Synthesis of Branched Polyethylene by Ethylene Homopolymerization with a Novel (α-Diimine)nickel Complex in the Presence of Methylaluminoxane

FANGMING ZHU, WEI XU, XINXING LIU, SHANGAN LIN

Institute of Polymer Science, Zhongshan University, Guangzhou 510275, China

ABSTRACT: Branched polyethylene (PE) was prepared with a novel (α-diimine)nickel(II) complex of 2,3-bis(2,6-dimethylphenyl)-butanediimine nickel dichloride {[2,6-$(CH_3)_2C_6H_3$—N=$C(CH_3)C(CH_3)$=N—2,6-$(CH_3)_2C_6H_3$]NiCl$_2$} activated by methylaluminoxane in the presence of a single ethylene monomer. The influences of various polymerization conditions, including the temperature, Al/Ni molar ratio, Ni catalyst concentration, and time, on the catalytic activity, molecular weight, degree of branching, and branch length of PE were investigated. According to gel permeation chromatography, the weight-average molecular weights of the polymers obtained ranged from 1.7×10^5 to 6.0×10^5, with narrow molecular weight distributions of 2.0–3.5. The degree of branching in the polymers rapidly increased with the polymerization temperature increasing; this led to highly crystalline to totally amorphous polymers, but it was independent of the Al/Ni molar ratio and catalyst concentration. At polymerization temperatures greater than 20°C, the resultant PE was confirmed by ^{13}C-NMR to contain significant amounts of not only methyl but also ethyl, propyl, butyl, amyl, and long branches (longer than six carbons). The formation of the branches could be illustrated by the chain walking mechanism, which controlled their specific spacing and conformational arrangements with one another. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1123–1132, 2002; DOI 10.1002/app.10398

Key words: late transition-metal catalysts; (α-diimine)nickel(II) complex; methylaluminoxane; polyethylene (PE); branched polyethylene; ethylene polymerization; branching

INTRODUCTION

Metallocene and late-transition-metal catalysts for ethylene polymerization have attracted considerable attention in academia and industry.[1–9] Usually, the polyethylene (PE) produced by these single active species catalysts has a narrower molecular weight distribution and displays excellent properties, but this can make such a polymer difficult to process.[10,11] Chain branching is one of the preferred methods for providing PE with good processability.[12–14] The copolymerization of ethylene with α-olefin has commonly been used to prepare branched PE.[15–19]

Recently, the synthesis of branched PE by ethylene homopolymerization with certain structure metallocene or later transition-metal catalysts has attracted much attention because of the resultant properties and applications.[20–29] Never-

theless, different structure catalysts lead to different specificities of the branching mechanism and ultimately control the polymer structures, including the molecular weight, molecular weight distribution, degree of branching, branch length, and branch distribution. Constrained-geometry catalysts[21–23] and monotitanocene catalysts[30] offer the possibility of yielding long-chain-branched PE from only ethylene polymerization. The results have been discussed in terms of a mechanism in which ethylene is copolymerized with macromonomers of α-olefin, which can be obtained via β-hydride elimination or chain transfer to ethylene monomers.[21,30] Although there is only a very low degree of long-chain branching, the rheology and processability of PE are essentially improved. Pellecchia et al.[31] found that the Cp*TiMe₃/B(C₆F₅)₃ catalytic system polymerized ethylene at high Ti concentrations to afford branched PE without any added comonomers. Products containing significant amounts of butyl branches were achieved by the copolymerization of ethylene and hexene-1 produced by a cationic Ti(II) species through a mechanism involving metallocycloheptane of Ti(II) intermediates. We examined ethylene polymerization with a monotitanocene/methylaluminoxane (MAO) catalyst in heptane used as a polymerization medium, from which the polymers obtained contained isolated ethyl and/or butyl branches.[32] Brookhart and coworkers[33,34] reported on a novel class of catalysts based on Ni(II) and Pd(II) diimine complexes for the production of PE containing mainly short-chain branches, particularly methyl branches. With variations in the catalyst structures and polymerization conditions, the resultant PE microstructures could be changed from being low branched to highly branched, giving rise to highly crystalline to totally amorphous polymers. These branches were suggested to be formed via a chain walking mechanism[25,33] rather than via ethylene copolymerization with oligomers produced *in situ*.

With MAO as a cocatalyst, the reported Ni(II)-based catalysts for ethylene polymerization were almost all (α-diimine)nickel dibromide complexes. In this study, a novel nickel(II) catalyst, 2,3-bis(2,6-dimethylphenyl)-butanediimine nickel dichloride {[2,6-(CH₃)₂C₆H₃—N=C(CH₃)C(CH₃)=N—2,6-(CH₃)₂C₆H₃]NiCl₂; **1**} was synthesized and activated by MAO for ethylene polymerization. The effects of the polymerization conditions on the catalytic activity and PE molecular structure, that is, the molecular weight, degree of branching, and branch type, were investigated.

EXPERIMENTAL

All operations were performed with Schlenk techniques under a dry nitrogen atmosphere. Polymerization-grade ethylene and extra-pure-grade nitrogen were further purified before being fed into the reactor by passage through a DC-IB gas purification instrument. Toluene was refluxed over metallic sodium for 24 h and distilled under a nitrogen atmosphere before use.

The catalyst complex **1** was synthesized according to the literature.[25,35] Solid MAO was prepared first by the controlled reaction of trimethylaluminum (TMA) with H_2O from $Al_2(SO_4)_3 \cdot 18H_2O$ dispersed in toluene for several hours, then by filtration, and finally by evaporation *in vacuo*. The TMA content retained in MAO was about 26.8 mol % as determined by ^1H-NMR.[36]

The polymerization runs were carried out under a purified ethylene atmosphere in 150-mL glass flasks equipped with magnetic stirrers. The solid MAO and toluene were introduced into the reactor at the desired temperature from −20 to 60°C (regulated by a water bath). After the solution was saturated with the ethylene monomer, the (α-diimine)nickel(II) complex **1**, dissolved and suspended in toluene, was rapidly injected into the reaction mixture, and the pressure was maintained at 0.13 MPa during full runs for 1 h. The polymerizations were terminated by the addition of 5 wt % HCl in ethanol. The polymers were washed with ethanol and dried *in vacuo* at 60°C to a constant weight.

The viscosity-average molecular weights of the polymers were calculated by $[\eta] = 6.67 \times 10^{-4} M_w^{0.67}$ (where M_w is the weight-average molecular weight), with $[\eta]$ measured in decahydronaphthalene at 135°C.[15] Gel permeation chromatography (GPC) analysis of the obtained polymers was performed on a Water 150C at 100°C with standard polystyrene as a reference and *o*-dichlorobenzene as a solvent. ^{13}C-NMR spectra of PE were recorded at 100°C in *o*-dichlorobenzene with an Inova 500-MHz spectrometer and were referenced against TMS with the resonance of the carbons of the PE sequences ($\delta = 30.00$ ppm) as a secondary standard. The PE samples were dissolved in *o*-dichlorbenzene/benzene-d_6 to form a 15 wt % solution. Differential scanning calorimetry (DSC) was conducted with a PerkinElmer DCS-7 system at 10°C/min.

Table I   Influences of T_p on Preparation of Branched PE with 1/MAO Catalyst

Run	T_p (°C)	Activity $\times 10^{-5}$ (g of PE/mol of Ni h)	$M_w{}^a \times 10^{-5}$	$M_w/M_n{}^a$	Degree of Branching[b]	$T_m{}^c$ (°C)
1	−20	Trace	—	—	—	—
2[d]	−20	1.5	6.0	2.1	—	138.3
3	−10	2.8	5.6	2.0	Trace	135.2
4	0	7.3	4.8	2.3	12.6	125.8
5	10	7.0	4.3	2.7	21.2	118.5
6	20	6.1	4.0	2.6	39.1	66.5, 95.8
7	40	3.2	2.9	3.5	69.5	No
8	60	3.1	1.7	3.2	92.1	No

Polymerization conditions: [Ni] = 1.3×10^{-4} mol/L, Al/Ni = 600 mol/mol, $P(C_2H_4)$ = 0.13 MPa, t_p = 1 h.
[a]Determined by GPC.
[b]Number of branches per 1000 carbon atoms in PE main chain determined by ^{13}C-NMR.
[c]Determined by DSC.
[d]Complex **1** reacted with MAO for 10 min at 30°C.

RESULTS AND DISCUSSION

As shown in Table I, the combination of the (α-diimine)nickel(II) complex of **1** with MAO, with respect to the ethylene homopolymerization, catalytic activity, and polymer microstructure, was extremely sensitive to the polymerization temperature (T_p). Except for run 2, in which active species were generated *in situ* by the MAO activation of **1** in the presence of ethylene, runs were performed according to the description in the Experimental section. Under low temperatures, such as −20°C, the catalyst exhibited hardly any activity for ethylene polymerization. The maximum catalytic activity of 7.3×10^{-5} g of PE/mol of Ni · h appeared at 0°C. Increasing T_p further led to the catalytic activity decreasing as a result of an enhancement in the acceleration of chain-transfer reaction at the same time that the solubility of ethylene decreased with increasing temperature. In addition, the **1**/MAO catalyst produced PE at −20°C (run 2) with an activity of 1.5×10^{-5} g of PE/mol of Ni · h after the complex **1** was reacted with MAO for 10 min at 30°C and ethylene was introduced. This suggests that the active cationic species could not be formed from the **1**/MAO system at too low a reaction temperature. The molecular weight of the obtained PE was observed to drop from $M_w = 6.0 \times 10^{-5}$ to $M_w = 1.7 \times 10^{-5}$ as T_p increased from −20 to 60°C. The result implied that, at a higher temperature, the rate of chain transfer was likely to increase. The degree of branching increased sharply with increasing T_p, which caused a corresponding decrease in the melting temperature (T_m) and broadened the

melting transition. No branches were detected in the PE produced at −10°C by ^{13}C-NMR, and it had a higher T_m value at 135.2°C. Completely amorphous ethylene homopolymer was produced at 40 or 60°C.

Data for ethylene polymerization with the **1**/MAO catalyst at various Al/Ni molar ratios are presented in Table II. The catalytic activity increased with the increasing Al/Ni molar ratio, but the highest activity was observed around 600. According to previous work, with MAO as a cocatalyst and (α-diimine)nickel(II) dibromide catalysts, the best Al/Ni molar ratio for higher catalytic activity is greater than 1000.[25] This can be explained by the fact that it is easier for MAO to activate catalyst **1** than the (α-diimine)nickel(II) dibromide complex. At lower Al/Ni ratios, a sharp drop in activity was noticed, and a minimum value of Al/Ni (ca. 200 mol/mol) was required with MAO used as a cocatalyst, the activation of **1** involved successive alkyation and cationation. In contrast, some of the Ni(II) active species would be deactivated at excessively high Al/Ni molar ratios; this would result in a relevant decrease in the polymerization activity. It is much more likely that, because MAO is a chain-transfer agent, a decrease in the molecular weight of PE would be found with increasing Al/Ni molar ratios and with a corresponding decrease in the catalytic activity. In addition, Al/Ni molar ratio charges do not distinctly affect the microstructure of branched PE.

The change in the polymerization rate (R_p) with the polymerization time (t_p) for the **1**/MAO catalyst is illustrated in Figure 1. R_p was calculated from the rate of ethylene addition to the

Table II   Influences of the Al/Ni Molar Ratio on Ethylene Polymerization with 1/MAO Catalyst

Run	Al/Ni (mol/mol)	Activity $\times 10^{-5}$ (g of PE/mol of Ni h)	$M_w{}^a \times 10^{-5}$	Degree of Branching[b]	$T_m{}^c$ (°C)
13	200	2.3	5.9	—	126.0
14	400	4.4	5.8	20.6	122.2
5	600	7.0	4.9	21.2	118.5
15	800	3.2	3.9	22.9	116.4

Polymerization conditions: [Ni] = 1.3×10^{-4} mol/L, P(C$_2$H$_4$) = 0.13 MPa, T_p = 10°C, t_p = 1 h, toluene used as polymerization medium.

[a]Determined with a viscometer.

[b]Number of branches per 1000 carbon atoms in PE main chain determined by ^{13}C-NMR.

[c]Determined by DSC.

polymerization reactor. For a lower T_p, R_p reached a maximum value within a short t_p, and then R_p decreased steeply. At a higher T_p, R_p decreased less after the maximum value. The dependence of the catalytic activity on the molar Ni catalyst concentration was investigated, and the results are shown in Table III. When ethylene was polymerized, with Ni concentrations of 1.0 $\times 10^{-4}$ to 2.0×10^{-4} mol/L and a constant Al/Ni molar ratio of 600, the catalytic activity almost

remained constant. This suggested that R_p was first-order in the Ni concentration. Too low a concentration would make catalyst poisoning by impurities from the toluene and monomer significant. Beyond 2.0×10^{-4} mol/L, R_p was so fast that the polymer became rapidly viscous. The degree of branching of PE slightly increased with the increase in the Ni concentration.

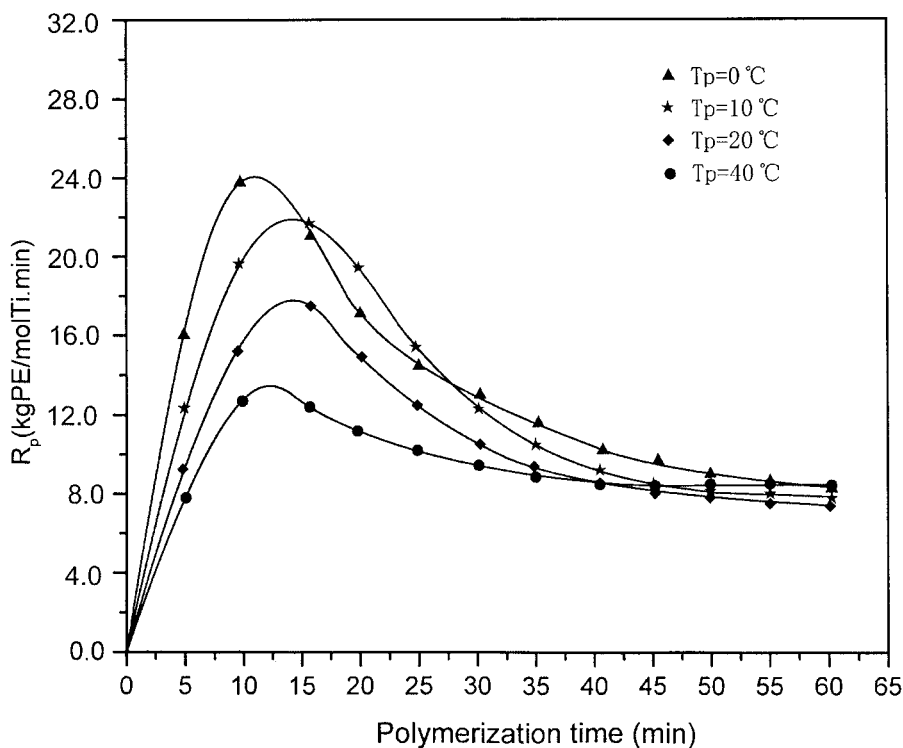A representative ^{13}C-NMR spectrum of PE, prepared with the **1**/MAO catalyst at 40°C, is

Figure 1   Variations in the R_p value of ethylene versus the polymerization time with the **1**/MAO catalyst. [Ni] = 1.3×10^{-4} mol/L; Al/Ni = 600 mol/mol; P(C$_2$H$_4$) = 0.13 MPa.

Table III   Influences of Catalyst Concentration on Ethylene Polymerization with 1/MAO Catalyst

Run	$[Ni] \times 10^4$ mol/L	Activity $\times 10^{-5}$ (g of PE/mol of Ni h)	$M_w{}^a \times 10^{-5}$	Degree of Branching^b	$T_m{}^c$ (°C)
9	0.75	4.9	5.0	20.0	120.1
10	1.00	6.8	5.1	—	119.4
5	1.30	7.0	4.9	21.2	118.5
11	2.00	6.6	4.6	—	118.8
12	2.70	4.2	4.7	25.6	115.9

Polymerization conditions: Al/Ni = 600 mol/mol, $P(C_2H_4)$ = 0.13 MPa, T_p = 10°C, t_p = 1 h, toluene used as polymerization medium.

^{a}Determined with a viscometer.

^{b}Number of branches per 1000 carbon atoms in PE main chain determined by ^{13}C-NMR.

^{c}Melting temperature Determined by DSC.

shown in Figure 2. According to the assignments of each resonance peak, based on chemical shift calculations performed with the method of Linderman and Adams,[37] the PE contained primarily not only methyl branches but also ethyl, propyl, butyl, amyl, and long branches (longer than six carbons), as listed in Table IV. The nomenclature used to designate the different carbon types is that of Usami and Takayama.[38] The carbon in branches is denoted xB_n, where n is the length of the branch and x is the carbon number starting with the methyl group as 1. xB_n is also used to mark the carbon of the methylene or branch point in the main chain, whereas x is replaced by Greek letters or br, respectively. For paired-branch prefixes, 1 and m are used, where m is the number of
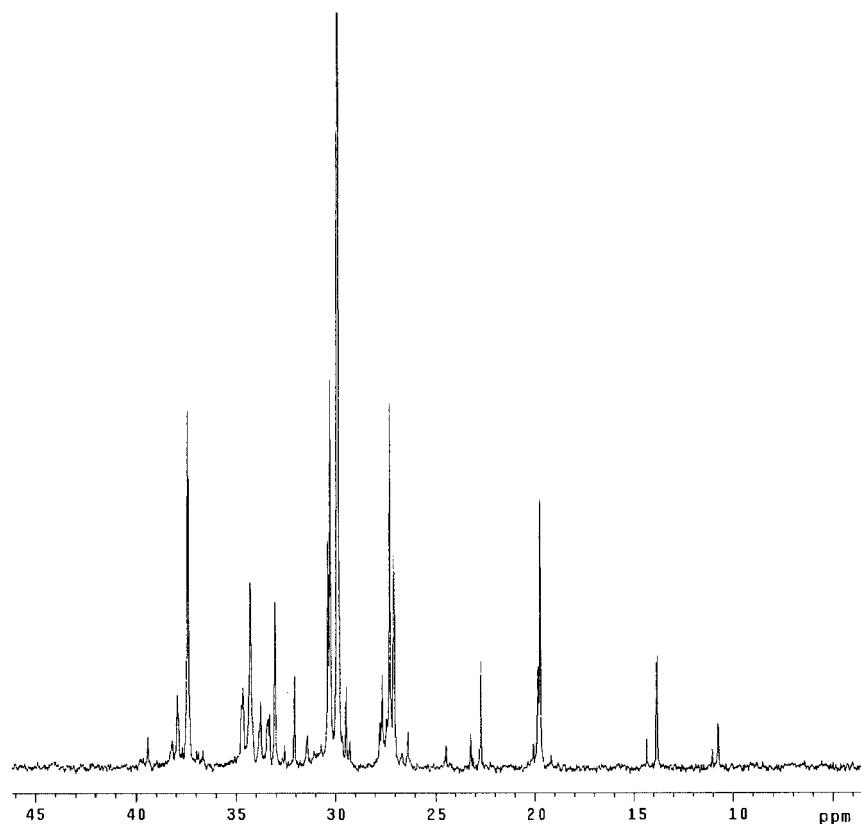

**Figure 2** ^{13}C-NMR spectrum of branched PE obtained from run 7 with the **1**/MAO catalyst at 40°C.

Table IV ^{13}C-NMR Chemical Shift Calculated and Observed and Their Assignments

Chemical Shift (ppm) Observed in				Chemical Shift (ppm) Calculated	Assignments
Figure 3(a)	Figure 3(b)	Figure 3(c)	Figure 2		
		11.13	11.13	11.16	1B$_2$
	14.14	14.14	14.14	13.98	1B$_{n \geq 4}$
			14.65	14.55	IB$_3$
19.90	19.92	19.92	19.91	19.93	1B$_1$, 1,5(6)-1B$_1$
	20.02	20.02	20.02	20.11	1,4-1B$_1$
			20.24	20.30	2B$_3$
	22.88	22.88	22.88	22.76	2B$_{n \geq 5}$
		23.36	23.38	23.32	2B$_4$
			24.61	24.58	1,5-β'B$_1$
		26.52	26.50	26.56	2B$_2$
	27.21	27.21	27.21	27.30	β'B$_{n \geq 2}$, $(n-1)$ B$_n$
27.41	27.42	27.42	27.42	27.37	βB$_1$, 1,4(4, 5, 6)-βB$_1$
	27.79	27.79	27.79	27.72	1,6-β'B$_1$
			29.40	29.45	3B$_4$
	29.58	29.58	29.58	29.61	4B$_{n \geq 6}$
30.00	30.00	30.00	30.00	29.96	δB$_{1 \sim n}$
30.35	30.37	30.37	30.37	30.31	γB$_1$
	30.49	30.49	30.48	30.48	γB$_{n \geq 2}$
			31.53	31.62	1,4-α'B$_{n \geq 2}$
	32.16	32.16	32.16	32.23	3B$_{n \geq 6}$
			32.65	32.65	3B$_5$
33.10	33.14	33.14	33.14	33.28	brB$_1$
	33.41	33.41	33.41	33.41	1,4-brB$_1$
	33.86	33.86	33.86	33.83	αB$_2$, 4B$_4$
	34.35	34.35	34.37	34.39	αB$_{n \geq 3}$
	34.78	34.78	34.73	34.72	1,4-α'B$_1$
			36.74	36.81	3B$_3$
37.43	37.47	37.47	37.42	37.35	αB$_1$, 1,4(5,6)-αB$_1$
			37.75	37.80	brB$_3$
	38.00	38.00	38.00	37.99	brB$_{n \geq 4}$
			38.25	38.24	1,4-brB$_n$
		39.46	39.46	39.44	brB$_2$

carbons between two tertiary carbons, 1 being the first tertiary carbon and m the next. The backbone carbons between branches are designated by Greek letters with primes. The presence of the δB$_{1 \sim n}$ resonance of EEEE sequences at 30.00 ppm suggests that branches with spacings longer than seven carbons appear as isolated branches. Resonances at 20.24, 24.61, and 27.90 ppm are assigned to 1,4-1B$_1$, 1,5-β'B$_1$, and 1,6-β'B$_1$ carbons, corresponding to the presence of 1,4-, 1,5, and 1,6-paired methyl branches. Scheme 1 is the proposed walking mechanism for ethylene chain propagation and branch formation.[34] In view of this mechanism, it seems significant that 1,2- and 1,3-paired methyl branches were not found in PE. Additionally, it is generally accepted that two odd or even carbon branches should be separated by an even number of methylene spacers; likewise, one odd carbon branch and one even carbon branch should be separated by an odd number of methylene spacers. However, it is difficult for the walking mechanism to explain the formation of two methyl branches separated by three methylene spacers such as 1,5-paired methyl branches. Two interesting resonances appeared at 31.53 and 38.25 ppm that were attributed to 1,4-α'B$_{n \geq 2}$ and 1,4-brB$_{n \geq 2}$ carbons.

The resultant polymers, prepared at various temperatures, produced different ^{13}C-NMR spectra, as shown in Figures 2 and 3(a–c). On the one hand, the degree of branching of PE increased with the elevation of T_p (Table I). These results strongly suggest the possibility of chain walking increasing with increasing temperature. The rea-
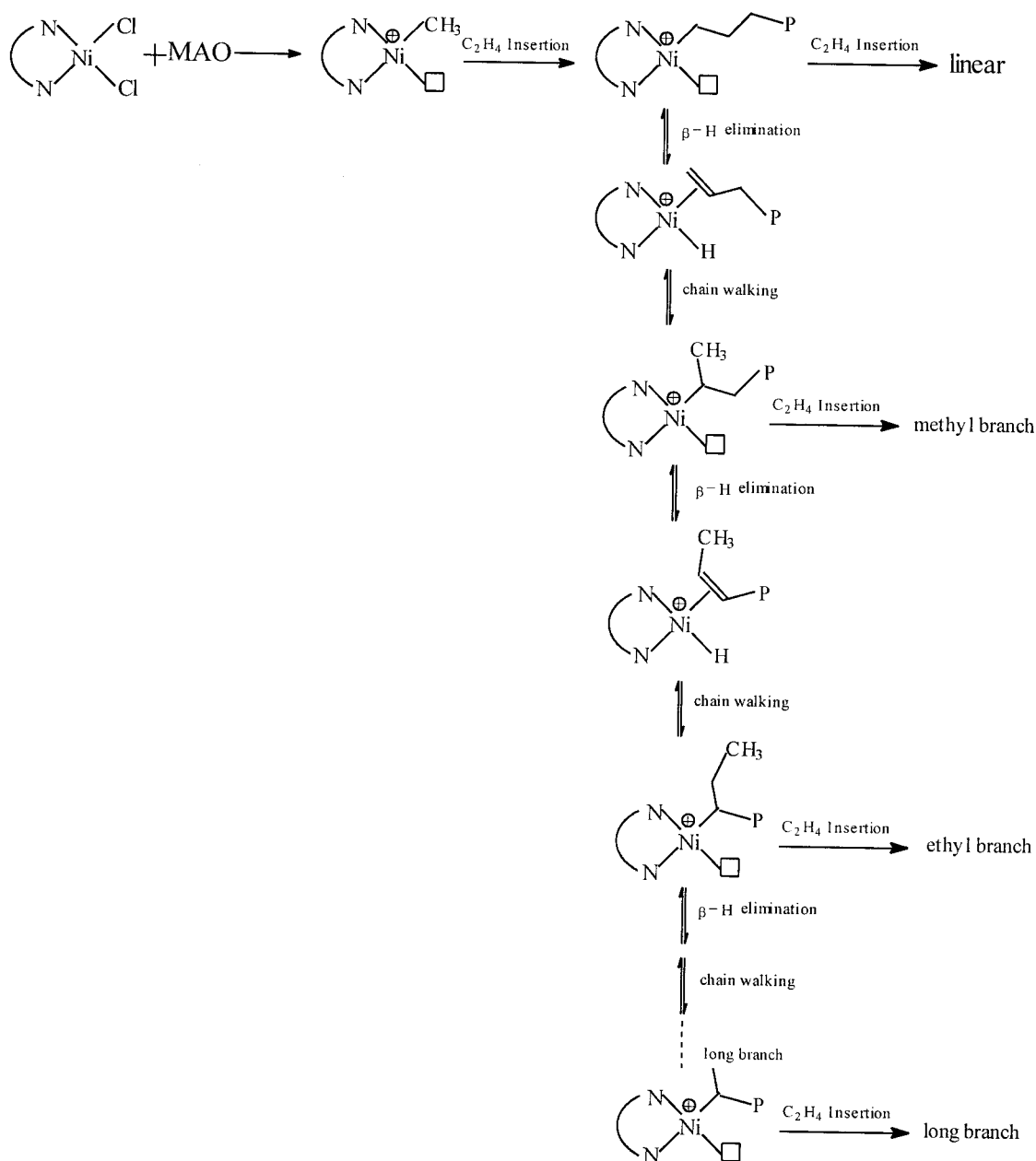
Scheme 1   Mechanism for the preparation of branched PE with the **1**/MAO catalyst.

son for this behavior appears to be that chain walking requires a higher energy of activation than ethylene insertion. On the other hand, the content of short branches, including ethyl, propyl, butyl, and amyl branches, increased with increasing T_p. The sample from run 3 prepared at $-10°C$ was a linear PE for which no branch signal was detected in its ^{13}C-NMR spectrum The polymer made at $0°C$ revealed only signals of methyl branches [Fig. 2(a)]. It is very surprising that long branches (longer than six carbons) were con-

firmed by the presence of the $3B_{n \geq 6}$ and $4B_{n \geq 6}$ carbon resonances at 32.16 and 29.58 ppm in Figure 3(b) of run 5 for the polymer produced at $10°C$, whereas short branches were not found. Some small resonances attributable to ethyl and butyl branches can be observed in Figure 3(c) for branched PE obtained at $20°C$.

The molecular weights and molecular weight distributions of all obtained PEs were determined by GPC. As shown in Table I, the polymers with higher molecular weights and rather narrow mo-
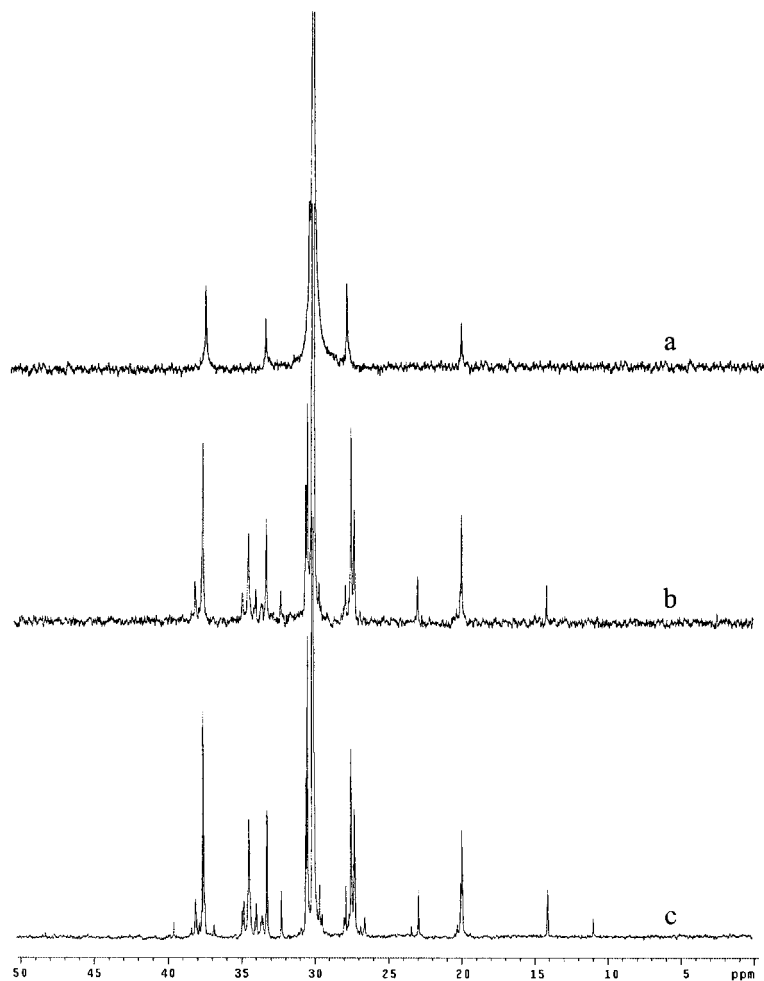
Figure 3   ^{13}C-NMR spectra of branched PE obtained from (a) run 4 at 0°C, (b) run 5 at 10°C, and (c) run 6 at 20°C.

lecular weight distributions of 2.0–3.5 showed characteristics of ethylene polymerization catalyzed by a single active species.

The DSC curves of PEs with different degrees of branching prepared with **1**/MAO at various values of T_p are exhibited in Figure 4. T_m decreased with an increased degree of branching of PE and gave rise to highly crystalline to totally amorphous polymers. The real linear PE produced at −10°C had a high T_m value of 138.3°C [Fig. 4(a)], whereas the highly branched PEs prepared at 40 and 60°C showed no melting peak [Fig. 4(e,f)]. The DSC curves become broader as the degree of branching increases, as shown in Figure 4(b,c). The DSC curve of branched PE produced at 20°C shows a much broader bimodal melting peak. The broadening of the DSC curve, and the appearance of the bimodal melting peak found at high branching numbers in the poly-

mers, could be due to factors such as the different sizes of crystals and imperfections in the crystalline lattice.

CONCLUSIONS

Ethylene homopolymerization catalyzed with a novel (α-diimine)nickel(II) complex of **1** in the presence of MAO produced branched PE. The catalytic activity and molecular weight of the obtained polymers depended on the Al/Ni molar ratio, Ni catalyst concentration, and T_p. The degree of branching and branch length of PE were mainly controlled by T_p. Increases in T_p resulted in increased branching and decreased molecular weights. According to ^{13}C-NMR characterization, the branches were primarily formed by isolated
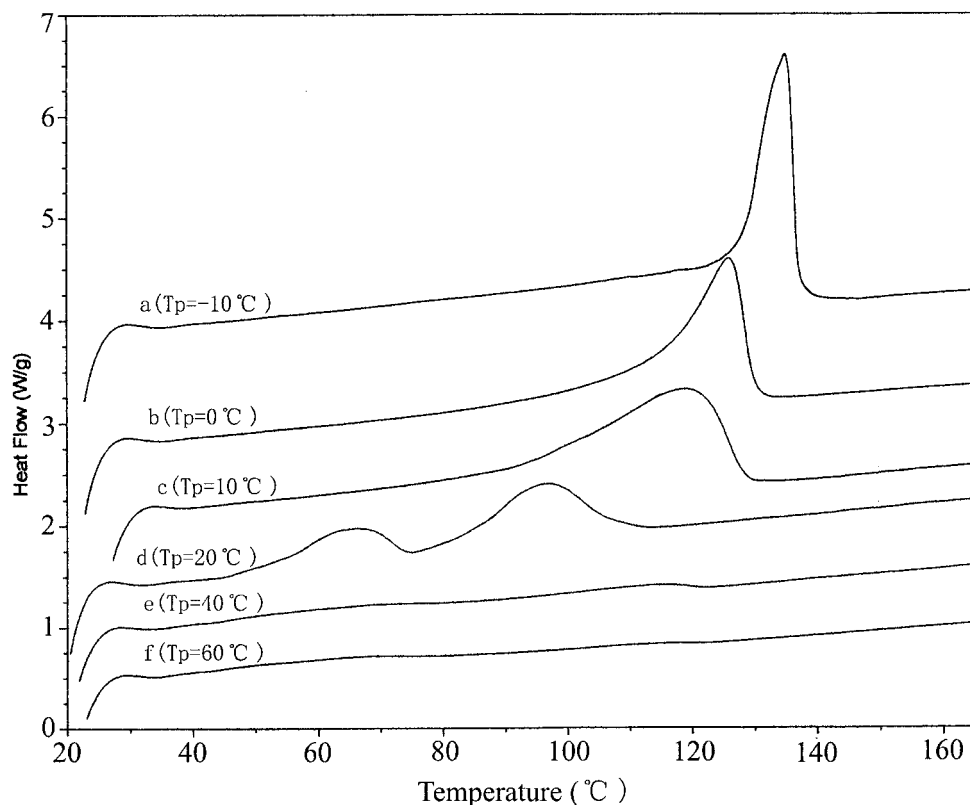
Figure 4   DSC curves of branched PE obtained from (a) run 3 at −10°C, (b) run 4 at 0°C (c) run 5 at 10°C, (d) run 6 at 20°C, (e) run 7 at 40°C, and (f) run 8 at 40°C.

methyl groups, but when the degree of branching was high, 1,4-, 1,5-, and 1,6- paired methyl branches could be found. With increasing T_p, the different branch types became evident in the following order: methyl, long branch (longer than six carbons), butyl, ethyl, propyl, and amyl. There were only methyl and long branches in the PE produced at 10°C. At T_p's above 20°C, the resultant PE contained not only significant amounts of methyl and long branches but also short branches (ethyl, propyl, butyl, and amyl). The chain-branching mechanism of the **1**/MAO catalysts was proposed to be a chain walking mechanism consisting of ethylene insertion and chain walking. Most of the catalyst system's behavior for ethylene polymerization could be interpreted with this mechanism; however, it was difficult to explain with this mechanism the presence of 1,5-paired methyl branches and long branches before other short branches.

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