

Ethylene polymerization and oligomerization catalyzed by bulky β -diketiminato Ni(II) and β -diimine Ni(II) complexes/methylaluminoxane systems

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Abstract

β -Diketiminato complexes $\text{Ni}\{(\text{N}(\text{Ar})\text{C}(\text{Me})_2\text{CH})\text{Br}$ (**9**), $\text{Ni}\{(\text{N}(\text{Ar})\text{C}(\text{Me})_2\text{CH})\text{PPh}_3\text{Br}$ (**10**) and β -diimine complexes $\text{Ni}\{(\text{N}(\text{Ar})\text{C}(\text{Me})_2\text{CH}_2)\text{Br}_2$ (**5**) ($\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$ (**a**), $2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**b**)) were used as catalyst precursors for ethylene polymerization in the presence of methylaluminoxane (MAO). High molecular weight ethylene polymers as well as short chain oligomers (C4–C8) were simultaneously produced from the catalysis reactions. Ethylene polymers obtained by using these β -N–N Ni(II)/MAO catalyst systems are mainly methyl branched. Small amounts of even number branches were also observed in the ^{13}C NMR spectra of the obtained ethylene polymers, which are believed generating from the incorporation of simultaneously produced α -olefins. Except methyl branch and the branches derived from the incorporation of α -olefin oligomers, the formation of other branch types via the chain walking process is not favored in β -diketiminato Ni(II) systems.

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Keywords: β -Diketiminato Ni(II) complexes; Ethylene; Polymerization; Oligomerization; Triphenylphosphine

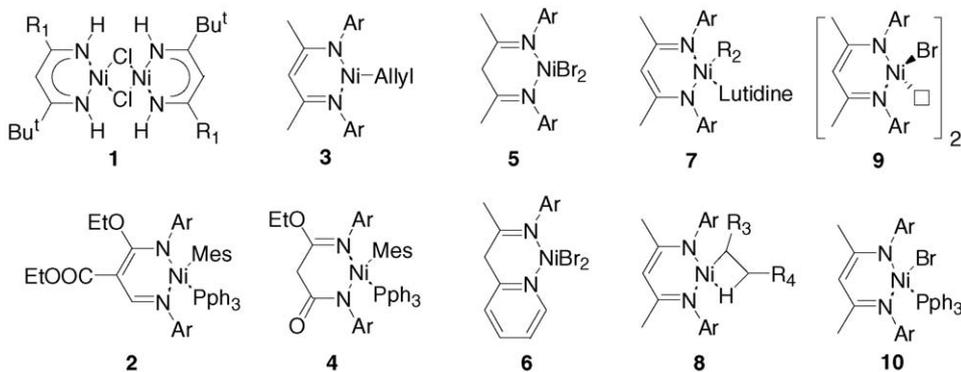
1. Introduction

The early report of the late transitional metal (LTM) catalyst can be traced back to the polymerization of butadiene catalyzed with diethyl bis(2,2'-bipyridyl)iron complexes developed by Yamamoto et al. in 1965 [1]. Later, Keim's researches founded base of the shell higher olefin process (SHOP) [2]. Due to the strong β -H elimination tendency of the LTM systems, rare LTM catalysts were found to produce solid ethylene polymers efficiently [3]. Until that, Brookhart and co-workers reported the cationic bulky α -diimine catalysts in 1995 [4]. Then, in 1998, Grubbs and co-workers reported the neutral salicylaldimine catalysts, which were capable of co-polymerizing the polar olefin monomers even in the polar solvent [5]. In the past decade, many researches on these two kinds of catalyst systems were carried out on topics including ligand structure [4,6], polymerization and branching mechanism [7]. The axial bulky aryl groups of the α -diimine ligands retard the chain transfer, and thus lead to

higher molecular weight polymers. This axial steric bulk concept had been validated with and extended to many kinds of fine contrived LTM catalyst systems, such as pyridine bis(imine) (PBI) Fe and Co catalyst systems, which produce high molecular weight linear ethylene polymers [8].

The researches on β -diketiminato metal complexes went afresh hot in the middle of 1990s [9]. The chemistry of the unsaturated three coordinate β -diketiminato LTM complexes were studied effectively by Holland and co-workers [10] and Warren and co-workers [11]. The works on the olefin polymerization with β -diketiminato transition metal catalysts, were recently reviewed in details by Gibson [12]. However, the researches on the ethylene polymerization by using β -diketiminato and analogous six-member-chelate-ring LTM catalyst systems are rare in the past decade [11a,13–15] (Fig. 1). The activities of these reported catalyst systems and corresponding characterization were listed in Table 1. Complexes of type **2** showed no activity either with methylaluminoxane (MAO) or with ethylaluminum sesquichloride (EASC) as cocatalyst. The amidoiminomalonate complex **4** shows high activities in the presence of MAO as cocatalyst, yielding oligomers with prevailing dimers (88.7%). Neither **3a**/BPh₃ nor **3a**/PMMAO are productive in catalyzing

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a : Ar = 2,6-diisopropylphenyl; **b** : Ar = 2,6-dimethylphenyl; Allyl = CH₂C(CO₂Me)CH₂, CH₂CHCH₂; Mes = mesityl; R₁ = piperidino; R₂ = methyl, ethyl, n-propyl, isopropyl; R₃ = H, methyl; R₄ = H, methyl, ethyl;

Fig. 1. Reported Ni(II) complexes of bidentate nitrogen ligand with six-membered chelating ring (**1–8**) and β -diketiminato Ni(II) bromide complexes (**9** and **10**) discussed.

Table 1
Ethylene oligomerization and polymerization catalyzed by compounds **2–8** in literature [11a,13–15]

Cat.	Cat. mol ($\times 10^{-6}$)	Co-cat. (ratio/type)	P_E (atm)	t (h)	TON	M_n	Refs.
1	~5.3	~55/MAO	0.375	1	1120	–	[15b]
2	10	MAO or EASC	29.6	–	Inactive	–	[14]
4	10	300/MAO	23.7	–	20530	(C4–C16)	[14]
3a	60	2/BPh ₃	6.9	18	81	–	[15a]
3a	110	PMAO	0.3	12	88	–	[15a]
5a	80	60/MAO	19	3.5	1800	–	[13a]
6a	2000	200/MAO	1	0.5	0.06 (g)	–	[13b]
8b	–	None	6.9	10	–	(C8–C18)	[11a]

ethylene polymerization to form solid polyethylene. Without the present of MAO, only ethylene oligomers (C8–C14) were obtained with complex **8a** at 6.9 atm ethylene pressure.

Bulky β -diketiminato complexes are catalyst precursors characterized by their axial steric bulk as α -diimine catalysts [4] and the neutral active center as salicylaldimine catalysts [5]. The ligand of the β -diketiminato complexes adopts a wedge shape configuration as compared with the open ligand configuration of the α -diimine complexes [6d]. In previous report, 1-hexene isomerization and dimerization were investigated by using **9**/MAO catalyst systems [16]. Result shows that the migration (chain-walking) of Ni(II) center on the alkyl chain were restrained by the coordination wedge of the β -diketiminato ligands. Here, β -diketiminato Ni(II) bromide complexes **9** and **10** were used as catalyst precursors in the presence of MAO for ethylene polymerization. Neutral ligand β -diimine Ni(II) complexes **5** were synthesized following the literature method [13a] and also used as catalyst precursors for comparison.

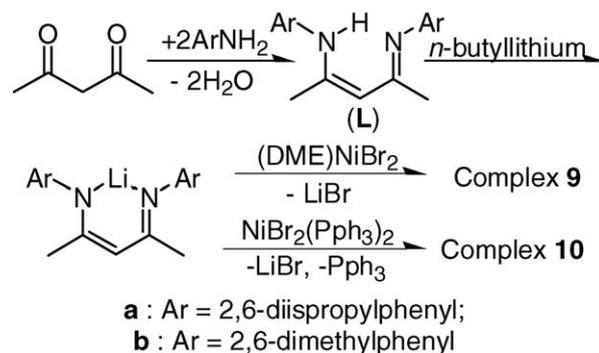
2. Result and discussion

2.1. Synthesis of β -diketiminato nickel complexes (**9** and **10**)

The synthetic routes of β -diketiminato Ni(II) complexes **9** and **10** are shown in Scheme 1. Complex **9** was synthesized according to the method in our previous report [16].

Ni{(N(C₆H₃R₂-2,6)C(Me)₂CH)}(PPh₃)Br (R = isopropyl **10a**, methyl **10b**) were readily obtained from reaction of lithium β -diketiminato salts with NiBr₂(PPh₃)₂. Hexane used to precipitate the target complex **10a** and **10b** should be enough to dissolve the PPh₃ released. These complexes are noteworthy thermal-stable, but sensitive to air and moisture.

The ¹H chemical shifts of these β -diketiminato complexes are paramagnetically induced by the unpaired spin of the Ni atom [17]. ¹H NMR spectra of **10a** and **10b** show that the equilibrium [10b,16] which shifts between monomer and dimer in the solution of **9a** and **9b** is interrupted by the introduction of PPh₃. ³¹P{¹H}NMR spectra of **10a** and **10b** show a single peak value around 135–136 ppm, and the sig-



Scheme 1. Synthesis of ligands and β -diketiminato Ni(II) complexes.

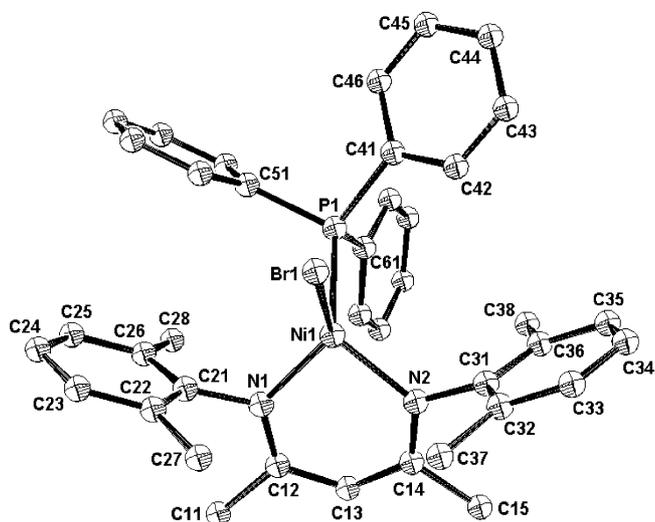


Fig. 2. Molecular structure of complex $\text{Ni}\{(\text{N}(\text{C}_6\text{H}_3\text{Me}_2-2,6)\text{C}(\text{Me})_2\text{CH})\}(\text{PPh}_3)\text{Br}$ (**10b**). Selected bond distances (\AA) and angles ($^\circ$): Ni(1)–N(1) 1.949 (2), Ni(1)–N(2) 1.939 (3), Ni(1)–Br(1) 2.3743 (8), Ni(1)–P(1) 2.3483 (11), N(2)–Ni(1)–N(1) 93.54 (11), P(1)–Ni(1)–Br(1) 95.52 (3), C(21)–N(1)–Ni(1) 115.57 (18), C(31)–N(2)–Ni(1) 114.9 (2). Hydrogen atoms are omitted for clarity.

nal corresponding to free PPh_3 at 6.0 ppm was not detected. The crystal structure of **10b** adopts a tetrahedral structure (Fig. 2).

2.2. Ethylene oligomerization and polymerization

The β -diketiminato Ni(II) systems catalyzed ethylene polymerization are characterized by simultaneous oligomerization. Considerable amounts of short-chain olefins as well as high molecular weight ethylene polymers were obtained (Fig. 3), indicating that there are at least two kinds of catalytically active species respectively for ethylene oligomerization and polymerization in the reaction systems. This character of the β -diketiminato Ni(II) systems differs from that of α -diimine catalyst system, especially the α -diimine Pd(II) system in which unreacted short-chain oligomer residuals were not observed [7a]. Total activities for producing oligomer and polymer and the ratios of polymer to oligomer increase with the increased

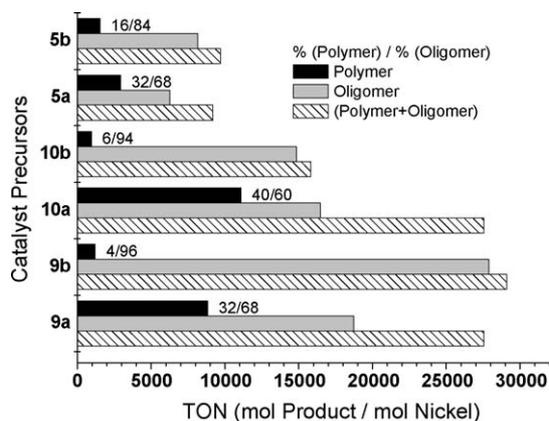


Fig. 3. Observed activities and polymer/oligomer ratios. Cond.: cat., 7×10^{-6} mol; MAO, ~ 250 mg; P_E , 150 psig, 30°C , 1.5 h, in 30 ml toluene.

Table 2

Ethylene oligomers^a obtained with **9a**/MAO at 150 psig

Temperature ($^\circ\text{C}$)	C4 (%)	C6 (%)	C8 (%)
0	84.3	12.6	3.1
20	78.8	18.6	2.6
40	41.3	43.3	15.4
60	60.6	30.0	9.4
80	72.5	21.1	6.4

Cat. 7×10^{-6} mol, MAO 275 mg, in 20 ml toluene.

^a Measured by GC–MS.

steric bulk of the complexes. The results suggest that bigger *ortho* substituents are more effective in stabilizing the Ni-alkyl active species and retarding the β -H elimination.

The data of the oligomer part products obtained with **9a**/MAO catalyst was listed in Table 2. The generation of these short chain olefins can be ascribed to the formation of highly electrophilic cationic species $[\text{Ni}(\text{II})\text{-R}]^+$ after the abstraction of the β -diketiminato ligand by MAO. As reported by Dubois et al., Groux et al. and Bryliakov et al., LM(halide) complexes combined with MAO give both cationic species as well as neutral species [18]. At 0°C , oligomers are mainly butylene. Below 40°C , the increased temperature leads to an increase in the proportions of longer oligomers (hexenes and octenes). Above 40°C , the proportions of longer oligomers fall with the increased temperature, and butylene proportions increase. This changing trend of oligomer proportions suggests that the increased temperature have a bigger impact on the β -H elimination than on the chain propagation in the oligomerization process. In addition, temperature also has impact on the distribution of C_n oligomer isomers ($n = 4, 6, \text{ or } 8$). The C8 oligomers are mainly 1-octene at 0°C and the proportions of other C8 isomers were observed increasing with the increased reaction temperature (Fig. 4). GC–MS confirmed that these C8 olefins include branched isomers and position isomers. In following discussion, activity refers merely to the polymer part, otherwise specified.

Table 3 lists polymerization data obtained by using different catalyst precursors at 30°C . Bulky catalyst systems (**9a**, **10a**

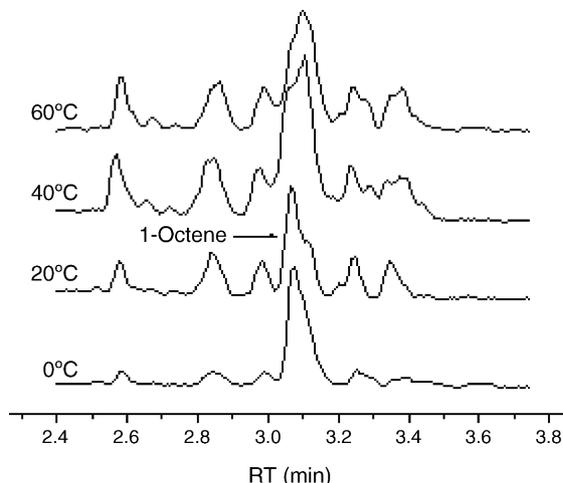


Fig. 4. C8 oligomers distribution obtained with **9a**/MAO at 150 psig of ethylene.

Table 3
Ethylene polymerization data for experiments at 30 °C

Entry	Cat.	Cat. mol ($\times 10^{-6}$)	P_E (psig)	PE (g)	Time (h)	TOF (/h)	M_n ($\times 10^{-3}$)	PDI	Branch (/1000 C) ^c	T_m (°C)
1 ^a	9a	7	150	1.732	1.5	5900	275	2.24	19	103.6
2 ^b	9a	10	20	0.656	8	300	223	2.78	–	105
3 ^a	9b	7	150	0.237	1.5	800	133	5.69	21	99.3 ^d /110.7
4 ^a	10a	7	150	2.175	1.5	7400	225	3.02	25	81.6
5 ^b	10a	10	20	0.415	8	190	179	2.54	–	102
6 ^a	10b	7	150	0.188	1.5	640	153	6.67	30	93.2 ^d /111.5
7 ^a	5a	7	150	0.574	1.5	1950	690/7	2.43/1.49	20	121.6
8 ^b	5a	10	20	0.651	8	290	87/4.8	3.90/1.51	–	114
9 ^a	5b	7	150	0.303	1.5	1030	517/1.9	2.79/2.59 ^e	29	117.6
10 ^b	5b	10	20	0.274	8	120	165/0.9	3.48/2.12	–	112

^a MAO 250 mg, toluene 30 ml.

^b MAO ~135 mg, toluene 20 ml.

^c [branch methyl carbon (total)/total carbon] \times 1000.

^d Main peak.

^e Value evaluated on Gauss distribution modal.

and **5a**/MAO) are observed more active for ethylene polymerization than less bulky catalyst systems (**9b**, **10b** and **5b**/MAO). The ethylene polymers obtained with big bulk catalysts (**9a**, **10a** and **5a**/MAO) have higher molecular weight and narrower distribution than that obtained with small bulk catalysts (**9b**, **10b** and **5b**/MAO). The branch rates of the polyethylenes obtained with less bulky catalyst systems are slightly higher than that of corresponding bulky ones (Table 3). The result suggests that the branching process is determined more by the free space between the two aromatic arms in β -diketiminatos Ni(II) systems, differing from the ethylene access factor by the size of the *ortho* substituents in α -diimine system [4a,7a]. The β -diketiminatos Ni(II)/MAO systems exhibit relatively lower activities than α -diimine Ni(II)/MAO analogues [4]. This activity decline should be ascribed to the weaker binding affinity of ethylene to the neutral Ni(II) center and the bigger binding restriction of ethylene to the metal center by the wedge shape ligand. Moreover, the activities of β -diketiminatos Ni(II)/MAO systems are sensitive to polymerization temperature. The highest activities are observed around 40 °C for **9a**/MAO and around 20 °C for **10a**/MAO (Table 4).

2.3. Polyethylene microstructure and branching mechanism

The ethylene polymers obtained with α -diimine Ni(II) and Pi(II) catalysts exhibit a branching rich structure, and multiple branching types including short and long, even and odd were observed [4,6,7]. In α -diimine systems, especially in the α -diimine Pd(II) system, these branches are believed to be formed via chain walking mechanism rather than by generating from the incorporation of short-chain oligomers [7a,19]. In following discussion, the used nomenclatures refer to Usami and Takayama for isolated branches [20a] and to Galland et al. [20b] for paired branches prefixes.

The ethylene polymers obtained with **9a**/MAO systems are basically methyl-branched, even if the polymerizations were carried out at higher temperature (Fig. 5). The branching structures of the ethylene polymers obtained with **10a**/MAO are similar to that obtained with **9a**/MAO (Fig. 6). The methyl-branched structure consists well with the ideas that the isomerization from 1-Ni-alkyl to 2-Ni-alkyl is favored in β -diketiminato Ni(II)/MAO system (Scheme 2) [16]. Aside from methyl branch, a small quantity of ethyl related carbon signals (1B2 11.190, 2B2 26.702,

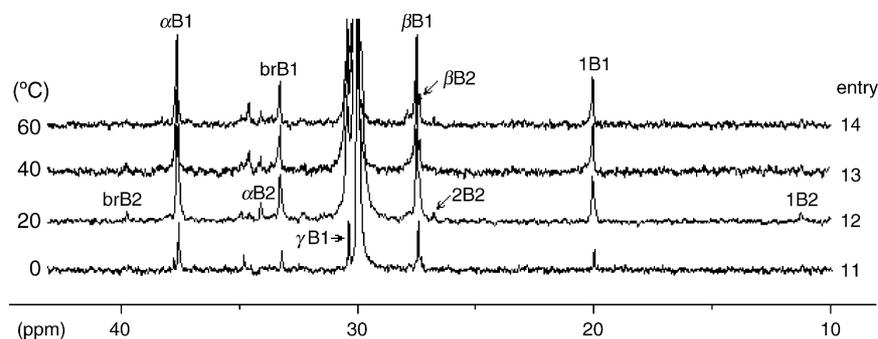
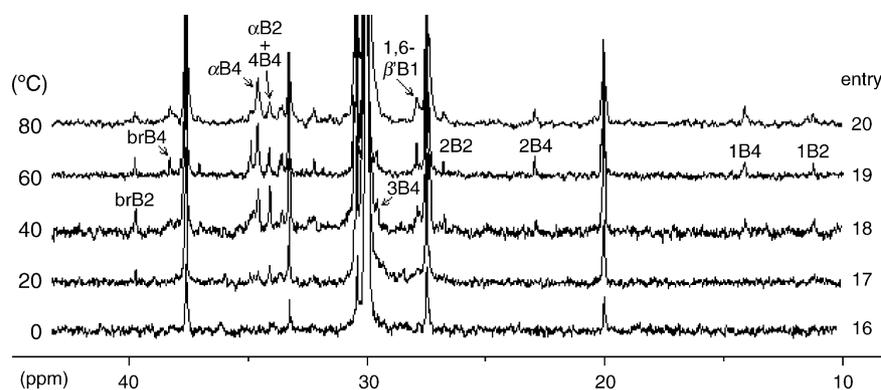
Table 4
Influence of temperature on ethylene polymerization

Entry	Cat.	Temperature (°C)	PE (g)	TOF (/h)	M_n ($\times 10^3$)	M_w/M_n , PDI	Me (/1000 C) ^a	Et (/1000 C) ^a	\geq C4 (/1000 C) ^a	T_m (°C)
11	9a	0	0.598	2030	813	2.41	7.6	–	–	110.4/118.7 ^b
12	9a	20	1.867	6320	781	2.55	13.7	1.5	–	99.5 ^b /113.5
13	9a	40	2.883	9810	224	2.64	20.2	1.7	–	78.6
14	9a	60	0.332	1130	107	13.04	33.7	2.2	–	94.4 ^b /110.5
15	9a	80	0.030	100	115	7.93	–	–	–	96.2 ^b /116
16	10a	0	0.442	1500	278	4.30	11.2	–	–	108.2/116.5 ^b
17	10a	20	2.249	7650	552	2.89	18.7	0.9	–	97.8 ^b /112.3
18	10a	40	0.974	3310	237	2.89	27.4	3.9	2.2	105.5 ^b /109.6
19	10a	60	0.836	2840	89	2.88	45.1	3.8	6.1	93.3/112.5 ^b
20	10a	80	0.102	350	84	7.73	–	–	–	93.7/113.4 ^b

P_E , 150 psig; Cat., 7×10^{-6} mol; MAO, 275 mg, 1.5 h, in 20 ml toluene.

^a Density of branches in chain = [methyl carbon of R/total chain carbon] \times 1000.

^b Main peak.

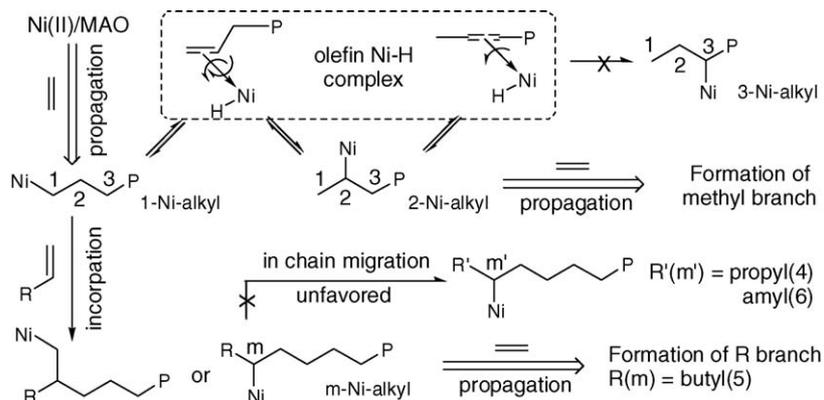
Fig. 5. ^{13}C NMR spectrum of polyethylene obtained with **9a**/MAO.Fig. 6. ^{13}C NMR spectrum of polyethylene obtained with **10a**/MAO.

$\alpha\text{B}2$ 34.059, $\text{brB}2$ 39.669) and butyl signals (1B4 14.058, 2B4 22.857, 3B4 29.527, $\text{brB}4$ 38.197, $\alpha\text{B}4$ 34.063) were also identified. Moreover, no specific resonance corresponding to odd number branches (propyl, amyl) was detected.

To understand of the origin of these ethyl and butyl branches, additional polymerization experiments were carried out with extra 6 ml 1-hexene added. Enhanced butyl related carbon resonance were observed in the ^{13}C NMR spectra of co-polymers (1B4 14.058, 2B4 22.857, 3B4 29.527, $\text{brB}4$ 38.197, $\alpha\text{B}4$ 34.063) (Fig. 7). As considering the highly initial 1-hexene concentration (6 ml), the incorporation rates by using **9a** and **10a**/MAO are very low with butyl branch number 6–8 per 1000 carbon. The low incorporation rate of α -olefins co-monomers were also reported in β -diketiminato Cr(III)/MAO system by

Theopold and co-workers [21] and should be ascribed to the wedge-shape configuration of the β -diketiminato ligand. Moreover, no minimal resonance corresponding to amyl and propyl was observed. This result suggests that the reinsertion of the coordinated inner olefin of the (olefin)Ni–H species, which formed after the β -H elimination of the 5-Ni-alkyl intermediate, is difficult in β -diketiminato Ni(II)/MAO catalyst systems. Here, these small quantities of even number branches observed in the ethylene homo-polymers can be safely ascribed to the incorporation of the simultaneously produced short chain α -olefins rather than chain walking process.

The incorporations of the α -olefin oligomers were also observed when complexes **9b**, **10b** and **5** were used as catalyst precursors (Fig. 8). Aside from methyl branch, polyethylene



Scheme 2. Presumed formation pathway of methyl-branched polyethylene.

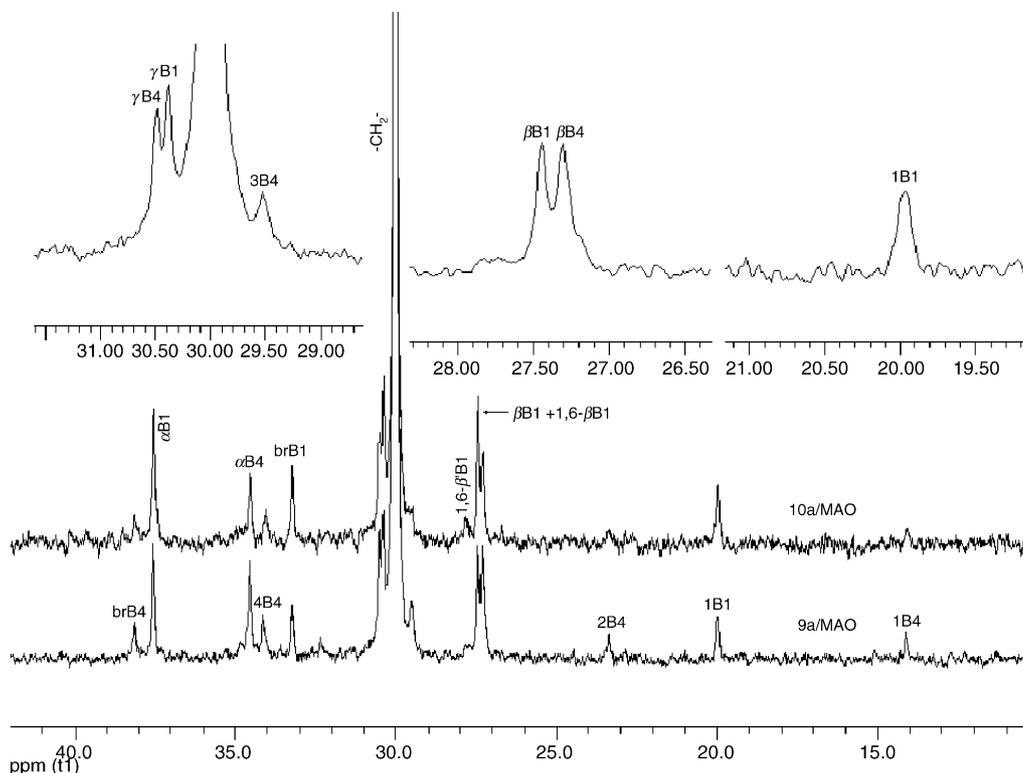


Fig. 7. ^{13}C NMR spectrum of only butyl branched poly(ethylene-co-1-hexene). Cond.: cat., 7×10^{-6} mol; 1-hexene 6 ml, P_E , 150 psig, 35°C , 2 h, in 14 ml toluene.

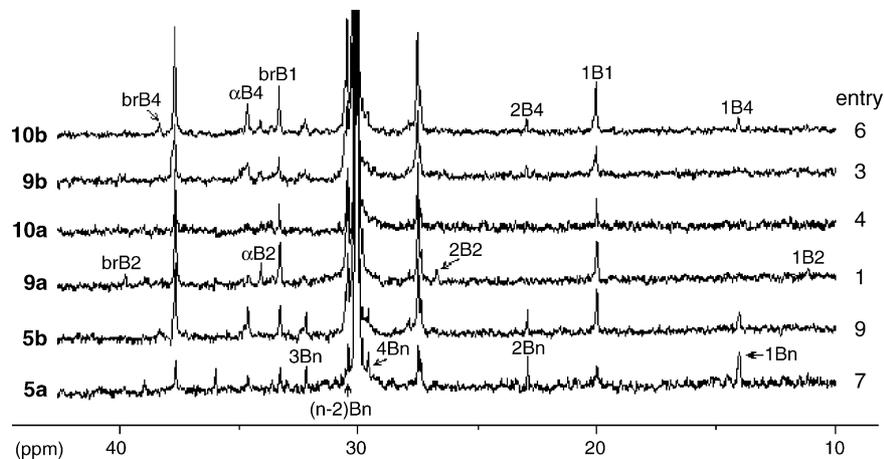
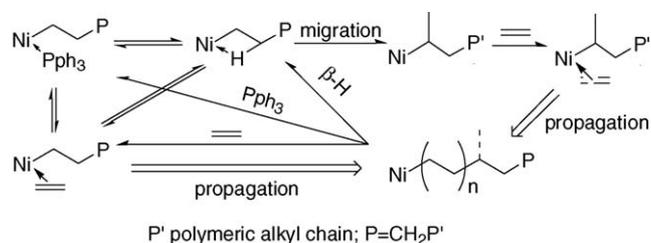


Fig. 8. ^{13}C NMR spectrum of polyethylene obtained with different catalyst precursors.

obtained with **5a**/MAO system obviously bears chain end structure (or longer branches) (1Bn 14.061, 2Bn 22.857, 3Bn 32.165, 4Bn 29.566, $(n-2)\text{Bn}$ 30.384, $(n-1)\text{Bn}$ 27.325). The chain end structure of low molecular weight products should have contribution to the bigger integral intensity of the signal at 14.06 ppm. DSC analysis demonstrates that ethylene polymers obtained with **5**/MAO systems are crystalline (see [supporting information](#)).

The influence of Pph_3 trapping in **10**/MAO system can be traced by detecting the methyl branch numbers of the obtained polymers (Table 4). At same polymerization temperature, the single and 1,6-paired methyl branch signals of the polyethylene obtained with **10a**/MAO are slightly higher than that obtained



Scheme 3. Presumed mechanism of ethylene polymerization by using **10a**/MAO.

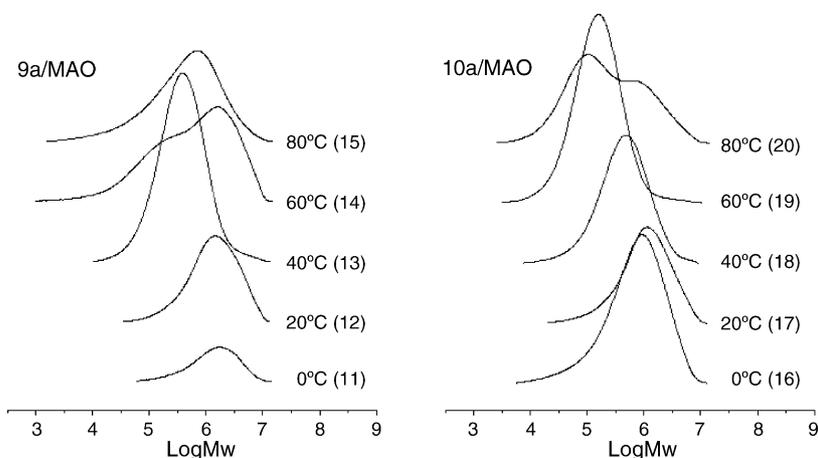


Fig. 9. GPC chromatograms of polyethylene obtained with **9a**/MAO and **10a**/MAO at different temperature (entry).

with **9a**/MAO (Figs. 6–8). This observation suggests that Pph_3 shares the vacant coordination site of Ni(II)-alkyl intermediates with α -olefins and β -H and is not involved in the chain-propagation status (Scheme 3). β -H atom is the inter-molecular part of Pph_3 coordinated intermediates, and this might offer extra opportunity for the formation of methyl branches [16]. This presumed scheme consists well with the coordination competition among 2,4-lutidine, β -H and ethylene as reported by Warren and co-workers [11]. At low temperature (entry 16), Pph_3 trapping results in relatively higher PDI value and lower molecular weight.

Bimodal GPC chromatograms corresponding to the high polymerization temperature in entries 14, 15 and 20 were observed (Fig. 9). This bimodal molecular distribution might be arisen from the possible coupling of the alkyl(polymeric) radicals due to the decomposition of Ni(II)-alkyl species [10a]. The portion of the higher molecular part obtained with **9a**/MAO is bigger than that obtained with **10a**/MAO. Moreover, this bimodal distribution result occurred at higher polymerization temperature in **10a**/MAO system, indicating that the active species might be stabilized in some degree by the introduction of Pph_3 .

3. Conclusion

In the presence of MAO, bulky β -diketiminato Ni(II) complexes and β -diimine Ni(II) complexes were used as catalyst precursors for ethylene polymerization. Ethylene polymerization carried out by using these six-membered chelate ring systems are characterized by simultaneous oligomerization. Due to the wedge-shaped ligand configuration of these catalyst precursors, the obtained ethylene polymers are basically methyl-branded. These small quantities of even number branches, observed in the ethylene homo-polymers, were ascribed to the incorporation of the simultaneously produced short chain α -olefins rather than chain walking process. The fourth ligand Pph_3 can stabilize the active species in some degree and result in ethylene polymers with slightly higher methyl-branch rate.

4. Experimental

4.1. General remarks

All necessary manipulations were performed by standard Schlenk techniques under nitrogen atmosphere or in a M. Braun glovebox. All the containers were thoroughly dried by heating under vacuum. Hexane and toluene were thoroughly dried over phosphorus pentoxide and sodium, respectively. MAO solid was prepared by the controlled hydrolyzation of the trimethylaluminum (TMA) at 0–60 °C by using $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ($\text{H}_2\text{O}/\text{Al}=1.3$) that was dispersed in toluene. 2,6-diisopropylaniline, 2,6-dimethylaniline, *n*-butyllithium were purchased from Aldrich. Other commercially available reagents were purchased and used as received. $(\text{DME})\text{NiBr}_2$ was prepared according to the reported literature [22]. Ligands $\{\text{N}(\text{C}_6\text{H}_3\text{R}_2-2,6)\text{C}(\text{Me})\}_2\text{CH}_2$ $\{\text{R} = \text{iPr}$ (**a**), Me (**b**) $\}$ and complexes **9** ($\text{Ni}\{\text{N}(\text{C}_6\text{H}_3\text{R}_2-2,6)\text{C}(\text{Me})\}_2\text{CH}\}\text{Br}$) were synthesized as the method in our previous report [16]. β -diimine Ni(II)Br₂ complexes **5** were synthesized as the method in literature [13a].

$\text{NiBr}_2(\text{Pph}_3)_2$ was prepared by refluxing NiBr_2 (0.1 mol) and Pph_3 (0.22 mol) in anhydrous ethanol, then the dark green solution was hot filtrated, condensed and cooled to crystallization. The $\text{NiBr}_2(\text{Pph}_3)_2$ was collected by filtration and dried in vacuum, obtained as bright green solid (>90%). Anal. Calcd. for $\text{C}_{32}\text{H}_{30}\text{Br}_2\text{NiP}_2$: C 58.19, H 4.07. Found: C 58.16, H 4.08.

4.2. $\text{Ni}\{\text{N}(\text{C}_6\text{H}_3\text{iPr}_2-2,6)\text{C}(\text{Me})\}_2\text{CH}\}\text{Br}$ (**10a**)

La 1.20 g (0.003 mol) was dissolved in 50 ml toluene and the solution was cooled to -78 °C and stirred. *n*-butyllithium 1.1 ml (hexane solution 2.6 M) was injected and the solution was allowed warm up to room temperature overnight. After that, 2.38 g $\text{NiBr}_2(\text{Pph}_3)_2$ (0.0032 mol) were added, and the slurry were stirred for 12 h at 80 °C. After hot filtration, the filtrate was condensed by vacuum to 10–15 ml, and the complexes were precipitated, washed twice by hexane and dried under vacuum. Green solid were obtained, 1.47 g (62.8%). ^1H NMR

(CD₂Cl₂) (ppm): 56.55 (4H, m-Ar), 36.85 (4H, CH(CH₃)₂), 9.58 (24H, CH(CH₃)₂), -27.08 (2H, p-Ar), -87.87 (6H, CH₃). ³¹P{¹H}NMR(C₆D₆): 136.08 ppm (s).

4.3. Ni{(N(C₆H₃Me₂-2,6)C(Me))₂CH}(PPh₃)Br (**10b**)

The synthesis of complex **10b** was performed as in the case of complex **10a**, by using **Lb** 0.92 g (0.003 mol), *n*-butyllithium 1.1 ml (hexane solution 2.6 M) and 50 ml toluene, NiBr₂(PPh₃)₂ 2.38 g (0.0032 mol) and a stirring time of 12 h at 80 °C. Product was obtained as black green solid, 1.54 g (76.4%). ¹H NMR (CDCl₃) (ppm): 42.58 (6H, CH₃-Ar), 40.68 (6H, CH₃-Ar), 39.41 (2H, m-Ar), 33.85 (2H, m-Ar), -33.34 (2H, p-Ar), -66.31 (6H, CH₃), -177.60 (1H, H-backbone). ³¹P{¹H}NMR(C₆D₆): 135.39 ppm (s).

4.4. Ethylene polymerization

A mechanically stirred 100 ml Parr reactor under an ethylene atmosphere was charged with MAO toluene solution 13 ml (MAO 275 mg). The system temperature was allowed to equilibrate at reaction temperature under a positive ethylene pressure (~200 mmHg). Catalyst precursor (7×10^{-6} mol) in 7 ml toluene was transferred into the reactor via cannula, and then the autoclave was immediately pressurized to desired pressure with ethylene and the polymerization begun. Usually, exothermic phenomena were observed at start. The system temperature might rush 5–10 °C higher than the desired polymerization temperature, and then was taken back by an inner cooler within 20 min. After 1.5 h polymerization, the autoclave was sat into a cooling bath and carefully vented at -10 °C (to reduce oligomer loss). Then the polymerization solution (~5 ml) was quickly collected and mixed with 15 ml cool ethanol in a 50 ml glass tube at -20 °C. Additional water was added into the tube to separate toluene phase from ethanol–water phase. The tube was sealed after the CH₄ bubble over and stored at -20 °C in refrigerator. The upper colorless toluene solution was used for GC or GC–MS analysis. The swelled polymer was excavated out and refluxed with HCl acidified ethanol in a flask for 8 h. The polymer was isolated by removal of the solvents, washed with ethanol and dried overnight in the vacuum oven.

4.5. Polymer characterization

¹³C NMR (100 MHz) of polymers were carried out in C₆D₄Cl₂ containing 0.05 M Cr(acac)₃ at 120 °C (393 K) following method in literature for better integration [23]. High-temperature gel permeation chromatography (GPC) was performed in 1,2,4-trichlorobenzene at 135 °C using Waters HPLC 150C equipped with Shodex columns. DCS traces of the polymers were obtained by heating polymer samples from 20 to 165 °C at 10 °C/min and holding for 3 min. The samples were cooled to -20 °C at 10 °C/min and held for 5 min. The temperature was then raised to 165 °C at 10 °C/min to obtain the reported data. *T_m* curves of these polymers are usually broad and the polymer *T_m* values are reported as the endothermic peak value.

4.6. Measurement

¹H NMR spectra were recorded on a Varian INOVA 500NB NMR spectrometer. Elemental analysis were determined with a Vario EL Series Elemental Analyzer from Elementar. The GC–MS data were recorded with a Finnigan Voyager GC-8000 Top Series GC–MS System with DB-5MS GC column. The GC spectrums were recorded with Varian CP3800 Series GC System with a HP-5MS GC column.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2005.12.027.

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