

Influence of activators on ethylene polymerization with diphenylmethylidene-(cyclopentadienyl)(fluorenyl)zirconium dichloride catalysts at high temperature

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Abstract

Ethylene polymerization was carried out with diphenylmethylidene-(cyclopentadienyl)(fluorenyl)zirconium dichloride ($\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$) activated with various activators such as methylaluminoxane (MAO), tetrakis(pentafluorophenyl)borates ($\text{R} \cdot \text{B}(\text{C}_6\text{F}_5)_4$, $\text{R} = \text{Me}_2\text{PhNH}$, Ph_3C , C_7H_7 , $\text{H}(\text{Et}_2\text{O})_n$), dimethylanilinium tetrakis(pentafluorophenyl)aluminate ($\text{Me}_2\text{PhNH} \cdot \text{Al}(\text{C}_6\text{F}_5)_4$) and tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$) to study the correlation between catalyst performance for ethylene polymerization and cocatalysts at high temperature. $\text{R} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ -activated catalysts showed relatively high activity but $\text{Al}(\text{C}_6\text{F}_5)_4$ -activated catalyst showed very low activity, presumably due to the low thermal stability. $\text{B}(\text{C}_6\text{F}_5)_3$ -activated catalyst also indicated low activity. This activity difference reflected the relative coordinative abilities of the anions and tightness of the ion-pairing. MAO-activated catalyst was comparable in activity and copolymerization reactivity with $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ -activated catalyst and these two catalyst produced high molecular weight ethylene/1-hexene copolymers in a high pressure process. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Metallocene; Ethylene polymerization; High temperature; Activator

1. Introduction

It is well known that the ligand structures of metallocene compounds influence the catalyst performance for polymerization of various α -olefins [1,2]. We also indicated that the ligand structures of metallocene compounds significantly affected the molecular weight of polyethylene produced at high temperature [3], and $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ -based catalysts could produce high molecular weight polyethylene with high activity even at high temperature [4,5].

Cocatalyst also plays an important role in α -olefin polymerization. Actually, it was found that *rac*-ethylenebis(indenyl)zirconiumdimethyl (*rac*- $\text{Et}(\text{Ind})_2\text{ZrMe}_2$)/trityl tetrakis(pentafluorophenyl)borate ($\text{Ph}_3\text{C} \cdot \text{B}(\text{C}_6\text{F}_5)_4$) catalyst indicated higher activity than *rac*- $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ /methylaluminoxane (MAO) catalyst for propylene polymerization [6]. Furthermore, Ewen et al. showed that isopropylidene(cyclopentadienyl)-(fluorenyl)zirconium dichloride ($\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$)/MAO catalyst was more stereospecific and more active than $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ -activated analogous catalyst, [7] presumably due to the formation of stronger con-

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Table 1

Results of ethylene polymerization with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ catalysts in combination with various activators at 150°C

| Run No. | Activator | Activity (kg/mmol Zr) | Mw ($\times 10^{-4}$) | Mw/Mn |
|---------|--|-----------------------|-------------------------|-------|
| 473 | $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ | 172 | 11.2 | 2.1 |
| 279 | $\text{C}_7\text{H}_7 \cdot \text{B}(\text{C}_6\text{F}_5)_4$ | 128 | 10.5 | 1.9 |
| 275 | $\text{Ph}_3\text{C} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ | 80 | 11.0 | 2.1 |
| 199 | $\text{H}(\text{Et}_2\text{O})_n \cdot \text{B}(\text{C}_6\text{F}_5)_4$ | 23 | 9.4 | 1.9 |
| 228 | $\text{Me}_2\text{PhNH} \cdot \text{Al}(\text{C}_6\text{F}_5)_4$ | 4 | – | – |

Polymerization conditions: ethylene pressure, 20 bar; solvent, C9–C13 hydrocarbon, 600 ml; polymerization time, 20 min; catalyst, $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{activator}/i\text{-Bu}_3\text{Al} = 0.25/0.5/62.5$ (μmol).

tact ion pair for $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ -activated catalyst. In addition, they also prepared trityl tetrakis(pentafluorophenyl)aluminate ($\text{Ph}_3\text{C} \cdot \text{Al}(\text{C}_6\text{F}_5)_4$) and reported that $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{-ZrCl}_2$ catalyst paired with $\text{Ph}_3\text{C} \cdot \text{Al}(\text{C}_6\text{F}_5)_4$ were significantly more stereospecific than the corresponding boron system [8]. The strong Lewis acid, $\text{B}(\text{C}_6\text{F}_5)_3$, was also studied for zirconocene polymerization catalyst but this compound was not useful for the activator of $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ catalyst for propylene polymerization [9].

As described above, for propylene polymerization, the effect of cocatalysts on catalyst performance has been studied. However, there is little information about this effect for ethylene polymerization at high temperature, although ethylene polymerization with MAO-

activated catalysts at high temperature were already reported [10–13].

Therefore, these propylene polymerization results induced us to study the effect of cocatalyst systems on ethylene polymerization at high temperature. In particular, it seems that the thermal stability of activators is very important factor for the preparation of the catalysts that can produce high molecular weight polyethylene with high activity at high temperature. We report here the results of ethylene homopolymerization and ethylene/ α -olefin copolymerization with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ catalysts paired with various activators such as MAO, $\text{R} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ ($\text{R} = \text{Me}_2\text{PhNH}$, Ph_3C , C_7H_7 , $\text{H}(\text{Et}_2\text{O})_n$), $\text{Me}_2\text{-PhNH} \cdot \text{Al}(\text{C}_6\text{F}_5)_4$ and $\text{B}(\text{C}_6\text{F}_5)_3$ at high temperature. Based on these results, the effect of activator on catalyst performance for ethylene polymerization at high temperature was discussed.

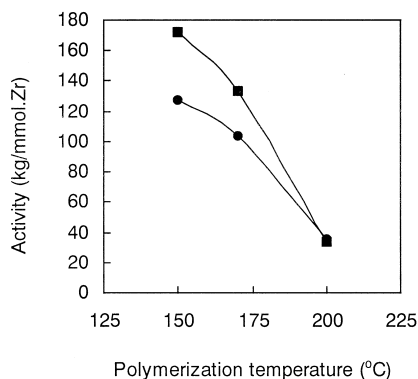


Fig. 1. Polymerization results with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ activated with various $\text{B}(\text{C}_6\text{F}_5)_4$ -based activators. Polymerization conditions: see Table 1; \blacksquare : $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$, \bullet : $\text{C}_7\text{H}_7 \cdot \text{B}(\text{C}_6\text{F}_5)_4$.

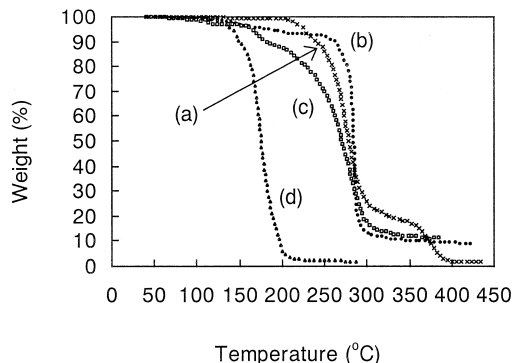


Fig. 2. TG analysis of $\text{R} \cdot \text{B}(\text{C}_6\text{F}_5)_4$, (a) $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$, (b) $\text{C}_7\text{H}_7 \cdot \text{B}(\text{C}_6\text{F}_5)_4$, (c) $\text{Ph}_3\text{C} \cdot \text{B}(\text{C}_6\text{F}_5)_4$, (d) $\text{H}(\text{Et}_2\text{O})_n \cdot \text{B}(\text{C}_6\text{F}_5)_4$.

2. Experimental

2.1. Materials

$\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ and $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ were synthesized according to the literature [14]. $\text{C}_7\text{H}_7 \cdot \text{B}(\text{C}_6\text{F}_5)_4$, $\text{Ph}_3\text{C} \cdot \text{B}(\text{C}_6\text{F}_5)_4$, $\text{H}(\text{Et}_2\text{O})_n \cdot \text{B}(\text{C}_6\text{F}_5)_4$ and $\text{Me}_2\text{PhNH} \cdot \text{Al}(\text{C}_6\text{F}_5)_4$ were synthesized according to the modified literature method [6]. $\text{B}(\text{C}_6\text{F}_5)_3$, $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$, *i*- Bu_3Al and MAO from Tosoh Akzo were used without purification. Toluene, C9–C13-mixed

hydrocarbon solvent, ethylene, 1-butene and 1-hexene were commercially obtained and purified according to the usual procedures.

2.2. Solution polymerization procedure

Polymerizations were carried out in a 1L 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-butene was

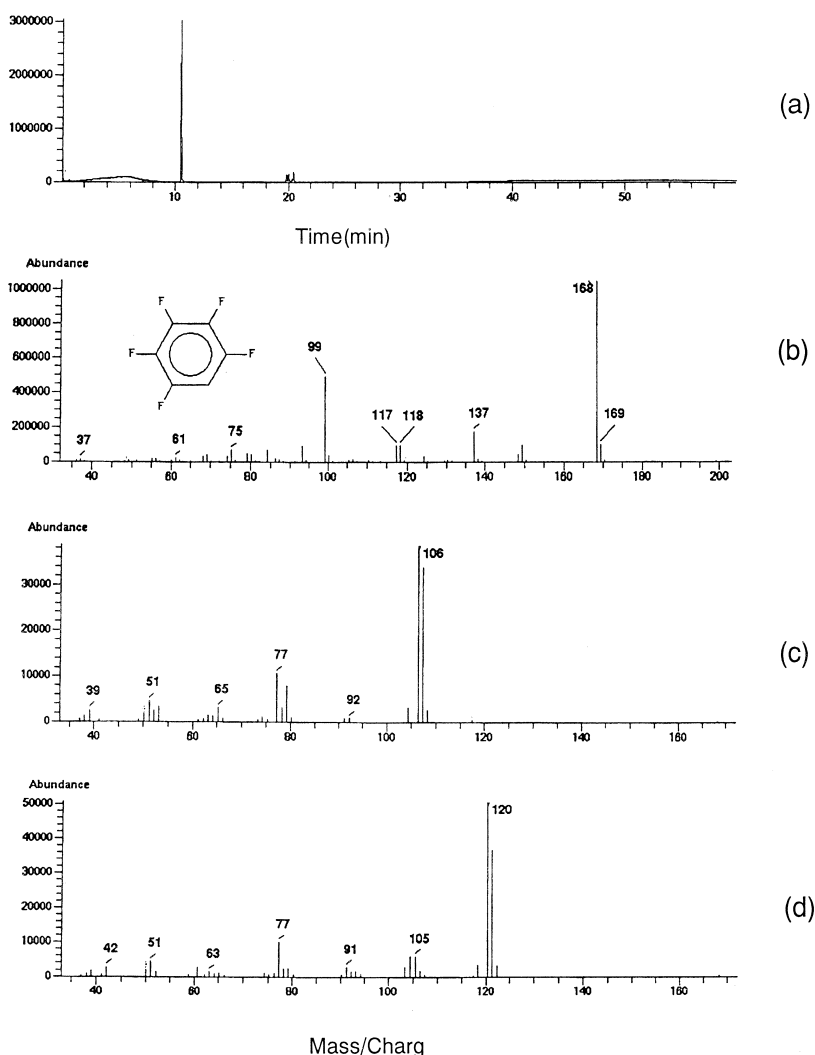


Fig. 3. GC-MS analysis of gas produced at 270–275°C for $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$, (a) TIC of $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$, (b) Scan at 10.490 min, (c) Scan at 19.933 min, (d) Scan at 20.392 min.

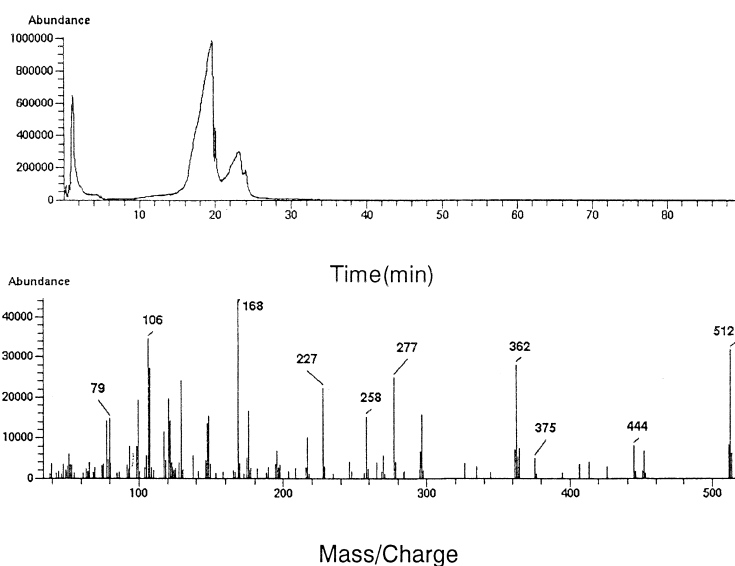


Fig. 4. MS analysis of gas produced at 270–275°C for $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$, Scan: 18.783 min.

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 the pressure constant during polymerization. After a certain polymerization time, ethylene 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.

2.3. Ethylene / α -olefin copolymerization procedure in a high pressure process

Copolymerization reactions were carried out in our pilot plant where the operating conditions were very close to the industrial ones. Polymerization temperature could be changed from 120°C to 280°C. Ethylene pressure range was up to 2000 bar. Polymerization temperature was controlled by catalyst feed rate. The average residence time was 60 s. Polymerization reactions were continuously carried out and unre-

acted ethylene and α -olefin were recycled. The melt polymer flowed out of the separator and could be pelletized.

2.4. Characterization of polymers

TG-DTA measurements were made using a Seiko DSC-200 at heating rate of 10°C/min from 40°C to 450°C under nitrogen. GC/MS study was performed with Hewlett-Packard 5989B instrument and EI-mass spectra was obtained with Jeol DX-303. Molecular weight and molecular weight distribution of the polymers

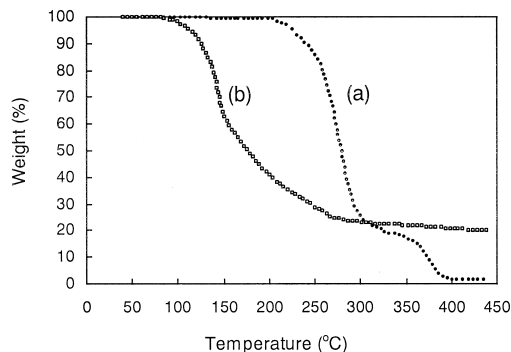
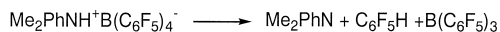


Fig. 5. TG analysis of $\text{Me}_2\text{PhNH} \cdot \text{M}(\text{C}_6\text{F}_5)_4$, (a) $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$, (b) $\text{Me}_2\text{PhNH} \cdot \text{Al}(\text{C}_6\text{F}_5)_4$.



Scheme 1. Decomposition pathway of $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$.

Table 2

The results of ethylene polymerization with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{B}(\text{C}_6\text{F}_5)_3/\text{i-Bu}_3\text{Al}$ catalyst

| Run No | $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ (μmol) | $\text{B}(\text{C}_6\text{F}_5)_3$ (μmol) | $\text{i-Bu}_3\text{Al}$ (μmol) | Zr/B/Al | Activity (kg/mmol Zr) |
|--------|--|---|---|----------|--------------------------|
| 319 | 0.5 | 5 | 125 | 1/10/250 | trace |
| 320 | 0.5 | 25 | 125 | 1/50/250 | trace |
| 404 | 1.0 | 10 | 250 | 1/10/250 | trace |

Polymerization conditions: ethylene pressure, 20 bar; polymerization temperature, 150°C; solvent, C9–C13 hydrocarbon, 600 ml; polymerization time, 20 min.

were determined by gel-permeation chromatography (GPC) using *o*-dichlorobenzene as solvent. Numbers of short chain branch and unsaturated end groups were analyzed from $^1\text{H-NMR}$ spectra recorded from 5 wt.% of 1,1,2,2-tetrachloroethane solution at room temperature by Jeol GSX-400 at 400 MHz. Cross fractionation chromatography (CFC) was made using a Mitsubishi Petrochemical CFC T-101.

3. Results and discussion

3.1. Comparison of various $\text{B}(\text{C}_6\text{F}_5)_4$ -based activators with $\text{Me}_2\text{PhNH} \cdot \text{Al}(\text{C}_6\text{F}_5)_4$

The results of ethylene polymerization with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ in combination with various activators at 150°C are given in Table 1. All these $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ catalysts with different $\text{B}(\text{C}_6\text{F}_5)_4$ -based activators produced high molecular weight polyethylene, although the activity was slightly different. The cationic part of $\text{B}(\text{C}_6\text{F}_5)_4$ -based activators are separated by the

reaction of $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ with $\text{B}(\text{C}_6\text{F}_5)_4$ -based activator in the presence of $\text{i-Bu}_3\text{Al}$ to form the active site. Therefore, it seems that the active sites of $\text{H}(\text{Et}_2\text{O})_n \cdot \text{B}(\text{C}_6\text{F}_5)_4$ -activated catalyst was deactivated, presumably due to the coordination of Et_2O to the active sites.

The influence of polymerization temperature on activity for ethylene polymerization using $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ paired with $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ or $\text{C}_7\text{H}_7 \cdot \text{B}(\text{C}_6\text{F}_5)_4$ are shown in Fig. 1. $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ -activated catalyst showed slightly higher activity than $\text{C}_7\text{H}_7 \cdot \text{B}(\text{C}_6\text{F}_5)_4$ -activated analogous catalyst in the temperature range from 150°C to 200°C. These results indicated that Me_2PhN released by the formation of active site was not coordinated to active site at high temperature.

TG diagrams of $\text{B}(\text{C}_6\text{F}_5)_4$ -based activators are shown in Fig. 2. All these activators were stable up to 150°C, although thermal stability was slightly different. These results suggested that the cationic part of $\text{B}(\text{C}_6\text{F}_5)_4$ -based activators affected the thermal stability but the structure of the anionic part was stable up to 150°C

Table 3

The effect of B/Zr ratio on activity for $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{i-Bu}_3\text{Al}$ catalyst

| Run No. | $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ (μmol) | $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ (μmol) | Zr/B/ $\text{i-Bu}_3\text{Al}$ | T_p^a (°C) | Activity (kg/mmol Zr) |
|---------|--|--|--------------------------------|--------------|--------------------------|
| 394 | 0.25 | 0.25 | 1/1/250 | 150 | 132 |
| 447 | 0.25 | 0.28 | 1/1.1/250 | 150 | 148 |
| 397 | 0.25 | 0.50 | 1/2/250 | 150 | 172 |
| 398 | 0.25 | 0.50 | 1/2/250 | 170 | 148 |
| 764 | 0.25 | 1.25 | 1/5/250 | 170 | 108 |
| 736 | 0.25 | 2.50 | 1/10/250 | 170 | 104 |

Polymerization conditions: ethylene pressure, 20 bar; solvent, C9–C13 hydrocarbon, 600 ml; 1-hexene, 20 ml; polymerization time, 20 min.
^aPolymerization temperature.

Table 4

The effect of B/Zr ratio on activity in Et(Ind)₂ZrCl₂/Me₂PhNH · B(C₆F₅)₄/i-Bu₃Al catalyst

| Run No. | Et(Ind) ₂ ZrCl ₂ (μmol) | Me ₂ PhNH · B(C ₆ F ₅) ₄ (μmol) | i-Bu ₃ Al (μmol) | Zr/B/Al | T _p ^a (°C) | Activity (kg/mmol Zr) |
|---------|--|---|--------------------------------|----------|----------------------------------|--------------------------|
| 144 | 1 | 2 | 250 | 1/2/250 | 150 | 40 |
| 165 | 1 | 15 | 250 | 1/15/250 | 150 | 53 |
| 145 | 5 | 10 | 1250 | 1/2/250 | 200 | 1 |
| 160 | 1 | 15 | 250 | 1/15/250 | 200 | 14 |

Polymerization conditions: ethylene pressure, 20 bar; solvent, C9–C13 hydrocarbon, 600 ml; 1-hexene, 20 ml; polymerization time, 20 min.

^aPolymerization temperature.

regardless of the structure of the cationic part. Therefore, all of Ph₂C(Cp)(Flu)ZrCl₂ catalysts with different B(C₆F₅)₄-based activators showed high activity at 150°C.

GC-MS analysis of Me₂PhNH · B(C₆F₅)₄ is shown in Fig. 3. Fractions of scan at 10.490, 19.993 and 20.392 min were identified C₆F₅H, PhMeNH and PhMe₂N whose molecular weight was 168, 107 and 121 respectively. Nevertheless, boron-based compounds were not detected in GC-MS analysis, which indicated that boron-based compounds might be absorbed in GC column.

MS analysis of direct injection is given in Fig. 4. B(C₆F₅)₃ whose molecular weight was 512 was detected in MS analysis of the direct injection of gas fraction at 270–275°C. Based on these analyses, Me₂PhNH · B(C₆F₅)₄ was thought to be decomposed to Scheme 1. In addition, it was thought that active center which was formed by the reaction of Ph₂C(Cp)(Flu)ZrCl₂, Me₂PhNH · B(C₆F₅)₄ and i-Bu₃Al was decomposed through the same reaction. Actually, this decomposition pattern has been already observed in the related cationic actinide complex, Cp'₂ThMe⁺BPh₄⁻ [15], and the in situ-generated, base-coordinated complexes [L₂ZrMe(NMe₂Ph)_n]⁺ · B⁻(4-C₆H₄F)₄⁻ [16]. Furthermore, Marks et al. [17] indicated that the identified metallocenium–fluoroborate decomposition pathways were divided into two categories: (i) decompositions involving the anions, e.g., the aryl transfer reactions and fluoride abstraction and (ii) cation self-decomposition, e.g., C–H activation reactions. These results

reveal that the cleavage of B–C bond is key step for thermal decomposition of active centers.

On the other hand, Ph₂C(Cp)(Flu)ZrCl₂ catalyst activated with Me₂PhNH · Al(C₆F₅)₄ showed very low activity for ethylene polymerization at 150°C. It is known that this catalyst showed high activity for propylene polymerization and we checked that this catalyst indicated high activity for ethylene polymerization at 40°C. The results indicate that the thermal stability of active center was closely connected with polymerization behavior at high temperature.

TG analysis of Me₂PhNH · B(C₆F₅)₄ and Me₂PhNH · Al(C₆F₅)₄ are shown in Fig. 5. It is clear that the decomposition of Me₂PhNH · Al(C₆F₅)₄ started at 130°C that was lower than the polymerization temperature, whereas Me₂PhNH · B(C₆F₅)₄ was stable up to 250°C. We speculate that the low activity of Me₂PhNH ·

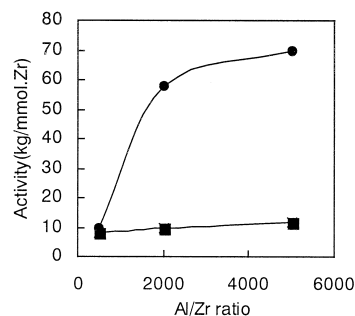


Fig. 6. Effect of Al/Zr ratio on activity of Ph₂C(Cp)(Flu)ZrCl₂/MAO catalyst, Polymerization conditions: see Table 1; ●: Polymerization temperature: 150°C, ■: Polymerization temperature: 200°C.

Table 5
Comparison of $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ with MAO in ethylene/1-butene copolymerization

| Run No. | Catalyst | Activity (kg/mmol Zr) | Methyl (No/1000C) | <i>Trans</i> -vinylene (No/1000C) | Vinyl (No/1000C) | Vinylidene (No/1000C) | Trisubstituted (No/1000C) |
|---------|--|--------------------------|----------------------|--------------------------------------|---------------------|--------------------------|------------------------------|
| 669 | $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2 / \text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4 / i\text{-Bu}_3\text{Al}^a$ | 72 | 35.6 | 0.59 | 0.09 | 0.09 | 0.92 |
| 703 | $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2 / \text{MAO}^b$ | 33 | 35.3 | 0.57 | 0.08 | 0.08 | 0.77 |

Polymerization conditions: ethylene pressure, 10 bar; solvent, C9–C13 hydrocarbon, 600 ml; 1-butene, 70 ml; polymerization temperature, 170°C; polymerization time, 20 min.

^a $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2 / \text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4 / i\text{-Bu}_3\text{Al} = 0.25 / 0.36 / 62.5$ (μmol).

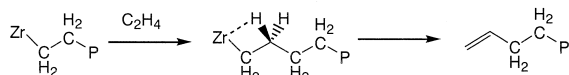
^b $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2 / \text{MAO} = 0.5 / 2500$ (μmol).

$\text{Al}(\text{C}_6\text{F}_5)_4$ -activated catalyst at 150°C arose from this low thermal stability of $\text{Me}_2\text{PhNH} \cdot \text{Al}(\text{C}_6\text{F}_5)_4$ compound.

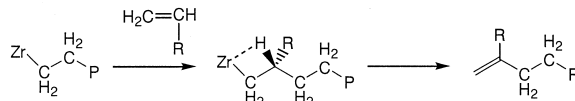
These results suggest that $\text{B}(\text{C}_6\text{F}_5)_3$ was formed by this decomposition reaction. Therefore, ethylene polymerization with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ paired with $\text{B}(\text{C}_6\text{F}_5)_3 / i\text{-Bu}_3\text{Al}$ was carried out at 150°C. These results are given in

Table 2. These catalyst systems were not active for ethylene polymerization at 150°C, indicating that $\text{B}(\text{C}_6\text{F}_5)_3$ anion was not contained in real active site. Of course, $\text{B}(\text{C}_6\text{F}_5)_3$ was useful activator for the metallocene catalysts, but high B:Zr ratio was needed to show high activity and the activity was lower than that of catalyst activated with $\text{R} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ [18]. We carried out

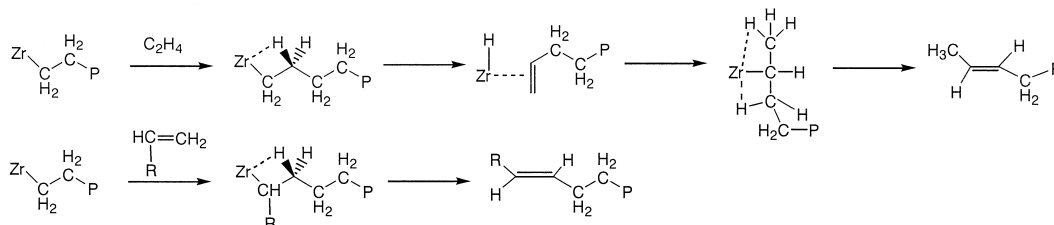
1) Vinyl end group : low



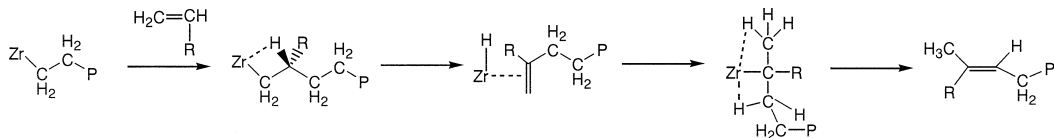
2) Vinylidene end group : low



3) *Trans* vinylene end group : high



4) Trisubstituted end group : high



Scheme 2. Chain transfer reactions in ethylene/ α -olefin copolymerization.

ethylene polymerization with the catalysts activated with $B(C_6F_5)_3$ and confirmed that the activity was lower than that of catalysts activated with $R \cdot B(C_6F_5)_4$. Marks et al. [19] studied the thermal stability of these cationic complexes and discovered several decomposition reaction pathways (cation/anion ligand redistribution, intramolecular C–H activation, fluoride abstraction, and intermolecular C–H activation). In addition, the relative coordinative tendencies of $MeB(C_6F_5)_3$ and $B(C_6F_5)_4$ was estimated from the solution spectroscopic information and structural dynamics of the ion-pairs and followed the order, $MeB(C_6F_5)_3 > B(C_6F_5)_4$. We speculate that the low activity of $B(C_6F_5)_3$ -activated catalyst may reflect the relative coordinative abilities of the anions. Based on these results, we concluded that $B(C_6F_5)_3$ was not better activator than $R \cdot B(C_6F_5)_4$ especially at high polymerization temperature.

The effect of B:Zr ratio on polymerization activity for $Ph_2C(Cp)(Flu)ZrCl_2$ catalysts activated with $Me_2PhNH \cdot B(C_6F_5)_4$ is shown in Table 3. The activity of $Me_2PhNH \cdot B(C_6F_5)_4$ -activated catalyst was not changed by B:Zr ratio, but the activity of $rac-Et(Ind)_2ZrCl_2$ catalyst activated with $Me_2PhNH \cdot B(C_6F_5)_4$ increased with the increase in B:Zr ratio at 200°C, although this was not observed for polymerizations at 150°C as shown in Table 4. The increase of activity for propylene polymerization with increasing B:Zr ratio was already reported [18].

Fink et al. [20] have studied the effect of $Me_2Si(Ind)_2ZrMe_2/Bu_3N \cdot B(C_6F_5)_4$ ratio on the properties of ethylene and propylene polymerization. For ethylene polymerization, activity increased with excess of $Me_2Si(Ind)_2ZrMe_2$. For propylene polymerization, maximum activity was observed at Zr:B ratio of 1:1. On the other hand, Bochmann and Lancaster [21] indicated the formation of dinuclear methyl-bridged complexes from the reaction of Cp'_2MMe_2 with $Ph_3C \cdot B(C_6F_5)_4$ and the polymerization with dimeric complexes was only possible when this compounds dissociate to Cp'_2MMe_2 and the active species $[Cp'_2MMe]^+$. The activity should therefore decrease with increasing concentration of Cp'_2MMe_2 . Theoretically a stoichiometric amount of $B(C_6F_5)_4$ compounds is enough to form active species from the reaction of Cp'_2MMe_2 and $B(C_6F_5)_4$ compounds but active species are decomposed at high temperature; therefore, excess of $B(C_6F_5)_4$ compounds may play an important role in stabilizing the active sites especially at high temperature.

3.2. Comparison of $Me_2PhNH \cdot B(C_6F_5)_4$ with MAO

The effect of Al:Zr ratio on activity for ethylene polymerization with $Ph_2C(Cp)(Flu)ZrCl_2/MAO$ catalyst is given in Fig. 6. Activity increased with increasing Al:Zr ratio and decreased with increasing polymerization temperature for ethylene polymerization. This tendency

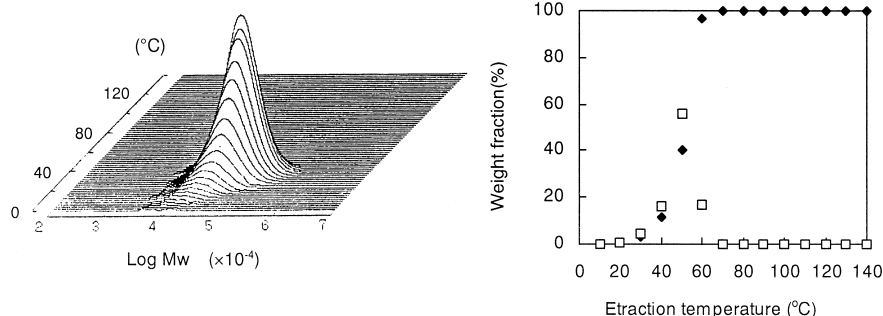


Fig. 7. TREF curve of copolymer with $Ph_2C(Cp)(Flu)ZrCl_2/Me_2PhNH \cdot B(C_6F_5)_4/i-Bu_3Al$. Sample No: 669, ◆: Integral line, □: differential line.

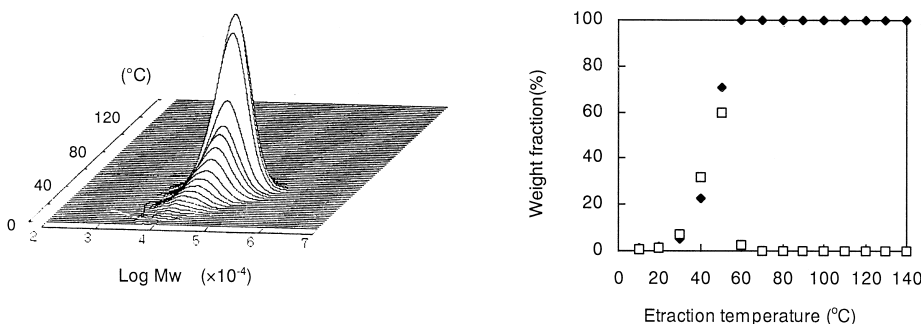


Fig. 8. TREF curve of copolymer with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{MAO}$. Sample No: 703; \blacklozenge : Integral line, \square : differential line.

is a general feature of conventional metallocene catalysts.

The results of ethylene/1-butene copolymerization with these two catalysts under low pressure at high temperature and the end group structures of these copolymers are shown in Table 5. It is clear that $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{i-Bu}_3\text{Al}$ catalyst showed higher activity than MAO-activated catalyst for copolymerization of ethylene and 1-butene under given polymerization conditions.

The terminal bond structures of these copolymers obtained with MAO-activated catalyst were roughly the same as those of copolymers obtained with $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{i-Bu}_3\text{Al}$ -activated catalyst [22]. *Trans*-vinylene [23] and trisubstituted [24] end groups are formed by the β -H transfer after isomerization from propagating chain containing ethylene or 1-butene as terminal unit as shown in Scheme 2. *Trans*-vinylene and trisubstituted end groups are ma-

ior, and vinyl and vinylidene are minor for copolymers obtained with both catalysts. These results indicate that these isomerization reactions are easily occurred in copolymerization under high temperature, low ethylene pressure and high-comonomer feed-rate conditions, regardless of cocatalysts.

CFC charts of these ethylene/1-butene copolymers are indicated in Figs. 7 and 8, respectively. The ethylene/1-butene copolymers with these two catalysts had narrow chemical composition distribution and CFC elution pattern of two copolymers was totally the same, indicating that copolymerization reactivity was mainly decided by metallocene compound.

3.3. Ethylene/1-hexene copolymerization in a high pressure process

The results of ethylene/1-hexene copolymerization with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ catalysts ac-

Table 6
Comparison of cocatalyst systems in a high pressure process

| Run No. | Cocatalyst | Activity (kg/mmol Zr) | Mw ($\times 10^{-4}$) | Mw/ Mn | Methyl (No/1000C) | <i>Trans</i> -vinylene (No/1000C) | Vinyl (No/1000C) | Vinylidene (No/1000C) | Trisubstituted (No/1000C) |
|---------|--|--------------------------|----------------------------|-----------|----------------------|--------------------------------------|---------------------|--------------------------|------------------------------|
| 36X002 | $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4$ ^a | 161 | 6.5 | 1.7 | 7.2 | 0.06 | 0.23 | 0.01 | 0.06 |
| 37X005 | $\text{C}_7\text{H}_7 \cdot \text{B}(\text{C}_6\text{F}_5)_4$ ^b | 203 | 6.6 | 1.8 | 6.0 | 0.08 | 0.19 | 0.01 | 0.10 |
| 37X012 | MAO ^c | 178 | 7.7 | 2.0 | 8.1 | 0.13 | 0.25 | 0.04 | 0.18 |

Polymerization conditions: polymerization temperature, 173–190°C; ethylene pressure, 950 bar; 1-hexene concentration, 30%.

^a $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{i-Bu}_3\text{Al} = 1/2/250$.

^b $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{C}_7\text{H}_7 \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{i-Bu}_3\text{Al} = 1/2/250$.

^c $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2/\text{MAO} = 1/4000$.

tivated with $\text{Me}_2\text{PhNH} \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{i-Bu}_3\text{Al}$, $\text{C}_7\text{H}_7 \cdot \text{B}(\text{C}_6\text{F}_5)_4/\text{i-Bu}_3\text{Al}$ and MAO in a high pressure process and end group structures of these copolymers are shown in Table 6. As same as the results of polymerizations under low pressure at high temperature, these three catalysts indicated roughly the same activity and comonomer incorporation ability, and the molecular weights of copolymers were also the same. The content of *trans*-vinylene and trisubstituted end groups of copolymers synthesized in a high pressure process were smaller than those of copolymers synthesized under low pressure at high temperature as shown in Table 5. For comparison of these three catalysts, the catalyst activated with MAO produced copolymers that have relatively high content of *trans*-vinylene and trisubstituted end groups. These results indicate that the difference in cocatalysts may affect the control of isomerization reactions as shown in Scheme 2. Vinyl end group becomes therefore major at low comonomer concentration under given polymerization conditions.

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