

# Ethylene/1-Octadecene Copolymerization Using $[\eta^5:\eta^1\text{-C}_5\text{Me}_4\text{-4-R}_1\text{-6-R-C}_6\text{H}_2\text{O}]\text{TiCl}_2$ Catalysts

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**ABSTRACT:** Copolymerization of ethylene with 1-octadecene was studied using  $[\eta^5:\eta^1\text{-C}_5\text{Me}_4\text{-4-R}_1\text{-6-R-C}_6\text{H}_2\text{O}]\text{TiCl}_2$  [ $R_1 = \text{tBu}$  (1), H (2, 3, 4);  $R = \text{tBu}$  (1, 2), Me (3), Ph (4)] as catalysts in the presence of  $\text{Al}(i\text{-Bu})_3$  and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ . The effect of the concentration of comonomer in the feed and Al/Ti molar ratio on the catalytic activity and molecular weight of the resultant copolymer were investigated. The substituents on the phenyl ring of the ligand affect considerably both the catalytic activity and comonomer incorporation. The 1/Al(*i*-Bu)<sub>3</sub>/

$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  catalyst system exhibits the highest catalytic activity and produces copolymers with the highest molecular weight, while the 2/Al(*i*-Bu)<sub>3</sub>/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  catalyst system gives copolymers with the highest comonomer incorporation under similar conditions. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1514–1519, 2011

**Key words:** polyethylene; 1-octadecene; copolymerization; constrained geometry catalyst; titanium complex

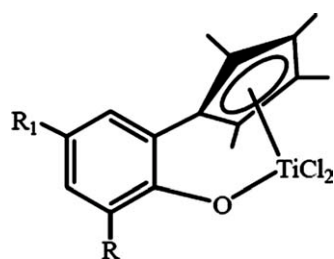
## INTRODUCTION

Constrained geometry metallocene catalysts have received extensive attention in the last decade because of their structural feature, good catalytic performance for olefin copolymerization, and their importance in industrial applications.<sup>1–7</sup> Among this category of catalysts, the constrained geometry catalysts with a pendent nitrogen donor on the cyclopentadienyl ligand have been widely studied for the copolymerization of ethylene with  $\alpha$ -olefins in both industry and academia.<sup>8–14</sup> Although a considerable number of catalysts with a pendent oxygen donor on the cyclopentadienyl ligand have also been reported,<sup>15–22</sup> the copolymerization of ethylene with  $\alpha$ -olefins catalyzed by this kind of catalysts has not been systematically studied so far. On the other hand, although the copolymerization of ethylene with short chain  $\alpha$ -olefins, such as 1-hexene and 1-octene, has been studied using different constrained geometry catalysts,<sup>23–27</sup> the copolymerization of ethylene with long chain  $\alpha$ -olefins, such as 1-hexadecene and 1-octadecene, has received less attention. It was reported that the dichlorozirconocene/methylaluminoxane catalyst system shows relatively low

comonomer incorporation for the copolymerization of ethylene with 1-hexadecene and produces low molecular weight copolymers.<sup>28,29</sup> Similar results were reported for the copolymerization of ethylene with 1-octadecene using the racemic ethylenebis(indenyl)zirconium dichloride/methylaluminoxane catalyst system and dimethylsilylenebis(indenyl)zirconium dichloride/methylaluminoxane catalyst system.<sup>30,31</sup> We have recently reported the copolymerization results of ethylene with 1-octadecene using constrained geometry complexes  $[\eta^5:\eta^1\text{-C}_5\text{H}_2\text{Ph}_2\text{-4-R}_1\text{-6-R-C}_6\text{H}_2\text{O}]\text{TiCl}_2$  as catalysts and  $\text{Al}(i\text{-Bu})_3$ / $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  as cocatalysts.<sup>32</sup> It was found that these catalyst systems show relatively low catalytic activity and produce low molecular weight copolymers with moderate comonomer incorporation. In recent years, we have also synthesized another series of constrained geometry catalyst precursors with similar structures  $[\eta^5:\eta^1\text{-C}_5\text{Me}_4\text{-4-R}_1\text{-6-R-C}_6\text{H}_2\text{O}]\text{TiCl}_2$  1–4 (Chart 1).<sup>33,34</sup> It was found that these complexes exhibit high catalytic activity for the polymerization of ethylene and propylene as well as the copolymerization of ethylene/norbornene, ethylene/5-ethylidene-2-norbornene upon activation with  $\text{Al}(i\text{-Bu})_3$  and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ .<sup>35–37</sup> Based on their structural feature and the electron-donating property of the tetramethylcyclopentadienyl group in their ligands, complexes 1–4 would be expected to be better precatalysts for the copolymerization of ethylene with  $\alpha$ -olefins than the above-mentioned diphenylcyclopentadienyl analogs  $[\eta^5:\eta^1\text{-C}_5\text{H}_2\text{Ph}_2\text{-4-R}_1\text{-6-R-C}_6\text{H}_2\text{O}]\text{TiCl}_2$ , by showing higher catalytic activity and producing copolymers with higher molecular

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R = <sup>t</sup>Bu (1, 2), Me (3), Ph (4)  
 R<sub>1</sub> = <sup>t</sup>Bu (1), H (2, 3, 4)

Chart 1 Complexes 1–4.

weight. In this article, we wish to present the results of ethylene/1-octadecene copolymerization catalyzed by **1-4**/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst systems under different conditions.

## EXPERIMENTAL

### Material and general procedures

All experiments involving air-sensitive compounds were performed using standard Schlenk tube or glove-box techniques in an atmosphere of high-purity nitrogen. Toluene was distilled from sodium/benzophenone ketyl under nitrogen prior to use. 1-Octadecene was dried over calcium hydride for several days and filtered under nitrogen prior to use. Al(*i*-Bu)<sub>3</sub> was purchased from Aldrich. Complexes **1-4**<sup>24</sup> and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>38,39</sup> were synthesized according to the literature procedures. Polymerization grade ethylene was further purified by passage through columns of 5 Å molecular sieves and MnO.

The <sup>13</sup>C-NMR data of the copolymers were obtained on a Varian Unity 400-MHz spectrometer at 125°C with *o*-C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> as the solvent and tetramethylsilane as the internal standard. The differential scanning calorimetry (DSC) analysis was performed on a NETZSCH DSC 204 differential scanning calorimeter. Each sample was heated from –20 to 150°C at a heating rate of 10°C/min two times and the data from the second scan are used. 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 on the copolymers (powder) was carried out on a Siemens D5005 at room temperature.

### Copolymerization of ethylene with 1-octadecene

A dry 250-mL steel autoclave with a magnetic stirrer was charged with a solution of appropriate amount

of 1-octadecene in toluene (80 mL), thermostated at the desired temperature, and saturated with ethylene (0.1 MPa). The polymerization reaction was started by injection of a mixture of Al(*i*-Bu)<sub>3</sub> and a catalyst in toluene (10 mL) and a solution of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in toluene (10 mL) at the same time. The vessel was repressurized to the needed pressure with ethylene immediately, and the pressure was maintained by continuously feeding ethylene. After a specified period, the polymerization was quenched by injecting acidified methanol [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/1-octadecene

The copolymerization of ethylene with 1-octadecene catalyzed by the complexes **1-4** in the presence of Al(*i*-Bu)<sub>3</sub> and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was studied in detail and the results are summarized in Table I. The catalytic activity of these catalyst systems is sensitive to the molar ratio of Al/Ti and the polymerization temperature when the concentration of the comonomer in the feed was kept unchanged. The highest catalytic activity was reached for these catalyst systems at about 80°C and therefore most of the polymerization experiments were carried out at this temperature. For the **1**/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst system, the catalytic activity increases with the increase in Al/Ti molar ratio and reaches the highest value with the Al/Ti ratio about 80. Further increase in the Al/Ti ratio results in a decrease in the catalytic activity (runs 1–3). Similar results were also observed previously for the polymerization of ethylene and propylene.<sup>33,35</sup> It is possible that excessive Al(*i*-Bu)<sub>3</sub> would consume some [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], and therefore result in that the catalyst could not be efficiently activated.<sup>24</sup> The comonomer content in the resultant copolymers was found to increase with the increase in polymerization temperature due to the decrease of the ethylene concentration. It was also observed that the comonomer content in the resultant copolymers decreases with the increase in ethylene pressure. Polymerization experiments (runs 2, 10–13) for different times were also carried out with the **1**/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst system, and the variations of the polymer yield and the catalytic activity with the polymerization time are plotted in Figure 1. It can be seen from the results of these experiments that the polymer yield increases little with the catalytic activity decreasing remarkably when the polymerization time is longer than 30 min, and the molecular weight distribution of the resultant copolymers increases while the comonomer

TABLE I  
Copolymerizations of Ethylene with 1-Octadecene (1-O) Catalyzed by 1–4/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]  
Catalyst Systems<sup>a</sup>

Run	Cat.	Al/Ti <sup>b</sup>	Time <sup>c</sup> (min)	[1-O] (mol/l)	Activity <sup>d</sup> (×10 <sup>3</sup> )	1-O content (mol%) <sup>e</sup>	<i>T<sub>m</sub></i> (°C) <sup>f</sup>	<i>M<sub>w</sub></i> <sup>g</sup> (×10 <sup>3</sup> )	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>g</sup>	<i>X<sub>c</sub></i> (%) <sup>h</sup>
1	1	60	10	0.4	26	7.6	94.9	18.7	2.56	14.4
2	1	80	10	0.4	30	7.5	96.5	16.6	2.84	14.6
3	1	100	10	0.4	27	7.4	96.4	12.8	2.68	15.1
4 <sup>i</sup>	1	80	10	0.4	22	6.6	99.6	17.1	2.34	16.3
5 <sup>j</sup>	1	80	10	0.4	21	8.2	91.3	13.2	2.86	13.4
6 <sup>k</sup>	1	80	10	0.4	32	5.3	102.7	18.1	2.44	17.9
7	1	80	10	0.2	26	4.2	112.1	19.5	2.51	20.0
8	1	80	10	0.6	37	11.5	81.7	13.3	2.42	8.1
9	1	80	10	0.8	35	14.1	67.3	11.6	2.27	3.8
10	1	80	5	0.4	33	7.7	94.5	15.7	2.25	14.1
11	1	80	15	0.4	25	7.4	96.3	16.8	2.92	14.5
12	1	80	30	0.4	17	7.2	96.5	17.1	3.24	14.7
13	1	80	60	0.4	9.1	7.1	96.6	17.3	3.47	14.8
14	2	80	10	0.2	19	4.4	107.4	18.4	2.43	19.3
15	2	80	10	0.4	23	8.6	89.9	15.5	2.41	12.5
16	2	80	10	0.6	34	12.4	77.8	12.8	2.32	6.7
17	2	80	10	0.8	31	15.5	61.1	11.2	2.36	3.1
18	3	80	10	0.2	7.6	3.6	108.5	15.3	2.31	21.4
19	3	80	10	0.4	9.0	7.1	93.5	12.7	2.38	15.3
20	3	80	10	0.6	7.8	10.1	83.2	11.8	2.21	10.2
21	3	80	10	0.8	7.2	12.9	74.3	10.2	2.13	6.1
22	4	80	10	0.2	6.1	3.4	106.4	10.5	2.34	21.8
23	4	80	10	0.4	7.2	6.7	92.5	8.2	2.01	16.1
24	4	80	10	0.6	6.6	8.1	84.3	7.1	1.98	13.9
25	4	80	10	0.8	4.8	11.2	74.6	6.2	2.11	8.7

<sup>a</sup> Conditions: ethylene pressure 0.4 MPa; catalyst amount 0.5 μmol for 1 and 2, 1.0 μmol for 3 and 4; toluene + 1-O total 100 ml; molar ratio of B/Ti 1.5; polymerization temperature 80°C.

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

<sup>c</sup> Polymerization time.

<sup>d</sup> Activity in kg/mol Ti·h.

<sup>e</sup> Determined by <sup>13</sup>C NMR spectroscopy.

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

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

<sup>h</sup> Crystallinity calculated as the ratio of the fusion heats of the samples and folded-chain polyethylene.<sup>46</sup>

<sup>i</sup> Polymerization temperature 60°C.

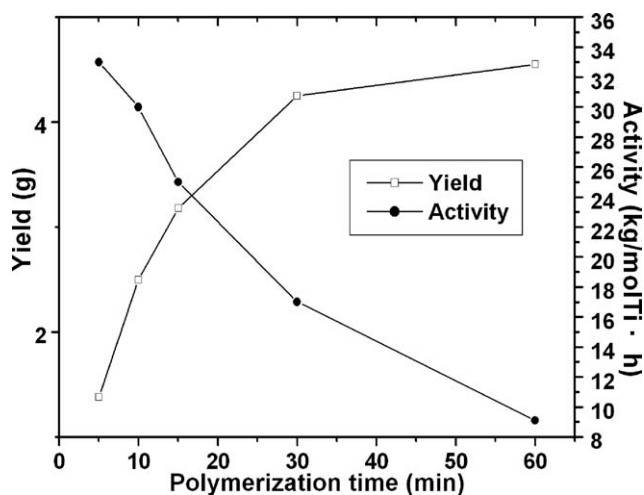
<sup>j</sup> Polymerization temperature 100°C.

<sup>k</sup> Ethylene pressure 0.6 MPa.

content in the copolymers decreases obviously with the increase in polymerization time. To obtain copolymers with relatively narrow molecular weight distribution and uniform comonomer content, most of the polymerization experiments were carried out for 10 min.

It can also be seen from the data in Table I that substituents R and R<sub>1</sub> on the phenyl ring of the ligand in the complexes 1–4 affect obviously their catalytic activity and the comonomer incorporation. With the R<sub>1</sub> being an electron-donating *tert*-butyl group, the 1/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst system displays higher catalytic activities comparing to the 2/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst system in which the R<sub>1</sub> group is replaced by a hydrogen atom. However, the latter catalyst system seems to produce copolymers with higher 1-octadecene incorporation in comparison to the former catalyst system.

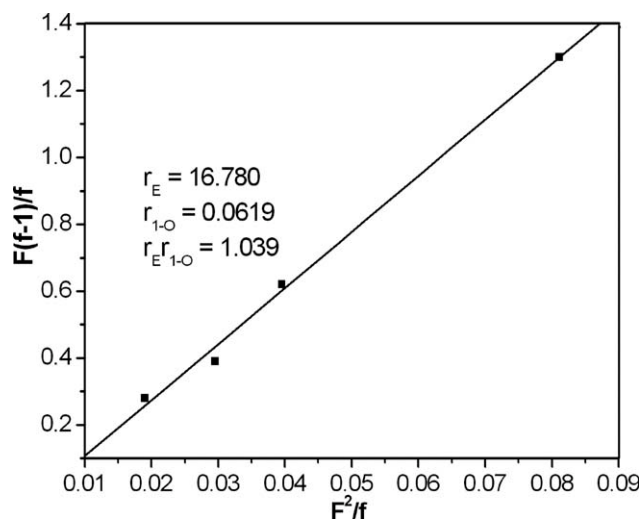
Furthermore, with the R<sub>1</sub> being a hydrogen atom and the R being a methyl group, the 3/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst system presents further lower catalytic activities and yields copolymers with lower 1-octadecene incorporation than the 2/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst system does. When the methyl group is replaced by a phenyl group, the 4/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst system shows the lowest catalytic activities and affords copolymers with further lower 1-octadecene incorporation. The general catalytic activity of these complexes for ethylene/1-octadecene copolymerization is in the same order as that for ethylene polymerization (1>2>3>4).<sup>33</sup> In addition, the catalytic activity of these complexes is higher than that of the complexes [η<sup>5</sup>: η<sup>1</sup>-C<sub>5</sub>H<sub>2</sub>Ph<sub>2</sub>-4-R<sub>1</sub>-6-R-C<sub>6</sub>H<sub>2</sub>O]TiCl<sub>2</sub>.<sup>32</sup> These results indicate that the electronic property of the R<sub>1</sub> group at the *para* position of the phenyl ring



**Figure 1** Plots of the polymer yield and the catalytic activity versus the polymerization time for ethylene/1-octadecene copolymerization with the 1/TIBA/B catalyst system.

significantly affects the catalytic activity of these catalysts, while both the steric and electronic effects of the R group at the *ortho* position of the phenyl ring on the catalytic activity and the comonomer incorporation ability of these catalysts are obvious. A less bulky R group would allow stronger interaction between the positively charged active catalyst and the negatively charged cocatalyst and therefore slow down the coordination and insertion rate of the bulky 1-octadecene (comparing 2 and 3). An electron-withdrawing R group would lower the stability of the positively charged active catalyst and thus decrease the catalytic activity of the catalyst (comparing 3 and 4).

The influences of the comonomer concentration in the feed on the catalytic activity of these catalyst systems and the comonomer incorporation were also examined by varying the feed concentration of 1-octadecene. As seen from Table I, the catalytic activity of all the four catalyst systems increases at first with the increase in comonomer concentration until reaching a maximum value and then begins to decrease. Similar results have previously been reported and explained by the comonomer effect.<sup>40–42</sup> The comonomer incorporation also increases with the increase in comonomer concentration for the ethylene/1-octadecene copolymerization as seen in Table I. The comonomer incorporation ability of these catalyst systems for the ethylene/1-octadecene copolymerization seems to be similar to that of the  $[\eta^5: \eta^1\text{-C}_5\text{H}_2\text{Ph}_2\text{-4-R}_1\text{-6-R-C}_6\text{H}_5\text{O}]\text{TiCl}_2$  catalyst systems under similar conditions.<sup>32</sup> The ethylene and 1-octadecene reactivity ratios ( $r_E$  and  $r_{OD}$  are the reactivity ratios of ethylene and 1-octadecene, respectively) for ethylene/1-octadecene copolymerization by 1/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst sys-

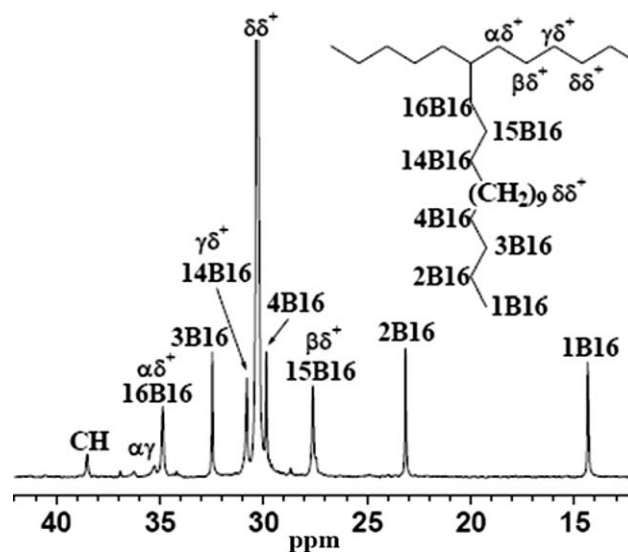


**Figure 2** Fineman-Ross plot for ethylene/1-octadecene copolymerization with the 1/TIBA/B catalyst system.

tem was calculated from Fineman-Ross plot as shown in Figure 2.<sup>43</sup> The values of  $r_E$  and  $r_{OD}$  are 16.78 and 0.0619, respectively, with the reactivity ratio products  $r_{OD}r_E$  being close to 1 ( $r_{OD}r_E = 1.039$ ), which demonstrates that ethylene/1-octadecene copolymerization reaction proceeds in largely a random manner.

### Characterizations of the copolymer

The microstructure of the obtained copolymers was investigated with <sup>13</sup>C-NMR spectroscopy. The <sup>13</sup>C-NMR spectrum of a typical ethylene/1-octadecene copolymer sample is shown in Figure 3. The percentage of comonomer incorporation in the polymer chain was calculated based on the <sup>13</sup>C-NMR analysis



**Figure 3** <sup>13</sup>C-NMR spectrum of a typical poly(ethylene-co-1-octadecene) sample with 11.5 mol % 1-octadecene incorporation by (run 8).

TABLE II  
Monomer Sequence Distribution Data of Selected Poly(ethylene-co-1-octadecene) Samples<sup>a</sup>

Run	Cat.	Incorp <sup>b</sup> (mol %)	Triads sequence distribuion <sup>b</sup>						Dyads (%) <sup>c</sup>		
			EEE	OEE + EEO	OEO	EOE	OOE + EOO	OOO	EE	EO + OE	OO
2	1	7.5	77.9	14.2	0.4	7.5	0	0	85.0	15.0	0
9	1	14.1	59.4	24.8	1.7	14.1	0	0	71.8	28.2	0
15	2	8.6	74.7	16.2	0.5	8.6	0	0	82.8	17.2	0
17	2	15.5	55.6	26.8	2.1	15.5	0	0	69.0	31.0	0
19	3	7.1	79.1	13.4	0.4	7.1	0	0	85.8	14.2	0
21	3	12.9	62.8	22.8	1.5	12.9	0	0	74.2	25.8	0
23	4	6.7	80.2	12.8	0.3	6.7	0	0	86.6	13.4	0
25	4	11.2	67.7	19.8	1.3	11.2	0	0	77.6	22.4	0

<sup>a</sup> Detailed polymerization conditions are given in Table I. E = ethylene unit, O = 1-octadecene unit.

<sup>b</sup> 1-Octadecene content (mol %) and sequence distribution were estimated by <sup>13</sup>C NMR spectroscopy.

<sup>c</sup> [EE] = [EEE] + 1/2 × [EEO + OEE], [EO] = [OEO] + [EOE] + 1/2 × {[EEO + OEE] + [OOE + EOO]}, [OO] = [OOO] + 1/2 × [OOE + EOO].

as described previously.<sup>32</sup> In addition to the comonomer concentration, it seems that the comonomer incorporation is also affected by the structure of the catalyst. As seen in Table I, the comonomer content of the copolymers obtained with catalyst 2 is somewhat higher than that of the copolymers produced by catalyst 1 under similar conditions, due probably to that the cationic active species from catalyst 2 carries more positive charge than the one from catalyst 1 does and therefore favors the coordination of the bulky comonomer more. The <sup>13</sup>C-NMR analysis indicates that the 1-octadecene units are essentially isolated by the ethylene units in almost all the resultant copolymers. A weak  $\alpha\gamma$  resonance (35.2 ppm) for the alternative sequence OEO can be seen, but no  $\alpha\alpha$  resonances (40.0–41.0 ppm) for the OOE and OOO block sequences can be observed in the <sup>13</sup>C-NMR spectra.<sup>44,45</sup> The calculated dyad and triad sequence distributions for two typical poly(ethylene-co-1-octadecene) samples from each catalyst in Table I are summarized in Table II. The gel permeation chromatography (GPC) analysis reveals that the molecular weight of the ethylene/1-octadecene copolymers ( $M_w = 6.2\text{--}19.5 \times 10^3$ ) produced by these catalysts is slightly higher than that of the copolymers obtained with the  $[\eta]^5: \eta^1\text{-C}_5\text{H}_2\text{Ph}_2\text{-4-R}_1\text{-6-R-C}_6\text{H}_2\text{O}]\text{TiCl}_2$  catalyst systems under similar conditions,<sup>32</sup> and the molecular weight distribution is basically unimodal and narrow, being characteristic for metallocene polyolefins. The copolymers produced by the 1/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst system possesses the highest molecular weight, while the ones formed from the 4/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst system under the same conditions show the lowest molecular weight. The difference in molecular weight for the copolymers produced by different catalysts should be resulted from both steric and electronic effects of the substituents on the ligand of the catalyst. The molecular weight of the copolymers is also

sensitive to the comonomer concentration in the feed for all catalyst systems.

The DSC thermograms of several copolymer samples (Fig. 4) obtained with the 1/Al(*i*-Bu)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst system show that the melting temperature of the copolymers decreases remarkably with the increase in the 1-octadecene incorporation. These results are similar to those previously reported by other authors with different homogeneous catalysts.<sup>28–31</sup> The decrease in melting point with the increase in comonomer content in the polymer chain is obviously caused by the increase in the branching degree of the polymer chain and thus the decrease in crystallinity. In addition, for samples with higher comonomer incorporation, a broad endothermic process in the region of 0–25°C occurs, which should be attributed to the glass transition in the amorphous regions of the polymer. The X-ray

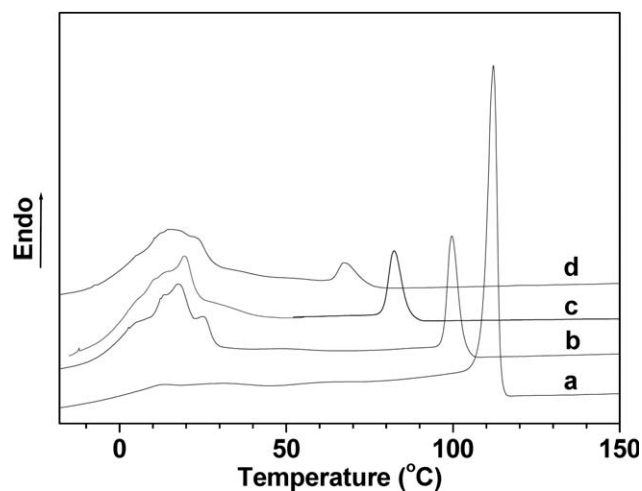
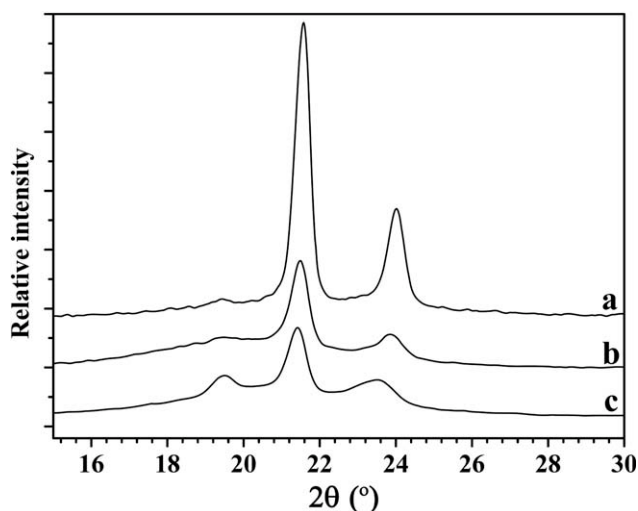


Figure 4 DSC diagrams of typical poly(ethylene-co-1-octadecene) samples with different 1-octadecene incorporations: (a) 4.2 mol % (run 7); (b) 7.5 mol % (run 2); c, 11.5 mol % (run 8); and (d) 14.1 mol % (run 9).



**Figure 5** XRD patterns of typical polymer samples recorded at room temperature: (a) polyethylene; (b) sample from run 7; (c) sample from run 2.

diffraction (XRD) patterns of several typical samples are shown in Figure 5. All the copolymers display the characteristic 110 and 200 diffractions of the orthorhombic cell of polyethylene, although there is some shifting in their position due to the known expansion of the unit cell in the copolymers as the comonomer content increases.<sup>31</sup>

## CONCLUSIONS

When activated with  $\text{Al}(i\text{-Bu})_3$  and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ , the constrained geometry complexes **1–4** are efficient catalysts for the copolymerization of ethylene with 1-octadecene. The catalytic activity, comonomer incorporation ability, and molecular weight of the produced copolymers can be affected by the catalyst structure and reaction conditions such as the polymerization temperature, ethylene pressure, and comonomer concentration. The  $1/\text{Al}(i\text{-Bu})_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  catalyst system shows the highest catalytic activity and produces copolymers with the highest molecular weight, while the  $2/\text{Al}(i\text{-Bu})_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  catalyst system gives copolymers with the highest comonomer incorporation under similar conditions.

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