乙烯聚合水杨醛亚胺锆配合物的合成、结构和固定化

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摘要：合成和表征了 2 个锆的配合物：Bis[*N*-(3-*tert*-butylsalicylidene) allylaminato] zirconium dichloride (**4**)和 Bis[*N*-(3-*tert*-butylsali-cylidene)-*iso*-butylaminato] zirconium dichloride (**5**),并且得到了配合物 **4** 的单晶结构。在引发剂的作用下,配合物 **4** 和苯乙烯进行自由基共聚,得到高分子化催化剂 **6**。在助催化剂 MMAO 的存在下,**4**,**5** 和 **6** 都可以催化乙烯聚合。最高活性为 3.7×10^6 g PE·(mol Zr)$^{-1}$·h^{-1}。

关键词：锆配合物；乙烯聚合；均相催化；高分子化催化剂
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Synthesis, Structure, Immobilization of Salicylaldiminato Zirconium Catalysts for Ethylene Polymerization

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Abstract: Two zirconium complexes, Bis[*N*-(3-*tert*-butylsalicylidene) allylaminato] zirconium dichloride (**4**) and Bis [*N*-(3-*tert*-butylsalicylidene)-iso-butylaminato] zirconium dichloride   (**5**), were prepared and characterized. The molecular structure of complex **4** has been determined by X-ray crystallographic analysis. The corresponding polymer-incorporated zirconium catalyst **6** was obtained by the co-polymerization of the olefin group of catalyst **4** with styrene in the presence of a radical initiator. All catalysts   (**4**, **5** and **6**) have been investigated for ethylene polymerization. These catalysts exhibit high activity up to 3.7×10^6 g PE $\cdot$ (mol Zr)$^{-1}$ $\cdot$ h^{-1} in the presence of modified methylaluminoxane (MMAO) as a co-catalyst. CCDC: 249504, **4**.

Key words: zirconium complexes; ethylene polymerization; homogeneous catalyst; polystyrene-incorporated catalyst

Polyolefins are of particular industrial and academic interests because of their diversities in structures and accordingly, the potential properties in applications. The polymer science was brand-new owing to the application of transition metal-based catalysts, among them Ziegler-Natta catalysts [1], the Shell Higher Olefin Process   (SHOP) developed by

Keim et al.[2], the metallocene catalyst[3], nickel(Ⅱ) and palladium(Ⅱ) complexes of bulky substituted diimine ligands [4], cationic iron and cobalt catalyst [5], and FI catalyst[6] are prominent examples.

Homogeneous polyolefin catalytic systems [7] are well-known for their high activities, good co-polymerization activities, narrow polydispersities, and excellent

control of stereo regularity. The industrial ethylene polymerization is usually performed in gas phase or slurry reactors from the point of view of practical considerations. However, for the case of homogeneous catalytic polymerization a continuous industrial process is impossible because they would cause "fouling", which means that the formed polymer is deposited at the reactor walls and causes the problems of the "boiler scale effect"[8]. Hence heterogeneous catalyst is of special interest in industrial application.

As part of our program to synthesize novel polyolefin catalysts, our group has prepared polymerized metallocene IVB complexes[9], Fe complexes and their polymer-incorporated catalyst[10] and nickel complexes[11]. Specifically, we are interested in polyolefin catalysts containing alkenyl groups for the case that they could be immobilized by co-polymeric method. The heterogeneous route of co-polymerization between complexes bearing alkenyl groups and styrene monomer has merits such as avoiding from inorganic ashes and catalyst poisoning and furthermore, the polystyrene material possesses benignant mechanical performance. Fujita et al.[6b,12] have demonstrated that as the alkyl group on the position of imine nitrogen changing from phenyl to cyclopropyl the complexes can display high ethylene polymerization activities. This article reports that zirconium complexes containing allyl and *iso*-butyl groups can display high ethylene polymerization activities, and the prepared polystyrene-incorporated catalyst **6** can also show a high ethylene polymerization activity. Noteworthily, it was observed that the polymerization behavior of Bis[*N*-(3-*tert*-butylsalicylidene) allylaminato] zirconium dichloride (complex **4**) was different from that of Bis [*N*-(3-*tert*-butylsalicylidene)-*iso*-butylaminato] zirconium dichloride (complex **5**) and the polystyrene-incorporated catalyst **6**.

1 Experimental

1.1 Materials and instruments

All air- and moisture-sensitive complexes were manipulated using standard Schlenk techniques under argon atmosphere. Dried solvents such diethyl ether,

tetrahydrofuran (THF), toluene and hexane were commercially available analytical grade reagents, dried over 4A molecular sieve and distilled over metal sodium. Dichloromethane (CH$_2$Cl$_2$) was distilled from calcium hydride (CaH$_2$). Modified methylalumoxane (MMAO) was Akzo-Nobel reagent as a 2.20 mol·L^{-1} toluene solution. Zirconium tetrachloride (ZrCl$_4$, purity 98%) and 1.6 mol·L^{-1} *n*-butyl lithium hexane solution were purchased from Acros Organics, USA. Azobisisobutyronitrile (AIBN) was recrystallized with ethanol and dried under vacuum for 8 h prior to use. Ethylene (99.9% purity) was from Guangming Institute of Chemical Industrial Design and Research and used as received. All other chemicals were obtained commercially and used as received.

IR spectra were recorded on a Bio-Rad FTS135 spectrometer as a KBr pellet. ^{1}H NMR spectra were recorded on a Bruker-300 spectrometer. EI-MS spectra were recorded on a Finigan MAT 8500 spectrometer (70 eV). Elemental analysis was performed on Elementar Analysensysteme Vario EL Ⅲ CHN Analyzer.

The characterization of the polystyrene-incorporated catalysts was performed using a Waters 410 gel permeation chromatograph at 35 ℃, THF was employed as an eluent at a flow rate of 1.0 mL·min^{-1}. The zirconium content of the polystyrene-incorporated catalyst was measured using the ICP-AES method with a TJA POEMS ICP analyzer after dry ashing and dilute nitric acid dissolution.

Polymer characterization: One-point intrinsic viscosity [η] was measured in Decalin at 135 ℃ using an Ubbelohde viscometer. The viscosity average molecular weight (M_v) values of polyethylene were calculated by the following equation[13]: [η]=6.2 × 10^{-4} $M_v^{0.7}$. The molecular weight distribution (M_w/M_n) values of polyethylene were determined using a PL GPC-220 Gel Permeation Chromatograph equipped with three PL gel columns (sets of PL gel 10 μm MIXED-BLS) at 150 ℃ using narrow standards calibration. Trichlorobenzene was employed as an eluent at a flow rate of 1.00 mL·min^{-1}. ^{13}C NMR spectra of polymer were recorded on av-400 spectrometer at 130 ℃ using o-dichlorobenzene as a solvent. Differential scanning

calorimetric analysis (DSC) were performed on a Perkin-Elmer DSC 7 series thermal analysis system with 5~6 mg of each of polymers, 50~150 ℃ temperature range, heating and cooling rate were 10.0 ℃·min^{-1}. The melting temperature T_m and the fusion enthalpy were recorded during the second heating course.

1.2 Synthesis

1.2.1 3-*tert*-butylsalicylaldehyde (**1**)

A solution of bromoethane (7.630 g, 0.070 mol) in diethyl ether (20 mL) was added to a stirred mixture of magnesium dust (1.848 g, 0.077 mol) in diethyl ether (30 mL), the dropping speed should be controlled so that diethyl ether was refluxed moderately. The mixture was kept stirring for an additional 0.5 h after the drop-feeding being completed. Then the mixture was transferred to a dropping funnel through a stainless tube and added dropwise to a solution of *o-tert*-butylphenol (9.000 g, 0.060 mol) in THF (40 mL) at room temperature and stirred for 2 h, a large number of white precipitation formed. Toluene (100 mL) was added and diethyl ether, and THF were removed under vacuum, then triethylamine (9.090 g, 0.090 mol), paraformaldehyde (4.700 g, 95% purity, 0.150 mol) and toluene (60 mL) were added, and the mixture was stirred for 8 h at 110 ℃. The resulting mixture was poured into 1 mol·L^{-1} hydrochloric acid (300 mL) at 0 ℃. The organic phase was collected and the aqueous phase was extracted with diethyl ether. The combined organic phase was dried over anhydrate sodium sulfate, filtered and evaporated in vacuum to give a yellow oil, which was purified by column chromatography on silica gel using petroleum ether (60~90 ℃) as an eluent to give 3-*tert*-butylsalicylaldehyde (9.078 g, 0.051 mol) as an orange oil in 85% yield. FTIR: 2 999, 2 960, 2 912, 2 872, 2 743, 1 651, 1 613, 1 483, 1 454, 1 432, 1 388, 1 363, 1 312, 1 266, 1 224, 1 197, 1 143, 1 091, 1 024, 948, 930, 854, 797, 753, 679, 625, 545, 508, 405 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.42(s, 9H, C(CH$_3$)$_3$), 6.96(q, 1H, aromatic-H), 7.37(d, 1H, aromatic-H), 7.53(d, 1H, aromatic-H), 9.89 (s, 1H, CH=O), 11.79 (s, 1H, OH) ppm.

1.2.2 *N*-(3-*tert*-butylsalicylidene)allylamine (**2**)

A mixture of allylamine (1.254 g, 0.022 mol), 3-*tert*-butylsalicylaldehyde (3.560 g, 0.020 mol) and 4A molecular sieve (3.077 g) in ethanol (40 mL) was stirred for 16 h at room temperature. The resulting mixture was filtered, the 4A molecular sieve was washed with ethyl acetate. The combined organic phase was concentrated in vacuum to afford a crude imine. Purification by column chromatography on silica gel using petroleum ether (60~90 ℃)/ethyl acetate (15∶1) as an eluent to give *N*-(3-*tert*-butylsalicylidene)allylamine (3.906 g, 0.018 mol) as an orange-red oil in 90% yield. FTIR: 3 083, 3 000, 2 957, 2 911, 2 874, 2 733, 2 657, 1 633, 1 496, 1 484, 1 457, 1 436, 1 391, 1 361, 1 309, 1 268, 1 200, 1 146, 1 089, 1 035, 986, 921, 854, 795, 751, 680, 605, 550, 408 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.44(s, 9H, ^{t}Bu), 4.24(d, 2H, -CH$_2$-), 5.22(q, 2H, -CH$_2$=), 6.00 (m, 1H, =CH), 6.81 (q, 1H, aromatic-H), 7.10 (d, 1H, aromatic-H), 7.31 (d, 1H, aromatic-H), 8.36 (s, 1H, CH=N), 14.02(s, 1H, OH) ppm.

1.2.3 *N*-(3-*tert*-butylsalicylidene)isobutylamine (**3**)

3 was prepared using a procedure similar to that for 2 as an orange-yellow oil in 85% yield. FTIR: 3 522, 3 056, 2 958, 2 872, 1 634, 1 606, 1 497, 1 484, 1 463, 1 436, 1 389, 1 361, 1 345, 1 307, 1 268, 1 200, 1 145, 1 090, 1 040, 1 006, 981, 958, 931, 854, 198, 751, 680, 625, 550, 509, 407 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.98(d, 6H, C(CH$_3$)$_2$), 1.42(s, 9H, C(CH$_3$)$_3$), 1.98(m, 1H, CH), 3.42(d, 2H, NCH$_2$), 6.81(q, 1H, aromatic-H), 7.09 (d, 1H, aromatic-H), 7.30 (d, 1H, aromatic-H), 8.30(s, 1H, CH=N), 14.19(s, 1H, OH) ppm.

1.2.4 Bis[*N*-(3-*tert*-butylsalicylidene)allylaminato] zirconium(IV) dichloride (**4**)

To a stirred solution of *N*-(3-*tert*-butylsalicylidene)allylamine (1.302 g, 6.00 mmol) in THF (20 mL), a 1.60 mol·L^{-1} *n*-butyllithium hexane solution (3.83 mL, 6.12 mmol) was added through a syringe at −78 ℃. The solution was allowed to warm to room temperature and stirred for 2 h. The resulting solution was added dropwise to a stirring ZrCl$_4$ (0.713 g, 3 mmol) in THF (20 mL) at −78 ℃. The mixture was allowed to warm to room temperature and stirred for 15 h. After

removal of the solvent, the residual solid was extracted with CH_2Cl_2, centrifuged following the removal of the volatile to give a yellow solid. The solid was recrystallized from a CH_2Cl_2/Hexane (1:3) solution to give the complex **4** as pale yellow needle crystals of 0.891 g in 50% yield. EI-MS (*m/z*): 594 (M+), 557, 543, 515, 499. FTIR: 3 078, 2 962, 2 910, 2 879, 1 608, 1 587, 1 561, 1 463, 1 451, 1 431, 1 407, 1 360, 1 325, 1 284, 1 267, 1 237, 1 203, 1 151, 1 091, 1 017, 990, 926, 878, 817, 800, 756, 709, 665, 619, 582, 535, 464, 429 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.52 (s, 18H, 2C(CH$_3$)$_3$), 4.25(s, 4H, 2-CH$_2$-), 4.97~5.09 (q, 4H, 2-CH$_2$=), 5.69(s, 2H, 2=CH-), 6.90(q, 2H, 2aromatic-H), 7.11(d, 2H, 2aromatic-H), 7.56~7.58(d, 2H, 2aromatic-H), 8.19 (s, 2H, 2CH=N). Anal. Found (calcd. for C$_{28}$H$_{36}$N$_2$O$_2$Cl$_2$Zr): C, 55.32 (56.57); H, 6.27 (6.06); N, 4.22(4.71) ppm.

1.2.5 Bis[*N*-(3-*tert*-butylsalicylidene)isobutylaminato] zirconium dichloride (**5**)

5 was prepared using a procedure similar to that for **4** as a pale yellow powder in 60% yield. EI-MS (*m/z*): 626 (M+), 590, 574. FTIR: 3 077, 2 959, 2 911, 2 870, 1 608, 1 588, 1 561, 1 469, 1 433, 1 405, 1 390, 1 360, 1 337, 1 317, 1 286, 1 267, 1 236, 1 204, 1 148, 1 092, 877, 815, 755, 703, 654, 583, 539, 431 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.91(d, 12H, 2C(CH$_3$)$_2$), 1.51(s, 18H, 2C(CH$_3$)$_3$), 1.88(m, 2H, 2CH), 3.43(s, 4H, 2NCH$_2$), 6.85 (q, 1H, aromatic-H), 7.20 (d, 1H, aromatic-H), 7.55 (d, 1H, aromatic-H), 8.14 (s, 1H, CH=N) ppm.

Anal found (calcd. for C$_{30}$H$_{44}$N$_2$O$_2$Cl$_2$Zr) (%): C, 57.86 (57.51); H, 7.28(7.03); N, 4.55(4.47).

1.2.6 Polystyrene supported catalyst (**6**)

A solution of complex **4** (0.260 g, 0.438 mmol), styrene (6 mL, 51.8 mmol) and AIBN (0.142 g, 0.086 mmol) in 30 mL toluene was stirred for 18 h at 70 ℃. The resulting reaction mixture was evaporated in vacuum to give a gel mixture, washed with toluene-hexane (1:3, *V/V*) and treated under vacuum to afford the polystyrene-incorporated catalyst as a pale yellow solid of 1.292 g. ICP-AES: 12.3 mg Zr/g GPC: M_n= 11 100, PDI (M_w/M_n)=1.34.

1.3 Crystal structure determination of the complex 4

The single crystal of complex **4** appropriate for X-ray structure analysis was sealed in a glass capillary. The intensity data were collected on a CCD-Bruker Smart APEX system with a graphite monochromator (Mo *K*α radiation, λ=0.071 073nm). All the data were collected at room temperature using the ω-2θ scan technique. The structure was solved by the direct method and subsequent difference. Fourier syntheses and refined on F^2 by a full-matrix least-squares method. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the structure factor calculation but not refined. All the calculations were carried out with a Siemens SHELXTL PLUS program. Selected data of bonds for complex **4** are summarized in Table 1.

CCDC: 249504, **4**.

Table 1 Selected data of bond distances (nm) and bond angles (°) for complex 4

Zr(1)-O(1)	0.196 6(3)	Zr(1)-O(2)	0.197 3(3)	Zr(1)-N(1)	0.232 1(4)
Zr(1)-N(2)	0.233 1(4)	Zr(1)-Cl(1)	0.242 23(17)	Zr(1)-Cl(2)	0.242 49(16)
N(1)-C(11)	0.127 3(6)	N(1)-C(12)	0.147 9(6)	N(2)-C(25)	0.128 7(6)
N(2)-C(26)	0.147 7(6)	O(1)-C(5)	0.133 8(5)	O(2)-C(19)	0.133 4(5)
O(1)-Zr(1)-O(2)	163.52(14)	N(1)-Zr(1)-N(2)	79.60(15)	O(2)-Zr(1)-N(1)	88.55(15)
Cl(1)-Zr(1)-Cl(2)	99.27(7)	O(1)-Zr(1)-N(2)	90.59(14)	O(2)-Zr(1)-N(2)	78.04(14)
O(1)-Zr(1)-Cl(1)	95.37(11)	O(1)-Zr(1)-N(1)	77.58(14)	O(2)-Zr(1)-Cl(1)	94.66(11)
N(1)-Zr(1)-Cl(1)	94.97(12)	N(2)-Zr(1)-Cl(1)	170.92(11)	O(1)-Zr(1)-Cl(2)	94.57(10)
O(2)-Zr(1)-Cl(2)	96.68(11)	N(1)-Zr(1)-Cl(2)	164.35(11)	N(2)-Zr(1)-Cl(2)	87.04(12)
C(11)-N(1)-C(12)	115.0(4)	C(11)-N(1)-Zr(1)	125.6(4)	C(25)-N(2)-C(26)	116.3(4)
C(12)-N(1)-Zr(1)	119.2(3)	C(25)-N(2)-Zr(1)	125.2(4)	C(26)-N(2)-Zr(1)	118.4(3)
C(19)-O(2)-Zr(1)	146.0(3)	C(5)-O(1)-Zr(1)	146.9(3)	C(5)-C(10)-C(11)	122.3(4)

Continued Table 1

O(1)-C(5)-C(6)	121.5(5)	O(1)-C(5)-C(10)	117.4(4)	O(2)-C(19)-C(24)	117.5(4)
C(27)-C(26)-N(2)	114.8(10)	N(2)-C(25)-C(24)	129.4(5)	C(27′)-C(26)-C(27)	39.1(14)
C(28)-C(27)-C(26)	131(3)	C(28′)-C(27′)-C(26)	154(4)		

Empirical formula: $C_{28}H_{36}Cl_2N_2O_2Zr$; Formula weight: 594.71; Temperature: 293(2) K; Wavelength: 0.071 073 nm; Crystal system: Monoclinic; Space group: C_2/c; Unit cell dimensions: a=2.155 5(11) nm, b=1.437 6(7) nm, c=1.934 8(9) nm; α=90°, β=91.212(7)°, γ=90°; Volume: 5.994(5) nm³; Z=8, Calculated density (D_c)=1.318 Mg·m⁻³; Absorption coefficient (μ): 0.571 mm⁻¹; F(000): 2 464; Crystal size: 0.30 mm × 0.15 mm × 0.10 mm; θ range for data collection: 1.70° to 25.01°. Limiting indices: $-25 \leqslant h \leqslant 25$, $-17 \leqslant k \leqslant 13$, $-23 \leqslant l \leqslant 21$; Reflections collected / unique: 12 280 / 5 279 (R_{int}=0.068 2); Completeness to θ=25.01°, 99.8%; Absorption correction: None; Max. and min. transmission: 0.945 2 and 0.847 5; Refinement method: Full-matrix least-squares on F^2; Data / restraints / parameters: 5 279 / 0 / 341; Goodness-of-fit on F^2: 1.067; Final R indices [$I>2\sigma(I)$]: R_1=0.058 0, wR_2=0.124 9; R indices (all data): R_1=0.105 3, wR_2=0.149 4; Largest diff. peak and hole: 0.865 × 10⁻³ and −0.547 × 10⁻³ e·nm⁻³.

1.4　Ethylene polymerization

Ethylene polymerization was carried out under atmospheric pressure in a 200 mL glass reactor equipped with a propeller-like stirrer. The reactor was treated by flame in vacuum for 1 h. After cooling to room temperature, the reactor was filled with ethylene gas under atmosphere pressure, then toluene, MMAO solution and a solution of complex were added one after another. After 30 min, ethylene gas feed was stopped and the resulting suspended liquid was poured into a solution of ethanol (200 mL) containing concentrated hydrochloric acid (2 mL). The polyethylene was collected by filtration, washed with ethanol, and dried in vacuum at 80 ℃ for 10 h.

In the case of ethylene polymerization under 0.45 MPa, a 500 mL glass reactor equipped with a propeller-like stirrer was first heated at 90 ℃ under vacuum for 1 h, then thermostated to a prescribed temperature, ethylene gas feed pressure was adjusted to 0.1 MPa and toluene (90 mL), a solution of MMAO

and then the toluene solution of catalyst was introduced into the reactor in turn, then the ethylene gas feed pressure was turned to a prescribed polymerization pressure. After 30 min, the ethylene gas feed was terminated. The resulting mixture was poured into a solution of ethanol (400 mL) containing concentrated hydrochloric acid (2 mL). The polymer was collected by filtration, washed with ethanol, and dried in vacuum at 80 ℃ for 10 h.

2　Results and discussion

2.1　Catalysts synthesis

The complexes synthesis route is shown in Scheme 1 and consists of three steps, the preparation of 3-substituent salicylaldehyde[14], the formylated phenol reacted with a primary amine to afford a Schiff Base, and the treatment of the Schiff Base lithium salt with $ZrCl_4$ to afford the corresponding zirconium complex[6b]. The manufacture procedure was found to be safe and productive.
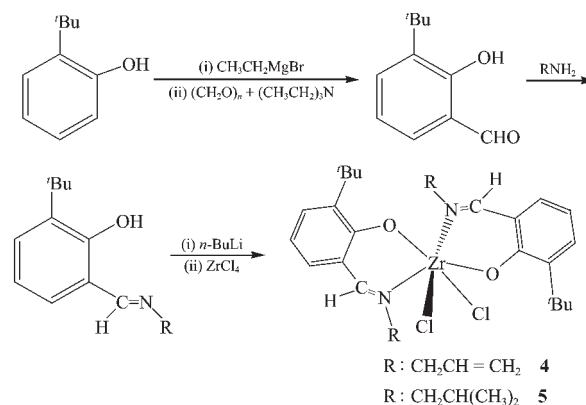
Scheme 1　Synthesis of **4**, **5**

The IR spectra of 3-*tert*-butylsalicylaldehyde (**1**) and *N*-(3-*tert*-butylsalicylidene) allylamine (**2**) did not show the stretch absorbance of hydroxy group using a method of smeared membrane, which may be explained by intramolecular hydrogen bond. The observed 3 522 cm⁻¹ absorbance of hydroxyl group for *N*-(3-*tert*-butyl-salicylidene) *iso*-butyllamine (**3**) suggests that the steric congestion of bulky isobutyl group can weaken

the intramolecular hydrogen bond.

Our previous works [9,10] have shown that metal complexes bearing alkenyl groups can co-polymerize with styrene in the presence of a radical initiator, and parallel GPC tests show that trace of unsupported complex could be rinsed off by toluene and hexane solution[10]. On the bases of these works and with some modification on reaction conditions the polystyrene-supported catalyst **6** were prepared by heating complex **4**, styrene and AIBN in toluene at 70 ℃ for 18 h. The tests of ICP-AES analysis result (12.3 mg Zr/g) and polymer characterization of GPC (M_n=11 100, PDI (M_w/M_n)=1.34) show that zirconium complex is fixed in the polystyrene chain.

2.2　Structure of complex 4

Single crystals appropriate for the X-ray structure analysis of complex **4** were obtained from dichloromethane solution using hexane layer diffusion. The X-ray crystallographic structure is shown in Fig.1, the coordination geometry around the central zirconium atom in complex **4** is close to octahedral. The two oxygen atoms are situated in trans position (O-Zr-O angle, 163.52(14)°), the two nitrogen atoms (N-Zr-N angle, 79.60 (15)°) and the two chlorine atoms (Cl-Zr-Cl angle, 99.27(7)°) are located *cis* to one another. The data of bond distances reveal that the ionic nature between zirconium atom and oxygen atom (Zr-O bond length, 0.197 0 nm) and the coordinative nature between zirconium atom and nitrogen atom (Zr-N bond length, 0.232 6 nm). The arrangement in crystal structure is correlated to bidental chelating effect of Schiff Base and the bond model between zirconium and other atoms, which reduces repulsion effect of charge, steric congestion of the ligands and
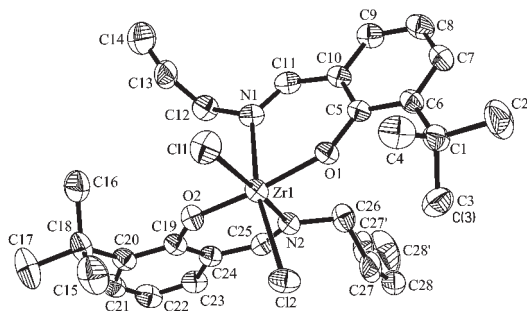

Fig.1　Molecular structure of complex **4**

maximizes the opportunity for other atoms to zirconium-bonding through the utilization of different zirconium *d*-orbital.

2.3　Ethylene polymerization

The zirconium complex **4** was investigated as an ethylene polymerization catalyst using modified methylalumoxane (MMAO) as a co-catalyst under ethylene at atmosphere pressure. The relationship between the polymerization activity and the polymerization time is displayed in Fig.2. Though the polyethylene yield increases, the activity of complex **4** is decreased with the polymerization time. The activity reaches the highest when the polymerization time is in the range of 35 to 40 minutes.
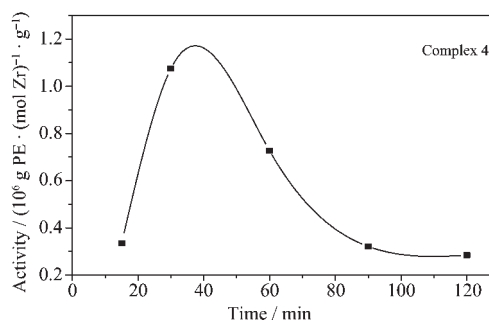
Polymerization condition: 12 ℃, 0.1 MPa ethylene pressure, 50 mL toluene, 1.111 μmol complex 4, 2.2 mol·L^{-1} MMAO toluene solution 0.5 mL

Fig.2　Relationship between the catalytic activity and polymerization time obtained with complex **4** using MMAO as co-catalyst

The polymerization performance of complex **4** and **5** as function of the amount of Al/Zr was studied. The relationship between the activity as well as the viscosity average molecular weight of the obtained polyethylene responding with the amount of Al/Zr are respectively shown in Fig.3 and Fig.4 (Conditions: complex **4**, 1.111 μmol, Complex **5**, 1.334 μmol, 0.1 MPa ethylene pressure, 50 mL toluene, 12 ℃, 30 min.).

Complex **4** shows a higher activity for ethylene polymerization and needs more amount of Al than complex **5** to display the highest activity. The M_v data of polyethylene obtained by complex **4** decreases much faster than that of complex **5** while the Al/Zr ratio increases. For the case of complex **5**, polymeriza-
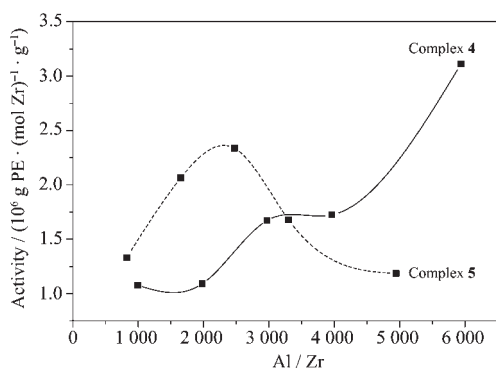
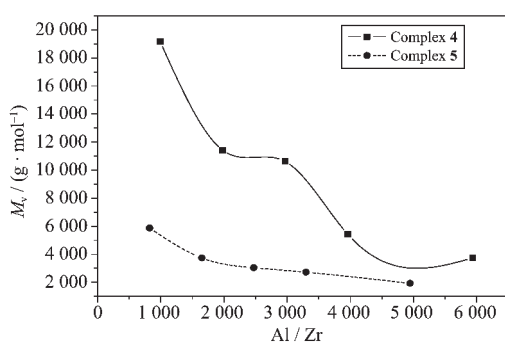Fig.3　Relationship between the activity and the amount of Al/Zr

Fig.4　Relationship between the viscosity average molecular weight of polyethylene and the amount of Al/Zr

tion activity as a function of the amount of Al displays a curve embodied an apex, this phenomena is reasonable because the initial complex needs to be activated by forming an alkylated species, the poison species need to be scavenged and excess alkylating reagents may lead to the formation of a hetero-dinuclear complex adducts, which are coordinative saturated and have no catalytic activity[15]. As for the complex **4**, the catalytic activities are enhanced while the molecular weight of the obtained polymers decreases along with the increasing amount of Al.

The polystyrene-incorporated catalyst **6** was investigated as an ethylene polymerization catalyst and the results are summarized in Table 2. The polystyrene-incorporated catalyst **6** displays a lower catalytic activity than complex **4** for ethylene polymerization under a low ethylene pressure, but the catalytic activity of catalyst **6** is higher than that of complex **4** under an atmospheric ethylene pressure, and the molecular weight of polyethylene obtained by

the polystyrene-incorporated catalyst **6** is higher than that obtained by complex **4**.

Table 2　Ethylene polymerization using the polystyrene-incorporated catalyst 6

Entry	T / ℃	Al/Zr	Activity[a]	M_v[b]
1	12	988	0.14	21 100
2	12	3 950	0.29	17 800
3	68	3 950	0.08	10 600
4	75	3 950	0.70	41 700
5	60	3 950	3.34	42 400
6	45	3 950	3.71	43 400

Conditions: 1.114 μmol (Zr); Entry 1~3, 0.1 MPa ethylene pressure, 50 mL toluene, 30 min; Entry 4~6, 0.45 MPa ethylene pressure, toluene 100 mL, 1 h; [a] 10^6 g PE·(mol Zr)$^{-1}$·h^{-1}, [b] obtained from the polyethylene solution in Decalin under 135 ℃.

2.4　Catalytic performance of complex 4

DSC analysis　(Fig.5) reveals that polyethylene obtained by complex **4** displays a bimodal apex. The bimodal phenomena become prominent as the amount of Al increases, suggesting the increase in the amount of low molecular weight polyethylene as seen in Fig.4.
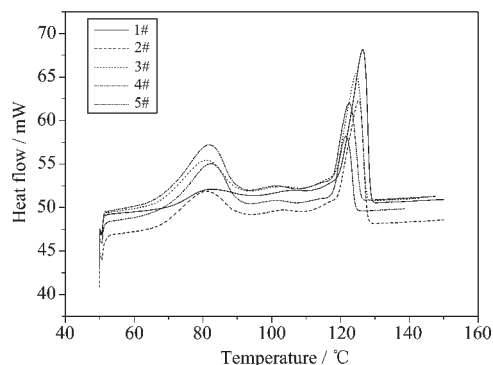
Curves were recorded by the second heating course. ΔH_m describes the fusion enthalpy of the crystalline polyethylene for the second heating course of the DSC analysis. Conditions for the produced polyethylene: 1#, Al/Zr=990　(ΔH_m: 19.09, 133.16 J·g^{-1}); 2#, Al/Zr=1 980　(ΔH_m: 49.36, 100.21 J·g^{-1}); 3#, Al/Zr=2 970 (ΔH_m: 53.65, 95.40 J·g^{-1}); 4#, Al/Zr=3 960 (ΔH_m: 73.62, 71.11 J·g^{-1}); 5#, Al/Zr=5 940　(ΔH_m: 76.68, 56.85 J·g^{-1}); 1.111 μmol complex **4**, 0.1 MPa ethylene pressure, 50 mL toluene.

Fig.5　DSC curves of polyethylene produced by complex **4** at various Al/Zr

High temperature GPC traces (Fig.6 and Table 3) indicate that the polyethylene obtained by complex **4** features a bimodel distribution and the composition of high molecular weight polyethylene decreases and the ratio of Al/Zr increases. In contrast, the polyethylene

<div align="center">Table 3　Results of high temperature GPC traces[a]</div>

Curve	Catalyst / μmol	Al/Zr	T / ℃	Solvent / mL	M_w	M_n	PDI
1	4 (1.111)	3960	12	Toluene (50)	10 400	680	15.3
2	4 (1.111)	990	12	Toluene (50)	39 800	1 250	31.8
3	6 (1.114)	3 950	45	Toluene (100)	70 100	1 766	39.7
4	5 (1.334)	4 948	12	Toluene (50)	2 660	837	3.2

[a] Polymerization was carried out for one hour under 0.45 MPa ethylene pressure, the polymerization for curve 1, 2 and 4 were all carried out for 30 min under 0.1 MPa ethylene pressure.

obtained by complex **5** was mono-model distribution. The bimodel distribution phenomenon of the polystyrene-incorporated catalyst **6** may be attributed to the complex **4** inclusion. These data indicate that there lay more than one active species when complex **4** is used in ethylene polymerization.
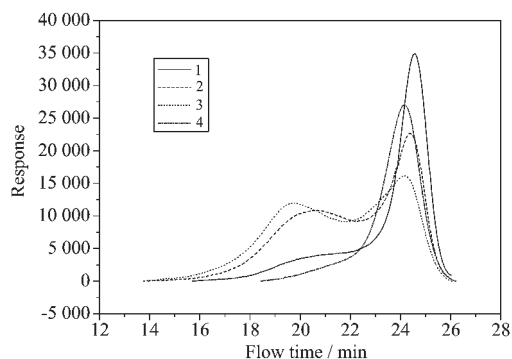

Fig.6　GPC curves for the obtained polyethylenes on various conditions

Quantitative ^{13}C NMR spectrum indicates that the polymer obtained by complex **4** under the condition of 3 960 Al/Zr ratio possess methine group （39.70 ppm） in addition to saturated linear hydrocarbon chain end according to Grant and Paul′s linear equation[17]. The amount of vinyl end group is only 4.77 percent that of methyl end group. These data indicate that the obtained bimodal polymer consists of linear structure and branched structure.

The difference in catalytic performance between complex **4** and complex **5** may be attributed to the group on the imine nitrogen in the structure of Schiff base Ⅳ-B complex. The single-crystal structure (Fig. 1) shows that the group on the imine nitrogen of complex is protruded from zirconium center since the bond angles of relative atoms are obtuse angles (C14-C13-C12 angle, 125.7°；C13-C12-N1 angle, 110.7°；C12-N1-Zr angle, 119.2°), the effect of the steric

congestion on the central mental could be neglected because allyl and isobutyl group differ little in size. Since there is a methylene group between vinyl, isopropyl group and nitrogen atom, the electronic effect can be insignificant. Considering that a molecular weight is determined by the relative rate of chain propagation and chain termination, and the β-H transfer is the main termination pathway for the Schiff base Ⅳ-B catalysts[6b] and there might lie a process of self-immobilization[8,11,16] for a catalyst bearing alkenyl group, the allyl subsituent on the nitrogen atom might use the self-immobilization process to bring about the bimodal results.

3　Conclusions

Two zirconium complexes (Complex **4**, **5**) of Schiff Base bearing short chain hydrocarbon groups and a polymer-incorporated catalyst **6** possess high catalytic activities for ethylene polymerization （10^6 g PE·(mol Zr)$^{-1}$·h^{-1}）. The catalytic lifetime of complex **4** was at least 35 minutes and catalytic activity was high. Noteworthily the catalytic performance of complex **4** was different from that of complex **5** because the relationship between catalytic activity together with the viscosity average molecular weight of polyethylene and the Al/Zr ratio was different. GPC traces and DSC analysis of polyethylene reveals that polymer obtained by complex **4** displays a bimodal apex while polymer obtained by complex **5** displays only one apex, indicating that the allyl group of complex **4** might be involved in the catalytically active species.

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