Binuclear titanocenes linked by the bridge combination of rigid and flexible segment: Synthesis and their use as catalysts for ethylene polymerization

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Abstract

Five novel binuclear titanocenes $(CpTiCl_2)_2[(C_5H_4)CH_2(p\text{-}C_6H_4)O(CH_2)_nO(C_6H_4\text{-}p)CH_2(C_5H_4)]$ ($n = 2$–6) (**16–20**) with the bridge combination of rigid and flexible segment were synthesized and characterized. In the presence of methylaluminoxane (MAO), the behaviors of these complexes toward ethylene polymerization were investigated. The results show that their catalytic behaviors are highly dependent on the length of flexible segment and polymerization conditions. With the length of flexible segment becoming longer, the catalytic activity increases, whereas the molecular weight (M_W) of the produced polyethylene (PE) decreases. In addition, the longer flexible segment is favorable to produce PE with broader molecular weight distribution (MWD).
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Keywords: Binuclear; Titanocene; Metallocene catalyst; Polyethylene

1. Introduction

Binuclear metallocenes used as catalysts for olefin polymerization can be divided roughly into two kinds in terms of the bridge [1], flexible bridge such as polymethylene [2–5], polysiloxane or silane [2,6–11] and rigid bridge such as phenylene [1,12,13], biphenylene [14,15], double bridges [16–18]. In general, binuclear metallocenes with a rigid bridge show higher activity and thermal stability [15]. In continuation of our previous investigation on binuclear metallocenes with rigid [1,12,14,19] or flexible bridge [3–5,20], here we report the synthesis of novel binuclear titanocenes $(C_5H_5TiCl_2)_2[(C_5H_4)CH_2(p\text{-}C_6H_4)O(CH_2)_nO(C_6H_4\text{-}p)CH_2(C_5H_4)]$ ($n = 2$–6) (**16–20**) with the bridge combination of rigid and flexible segment. The behaviors of these complexes toward ethylene polymerization were investigated.

2. Experimental

2.1. General procedures

All manipulations involving air- or moisture-sensitive compounds were performed under an atmosphere of argon using standard Schlenk techniques. Elemental analyses were conducted on a Perkin-Elmer 240 elemental analyzer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400 instrument at ambient temperature using $CDCl_3$ as solvent and tetramethylsilane as internal standard. The intrinsic viscosity $[\eta]$ of PE in decahydronaphthalene was measured with a modified Ubbelohde viscometer at 135 °C. The viscosity-averaged molecular weight (M_η) was calculated according to the equation $[\eta] = 6.67 \times 10^{-4} M_\eta^{0.67}$ (ml/g) [21]. The molecular weight distributions (MWD) of PE were determined by gel-permeation chromatography (GPC, Waters 150, 135 °C) with standard polystyrene as a calibration reference. The melting point temperatures (T_m) of PE were recorded with a Perkin-Elmer DSC-7 differential scanning calorimeter.

All chemical reagents used were of analytical grade and were further purified as given in the literature. Toluene,

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tetrahydrofuran (THF), diethyl ether, and hexane were freshly distilled under argon from purple sodium/benzophenone ketyl solutions. CH_2Cl_2 was distilled under argon from CaH_2. Cyclopentadiene was freshly distilled from its dimer. Methylaluminoxane (MAO) (10% in toluene) was purchased from Witco. Ethylene (polymer grade) was purified via bubbling through triisobutylaluminum in toluene. Cyclopentadienyltitaniumtrichloride ($CpTiCl_3$) [22] was prepared according to the literature.

2.2. Synthesis of compounds

2.2.1. p-$CH_3C_6H_4O(CH_2)_nOC_6H_4CH_3$-$p$ ($n = 2$–6) (1–5)

p-Cresol (21.60 g, 0.20 mol) was added to a stirred solution of sodium hydroxide (8.80 g, 0.22 mol) in 150 ml of ethanol at room temperature. After stirring for 0.5 h, 0.10 mol of $Br(CH_2)_nBr$ ($n = 2$–6) was added. The reaction mixture was stirred for another 8 h under refluxing and then poured into water (500 ml). The resulting mixture was cooled to room temperature and filtered. The remaining solid was washed with water ($2 \times$ 30 ml) and ethanol ($2 \times$ 20 ml), and then dried in vacuo to give the products as white solids.

1: yield: 8.18 g (33.8%); m.p. 137–138 °C; ^{1}H NMR: $\delta = 2.30$ (s, 6H, $2 \times CH_3$), 4.29 (s, 4H, $2 \times CH_2$), 6.86 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$), 7.09 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$).

2: yield: 14.4 g (56.3%); m.p. 98–100 °C; ^{1}H NMR: $\delta = 2.24$ (m, 2H, CH_2), 2.28 (s, 6H $2 \times CH_3$), 4.12 (t, $J = 6.4$ Hz, 4H, $2 \times CH_2$), 6.78 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$), 7.07 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$).

3: yield: 17.2 g (63.8%); m.p. 109–111 °C; ^{1}H NMR: $\delta = 1.95$ (m, 4H, $2 \times CH_2$), 2.28 (s, 6H $2 \times CH_3$), 3.99 (t, $J = 5.2$ Hz, 4H, $2 \times CH_2$), 6.78 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$), 7.06 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$).

4: yield: 24.6 g (86.6%); m.p. 68–70 °C; ^{1}H NMR: $\delta = 1.65$ (m, 2H, CH_2), 1.84 (m, 4H, $2 \times CH_2$), 2.28 (s, 6H $2 \times CH_3$), 3.95 (t, $J = 6.4$ Hz, 4H, $2 \times CH_2$), 6.80 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$), 7.06 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$).

5: yield: 27.2 g (91.3%); m.p. 88–91 °C; ^{1}H NMR: $\delta = 1.52$ (m, 4H, $2 \times CH_2$), 1.79 (m, 4H, $2 \times CH_2$), 2.28 (s, 6H $2 \times CH_3$), 3.93 (t, $J = 6.4$ Hz, 4H, $2 \times CH_2$), 6.78 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$), 7.05 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$).

2.2.2. p-$BrCH_2C_6H_4O(CH_2)_nOC_6H_4CH_2Br$-$p$ ($n = 2$–6) (6–10)

A mixture of **1** (6.05 g, 25 mmol), N-bromosuccinimide (9.10 g, 51 mmol), dibenzoyl peroxide (0.50 g, 2 mmol) and CCl_4 (80 ml) was refluxed 5 h under stirring. The solvent was removed in vacuo, and water (400 ml) was added. The resulting mixture was stirred and filtered. The remaining solid was washed with water ($3 \times$ 100 ml), recrystallized from THF and dried in vacuo to afford compound **6** in form of white crystals. Yield: 5.56 g (55.6%); m.p. 178–180 °C; ^{1}H NMR: $\delta = 4.32$ (s, 4H, $2 \times CH_2$), 4.50 (s, 4H, $2 \times CH_2$), 6.90 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$), 7.32 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$).

2–**5** ($n = 3$–6) (25 mmol), N-bromosuccinimide (9.10 g, 51 mmol), dibenzoyl peroxide (0.50 g, 2 mmol) and CCl_4 (80 ml) were mixed together and refluxed for 2 h under stirring.

After a few minutes a white solid was formed, floating on the CCl_4 surface. The reaction mixture was filtered while it was still hot and the solid was washed with CCl_4 ($2 \times$ 15 ml). The combined filtrate and washing solutions were concentrated to 25 ml and cooled to 0 °C. After filtration, the solid was recrystallized from $CHCl_3$ and dried in vacuo affording white needles.

7: yield: 6.1 g (58.9%); m.p. 143–146 °C; ^{1}H NMR: $\delta = 2.25$ (m, 2H, CH_2), 4.15 (t, $J = 6.0$ Hz, 4H, $2 \times CH_2$), 4.50 (s, 4H $2 \times CH_2$), 6.86 (d, $J = 8.8$ Hz, 4H, $2 \times C_6H_4$), 7.30 (d, $J = 8.8$ Hz, 4H, $2 \times C_6H_4$).

8: yield: 7.1 g (66.4%); m.p. 137–139 °C; ^{1}H NMR: $\delta = 1.98$ (m, 4H, $2 \times CH_2$), 4.04 (t, $J = 5.2$ Hz, 4H, $2 \times CH_2$), 4.51 (s, 4H $2 \times CH_2$), 6.85 (d, $J = 8.8$ Hz, 4H, $2 \times C_6H_4$), 7.31 (d, $J = 8.8$ Hz, 4H, $2 \times C_6H_4$).

9: yield: 6.26 g (56.7%); m.p. 112–114 °C; ^{1}H NMR: $\delta = 1.64$ (m, 2H, CH_2), 1.85 (m, 4H, $2 \times CH_2$), 3.98 (t, $J = 6.4$ Hz, 4H, $2 \times CH_2$), 4.50 (s, 4H $2 \times CH_2$), 6.84 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$), 7.30 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$).

10: yield: 6.35 g (55.7%); m.p. 116–119 °C; ^{1}H NMR: $\delta = 1.53$ (m, 4H, $2 \times CH_2$), 1.81 (m, 4H, $2 \times CH_2$), 3.96 (t, $J = 6.4$ Hz, 4H, $2 \times CH_2$), 4.50 (s, 4H $2 \times CH_2$), 6.84 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$), 7.29 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$).

2.2.3. p-$(LiC_5H_4CH_2)C_6H_4O(CH_2)_nOC_6H_4$ $(CH_2C_5H_4Li)$-p ($n = 2$–6) (11–15)

A solution of **6**–**10** ($n = 2$–6) (5 mmol) in THF (30 ml) was added to a stirred solution of cyclopentadienyl sodium (10 mmol) in 20 ml of THF at 0 °C. The temperature of the reaction mixture was allowed to rise gradually to room temperature and the mixture was stirred for 2 h. The solvent was removed in vacuo and the residue was extracted with diethyl ether ($3 \times$ 25 ml). The combined extracts were added to a stirred solution of n-BuLi (6.3 ml, 1.6 M, 10 mmol) in hexane at 0 °C. The mixture was stirred for additional 8 h and filtered. The solid was washed with diethyl ether ($2 \times$ 15 ml) and dried in vacuo to afford the **11**–**15** as pale yellow powders in yields of 91.9–95.0%.

2.2.4. p-$[(C_5H_5TiCl_2)C_5H_4CH_2]C_6H_4O(CH_2)_nOC_6H_4$ $[CH_2C_5H_4(TiCl_2C_5H_5)]$-$p$ ($n = 2$–6) (16–20)

11–**15** ($n = 2$–6) (4 mmol) were added to a stirred solution of $C_5H_5TiCl_3$ (8 mmol, 1.75 g) in 40 ml of toluene at 0 °C. The suspension was warmed up to room temperature and stirred overnight, then filtered. The solid was extracted with CH_2Cl_2 ($3 \times$ 30 ml). The combined extraction liquid was concentrated to 10 ml and cooled to −15 °C. After filtration, the solid was recrystallized from CH_2Cl_2/cyclohexane (1/2) to afford **16**–**20** as red powders.

16: yield: 1.32 g (44.8%). $C_{36}H_{34}Cl_4O_2Ti_2$: (736.20) elemental analysis (%), found: C, 58.91%; H, 4.72%. Calc.: C, 58.73%; H, 4.65%. ^{1}H NMR: $\delta = 4.04$ (s, 4H, $2 \times CH_2$), 4.29 (s, 4H, $2 \times CH_2$), 6.35 (t, $J = 2.8$ Hz, 4H, $2 \times C_5H_4$), 6.44 (t, $J = 2.8$ Hz, 4H, $2 \times C_5H_4$), 6.49 (s, 10H, $2 \times C_5H_5$), 6.87 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$), 7.12 (d, $J = 8.4$ Hz, 4H, $2 \times C_6H_4$); ^{13}C NMR $\delta = 36.1$ (CH_2), 66.7 (CH_2), 114.9 (C_6H_4), 116.3 (C_5H_4), 119.8 (C_5H_5), 122.5 (C_5H_4), 130.1 (C_6H_4), 131.9 (C_6H_4), 138.2 (C_5H_4), 157.4 (C_6H_4).

17: yield: 1.44 g (48.0%). $C_{37}H_{36}Cl_4O_2Ti_2$: (750.23) elemental analysis (%), found: C, 59.34%; H, 4.89%. Calc.: C, 59.23%; H, 4.84%. ^{1}H NMR: $\delta = 2.22$ (m, 2H, CH_2), 4.02 (s, 4H, $2\times CH_2$), 4.12 (t, $J = 5.8$ Hz, 4H, $2\times CH_2$), 6.34 (t, $J = 2.4$ Hz, 4H, $2\times C_5H_4$), 6.44 (t, $J = 2.8$ Hz, 4H, $2\times C_5H_4$), 6.45 (s, 10H, $2\times C_5H_5$), 6.83 (d, $J = 8.4$ Hz, 4H, $2\times C_6H_4$), 7.10 (d, $J = 8.4$ Hz, 4H, $2\times C_6H_4$); ^{13}C NMR $\delta = 28.9$ (CH_2), 36.0 (CH_2), 64.7 (CH_2), 114.6 (C_6H_4), 116.4 (C_5H_4), 119.8 (C_5H_5), 122.5 (C_5H_4), 130.1 (C_6H_4), 131.9 (C_6H_4), 138.2 (C_5H_4), 157.4 (C_6H_4).

18: yield: 1.53 g (50.1%). $C_{38}H_{38}Cl_4O_2Ti_2$: (764.25) elemental analysis (%), found: C, 59.91%; H, 5.08%. Calc.: C, 59.72%; H, 5.01%. ^{1}H NMR: $\delta = 1.95$ (m, 4H, $2\times CH_2$), 4.00 (s, 4H, $2\times CH_2$), 4.02 (s, 4H, $2\times CH_2$), 6.35 (t, $J = 2.4$ Hz, 4H, $2\times C_5H_4$), 6.44 (t, $J = 2.8$ Hz, 4H, $2\times C_5H_4$), 6.50 (s, 10H, $2\times C_5H_5$), 6.81 (d, $J = 8.8$ Hz, 4H, $2\times C_6H_4$), 7.10 (d, $J = 8.0$ Hz, 4H, $2\times C_6H_4$); ^{13}C NMR $\delta = 26.0$ (CH_2), 36.1 (CH_2), 67.5 (CH_2), 114.5 (C_6H_4), 116.4 (C_5H_4), 119.8 (C_5H_5), 122.6 (C_5H_4), 130.3 (C_6H_4), 131.3 (C_6H_4), 138.2(C_5H_4), 157.7 (C_6H_4).

19: yield: 1.60 g (51.4%). $C_{39}H_{40}Cl_4O_2Ti_2$: (778.28) elemental analysis (%), found: C, 60.33%; H, 5.22%. Calc.: C, 60.19%; H, 5.18%. ^{1}H NMR: $\delta = 1.63$ (m, 2H, CH_2), 1.83 (m, 2H, $2\times CH_2$), 3.95 (t, $J = 6.4$ Hz, 4H, $2\times CH_2$), 4.02 (s, 4H, $2\times CH_2$), 6.35 (t, $J = 2.8$ Hz, 4H, $2\times C_5H_4$), 6.44 (t, $J = 2.8$ Hz, 4H, $2\times C_5H_4$), 6.49 (s, 10H, $2\times C_5H_5$), 6.81 (d, $J = 8.8$ Hz, 4H, $2\times C_6H_4$), 7.10 (d, $J = 8.4$ Hz, 4H, $2\times C_6H_4$); ^{13}C NMR $\delta = 22.7$ (CH_2), 29.0 (CH_2), 36.1 (CH_2), 67.8 (CH_2), 114.6 (C_6H_4), 116.4 (C_5H_4), 119.8 (C_5H_5), 122.5 (C_5H_4), 130.3 (C_6H_4), 131.3 (C_6H_4), 138.3 (C_5H_4), 157.7 (C_6H_4).

20: yield: 1.16 g (46.1%). $C_{40}H_{42}Cl_4O_2Ti_2$: (792.31) elemental analysis (%), found: C, 60.92%; H, 5.43%. Calc.: C, 60.64%; H, 5.34%. ^{1}H NMR: $\delta = 1.52$ (m, 4H, $2\times CH_2$), 1.80 (m, 4H, $2\times CH_2$), 3.94 (t, $J = 6.0$ Hz, 4H, $2\times CH_2$), 4.02 (s, 4H, $2\times CH_2$), 6.36 (t, $J = 2.4$ Hz, 4H, $2\times C_5H_4$), 6.44 (t, $J = 2.4$ Hz, 4H, $2\times C_5H_4$), 6.49 (s, 10H, $2\times C_5H_5$), 6.81 (d, $J = 8.0$ Hz, 4H, $2\times C_6H_4$), 7.10 (d, $J = 8.0$ Hz, 4H, $2\times C_6H_4$); ^{13}C NMR $\delta = 25.9$ (CH_2), 29.2 (CH_2), 36.1 (CH_2), 67.9 (CH_2), 114.6 (C_6H_4), 116.4 (C_5H_4), 119.8 (C_5H_5), 122.5 (C_5H_4), 130.1 (C_6H_4), 131.2 (C_6H_4), 138.8 (C_5H_4), 157.8 (C_6H_4).

2.3. Polymerizations of ethylene

The polymerizations were carried out in a 50 ml glass reactor. The reactor was filled with a proper amount of toluene and MAO solution and saturated with a continuous flow of ethylene under atmospheric pressure. The polymerization was initiated by injection of the catalyst solution. The reaction mixture was stirred for an appropriate period at the desired temperature. A mixture of ethanol (150 ml) and hydrochloric acid (10 ml) was added to quench the reaction. The precipitated PE was filtered, washed repeatedly with water and ethanol, and then dried in vacuo at 60 °C.

In analogous procedure, the ethylene polymerizations were carried out in a 100 ml autoclave under high ethylene pressure.

3. Results and discussions

3.1. Synthesis and characterizations of complex **16**–**20**

The α,ω-bis (4-bromomethylphenoxy)alkanes **6**–**10** [23] were prepared according to Scheme 1 starting with *p*-cresole via the α,ω-bis (4-methylphenoxy)alkanes **1**–**4** [24–26] and **5**. They react with cyclopentadienyl sodium and butyl lithium with formation of the air- and moisture-sensitive dilithium salts **11**–**15** (Scheme 2), which were isolated as pale yellow powders. Reaction with $C_5H_4TiCl_3$ affords the dinuclear titanium complexes **16**–**20**. Their ^{1}H NMR spectra show two sets of triplets at 6.34–6.44 ppm similar to analogous bridged binuclear titanocenes [1,12,14,19].

3.2. Polymerization results of ethylene with complex **16**–**20**

Complexes **16**–**20** have been studied as catalysts in combination with MAO for ethylene polymerization. Table 1 demonstrates that the catalytic behaviors of these complexes **16**–**20** are highly depended on the length of flexible segment in the bridge. The catalytic activity increases with lengthen-
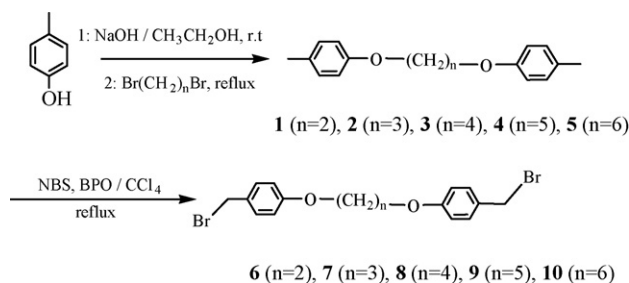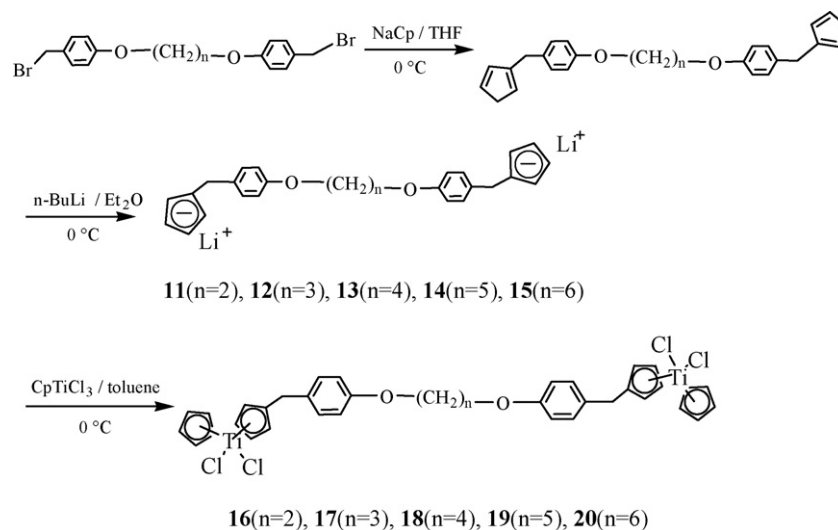
Scheme 1.

Table 1
Ethylene polymerization results using complexes **16**–**20**

Complex	[Cat][a]	MAO/Ti	Temperature (°C)	Time (h)	Activity[b]	$M_\eta \times 10^5$	MWD	m.p. (°C)
16	5	2000	25	0.5	1.60	5.97	3.99	136.7
17	5	2000	25	0.5	2.45	5.65	4.19	134.2
18	5	2000	25	0.5	2.84	5.10	4.88	135.9
19	5	2000	25	0.5	3.30	5.05	5.26	135.7
20	5	2000	25	0.5	3.62	4.11	5.35	135.4
Cp$_2$TiCl$_2$	20	500	20	0.5	0.89	2.89	1.92	132.9

[a] [Cat]: 10^{-5} mol Ti/l.

[b] Activity: 10^5 g of PE/mol Ti h; V(toluene) = 25 ml, 1 bar.

11(n=2), **12**(n=3), **13**(n=4), **14**(n=5), **15**(n=6)

16(n=2), **17**(n=3), **18**(n=4), **19**(n=5), **20**(n=6)

Scheme 2.

ing of the flexible segment (**16** < **17** < **18** < **19** < **20**). That is in accordance with the activity tendency of polysiloxane or polymethylene bridged binuclear zirconocenes [2,7] and can be attributed to the stronger steric hindrance of binuclear metallocenes caused by the shorter bridge, which prevents the monomer accessing to the coordination sites. In addition, an intramolecular deactivation of the active species in the same molecules may be restricted by long bridge. The M_η of the produced PE decreases in the order **16** > **17** > **18** > **19** > **20**, which can be interpreted by the steric hindrance of the shorter bridge which suppresses the β-H transfer to the active species, favorable for producing PE with higher molecular weight [7]. As expected, the MWD of PE produced by **16**–**20** (MWD = 3.99–5.35) are obviously broader than that of PE produced by $(C_5H_5)_2TiCl_2$ (MWD = 1.92) [1], moreover, it increase with the length of flexible segment in the bridge of these complexes becoming longer (**16** < **17** < **18** < **19** < **20**). The reason may be that the interaction between two metals creates more than one kind of active species during the polymerization [27]. The melting points of the PE produced by the novel complexes **16**–**20** were all higher than 130 °C, which indicates that the PE are highly linear and highly crystalline PE [14,27].

Table 2 shows, that the catalytic activity of complex **19** decreases faster than that of the 4,4-bis (methylene)biphenylene bridged dinuclear titanocene $(CpTiCl_2)_2[C_5H_4CH_2C_6H_4\text{-}p\text{-}C_6H_4CH_2C_5H_4]$ (**21**) [14] with rising of polymerization temperature. The reason may be that the introduction of a flexible segment $[-O(CH_2)_nO-]$ into the bridge lowers the thermal stability of the active species formed in the process of ethylene polymerization. Compared with ethylene polymerization catalyzed by complex **21**, a lower catalyst concentration is more favorable to reach a high activity for complex **19**.

3.3. Effects of polymerization conditions on ethylene polymerization with complex 19

Complex **19** was used to test the effect of the polymerization conditions such as catalyst concentration, mole ratio of MAO/Ti, polymerization temperature, polymerization time and ethylene pressure. The preliminary results show that a proper catalyst concentration and mole ratio of MAO/Ti are favorable for reaching high catalytic activity and producing PE with high molecular weight (Figs. 1 and 2).

Table 2
Ethylene polymerization results using complexes **19** and **21**

Complex	[Cat][a]	MAO/Ti	Temperature (°C)	Time (h)	Activity[b]	$M_\eta \times 10^5$
19	5	2000	25	0.5	3.30	5.05
	5	2000	40	0.5	0.55	3.19
	5	2000	55	0.5	0.47	1.55
	10	2000	25	0.5	2.04	5.84
	20	2000	25	0.5	1.58	4.92
21	20	500	20	0.5	1.97	3.13
	20	500	40	0.5	1.95	1.47
	20	500	60	0.5	1.18	0.65
	10	500	40	0.5	0.88	1.89
	30	500	40	0.5	1.40	1.31

[a] [Cat]: 10^{-5} mol Ti/l.
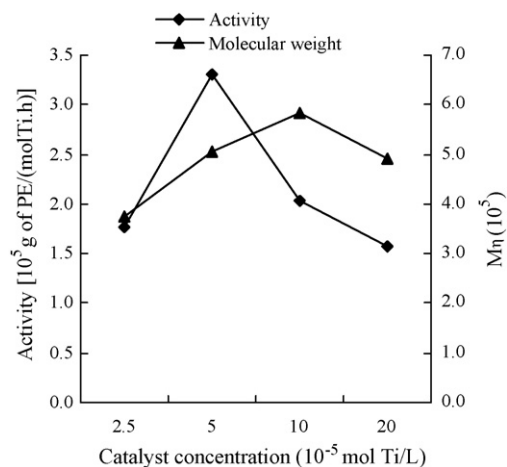[b] Activity: 10^5 g of PE/mol Ti h; V(toluene) = 25 ml, 1 bar.

Fig. 1. Influence of catalyst concentration on the catalytic activity and viscosity-average-molecular weight of PE. {Polymerization conditions: n(MAO)/n(Ti) = 2000, 0.5 h, 25 °C, 1 bar, V(toluene) = 25 ml}.
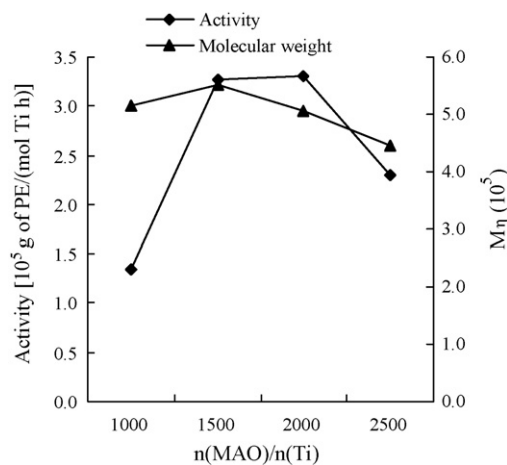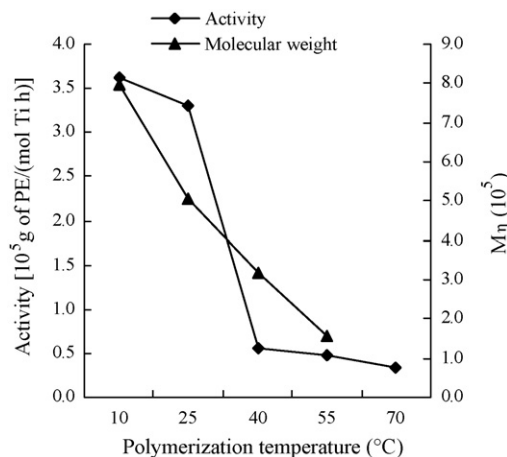

Fig. 2. Influence of MAO/Ti mole ratio [n(MAO)/n(Ti)] on the catalytic activity and viscosity-average-molecular weight of PE. {Polymerization conditions: [Cat] = 5 × 10⁻⁵ mol Ti/l, 0.5 h, 25 °C, 1 bar, V(toluene) = 25 ml}.
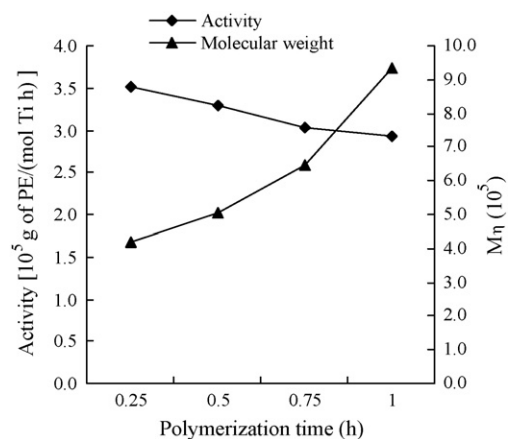

Fig. 3. Influence of polymerization temperature on the catalytic activity and viscosity-average-molecular weight of PE. {Polymerization conditions: n(MAO)/n(Ti) = 2000, [Cat] = 5 × 10⁻⁵ mol Ti/l, 0.5 h, 1 bar, V(toluene) = 25 ml}.

Fig. 4. Influence of polymerization time on the catalytic activity and viscosity-average-molecular weight of PE. {Polymerization conditions: n(MAO)/n(Ti) = 2000, [Cat] = 5 × 10⁻⁵ mol Ti/l, 25 °C, 1 bar, V(toluene) = 25 ml}.

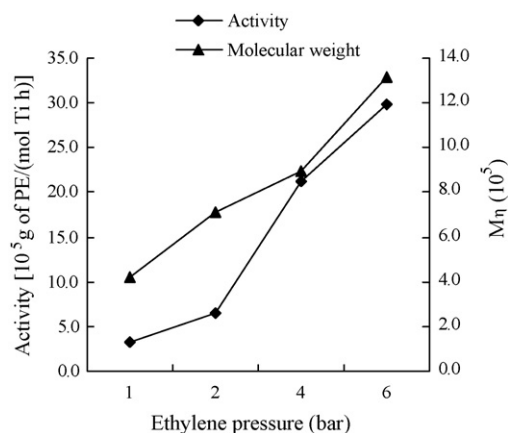Fig. 5. Influence of ethylene pressure on the catalytic activity and viscosity-average-molecular weight of PE. {Polymerization conditions: n(MAO)/n(Ti) = 2000, [Cat] = 5 × 10⁻⁵ mol Ti/l, 25 °C, 0.25 h, V(toluene) = 25 ml}.

Fig. 3 illustrates the effect of the temperature on ethylene polymerization. Both the catalytic activity and M_η of PE decrease rapidly with rising temperature, which demonstrates that higher temperature leads to faster deactivation of active species [28].

Fig. 4 demonstrates that the catalytic activity decreases with the prolongation of time, however M_η of PE is still increasing, which is in agreement with the common sense of homogeneous polymerization by metallocene/MAO.

Fig. 5 illustrates the effect of the ethylene pressure on polymerization. High ethylene pressure is effective for both increasing of catalytic activity and M_η of the produced PE.

4. Conclusion

The novel binuclear titanocenes (CpTiCl₂)₂[(C₅H₄)CH₂(p-C₆H₄)O(CH₂)$_n$O(C₆H₄-p)CH₂(C₅H₄)] (n = 2–6) (**16–20**) have been synthesized and successfully used as homogeneous catalysts with MAO as cocatalyst for ethylene polymerization. The

results show that the bridge including flexible and rigid segment effectively improved the catalytic behaviors of metallocene catalyst. The increase of the length of flexible segment is obviously favorable to rise the catalytic activities and broaden the MWD of PE (**16 < 17 < 18 < 19 < 20**). Both catalytic activities and MW of PE obtained from these complexes are remarkable higher than those of Cp_2TiCl_2, especially, the MWD (3.99–5.35) of PE obtained from all these complexes are much more broader than that of PE produced by Cp_2TiCl_2.

Acknowledgements

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