

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

Seok Kyun Noh <sup>a,\*</sup>, Woosung Jung <sup>a</sup>, Hyunsook Oh <sup>a</sup>, Yong Rok Lee <sup>a</sup>, Won Seok Lyoo <sup>b</sup>

<sup>a</sup> School of Chemical Engineering and Technology, Yeungnam University, 214-1 Daedong, Gyeongsan 712-749, Republic of Korea

<sup>b</sup> School of Textiles, Yeungnam University, Gyeongsan 712-749, Republic of Korea

Received 30 June 2006; received in revised form 9 August 2006; accepted 17 August 2006

Available online 30 August 2006

### 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.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Metallocene catalyst; Dinuclear metallocene; Half-titanocene; Styrene polymerization; Syndiotactic polystyrene

### 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

\* Corresponding author. Tel.: +82 53 810 2526; fax: +82 53 810 4631.  
E-mail address: [sknoh@yumail.ac.kr](mailto:sknoh@yumail.ac.kr) (S.K. Noh).

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-

Download English Version:

<https://daneshyari.com/en/article/1328457>

Download Persian Version:

<https://daneshyari.com/article/1328457>

[Daneshyari.com](https://daneshyari.com)