Polymerization of propylene catalyzed by α-diimine nickel complexes/methylaluminoxane: catalytic behavior and polymer properties

Hamid Pourtaghi-Zahed & Gholam Hossein Zohuri

ORIGINAL PAPER

Polymerization of propylene catalyzed by α-diimine nickel complexes/methylaluminoxane: catalytic behavior and polymer properties
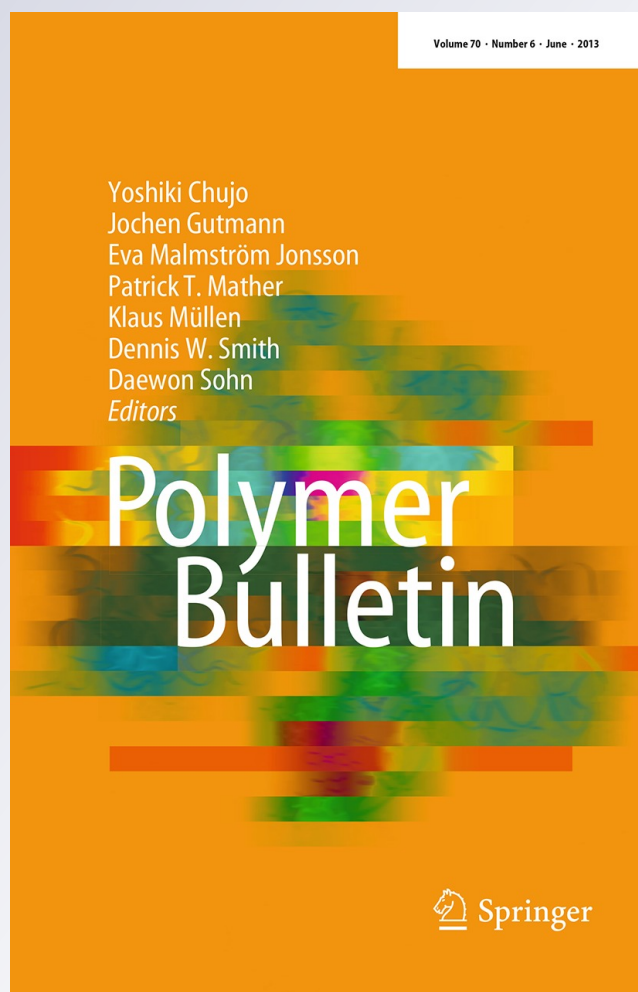
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Abstract   α-Diimine nickel dibromide complexes of dibromo[*N,N'*-bis(2,6-diiso-propylphenyl)-2,3-butanediimine]nickel(II) (**A**) and dibromo[*N,N'*-(phenanthrene-9,10-diylidene)bis(2,6-diisopropylaniline)]nickel(II) (**B**) were synthesized under controlled conditions. The catalysts **A**, **B** and mixed of 1:1 weight ratio of them (**C**) were activated by methylaluminoxane and were used for propylene polymerization in a semi-batch reactor. In study of the catalytic systems behavior, activities, glass transition temperature (T_g) and viscosity average molecular weight (M_v) values related to the catalyst **C** were between those related to the catalysts **A** and **B** under same conditions. The highest and the lowest molecular weights of the obtained polymers were produced by the catalysts **B** and **A** which were about 80,000 and 70,000 (g/mol) under same conditions, respectively. The T_g of polypropylenes produced by the catalysts was about −34 °C. The resulting polymers had similar behavior with ethylene-propylene copolymer which it could be due to formation of ethylene-type units in the polymer chain.

Keywords   Nickel-based catalyst · Late transition metal · Polymerization · Polypropylene · Chain-walking

Introduction

In 1995, Brookhart and coworkers synthesized a new class of Ni(II) and Pd(II) polymerization catalysts stabilized by bulky α-diimine ligands. The α-diimine complexes based on nickel(II) activated by MAO are able to polymerize α-olefins to form high molecular weight polymers [1–6]. Compared to the early Ziegler–Natta

H. Pourtaghi-Zahed · G. H. Zohuri (✉)
Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad,
PO Box 1436, Mashhad, Iran
e-mail: zohuri@um.ac.ir

and metallocene catalysts, the late transition metal complexes show better tolerance to the functional groups, which make them have an ability to form copolymers with a variety of polar-functionalized comonomers [1, 7, 8].

Marked chain isomerization mechanism (chain-walking) of nickel and palladium complexes allows them to produce polymers with a broad spectrum of branching topologies, ranging from relatively linear to hyperbranched or dendritic. Recently, a new family of polypropylenes (PPs) has been synthesized by bulky α-diimine/nickel catalysts, which those differ from PP produced by the early transition metal catalysts due to chain-walking events that often result in unique microstructures with ethylene-type runs (sequences of CH_2) in the PP chain [3, 9–12]. The nickel α-diimine catalysts produce moderately syndiotactic PPs with an array generated by inversions and 3,1-enchainments as well as different types of short- and long-chain branches [9, 12, 13].

In this study, the catalysts **A** and **B** were synthesized as late transition metal α-diimine nickel complexes. The catalysts were bearing bulky substituent (isopropyl) in the *ortho*-position of the aryl group. Propylene polymerization was carried out using the catalysts **A**, **B** and mixed of 1:1 w/w of them (**C**) in the presence of MAO. The catalytic performance in propylene polymerization is influenced by factors such as reaction temperature, monomer pressure, and cocatalyst/catalyst molar ratio. Therefore, for all the catalysts the effect of mentioned factors on catalyst activity, M_v and the apparent property and behavior of produced polymers were studied.

Experimental

Materials and propylene polymerization

Methanol and dichloromethane were supplied by Merck Chemical Co. (Darmstadt, Germany) and were used without any purification. Toluene was obtained from Arak Petrochemical Co. (Arak, Iran), it was dried by refluxing over sodium wire/benzophenone and then distilled under dry N_2 and stored over activated 4 Å/13× type molecular sieves. Toluene was used as solvent of the catalyst slurry and polymerization medium. 4-Toluenesulfonic acid, diacetyl(2,3-butanedione), 9,10-phenanthrenequinone and aniline compounds were supplied by Merck Chemical Co. (Darmstadt, Germany) and were used in ligands synthesis. Methylaluminoxane (MAO) was purchased from Sigma Aldrich Chemicals (Steinheim, Germany) as 10 wt% (1.5 M) solution in toluene. 1,2-Dimethoxyethane nickel(II) bromide [(DME)NiBr$_2$] were supplied by Sigma Aldrich Chemicals (Steinheim, Germany) with purity 97 % and was applied in the synthesis of the catalysts. Polymer-grade propylene was obtained from Arak Petrochemical Co. (Arak, Iran) and it was used after passing through a column of activated 4 Å/13× type molecular sieves. Nitrogen was obtained from Roham Gas (Tehran, Iran) dried by passage through KOH, activated silica gel and 4 Å/13× type molecular sieve columns. All manipulations were carried out under an atmosphere of dried and purified nitrogen using Schlenk or dry box techniques.

Polymerization runs were carried out in a stainless steel Buchi AG reactor (CH-8610) using the catalysts **A**, **B** and mixed of 1:1 w/w of them (**C**). The reactor temperature was adjusted by a thermostatic bath. The dried toluene (100 ml) was used as solvent. MAO solution (10 wt% in toluene) was used as a cocatalyst. Monomer injection system was equipped with mass flow controller (MFC) that loading of reactor was accomplished with the flow control of propylene gas. Toluene was saturated with the monomer gas prior to the polymerization. The catalysts **A** (3.0×10^{-3} mmol), **B** (3.0×10^{-3} mmol) and mixed of 1:1 w/w of them (3.0×10^{-3} mmol) were suspended in toluene and was transferred into the reactor under flow of nitrogen. After the desired reaction time, polymerization ended with transfer of reaction mixture into methanol containing HCl (5 %). Reaction mixture was filtered and the polymer was washed with methanol and water several times and was dried for 12 h at 40 °C.

PP and complex characterization

Direct application of Mark–Houwink equation of the form $[\eta] = 1.58 \times 10^{-4}$ $M_v^{0.77}$ dl g^{-1}, displayed the so-called viscosity average molecular weight, M_v [14]. M_v of polymer samples were measured in decaline (decahydronaphthalene) at 135 °C by means of Ubbelohde suspended level dilution viscometer [15]. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch 200 F3 DSC instrument under an N_2 atmosphere. The samples were heated from -100 to $+200$ °C with a rate of 10 °C/min. The T_g of polymers were determined by DSC. Melting points (mp) were determined in open capillary tubes in an Electrothermal IA 9000 melting point apparatus. ^{1}H NMR and ^{13}C NMR analyses of ligands were performed on Bruker BRX-100 Avance and Bruker Avance 400 spectrometers, respectively. Mass spectra (MS) were recorded with a Varian MAT CH7 mass spectrometer. Elemental analysis for CHN was carried out by CHNS type Thermo Finnigan 1112EA microanalyzer.

Ligands and catalysts preparation

*Synthesis of ligand **1**, [N,N′-bis(2,6-diisopropylphenyl)-2,3-butanediimine]*

The ligand was synthesized through the reaction of 2,3-butanedione (5.0 mmol, 0.43 ml in 15 ml methanol), 2,6-diisopropylaniline (10.0 mmol, 1.88 ml) and in the presence of trace amount of 4-toluenesulfonic acid as a catalyst. The solution was stirred for 24 h at 40 °C. A yellow solid was obtained by solvent removing method. The solid was washed and crystallized with cold methanol and dried. The yield of the reaction was about 85 %; mp: 100 °C. ^{1}H NMR (CDCl$_3$, 100 MHz): δ 7.05–7.30 (m, 6H, Ar–*H*), 2.72 (septet, 4H, C*H*–(Me)$_2$), 2.24 (s, 6H, N=C–C*H*$_3$), 1.24, 1.17 (d, 24H, CH–(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 167.2 (*C*=N), 146.7, 135.1, 123.9, 123.2 (Ar–*C*), 28.5 (*C*H–(Me)$_2$), 23.6, 23.1 (CH–(*C*H$_3$)$_2$), 16.8 (*C*H$_3$–C=N). EI-MS: *m/z* 404 [M$^+$]. Anal. Calc. for C$_{28}$H$_{40}$N$_2$: C, 83.11; H, 9.96; N, 6.93. Found: C, 83.07; H, 10.02; N, 6.88.

*Synthesis of ligand **2**, [N,N′-(phenanthrene-9,10-diylidene)bis(2,6-diisopropylaniline)]*

To prepare the ligand, suspension of 9,10-phenanthrenequinone (4.8 mmol, 1.0 g) in methanol (10 ml) was added to a stirred solution of 2,6-diisopropylaniline (14.4 mmol, 2.70 ml) in methanol (10 ml) containing a trace amount of 4-toluene-sulfonic acid. The reaction mixture was heated to reflux for 48 h. After removal of the solvent, the precipitated green solid was washed with cold methanol several times and dried. The yield of the reaction was about 50 %; mp: 159 °C. ^{1}H NMR (CDCl$_3$, 100 MHz): δ 6.97–8.24 (m, 14H, Ar–H), 3.21 (septet, 4H, CH–(Me)$_2$), 1.42, 1.27 (d, 24H, CH–(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ 161.5, 159.7 (C=N), 150.2, 147.3, 141.6, 139.3, 136.5, 135.1, 134.2, 132.1, 131.4, 129.7, 129.5, 125.3, 124.2, 118.6 (Ar–C), 29.5, 27.7 (CH–(Me)$_2$), 24.4, 23.5 (CH–(CH$_3$)$_2$). EI-MS: m/z 526 [M$^+$]. Anal. Calc. for C$_{38}$H$_{42}$N$_2$: C, 86.64; H, 8.04; N, 5.32. Found: C, 86.57; H, 8.09; N, 5.30.

*Synthesis of catalyst **A**, dibromo[N,N′-bis(2,6-diisopropylphenyl)-2,3-butanediimine]nickel(II)*

(DME)NiBr$_2$ (1.2 mmol, 0.37 g) and ligand **1** (1.2 mmol, 0.48 g) were combined in a Schlenk flask under a nitrogen atmosphere to prepare catalyst **A**. Methylene chloride (25 ml) was added to the solid mixture. The produced suspension was stirred for 24 h at room temperature. Solvent removal of the suspension resulted brown solid. The solid was washed with Et$_2$O several times and dried in vacuum. The yield of the reaction was about 71 %; decomposed at temperature above 300 °C. EI-MS: *m/z* 543 [M$^+$−Br], 463 [M$^+$−2Br], 404 [M$^+$−NiBr$_2$]. Anal. Calc. for C$_{28}$H$_{40}$N$_2$NiBr$_2$: C, 53.97; H, 6.47; N, 4.49. Found: C, 53.76; H, 6.53; N, 4.45.

*Synthesis of catalyst **B**, dibromo[N,N′-(phenanthrene-9,10-diylidene)bis(2,6-diisopropylaniline)]nickel(II)*

The synthesis of complex **B** was carried out according to the complex **A**, using the ligand **2** (1.2 mmol, 0.63 g) and (DME)NiBr$_2$ (1.2 mmol, 0.37 g). The complex **B** was isolated as a brown powder. The yield of the reaction was about 80 %; decomposed at temperature above 300 °C. EI-MS: *m/z* 665 [M$^+$−Br], 585 [M$^+$−2Br], 526 [M$^+$−NiBr$_2$]. Anal. Calc. for C$_{38}$H$_{42}$N$_2$NiBr$_2$: C, 61.24; H, 5.68; N, 3.76. Found: C, 60.97; H, 5.75; N, 3.71.

Structures of the catalysts **A** and **B** are shown in Fig. 1.

Result and discussion

Propylene polymerization reactions using the prepared catalysts **A**, **B** and mixed of 1:1 w/w of them (**C**) were carried out at the different polymerization conditions. The activity of the catalyst, R_p (average) is expressed as g PP/mmol Ni.h. Figure 2 shows the effect of Al/Ni molar ratio on the polymerization behavior of propylene
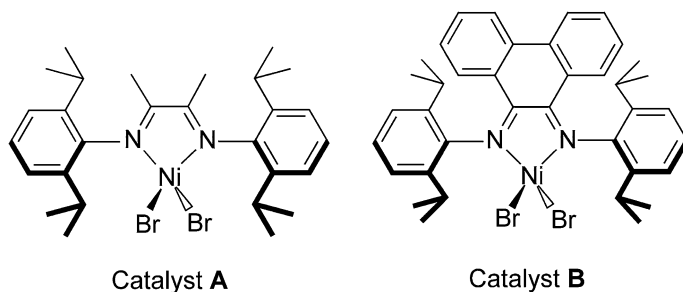
Fig. 1 Possible structure of the catalysts used for polymerization of propylene

using of the catalysts **A**, **B**, and **C**. MAO was used as a cocatalyst. In general, the role of MAO in polymerization can be included alkylation, generation of cationic active species and stabilization of these species by coordinative contact with its counterion. However, excess MAO inhibits the coordination of monomer with the active center and results in a slight decrease in the catalytic activity [1, 16].

As displayed in Fig. 2, activity of the catalytic systems increased significantly with increasing Al/Ni molar ratio up to 2,000:1 while decreased in the molar ratios higher than 2,000. However, activity of the catalyst **C** in the molar ratio of 2,000 was about 138 (g PP/mmol Ni.h) between activity of the catalysts **A** and **B** which were about 117 and 164 (g PP/mmol Ni.h), respectively. The influence of Al/Ni molar ratio on the M_v of the polymers obtained using the catalytic systems were investigated (Fig. 3). Increasing the Al/Ni molar ratio up to 2,000 increased M_v values, while further increase in the ratio decreased M_v of the obtained polymers. The competition between chain transfer to aluminum and propagation reactions increases in the ratio higher than 2,000 as reported [17, 18]. As shown in Fig. 3,
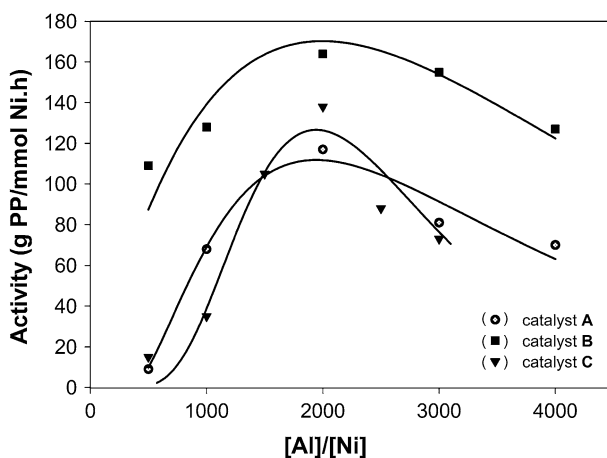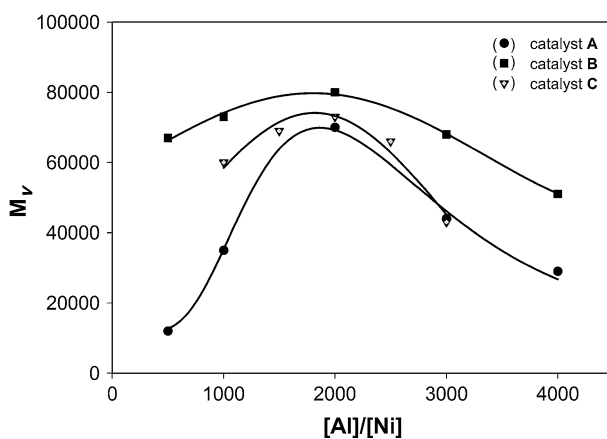

Fig. 2 Effect of Al/Ni molar ratio on activity of the catalytic systems. Polymerization conditions: [Ni] = 3 × 10^{-5} mol/l, temperature = 30 °C, monomer pressure = 4 bar, reaction time = 30 min, toluene = 100 ml

the M_v values related to catalyst **C** are between the M_v values related to the catalysts **A** and **B**, in the Al/Ni molar ratio range from 1,000 to 3,000 which studied.
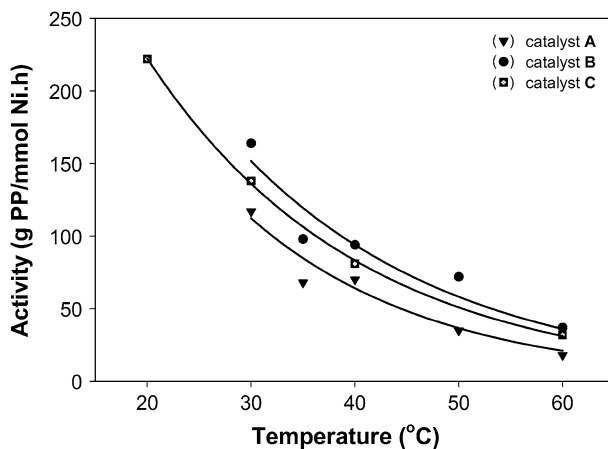
The influence of polymerization temperature on activity of the catalytic systems and M_v of the resulting polymers was investigated in temperature range from 30 to 60 °C (for the catalysts **A** and **B**) and from 20 to 60 °C (for the catalyst **C**), while the [Al]/[Ni] ratio was kept constant at 2,000:1. As displayed in Figs. 4 and 5, increasing temperature in the studied range decreased activity of the catalytic systems and M_v values of the obtained polymers. The decrease of the catalyst activity with increasing temperature in the polymerization medium could be attributed to the catalyst irreversible deactivation and reducing the solubility of the monomer gas in the polymerization medium. Also higher rate of chain transfer and termination reactions than propagation reaction could be result of increasing polymerization temperature that leads to form shorter chains [16, 19, 20]. Figures 4 and 5 show that the M_v values and activities related to the catalyst **C** are between those related to the catalysts **A** and **B**, in the temperature range from 30 to 60 °C. The M_v values of polymers formed by the catalysts **A**, **B**, and **C** were about 58,000, 75,000 and 70,000 (g/mol), also activities of the catalysts **A**, **B**, and **C** were about 70, 94, and 81 (g PP/mmol Ni.h) in the polymerization temperature of 40 °C, respectively.

The influence of monomer pressure in the range of 2.5–8 bars on behavior of the catalysts **A** and **B** was studied, while the [Al]/[Ni] ratio and polymerization temperature were kept constant at 2,000:1 and 30 °C, respectively. According to runs **1–8** (Table 1), the highest productivity was obtained at the monomer pressure of +4 bars. The higher of the pressure the higher of the monomer concentration close to the catalyst active centers which could increase temperature in the polymerization environment. Increasing activity in the higher pressure may encapsulate the active centers because of the formed rubber-like polymer. Therefore, the higher activity and the higher increase of the reaction temperature
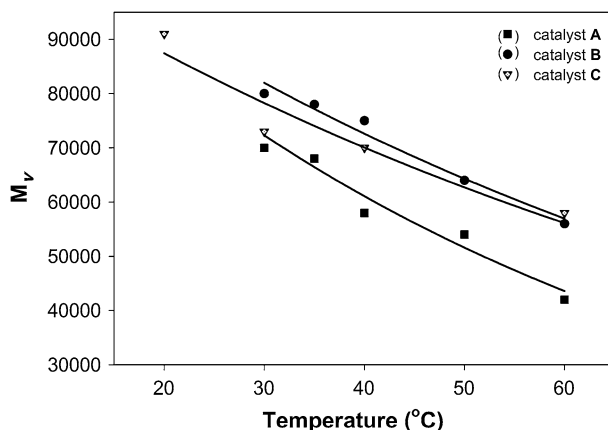

Fig. 3 Influence of Al/Ni molar ratio on M_v of the obtained polymers. Polymerization conditions: [Ni] = 3 × 10^{-5} mol/l, temperature = 30 °C, monomer pressure = 4 bar, reaction time = 30 min, toluene = 100 ml

Fig. 4 Effect of reaction temperature on activity of the catalytic systems. Polymerization conditions: $[Ni] = 3 \times 10^{-5}$ mol/l, $[Al]/[Ni] = 2,000{:}1$, monomer pressure = 4 bar, reaction time = 30 min, toluene = 100 ml

Fig. 5 Influence of reaction temperature on M_v of the obtained polymers. Polymerization conditions: $[Ni] = 3 \times 10^{-5}$ mol/l, $[Al]/[Ni] = 2,000{:}1$, monomer pressure = 4 bar, reaction time = 30 min, toluene = 100 ml

could decay the active centers quickly [21, 22]. In order to study increasing temperature with increasing pressure from 2.5 to 8 bars, the propylene polymerization was carried out using the catalyst **C** at low temperature (20 °C). The highest activity of the catalyst **C** was about 222 (g PP/mmol Ni.h) at a monomer pressure of +4 bars and reaction temperature of 20 °C, it was higher than activity of the catalysts **A** and **B** which were about 117 and 164 (g PP/mmol Ni.h), respectively, at a monomer pressure of +4 bars and reaction temperature of 30 °C (Table 1). As expected, the M_v values of the polymers obtained using the catalytic systems increased with increasing pressure from 2.5 to 8 bars (runs **1–13**, Table 1).

Table 1 Influence of reaction time and pressure on polymerization of propylene using catalysts **A**, **B** and mixed of 1:1 w/w of them (**C**)

Run	Catalytic system	Pressure (bar)	Time (min)	Temperature (°C)	Yield[a] (g)	Activity[b]	M_v (g/mol)
1	**A**	2.5	30	30	0.087	58	5.40×10^4
2	**A**	4	30	30	0.175	117	7.00×10^4
3	**A**	6	30	30	0.157	105	7.50×10^4
4	**A**	8	30	30	0.145	97	7.70×10^4
5	**B**	2.5	30	30	0.052	35	5.00×10^4
6	**B**	4	30	30	0.246	164	8.00×10^4
7	**B**	6	30	30	0.205	137	8.60×10^4
8	**B**	8	30	30	0.157	105	8.70×10^4
9	**C**	2.5	30	20	0.118	136	7.43×10^4
10	**C**	4	30	20	0.333	222	9.10×10^4
11	**C**	6	30	20	0.289	193	1.15×10^5
12	**C**	7	30	20	0.283	189	1.19×10^5
13	**C**	8	30	20	0.279	186	1.23×10^5
14	**A**	4	5	30	0.009	36	–
15	**A**	4	15	30	0.095	128	6.50×10^4
16	**A**	4	45	30	0.216	96	1.11×10^5
17	**A**	4	60	30	0.195	65	1.22×10^5
18	**B**	4	5	30	0.04	160	2.70×10^4
19	**B**	4	15	30	0.259	173	6.90×10^4
20	**B**	4	45	30	0.256	114	1.20×10^5
21	**B**	4	60	30	0.267	89	1.40×10^5
22	**C**	4	5	20	0.042	168	1.50×10^4
23	**C**	4	15	20	0.157	209	5.40×10^4
24	**C**	4	45	20	0.349	155	1.09×10^5
25	**C**	4	60	20	0.354	118	1.24×10^5

Polymerization conditions: [Ni] = 3×10^{-5} mol/l, [Al]/[Ni] = 2,000:1, monomer pressure = 4 bar, toluene = 100 ml

[a] Yield in (g PP)

[b] Activity in (g PP/mmol Ni.h)

In order to study the catalysts lifetime, propylene polymerization was carried out with the selected reaction times of 5, 15, 30, 45, and 60 min at reaction temperature of 30 °C for the catalysts **A** and **B**, and 20 °C for the catalyst **C**. The maximum activity was obtained after 15 min of the polymerization for the catalysts **A** and **B** at 30 °C and for the catalyst **C** it was obtained after 30 min at 20 °C (Table 1). The catalyst activity decreased after the maximum time of polymerization because of possible encapsulation of active centers of the catalyst in rubbery polymer and decay of some active centers due to the sudden increase of the reaction temperature [23, 24]. Increasing M_v values during the polymerization time represented chain growth during the reaction time [23, 25]. The maximum values of M_v for the

polymers obtained by the catalysts **A** and **B** were about 122,000 and 140,000 (g/mol), respectively, at reaction time of 60 min and temperature of 30 °C. Also the maximum value of M_v for the polymer formed by the catalyst **C** was about 124,000 (g/mol) at reaction time of 60 min and temperature of 20 °C (runs **17**, **21**, and **25**, Table 1).

The activity of the catalyst **B** was higher than the catalyst **A**. For example, runs **1** and **3** (Table 2) show that activities of the catalysts **A** and **B** in the polymerization of propylene were 117 and 164 (g PP/mmol Ni.h) under same conditions, respectively. According to the structures of the catalysts **A** and **B**, presence of an electron-withdrawing phenanthrene group in the catalyst **B** instead of electron-donating methyl groups caused increase in positive charge of nickel and increase the catalyst activity [26, 27]. The M_v value of the PP formed by the catalyst **B** was about 80,000 (g/mol) higher than 70,000 (g/mol) for M_v value of the polymer obtained by the catalyst **A** under same conditions (runs **1** and **3**, Table 2). The behavior suggests that the α-diimine nickel complexes based on 9,10-phenanthrenequinone (**B**) can introduce more steric demands on the axial faces than those based on 2,3-butanedione (**A**) [1]. The T_g of PPs obtained by the catalysts **A**, **B**, and **C** were about −33.3, −34.4, and −33.6, respectively (runs **1**, **3**, and **5**, Table 2). Tables and Figures show that the activities, T_g and M_v values related to the catalyst **C** were between those related to the catalysts **A** and **B** under same conditions.

PPs formed by the α-diimine nickel catalysts (**A**, **B**, and **C**) had approximately the rubber-like behavior and were completely transparent. Also, the T_g of resulting PPs was near to T_g of ethylene-propylene copolymer with ethylene content of about 20–30 % (Table 2) [21, 28]. It can be realized to the probability of formation of ethylene-type units (sequences of CH_2) in polymer chain. The resemblance of behavior of these propylene homopolymers to ethylene–propylene copolymer suggests that the monomer was incorporated via 2,1-insertion of propylene and chain-walking based on 3,1-enchainment to give sequences of CH_2 in the polymer chain. As displayed in Scheme 1, presence of ethylene-type runs is a result of 2,1-insertion of propylene and also chain-walking, in which the metal center

Table 2 Influence of type of catalytic system on some characteristic of the obtained polymer

Run	Catalytic system	Temperature (°C)	Yield[b] (g)	Activity[c]	T_g (°C)	M_v (g/mol)
1	**A**	30	0.175	117	−33.3	7.0×10^4
2	**A**	40	0.105	70	–	5.8×10^4
3	**B**	30	0.246	164	−34.4	8.0×10^4
4	**B**	40	0.141	94	–	7.5×10^4
5	**C**[a]	30	0.207	138	−33.6	7.3×10^4
6	**C**	40	0.121	81	–	7.0×10^4

Polymerization conditions: [Ni] = 3×10^{-5} mol/l, [Al]/[Ni] = 2,000:1, monomer pressure = 4 bar, reaction time = 30 min, toluene = 100 ml

[a] Mixed of 1:1 w/w of the catalysts **A** and **B**

[b] Yield in (g PP)

[c] Activity in (g PP/mmol Ni.h)
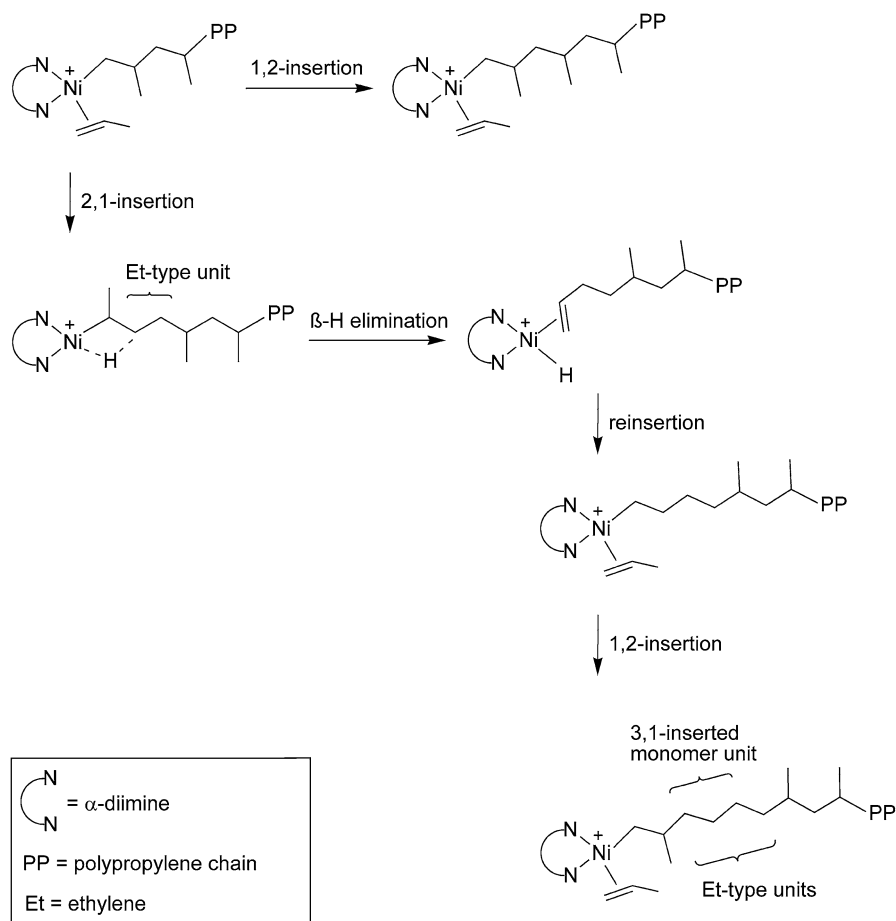
Scheme 1 Mechanism of ethylene-type unit formation via 2,1-insertion of propylene and chain-walking based on 3,1-enchainment

migrates along the growing polymer chain through a series of β-hydride elimination and reinsertion events [9, 13, 29].

Conclusion

Propylene polymerization was catalyzed with the α-diimine Ni(II) catalysts (**A**, **B**, and **C**) in the presence of MAO as cocatalyst. To obtain optimum conditions in the polymerization, effects of the Al/Ni molar ratio, temperature, pressure of monomer and reaction time were studied. The activities of the catalysts **A**, **B**, and **C** were about 117, 164, and 138 (g PP/mmol Ni.h) and M_v values of the polymers formed by the catalysts **A**, **B**, and **C** were about 70,000, 80,000, and 73,000 (g/mol), respectively, at [Al]/[Ni] ratio of 2,000:1, temperature of 30 °C and monomer

pressure of +4 bars. The activity of the catalyst **B** was higher than the catalyst **A** which was due to presence of an electron-withdrawing phenanthrene group in the catalyst **B** structure. The activities of the catalytic systems and M_v of the obtained polymers decreased with increasing temperature, while those increased with increasing Al/Ni molar ratio up to 2,000:1. Increasing pressure of the monomer to 8 bars increased the M_v of the resulting polymers. In addition, performance of the catalyst **C** was between performance of the catalysts **A** and **B** in the propylene polymerization under same conditions. PP formed by the catalysts (**A**, **B**, and **C**) had approximately the rubber-like behavior. The T_g of resulting PPs was closed to the T_g of reported ethylene-propylene copolymer. This behavior was due to formation of ethylene-type units in a result of 2,1-insertion of propylene and 3,1-enchainment (chain-walking) using α-diimine nickel-based catalyst. So it is possible with these kinds of catalyst structures to obtain propylene–ethylene copolymer structure like with the same T_g behavior. The behavior was not observed with previous catalysts used such as metallocene and Ziegler–Natta catalysts.

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