Received: 10 November 2009

Revised: 27 February 2010

(wileyonlinelibrary.com) DOI 10.1002/aoc.1674

Accepted: 17 April 2010

Published online in Wiley Online Library: 28 June 2010

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Chemistry

The bridged cyclopentadienyl indenyl (fluorenyl) zirconocene complexes for polyethylene macromonomers

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The synthesis of long-chain branched polyethylene includes the generation of vinyl-terminated polyethylene macromonomers and the copolymerization of these macromonomers with ethylene. Four new bridged cyclopentadienyl indenyl (fluorenyl) zirconocene complexes 1a-b, 2a-b were prepared and showed high activities for ethylene homopolymerization upon the activation of methylaluminoxane. The steric bulk of bridged substituent has a profound effect on the catalytic activity as well as on the molecular weight of resulting polyethylene. Complex 1b showed the highest activity of up to 5.32×10^6 g PE/(mol Zr h) for ethylene homopolymerization at 70°C, which was higher than that of Cp₂ZrCl₂. The polyethylenes produced with complexes 1a-d/MAO are mostly vinyl-terminated, possess low molecular weight and fit as macromonomers. The (p-MePh)₂Cbridged cyclopentadienyl indenyl zirconocene complex 1a could produce polyethylene macromonomer with selectivity for the vinyl-terminal as high as 94.9%. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: zirconocene; ethylene polymerization; polyethylene macromonomer

Introduction

Metallocene catalysts have attracted considerable attention due to their high catalytic activities for olefin polymerizations and fine control over polyolefin size dimensions and microstructure.^[1,2] Modification of the ligand environment on the catalyst affords polymers with different physical characteristics such as molecular weight (M_w) , molecular weight distribution and branch length.^[3,4] The length of branches dramatically affects the processability and rheological properties of polyolefin^[5] and the frequency of longchain branches in the range of 0.01-3 long chain branches per 1000 carbon atoms can be a remarkable influence on the physical properties of polyolefin.^[6]

It is difficult to incorporate α -olefins with more than eight carbon atoms into growing chains by Ziegler-Natta catalysts,^[7] but metallocene catalysts can copolymerize α -olefins with vinyl end-group chains to form long chain branched (LCB) polymers.^[8-10] These vinyl end-group chains can be considered as macromonomers.^[11] Dow Chemical Company^[10] first used the constrained geometry catalyst (CGC) to get LCB polyethylene up to 0.34 long chain branches/1000 carbon atoms. Then some metallocenes such as Et(Ind)₂ZrCl₂^[11] and Cp₂ZrCl₂^[12] were used as single catalysts to produce LCB polyethylene with narrow molecular weight distribution. In comparison with the singlesite nature of metallocene complexes, the non-metallocene nickel complex, $\{[2-C_6H_4(C_6H_5)] - N = C(CH_3) - C(CH_3) = N - [2-C_6H_4]$ (C_6H_5)]NiBr₂,^[13] afforded LCB polyethylene but with a broad or bimodal molecular weight distribution.

Besides the method utilizing one catalyst, two different metal complexes are often combined to produce LCB PE. In this method, one is the catalyst for producing PE macromonomer and the other is the catalyst for copolymerization. There are also three ways to carry out the copolymerization:^[14] the separated macromonomer copolymerizes with ethylene in the presence of the second catalyst (copolymerization), or second catalyst is added to the same reactor after the macromonomer is produced but not separated (tandem), or the two catalysts are added simultaneously to the reactor (simultaneous).

In order to obtain LCB PE, it is necessary to obtain vinylterminated PE macromonomers of suitable molecular weights. Because studies showed that only vinyl-terminated oligomers were incorporated into growing polymer chains,^[15] longer branches did not benefit incorporation and shorter branches were found not to influence the rheological properties,^[6,16] the branch length of LCB polymer must exceed the entanglement molar mass (M_e) of around 1300 g/mol for polyethylene.^[4] The PE macromonomers were produced by Markel *et al.*^[17] with Cp_2ZrCl_2/MAO in hexane. Sperber and Kaminsky^[14] reported that bridged metallocene system of [Me₂C(Cp₂)]ZrCl₂/MAO produced macromonomers with $M_{\rm w}$ ranging from 1200 to 4500 g/mol and terminal double bond contents up to 96-98%. In addition, Fujita et al.^[18] used the non-metallocene complexes [(2-OH-3-R¹-5-R²)-C₆H₃-CH=N-R³]₂ZrCl₂ to synthesize PE macromonomers with vinyl-terminal content of 90–96% and *M*_w of 2000–14 000 g/mol.

Recently, we reported^[19,20] that the bridged cyclopentadienyl indenyl zirconocene complexes [(R-Ph)₂C(Cp)(Ind)]ZrCl₂ showed high activities for ethylene polymerization and afforded polyethylenes of low molecular weights. Further analysis showed that the obtained PEs possessed a high percentage of vinylterminal groups. The results implied that these zirconocene complexes can homopolymerize ethylene to provide polyethylene macromonomers. In order to obtain PE macromonomers

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of various molecular weights as well as with high vinyl-terminal content, in the work described herein we take advantage of two reported *ansa*-cyclopentadienyl indenyl zirconocene complexes and synthesize two new analogous complexes to examine their ethylene polymerization behavior. In addition, two new *ansa*-cyclopentadienyl fluorenyl zirconocene complexes were also synthesized and it was further attempted to copolymerize ethylene with PE macromonomers using three different copolymerization methods.

Experimental

General Procedures

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques unless otherwise indicated. Toluene, diethyl ether (Et₂O) and tetrahydrofuran (THF) were refluxed over sodium benzophenone. Dichloromethane (CH₂Cl₂) was refluxed over CaH₂. Chloroform-*d* was dried over calcium hydride under argon and stored in the presence of activated 4 Å molecular sieves. *n*-BuLi (2.5 M in *n*-hexane) was purchased from Chemetall. The cocatalyst methylaluminoxane (MAO, 1.53 M in toluene) was purchased from Witco. Polymer-grade ethylene was directly used for polymerization.

¹H NMR spectra were recorded on a Bruker Avance-500 spectrometer with CDCl₃ as solvent. Chemical shifts for ¹H NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane (TMS). Elemental analyses were carried out on an EA-1106 type analyzer. Differential scanning calorimetry analyses (DSC) were performed on a Universal V2.3C TA instrument at a heating rate of 10 °C/min. ¹³C NMR spectra of polymers were recorded on a Bruker Avance-500 spectrometer with 1,2-dichlorobenzene-*d* at 100 °C. Intrinsic viscosities were determined in decahydronaphthalene at 135 °C and viscosity average molecular weights of PEs were calculated according to the equation:^[21] [η] (dl/g) = 6.77 × 10⁻⁴ $M_{\eta}^{0.67}$.

Synthesis of Fulvenes

$(p-CH_3-Ph)_2C=(C_5H_4)$

Cyclopentadienyl sodium (27 ml, 1.56 mol/l, 42.1 mmol) in THF was added to a solution of $(p-CH_3-Ph)_2CO$ (7.1 g, 33.8 mmol) in Et₂O (30 ml). The solution was stirred at room temperature for 3 days. The reaction was slowly quenched by addition of water (50 ml) at 0 °C; the organic layer was washed with water and dried over MgSO₄, filtered and concentrated *in vacuo* to produce red viscous oil. The crude product was purified by chromatography on silica gel with petroleum ether as eluant. A red crystal was obtained (4.12 g, yield 47.1%).

$(p-CH_3-Ph)[p-C(CH_3)_3-Ph]C=(C_5H_4)$

This compound was obtained as a viscous oil by using a similar procedure (4.24 g, yield 54.8%).

Synthesis of Preligands

$(p-CH_3-Ph)_2C(C_5H_5)(C_9H_7)$

Indenyl lithium (1.05 g, 12.9 mmol) in Et₂O (20 ml) was added to a solution of $(p-CH_3-Ph)_2C=(C_5H_4)$ (2.5 g, 12.9 mmol) in Et₂O (20 ml) at 0 °C. The mixture was warmed to room temperature and stirred

for 3 days. Then the reaction was slowly quenched by addition of water (50 ml) at 0 °C; the organic layer was washed with water three times and dried over MgSO₄, filtered and concentrated *in vacuo* to produce yellow viscous oil. The crude product was purified by chromatography on silica gel with petroleum ether as eluant. A pale yellow solid powder was obtained (1.8 g, yield 49.7%).

$(p-CH_3-Ph)[p-C(CH_3)_3-Ph]C(C_5H_5)(C_9H_7)$

The compound was obtained as a pale yellow solid powder using a similar procedure (2.4 g, yield 32.8%).

$(p-CH_3-Ph)_2C(C_5H_5)(C_{13}H_9)$

A solution of fluorenyl lithium (1.32 g, 7.7 mmol) in 20 ml of Et₂O was added dropwise to a solution of $(p-CH_3-Ph)_2C=(C_5H_4)$ (2.0 g, 7.7 mmol) in 30 ml of Et₂O. After being stirred for about 24 h, the reaction solution was hydrolyzed with 20 ml of water. The white solid $(p-CH_3-Ph)_2C(C_5H_5)(C_{13}H_9)$ precipitated (1.9 g, yield 57.8%).

$(p-CH_3-Ph)[p-C(CH_3)_3-Ph]C(C_5H_5)(C_{13}H_9)$

Similarly, fluorenyl lithium salt (1.15 g, 6.7 mmol) and (p-CH₃-Ph)[p-C(CH₃)₃-Ph]C=(C₅H₄) (2.0 g, 6.7 mmol) gave (p-CH₃-Ph)[p-C(CH₃)₃-Ph]C(C₅H₅)(C₁₃H₉) as a white solid (1.8 g, yield 57.9%).

Synthesis of Complex [(p-CH₃-Ph)₂C(C₅H₄)(C₉H₆)]ZrCl₂ (1a)

A hexane solution of *n*-butyllithium (2.50 mol/l, 1.9 ml, 4.8 mmol) was added to a solution of $(p-CH_3-Ph)_2C(C_5H_5)(C_9H_7)$ (0.9 g, 2.4 mmol) in Et₂O (30 ml) at 0 $^{\circ}$ C. The resulting suspension was stirred for 12 h at room temperature. After removal of solvent in vacuo, the dilithium salt was obtained as a white solid. The solution of dilithium salt in CH₂Cl₂ (50 ml) was added dropwise into the suspension of ZrCl₄ (0.56 g, 2.4 mmol) in CH₂Cl₂ (30 ml) at 0 °C. The mixture was stirred at room temperature overnight. The solvent was removed in vacuo to yield a yellow solid which was redissolved in *n*-hexane leaving a precipitate of LiCl. The filtrate was reduced to 80 ml *in vacuo* and stored at -20° C to give a yellow powder (312 mg, yield 24.3%). ¹H NMR (500 MHz, 298 K, CDCl₃): δ 7.76 (d, 2H, ${}^{3}J = 8.1$ Hz, Ph), 7.73 (dd, 1H, ${}^{3}J = 8.0$, ${}^{4}J = 1.5$ Hz, Ph), 7.65 (d, 1H, ${}^{3}J = 8.7$ Hz, Ind), 7.58 (dd, 1H, ${}^{3}J = 8.0$, ${}^{4}J = 1.5$ Hz, Ph), 7.32 (quasi t, 1H, Ind), 7.20 (d, 1H, ³J = 8.3 Hz, Ph), 7.18 (d, 2H, ${}^{3}J = 8.1$ Hz, Ph), 7.14 (d, 1H, ${}^{3}J = 8.3$ Hz, Ph), 6.90 (d, 1H, ³J = 3.3 Hz, Ind), 6.78 (*quasi* t, 1H, Ind), 6.58–6.54 (m, 2H, Cp), 6.40 (d, 1H, ${}^{3}J = 8.9$ Hz, Ind), 6.26 (d, 1H, ${}^{3}J = 3.3$ Hz, Ind), 5.87 (dd, 1H, $^{3}J = 5.4$ Hz, $^{4}J = 2.4$ Hz, Cp), 5.72 (dd, 1H, $^{3}J = 5.4$ Hz, $^{4}J = 2.4$ Hz, Cp), 2.33 (s, 6H, CH₃), 1.33-1.26 (m, 4H, hexane-CH₂), 0.88 (t, 3H, ${}^{3}J = 6.5$ Hz, hexane-CH₃); IR (KBr, cm⁻¹): 3089m, 3023m, 2954s, 2921s, 2856m, 1608 w, 1509s, 1459s, 1409m, 1379m, 1234 w, 1211 w, 1189m, 1124m, 1051m, 1041m, 1021m, 1002 w, 867 w, 806s, 784s, 747s, 724m, 580s, 520m, 468s; MS (*m*/*z*): 532 (100, M⁺), 496 (24, M⁺ – Cl), 441 [41, M⁺ – (CH₃-C₆H₄)], 372 (12, M⁺ – ZrCl₂). Anal. calcd for C₂₉H₂₄ZrCl₂·0.5C₆H₁₄: C, 66.53; H, 5.41. Found: C, 67.44, H, 5.40%.

Synthesis of Complex {(p-CH₃-Ph)[p-C(CH₃)₃-Ph]C(C₅H₄)(C₉ H₆)}ZrCl₂ (1b)

Following the procedure described for complex **1a**, 2.50 mol/l *n*butyllithium in hexane (1.8 ml, 4.50 mmol), (*p*-CH₃-Ph)[*p*-C(CH₃)₃-Ph]C(C₅H₅)(C₉H₇) (0.9 g, 2.24 mmol) and ZrCl₄ (0.52 g, 2.24 mmol) were used to give **1b** as a yellow crystal (132 mg, yield 10.3%). Two diastereomers existed. ¹H NMR (500 MHz, 298 K, CDCl₃): δ 7.79 (d, 0.8H, ³J = 8.1 Hz, Ph), 7.78 (d, 1.2H, ³J = 8.6 Hz, Ph), 7.76 (dd, 1H, ${}^{3}J = 8.1$ Hz, ${}^{4}J = 2.1$ Hz, Ph), 7.65 (d, 1H, ${}^{3}J = 8.7$ Hz, Ind), 7.58 (dd, 1H, ${}^{3}J = 8.1$ Hz, ${}^{4}J = 2.1$ Hz, Ph), 7.40 (dd, 0.4H, ³J = 8.0, ⁴J = 2.1 Hz, Ph), 7.37 (d, 1.2H, ³J = 8.6 Hz, Ph), 7.34–7.30 (m, 1.4H, 1H-Ind, 0.4H-Ph), 7.23 (d, ${}^{3}J = 8.0$ Hz, 0.6H, Ph), 7.20 (d, ${}^{3}J = 8.1$ Hz, 0.8H, Ph), 7.14 (d, ${}^{3}J = 8.0$ Hz, 0.6H, Ph), 6.89 (m, 1H, Ind), 6.72-6.68 (m, 1H, Ind), 6.58-6.54 (m, 2H, Cp), 6.38 (dd, 0.6H, ${}^{3}J = 8.9$ Hz, ${}^{4}J = 0.7$ Hz, Ind), 6.31 (dd, 0.4H, ${}^{3}J = 8.9$ Hz, ${}^{4}J = 0.7$ Hz, Ind), 6.29 (d, 0.6H, ${}^{3}J = 3.5$ Hz, Ind), 6.25 (d, 0.4H, ³J = 3.5 Hz, Ind), 5.89 (dd, 0.4H, ³J = 5.3 Hz, ⁴J = 2.8 Hz, Cp), 5.86 $(dd, 0.6H, {}^{3}J = 5.3 Hz, {}^{4}J = 2.8 Hz, Cp), 5.74 (dd, 0.6H, {}^{3}J = 5.3 Hz,$ ⁴J = 2.8 Hz, Cp), 5.72 (dd, 0.4H, ³J = 5.3 Hz, ⁴J = 2.8 Hz, Cp), 2.35 (s, 1.8H, CH₃), 2.34 (s, 1.2H, CH₃), 1.2 (s, 9H, C(CH₃)₃); IR (KBr, cm⁻¹): 3049m, 3028m, 2959s, 2867m, 1608 w, 1510s, 1461m, 1409m, 1362m, 1266m, 1130m, 1111m, 1078m, 1041s, 952 w, 866 w, 825s, 803s, 742s, 723m, 589s, 508s, 468s; MS (m/z): 574 (100, M⁺), 538 (11, M⁺ - Cl), 483 [14, M⁺ - (CH₃-C₆H₄)], 442 {13, M⁺ - [C(CH₃)₃- $C_{6}H_{4}$]. Anal. calcd for $C_{32}H_{30}ZrCl_{2}$: C, 66.64; H, 5.24. Found: C, 66.97; H, 5.81%.

Synthesis of Complex [(p-CH₃-Ph)₂C(C₅H₄)(C₁₃H₈)]ZrCl₂ (2a)

To a solution of $(p-CH_3-Ph)_2C(C_5H_5)(C_{13}H_9)$ (1.0g, 2.4 mmol) in 30 ml of Et₂O, 1.75 mol/l *n*-butyllithium in hexane (2.8 ml, 4.9 mmol) was added dropwise at -78 °C. After being stirred overnight, ZrCl₄ (0.55 g, 2.4 mmol) was added directly to the solution as a solid. The resulting suspension was stirred for 8 h at room temperature, and then filtered. The solid residue was recrystallized in toluene to give complex 2a as a red crystal (350 mg, yield 25.4%). ¹H NMR (500 MHz, 298 K, CDCl₃): δ 8.19 (d, 2H, ${}^{3}J = 8.3$ Hz, Flu), 7.80 (dd, 2H, ${}^{3}J = 8.3$ Hz, ${}^{4}J = 1.9$ Hz, Ph), 7.77 (dd, 2H, ${}^{3}J = 8.3$ Hz, ${}^{4}J = 1.9$ Hz, Ph), 7.56 (*quasi* t, 2H, Flu), 7.27-7.21 (m, 4H, 2H-toluene-Ph, 2H-Ph), 7.18-7.15 (m, 3H, toluene-Ph), 7.13 (d, 2H, ³J = 8.3 Hz, Ph), 7.01 (*quasi* t, 2H, Flu), 6.45 (d, 2H, ³J = 8.3 Hz, Flu), 6.37 (quasi t, 2H, Cp), 5.79 (quasi t, 2H, Cp), 2.35 (s, 3H, toluene-CH₃), 2.34 (s, 6H, CH₃); IR (KBr, cm⁻¹): 3112m, 3083m, 3024s, 2968 w, 2918s, 1590m, 1512m, 1504m, 1494m, 1462s, 1427s, 1326s, 1212m, 1126m, 1082m, 1042s, 1018m, 952 w, 896 w, 823s, 786m, 753s, 730s, 695m, 473s; MS (*m/z*): 582(63, M⁺), 546 (14, M^+ – Cl), 491 [100, M^+ – (CH₃-C₆H₄)], 422 (14, M^+ – ZrCl₂). Anal. calcd for C₃₃H₂₆ZrCl₂·C₇H₈: C, 70.98; H, 5.06. Found: C, 71.30; H, 5.42%.

Synthesis of Complex {(p-CH₃-Ph)[p-C(CH₃)₃-Ph]C(C₅H₄)(C₁₃ H₈)}ZrCl₂ (2b)

Following the procedure described for **2a**, $(p-CH_3-Ph)[p-C(CH_3)_3-Ph]C(C_5H_5)$ ($C_{13}H_9$) (1.1 g, 2.36 mmol), 2.50 mol/l *n*-butyllithium in hexane (1.9 ml, 4.75 mmol) and ZrCl₄ (0.55 g, 2.36 mmol) were used to give **2b** as an orange crystal (226 mg, yield 15.3%). ¹H NMR (500 MHz, 298 K, CDCl_3): δ 8.19 (d, 2H, ³J = 8.4 Hz, ⁴J = 0.9 Hz, Flu), 7.80 (d, 2H, ³J = 8.3 Hz, Ph), 7.77 (dt, 2H, ³J = 8.3 Hz, ⁴J = 2.3 Hz, Ph), 7.58–7.55 (m, 2H, Flu), 7.41 (dd, 1H, ³J = 8.3 Hz, ⁴J = 2.1 Hz, Ph), 7.36 (dd, 1H, ³J = 8.3 Hz, ⁴J = 2.1 Hz, Ph), 7.36 (dd, 1H, ³J = 8.3 Hz, ⁴J = 2.1 Hz, Ph), 7.36 (dd, 1H, ³J = 8.3 Hz, ⁴J = 2.1 Hz, Ph), 7.36 (dd, 1H, ³J = 8.3 Hz, Flu), 6.37 (d, 1H, ³J = 8.3 Hz, Flu), 6.45 (d, 1H, ³J = 8.3 Hz, Flu), 6.37 (d, 1H, ³J = 8.3 Hz, Flu), 6.35 (m, 2H, Cp), 5.82-5.78 (m, 2H, Cp), 2.36 (s, 3H, CH₃), 2.35 (s, 3H, toluene-CH₃), 1.32 (s, 9H, C(CH₃)₃); IR (KBr, cm⁻¹): 3115m, 3031m, 2959s, 2865m, 1595 w, 1510s, 1493m, 1460s, 1428s, 1409m, 1328m, 1214m, 1128m, 1081m, 1043m, 1017m, 823s, 808m, 753s, 730s, 695m, 587s, 475s; MS (*m/z*): 626 (100, M⁺), 588 (14,

$$\begin{split} & \mathsf{M^+-Cl}, 535\,[53,\mathsf{M^+-(CH_3-C_6H_4)}], 491\,\{14,\mathsf{M^+-[C(CH_3)_3-C_6H_4]}\}, \\ & \mathsf{491}\,(13,\mathsf{M^+-ZrCl_2}). \, \mathsf{Anal. \, calcd \, for \, C_{36}H_{32}ZrCl_2\cdot C_7H_8; \, C, \, 71.84; \, H, } \\ & \mathsf{5.61. \, Found: \, C, \, 71.60; \, H, \, 5.92\%. } \end{split}$$

Homopolymerization

A 100 ml autoclave, equipped with a magnetic stirrer, was evacuated under vacuum, and then filled with ethylene. Toluene was injected into the reactor. After equilibrating, the appropriate volume of catalyst solution and cocatalyst were injected to start the reaction. The ethylene pressure was kept constant during the reaction. The polymerization was carried out for 30 min and then quenched with 30 ml 3% HCl in ethanol. The collected polymer was washed to neutral with ethanol and then dried overnight in a vacuum oven at 60 °C to constant weight.

Copolymerization

All copolymerizations were carried out in a 100 ml autoclave reactor. According to the conventional copolymerization, the macromonomer was first added to the dry reactor, then toluene and MAO were introduced. After equilibrating, the appropriate catalyst solution of **2a** was injected to initiate the copolymerization. For the tandem copolymerization, a conventional ethylene polymerization was done using the toluene solution of complex 1a after the reactor was set with the toluene, MAO, temperature, and ethylene pressure and stirred for 30 min. Then a solution of complex 2a in toluene was added to start the copolymerization. The simultaneous copolymerization was carried out by injecting a mixture of 1a and 2a after the reactor was set. The polymer product was then quenched with 30 ml of 3% HCl in ethanol. The precipitated polymer was filtered, and extracted with hot toluene for 24 h in a Soxhlet apparatus to separate the residue macromonomer from high molecular weight component. Then the macromonomer and polyethylene were dried overnight in a vacuum oven at 60 °C.

Results and Discussion

Synthesis of Zirconocene Complexes

The new *ansa*-cyclopentadienyl indenyl (or fluorenyl) zirconocene complexes **1a-b** and **2a-b** were synthesized as illustrated in Scheme 1. For comparison purposes, complexes **1c-d** were synthesized according to our previous paper.^[19]

The bridged cyclopentadienyl indenyl (or fluorenyl) preligand compounds were synthesized analogously to the literature.^[22,23] The substituted diphenylfulvenes were prepared by the reaction of substituted benzophenons with cyclopentadienyl sodium in ether. Then the indenyl (or fluorenyl) lithium salt was allowed to react with the fulvenes. After hydrolysis, the preligand compounds were precipitated from diethyl ether as white solids. The preligands were treated with two equivalents of *n*-butyl lithium in diethyl ether and reacted respectively with one equivalent of zirconium tetrachloride to afford zirconocene complexes 1a-b and 2a-b after recrystallization from toluene. All the complexes were characterized by ¹H NMR spectroscopy and elemental analysis methods.

Synthesis of Polyethylene Macromonomer

Vinyl-terminated PE macromonomers were usually obtained with low AI:Zr molar ratios.^[18] In this work, an AI:Zr molar ratio of



Scheme 1. Synthetic route of substituted ansa-zirconocene complexes.



Figure 1. Influence of ethylene pressure on molecular weight (polymerization conditions: $[Zr] = 50 \ \mu mol/l$, Al: Zr = 500, 90 °C, 30 min, 25 ml toluene).

500 was adopted for most of the polymerization runs. Upon the activation of methylaluminoxane, all complexes are effective for the polymerization of ethylene in toluene.

The molecular weight and high vinyl-terminal content of macromonomer are particular important to synthesize LCB polyethylene. From Fig. 1, in the presence of MAO complexes 1a-c catalyzed ethylene polymerization to give polyethylenes with molecular weight ranging from 3300 to 10 300 g/mol by changing ethylene pressure from 5 to 10 bar. The obtained polymers/oligomers possessed high vinyl-terminal percentages of 80.7–94.9%, as depicted in Table 1. Markel *et al.*^[17] reported that Cp₂ZrCl₂ catalyzed ethylene polymerization to get PE macromonomers with M_n of 12 933 g/mol and 89.5% vinyl-terminated group in hexane, and with M_n of 25 154 g/mol and 91.4% vinyl-terminated group in toluene. In comparison with that, complexes **1a**–**d** afforded polyethylenes with lower molecular weights. Complex **1b** displayed higher catalytic activities than Cp₂ZrCl₂, but with similar selectivity for vinyl-terminated groups (Table 1: runs 4 and 11).

From Table 1, it is clear that low catalyst concentration (run 4 vs 5) and high polymerization temperature (run 3 vs 4 and run 8 vs 9) were favorable for producing vinyl-terminals and macromonomers with low molecular weight. These results are similar to other reported *ansa*-metallocene catalyst systems. Rulhoff and Kaminsky^[24] used [CMe₂(Cp)₂]ZrCl₂ to produce PE and also found that high polymerization temperature of 90 °C and low ethylene concentration of 0.05 mol/l were of benefit to the formation of low-molecular-weight macromonomers.

The influence of polymerization temperature on catalytic activity differed for individual complexes. The newly synthesized complexes **1a-b** displayed higher catalytic activities than those of complexes **1c-d**, as shown in Fig. 2. Furthermore, polymerization temperature for maximal catalytic activities of complexes **1a-c** decreased from 90 to 70 and 60 °C, indicating that the increase in the steric bulk of the *para*-substituent led to a decrease in the thermal stability of corresponding zirconocene complex.

End group analyses using ¹H NMR^[25] revealed that the majority of the unsaturated oligomer chains obtained with individual *ansa*complexes **1a-d** ended in a vinyl group, with the rest ending in a vinylidene group, whereas Cp_2ZrCl_2/MAO system produced macromonomers mainly with vinyl-terminal and a few with vinylene end groups. It is possible that the two kinds of metallocene complexes experience different transition states (Scheme 2).^[26]

Table 1. Ethy	lene polymerization	by complex	1a-d/MAO	catalyst s	ystem
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		[Catalyst]			M			Terminal selectivity (%)		
Run	Catalyst	(10^{-4} mol/l)	Al:Zr	P _{ethylene} (bar)	T_P (°C)	Activity ^b	(g/mol)	Vinyl	Vinylidene	Vinylene
1	1a	0.5	500	10	90	19.7	3 300	80.7	19.3	
2	1a	0.5	500	5	90	9.49	8 900	94.9	5.1	
3	1b	0.5	500	10	60	38.0	7 300	68.8	31.2	
4	1b	0.5	500	10	90	44.1	4 400	88.9	11.1	
5	1b	1.0	500	10	90	39.2	5 600	83.5	16.5	
6	1b	0.5	200	10	90	21.4	4 500	84.3	15.7	
7	1b	0.5	2000	10	90	77.2	7 500	86.9	13.1	
8	1c	0.5	500	10	60	12.7	5 300	74.2	25.8	
9	1c	0.5	500	10	90	9.52	4 900	85.8	14.2	
10	1d	0.5	500	10	90	15.3	2 700	80.0	20.0	
11	Cp_2ZrCl_2	0.5	500	10	90	25.1	28 000	89.7		10.3

а

^a Polymerization runs were performed in 25 ml of toluene over 30 min.

^b 10^{5} g PE/(mol Zr h)

^c Calculated by the data of ¹H NMR assuming each polymer chain is olefin terminated.^[25]



Figure 2. Influence of polymerization temperature on activity (polymerization conditions: $[Zr] = 50 \,\mu$ mol/l, Al : Zr = 500, 30 min, 10 bar ethylene, 25 ml toluene).

The possible mechanism of forming a vinyl end group is β -H transfer to the metal center as reported by Chien *et al.*^[26] The vinylene end group is formed by β -H transfer after isomerization from propagating chains containing ethylene as a terminal unit under the Cp₂ZrCl₂/MAO system.^[27] In addition, as Seppälä *et al.* has reported,^[11] the small number of vinylidene end groups formed in the system of complexes **1a**-**d**/MAO perhaps may result from the insertion of macromonomer. This mechanism can explain why high catalyst concentration is disadvantageous for forming vinyl-terminated groups (run 4 vs 5).

For ansa-zirconocene complexes **1a**–**d**, the substituents on the phenyl groups of bridge carbon had a significant effect on the activity. Complex **1b** with *para*-^tBu and *para*-Me substituents on phenyl groups exhibited the highest catalytic activity of 5.23×10^6 g PE/(mol Zr h), which is about 2.5 times more active than complex **1a** with two *para*-Me substituents on phenyl under the same conditions.

Compared with the bridged cyclopentadienyl indenyl zirconium complexes, the bridged cyclopentadienyl fluorenyl zirconium complexes (**2a**-**b**) could not catalyze ethylene homopolymer-

Table 2. Ethylene polymerization by complex 2a-b/MAO system ^a								
Run	Catalyst	T_{P} (°C)	Yield (g)	Activity ^b	M_{η}^{c} (g/mol)			
12	2a	60	0.330	5.28	300 000			
13	2a	90	0.965	15.44	232 000			
14	2b	60	0.096	1.54	161 000			
15	2b	90	0.871	13.94	109 000			
^a Polymerization runs were performed with $[Zr] = 5.0 \times 10^{-5}$ mol/l, Al : Zr = 500, 10 bar of ethylene pressure in 25 ml of toluene over 30 min. ^b 10 ⁵ g PE/(mol Zr h) ^c Intrinsic viscosity was determined in decahydronaphthalene at 135°C and viscosity average molecular weight was calculated using the relation ^[21] [n] = 6.77 × 10 ⁻⁴ M ^{0.67}								

ization to provide PE macromonomers (Table 2). The ¹³C NMR spectroscopic analyses indicate that these polymers are linear polyethylenes with double bond end-groups.

Complex **2a** showed higher catalytic activity than complex **2b** but both complexes reached the highest activity at the polymerization temperature of 90 °C (Fig. 3), which indicates that the two complexes exhibit highly thermal stability. In comparison with the analogous complex of $[(p-tBu-Ph)_2C(Cp)(Flu)]ZrCl_2^{[28]}$, complexes **2a** and **2b** displayed higher catalytic activities. Obviously, increasing the steric bulk of substituted phenyl leads to a fall of catalytic activity.

Copolymerization Attempt of Macromonomer with Ethylene

Kaminsky *et al.*^[24] reported that *ansa*-cyclopentadienyl fluorenyl zirconium complex [Ph₂C(Cp)(Flu)]ZrCl₂ can catalyze the copolymerization of PE macromonomer with propylene to give LCB polypropylene. In this work, with the aim of synthesizing LCB PE, complex **2a** was chosen as the catalyst for copolymerization due to its having a higher catalytic activity and affording higher molecular weight PE than those of complex **2b**; complex **1a** was selected to synthesize polyethylene macromonomers. All results are listed in Table 3. (1) Vinyl end group

$$Zr \xrightarrow{C}_{H_2}^{H_2} PE \xrightarrow{\beta-H \text{ transfer}} Zr \xrightarrow{C}_{H_2}^{H_2} PE \xrightarrow{H} Zr \xrightarrow{PE} Ir \xrightarrow{PE} Ir$$

(2) Vinylidene end group



(3) Vinylene end group



Scheme 2. The β -H transfer reaction in ethylene polymerization.



Figure 3. Influence of polymerization temperature on activity (polymerization conditions: $[Zr] = 50 \,\mu mol/I$, Al : Zr = 500, 30 min, 10 bar ethylene, 25 ml toluene).

The method of 'copolymerization' was attempted to produce LCB PE first. The separated polyethylene macromonomer sample from run 1 was copolymerized with ethylene using **2a**/MAO system, but the weight of recovered macromonomer was equal to input and the molecular weight of the polymer fraction was similar to that of run 13 (with the melting point of 134.2 °C), suggesting that macromonomer does not copolymerize with ethylene. Further studies show that the 'tandem' method just gives macromonomer and does not produce any high molecular weight PE (run 18). Finally, the method of 'simultaneous' polymerization was carried out. In comparison with the homopolyethylene obtained with **2a**/MAO (run 13), polymer samples obtained in runs 16 and 17 possessed rather low viscosity average molecular weight. Meanwhile, the melting points of these polymers had almost the same value. Sperber and Kaminsky reported^[14] that the

 Table 3.
 Different copolymerization methods with the complex 1a, 2a/MAO system^a

R = polyethylene macromonomer

					Insoluble polymer		
Run	C _{cat 1a} (mmol/l)	C _{cat 2a (mmol/l)}	Al : Zr	Yield (g)	m _{Insol} b (g)	<i>M</i> _η ^c (×10 ⁵)	T_{m}^{d} (°C)
16 ^e	0.5	0.5	500	1.137	0.455	1.74	133.9
17 ^e	0.5	0.5	250	0.782	0.447	1.05	133.0
18 ^f	0.5	0.5	500	2.111	0		

 a Polymerization conditions: ethylene pressure = 10 bar; $T_P=90\,^\circ\text{C}$, in 25 ml of toluene; 30 min.

^b The insoluble polymer was obtained by extracting the bulk polymer sample with hot toluene for 24 h in a Soxhlet apparatus

^c Intrinsic viscosity was determined in decahydronaphthalene at 135 °C and viscosity average molecular weight was calculated using the equation:^[21] [η] = 6.77 × 10⁻⁴ $M_{\eta}^{0.67}$.

^d Melting point was determined by differential scanning calorimetry. ^e Copolymerization with the 'simultaneous' method: **1a** and **2a** were added simultaneously.

^f Copolymerization with the 'tandem' method: after **1a**/MAO had been polymerized for 30 min, **2a**/MAO was added.

melting point of the synthesized LCB PE decreases with increasing the side-chain percentage. For that reason, LCB PE might not have been produced in this work. The low molecular weights of isolate polymers are probably a result of the interaction of mixed complexes.

Conclusion

Four new bridged cyclopentadienyl indenyl (fluorenyl) zirconocene complexes, **1a**-**b** and **2a**-**b**, were prepared and showed moderate to high activities for ethylene homopolymerization. The steric bulk of the bridging group displays an important influence on the catalytic activity and thermal stability. The bridged cyclopentadienyl indenyl zirconocene complexes **1a**-**d** can catalyze ethylene homopolymerization to afford vinyl-terminated PE macromonomer in high percentages (68.8–94.9%) with molecular weights ranging from 2.7 × 10³ to 10.3 × 10³ g/mol. Polymerization conditions such as ethylene pressure, polymerization temperature and catalyst concentration dramatically influence the vinyl selectivity and the molecular weight of obtained macromonomer.

After attempting three different copolymerization methods, the combined systems of *ansa*-cyclopentadienyl indenyl zirconocene **1a** and *ansa*-cyclopentadienyl fluorenyl zirconocene **2a**/MAO probably do not afford the long-chain branched PE.

Acknowledgments

This work is subsidized by the National Basic Research Program of China (2005CB623801), National Natural Science Foundation of China (NNSFC, 20604009, 20774027), the Program for New Century Excellent Talents in University (for H. Ma, NCET-06-0413) and the Key (Keygrant) Project of Chinese Ministry of Education (no. 109064). All the financial support is gratefully acknowledged.

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