Profiles of ethylene polymerization with zirconocene–trialkylaluminum/borane compound

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Abstract

Ethylene polymerization was conducted with bis(cyclopentadienyl)zirconium dichloride (**1**) and *rac*-dimethylsilylenebis(indenyl)zirconium dichloride (**2**) combined with trialkylaluminum (AlR$_3$; R = methyl (Me), ethyl (Et), isobutyl (*i*Bu))/triphenylcarbenium tetrakis(pentafluorophenyl)borate (Ph$_3$CB(C$_6$F$_5$)$_4$) or tris(pentafluorophenyl)borane (B(C$_6$F$_5$)$_3$) to study the effect of cocatalysts on polymerization rate (R_p). When AlMe$_3$ was used, no activity or very low activity was observed with both zirconocenes regardless of the borane compounds used. The replacement of AlMe$_3$ to AlEt$_3$ or Al*i*Bu$_3$ with **1**–AlR$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ caused polymerization and induction time was observed to reach the maximum R_p. Especially in the case of using AlEt$_3$, it took about 30 min to show the activity. When B(C$_6$F$_5$)$_3$ was used, AlEt$_3$ was not effective but Al*i*Bu$_3$ gave the highest activity among all the combinations of AlR$_3$ and the borane compounds. In the case of polymerization with **2** using Ph$_3$CB(C$_6$F$_5$)$_4$, high activity was observed with both AlEt$_3$ and Al*i*Bu$_3$ without any induction period. When B(C$_6$F$_5$)$_3$ was used instead of Ph$_3$CB(C$_6$F$_5$)$_4$, very low activity was observed with AlEt$_3$. On the other hand, high activity was observed with Al*i*Bu$_3$, and the maximum R_p was found at the beginning of the polymerization. The effect of AlR$_3$ on the formation of active species was discussed based on these results. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ethylene polymerization; Zirconocene catalyst; Trialkylaluminum; Cation-forming reagent

1. Introduction

Active species for olefin polymerization derived from group 4 metallocene catalysts have been considered to be metallocenium cation M$^+$(IV). Jordan et al. [1] found that a cationic zirconocene complex, [Cp$_2$ZrCH$_3$(THF)]$^+$-[BPh$_4$]$^-$ (Cp = cyclopentadienyl, THF = tetrahydrofuran, Ph = phenyl), was active for ethy-

lene polymerization in a polar solvent without any cocatalysts. After that finding, much effort has been focused on the development of cationic metallocene complexes and cocatalysts for olefin polymerizations.

Marks et al. [2–5] synthesized a cationic zirconocene catalyst, [Cp$_2$ZrCH$_3$]$^+$[CH$_3$B-(C$_6$F$_5$)$_3$]$^-$, through a reaction of bis(cyclopentadienyl)zirconium dimethyl (Cp$_2$Zr(CH$_3$)$_2$) with tris(pentafluorophenyl)borane (B(C$_6$F$_5$)$_3$), and studied the structure, solution dynamic and catalytic activity for olefin polymerization.

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Bochmann and Lancaster [6,7] isolated some binuclear and heterobinuclear zirconocene and hafnocene complexes through a reaction of dialkylmetallocene and triphenylcarbenium tetrakis(pentafluorophenyl)borate $(Ph_3CB(C_6F_5)_4)$, and applied them for propylene polymerization. On the basis of the activity in propylene polymerization with trimethylaluminum $(AlMe_3)$ / $Ph_3CB(C_6F_5)_4$ at the different molar ratio of Al/Zr, they proposed dormant states of the active sites for olefin polymerization. Beck et al. [8] and Haselwander et al. [9] studied binuclear zirconocene cations by solution ^1H NMR spectroscopy. They found the equilibrium between solvent-separated ion pairs and associated ion pairs of the $[Cp_2ZrCH_3]^+[CH_3B(C_6F_5)_3]^-$ complex in benzene-d_6 solution. Tritto et al. [10] studied the structure of cation-like and binuclear zirconocene complexes by means of ^{13}C NMR spectroscopy using ^{13}C-enriched $Cp_2Zr(^{13}CH_3)_2$ in toluene-d_8 solution. Beck et al. [8], Haselwander et al. [9] and Herfert and Fink [11] hypothesized that the binuclear ion pairs were active for ethylene polymerization. However, there is room for argument on this point.

Chien et al. [12–14] reported effect of counter-ions for isospecific polymerization of propylene catalyzed by *rac*-ethylenebis(indenyl)zirconium dimethyl (rac-Et(Ind)$_2$Zr(CH$_3$)$_2$) or *rac*-ethylenebis(indenyl)zirconium dichloride (rac-Et(Ind)$_2$ZrCl$_2$)/triethylaluminum $(AlEt_3)$ combined with $Ph_3CB(C_6F_5)_4$ or $B(C_6F_5)_3$, and found that $Ph_3CB(C_6F_5)_4$ showed much higher activity than $B(C_6F_5)_3$. They suggested the existence of free Zr cation which enhanced the activity for propylene polymerization.

Rate–time profile of polymerization gives important information for the formation of active species and decay process. A large number of attempts have been made on the polymerization profiles with metallocene-methylaluminoxane (MAO) to study the effect of polymerization temperature, concentration of metallocene, molar ratio of metallocene to MAO and aging condition of metallocene with MAO [14–24].

Although some investigations have been reported to study the effect of trialkylaluminum (AlR_3) and/or borane compound on the activity for the olefin polymerization with metallocene catalysts [12–14,25–28], few data have been reported about the polymerization profile with the metallocene–AlR$_3$/borane compound systems.

In this study, we have conducted the polymerization of ethylene with zirconocene dichloride–AlR$_3$/borane compound to study the effect of cocatalyst system on the polymerization rate and profile. The mechanisms of active-site formation were discussed on the basis of the rate–time profiles.

2. Experimental

2.1. Materials

Bis(cyclopentadienyl)zirconium dichloride $(Cp_2ZrCl_2$, **1**) and *rac*-dimethylsilylenebis(indenyl)zirconium dichloride (rac-Me$_2$Si(Ind)$_2$-ZrCl$_2$, **2**) were commercially obtained from Aldrich and Witco, respectively, and used without further purification. AlMe$_3$, AlEt$_3$ and triisobutylaluminum $(AliBu_3)$ were donated from Tosoh Akzo and used without further purification. $Ph_3CB(C_6F_5)_4$ and $B(C_6F_5)_3$ were donated from Asahi glass and used without further purification. Ethylene was donated from Mitsubishi Chemical and purified by passing it through a column of molecular sieves 3A. Toluene was commercially obtained and dried over CaH$_2$.

2.2. Polymerization of ethylene

Polymerization of ethylene was conducted at 40°C in a 300-ml glass reactor equipped with a magnetic stirrer. After 190 ml of toluene was added to the reactor, the solvent was saturated with an atmospheric pressure of ethylene. Toluene (10 ml), metallocene catalyst (1.0

Table 1
Results of ethylene polymerization with Cp_2ZrCl_2 (**1**)–AlR_3/$Ph_3CB(C_6F_5)_4$[a]

Run	AlR_3	t[b] (min)	Yield (kg PE/mol Zr)	$M_n \, 10^{-4}$[c]	M_w/M_n[c]	N[d] (mol PE/mol Zr)
1	$AlMe_3$	60	22.0	2.1	2.8	
2(a)	$AlEt_3$	5	0.0			
2(b)		10	0.0			
2(c)		20	0.0			
2(d)		30	3.5			
2(e)		45	29.2	3.3	2.4	0.89
2(f)		60	126	3.4	2.4	3.7
2(g)		75	153	3.3	2.5	4.6
2(h)		90	157	3.3	2.5	4.7
3(a)	$AliBu_3$	5	46.6	13.0	2.7	0.36
3(b)		10	95.5	13.8	2.6	0.69
3(c)		20	198	13.8	2.6	1.4
3(d)		30	298	14.8	2.5	2.0
3(e)		45	432	13.5	2.6	3.2
3(f)		60	553	15.4	2.3	3.6

[a] Polymerization conditions: $Cp_2ZrCl_2 = 1.0$ μmol, $AlR_3 = 0.5$ mmol, $Ph_3CB(C_6F_5)_4 = 1.0$ μmol polymerization temperature = 40°C, ethylene = 1 atm.
[b] Polymerization time.
[c] Number-average molecular weight and molecular weight distribution of polyethylene determined by GPC.
[d] Number of polymer chains.

μmol) and AlR_3 (0.5 mmol) were premixed in a 100-ml glass flask at 25°C for 5 min. Polymerization was started by introducing the catalyst solution and borane compound (1.0 μmol in 1.0 ml of toluene solution). Consumption of ethylene was monitored by a gas flow meter. Reaction medium was sampled through an equipped seal septum with a syringe and quenched in methanol. During the polymerization, temperature was kept at 40°C. Polymerization was terminated by adding dilute hydrochloric acid solution in methanol. The polyethylene obtained was adequately washed with plenty of methanol and dried *i. vac.* at 60°C for 6 h.

Table 2
Results of ethylene polymerization with Cp_2ZrCl_2 (**1**)–AlR_3/$B(C_6F_5)_3$[a]

Run	AlR_3	t[b] (min)	Yield (kg PE/mol Zr)	$M_n \, 10^{-4}$[c]	M_w/M_n[c]	N[d] (mol PE/mol Zr)
4	$AlMe_3$	60	0			
5	$AlEt_3$	60	0			
6(a)	$AliBu_3$	5	255	8.9	3.0	2.5
6(b)		10	362	8.7	3.5	4.2
6(c)		20	455	8.4	3.3	5.4
6(d)		30	529	9.1	3.6	5.8
6(e)		45	631	9.7	3.5	6.5
6(f)		60	714	10.4	3.5	6.8

[a] Polymerization conditions: $Cp_2ZrCl_2 = 1.0$ μmol, $AlR_3 = 0.5$ mmol, $B(C_6F_5)_3 = 1.0$ μmol polymerization temperature = 40°C, ethylene = 1 atm.
[b] Polymerization time.
[c] Number-average molecular weight and molecular weight distribution of polyethylene determined by GPC.
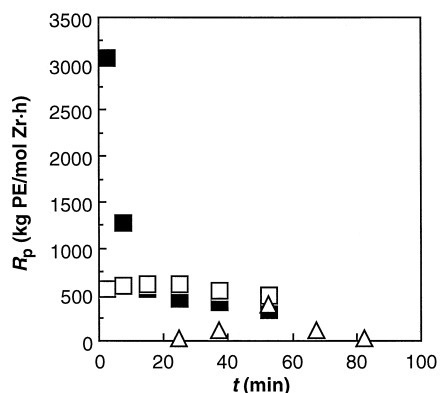[d] Number of polymer chains.

Fig. 1. Plots of polymerization rate (R_p) against polymerization time with **1**; ($\triangle$) $AlEt_3/Ph_3CB(C_6F_5)_4$, ($\square$) $AliBu_3/Ph_3CB-(C_6F_5)_4$, ($\blacksquare$) $AliBu_3/B(C_6F_5)_3$.

2.3. Analytical procedure

Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were measured at 140°C by means of gel-permeation chromatography (GPC, Waters 150CV) using *o*-dichlorobenzene as a solvent and calibrated with standard polystyrene samples. M_n of polyethylene was converted using the *Q*-factor by the following equations: $M_n =$

$M_n(PS) \cdot Q_{PE}/Q_{PS}$ ($M_n(PS)$, M_n calibrated with polystyrene standards; Q_{PP}, *Q*-factor of polyethylene = 17.7; Q_{PS}, *Q*-factor of polystyrene = 41.3) [29].

3. Results and discussion

3.1. Polymerization with Cp_2ZrCl_2 (**1**)

Polymerization of ethylene was performed at 40°C under an atmospheric pressure with **1** using $AlR_3/Ph_3CB(C_6F_5)_4$ or $B(C_6F_5)_3$ as co-catalysts. The results are summarized in Tables 1 and 2, respectively.

In the case of using $Ph_3CB(C_6F_5)_4$ as a cation-forming reagent, the order of average polymerization activity for 1 h decreased in the following order: $AliBu_3 > AlEt_3 > AlMe_3$. In the polymerization with $AlEt_3$, **1** showed moderate activity after a remarkably long induction time (about 30 min). The molecular weight of polyethylene obtained with $AliBu_3$ was higher than that with $AlEt_3$. When $B(C_6F_5)_3$ was used as a cation-forming reagent, the polymerization

Table 3
Results of ethylene polymerization with *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ (**2**)–AlR$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$[a]

Run	AlR$_3$	t[b] (min)	Yield (kg PE/mol Zr)	M_n 10^{-4}[c]	M_w/M_n[c]	N[d] (mol PE/mol Zr)
7	AlMe$_3$	60	56.3	1.8	2.8	
8(a)	AlEt$_3$	2	301	1.6	3.2	18.8
8(b)		5	525	1.5	3.0	35.3
8(c)		10	841	1.5	3.1	56.1
8(d)		15	1121	1.7	2.8	66.5
8(e)		20	1275	1.7	3.2	76.5
8(f)		30	1454	1.8	3.0	81.3
9(a)	AliBu$_3$	2	405	6.4	4.2	6.3
9(b)		5	904	6.6	4.3	13.7
9(c)		10	1193	7.1	4.6	16.9
9(d)		15	1475	7.5	4.4	19.7
9(e)		20	1670	7.7	4.0	21.7
9(f)		30	1867	8.1	4.7	23.1

[a] Polymerization conditions: *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ = 1.0 μmol, AlR$_3$ = 0.5 mmol, Ph$_3$CB(C$_6$F$_5$)$_4$ = 1.0 μmol polymerization temperature = 40°C, ethylene = 1 atm.
[b] Polymerization time.
[c] Number-average molecular weight and molecular weight distribution of polyethylene determined by GPC.
[d] Number of polymer chains.

Table 4
Results of ethylene polymerization with *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ (**2**)–AlR$_3$/B(C$_6$F$_5$)$_3$[a]

Run	AlR$_3$	t[b] (min)	Yield (kg PE/mol Zr)	M_n 10^{-4}[c]	M_w/M_n[c]	N[d] (mol PE/mol Zr)
10	AlMe$_3$	60	0			
11(a)	AlEt$_3$	5	40.8	1.9	2.3	2.1
11(b)		10	48.1	1.9	2.7	2.6
11(c)		20	55.9	1.9	2.8	2.9
11(d)		30	58.7	1.9	2.5	3.1
11(e)		45	58.7			
12(a)	Al*i*Bu$_3$	2	290	3.0	6.8	9.7
12(b)		5	669	4.5	6.4	14.9
12(c)		10	1245	7.0	5.3	17.7
12(d)		15	1802	7.0	5.3	25.7
12(e)		20	2253	6.9	5.3	32.8
12(f)		30	2919	8.2	5.7	35.8

[a] Polymerization conditions: *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ = 1.0 μmol, AlR$_3$ = 0.5 mmol, B(C$_6$F$_5$)$_3$ = 1.0 μmol polymerization temperature = 40°C, ethylene = 1 atm.
[b] Polymerization time.
[c] Number-average molecular weight and molecular weight distribution of polyethylene determined by GPC.
[d] Number of polymer chains.

proceeded with Al*i*Bu$_3$, however, no activity was observed with AlMe$_3$ and AlEt$_3$.

Polymerization rate (R_p) at polymerization time $t(t = (t_1 + t_2)/2)$ was determined according to the following equation:

$$R_p = (Y_2 - Y_1)/(t_2 - t_1)$$

where Y_1 and Y_2 are yields of polyethylene at polymerization time t_2 and t_1 determined by the consumption of ethylene, respectively. The R_p values with **1** against the polymerization time are displayed in Fig. 1. In the case of using Ph$_3$CB(C$_6$F$_5$)$_4$ as a cation-forming reagent, induction time to reach the maximum R_p was observed with both AlEt$_3$ and Al*i*Bu$_3$. When B(C$_6$F$_5$)$_3$ was used with Al*i*Bu$_3$, R_p showed maximum value at the beginning of polymerization, and then rapidly dropped.

R_p can be expressed by the following equation:

$$R_p = k_p[M]^a[C^*]$$

where k_p, $[M]$, a and $[C^*]$ are, respectively, the rate constant of propagation, monomer concentration, reaction order and the number of active centers. The $[M]$ value is constant during the polymerization. Therefore, the time dependence of R_p should derive from the change of k_p and/or $[C^*]$ during the polymerization. The number of polymer chains (N = mol polyethylene/mol Zr) and the polymer yield show almost the same profile with the increase in polymerization time. Furthermore, the decrease of molecular weight of resulting polyethylenes could not be observed in spite of the decrease of
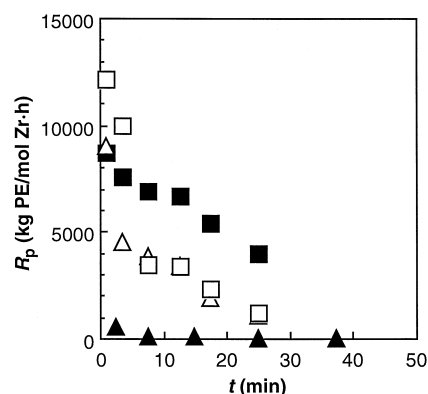

Fig. 2. Plots of polymerization rate (R_p) against polymerization time with **2**; (△) AlEt$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$, (□) Al*i*Bu$_3$/Ph$_3$CB-(C$_6$F$_5$)$_4$, (▲) AlEt$_3$/B(C$_6$F$_5$)$_3$, (■) Al*i*Bu$_3$/B(C$_6$F$_5$)$_3$.

Table 5
Summary of ethylene polymerization with zirconocene–AlR$_3$/borane compound systems

Zirconocene catalyst	AlR$_3$	Borane compound	Induction time[a] (min)	$R_p$max[b]	Activity[c]	M_n^d 10^{-4}	M_w/M_n^e
Cp$_2$ZrCl$_2$	AlMe$_3$	Ph$_3$CB(C$_6$F$_5$)$_4$	–	–	22	2.1	2.8
		B(C$_6$F$_5$)$_3$			0	–	–
	AlEt$_3$	Ph$_3$CB(C$_6$F$_5$)$_4$	52.5	387	153	3.3	2.5
		B(C$_6$F$_5$)$_3$			0	–	–
	AliBu$_3$	Ph$_3$CB(C$_6$F$_5$)$_4$	15	615	553	14.1	2.6
		B(C$_6$F$_5$)$_3$	–	3060	714	9.2	5.2
rac-Me$_2$Si(Ind)$_2$ZrCl$_2$	AlMe$_3$	Ph$_3$CB(C$_6$F$_5$)$_4$	–	–	56	1.8	2.8
		B(C$_6$F$_5$)$_3$			0	–	–
	AlEt$_3$	Ph$_3$CB(C$_6$F$_5$)$_4$	–	9030	2900	1.6	3.1
		B(C$_6$F$_5$)$_3$	–	490	117	1.9	2.7
	AliBu$_3$	Ph$_3$CB(C$_6$F$_5$)$_4$	–	12,200	3730	7.2	4.4
		B(C$_6$F$_5$)$_3$	–	8700	5840	6.1	5.8

[a] Induction time to reach the maximum R_p.
[b] Maximum R_p (kg PE/mol Zr h).
[c] Average value for 1 h (kg PE/mol Zr h).
[d] Average value of M_n.
[e] Average value of M_w/M_n.

R_p. These results suggest that the decrease of R_p with the increase of polymerization time is not caused by the decrease of k_p but the decrease of $[C^*]$.

3.2. Polymerization with rac-Me$_2$Si(Ind)$_2$ZrCl$_2$ (2)

Polymerization of ethylene was conducted at 40°C under an atmospheric pressure with **2** using AlR$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ or B(C$_6$F$_5$)$_3$ as co-catalysts. The results are summarized in Tables 3 and 4, respectively. The order of average activity for 1 h polymerization decreased in the following order in the case of using Ph$_3$CB-(C$_6$F$_5$)$_4$: AliBu$_3$ > AlEt$_3$ > AlMe$_3$. When B(C$_6$F$_5$)$_3$ was used, the order of activity was the same with that using Ph$_3$CB(C$_6$F$_5$)$_4$, however, the activity with AlEt$_3$ was very low and no activity was observed with AlMe$_3$.

The R_p values with **2** against the polymerization time are displayed in Fig. 2. R_p showed the maximum value at the beginning of polymerization and decayed regardless of AlR$_3$ and cation-forming reagents used. The R_p value with B(C$_6$F$_5$)$_3$ decayed slower than that with Ph$_3$CB(C$_6$F$_5$)$_4$. The decrease of R_p would de-
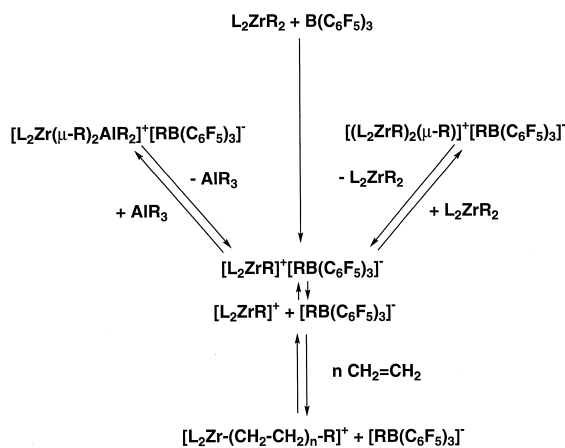
rive from the decrease of $[C^*]$ for the same reason in the polymerization with **1**.

3.3. Mechanistic study in formation of active species

As described above, the activity and rate–time profiles of ethylene polymerization were strongly depended on the combination of zirconocene, trialkylaluminum and borane compound. The summary of ethene polymerizations
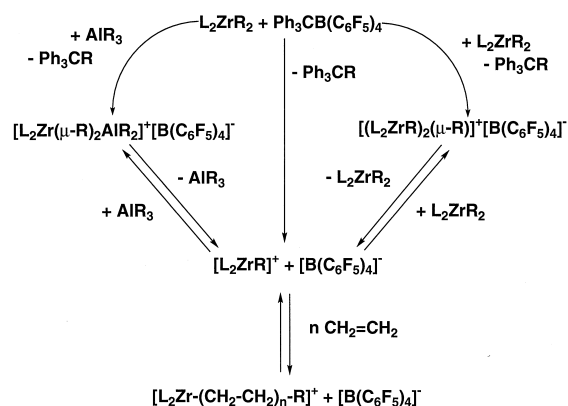
Scheme 1. Proposed reaction mechanism in the formation of active species with zirconocene–AlR$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$.

$$L_2ZrR_2 + B(C_6F_5)_3$$

$$[L_2Zr(\mu\text{-}R)_2AlR_2]^+[RB(C_6F_5)_3]^- \qquad [(L_2ZrR)_2(\mu\text{-}R)]^+[RB(C_6F_5)_3]^-$$

$$- AlR_3 \qquad\qquad - L_2ZrR_2$$
$$+ AlR_3 \qquad\qquad + L_2ZrR_2$$

$$[L_2ZrR]^+[RB(C_6F_5)_3]^-$$

$$[L_2ZrR]^+ + [RB(C_6F_5)_3]^-$$

$$n\ CH_2=CH_2$$

$$[L_2Zr\text{-}(CH_2\text{-}CH_2)_n\text{-}R]^+ + [RB(C_6F_5)_3]^-$$

Scheme 2. Proposed reaction mechanism in the formation of active species with zirconocene–AlR_3/$B(C_6F_5)_3$.

with zirconocene–AlR_3/borane compound systems is listed in Table 5. Schemes 1 and 2 show the proposed reaction mechanisms using $Ph_3CB(C_6F_5)_4$ and $B(C_6F_5)_3$ as cation-forming reagents, respectively. In the polymerization with $AlMe_3$, no activity or very low activity was found in each zirconocene catalyst by using any kinds of cation-forming reagents. This result could be due to the stability of $[L_2Zr(\mu\text{-}Me)_2AlMe_2]^+[B(C_6F_5)_4]^-$ and $[L_2Zr(\mu\text{-}Me)_2AlMe_2]^+[MeB(C_6F_5)_3]^-$ (L_2 = ligand; Cp_2 for **1** and $Me_2Si(Ind)_2$ for **2**) which formed by the zirconocene, $AlMe_3$ and counter-ion.

The induction time before the maximum R_p with **1**–AlR_3 (R = Et, iBu)/$Ph_3CB(C_6F_5)_4$, especially in the case of using $AlEt_3$, could be explained by the formation of dormant complexes, $[Cp_2Zr(\mu\text{-}R)_2AlR_2]^+[B(C_6F_5)_4]^-$ or binuclear $[(Cp_2ZrR)_2(\mu\text{-}R)]^+[B(C_6F_5)_4]^-$ (R = Et, iBu), similarly to the case of $AlMe_3$. When $AlEt_3$ was applied, these complexes should be so stable that it took considerably long time to form the activated free ion. While in the polymerization with **2**–AlR_3 (R = Et, iBu)/$Ph_3CB(C_6F_5)_4$, almost no induction time was observed. Active species were formed without staying the dormant complexes probably due to the steric hindrance of bridged bis(indenyl) ligand and the alkyl group.

In the case of using $B(C_6F_5)_3$ as a cation-forming reagent, high activity was observed with AliBu_3, while no activity or very low activity was found with $AlEt_3$ in the polymerization with both **1** and **2**. Two reasons could be considered to explain this tendency. One is the stability of dormant site as $[L_2Zr(\mu\text{-}Et)_2AlEt_2]^+[EtB(C_6F_5)_3]^-$ or binuclear $[(L_2ZrEt)_2(\mu\text{-}Et)]^+[EtB(C_6F_5)_3]^-$. The other is the stability of ion pair $[L_2ZrR]^+[RB(C_6F_5)_3]^-$ which might have very small k_p in ethene polymerization. In these cases, the alkyl group of AlR_3 should significantly affect the nature of these species. Chien et al. suggested dissociation of the ion pair to free ion in the rac-$Et(Ind)_2$-$ZrMe_2$–$B(C_6F_5)_3$ system which has very large k_p for polymerization [14]. Beck et al. [8] and Haselwander et al. [9] reported existence of solvent-separated ion pairs and associated ion pairs in both Cp_2ZrMe_2–$B(C_6F_5)_3$ and rac-dimethylsilylenebis(indenyl)zirconium dimethyl (rac-$Me_2Si(Ind)_2ZrMe_2$)–$B(C_6F_5)_3$. High activity with AliBu_3/$B(C_6F_5)_3$ could be explained by the formation of free ion or solvent-separated ion pairs due to the isobutyl groups which enhance separation of dormant complexes and/or $[L_2ZrR]^+[RB(C_6F_5)_3]^-$ ion pair.

4. Conclusions

Activity and rate–time profiles of ethylene polymerization with zirconocene catalysts (**1**, **2**)–AlR_3 (R = Me, Et, iBu)/borane compound ($Ph_3CB(C_6F_5)_4$, $B(C_6F_5)_3$) were studied. In summary, not only AlR_3 but the borane compound used as a cation-forming reagent affected the induction time and activity of ethylene polymerization. Very low activity or no activity was observed with $AlMe_3$ independent of borane compound used. In the case of using $Ph_3CB(C_6F_5)_4$, high activity was observed with both $AlEt_3$ and AliBu_3. On the other hand, when $B(C_6F_5)_3$ was used, high activity was observed only with AliBu_3.

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