

# Ethylene/ $\alpha$ -Olefin Copolymerization Using Diphenylcyclopentadienyl-phenoxytitanium Dichloride/ $\text{Al}(\text{i-Bu})_3$ /[ $\text{Ph}_3\text{C}$ ][ $\text{B}(\text{C}_6\text{F}_5)_4$ ] Catalyst Systems

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**ABSTRACT:** Copolymerization of ethylene with 1-octene and 1-octadecene using constrained geometry catalysts 2-(3,4-diphenylcyclopentadienyl)-4,6-di-*tert*-butylphenoxytitanium dichloride (1), 2-(3,4-diphenylcyclopentadienyl)-6-*tert*-butylphenoxytitanium dichloride (2), 2-(3,4-diphenylcyclopentadienyl)-6-methylphenoxytitanium dichloride (3), and 2-(3,4-diphenylcyclopentadienyl)-6-phenylphenoxytitanium dichloride (4) was studied in the presence of  $\text{Al}(\text{i-Bu})_3$  and [ $\text{Ph}_3\text{C}$ ][ $\text{B}(\text{C}_6\text{F}_5)_4$ ](TIBA/B). The effect of the catalyst structure, comonomer, and reaction conditions on the catalytic activity, comonomer incorporation,

and molecular weight of the produced copolymers was also examined. The 1/TIBA/B catalyst system exhibits high catalytic activity and produces high molecular weight copolymers. The melting temperature and the degree of crystallinity of the copolymers show a decrease with the increase in the comonomer incorporation. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3030–3036, 2008

**Key words:** titanium catalysts; ethylenepolymerization; polyolefins; 1-octadecene; 1-octene

## INTRODUCTION

Copolymers of ethylene with  $\alpha$ -olefins are important polymer materials in industry because of their excellent performance. Therefore, there has been a continuing interest in the investigation on ethylene/ $\alpha$ -olefin copolymerization.<sup>1–5</sup> It is well known that the properties of ethylene copolymers are influenced by molecular weight, molecular weight distribution, kinds and content of comonomer, and monomer sequence distribution. In turn, some of these factors are dependent on the nature of the catalyst.<sup>6</sup> So far, many catalyst systems have been studied for the copolymerization of ethylene with  $\alpha$ -olefin. Among these catalysts, the constrained geometry catalysts (CGC) exhibit high catalytic activities and produce ethylene/ $\alpha$ -olefin copolymers with uniform compositions and narrow molecular weight distributions.<sup>7–11</sup> The CGC with a pendent nitrogen donor on the cyclopentadienyl ligand have been widely studied for the copolymerization of ethylene with  $\alpha$ -olefin in both industry and academia.<sup>12–14</sup> A considerable number of catalysts with a pendent oxygen donor

on the cyclopentadienyl ligand have also been reported,<sup>15–17</sup> but the copolymerization of ethylene with  $\alpha$ -olefin catalyzed by this kind of catalysts has not been systematically studied so far.

Recently, we reported the synthesis of diphenylcyclopentadienyl-phenoxytitanium dichlorides **1–4** (Chart 1), a type of CGC precursors with a pendent oxygen donor, and the ethylene polymerization catalyzed by these complexes in the presence of  $\text{Al}(\text{i-Bu})_3$  and [ $\text{Ph}_3\text{C}$ ][ $\text{B}(\text{C}_6\text{F}_5)_4$ ](TIBA/B).<sup>18</sup> It was found that these complexes exhibited high catalytic activity for the ethylene polymerization upon activation. Based on their structural feature, it would be expected that these complexes might be converted into good catalysts for the copolymerization of ethylene with  $\alpha$ -olefin upon activation. In this article, we present the results of ethylene/1-octene and ethylene/1-octadecene copolymerization catalyzed by the **1–4**/TIBA/B catalyst systems under different conditions.

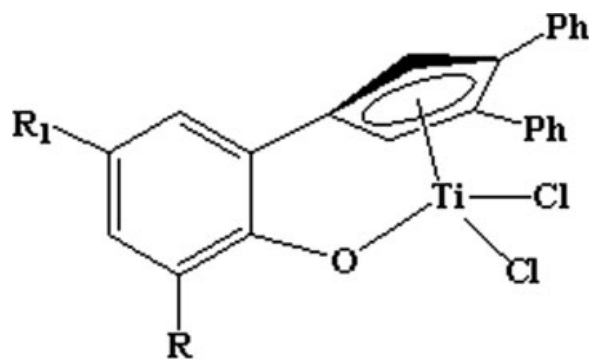
## EXPERIMENTAL

### Materials and general procedures

All experiments involving air-sensitive compounds were performed using standard Schlenk techniques in an atmosphere of high-purity nitrogen or glove-box techniques. Toluene was distilled from sodium/benzophenone ketyl under nitrogen before use. 1-Octene and 1-octadecene were dried over calcium

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- 1:  $R_1 = {}^t\text{Bu}$   $R = {}^t\text{Bu}$   
 2:  $R_1 = \text{H}$   $R = {}^t\text{Bu}$   
 3:  $R_1 = \text{H}$   $R = \text{Me}$   
 4:  $R_1 = \text{H}$   $R = \text{Ph}$

Chart 1 Structure of complexes 1–4.

hydride for several days and filtered under nitrogen before use.  $\text{Al}({}^t\text{Bu})_3$  was purchased from Aldrich. Complexes 1–4<sup>18</sup> and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ <sup>19–21</sup> were synthesized according to the literature procedures. Polymerization grade ethylene was further purified by passage through columns of 5 Å molecular sieves and  $\text{MnO}$ .

The  $^{13}\text{C}$  NMR data of the copolymers were obtained on a Varian Unity 400-MHz spectrometer at 125°C with  $o\text{-C}_6\text{D}_4\text{Cl}_2$  as the solvent and tetramethylsilane as the internal standard. The comonomer content in the copolymers was calculated by the  $^{13}\text{C}$  NMR integrated peak area with eq. (3). If  $I(\text{CH})$ ,  $X$ , and  $I$  is the integrated peak area of methine carbon signals, ethylene carbon signals, and all carbon signals, respectively, then eqs. (1) and (2) can be written as:

$$n_{\text{com}} \times I(\text{CH}) + X = I \quad (1)$$

where  $n_{\text{com}}$  is the number of carbons of the comonomer.

$$\text{Content}_{\text{comonomer}}(\text{mol}\%) = \frac{I(\text{CH})}{I(\text{CH}) + X/2} \times 100 \quad (2)$$

By rearranging eqs. (1) and (2), one obtains:

$$\text{Content}_{\text{comonomer}}(\text{mol}\%) = \frac{2 \times I(\text{CH})}{I - (n_{\text{com}} - 2) \times I(\text{CH})} \times 100 \quad (3)$$

The differential scanning calorimetry (DSC) analysis was performed on a NETZSCH DSC 204 differential scanning calorimeter. Each sample was heated from 40 to 160°C at a heating rate of 10°C/min and

reheated at the same rate. The molecular weights and polydispersity indices of the polymer samples were determined at 150°C on a PL-GPC 220 high-temperature chromatograph with 1,2,4-trichlorobenzene as the solvent, and the calibration made with polystyrene standard. X-ray diffraction (XRD) analysis was carried out on a Siemens D5005 at room temperature.

### Copolymerization of ethylene with $\alpha$ -olefin

A dry 250-mL steel autoclave with a magnetic stirrer was charged with a solution of appropriate amounts of  $\alpha$ -olefin in toluene (80 mL), thermostated at the desired temperature, and saturated with ethylene (1 atm). The polymerization reaction was started by injection of a mixture of a catalyst and  $\text{Al}({}^t\text{Bu})_3$  in toluene (10 mL) and a solution of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in toluene (10 mL) at the same time. The vessel was repressurized to needed pressure with ethylene immediately, and the pressure was maintained by continuously feeding ethylene. After a certain period of time, the polymerization was quenched by injecting acidified methanol [ $\text{HCl}$  (3M)/methanol = 1 : 1]. The polymer was collected by filtration, washed with water and methanol, and dried at 60°C *in vacuo* to a constant weight.

## RESULTS AND DISCUSSION

### Copolymerization of ethylene with 1-octene and 1-octadecene

The copolymerization results of ethylene/1-octene and ethylene/1-octadecene catalyzed by 1–4/TIBA/B catalyst systems under different conditions are summarized in Tables I and II, respectively. It can be seen that the effect of the substituents  $R$  and  $R_1$  on the phenolate of the ligand in 1–4 on their catalytic activity is obvious. With the  $R$  and  $R_1$  being an electron-donating *tert*-butyl group, the 1/TIBA/B catalyst system displays a high catalytic activity of  $7.08 \times 10^3$  kg/(mol<sub>Ti</sub> h) (Run 3 in Table I). Under the same conditions, When the  $R_1$  group is replaced by a hydrogen atom, the 2/TIBA/B catalyst system exhibits a lower catalytic activity of  $5.88 \times 10^3$  kg/(mol<sub>Ti</sub> h) (Run 13 in Table I); with the  $R_1$  being a hydrogen atom and the  $R$  being a methyl group, the 3/TIBA/B catalyst system presents a further lower catalytic activity of  $3.55 \times 10^3$  kg/(mol<sub>Ti</sub> h) (Run 16 in Table I); and with the  $R_1$  being a hydrogen atom and the  $R$  being an electron-withdrawing phenyl group, the 4/TIBA/B catalyst system presents the lowest catalytic activity of  $2.56 \times 10^3$  kg/(mol<sub>Ti</sub> h) (Run 19 in Table I). The same trend was also observed with the 1–4/TIBA/B catalyst systems for the ethylene/1-octadecene copolymerization. The

**TABLE I**  
Copolymerization Results of Ethylene with 1-Octene by the 1-4/TIBA/B Catalyst Systems<sup>a</sup>

| Run | Cat. | Al/Ti <sup>b</sup> | T (°C) <sup>c</sup> | 1-Octene (mol/L) <sup>d</sup> | Activity (10 <sup>3</sup> ) <sup>e</sup> | 1-Octene content (mol %) <sup>f</sup> | M <sub>w</sub> (10 <sup>3</sup> ) <sup>g</sup> | PDI <sup>g</sup> | T <sub>m</sub> (°C) <sup>h</sup> | X <sub>c</sub> (%) <sup>i</sup> |
|-----|------|--------------------|---------------------|-------------------------------|--|---------------------------------------|--|------------------|----------------------------------|---------------------------------|
| 1   | 1    | 120                | 70                  | 0.05                          | 3.85                                     | 2.1                                   | 22.2   | 2.70             | 111.1                            | 33.8                            |
| 2   | 1    | 120                | 70                  | 0.10                          | 5.08                                     | 4.3                                   | 21.4   | 2.68             | 109.6                            | 33.1                            |
| 3   | 1    | 120                | 70                  | 0.15                          | 7.08                                     | 6.0                                   | 20.6   | 2.72             | 107.4                            | 32.0                            |
| 4   | 1    | 120                | 70                  | 0.20                          | 5.78                                     | 8.5                                   | 17.4   | 2.75             | 104.6                            | 30.6                            |
| 5   | 1    | 120                | 70                  | 0.25                          | 4.28                                     | 9.8                                   | 14.2   | 2.93             | 102.1                            | 28.5                            |
| 6   | 1    | 120                | 70                  | 0.30                          | 2.26                                     | 11.0                                  | 10.1   | 3.19             | 98.4                             | 25.7                            |
| 7   | 1    | 60                 | 70                  | 0.15                          | 3.55                                     | n.d. <sup>j</sup>                     | n.d.   | n.d.             | n.d.                             | n.d.                            |
| 8   | 1    | 90                 | 70                  | 0.15                          | 5.07                                     | n.d.                                  | n.d.   | n.d.             | n.d.                             | n.d.                            |
| 9   | 1    | 150                | 70                  | 0.15                          | 5.82                                     | n.d.                                  | n.d.   | n.d.             | n.d.                             | n.d.                            |
| 10  | 1    | 120                | 50                  | 0.15                          | 5.05                                     | 4.8                                   | 24.8   | 2.25             | n.d.                             | n.d.                            |
| 11  | 1    | 120                | 90                  | 0.15                          | 6.97                                     | 6.6                                   | 15.6   | 2.32             | n.d.                             | n.d.                            |
| 12  | 2    | 120                | 70                  | 0.05                          | 2.10                                     | 2.4                                   | 18.3   | 2.60             | 105.1                            | 31.1                            |
| 13  | 2    | 120                | 70                  | 0.15                          | 5.88                                     | 6.6                                   | 16.8   | 2.73             | 101.9                            | 29.6                            |
| 14  | 2    | 120                | 70                  | 0.30                          | 1.54                                     | 11.2                                  | 6.2  | 2.95             | 93.3                             | 22.1                            |
| 15  | 3    | 120                | 70                  | 0.05                          | 0.81                                     | 2.9                                   | 13.1   | 2.58             | 106.2                            | 32.2                            |
| 16  | 3    | 120                | 70                  | 0.15                          | 3.55                                     | 7.5                                   | 11.6   | 2.81             | 104.8                            | 30.8                            |
| 17  | 3    | 120                | 70                  | 0.30                          | 1.01                                     | 11.6                                  | 4.3  | 3.05             | 95.3                             | 22.9                            |
| 18  | 4    | 120                | 70                  | 0.05                          | 0.51                                     | 2.7                                   | 14.5   | 2.63             | 105.8                            | 31.9                            |
| 19  | 4    | 120                | 70                  | 0.15                          | 2.56                                     | 7.2                                   | 13.3   | 2.71             | 103.2                            | 30.3                            |
| 20  | 4    | 120                | 70                  | 0.30                          | 0.68                                     | 11.5                                  | 5.0  | 2.92             | 94.6                             | 22.6                            |

<sup>a</sup> Reaction conditions: ethylene pressure 6 atm, catalysts 1-4 1 μmol, toluene + 1-octene total 100 mL, molar ratio of B/Ti 1.5, polymerization time 10 min.

<sup>b</sup> Molar ratio of Al/Ti.

<sup>c</sup> Polymerization temperature.

<sup>d</sup> Concentration of 1-octene in the feed.

<sup>e</sup> Activity in kg/(mol<sub>Ti</sub>h).

<sup>f</sup> Determined by <sup>13</sup>C NMR.

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

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

<sup>i</sup> Crystallinity calculated as the ratio of the fusion heats of the samples and folded-chain polyethylene.<sup>22</sup>

<sup>j</sup> n.d., not determined.

**TABLE II**  
Copolymerization Results of Ethylene with 1-Octadecene by the 1-4/TIBA/B Catalyst Systems<sup>a</sup>

| Run | Cat. | 1-Octadecene (mol/L) <sup>b</sup> | Activity (10 <sup>3</sup> ) <sup>c</sup> | 1-Octadecene content (mol %) <sup>d</sup> | M <sub>w</sub> (10 <sup>3</sup> ) <sup>e</sup> | PDI <sup>e</sup> | T <sub>m</sub> (°C) <sup>f</sup> | X <sub>c</sub> (%) <sup>g</sup> |
|-----|------|-----------------------------------|--|---|--|------------------|----------------------------------|---------------------------------|
| 1   | 1    | 0.05                              | 5.13                                     | 0.8                                       | 34.6   | 2.32             | 116.2                            | 34.1                            |
| 2   | 1    | 0.10                              | 6.63                                     | 1.6                                       | 31.3   | 2.41             | 114.7                            | 33.0                            |
| 3   | 1    | 0.15                              | 7.82                                     | 2.5                                       | 25.1   | 2.28             | 112.6                            | 30.8                            |
| 4   | 1    | 0.20                              | 9.15                                     | 3.1                                       | 16.7   | 2.45             | 108.7                            | 27.5                            |
| 5   | 1    | 0.25                              | 10.64                                    | 4.1                                       | 12.3   | 2.33             | 104.4                            | 23.4                            |
| 6   | 1    | 0.30                              | 8.14                                     | 5.2                                       | 9.3  | 2.15             | 99.3                             | 18.7                            |
| 7   | 2    | 0.15                              | 6.42                                     | 2.7                                       | 19.5   | 2.38             | 99.8                             | 28.3                            |
| 8   | 2    | 0.25                              | 8.82                                     | 4.6                                       | 8.2  | 2.44             | 92.1                             | 19.7                            |
| 9   | 2    | 0.30                              | 6.01                                     | 5.5                                       | 6.0  | 2.25             | 88.5                             | 13.4                            |
| 10  | 3    | 0.15                              | 2.38                                     | 3.0                                       | 12.4   | 2.35             | 100.9                            | 29.2                            |
| 11  | 3    | 0.25                              | 4.15                                     | 5.3                                       | 3.7  | 2.42             | 95.3                             | 21.3                            |
| 12  | 3    | 0.30                              | 2.22                                     | 6.0                                       | 3.2  | 2.31             | 90.4                             | 15.4                            |
| 13  | 4    | 0.15                              | 1.75                                     | 2.9                                       | 15.4   | 2.37             | 100.5                            | 28.8                            |
| 14  | 4    | 0.25                              | 3.22                                     | 4.9                                       | 6.0  | 2.42             | 94.2                             | 20.9                            |
| 15  | 4    | 0.30                              | 1.27                                     | 5.7                                       | 4.2  | 2.27             | 89.7                             | 14.6                            |

<sup>a</sup> Reaction conditions: ethylene pressure 6 atm, catalysts 1-4 1 μmol, toluene + 1-octadecene total 100 mL, molar ratio of Al/Ti 120, molar ratio of B/Ti 1.5, Polymerization temperature 70°C, polymerization time 10 min.

<sup>b</sup> Concentration of 1-octadecene in the feed.

<sup>c</sup> Activity in kg/(mol<sub>Ti</sub>h).

<sup>d</sup> Determined by <sup>13</sup>C NMR.

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

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

<sup>g</sup> Crystallinity calculated as the ratio of the fusion heats of the samples and folded-chain polyethylene.<sup>22</sup>

TABLE III  
Effect of Polymerization Time on the Catalytic Activity of 1-4/TIBA/B Catalyst Systems for the Ethylene/1-Octene Copolymerization<sup>a</sup>

| Run | Cat. | Time (min) | Polymer yield (mg) | Activity (10 <sup>3</sup> ) <sup>b</sup> |
|-----|------|------------|--------------------|--|
| 1   | 1    | 5          | 653                | 7.83                                     |
| 2   | 1    | 10         | 1180               | 7.08                                     |
| 3   | 1    | 30         | 1380               | 2.76                                     |
| 4   | 2    | 5          | 565                | 6.78                                     |
| 5   | 2    | 10         | 980                | 5.88                                     |
| 6   | 2    | 30         | 1130               | 2.26                                     |
| 7   | 3    | 5          | 482                | 5.78                                     |
| 8   | 3    | 10         | 592                | 3.55                                     |
| 9   | 3    | 30         | 632                | 1.26                                     |
| 10  | 4    | 5          | 351                | 4.21                                     |
| 11  | 4    | 10         | 427                | 2.56                                     |
| 12  | 4    | 30         | 440                | 0.88                                     |

<sup>a</sup> Reaction conditions: ethylene pressure 6 atm, catalysts 1-4 1  $\mu$ mol, toluene + 1-octene total 100 mL, 1-octene 0.15 mol/L, molar ratio of Al/Ti 120, molar ratio of B/Ti 1.5, and polymerization temperature 70°C.

<sup>b</sup> Activity in kg/(mol<sub>Ti</sub>h).

general catalytic activity of these complexes (**1** > **2** > **3** > **4**) for the copolymerization of ethylene with 1-octene and 1-octadecene is in the same order as that observed for ethylene homopolymerization.<sup>18</sup> These results might be mainly ascribed to the electronic effect of the *R* and *R*<sub>1</sub> groups because it has been well known that the catalytic activity of metallocene catalysts could be increased by electron-donating groups on the ligand and decreased by electron-withdrawing groups, while the steric effect of the *R* group at the ortho position of the phenolate seems also to play a role in determining the order of the catalytic activity of these catalysts considering that the catalytic activity of **2** is obviously higher than that of **3**. In principle, the bulky *tert*-butyl at the ortho position of the phenolate has a higher tendency for protecting the O-Ti bonding toward catalyst decomposition. It is well known that the alkoxy-Ti bond can be readily replaced by alkyl-Ti bonding upon treatment with trialkylaluminum or MAO.<sup>23</sup> To examine the difference in decomposition rate of these catalysts, the effect of polymerization time on the catalytic activity of these catalyst systems for the ethylene/1-octene copolymerization was investigated. The results are listed in Table III. It was found that the catalytic activity of the **3** and **4**/TIBA/B catalyst systems decreases more quickly with the increase in polymerization time from 5 to 10 min. These results confirm that catalysts with a smaller *R* group decompose faster during the polymerization. On the other hand, the substituents *R* and *R*<sub>1</sub> affect the comonomer incorporation. The order of comonomer incorporation ability of **1-4** for the copolymerization of ethylene with 1-octene and 1-octadecene is

**3** > **4** > **2** > **1**. This result suggests that both *R* and *R*<sub>1</sub> affect the comonomer incorporation.

The effect of the Al/Ti molar ratio and the polymerization temperature on the ethylene/1-octene copolymerization reaction was examined with the **1**/TIBA/B catalyst system. It is found that the catalytic activity increases with the increase of Al/Ti molar ratio until reaching the maximum value of 7.08  $\times 10^3$  kg/(mol<sub>Ti</sub> h) at Al/Ti = 120. Further increase in the Al/Ti mol ratio results in a decrease in the catalytic activity. Similar phenomenon has been observed previously.<sup>24,25</sup> The catalytic activity is also dependent on the polymerization temperature, and the highest catalytic activity was obtained at 70°C, which reflects the nature of tight interaction between the catalyst cation and the cocatalyst anion in the CGC systems.<sup>26</sup> The comonomer incorporation was also found to increase with the increase in polymerization temperature. Similar results have been reported earlier.<sup>27</sup>

The influence of the concentration of comonomer in the feed on the catalytic activity of these catalyst systems and the comonomer incorporation was also examined by conducting the copolymerization of ethylene with 1-octene or 1-octadecene under different comonomer concentrations. As seen from the data in Tables I and II, the catalytic activity for all catalyst systems increases first with the increase in comonomer concentration until reaching a maximum value and then decreases, which can be explained by the so-called comonomer effect.<sup>28-31</sup> The comonomer incorporation also increases with the increase in comonomer concentration for both ethylene/1-octene and ethylene/1-octadecene copolymerization as seen in Tables I and II. The comonomer incorporation ability for 1-octene is higher than that for the long-chain 1-octadecene under similar conditions (Runs 1-6 in Table I and Runs 1-6 in Table II), which could be attributed to that the coordination ability of the bulkier 1-octadecene is lower than that of 1-octene.<sup>32</sup> Similar results have been reported for other metallocene catalyst systems.<sup>30</sup> The comonomer incorporation ability of our catalyst systems seems to be similar to that of the [Me<sub>2</sub>Si( $\eta$ <sup>5</sup>-Me<sub>4</sub>C<sub>5</sub>)(N<sup>t</sup>Bu)]TiCl<sub>2</sub>/MAO catalyst system under the similar conditions.<sup>33</sup> However, the catalytic activity of our catalyst systems is lower than that of the latter catalyst system, which may be attributed to the presence of two electron-withdrawing phenyl groups on the cyclopentadienyl group of the ligand. The molecular weight of the copolymers produced by our catalyst systems is much lower compared to the one of the copolymers from the latter catalyst system due probably to that the more open coordination environment of our catalysts makes the  $\beta$ -hydride elimination reaction to happen easily. We did not try to get copoly-

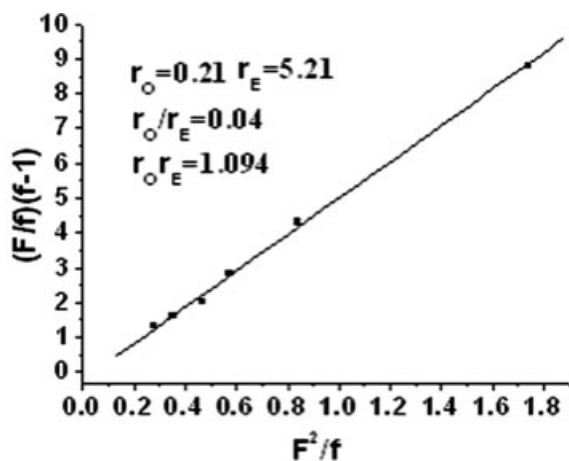


Figure 1 Fineman-Ross plot for ethylene/1-octene copolymerization with the 1/TIBA/B catalyst system.

mers with higher comonomer contents by further increasing the comonomer concentration, because the molecular weight of the produced copolymers is too low.

The ethylene and comonomer reactivity ratios ( $r_E$ ,  $r_O$ , and  $r_{OD}$  are the reactivity ratios of ethylene, 1-octene, and 1-octadecene, respectively) for the ethylene/1-octene and ethylene/1-octadecene copolymerization by 1/TIBA/B catalyst system were calculated from Fineman-Ross plots<sup>34</sup> as shown in Figures 1 and 2, respectively. The monomer reactivity ratios of  $r_E$  and  $r_O$  are 5.21 and 0.21, respectively, in the ethylene/1-octene copolymerization, while the values of  $r_E$  and  $r_{OD}$  are 13.17 and 0.081, respectively, in the ethylene/1-octadecene copolymerization. The ratio of  $r_O/r_E$  and  $r_{OD}/r_E$  are 0.04 and 0.006, respectively, which can be used to compare the relative comonomer incorporation ability.<sup>35,36</sup> Both values of reactivity ratio products  $r_O r_E$  and  $r_{OD} r_E$  are close to 1 ( $r_O r_E = 1.094$ ,  $r_{OD} r_E = 1.067$ ), which demonstrates that

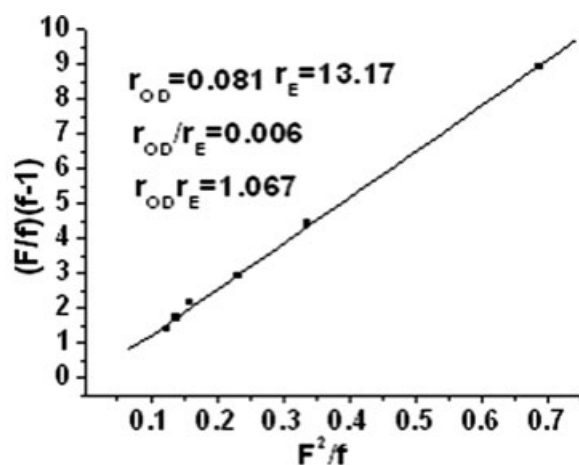


Figure 2 Fineman-Ross plot for ethylene/1-octadecene copolymerization with the 1/TIBA/B catalyst system.

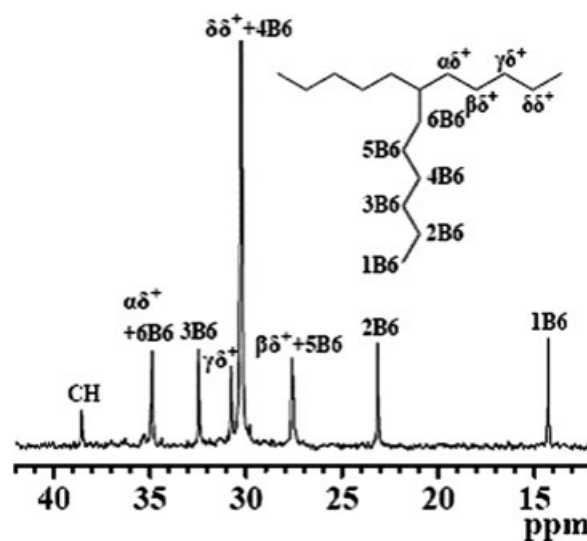


Figure 3  $^{13}\text{C}$  NMR spectrum of a poly(ethylene-co-1-octene) sample (Run 6 in Table I).

ethylene/1-octene and ethylene/1-octadecene copolymerization reactions proceed in a random manner.

### Characterizations of the copolymers

The obtained copolymers were characterized by means of  $^{13}\text{C}$  NMR, GPC, DSC, and XRD. The microstructure of the copolymers was analyzed with  $^{13}\text{C}$  NMR spectroscopy. Typical  $^{13}\text{C}$  NMR spectra of poly(ethylene-co-1-octene) and poly(ethylene-co-1-octadecene) samples are presented in Figures 3 and 4, respectively. The carbon assignments were established according to the rules of Linderman and Adams.<sup>37</sup> It can be seen clearly from the  $^{13}\text{C}$  NMR spectra that the 1-octene or 1-octadecene units in the copolymers are isolated by the ethylene units, and no

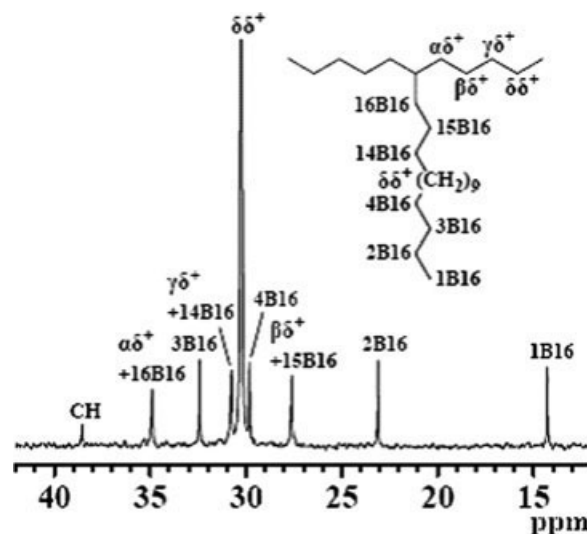
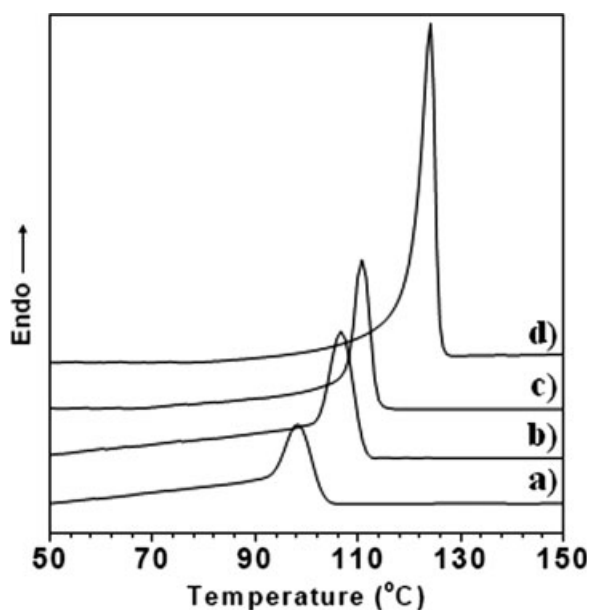


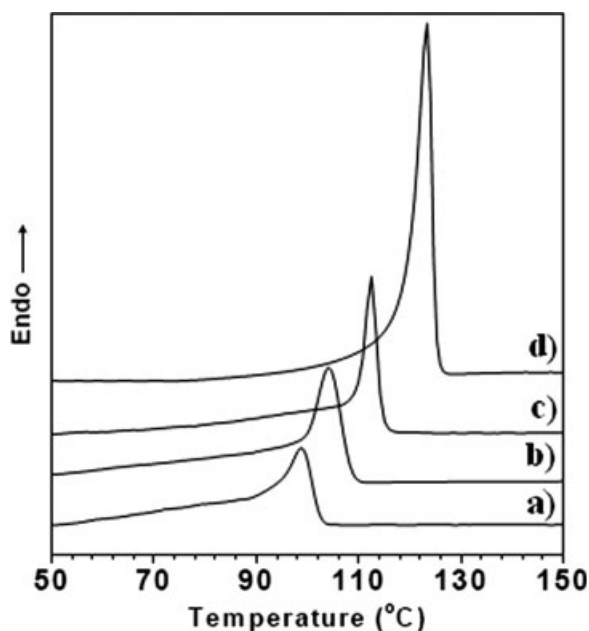
Figure 4  $^{13}\text{C}$  NMR spectrum of a poly(ethylene-co-1-octadecene) sample (Run 6 in Table II).



**Figure 5** DSC melting curves of poly(ethylene-*co*-1-octene) samples by the 1/TIBA/B catalyst system (a) Run 6 in Table I, (b) Run 3 in Table I, (c) Run 1 in Table I, and (d) polyethylene.

$\beta\beta$  resonance (24.5 ppm) for alternative sequence and  $\alpha\alpha$  resonance (40.0 ~ 41.0 ppm) for block type sequences was observed.<sup>38</sup>

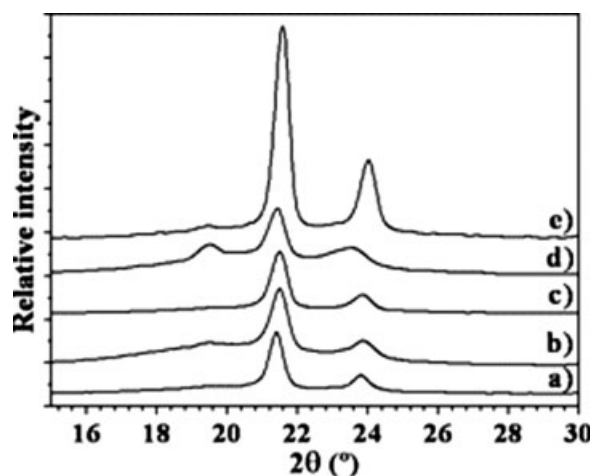
The GPC analysis reveals that the molecular weights of the poly(ethylene-*co*-1-octene)s and poly(ethylene-*co*-1-octadecene)s obtained with these catalyst systems is relatively low, as seen in Tables I and



**Figure 6** DSC melting curves of poly(ethylene-*co*-1-octadecene) samples by the 1/TIBA/B catalyst system (a) Run 6 in Table II, (b) Run 5 in Table II, (c) Run 3 in Table II, and (d) polyethylene.

II. The copolymers produced by the 1/TIBA/B catalyst system possess the highest molecular weight, while the copolymers from the 3/TIBA/B catalyst system under the same conditions show the lowest molecular weight, which may be ascribed to that a smaller R group at the ortho position of the phenolate of the ligand favors the  $\beta$ -hydride elimination reaction. As mentioned earlier, the molecular weight of the copolymers is sensitive to the comonomer concentration in the feed and decreases quickly with the increase in the comonomer concentration (Runs 1–6 in Table I and Runs 1–6 in Table II), which is in agreement with the results observed with other catalyst systems.<sup>5,36</sup> The molecular weight of the obtained copolymers also decreases with the increase in polymerization temperature as can be seen in Table I.

DSC measurements on the copolymer samples indicate that both the melting temperature and the degree of crystallinity of the poly(ethylene-*co*-1-octene)s and poly(ethylene-*co*-1-octadecene)s decrease with the increase in the comonomer content as shown in Tables I and II. The DSC curves of some typical poly(ethylene-*co*-1-octene) and poly(ethylene-*co*-1-octadecene) samples are shown in Figures 5 and 6, respectively. The X-ray diffraction (XRD) analysis on some typical copolymer samples was conducted for qualitatively probing the crystallinity of the copolymers. The XRD patterns of several typical samples are shown in Figure 7. It can be seen that these copolymers all display the 110 and 200 reflections, which are characteristic of the orthorhombic cell of polyethylene, although there is some shifting in their position due to the known expansion of the unit cell in ethylene copolymers as the comonomer content increases.<sup>5</sup>



**Figure 7** X-ray diffractograms of polymer samples by the 1/TIBA/B catalyst system (a) Run 3 in Table I, (b) Run 6 in Table I, (c) Run 3 in Table II, (d) Run 6 in Table II, and (e) polyethylene.

## CONCLUSIONS

The constrained geometry (diphenylcyclopentadienyl-phenoxy)titanium dichlorides **1–4**, activated with TIBA/B, are efficient catalysts for the copolymerization of ethylene with 1-octene and 1-octadecene. The catalytic activity, comonomer incorporation, and molecular weight of the produced copolymers can be controlled by the variation of catalyst structure, comonomer, and reaction parameters such as the reaction temperature and comonomer concentration. The **1**/TIBA/B catalyst system exhibits high catalytic activity and produces copolymers with high molecular weight, while the **3**/TIBA/B catalyst systems yield copolymers with high comonomer incorporation under the same conditions.

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