

# A silica-supported titanium(IV) complex bearing [O<sup>-</sup>NS] tridentate ligand and its behavior in ethylene homo- and copolymerization with 1-hexene

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## Abstract

A silica-supported titanium(IV) complex (**I**) bearing [O<sup>-</sup>NS] tridentate ligand was prepared for the first time. Its performance in ethylene homo- and copolymerization with 1-hexene were studied. The effects of various polymerization conditions including Al/Ti molar ratio, temperature, ethylene pressure and the mixture of modified methylaluminoxane (MAO) and triethylaluminum (AlEt<sub>3</sub>) as cocatalyst on the catalytic activities and properties of the obtained polymer were investigated. The results showed that the good catalytic activities and incorporation of 1-hexene in copolymer can be reached. Ethylene polymerization with such supported catalyst system gave polymers with higher molecular weight, higher melting temperature and better morphology than those obtained with the corresponding homogeneous catalyst.

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**Keywords:** Titanium catalyst; Silica-supported catalyst; Ethylene polymerization; Ethylene copolymerization

## 1. Introduction

In recent years, numerous efforts are being directed toward developing new single-site non-metallocene catalysts [1–9], as well as allowing access to previously inaccessible polymers [10–12]. Of the successful non-metallocene catalysts developed [1–3], the complexes possessing phenoxyimine ligands are one of the promising examples [13–15] which show excellent performance in living ethylene polymerization [16–19], living propylene polymerization with excellent stereoselectivity [20–22], living copolymerization of ethylene with  $\alpha$ -olefins [23], and the synthesis of functional and block copolymers of propylene [24].

Tang and co-workers recently reported that titanium(IV) catalysts bearing a [O<sup>-</sup>NP] ligand were robust and highly active for ethylene homo- and copolymerization with 1-hexene and norbornene [25]. Moreover, a series of novel titanium(IV) complexes (**I**) (Scheme 1) bearing [O<sup>-</sup>NS] tridentate ligand

developed by Tang and co-workers were proved to be good catalysts for olefin polymerization [26,27].

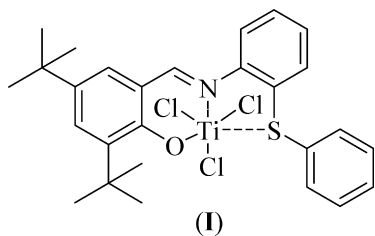
A significant impediment to the industrial application of such homogeneous catalysts is the cost reflected in the requirement that a very large excess of methylaluminoxane (MAO) must be employed to obtain high catalytic activity and catalyst stability. Moreover, homogeneous catalytic system has other drawbacks: the lack of morphology control of the polymers and reactor fouling. An approach to overcome these problems is immobilizing homogeneous catalyst on various carriers. As a result, low amount of MAO even alkylaluminum in some extent might be utilized in such heterogeneous catalytic system to reach good catalytic activity and smooth polymerization kinetics [28]. Furthermore, the immobilized homogeneous catalysts can improve polymer morphologies and the ability to be used in gas-phase and slurry-phase reactors with existing industrial technology.

A variety of carriers for immobilizing single-site catalyst has been reported, such as SiO<sub>2</sub> [29,30], Al<sub>2</sub>O<sub>3</sub> [31], MgCl<sub>2</sub> [32,33], zeolites and mesoporous materials [34–37], montmorillonite [38], organic–inorganic hybrid [39,40], polymer [41–44] and so on. Silica, with high surface area, porosity, good mechanical properties and stability under processing conditions [45,46],

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Scheme 1. [O<sup>-</sup>NS] titanium(IV) complex (**I**).

is widely used as support on which the homogeneous single-site catalyst is directly impregnated, or through its modified surface. Herein, a silica-supported titanium(IV) complex (**I**) bearing [O<sup>-</sup>NS] tridentate ligand was prepared and its catalytic behaviors in ethylene homopolymerization and copolymerization with 1-hexene in different solvents in the presence of MMAO or the mixture of MMAO and AlEt<sub>3</sub> were studied. The properties and morphology of the obtained polymer were also investigated.

## 2. Experimental

### 2.1. Materials

Silica ES70 was kindly provided by INEOS Silicas Company. Modified methylaluminoxane was purchased from Akzo Chemical as a 1.9 M toluene solution. Toluene (Aldrich, 99.5%) and *n*-hexane (Aldrich, 98.5%) were distilled over sodium/benzophenone ketyl prior to use. 1-Hexene (Acros, 97%) was distilled from sodium/benzophenone ketyl before use. Polymerization-grade ethylene was purified before use. The catalyst (**I**) was prepared according to published procedures [26].

All manipulations of air- and/or moisture-sensitive compounds were performed under an inert atmosphere using a glovebox and/or standard Schlenk techniques.

### 2.2. Preparation of silica-supported catalyst

The measured ES70 silica was calcinated at 400 °C for 6 h in a nitrogen atmosphere, then it was treated by MMAO ([Al]/[Si–OH] = 4; the content of OH group in SiO<sub>2</sub> [Si–OH] was 1.96 mmol/g determined by titration with AlEt<sub>3</sub>) in a Schlenk flask at 60 °C for 2 h. The modified silica (MSi) was washed by toluene (20 mL × 3) and dried to constant weight at room temperature under vacuum.

The catalyst (**I**) was added to a suspension of modified silica mentioned above (**I**: MSi = 1 mmol: 1.0 g). The resulting suspension was stirred at 60 °C for 12 h. The mixture was filtered, washed with toluene (20 mL × 3) and then *n*-hexane (20 mL × 3), and dried to constant weight under vacuum. The silica-supported catalyst (**SC**) was then obtained as a fluid brown powder.

### 2.3. Ethylene homopolymerization and copolymerization with 1-hexene

A 300 mL stainless-steel autoclave equipped with magnetic stirrer was dried under vacuum at 80 °C in an oil bath for 1 h, sub-

sequently cooled to the desired reaction temperature, and then purged with ethylene three times. Freshly distilled toluene (or *n*-hexane if necessary) was transferred to the reactor via a gas-tight syringe. The 1-hexene (in the case of the copolymerization) and MMAO (or the mixture of MMAO and AlEt<sub>3</sub> if necessary) were added. After stirring for 5 min, the supported catalyst was introduced into the autoclave with some toluene. The system was maintained at desired ethylene pressure throughout the polymerization run with a continuous feed of ethylene gas. After the polymerization run for 1 h, the autoclave was cooled quickly to room temperature and the residual ethylene was released slowly. Then the reaction mixture was poured into a solution of HCl/ethanol (10%, v/v). The polymer was isolated by filtration, washed with ethanol, and dried at 60 °C under vacuum for 12 h.

### 2.4. Characterization of silica-supported catalyst

Inductively coupled plasma (ICP) spectroscopy was used to determine the titanium content of the supported catalyst using Prodigy ICP-AES (Leeman Co.) in Shanghai Institute of Organic Chemistry, CAS. Scanning electron microscope (SEM) (JEOL JSM-6360LV) was used to observe the morphologies of calcinated SiO<sub>2</sub> and SiO<sub>2</sub>/MMAO.

### 2.5. Characterization of polymers

$M_w$ ,  $M_n$  and  $M_w/M_n$  (PDI) of polymers were determined using a gel permeable chromatography (GPC) (Waters Alliance 2000 series) at 135 °C (using polystyrene calibration, 1,2,4-trichlorobenzene as the solvent at a flow rate of 1.0 mL/min). Carbon-13 nuclear magnetic resonance (<sup>13</sup>C NMR) spectra of copolymers were recorded at 110 °C using *o*-dichlorobenzene-*d*<sub>4</sub> as the solvent. Polymer melting temperatures ( $T_m$ ) were determined on a differential scanning calorimetry (DSC) (Perkin-Elmer Instruments Pyris 1) calibrated with indium, using a heating rate of 10 °C/min in the temperature range of 50–200 °C. The heating cycle was performed twice, but only the results of the second cycle were reported, since the former was influenced by the mechanical and thermal history of the samples. The morphologies of polymers were observed using SEM (JEOL JSM-6700F).

## 3. Resulting and discussion

### 3.1. Preparation and characterization of supported catalyst

A silica-supported titanium(IV) complex (**I**) (**SC**) bearing [O<sup>-</sup>NS] tridentate ligand was prepared for the first time using one traditional method of immobilization for other homogenous catalyst in order to study its catalytical behavior in ethylene polymerization. The titanium content of such silica-supported catalyst was 1.8 wt% determined by ICP. The further investigation into the effect of different carriers and the various immobilization methods on the behavior of **SC** in ethylene polymerizations will be reported in our another work.

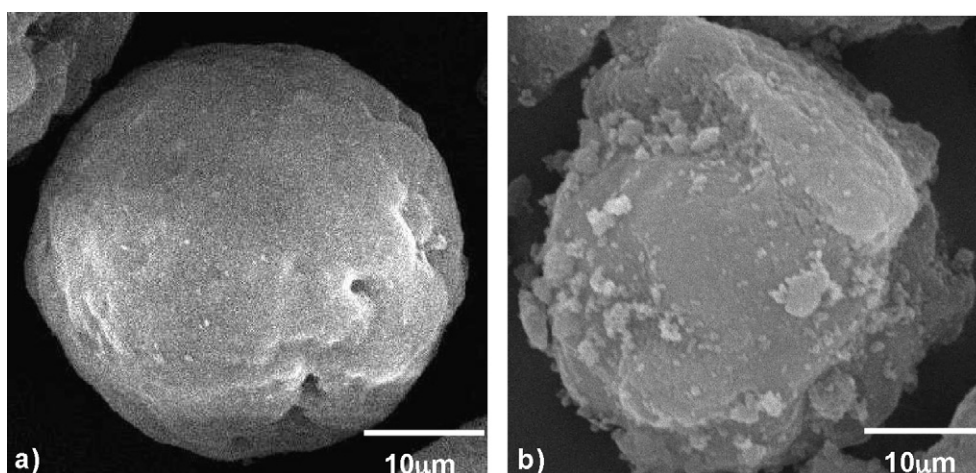


Fig. 1. SEM photographs of (a) calcinated silica and (b) silica treated with MMAO.

The morphologies of calcinated  $\text{SiO}_2$  and  $\text{SiO}_2/\text{MMAO}$  are shown in Fig. 1. The smooth surface of calcinated  $\text{SiO}_2$  became loose and rough after the treatment with MMAO and will benefit the adsorption of catalyst (I) onto the surface of silica during the immobilization of catalyst. The elemental analysis on the surface of supported catalyst via X-ray photoelectron spectroscopy (XPS) is under investigation in order to show the possible mechanism of immobilization.

### 3.2. Ethylene polymerization

The results of ethylene polymerization with the supported catalyst in the presence of MMAO are summarized in Table 1.

The first ethylene polymerization was carried out using SC at  $[\text{Al}]/[\text{Ti}] = 2000$  and the catalytic activity of SC was  $2.42 \times 10^5 \text{ g PE mol}^{-1} \text{ Ti h}^{-1}$ . While the highest activity was achieved at  $[\text{Al}]/[\text{Ti}]$  of 1000. And then, with the decrease of  $[\text{Al}]/[\text{Ti}]$  molar ratio from 1000 to 100, the catalytic activity decreased from  $2.71 \times 10^5 \text{ g PE mol}^{-1} \text{ Ti h}^{-1}$  (Entry 2) to  $0.68 \times 10^5 \text{ g PE mol}^{-1} \text{ Ti h}^{-1}$  (Entry 5). The possible explanation should be the role of MMAO in the activation and

reactivation of catalyst and the elimination of impurity in the system reduced when the amount of MMAO decreased. It was worth noting that the silica-supported catalyst showed quite good thermostability at  $80^\circ\text{C}$  with the catalytic activity of  $3.53 \times 10^5 \text{ g PE mol}^{-1} \text{ Ti h}^{-1}$  (Entry 6) which was even higher than that of  $50^\circ\text{C}$ . Such characteristic will benefit the performance of catalyst in industrial experiment. The detail study of polymerization at  $80^\circ\text{C}$  and higher temperatures are in progress. The results of Entries 7, 8 and 2 showed that the catalytic activities of SC were slightly increased with the increase in ethylene pressure from 0.5 to 1.0 MPa. However, the supported catalyst showed relative lower activity than that of corresponding homogeneous catalyst, which was the same as many supported catalyst systems reported in literatures.

One of important considerations to immobilize homogeneous catalyst on carries is to reduce the amount of expensive MMAO, which is cocatalyst in many homogeneous catalytic systems, even utilize cheaper alkylaluminium as substitute to reduce the production cost. So, some experiments were carried out in order to know the role of  $\text{AlEt}_3$  in ethylene polymerization using SC. The results are shown in Table 2.

Table 1  
Ethylene polymerization with the supported catalyst in the presence of MMAO<sup>a</sup>

Entry	$[\text{Al}]/[\text{Ti}]$	$P_E$ (MPa)	$T$ ( $^\circ\text{C}$ )	Yield (g)	Activity <sup>b</sup>	$M_w^c$ ( $\times 10^4$ )	$M_w/M_n^c$	$T_m^d$ ( $^\circ\text{C}$ )	$X_c^e$ (%)
1	2000	1.0	50	1.209	2.42	35.1	7.6	137.6	56.5
2	1000	1.0	50	1.355	2.71	21.7	2.6	137.3	58.6
3	500	1.0	50	0.858	1.72	n.d. <sup>f</sup>	n.d.	137.6	51.6
4	200	1.0	50	0.637	1.27	n.d.	n.d.	136.7	45.6
5	100	1.0	50	0.342	0.68	n.d.	n.d.	137.3	45.3
6	1000	1.0	80	1.766	3.53	13.4	4.6	136.6	72.2
7	1000	0.5	50	1.042	2.08	n.d.	n.d.	137.7	56.6
8	1000	0.8	50	1.161	2.32	n.d.	n.d.	137.4	48.3
9 <sup>g</sup>	1000	1.0	50	2.031	4.06	n.d.	n.d.	127.5	44.6

<sup>a</sup> Polymerization conditions: SC:  $5 \mu\text{mol Ti}$ ; cocatalyst is MMAO; toluene 100 mL;  $t = 1 \text{ h}$ .

<sup>b</sup>  $10^5 \text{ g PE mol}^{-1} \text{ Ti h}^{-1}$ .

<sup>c</sup> Determined by GPC.

<sup>d</sup> Determined by DSC.

<sup>e</sup> Crystallinity determined from  $X_c$  (%) =  $(\Delta H_m / \Delta H_m^*) \times 100$ ,  $\Delta H_m^* = 293 \text{ J/g}$  for HDPE [47].

<sup>f</sup> n.d.: not determined.

<sup>g</sup>  $5 \mu\text{mol}$  homogeneous catalyst in toluene, other conditions were all the same.

Table 2  
Ethylene polymerization with the silica-supported catalyst in the presence of MMAO/ $\text{AlEt}_3$ <sup>a</sup>

Entry	[MMAO]/[ $\text{AlEt}_3$ ]/[Ti]	Yield (g)	Activity <sup>b</sup>	$M_w^c$ ( $\times 10^4$ )	$M_w/M_n^c$	$T_m^d$ ( $^\circ\text{C}$ )	$X_c^e$ (%)
1	500/500/1	1.612	3.22	18.8	19.6	136.4	65.6
2	100/500/1	1.565	3.13	50.0	13.3	138.4	62.4
3 <sup>f</sup>	500/500/1	1.792	3.58	n.d. <sup>g</sup>	n.d.	136.8	65.0
4 <sup>f</sup>	100/500/1	0.326	0.65	n.d.	n.d.	136.8	51.3

<sup>a</sup> Polymerization conditions: **SC**: 5  $\mu\text{mol}$  Ti; cocatalyst is the mixture of MMAO and  $\text{AlEt}_3$ ; toluene 100 mL,  $P_E = 1.0$  MPa,  $T = 50$   $^\circ\text{C}$ ,  $t = 1$  h.

<sup>b</sup>  $10^5$  g PE  $\text{mol}^{-1}\text{Ti h}^{-1}$ .

<sup>c</sup> Determined by GPC.

<sup>d</sup> Determined by DSC.

<sup>e</sup> Crystallinity determined from  $X_c$  (%) =  $(\Delta H_m / \Delta H_m^*) \times 100$ ,  $\Delta H_m^* = 293$  J/g for HDPE [22].

<sup>f</sup> Hexane 100 mL.

<sup>g</sup> n.d.: not determined.

Table 3  
Ethylene copolymerization with 1-hexene<sup>a</sup>

Entry	1-Hexene (mmol)	[Al]/[Ti]	$P_E$ (MPa)	$T$ ( $^\circ\text{C}$ )	Yield (g)	Activity <sup>b</sup>	$M_w^c$ ( $\times 10^4$ )	$M_w/M_n^c$	$T_m^d$	H% <sup>e</sup> (mol%)
1	80	1000	1.0	50	1.344	2.69	17.6	3.2	116.6	2.71
2	160	1000	1.0	50	1.292	2.58	28.8	2.6	105.6	4.68
3	80	500	1.0	50	0.494	0.99	n.d. <sup>f</sup>	n.d.	120.1	n.d.
4	80	1000	1.0	80	2.477	4.95	11.1	2.9	114.8	1.83
5	80	1000	0.5	50	0.999	2.00	31.7	6.1	110.5	1.88
6 <sup>g</sup>	80	500/500/1	1.0	50	1.158	2.32	47.4	20.0	116.0	n.d.

<sup>a</sup> Polymerization conditions: **SC** 5  $\mu\text{mol}$  Ti; solvent: toluene  $V_{\text{total}} = 100$  mL.

<sup>b</sup>  $10^5$  g copolymer  $\text{mol}^{-1}\text{Ti h}^{-1}$ .

<sup>c</sup> Determined by GPC.

<sup>d</sup> Determined by DSC.

<sup>e</sup> H% is incorporation ratio of 1-hexene in copolymer, determined by  $^{13}\text{C}$  NMR.

<sup>f</sup> n.d.: not determined.

<sup>g</sup> Cocatalyst is the mixture of MMAO and  $\text{AlEt}_3$ .

With the mixture of MMAO and  $\text{AlEt}_3$  as cocatalyst, the **SC** performed well in ethylene polymerization both in toluene and in *n*-hexane, except for Entry 4. It was probably due to the combined role of  $\text{AlEt}_3$  as cocatalyst and scavenger of impurity in polymerization system. The influence of MMAO/ $\text{AlEt}_3$ /Ti molar ratio on the behavior of **SC** in ethylene polymerization and the catalytic mechanism of such system are under investigation.

### 3.3. Properties of the resulting polyethylenes

The molecular weights ( $M_w$ ) of the polymer resins obtained with **SC**/MMAO system are much higher than those of polyethylenes (PEs) obtained with **I**/MMAO system ( $M_w = 21.7 \times 10^4$  (Table 1, Entry 2) versus  $M_w = 2.96 \times 10^4$  (literature [13b], Table 2, Entry 2). The main reason is that the chain transfer rate is lower than **I**/MMAO system. The

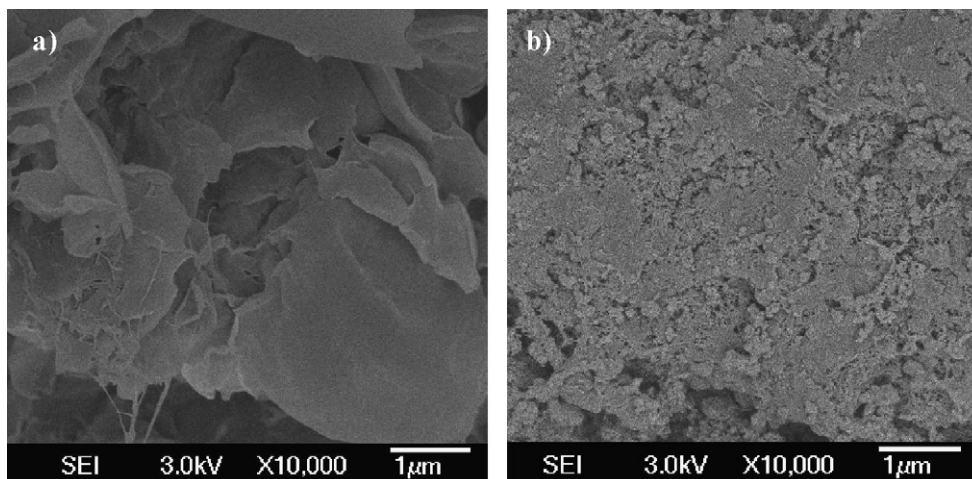


Fig. 2. Surface morphology of the obtained PE (a) by homogeneous catalyst (**I**) and (b) by silica-supported catalyst (**SC**).



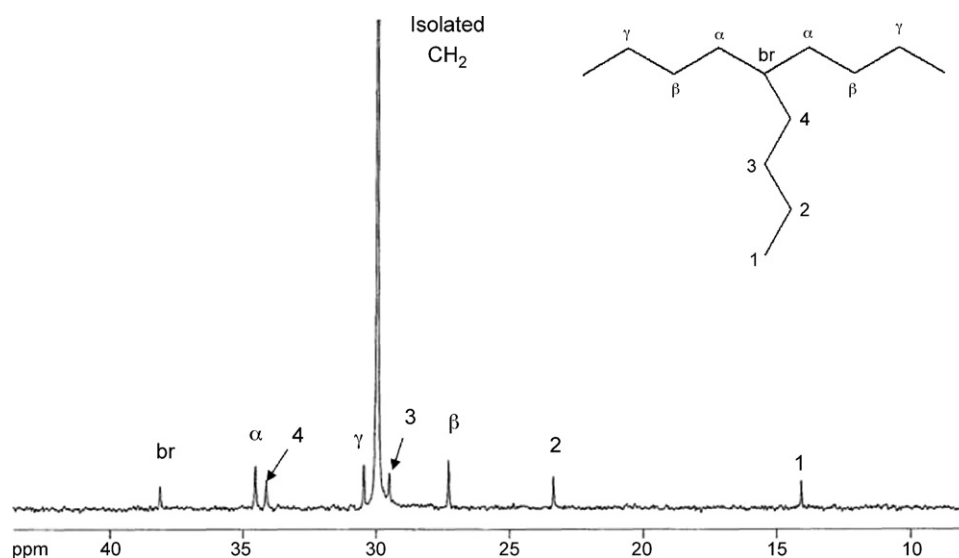


Fig. 3.  $^{13}\text{C}$  NMR spectrum of ethylene/1-hexene copolymer obtained with SC/MMAO (Entry 2 in Table 3).

molecular weight distributions (PDI) the polymer obtained with SC/MMAO/ $\text{AlEt}_3$  become much broader, which might be due to the formation of multiple active centers in such catalytic system. The melting temperatures ( $T_m$ ) and crystallinities ( $X_c$ ) of PEs obtained with SC system are about  $10^\circ\text{C}$  higher than those of PEs obtained with homogeneous catalytic system (as shown in Table 1).

In the case of ethylene polymerization using SC, the autoclave showed much less fouling than that of homogeneous catalyst. From SEM images of the resultant PEs as shown in Fig. 2, we could observed the different surface morphology of the PEs between the homogeneous catalyst and the SC system. The polyethylene obtained via silica-supported catalyst has a more compact morphology than that using homogeneous catalyst, although the “replicate effect of support” was not obvious. The further research on the choice of silica or other carriers and the conditions of immobilization and polymerization are necessary to be done for the development of polymer’s morphology.

### 3.4. Ethylene copolymerization with 1-hexene

The results of ethylene copolymerization with 1-hexene are summarized in Table 3.

The copolymerization was carried out with 1-hexene in feed at 80 and 160 mmol. Overall, the catalytic activities in such two cases were found to be similar to ethylene homopolymerization. When the amount of 1-hexene was increased from 80 to 160 mmol, the activity in copolymerization decreased

Table 4

Calculated and observed  $^{13}\text{C}$  NMR chemical shifts and assignments

Chemical shift exptl. (ppm)	Chemical shift from Ref. [49] (ppm)	Assignments
14.08	13.86	<b>1</b>
23.35	22.90	<b>2</b>
27.29	27.52	<b><math>\beta</math></b>
29.51	29.96	<b>3</b>
29.98	29.96	Isolated $\text{CH}_2$
30.47	30.21	<b><math>\gamma</math></b>
34.13	34.22	<b>4</b>
34.47	34.47	<b><math>\alpha</math></b>
38.14	37.05	<b>br</b>

(Entry 1 and 2) that is so-called comonomer effect [48]. When  $[\text{Al}]/[\text{Ti}]$  was reduced from 1000 to 500, the activity was sharply decreased. The activity of ethylene copolymerization with 1-hexene in the different conditions showed a similar trend to that of ethylene homopolymerization. The SC/MMAO/ $\text{AlEt}_3$  system also showed good performance in the copolymerization of ethylene and 1-hexene (Entry 6). The melting temperatures around  $110^\circ\text{C}$  of the resultant copolymers indicated that they are characteristic linear low density polyethylene (LLDPE).

### 3.5. Properties of the resulting copolymers

The example of  $^{13}\text{C}$  NMR spectrum of the resulting copolymer is shown in Fig. 3. From Fig. 3, no 1-hexene continuous incorporation could be observed. The presence of butyl branches

Table 5

Dyad-triad sequence distribution of ethylene/1-hexene copolymers prepared with SC system in different polymerization condition (see Table 3)<sup>a</sup>

Entry	H%	[EE]	[EH]	[HH]	[EEE]	[HEE]	[HEH]	[EHE]	[HHE]	[HHH]	$n_E$	$n_H$
1	2.71	91.9	8.1	0.0	91.0	6.3	0.0	2.7	0.0	0.0	35.9	1.0
2	4.68	94.5	5.5	0.0	89.4	7.3	0.0	3.3	0.0	0.0	20.1	1.0
5	1.88	92.9	7.1	0.0	93.0	5.3	0.0	1.7	0.0	0.0	53.1	1.0

<sup>a</sup> Composition is in mol%; H and E stand for 1-hexene and ethylene, respectively.

is confirmed by the peak at 23.37 ppm, corresponding to the carbon **2**. The signals at 14.05 and 38.10 ppm are superposed to the signals of carbons **1** and **br** from butyl branches. Chemical shifts and assignments of carbons in the polymer chain are summarized in Table 4.

The microstructure of ethylene/1-hexene copolymers is studied by  $^{13}\text{C}$  NMR (Table 5). The absence of [HHH], [EHH] and [HEH] triads suggests random copolymerization. The comonomer average sequence lengths and ethylene reactivity ratios were calculated from the  $^{13}\text{C}$  NMR data [50,51]. Sequence length calculation showed that copolymers are formed by ca. 20–53 ethylene units between 1-hexene ones.

#### 4. Conclusions

Titanium(IV) complexes (**I**) bearing  $[\text{O}^-\text{NS}]$  tridentate ligand and was immobilized on silica and showed good activities for ethylene homo- or copolymerization with 1-hexene. Especially,  $\text{AlEt}_3$  can partially substitute expensive MMAO as cocatalyst. The PEs obtained with **SC** system have higher molecular weight, higher melting temperature and more compact morphology than those obtained with homogeneous catalyst. Detailed investigations into the use of different carriers, the application of different methods in immobilization and the various polymerization conditions for ethylene homo- and copolymerization with various comonomer, such as  $\alpha$ -olefin and cyclo-olefin are in progress and will be reported in the near future.

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