Copolymerization of Ethylene with 1-Hexene Promoted by Novel Multi-Chelated Non-Metallocene Complexes with Imine Bridged Imidazole Ligand

LIFU MA,[1] HONGLI WANG,[1] JIANJUN YI,[2] QIGU HUANG,[1] KEJING GAO,[3] WANTAI YANG[1]

[1]State Key Laboratory of Chemical Resource Engineering, Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, The College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029

[2]Lab for Synthetic Resin Research Institution of Petrochemical Technology, China National Petroleum Corporation, Beijing 100083, China

[3]Beijing Research Institute of Chemical Industry, Sinopec, Beijing 100013, China

ABSTRACT: A series of novel bridged multi-chelated non-metallocene catalysts is synthesized by the treatment of N,N-imidazole, N,N-dimethylimidazole, and N,N-benzimidazole with n-BuLi, 2,6-dimethylaniline, and MCl_4 (M = Ti, Zr) in THF. These catalysts are used for copolymerization of ethylene with 1-hexene after activated by methylaluminoxane (MAO). The effects of polymerization temperature, Al/M molar ratio, and pressure of monomer on ethylene copolymerization behaviors are investigated in detail. These results reveal that these catalysts are favorable for copolymerization of ethylene with 1-hexene featured high catalytic activity and high comonomer incorporation. The copolymer is characterized by ^{13}C NMR, WAXD, GPC, and DSC. The results confirm that the obtained copolymer features broad molecular weight distribution (MWD) about 33–35 and high 1-hexene incorporation up to 9.2 mol %, melting temperature of the copolymer depends on the content of 1-hexene incorporation within the copolymer chain and 1-hexene unit in the copolymer chain isolates by ethylene units. The homopolymer of ethylene has broader MWD with 42–46. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 417–424, 2010

KEYWORDS: broad molecular weight distribution; copolyethylene; copolymerization; metallocene catalysts; methylaluminoxane; non-metallocene complexes; Ziegler-Natta polymerization; polyethylene

INTRODUCTION Mononuclear metallocene and constrained geometry configuration (CGC) are excellent single site catalyst for ethylene polymerization producing polymer ethylene (PE) with excellent mechanical and optical properties.[1–3] However, there still are some limitations in polymer processing due to the narrow molecular weight distribution (MWD).[4] There are three approaches to control the MWD of PE, using a series of reactors under different polymerization conditions, employing different catalytic systems in one-pot[5,6] and designing metallocene precatalytic systems that can produce multicatalytic species during the polymerization process. In recent years, a variety of multinuclear bridged metallocene complexes bearing polymethylene,[7] polysiloxane or sila,[8–13] benzylene,[14] p-bisbenzylene,[15] polymethylene or polysiloxane double bridges,[16,17] and other ligands[18,19] have been prepared and used as catalysts in ethylene polymerization due to their ability of MWD tailoring through the cooperative effect among metal centers, ligand structures and the nature of the bridges. Petersen and coworkers[20] reported the synthesis of dinuclear metallocene titanium and zirconium complexes bearing a bridged bis(cyclopentadienyl) ligand. Huang and coworkers[21] employed mono-bridged hetero-, or homo-binuclear complexes with different substituted cyclopentadienyl ligands to promote the polymerization of ethylene. Green and coworkers,[22] Alt et al.,[18] and Noh et al.[23] synthesized a lot of multinuclear metallocenes and studied their behaviors in the polymerization of ethylene.

In our previous work,[24] we reported a kind of novel bridged non-metallocene catalysts for ethylene polymerization to producing broad MWD and linear polyethylene. Herein, we synthesize a series of novel bridged multi-chelated non-metallocene catalysts bearing substituted or unsubstituted imidazole ligands differed from the previous work. These catalysts exhibit high catalytic activity for copolymerization of ethylene with 1-hexene featured broad MWD and high comonomer incorporation. The effects of performing conditions, such as
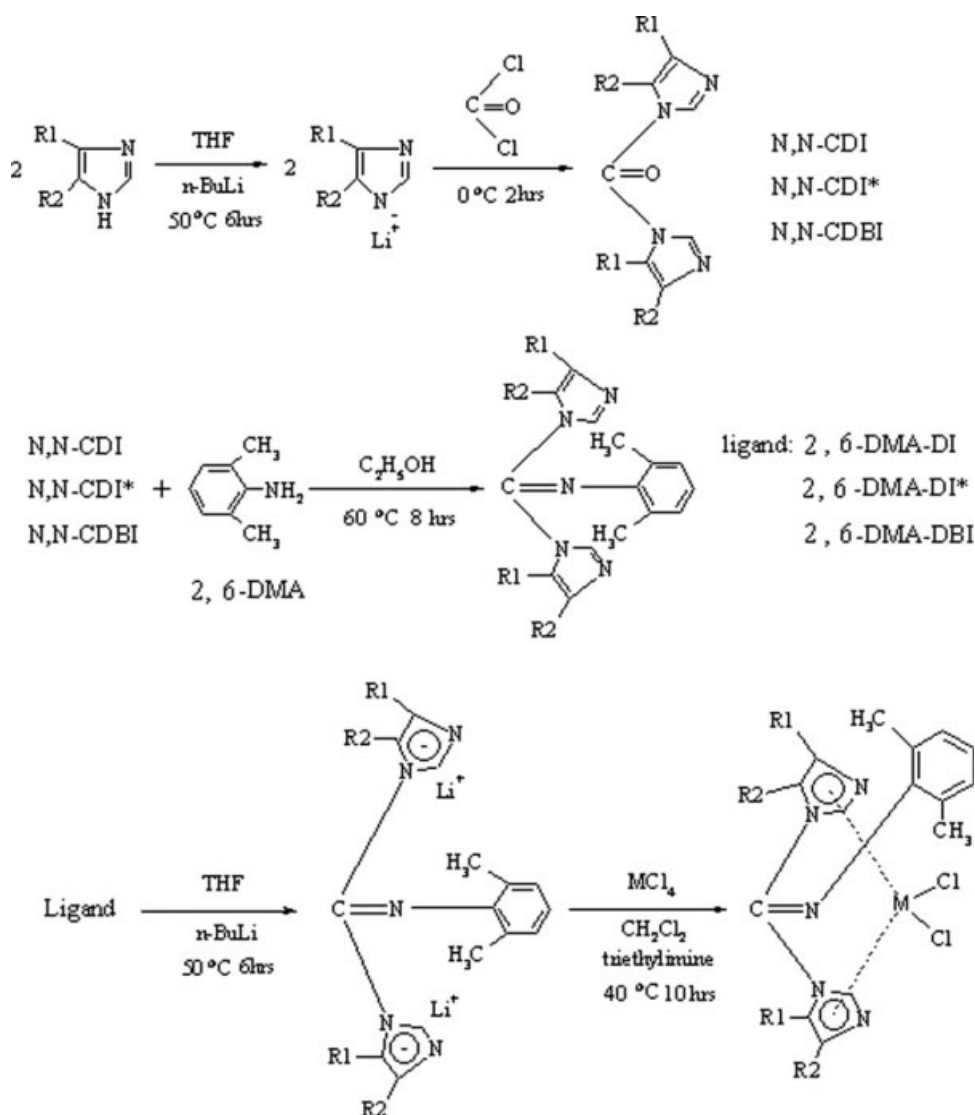
SCHEME 1 The synthesis course of the non-metallocene catalysts.

polymerization temperature, ratio of Al/M and monomer pressure on the polymerization behaviors are investigated as well.

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. Toluene, benzene, THF, and n-hexane were further purified by refluxing over metal sodium under nitrogen for 48 h and distilled before use. Toluene, benzene, n-hexane, THF, MCl_4 (M = Ti or Zr), Methylaluminoxane (MAO) with 10% in toluene, and n-BuLi with 2.5 M in n-hexane were purchased from Aldrich. The ligands, 1, 2-R_1, R_2-N, N-imidazole (R_1, R_2 = H, methyl), and benzimidazole were purchased from Acros. 1-hexene (98%) from Fluka was purified by distillation over CaH_2 and stored in a Schlenk tube containing 5A molecular sieves under high-purity nitrogen.

Synthesis of Catalyst Precursors

Imidazole 5.00 g (0.0735 mol) was added in a 500-mL flask. THF 100 mL was introduced into the flask and stirred it till the imidazole totally dissolved. 29.4 mL (0.0735 mol) n-BuLi was dripped into the solution at 5 °C. The mixture was heated to 40 °C and stirred for 6 h. Subsequently, the phosgene was introduced into the reactor and the mixture was stirred for 2 h at 0 °C. The ratio of imidazole to phosgene was 2:1. The mixture was filtered and the filtrate was kept in refrigerator at −15 °C, 5.90 g white crystal N,N-carbonyldiimidazole (N,N-CDI) was obtained.

The imine bridged imidazole compound was synthesized as following procedures. N,N-CDI (0.60 g) dissolved in 70 mL anhydrous alcohol and 0.34 g of 2,6-dimethylaniline (2,6-DMA) was introduced and stirred for 8 h at 60 °C. The mixture was filtered at room temperature and the filtrate was crystallized at −10 °C. Then the compound was recrystallized from 50 mL petroleum ether at −10 °C, from which 0.89 g 2,6-dimethylanilin-diimidazole (2,6-DMA-DI) was obtained (Scheme 1), ^{1}H NMR (DMSO): δ = 7.25 (s, 2H[2]),

TABLE 1 The Parameters for Cat.**1** to Cat.**6**

Catalysts	Metals	Ligands	Microanalysis	^{1}H NMR
Cat.**1**	Ti	2,6-DMA-DI	($C_{15}N_5H_{13}TiCl_2$) (382): Calcd. C 44.05, H 2.53, N 19.82; Found C 44.11, H 2.58, N 19.80	(DMSO): δ = 7.25 (s, 2H^2), 7.18 (d, 2H^4, 2H^5, $J_{4,5}$ = 3.6 Hz), 2.33 (s, 6H, dimethylaniline), 6.61 (d, 2H, dimethylaniline, $J_{4,5}$ = 3.0 Hz), 6.82 (m, 1H, dimethylaniline)
Cat.**2**	Zr	2,6-DMA-DI	($C_{15}N_5H_{13}ZrCl_2$) (425): Calcd. C 42.27, H 2.51, N 19.40; Found C 42.31, H 2.53, N 19.36	
Cat.**3**	Ti	2,6-DMA-DI*	($C_{19}N_5H_{21}TiCl_2$) (438): Calcd. C 52.05, H 4.79, N 15.98; Found C 52.11, H 4.84, N 15.80	(DMSO): δ = 7.20 (s, 2H^2), 3.90 (s, 12H, methyl), 2.33 (s, 6H, dimethylaniline), 6.61 (d, 2H, dimethylaniline, $J_{4,5}$ = 3.0 Hz), 6.82 (m, 1H, dimethylaniline)
Cat.**4**	Zr	2,6-DMA-DI*	($C_{19}N_5H_{21}ZrCl_2$) (481): Calcd. C 47.40, H 4.37, N 14.55; Found C 47.45, H 4.42, N 14.59	
Cat.**5**	Ti	2,6-DMA-BDI	($C_{23}N_5H_{17}TiCl_2$) (482): Calcd. C 57.26, H 3.53, N 14.52; Found C 57.31, H 3.58, N 14.57	(DMSO): δ = 8.25 (s, 2H^2), 7.61 (d, 2H^5, 2H^8, $J_{5,6}$ = 3.0 Hz), 7.18–7.21 (m, 2H^6, 2H^7), 2.33 (s, 6H, dimethylaniline), 6.61 (d, 2H, dimethylaniline, $J_{4,5}$ = 3.0 Hz), 6.82 (m, 1H, dimethylaniline)
Cat.**6**	Zr	2,6-DMA-BDI	($C_{23}N_5H_{17}ZrCl_2$) (525): Calcd. C 52.51, H 3.24, N 13.33; Found C 52.56, H 3.29, N 13.38	

2,6-DMA-DI: 2,6-dimethylanilin-diimidazole; 2,6-DMA-DI*: methyl substituted 2, 6-dimethylanilin-diimidazole; 2,6-DMA-DBI: 2,6-dimethylanilin-dibenzimidazole.

7.18 (d, 2H^4, 2H^5, $J_{4,5}$ = 3.6 Hz), 2.33 (s, 6H, dimethylaniline), 6.61 (d, 2H, dimethylaniline, $J_{4,5}$ = 3.0 Hz), 6.82 (m, H, dimethylaniline); 2,6-DMA-DI ($C_{15}N_5H_{15}$) (265): Calcd. C 66.38, H 3.85, N 29.81; Found C 66.40, H 3.87, N 29.79. The ligand 2,6-DMA-DI was treated with *n*-BuLi in THF for 6 h at 40–50 °C. 2,6-DMA-DI titanium complex (Cat.**1**) was prepared by the treatment of ligand (0.60 g) with TiCl$_4$ (0.31 g) in 70 mL methylene chloride in the presence of 0.60 mL triethylamine. The reaction lasted for 10 h at 40 °C. The mixture was filtrated and the solvent was removed. The residue was dried by vacuum for 8 h at 40 °C and 0.63 g Cat.**1** was obtained (Scheme 1). 2,6-DMA-DI and Cat. **1** were confirmed by ^{1}H NMR and microanalysis (Table 1). The ligand methyl substituted 2,6-dimethylanilin-diimidazole (2,6-DMA-DI*) derived from methyl substituted imidazole, 2,6-dimethylanilin-dibenzimidazole (2,6-DMA-DBI) from benzimidazole and Cat.**2**–**6** were synthesized according to the foregoing method. Their ^{1}H NMR and microanalysis data were compiled in Table 1.

Polymerization Procedure

All polymerizations were carried out in a 300 mL autoclave with cooling and heating jacket, after purging all moisture and oxygen by a high-vacuum pump, the reactor was sealed under a nitrogen atmosphere. Freshly distilled toluene (80 mL), desired amount of non-metallocene catalyst and MAO were added in order. The mixture was stirred for 15 min for preactivation. After that, desired amount of 1-hexene was added, ethylene was introduced up to desired pressure and the reactor was heated to desired temperature by oil bath. Under the desired ethylene pressure, the reaction system was stirred for 60 min. Finally, the polymerization was terminated with 10 wt % HCl in alcohol. The obtained copolymer was filtered and washed with alcohol and water for three times, then dried overnight in a vacuum oven at 80 °C.

Characterization

^{13}C NMR spectra of the copolymer samples were obtained on an INOVA500 MHz (for hydrogen) instrument. The conditions used for quantitative ^{13}C NMR were 15 wt % samples in ortho-dichlorobezene-d_4 at 125 °C. The average molecular weight and MWD were measured by PL-GPC200 instrument using standard polystyrene as reference and 1,2,4-trichlorobenzene as solvent at 150 °C. DSC thermograms were recorded with a PA5000-DSC instrument at a rate of 10 K/min. WAXD was recorded with an X-ray diffraction instrument, using Ni films to sieve wave, using CuKα radiation (λ = 1.5405 × 10^{-10} m). WAXD intensities were recorded from 5 to 40° with a continuous scanning speed.

RESULTS AND DISCUSSION

Copolymerization of Ethylene with 1-Hexene

The six newly synthesized non-metallocene catalysts (Cat.**1** to Cat.**6**) are investigated for copolymerization of ethylene with 1-hexene, using MAO as cocatalyst. These results are compiled in Table 2.

From Table 2, it could be noticed that each of the six catalysts exhibits high activity for homo and copolymerization of

TABLE 2 The Copolymerization of Ethylene with 1-Hexene Mediated by Novel Non-Metallocene Catalysts at 50 °C in 80 mL Toluene for 1 h[a]

Run	Catalysts	A^b ($\times 10^{-4}$)	$M_w{}^c$ ($\times 10^{-6}$)	$M_w/M_n{}^c$	1-hex^d (mol %)	$T_m{}^e$
1	Cat.**1**	1.46	1.11	33.2	4.6	118.1
2	Cat.**2**	1.88	1.21	33.6	6.7	_
3	Cat.**3**	2.42	1.12	34.5	5.1	112.2
4	Cat.**4**	3.21	1.28	35.2	9.2	_
5	Cat.**5**	2.86	1.17	33.2	4.3	122.8
6	Cat.**6**	3.32	1.27	33.9	6.8	_
7[f]	Cat.**1**	0.61	1.06	42.0	_	128.8
8[f]	Cat.**2**	0.84	1.12	43.0	_	129.0
9[f]	Cat.**3**	1.64	1.08	43.5	_	129.2
10[f]	Cat.**4**	2.01	1.18	46.0	_	129.7
11[f]	Cat.**5**	1.86	1.12	43.2	_	130.8
12[f]	Cat.**6**	2.12	1.17	43.9	_	129.8

[a] M; Al/M, 200/1 in mol; 1-hexene, 4 mL; MAO as cocatalyst.
[b] Catalytic activity, g PE/g M.h (M: Ti and Zr).
[c] Measured by GPC, 1,2,4-trichlorobenzene as solvent, PS as reference.
[d] The molar content of 1-hexene incorporation within copolymer chain.
[e] Melting point, measured by DSC.
[f] Homopolymerization of ethylene under the same conditions.

ethylene with 1-hexene. Non-metallocene titanium complexes for copolymerization of ethylene with 1-hexene are less effective than the zirconium analogues with the same ligand, for example, the catalytic activity of 1.46×10^4 g PE/g Ti.h for Cat.**1** and 1.88×10^4 g PE/g Zr.h for Cat.**2** (run 1, 2 in Table 2). On the other hand, the complexes with methyl or phenyl ring substituted ligands exhibit obviously higher catalytic activity for homopolymerization of ethylene and copolymerization of ethylene with 1-hexene (runs 3–6 and runs 9–12 in Table 2) than that with unsubstituted ones (runs 1–2 and runs 7–8 in Table 2). It exhibits that the replacement of hydrogen by methyl or phenyl in this kind of catalysts is more preferable for polymerization of ethylene and copolymerization of ethylene with 1-hexene. The results indicate that the presence of methyl or phenyl ring moiety meets the electronic coordination requirements for high activity; it might be attributable to the electronic and steric effects of methyl or phenyl ring substituent. Therefore, the overall catalytic activity is enhanced. We can also notice from Table 2 that the positive "comonomer effective"[25,26] took place for all these catalysts. The catalytic activity for copolymerization of ethylene with 1-hexene was obviously higher than that of the homopolymerization of ethylene catalyzed by the same catalyst under the same conditions.

It is shown in Table 2 that the weight average molecular weight of the obtained polymers is relatively high, ranged in $1.06–1.28 \times 10^6$ g/mol. The high molecular weight mainly attributes to the electron effect caused by the presence of the bridged ligands with multi-nitrogen atoms, which results in an increase of electron density at the metal center and also at the β-carbon. Consequently, the β-hydrogen elimination and chain transfer to monomer reactions will be diminished during the polymerization process. Additionally, the

molecular weight of the obtained polymer by the catalysts with methyl or phenyl substituted ligand and unsubstituted ligand has the same change tendency. These results reveal that the effects of ligand structure and transition metal on weight average molecular weight of the polymer are nearly unobservable. It also could be found from Table 2 that the polyolefins promoted by these kinds of newly synthesized non-metallocene catalysts feature outstanding broad M_w/M_n ratio of 33.2–46.0. But the MWD of the copolymer is narrower than that of the homopolymer. The result consists with the report.[27,28] The MWD of these copolymers aren't obviously relative to the content of 1-hexene incorporation.

From Table 2, one could notice that the melting point of these homopolymers obtained is relatively low, ranged at 128.8–130.8 °C (run 7–12 in Table 2). It is possible that the lower molecular weight fraction of the polymer blends in the higher molecular weight fraction as a lubricant in the polymer, which impacts on the crystallization of polyethylene and results in lower melting point of these polymers. However, the melting points of the copolymers considerably depend on the content of 1-hexene incorporation. The higher the content of 1-hexene incorporation, the lower the melting points of the copolymers are. When the content of 1-hexene incorporation is up to 6.7 mol % (run 2 in Table 2), the copolymer exhibits no endothermal phenomena on the DSC record. Wu and coworkers[29] reports branched polyethylene with branching degree of 62.5/1000C catalyzed by α-diimine nickel (II) catalyst shows no melting endothermic character. The thermal properties of the branched polyethylene depend on the branching degree, distribution and structure. Li and coworkers[30] confirms that the copolyethylene with 1-hexene incorporation content of 5.29 mol % promoted by bis(b-enaminoketonato) titanium complexe/MAO obviously shows

TABLE 3 Contents of Different Monomer Triads in ^{13}C NMR of the Copolymer (Run 4 in Table 2)

Mole Fractions		Triad Distributions						
[E]	[H]	[EHE]	[EHH]	[HHH]	[HEH]	[HEE]	[EEE]
90.8	9.2	8.8	0.47	0.18	0.36	16.35	73.84

bad crystalline property with crystallinity of 8.9%.The crystallinity of the copolymer considerably decreases with increase of 1-hexene incorporation content.

The ^{13}C NMR spectrum of the copolymer promoted by Cat.**4** (run 4 in Table 3) is performed (Fig. 1). The chemical shift assignments for the peaks are listed in Table 2.[31] They are obtained by comparing the observed ones to those calculated with the empirical method of Grant and Paul.[32]

As seen Table 3, the E–O copolymer contains the sequences of EHHE, EHE, HHE, HHH, HEEH, HEE, EEE, and other sequences. According to the ^{13}C NMR spectrums of ethylene/1-hexene copolymers obtained via these non-metallocene catalysts, the signals content of the copolymer are high at δ 38.31, 30.20, and 27.37 ppm, which are assigned to the sequences of EHE, HEE, EEE. Moreover, these sequences (HEH, HEEH) in which 1-hexene unit separated by one or two ethylene units are appeared and the resonances ranging from δ 35.0 to 41.0 ppm and 34.03 ppm can confirm the possibility of HH dyad and HHH triad sequences, indicating the trend of 1-hexene toward forming relative long sequences in the ethylene/1-hexene copolymer. But, the signals of long 1-hexene sequences are weak.

Based on the ^{13}C NMR result, the microstructure of the obtained copolymer is determined. Additionally, to determine more precisely the microstructure of the analyzed copolymer, the structural parameters, such as comonomer mole fractions and the reactivity ratios of the comonomers are calculated using the Randall method.[33] The results are presented
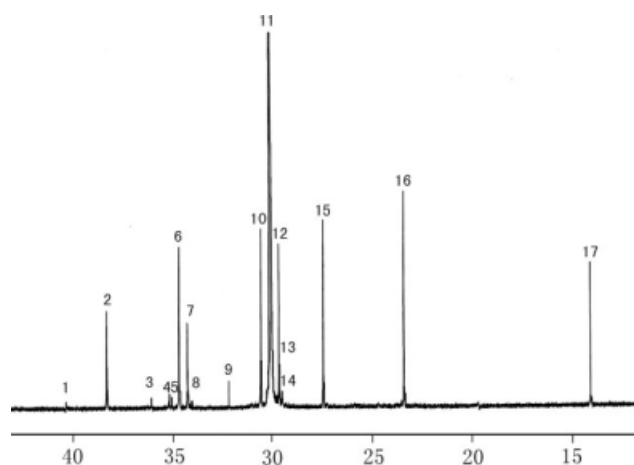
FIGURE 1 The ^{13}C NMR spectrum of the copolymer promoted by Cat.**4** (run 4 in Table 2).

TABLE 4 The Observed Signals Assignment for the Copolymer of Ethylene/1-Hexene (Run 4 in Table 2)

Peak No.[a]	Carbon Type	Monomer Sequence	Chemical Shift	
			Calculated	Found
1	$\alpha\alpha$	EHHE	40.18	40.35
2	CH	EHE	38.13	38.26
3	CH	HHE	35.85	36.03
4	$\alpha\gamma$	HHEH+EHEH	35.00	35.13
5	$\alpha\delta^+ + CH_2(4)$	HHEE+HHE	34.90	35.04
6	$\alpha\delta^+$	EHEE	34.54	34.65
7	$CH_2(4)$	EHE	34.13	34.25
8	CH	HHH	33.47	34.03
9	$\gamma\gamma$	HEEH	30.94	32.17
10	$\gamma\delta^+$	HEEE	30.47	30.50
11	$\delta^+\delta^+$	(EEE)n	29.98	30.20
12	$CH_2(3)$	EHE	29.51	29.66
13	$CH_2(3)$	HHE	29.34	29.56
14	$CH_2(3)$	HHH	29.18	29.44
15	$\beta\delta^+$	EHEE	27.28	27.36
16	$CH_2(2)$	EHE+HHE+HHH	23.36	22.84
17	CH_3	EHE+HHE+HHH	14.12	14.06

[a] The peak numbers labeled in Figure 1.

in Table 4. As seen in Table 4, the ethylene/1-hexene copolymer catalyzed by these non-metallocene catalysts mainly contains the triad distributions of EHE, EEE, and HEE, but these triad distribution concentrations (HHH, HHE, HEH) are very low, indicating the trend of 1-hexene toward forming isolated by one or more ethylene units and uniform sequences in the ethylene/1-hexene copolymer. The result of the monomer reactivity ratio also confirms that the 1-hexene units within the copolymer chain are mostly isolated by ethylene units. Additionally, for the products of the comonomers reactivity ratios, the values $r_E = 13.51$ for ethylene and $r_H = 0.059$ for 1-hexene, with $r_E \cdot r_H = 0.8$. The value of $r_E \cdot r_H$ is close to 1, reflecting a pronounced tendency for the random distribution of the comonomers in the copolymer chain. Consequently, unlike ethylene/1-hexene copolymers obtained by metallocene catalysts, in which the copolymers with high 1-octene content contained abundance of signals of HH dyad and HHH triad sequences besides the alternating and isolated H units. The ethylene/1-hexene copolymers obtained by these non-metallocene catalysts are not only improved the incorporation of 1-hexene into the polyethylene main chain, but also optimized the uniformity for the whole copolymer molecular chain because of the copolymers mainly containing the isolated and uniform H units.

Although the concentration of the comonomer in feed is the same for these investigated catalysts (Cat.**1** to Cat.**6**), the results of the calculations show that the obtained copolymer with these non-metallocene catalysts has a high contribution of the comonomer in the product. Therefore, the

TABLE 5 The Effect of Conditions on the Copolymerization of Ethylene with 1-Hexene Catalyzed with Cat.4 in 80 mL Toluene for 1 h[a]

Run	T (°C)	Al/Zr (mol/mol)	P^b (MPa)	h–f[c] (mL)	A[d] ($\times 10^{-4}$)	M_w[e] ($\times 10^{-6}$)	M_w/M_n[e]	1-hex[f] (mol %)	T_m[g]
13	40	200	0.5	4	2.42	1.06	31. 2	5.2	112.2
4	50	200	0.5	4	3.21	1.28	35.2	9.2	_
14	60	200	0.5	4	2.61	1.02	36.1	7.8	_
15	50	150	0.5	4	2.01	0.98	34.4	7.6	_
16	50	250	0.5	4	2.56	1.03	36.6	6.4	_
17	50	200	0.1	4	1.48	0.92	35.1	12.8	_
18	50	200	0.25	4	1.77	0.94	35.8	10.6	_
19	50	200	0.3	4	2.45	1.03	35.5	9.4	_
20	5	200	0.5	1	2.85	1.06	35.1	6.7	_
21	50	200	0.5	2	2.98	1.03	35.2	7.8	_
22	50	200	0.5	6	3.01	0.96	35.4	9.2	_

[a] Polymerization conditions: the catalyst concentration, 1.0×10^{-4} M.
[b] Pressure of the ethylene.
[c] The adding amount of 1-hexene in feed (mL).
[d] Catalytic activity in g of PE/g of Zr.h.
[e] Determined by GPC.
[f] The molar content of 1-hexene incorporation within copolymer chain.
[g] Melting point determined by DSC.

incorporation of α-olefins into the polyethylene chain is more effective in case of these non-metallocene catalysts compared to the convenient Z–N catalyst.

But the ^{13}C NMR spectrum of the homopolymer of ethylene promoted by Cat.**4** (run 10 in Table 2) exhibits only one signal at δ 30.00 ppm, which attributes to the methylene of PE. It is confirmed that the polymer features linear structure.

The WAXD pattern of the polyethylene catalyzed by these catalysts (runs 1,3,5,7–12 in Table 2) shows three diffraction signals, which are at $2\theta = 21.5$, sharp, for (110) plane, $2\theta = 23.9$, middle, for (200) plane, and $2\theta = 31.5$, weak, for (020) plane, respectively. These signals attribute to the character of PE crystal.[34] But for those copolymers with high 1-hexene incorporation (runs 2, 4, 6 in Table 2), no sharp signal, just weak and broad peaks are observed on their WAXD diffractograms.

Meanwhile, high catalytic activity of these six catalysts for ethylene polymerization is exhibited even at fairly low Al/M ratio of 200, which results in lower cost for industrial production.

Comparing with other catalysts used in this work (in Table 2), Cat.**4** is preferable for ethylene polymerization. So the effects of polymerization conditions, such as temperature, Al/Zr ratio, and pressure of monomer on ethylene polymerization are investigated in detail. The results are listed in Table 5.

From Table 5 we could notice that the catalytic activity increases with the increasing of temperature within the range of 40–50 °C (run 13 and run 4 in Table 5) and shows a maximum value of 3.21×10^4 g of PE/g of Zr.h at 50 °C. However, it decreases to 2.61×10^4 g of PE/g of Zr.h at 60 °C (run 14 in Table 5) because of both the lower monomer concentration and the faster deactivation rate of the active species at relatively high temperature. The weight average molecular weight of the polymer is obviously relative to the

polymerization temperature (40–60 °C), at 50 °C the peak value of 1.28×10^6 g/mol is shown (run 4 in Table 5) and the MWD of the obtained polymer becomes broader slightly as increasing temperature (runs 13, 4, and 14 in Table 5).

MAO is used as cocatalyst for alkylation, chain-transfer agent, and deimpurifier. Trimethylaluminum (TMA) in MAO could reduce oxidation state of Ti (IV) to Ti (III), Ti (IV) is favorable for α-olefin polymerization.[35] From Table 4, it is found that Cat.**4** shows high activity at Al/Zr (mol/mol) = 150–250 (runs 15, 4, and 16 in Table 5) and exhibits a maximum value of 3.21×10^4 g of PE/g of Zr/h at Al/Zr = 200. However, the catalytic activity is obviously lower at higher or lower ratio of Al/Zr, 2.1×10^4 g of PE/g of Zr.h at Al/Zr = 150 and 2.56×10^4 g of PE/g of Zr.h at Al/Zr = 250 (runs 15 and 16 in Table 5), respectively. The weight average molecular weight of the obtained polymer increases from 9.8×10^5 to 12.8×10^5 g/mol with the increasing of the ratio of Al/Zr from 150 to 200 (runs 15 and 4 in Table 5). When the ratio of Al/Zr increases from 200 to 250, however, the value of weight average molecular weight decreases slightly from 1.28×10^6 to 1.03×10^6 g/mol (runs 4 and 16 in Table 5). In short, the catalytic activity of the non-metallocene complexes and the molecular weight of the obtained polymer are greatly depended upon the amount of MAO.

Moreover, higher pressure of monomer leads to higher catalytic activity and molecular weight (runs 17, 18, 19, and 4 in Table 5). From Table 5, it could be also noticed that the MWD of the obtained polyethylene is obviously broad but changes slightly even at different polymerization conditions.

Broad Molecular Weight Distribution

Table 2 shows that the polyolefins catalyzed by these non-metallocene catalysts have broader MWD, for example, the polyethylene and the copolymer of ethylene with 1-hexene
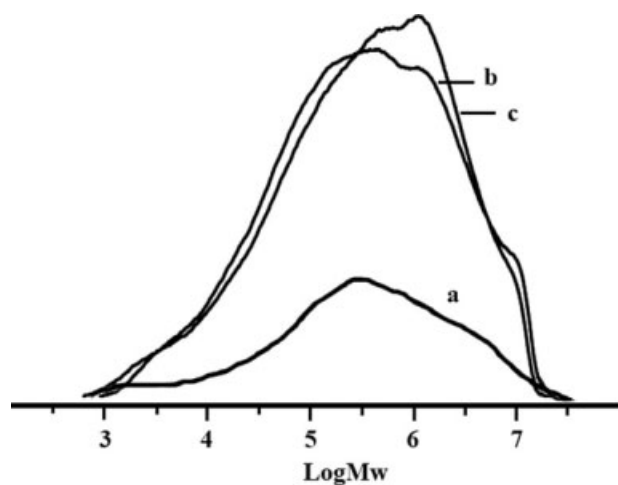
FIGURE 2 The GPC plots of the obtained polyolefins (a) run 10, (b) run 4, and (c) run 3 (Table 2).

catalyzed by cat.**4** (runs 10 and 4 in Table 2) exhibit broader M_w/M_n ratio of 46.0 and 35.2, respectively, than the MWD of the polymers promoted by traditional Z-N catalyst and metallocene complexes. Cat.**3** having the same ligand as cat.**4** for the copolymerization of ethylene with 1-hexene produces the copolymer with broader M_w/M_n ratio of 34.5. The GPC plots of the obtained polymers are shown in Figure 2.

The value of M_w/M_n is relative large, indicating the formation of more than one active species and/or the changing nature of the active species are taken place during the course of the polymerization. This phenomenon is operative strong evidence for the presence of different active species. It has recently been provided by Barabanov et al.,[36] who used ^{14}CO radiotagging to determine the number of active species and propagation rate constant in homogeneous polymerization. It is hard, at present, to specify the real active species in the catalytic system. However, it is likely that the active species would be $[2,6\text{-DMA-DITi(Zr)Me}_2]^+$, $[2,6\text{-DMA-DI*Ti(Zr)Me}_2]^+$, and $[2,6\text{- DMA-DBITi(Zr)Me}_2]^+$ because $[Cp^*Ti(Zr)Me_2]^+$ has been proposed as an active polymerization catalyst[37,38] and the deactivation of $[2,6\text{-DMA-DITi(Zr)Me}_2]^+$ would take place by the reduction of the central metal such as reductive elimination of the two alkyl groups.

The catalysts synthesized are mononuclear non-metallocene complexes; however, there are two different coordinative connection fashions of metal atom and nitrogen atom in imidazole or dimethylaniline, which cause a difference in electron density and steric hindrance between each other. Lewis acid–base interaction, chain transfer to aluminum (MAO)[39] and the stepwise dissociation of bridged imidazole ligands might be conceivable, too.[40] Therefore, more than one kind of active species appear during the polymerization, which are preferable for the broad MWD of PE. The low molecular weight polymer fraction attributes to highly active but unstable active species, as well as less active but more stable species produce the high molecular weight polymer.[41] So the

obviously broader M_w/M_n ratio of 46.0 is obtained and the processability of the polymer obtained might be improved.

CONCLUSIONS

The bridged multi-chelated non-metallocene catalysts consisting of heterocyclic ligands (Cat.**1** to Cat.**6**) exhibit high catalytic activity for ethylene polymerization and copolymerization of ethylene with 1-hexene. Zirconium complexes are more favorable for ethylene polymerization and copolymerization of ethylene with 1-hexene. Polymerization conditions, such as temperature, pressure of ethylene and Al/M ratio show considerable effects on the catalytic activity and weight average of molecular weight of the obtained polymers. The ^{13}C NMR results confirm that the homopolymer of ethylene catalyzed by these bridged non-metallocene catalysts show linear structure and the copolymers have high content of 1-hexene incorporation within the copolymer chain. 1-hexene units within the copolymer chain are isolated by one, two or more units of ethylene. Block distribution of ethylene units are dominant in the copolymer chain. The DSC results show that the melting points of the obtained polymer are depended on the content of 1-hexene incorporation, obviously decreased with increasing of the content of 1-hexene incorporation. The GPC results confirm that the obtained polymers feature relatively high molecular weight and dramatic broad M_w/M_n ratio of 42 to 46 for polyethylene, and 33 to 35.2 for copolymer of ethylene with 1-hexene. The MWD of the obtained polymers are independent of the polymerization conditions. The reactivity ratio, r_E is larger than r_H. The result reveals that 1-hexene unit within the copolymer chain is isolated by ethylene units, but long sequence of ethylene units exists.

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