# Ethylene Polymerization by 3-Oxa-Pentamethylene Bridged Asymmetric Dinuclear Titanocene/MAO System

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**ABSTRACT:** An asymmetric 3-oxa-pentamethylene bridged dinuclear titanocenium complex $(CpTiCl_2)_2(\eta^5\text{-}\eta^5\text{-}C_9H_6(CH_2CH_2OCH_2CH_2)C_5H_4)$ (**1**) has been prepared by treating two equivalents of $CpTiCl_3$ with the corresponding dilithium salts of the ligand $C_9H_7(CH_2CH_2OCH_2\ CH_2)C_5H_5$. The complex **1** was characterized by $^1$H-, $^{13}$C-NMR, and elemental analysis. Homogenous ethylene polymerization catalyzed using complex **1** has been conducted in the presence of methylaluminoxane (MAO). The influences of reaction parameters, such as [MAO]/[Cat] molar ratio, catalyst concentration, ethylene pressure, temperature, and time have been studied in detail. The results show that the catalytic activity and the molecular weight (MW) of polyethylene produced by **1**/MAO decrease gradually with increasing the catalyst concentration or polymerization temperature. The most important feature of this catalytic system is the molecular weight distribution (MWD) of polyethylene reaching 12.4, which is higher than using common mononuclear metallocenes, as well as asymmetric dinuclear titanocene complexes like $[(CpTiCl_2)_2(\eta^5\text{-}\eta^5\text{-}C_9H_6(CH_2)_nC_5H_4)]$ ($n$ = 3, MWD = 7.31; $n$ = 4, MWD = 6.91). The melting point of polyethylene is higher than 135°C, indicating highly linear and highly crystalline polymers. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 504–509, 2008

**Key words:** asymmetric dinuclear titanocene; metallocene catalyst; ethylene polymerization; polyethylene

## INTRODUCTION

The molecular weight (MW) and the molecular weight distribution (MWD) of polyolefin influence directly its mechanical and rheological properties. High MW polyolefins have superior physical properties, but it is difficult to process. The broad MWD is favorable to improve flowability at high shear rates. Therefore, producing polyolefins with broad MWD has become an attractive research project in the development of metallocene polyolefin techniques.[1-3]

Up to now, several methods have been used for producing broad MWD polyolefins. The simplest way is blending the polyolefin with different average MW. However, miscibility problems might occur in the processing.[4] Another way is carrying out the polymerization in a series of reactors with various polymerization conditions. However, this method involves additional processes and increases the capital cost.[5] The third way is to mix individual mononuclear catalysts in a single reactor, which also causes difficulties in obtaining the desired multi modal polyolefin because of the averaging effect.[6]

Dinuclear or multi-nuclear metallocenes have been improved to be an effective new catalyst to produce broad or bimodal MWD polyolefins[7-10]. Alt and coworkers[11] has studied systematically polymethylene bridged asymmetric dinuclear metallocene complexes of Ti, Zr, and Hf to produce polyethylene with broad MWD. A typical bimodal polyethylene has been obtained from the dinuclear ansa zirconocene/methylaluminoxane (MAO) system.[12] Our previous research proved that dinuclear metallocenes were efficient catalysts to produce high MW polymers with broad MWD, not only in methylmethacrylate polymerization, but also in ethylene polymerization.[13-18]

Here, we report a novel 3-oxa-pentamethylene bridged asymmetric dinuclear titanocene/MAO system, which is a useful catalyst to produce polyethylene with high MW and broad MWD.

## EXPERIMENTAL

All reactions were carried out under a dry, oxygen-free atmosphere using standard Schlenk techniques with a double manifold vacuum line. Argon gas was purified by passage through a column of molecular sieve (4 Å) and Drierite (8 mesh).

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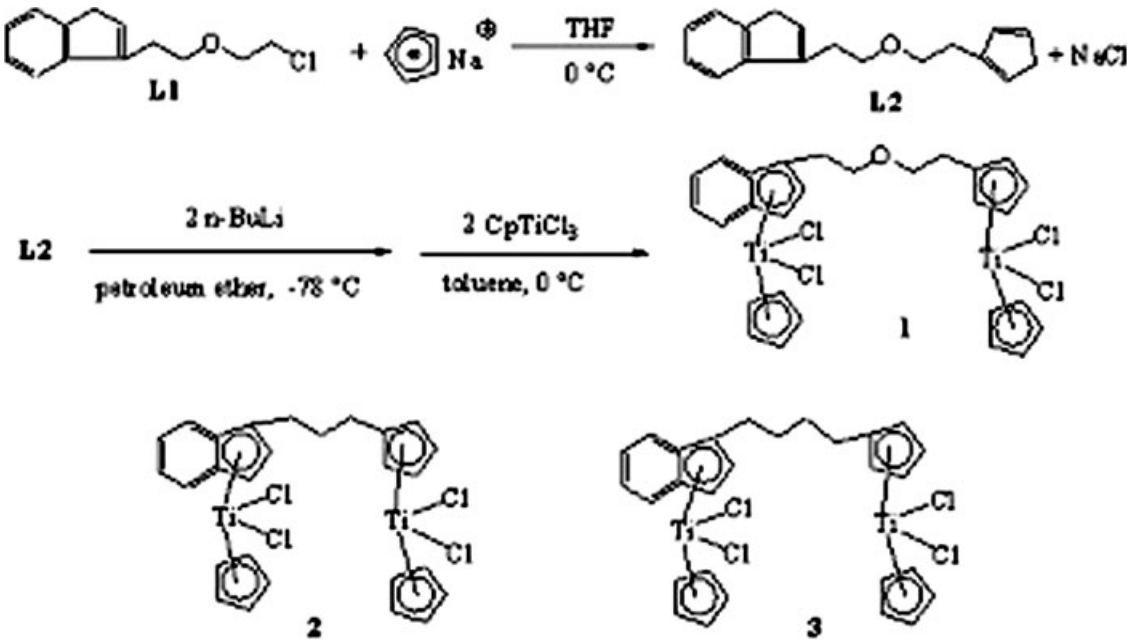



**Scheme 1**

## Materials

Tetrahydrofuran, diethyl ether, hexane, and toluene were distilled from sodium-benzophenone ketyl prior to use. Methylene chloride was distilled from calcium hydride prior to use. 2,2′-dichlorodiethyl ether purchased from Aldrich was used after distilling from calcium hydride. $CpTiCl_3$ was synthesized according to the literature.[19] MAO (10 wt % in toluene, provided by Witco) was used without further purification. Ethylene (Polymer grade) was purified by bubbling through a solution of triethylaluminium in toluene.

## Measurements

$^1$H-NMR spectra were recorded on a Bruker Avance DMX500 spectrometer at ambient temperature; chemical shifts were referenced with respect to tetramethylsilane. Elemental analysis was conducted on a Perkin-Elmer 240 elemental analyzer. The MW of polyethylene was measured in decahydronaphthalene at 135°C by a modified Ubbelohde-type viscometer according to $[\eta] = 6.67 \times 10^{-4} M_\eta^{0.67}$(mL/g). The MW distribution of some polymers with orthodichlorobenzene as solvent were determined by gel-permeation chromatography (GPC, Waters 150, 135°C) using polystyrene as a standard. The melting temperatures ($T_m$) of the polymers were measured by a differential scanning calorimeter (Perkin Elmer DSC-7).

## Synthesis

Preparation of $C_9H_7(CH_2CH_2OCH_2CH_2)C_5H_5$ (L2)

A solution of $C_5H_5Na$ (10.0 mL, 1.00 mol/L) in THF (50.0 mL) was cooled to 0°C and treated dropwise for 30 min with a solution of $C_9H_7(CH_2CH_2OCH_2CH_2)Cl$ (**L1**) (2.22 g, 10.0 mmol) prepared form $C_9H_7Li$ and $Cl(CH_2CH_2OCH_2CH_2)Cl$ in THF according to Alt and coworkers.[11] The resulting solution was warmed to room temperature and stirred for 6 h. Volatiles were removed *in vacuo* and the yellowish paste was extracted with pentane. The filtrate was concentrated *in vacuo* to get the products as light yellow oil (5.20 g, 40% in yield). GC-MS m/z (%): 252 ($M^+$, 35 %), 128 ($M^+$—$HC_9H_7$, 98%), 77 ($M^+$—$O(CH_2)_2C_9H_7$). $^1$H-NMR ($CDCl_3$, 20°C, δ ppm): 7.58–7.31 (m, 4H, $C_9H_7$), 6.60(t, 1H, allylic indene-H)[1.6], 6.59–6.22(m, 3H, $C_5H_5$), 3.91–3.89(m, 2H, $OCH_2$), 3.87–3.86(m, 2H, $OCH_2$),3.44(d, 2H, alkyl indene-H)[1.6], 3.08–3.04(m, 2H, $C_5H_5$), 3.04–2.99(m, 2H, $C_9H_7CH_2$), 2.85–2.82(m, 2H, $C_5H_5CH_2$).

Preparation of $(CpTiCl_2)_2(\eta^5\text{-}\eta^5\text{-}C_9H_6(CH_2CH_2OCH_2CH_2)C_5H_4)$ (1)

A solution of $C_5H_5TiCl_3$ (2.2 g, 10.0 mmol) in toluene (30.0 mL) was cooled to 0°C and treated dropwise over 30 min with a solution of $Li_2[C_9H_6(CH_2CH_2OCH_2CH_2)C_5H_4]$ (1.3 g, 5.0 mmol) prepared from *n*-BuLi and $C_9H_7(CH_2CH_2OCH_2CH_2)C_5H_5$ (**L2**) in toluene (20.0 mL). The resulting solution was warmed up to room temperature and stirred for 24 h. Volatiles were removed *in vacuo* and the resulting residue was extracted with $CH_2Cl_2$. Recrystallization in toluene resulted in a reddish brown solid of **1** (1.8 g, 60.0 % yield). $C_{28}H_{28}OCl_4Ti_2$ elemental analysis (%), Calcd: C 54.41%; H 4.57%. Found: C 54.26%; H 4.63%. $^1$H-NMR ($CDCl_3$, 20°C, δ ppm): 7.71–7.35 (m, 4H, $C_9H_6$), 6.68–6.60(m, 2H, $C_9H_6$), 6.53(s, 5H, $C_5H_5$),

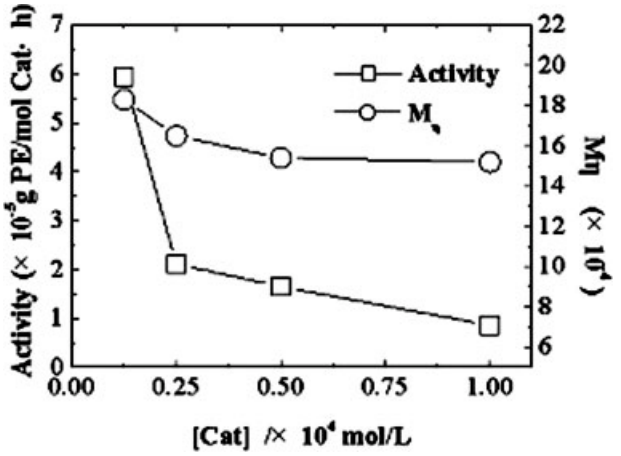



**Figure 1** Influence of the catalyst concentration on catalytic activity and molecular weight of polyethylene. [○]: Activity of **1**/MAO, □: $M_\eta$ of **1**/MAO]. Polymerization conditions: [MAO]/[Cat]=1000, $T_p$ = 40°C, $t_p$ = 30 min, $P_e$ = 1 bar, $V_{toluene}$ = 25 mL.

6.41–6.36(m, 2H, $C_5H_4$), 6.34(m, 1H, $C_5H_4$), 6.28(m, 1H, $C_5H_4$), 6.22(s, 5H, $C_5H_5$), 3.76–3.63(m, 4H, $OCH_2$×2), 3.37(m, 1H, $C_9H_6CH_2$), 3.25(m, 1H, $C_9H_6CH_2$), 2.96(m, 2H, $C_5H_4CH_2$). $^{13}$C-NMR ($CDCl_3$, 20°C, δ ppm): ($C_q$): 140.2, 135.9, 135.8, 127.7; (CH): 128.0, 127.3, 126.9, 124.8, 123.6, 123.2 120.5, 119.8, 119.2, 118.8, 116.0, 115.6, 104.7; ($CH_2$): 70.2, 70.1, 31.2, 29.3. IR (KBr, $cm^{-1}$): 3100, 2928, 2859, 1647, 1437, 1111, 823, 752, 669, 418.

## Polymerization

### Ethylene polymerization under atmospheric pressure

Homogeneous ethylene polymerizations were carried out in a 100-mL glass reactor. The reactor was filled with a proper amount of toluene and MAO solution.

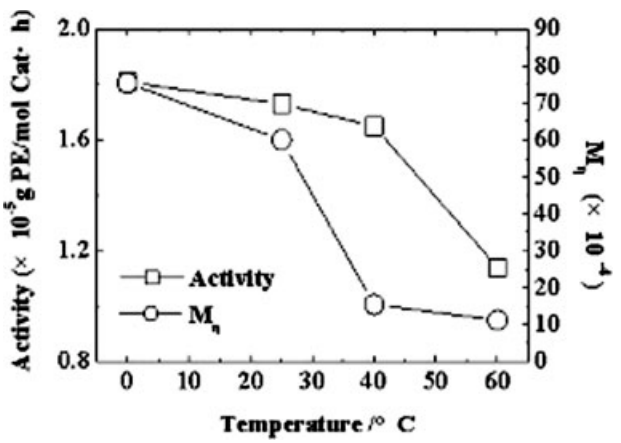



**Figure 2** Influence of the polymerization temperature on catalytic activity and molecular weight of polyethylene. [○]: Activity of **1**/MAO, □: $M_\eta$ of **1**/MAO]. Polymerization conditions: [Cat] = 2.5 × $10^{-5}$ mol/L, [MAO]/[Cat] = 2400, $t_p$ = 30 min, $P_e$ = 1 bar, $V_{toluene}$ = 25 mL.

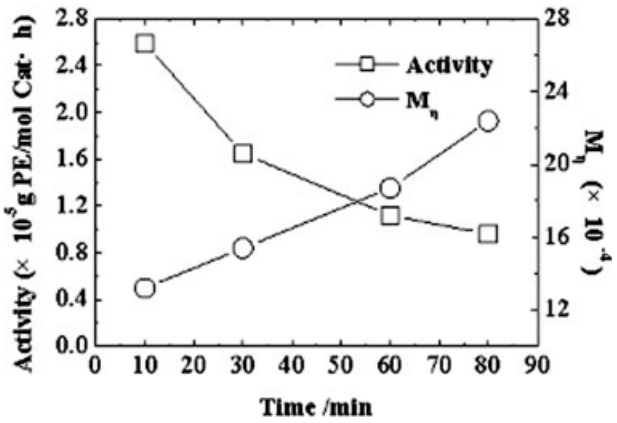



**Figure 3** Influence of the polymerization time on catalytic activity and molecular weight of polyethylene. [○]: Activity of **1**/MAO, □: $M_\eta$ of **1**/MAO]. Polymerization conditions: [Cat] = 2.5 × $10^{-5}$ mol/L, [MAO]/[Cat] = 2400, $T_p$ = 40°C, $P_e$ = 1bar, $V_{toluene}$ = 25 mL.

The system was then saturated with a continuous flow of ethylene under atmospheric pressure. The polymerization was initiated by injection of the catalyst. After the reaction, the resulting polyethylene crops were precipitated in acidified ethanol, filtered, and dried under vacuum at 75°C until constant weight.

### Ethylene polymerization under high-pressure

A 100-mL autoclave was filled with toluene and MAO solution. After heating the reactor to the polymerization temperature the catalyst solution was injected into the reactor followed by pressurizing the reactor immediately with ethylene. At the end of the reaction, the resulting polyethylene was treated and separated using the same procedures as aforementioned.

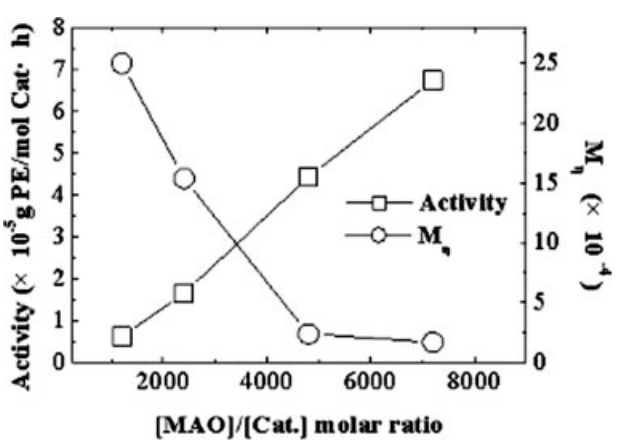



**Figure 4** Influence of the [MAO]/[Cat] molar ratio on catalytic activity and molecular weight of polyethylene. [○]: Activity of **1**/MAO, □: $M_\eta$ of **1**/MAO]. Polymerization conditions: [Cat] = 1.0 × $10^{-4}$ mol/L, $T_p$ = 40°C, $t_p$ = 30 min, $P_e$ = 1 bar, $V_{toluene}$ = 25 mL.

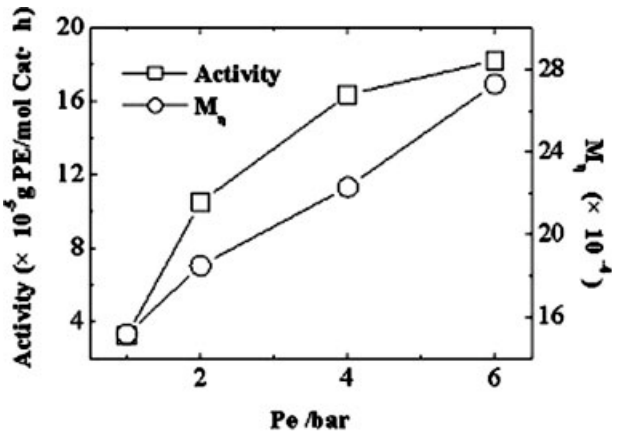



**Figure 5** Influence of the ethylene pressure on catalytic activity and molecular weight of polyethylene. [○]: Activity of **1**/MAO, □: $M_\eta$ of **1**/MAO]. Polymerization conditions: [Cat]=1.0 × $10^{-4}$ mol/L, [MAO]/[Cat] = 4800, $t_p$ = 10 min, $T_p$ = 25°C, $V_{toluene}$ = 25 mL.

## RESULTS AND DISCUSSION

### Synthesis and characterization

The 3-oxa-pentamethylene bridged asymmetric dinuclear metallocene complex $(CpTiCl_2)_2(\eta^5\text{-}\eta^5\text{-}C_9H_6(CH_2CH_2OCH_2CH_2)C_5H_4)$ (**1**) was prepared by reaction of the dilithium salts of the corresponding ligand $C_9H_7(CH_2CH_2OCH_2CH_2)C_5H_5$ (**L2**) with two equivalents of $CpTiCl_3$ in toluene at 0°C (Scheme 1). The ligand **L2** was prepared in 40% yield by treatment of cyclopentadienyl sodium with one equivalent of $C_9H_7(CH_2CH_2OCH_2CH_2)Cl$ (**L1**) in THF. The dinuclear complex was separated as reddish brown solid, which is soluble in common organic solvents.

The $^1$H-NMR spectrum of complex **1** proves the assigned dinuclear metallocene structure. The four resonances between 7.35 and 7.71 ppm which are well separated in the aromatic region are assigned to the four protons of the six-membered ring in the indenyl group. The resonances appearing at 6.68–6.60 ppm as multiplets are due to two protons of the five-membered ring side at the indenyl fragment. The most obvious feature in the spectra are the sharp singlets at 6.53 and 6.22 ppm which result from the 10 protons of two kinds of cyclopentadienyl moieties, the former one is related to the CpTi bonded to the indenyl group, the latter one is related to the other CpTi bonded to the $C_5H_4(CH_2)_2O$ residue. Additionally, there are two sets of multiplets in the high field region which are assigned to the two protons of the methylene in the $C_9H_6CH_2$ residue. The $^{13}$C-NMR spectrum of the complex is in agreement with the mentioned structure.

### Homogeneous ethylene polymerization

#### Influence of the conditions on ethylene polymerization

As shown in Figure 1, the catalytic activity of complex **1** and the MW of polyethylene decrease gradually with increasing of the catalyst concentration. Increasing the catalyst concentration increases the chance of bimolecular deactivation of the catalyst.[7,8]

Figure 2 demonstrates the influence of the polymerization temperature on the catalytic activity and the MW of polyethylene. The activity of the catalyst decreases with increasing temperature above 0°C. This may contribute to the deactivation process because of the poor thermal stability of the cationic methyl complex formed in the presence of MAO. The MW of polyethylene also depends on the polymerization temperature. A competition between the termination and propagation steps determines the MW of polyethylene. A higher temperature is favorable to increase the rate of β-hydride chain transfer over the propagation rate, which causes the formation of a polymer with lower MW.[20]

The influence of the polymerization time on ethylene polymerization is shown in Figure 3. It demonstrates a decrease of the catalytic activity of **1** with prolonging reaction time, because of the deactivation of the catalyst. The MW of polyethylene produced increases from 13.27 to 22.43 ×$10^4$ g/mol.

As shown in Figure 4, the catalytic activity of **1**/MAO increases constantly from 0.62 to 6.74 × $10^5$ g PE mol $Cat^{-1}$ $h^{-1}$. with increasing molar ratio [MAO]/[Cat] from 1200 to 7200. A high amount of MAO favorizes the stabilization of the active metal centers.

**TABLE I**
**Comparison of the Three Different Bridged Asymmetric Dinuclear Metallocenes on Ethylene Polymerization**

| Cat | [Cat] × $10^4$ mol/L | [MAO]/[Cat] | $T_p$ (°C) | $t_p$ (min) | $P_e$ (bar) | Activity × $10^{-5}$ g PE mol $Cat^{-1}$ $h^{-1}$ | $M_\eta$ × $10^{-4}$ | $M_w/M_n$ | $T_m$ (°C) |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 1.0 | 4800 | 25 | 5 | 4 | 16.38 | 22.3 | 12.40 | 135.80 |
| **1** | 0.5 | 2400 | 0 | 30 | 1 | 1.81 | 75.5 | 12.25 | 137.80 |
| **2**[a] | 1.0 | 1000 | 40 | 30 | 1 | 1.75 | 14.2 | 7.31 | 132.50 |
| **3**[b] | 1.0 | 1000 | 40 | 30 | 1 | 1.99 | 11.4 | 6.91 | 132.32 |

[a] **2**: $(CpTiCl_2)_2(\eta^5\text{-}\eta^5\text{-}C_9H_6(CH_2)_3C_5H_4)$.
[b] **3**: $(CpTiCl_2)_2(\eta^5\text{-}\eta^5\text{-}C_9H_6(CH_2)_4C_5H_4)$.

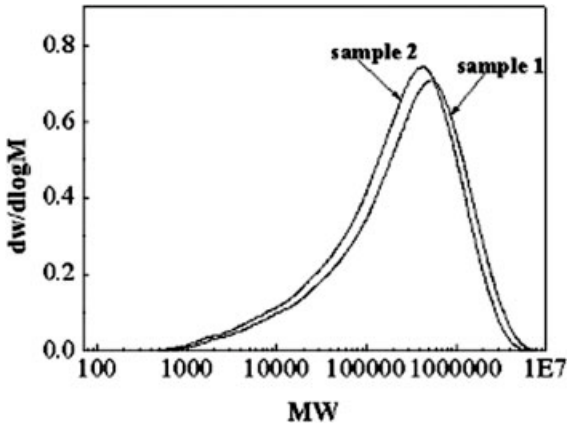


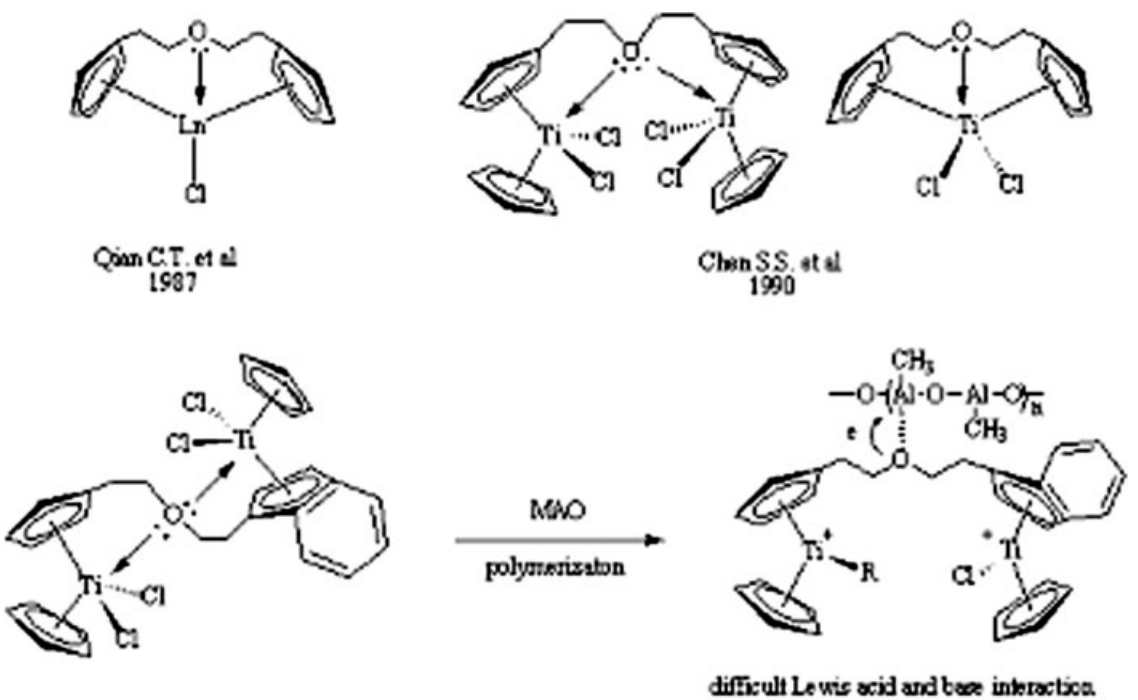

**Figure 6** HT-GPC diagrams of polyethylene provided by **1**/MAO. Polymerization conditions: sample 1 ([Cat]=1.0 × $10^{-4}$ mol/L, [MAO]/[Cat] = 4800, $t_p$ = 5 min, $T_p$ = 25°C, $P_e$ = 4 bar, $V_{toluene}$ = 25 mL); sample 2 ([Cat] = 0.5 × $10^{-4}$ mol/L, [MAO]/[Cat] = 2400, $t_p$ = 30 min, $T_p$ = 0°C, $P_e$ = 1 bar, $V_{toluene}$ = 25 mL).

As shown in Figure 5, the activity of the dinuclear titanocene **1** for ethylene polymerization under high-pressure, is more than three times higher than that in ethylene polymerization under standard atmosphere. For example, when the ethylene pressure raises from 1 to 2 bar, the activity of **1**/MAO increases from 3.42 to 10.52 × $10^5$g PE mol $Cat^{-1}$ $h^{-1}$. The MW of the polymer produced increases directly with increasing ethylene pressure. This can be explained by a higher solubility of ethylene in toluene at higher ethylene pressure.

### Comparison of the catalytic properties of the 3-oxa-pentamethylene bridged asymmetric dinuclear metallocene with those of alkylidene bridged asymmetric dinuclear complexes on ethylene polymerization

A longer alkylidene or polysiloxane bridge improves the catalytic activity of dinuclear metallocenes which was discovered by Noh eta l.[21-25] and Alt et al.[11,12] However, we found that the composition of the bridge is more important than their length. Although the length of the bridge in complex **1** is longer than in complex **2** and **3** (Scheme 1), the catalytic activity of **1** is between those of complex **2** and **3**.[26] The most obvious difference of the three catalytic systems is the melting temperature and the MW distribution of polyethylene produced. As shown in Table I, the melting temperature of polyethylene produced by **1**/MAO is 2–5°C higher than those of polyethylene produced by **2**/MAO and **3**/MAO. That may explain that the polyethylene obtained by **1**/MAO is highly linear and highly crystalline.[27] As shown in Figure 7, the $^{13}$C-NMR spectrum (methylene and methane region) of polyethylene obtained by the **1**/MAO system also shows only one strong signal at 30ppm for the methylene units.

The MW distribution of polyethylene produced by **1**/MAO is 12.40, much wider than those of complexes **2** and **3**. From Noh's study, a Lewis acid and base interaction might exist between the aluminum atoms in MAO and the oxygen atoms in the polysiloxane bridge of the dinuclear metallocene during ethylene polymerization.[21] This effect would change




**Scheme 2**

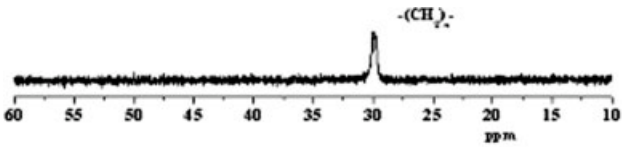



**Figure 7** The $^{13}$C-NMR spectrum of polyethylene obtained by **1**/MAO (in orthodichlorobezene-$d_4$ at 130°C).

the electron density of the active species which might create different active species. Additionally, a coordination effect determined by X-ray photoelectron spectra between the oxygen atom of the 3-oxa-pentamethylene bridge and the metal atoms has been reported.[28,29] We suppose that pseudo five or six membered rings exist in the dinuclear metallocenes (Scheme 2) causing difficulties during ethylene polymerization using MAO as a cocatalyst, because of a hindered Lewis acid and base interaction. A coordinative bond between the metal atom and the oxygen atom already exists, therefore a big steric hindrance avoids that the oxygen atom attacks the Lewis acidic aluminum cocatalyst MAO. As shown in Figure 6, the HT-GPC plot of polyethylene produced by complex **1** did not exhibited a bimodal distribution; however, the MW distribution of PE obtained by **1**/MAO is much wider than that of PE produced using mononuclear metallocenes. These results indicate that an interaction between two metals creates more than one kind of active species during the polymerization process, but the difference between two active species is not enough to produce polyethylene with a bimodal distribution.

## CONCLUSIONS

A new 3-oxa-pentamethylene bridged asymmetric dinuclear titanocene complex has been synthesized and successfully used as catalyst for ethylene polymerization. The catalytic activity of **1**/MAO is similar with that of known alkylidene-bridged asymmetric dinuclear titanocene complexes. The melting points and the MW distribution of the resulting polyethylene products are much higher than those of the alkylidene-bridged asymmetric dinuclear titanocene complexes. The new **1**/MAO system is an efficient catalyst for ethylene polymerization producing polyethylene with high MW distribution.

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## References

1. Brintzinger, H. H.; Fischer, D.; Muehaupt, R.; Rieger, B.; Waymouth Angew Chem 1995, 107, 1255.
2. Kaminsky, W. J Chem Soc Dalton Trans 1998, 5, 1413.
3. Alt, H. G.; Koeppl, A. Chem Rev 2000, 100, 1205.
4. Aguilar, M.; Martin, S.; Vega, J. F.; Munoz-Escalona, A.; Martinez-Salazar, J. J Poly Sci Part B: Polym Phys 2005, 43, 2963.
5. Agnillo, L.; Soares, J. B. P.; Penlidis, A. J Polym Sci Part A: Poly Chem 1998, 36, 831.
6. Cho, H. S.; Chung, J. S.; Lee, W. Y. J Mol Cat A: Chem 2000, 159, 203.
7. Juengling, S.; Muelhaupt, R.; Plenio, H. J Organomet Chem 1993, 460, 191.
8. Chien, J. A.; Wang, B. P. J Polym Sci Part A: Polym Chem 1988, 26, 3089.
9. Reddy, K. P.; Petersen, J. L. Organometallics 1989, 8, 2107.
10. Ewen, J. A. J Am Chem Soc 1984, 106, 6355.
11. Deppner, M.; Burger, R.; Alt, H. G. J Organomet Chem 2004, 689, 1194.
12. Alt, H. G.; Ernst, R.; Bohmer, I. K. J Organomet Chem 2002, 658, 259.
13. Zhang, Z. H.; Sun, J. Q.; Hu, W. Q. J Zhejiang Univ (Eng Sci) 2004, 38, 649.
14. Sun, J. Q.; Ban, Q.; Xu, Y. J. J Zhejiang Univ (Eng Sci) 2004, 38, 1061.
15. Ban, Q.; Sun, J.Q. Chem J Chin Univ 2003, 24, 2304.
16. Hu, W. Q.; Sun J. Q.; Pan, Z. D.; Wu, Z. L. J Zhejiang Univ (Sci) 2000, 1, 157.
17. Sun, J. Q.; Pan, Z. D.; Hu, W. Q.; Yang, S. L. Eur Polym J 2002, 38, 545.
18. Liu, X. J.; Sun, J. Q.; Zhang, H. Y.; Xiao, X. H.; Lin, F. Eur Polym J 2005, 41, 1519.
19. Richard, D. G. J Am Chem Soc 1960, 82, 4211.
20. Bochmann, M.; Lancaster, S. J. Organometallics 1993, 12, 633.
21. Noh, S. K.; Kim, S. H.; Kim, J. H.; Lee, D. H.; Yoon, K. B.; Lee, H. B.; Lee, S. W.; Huh, W. S. J Polym Sci Part A: Polym Chem 1997, 35, 3717.
22. Noh, S. K.; Byun, G. G.; Lee, C. S.; Lee, D. H.; Yoon, K. B.; Kang, K. S. J Organomet Chem 1996, 518, 1.
23. Lee, D. H.; Yoon, K. B.; Lee, E. H.; Noh, S. K.; Lee, C. S.; Huh, W. S. Macromol Rapid Commun 1996, 17, 325.
24. Lee, D. H.; Yoon, K. B.; Lee, E. H.; Noh, S. K.; Byun, G. G.; Lee, C.S. Macromol Rapid Commun 1995, 16, 265.
25. Noh, S. K.; Kim, J. M.; Jung, J.; Ra, C. S.; Lee, D. H.; Lee, H. B.; Lee, S. W.; Huh, W. S. J Organomet Chem 1999, 580, 90.
26. Lin, F.; Sun, J. Q.; Liu, X. J.; Lang, W. K.; Xiao, X. H. J Appl Polym Sci 2006, 101, 3317.
27. Ushioda, T.; Green, M. L. H.; Haggitt, J.; Yan, X. F. J Organomet Chem 1996, 518, 155.
28. Qian, C. T.; Xie, Z. W.; Huang, Y. Z. J Organomet Chem 1987, 323, 285.
29. Chen, S. S.; Chen, Y. X.; Wang, J. T. Acta Chim Sin 1990, 48, 298.