Preparation of new dinuclear half-titanocene complexes with *ortho*- and *meta*-xylene linkages and investigation of styrene polymerization

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ABSTRACT

Half-titanocene is well-known as an excellent catalyst for the preparation of SPS (syndiotactic polystyrene) when activated with methylaluminoxane (MAO). Dinuclear half-sandwich complexes of titanium bearing a xylene bridge, $(TiCl_2L)_2\{(\mu\text{-}\eta^5, \eta^5\text{-}C_5H_4\text{-}ortho\text{-}(CH_2\text{-}C_6H_4\text{-}CH_2)C_5H_4\}$, (**4** (L = Cl), **7** (L = O-2,6-iPr$_2$C$_6$H$_3$)) and $(TiCl_2L)_2\{(\mu\text{-}\eta^5, \eta^5\text{-}C_5H_4\text{-}meta\text{-}(CH_2\text{-}C_6H_4\text{-}CH_2)C_5H_4\}$ (**5** (L = Cl), **8**(L = O-2,6-iPr$_2$C$_6$H$_3$)), have been successfully synthesized and introduced for styrene polymerization. The catalysts were characterized by ^{1}H- and ^{13}C NMR, and elemental analysis. These catalysts were found to be effective in forming SPS in combination with MAO. The activities of the catalysts with rigid *ortho*- and *meta*-xylene bridges were higher than those of catalysts with flexible pentamethylene bridges. The catalytic activity of four dinuclear half-titanocenes increased in the order of **4 < 5 < 7 < 8**. This result displays that the *meta*-xylene bridged catalyst is more active than the *ortho*-xylene bridged and that the aryloxo group at the titanium center is more effective at promoting catalyst activity compared to the chloride group at the titanium center. Temperature and ratio of [Al]:[Ti] had significant effects on catalytic activity. Polymerizations were conducted at three different temperatures (25, 40, and 70 °C) with variation in the [Al]:[Ti] ratio from 2000 to 4000. It was observed that activity of the catalysts increased with increasing temperature, as well as higher [Al]:[Ti]. Different xylene linkage patterns (*ortho* and *meta*) were recognized to be a principal factor leading to the characteristics of the dinuclear catalyst due to its different spatial arrangement, causing dissimilar intramolecular interactions between the two active sites.

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1. Introduction

Syndiotactic polystyrene (SPS) is a highly crystalline polymer with a melting temperature (T_m) near 270 °C. The relatively fast crystallization rate, low specific gravity, low dielectric constant, high modulus of elasticity, and excellent resistance to chemicals make SPS a potential material for a large number of applications in the automotive, electronic, and packaging industries [1,2]. Ishihara succeeded in the synthesis of SPS in 1985 by using homogeneous organometallic catalytic systems based on titanium compounds and methylaluminoxane (MAO) [3]. Since then, a variety of titanium compounds have been examined for their ability to produce SPS in the presence of MAO [4–6]. As a result of such research, it turned out that structural characteristics of half-titanocenes based on the electronic and steric effects of CṕTiX$_3$ determined not only catalytic activity of the catalyst but also degree of stereoregularity and molecular weight of the SPS. Recently,

the utility of titanium-based half-metallocene with a variety of substituents at the metal site, such as aryloxo, amide, and ketimide as an olefin polymerization catalyst, has been investigated extensively [7–9]. These studies demonstrated clearly that the effect of the substituent on both Cp and titanium plays an essential role not only regarding catalytic activity, but also for monomer reactivity in the polymerization of styrene and copolymerization with ethylene.

Investigation of the properties of dinuclear metallocenes has been a topic of this lab's research since these metallocenes may offer cooperative effects between two active sites that could provide an effective tool for the discovery of a new class of catalysts for olefin polymerization [10,11]. In fact, the dinuclear metallocene systems display not only the defining characteristics of well-defined mononuclear metallocenes, but also a strong dependence upon the nature of the bridging ligand [12–18]. The initial attempts to exploit dinuclear half-titanocenes were performed by Royo et al. and Flores et al. [19–21]. It was found that the activity for the dinuclear half-titanocenes is one order of magnitude lower than that of the mononuclear half-titanocene [18,21]. Osakada reported also

the higher activity of dinuclear zirconium metallocene catalyst comparing to the corresponding normal metallocene due to the bridge effect [25]. To the contrary, Do and coworkers reported that the activity of dinuclear half-titanocene with two phenyl spacers was, in actuality, similar to the mononuclear half-titanocene, demonstrating that the nature of the bridging unit in dinuclear metallocenes exerted a significant influence on determining the characteristics of the catalysts [22]. We have also reported that *para*-xylene bridged dinuclear half-titanocene exhibited greater activity than the polymethylene bridged, demonstrating the effect of the bridge rigidity on the catalyst [14,15].

Much work has been performed to establish the effect of the bridge nature in dinuclear metallocenes; however, the topics related to the geometric effect of the bridging ligand on dinuclear metallocenes have not been well established. Herein, it is the intent of the authors to describe an efficient preparative route to make four novel dinuclear half-titanocenes with *meta*- and *ortho*-xylene bridges as new metallocenes in order to understand the influence of the geometric arrangement of dinuclear metallocenes on catalytic behavior as shown in Scheme 1. The results of styrene polymerization using these catalysts have exhibited some meaningful aspects to point out the effect of space orientation of the two active sites.

2. Experimental

2.1. General considerations

All manipulations were performed either under a dry, oxygen-free atmosphere using standard Schlenk techniques or under a double manifold vacuum line. Nitrogen gas was purified by passage through a column of molecular sieve (4 Å) and Drierite (8 mesh). Tetrahydrofuran (THF), diethyl ether, hexane, and toluene were distilled from sodium/benzophenone ketyl prior to use. Methylene chloride and trimethylsilyl chloride (97%, Aldrich Co., City, State, Country) were distilled from calcium hydride prior to use. α,α′-Dibromo-*o*-xylene (96%, Aldrich Co.), α,α′-dibromo-*m*-xylene (97%, Aldrich Co.), sodium cyclopentadienylide (2.0 M solution in THF, Aldrich Co.), sodium hydride (as a 60% dispersion in mineral oil, Aldrich Co.), *n*-BuLi (2.5 M solution in hexane, Aldrich Co.), titanium chloride (Aldrich Co.), and modified methylaluminoxane (MMAO, 5.9 wt.% Al, Akzo, City, State, USA) were used without further purification. ^1H NMR (300 MHz) and ^{13}C NMR (75.46 MHz) spectra were recorded using a Bruker VNS-300 FT-NMR spectrometer. Elemental analysis was conducted on an EA 1108 elemental analyzer (FISONS Instrument, City, Italy).
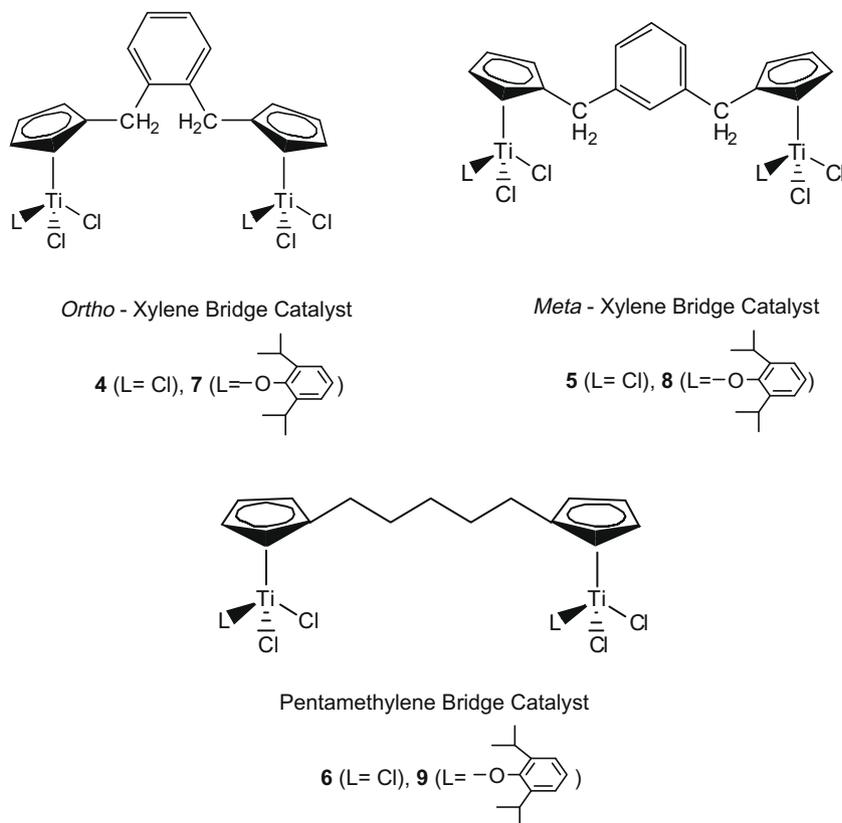
Molecular weight and molecular weight distribution were measured by a Waters GPC (Alliance GPC 2000, City, State, Country) with a polystyrene gel column (Styragel HT 3, 4, 5) at 140 °C using 1,2,4-trichlorobenzene. The molecular weight was calculated by a standard procedure based on calibration with standard polystyrene samples. Differential scanning calorimetric (DSC) data were recorded with a Pyris 6 DSC (Perkin Elmer, City, State, Country) under a nitrogen atmosphere [conditions: heating from 25 to 300 °C (20 °C/min); cooling from 300 to −55 °C (10 °C/min)].

Catalysts **6** and **9** having pentamethylene bridge were prepared by the literature method [12,15].

2.2. Synthesis

2.2.1. Synthesis of $(TiCl_3)_2\{(\mu-\eta^5, \eta^5-C_5H_4$-ortho-$(CH_2-C_6H_4-CH_2)C_5H_4\}$, 4

α,α′-Bis(trimethylsilyl)cyclopentadienyl-*ortho*-xylene (**3o**) was synthesized according to literature methods [23]. A solution of **3o** (3.0 g, 7.93 mmol) in methylene chloride (50 mL) was added dropwise to 1.74 mL (15.86 mmol, 2.0 eq) of $TiCl_4$ at -78 °C; an

Ortho - Xylene Bridge Catalyst

4 (L= Cl), **7** (L=—O—⟨⟩)

Meta - Xylene Bridge Catalyst

5 (L= Cl), **8** (L=—O—⟨⟩)

Pentamethylene Bridge Catalyst

6 (L= Cl), **9** (L= —O—⟨⟩)

Scheme 1. Structure of dinuclear half-titanocenes.

immediate solution color change from clear to greenish black was observed. After the addition (≈10 min), the solution was allowed to warm to room temperature and stirred overnight. Methylene chloride was removed under vacuum and the residue extracted with ether. The final solid was obtained as a greenish yellow product after washing with hexane.

Compound **4**: Yield: 2.77 g (65%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.20 (s, 4H, C$_6$H$_4$), 6.86 (t, 4H, C$_5$H$_4$), 6.68 (t, 4H, C$_5$H$_4$), 4.14 (s, 4H, CH$_2$); ^{13}C NMR (CDCl$_3$): δ 141.9, 136.1, 130.6, 128.2, 123.4, 34.8. Anal. Calc. for C$_{18}$H$_{16}$Cl$_6$Ti$_2$: C, 39.98; H, 2.98. Found: C, 40.26; H, 3.20%.

2.2.2. Synthesis of (TiCl$_3$)$_2${(μ-η^5, η^5-C$_5$H$_4$-meta-(CH$_2$–C$_6$H$_4$–CH$_2$)C$_5$H$_4$}, **5**

This reaction proceeded in an analogous fashion to the above reaction with the following exceptions: α,α'-Bis(trimethyl-silyl)cyclopentadienyl-*meta*-xylene (**3m**) was used in place of **3o**. α,α'-Bis(trimethylsilyl)cyclopentadienyl-*meta*-xylene (**3m**) was synthesized according to literature methods [22]. Purification re-sulted in a greenish yellow solid of **5**.

Compound **5**: Yield: 2.81 g (66%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.15 (s, 4H, C$_6$H$_4$), 6.93 (t, 4H, C$_5$H$_4$), 6.78 (t, 4H, C$_5$H$_4$), 4.16 (s, 4H, CH$_2$); ^{13}C NMR (CDCl$_3$): δ 142.8, 138.3, 129.5, 127.8, 123.7,

37.6. Anal. Calc. for C$_{18}$H$_{16}$Cl$_6$Ti$_2$: C, 39.98; H, 2.98. Found: C, 40.18; H, 3.41%.

### 2.2.3. Synthesis of {Ti(O-2,6-iPr$_2$C$_6$H$_3$)Cl$_2$}$_2${(μ-η^5, η^5-C$_5$H$_4$-ortho-(CH$_2$-C$_6$H$_4$-CH$_2$)C$_5$H$_4$}, **7**

To a solution of **4** (1.0 g, 1.8 mmol) in methylene chloride was added Li(O-2,6-iPr$_2$C$_6$H$_3$) (0.72 g, 3.6 mmol) at -30 °C. The solution was warmed to RT slowly and stirred overnight. The solvent was then removed *in vacuo* to leave a dark orange residue that was ex-tracted into hexane, separated, and recrystallized from hexane at -30 °C to give the final product as a light orange solid.

Compound **7**: Yield: 0.62 g (42%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.12 (s, 4H, C$_6$H$_4$), 7.09 (m, 6H, C$_6$H$_3$), 6.44 (t, 4H, C$_5$H$_4$), 6.37 (t, 4H, C$_5$H$_4$), 4.22 (s, 4H, CH$_2$), 3.24 (m, 4H, CH), 1.25 (d, 24H, CH$_3$); ^{13}C NMR (CDCl$_3$): δ 164.2, 138.9, 138.3, 137.0, 130.3, 127.6, 124.6, 123.4, 120.9, 120.0, 34.1, 26.9, 23.6. Anal. Calc. for C$_{42}$H$_{50}$Cl$_4$Ti$_2$O$_2$: C, 61.19; H, 6.11%. Found: C, 61.04; H, 6.04%.

2.2.4. Synthesis of {Ti(O-2,6-iPr$_2$C$_6$H$_3$)Cl$_2$}$_2${(μ-η^5, η^5-C$_5$H$_4$-meta-(CH$_2$–C$_6$H$_4$–CH$_2$)C$_5$H$_4$}, **8**

A method similar to those used to make **7** was also applied. The only exception was introduction of **5** in place of **4**. The final product **8** was separated in 45% yield as a pale orange solid.
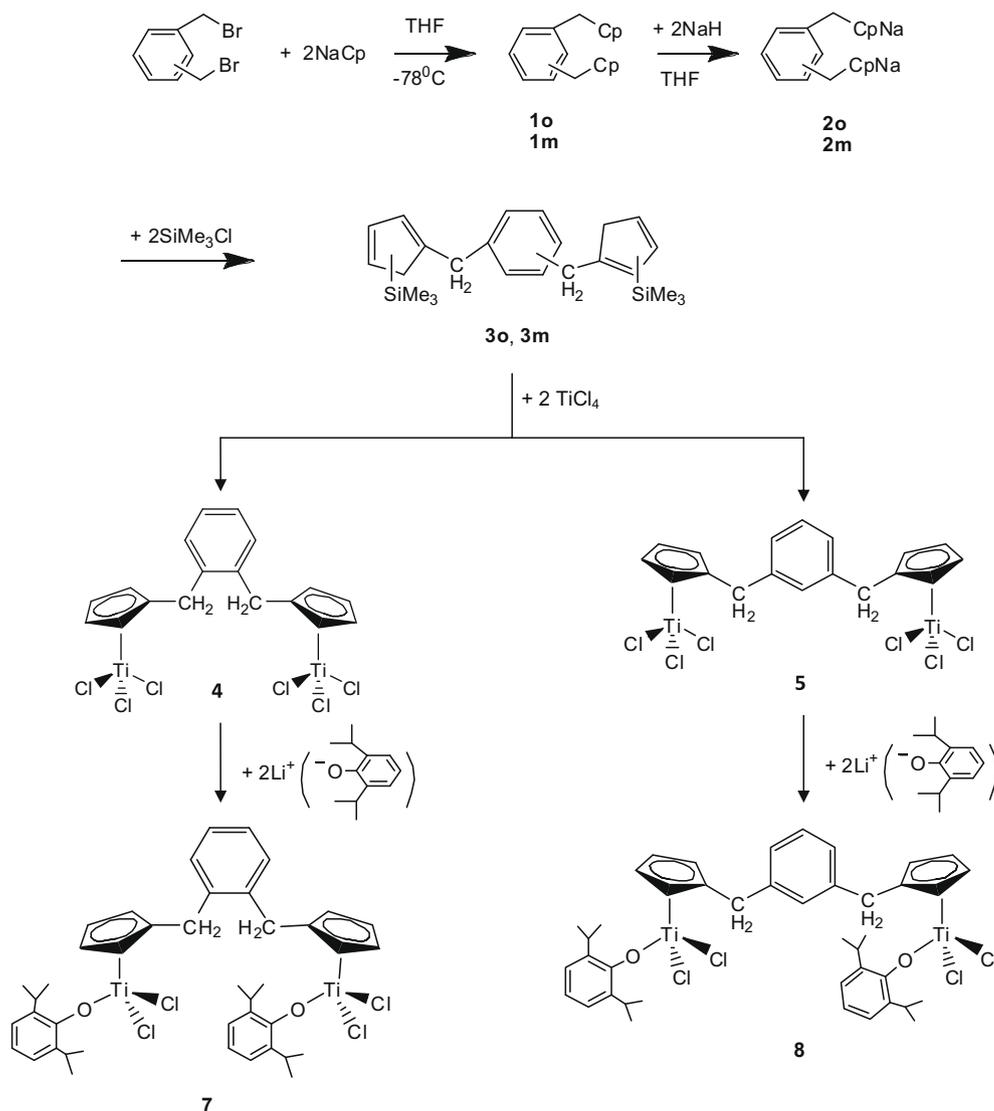
Scheme 2. Synthesis of dinuclear half-titanocenes.

Compound **8**: Yield: 0.66 g (45%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.14 (s, 4H, C$_6$H$_4$), 7.08 (m, 6H, C$_6$H$_3$), 6.45 (t, 4H, C$_5$H$_4$), 6.37 (t, 4H, C$_5$H$_4$), 4.22 (s, 4H, CH$_2$), 3.24 (m, 4H, CH), 1.25 (d, 24H, CH$_3$); ^{13}C NMR (CDCl$_3$): δ 164.2, 138.9, 138.3, 137.1, 130.4, 127.7, 124.6, 123.4, 121.0, 120.0, 34.1, 27.0, 23.6. Anal. Calc. for C$_{42}$H$_{50}$Cl$_4$Ti$_2$O$_2$: C, 61.19; H, 6.11. Found: C, 61.50; H, 6.55%.

2.3. Styrene polymerization

Polymerizations were carried out in a 300-mL Schlenk flask. The reactor was filled with the proper amount of toluene, MMAO, and styrene. Polymerization was initiated by injection of the catalyst. After 1 h, polymerization was stopped by adding 10% acidified methanol. Polymers were filtered and washed with methanol and dried under vacuum to a constant weight. The SPS was separated by removing atactic PS *via* extraction using refluxing MEK for 24 h and the ratio of the separated SPS to the total polystyrene was defined as syndiotactic index (SI). The insoluble portions after the extraction were dried under vacuum and analyzed by the instrument.

3. Results and discussion

3.1. Synthesis and characterization

Dinuclear half-titanocenes with *ortho*- and *meta*-xylene bridges, (TiCl$_2$L)$_2${(μ-η^5, η^5-C$_5$H$_4$-*ortho*-(CH$_2$–C$_6$H$_4$–CH$_2$)C$_5$H$_4$} (**4** (L = Cl), **7** (L = O-2,6-iPr$_2$C$_6$H$_3$)) and (TiCl$_2$L)$_2${(μ-η^5, η^5-C$_5$H$_4$-*meta*-(CH$_2$–C$_6$H$_4$–CH$_2$)C$_5$H$_4$} (**5** (L = Cl), **8**(L = O-2,6-iPr$_2$C$_6$H$_3$)), were conveniently prepared in modest yields (40–70%) by treating the respective trimethylsilyl derivatives of the ligands with 2.0 eq of TiCl$_4$ in methylene chloride as shown in Scheme 2. The preparative route to obtain new compounds was different from the synthetic procedure to make the corresponding catalyst with a *para*-xylene bridge [14]. It was found that biscyclopentadienyls connected through *ortho*- or *meta*-xylene **1o** and **1m** gave rise to the formation of polymeric structure which was difficult to be separated as a stable compound. The best way to overcome these complications was to conduct a one-pot reaction from the first step to the third step to form trimethylsilyl derivatives **3o** and **3m** without separation of any intermediate compound [23,24]. *In situ* reaction of **1o** and **1m** with excess sodium hydride readily produced the dianion species **2o** and **2m**, respectively, conveniently recognizable due to the vigorous evolution of hydrogen gas. Reaction of the corresponding disodium salts with SiMe$_3$Cl yielded **3o** and **3m**, stable enough to be separated for identification. Methylene chloride was an effective solvent for the reaction between ditrimethylsilyl derivatives **3** and TiCl$_4$. At -78 °C in methylene chloride, catalysts **4** and **5** were formed by the reaction of the trimethylsilyl derivatives of complexes **3o** and **3m** with 2.0 eq of TiCl$_4$ in about 65% yield [24]. Preparation of aryloxo-substituted, xylene-bridged, dinuclear half-titanocenes **7** and **8** were achieved in 50% yield by treating catalysts **4** and **5** with 2.0 eq of the corresponding aryloxo lithium salts for 15 h at RT. For reactivity comparison, the dinuclear half-titanocenes **6** and **9** with pentamethylene bridges were also synthesized. Catalysts **4**, **5**, **7**, and **8** were characterized by ^{1}H- and ^{13}C NMR, and elemental analysis.

The NMR spectrum of catalyst **4** indicates the predicted resonances for the bridging *meta*-xylene-biscyclopentadienyl ligand that appears as: two sets of pseudotriplets at 6.86 and 6.68 ppm due to the AA′BB′ system of cyclopentadienyl protons; a singlet at 4.14 ppm for methylene protons; a multiplet between 7.00 and 7.20 ppm for phenyl protons. The ^{1}H NMR spectrum of catalyst **5** exhibited a slight difference from catalyst **4** (Experimental section). Formation of aryloxo compounds **7** and **8** was quite easily

identified by ^{1}H- and ^{13}C NMR spectra. Resonances of the isobutyl group of **7** and **8** appeared at 3.24 ppm (septet) and 1.25 ppm (doublet), assigned to CH and two CH$_3$, respectively. The most distinctive change in the proton NMR spectrum due to aryloxo substitution at titanium was represented by the chemical shift change of protons at the cyclopentadienyl ring, as well as the value of $\delta\delta = [\delta_d - \delta_p]$, the chemical shift difference between the distal and proximal protons in the cyclopentadienyl ring. Chemical shifts of the cyclopentadienyl protons of catalyst **7** were moved to 6.44 and 6.37 ppm from 6.86 and 6.68 ppm of those of catalyst **4**, indicating that aryloxo substitution caused a 0.42 and 0.31 ppm upfield shift of cyclopentadienyl protons. This may be understood by the electron density increase around the metal center due to the superb electron pushing power of the aryloxo group. The value of $\delta\delta = [\delta_d - \delta_p]$ of catalyst **4** was 0.18 ppm, much larger than 0.07 ppm of catalyst **7**. This kind of trend was seeing between catalysts **5** and **8** as well. A detailed correlation of the values of $\delta\delta$ with the geometric characteristics of dinuclear metallocene may not be simply overviewed, but one point was noted. The large $\delta\delta$ value for the dinuclear metallocene displayed the relatively small steric interactions around the metal center due to the enlarged separation between the connected cyclopentadienyl rings [20]. It is not so unreasonable that the reduced $\delta\delta$ value of compounds **7** and **8** were merely the reflection of the aryloxo group, larger than the chloride, leading to more substantial steric interactions around the titanium.

3.2. Polymerization

In order to probe the catalytic properties of the prepared catalysts, styrene polymerization was conducted in the presence of MMAO with pentamethylene bridged dinuclear half-titanocenes **6** and **9**, and simultaneously examined for comparison. In a series of experiments, the catalysts were used in toluene at 25, 40, and 70 °C, at two ratios of [Al]:[Ti]; the results are summarized in Table 1. Table 1 reveals that the catalytic activity of the six catalysts increased in the order of **6** (232) < **9** (376) < **4** (398) < **5** (450) < **7** (501) < **8** (603) at 70 °C, [Al]:[Ti] = 4000 (activity unit = kg of polymer/(mol of Ti-h). At 40 °C, this tendency remained unchanged; however, abnormal activity data came from the experiment at 25 °C, probably due to an irregular initiation rate of the catalysts. This result exhibited a very meaningful implication that the geometric characteristics might play a significant role in directing the catalytic activity of the dinuclear half-titanocenes with the isomeric xylene bridge. Firstly, four xylene bridged catalysts displayed much higher activity than the two pentamethylenes. Activities of catalysts **4**, **5**, **7**, and **8** with a xylene bridge were at least 1.5 times larger than those of catalysts **6** and **9** with pentamethylene bridges, at a [Al]:[Ti] ratio of 4000 at 40 and 70 °C. Secondly, *meta*-xylene bridged catalysts exhibited much higher activities than the corresponding *ortho*-xylene bridged catalysts. For instance, activity of **5** with a [Al]:[Ti] ratio of 4,000 and a 70 °C polymerization temperature was 450 kg of polymer/(mol of Ti-h), larger than the activity of **4**, 398 kg of polymer/(mol of Ti-h). Thirdly, regardless of the bridge nature of the catalysts, having an aryloxo substituent at the titanium represented much larger activities than those having chloride at the titanium. Catalysts **7**, **8**, and **9** with an aryloxo group showed 20–60% higher activity than catalysts **4**, **5**, and **6** with chloride.

The different activity trend between the xylene and pentamethylene linkages may be understood both by steric and electronic factors. It is not surprising that the presence of a xylene bridge can deliver more electrons to the metal center than the linear pentamethylene bridge [14,15]. Electron density increase to the active site should lead to an increase in activity. In terms of steric circumstances, the most principal difference of xylene from pentamethyl-

Table 1
Results of styrene polymerization using the new dinuclear half-titanocene catalysts.

Catalyst	T_p[a] (°C)	[Al]/[Ti]	Activity[b]	T_m (°C)	S.I.[c]	Mw × 10^{-3}	Mw/Mn
4	25	2000	75	267.6	92.8	105	2.8
	25	4000	186	267.3	94.7	101	2.5
	40	2000	123	267.1	90.4	70	1.8
	40	4000	286	264.8	91.1	55	1.7
	70	2000	139	262.8	90.3	50	3.6
	70	4000	398	267.1	91.6	44	3.3
5	25	2000	180	266.7	91.1	116	3.6
	25	4000	335	271.3	98.9	106	2.9
	40	2000	220	271.4	94.8	71	3.2
	40	4000	392	271.5	97.3	64	2.1
	70	2000	252	262.2	92.2	33	2.4
	70	4000	450	267.5	94.8	30	2.2
6	25	2000	102	267.9	93.4	98	2.2
	25	4000	172	264.6	96.5	86	1.9
	40	2000	112	268.3	95.5	85	1.6
	40	4000	186	262.7	97.8	76	1.8
	70	2000	137	262.1	92.3	40	1.9
	70	4000	232	263.3	94.4	37	1.8
7	25	2000	84	269.1	96.2	128	3.4
	25	4000	187	269.9	98.7	114	3.1
	40	2000	155	262.8	91.6	73	1.9
	40	4000	492	266.7	94.1	68	2.1
	70	2000	150	268.6	89.4	41	2.1
	70	4000	501	264.9	96.6	38	2.4
8	25	2000	108	270.8	97.6	114	2.4
	25	4000	223	268.9	98.6	109	3.1
	40	2000	200	263.6	92.7	83	2.1
	40	4000	582	267.5	98.8	62	2.5
	70	2000	246	269.1	93.9	38	3.3
	70	4000	603	264.9	98.9	33	2.5
9	25	2000	56	264.1	94.2	92	2.4
	25	4000	132	265.3	95.6	87	1.8
	40	2000	140	262.9	92.3	91	2.1
	40	4000	231	262.8	96.7	82	1.8
	70	2000	245	266.6	91.1	41	2
	70	4000	376	265.7	96.8	36	1.7

Reaction conditions: styrene concentration, 1.32 mol/l; [Ti] = 0.83 × 10^{-6} mol/l.
[a] T_p = Polymerization temperature.
[b] Activity = kg-polymer/mol-Ti-h-atm.
[c] S.I. = Syndiotactic index.

ene is rigidity. The xylene bridge is stiff enough to prohibit any possible intramolecular approach between the two titanium centers. Conversely, pentamethylene would have no problem allowing the approach of two titanium centers given the flexibility inherent to a carbon single bond. As a consequence, the larger activity of the catalysts bearing the xylene bridge compared to those with the pentamethylene bridge can be attribute to the increased electron density at the titanium center and less steric disturbance between the two titanium centers. It is worthwhile to point out an effect of the geometric differences between the *ortho* and *meta* linkages of the xylene on catalytic activity. It was found that *meta*-xylene bridge catalysts **5** and **8** displayed activities larger than the *ortho*-xylene bridged **4** and **7**. The range in activity differences of **5** from **4** was actually larger than those of **8** from **7**, suggesting that aryloxo substitution attenuated the geometric effect. It is not unreasonable that a widened angle of *meta* geometry, compared to *ortho* geometry, would be the reason for a faster rate of polymerization given a bigger active site. From previous work of this lab with the *para*-xylene catalyst, it was confirmed that the dinuclear half-titanocene with the *para*-xylene bridge represented the greatest activity among the three isomers, followed by the catalyst with *meta*-xylene bridge. Substituent effects of the half-titanocene on polymerization properties have been demonstrated by Nomura as well [7–9]. By substitution of chloride with the aryloxo group at the titanium of the half-titanocene, copolymerization ability was improved considerably in terms of activity as well as comonomer reactivity. Catalysts **7**, **8**, and **9** may be able to effectively delocalize the cationic charge of the active site through the phenyl ring that delivers the resonance stabilization to the active species, inducing overall activity enhancement.

It was observed that the activity of the dinuclear half-titanocenes is sensitively affected by polymerization temperature and the [Al]:[Ti] ratio. All the catalysts, irrespective of type, displayed a maximum activity at 70 °C that decreased upon lowering of polymerization temperature. Activities of catalysts **7**, **8**, and **9** at 70 °C were 2.7 times larger than those at 25 °C. Activity differences according to polymerization temperature among the catalysts with two chlorides at the titanium were much smaller than those among the catalysts with the aryloxo group. In all cases, the activities at [Al]:[Ti] = 4000 were much greater than those at 2000. With catalyst **7**, the activity at [Al]:[Ti] = 4,000 was more than three times larger than those at 2000. It should be noted that the higher activity at the higher reaction temperature with the higher amount of cocatalyst is not unusual at all.

The variation in molecular weight and molecular weight distribution does not seem to be very sensitive to catalyst structure. Among catalysts **7**, **8**, and **9**, the *ortho*-xylene bridged **7** gave rise to the formation of the highest molecular weight SPS, while SPS formed by the catalyst with the pentamethylene bridge exhibited the lowest molecular weight. Nearly identical molecular weights were found from the polymers produced by respective catalysts with the aryloxo group and chloride. Molecular weight distributions of polymers by catalysts bearing either *ortho*- or *meta*-xylene bridges ranged from 1.7 to 3.6 and were relatively wider than those

(1.8–2.4) by the catalyst bearing the pentamethylene bridge. Dependence of the molecular weights of SPS upon polymerization temperature follows the general tendency that polymerization at lower temperatures produces larger molecular weights regardless of the catalyst structure. Molecular weight of SPS generated by the xylene bridged catalysts at 25 °C ranged between 100 000 and 128 000. However, molecular weights of polymers at 70 °C ranged from 30 000 to 50 000. Effects of cocatalyst amount on molecular weight was found not to be significant, although SPS from [Al]:[Ti] = 2000 represented lower molecular weights compared to those from [Al]:[Ti] = 4000. This result illustrates that the polymerization temperature is the major element to adjust molecular weight of SPS using the catalysts in this study.

The dinuclear catalysts mentioned herein were very efficient in preparing syndiotactic polystyrene (SPS) with high stereoregularity. All the SPS possessed a syndiotactic index (SI) from 90% to 99%. When comparing SI's of the polystyrenes, it was interesting that the catalysts with the aryloxo group (**7**, **8**, **9**) seemed to form polymers with slightly higher SI values than those with the corresponding chloride group (**4**, **5**, **6**). The polymers generated by catalysts **4** and **7**, having an *ortho*-xylene bridge, exhibited syndiotacticity relatively lower than those made by catalysts bearing a *meta*-xylene bridge, as well as pentamethylene bridge. Generally speaking, the structure of the bridging ligand of the dinuclear half-titanocenes does not seem to have a crucial effect upon differentiating the stereochemical process of polymerization despite the abovementioned difference. This result can be attributed to the mechanistic property of styrene polymerization *via* half-titanocene. It is accepted that a perfect regioselective insertion of a coordinated styrene monomer to the metal-carbon bond *via* a secondary 2,1-insertion mode led to the generation of syndiotactic stereoregularity due to π-bonding of the terminal styrene unit of the growing chain to the metal center. This indicates that the stereoregular configuration is induced by a repulsing interaction between the phenyl ring of the last unit of the growing chain and the phenyl ring of the incoming monomer and accounts for the finding that in the case of syndiospecific styrene polymerization, variation of the catalyst ligand sphere has only a minor effect on polymer structure. Many homogenous metallocene catalysts were able to produce SPS with a decrease in syndiotacticity and melting temperature as polymerization temperature increased [7,8,14]. This general trend has also been demonstrated in this experiment.

4. Summary

Preparation of dinuclear half-titanocenes with *ortho*- and *meta*-xylene bridges [{Ti(η^5-cyclopentadienyl)Cl$_2$L}$_2$-*ortho*, *meta*-(CH$_2$–C$_6$H$_4$–CH$_2$)] (L = Cl (**4**, **5**), L = O-2,6-*i*Pr$_2$C$_6$H$_3$ (**7**, **8**)) has been achieved by the reaction of the respective trimethylsilyl derivatives of the ligands with 2.0 eq of TiCl$_4$ in methylene chloride. The preparative route to obtain new compounds was the improved synthetic procedure to make the corresponding catalyst with the *para*-xylene bridge. Catalysts **4**, **5**, **7**, and **8** were characterized by ^{1}H and ^{13}C NMR, and elemental analysis. The ^{1}H NMR spectrum of catalyst **4** indicated the predicted resonances for the bridging *meta*-xylene-biscyclopentadienyl ligand that appears as: two sets of pseudotriplets at 6.86 and 6.68 ppm due to the AA'BB' system of the cyclopentadienyl protons; a singlet at 4.14 ppm for the methylene protons; a multiplet between 7 and 7.20 ppm for the phenyl protons. Chemical shifts of the cyclopentadienyl protons of catalyst **7** moved to 6.44 and 6.37 ppm from 6.86 and 6.68 ppm of those of catalyst **4**, indicating that aryloxo substitution

caused a 0.42 and 0.31 ppm upfield shift of the cyclopentadienyl protons. It is suggested that the reduced value of δ of compounds **7** and **8** likely reflects the larger size of the aryloxo group over the chloride that lead to greater steric interaction around the titanium. The catalytic activity of the six catalysts increased in the order of **6** < **9** < **4** < **5** < **7** < **8**, at 40 and 70 °C, [Al]:[Ti] = 4000 (activity unit = kg of polymer/(mol of Ti-h). This result was understood as the geometric characteristics of the catalysts due to the presence of the *ortho*- and *meta*-xylene bridge. The different activity trend between the xylene and pentamethylene linkage may be understood both by steric and electronic factors. The variation in molecular weight and molecular weight distribution does not seem to be very sensitive to catalyst structure. The *ortho*-xylene bridged **7** gave rise to the formation of the highest molecular weight SPS while the SPS formed by the catalyst with the pentamethylene bridge exhibited the lowest molecular weight. All the SPS generated in this study possessed a syndiotactic index (SI) from 90% to 99%. It was found that the polymers generated by catalysts **4** and **7** having the *ortho*-xylene bridge exhibited relatively lower syndiotacticity than the others made by the catalysts with the *meta*-xylene bridge, as well as the pentamethylene bridge. Generally speaking, the structure of the bridging ligand of the dinuclear half-titanocenes does not seem to have a crucial effect upon differentiating the stereochemical process of polymerization.

Acknowledgements

References

[1] R. Po, N. Cardi, Prog. Polym. Sci. 21 (1996) 47–88.
[2] J. Cano, K. Kunz, J. Organomet. Chem. 692 (2007) 4411.
[3] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, Macromolecules 19 (1986) 2465.
[4] N. Tomotsu, N. Ishihara, T.H. Newman, M.T. Malanga, J. Mol. Catal. A 128 (1998) 167.
[5] P. Longo, A. Proto, A. Zambelli, Macromol. Chem. Phys. 196 (1995) 3015.
[6] N. Tomotsu, N. Ishihara, Catal. Surv. Jpn. 1 (1997) 89.
[7] H. Zhang, K. Nomura, J. Am. Chem. Soc. 127 (2005) 1.
[8] H. Zhang, K. Nomura, Macromolecules 39 (2006) 5266.
[9] K. Itagaki, M. Fujiki, K. Nomura, Macromolecules 40 (2002) 6489.
[10] Dong-ho Lee, Seok Kyun Noh, Curr. Trend Polym. Sci. 8 (2003) 223.
[11] L. Li, M.V. Metz, H. Li, M.C. Chen, T.J. Marks, L. Liable-Sands, A. Rheingold, J. Am. Chem. Soc. 124 (2002) 12725.
[12] N.T.L. Thanh, S.K. Noh, W.S. Lyoo, D.H. Lee, Chin. J. Polym. Sci. 26 (5) (2008) 611.
[13] S.K. Noh, S. Kim, Y. Yang, W.S. Lyoo, D.H. Lee, C. Lee, Eur. Polym. J. 40 (2004) 227.
[14] S.K. Noh, W. Jung, H. Oh, Y.R. Lee, W.S. Lyoo, J. Organomet. Chem. 691 (2006) 5000.
[15] D.H. Kum, W. Jung, K. Kim, S.K. Noh, D.H. Lee, W.S. Lyoo, Polymer (Korea) 30 (1) (2006) 64.
[16] J. Jung, S.K. Noh, D.H. Lee, S.K. Park, H.J. Kim, J. Organomet. Chem. 595 (2000) 147.
[17] S.K. Noh, J. Kim, J. Jung, C.S. Ra, D.H. Lee, H.B. Lee, S.W. Lee, W.S. Huh, J. Organomet. Chem. 580 (1999) 90.
[18] S.K. Noh, S. Kim, J. Kim, D.H. Lee, K.B. Yoon, H.B. Lee, S.W. Lee, W.S. Huh, J. Polym. Sci., Part A: Polym. Chem. 35 (1997) 3717.
[19] T. Cuenca, J.C. Flores, R. Gomez, P. Gomez-sal, M. Parra-Hake, P. Royo, Inorg. Chem. 32 (1993) 3608.
[20] S. Ciruelos, T. Cuenca, J.C. Flores, R. Gomez, P. Gomez-sal, P. Royo, Organometallics 12 (1993) 944.
[21] J.C. Flores, T.E. Ready, J.C.W. Chien, M.D. Rausch, J. Organomet. Chem. 562 (1998) 11.
[22] M.H. Lee, S.K. Kim, Y. Do, Organometallics 24 (2005) 3618.
[23] X. Liu, J. Sun, H. Zhang, X. Xiao, F. Lin, Eur. Polym. Sci. 41 (2005) 1519.
[24] L. Resconi, F. Piemontesi, I. Cumurati, O. Sudmeijer, I.E. Nifan'ev, P.V. Ivchenko, L.G. Kuz'mina, J. Am. Chem. Soc. 120 (1998) 2308.
[25] J. Kuwabara, D. Takeuchi, K. Osakada, Organometallics 24 (2005) 2705.