

## (Co)polymerization of ethylene via nonmetallocene catalysts with diphenyl phosphoroso schiff-base ligand

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**ABSTRACT:** A series of novel nonmetallocene catalysts [N, O, P] with diphenyl phosphoroso ligands were synthesized by the treatment of phthalaldehyde, substituted phenols, chlorodiphenyl phosphine with metal halides of  $\text{TiCl}_4$  and  $\text{ZrCl}_4$ . The catalyst microstructure was characterized by  $^1\text{H}$  NMR and EA. After activated by methylaluminoxane (MAO), these [N, O, P] catalysts were utilized to catalyze the polymerization of ethylene and the copolymerization of ethylene with 1-octene. The results indicated that the obtained catalysts were highly efficient for ethylene polymerization and ethylene/1-octene copolymerization. Structures and properties of the obtained polymers were measured by WAXD, DSC, GPC, and  $^{13}\text{C}$  NMR. The results indicated that polyethylene catalyzed by Cat.3 possessed the highest weight-average molecular weight of  $1.025 \times 10^6$  g/mol and the highest melting point of  $136.3^\circ\text{C}$ . The copolymer of ethylene/1-octene catalyzed by Cat.1 exhibited the highest 1-octene incorporation content of 0.63 mol %. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42225.

**KEYWORDS:** catalysts; copolymers; differential scanning calorimetry (DSC); polyolefins; properties and characterization

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### INTRODUCTION

Homogeneous catalysts are favorable for coordination polymerization of olefins.<sup>1–4</sup> One of them, nonmetallocene catalyst which include early-,<sup>5</sup> middle-,<sup>6</sup> and late-transition-metal<sup>7</sup> and lanthanide<sup>8</sup> species incorporating noncyclopentadiene-based ligands has attracted much more attention for its excellent capacity in olefins (co)polymerization. [N,N,O,O],<sup>9</sup> [N,O,O],<sup>10</sup> [NNO],<sup>11</sup> and [O,S,O,S]<sup>12,13</sup> *et al.* have been studied for olefins (co)polymerization.

Edit<sup>14</sup> reported the living polymerization of 1-hexene catalyzed by  $\text{C}_2$ -symmetrical zirconium catalyst with  $\text{B}(\text{C}_6\text{F}_5)_3$  as cocatalyst. Rieko<sup>15</sup> studied FI-Ti catalysts having fluorinated substituents for olefins polymerization and the polymerization behaviors. The properties of the polyolefins are improved because of  $\alpha$ -olefins incorporated within the copolymer chains by these catalysts. Mikhail<sup>16</sup> synthesized ethylene/1-hexene copolymers using supported catalysts of different composition. The copolymer of ethylene with 1-hexene showed excellent properties including stretchability and toughness.<sup>17</sup> Endre<sup>18</sup> prepared copolymers of ethylene with 1-octene by zirconium and hafnium catalysts with diimine ligands. The resultant copolymers were featured with multiple melting peaks and wide MWDs. Habib<sup>19</sup> reported 2-aminophenyl diphenylphosphinite ligand which was stable in water and air. This provided new

idea for preparing nonmetallocene catalysts with novel structures. Although constrained geometry catalyst (CGC),<sup>20</sup> Monocyclopentadienylamido Complex<sup>21</sup> were efficient for the copolymerization of ethylene with 1-octene, the comonomer incorporation content was higher and the resultant copolymer showed lower melting temperature or became amorphous.

Our previous work<sup>22</sup> showed that the 1-octene incorporation content was *ca* 0.34mol % for the copolymer of ethylene with 1-octene, the copolymer performed better thermal properties. Its melting temperature was *ca*  $130^\circ\text{C}$ . This copolymer should be useful to make PE100 (a brand of PE tube, this material can be used for 50 years under 10 MPa pressure at  $20^\circ\text{C}$ ) and polyethylene of raised temperature resistance (PE-RT) which could be serviced at  $95^\circ\text{C}$  in long term in application. Currently, the materials for making PE100 through the copolymerization of ethylene with 1-butene or 1-hexene catalyzed by supported Ziegler–Natta catalyst and the materials for making PE-RT through the copolymerization of ethylene with 1-hexene promoted by metallocene catalysts. CGC was not favorable for producing PE100 and PE-RT because of the high incorporation content of the comonomers, such as 1-hexene and 1-octene. Nozaki<sup>23</sup> described that the ancillary ligand structure can obviously influence on monomer insertion fashions, the catalytic activity and the obtained polymers' molecular weight.

Herein, the work based on a kind of novel nonmetallocene catalysts bearing diphenyl phosphoro schiff-base ligands was reported. These novel catalysts can catalyze copolymerization of ethylene and 1-octene. The effects of the catalyst structure regarding of the ancillary ligand substitute groups on the *p*-position correspond to the chelated oxygen atom and reaction conditions on the polymerization were investigated.

## EXPERIMENTAL

### General Remarks

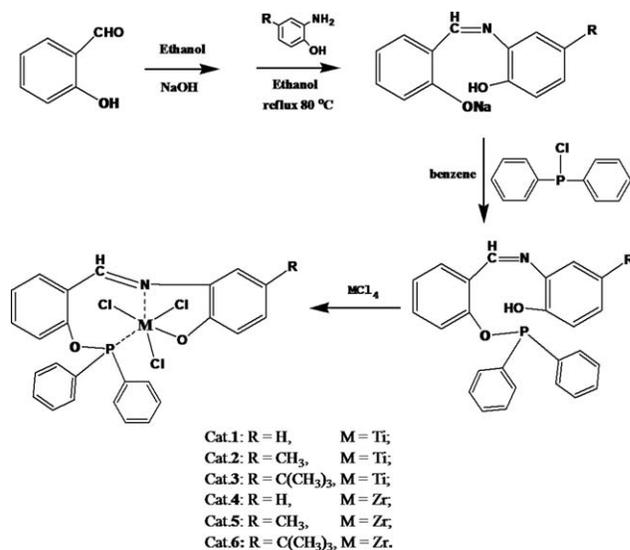
All operations of air- and moisture-sensitive materials were performed using the rigorous repellency of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line under a nitrogen atmosphere. Salicylaldehyde (99%) and chlorodiphenyl phosphine (99%) were purchased from J&K in China; 2-amino-4-methylphenol (98%), 2-amino-5-methylphenol (98%), and 2-amino-4-*t*-butylphenol (98%) were purchased from TCI in China. Methylaluminoxane (MAO) with 10 wt % in toluene was purchased from Acros Organics Agent in China. Toluene and THF from Beijing Chemicals Company were further purified by refluxing over sodium under normal pressures for 48 h prior to use.

### Characterization

$^1\text{H}$  NMR spectra were recorded on a Varian INOVA600 MHz spectrometer in  $\text{DMSO}-d_6$  solution at  $25^\circ\text{C}$  and tetramethylsilane used as reference. All  $^1\text{H}$  chemical shifts were reported in ppm relative to proton resonance in  $\text{DMSO}-d_6$  at  $\delta$  2.62 ppm. Elemental analyses were performed on a Perkin–Elmer 2400 microanalyzer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5DXC FTIR spectrograph. The spectra were obtained at  $40\text{ cm}^{-1}$  resolution, and average data were obtained from at least 32 scans in the standard wavenumber range from 500 to  $4000\text{ cm}^{-1}$ . Mass spectrum was recorded by Esquire-LC mass spectroscopy.  $^{13}\text{C}$  NMR spectra were recorded on an INOVA500 MHz instrument operating at 125 MHz. The condition used for quantitative  $^{13}\text{C}$  NMR was of the copolymer content up to 15 wt % in solution, using *ortho*-dichlorobenzene ( $d_4$ ) as the solvent at  $125^\circ\text{C}$ . Hexamethyl disiloxane was used as internal chemical shifts reference. The 1-octene incorporation was estimated from  $^{13}\text{C}$  NMR spectra according to the literature.<sup>24</sup> The average molecular weight and molecular weight distribution were measured by PL–GPC200 instrument using standard polyethylene as reference and 1, 2, 4-trichlorobenzene as solvent at  $150^\circ\text{C}$ . DSC thermograms were recorded with a PA5000-DSC instrument at a rate of 10 K/min. WAXD curves were recorded with a Rigaku D/max 3A instrument, using Ni films to sieve wave, using Cu K $\alpha$  radiation ( $\lambda = 1.5405 \times 10^{-10}$  m). WAXD intensities were recorded from  $5^\circ$  to  $40^\circ$  with a continuous scanning speed.

### Synthesis of Catalyst Precursors

Salicylaldehyde 1 mL (9.5 mmol) was treated with 0.38 g (9.5 mmol) NaOH for 3 h in 60 mL anhydrous alcohol at room temperature. The solvent was removed off, the residue, salicylaldehyde sodium (1.29 g) with yellow color, was reacted with 0.62 g (5 mmol) of 2-amino-phenol in 30 mL anhydrous alcohol for 1 h at room temperature. Then the mixture was refluxed for 8 h at  $80^\circ\text{C}$ . Subsequently, the mixture was cooled to room



**Scheme 1.** Synthesis of the nonmetallocene catalysts.

temperature. After filtered, the red precipitate was further dissolved in 50 mL anhydrous benzene and reacted with an equivalent of chlorodiphenyl phosphine (0.50 mL) at  $0^\circ\text{C}$ . Heated the system to room temperature and kept it stirring for 1 h. After filtered, the residue was dissolved in mixture of acetone and benzene (50 mL, 1 : 1 in volume). The mixture was concentrated to *ca* 10 mL and kept it at  $-10^\circ\text{C}$  to recrystallize. About 0.39 g of ligand (La) with brown color in yield of 34.1% was obtained (Scheme 1). **La** ( $\text{C}_{25}\text{H}_{20}\text{NPO}_2$ ,  $F_W = 397$ ):  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  6.59–7.87 (m, 18H, benzene),  $\delta$  9.80 (s, 1H, CH=N),  $\delta$  9.7 (s, 1H, OH); EA. Calcd (%): C, 76.74; H, 4.01; N, 3.75; P, 7.43; found: C, 76.75; H, 4.02; N, 3.76; P, 7.41. FT-IR ( $\text{cm}^{-1}$ , KBr): 1612 (C=N). MS [ $m/z$  (%): 398 (100).

La Ti complex (Cat.1) was prepared by the treatment of La 0.20 g (0.8 mmol) in 50 mL toluene with  $\text{TiCl}_4$  (0.09 mL, 0.8 mmol) by a syringe at  $0^\circ\text{C}$ . The reaction was lasted for 6 h at  $40^\circ\text{C}$ . The solvent was removed off. The residue was extracted with hexane (30 mL  $\times$  4) and dried by vacuum. Cat.1 was obtained (0.21 g, 47.9%; Scheme 1). Cat.1 was confirmed by  $^1\text{H}$  NMR and microanalysis (Table I). The ligand Lb derived from 2-amino-4-methylphenol, Lc from 2-amino-4-*t*-butylphenol. **Lb** ( $\text{C}_{26}\text{H}_{22}\text{NPO}_2$ ,  $F_W = 411$ ),  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  2.02 (s, 3H),  $\delta$  6.61–7.91 (m, 17H, benzene),  $\delta$  9.77 (s, 1H, CH=N),  $\delta$  9.9 (s, 1H, OH); EA. Calcd (%): C, 76.84; H, 4.19; N, 3.45; P, 7.29; found: C, 76.85; H, 4.17; N, 3.46; P, 7.28. FT-IR ( $\text{cm}^{-1}$ , KBr): 1609 (C=N). MS [ $m/z$  (%): 412 (100). **Lc** ( $\text{C}_{29}\text{H}_{28}\text{NPO}_2$ ,  $F_W = 453$ ),  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ ):  $\delta$  1.10 (s, 9H),  $\delta$  6.35–7.96 (m, 17H, benzene),  $\delta$  9.34 (s, 1H, CH=N),  $\delta$  10.0 (s, 1H, OH); EA. Calcd: C, 76.77; H, 6.17; N, 3.08; P, 6.62; found: C, 76.81; H, 5.99; N, 3.06; P, 6.59. FT-IR ( $\text{cm}^{-1}$ , KBr): 1615 (C=N). MS [ $m/z$  (%): 454 (100). Cat.1–6 were synthesized according to the similar method mentioned above. The  $^1\text{H}$  NMR and microanalysis data were compiled in Table I.

### Polymerization Procedure

All polymerization manipulations were carried out in a 300 mL reaction flask after purging all moisture and oxygen by a high-

**Table I.** The Parameters for Catalysts Cat.1–6

Cat.	Metal	Ligand	<i>p</i> - <sup>a</sup>	Microanalysis	<sup>1</sup> H NMR	FT-IR (cm <sup>-1</sup> , KBr)
Cat.1	Ti	La	H	C <sub>25</sub> H <sub>19</sub> O <sub>2</sub> NPTiCl <sub>3</sub> (550): Calcd. (%): C, 56.93; H, 3.83; N, 2.55; P, 5.65; found: C, 56.95; H, 3.79; N, 2.56; P, 5.65	(DMSO): δ = 6.62-7.91 (m, 18H, benzene), and δ = 9.74 (s, 1H, CH=N)	1606 (C=N)
Cat.2	Ti	Lb	CH <sub>3</sub>	C <sub>26</sub> H <sub>21</sub> O <sub>2</sub> N- PTiCl <sub>3</sub> (564):Calcd.(%): C, 57.45; H, 4.02; N, 2.45; P, 5.39; found: C, 57.44; H, 4.00; N, 2.46; P, 5.40	(DMSO):δ = 2.02 (s, 3H, methyl on benzene), δ = 6.61-7.91 (m, 17H, benzene), and δ = 9.77 (s, 1H, CH=N)	1595 (C=N)
Cat.3	Ti	Lc	t-butyl	C <sub>29</sub> H <sub>27</sub> O <sub>2</sub> N- PTiCl <sub>3</sub> (606):Calcd.(%): C, 58.98; H, 4.57; N, 2.37; P, 5.25; found: C, 58.95; H, 4.56; N, 2.35; P, 5.27	(DMSO):δ = 1.10 (s, 9H, t- butyl on benzene), δ = 6.35- 7.96 (m, 17H, benzene), δ 9.34 (s, 1H, CH=N)	1611 (C=N)
Cat.4	Zr	La	H	C <sub>25</sub> H <sub>19</sub> O <sub>2</sub> NPZrCl <sub>3</sub> (594): Calcd.(%): C, 51.92; H, 3.12; N, 1.56; P, 5.81; found: C, 51.91; H, 3.10; N, 1.59; P, 5.83	(DMSO):δ = 6.61-7.91 (m, 18H, benzene), and δ = 9.76 (s, 1H, CH=N)	1591 (C=N)
Cat.5	Zr	Lb	CH <sub>3</sub>	C <sub>26</sub> H <sub>21</sub> O <sub>2</sub> NPZrCl <sub>3</sub> (608): Calcd. (%): C, 52.70; H, 3.55; N, 1.86; P, 5.24; found: C, 52.72; H, 3.57; N, 1.86; P, 5.21	(DMSO): δ = 2.02 (s, 3H, methyl on benzene), δ = 6.61-7.91 (m, 17H, benzene), and δ = 9.73 (s, 1H, CH=N)	1579 (C=N)
Cat.6	Zr	Lc	t-Butyl	C <sub>29</sub> H <sub>27</sub> O <sub>2</sub> N- PZrCl <sub>3</sub> (650):Calcd.(%): C, 54.98; H, 4.26; N, 2.21; P, 4.68; found: C, 54.96; H, 4.27; N, 2.18; P, 4.69	(DMSO):δ = 1.11 (s, 9H, t- butyl on benzene), δ = 6.34- 7.96 (m, 17H, benzene), δ = 9.33 (s, 1H, CH=N)	1598 (C=N)

<sup>a</sup>Substitute groups on the *p*-position corresponding to the chelated oxygen atom.

vacuum pump. Freshly distilled solvent (100 mL), desired amount of catalysts Cat.1–6 and MAO were introduced in order. Then injected desired amount of 1-octene using as comonomer, charged ethylene up to desired pressure and heated the reactor to desired temperature. The system was stirred for 30 min. Finally the reaction was terminated with 10 wt % HCl in alcohol. The obtained product was filtered and washed, then dried to constant weight in a vacuum oven at 80°C. Weighted it and calculated the catalytic activity.

## RESULTS AND DISCUSSION

### Ethylene (Co-) Polymerization

The novel nonmetallocene catalysts Cat.1–6 were utilized for ethylene (co-)polymerization with MAO as cocatalyst. The effects of center metal atoms (Ti and Zr) and the structure of catalyst ligand on ethylene (co-) polymerization are compiled in Table II.

From Table II, the results indicate that these nonmetallocene catalysts are favorable for both homopolymerization of ethylene and copolymerization of ethylene with 1-octene with high catalytic activity up to  $3.12 \times 10^6$  gPE(molZr.h)<sup>-1</sup> and  $2.03 \times 10^6$

gPE (molZr.h)<sup>-1</sup>, respectively, catalyzed by Cat.4. The catalytic activity of the catalysts Cat.1 and Cat.4 with ligand La increases successively for homopolymerization of ethylene and copolymerization of ethylene with 1-octene. Cat.2 and Cat.5 with ligand Lb, Cat.3 and Cat.6 with ligand Lc show the similar tendency for homopolymerization of ethylene and copolymerization of ethylene with 1-octene. The result confirms that Zr complex with the same ancillary ligand exhibits higher catalytic activity than Ti complex for ethylene (co)polymerization. But the obtained polymers catalyzed by Ti complexes show higher weight average molecular weight and higher 1-octene incorporation content within the polymer chains than Zr complexes. We can also notice from Table II that the ancillary ligands of these catalysts influence ethylene (co-)polymerization behavior. The ancillary ligand substitute groups on the *p*-position correspond to the chelated oxygen atom are changed from H, CH<sub>3</sub> to C(CH<sub>3</sub>)<sub>3</sub>. Ti complexes Cat.1 to Cat.3 (runs 1–6 in Table II) for ethylene (co)polymerization, the catalytic activities show slight changing, but the catalytic activity for the copolymerization of ethylene with 1-octene is higher than that for the

**Table II.** Effects of the Transition Metal Atoms and the Ancillary Ligand Structure of the Catalysts on Ethylene (co-) Polymerization

Run	Catalysts	$A^a (\times 10^{-6})$	O-cont <sup>b</sup> (mol %)	$M_w^c (\times 10^{-5})$	$M_w/M_n^c$	$T_m^d (^\circ\text{C})$
1	Cat.1 (Ti, La)	1.16	-	9.47	2.16	135.0
2 <sup>e</sup>		1.98	0.63	9.55	2.33	128.6
3	Cat.2 (Ti, Lb)	1.09	-	9.63	2.33	135.2
4 <sup>e</sup>		1.86	0.51	9.70	3.16	131.3
5	Cat.3 (Ti, Lc)	1.01	-	10.25	2.31	136.3
6 <sup>e</sup>		1.53	0.47	10.31	3.08	131.7
7	Cat.4 (Zr, La)	2.03	-	6.92	2.35	135.1
8 <sup>e</sup>		3.12	0.58	6.97	2.47	130.2
9	Cat.5 (Zr, Lb)	1.92	-	7.38	2.71	135.1
10 <sup>e</sup>		2.42	0.33	7.48	3.76	132.1
11	Cat.6 (Zr, Lc)	1.74	-	8.16	2.47	135.1
12 <sup>e</sup>		2.13	0.28	8.23	3.15	132.8

<sup>a</sup>Catalytic activity, gPE/molTi(Zr).h.

<sup>b</sup>Incorporation content of 1-Octene, determined by <sup>13</sup>C NMR.

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

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

<sup>e</sup>Comonomer: 1-octene 5 mL.

Reaction conditions: pressure of ethylene,  $0.2 \times 10^6$  Pa; catalyst concentration,  $1.8 \times 10^{-4}$  mol·L<sup>-1</sup>; Al/M in mol, 600; reaction temperature, 60°C; solvent, toluene, 100 mL; polymerization time, 30 min.

homopolymerization of ethylene. However, the weight average molecular weight of the obtained polymers exhibit obvious changing, from  $9.47 \times 10^5$ ,  $9.63 \times 10^5$  to  $10.25 \times 10^5$  g/mol for the homopolymers of ethylene, from  $9.55 \times 10^5$ ,  $9.70 \times 10^5$  to  $10.31 \times 10^5$  g/mol for the copolymers of ethylene with 1-octene, as the ancillary ligand substitute groups change from H, CH<sub>3</sub> to C(CH<sub>3</sub>)<sub>3</sub>. Zr complexes Cat.4 to Cat.6 (runs 7–12 in Table II) reveal the similar tendency. The results show that the catalyst with a bulk group on the ancillary ligand, such as *t*-butyl, has the lowest catalytic activity for ethylene (co)polymerization, and the resultant (co)polymers possess the highest weight average molecular weight and the lowest incorporation content of 1-octene within the copolymer chains.

The effects of polymerization conditions, such as temperature, Al/Ti ratio and concentration of the catalyst on copolymerization of ethylene with 1-octene catalyzed by Cat.1 were investigated in detail. The results are listed in Table III.

From Table III, we can notice that Cat.1 features rather high tolerance to reaction conditions and exhibits high catalytic activity between  $0.96 \times 10^6$  and  $1.98 \times 10^6$  gPE(molM·h)<sup>-1</sup>. While the catalytic activity reaches the highest value of  $1.98 \times 10^6$  gPE(molM·h)<sup>-1</sup> (run 2 in Table III) at 60°C. As the polymerization temperature becomes lower or higher, the catalytic activity decreases. Because high temperature can promote chain propagation rate, but deactivate the active species. It is optimal at 60°C for balancing the two factors. The higher the temperature is, the lower the MW becomes. It is possible that the MWs of the obtained polymers depend on the chain propagation and the termination rate.<sup>25</sup> Higher temperature speeds up the chain transfer to MAO and

monomer. The incorporation of 1-octene changes slightly with the changing of temperature.

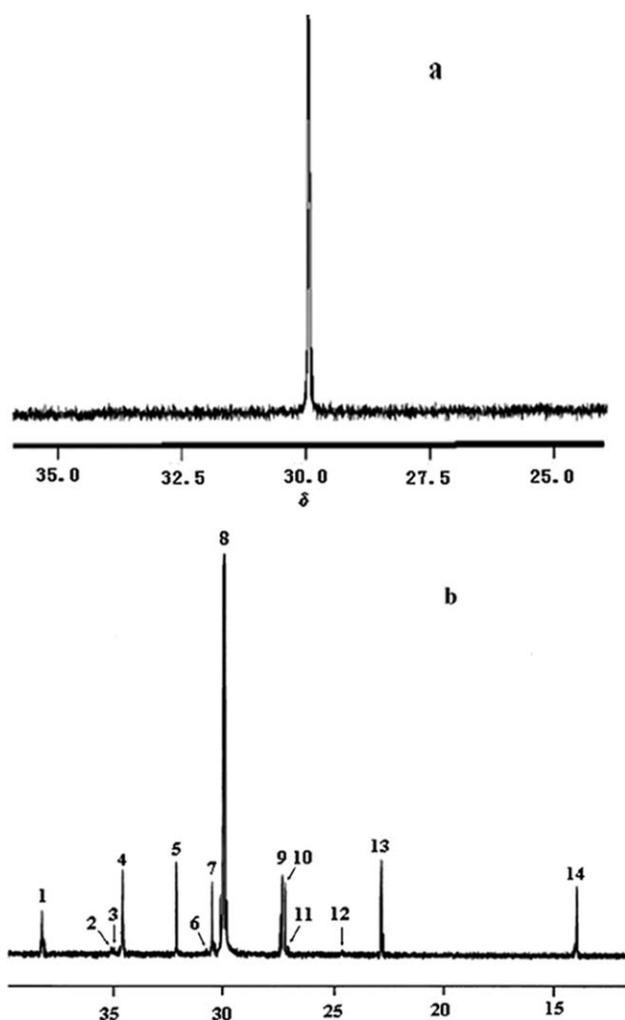
As shown in Table III, when catalyst concentration is  $1.8 \times 10^{-4}$  mol/L, catalytic activity exhibits the highest value of  $1.98 \times 10^6$  gPE(mol<sup>-1</sup>Ti<sup>-1</sup>h<sup>-1</sup>). Lower or higher the value of the catalyst concentration (runs 27 and 28 in Table III) is carried out, the catalytic activity is decreased. Because the active centers of the catalyst are devitalized by impurity easily. But too higher catalyst concentration leads to fast polymer chain aggregation.

The 1-octene in feed influences incorporation of 1-octene. For example, 1 mL 1-octene is charged into the reaction system, the resultant copolymer shows that insertion content of 1-octene is 0.31 mol %. While the amount of 1-octene is up to 5 mL in feed, the insertion content of 1-octene within the copolymer chain becomes 0.63 mol %. However, increasing it to 10 mL in feed, the insertion content of 1-octene slightly raises to 0.65 mol % (runs 29, 2, and 30 in Table III). The result indicates that there is a limit to amount of 1-octene in feed. When it is enough for the polymerization, the extra 1-octene would not work anymore.

When Al/Ti ratio in mol is 600, the catalytic activity for the copolymerization of ethylene with 1-octene reaches the maximum value of  $1.98 \times 10^6$  gPE(molM·h)<sup>-1</sup> and the weight average molecular weight of the obtained copolymer also reaches its peak value of  $10.31 \times 10^5$  g/mol. When the value of Al/Ti ratio in mol is lower or higher, the catalytic activity and MWs of the obtained copolymers are decreased. It is possible that both purifying in the reaction system and chain transfer consume MAO. However, too much MAO prevents monomer from approaching to active center and reduces the center metal to lower oxide

**Table III.** Effects of Polymerization Conditions on Copolymerization of Ethylene with 1-Octene Catalyzed by Cat.1

Run	$T^a$ (°C)	$C^b$ ( $\times 10^4$ )	1-octene <sup>c</sup> (ml)	Al/M <sup>d</sup>	$A^e$ ( $\times 10^{-6}$ )	$M_w^f$ ( $\times 10^{-5}$ )	$M_w/M_n^f$	$T_m^g$ (°C)	O-Cont <sup>h</sup> (mol %)
13	50	1.8	5	600	1.43	10.53	2.81	129.2	0.61
2	60	1.8	5	600	1.98	9.55	2.33	128.6	0.63
14	70	1.8	5	600	1.35	9.59	3.11	129.0	0.62
15	60	1.0	5	600	1.24	10.47	2.81	131.8	0.52
16	60	5.0	5	600	0.96	9.16	2.67	131.6	0.41
17	60	1.8	1	600	1.42	10.04	2.79	131.8	0.31
18	60	1.8	10	600	1.85	10.25	2.64	127.6	0.65
19	60	1.8	5	400	1.25	9.17	2.17	130.3	0.56
20	60	1.8	5	800	1.09	9.36	3.73	131.5	0.52

<sup>a</sup> Reaction temperature.<sup>b</sup> Catalyst concentration.<sup>c</sup> 1-Octene in feed.<sup>d</sup> Al/M in mol.<sup>e</sup> Activity of catalysts, g PE( $\text{mol}^{-1}\text{M}^{-1}\text{h}^{-1}$ ).<sup>f</sup> Results of GPC.<sup>g</sup> Results of DSC.<sup>h</sup> Incorporation content of 1-Octene, results of  $^{13}\text{C}$  NMR.Reaction conditions: pressure of ethylene,  $0.2 \times 10^6$  Pa; dissolvent, toluene, 100 mL; polymerization time, 30 min.**Figure 1.** The  $^{13}\text{C}$  NMR spectra of (a) polyethylene from run 1 and (b) ethylene/1-octene copolymer from run 2 in Table II.

status which is less favorable for polymerization,<sup>25</sup> and also makes chain transfer easier.

#### Characterization of the Polymers

The  $^{13}\text{C}$  NMR spectrum of the polyethylene promoted by Cat.1 (run 1 in Table II) is shown as Figure 1(a). The result suggests that the obtained polymer exhibits only one signal at  $\delta = 30.4$  ppm, attributed to the character of methylene group of PE, which confirms that the obtained polymer is linear polyethylene without branch.

The nomenclature suggested by Kimura<sup>24</sup> about the monomer unit sequence within the copolymer chain was employed. The chemical shift assignments for each peak of  $^{13}\text{C}$  NMR spectrum were carried out [Figure 1(b)] and the results were presented in Table IV. As revealed by the result, the ethylene/1-octene copolymer catalyzed by Cat.1/MAO contains the sequences of EOE, EEE, OEE, EOEE, OEEE, and EOEO. The signal at  $\delta 30.0$  ppm is assigned to the  $S_{\delta\delta}$  carbon in ethylene sequence of polyethylene. These signals at  $\delta 27.17$  and  $34.65$  ppm, are near to assign to  $\text{CH}_2$  (5) and  $\text{CH}_2$  (6), confirming the trend of ethylene monomer to form long sequence. These sequences (EEO, OEEO) in which 1-octene unit separated by one or two ethylene units are appeared at  $\delta 24.40$  (peak No. 12) and  $\delta 30.83$  (peak No. 6), respectively. The resonance signal at higher than  $\delta 35$  ppm confirms the possibility of OO dyad. The signal at  $\delta 34.03$  ppm assigned to OOO triad sequences is near disappeared, indicating the trend of 1-octene untoward forming relative long sequences in the ethylene/1-octene copolymer. This result indicates that this copolymer structures are unlike ethylene/1-octene copolymers catalyzed by the CGC's *o*-phenylene-bridged Cp/amido titanium complexes in which the copolymers with high 1-octene incorporation content contained abundance of OO dyad and OOO triad sequences besides the alternating and isolating O units. The ethylene/1-octene copolymer

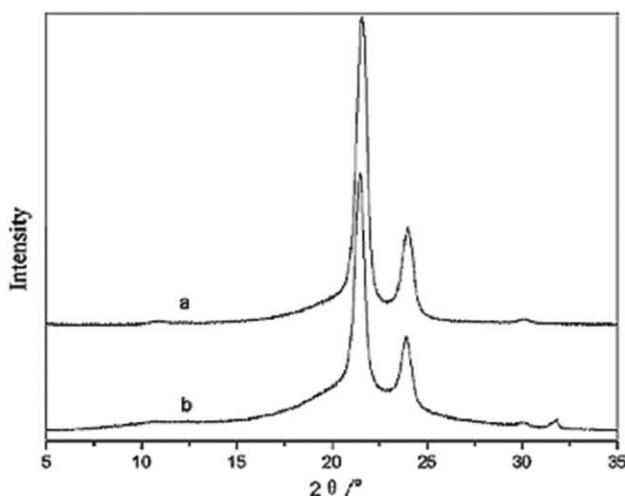
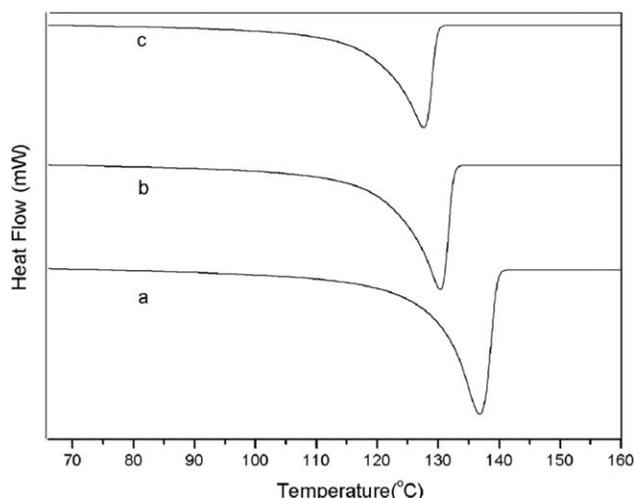
**Table IV.** The Observed Signals Assignment for the Copolymer of Ethylene/1-Octene (Run 2 in Table II)

Peak no. <sup>a</sup>	Carbon type	Monomer sequence	Chemical shift	
			Calculated	Found
1	CH	EOE	38.13	38.32
2	$\alpha\delta + \text{CH}_2(6)$	EEOO+EEO	34.90	35.13
3	$\alpha\gamma$	EOEO	35.00	34.97
4	$\alpha\delta + \text{CH}_2(6)$	EOEE+EOE	34.54	34.65
5	$\text{CH}_2(3)$	EOE+OOE+OOO	32.31	32.23
6	$\gamma\gamma$	OEEO	30.94	30.83
7	$\gamma\delta^+$	OEEE	30.47	30.50
8	$\delta^+ \delta^+$	(EEE) <sub>n</sub>	29.98	30.00
9	$\beta\delta$	OEE	27.42	27.36
10	$\text{CH}_2(5)$	EOE+OOE+OOO	27.29	27.31
11	$\beta\delta^+$	EOEE	26.89	27.11
12	$\beta\beta$	OEO	24.46	24.40
13	$\text{CH}_2(2)$	EOE+OOE+OOO	23.36	22.63
14	$\text{CH}_3$	EOE+OOE+OOO	14.12	14.05

<sup>a</sup>The peak numbers labeled in Figure 1(b).

obtained by Cat.1 is not only improved the incorporation of 1-octene into the polyethylene main chain, but also optimized the uniformity for the whole copolymer molecular chain because of the copolymer mainly containing the isolated and uniform O units.

Based on the <sup>13</sup>C NMR result, the microstructures of the obtained copolymers were determined. The ethylene/1-octene copolymer catalyzed by Cat.1 mainly contains the triad distributions of EOE, EEE, and OEE, but these triad distribution concentrations (OOO, OOE, OEO) are very low, indicating the trend of 1-octene toward forming isolated by one or more ethylene units and uniform sequences in the ethylene/1-octene copolymer. O mole fraction is 0.63%, implying that the rate of

**Figure 2.** WAXD spectrums of ethylene homopolymer (a, run 1 in Table II) and ethylene/1-octene copolymer (b, run 2 in Table II).**Figure 3.** DSC curves correspond to the second heating of ethylene homopolymer (a, run 1 in Table II) and ethylene/1-octene copolymer (b, run 10 in Table II; c, run 2 in Table II).

1-octene insertion within the copolymer chain catalyzed by Cat.1 is barely of 0.63mol %. So the catalysts with the specific structure are effective in producing the copolymers of ethylene/1-octene which are useful for making PE100 or PE-RT tubes. But, not effective in producing the copolymers with very high rate of 1-octene insertion within the copolymer chain, the materials are just good elastic with bad mechanical property.

There are evident diffraction peaks at 21.62° and 24.01° which are resulted from diffraction of crystal surfaces (110) and (200). As shown in Figure 2, intensity of spectrum Figure 2(b) is much lower than that of spectrum Figure 2(a). It is possible that homopolymer of ethylene has regular chain structure with higher crystallinity. While the insertion of 1-octene breaks the regularity of the copolymer chains and results in lower crystallinity. However, the 1/2 width and the 2θ values of peaks to polyethylene and copolymer are the same, which indicates that the insertion of 1-octene within the copolymer chain does not influence the crystallizing property of polyethylene segments.

As shown in Figure 3, the melting points of the obtained polymers decrease in order from 136.3°C to 128.6°C. Crystallization enthalpy of homopolyethylene [Figure 3(a)] is 231.7 J/g and crystallinity is 79.9% which are calculated from area integration. However, the Crystallization enthalpy of the copolymers [Figure 3(b,c)] is 189.3 and 180.9 J/g, respectively. Using the same method, we figured out that the crystallinity of copolymers [Figure 3(b,c)] is 65.3% and 62.4%, respectively. The results are agreed with that of <sup>13</sup>C NMR and X-ray analysis. The reducing of melting points is ascribed to insertion of 1-octene which destroys the regularity of polymer chain. The more comonomer insertion is, the lower  $T_m$  becomes.

## CONCLUSIONS

These novel nonmetallocene catalysts [N, O, P] with diphenyl phosphoroso schiff-base ligands with different substitutes on *p*-position corresponding to the chelated oxygen atom and early transition metals, activated by MAO, are utilized to catalyze

ethylene homopolymerization and copolymerization of ethylene and 1-octene. The highest catalytic activity can be up to  $2.03 \times 10^6$  gPE (molZr.h)<sup>-1</sup> obtained by Cat.4 with ligand La and transition metal Zr. The <sup>13</sup>C NMR result confirms that 1-octene trends toward forming isolated by one or more ethylene units in the ethylene/1-octene copolymer chain and 1-octene mole fraction is 0.63mol %. WAXD result reveals that regularity of the polymer chain depends on the amount of comonomer insertion rate. The more the insertion rate is, the lower the regularity becomes. As shown in DSC spectrum, polymer melting point decreases with 1-octene insertion rate increasing. On the basis of GPC results, MWs of polymers are rather high and MWDs are narrow. These results imply that the polymerization behavior follows the single mechanism.<sup>26</sup>

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