

Effect of ligand structures on high temperature homo- and copolymerization of ethylene by cationic hafnocene catalysts based on tetrakis(pentafluorophenyl) borate

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Received 16 August 1999; accepted 22 November 1999

Abstract

Ethylene (Et) polymerization and Et/ α -olefin copolymerization were carried out with various hafnocenes activated with dimethylanilinium tetrakis(pentafluorophenyl)borate ($\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ /triisobutylaluminum (*i*- Bu_3Al) to study the relationship between ligand structures and catalyst performance at high temperature. Dimethylsilylene(bisindenyl)hafnium dichloride ($\text{Me}_2\text{Si}(\text{Ind})_2\text{HfCl}_2$)-based catalyst produced highest molecular weight polyethylene among indenyl-based catalysts. Hydrogenation of the indenyl ligand resulted in the decrease in activity and copolymerization reactivity, presumably due to the increased mobility of the ligand framework at high temperature. Diphenylmethylidene(cyclopentadienyl)(fluorenyl)hafnium dichloride ($\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$)-based catalyst produced higher molecular weight polyethylene than zirconium analog and indenyl-based hafnocene catalysts, but the activity was drastically dependent upon the alkylaluminum compound. This phenomenon was not observed in the corresponding zirconium catalyst. A broad chemical composition distribution, which was observed in Et/1-hexene copolymers obtained with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ -based catalyst, was attributed to the small amount of zirconium contamination. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hafnocene; Ligand; Ethylene polymerization; High temperature

1. Introduction

In contrast of conventional multi site Ziegler–Natta catalysts, single site metallocene catalysts produce uniform ethylene (Et)/ α -olefin copolymers. Therefore, great interest has been focused on the copolymerization of Et and α -olefin with these catalysts from the academic and industrial point of view. Whereas, it is well

known that the molecular weights of Et copolymers obtained with conventional metallocene catalysts such as dicyclopentadienyl zirconium dichloride (Cp_2ZrCl_2) activated with methylaluminoxane (MAO) decrease with increasing polymerization temperature [1]. This feature is a disadvantage for applying metallocene catalysts for high temperature polymerization. Nevertheless, few papers [2–5] have been published on the performance of Et polymerization with metallocene catalysts at high temperature, although it is well known that the molecular weights of

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polyethylene are dependent upon the ligand structures of metallocenes [6,7].

From this point of view, we have studied the Et polymerization with various metallocene catalysts at high temperature, and reported that Cp_2ZrCl_2 , *rac*-(ethylene)bis(indenyl)zirconium dichloride (*rac*-Et(Ind)₂ZrCl₂) and *rac*-(dimethylsilyl)bis(2,4-dimethylcyclopentadienyl)zirconium dichloride (*rac*-Me₂Si(2,4-Me₂Cp)₂ZrCl₂) activated with dimethylanilinium tetrakis(pentafluorophenyl)borate (Me₂PhNH · B(C₆F₅)₄)/triisobutylaluminum (*i*-Bu₃Al) produced low molecular weight polyethylenes [8], but Ph₂C(Cp)(Flu)ZrCl₂ and its derivatives-based catalysts produced high molecular weight polyethylene with high activity even at high temperature [9]. Nevertheless, the catalysts that can produce higher molecular weight polyethylene at high temperature are needed.

On the other hand, employing hafnocene/MAO catalysts affords higher molecular weight polymers than zirconium analogs [10], but the low activity is a significant disadvantage for these catalysts [11]. However, we have already found that the activity of hafnocene-based catalysts could be enhanced by using Me₂PhNH · B(C₆F₅)₄/*i*-Bu₃Al as activator instead of MAO [12]. These results induced us to carry out the Et polymerization with various hafnocenes activated with Me₂PhNH · B(C₆F₅)₄/*i*-Bu₃Al.

In the present paper, we report the results of Et homopolymerization and copolymerization of Et and α -olefin with various hafnocene compounds in combination with Me₂PhNH · B(C₆F₅)₄/*i*-Bu₃Al as cocatalyst at high temperature, and discuss the relationship between the ligand structures and catalyst performance.

2. Experimental part

2.1. Materials

rac-Et(Ind)₂HfCl₂, *rac*-dimethylsilylene(bis-indenyl)hafnium dichloride (*rac*-Me₂Si(Ind)₂-HfCl₂), *rac*-Me₂Si(H₄-Ind)₂HfCl₂, *rac*-Me₂-

Si(2,4-Me₂Cp)₂HfCl₂, Me₂C(Cp)(Flu)-HfCl₂, MePhC(Cp)(Flu)HfCl₂, diphenylmethylidene(cyclopentadienyl)(fluorenyl)hafnium dichloride (Ph₂C(Cp)(Flu)HfCl₂) and these zirconium analogs were synthesized according to the literature [13–17]. Me₂PhNH · B(C₆F₅)₄, Ph₃C · B(C₆F₅)₄, Et₃Al, *i*-Bu₃Al, *n*-Hex₃Al, *n*-Oct₃Al and MAO from Tosoh Akzo were used without purification. C₇H₇ · B(C₆F₅)₄ was synthesized according to the modified literature method [18–20]. Toluene, C₉–C₁₃ mixed hydrocarbon solvent, Et and 1-hexene were commercially obtained and purified according to the usual procedures.

3. Polymerization procedure

3.1. Solution polymerization

Polymerizations were carried out in a 1-l autoclave equipped with a magnetic stirrer, a thermometer tube and various inlets. The autoclave was flushed several times with nitrogen and filled with 600 ml of C₉–C₁₃ mixed hydrocarbon solvent and if needed, 1-hexene was added. After that, autoclave was heated up to the polymerization temperature. Polymerization was started by adding the catalyst components. Ethylene was continuously supplied to keep constant during polymerization. After polymerization time, Et was released and polymerization was terminated by adding ethanol. Obtained polymer was adequately washed with plenty of ethanol and dried at 60°C under reduced pressure to constant weight.

3.2. Characterization of polymers

Differential scanning calorimetry (DSC) measurements were made using a SEIKO DSC-200 at a heating rate of 10°C/min. Molecular weight and molecular weight distribution of the polymer were determined by gel-permeation chromatography (GPC) using *o*-dichlorobenzene as solvent.

4. Results and discussion

4.1. Indenyl-based catalysts

Metal species is an important factor for deciding the catalyst performance as well as ligand structures. Ethylene polymerization with various hafnocenes activated with $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$ was carried out to study the relationship between the ligand structures of metallocene compound and the molecular weights of polyethylene in addition to the activity. The activity and the molecular weights of polyethylene are summarized in Table 1. For comparison, the results of Et polymerization with zirconium analogs are also indicated.

Using $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$ as cocatalyst enhanced activity and all of indenyl-based hafnocene catalysts produced higher molecular weight polyethylene than zirconium analogs. Dimethylsilylene (Me_2Si)-bridged hafnocene produced higher molecular weight polyethylene than Et-bridged hafnocene though slightly lower activity. Naga et al. [21] indicated that $\text{Et}(\text{Ind})_2\text{HfCl}_2/\text{MAO}$ produced higher molecular weight polyethylene than $\text{Me}_2\text{Si}(\text{Ind})_2\text{HfCl}_2$ analogous catalyst at 40°C. This result indicates that cocatalyst and polymerization temperature influence the molecular weights of polyethylene. Hydrogenation of indenyl ligands gave rise to the decrease in the molecular weights of polyethylene and activity. We

have already reported that diphenylmethylene(cyclopentadienyl)(octahydrofluorenyl)zirconium dichloride ($\text{Ph}_2\text{C}(\text{Cp})(\text{H}_8\text{Flu})\text{ZrCl}_2$)/ $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$ catalyst produced lower molecular weight polyethylene than $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ -based catalyst [22]. On the other hand, the slightly higher molecular weight of polyethylene obtained with tetrahydroindenyl-based complexes such as $\text{Et}(\text{H}_4\text{-Ind})_2\text{-ZrCl}_2$ or $\text{Me}_2\text{Si}(\text{H}_4\text{-Ind})_2\text{ZrCl}_2$ activated with MAO, as compared with indenyl-based zirconocene analogous catalysts, was observed at low temperature [23]. These results indicate that stereo rigidity of ligand structure of metallocene compound is a key factor for the production of high molecular weight polyethylene at high temperature.

The results of Et/1-hexene copolymerization with these hafnocene-based catalysts are shown in Table 2. The molecular weights of copolymers with these catalysts decreased with 1-hexene incorporation into polymer structure and $\text{Me}_2\text{Si}(\text{Ind})_2\text{HfCl}_2$ -based catalyst produced much higher molecular weight copolymers than $\text{Me}_2\text{Si}(\text{H}_4\text{-Ind})_2\text{HfCl}_2$ -based catalyst. Chien and He already reported that the hydrogenated complexes produced copolymers with lower molecular weight than their nonhydrogenated analogs for $\text{Et}(\text{H}_4\text{-Ind})_2\text{ZrCl}_2/\text{MAO}$ vs. $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ in copolymerization of Et and propylene [24]. The highest molecular weight copolymers obtained with $\text{Me}_2\text{Si}(\text{Ind})_2\text{HfCl}_2$ -based catalyst

Table 1
Results of Et polymerization with various hafnocene-based catalysts

Run no.	Metallocene	(μmol)	Zr/B/Al	Activity (kg/mmol M)	M_w ($\times 10^{-4}$)	M_w/M_n
222	$\text{Et}(\text{Ind})_2\text{HfCl}_2$	1.0	1/2.0/250	30	10.8	3.0
720	$\text{Me}_2\text{Si}(\text{Ind})_2\text{HfCl}_2$	1.0	1/1.2/250	14	20.3	2.1
743	$\text{Me}_2\text{Si}(\text{H}_4\text{-Ind})_2\text{HfCl}_2$	1.0	1/1.2/250	7	7.8	1.9
099	$\text{Et}(\text{Ind})_2\text{ZrCl}_2$	1.0	1/2.0/250	40	2.6	1.9
301	$\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$	2.5	1/2.0/250	5	2.8	2.1
304	$\text{Me}_2\text{Si}(\text{H}_4\text{-Ind})_2\text{ZrCl}_2$	2.5	1/2.0/250	6	3.9	2.3

Polymerization conditions: polymerization temperature, 150°C; polymerization time, 20 min; solvent, C9–C13 hydrocarbon, 600 ml; catalyst: metallocene/ $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$.

Table 2
Results of Et/1-hexene copolymerization with various hafnocene-based catalysts

Run no.	Metallocene	(μmol)	Zr/B/Al	1-Hexene (ml)	Activity (kg/mmol M)	M_w ($\times 10^{-4}$)	M_w/M_n	T_m ($^{\circ}\text{C}$)
178	Et(Ind) ₂ HfCl ₂	1.0	1/2.0/250	20	31	6.4	2.5	102,120
721	Me ₂ Si(Ind) ₂ HfCl ₂	1.0	1/1.2/250	20	12	12.0	2.0	89
744	Me ₂ Si(H ₄ -Ind) ₂ HfCl ₂	1.0	1/1.2/250	20	9	1.7	1.7	106
144	Et(Ind) ₂ ZrCl ₂	1.0	1/2.0/250	20	40	2.0	2.2	124
303	Me ₂ Si(Ind) ₂ ZrCl ₂	1.0	1/2.0/250	20	6	very low	–	–
305	Me ₂ Si(H ₄ -Ind) ₂ ZrCl ₂	1.0	1/2.0/250	20	7	very low	–	–

Polymerization conditions: polymerization temperature, 150 $^{\circ}\text{C}$; polymerization time, 20 min; solvent, C9–C13 hydrocarbon, 600 ml; catalyst: metallocene/Me₂PhNH · B(C₆F₅)₄/i-Bu₃Al.

apparently result from the favorable combination of electric and steric effects induced by silylene bridge and the nonhydrogenated ligand framework. We have already reported that β -H transfer from propagating chain containing primary inserted α -olefin as terminal unit was major chain transfer reaction for the copolymerization of Et and α -olefin at high temperature [8]. We suppose that this type of chain transfer reaction is easily occurred for the copolymerization with Me₂Si(H₄-Ind)₂HfCl₂-based catalyst compared with Me₂Si(Ind)₂HfCl₂-based catalyst.

Melting point of copolymers with hafnocene-based catalysts was lower than that of copolymers with analogous zirconocene-based catalysts, indicating that hafnocene/Me₂-PhNH · B(C₆F₅)₄/i-Bu₃Al catalysts are more effective for inserting α -olefin into Et copolymer than analogous zirconocene catalysts, which is the same as MAO-activated catalysts. We

have already reported that comonomer incorporation into copolymers decreased with the increase in polymerization temperature [9], therefore, high comonomer incorporation ability of hafnocene-based catalysts is a very useful character for the production of Et copolymers at high temperature. Furthermore, another important point is that melting point of copolymers obtained with Me₂Si(Ind)₂HfCl₂-based catalyst is lower than that of copolymers obtained with Me₂Si(H₄-Ind)₂HfCl₂-based catalyst, indicating that copolymerization reactivity was different. This phenomenon is not completely understood now, but Chien et al. showed that copolymerization reactivity of Me₂Si(Ind)₂ZrCl₂ and Me₂Si(H₄-Ind)₂ZrCl₂ activated with MAO was roughly the same for Et/propylene copolymerization at 50 $^{\circ}\text{C}$. In addition, Lehmus et al. [25] revealed that indenyl complex showed better copolymerization reactivity than tetrahydroindenyl complex for Et/1-hexene copolymeriza-

Table 3
Effect of B/Hf ratio on catalyst performance for Me₂Si(Ind)₂HfCl₂/Me₂PhNH · B(C₆F₅)₄/i-Bu₃Al

Run no.	(μmol)	Zr/B/Al	1-Hexene (ml)	Activity (kg/mmol Hf)	M_w ($\times 10^{-4}$)	M_w/M_n	T_m ($^{\circ}\text{C}$)
720	1.0	1/1.2/250	0	14	20.3	2.1	–
747	0.5	1/5.0/250	0	36	19.7	2.1	–
721	1.0	1/1.2/250	20	12	12.0	2.0	89
748	0.5	1/5.0/250	20	30	9.9	2.0	90

Polymerization conditions: polymerization temperature, 150 $^{\circ}\text{C}$; polymerization time, 20 min; solvent, C9–C13 hydrocarbon, 600 ml.

Table 4
Effect of bridge structure on catalyst performance

Run no.	Metalocene	Activity (kg/mmol Hf)	M_w ($\times 10^{-4}$)	M_w/M_n	T_m ($^{\circ}\text{C}$)
186	$\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$	4	17.0	3.2	79,119
829	$\text{MePhC}(\text{Cp})(\text{Flu})\text{HfCl}_2$	15	11.2	3.1	81,116
957	$\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$	23	22.0	2.0	83,113
185	$\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$	6	3.2	2.5	–
002	$\text{MePhC}(\text{Cp})(\text{Flu})\text{ZrCl}_2$	32	3.6	2.0	–
397	$\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$	172	8.0	2.0	117

Polymerization conditions: Et pressure, 20 bar; 1-hexene, 20 ml; solvent, C9–C13 hydrocarbon, 600 ml; polymerization time, 20 min; catalyst: metalocene/ $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al} = 1/2/250$ (μmol).

tion and the difference in comonomer response was more emphasized for Et/1-hexadecene copolymerization. Based on these results, we speculate that the increased mobility of the tetrahydroindenyl ligand inhibit the coordination of the bulky monomer at high temperature.

The effect of the ratio ($\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{Me}_2\text{Si}(\text{Ind})_2\text{HfCl}_2$) on catalyst performance is given in Table 3. The catalytic activities for Et polymerization and Et/1-hexene copolymerization increased with increasing B/Hf mole ratio, whereas the molecular weights and comonomer incorporation did not changed. This phenomenon was also observed in Et [26] or propylene [27] polymerization with zirconocene catalysts, but the degree of this activity enhancement was higher than that of zirconium analogs. This may relate to the low stability of hafnium-based catalyst. We speculate that

reactivation reaction with excess $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ occurred.

4.2. Fluorenyl-based catalysts

The effect of substituent groups of the bridge structure of hafnocene compounds containing fluorenyl ligand on catalyst performance is shown in Table 4, and the effect of polymerization temperature on activity and the molecular weights of copolymers are given in Table 5. The activity and the molecular weights of copolymers were enhanced by changing methyl to phenyl groups on bridge structure. This phenomenon was also observed in the corresponding zirconium catalysts, but the effect of introducing phenyl substituent groups on the activity was lower than that of analogous zirconocene catalyst. Nevertheless, the weight-average

Table 5
Effect of polymerization temperature on catalyst performance for Et/1-hexene copolymerization

Run no.	Metalocene	Hf/B/Al (μmol)	T_p ($^{\circ}\text{C}$)	Activity (kg/mmol M)	M_w ($\times 10^{-4}$)	M_w/M_n	T_m ($^{\circ}\text{C}$)
1005	$\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2^a$	1.0/1.2/250	150	16	23.0	2.0	80
1044		1.0/1.2/250	170	13	16.0	1.9	87
1050		1.0/1.2/250	200	3	8.9	1.9	80
0397	$\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$	0.25/0.5/62.5	150	172	8.0	2.0	117
0398		0.25/0.5/62.5	170	148	6.6	2.0	120
0399		0.25/0.5/62.5	200	40	4.7	2.0	117

Polymerization conditions: Et pressure, 20 bar; 1-hexene, 20 ml; solvent, C9–C13 hydrocarbon, 600 ml; polymerization time, 20 min; catalyst: metalocene/ $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$.

^aZirconium contamination was very low (see Fig. 1).

Table 6
Effect of aluminium compound on $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ -based catalyst

Run no.	Catalyst	(μmol)	Activity (kg/mmol Hf)
0957	$\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2/\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$	1/2/250	23
1059	$\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2/\text{C}_7\text{H}_7 \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$	1/2/250	13
1055	$\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2/\text{Ph}_3\text{C} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$	1/2/250	8
1013	$\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2/\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{Et}_3\text{Al}$	3/6/750	trace
1079	$\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2/\text{PMAO}$	1/10000	6

Polymerization conditions: Et pressure, 20 bar; 1-hexene, 20 ml; solvent, C9–C13 hydrocarbon, 600 ml; polymerization time, 20 min; polymerization temperature, 170°C.

molecular weight of copolymers obtained with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ -based catalyst produced at 200°C was 89 000. Melting point of copolymers was 80°C, indicating that this catalyst was very effective for inserting α -olefin into Et copolymer. These results indicate that this catalyst is very effective for the production of Et/ α -olefin copolymers with high α -olefin content at high temperature.

The results of Et/1-hexene copolymerization with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ in conjunction with various activators are recorded in Table 6. $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$ -activated catalyst showed highest activity and the activity decreased in the following order: $\text{C}_7\text{H}_7 \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al} > \text{Ph}_3\text{C} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$. This order was as same as that of the corresponding zirconium catalysts [26]. Furthermore, $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{Et}_3\text{Al}$ and MAO-activated catalysts were less active than $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$ system. On the other hand, $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ -based catalyst

in conjunction with $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{Et}_3\text{Al}$ showed high activity as shown in Table 7. These results indicate that the selection of alkylaluminium compounds is important for $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ -based catalyst. Mühlaupt et al. [28] recently reported that $\text{rac-Me}_2\text{-Si}(2\text{-Me-Benz[e]Ind})_2\text{ZrMe}_2$ activated with $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{Et}_3\text{Al}$ was not a useful catalyst for propylene polymerization, whereas the polymerization using $i\text{-Bu}_3\text{Al}$ gave polypropylenes with comparable of MAO-activated catalyst. The enhanced reduction of the transition metal center with Et_3Al compared to $i\text{-Bu}_3\text{Al}$ possibly accounts for the observed behavior. We speculate that the activity dependence on alkylaluminum was attributed to this phenomenon.

The effect of the introduction of *tert*-butyl substituent groups at 2,7-position of fluorenyl ligand, and diphenylsilylene-bridge structure on catalyst performance is indicated in Table 8. The slight increase in activity and the molecular

Table 7
Effect of aluminium compound on $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ -based catalyst

Run no.	Alkylaluminium	1-Hexene (ml)	Activity (kg/mmol Zr)	T_m (°C)
507	Et_3Al	20	96	121
398	$i\text{-Bu}_3\text{Al}$	20	148	120
494	$n\text{-Hex}_3\text{Al}$	20	136	120
496	$n\text{-Oct}_3\text{Al}$	20	160	120

Polymerization conditions: Et pressure, 20 bar; solvent, C9–C13 hydrocarbon, 600 ml; polymerization time, 20 min; polymerization temperature, 170°C; catalyst: $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{Al-compound} = 0.25/0.5/62.5 \mu\text{mol}$.

Table 8

Effect of substituent or bridge structures on catalyst performance for Et/1-hexene copolymerization

Run no.	Metalocene	Hf/B/Al (μmol)	Activity ($\text{kg}/\text{mmol M}$)	M_w ($\times 10^{-4}$)	M_w/M_n	T_m ($^{\circ}\text{C}$)
0817	$\text{Ph}_2\text{C}(\text{Cp})(2,7\text{-}t\text{-Bu}_2\text{Flu})\text{HfCl}_2$	0.5/1.0/125	28	17.2	2.2	83,114
1230	$\text{Ph}_2\text{Si}(\text{Cp})(\text{Flu})\text{HfCl}_2$	1.0/1.2/250	trace	–	–	–
0409	$\text{Ph}_2\text{C}(\text{Cp})(2,7\text{-}t\text{-Bu}_2\text{Flu})\text{ZrCl}_2$	0.25/0.5/62.5	144	8.6	1.7	120
1350	$\text{Ph}_2\text{Si}(\text{Cp})(\text{Flu})\text{ZrCl}_2$	1.0/1.2/250	14	11.0	2.0	120

Polymerization conditions: Et pressure, 20 bar; 1-hexene, 20 ml; solvent, C9–C13 hydrocarbon, 600 ml; polymerization time, 20 min; polymerization temperature, 170 $^{\circ}\text{C}$; catalyst: metalocene/ $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$.

weights of polyethylene by the introduction of *t*-butyl substituent groups was observed though significantly lower activity than zirconium analog. Diphenylsilylene-bridge structure was less effective for the Et polymerization activity at high temperature and this phenomenon was also observed in zirconium analog. Chen et al. [29] indicated that the replacement of the carbon bridge with the silylene bridge resulted in a large drop in syndiotacticity for propylene polymerization with Cs-symmetric metallocene. In addition, Ewen et al. [30] indicated that this was attributed to the difference of the metal-centroid angles, thus, less steric hindrance are responsi-

ble for the higher activity of the carbon-bridged metallocene than silylene-bridged analog.

4.3. Chemical composition distribution of copolymers obtained with hafnium-based catalysts

$\text{Me}_2\text{Si}(\text{Ind})_2\text{HfCl}_2$ - and $\text{Et}(\text{H}_4\text{-Ind})_2\text{HfCl}_2$ -based catalysts produced Et/1-hexene copolymers with single melting point as shown in Table 2, indicating that these copolymers had narrow chemical composition distributions. However, $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ -based catalyst produced copolymers with two melting points as shown in Table 4. We have already reported that Et/1-hexene copolymers obtained with $\text{Et}(\text{Ind})_2\text{HfCl}_2/\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$ catalyst had a broad chemical composition distribution [12].

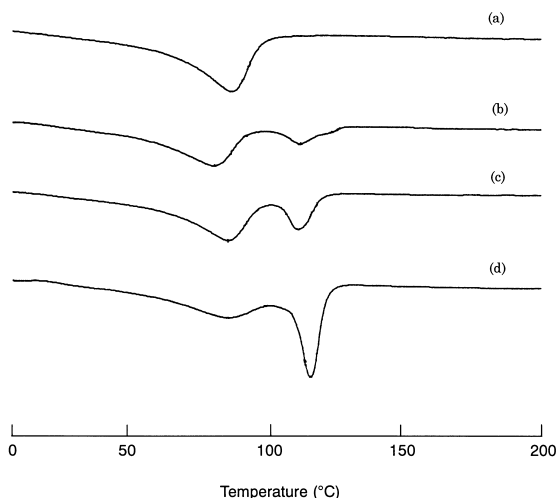


Fig. 1. DSC diagrams of Et/1-hexene copolymers with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ -based catalysts containing different amount of zirconium as contamination. (a) Zirconium contamination: < 0.01 wt.%. (b) Zirconium contamination: 0.03 wt.%. (c) Zirconium contamination: 0.16 wt.%. (d) Zirconium contamination: 0.35 wt.%.

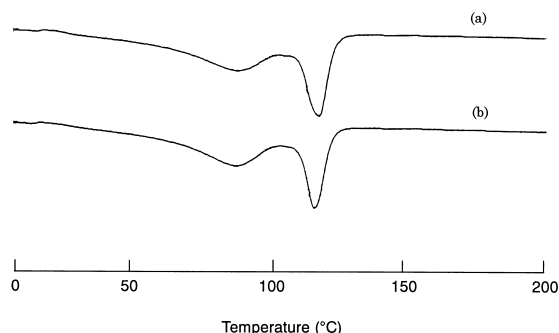


Fig. 2. DSC diagrams of Et/1-hexene copolymers obtained with pure $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ and the mixture of $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ -based catalysts. (a) 0.35 wt.% of zirconium contaminated $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ catalyst. (b) Pure $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ catalyst mixed with 0.35 wt.% of $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ catalyst.

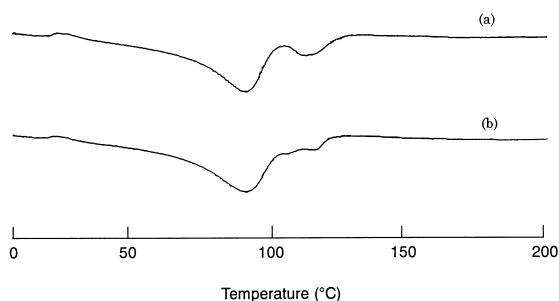


Fig. 3. DSC diagrams of Et/1-hexene copolymers obtained with pure $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ and the mixture of $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ -based catalysts. (a) 0.03 wt.% of zirconium contaminated $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ catalyst. (b) Pure $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ catalyst mixed with 0.03 wt.% of $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ catalyst.

Two active sites model was reported for the explanation of a broad chemical composition distribution in copolymerization of Et and 1-hexene with $\text{Cp}_2\text{ZrCl}_2/\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$ catalyst [31]. In this mechanism, anionic character of $i\text{-Bu}_3\text{Al}$ had an important role in the formation of two active sites, because Et_3Al -activated catalyst produced copolymers with a single chemical composition distribution. Therefore, the broad chemical composition of copolymers obtained with hafnium-based catalysts is not based on this mechanism because $\text{Me}_2\text{Si}(\text{Ind})_2\text{HfCl}_2/\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}$ catalyst synthesized the copolymers with a uni-modal chemical composition distribution.

On the other hand, it is well known that HfCl_4 contains small amount of ZrCl_4 as contamination. Kaminsky and Schlobohm [10] and Kioka et al. [16] reported that each catalyst synthesized its own polymer. Based on these results, $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ complexes containing different amount of zirconium were synthesized from HfCl_4 containing different amount of ZrCl_4 as contamination.

DSC charts of Et/1-hexene copolymers obtained with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ -based catalysts containing different amount of zirconium as contamination are indicated in Fig. 1. Et/1-hexene copolymers obtained with pure $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ -based catalyst showed

DSC curve with single peak, indicating that the chemical composition distribution of this copolymers was a uni-modal. In addition, the second peak increased with the increase in the amount of zirconium contamination and this melting point was in good agreement with that of copolymers with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ -based catalyst. These results strongly suggest that the small amount of zirconium contamination give rise to the broad chemical composition distribution of copolymers with hafnium-based catalysts. Figs. 2 and 3 show DSC charts of Et/1-hexene copolymers obtained with zirconium contaminated $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{HfCl}_2$ -based catalyst and the mixture of $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ with pure $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ catalyst. DSC diagrams of these two catalysts were roughly the same regardless of the concentration of zirconium contamination.

Therefore, we conclude that a broad chemical composition distribution of copolymers obtained with hafnium-based catalysts is attributed to the small amount of zirconium contamination.

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