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Polymerization of Ethylene Initiated with Trisiloxane-bridged Heterometallic Dinuclear Metallocene

Dong-ho Lee*, Hun-bong Lee, Woo Sik Kim, Kyung Eun Min, Lee Soon Park, Kwan Ho Seo, and Inn Kyu Kang

Department of Polymer Science, Kyungpook National University, Taegu 702-701, Korea

Seok Kyun Noh and Chang Keun Song

School of Chemical Engineering and Technology, Yeungnam University, Kyungsan 712-749, Korea

Sang Sun Woo and Hyun Joon Kim

R&D Center, Samsung General Chemicals, Ltd., Taejon 305-714, Korea

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Abstract : The new trisiloxane-bridged heterometallic dinuclear metallocenes, hexamethyltrisiloxanediyl (cyclopentadienyltitanium trichloride)(cyclopentadienylindenyl zirconium dichloride), Cl_3Ti-$Cp(CH_3)_2Si$-O-$Si(CH_3)_2$-O-$Si(CH_3)_2$-Cp-$ZrIndCl_2$ (1) and hexamethyltrisiloxanediyl(cyclopentadienylindenylhafnium dichloride)(cyclopentadienylindenyl zirconium dichloride), Cl_2IndHf-$Cp(CH_3)_2Si$-O-$Si(CH_3)_2$-O-$Si(CH_3)_2$-Cp-$ZrIndCl_2$ (2) connecting two dissimilar metallocenes were synthesized and used for ethylene polymerization in the presence of modified methylaluminoxane (MMAO) cocatalyst. The catalytic activity of heterometallic dinuclear metallocenes, **1** and **2** was lower than that of corresponding mononuclear metallocene as well as two physically mixed catalysts, $CpTiCl_3/Cp_2ZrCl_2$ and Cp_2HfCl_2/Cp_2ZrCl_2. On the other hand, MWD of PE obtained with **1** and **2** was remarkably broader (M_w/M_n became up to 9.4) than those of PEs prepared with the corresponding mononuclear metallocenes and mixed catalysts. With analysis by GPC and CFC, it was found that PE produced by the heterometallic dinuclear metallocenes exhibited the definite bimodal GPC curves that should cause the broadening of MWD.

Introduction

Since the discovery that Cp_2ZrCl_2 with a methylaluminoxane cocatalyst acts as a homogeneous catalyst for ethylene polymerization, many efforts have been devoted to the developments of the various kinds of metallocenes that polymerized not only ethylene, propylene, styrene but polar monomers.[1] Recently the synthesis[2] of polysiloxane-bridged ansa-metallocenes and their polymerization behaviors[3,4] were reported. In addition, we studied the polymerization of ethylene[5] and styrene[6] by using various polysiloxane-bridged dinuclear metallocenes as a polymerization catalyst.

Our interests in the polysiloxane-bridged dinuclear metallocenes are originated from the idea that these compounds could be a suitable model for the immobilized metallocenes[7] on the silica surface.

As a part of our research work, here we described the polymerization of ethylene initiated with the new siloxane-bridged heterometallic dinuclear metallocenes, hexamethyltrisiloxanediyl(cyclopentadienyltitanium trichloride)(cyclopentadienylindenylzirconium dichloride), Cl_3Ti-$Cp(CH_3)_2Si$-O-Si-$(CH_3)_2$-O-$Si(CH_3)_2Cp$-$ZrIndCl_2$ **(1)** and hexamethyltrisiloxanediyl(cyclopentadienylindenylhafnium dichloride)(cyclopentadienylindenylzirconium dichloride), Cl_2IndHf-$Cp(CH_3)_2Si$-O-$Si(CH_3)_2$-O-Si-

*e-mail : leedh@knu.ac.kr

$(CH_3)_2$Cp-ZrIndCl$_2$ (2) containing two dissimilar metallocenes with trisiloxane connection. The molecular weight distribution (MWD) and thermal properties of the obtained polyethylene (PE) were examined. The fractionation of PE was carried out by cross fractionation chromatography (CFC).

Experimental

Materials. Ethylene (polymerization grade, 99.5% purity, Korea Petrochemical Ind. Co., Korea) was dried by passing through two column of P_2O_5. Monometallic metallocenes such as cyclopentadienyltitanium trichloride ($CpTiCl_3$), biscyclopentadienylzirconium dichloride (Cp_2ZrCl_2), bisindenylzirconium dichloride (Ind_2ZrCl_2) and biscyclopentadienylhafnium dichloride (Cp_2HfCl_2) were purchased from Strem Chemicals Inc., U.S.A. and used as received. As a cocatalyst, the modified methylaluminoxane (MMAO, Type-4, 7.56 wt% Al, Akzo, U.S.A) was used without further purification. 1,5-Dibromopentane (Aldrich Chem. Co., U.S.A) and 1,5-dichlorohexamethyltrisiloxane (United Chem. Tech. Inc., U.S.A) were used after drying with P_2O_5.

Synthesis of Trisiloxane-bridged Heterometallic Dinuclear Metallocene Catalyst. The trisiloxane-bridged heterometallic dinuclear titanium/zirconium complex, **1** was prepared by the reaction of the dithallium salt of 1,5-dicyclopentadienylhexamethyltrisiloxane[2] with one equivalent of indenylzirconium trichloride at room temperature in THF, followed by the addition of one equivalent of $TiCl_4$ after 3 h stirring. After completing reaction by stirring overnight at room temperature, recrystallization from CH_2Cl_2-hexane gave a pale yellow green solid product in ca. 45% yield. The trisiloxane-bridged heterometallic dinuclear hafnium/zirconium complex, **2** was obtained by using indenylhafnium trichloride instead of $TiCl_4$ in the previous procedure. Indenylzirconium trichloride and indenylhafnium trichloride were prepared according to the literature.[8]

The structure of products was confirmed by ^{1}H-NMR (300 MHz, $CDCl_3$, 25°C) : **1** : δ = 7.64(m; 2H), 7.29(m; 2H), 7.22(t; 2.4Hz, 2H), 7.03(t; 2.4Hz, 2H), 6.86(t; 3.3Hz, 1H), 6.56(t; 2.4Hz, 2H), 6.50(d; 3.3Hz, 2H), 6.08(t; 2.4Hz, 2H), 0.41(s; Si-CH_3, 6H), 0.35(s; Si-CH_3, 6H), 0.05(s; Si-CH_3, 6H), **2** : δ = 7.62(m; 4H), 7.28(m; 4H), 6.84(m; 2H), 6.56(m; 4H), 6.49(m; 4H), 6.07(m; 4H), 0.34(s; Si-CH_3, 12H), 0.02(s; Si-CH_3, 6H). The metal contents (wt%) of **1** and **2** were measured by inductively coupled plazma emission spectrophotometer (ICP, JY-38 Plus, France) and found to be Ti 5.7 (calc., 6.3) and Zr 10.8 (calc., 11.9) for **1** and Hf 17.6 (calc., 18.3) and Zr 9.0 (calc., 9.3) for **2**, respectively.

Polymerization and Polymer Characterization. All operations were carried out under a nitrogen atmosphere. In a 400 mL glass reactor were introduced sequentially the proper amounts of toluene and MMAO solution, and then the system was saturated with ethylene. With continuous flow of ethylene, the polymerization was initiated by injecting the solution of heterometallic dinuclear metallocene. Melting temperature (T_m) of PE was measured by means of differential scanning calorimetry (DSC) (Dupont TA 2000) at 20°C/min. Molecular weight and polydispersity index (M_w/M_n) were determined by means of gel-permeation chromatography (GPC) (Waters 150C) in 1,2,4-trichlorobenzene solvent at 135°C and data were analyzed using polystyrene calibration curves. The fractionation chromatograms were obtained by using cross fractionation chromatography (CFC, Mitsubishi Petrochem. Co. Ltd., Japan) in o-dichlorobenzene. Approximately 6 mg of PE was loaded onto a column of inert packing by slow cooling, stepwise elution from 0 to 140°C with a flow rate of 1 mL/min.

Results and Discussion

PE of wide MWD can be obtained by using a mixture of different mononuclear metallocenes[9] and dinuclear metallocenes[10] or a hybrid catalyst of Ziegler-Natta and metallocene catalysts.[11,12]

To examine the difference of mononuclear metallocene mixture and heterometallic dinuclear metallocene in MWD of the produced PEs, the first heterometallic dinuclear titanium/zirconium complex, **1** and hafnium/zirconium complex, **2** were synthesized. With **1** and **2**, the ethylene polymerizations were carried out in the presence of MMAO cocatalyst and the results are shown in

Table I. Polymerizations of Ethylene Initiated with Monometallic Metallocenes and Their Mixtures, Hexamethyltrisiloxanediyl(cyclopentadienyltitanium trichloride)(cyclopentadienylindenylzirconium dichloride) (1) and Hexamethyltrisiloxanediyl(cyclopentadienylindenylhafnium dichloride)(cyclopentadienylindenylzirconium dichloride) (2) in the presence of MMAO Cocatalyst (Polymerization Conditions : [Al]/[M]=10000, 70 °C, 2 h)

Catalyst[a]	Activity[c]	M_w (x10^{-3})	M_w/M_n	T_m (°C)
$CpTiCl_3$ (3.20)	15.9	412	2.2	130.1
Cp_2ZrCl_2 (0.56)	2125.4	59	2.6	133.4
$CpIndZrCl_2$ (0.73)	1758.7	37	2.6	133.9
Cp_2HfCl_2 (0.73)	417.4	140	2.4	133.8
$CpTiCl_3/Cp_2ZrCl_2$ (0.90/0.91)	1649.2	61	3.2	133.6
Cp_2HfCl_2/Cp_2ZrCl_2 (0.91/0.91)	1318.1	81	5.6	131.6
1 (0.75)[b]	14.6	101	8.7	132.7
2 (0.84)[b]	31.8	113	9.4	132.8

[a]Concentration in mol/L (× 10^{-6}).
[b][M] = [Ti]+[Zr] or [Hf]+[Zr].
[c]Activity in kg-PE/(mol-M · h · atm).

Table I. For comparison, some experimental data for the mononuclear metallocenes and their mixtures were also included.

Among the examined mononuclear metallocenes, $CpTiCl_3$ exhibited the lowest catalytic activity but the highest weight-average molecular weight (M_w). In the case of Cp_2HfCl_2, the activity was about 25 times higher than that of $CpTiCl_3$, but about 5 times lower than that of Cp_2ZrCl_2.

The catalytic activity and M_w of PE for Cp_2ZrCl_2 were slightly larger than those for $CpIndZrCl_2$ while M_w/M_n of PE for both zirconocenes were almost identical, which intimated that the effect of cyclopentadienyl and indenyl ligands on MWD was not so significant.

Two physically mixed catalysts, $CpTiCl_3/Cp_2ZrCl_2$ and Cp_2HfCl_2/Cp_2ZrCl_2 were less active than Cp_2ZrCl_2 at 70 °C. These results were consistent with the presence of relatively lower active catalysts, $CpTiCl_3$ and Cp_2HfCl_2 compared to Cp_2ZrCl_2. As expected, M_w/M_n of PE prepared with the mixed catalysts was larger than that of PE with mononuclear metallocenes. Interestingly, M_w of PE from the mixed catalysts was close to that of PE from Cp_2ZrCl_2.

For the ethylene polymerization initiated with the synthesized heterometallic dinuclear metallocenes, **1** and **2**, much smaller activities were observed in comparison to those for the other catalysts as shown in Table I. On the other hand, M_w of PE obtained with **1** and **2** was higher than that of PE with Cp_2ZrCl_2, $CpIndZrCl_2$ and mixed catalysts. The melting temperature (T_m) of the produced PE was not significantly different among them.

The most remarkable result was the unusually broad MWD of PE produced by the synthesized **1** and **2**. In the case of **2**, M_w/M_n of PE exceeded that of PE obtained with the mixed catalysts Cp_2HfCl_2/Cp_2ZrCl_2 by a factor of about 2. This outcome was clearly demonstrated in Figure 1.

The GPC curves for the mixed catalysts, $CpTiCl_3/Cp_2ZrCl_2$ (curve A) and Cp_2HfCl_2/Cp_2ZrCl_2 (curve B) was almost identical to that of PE produced with Cp_2ZrCl_2 because the catalyst activity of Cp_2ZrCl_2 is much higher than that of $CpTiCl_3$ and Cp_2HfCl_2. In contrast, PE produced by the heterometallic dinuclear metallocenes exhibited the definite bimodal GPC curves (curves C and D) that should cause the broadening of MWD. The peaks of curves C and D were corresponding to those of monozirconocenes as shown with curve E (mixture of PE obtained with Cp_2HfCl_2 and Cp_2ZrCl_2 separately).

The samples of PE-1 obtained with the mixed catalyst of Cp_2HfCl_2/Cp_2ZrCl_2 and PE-2 prepared by heterometallic dinuclear metallocene **2** were fractionated with cross fractionation chromatography (CFC)[13] and the chromatograms are shown in Figure 2.

As shown in the TREF(on-line temperature-rising elution fractionation) diagrams (A), the range of

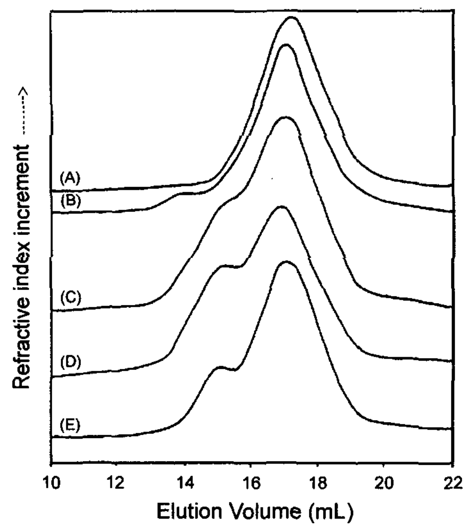

Figure 1. Gel permeation chromatograms of PEs prepared with mononuclear metallocene mixtures such as $CpTiCl_3/Cp_2ZrCl_2$ (A) and Cp_2HfCl_2/Cp_2ZrCl_2 (B), and heterometallic dinuclear metallocenes of hexamethyltrisiloxanediyl(cyclopentadienyltitanium trichloride)(cyclopentadienylindenylzirconium dichloride) (C), hexamethyltrisiloxanediyl(cyclopentadienylindenylhafnium dichloride)(cyclopentadienylindenylzirconium dichloride) (D) and mixture of PE obtained by Cp_2HfCl_2 and Cp_2ZrCl_2 (E) in the presence of MMAO cocatalyst.

elution temperature (T_e) of PE-1 was slightly narrower than that of PE-2 and elution was completed at around 102°C for PE-1 as well as PE-2. In addition, 19.6 wt% of PE-1 was eluted at 60 ~ 90°C while 12.5 wt% of PE-2 at 50 ~ 90°C. At the birds eye views of cross fractionation chromatograms (B) showing the relation of molecular weight (arbitrary scale) and T_e, the polymer of low molecular weight and narrow MWD was eluted at lower temperature than that of high molecular weight and wide MWD. In addition, the boundary of fractions having low and high T_e for PE-1 exhibited clearer cut than that for PE-2 as shown in the contour-type chromatograms (C). With these observations of CFC, it was considered that PE-1 was a heterogeneous mixture of PEs which are produced independently by two metallocenes, Cp_2HfCl_2 and Cp_2ZrCl_2 while PE-2 was not simple mixture of polymers generated by two transition metal centers.

In conclusion, it was found that the heterometallic dinuclear metallocenes such as **1** and **2** produced PE having wider MWD than the simple mixture of mononuclear metallocenes.

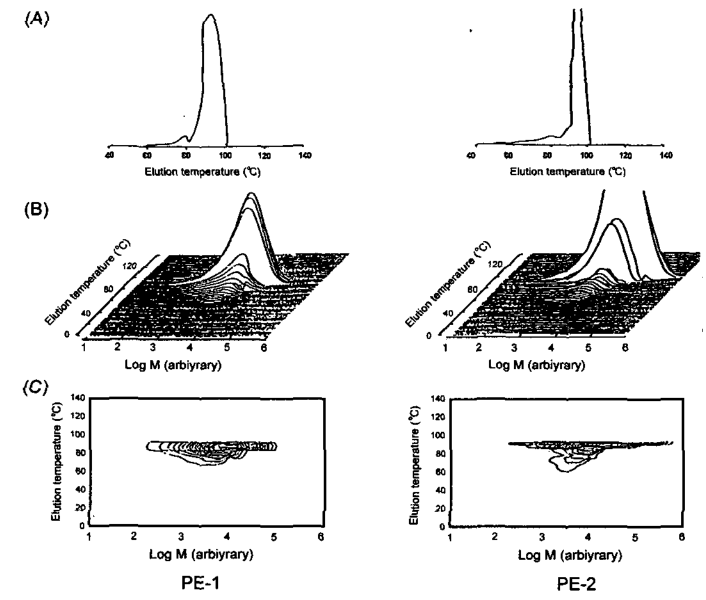

Figure 2. Cross fractionation chromatograms of PE-1 prepared with mononuclear metallocene mixture, Cp_2HfCl_2/Cp_2ZrCl_2, and PE-2 with heterometallic dinuclear metallocene, hexamethyltrisiloxanediyl(cyclopentadienylindenylhafnium dichloride)(cyclopentadienylindenylzirconium dichloride) in the presence of MMAO cocatalyst ; TREF diagram (A), birds eye views CFC chromatogram (B) and contour-type CFC chromatogram (C).

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