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Synthesis of polymer supported borate cocatalysts and their application to metallocene polymerizations

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Abstract

Polymer supported borate complexes were synthesized using poly(styrene-*co*-4-bromostyrene) and polystyrene-beads as carriers. These complexes were reacted with *rac*-Et[Ind]$_2$ZrCl$_2$ (Ind = indenyl) or Ph$_2$C[(Cp)Flu]ZrCl$_2$ (Cp = cyclopentadienyl, Flu = Fluorenyl) in toluene, at a molar ratio of [Zr]/[B] = 1, to obtain polymer supported catalysts. Polymerizations of ethylene and propylene were conducted over them in the presence of $Al(i\text{-}C_4H_9)_3$ as an activator. When poly(styrene-*co*-4-bromostyrene) was used as the carrier, the resulting soluble catalyst showed high activity comparable to those of the corresponding homogeneous catalysts for ethylene polymerization. For propylene polymerization, however, those catalysts showed low-activity. Even though the insoluble catalysts prepared with polystyrene-beads as carrier displayed far less activities for both ethylene and propylene polymerizations, it was found that the shape of polyethylene obtained at 40°C is a replica of the carrier particle. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Metallocene catalyst; Olefin polymerization; Polymer supported cocatalyst

1. Introduction

Recently, there have been an increasing number of investigations on the development of supported-type metallocene catalysts for practical applications. The synthetic method of heterogeneous metallocene catalysts reported so far can be roughly classified into the following three categories: (1) immobilization of methylalumoxane (MAO) on the carrier followed by contact with a metallocene complex [1,2]; (2) direct impregnation of a metallocene complex on the carrier [3–6]; and (3) Immobilization of metallocene ligands on the carrier followed by contact with transition metal salts [7–10].

Generally, the first method affords high-performance catalysts with a reduced amount of additional MAO. The second method leads to a loss of catalyst activity probably due to side reactions, which may occur between the metallocene complexes and some functional groups on the carrier surface. In addition, the metallocene catalysts supported on the SiO_2 carrier showed different stereospecificity from that of the original metallocene catalyst [5]. Whereas, the catalyst prepared according to the third method displays a variety of catalyst performance depending upon the carrier used. For example, the use of polysiloxanes as the carrier gives catalysts with fairly high activities, but the corresponding SiO_2-supported catalysts are far less active [11,12].

Much effort has also been put into developing a novel cocatalyst that can replace MAO, and a major improvement has been the use of non-coordinating, bulky anions for the formation of a cationic Zr complex [13–25]. There are, however, very few reports concerning the immobilization of these anions on the carrier [26–28].

With this viewpoint, we have prepared polymer supported borate cocatalysts using poly(styrene-*co*-4-bromostyrene) and poly(styrene-*co*-2%-divinylbenzene) beads as the carrier. This paper reports the synthetic method of those cocatalysts together with the results of ethylene and propylene polymerizations with typical zirconocenes using them as cocatalysts.

2. Experimental part

2.1. Materials

Tris(pentafluorophenyl)boron ($B(C_6F_5)_3$), triphenylcarbenium tetrakis(pentafluorophenyl)borate ($[Ph_3C]^+[B(C_6F_5)_4]^-$), tri(isobutyl)aluminum ($Al(i\text{-}C_4H_9)_3$) (donated by Tosoh Akzo Co., Japan), diphenylmethylene (cyclopentadienyl) (9-fluorenyl)zirconium dichloride (Ph$_2$C[(Cp)Flu]ZrCl$_2$) (donated by Mitsui Chemical Co. Japan), and 2,2′-azobis

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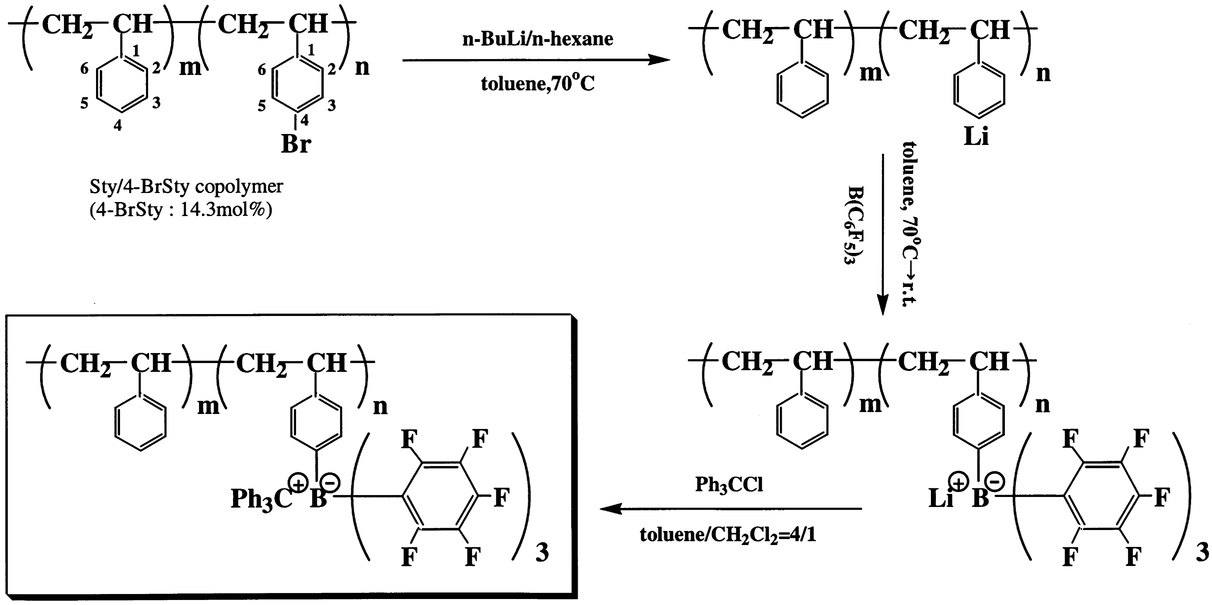

Fig. 1. Preparation scheme of PS-B.

(isobutyronitrile) (AIBN) (from Tokyo Chemical Industry Co., Japan) were used without further purification. Styrene, 4-bromostyrene, toluene, hexane, dichloromethane (from Kanto Chemicals Co., Japan), and polystyrene beads, poly(styrene-*co*-2%-divinylbenzene), (obtained from Acros Organics, USA) were purified according to the usual procedures [29]. Ethylene and propylene (donated by Mitsui Chemical Co., Japan) were purified by passing

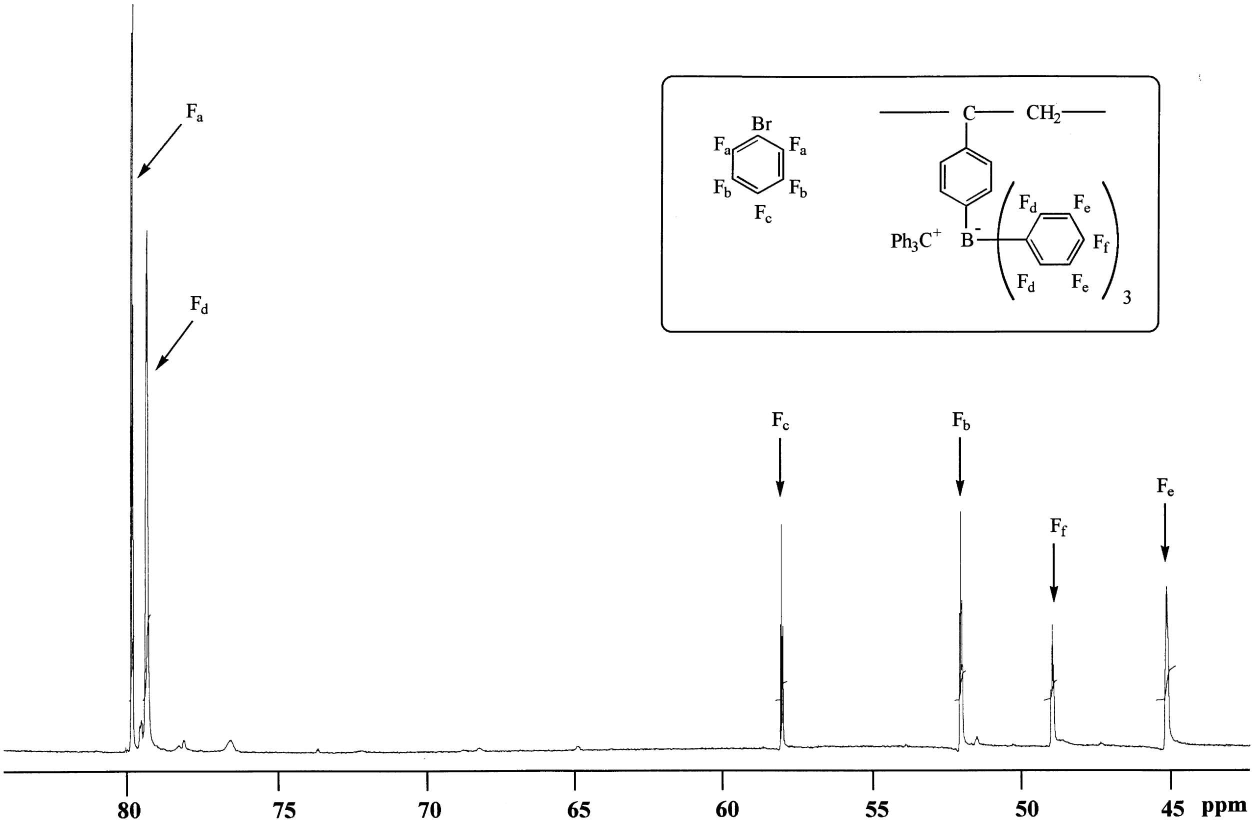

Fig. 2. ^{19}F NMR spectrum of PS-B containing bromopentafluorobenzene as a reference.

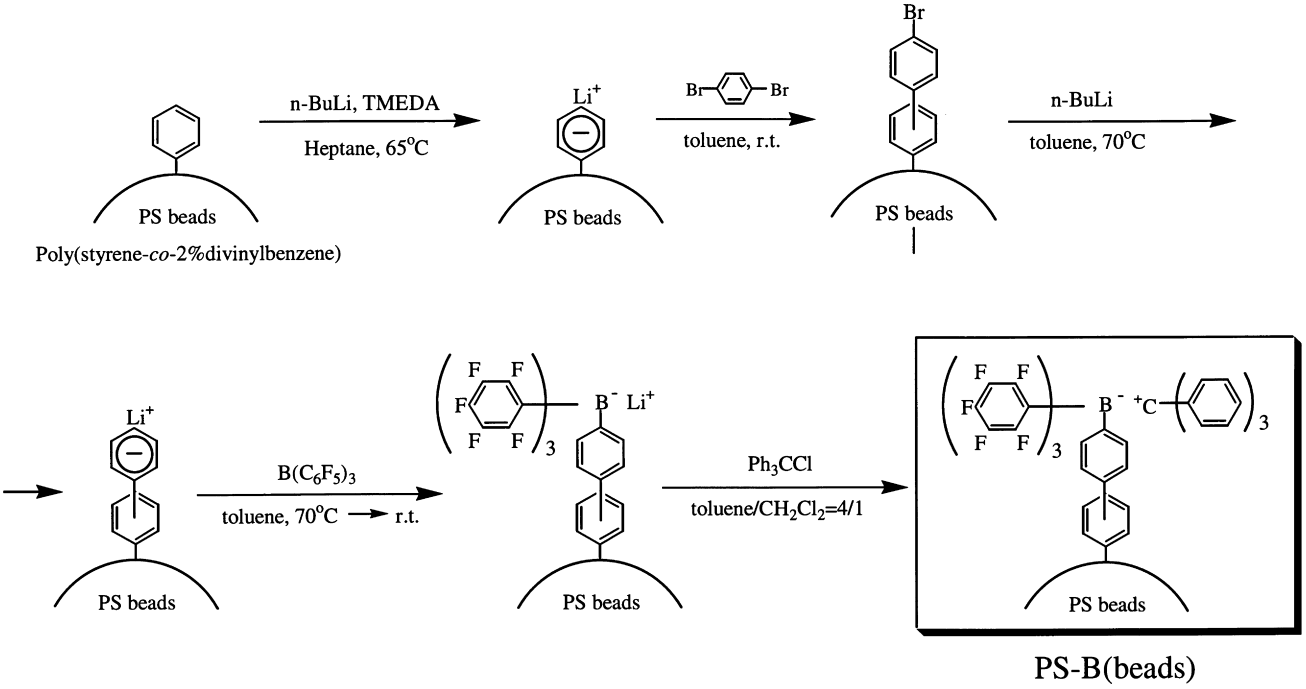

Fig. 3. Preparation scheme of PS-B(beads).

them through NaOH and P_2O_5 columns. *rac*-Ethylene-bis(1-indenyl)zirconium dichloride (*rac*-Et[Ind]$_2$ZrCl$_2$) was prepared according to the literatures [30,31].

2.2. Preparation of the cocatalyst supported on poly(sytrene-co-4-bromostyrene) (PS-B)

The synthetic method of the borate cocatalyst supported on poly(styrene-*co*-4-bromostyrene) (PS-B) is schematically shown in Fig. 1. To 100 cm^3 three-neck flask equipped with a magnetic stirrer, styrene (107 mmol), 4-bromostyrene (15.3 mmol), AIBN (0.15 mmol) and 35 cm^3 of toluene were introduced under nitrogen atmosphere. The copolymerization was carried out at 60°C for 12 h and the reaction mixture was poured into excess methanol. The polymer was separated by filtration and dried in vacuo at 60°C to yield 2.55 g of poly(styrene-*co*-4-bromostyrene). The content of 4-bromostyrene in the copolymer was calculated by ^{13}C NMR spectroscopy from the intensities of two peaks at 125.7 and 119.3 ppm, which were assignable to the phenyl C_1 carbons of styrene and 4-bromostyrene (Fig. 1), respectively, and estimated to be 14.3 mol.% (1.2 mmol-Br/g-polymer). The number average molecular weight ($\bar{M}_n$) and polydispersity ($\bar{M}_w/\bar{M}_n$) of the copolymer determined by GPC were 6.7×10^4 and 2.0, respectively.

Toluene solution (50 cm^3) containing 1.9 g of copolymer (Br: 2.4 mmol) was added dropwise to a 300 cm^3 of 8.7×10^{-3} M *n*-BuLi solution in toluene at 70°C. Disappearance of the peak at 119.3 ppm in ^{13}C NMR spectra confirmed that all the Br groups were completely lithiated. After 5 h at 70°C, 26 cm^3 of 0.1 M $B(C_6F_5)_3$ solution in toluene was added. The reaction mixture was slowly cooled down to room temperature and stirred for 8 h. The product was reacted with 90 cm^3 of 6.4×10^{-2} M Ph_3CCl solution in dichloromethane for 12 h to substitute Li cation for triphenylcarbenium cation. The reaction mixture was filtered to remove the precipitate LiCl and the solution was condensed by evaporation. The yellowish solid product was adequately washed with hexane to obtain the poly(styrene-*co*-4-bromostyrene) supported borate cocatalyst. Fig. 2 displays the ^{19}F NMR spectrum of PS-B measured in $CDCl_3$ at room temperature using bromopentafluorobenzene as a reference. The borate content was estimated from the intensity of F_a and F_d peaks, was found to be 0.92 mmol of borate/g-polymer. The result indicates that approximately 75 mol.% of the 4-bromostyrene units are transformed to the borate complex.

2.3. Preparation of PS-B supported catalyst

The cocatalyst on the PS-B was reacted with an equimolar amount ($[Zr]/[B] = 1$) of *rac*-Et[Ind]$_2$ZrCl$_2$ or Ph$_2$C[(Cp)Flu]ZrCl$_2$ in 20 cm^3 of toluene at 60°C for 1 h. The resulting PS-B supported catalysts were soluble in toluene. After removing toluene by evaporation, 30 cm^3 of heptane was added, and the solid fraction was separated by decantation under nitrogen atmosphere. The contents of Zr in the PS-B supported *rac*-Et[Ind]$_2$ZrCl$_2$ and Ph$_2$C[(Cp)Flu]ZrCl$_2$ catalysts were calculated, respectively, to be 0.51 and 0.17 mmol of Zr/g-PS-B (ca 55.4 and 18.5% formation of a potential active species) by subtracting the Zr contents in the heptane solution part, which were

Table 1
Results of ethylene polymerization with the *rac*-Et[Ind]$_2$ZrCl$_2$ (1)/PS-B catalyst (polymerization conditions: Zr = B = 0.0025 mmol, Al/Zr = 40, solvent = 0.3 dm^3 of toluene, ethylene = 2 atm, reactor = 1 dm^3 glass autoclave equipped with mechanical stirrer, polymerization time = 5 min)

Run no.	Catalyst system	Aging conditions[a]	T_p (°C)	Activity ($\times 10^{-3}$ Kg /PE/mol-Zr.h)	T_m (°C)	$\bar{M}_w$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$
1	(1)/PS-B/Al(i-C_4H_9)$_3$	None	40	Trace	N.d.[b]	N.d.[b]	N.d.[b]
2	(1)/PS-B/Al(i-C_4H_9)$_3$	r.t., 1 h	40	1.62	N.d.[b]	N.d.[b]	N.d.[b]
3	(1)/PS-B/Al(i-C_4H_9)$_3$	60°C, 1 h	40	36.3	137.8	4.7	2.6
4	(1)/PS-B/Al(i-C_4H_9)$_3$	60°C, 1 h	70	49.2	137.4	2.6	2.2
5	(1)/PS-B/Al(i-C_4H_9)$_3$	60°C, 1 h	100	51.6	135.6	1.4	2.4
6	(1)/[Ph_3Cl][B(C_6F_5)$_4$]/Al(i-C_4H_9)$_3$	r.t., 15 min	40	27.4	137.8	8.4	2.9
7	(1)/[Ph_3Cl][B(C_6F_5)$_4$]/Al(i-C_4H_9)$_3$	r.t., 15 min	70	52.8	137.4	3.8	2.4
8	(1)/[Ph_3Cl][B(C_6F_5)$_4$]/Al(i-C_4H_9)$_3$	r.t., 15 min	100	32.6	135.1	1.8	2.0

[a] The catalyst system was aged under described conditions in nitrogen atmosphere.
[b] N.d.: not determined.

determined by ICP analysis, from the total amount of Zr employed. The reactions between the borate and zirconocenes did not proceed quantitatively, which might be due to the steric hindrance around the borate supported on poly(styrene-*co*-4-bromostyrene).

2.4. Preparation of the borate cocatalyst supported on polystyrene beads (PS-B(beads))

The synthesis of the borate cocatalyst supported on poly(styrene-*co*-2%-divinylbenezene) beads (PS-B(beads)) is illustrated in Fig. 3. The brominated PS beads were prepared by the reaction of lithiated PS beads and 1,4-dibromobenzene at room temperature for 24 h. The product was successively washed with THF, diethyl ether, water, toluene and methanol and then dried in vacuo at 60°C for 6 h. The brominated PS beads (5.03 g, Br: 4.5 mmol) were lithiated once again with 13.5 mmol of *n*-BuLi in 150 cm^3 of toluene at 70°C for 8 h, followed by decantation and adequate washing with hexane. The lithium content in the product was estimated to be 0.62 mmol-Li/g by titration. To 36 cm^3 of toluene suspension of lithiated PS beads (4.3 g, Li: 2.67 mmol), 44 cm^3 of 0.1 M B(C_6F_5)$_3$ solution in toluene was added dropwise at room temperature and stirred for 18 h. The product was reacted with 20 cm^3 of 0.4 M Ph_3CCl solution in dichloromethane for 12 h at room temperature to substitute the Li cation for triphenylcarbenium cation. The resulting polystyrene-beads supported borate compounds were dried in vacuo. The supported cocatalyst, PS-B (beads), was insoluble in ordinary organic solvents. Therefore, the borate content in PS-B (beads) was estimated from the elemental analysis of fluoride to be 0.18 mmol of borate/g-PS-B (beads).

2.5. Preparation of the PS-B (beads) supported catalyst

The cocatalyst on the PS-B (beads) was reacted with the mixture of *rac*-Et[Ind]$_2$ZrCl$_2$ ([Zr]/[B] = 1) and Al(i-C_4H_9)$_3$ ([Al]/[Zr] = 40) in toluene at 60°C for 1 h. The reaction mixture was separated by decantation and the solid fraction was subjected to the ICP analysis. The Zr content in the catalyst was found to be 0.14 mmol of Zr/g-PS-B (beads), indicating that approximately 80 mol.% of the borate forms a potential active complex with *rac*-Et[Ind]$_2$ZrCl$_2$.

2.6. Polymerization procedures

Polymerizations of ethylene and propylene were carried out either in a 1 dm^3 glass autoclave equipped with a mechanical stirrer or in a 0.1 dm^3 stainless steel autoclave with a magnetic stirrer. The Glass autoclave was first filled with ethylene or propylene, followed by the introduction of 0.3 dm^3 of toluene. After the reactor was heated up to the polymerization temperature, a given amount of catalyst solution was added to initiate the polymerization. The monomers were continuously supplied into the reactor during the polymerization to maintain the monomer pressure at the initial level. To a stainless steel autoclave, 30 cm^3 of toluene and given amount of the catalyst solution were introduced. The reactor was degassed at liquid nitrogen temperature and 0.29 mol of monomer (7 dm^3 at STP) was introduced. Polymerization was started by rapidly warming up to the polymerization temperature, and terminated by adding acidic methanol. The precipitated polymers were washed with excess methanol and then extracted with either boiling 2-butanone for 8 h to remove the PS-B or with *o*-dichlorobenzene (ODCB) for 8 h to remove the PS-B (beads).

2.7. Analytical procedures

The molecular weight and polydispersity of polymer were measured at 145°C by GPC (gel-permeation chromatography, Senshu Scientific SSC7100) using ODCB as the solvent. Thermal transitions were measured on a Seiko DSC220C differential scanning calorimeter with the rate of 10°C/min. The microstructure of the polymer was mainly determined by ^{13}C NMR spectroscopy. The ^{13}C NMR spectra were recorded at 140°C using a Varian Gemini 300 spectrometer operating at 75 MHz. The content of borate

Table 2
Results of propylene polymerization with the *rac*-Et[Ind]$_2$ZrCl$_2$ (1)/PS-B and Ph$_2$C[(Cp)Flu]ZrCl$_2$(2)/PS-B catalysts (polymerization conditions: Zr = B = 0.005 mmol (Run nos. 8–10), 0.0025 mmol (Run nos. 11–13), Al/Zr = 40, solvent = 0.3 dm^3 of toluene, reactor = 1 dm^3 glass autoclave equipped with mechanical stirrer, propylene = 2 atm, polymerization time = 5 min)

Run no.	Catalyst system	T_p (°C)	Activity ($\times 10^{-3}$ Kg/PE/mol-Zr.h)	T_m (°C)	$\bar{M}_w$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$	Pentad distribution (%)
9[a]	(1)/PS-B/Al(i-C_4H_9)$_3$	40	3.67	141.0	3.0	2.5	88.4 ([*mmmm*])
10[a]	(1)/PS-B/Al(i-C_4H_9)$_3$	70	4.68	113.1	1.0	3.2	N.d.[b]
11[a]	(2)/PS-B/Al(i-C_4H_9)$_3$	40	0.784	128.6	42	2.6	81.4([*rrrr*])
12[c]	(1)/[Ph_3Cl][B(C_6F_5)$_4$]/Al(i-C_4H_9)$_3$	40	56.2	135.6	4.2	2.2	88.5([*mmmm*])
13[c]	(1)/[Ph_3Cl][B(C_6F_5)$_4$]/Al(i-C_4H_9)$_3$	70	34.0	117.9	2.8	2.0	N.d.[b]
14[c]	(1)/[Ph_3Cl][B(C_6F_5)$_4$]/Al(i-C_4H_9)$_3$	100	24.6	87.2	0.9	2.1	N.d.[b]
15[c]	(2)/[Ph_3Cl][B(C_6F_5)$_4$]/Al(i-C_4H_9)$_3$	40	19.5	126.5	42	1.9	83.2([*rrrr*])

[a] Catalyst system was aged at 60°C for 1 h in nitrogen atmosphere.
[b] N.d.: not determined.
[c] Catalyst system was aged at room temperature for 15 min in nitrogen atmosphere.

in PS-B was estimated by ^{19}F NMR with bromopentafluorobenzene (C_6F_5Br) as a reference. The ^{19}F NMR spectrum was taken at room temperature using the ^{19}F NMR (Varian Unity Plus 500) operating at 475 MHz. The content of borate in PS-B (beads), which was insoluble in organic solvents, was determined from elemental analysis. The contents of Zr in the catalysts were measured by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer) Seiko Instruments SPS7700. The morphology of polymer was observed by scanning electron microscope (SEM, Hitachi S4100).

3. Results and discussion

Polymerization of ethylene was conducted with the *rac*-Et[Ind]$_2$ZrCl$_2$/PS-B/Al(i-C_4H_9)$_3$ catalyst system. As shown in Table 1, the catalyst performance is markedly dependent upon the aging conditions. The catalyst system aged at 60°C for 1 h displayed a very high activity comparable to that of the corresponding [Ph_3C][B(C_6F_5)$_4$] cocatalyst system. Moreover, the activity slightly increases with the polymerization temperature up to 100°C probably due to the enhanced stability of the active species, while that of the [Ph_3C][B(C_6F_5)$_4$] cocatalyst system reaches a maximum value and then decreases at higher polymerization temperature. No activity of the heptane solution counterpart from the catalyst preparation and narrow polydispersity ($\bar{M}_w/\bar{M}_n = 2.2$–$2.6$) of the obtained polymers suggest that homogeneous active species remained attached with the PS-B under the polymerization conditions. In addition, the deactivation of active species at high temperature hardly seems to proceed by supporting them on the carrier (Run no. 5).

Polymerization of propylene was carried out with *rac*-Et[Ind]$_2$ZrCl$_2$/PS-B/Al(i-C_4H_9)$_3$, Ph$_2$C[(Cp)Flu]ZrCl$_2$/PS-B/Al(i-C_4H_9)$_3$, and corresponding [Ph_3C][B(C_6F_5)$_4$] cocatalyst systems. Table 2 summarizes the results of polymerization and the analytical data of the resulting polymers. Contrary to ethylene polymerization, the PS-B supported catalysts displayed low-activities for propylene polymerization. ^{13}C NMR spectra of crude polymers obtained in Run nos. 9 and 11 are illustrated in Fig. 4. ^{13}C NMR confirmed that the present catalyst selectively produced syndiotactic polypropylene.

Typical results of ethylene and propylene polymerizations obtained with the aged *rac*-Et[Ind]$_2$ZrCl$_2$/PS-B(beads)/Al(i-C_4H_9)$_3$catalyst system are shown in Table 3. Even though the activities of the *rac*-Et[Ind]$_2$ZrCl$_2$/PS-B (beads) catalyst were much lower than those of the corresponding homogeneous PS-B and [Ph_3C][B(C_6F_5)$_4$] catalyst systems, the linear increase in the yield–time profile of ethylene polymerization, as illustrated in Fig. 5, indicates the enhanced life time of active species on the PS-B (beads). It is often observed that the melting point of polypropylene obtained by the homogeneous catalyst system markedly decreases with polymerization temperature; however, the decrease in melting points of the resulting polypropylene by the present catalyst system was not so drastic even when the polymerization temperature was elevated up to 100°C. The obtained polypropylene was found to consist of a polymer mixture with different tacticity polymers, which could be further separated by extracting with boiling pentane. The analytical data for each fraction are shown in Table 4. The ^{13}C NMR spectra of the polymers, illustrated in Fig. 6, suggest that at least two kinds of active species, isospecific and aspecific, exist in the catalyst system. Although the reason why atactic polypropylene was obtained from a C_2 symmetric metallocene complex is not clear at this moment, the steric environment inside the micropore in the swollen polystyrene beads might affect the stereospecificity of the active species formed on the PS-B (beads). It was also found from the ^{13}C NMR spectrum shown in Fig. 6(a) that the polypropylene obtained from the boiling pentane insoluble fraction is much more isotactic compared with that obtained with the

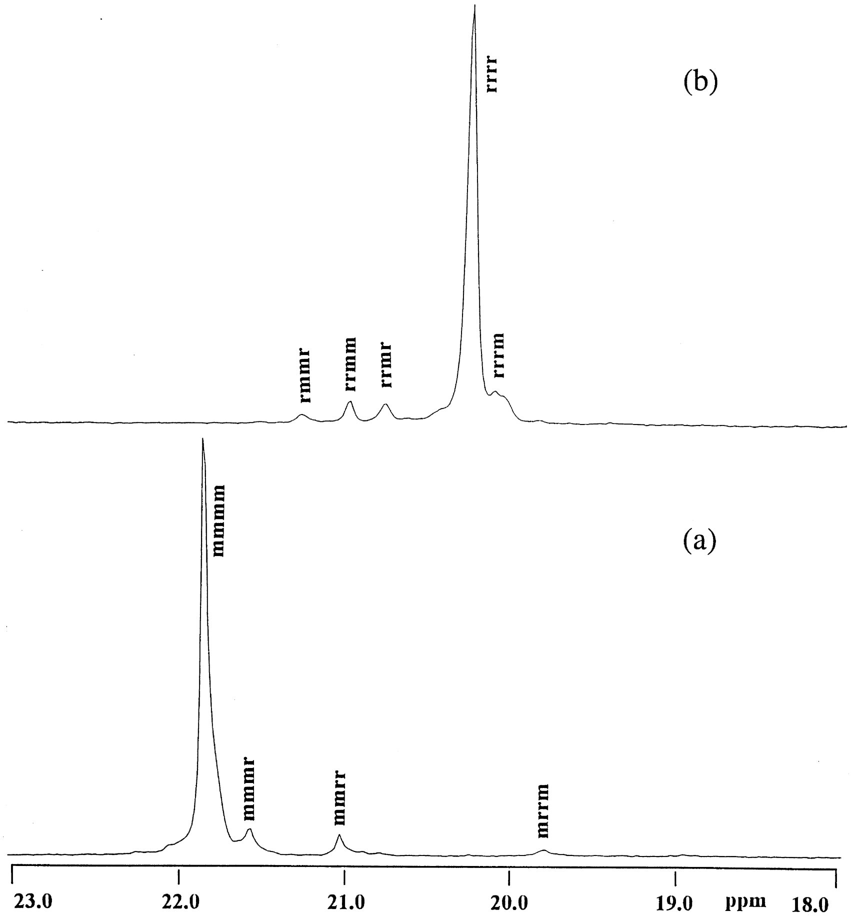

Fig. 4. ^{13}C NMR spectra of (a) isotactic polypropylene (Run no. 9) and (b) syndiotactic polypropylene (Run no. 11).

corresponding homogeneous metallocene catalyst. When the $Ph_2C[(Cp)Flu]ZrCl_2$ catalyst was employed for propylene polymerization, only trace amounts of the polymer were produced.

To obtain morphological information on the obtained polymers, both the PS-B (beads) and polyethylene (Run no. 17) was observed by SEM. The SEM pictures, shown in Fig. 7, clearly indicate that the shape of the polymer particles is a replica of that of the carrier particle.

In conclusion, two types of polymer supported borate cocatalysts using poly(styrene-*co*-4-bromostyrene) (PS-B) and poly(styrene-*co*-2%-divinylbenzene) (PS-B(beads)) were prepared and employed for ethylene and propylene polymerizations combined with Al(i-C_4H_9)$_3$. In the case of

Table 3
Typical results of ethylene and propylene polymerizations with the *rac*-Et[Ind]$_2$ZrCl$_2$/PS-B (beads)/Al(I-C_4H_9)$_3$ catalyst (catalyst system was aged at 60°C for 1 h in nitrogen atmosphere)

Run no.	Monomer	T_p (°C)	Activity(kg-polymer/mol-Zr.h)	T_m (°C)	$\bar{M}_w$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$
16[a]	Ethylene	0	255	140.5	16.0	4.6
17[a]	Ethylene	40	646	141.5	8.5	4.7
18[a]	Ethylene	70	720	139.9	6.1	3.7
19[b]	Propylene	40	14.2	146.9	3.7	6.6[c]
20[b]	Propylene	70	45.1	129.7	1.0	5.2[c]
21[b]	Propylene	100	10.7	122.7	0.8	4.5
22[b]	Propylene	140	1.8	82.1	0.3	2.5

[a] Polymerization conditions: Catalyst = 20 mg (Zr = 0.0028mmol, B = 0.0036mmol), solvent = 0.3 dm^3 of toluene reactor = 1 dm^3 glass autoclave equipped with mechanical stirrer, ethylene = 4 atm, polymerization time = 1 h.

[b] Polymerization conditions: Catalyst = 20 mg (Zr = 0.0028 mmol, B = 0.0036 mmol), solvent = 30 cm^3 of toluene reactor = 0.1 dm^3 Stainless steel autoclave equipped with magnetic stirrer propylene = 7 dm^3 (STP) polymerization time = 15 h.

[c] Bimodal GPC curve was observed.

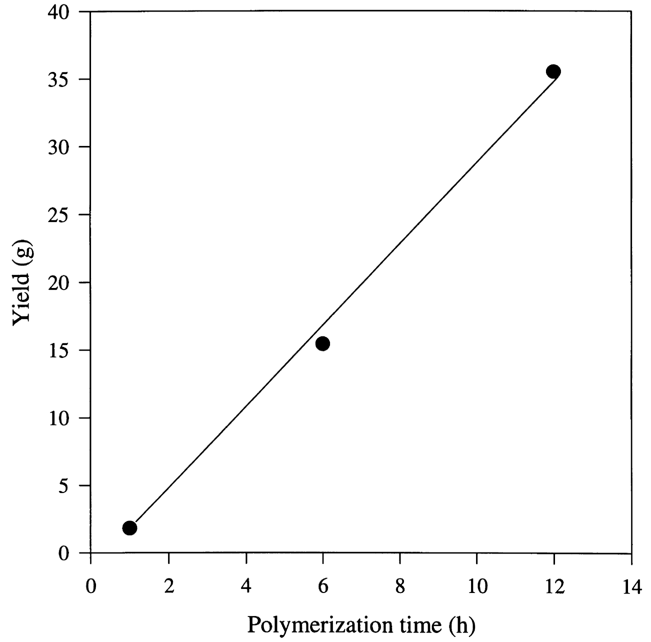

Fig. 5. Yield of polyethylene as a function of polymerization time on the polymerization of ethylene with the *rac*-Et[Ind]$_2$ZrCl$_2$/PS-B(beads)/Al(*i*-C$_4$H$_9$)$_3$ catalyst at 40°C.

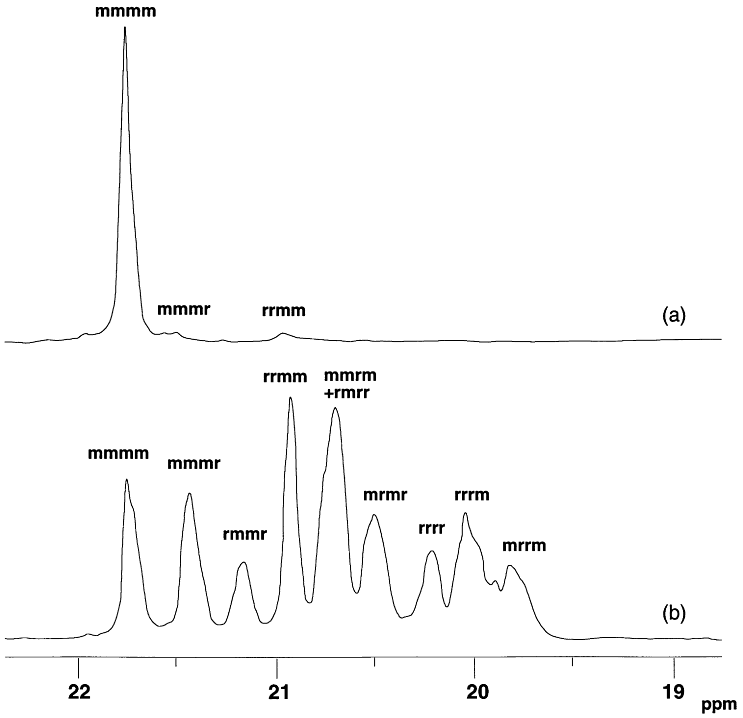

Fig. 6. ^{13}C NMR spectra of fractionated polypropylene: (a) boiling pentane insoluble fraction; and (b) boiling pentane soluble fraction.

Table 4
Fractionation of propylene obtained in Run no. 19

	Wt.%	T_m (°C)	$\bar{M}_w$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$	[*mmmm*][a] (%)
Boiling pentane insoluble fraction	50.5	150.7	8.6	2.6	95.1
Boiling pentane soluble fraction	49.5	N.d.[b]	1.0	2.3	10.0

[a] Determined by ^{13}C NMR analysis.

[b] N.d.: not detected.

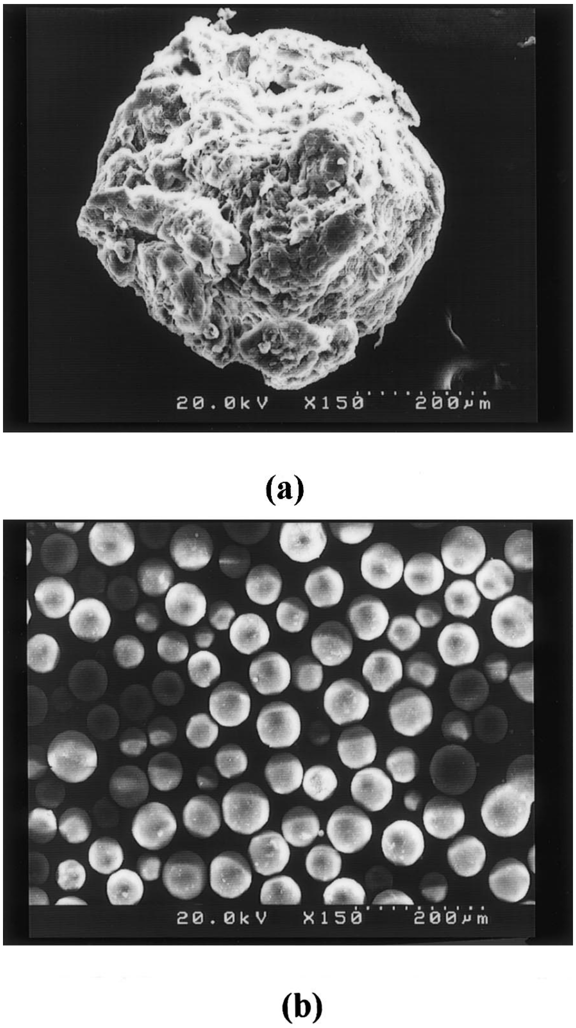

Fig. 7. SEM photographs of: (a) polyethylene (Run no. 17); and (b) polystyrene beads.

PS-B as the carrier, the resulting soluble catalysts showed very high activity for ethylene polymerization, but were not so active for propylene polymerization. The insoluble catalyst with PS-B (beads) as the carrier displayed low activity for both polymerization, however, the obtained polyethylene particles replicated the sphere shape of the carrier.

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