston, C. L. Organometallics 1995, 14, 584.

19. Gao, H.; Angelici, R. J. J Am Chem Soc 1997, 119, 6937.

20. Möhring, P. C.; Coville, N. J. J Mol Catal 1992, 77, 41.

21. Resconi, L.; Bossi, S.; Abis, L. Macromolecules 1990, 23, 4489.

22. Chien, J. C. W.; De, H. J Polym Sci Polym Chem Ed 1991, 29, 1595.