

Investigation of Ethylene and Styrene Copolymerization Initiated with Dinuclear Constrained Geometry Catalysts Holding Polymethylene as a Bridging Ligand and Indenyl as a Cyclopentadienyl Derivative

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ABSTRACT: A series of polymethylene-bridged dinuclear constrained geometry catalysts (CGC) $[\text{Me}_2\text{Si}(\text{Ind})(\text{N}^t\text{Bu})\text{TiCl}_2]_2[(\text{CH}_2)_n]$ (**1**, $n = 6$; **2**, $n = 9$; **3**, $n = 12$) were synthesized to study the copolymerization of ethylene and styrene. The experiments display that the polymerization activity of the dinuclear catalysts increased in the order of $1 < 2 < 3$, which indicated that the dinuclear CGC with the longest methylene units as a bridge showed the greatest activity. According to the activity correlation with the monomer ratio, all the catalysts exhibited maximum polymerization activity at the monomer ratio of $([\text{styrene}]/[\text{ethylene}])$ of 2. The dinuclear CGC **2** and **3** represented excellent characteristics of styrene reactivity while catalyst **1** represented considerably low styrene reactivity. The

relation between the molecular weights of the polymers and the catalysts used in the polymerization is not straightforward. The steric interference in catalyst **1**, containing just six methylene bridges, can be applied to explain not only the strikingly decreased activity but also the very low styrene content in the copolymer. In contrast, the electronic effect seems to be more pronounced in manipulating the polymerization properties of catalysts **2** and **3** having nine and 12 methylene bridges, respectively. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2469–2474, 2003

Key words: metallocene catalysts; polyolefins; polystyrene; copolymerization

INTRODUCTION

The group 4 monocyclopentadienylamido catalysts have been famous as extremely efficient catalysts to incorporate styrene into the polyethylene backbone. One of the key features of these catalysts is the opened nature of the active site, which is capable of delivering a pronounced amount of bulky comonomers such as α -olefins and styrene into polyethylene compared to the normal bent-metallocene catalysts.^{1–3} While these kinds of catalyst derivatives and their polymerization properties have been examined extensively, dinuclear constrained geometry catalysts (CGC) having two CGC linked with the bridging ligands as a polymerization catalyst have rarely been investigated.^{4–6} Dinuclear metallocenes have been paid attention to for being a new kind of catalyst for olefin polymerization, which could be potentially useful in catalysis if two metal centers show cooperative electronic and spatial

effects on polymerization.^{6–10} Another important point to be expected for dinuclear metallocene is that the nature of the bridging ligand could be the third element to characterize the properties of the dinuclear catalyst together with the metal and cyclopentadienyl derivatives.

In reality, we have demonstrated clearly that the structural feature of the bridging ligand in dinuclear metallocenes exerts an influence on the catalytic properties to distinguish not only between the dinuclear metallocenes and the well-defined mononuclear metallocenes but also among the dinuclear metallocenes.^{5,9,10} On the basis of this knowledge, we investigated the polymerization behavior of dinuclear CGC. Included in this article is a characteristic family of polymethylene-bridged dinuclear CGC used to describe the effect of the presence of a bridging ligand on the catalytic properties of ethylene and styrene copolymerization (Scheme 1):

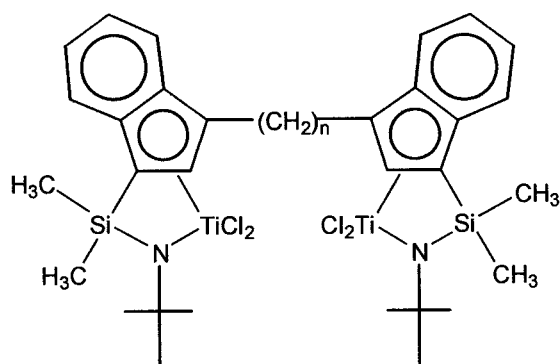
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EXPERIMENTAL

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



Scheme 1

was purified by passage through a column of molecular sieves (4 Å) and Drierite (8 mesh). Tetrahydrofuran, diethyl ether, hexane, toluene, and pentane were distilled from sodium benzophenone ketyl prior to use. Methylene chloride was distilled from calcium hydride prior to use. 1,6-Dibromohexane, 1,9-dibromononane, and 1,12-dibromododecane, purchased from Aldrich (The Netherlands), were used after distilling from calcium hydride. Modified methylaluminoxane (MMAO, type 4, 6.4 wt % Al; Akzo) was used without further purification. ^1H (300 MHz)-NMR and ^{13}C (75.46 MHz)-NMR spectra were recorded using a Bruker DPX-300 FT-NMR spectrometer (Germany). Mass spectra were performed on a Autospec-Ultima E. IR spectra were recorded on a Jasco FT/IR-5300 spectrophotometer between 4000 and 200 cm^{-1} .

Synthesis of $[\text{Me}_2\text{Si}(\text{Ind})(\text{N}^t\text{Bu})\text{TiCl}_2]_2[(\text{CH}_2)_6]$, **1**

A solution of $[\text{MeSi}(\text{C}_9\text{H}_5)(\text{NH}^t\text{Bu})]_2[(\text{CH}_2)_6]$ (2.7 g, 4.71 mmol) in THF 40 mL was treated with 4 equiv of *n*-BuLi (2.5M hexane solution, 4 mL, 9.9 mmol) at -78°C and warmed to 60°C . After stirring for 12 h, the resulting orange solution of the tetralithium salt was cooled to -78°C . $\text{TiCl}_3(\text{THF})_3$ (3.35 g, 9.04 mmol) in THF, 30 mL, was added dropwise to the solution of the tetralithium salt at -78°C . The black-brown solution was warmed to room temperature to stir for an

additional 3 h. AgCl (1.3 g, 9.0 mmol) was added as a solid, and the silver mirror precipitated immediately. THF was removed *in vacuo* after 30 min and the residue was extracted with toluene. After filtering and removing toluene, the residue was extracted with hexane. Recrystallization of the resulting solution gave the product as a reddish brown solid (1.79 g, 48%).

^1H -NMR (CDCl_3): δ 7.71 (d, 2H, C_9H_6), 7.62 (d, 2H, C_9H_6), 7.40 (t, 2H, C_9H_6), 7.26 (t, 2H, C_9H_6), 6.31 (s, 2H, C_9H_6), 3.02 (m, 4H, CH_2), 1.70 (m, 4H, CH_2), 1.41 (m, 4H, CH_2), 1.33 (s, 18H, $\text{C}(\text{CH}_3)_3$), 0.88 (s, 6H, $\text{Si}-\text{CH}_3$), 0.64 (s, 6H, $\text{Si}-\text{CH}_3$); ^{13}C -NMR (CDCl_3): δ 138.8, 135.8, 135.0, 128.5, 128.1, 127.9, 127.3, 124.5, 96.7, 63.0, 32.3, 29.7, 29.2, 29.0, 3.3, 1.0. High-resolution mass spectrum: $[\text{P}^+]$ $\text{C}_{36}\text{H}_{52}\text{N}_2\text{Si}_2\text{Cl}_4\text{Ti}_2$, $m/z = 804$ (M^+ , 15%), 769 (M^+-Cl , 30%).

Synthesis of $[\text{Me}_2\text{Si}(\text{Ind})(\text{N}^t\text{Bu})\text{TiCl}_2]_2[(\text{CH}_2)_9]$, **2**

Methods similar to those used to make **1** were also applied. The only exception was the introduction of $[\text{MeSi}(\text{C}_9\text{H}_5)(\text{NH}^t\text{Bu})]_2[(\text{CH}_2)_9]$ in place of $[\text{MeSi}(\text{C}_9\text{H}_5)(\text{NH}^t\text{Bu})]_2[(\text{CH}_2)_6]$. The final product was separated in 70% yields as a reddish brown solid.

^1H -NMR (CDCl_3): δ 7.71 (d, 2H, C_9H_6), 7.64 (d, 2H, C_9H_6), 7.41 (t, 2H, C_9H_6), 7.27 (t, 2H, C_9H_6), 6.32 (s, 2H, C_9H_6), 2.99 (m, 4H, CH_2), 1.69 (m, 4H, CH_2), 1.41 (m, 10H, CH_2), 1.33 [s, 18H, $\text{C}(\text{CH}_3)_3$], 0.88 (s, 6H, $\text{Si}-\text{CH}_3$), 0.64 (s, 6H, $\text{Si}-\text{CH}_3$); ^{13}C -NMR (CDCl_3): δ 139.1, 135.8, 135.0, 128.1, 127.9, 127.2, 124.5, 96.7, 63.0, 32.3, 30.0, 29.4, 29.3, 29.1, 3.40, 1.07. High-resolution mass spectrum: $[\text{P}^+]$ $\text{C}_{39}\text{H}_{58}\text{N}_2\text{Si}_2\text{Cl}_4\text{Ti}_2$, $m/z = 846$ (M^+ , 13%), 811 (M^+-Cl , 35%).

Synthesis of $[\text{Me}_2\text{Si}(\text{Ind})(\text{N}^t\text{Bu})\text{TiCl}_2]_2[(\text{CH}_2)_{12}]$, **3**

Methods similar to those used to make **1** were also applied. The only exception was the introduction of $[\text{MeSi}(\text{C}_9\text{H}_5)(\text{NH}^t\text{Bu})]_2[(\text{CH}_2)_{12}]$ in place of $[\text{MeSi}(\text{C}_9\text{H}_5)(\text{NH}^t\text{Bu})]_2[(\text{CH}_2)_6]$. The final product was separated in 55% yields as a reddish brown solid.

TABLE I
Results of Ethylene-Styrene Copolymerization with Catalyst 1, $[\text{Me}_2\text{Si}(\text{Ind})(\text{N}^t\text{Bu})\text{TiCl}_2]_2[(\text{CH}_2)_6]$

[S]/[E]	DCGC-6					
	Activity ^a	S (mol %) ^b	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	M_w ($\times 10^{-4}$)	M_w/M_n
0.0	21	—	n.d	126.3	2.4	3.4
1.0	16	6.3	n.d	99.4	2.0	3.2
2.0	18	7.5	n.d	76.8	2.1	2.8
5.0	11	11.5	-14.0	—	2.0	2.5
10.0	10	19.2	-9.2	—	1.9	2.0

Polymerization condition: $[\text{Ti}] = 2.0 \times 10^{-5}$ mol/L; $[\text{Al}]/[\text{Ti}] = 2000$; polymerization time: 2 h; ethylene pressure: 1 atm; polymerization temperature: -70°C . S, styrene; E, ethylene n.d. = not detected.

^a kg polymer/mol of $[\text{Ti}] \cdot \text{h} \cdot \text{atm}$.

^b Composition of styrene estimated by ^{13}C -NMR.

TABLE II
Results of Ethylene–Styrene Copolymerization with Catalyst 2, $[\text{Me}_2\text{Si}(\text{Ind})(\text{N}^t\text{Bu})\text{TiCl}_2]_2[\text{CH}_2]_9$

[S]/[E]	DCGC-9					
	Activity ^a	S (mol %) ^b	T_g (°C)	T_m (°C)	M_w ($\times 10^{-4}$)	M_w/M_n
0.0	125	—	n.d	128.2	2.7	2.2
1.0	145	6.6	n.d	91.3	2.5	2.2
2.0	163	11.3	n.d	65.9	2.5	2.1
5.0	98	27.0	-18.5	—	2.1	1.9
10.0	88	38.8	-8.2	—	2.0	1.5

Polymerization condition: $[\text{Ti}] = 2.0 \times 10^{-5}$ mol/L; $[\text{Al}]/[\text{Ti}] = 2000$; polymerization time: 2 h; ethylene pressure: 1 atm; polymerization temperature: 70°C. S, styrene; E, ethylene n.d. = not detected.

^a kg polymer/mol of $[\text{Ti}] \cdot \text{h} \cdot \text{atm}$.

^b Composition of styrene estimated by ¹³C-NMR.

¹H-NMR (CDCl_3): δ 7.71 (d, 2H, C_9H_6), 7.65 (d, 2H, C_9H_6), 7.42 (t, 2H, C_9H_6), 7.27 (t, 2H, C_9H_6), 6.32 (s, 2H, C_9H_6), 3.00 (t, 4H, CH_2), 1.69 (m, 4H, CH_2), 1.34 (m, 4H, CH_2), 1.33 [s, 18H, $\text{C}(\text{CH}_3)_3$], 1.23 (m, 10H, CH_2), 0.88 (s, 6H, $\text{Si}-\text{CH}_3$), 0.64 (s, 6H, $\text{Si}-\text{CH}_3$); ¹³C-NMR (CDCl_3): δ 139.1, 135.8, 135.0, 128.5, 128.1, 127.8, 127.2, 124.5, 96.6, 63.0, 32.3, 30.0, 29.5, 29.4, 29.3, 29.1, 3.38, 1.05. High-resolution mass spectrum: $[\text{P}^+]$ $\text{C}_{42}\text{H}_{64}\text{N}_2\text{Si}_2\text{Cl}_4\text{Ti}_2$, $m/z = 888$ (M^+ , 16%), 853 ($\text{M}^+ - \text{Cl}$, 36%).

Polymerization

Ethylene homopolymerizations and copolymerizations were carried out in a 400-mL glass reactor. The reactor was filled with a proper amount of styrene, toluene, and the MMAO 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 for 2 h. The polymers were precipitated in acidified methanol, filtered, and dried under a vacuum to a constant weight.

RESULTS AND DISCUSSION

The dinuclear CGC **1**, **2**, and **3** were tested with MMAO as a cocatalyst in the copolymerization of ethylene and styrene. The polymerizations were conducted at 70°C and an $[\text{Al}]/[\text{Ti}]$ ratio of 2000 and the

results are given in Tables I–III and Figures 1 and 2. These results demonstrate some important points to be noted to characterize the dinuclear CGC as a new catalyst for ethylene–styrene copolymerization.

The most important feature that we observed is the clear distinction among the three dinuclear CGC. As shown in Figure 1, the polymerization activity of the dinuclear catalysts increased in the order of **1** \ll **2** $<$ **3**, which indicated that the dinuclear CGC with 12 methylenes as a bridge represented greater activity than the other two dinuclear CGC. Very interestingly, the dinuclear CGC **1** with six methylene bridging units displaying particularly low activity while the dinuclear CGC **2** with nine methylene bridging units shows a similar activity to the dinuclear CGC **3** with twelve methylene bridges. For instance, at the monomer ratio ($[\text{styrene}]/[\text{ethylene}]$) of 2, the activity of catalyst **1** was just 18 kg polymer/mol Ti h atm, while the activities of catalysts **2** and **3** were 163 and 167 kg polymer/mol Ti h atm, respectively, which were more than nine times larger than that of catalyst **1**. The second point can be delivered by the activity correlation with the monomer ratio according to the catalysts. All the catalysts exhibited maximum polymerization activity at a monomer ratio of 2, which decreased with changes of the monomer ratio. Although the actual activity value at the monomer ratio of 2 is slightly smaller than the activity of ethylene homopolymeriza-

TABLE III
Results of Ethylene–Styrene Copolymerization with Catalyst 3, $[\text{Me}_2\text{Si}(\text{Ind})(\text{N}^t\text{Bu})\text{TiCl}_2]_2[\text{CH}_2]_{12}$

[S]/[E]	DCGC-12					
	Activity ^a	S (mol %) ^b	T_g (°C)	T_m (°C)	M_w ($\times 10^{-4}$)	M_w/M_n
0.0	145	—	n.d	130.4	2.1	2.5
1.0	154	6.5	n.d	108.0	1.9	2.3
2.0	167	11.8	n.d	79.7	1.8	2.2
5.0	121	28.1	-19.5	—	1.6	2.3
10.0	107	40.9	-8.6	—	1.7	1.5

Polymerization condition: $[\text{Ti}] = 2.0 \times 10^{-5}$ mol/L; $[\text{Al}]/[\text{Ti}] = 2000$; polymerization time: 2 h; ethylene pressure: 1 atm; polymerization temperature: 70°C. n.d. = not detected.

^a kg polymer/mol of $[\text{Ti}] \cdot \text{h} \cdot \text{atm}$.

^b Composition of styrene estimated by ¹³C-NMR.

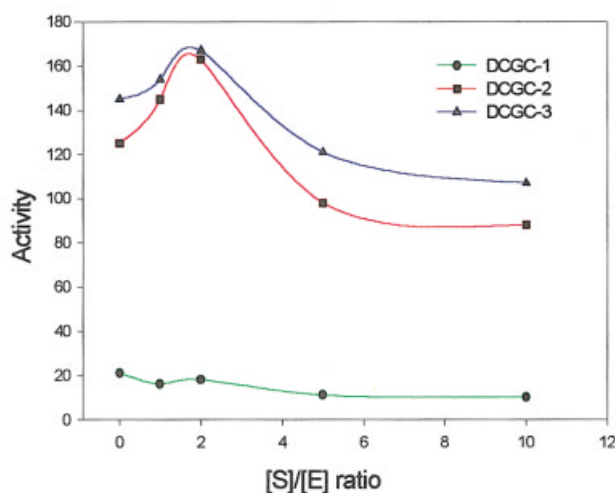


Figure 1 Variation of activity with [styrene]/[ethylene] ratio. Activity: kg polymer/mol of [Ti] · h · atm.

tion in the case of the catalyst **1**, the activity point at the monomer ratio of 2 is still on the top throughout the correlation curve as shown in Figure 1. Because of this aspect, we regarded the activity trend of catalyst **1** as an identical trend with the other two cases. In contrast to the analogy of the activity transition mode, the actual activity numbers of the catalysts are not analogous as mentioned earlier. It is remarkable that the monomer ratio of 2, resulting in the maximum activity, does not vary with the characteristics of the catalyst structure. This observation may imply that the nature of the bridging ligand does play a significant role in influencing the polymerization activity of the dinuclear CGC.^{9,10} The existence of the maximum value of the activity according to the monomer ratio could be interpreted as a comonomer effect that had often been observed in ethylene-propylene copolymerization.¹¹ Also, the depreciation of the activity after the maximum point in accordance with the improvement of the [styrene]/[ethylene] ratio can be understood as a general tendency to follow the reported experiments.¹²

The variation of the styrene content in copolymer with the monomer ratio of [styrene]/[ethylene] in the feed is plotted in Figure 2. Surprisingly, a general changing shape of the styrene contents in the formed copolymers is likely to very much resemble the case of the activities. As shown in Figure 2, two sets of trends were revealed from the styrene content in the copolymers. The first set consists of two similar slopes of lines from catalysts **2** and **3** that held nine and 12 methylenes as a bridge, respectively, on the topside and the other is one line downside from catalyst **1** having six methylenes as a bridge. Similar to the case for the activity, a few noticeable points based on these results can be mentioned: The styrene contents in the polyethylene

backbone produced by catalyst **1** were considerably less than those in the copolymers produced by the other two catalysts. This phenomenon was intensified as the monomer ratio increased. At the monomer ratio of 1, the styrene content in the copolymer formed by catalyst **1** is 6.3%, which is a similar value to the styrene contents of 6.6 and 6.5% in copolymers generated by catalysts **2** and **3**, respectively. However, at the monomer ratio of 5, the copolymer produced by catalyst **1** contained just 11.5% of styrene, while those formed by catalysts **2** and **3** included 27 and 28% of styrene, respectively. Actually, these quantities of the comonomer contents in the copolymers produced by dinuclear CGC **2** and **3** are larger than those of the previously known results, which demonstrates the excellent characteristics of styrene reactivity of the mentioned catalysts compared to the normal mononuclear CGC.¹² If we look at the slopes of the lines in Figure 2, we can realize that each catalyst represented a unique and consistent relationship with the styrene content in the copolymer. This expresses that the styrene reactivity of the dinuclear CGC is sensitive to the property of the bridging ligand.

The molecular weights of the polymers produced from the dinuclear CGC at 70°C were measured by GPC. The relation found between the molecular weights of the polymers and the catalyst used in polymerization is not straightforward. As shown in the tables, the molecular weights of the polymers manufactured by catalyst **2** are the greatest among those of polymers formed by three dinuclear CGC. On the other hand, catalyst **3** not only shows the highest activity but also produces the highest styrene-content copolymers. However, it gives rise to the formation of the polymers with the lowest molecular weights. It is

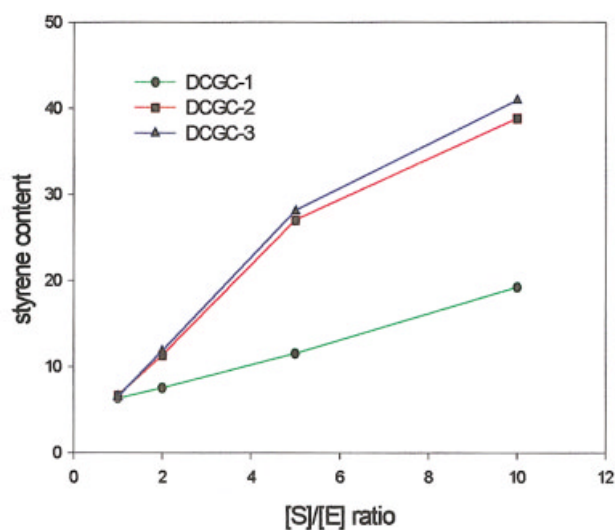


Figure 2 Variation of styrene content in copolymer with [styrene]/[ethylene] ratio in feed. Styrene content: mol %.

interesting that catalyst **1**, which exhibited extremely low activity and gave the formation of copolymers containing a small content of styrene, generates the intermediate molecular weight polymers. Consequently, the dinuclear CGC holding the longest methylene linkage forms the shortest copolymers although the differences of molecular weights of the produced polymers are not significantly large. The second point related to the molecular weight is the variation of the molecular weight with the [styrene]/[ethylene] ratio. The molecular weight of the produced copolymers decreases consistently with an increase in the [styrene]/[ethylene] ratio regardless of the introduced catalyst in the polymerization. This outcome is well in accord with the observation reported by mononuclear CGC.¹³

On the basis of the results obtained from ethylene/styrene copolymerization, it was clearly demonstrated that the activity, the styrene content in copolymer, and the molecular weight of the copolymer were varied with the characteristics of the dinuclear CGC with polymethylene bridges. We thus would like to relate electronic and steric influences to the catalytic activity and styrene content in the polymer to understand the tendency noted in the experiments.

Concerning the influence of the electronic effect on the activity, it is generally recognized that increasing the electron density at the metal center results in increased activity. In our investigation, the polymerization activity of the catalysts decreased in the order $3 > 2 \gg 1$, which indicated that the dinuclear CGC with 12 methylene units as a bridge represented the greatest activity in the three catalysts while the dinuclear CGC with six methylene units as a bridge displayed an extremely low activity. The polymerization behavior of catalyst **2** having nine methylene bridges and catalyst **3** having 12 methylene bridges looks similar. This outcome suggests that there is a distinctive effect on the polymethylene linkage that leads to slow down or accelerate the activity. One of the effects would be an electron-donating nature of the polymethylene that would increase polymerization activity.^{9,10} According to this proposal, it is acceptable that the dinuclear CGC containing a longer methylene bridge exhibits a greater activity as shown in our experiments. However, it is hard to believe that the dramatic loss in activity of catalyst **1** is attributed to the difference of the electron-donating power between six methylene linkage and nine or 12 methylene linkage as a single convincing factor. We suppose, in this case, that the steric circumstance will prevail to determine the apparent activity of the dinuclear CGC. In the same manner, the electronic effect should not be a major factor to control the styrene reactivity of the dinuclear CGC, although it is not so surprising to suggest that the more electron-deficient center would be more receptive to interact with an electron-rich styrene compared to ethylene. On the basis of this suggestion,

catalyst **1**, sustaining the least electron-donating bridge, is expected to exhibit the highest styrene reactivity. However, the results are just opposite to the expectation. Consequently, it is very difficult to explain an impressive distinction of styrene reactivity revealed in three dinuclear CGC with the electronic effect solely. Once again, we assume that the steric effect would be a significant element to control a comonomer response.

The influence of the stereochemical environment around the active center on the catalytic properties is fairly complicated. Sometimes, slight changes in steric circumstances have detrimental effects on catalytic behavior. It is generally accepted that steric congestion around the metal center prevents facile access to the coordination site to slow down the propagation rate. On this basis, it would be anticipated that the dinuclear CGC with a shorter bridge experiences more steric disturbance from the other end than does the one with a longer bridge. If this occurs, the lowest activity should be observed by catalyst **1** holding the shortest methylene connection. The sudden activity elevation of dinuclear CGC with between nine and six methylene bridges is hard to rationalize clearly. We suppose that two ends of the dinuclear CGC could interact with each other to be part of one bulky substituent on the active site enough to interfere with monomer's approach to it. At the distance of six methylene units, this effect might be maximized to decrease the activity drastically.¹⁰ This kind of steric interaction will prevent styrene monomer coordination to the active site more strongly than with the ethylene monomer due to a bigger size, which will lead to a decrease of the styrene content in the copolymer. From the distance between the two metal fragments of nine methylenes, the steric disturbance seems to be depreciated to transfer its position to the electronic effect, playing a major role to identify the polymerization properties of the dinuclear CGC **2** and **3**. In summary, the steric interference in catalyst **1** having six methylene bridges can be applied to explain not only the strikingly decreased activity but also the very low styrene content in the copolymer. In contrast, the electronic effect is likely to be more pronounced in influencing the polymerization behavior of the catalysts having nine and 12 methylene bridges.

CONCLUSIONS

The copolymerization of ethylene and styrene was investigated using a series of polymethylene-bridged dinuclear CGC: $[\text{Me}_2\text{Si}(\text{Ind})(\text{N}^t\text{Bu})\text{TiCl}_2]_2[(\text{CH}_2)_n]$ (**1**, $n = 6$; **2**, $n = 9$; **3**, $n = 12$). The polymerization studies revealed that (i) catalyst **3**, holding the longest bridging ligand, exhibited not only the largest activity but also the highest comonomer reactivity, (ii) the molecular weights of the ethylene/styrene copolymers produced by the

dinuclear CGC did not show much difference according to the employed catalysts, and (iii) the catalytic activities as well as the comonomer response of the dinuclear CGC in this study were comparable to the mononuclear CGC. The lowest activity of catalyst **1**, containing the shortest bridge, is attributed to the steric hindrance caused by the interaction between two metal fragments as well as the influence of a relatively small electron donation from the bridging ligand. An increase in steric perturbation around the active site led not only to a decrease in catalytic activity but also a reduction of styrene content in the copolymers due to preventing facile olefin access to the active site. The high activities of catalysts **2** and **3** can be understood not only by the electron-donating ability of the polymethylene bridges but also by the reduction of the steric interaction between two metal sites. Catalyst **3**, displaying the greatest activity as well as producing the highest styrene-content copolymers, gives rise to the formation of polymers with the lowest molecular weight.

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