

Ethylene Polymerization by Diphenyl Ether Bridged Dinuclear Titanocenes/MAO

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ABSTRACT: Two diphenyl ether bridged dinuclear titanocenes, $(C_5H_5TiCl_2)_2[(RC_5H_3)CH_2](p-C_6H_4)O(C_6H_4-p)[CH_2(C_5H_3R)]$ [R = H(5), Me(6)] have been synthesized and characterized by ¹H-NMR spectroscopy and elemental analysis. In the presence of methylaluminoxane (MAO), 5 and 6 are efficient catalysts for ethylene polymerization. The influences of the polymerization conditions such as [MAO]/[Cat] molar ratio, catalyst concentration, polymerization temperature and time have been studied in detail. Compounds 5 and 6 produce 10⁵ g polyethylene (PE)/(mol Ti h), which is in the same range as that produced by the binuclear titanocenes $\{(C_5H_5TiCl_2)_2[(C_5H_4CH_2)(p-C_6H_4)(C_6H_4-p)(CH_2C_5H_4)]\}$ (7) and $(C_5H_5TiCl_2)_2(C_5H_4CH_2$

$CH_2OCH_2CH_2C_5H_4)$ (8). However, the molecular weight of PE is somewhat higher than that of PE using 7 and 8. The high temperature gel permeation chromatography (GPC) results show that the molecular weight distributions of PE produced by 5 and 6 (MWD = 6.17 and 7.56) were obviously broader than those of PE produced by 7 (MWD = 4.28) and 8 (MWD = 5.90). The melting points of the PE produced by 5 and 6 are higher than 132°C, indicating a highly linear and highly crystalline PE. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3702–3706, 2008

Key words: binuclear titanocene; diphenyl ether bridges; metallocene catalysts; polyethylene; polymerization

INTRODUCTION

The study of dinuclear metallocene catalysts in olefin polymerization has gained much interest in the last 10 years because of the cooperative effect of two metal centers. Previous studies demonstrated that the type and structure of the bridge between the two cyclopentadienyl ligands played an important role not only for the catalytic activity but also for the molecular weight and the molecular weight distribution (MWD) of the resulting polyolefin. Therefore, design and synthesis of novel dinuclear catalysts considering electronic and steric effects is a trend of recent studies.^{1–10} Our previous work on phenylene or diphenylene bridged binuclear metallocenes showed that rigid bridging ligands are favorable for increasing the catalytic activity and producing polyolefins with broader molecular weight distribution.^{11–13} In addition, our research on flexible diethyl ether bridged binuclear metallocenes indicated that the oxygen atom in the bridge might be favorable to stabilize the active species and therefore increases the catalytic performance.¹⁴ In continuation of our previ-

ous work, a new bridge containing not only a rigid aromatic hydrocarbon but also oxygen as a heteroatom was used for the synthesis of two biphenyl ether bridged binuclear titanocenes. In the presence of MAO, both new titanocene complexes were used as catalysts for ethylene polymerization with an anticipation to produce PE with broad molecular weight distributions.

EXPERIMENTAL

All manipulations including air- or moisture-sensitive procedures were performed under an argon atmosphere with standard Schlenk techniques.

Materials

Toluene, 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 and methylcyclopentadiene were freshly distilled from their dimers. All other chemical reagents were commercially available and used without further purification. Methylaluminoxane (MAO) (10% in toluene) was purchased from Witco. Ethylene (polymer grade) was purified via bubbling through triisobutylaluminum in

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toluene. CpTiCl_3 ¹⁵ and 4,4'-bis(bromomethyl)diphenyl ether¹⁶ were synthesized according to the literature.

Measurements

¹H NMR spectra were recorded on a Bruker Advance 400 instrument at ambient temperature. Chemical shifts were referenced with respect to tetramethylsilane. Elemental analysis was conducted on a Perkin–Elmer 240 elemental analyzer. Electron impact mass spectra (EIMS) were measured on an HP 6890/5973 gas chromatography/mass spectrometry instrument (70 eV and 50–270°C). The intrinsic viscosity $[\eta]$ of PE in decahydronaphthalene was measured with an 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). The molecular weight distributions 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.

Synthesis

Synthesis of Complexes 5 and 6

A solution of 4,4'-bis(bromomethyl)diphenyl ether (1.77 g, 5.00 mmol) in THF (40 mL) was added slowly to a stirred solution of cyclopentadienyl sodium (10.00 mmol) in THF (30 mL) at 0°C and stirred for additional 2 h. The solvent was removed in vacuum and the resulting mixture was extracted with diethyl ether (3 × 30 mL). The combined extraction solutions were added to a stirred solution

of *n*-BuLi (8 mL, 1.5M, 12.00 mmol) in hexane at 0°C. The reaction mixture was warmed up to room temperature, stirred overnight, and then filtered. The residue was washed with diethyl ether (3 × 20 mL) and dried in vacuum to yield an air-sensitive pale yellow powder. The powder was added slowly to a stirred yellow solution of CpTiCl_3 (1.31 g, 6.00 mmol) in 60 mL of toluene at 0°C. After stirring overnight at room temperature, the mixture was filtered and the residue was extracted with CH_2Cl_2 (3 × 40 mL). The combined extraction solutions were concentrated and cooled to -15°C. Subsequently, a red powder precipitated from the solution and was isolated by filtration and washed several times by cold pentane yielding 5 as a red powder.

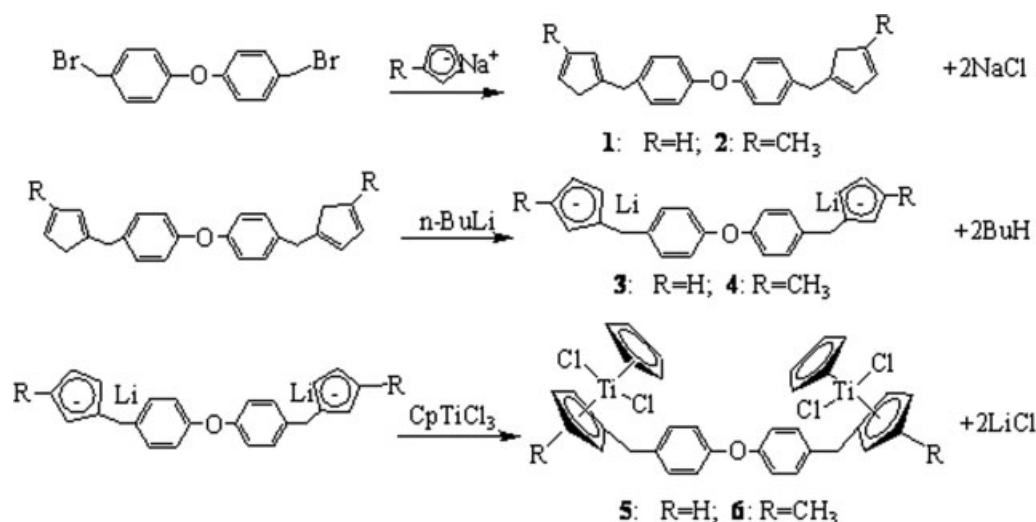
Yield: 1.12 g (43.4%). Elemental analysis: $\text{C}_{34}\text{H}_{30}\text{OTi}_2\text{Cl}_4$ (%), found: C 59.12, H 4.40; calc. C: 59.00, H 4.37; ¹H NMR (CDCl_3 , δ , ppm): 4.08 (s, 4 H, CH_2), 6.36 (t, $J = 2.4$ Hz, 4 H, C_5H_4), 6.45 (t, $J = 2.4$ Hz, 4 H, C_5H_4), 6.52 (s, 10 H, C_5H_5), 6.91 (d, $J = 8.4$ Hz, 4 H, C_6H_4), 7.16 (d, $J = 8.4$ Hz, 4 H, C_6H_4).

Complex 6 was synthesized in analogy to 5 and isolated as a red powder.

Yield: 1.11 g (41%). Elemental analysis: $\text{C}_{36}\text{H}_{34}\text{OTi}_2\text{Cl}_4$ (%), found: C 60.15, H 4.69; calc. C: 60.04, H 4.76; ¹H NMR (CDCl_3 , δ , ppm): 2.22 (s, 6 H, CH_3), 3.84 ~ 3.94 (m, 4 H, CH_2), 6.27–6.49 (m, 6 H, 2 × C_5H_3), 6.45 (s, 5 H, C_5H_5), 6.47 (s, 5 H, C_5H_5), 6.90 (d, $J = 8.4$ Hz, 4 H, C_6H_4), 7.13 (d, $J = 8.4$ Hz, 4 H, C_6H_4).

Polymerizations

The polymerizations were carried out in a 50 mL glass reactor. A solution of MAO in toluene was saturated with ethylene at 1 bar. The polymerization



Scheme 1 Synthesis route for diphenyl ether bridged dinuclear titanocenes.

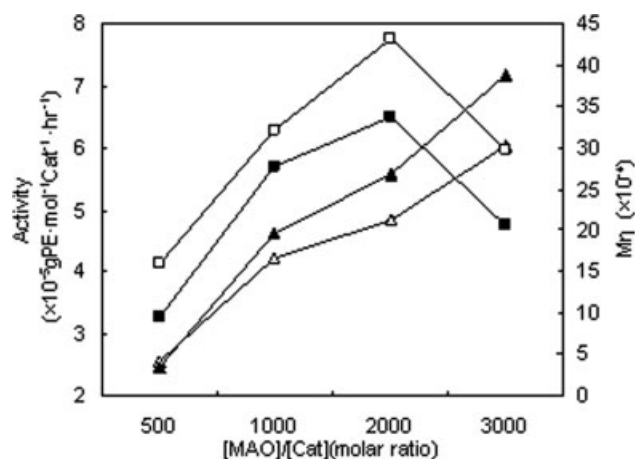


Figure 1 Influence of the [MAO]/[Cat] molar ratio on catalytic activity and molecular weight of PE [Δ , Activity of 5/MAO; \blacktriangle , Activity of 6/MAO; \square , M_n of 5/MAO; \blacksquare , M_n of 6/MAO]. [Polymerization conditions: [Cat] = 1.0×10^{-4} mol/L, T_p = 40°C, t_p = 30 min, P_e = 1 bar, V (toluene) = 25 mL].

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. The precipitated PE was then filtered, washed repeatedly with water and ethanol, and then dried *in vacuo* at 60°C.

RESULTS AND DISCUSSION

Synthesis and characterization of the binuclear titanocenes 5 and 6

According to Scheme 1, (4-C₅H₄CH₂C₆H₄)₂O (1) and (4-MeC₅H₃CH₂C₆H₄)₂O (2) were prepared from 4,4'-bis(bromomethyl)diphenyl ether, reacted *in situ* with butyl lithium to give the dilithium salts 3 and 4 which reacted with two equivalents of CpTiCl₃ at 0°C yielding the bridged binuclear titanocenes 5 and 6 which were isolated as red powders.

Complex 6 has one methyl substituent on two of the four cyclopentadienyl rings. Therefore, the different steric environment related to 5 causes complicated isomers as similar discussion in literature.¹⁷ In accordance with that, the ¹H-NMR spectrum of the isolated complex 6, which is a mixture of those isomers, shows an unresolved multiplet at δ = 3.84–3.94 ppm for the CH₂ groups instead of one sharp singlet at 4.08 ppm in 5 and two singlet peaks at 6.45 and 6.47 ppm for the two unsubstituted C₅H₅ ligands in contrast to the two pseudo-triplets at 6.34–6.45 ppm corresponding to the pseudo-A₂B₂ splitting pattern of the C₅H₄ groups in 5, like in other bridged binuclear metallocenes.^{12–14}

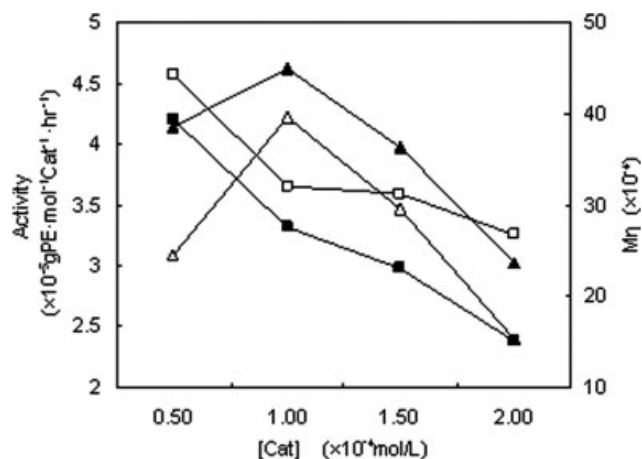


Figure 2 Influence of the catalyst concentration on catalytic activity and molecular weight of PE. [Δ , Activity of 5/MAO; \blacktriangle , Activity of 6/MAO; \square , M_n of 5/MAO; \blacksquare , M_n of 6/MAO]. [Polymerization conditions: [MAO]/[Cat] = 1000, T_p = 40°C, t_p = 30 min, P_e = 1 bar, V (toluene) = 25 mL].

Ethylene polymerization

Influences of the polymerization parameters

Complexes 5 and 6 have been used as catalysts in combination with MAO for ethylene polymerization. The influence of the reaction parameters, such as [MAO]/[Cat] molar ratio, catalyst concentration, temperature and time have been studied in detail.

The catalytic activity of the new metallocene catalysts is strongly dependent on the amount of MAO. As shown in Figure 1, the catalytic activity of complexes 5 and 6 increases linearly with increasing

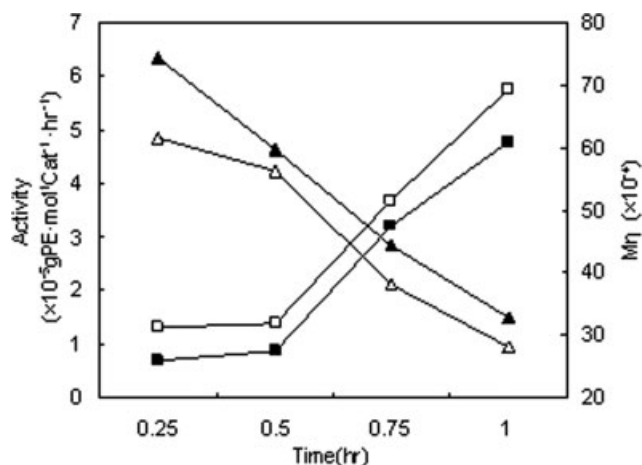


Figure 3 Influence of the polymerization time on catalytic activity and molecular weight of PE. [Δ , Activity of 5/MAO; \blacktriangle , Activity of 6/MAO; \square , M_n of 5/MAO; \blacksquare , M_n of 6/MAO]. [Polymerization conditions: [Cat] = 1.0×10^{-4} mol/L, [MAO]/[Cat] = 1000, T_p = 40°C, P_e = 1 bar, V (toluene) = 25 mL].

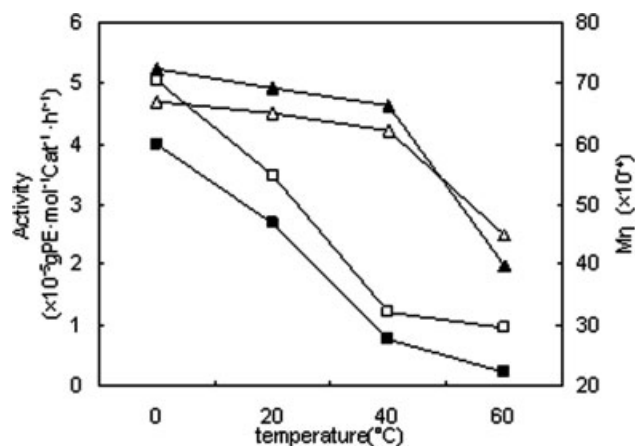


Figure 4 Influence of the polymerization temperature on catalytic activity and molecular weight of PE. [Δ , Activity of 5/MAO; \blacktriangle , Activity of 6/MAO; \square , M_n of 5/MAO; \blacksquare , M_n of 6/MAO]. [Polymerization conditions: $[\text{Cat}] = 1.0 \times 10^{-4}$ mol/L, $[\text{MAO}]/[\text{Cat}] = 1000$, $t_p = 30$ min, $P_e = 1$ bar, V (toluene) = 25 mL].

$[\text{MAO}]/[\text{Cat}]$ molar ratio. This phenomenon is in agreement with other reports in literature.¹⁴ Previously we could show that the activity of the system $(\text{CpTiCl}_2)_2[\text{C}_5\text{H}_4\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{CH}_2\text{C}_5\text{H}_4]$ (7)/MAO reached a maximum at a $[\text{MAO}]/[\text{Cat}]$ molar ratio of 1500.¹² The difference between the systems 5/MAO, 6/MAO, and 7/MAO might be caused by the hetero-atom oxygen in the bridge of 5 and 6, which attacks the Lewis acidic aluminum cocatalyst MAO and leads to a still favorable increase of the catalytic activity at high MAO concentrations. The molecular weight of PE produced by 5/MAO and 6/MAO reaches a maximum and then decreases at a $[\text{MAO}]/[\text{Cat}]$ molar ratio larger than 2000, which might be a result of a chain transfer to the excess MAO.¹³

Figure 2 shows the effect of the catalyst concentration on polymerization. The catalytic activity of complexes 5 and 6 reaches a maximum at $[\text{Cat}] = 1.0 \times 10^{-4}$ mol/L before it decreases gradually. However, the molecular weight of PE decreases with increasing catalyst concentration. That demonstrates

that an increasing catalyst concentration increases the chance of bimolecular deactivation of the catalyst. On the other hand, at high catalyst concentration, the high MAO concentration used will cause a chance for chain transfers.

The influence of the polymerization time on ethylene polymerization is shown in Figure 3. It shows that the catalytic activity of complexes 5 and 6 decreases with prolonging reaction time. However, the molecular weight of polyethylene increases gradually, the reason may be that the surviving active species in the catalyst system are still catalyzing ethylene polymerization. We suggest that the introduction of the oxygen atom in the bridge will increase the electron density around the catalytic active sites, improving their stability.

Figure 4 demonstrates the influence of the polymerization temperature on the catalytic activity and the molecular weight of polyethylene. There is only a small decrease of the activity between 0 and 40°C, but the activity decreases rapidly at higher temperature, indicating a decomposition of the catalysts at higher temperatures. The molecular weight of PE obtained using complexes 5 and 6 is decreasing analogously. The reason for that behavior should be that the competition between the termination and propagation steps determines the molecular weight of polyethylene. Higher temperature is favorable for increasing the rate of β -hydride chain transfer over the propagation rate, which leads to a polymer with lower molecular weight.¹⁸

Comparison to the correspondent catalyst 7, 8, and Cp_2TiCl_2

Table I and Figure 5 show the results of GPC and DSC determination of PE produced using the complexes 5 and 6 in comparison with PE made by $\{(\text{C}_5\text{H}_5\text{TiCl}_2)_2[(\text{C}_5\text{H}_4\text{CH}_2)(p\text{-C}_6\text{H}_4)(\text{C}_6\text{H}_4\text{-}p)(\text{CH}_2\text{C}_5\text{H}_4)]\}$ (7), $(\text{C}_5\text{H}_5\text{TiCl}_2)_2(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4)$ (8), and Cp_2TiCl_2 . The high melting points above 132°C indicate a high linear and high crystalline PE. The

TABLE I
Comparison of 5 and 6 with Corresponding Binuclear Catalysts 7, 8, and Cp_2TiCl_2

| Cat. | $[\text{Cat}] \times 10^4$ (mol/L) | T_p | $[\text{MAO}]/[\text{Cat}]$ | Activity $\times 10^{-5}$ g PE/mol Cat h | $M_n \times 10^{-4}$ | M_w/M_n | T_m (°C) |
|----------------------------|---------------------------------------|-------|-----------------------------|--|----------------------|-----------|---------------|
| 5 | 1.0 | 40 | 1000 | 4.02 | 31.99 | 6.17 | 132.1 |
| 6 | 1.0 | 40 | 1000 | 4.42 | 27.65 | 7.56 | 134.1 |
| 7 | 1.0 | 40 | 1000 | 3.90 | 14.7 | 4.28 | 134.0 |
| 8 | 1.0 | 30 | 1000 | 3.58 | 2.15 | 5.90 | 129.0 |
| Cp_2TiCl_2 | 2.0 | 40 | 500 | 0.80 | 20.31 | 2.15 | 131.5 |

Polymerization conditions: $[\text{Cat}] = 1.0 \times 10^{-4}$ mol/L, $[\text{MAO}]/[\text{Cat}] = 1000$, $t_p = 30$ min, $P_e = 1$ bar, V (toluene) = 25 mL.

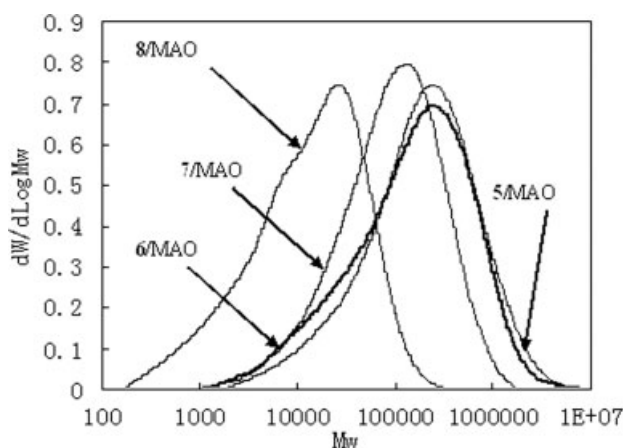


Figure 5 HT-GPC diagrams of PE provided by 5/MAO, 6/MAO, 7/MAO, and 8/MAO. [Polymerization conditions: [Cat] = 1.0×10^{-4} mol/L, [MAO]/[Cat] = 1000, t_p = 30 min, P_e = 1 bar, V (toluene) = 25 mL].

activities of 5 and 6 are higher than those of 7, 8, and Cp_2TiCl_2 . It is obvious that the hetero atom oxygen in bridge not only increases the length of bridge but also creates an electron-donating effect to the metal centers. Both aspects might be favorable to increase the activity of the complexes.^{12,19} On the other hand, the molecular weight distributions of PE produced by 5 and 6 are broader than those of PE produced by 7, 8, and Cp_2TiCl_2 . A reason for that should be the mobility of the molecules 5 and 6 around the central oxygen atom in solution. This mobility is reduced by the MeCp ligands in 6, resulting in two isomers of 6 in comparison to 5 and therefore, in a little bit broader molecular weight distribution.

CONCLUSIONS

Two new diphenyl ether bridged dinuclear titanium metallocenes 5 and 6 were synthesized and successfully used for ethylene polymerization in the pres-

ence of MAO. The catalytic activity of both complexes is higher than that of complex 7, 8, and the mononuclear catalysts Cp_2TiCl_2 . The molecular weight distributions of PE obtained with these dinuclear complexes are much wider than those of the corresponding rigid metallocenes. These results indicate that introduction of the hetero-atom oxygen into the bridges of 5 and 6 greatly improves the catalytic performance.

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