

Copolymerization characteristics of homogeneous and in situ supported $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst

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Abstract

A newly synthesized catalyst, a pentamethylene bridged dinuclear zirconocene ($[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$), and its in situ supported catalyst were tested in a ethylene/1-hexene copolymerization and their performance was compared with those of Cp_2ZrCl_2 and $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$. When homogeneous $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst was used in the copolymerization, its activity decreased with comonomer incorporation (a negative comonomer effect) and it produced copolymer with a lower comonomer content than other catalysts, both of which were ascribed to the steric effect of the $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst. With in situ supported catalysts, the activity did not change much with the increase of 1-hexene content in contrast to the homogeneous catalysts. In situ supported catalysts produced copolymers with higher content of 1-hexene and lower melting point and crystallinity. The changes in the molecular weight and its distribution of the copolymer with in situ supporting were significant and dependant on the nature of the catalyst.

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1. Introduction

Metallocene catalysts with 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. They can also produce LLDPE with a low melting point and crystallinity which have improved processability and optical properties as resins for the blown and cast film manufacture [1].

Of these catalysts, various dinuclear metallocenes which contain two mechanically linked metallocene units recently have been prepared as new polymerization catalysts since the cooperative electronic and chemical interaction between two centers of these catalysts can yield a special catalytic activity. Jüngling and Mülhaupt [2] tested a phenylene bridged dinuclear zirconocenes in propylene polymerization and suggested an electron-drawing effect interacting two zirconium centers via the bridge. Green and coworkers [3] performed olefin polymerization with a dimethylsilyl-bridged dinuclear metallocene and found the effect of the bridge structure and ligand on the reaction characteristics of the catalysts. Hermann et al. [4] studied on a tin-bridged dinuclear

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zirconocene and proposed that only one center of the dinuclear complex is active during polymerization. Noh et al. [5,6] performed a systematic polymerization study on the dinuclear metallocenes with polymethylene and polysiloxane bridges. They found that dinuclear metallocenes display not only the distinguished properties from the mononuclear metallocene, but also strong dependence upon the length as well as the type of the bridge ligand. However, these studies were rather confined to homopolymerization so it is worth extending research work on the dinuclear zirconocenes to copolymerization experiments for its future use in production of copolymer.

The dinuclear zirconocene catalysts also need to be supported before their application to the existing industrial processes, since homogeneous catalyst are unsuitable for gas phase and slurry process. Metallocene catalysts usually have been supported on silica [7] or other supports [8–11]. But the activity of the supported catalyst is significantly reduced and it is not easy to mount bulky catalysts on such conventional support. As an effort to overcome these problems, authors applied an in situ supporting method to various metallocenes including a dinuclear zirconocene ($[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$) and obtained high activities in ethylene polymerization and polymers with good morphology [12]. The in situ supporting method, developed by Chu et al. [13], consists of introducing a metallocene catalyst into the reaction mixture containing MAO-treated silica (SMAO) and a co-catalyst and performing polymerization. Therefore, it is meaningful to prepare the in situ supported dinuclear zirconocene and test its copolymerization behavior for its application to production of LLDPE.

In this work, the copolymerization characteristics of a pentamethylene bridged dinuclear zirconocene ($[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$) and its in situ supported catalyst were studied in ethylene/1-hexene copolymerization and compared with those of other commercial catalysts (Cp_2ZrCl_2 and $rac-Et(Ind)_2ZrCl_2$). The changes in the catalytic activity, molecular weight of the copolymer and its distribution with incorporation of comonomer were examined to find the relationship between the catalytic behavior and the catalyst structure and the effect of the in situ supporting on the copolymerization behavior of metallocene catalysts.

2. Experimental

2.1. Materials

Nitrogen and ethylene gases were purified by passing through columns packed with molecular sieves 4A and Ridox[®] oxygen scavenger (from Fisher Scientific). Tetrahydrofuran (THF), hexane, toluene, diethylether (from Junsei) and 1-hexene (from Acros) were distilled over sodium/benzophenone ketyl under nitrogen. Modified methyl aluminoxane (MMAO, from Akzo Noble), trimethyl aluminum (TMA, from Aldrich), and MAO treated silica (SMAO, from Witco) which contains 23 wt.% aluminum were used without further purification. Commercial catalysts including bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2 , from Strem) and *rac*-ethylenebis(indenyl)zirconium dichloride ($rac-Et(Ind)_2ZrCl_2$, from Aldrich) were used as purchased.

In preparation of the dinuclear zirconocene catalyst, indene, *n*-butyl lithium (*n*-BuLi), tributyl tinchloride (Bu_3SnCl), trimethyl tinchloride (Me_3SnCl), sodium cyclopentadienid ($CpNa$), and 1,5-dibromopentane were purchased from Aldrich and used without further treatment.

2.2. Preparation of $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst

A pentamethylene bis(cyclopentadienylindenyl) zirconium dichloride ($[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$), was prepared in a large scale using the recipe developed by Noh et al. [5]. All operations were performed under nitrogen by 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, $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$, was finally obtained from recrystallization of the resultant mixture at -78 °C. The synthesized catalyst was characterized with FT-NMR spectrometer (VARIAN, MERCURY-300).

For preparation of the supported catalyst, SMAO powder was introduced into the reaction mixture

containing the metallocene catalyst and co-catalyst (TMA) to induce an in situ supporting effect during the polymerization process.

2.3. Polymerization

Reaction experiments were performed in a glass reactor of 250 ml volume. The reaction temperature was controlled by circulating a heating medium through the reactor jacket. The polymerization temperature was maintained at 60 °C. The reaction mixture was stirred by a magnet drive. The consumption rate of ethylene during the reaction was monitored by a mass flow meter.

The reactor was dried and purged with nitrogen before adding toluene (150 ml) and 1-hexene into the reactor at the set temperature. The reaction mixture was saturated with ethylene and the ethylene pressure was kept at a constant value of 0.1 MPa. For polymerizations with homogeneous catalyst, MAO was injected into the reactor and the polymerization was initiated by injecting metallocene. For reactions with in situ supported catalyst, TMA, metallocene and MAO-treated silica were introduced sequentially into the reactor before initiating the reaction. It was shown previously that TMA needs to be added as co-catalyst instead MMAO in reactions with in situ supported catalysts [12,13] After the reaction were carried out for 1 h, the resulting polymer was precipitated in an excess amount of methanol, filtered, and dried in a vacuum oven for 1 day.

2.4. Analysis

The average molecular weight (\bar{M}_w) and molecular weight distribution (MWD) of the polymer product were determined by gel-permeation chromatography (PL-GPC 210) at 145 °C, using 1,2,4-trichlorobenzene as eluent. The calibration curve for the molecular weight was prepared with polystyrene standards. The melting point (T_m) and crystallinity (X_c) of polymer were measured by differential scanning calorimeter (DSC, TA 2010). The sample was scanned while being heated from 25 to 200 °C at a rate of 10 °C/min, cooled and re-scanned using the same heating schedule. The 1-hexene percentage in the polymer chain was obtained by FT-IR (Biorad FTS-7). The data was analyzed by the calibration curve for the ratio of the

peak areas at 1380 and 1370 cm^{-1} as suggested by Nowlin et al. [14]. The film specimen was prepared by extrusion at 190 °C, 10 MPa for 30 s.

3. Results and discussion

3.1. Copolymerization characteristics of homogeneous $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst

$[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst synthesized was obtained as brown powder and was found to have the correct ^1H NMR spectra for the given catalyst structure (Fig. 1).

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

Table 1 shows the characteristics of copolymerization over homogeneous catalysts including $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$, Cp_2ZrCl_2 and $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$. As the 1-hexene charge increased the activity of $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst decreased, while those of Cp_2ZrCl_2 and $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ increased. The decrease of the activity of $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ with injection of comonomer, called a 'negative comonomer effect', is not usual but similar results have been reported for other bulky catalysts such as $\text{MeSi-[2-Me-4-Ph-Ind]}_2\text{ZrCl}_2$ [15] and $\text{rac-Me}_2\text{Si(2,4,6-Me}_2\text{-Ind)}_2\text{ZrCl}_2$ [16]. The percentage of 1-hexene in polymer from $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst was the least and increased at a slower rate compared to other catalysts. The $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ catalyst with an ansa-structure incorporated the highest amount of 1-hexene and the Cp_2ZrCl_2 catalyst also produced polymer with higher content of 1-hexene than that from $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst.

These unique copolymerization characteristics of $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst seem to be related to its structure of dinuclear zirconocene in which two metal centers are connected by a rigid pentamethyl group. Noh et al. [5] found that such steric hindrance of polymethylene bridged dinuclear zirconocene catalyst reduced the catalyst activity in ethylene polymerization in comparison to the mononuclear catalyst. As the 1-hexene content in the polymer

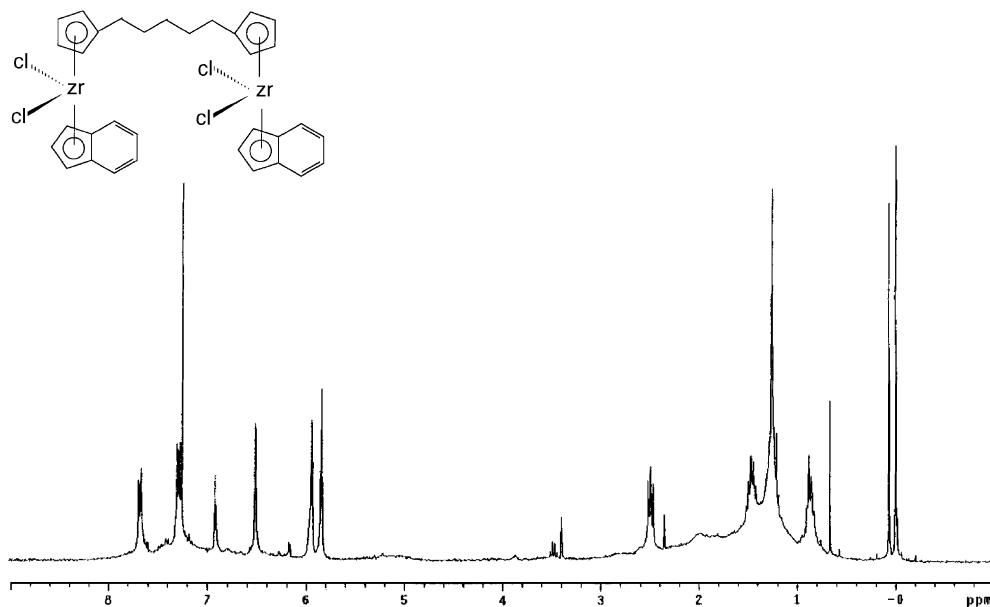


Fig. 1. Structure of the $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst and its ^1H NMR spectra.

Table 1

Properties of ethylene/1-hexene copolymers from homogeneous metallocene catalysts^a

| $[\text{H}]^b$ in reaction medium (mol/l) | Activity ^c | $[\text{H}]^b$ in polymer (mol.%) | X_c^d (%) | T_m^e (°C) | \bar{M}_w (g/mol) | M_w/M_n |
|--|-----------------------|-----------------------------------|-------------|--------------|---------------------|-----------|
| $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ | | | | | | |
| 0 | 3581 | 0.0 | 57.1 | 135.2 | 577600 | 2.70 |
| 0.053 | 2041 | 2.1 | 48.0 | 124.9 | 260600 | 3.17 |
| 0.107 | 1995 | 2.5 | 47.1 | 121.5 | 250100 | 2.98 |
| 0.213 | 1958 | 3.3 | 43.3 | 117.4 | 169400 | 2.85 |
| 0.320 | 1900 | 3.6 | 40.1 | 113.4 | 80000 | 2.70 |
| Cp_2ZrCl_2 | | | | | | |
| 0 | 3205 | 0 | 66.4 | 139 | 155100 | 2.71 |
| 0.053 | 6730 | 2.4 | 55.1 | 122.8 | 71400 | 2.43 |
| 0.107 | 6340 | 3.1 | 49.2 | 118.8 | 44900 | 2.21 |
| 0.213 | 6564 | 4.1 | 43.1 | 110.3 | 24100 | 1.93 |
| 0.320 | 6755 | 4.5 | 33.2 | 103.5 | 20200 | 1.98 |
| $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ | | | | | | |
| 0 | 3610 | 0 | 61.6 | 132 | 307400 | 2.7 |
| 0.053 | 6108 | 2.8 | 39.6 | 116 | 260500 | 2.89 |
| 0.107 | 7884 | 3.0 | 32.1 | 106 | 200500 | 2.86 |
| 0.213 | 7444 | 4.9 | 16.5 | 95 | 142700 | 2.79 |
| 0.320 | 11216 | 6.0 | 8.5 | 83 | 107700 | 2.81 |

^a Reaction conditions: co-catalyst MMAO; Al/Zr = 1000 (mole ratio of [Al] in the MMAO to [Zr] in the metallocene); temperature, 60 °C; pressure, 1 atm; time, 1 h; [Zr] in $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ = 2.64 μmol ; [Zr] in Cp_2ZrCl_2 = 2.56 μmol ; [Zr] in $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ = 2.41 μmol .

^b [H] means the concentration of 1-hexene.

^c Activity = [kg of polymer/mol. of Zr atm h].

^d Crystallinity of polymer (%) = $\Delta H_f \times 100 / \Delta H_f^0$ (ΔH_f is the heat of fusion of the samples as determined from the DSC curve, ΔH_f^0 is the heat of fusion folded-chain polyolefin crystals, 269.9 J/g for polyethylene).

^e Melting temperature of polymer.

increased, a steric congestion around the metal center due to bulkier comonomer and the bulky catalyst became worse to result in a severe inhibition of diffusion of ethylene or 1-hexene to the active sites of dinuclear zirconocene and insertion into the propagation chain. This steric hindrance seems to have caused a decrease in the propagation rate, which leads to a reduced activity at higher comonomer content. This steric effect seems to have overcompensated the activity enhancement due to increased polymer solubility with 1-hexene incorporation (“comonomer effect”) [17] so that overall catalytic activity decreased with comonomer incorporation. It also makes incorporation of 1-hexene into the polymer more difficult to result in a lower content of comonomer than other metallocenes.

The crystallinity of the copolymer obtained from $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ decreased at a slower rate with comonomer incorporation than those of the other catalysts. And its melting temperature decreased at a lower rate to result in the highest melting point among those for the three metallocenes. The lower rates of the decrease in the crystallinity and melting point of the copolymers obtained from the $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst originate from the lower contents of 1-hexene in those copolymers than those in the copolymers from other catalysts. The existence of 1-hexene in the copolymer makes the crystalline ethylene chain amorphous and lowers the melting point of the copolymer.

The molecular weight of the copolymers from $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst decreased rapidly with comonomer incorporation even though it was very high at zero comonomer content. The higher molecular weight of the homopolymer obtained from $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst than those for other catalysts was ascribed to the steric hindrance of the catalyst which caused inhibition of β -hydride transfer to the metal [18]. The decrease of the molecular weight with comonomer incorporation is common for copolymerization with metallocenes and is known to be due to 1-hexene incorporation favoring chain termination reactions [19].

The polydispersity of the copolymer from $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst became a little bit broader as the 1-hexene charge in the reactor increased and then decreased to the original level of the homopolymer. It contrasted to the steady decrease of

the polydispersity of the copolymer from Cp_2ZrCl_2 or the constancy of the polydispersity of the copolymer from $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$. But almost all the values of the polydispersity remained below 3.0.

3.2. Copolymerization over in situ supported catalysts

The $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst was supported by an in situ method and its copolymerization characteristics were analyzed with respect to those of homogeneous catalyst. These results are as shown in Table 2 along with those of other commercial metallocenes. The reaction profiles during copolymerization with $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst (Fig. 2) show that the reaction characteristics change significantly with in situ supporting. With in situ supported catalyst the ethylene consumption rate was maintained at a rather constant value, while the homogeneous catalyst showed a decaying type of reaction profile. The profile for the in situ supported $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst in the copolymerization looks similar to the typical profile for a supported metallocene catalyst, which indicates that in situ supporting is effective in stabilizing the catalytic activity like the conventional supporting method.

Fig. 3 shows the changes in the catalytic activities with 1-hexene incorporation for $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ and other metallocenes. The level of the activities of in situ supported catalysts decreased to the one-third to one-tenth of those for the homogeneous catalyst. However, the activities of in situ supported catalysts did not change much with 1-hexene incorporation in contrast to the large decrease or increase in the activities of homogeneous catalysts. The lower activity of an in situ supported catalyst seems to be caused by blocking a side of the metallocene catalyst by the support. The “negative comonomer effect” or “comonomer effect” during copolymerization shown by the homogeneous catalysts was not apparent for in situ supported catalyst.

Fig. 4 shows the changes in the 1-hexene content in the copolymer with in situ supporting. In situ supported $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst produced copolymers with higher comonomer content than its homogeneous counterpart. Similar results were obtained for other in situ supported catalysts,

Table 2

Properties of ethylene/1-hexene copolymers from in situ supported metallocene catalysts^a

| [H] ^b in reaction medium (mol/l) | Activity ^c | [H] ^b in polymer mol.%) | X _c ^d (%) | T _m ^e (°C) | \bar{M}_w (g/mol) | M _w /M _n |
|---|-----------------------|------------------------------------|---------------------------------|----------------------------------|---------------------|--------------------------------|
| In situ supported [(CH ₂) ₅ (C ₅ H ₄) ₂][(C ₉ H ₇)ZrCl ₂] ₂ | | | | | | |
| 0 | 462 | 0.0 | 43.7 | 136.8 | 504500 | 2.50 |
| 0.053 | 432 | 2.9 | 34.8 | 123.2 | 243300 | 2.64 |
| 0.107 | 419 | 3.2 | 34.3 | 119.9 | 233600 | 3.09 |
| 0.213 | 599 | 3.5 | 31.0 | 114.1 | 199600 | 3.37 |
| 0.320 | 455 | 3.8 | 30.7 | 110.0 | 133700 | 3.58 |
| In situ supported Cp ₂ ZrCl ₂ | | | | | | |
| 0 | 994 | 0 | 63.2 | 133.7 | 240500 | 3.20 |
| 0.053 | 1084 | 2.8 | 38.5 | 121.8 | 171600 | 3.00 |
| 0.107 | 788 | 3.2 | 31.2 | 115.6 | 99800 | 3.80 |
| 0.213 | 850 | 4.4 | 27.5 | 105.7 | 55100 | 4.27 |
| 0.320 | 834 | 4.8 | 18.8 | 91.7 | 40000 | 3.77 |
| In situ supported rac-Et(Ind) ₂ ZrCl ₂ | | | | | | |
| 0 | 1603 | 0 | 57.8 | 133.2 | 232100 | 2.69 |
| 0.053 | 2357 | 2.7 | 39.8 | 115.6 | 224100 | 2.88 |
| 0.107 | 2763 | 3.1 | 27.6 | 103.8 | 76900 | 2.79 |
| 0.213 | 1166 | 4.9 | 11.4 | 89.0 | 48600 | 2.64 |
| 0.320 | 1137 | 6.7 | 6.2 | 78.8 | 46100 | 2.12 |

^a Reaction conditions: co-catalyst TMA; [Al]/[Zr] = 1000 (mole ratio of [Al] in the TMA to [Zr] in the metallocene); temperature, 60 °C; pressure, 1 atm; time, 1 h; [Al] in SMAO used for in situ supporting = 1.4 mmol; [Zr] in [(CH₂)₅(C₅H₄)₂][(C₉H₇)ZrCl₂]₂ = 2.64 μmol; [Zr] in Cp₂ZrCl₂ = 2.56 μmol; [Zr] in rac-Et(Ind)₂ZrCl₂ = 2.41 μmol.

^b [H] means the concentration of 1-hexene.

^c Activity = [kg of polymer/mol. of Zr atm h].

^d Crystallinity of polymer (%) = $\Delta H_f \times 100 / \Delta H_f^0$ (ΔH_f is the heat of fusion of the samples as determined from the DSC curve, ΔH_f^0 is the heat of fusion folded-chain polyolefin crystals, 269.9 J/g for polyethylene).

^e Melting temperature of polymer.

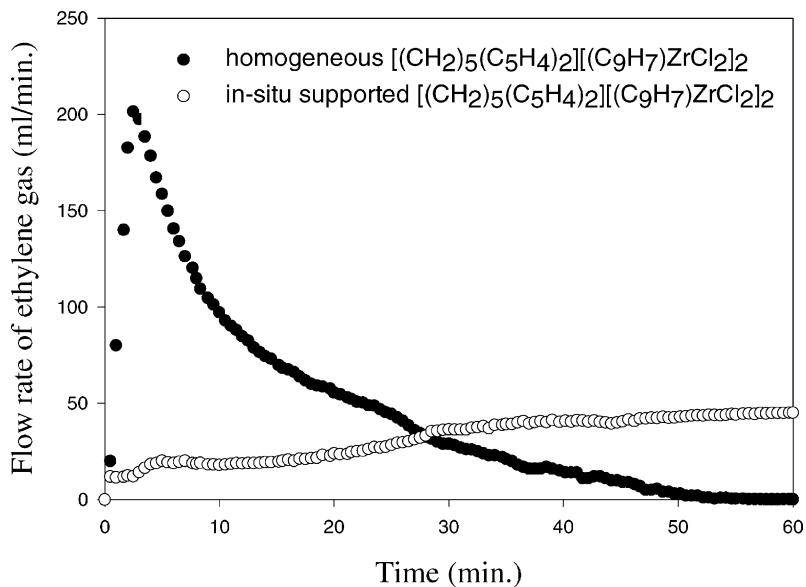
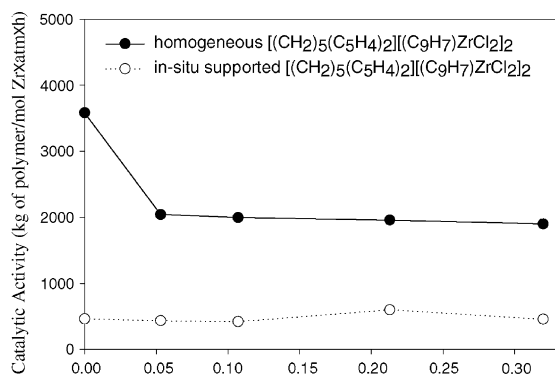
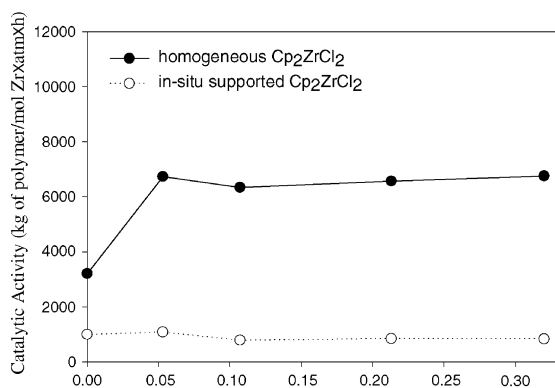


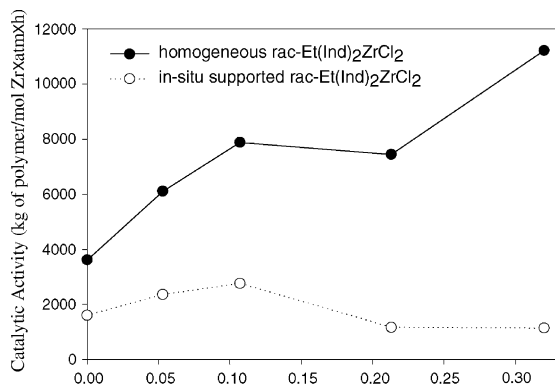
Fig. 2. Kinetic behavior of ethylene/1-hexene copolymerization with [(CH₂)₅(C₅H₄)₂][(C₉H₇)ZrCl₂]₂ catalysts (2.64 μmol Zr; Al_{[MAO]or[TMA] / Zr = 1000; Al of SMAO, 1.4 mmol; 60 °C; 1 atm).}



(a) 1-Hexene in the reaction medium (mol/L)

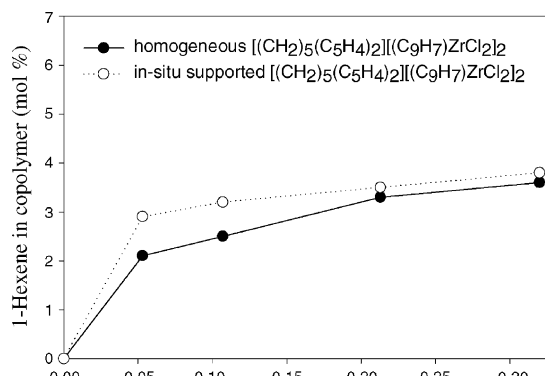


(b) 1-Hexene in the reaction medium (mol/L)

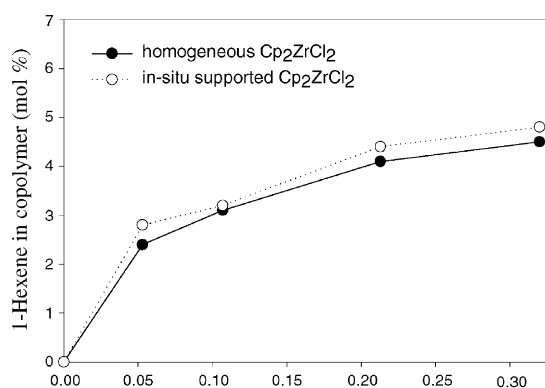


(c) 1-Hexene in the reaction medium (mol/L)

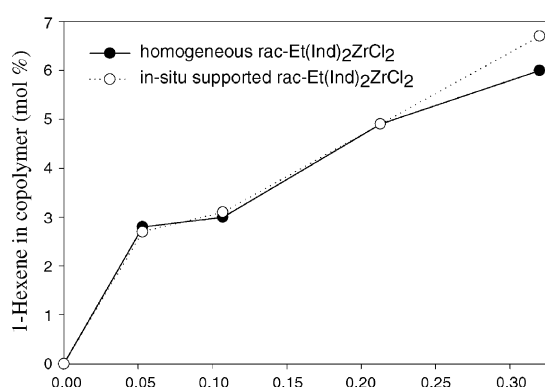
Fig. 3. Trends of catalytic activity of different homogeneous and in situ supported metallocene catalysts in ethylene/1-hexene copolymerization ($[(CH_2)_5(C_5H_4)_2] [(C_9H_7)ZrCl_2]_2$ 2.64 μ mol Zr; Cp_2ZrCl_2 2.56 μ mol Zr; $rac-Et(Ind)_2ZrCl_2$ 2.41 μ mol Zr; $Al_{[MAO]or[TMA]}/Zr = 1000$; Al of SMAO, 1.4 mmol; 60 °C; 1 atm; 1 h).



(a) 1-Hexene in the reaction medium (mol/L)



(b) 1-Hexene in the reaction medium (mol/L)



(c) 1-Hexene in the reaction medium (mol/L)

Fig. 4. Trends of 1-hexene content in the copolymer from different homogeneous and in situ supported metallocene catalysts in ethylene/1-hexene copolymerization ($[(CH_2)_5(C_5H_4)_2] [(C_9H_7)ZrCl_2]_2$ 2.64 μ mol Zr; Cp_2ZrCl_2 2.56 μ mol Zr; $rac-Et(Ind)_2ZrCl_2$ 2.41 μ mol Zr; $Al_{[MAO]or[TMA]}/Zr = 1000$; Al of SMAO, 1.4 mmol; 60 °C; 1 atm; 1 h).

even though the degrees of the changes were smaller. These observations were different from the results for the metallocenes supported by a conventional method, where the steric hindrance from the support decreases the amount of 1-hexene incorporated [19]. It seems that these differences are due to the fact that for in situ supported catalysts new catalytic sites are continuously formed on the surface of the silica particles by the metallocene remaining in the liquid phase during polymerization. According to Chu et al. [13], the active sites of in situ supported metallocenes are generated continuously by interaction of the homogeneous catalyst with the silica treated with MAO. On the newly formed catalytic sites of in situ supported metallocene there would be less amount of polymer matrix formed than on the sites of the homogeneous catalyst which have participated in the reaction from the beginning. Therefore, it would be easier for 1-hexene to approach and get incorporated to the sites of the in situ supported catalysts than the sites of the homogeneous catalyst so that a higher content of comonomer in the polymer is obtained by the in situ supported catalysts.

As the copolymers prepared from in situ supported catalysts including $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ contained higher amount of 1-hexene than those from the homogeneous catalysts, their crystallinity decreased accordingly (Fig. 5). The melting points of the copolymer from in situ supported catalysts were also found to be slightly lower than those for the homogeneous catalyst (Table 2).

When the molecular weights of the copolymers were compared (Fig. 6), those from the in situ supported catalysts decreased with increased comonomer charge as in the case of homogeneous catalysts. But the relative magnitudes of the molecular weight of the polymers from the homogeneous and in situ supported catalysts depended on the nature of the catalyst. For the $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst, in situ supported catalyst produced polymers with higher molecular weight than the homogeneous catalyst at the comonomer concentration over 0.1 mol/l, while it gave lower molecular weight at the comonomer concentration lower than 0.1 mol/l. The molecular weights of the polymers from the in situ supported Cp_2ZrCl_2 were higher than those for the homogeneous Cp_2ZrCl_2 catalyst, while the reverse was true in the case of $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$. These behaviors contrast to

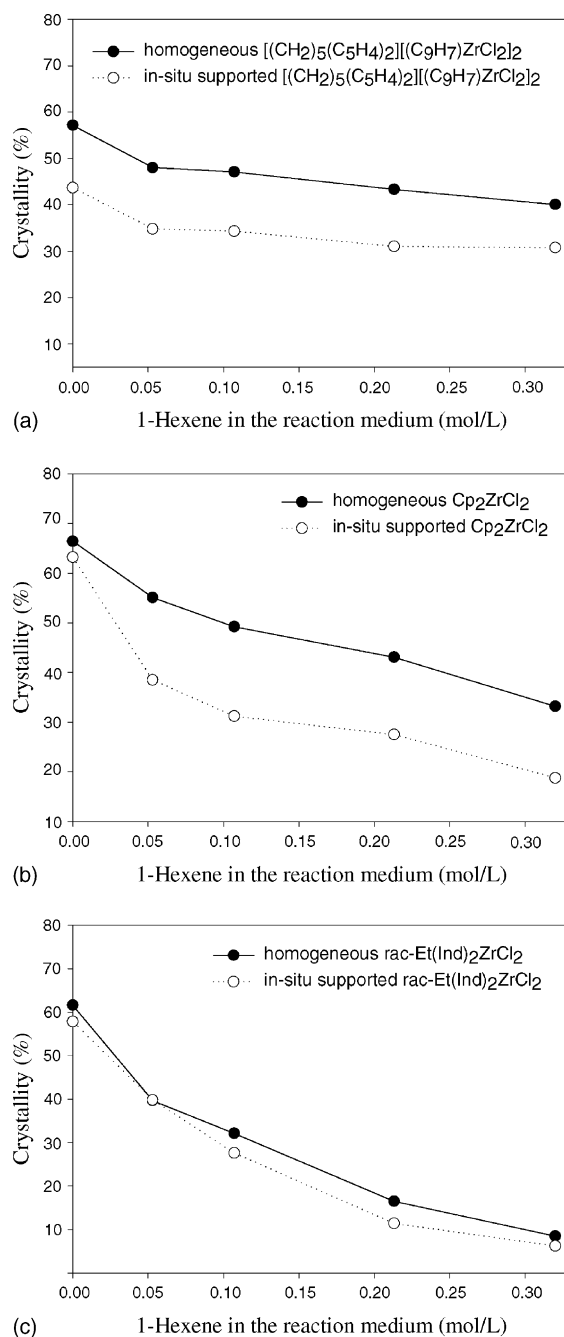
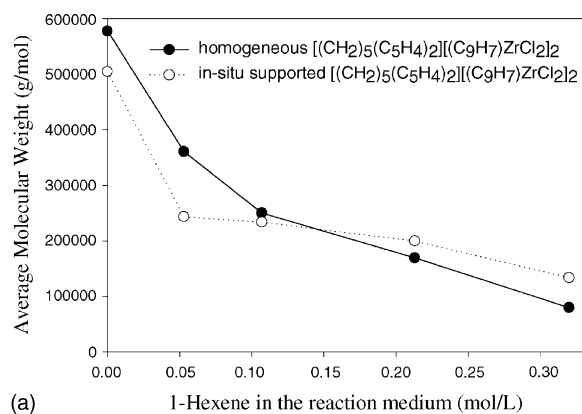
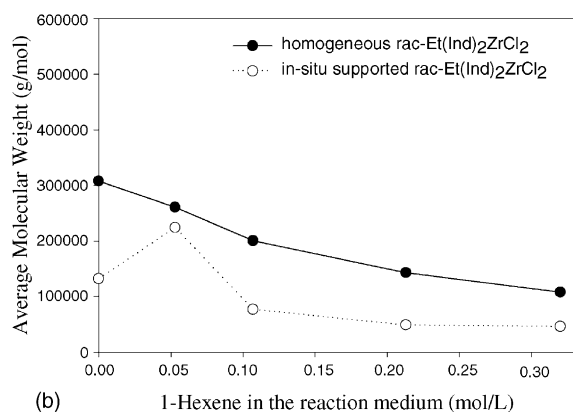


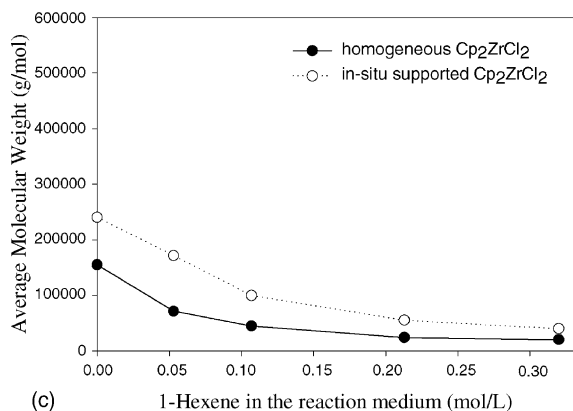
Fig. 5. Trends of crystallinity of the copolymer from different homogeneous and in situ supported metallocene catalysts in ethylene/1-hexene copolymerization ($[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ 2.64 $\mu\text{mol Zr}$; Cp_2ZrCl_2 2.56 $\mu\text{mol Zr}$; $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ 2.41 $\mu\text{mol Zr}$; $\text{Al}_{[\text{MAO}] \text{ or } [\text{TMAI}]} / \text{Zr} = 1000$; Al of SMAO, 1.4 mmol; 60 °C; 1 atm; 1 h).



(a)



(b)



(c)

Fig. 6. Trends of average molecular weight of the copolymer from different homogeneous and in situ supported metallocene catalysts in ethylene/1-hexene copolymerization ($[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ 2.64 μ mol Zr; Cp_2ZrCl_2 2.56 μ mol Zr; $rac-Et(Ind)_2ZrCl_2$ 2.41 μ mol Zr; $Al_{[MAO]_{or}[TMA]}/Zr = 1000$; Al of SMAO, 1.4 mmol; 60 °C; 1 atm; 1 h).

those of catalysts supported by a traditional method, since the molecular weight of copolymer from the supported catalyst is known to be higher than that for the homogeneous catalyst. The increase in the molecular weight of copolymer from supported metallocene was ascribed to the steric hindrance of support preventing β -hydride transfer [19]. This explanation can be partly applicable to the in situ supported catalyst since the polymerization over the in situ supported catalyst also takes place on the surface of support (SMAO). It was also found that chain transfer to the excess alkyl aluminum co-catalyst in the reaction mixture inhibit chain growth significantly in the polymerization over in situ supported metallocenes [20]. The steric hindrance by the support seemed to increase the molecular weight of the polymer from in situ supported catalysts while the inhibition by the excess TMA seemed to decrease it. So the different value of molecular weight for each catalyst may be the result from different combination of these effects. But how these factors affected the copolymerization with different catalyst at various comonomer concentrations are not clear from the obtained result.

The polydispersity of the copolymer from the in situ supported $[(CH_2)_5(C_5H_4)_2][(C_9H_7)ZrCl_2]_2$ catalyst increased steadily with increased 1-hexene content, while that of the copolymer from the homogeneous catalyst decreased at 1-hexene concentrations higher than 0.05 mol/l (Table 2). In case of in situ supported Cp_2ZrCl_2 , the polydispersity increased significantly with incorporation of the comonomer, while that of the copolymer from the homogeneous Cp_2ZrCl_2 catalyst decreased continuously. On the other hand, the polydispersity of the copolymer from in situ supported $rac-Et(Ind)_2ZrCl_2$ decreased as the amount of comonomer in the polymer increased, which also contrast to the constant polydispersity of the polymer from homogeneous $rac-Et(Ind)_2ZrCl_2$. These results show that molecular weight distribution of the polymer from metallocene catalysts changes considerably with in situ supporting.

These results indicate that in situ supported metallocenes produce copolymer products with a higher 1-hexene content, lower crystallinity and lower melting point than their homogeneous forms. But the changes in the molecular weight and its distribution of the copolymer product with in situ supporting were rather dependent on the nature of the catalyst. These

results show that the copolymerization characteristics of the metallocene catalysts change significantly with in situ supporting. Therefore, it seems necessary to study the behavior of in situ supported metallocene catalysts in copolymerization further for the industrial application of this efficient supporting method.

4. Conclusions

The newly synthesized pentamethylene bridged dinuclear zirconocene catalyst was tested in ethylene/1-hexene copolymerization and its performance was compared with those of Cp_2ZrCl_2 and $\text{rac-Et(Ind)}_2\text{ZrCl}_2$. The dinuclear zirconocene catalyst showed a decrease in the catalytic activity with increased comonomer charge (a negative comonomer effect), which contrast to the cases of other metallocenes. The copolymer from that catalyst also had a lower comonomer content and showed a rapid drop of the molecular weight with incorporation of comonomer. These unique characteristics of $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst were ascribed to the steric hindrance of the catalyst with a dinuclear structure.

When the metallocene catalysts including $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ were supported by in situ method, their copolymerization characteristics changed significantly. Their catalytic activity did not change much with the increase in 1-hexene content even though the level of the activities of in situ supported catalysts was lower. With in situ supported catalysts, higher amount of 1-hexene was incorporated to yield polymers with lower melting point and crystallinity in comparison to the homogeneous catalysts. The molecular weight and polydispersity of the polymer from in situ supported $[(\text{CH}_2)_5(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ catalyst became lower at a low comonomer content but reached higher values at high concentrations than those from homogeneous catalyst, which were different from the behaviors of Cp_2ZrCl_2

and $\text{rac-Et(Ind)}_2\text{ZrCl}_2$. These data on the copolymerization characteristics of various in situ supported catalysts would be useful for industrial application of the in situ supporting method to metallocene catalysts.

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