Ethylene Polymerization by Alkylidene-Bridged Asymmetric Dinuclear Titanocene/MAO Systems

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ABSTRACT: Two asymmetric alkylidene-bridged dinuclear titanocenium complexes $(CpTiCl_2)_2(\eta^5\text{-}\eta^5\text{-}C_9H_6(CH_2)_nC_5H_4)$, **1** ($n = 3$) and **2** ($n = 4$) have been prepared by treating two equivalents of $CpTiCl_3$ with the corresponding dilithium salts of the ligands $C_9H_7(CH_2)_nC_5H_5$ ($n = 3, 4$). Additionally, $Ti(\eta^5\text{:}\eta^5\text{-}n\text{-}BuC_5H_4C_5H_5)Cl_2$ (**3**) and $Ti(\eta^5\text{:}\eta^5\text{-}n\text{-}BuC_9H_6C_5H_5)Cl_2$ (**4**) were synthesized as corresponding mononuclear complexes. All complexes were characterized by ^1H, ^{13}C NMR, and IR spectroscopy. Homogenous ethylene polymerization catalyzation using those complexes 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 showed that the catalytic activities of both dinuclear titanocenes were higher than those of the corresponding mononuclear titanocenes. Although the two dinuclear complexes were different in only one [CH_2] unit, the catalytic activity of **2** was about 50% higher than that of **1**; however, the molecular weight of polyethylene (PE) obtained by **2** was lower than that obtained from **1**. The molecular weight distribution of PE produced by these dinuclear complexes reached 6.9 and 7.3, respectively. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3317–3323, 2006

Key words: alkylidene bridge; dinuclear; metallocene catalysts; polyethylene; polymerization

INTRODUCTION

During the last decade, a variety of dinuclear metallocene compounds containing two mechanically linked metallocene units have been prepared and their catalytic properties were examined because dinuclear complexes are potentially useful as a new kind of polymerization catalyst, due to cooperative electronic and chemical interaction between two centers, ascribed as a "synergism effect."[1–4] Petersen[5] and Royo[6,7] prepared a variety of dimethylsily-bridged homodinuclear metallocene complexes of titanium and zirconium. Muelhaupt[4] first studied olefin polymerization using phenylene-bridged dinuclear zirconocenes and discovered cooperative effects. In 1996, Green[8] reported the synthesis of a series of homo- and heterodinuclear metallocenes of Group IV metals and investigated their catalytic activity in the polymerization of ethylene and propylene. The resulting PE showed high melting points (T_m) in the range of 137–140°C, indicating a high linear crystallinity. Soga[9] synthesized a new type of biphenyl-bridged dinuclear zirconocenes and examined their polymerization activity. In the presence of MAO, the catalysts showed an extremely high catalytic activity and high thermal stability on ethylene polymerization. A systematic polymerization study of dinuclear metallocenes was performed by Noh[10–14] using polysiloxane- and polymethylene-bridged dinuclear zironocenes. They found increasing polymerization activity with longer bridges. A higher electron density delivered by a longer polymethylene bridge seems to stabilize the active site of the catalysts and accelerates the rate of polymerization. More recently, Alt[15] prepared a series of asymmetric alkylidene-bridged dinuclear metallocene complexes of zirconium and hafnium and investigated the polymerization of ethylene using those dinuclear complexes. Their results showed that a longer alkylidene bridge improves the catalytic activity of the dinuclear metallocenes. In addition, the results verified their hypothesis that the PE obtained from those dinuclear complexes had higher molecular weight distribution (MWD) than those produced with corresponding mononuclear complexes. We found in our recent research that dinuclear metallocenes were efficient catalysts to produce high molecular weight polymers with broad MWD, not only in methyl methacrylate polymerization, but also in ethylene polymerization.[16–21]

The present study approves again that **1**/MAO and **2**/MAO were both efficient catalysts to produce PE with broad MWD. In addition, according to Noh and Alt's results—the longer the bridge of dinuclear metallocenes, the higher the catalytic activity—we have designed and synthesized **1** and **2**, which contain asymmetric ligands and have only one [CH_2] unit difference in the bridge. Compared with corresponding mononuclear metallocene, the catalytic properties in ethylene polymerization were more valuable to be examined in detail.

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 passing it through a column of molecular sieve (4 Å) and Drierite (8 mesh).

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. 1,3-Dibromopropane and 1,4-dibromobutane purchased from Aldrich were used after distilling from calcium hydride. $CpTiCl_3$,[22] $C_9H_7(CH_2)_nC_5H_5$ (n = 3,4)[15] were synthesized according to the literature. MAO (10 wt % in toluene, provided by Witco) was used without further purification. Ethylene (polymer grade) was purified by bubbling through triethylaluminium in toluene.

Measurements

NMR spectra were recorded on a Bruker Avance DMX500 spectrometer at ambient temperature; chemical shifts were referenced with respect to tetramethylsilane. The molecular weight of polyethylene was measured in decahydronaphthalene at 135°C by a modified Ubbelohde-type viscometer using $[\eta] = 6.67 \times 10^{-4} M_\eta^{0.67}$ (mL/g). The molecular weight distribution of some polymers with orthodichlorobenzene as solvent were determined by gel-permeation chromatography (GPC, Waters 150, 135°C), using polystyrene columns 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 $(CpTiCl_2)_2(\eta^5-\eta^5-C_9H_6(CH_2)_3C_5H_4)$ (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 dropwisely for 30 min with a solution of $Li_2[C_9H_6(CH_2)_3C_5H_4]$

prepared from $C_9H_7(CH_2)_3C_5H_5$ and n-BuLi (1.2 g, 5.0 mmol) in THF (20.0 mL) according to Alt.[15] 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, 62.0% yield).

^{1}H NMR ($CDCl_3$, 20°C, δ ppm): 7.62–7.53 (m, 2H, C_9H_6), 7.37–7.27 (m, 2H, C_9H_6), 6.63–6.60 (m, 2H, C_9H_6), 6.55 (s, 5H, C_5H_5), 6.43 (t, ^3J = 2.5 Hz, 2H, C_5H_4) 6.34 (t, ^3J = 2.5 Hz, 2H, C_5H_4), 6.18 (s, 5H, C_5H_5), 3.17–3.12 (m, 2H, CH_2), 2.94–2.80 (m, 2H, CH_2), 2.11–1.99 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 20°C, δ ppm): (C_q):138.8, 130.3, 129.3, 127.5; (CH): 128.1, 127.3, 126.3, 126.1, 124.5, 120.5, 119.6, 119.1, 115.8, 115.4, 104.7; (CH_2): 30.7, 29.2, 28.5. IR (KBr, cm^{-1}): 3108, 2930, 2859, 1459, 1440, 1065, 1016, 821, 752, 405.

Preparation of $(CpTiCl_2)(\eta^5-\eta^5-C_9H_6(CH_2)_4C_5H_4)$ (2)

This complex was synthesized in analogy to **1** using $Li_2[C_9H_6(CH_2)_4C_5H_4]$[15] and isolated as a reddish brown solid (1.8 g, 60.0% yield).

^{1}H NMR ($CDCl_3$, 20°C, δ ppm): 7.68–7.57 (m, 2H, C_9H_6), 7.38–7.31 (m, 2H, C_9H_6), 6.60–6.52 (m, 2H, C_9H_6), 6.54 (s, 5H, C_5H_5), 6.43 (t, ^3J = 2.5 Hz, 2H, C_5H_4), 6.34 (t, ^3J = 2.5 Hz, 2H, C_5H_4), 6.20 (s, 5H, C_5H_5), 3.18–3.14 (m, 1H, CH_2), 3.02–2.98 (m, 1H, CH_2), 2.82–2.77 (m, 2H, CH_2), 1.75–1.67 (m, 4H, 2× CH_2). ^{13}C NMR ($CDCl_3$, 20°C, δ ppm): (C_q): 139.0, 130.7, 129.5, 127.8; (CH): 128.0, 127.3, 126.3, 125.9, 124.6, 123.0, 122.7, 119.8, 118.8, 116.2, 115.5, 104.8; (CH_2): 30.6, 30.0, 29.3, 28.7. IR (KBr, cm^{-1}): 3110, 2943, 2856, 1437, 1017, 820, 752, 444.

Preparation of $Ti(\varsigma^5:\varsigma^5-n\text{-}BuC_5H_4 C_5H_5)Cl_2$ (3)

A solution of n-BuBr (0.7 g, 5.0 mmol) in THF (20.0 mL) was cooled to 0°C and treated dropwisely for 20 min with a solution of C_5H_5Na (6.2 mL, 1.2 mol/L, 5.0 mmol) in THF. The resulting solution was warmed up to room temperature and stirred for 5 h. Then the reaction mixture was added to a suspension of NaH (0.1g , 5.0 mmol) in THF (20.0 mL) at 0°C. The resulting mixture was warmed up to room temperature and stirred until no gas was evolved. The mixture was filtered and the filtrate was added to a solution of $C_5H_5TiCl_3$ (1.1 g, 5.0 mmol) in toluene (20.0 mL) at 0°C. The resulting solution was then 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 of the resulting solid yielded **3** as a reddish solid (0.8 g, 53.3% yield).

^{1}H NMR ($CDCl_3$, 20°C, δ ppm): 6.55 (s, 5H, C_5H_5), 6.43 (t, ^3J = 2.6 Hz, 2H, C_5H_4), 6.36 (t, ^3J = 2.6 Hz, 2H, C_5H_4), 2.73 (t, 2H, ^3J = 7.7 Hz, CH_2), 1.57–1.54 (m, 2H, CH_2), 0.92 (t, ^3J = 7.3 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$,

20°C, δ ppm): (C$_q$): 139.6; (CH): 122.8, 119.6, 116.0; (CH$_2$): 32.5, 30.8, 22.3; (CH$_3$): 13.8. IR (KBr, cm^{-1}): 3105, 2954, 2927, 2858, 1496, 1444, 1049, 1015, 857, 825, 418.

Preparation of Ti(ç^5:ç^5-n-BuC$_9$H$_6$ C$_5$H$_5$)Cl$_2$ (4)

A solution of n-BuBr (0.7 g, 5.0 mmol) in THF (20.0 mL) was cooled to 0°C and treated dropwisely for 20 min with a solution of C$_9$H$_7$Li (0.6 g, 5.0 mmol) in THF (20.0 mL). The resulting solution was warmed up to room temperature and stirred for 6 h. Volatiles were removed *in vacuo* and the yellowish paste was extracted with pentane. The yellow filtrate was then added to a solution of n-BuLi (4.2 mL, 1.2 mol/L, 5.0 mmol) in pentane at −78°C. The reaction mixture was warmed up to room temperature and stirred for 6 h. The resulting suspension was cooled to 0°C and treated dropwisely for 20 min with a solution of C$_5$H$_5$TiCl$_3$ (1.1 g, 5.0 mmol) in toluene (30.0 mL). Volatiles were removed *in vacuo* and the resulting residue was extracted with CH$_2$Cl$_2$. Recrystallization of the resulting solid yielded **4** as reddish solid (1.0 g, 58.8% yield).

^{1}H NMR (CDCl$_3$, 20°C, δ ppm): 7.70–7.58 (m, 2H, C$_9$H$_6$), 7.37–7.34 (m, 2H, C$_9$H$_6$), 6.63–6.59 (m, 2H, C$_9$H$_6$), 6.53 (s, 5H, C$_5$H$_5$), 3.16–3.08 (m, 1H, CH$_2$), 2.95–2.87 (m, 1H, CH$_2$), 1.63–1.61 (m, 2H, CH$_2$), 1.41–1.38 (m, 2H, CH$_2$), 0.94 (t, ^3J = 7.3 Hz, 3H, CH$_3$). ^{13}C NMR (CDCl$_3$, 20°C, δ ppm): (C$_q$): 127.2, 126.4, 126.1, 124.5; (CH): 120.4, 119.2; (CH$_2$): 32.1, 28.8, 22.8; (CH$_3$): 13.9. IR (KBr, cm^{-1}): 3107, 2954, 2928, 2859, 1437, 1016, 832, 750, 670, 519.

Polymerization

Ethylene polymerization under standard atmosphere

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. The system was then saturated with ethylene. With a continuous flow of ethylene the polymerization was initiated by injection of the catalysts and polymerized during the given time. The resulting polyethylene crops were precipitated in acidified ethanol, filtered, and dried under vacuum to 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, to start the polymerization immediately. The polyethylene crops were treated
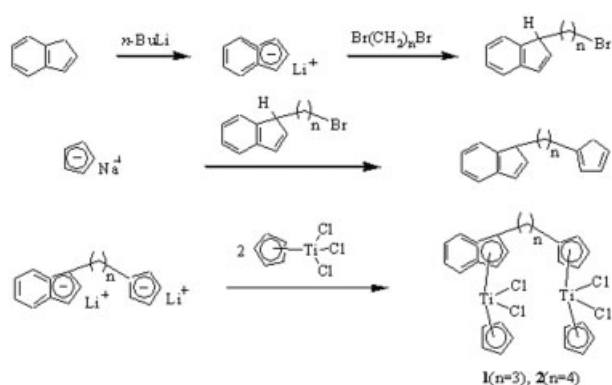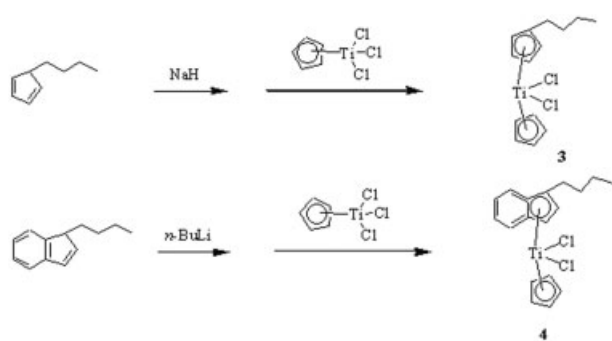

Scheme 1

and separated using the same procedures mentioned earlier.

RESULTS AND DISCUSSION

Synthesis and characterization

The alkylidene-bridged dinuclear metallocene complexes (CpTiCl$_2$)$_2$(η^5-η^5-C$_9$H$_6$(CH$_2$)$_3$C$_5$H$_4$) (**1**) and (CpTiCl$_2$)$_2$(η^5-η^5-C$_9$H$_6$(CH$_2$)$_4$C$_5$H$_4$) (**2**) are prepared by the reaction of the dilithium salts of the corresponding ligands C$_9$H$_7$(CH$_2$)$_3$C$_5$H$_5$ and C$_9$H$_7$(CH$_2$)$_4$C$_5$H$_5$, respectively, with two equivalents of CpTiCl$_3$ in toluene at 0 °C (Scheme 1). The ligands were prepared in 95% yields by treatment of the corresponding bromide compounds C$_9$H$_7$(CH$_2$)$_3$Br and C$_9$H$_7$(CH$_2$)$_4$Br, respectively, with one equivalent of sodium cyclopentadienyl in THF following the procedure of Alt.[15] Both dinuclear complexes are separated as reddish brown solids, which are soluble in common organic solvents. The corresponding mononuclear metallocenes **3** and **4** are prepared according to the literature (Scheme 2).[23,24]

The ^{1}H NMR spectra of the complexes **1** and **2** prove the assigned dinuclear metallocenes structure.[15] They show two sets of well separated resonances in the aromatic region. The four resonances between 7.3 and

Scheme 2

7.6 ppm are assigned to the four protons of the six-membered ring in indenyl fragment. The resonances appearing at 6.6 ppm as multiplets are due to two protons of the five-membered ring side at the indenyl group. The sharp singlets at 6.55/6.54 and 6.18/6.20 ppm result from the 10 protons of two kinds of cyclopentadienyl moieties, the first one is related to the CpTi bonded to the indenyl group, the later one is related to the other CpTi bonded to the $(CH_2)_nC_5H_4$ residue. The resonances of the related cyclopentadienyl groups in the corresponding mononuclear complexes **3** and **4** appear as singlets at 6.55 and 6.53 ppm, respectively. That proves that both metal centers in the dinulear metallocene complexes **1** and **2** have a different electron density. The triplet signals at 6.43 and 6.34 ppm result from the four protons of the cyclopentadienyl bonded to the bridge. The resonances of the bridging methylene protons display as three multiplets between 3.17 and 1.99 ppm for **1** and four multiplets between 3.18 and 1.67 ppm for **2**, respectively. The ^{13}C NMR spectra of the complexes demonstrate the mentioned feature well.

Homogeneous ethylene polymerization

Influence of the conditions on the ethylene polymerization

The complexes **1** and **2** were employed for ethylene polymerization in the presence of MAO. The catalytic activity and the molecular weight of polyethylene are remarkable dependent on the molar ratio of [MAO]/[Cat] (Fig. 1). With increasing molar ratio [MAO]/[Cat] from 500 to 2000, the activity of **1** (from 1.21 $\times$ 10^5 to 1.99 $\times$ 10^5 g PE/(mol Cat h) and **2** (from 1.70 $\times$ 10^5 to 2.90 $\times$ 10^5 g PE/(mol Cat h) both increases consistently. The activity of **2** is about 50% higher than

Figure 2 Influence of the catalyst concentration on catalytic activity and molecular weight of polyethylene. [○: Activity of **1**/MAO, ●: Activity of **2**/MAO, □: M_η of **1**/MAO, ■: M_η of **2**/MAO]. Polymerization conditions: [MAO]/[Cat] = 1000, T_p = 40°C, t_p = 30 min, P_e = 1 bar, $V_{toluene}$ = 25 mL.

that of **1**, which demonstrates that the dinuclear catalyst with more [CH_2] units in the bridge causes higher activity.[14,15] With a longer bridge the bimolecular deactivation process could also be suppressed because of the intramolecular remoteness as well as the intermolecular access disturbance of two active sites.[10] In addition, the dinuclear metallocene **1** generated greater molecular weight polyethylenes than by **2**. This behaviors is very well in accordance with the molecular weight tendency observed with the polysiloxane-bridged dinuclear zirconocenes.[10,11]

As shown in Figure 2, the catalytic activity of **1** and **2** and the molecular weight of polyethylene received using these catalysts decrease gradually with increasing of the catalyst concentration. Increasing the catalyst concentration implies much more active centers

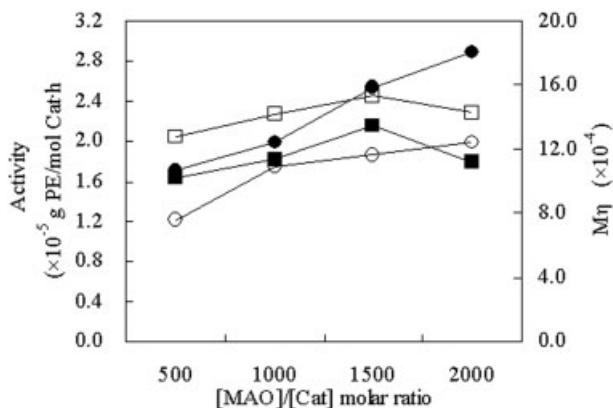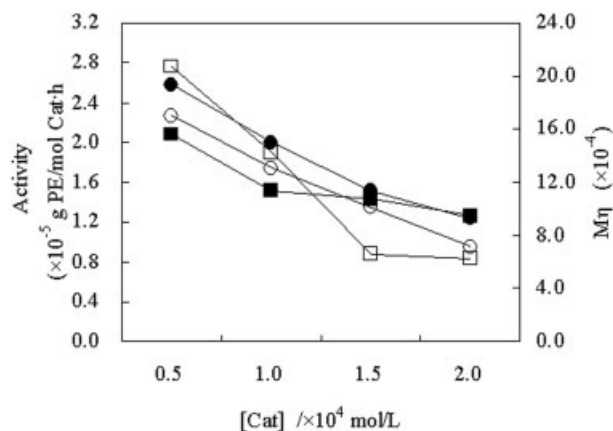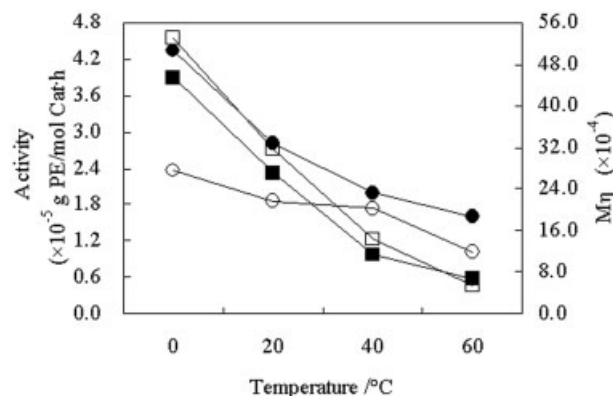**Figure 1** Influence of the [MAO]/[Cat] molar ratio on catalytic activity and molecular weight of polyethylene. [○: activity of **1**/MAO, ●: activity of **2**/MAO, □: M_η of **1**/MAO, ■: M_η of **2**/MAO]. Polymerization conditions: [Cat] = 1.0 $\times$ 10^{-4} mol/L, T_p = 40°C, t_p = 30 min, P_e = 1 bar, $V_{toluene}$ = 25 mL.

Figure 3 Influence of the polymerization temperature on catalytic activity and molecular weight of polyethylene. [○: Activity of **1**/MAO, ●: Activity of **2**/MAO, □: M_η of **1**/MAO, ■: M_η of **2**/MAO]. Polymerization conditions: [Cat] = 1.0 $\times$ 10^{-4} mol/L, [MAO]/[Cat] = 1000, t_p = 30 min, P_e = 1 bar, $V_{toluene}$ = 25 mL.
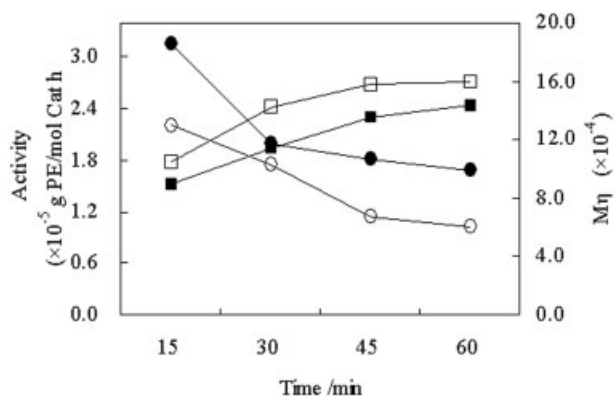
Figure 4 Influence of the polymerization time on catalytic activity and molecular weight of polyethylene. [○: Activity of **1**/MAO, ●: Activity of **2**/MAO, □: M_η of **1**/MAO, ■: M_η of **2**/MAO]. Polymerization conditions: [Cat] = 1.0×10^{-4} mol/L, [MAO]/[Cat] = 1000, T_p = 25°C, P_e = 1 bar, $V_{toluene}$ = 25 mL.

Figure 6 Polymerization activities of **1**/MAO, **2**/MAO, and a mixture (1:1M ratio) of **3**/MAO and **4**/MAO for ethylene polymerization at different ethylene pressure. Polymerization conditions: [Cat] = 1.0×10^{-4} mol/L, [MAO]/[Cat] = 1000, t_p = 5 min, T_p = 40°C, $V_{toluene}$ = 25 mL.

during the polymerization process, making less ethylene available per mole of active enters and increases the chance of the bimolecular deactivation of the catalyst.[2,4]

Figure 3 demonstrates the influence of the polymerization temperature on the catalytic activity and the molecular weight of polyethylene. It shows that 0 °C is the optimum polymerization temperature. The activity of the catalysts decreases with increasing temperature above 0°C. This may be contributed to a decreasing solubility of ethylene in toluene at higher temperatures as well as a deactivation process due to the poor thermal stability of the cationic methyl complex formed in the presence of MAO as the active center.[25] The molecular weight of polyethylene also depends
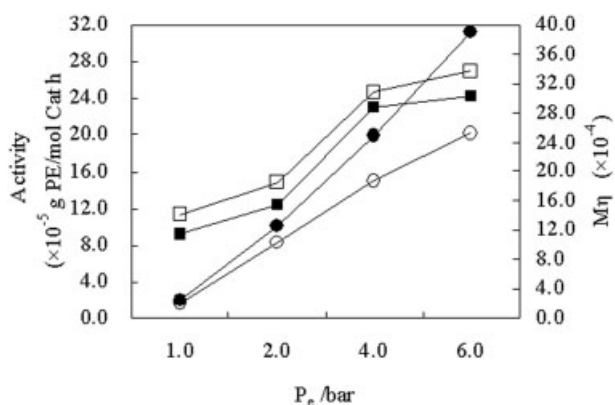
upon the polymerization temperature. A competition between the termination and propagation steps determines the molecular weight of polyethylene. A higher temperature is favorable to increase the rate of β-hydride chain transfer over the propagation rate, which causes the formation of a polymer with lower molecular weight.

The influence of the polymerization time on ethylene polymerization is shown in Figure 4. It demonstrates a decrease of the catalytic activity of **1** and **2** with prolonging reaction time, due to the deactivation of the catalysts. The molecular weight of polyethylene produced by both dinuclear catalysts increases from 10.5×10^4 to 16.0×10^4 g/mol by **1**/MAO and from 8.9×10^4 to 14.3×10^4 g/mol by **2**/MAO, respectively.

For ethylene polymerization under high-pressure, the activities of the dinuclear titanocenes **1** and **2** (as

Figure 5 Influence of the ethylene pressure on catalytic activity and molecular weight of polyethylene. [○: Activity of **1**/MAO, ●: Activity of **2**/MAO, □: M_η of **1**/MAO, ■: M_η of **2**/MAO]. Polymerization conditions: [Cat] = 1.0×10^{-4} mol/L, [MAO]/[Cat] = 2000, t_p = 5 min (under high pressure) and t_p = 30 min (under atmosphere), T_p = 25°C, $V_{toluene}$ = 25 mL.
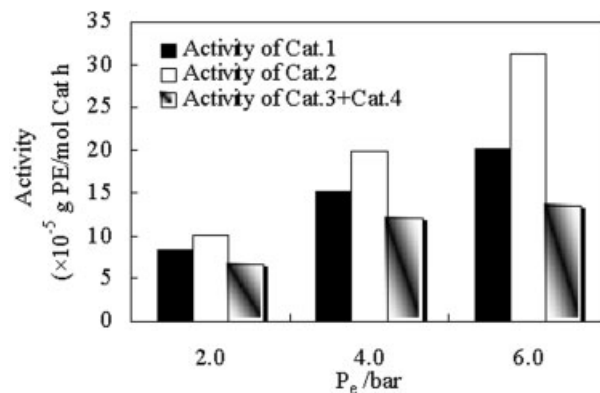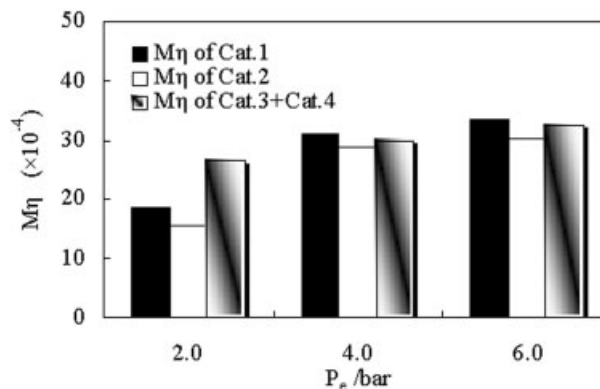

Figure 7 Molecular weights of resulting polyethylenes of **1**/MAO, **2**/MAO, and a mixture (1:1M ratio) of **3**/MAO and **4**/MAO for ethylene polymerization at different ethylene pressure. Polymerization conditions: [Cat] = 1.0×10^{-4} mol/L, [MAO]/[Cat] = 1000, T_p = 40°C, t_p = 30 min, $V_{toluene}$ = 25 mL.
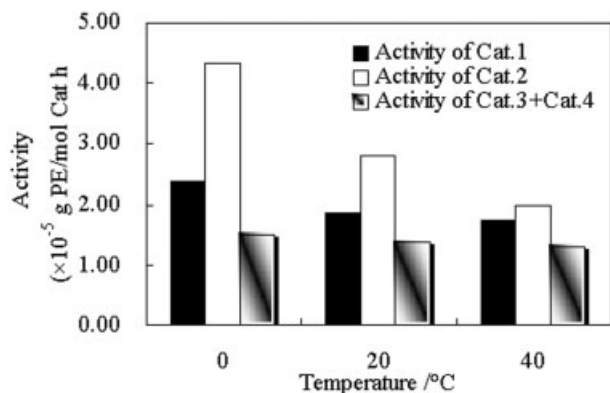
Figure 8 Polymerization activities of **1**/MAO, **2**/MAO, and a mixture (1 : 1M ratio) of **3**/MAO and **4**/MAO for ethylene polymerization at different temperatures. Polymerization conditions: [Cat] = 1.0 × 10^{-4} mol/L, [MAO]/[Cat] = 1000, t_p = 30 min, P_e = 1 bar, V_{toluene} = 25 mL.

shown in Fig. 5) are almost one order of magnitude 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** increases from 1.75 × 10^5 to 8.21 × 10^5 g PE/(mol Cat h). The molecular weight of the polymer produced using both dinuclear titanocenes 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 activity of the asymmetric dinuclear metallocenes with those of corresponding mononuclear complexes on ethylene polymerization

Figure 6 shows that the catalytic activity of dinuclear titanocenes is higher than that of the mixture (1 : 1M ratio) of the mononuclear complexes **3** and **4**. Especially, the activity of **3** at 6 bar is two times higher than that of the mixture of both complexes. This observation promises advantages for industrial use of the catalysts, because commercial ethylene polymerization is mainly done at high pressure. Figure 7 shows the influence of the ethylene pressure on the molecular weight of the polymer. The polymer molecular weight of the products produced using three different catalysts systems increase with raising the ethylene pressure. **1**/MAO produces a polymer with a higher molecular weight than does **2**/MAO, but both with a lower molecular weight than the mixture of **3** and **4** at 2 bar ethylene pressure. On the other hand, the molecular weights of the products received using **1**/MAO, **2**/MAO, or the mixture of **3** and **4** are nearly the same with continually increasing ethylene pressure.

Figure 8 demonstrates that the activities of the dinuclear titanocenes are higher than that of the mixed mononuclear catalyst system with increasing reaction

temperature. This behavior is very well in accordance with the activity tendency in polymethylene-bridged dinuclear zirconocenes.[15] Figure 9 shows that at low temperature the molecular weights of the polymer produced by dinuclear catalysts are higher than that of the mixed mononuclear catalyst system, but at higher temperature the instance is exactly reversed. This implies that the β-hydride chain transfer in dinuclear catalysts is more frequently than that in a mixed mononuclear catalyst system.

Our experiments show (Table I) that the activity of the catalysts decrease in the order **2** > **1** > **3** + **4** > **3** > **4**, indicating a higher activity of dinuclear titanocenes with more (CH$_2$) units as a bridge. In addition, the dinuclear metallocene complexes **1** and **2** show a higher activity than the corresponding mononuclear complexes **3**, **4**, and the 1 : 1 mixture of **3** and **4**. The "synergism effect" of the dinuclear metallocenes exhibits a buildup tendency in catalytic activity.[4]

The HT-GPC curves in Figure 10 demonstrate that a mixture (1 : 1M ratio) of **3** and **4** shows a bimodal distribution curve and the MWD (=10.90) is higher than that received using the dinuclear metallocenes **1** (MWD = 7.31) and **2** (MWD = 6.91). Meanwhile, the MWD of **1** and **2** is higher than that of the phenylenedimethylene-bridged homobinuclear titanocene in our previous study.[21] This might be attributed to the asymmetric ligands of **1** and **2**, causing the difference in electron density and steric hindrance between the two active centers in one catalyst. Although the spectra of the MWD of PE obtained from **1** and **2** are unimodal distribution, they are obviously broader than those obtained using general mononuclear metallocene catalysts (MDW ≈ 2), indicating that the interaction between two metals created more than one kind of active species during the polymerization
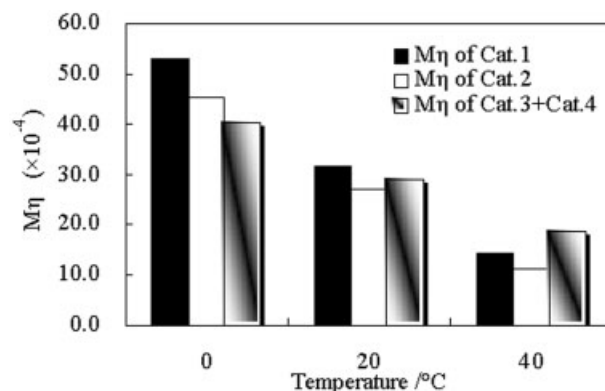

Figure 9 Molecular weights of resulting polyethylenes of **1**/MAO, **2**/MAO, and a mixture (1 : 1M ratio) of **3**/MAO and **4**/MAO for ethylene polymerization at different temperatures. Polymerization conditions: [Cat] = 1.0 × 10^{-4} mol/L, [MAO]/[Cat] = 1000, t_p = 30 min, P_e = 1 bar, V_{toluene} = 25 mL.

TABLE I
Comparison of the Asymmetric Dinuclear Metallocenes with Corresponding Mononuclear Complexes as Catalysts on Ethylene Polymerization

Cat	[Cat] (10^4 mol L^{-1})	[MAO]/[Cat]	T_p (°C)	t_p (min)	Activity (10^{-5} g PE/mol Cat/h)	M_η (10^{-4})	M_w/M_n	T_m (°C)
1	1.0	1000	40	30	1.75	14.2	7.31	132.50
2	1.0	1000	40	30	1.99	11.4	6.91	132.32
3	2.0	500	40	30	1.07	11.3	–	132.13
4	2.0	500	40	30	1.06	15.5	–	129.66
3+4[a]	2.0	500	40	30	1.30	15.8	10.90	133.84

Polymerization condition: 1 bar, 25 mL toluene.
[a] Mixture of 3 and 4 (1 : 1 molar ratio).

process. Moreover, the dinuclear titanocene with more (CH$_2$) units as a bridge exhibits a broader molecular weight distribution, which was similar with that of the asymmetric dinuclear zironocenes.[15]

The melting points of polyethylene range between 129 and 133°C, indicating that these are highly linear and highly crystalline polymers.[8]

CONCLUSIONS

Two new alkylidene-bridged asymmetric dinuclear titanocenes have been synthesized and successfully used as catalysts for ethylene polymerization. It could be found that the polymerization activity increases in the order of the bridge length in these dinuclear catalysts. The molecular weight of the produced PE is exactly reverse with the activity of the catalyst used. The activities of the dinuclear catalysts are higher than those of the corresponding mononuclear metallocenes, especially in high-pressure ethylene polymerization. The polyethylene obtained from dinuclear titanocenes has a broad molecular weight distribution (MWD = 6.9–7.3), which is wider than that of PE received using general mononuclear metallocene catalysts (MWD ≈ 2).
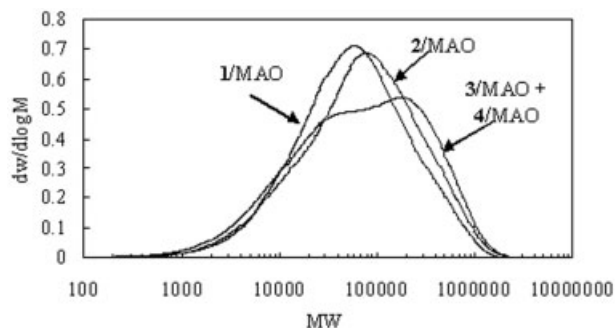

Figure 10 HT-GPC diagram of polyethylene provided by **1**/MAO, **2**/MAO, and a mixture (1 : 1M ratio) of **3**/MAO and **4**/MAO. Polymerization conditions: [Cat] = 1.0 × 10^{-4} mol/L, [MAO]/[Cat] = 1000, t_p = 30 min, T_p = 40°C, P_e = 1 bar, $V_{toluene}$ = 25 mL.

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