

The synthesis and catalytic activity of poly(bis(imino)pyridyl) iron(II) metallodendrimer

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Abstract

The first and second generation carbosilane dendrimers with silicon hydride terminated were synthesized, and then reacted with bis(imino)pyridyl containing allyl [4-CH₂=CHCH₂-2,6-*i*-Pr₂C₆H₃N=CMe(C₅H₃N)MeC=N(2,6-*i*-Pr₂C₆H₃)], in the presence of H₂PtCl₆ as a hydrosilylation catalyst, to afford the first and second generation carbosilane supported ligands. Complexation reactions with FeCl₂ · 4H₂O give rise to iron-containing carbosilane dendrimers with FeCl₂ moieties bound on the periphery. The metallodendrimers were used as catalyst precursors, activated with modified methylaluminoxane, for the polymerization of ethylene. In the case of low Al/Fe molar ratio, the metallodendrimers display much higher catalytic activity towards ethylene polymerization and produce much higher molecule weight polyethylenes than the corresponding single-nuclear complex under the same conditions.

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1. Introduction

The late transition metal catalysts for olefin polymerization have attracted intense interest because of the potential to yield polymers with different microstructures and more tolerant of functionalized monomers [1–3]. In 1998, Brookhart's and Gibson's groups independently discovered that iron(II) pyridinebisimine complexes can be activated with methylaluminoxane (MAO) to afford highly active catalysts for the polymerization of ethylene [4–6]. In general, however, the iron catalysts produce the polyethylene with low molecular weight and broad molecular weight distribution. One way to solve this problem is to immobilize the catalysts on inor-

ganic materials such as silica [7–11] and organic materials such as polystyrene and polyethylene [11–14]. By means of heterogeneous iron catalyst, high molecular weight polyethylenes can easily be obtained at the expense of catalytic activity. Another potential way is to immobilize the catalysts onto the periphery of dendrimers [15–17].

The synthesis of metallodendrimers has been developed at a prolific rate in recent years, and a number of metallodendrimers for catalysis have also been reported lately [18–20]. This inspires us to synthesize metallodendrimer precatalysts for the polymerization of olefin. Herein we selected carbosilane dendrimers as the solid support, and the dendrimers were modified by bis(imino)pyridyl bearing allyl group. We hoped to get high activity for ethylene polymerization and high molecule weight polyethylenes. This article describes the preparation and characterization of the iron metallodendrimers,

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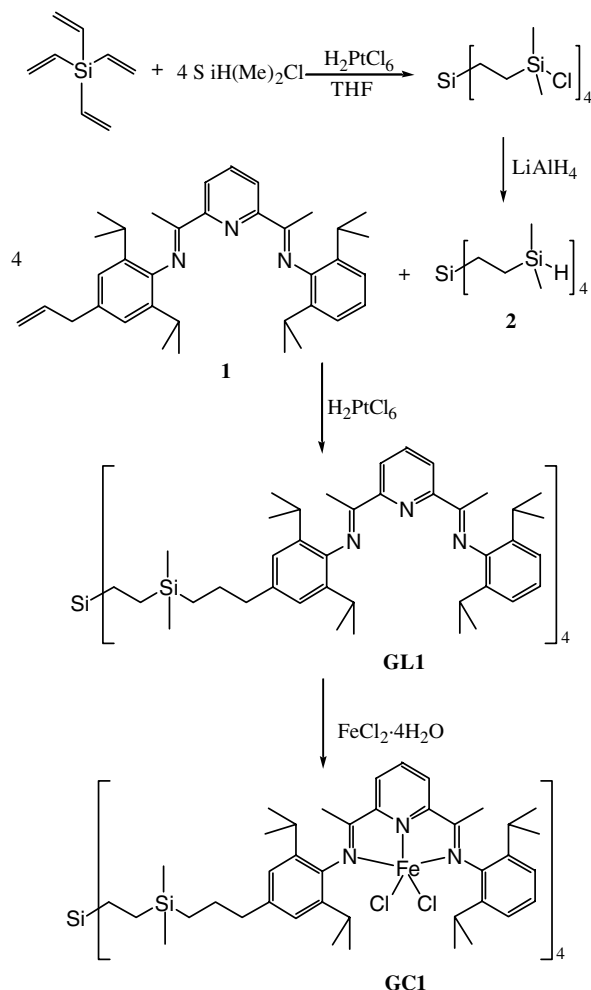
and the comparison study of the metallodendrimers and the corresponding single-nuclear complex.

2. Results and discussion

2.1. Synthesis and characterization of metallodendrimers

A general synthetic route for the first and second generation iron metallodendrimers **GC1** and **GC2** is shown in Schemes 1 and 2. The tetra(Si–H)silane **2** and octa(Si–H)silane **4**, as clear, colorless liquid, were prepared via Pt-catalyzed hydrosilylation reactions of the corresponding tetravinylsilane and octavinylsilane with chlorodimethylsilane, respectively, and succedent deoxidization reactions of the resulting silanes chloride with LiAlH_4 in diethyl ether, according to the literatures [21,22].

The dendritic bis(imino)pyridyl ligands were prepared in good yields (**GL1**, 68%; **GL2**, 43%) by Pt-catalyzed hydrosilylation reactions of the bis(imino)pyridyl containing an allyl with the corresponding carbosilane



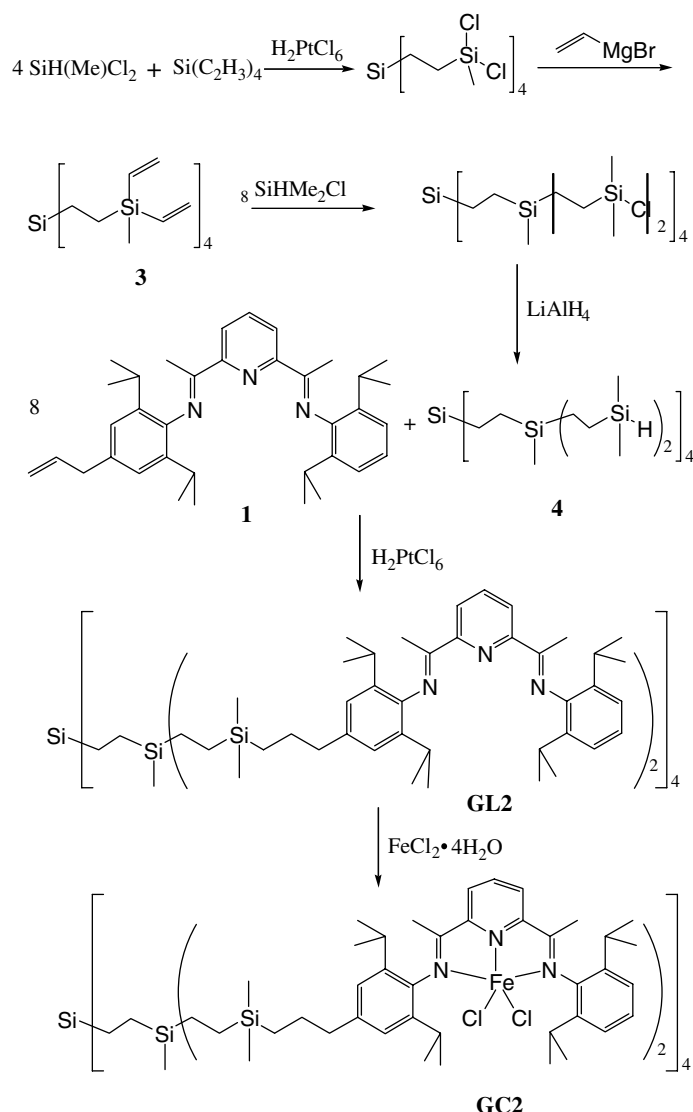
Scheme 1.

dendrimers containing Si–H capping groups **2** and **4**, respectively. During the synthesis of the dendritic bis(imino)pyridyl ligands, FTIR was used to detect the conversion extent of carbosilane dendrimers with Si–H capping groups. As shown in Fig. 1, the carbosilane dendrimers **2** displays a strong and sharp resonance at 2108 cm^{-1} for Si–H bands, while the dendritic bis(imino)pyridyl ligands **GL1** does not show any resonance at 2108 cm^{-1} , indicating that the hydrosilylation reactions were completely. The data of ^1H and ^{13}C NMR also confirm the structures of the functionalized carbosilane dendrimers **GL1** and **GL2**. For example, neither Si–H resonance (δ 3.82) nor vinyl resonances (δ 6.10–5.00) were observed.

Dendritic precatalysts **GC1** and **GC2** were obtained as blue powders (yields: **GC1**, 95%, **GC2**, 93%) by the complexation reactions of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ with the corresponding dendritic ligands **GL1** and **GL2**, respectively. They were characterized by FTIR spectroscopy, mass spectroscopy. After complexation, the absorption of C=N bonds shifts from 1643 to 1590 cm^{-1} , as shown in Fig. 1, and the determination results of iron content accord with calculation values very well.

2.2. Polymerization of ethylene using the metallodendrimers

The polymerizations of ethylene were conducted at an atmospheric pressure of ethylene in toluene using the iron metallodendrimers **GC1** and **GC2** as well as single-nuclear complex $[\text{2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}(\text{C}_5\text{H}_3\text{N})\text{MeC}=\text{NC}_6\text{H}_3^i\text{Pr}_2\text{-2,6}]\text{FeCl}_2$ (**C1**) activated with modified methylaluminoxane (MMAO). We investigated the effect of Al/Fe molar ratios and the temperature of reaction on the activities of precatalyst **GC1** and **C1** for ethylene polymerization, to evaluate the dendritic catalysts. As shown in Fig. 2, the activities of both **GC1** and **C1** decrease gradually with reaction temperature. These results were consistent with those for **C1** reported by Gibson [6]. Fig. 3 shows that the molar ratios of Al/Fe influence considerably the activities of both precatalysts. When Al/Fe molar ratio is higher than 1200, the activities of both precatalysts are comparable. It is very interesting, however, that the activity of **GC1** is much higher than that of **C1** at low Al/Fe molar ratio. For example, when Al/Fe molar ratio equals 300, the activity of **GC1** is still high up to $2.42 \times 10^3\text{ kg PE/mol}_{\text{Fe}}\text{ h bar}$, while that of **C1** is only $0.98 \times 10^3\text{ kg PE/mol}_{\text{Fe}}\text{ h bar}$. The reason for the much higher activity of dendritic catalyst **GC1**, in the case of low Al/Fe molar ratios, could derive from the “steric crowding” of the molecule in combination with MMAO counter anions that are formed in the activation step. This result also indicates that the “steric crowding” of dendritic iron catalyst could restrain iron active center from deactivation in some degree.



Scheme 2.

The typical results of ethylene polymerizations with the iron metallodendrimers **GC1** and **GC2** as well as their mother complex **C1** activated with MMAO are shown in Table 1. The data, listed in Entries 5–9, indicate that **GC2** and **GC1** display similar performance. In the case of high Al/Fe molar ratio (for instance, Al/Fe = 1500), the metallodendrimers and single-nuclear complex **C1** exhibit similar activities, but the both metallodendrimers yield much higher molecular weight polyethylenes with higher melting temperature (Entry 6, **GC1**: $M_v = 84.2$ kg/mol, $T_m = 132.2$ °C. Entry 9, **GC2**: $M_v = 85.3$ kg/mol, $T_m = 132.3$ °C) than their mother complex **C1** (Entry 3: $M_v = 21.7$ kg/mol, $T_m = 125.7$ °C). In the case of low Al/Fe molar ratio (for example, Al/Fe = 500), the both metallodendrimers not only display much higher activities (**GC1**, Entry 4: 2.52×10^3 kg PE/mol_{Fe} h bar. **GC2**, Entry 7: 2.55×10^3 kg PE/mol_{Fe} h bar) than the corresponding single-nuclear

complex **C1** (Entry 1: 1.14×10^3 kg PE/mol_{Fe} h bar), but also yield much higher molecular weight polyethylenes with higher T_m s (Entry 4, **GC1**: $M_v = 136.7$ kg/mol, $T_m = 133.9$ °C. **GC2**, Entry 7: $M_v = 137.7$ kg/mol, $T_m = 134.1$ °C) than their mother complex **C1** (Entry 1: $M_v = 62.5$ kg/mol, $T_m = 127.9$ °C). These results indicate that the ‘steric crowding’ of dendritic iron catalyst could control chain transfer during ethylene polymerization in some extent.

3. Conclusion

Two new peripherally bound iron metallodendrimers **GC1** and **GC2**, with four and eight bis(imino)pyridyl situated on the dendritic surface, were synthesized via hydrosilylation and complexation reactions. These polynuclear iron complexes display much higher catalytic

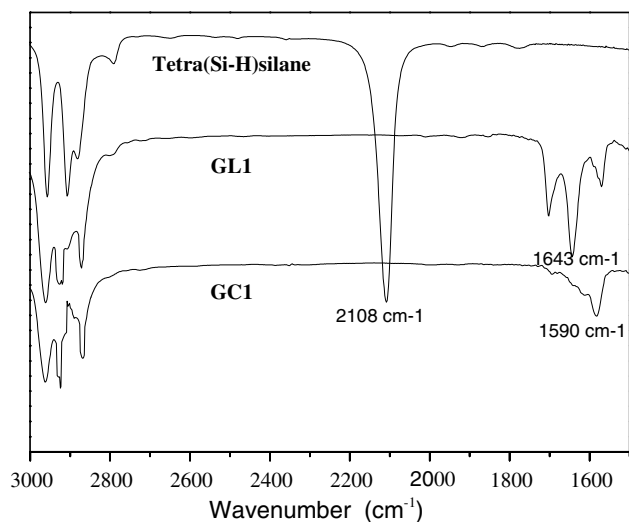


Fig. 1. FTIR spectra of the tetra(Si-H)silane, dendritic Ligand **GL1** and dendritic precatalyst **GC1**.

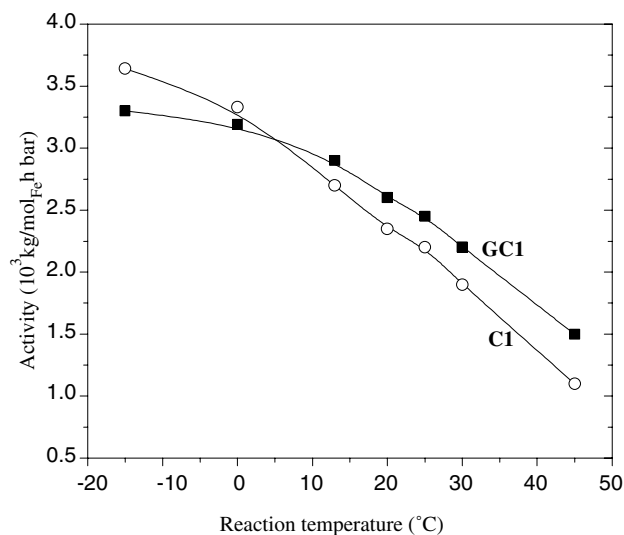


Fig. 2. Plot of catalytic activity versus reaction temperature. 2.0 μmol Fe (0.5 μmol **GC1** or 2.0 μmol **C1**), Al/Fe = 1000 (molar ratio), V_{total} = 50 mL, polymerization for 10 min.

activity for ethylene polymerization and produce much higher molecular weight polymers than the corresponding single-nuclear complex in the case of low Al/Fe molar ratios.

4. Experimental

4.1. General procedures and materials

All work involving air and moisture sensitive compounds was carried out using standard Schlenk techniques. NMR data were obtained on a Bruker 300 MHz spectrometer at ambient temperature, CDCl_3 as

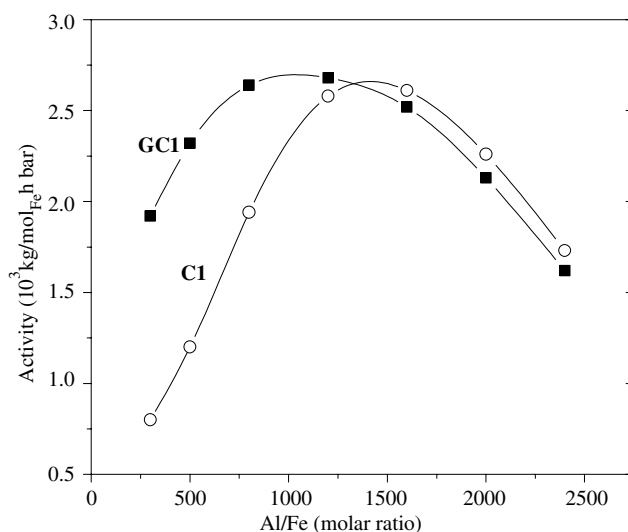


Fig. 3. Plot of catalytic activity versus Al/Fe molar ratio. 2.0 μmol Fe (0.5 μmol **GC1** or 2.0 μmol **C1**), V_{total} = 50 mL, polymerization at 25 °C for 10 min.

solvent and TMS as internal standard. Infrared spectra were recorded on a Bio-Rad FTS135 spectrometer. Mass spectra were obtained using electron impact (EI-MS) and LDI-1700 (Linear Scientific Inc.). Elemental analysis of Fe was conducted using AAS (PE AA800). DSC measurements were performed with a Perkin-Elmer Pyris 1 Differential Scanning Calorimeter. The intrinsic viscosity was measured in decalin. At 135 °C using an Ubbelohde viscometer, and the average of molecular weight was calculated by the following equation [23].

$$[\eta] = 6.2 \times 10^{-4} M_v^{0.7}.$$

Modified methylaluminoxane (MMAO, 7% Aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. The pyridinebisimine iron complex $[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}(\text{C}_5\text{H}_3\text{N})\text{MeC}=\text{NC}_6\text{H}_3\text{Pr}_2\text{-}2,6]\text{FeCl}_2$ (**C1**) was prepared in good yields according to a published procedure by Gibson and coworkers [6]. The ligand $[4\text{-CH}_2=\text{CHCH}_2\text{-}2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CMe}(\text{C}_5\text{H}_3\text{N})\text{MeC}=\text{NC}_6\text{H}_3\text{Pr}_2\text{-}2,6]$ (**1**) was prepared according to a published procedure by Jin and colleagues [12]. The Octa(vinyl)silane (**3**) was prepared according to a published procedure by Roovers [21]. Toluene was dried over sodium with dibenzophenone as indicator, and the other chemicals were commercially available and used without further purification.

4.2. Synthesis of dendritic ligands

4.2.1. Tetra(Si-H)silane (**2**)

To a 100 mL of flask was added tetravinylsilane 1.36 g (10 mmol), tetrahydrofuran (THF) 30 mL, chlorodimethylsilane 7.5 g (80 mmol), and H_2PtCl_6 (1.0 mg)

Table 1

The results of ethylene polymerization with iron precatalysts^a

Entry	Catalyst	Al/Fe (molar ratio)	Yield (g)	Activity (10 ³ kg PE/mol _{Fe} h bar)	<i>T</i> _m ^b (°C)	<i>M</i> _v ^c 10 ³ g/mol)
1	C1	500	0.38	1.14	127.9	62.5
2		1000	0.55	1.65	126.3	36.7
3		1500	1.00	3.00	125.7	21.7
4	GC1	500	0.84	2.52	133.9	136.7
5		1000	0.97	2.91	132.2	97.2
6		1500	0.96	2.88	132.2	84.2
7	GC2	500	0.85	2.55	134.1	137.7
8		1000	1.01	3.03	132.8	98.0
9		1500	1.00	3.00	132.3	85.3

^a Polymerization condition: 2.0 mol Fe (0.5 μmol **GC1** or 2.0 μmol **C1**), Al/Fe = 1000 (molar ratio), *V*_{total} = 50 mL, polymerization for 10 min.^b Melting temperature determined by DSC with a heating rate of 20 °C/min in nitrogen.^c Viscosity-average molecular weights calculated from the equation $[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$ [22].

as a catalyst, the solution was stirred and refluxed for 2 and 8 h at room temperature. The excess chlorodimethylsilane and THF were removed under reduced pressure. The residual was dissolved in 30 mL THF and transferred to 200 mL of diethyl ether. To the solution LiAlH₄ (1.7 g, 44 mmol) was added dropwise, stirred at room temperature overnight, and then was filtered through Celite. The filtrate was added cautiously to 200 mL of ice-cooled concentrated hydrochloric acid. The aqueous layer was extracted twice with Et₂O, the combined organic layers were washed twice with water and once with saturated NaCl. The organic layer was dried over anhydrous MgSO₄ and filtered. Most of the solvent were removed using a rotary evaporator, the residual liquid was distilled at reduced pressure to give tetra(Si–H)silane **2** (2.3 g, 56%) as a clear, colorless liquid. ¹H NMR (CDCl₃): δ 3.82 (s, 4H, SiH), 0.55 (m, 16H, CH₂), 0.075 (s, 24H, CH₃). ¹³C NMR (CDCl₃): δ –4.48, 4.68, 6.85. IR ν(Si–H): 2108 cm^{–1}. EI-MS (70 ev): *m/z* = 376 [M⁺].

4.2.2. Octa(Si–H)silane (**4**)

The prepared procedure is similar to that used for tetra(Si–H)silane **2**. Yield: 38%. ¹H NMR (CDCl₃): δ 3.82 (s, 8H, SiH), 0.58 (m, 32H, SiMeCH₂CH₂SiMe₂), 0.40 (m, 16H, SiCH₂CH₂SiMe), 0.09 (m, 60H, Si(CH₃)₂ and SiCH₃). ¹³C NMR (CDCl₃): δ –4.22, –3.84, 6.82, 8.93, 10.32, 10.44. IR ν(Si–H): 2115 cm^{–1}. EI-MS (70 ev): *m/z* = 1008 [M⁺].

4.2.3. Dendritic ligand **GL1**

To a 100 mL of flask was added bis(imino)pyridyl **1** (0.887 g, 1.7 mmol), tetra(Si–H)silane **2** (0.159 g, 0.42 mmol) in 30 mL THF, and H₂PtCl₆ (1 mg), the solution was stirred and refluxed at 70 °C for 24 h. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on a silica gel with hexane/ethyl acetate (15/1) as the eluent, affording compound **GL1** (0.7 g, 68%) as a yellow powder. ¹H NMR (CDCl₃): δ 8.43

(br, 8H, Py–H_m), 8.09 (br, 4 H, Py–H_p), 7.18 (d, 8 H, Ph–H_m), 7.15 (t, 4H, Ph–H_p), 6.84 (s, 8H, Ph–H_m), 2.77 (br, 16 H, CH(Me)₂), 2.58 (m, 8H, SiCH₂CH₂CH₂Ph), 2.31 (s, 24H, N=CCH₃), 1.27 (m, 8H, SiCH₂CH₂CH₂Ph), 1.17 (br, 96H, C(CH₃)₂), 0.58–0.66 (m, 24H, SiCH₂CH₂Si and SiCH₂CH₂CH₂Ph), 0.09 (s, 24H, Si(CH₃)₂). IR ν(C=N): 1643 cm^{–1}. MS: LDI-1700 (Linear Scientific Inc, 337 nm, 30 kV). Found: 2457. (Calc: 2464).

4.2.4. Dendritic ligand **GL2**

The prepared procedure is similar to that used for tetra(Si–H)silane **GL1**. Yield: 43%. ¹H NMR (CDCl₃): δ 8.46 (br, 16H, Py–H_m), 8.12 (br, 8H, Py–H_p), 7.17 (d, 16H, Ph–H_m), 7.09 (t, 8H, Ph–H_p), 6.81 (s, 16H, Ph–H_m), 2.77 (br, 32H, CH(Me)₂), 2.56 (m, 16H, SiCH₂CH₂CH₂Ph), 2.31 (s, 48H, N=CCH₃), 1.28 (m, 16H, SiCH₂CH₂CH₂Ph), 1.17 (br, 192H, C(CH₃)₂), 0.55–0.70 (m, 32H, SiCH₂CH₂Si and SiCH₂CH₂CH₂Ph), 0.09 (s, 48H, Si(CH₃)₂). IR ν(C=N): 1641 cm^{–1}. MS: LDI-1700 (Linear Scientific Inc, 337 nm, 30 kV). Found: 5146. (Calc: 5184)

4.3. Synthesis of dendritic precatalysts

4.3.1. Dendritic precatalyst **GC1**

To a 100 mL flask was added **GL1** (0.49 g, 0.2 mmol) in 30 mL THF, and FeCl₂·4H₂O (0.159 g, 0.8 mmol), and stirred at room temperature for 4 h. The solution was concentrated, and then hexane was added to afford precipitate as a yellow powder. The crude product was washed twice with diethyl ether, filtered, and dried at vacuum to afford **GC1** (0.62 g, 95%). IR ν(C=N): 1590 cm^{–1}. Calc: Fe, 75.4 mg/g. Found: Fe, 75.5 mg/g.

4.3.2. Dendritic precatalyst **GC2**

The prepared procedure is similar to that used for tetra(Si–H)silane **GL1**. Yield: 93%. IR ν(C=N): 1588 cm^{–1}. Calc: Fe, 72.2 mg/g. Found: Fe, 72.4 mg/g.

4.4. Polymerization procedure

Ethylene polymerization was carried out under atmospheric pressure in toluene in a 150 mL glass reactor equipped with a mechanical stirrer. Toluene (40 mL) was introduced into the nitrogen-purged reactor and stirred vigorously (600 rpm). The toluene was kept at a prescribed polymerization temperature, and then the ethylene gas feed (100 L/h) was started. After 10 min, polymerization was initiated by the addition of a toluene solution of MMAO and then a toluene solution of the complex into the reactor with vigorous stirring (600 rpm). After a prescribed time, isobutyl alcohol (10 mL) was added to terminate the polymerization reaction, and the ethylene gas feed was stopped. The resulted mixture was added to the acidic methanol (1 mL concentrated HCl in 500 mL methanol). The solid polyethylene was recovered by filtration, washed with methanol, and dried at 60 °C for 24 h in a vacuum oven.

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