

# Synthesis and characterization of ethylene-propylene copolymer and polyethylene using $\alpha$ -diimine nickel catalysts

Hamid Pourtaghi-Zahed · Gholam Hossein Zohuri

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**Abstract** Nickel-based catalysts of dibromo[*N,N'*-bis(2,6-diisopropylphenyl)-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 were used for ethylene-propylene (EP) copolymerization and ethylene polymerization. Methylaluminoxane (MAO) was used as a co-catalyst. The polymers were characterized by means of FT-IR,  $^1\text{H}$  NMR and DSC (Differential scanning calorimetry). In ethylene polymerization using mixed of 1:1 w/w of the catalysts **A** and **B** degree of branching polymer chain decreased with increasing monomer pressure while increased with enhancing polymerization temperature. In ethylene-propylene copolymerization using mixed of 1:1 w/w of **A** and **B**, the catalytic system showed the maximum activity at about  $[\text{Al}]/[\text{Ni}]=2000:1$  ratio and further addition of MAO did not affect the activity of the catalyst. Increasing the copolymerization temperature from 20 to 80 °C decreased the productivity of the catalytic system while increased the ethylene content of the copolymer. Decreasing relative pressure of  $P_{P_r}/P_{E_t}$  from 9:1 to 1:1 increased the ethylene contents of the copolymers from 51 % to 72 % while decreased the viscosity average molecular weight ( $M_v$ ) and glass transition temperature ( $T_g$ ) of the products. A copolymer with more rubber-like behavior was obtained in relative pressure of  $P_{P_r}/P_{E_t}$  (5:1) and total pressure of 5 bars.

**Keywords** Nickel-based catalyst · Late transition metal · Copolymerization · NMR

## Introduction

Ethylene-propylene copolymer is a family of amorphous products with elastomeric character. Ethylene-propylene elastomers (EPM) are amorphous materials with a glass transition temperature of  $-50$  to  $-60$  °C. The commercial EP copolymers are generally made using homogeneous specific vanadium-based and heterogeneous isospecific titanium-based Ziegler-Natta catalysts. Single site metallocene catalysts based on zirconium and titanium activated with MAO are used to produce EPM, too [1–4].

In 1995, Brookhart and coworkers synthesized a new class of Ni(II) and Pd(II) polymerization catalysts stabilized by bulky  $\alpha$ -diimine ligands.  $\alpha$ -Diimine complexes based on nickel(II) activated by MAO are able to polymerize  $\alpha$ -olefins to form high molecular weight polymers and are also used in copolymerization of ethylene and propylene monomers. Ni(II) catalysts bearing various ligands are used for polymerizing ethylene to give a variety of materials, ranging from highly viscous liquids to rigid linear polyethylenes [5–10].

In the present study, the catalysts **A** and **B** were synthesized as late transition metal  $\alpha$ -diimine nickel complexes. These catalysts and mixed of 1:1 w/w of them were used for ethylene-propylene copolymerization and ethylene polymerization. The activities of the catalysts (**A** and **B**), degree of branching of polyethylene,  $M_v$ , and the apparent property of produced polymers were studied. The catalytic performance in ethylene-propylene copolymerization is influenced by factors such as reaction temperature, relative pressure of propylene/ethylene, total monomer pressure and cocatalyst/catalyst molar ratio. Therefore, effect of mentioned factors on the copolymerization was studied.

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## Experimental

### Materials and characterization

Methanol and dichloromethane (Merck, Germany) were used without any purification. Toluene (Arak Petrochemical Co, Iran) was dried by refluxing over a sodium wire and benzophenone mixture and then distilled under dry N<sub>2</sub> and stored over activated 4 Å/13X 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 (Merck, Germany) were used in ligands synthesis. Methylaluminoxane (MAO) (Sigma Aldrich Chemicals, Germany) was purchased as a 10 wt % (1.5 M) solution in toluene. 1,2-Dimethoxyethane nickel(II) bromide [(DME)NiBr<sub>2</sub>] (Sigma Aldrich Chemicals, Germany) with purity 97 % was applied in the synthesis of the catalysts. Polymer grade ethylene and propylene (Arak Petrochemicals Co, Iran) were used after passing through a column of activated 4 Å/13X type molecular sieves. Nitrogen (Roham Gas, Iran) dried by passage through KOH, activated silica gel and 4 Å/13X 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 stainless steel Buchi AG reactor (CH-8610) using catalysts **A**, **B** and mixed of 1:1 of them. The reactor temperature was adjusted by a thermostatic bath. Dry toluene (200 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 mixed of ethylene and propylene gasses in a fixed ratio. Toluene was saturated with a constant ratio from mixture of the both gases prior to the copolymerization. Ethylene polymerization was also carried out in the reactor after toluene saturated with ethylene at different pressures and temperatures. A mixed of 1:1 w/w of the catalysts **A** and **B** ( $3.0 \times 10^{-3}$  mmol) was 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.

Direct application of Mark-Houwink equation of the form  $[\eta] = 3.8 \times 10^{-4} M_v^{0.74} \text{ dL.g}^{-1}$ , displayed the so-called viscosity average molecular weight,  $M_v$  [11, 12].  $M_v$  of copolymer samples were measured in decaline (decahydronaphthalene) at 135 °C by means of Ubbelohde suspended level dilution viscometer. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch 200F3 DSC instrument under an N<sub>2</sub> atmosphere. The samples were heated from -100 to +200 °C with a rate of 10 °C/min. The  $T_g$  of copolymers

were determined by DSC. The molar proportions of ethylene and propylene units in EP copolymers were determined using an IR method (Shimadzu FTIR-4300) [13, 14]. For polyethylene, the number of branches in 1,000 carbons was determined by <sup>1</sup>H NMR (Bruker BRX-100 Avance) spectrum according to the literature [15]. Melting points (mp) were determined in open capillary tubes in an Electrothermal IA 9000 melting point apparatus. <sup>1</sup>H NMR and <sup>13</sup>C NMR analyses of ligands were performed on Bruker BRX-100 Avance and Bruker Avance 400 spectrometers, respectively. MS spectra were recorded with a Varian MAT CH7 mass spectrometer. Elemental analysis for CHN was carried out by CHNS type Thermo Finnigan 1112EA microanalyzer.

### Synthesis of ligands and complexes

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

#### *Synthesis of Ligand 1, [N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine] and catalyst A*

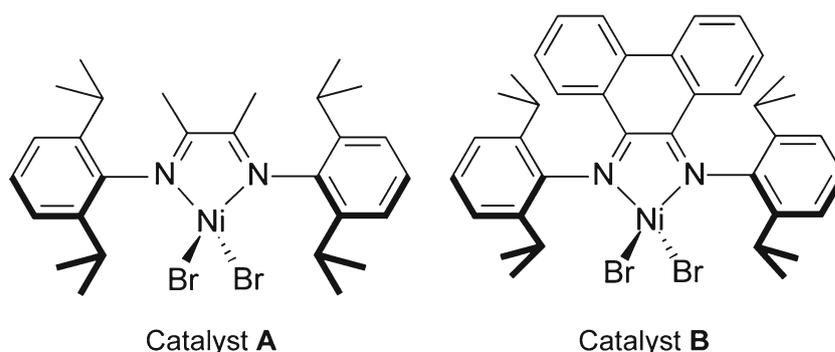
The ligand was synthesized through the reaction of 2,3-butanedione (5.0 mmol, 0.43 ml in 15 ml methanol), 2,6-diisopropylaniline (10.0 mmol, 1.88 ml) and in the presence of trace amount of 4-toluenesulfonic acid as a catalyst. The solution was stirred for 24 h at 40 °C. A yellow solid was obtained by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

(DME)NiBr<sub>2</sub> (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<sub>2</sub>O several times and dried in vacuum. The yield of the reaction was about 71 %; mp: > 300 °C. EI-MS: m/z 543 [M<sup>+</sup>-Br], 463 [M<sup>+</sup>-2Br], 404 [M<sup>+</sup>-NiBr<sub>2</sub>]. Anal. Calc. for C<sub>28</sub>H<sub>40</sub>N<sub>2</sub>NiBr<sub>2</sub>: C, 53.97; H, 6.47; N, 4.49. Found: C, 53.76; H, 6.53; N, 4.45.

#### *Synthesis of Ligand 2, [N,N'-(phenanthrene-9,10-diylidene)bis(2,6-diisopropylaniline)] and catalyst B*

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)

**Fig. 1** Structures of catalysts used for polymerization of ethylene and its copolymerization with propylene



in methanol (10 ml) containing a trace amount of 4-toluenesulfonic acid. The reaction mixture was heated to reflux for 48 h. After removal of 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.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  6.97–8.24 (m, 14 H, Ar-H), 3.21 (septet, 4 H,  $\text{CH}(\text{Me})_2$ ), 1.42, 1.27 (d, 24 H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  161.5, 159.7 ( $\text{C}=\text{N}$ ), 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 ( $\text{CH}(\text{Me})_2$ ), 24.4, 23.5 ( $\text{CH}(\text{CH}_3)_2$ ). EI-MS:  $m/z$  526 [ $\text{M}^+$ ]. Anal. Calc. for  $\text{C}_{38}\text{H}_{42}\text{N}_2$ : C, 86.64; H, 8.04; N, 5.32. Found: C, 86.57; H, 8.09; N, 5.30.

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

## Result and discussion

In order to investigate the catalysts behavior, polymerization reactions were carried out at the various conditions. MAO was used as a cocatalyst. The molar ratio of cocatalyst/catalyst (Al/Ni molar ratio) was varied from 500:1 to 5,000:1. Table 1 shows the effect of Al/Ni molar ratio on copolymerization behavior of ethylene-propylene using mixed of the catalysts **A** and **B**. As shown in Fig. 2, the catalytic activity increased significantly with increasing Al/Ni molar ratio up to 2,000 while increased slightly in the molar ratios higher than 2,000. Also ethylene contents (Et %) of the copolymers increased with increasing Al/Ni molar ratio linearly. 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 increase in catalytic activity [16, 17].

The influence of Al/Ni molar ratio on the  $M_v$  was investigated (Table 1). Increasing the Al/Ni molar ratio up to 4,000 increased  $M_v$  values; however, further increase in the ratio decreased  $M_v$  of obtained copolymer. The competition between chain transfer to aluminum and propagation reactions increases in the ratio higher than 4,000 as reported [14, 17, 31]. The highest  $M_v$  was obtained at 4,000 molar ratio.  $M_v$  and ethylene content of the copolymer at 4,000 molar ratio (run 5, Table 1) were 255,000 g/mol and 64 %, respectively. Since rubber-like copolymer was obtained at Al/Ni molar ratio of 1,500–2,000, this ratio was used for further studies.

Copolymerization reactions were performed in the temperature range from 20 to 80 °C (Table 1). The copolymerization was affected using the optimum conditions that had been previously obtained (run 1–6, Table 1). Increasing temperature in the studied range decreased the catalyst activity while increased ethylene contents of the products. The highest activity of the catalytic system (1,080 g polym/mmol Ni.h) and lowest percentage of ethylene (59 %) were obtained at 20 °C (run 3, Table 1), while the lowest catalytic activity (50 g polym/mmol Ni.h) and highest ethylene content (70.4 %) were obtained at 80 °C (run 10, Table 1). The most rubber-like polymer was obtained at 20 °C. Decreasing monomer solubility in toluene or decreasing monomer concentration in the polymerization medium and destruction of some of the catalytic active centers with increasing temperature can affect decreasing the catalyst activity [14, 16, 32, 33]. The values of the reactivity ratio for ethylene and  $\alpha$ -olefin pairs are dependent on the temperature of copolymerization. One of the factors that can show the temperature effect on the amount of reactivity ratio of the monomers is a diffusion limitation for heavier  $\alpha$ -olefin which can be serious at high temperature [17–19].

The  $M_v$  decreased from 222,000 to 43,000 g/mol by increasing of the reaction temperature from 20 to 80 °C (Table 1). Higher rate of chain-transfer and termination reactions than propagation reaction could be result of increasing copolymerization temperature that leads to form shorter chains [10, 16, 20].

The influence of propylene/ethylene relative pressure ( $P_P/P_E$ ) of 1:1, 3:1, 5:1, 7:1 and 9:1 on copolymerization behavior

**Table 1** Influence of MAO concentration, temperature and monomer relative pressure on copolymerization of ethylene-propylene using mixed nickel-based catalysts **A** and **B**

Run	[Al]/[Ni]	Temperature (°C)	$P_{Pr}/P_{Et}$	Yield <sup>a</sup> (g)	Activity <sup>b</sup>	Et (%)	$M_v$ (g/mol)
1	500:1	20	1:5	0.349	233	57.6	$1.75 \times 10^5$
2	1000:1	20	1:5	1.140	760	58.1	$1.97 \times 10^5$
3	2000:1	20	1:5	1.620	1080	59.0	$2.22 \times 10^5$
4	3000:1	20	1:5	1.608	1072	61.8	$2.53 \times 10^5$
5	4000:1	20	1:5	1.674	1116	63.9	$2.55 \times 10^5$
6	5000:1	20	1:5	1.875	1250	64.5	$2.50 \times 10^5$
7	2000:1	30	1:5	1.515	1010	65.0	$2.29 \times 10^5$
8	2000:1	40	1:5	0.700	467	63.5	$1.52 \times 10^5$
9	2000:1	60	1:5	0.240	160	69.5	$1.18 \times 10^5$
10	2000:1	80	1:5	0.075	50	70.4	$4.30 \times 10^4$
11	2000:1	20	1:1	3.825	2550	72.2	$3.89 \times 10^5$
12	2000:1	20	3:1	2.482	1655	64.4	$3.72 \times 10^5$
13	2000:1	20	7:1	1.342	895	56.0	$2.02 \times 10^5$
14	2000:1	20	9:1	0.732	488	51.5	$1.36 \times 10^5$

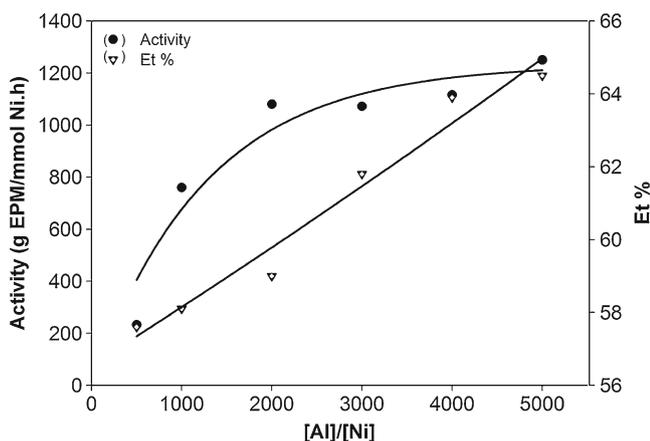
Copolymerization conditions: cat A/cat B=1:1 w/w, [Ni]= $1.5 \times 10^{-5}$  mol/L,  $P_t=5$  bar, reaction time=30 min, 200 ml toluene

<sup>a</sup>Yield in (g polym)

<sup>b</sup>Activity in (g polym/mmol Ni.h)

was studied. The best elastomeric figure was observed at the  $P_{Pr}/P_{Et}=5:1$  relative pressure. Table 1 shows the catalytic activity behavior,  $M_v$ , and ethylene contents of the copolymers when the  $P_{Pr}/P_{Et}$  was varied from 1:1 to 1:9. The catalyst activity and ethylene contents of the copolymers decreased with increasing of the propylene relative pressure. The different reactivities of the olefins are important for the copolymerization. The comonomer reactivity ratio in copolymerization with ethylene appears to decrease with increasing steric hindrance around the double bond in the  $\alpha$ -olefin in to the following order: ethylene > propylene > 1-butene > linear  $\alpha$ -olefin > branched  $\alpha$ -olefin [21].

Increasing propylene relative pressure significantly affected  $M_v$  to lower values (Table 1). The most likely  $\beta$ -H chain elimination has been reported to have higher rate constant for propylene compared to ethylene due to labile  $\beta$ -hydrogen being associated with the former [12].



**Fig. 2** Effect of Al/Ni molar ratio on catalyst activity and ethylene contents of obtained polymers. Copolymerization conditions: cat A/cat B=1:1 w/w, [Ni]= $1.5 \times 10^{-5}$  mol/L, temperature=20 °C,  $P_{Pr}/P_{Et}=5:1$ ,  $P_t=5$  bar, reaction time=30 min, toluene=200 ml

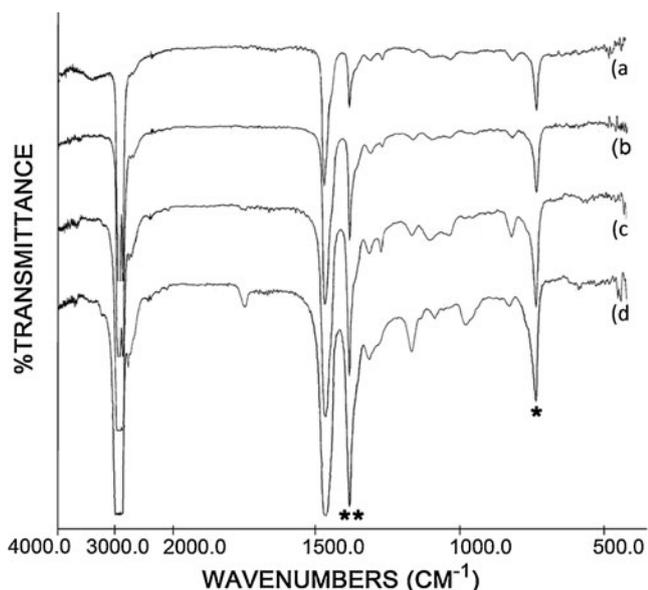
FTIR spectra of some copolymers obtained in different propylene/ethylene relative pressure are shown in Fig. 3. Spectra a, b, c and d are related to the runs **11**, **12**, **3** and **14** in the Table 1, respectively. As shown in Fig. 3, the spectral regions of  $722 \text{ cm}^{-1}$  with sign of (\*) and  $1,377 \text{ cm}^{-1}$  with sign of (\*\*) in each spectrum are related to the  $\text{CH}_2$  rocking and symmetric bending of  $\text{CH}_3$ , respectively. An increase of the spectral regions at  $722 \text{ cm}^{-1}$  corresponds to a decrease of propylene concentration in the copolymer while an increase of the bands at  $1,371 \text{ cm}^{-1}$  corresponds to an increase of propylene concentration in the copolymer [4].

The influence of total monomer pressure in the range of 3 to 9 bars on the catalyst behavior was studied. Figure 4 shows activity of the catalyst and  $M_v$  versus the pressure. The highest productivity can be obtained at a total pressure about +6 bars. The higher of total 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 rubber-like of the polymer formed. Accordingly, the higher activity and the higher increase of the reaction temperature could decay the active centers quickly [14, 22].

Also, Fig. 4 shows that the  $M_v$  of the copolymers linearly increases from 116,000 to 389,000 (g/mol) with increasing pressure from 3 to 9 bars.

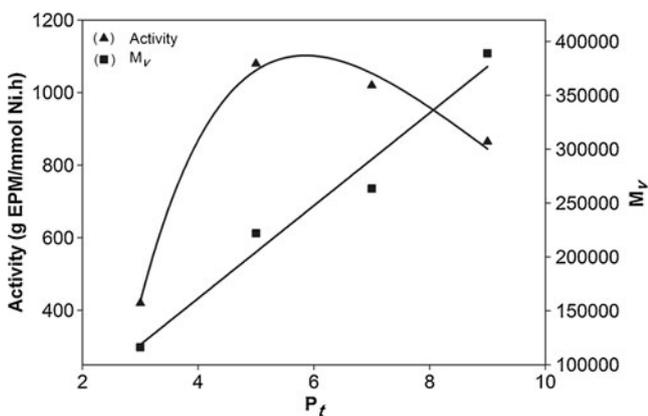
The  $T_g$  of EP copolymers decreased with increasing ethylene contents of the copolymers (see Fig. 5). The decrease in  $T_g$  with increasing ethylene content of the copolymer could be due to the loss of elastomeric behavior of the copolymer [14].

The catalyst activity and  $M_v$  of obtained copolymers versus the reaction times are illustrated in Fig. 6. The copolymerization was affected using the optimum conditions that had been previously obtained. The selected times of copolymerization were 5, 15, 30, 45, and 60 min under the same

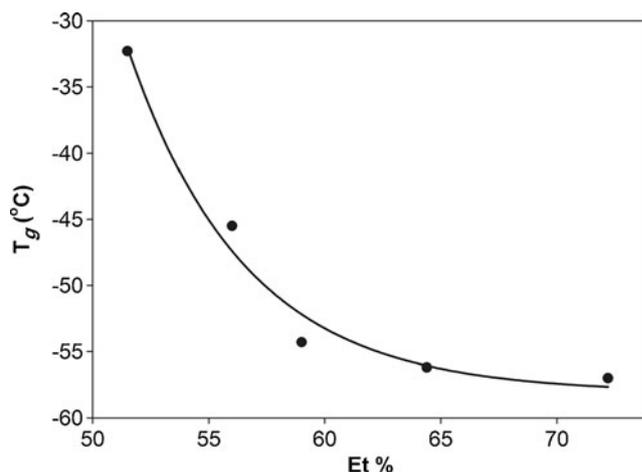


**Fig. 3** Comparing of the spectral regions (\*) (CH<sub>2</sub> rocking) and (\*\*) (symmetric bending CH<sub>3</sub>) in the FTIR spectrum obtained from 4 samples of ethylene-propylene copolymers. Run:spectrum sign=11:a, 12:b, 3:c, 14:d

conditions. As shown in Fig. 6, the catalyst activity rose quickly to a maximum activity of about 1,200 (g polym/mmol Ni.h) in about 15 min and decreased gradually to a minimum activity in 60 min which studied. The catalyst activity was decreased during the copolymerization time because of possible the encapsulation of active centers of the catalyst in rubbery polymer with a probable gel effect and the decay of some active centers due to the sudden increase of the reaction temperature. Increasing  $M_v$  during the copolymerization time represented chain growth during the reaction time that  $M_v$  rose to a maximum value of about 250,000 (g/mol) at the time of 60 min (Fig. 6) [14, 23, 24].



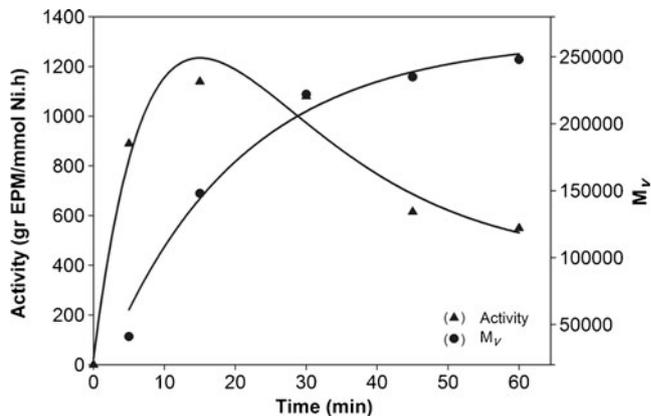
**Fig. 4** Effect of total monomer pressure on catalyst activity and  $M_v$  of obtained polymers. Copolymerization conditions: cat A/cat B=1:1 w/w, [Ni]= $1.5 \times 10^{-5}$  mol/L, [Al]/[Ni]=2000:1, temperature=20 °C,  $P_{P_i}/P_{E_i}$ =5:1, reaction time=30 min, toluene=200 ml



**Fig. 5** Effect of the ethylene content in the copolymer on  $T_g$ . Copolymerization conditions: [Ni]= $1.5 \times 10^{-5}$  mol/L, [Al]/[Ni]=2000:1, temperature=20 °C,  $P_i$ =5 bar, reaction time=30 min, toluene=200 ml

The yield of polymerization is expressed as g polymer obtained during the whole time of polymerization. The influence of polymerization conditions such as temperature and time of reaction, monomer pressure, cocatalyst/catalyst molar ratio and type of catalyst on the yield of polymerization is shown in the Tables 1 and 2. Similar behavior was observed for yield of polymerization and catalytic activity against different polymerization conditions, in this work.

According to runs 1, 2 and 3 (Table 2), in the system of ethylene polymerization with the same conditions used for the copolymerization, enhancing ethylene pressure from 1.4 to 4 bars caused increase catalyst activity and decrease degree of branching (from 82 branches to number of trace branches in 1,000 carbon atoms). In the polymerization system using nickel-based catalyst, the polymer chains are branched via  $\beta$ -H elimination and chain walking (Scheme 1) [25–28].



**Fig. 6** Effect of reaction time on catalyst activity and  $M_v$  of obtained polymers. Copolymerization conditions: cat A/cat B=1:1 w/w, [Ni]= $1.5 \times 10^{-5}$  mol/L, [Al]/[Ni]=2000:1, temperature=20 °C,  $P_{P_i}/P_{E_i}$ =5:1,  $P_i$ =5 bar, toluene=200 ml

**Table 2** Behavior of the catalysts **A**, **B** and mixed of 1:1 w/w of them in the ethylene polymerization and copolymerization of ethylene-propylene

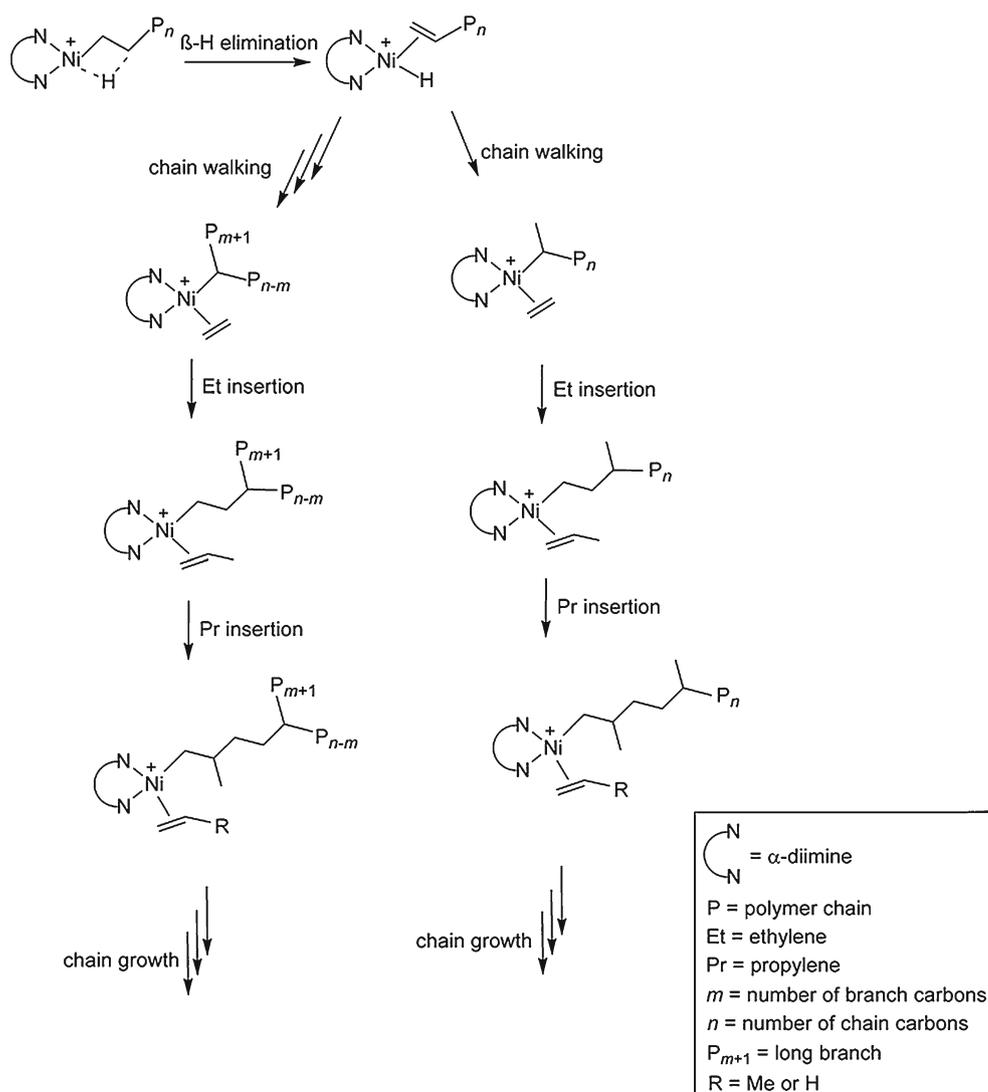
Run	cat <b>A</b> /cat <b>B</b> (w/w)	T (°C)	P <sub>t</sub> (bar)	P <sub>Pr</sub> /P <sub>Et</sub>	Yield <sup>a</sup> (g)	Activity <sup>b</sup>	branches/1000 C	Et (%)	M <sub>v</sub> (g/mol)
1	1:1	20	1.4	0 : 1.4	2.775	1850	82	–	–
2	1:1	20	2	0 : 2	3.345	2230	68	–	–
3	1:1	20	5	0 : 5	12.615	8410	Trace	–	–
4	1:0	20	2	0 : 2	2.917	1945	63	–	–
5	0:1	20	2	0 : 2	3.765	2510	92	–	–
6	1:1	40	2	0 : 2	1.710	1140	109	–	–
7	1:1	60	2	0 : 2	1.446	964	132	–	–
8	1:0	20	5	5 : 1	1.380	920	–	63.7	21.1 × 10 <sup>4</sup>
9	0:1	20	5	5 : 1	1.920	1280	–	57.1	24.3 × 10 <sup>4</sup>
10	1:1	20	5	5 : 1	1.620	1080	–	59.0	22.2 × 10 <sup>4</sup>

Polymerization conditions: [Ni]=1.5 × 10<sup>-5</sup> mol/L, [Al]/[Ni]=2000:1, reaction time=30 min, 200 ml toluene

<sup>a</sup> Yield in (g polym)

<sup>b</sup> Activity in (g polym/mmol Ni.h)

**Scheme 1** Mechanism of branch formation in the copolymer chain via insertion propylene and chain walking using  $\alpha$ -diimine nickel catalyst



The catalysts **A** and **B** created 63 and 92 branches/1,000 carbons in polyethylenes (runs **4** and **5**, Table 2) respectively and also white rubbery material was produced. The behavior of the catalysts **A** and **B** was studied to produce more rubber-like polymer with a high level of branching. Increasing the polymerization temperature increased the degree of branching of polyethylene whereas considerably decreased rubber-like behavior that was probably due to decreasing  $M_v$  of polymer (runs **6** and **7**, Table 2) [26, 28].

For this reason, the copolymerization of ethylene-propylene was applied using nickel-based catalysts at low temperature (20 °C) under controlled conditions for preparation more rubber-like polymer with higher  $M_v$ . In copolymerization using these types of catalysts under controlled conditions, polymer chain is branched via the insertion of propylene and chain walking. The nickel-based catalysts can create short and long branches in the chain through the  $\beta$ -H elimination reactions and chain walking (Scheme 1) [27].

The activity of catalysts **A** and **B** in the copolymerization of ethylene with propylene were 920 and 1,280 (g copolymer/mmol Ni.h), respectively (runs **8** and **9**, Table 2). The  $M_v$  of the copolymers produced using catalysts **A** and **B** were 211,000 and 243,000 (g/mol), respectively. The activity of the catalyst **B** was higher than the catalyst **A**. The behavior could be due to less electron density around the nickel metal center which increased activity of the catalyst **B**. 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 catalyst activity [29, 30]. The catalyst **B** produced a polymer with different  $M_v$  compared to the catalyst **A**. Copolymerization using mixed catalysts **A** and **B** led to form several catalytic active centers with different behavior which applying this catalytic system has contributed to produce a large range of molecular weight (runs **8**, **9** and **10**, Table 2). According to the optimum conditions obtained previously and also run **10** (Table 2), to produce the most rubber-like copolymer, the activity of mixed of 1:1 w/w of the catalysts **A** and **B** in copolymerization of ethylene-propylene was 1,080 (g EPM/mmol Ni.h). The copolymer was colorless and the ethylene content,  $M_v$  and  $T_g$  of the copolymer were 59 %, 222,000 (g/mol) (run **10**, Table 2) and -54.3 °C, respectively.

## Conclusion

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**. Increasing the ethylene polymerization temperature increased the degree of branching of polyethylene whereas considerably decreased rubber-like behavior of obtained polymer. Ethylene-

propylene copolymerization was catalyzed with mixed of 1:1 w/w of  $\alpha$ -diimine nickel catalysts in the presence of MAO as cocatalyst. To obtain optimum conditions in copolymerization, variables of the Al/Ni molar ratio, temperature, relative pressure of monomers, total pressure and reaction time were studied. Activity of the catalytic system and  $M_v$  of the copolymers increased with increasing Al/Ni molar ratio while decreased with increasing temperature. Increasing the total pressure of monomers to 9 bars increased the  $M_v$  of copolymers linearly. Decreasing relative pressure of  $P_{Pr}/P_{Et}$  from 9:1 to 1:1 increased the ethylene contents of the copolymers from 51 % to 72 % while decreased the  $M_v$  of the product from 389,000 to 136,000 (g/mol). But suitable conditions for the preparation of ethylene-propylene copolymer with the desirable elastomeric like behavior was obtained at the Al/Ni molar ratio of 2,000, temperature of 20 °C,  $P_{Pr}/P_{Et}$  relative pressure of 5:1 and total pressure about 5 bars.

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