

## Synthesis and styrene polymerization properties of dinuclear half-titanocene complexes with xylene linkage

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### Abstract

The new dinuclear half-sandwich complexes of titanium with xylene bridge,  $[\text{Ti}(\eta^5\text{-cyclopentadienyl})\text{Cl}_2\text{L}]_2[\text{CH}_2\text{-C}_6\text{H}_4\text{-CH}_2]$  ( $\text{L} = \text{Cl}$  (**3**),  $\text{L} = \text{O-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3$  (**4**),  $\text{L} = \text{N}(\text{SiMe}_3)(2,6\text{-Me}_2\text{C}_6\text{H}_3)$  (**5**)), have been synthesized. The complexes **4** and **5** have been prepared by the reaction of the complex **3** with the corresponding lithium salts of aryloxy and anilide. Structure of these complexes has been characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The change of substituent from chloride, **3**, to anilide, **5**, at titanium resulted in chemical shift change of cyclopentadienyl protons from 6.92 and 6.79 to 6.13 and 5.95 ppm probably due to the positive electron density delivery from the anilide group. It was found that all three half-titanocenes were effective catalyst for the generation of SPS (syndiotactic polystyrene). Xylene bridged dinuclear catalyst (**4**) with aryloxy substituent exhibited very high activity (458 kg of SPS/(mol of  $[\text{Ti}]_h$ ), at 40 °C, whereas the analogous hexamethylene bridged dinuclear half-titanocene catalyst (**7**) showed a lower activity (80.7 kg of SPS/(mol of  $[\text{Ti}]_h$ ) under the same conditions. While the catalyst **3** was the most active catalyst among three complexes less than 40 °C the catalyst **5** exhibited the highest activity at 70 °C. Xylene linkage was suggested to be too stiff to permit any kind of intramolecular interaction between two active centers. Lack of steric disturbance due to the rigidity of the xylene bridge might give rise to the similar properties of dinuclear metallocene to the corresponding mononuclear metallocene to result in not only the facile coordination of monomer at the active center to lead high activity but also the easier  $\beta\text{-H}$  elimination comparing to the dinuclear catalysts with the flexible bridge to result in the formation of lower molecular weight polymer.

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### 1. Introduction

After the first finding of syndiotactic polystyrene (SPS) in 1985, the preparation of SPS has gained much interest in the last 20 years particularly in catalyst and polymerization study to lead to a fast commercialization of this polymer [1–4]. Since 1985, a variety of titanium compounds have been examined for their ability to produce SPS in the presence of methylaluminoxane (MAO). As a result of these researches, it turned out that the half-titanocene compounds based on  $\text{Cp}'\text{TiX}_3$  showed high polymerization activities for styrene at high degrees of syndiotacticity [5–

7]. A comparison of the polymerization property of titanium half-titanocenes according to  $\text{Cp}'$  (cyclopentadienyl) derivatives revealed that  $\text{Cp}^*$  (pentamethylcyclopentadienyl) derivatives gave a higher degree of stereoregularity, much higher molecular weights and predominantly an increased polymerization activity. This consequence of the  $\text{Cp}^*$  complex in relation to the Cp (unsubstituted cyclopentadienyl) complex was able to be understood by a better stabilization of the electron deficient active site by  $\text{Cp}^*$ , which is a stronger electron donor than Cp. Recently, the utility of titanium-based half-metallocene with a variety of substituents at the metal such as aryloxy, amide, ketimide as an olefin polymerization has been investigated extensively [7–12]. These studies demonstrate clearly that the effect of substituents on both Cp and titanium plays

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an essential role not only for the catalytic activity but also for monomer reactivities in styrene polymerization as well as ethylene copolymerization.

Recently a variety of dinuclear compounds, which contain two mechanically linked metallocene units, have been prepared to examine their catalytic properties [13,14]. We have been interested in investigating the properties of dinuclear metallocenes, since these metallocenes are able to offer the opportunity of cooperative effects between two active sites which could be potentially utilized to discover a new class of catalysts for olefin polymerization [15–19]. In reality the dinuclear metallocene systems displayed not only the distinguished characters from the well-defined mononuclear metallocenes, but also a strong influence upon the nature of the bridging ligand. Differently from the other metallocene catalysts polymerization properties of the dinuclear complex that holds two half-titanocene fragments through the bridging ligand have not been explored until very recently. The initial attempt to exploit dinuclear half-titanocene was performed by Royo although he did not pay attention to the styrene polymerization study [20,21]. Flores and coworkers described the synthesis of the dinuclear half-titanocenes with indenyl as a Cp derivative and ethylene as a bridge and study of the effects on activity and syndiospecificity resulting from possible cooperative chemical behavior between two active centers [22]. It turned out that the activity for the dinuclear half-titanocenes is one order of magnitude lower than that for the mononuclear half-titanocene [22]. On the contrary, Do and coworkers reported recently that the activity of dinuclear half-titanocene with two phenyl spacer were actually similar to the mononuclear half-titanocene, which demonstrated clearly the nature of the bridging unit in dinuclear metallocene played a significant role to exhibit the characteristics of the catalyst [23].

An extensive polymerization study with the dinuclear half-titanocene has been probed by our group in recent years [15–19]. According to the polymerization results some noticeable points have been revealed to display that the effects of bridge structure exerted a major influence on catalyst properties.

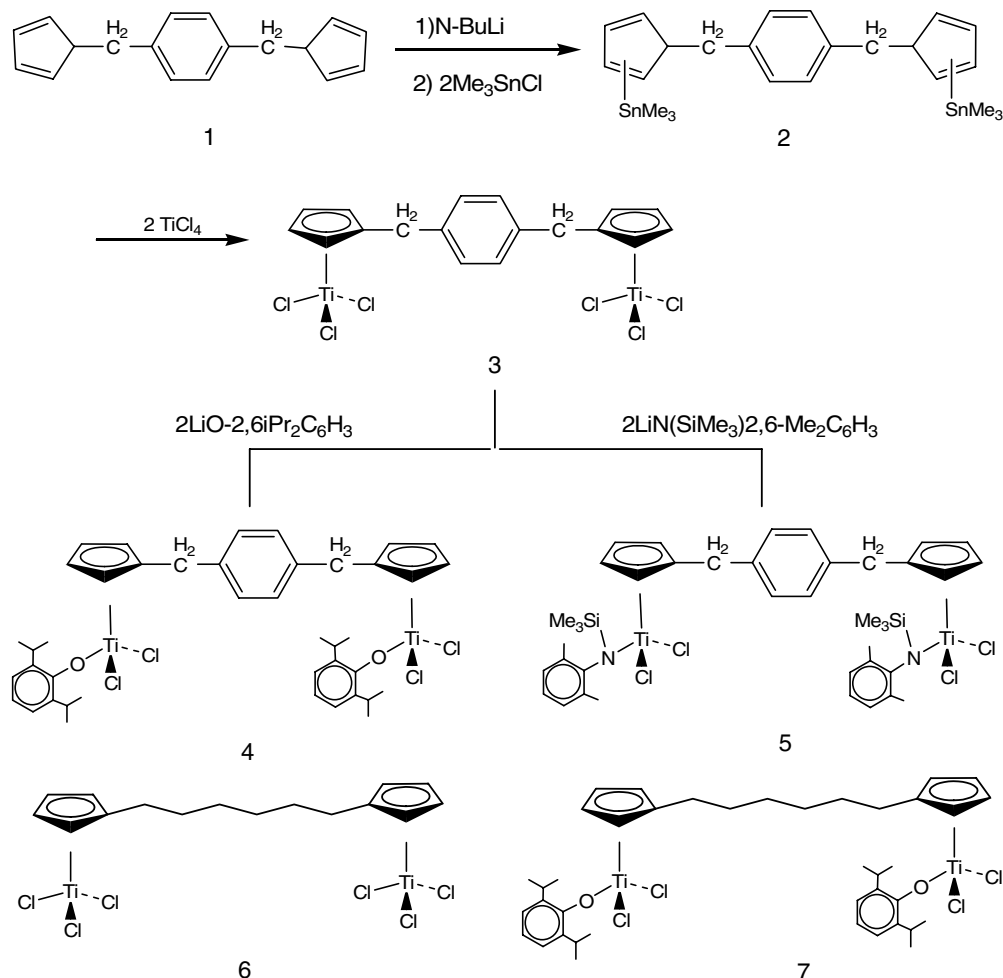
In this paper we report efficient synthetic route to dinuclear half-titanocenes with xylene bridge as a new dinuclear metallocene and the results of styrene polymerization using these catalysts with the emphasis on the nature of bridging ligand. This research has been designed to figure out how the bridge stiffness can operate on the property of the dinuclear half-titanocene.

## 2. Results and discussion

### 2.1. Synthesis and characterization of dinuclear half-titanocene

Preparation of three dinuclear half-titanocenes distinguished by the substituent at titanium center has been achieved satisfactorily by the procedure as shown in

**Scheme 1.** Xylene-bridged dinuclear half-titanocene **3** is prepared by the reaction of distannylated derivative [24] of the ligand **2** with 2 equiv. of  $\text{TiCl}_4$  in toluene at  $0^\circ\text{C}$  followed by 4 h reaction after warming the reaction mixture to room temperature (**Scheme 1**). The complexes **4** and **5** were prepared by treating the catalyst **3** with 2 equiv. of the corresponding lithium salts of aryloxy and anilide compound in proper solvent for 10 h at RT respectively. Accordingly all three dinuclear half-titanocenes were able to be prepared in about 50% yields. These catalysts are sensitive to moisture and separated as a orange solid. For comparison the known hexamethylene bridged dinuclear half-titanocenes **6** and **7** have also been made [19]. The dinuclear metallocenes **3**, **4**, and **5** are characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, and mass spectrometry.  $^1\text{H}$  NMR spectra of the complexes **3**, **4**, and **5** have been utilized conveniently to identify the assigned dinuclear half-metallocene structure. The proton NMR spectra of these compounds show two well separated triplet resonances in the vinyl region. The two triplets exhibited 6.92 and 6.79 ppm for **3**, 6.49 and 6.39 ppm for **4**, and 6.13 and 5.95 ppm for **5** are assigned as the four protons residing on Cp ring fragment. The most significant feature is the change of chemical shift of Cp ring protons as shown above by changing the substituent at titanium. Switching chloride of **3** to oxygen of **4** resulted in 0.5 ppm highfield shift of Cp protons. This tendency was sustained by converting oxygen of **4** into nitrogen of **5**. This feature is actually good indication of the half-titanocene complex formation with the more electron supply since the donation of more electrons by the substituent change from chloride to aryloxy and anilide group should cause a greater shielding effect for the catalyst. Presence of sharp singlet at 4.16 ppm for **3** indicated four protons of methylene protons between Cp and phenyl ring. The direction of chemical shift change is in accord with that of the Cp ring protons toward the highfield by changing substituent pattern. The  $^{13}\text{C}$  NMR spectra of the complexes demonstrate the mentioned structural feature as well. The important point associated with the chemical shift is the downfield chemical shift around 140 ppm from the bridgehead *ipso*-carbon of Cp ring connected to xylene bridging ligand. It is known that the  $^{13}\text{C}$  resonance due to Cp ring bridgehead carbon appears to be sensitive to the mode of coordination of the ligand. For most dinuclear transition metal derivatives containing Cp ring as a part of the bridging unit, the  $^{13}\text{C}$  resonance of Cp ring bridgehead carbon is typically found downfield from the other carbon resonances, which are less sensitive to the mode of coordination. In our case this suggestion is actually very well accord with the observation, that in all of three new complexes the chemical shifts of the bridgehead carbons exhibited downfield near 140 ppm. The EI mass spectra for the dinuclear half-titanocenes **3–5** were very informative and convenient to identify their composition, because in all of these compounds there are multiple chlorines showing a second isotope appearance in the mass spectra. The peaks for the molecu-



Scheme 1.

lar ions ( $m/e$  540.77 of **3**;  $m/e$  824.39 of **4**;  $m/e$  854.57 of **5**) are obviously recognized from the characteristic isotope ratios of the ions separated two mass units principally due to the presence of six (the catalyst **3**) and four (the catalysts **4** and **5**) chlorides.

## 2.2. Polymerization of styrene

Half-titanocene is well-known as an excellent catalyst when activated with methylaluminoxane (MAO) for the preparation of SPS [3]. In order to investigate the catalytic behaviors of the dinuclear half-titanocenes **3**, **4**, and **5** along with the hexamethylene bridged catalysts **6** and **7** these were delivered for the polymerization of styrene in the presence of MMAO ([Al]/[Ti] ratio of 2000 and 4000). A series of styrene polymerization runs have been carried out at three different temperatures and the results are shown in Table 1 and Fig. 1.

### 2.2.1. Polymerization activity

The catalytic activity with five dinuclear half-titanocenes increased in the order of **5** < **6** < **7** < **3** < **4** below 40 °C, which illustrated that the activity of dinuclear half-titanoc-

enes seemed to be compounded by a variety of factors such as reaction temperature, structure of bridge and character of substituent at metal. The prime feature concerned with the catalytic activity was the manifested difference between xylene and hexamethylene bridge. The catalysts (**3** and **4**) with xylene as a bridge represented greater activity than those (**6** and **7**) with hexamethylene bridge except the catalyst **5** containing anilide substitution. Activities of the catalyst **3** (722 kg-polymer/mol-Ti-h-atm.) and **4** (819 kg-polymer/mol-Ti-h-atm.) with xylene bridge are approximately 2–3 times larger than those of the catalyst **6** (250 kg-polymer/mol-Ti-h-atm.) and **7** (450 kg-polymer/mol-Ti-h-atm.) with six methylene bridge at 40 °C. This can be explained by the factor that the more electron density delivered by the adoption of xylene group as a link would stabilize the electron deficient active site more efficiently in some extent to give a greater polymerization rate. This observation may imply that the property of bridging ligand does play an important role in determining polymerization activity of the dinuclear metallocene which is actually well in accord with the reported results [15,18]. The different polymerization behavior represented by the xylene bridged catalyst from the hexamethylene bridged one may

Table 1  
Results of styrene polymerization by use of the dinuclear half-titanocenes

Catalyst	$T_p^a$ (°C)	[Al]/[Ti]	Activity <sup>b</sup>	SI <sup>c</sup>	$M_w$ ( $\times 10^{-4}$ )	$M_w/M_n$
3	25	2000	87	90.2	17.5	2.3
	25	4000	283	93.2	14.5	2.2
	40	2000	277	91.3	11.4	2.1
	40	4000	722	90.0	11.5	2.0
	70	2000	253	91.1	4.48	2.5
	70	4000	639	90.6	4.25	1.4
4	25	2000	108	91.1	17.6	2.3
	25	4000	627	96.2	13.2	2.1
	40	2000	458	97.4	10.9	2.4
	40	4000	819	91.2	10.7	2.1
	70	2000	169	93.3	3.8	3.0
	70	4000	699	91.3	3.8	2.9
5	25	2000	24	93.8	19.1	1.7
	25	4000	36	91.6	17.1	1.6
	40	2000	84	94.3	10.7	2.0
	40	4000	277	94.5	10.2	2.2
	70	2000	361	90.2	3.1	2.3
	70	4000	421	90.7	4.0	2.3
6	25	2000	110	95.3	23.1	2.1
	25	4000	198	93.8	21.6	2.0
	40	2000	128	91.4	15.0	1.7
	40	4000	250	93.7	13.3	1.9
7	25	2000	132	97.0	21.4	2.6
	25	4000	200	94.2	17.3	2.5
	40	2000	220	97.1	14.3	2.8
	40	4000	450	95.8	14.4	2.5

Reaction condition: styrene, 4.58 ml; catalyst,  $0.83 \times 10^{-6}$  mol (2  $\mu$ mol/ml of toluene); MAO, 4.1 wt%.

<sup>a</sup>  $T_p$  = Polymerization temperature.

<sup>b</sup> Activity = kg-polymer/mol-Ti-h-atm.

<sup>c</sup> SI = Syndiotactic index.

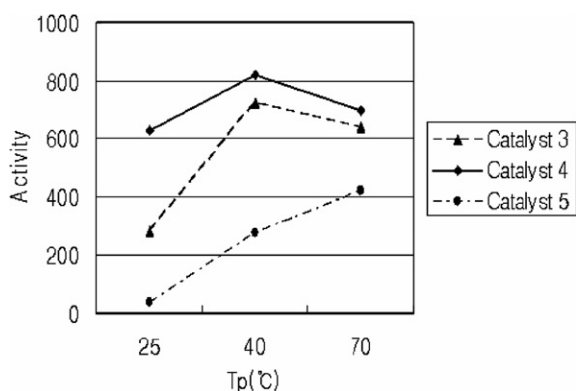
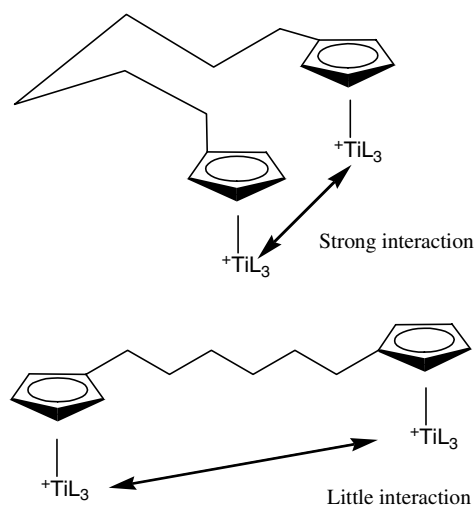


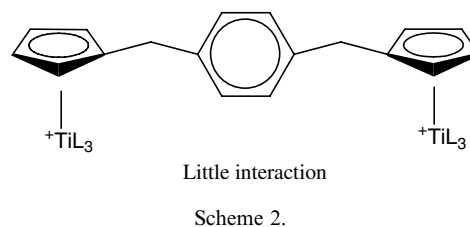
Fig. 1. Correlation of activity with the polymerization temperature of the catalysts 3, 4, and 5. [Al]/[Ti] = 4000;  $A$  = activity (kg-polymer/mol-Ti-h-atm.);  $T_p$  = polymerization temperature.

also be interpreted by the steric factor as well as the electronic factor. The biggest distinctive feature between xylene and hexamethylene bridge would be a rigidity. Xylene linkage is so stiff enough to prevent any kind of intramolecular interaction between two metal centers (Scheme 2). On the contrary hexamethylene is sufficiently flexible to draw a close contact of two active centers. This contact is able to

Hexamethylene bridged dinuclear half – titanocene



Xylene bridged dinuclear half – titanocene



provide not only the opportunity to transfer electronic information of the active site from one side to the other but also the perturbation effect to reduce a monomer coordination opportunity to the vacant site to slow down the propagation rate. On this basis it is not so surprising to anticipate that the dinuclear half-titanocenes 3 and 4 with xylene bridge experience more electron supply at the same time less steric perturbation to lead the higher activity than the catalysts 6 and 7.

Another important observation related to the activity of dinuclear half-titanocenes is that the activity is sensitively affected by the property of substituent at titanium center. Table 1 shows the relation between polymerization activities and polymerization temperature according to the substitution pattern at titanium of the catalysts. It is worthwhile to notice that the catalyst 5 holding anilide group at titanium with xylene bridge displays particularly lower activity (277 kg-polymer/mol-Ti-h-atm.) than the other four catalysts at 40 °C. Interestingly, the activity of the catalyst 5 exhibited a steady increase (421 kg-polymer/mol-Ti-h-atm.) according to the polymerization temperature rising (Fig. 1). On the other hand, the activities of 3 and 4 with chloride and aryloxy group at titanium, respectively, displayed a descending pattern by the poly-

merization temperature rising, which is an opposite temperature dependence to the catalyst **5** [10]. In addition, with the identical bridge ligand the catalysts **4** and **7** having aryloxy substituent at titanium showed much higher activities than the catalysts **3** and **6** having chloride group. This might be understood by the implication that the substituent factor along with the bridge factor may exert a significant influence on the polymerization behavior of the dinuclear half-titanocene. Substituent effect of half-titanocene on polymerization properties has been demonstrated very well by Nomura [8–12]. By the substitution of chloride to aryloxy group at titanium of half-titanocene copolymerization ability has been improved considerably in terms of activity as well as comonomer reactivity. Consequently, the activity progress resulted from the aryloxy substitution in our study can be understood as a coincident outcome in the activity tendency regardless of dinuclearity of the half-titanocene [8–12]. In spite of the excellent copolymerization property half-titanocene revealed a critical drawback for the practical application. It turned out that the system of aryloxy or anilide substituted half-titanocene was extremely sensitive to the polymerization temperature probably due to the partial decomposition of catalytically active species above 40 °C. However, our case represented that the presence of anilide at titanium was found to be beneficial to improve thermal stability of the dinuclear half-titanocene. Concerning the effect of nitrogen substitution at titanium center on thermal stability of the metallocene, it is known that CGC (constrained geometry catalyst) constituted by the nitrogen–titanium bond along with Cp–titanium bond is one of the most stable catalysts thermally. At this moment the authors do not have a firm evidence to answer the reason why dinuclear half-titanocene showed a different thermal dependence from the normal half-titanocene just with the anilide group at metal.

### 2.2.2. Stereoregularity and molecular weight

Influence of the catalyst structure and polymerization condition on SI can be indicated. It was observed that there was little noticeable trend between the catalyst structure and syndiotacticity of the formed SPS, which is actually not only unusual but also entirely dissimilar outcome to the occasion for the activity. As shown in Table 1 regardless of both the catalyst structure and polymerization temperature very high degree (SI > 90%) of SPS were still able to be manufactured by use of all five dinuclear half-titanocenes **3–7**. These results suggest that the structure of the bridging ligand of the dinuclear half-titanocenes does not seem to have a crucial effect to differentiate stereochemical process of polymerization.

Contrary to the stereoregularity, the variation of molecular weight of SPS does seem to be very much dependent upon both catalyst structure and polymerization temperature. It is remarkable that molecular weights of SPS from the xylene bridged dinuclear half-titanocenes **3**, **4**, and **5** were significantly smaller than those of from the hexamethylene bridged catalysts **6** and **7**. At 25 °C the molecular

weight of SPS from **6** and **7** are 23,000 and 21,000, respectively, which are about 20–30% greater than 17,500 from **3** and **4**. At higher temperature polymerization molecular weight difference among the catalysts became more escalated. At 70 °C molecular weights of SPS by the catalysts containing xylene linkage became extremely low to have the range of just 3000–4000 value, which clearly represents that molecular weight of SPS by the catalyst having xylene bridge were very sensitively reflected by the polymerization temperature. These experiments illustrate that the nature of the bridge of the dinuclear half-titanocenes between two titanium centers is one of the major elements to adjust molecular weight of SPS. In addition, molecular weights of the generated SPS can be brought up to some extent as the anilide group was positioned at titanium metal. It was found interestingly that the solubility of SPS in chloroform was strongly dependent upon the structure of the catalyst employed in polymerization. For instance, SPS formed by the catalyst **6** and **7** with hexamethylene connection were well dissolved in chloroform. On the other hand, SPS prepared by the xylene bridged dinuclear half-titanocenes **3** and **4** were hardly soluble in chloroform even at the elevated temperature. In order to figure out this observation X-ray diffraction pattern of SPS has been determined. It turned out that peak intensities as well as sharpness displayed by SPS from the catalysts **3** and **4** were clearly more prominent than those from the catalysts **6** and **7**. It is believed that solubility of SPS is more dependent on the crystallinity than the molecular weight of the polymer.

The relationship of the characteristics of the dinuclear half-titanocene catalyst with both molecular weight and crystallinity of the synthesized SPS can be rationalized by the distinction of steric circumstance arisen by xylene and hexamethylene bridge. Stiffness of xylene bridge is supposed to prevent interaction between two active sites as mentioned in the previous section. On this basis it is quite reasonable to anticipate that the dinuclear half-titanocene with xylene linkage would have more frequencies to proceed  $\beta$ -H elimination to terminate propagation for the delivery of low molecular weight polymer containing vinyl end group. The produced low molecular weight SPS were expected to create well arranged crystalline structure, which is definitely resistant to be invaded by the solvent molecule. In summary, structure of the catalyst originated by the bridge nature does show a pronounced effect on not only molecular weight but also crystallinity of the formed SPS. This phenomenon is able to be understood by the stereochemical reason of the characteristics of the dinuclear half-titanocene containing xylene bridge.

### 3. Summary

The new dinuclear half-sandwich titanocenes with xylene bridge have been successfully synthesized by treating 2 equiv. of the lithium salts of aryloxy and arylamide ligands with the trichloride complex **3**. It was found that the new dinuclear half-titanocenes **4** and **5** including the catalyst **3**

were effective catalyst for the generation of SPS in the presence of MAO. In order to investigate the polymerization properties of the catalysts polymerization of styrene using the dinuclear half-titanocene has been conducted in the presence of MMAO. The important feature is that the activity increases in the order of  $6 < 7 < 3 < 4$  which indicates the presence of xylene bridge between two active sites with aryloxy group at titanium is more effective to improve polymerization activity of the dinuclear half-titanocene. This observation could be interpreted by the implication that not only the steric factor but also electronic factor may play cooperatively to guide the final polymerization properties of the dinuclear half-titanocene. In contrast to the activity the molecular weights of SPS from the xylene bridged catalysts were actually smaller than those from the polymethylene bridged ones probably due to the rigid nature of xylene group to cause a faster termination process. The other important feature for the dinuclear half-titanocene is that the activity of the catalyst was found to be sensitively affected by the substituent property at titanium. All the outcomes represent the implication that not only the electronic effect but also the steric character of the active site induced by the introduction of a rigid xylene linkage on dinuclear half-titanocene are interacting together to give rise to the final polymerization behaviors of the catalysts.

## 4. Experimental

### 4.1. General considerations

All reactions were carried out under a dry, oxygen-free atmosphere using standard Schlenk techniques with 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, toluene, and pentane were distilled from sodium-benzophenone ketyl prior to use. Sodium cyclopentadienylide (2 M solution in THF, Aldrich Co.), *n*-BuLi (2.5 M solution in hexane, Aldrich), trimethyltin chloride (Aldrich Co.), titanium chloride (Aldrich Co.), modified methylaluminoxane (MMAO, type 4, 6.4 wt.% Al, Akzo, USA) were used without further purification.  $^1\text{H}$  (300 MHz) NMR and  $^{13}\text{C}$  (75.46 MHz) NMR spectra were recorded using Bruker DPX-300 FT-NMR spectrometer. Mass spectra were performed on Autospec-Ultima E. IR spectra were recorded on Jasco FT/IR-5300 spectrophotometer between 4000 and  $200\text{ cm}^{-1}$ .

Molecular weight and molecular weight distribution were measured by Waters GPC (Alliance GPC 2000) with polystyrene gel column (Styragel HT 3, 4, 5) at  $140\text{ }^\circ\text{C}$  using 1,2,4-trichlorobenzene. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples. Differential scanning calorimetric (DSC) data were recorded by Pyris 6 DSC (Perkin Elmer) under nitrogen atmosphere [conditions: heating from 25 to  $300\text{ }^\circ\text{C}$  ( $20\text{ }^\circ\text{C}/\text{min}$ ); cooling from 300 to  $-55\text{ }^\circ\text{C}$  ( $10\text{ }^\circ\text{C}/\text{min}$ ).

### 4.2. Synthesis of $[(\text{C}_5\text{H}_4)\text{TiCl}_3]_2[\text{CH}_2(\text{C}_6\text{H}_4)\text{CH}_2]_2$ (3)

A solution of  $[\text{Me}_3\text{Sn}(\text{C}_5\text{H}_4)]_2[\text{CH}_2(\text{C}_6\text{H}_4)\text{CH}_2]$  **2** (5.01 g, 8.95 mmol) in toluene 100 ml was treated with 2 equiv. of  $\text{TiCl}_4$  (2.4 ml, 18 mmol) at  $0\text{ }^\circ\text{C}$  to observe an immediate solution color change to blackish brown. The black brown solution was warmed to room temperature to stir for additional 4 h. After filtering and removing toluene the residue was extracted with ether. The resulting solid formed by the evaporation of ether has been washed by hexane to give greenish yellow product in modest yields (1.88 g, 39%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.18 (s, 4H,  $\text{C}_6\text{H}_4$ ), 6.92 (t, 4H,  $\text{C}_5\text{H}_4$ ), 6.79 (t, 4H,  $\text{C}_5\text{H}_4$ ), 4.16 (s, 4H,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  143.3, 137.1, 129.9, 124.1, 124.1, 123.6, 37.7. High resolution mass spectrum:  $[\text{P}^+]$   $\text{C}_{18}\text{H}_{16}\text{Cl}_6\text{Ti}_2$ ,  $m/z = 540$  ( $\text{M}^+$ ).

### 4.3. Preparation of $[(\text{C}_5\text{H}_4)\text{Ti}(\text{O}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{Cl}_2]_2[\text{CH}_2(\text{C}_6\text{H}_4)\text{CH}_2]_2$ (4)

To a  $\text{CH}_2\text{Cl}_2$  solution of  $[(\text{C}_5\text{H}_4)\text{TiCl}_3]_2[\text{CH}_2(\text{C}_6\text{H}_4)\text{CH}_2]_2$  (**3**) (1 g, 1.8 mmol) HO-2,6-*iPr*<sub>2</sub> $\text{C}_6\text{H}_3$  (0.685 ml, 4 mmol) was added at  $-25\text{ }^\circ\text{C}$ . The solution was warmed to RT slowly and stirred for 10 h. The solvent was then removed in vacuo to give yellowish materials. The materials that were soluble in hexane was separated and recrystallized in hexane at  $-30\text{ }^\circ\text{C}$  to result in the product as an orange solid (0.58 g, 38%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.12 (s, 4H,  $\text{C}_6\text{H}_4$ ), 7.05 (m, 6H,  $\text{C}_6\text{H}_3$ ), 6.49 (t, 4H,  $\text{C}_5\text{H}_4$ ), 6.39 (t, 4H,  $\text{C}_5\text{H}_4$ ), 4.13 (s, 4H,  $\text{CH}_2$ ), 3.23 (m, 4H, CH), 1.21 (d, 24H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  164.6, 140.2, 138.6, 138.1, 137.9, 129.7, 125.0, 123.9, 124.4, 121.0, 37.0, 27.6, 24.1. High resolution mass spectrum:  $[\text{P}^+]$   $\text{C}_{42}\text{H}_{50}\text{Cl}_4\text{O}_2\text{Ti}_2$ ,  $m/z = 824$  ( $\text{M}^+$ ).

### 4.4. Preparation of $[(\text{C}_5\text{H}_4)\text{Ti}\{\text{N}-(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{SiMe}_3\}\text{Cl}_2]_2[\text{CH}_2(\text{C}_6\text{H}_4)\text{CH}_2]_2$ (5)

To a toluene solution of  $[(\text{C}_5\text{H}_4)\text{TiCl}_3]_2[\text{CH}_2(\text{C}_6\text{H}_4)\text{CH}_2]_2$  (**3**) (0.8 g, 1.5 mmol)  $\text{LiN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{SiMe}_3$  (0.589 ml, 3 mmol) was added at  $-35\text{ }^\circ\text{C}$ . The solution was warmed to RT slowly and stirred for 10 h. The solvent was then removed in vacuo to give yellowish materials. The materials that were soluble in hexane was separated and recrystallized in hexane at  $-30\text{ }^\circ\text{C}$  to result in the product as an orange solid (0.49 g, 39%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.04 (s, 4H,  $\text{C}_6\text{H}_4$ ), 6.94 (m, 6H,  $\text{C}_6\text{H}_3$ ), 6.13 (t, 4H,  $\text{C}_5\text{H}_4$ ), 5.95 (t, 4H,  $\text{C}_5\text{H}_4$ ), 3.95 (s, 4H,  $\text{CH}_2$ ), 2.11 (s, 12H,  $\text{CH}_3$ ), 0.3 (s, 18H,  $\text{SiMe}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  160.0, 138.7, 138.2, 133.7, 129.5, 129.4, 128.8, 128.5, 125.2, 122.4, 121.2, 37.4, 21.1, 3.2. High resolution mass spectrum:  $[\text{P}^+]$   $\text{C}_{40}\text{H}_{52}\text{Cl}_4\text{N}_2\text{Si}_2\text{Ti}_2$ ,  $m/z = 854$  ( $\text{M}^+$ ).

## 5. Polymerization

Toluene polymerizations were carried out in a 150 ml glass reactor. The reactor was filled with proper amount

of styrene, toluene and MMAO. The polymerization was initiated by injection of the catalysts and polymerized for 2 h. The polymerization was terminated by the addition of acidified methanol, filtered, and dried under vacuum to constant weight. The polymer sample obtained in the polymerization was added into a flask containing MEK (100 ml) equipped with a reflux condenser, and the mixture was refluxed for 24 h to separate MEK-insoluble fractions. These fractions were analyzed by the instruments.

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