Polymer-incorporated iron catalysts for ethylene polymerization—a new approach to immobilize iron olefin catalysts on polystyrene chains

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Received (in Montpellier, France) 14th March 2002, Accepted 16th May 2002
First published as an Advance Article on the web 20th August 2002

2,6-Bis(imino)pyridyl iron catalysts bearing allyl groups [ArN=C(Me)][Ar′N=C(Me)]$C_5H_3NFeCl_2$ (Ar = Ar′ = 4-allyl-2,6-(i-Pr)$_2C_6H_2$ (**Cat-1**); Ar = 2,6-(i-Pr)$_2C_6H_3$, Ar′ = 4-allyl-2,6-(i-Pr)$_2C_6H_3$ (**Cat-2**)) have been synthesized and characterized. The corresponding polymer-incorporated iron catalysts **PC-1**, **PC-2** and their SiO_2-supported core–shell structure catalysts **SC-1** and **SC-2** were obtained by the co-polymerization of the olefin groups of **Cat-1** or **Cat-2** with styrene in the presence of a radical initiator. All three types of catalysts (**Cat-1** and **Cat-2**; **PC-1** and **PC-2**; **SC-1** and **SC-2**) have been investigated for ethylene polymerization. As a result, these catalysts were found to exhibit high activity using modified methylaluminoxane (MMAO) as a co-catalyst. Among them, the polymer-incorporated SiO_2 core–shell catalysts displayed very high activity ($\sim$3181 g (mmol Fe)$^{-1}$ h^{-1}) with product molecular weights in the range 25–93 × 10^4. The particle morphology of polyethylene produced by the core–shell structure catalysts (**SC-1** and **SC-2**) was improved.

1 Introduction

The polymerization of olefins by late transition metal complexes is at an exciting juncture. Late transition metal catalysts are particularly attractive because of their potential for tolerating heteroatomic functionalities, which may open up the possibility for copolymerizations of polar monomers.[1,2] In prior studies, Brookhart *et al.*,[3–7] and Gibson *et al.*[8–10] have reported highly active ethylene and propylene polymerization catalysts based on iron(II) and cobalt(II) bearing 2,6-bis(imino)pyridyl ligands. We were attracted by the potential for using iron as an ethylene polymerization active center due to its low cost and high activity. However, practical considerations have indicated that industrial ethylene polymerization is performed usually in the heterogeneous mode with supported catalysts. Traditional supports, such as high surface area silica or alumina, have reactive surfaces[11–13] that can lead to catalyst deactivation and thus alternative supports are desirable.

Recently, on the basis of long experience in polymer-supported metallocene catalysts for olefin polymerization,[14a,b] we successfully developed a series of novel polymer-incorporated late transition metal catalysts for ethylene polymerization. This article reports the preparation and characterization of the polystyrene-incorporated iron catalysts and the more practicable shell–core polystyrene-incorporated iron catalysts, as well as the results on their use in ethylene polymerization (Scheme 1).

2 Experimental

2.1 General considerations and materials

Dried solvents (hexane, toluene, tetrahydrofuran, methanol, dichloromethane) used for complex synthesis and ethylene polymerization were refluxed over an appropriate drying agent and distilled prior to use. Diacetylpyridine, 2,6-diisopropylbenzeneamine, SiO_2 used as support were purchased from Aldrich Chemical Co. Inc. Modified methylaluminoxane (MMAO) was purchased from Acros Organics as 10% weight of a toluene solution and used without further purification. Styrene and divinylbenzene for co-polymerization were purchased from Aldrich Chemical Co. Inc. and redistilled prior to use.

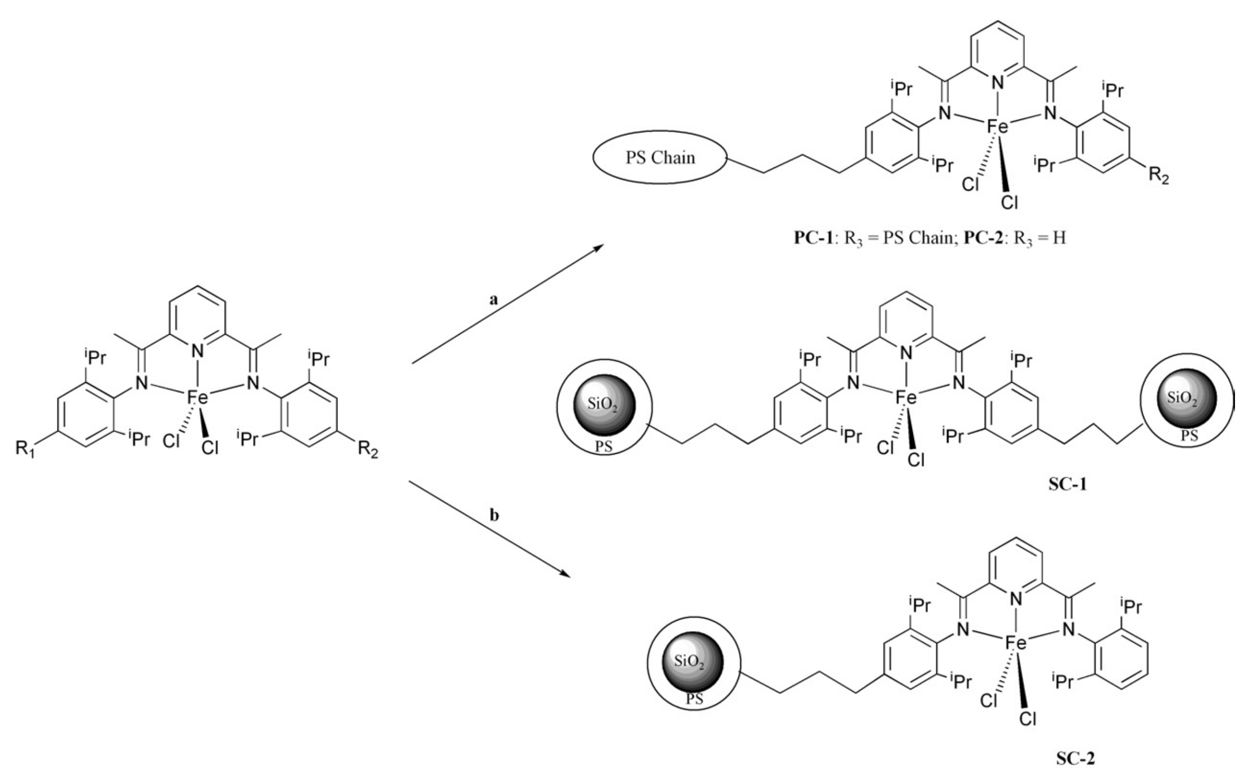
2.2 Ligand and complex analyses

IR spectra of the complexes were measured on a Bio-Rad FTS135 spectrometer. ^{1}H-NMR spectra and ^{13}C NMR spectra were recorded on a Unity-400 spectrometer. EI-MS spectra were recorded on a Finigan MAT 8500 spectrometer (70 eV), and elemental analysis was performed on Perkin Elmer Series II CHN/O Analyzer 2400.

2.3 Polymer characterization

^{13}C NMR data for polyethylene were obtain using *o*-dichlorobenzene as a solvent at 130 °C. The intrinsic viscosity [η] was measured in Decalin at 135 °C using an Ubbelohde viscometer. Viscosity average molecular weight (M_v) were calculated by using the following equation $[\eta] = 2.3 \times 10^{-4}\ M_v^{0.82}$. Molecular weight distribution (M_w/M_n) values of polyethylene were determined using a PL GPC-220 gel permeation chromatograph at 150 °C using narrow standards calibration and equipped with three PL gel columns (sets of PL gel 10 μm MIXED-B LS). Trichlorobenzene was employed as a solvent at a flow rate of 1.00 mL min^{-1}. GPC characterizations of the polystyrene-incorporated catalysts were made on a Waters 410 GPC Report at 35 °C. Tetrahydrofuran (THF) was employed as a solvent at a flow rate of 1.00 mL min^{-1}. Elemental analysis for Fe in polystyrene-incorporated catalysts and shell–core iron catalysts was done using the ICP method

DOI: 10.1039/b202715c



Scheme 1 The synthesis of polystyrene-incorporated catalysts **PC-1**, **PC-2** and shell–core polystyrene-incorporated catalysts **SC-1**, **SC-2**. a. Styrene, AIBN, toluene, 79–80 °C; b, SO_2, styrene, divinylbenzene, AIBN, toluene, 79–80 °C.

with a TJA POEMS ICP analyzer after dry ashing and dilute nitric acid dissolution.

2.4 Synthesis

All manipulations and reactions were performed with the exclusion of oxygen and moisture under argon using standard Schlenk technigues in oven-dried glassware. 4-Allyl-2,6-diisopropylaniline was prepared from 2,6-diisopropylaniline according to reference 15.

2.4.1 Synthesis of 2,6-diacetylpyridine bis(4-allyl-2,6-diisopropylaniline) (L-1). A solution containing 2,6-diacetylpyridine (0.30 g, 1.84 mmol), 4-ally-2,6-diisopropylaniline (0.80 g, 3.68 mmol) and formic acid (2 ml) in 30 ml dry methanol was kept to reflux under argon for 14 hours. The resulting yellow solid was collected by filtration and washed with cold methanol (3 × 5 ml). Yellow crystals (0.70 g, 68%) of **L-1** were isolated by recrystallization from CH_2Cl_2–hexane (1:4). IR (KBr): ν(C=N) 1639 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 8.47 (d, 2H, Py-H_m), 7.92 (t, 1H, Py-H_p), 6.98 (s, 4H, Ph-H_m), 6.04 (m, 2H, CH=C), 5.12 (m, 4H, C=CH_2), 3.40 (d, 4H, CH_2-C=C), 2.75 (m, 4H, CH$(Me)_2$), 2.27 (s, 6H, CH_3), 1.15 (d, 24H, C$(CH_3)_2$); ^{13}C-NMR ($CDCl_3$): 167.04 (C=N), 155.15 (Py-C), 144.57 (Ph-C), 138.12 (Ph-C), 136.79 (Py-C), 135.69 (Ph-C), 134.75 (–CH=), 123.16 (Py-C), 122.12 (Ph-C), 115.34 (=CH_2), 40.25 (–CH_2–), 28.31 (C$(Me)_2$), 23.24 (CH_3), 22.92 (CH_3), 17.14 (CH_3). $C_{39}H_{51}N_3$ (561.86 g mol^{-1}): Anal. Calcd.: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.03; H, 9.13; N, 7.55%.

2.4.2 Synthesis of 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine (L-2). A solution of 2,6-diacetylpyridine (0.30 g, 1.84 mmol), 2,6-diisopropylaniline (0.33 g, 1.84 mmol) and formic acid (2 ml) in 30 ml dry methanol was stirred at room temperature for two days. The monosubstituted yellow solid product (0.52 g, 87.1%) was collected by filtration, washed with cold methanol, and identified as the desired monoimine by ^{1}H-NMR. This monoimine (0.50 g, 1.55 mmol) was dissolved in 25 ml hot methanol, followed by the addition of 5 ml CH_2Cl_2, 2 ml formic acid and excess 4-allyl-2,6-diisopropylaniline. The solution was stirred in a sealed flask at 50 °C for 2 days, and a yellow solid formed. This solid was determined to be the desired ligand (**L-2**) (0.65 g, 80.4%). IR(KBr): ν(C=N) 1639 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 8.46–8.50 (br, 2H, Py-H_m), 7.90–7.96 (br, 1H, Py-H_p), 7.17 (d, 2H, Ph-H_m), 7.11 (t, 1H, Ph-H_p), 6.98 (s, 2H, Ph-H_m), 6.05 (br, 1H, –CH=C), 5.10 (t, 2H, C=CH_2), 3.41 (d, 2H, CH_2–C=C), 2.77 (br, 4H, CH$(Me)_2$), 2.27 (s, 6H, CH_3), 1.14–1.17 (br, 24H, C$(CH_3)_2$). ^{13}C-NMR ($CDCl_3$): 167.04 (C=N), 155.21 (Py-C), 146.51 (Ph-C), 144.59 (Ph-C), 138.16 (Ph-C), 136.81 (Py-C), 135.77 (Ph-C), 135.71 (Ph-C), 134.78 (–CH=), 123.56 (Py-C), 123.17 (Py-C), 122.99 (Ph-C), 122.13 (Ph-C), 115.32 (=CH_2), 40.26 (–CH_2–), 28.33 (C$(Me)_2$), 23.24 (CH_3), 22.91 (CH_3), 17.13 (CH_3). $C_{36}H_{47}N_3$ (521.79 g mol^{-1}): : Anal. Calcd.: C, 82.87; H, 9.08; N, 8.05. Found: C, 82.20; H, 9.13; N, 8.11%.

2.4.3 Synthesis of 2,6-diacetylpyridine bis(4-allyl-2,6-diisopropylaniline) iron dichloride (Cat-1) and [2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine] iron dichloride (Cat-2). A solution containing $FeCl_2 \cdot 4H_2O$ (0.20 g, 1.00 mmol) and **L-1** (0.60 g, 1.07 mmol) in 40 ml THF was stirred for 5 h and then evaporated under vacuum. The residue was washed with diethyl ether (3 × 10 ml), and recrystallized from CH_2Cl_2–hexane (3:1) at −20 °C to afford blue crystals of **Cat-1** (0.66 g, 95.9%). IR(KBr): ν(C=N) 1621 cm^{-1}. EI-MS (70 eV): m/z 653 ($M^+ - Cl$, 10%), 562 ($M^+ - FeCl_2$, 100), 520 ($M^+ - FeCl_2 - C_3H_6$, 5). $C_{39}H_{51}N_3FeCl_2$ (688.61 g mol^{-1}): Anal. Calcd.: C, 68.03; H, 7.47; N, 6.10. Found: C, 67.70; H, 7.39; N, 6.13%.

An analogous method was used for the preparation of **Cat-2** (97.2%). IR(KBr): ν(C=N) 1619 cm^{-1}. EI-MS (70 eV): m/z 522 ($M^+ - FeCl_2$, 100%), 576 ($M^+ - 2Cl$, 20). $C_{36}H_{47}N_3FeCl_2$ (648.54 g mol^{-1}): Anal. Calcd.: C, 66.67; H, 7.31; N, 6.48. Found: C, 66.74; H, 7.27; N, 6.52%.

2.4.4 Preparation of polymer-incorporated catalysts PC-1 and PC-2. Under argon atmosphere, a solution containing **Cat-1** (0.34 g, 0.49 mmol), styrene (5 ml) and AIBN (0.20 g, 1.22 mmol) in 30 ml toluene was kept at 79–80 °C under stirring for 8 h. The solution was evaporated under reduced pressure and the residue was washed with a mixed solution of hexane–toluene (2:1) to afford the solid polymer-incorporated catalyst **PC-1**. ICP-AES: 4.00 mg Fe/g poly.; GPC: M_w 22 598, M_n 15 406, polydispersity index 1.446. An analogous method was used for preparation of polymer-incorporated catalyst **PC-2**. ICP-AES: 2.81 mg Fe/g poly.; GPC: M_w 17 959, M_n 13 000, polydispersity index 1.38.

2.4.5 Preparation of shell–core polymer-incorporated iron catalysts SC-1 and SC-2. To a solution of 5 ml styrene in 10 ml toluene was added 2.0 g of SiO_2 under nitrogen atmosphere, followed by vigorous stirring at 40 °C for 30 min. Then the solution of 0.17 g (0.245 mol) **Cat-l** in 5 ml toluene and 0.25 ml of divinyl benzene were transferred to the above suspension by syringe. 0.20 g of AIBN was added. The suspension was kept at 79–80 °C under stirring for 8 h. The precipitate was separated and washed with toluene then dried under reduced pressure to afford the shell–core polymer-incorporated iron catalyst **SC-1**. ICP-AES: 1.69 mg Fe/g cat. An analogous method was used for the preparation of shell–core polymer-incorporated iron catalyst **SC-2**. ICP-AES: 1.44 mg Fe/g cat.

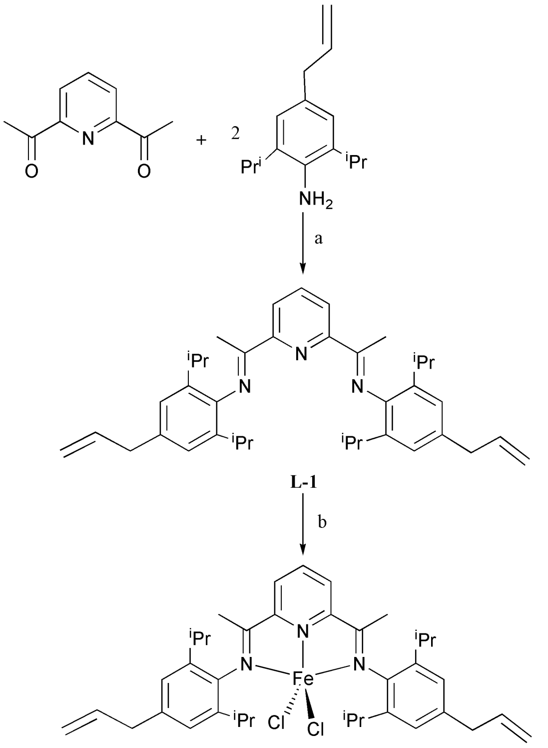
2.5 Ethylene polymerization

Ethylene polymerization was carried out under appropriate ethylene pressure in toluene or hexane in a 500 mL glass reactor equipped with a propeller-like stirrer. Solvent (100 mL) was introduced into the argon-purged reactor and stirred (800 rpm). The solvent was thermostated to a prescribed polymerization temperature, and the ethylene gas feed was started after 20 min. Polymerization was initiated by adding a toluene solution of co-catalyst (MMAO) and then catalyst (in a solution of toluene or as solid particles) into the reactor with vigorous stirring (800 rpm). After a prescribed time, the ethylene gas feed was terminated. To the resulting mixture, ethanol (500 mL) and concentrated HCl (1 mL) were added. The polymer was collected by filtration, washed with methanol (100 mL) and dried *in vacuo* at 70 °C for 15 h.

3 Result and discussion

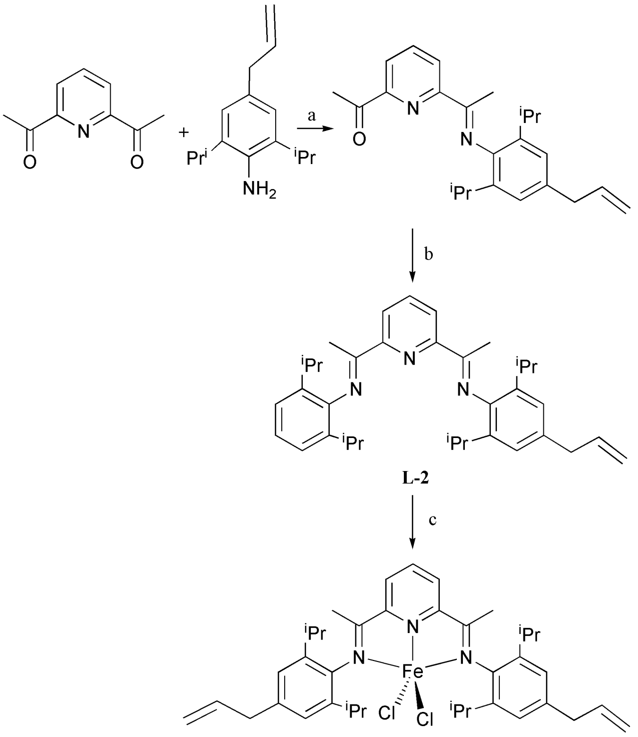
3.1 Synthesis and characterization of the polymer-incorporated iron catalysts and shell–core polymer-incorporated iron catalysts

The reaction of 2,6-diacetylpyridine and primary amine was carried out in the presence of formic acid in methanol solution. Different molar ratios of the starting materials gave two different kinds of products. Treatment of 2,6-diacetylpyridine with an excess of 4-allyl-2,6-diisopropylaniline led to the formation of 2,6-diacetylpyridinebis(4-allyl-2,6-diisopropylaniline) (**L-1**) (Scheme 2), while an equimolar ratio of 2,6-diacetylpyridine with 4-allyl-2,6-diisopropylaniline or 2,6-diisopropylaniline gave the monoimine product, which could further react with the primary amine to form the unsymmetrical 2,6-diimine-pyridine ligand (**L-2**) (Scheme 3). **L-1** and **L-2** can be used as tridentate ligands and coordinated with $FeCl_2 \cdot 4H_2O$ in THF solution to form complexes (**Cat-1** and **Cat-2**) in high yields. **Cat-1** and **Cat-2** were blue needle-like crystals, which were obtained by recrystallization from CH_2Cl_2–hexane (3:1).



Scheme 2 The synthesis of **Cat-1**. a, Methanol, H^+, heat; b, $FeCl_2 \cdot 4H_2O$, THF.

Alt *et al.* reported that metallocene catalysts with ω-alkenyl substituents showed self-immobilization in ethylene polymerization by the co-polymerization of the alkenyl group with ethylene.[16] Recently Herrmann *et al.* described that bis(imino)-pyridyliron complexes with ω-alkenyl groups acted as self-immobilized catalysts for ethylene polymerization.[17] The allyl groups in **Cat-1** and **Cat-2** are also active and can be co-polymerized with styrene in the presence of a radical initiator (AIBN) resulting in the corresponding polymer-incorporated catalysts **PC-1** and **PC-2**. In order to co-polymerize the complexes with styrene sufficiently, it was necessary to control the temperature in the range of 79 °C to 81 °C. The higher



Scheme 3 The synthesis of **Cat-2**. a, Methanol, H^+; b, 4-allyl-2,6-diisopropylaniline, 2-propanol, H^+, heat; c, $FeCl_2 \cdot 4H_2O$, THF.

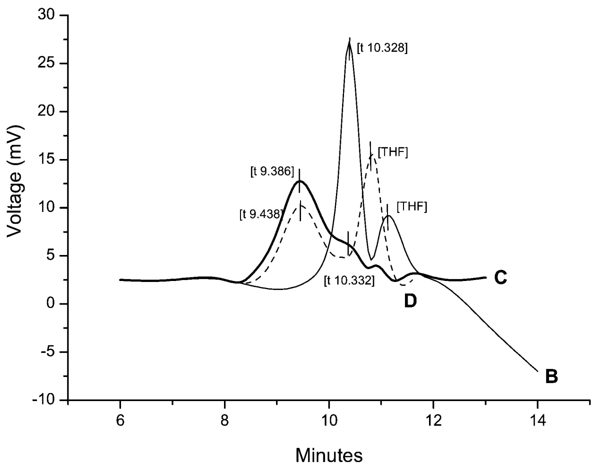


Fig. 1 The results of GPC characterization.

temperature would lead to enhancement of the rate of homopolymerization of styrene. When the co-polymerization is complete, the mixed solvent hexane–toluene (2:1) was used to precipitate the polymer-incorporated catalysts and wash away the remnants of iron compounds, which did not co-polymerize with styrene. According to the results of ICP characterization, it was deduced that the molar ratios of the starting materials (**Cat-1**:styrene and **Cat-2**:styrene) were 1:88.3 and the corresponding copolymer unit ratios in **PC-1** and **PC-2** were 1:134 and 1:191. In the structures of the polymer-incorporated catalysts **PC-1** and **PC-2**, the active center was connected to the polystyrene chains through only one or two carbon–carbon bonds. The low content of active centers and the electronic paramagnetism of Fe(II) make the IR and ^{1}H NMR characterization inefficient. Further parallel GPC tests of three samples (B, **Cat-2**; C, **PC-2** mixed with trace of **Cat-2**, 4.67 mg Fe/g poly.; D, **PC-2**, 2.81 mg Fe/g poly.) were carried out. Fig. 1 shows that the trace of **Cat-2** in **PC-2** (curve C) can be distinguished by the rinsing time (10.332 min for **Cat-2**, 9.386 min for **PC-2**). No peak appears around 10.332 min in curve D (9.438 min for **PC-2**, 10.859 min for THF solvent), demonstrating that the iron content in **PC-2** (2.81 mg Fe/g poly.) is almost incorporated in polystyrene blocks. The rinsing time of the solvent THF was affected by the tested samples so that it was different in the three curves.

The shell–core iron incorporated catalysts **SC-1** and **SC-2** were prepared by using SiO_2 beads to support the light cross-linked polystyrene-incorporated iron catalysts. Co-polymerization among iron compounds, styrene and divinylbenzene was controlled under similar condition to the preparation of **PC-1** and **PC-2**. The cross-linking degree of the polystyrene-incorporated catalysts plays an important role in the preparation of shell–core catalysts. Polymer-incorporated iron catalysts with high cross-linking degrees are insoluble in toluene and can not cover the surface of the SiO_2 beads, whereas for the polystyrene-incorporated iron catalysts with too low cross-linking degrees the shell–core catalysts will be frail and easily disintegrated because of the swelling effect of polystyrene in toluene. In this article, polystyrene-incorporated catalysts with a cross-linking degree of 4.07% (calculated according to the starting materials) were chosen.

3.2 Polymerization of ethylene

The results of ethylene polymerization tests are collected in Table 1

Several features are noteworthy. Unlike the cases of **Cat-1** and **Cat-2**, ethylene polymerization catalyzed by **PC-1** and **PC-2** proceeds smoothly without an immediate exotherm and a decrease in activity. The dispersion of iron complexes among the polystyrene blocks did not approach too high concentrations of active centers in the polymerization system and resulted in ethylene polymerization at a smooth pace. As a result, **PC-1** was found to display a activity of 430 kg of polyethylene (mol Fe)$^{-1}$ h^{-1} at 25 °C which was lower than the activity of ethylene polymerization catalyzed by **Cat-1** under the same polymerization conditions (1590 kg of polyethylene (mol Fe)$^{-1}$ h^{-1}). However, **PC-2** was found to display a higher activity than **Cat-2** under the same polymerization conditions (at 13 °C, **PC-2**: 2466 kg of polyethylene (mol Fe)$^{-1}$ h^{-1}; **Cat-2**: 1588 kg of polyethylene (mol Fe)$^{-1}$ h^{-1}). The different polymer configuration of the polymer-incorporated catalysts **PC-1** and **PC-2** may contribute to this observation.

Although the polymer-incorporated iron catalysts **PC-1** and **PC-2** are active for ethylene polymerization and avoid

Table 1 Results of ethylene polymerization[a]

						molecular weight		
Entry[b]	Pro-catalyst	T/°C	Pressure/MPa	Al/Fe (molar ratio)	Activity/g (mmol Fe)$^{-1}$ h^{-1}	M_w[c]	M_n[c]	M_w/M_n[c]
1		25	0.1	1600	1590	142 302	3001	47.42
2	**Cat-1**	0	0.1	1600	1900	187 123	8725	21.45
3		13	0.1	2200	1588	89 658	968	92.62
4	**Cat-2**	0	0.1	2200	4017	179 882	7776	23.13
5		25	0.1	1200	365	—	—	—
6	**PC-1**	25	0.1	1600	430	99 935	1456	68.64
7		60	0.24	1600	3130	182 427	6734	27.09
8		13	0.1	1650	2233	—	—	—
9	**PC-2**	13	0.1	2200	2466	129 216	2727	47.38
10		60	0.24	2200	3900	153 632	6514	23.58
11		51	0.1	1200	636		31.24×10^4[d]	
12	**SC-1**	60	0.3	1200	3085		25.47×10^4[d]	
13		51	0.3	1200	2507		93.97×10^4[d]	
14		51	0.1	1600	1086		30.56×10^4[d]	
15	**SC-2**	60	0.3	1600	3181		28.13×10^4[d]	
16		51	0.3	1600	2623		86.98×10^4[d]	

[a] All of the pro-catalysts activated with MMAO; ethylene polymerization time, 1 h. [b] Entries 1–10, 50 ml of toluene solvent; entries 11, 13, 14, 16, 100 ml of hexane solvent; entries 12, 15, 100 ml of toluene solvent. [c] Determined by GPC at 135 °C. [d] Polymer did not dissolve wholly in trichlorobenzene under GPC measurement conditions. The results were obtained from polyethylene soluble in Decalin under intrinsic viscosity measurement conditions.

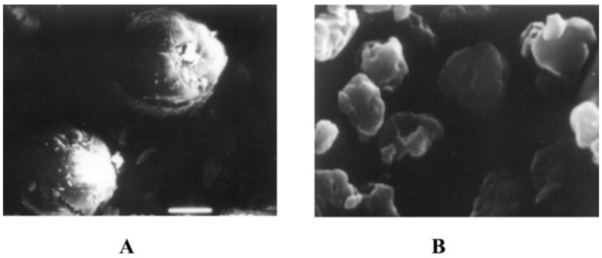


Fig. 2 (A) Scanning electron microscope image of a **SC-1** particle (scale bar, 10 μm). (B) Scanning electron microscope image of a polyethylene bead resulting from the **SC-1** catalyst (scale bar, 100 μm).

immediate exotherm, the morphology of the polyethylene catalyzed by **PC-1**, **PC-2** is a little poor, with particles of varied and ill-defined shapes. The further synthesis of the shell–core iron catalysts **SC-1** and **SC-2** is expected to control the particle morphology.

The shell–core polymer-incorporated catalysts **SC-1** and **SC-2** were prepared using SiO_2 beads as the core to support the polymer-incorporated catalysts so that fewer active centers were enwrapped in the inner spherical particles to exhibit high activity. As the result, **SC-1** exhibited a very high activity of 3085 kg of polyethylene (mol Fe)$^{-1}$ h^{-1} at 60 °C and 0.3 MPa of ethylene pressure with a viscosity average molecular weight (M_v) value of 25.47×10^4 and **SC-2** was found to display a very high activity of 3181 kg of polyethylene (mol Fe)$^{-1}$ h^{-1} at 60 °C and 0.3 MPa of ethylene pressure with a viscosity average molecular weight (M_v) value of 28.13×10^4. The most exciting fact was that the shell–core iron catalysts **SC-1** and **SC-2** gave unexpectedly high molecular weight polyethylene. Polyethylene with a very high viscosity average molecular weight (M_v) value of 93.97×10^4 was obtained at 51 °C by using **SC-1** as the catalyst, and polyethylene with a viscosity average molecular weight (M_v) value of 86.98×10^4 was obtained at 51 °C by using **SC-2** as catalyst. In comparison, **PC-2**/MAO provided polyethylene with a viscosity average molecular weight (M_W) value of 18.24×10^4 at 60 °C and 0.24 MPa of ethylene pressure,[18] and 2,6-diacetylpyridinebis(2,6-diisopropylaniline)iron dichloride reported by Gibson *et al.* provided polyethylene with a molecular weight (M_w) value of 2.76×10^4 at 60 °C and 1.33 MPa ethylene pressure.[8] The explanation of such results is still under research.

The SiO_2 core increases the rigidity of the catalyst beads and affords a suitable spherical mode for polyethylene products. Polyethylene samples resulting from **SC-1** and **SC-2** were isolated in the form of discrete spherical beads (Fig. 2).

All the iron catalysts including **Cat-1**, **Cat-2**, **PC-1**, **PC-2**, **SC-1**, **SC-2** produce essentially linear polyethylene with a broad molecular weight distribution. The bimodality of polyethylene is attributed to the additional chain termination mechanism (chain transfer to aluminium), which predominates at high concentrations of aluminium activator and at short reaction times. ^{13}C-NMR analyses of the polyethylene generated by all the iron catalysts reveal that the resonances at 14.1 ppm, 22.85 ppm, 29.57 ppm, 29.69 ppm, 32.21 ppm are obvious in all tests, by which the saturated end group in the polymer chains is identified. This end group arises from chain transfer to aluminium followed by hydrolysis during the acid workup.[19]

In summary, the shell–core polymer-incorporated iron catalysts described herein represent a significant polyolefin technology, which may be applicable to some other olefin polymerization catalysts based on late transition metals. To the best of our knowledge, these are the first reported polymer-incorporated and shell–core polymer-incorporated late transition metal catalysts for olefin polymerization.

Acknowledgements

Financial support by the National Natural Science Foundation of China and by the Special Funds for Major State Basic Research Projects (G 1999064800) is gratefully acknowledged.

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