Polymerization of Ethylene Using a Series of Binuclear and a Mononuclear Ni (II)-Based Catalysts

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ABSTRACT: A novel series of homo-, bi-, and mononuclear Ni(II)-based catalysts (BNC_n $n = 1$–4, MNC_4) were used for ethylene polymerization. The optimum conditions for the catalyst BNC_4 (the highest catalytic activity) was obtained at [Al]/[Ni]=2000/1, $T_p = 42$ °C, and $t_p = 20$ min that was 1073 g PE/mmol Ni h. In theoretical study, steric and electronic effects of substituents and diimine backbone led to prominent influence on the catalyst behavior. The highest M_V was resulted from polymerization using BNC_4; however, the highest unsaturation content was obtained from BNC_1. GPC analysis showed a broad MWD (PDI = 17.8). BNC_1 and BNC_2 in similar structures showed broad peaks in DSC thermogram, while BNC_3 and BNC_4 with more electronic effects showed a peak along with a wide shoulder. Monomer pressure increasing showed enhancing in activity of the BNC_4, meanwhile a peak with shoulder to a single peak in DSC thermogram and uniformity in morphology of the resulted polymer were observed. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *54*, 3000–3011

KEYWORDS: branch; binuclear nickel complex; catalysts; α-diimine catalyst; FTIR; late transition metal catalysts; polyethylene (PE); structural study

INTRODUCTION Multinuclear catalysts are a class of multisite catalysts which can be multi- or monometallic center. During last decades, multinuclear catalysts have seen impressive progress.[1–7] Albeit mechanisms of these types of catalysts are still in ambiguous due to complexity of theirs function through the polymerization; however, there is two main supposed structure include cooperation and independent effect of active centers. Distance between the active centers and the presence of weakly basic substituents are two important factors that can control the cooperative effect of metal centers in olefin homo- and copolymerization of polar monomers, especially.[8–15] According to the literatures, multinuclear catalysts have shown various results in comparison to correspond mononuclear catalysts such as both lower and higher catalyst activity, bimodal to wide range molecular weights distribution, isotacticity, and microstructures.[16–23]

There are several structures in multinuclear catalysts containing metallocene and postmetallocene based and even combination of them.[24–28] The diversity of bridge between the metal centers has given more variety to these types of catalysts which can be rigid or flexible or even counter-ion of cocatalyst.[29–33] Homogenous late transition metal catalysts considered as being one of the interesting research fields in mono and multinuclear catalyst of the olefin polymerization due to their unique reactivity patterns and unusual catalytic properties such as producing branched polyethylene (PE) without any α-olefin comonomers and chemical stability due to less oxophilic properties.[34–40] Furthermore, the key feature of these catalysts is the symmetrical and unsymmetrical presence of ligands which effectively affect these catalysts behavior.[41,42] All this variety in structures can enhance by homo and heterometallic centers. In the most of these catalysts, presence of chelate ligands with aromatic rings cause increasing in thermal stability, performance and more steric and electronic effects.[43,44] There is some binuclear structure of diimine catalysts in Scheme 1 which are related to our work. Catalysts a and b were activated with methylaluminoxane (MAO) and produced PE oligomers and waxes with broad MWDs. Catalysts c, d, and e showed higher catalytic activities, producing higher molecular weight PE with higher degree of branching in comparison to mononuclear analogous.[26,45–48] Besides of all practical experiments, many articles about theoretical study on structures of the catalysts have been published. These studies can help researchers to better judge on the structures, mechanisms, performances

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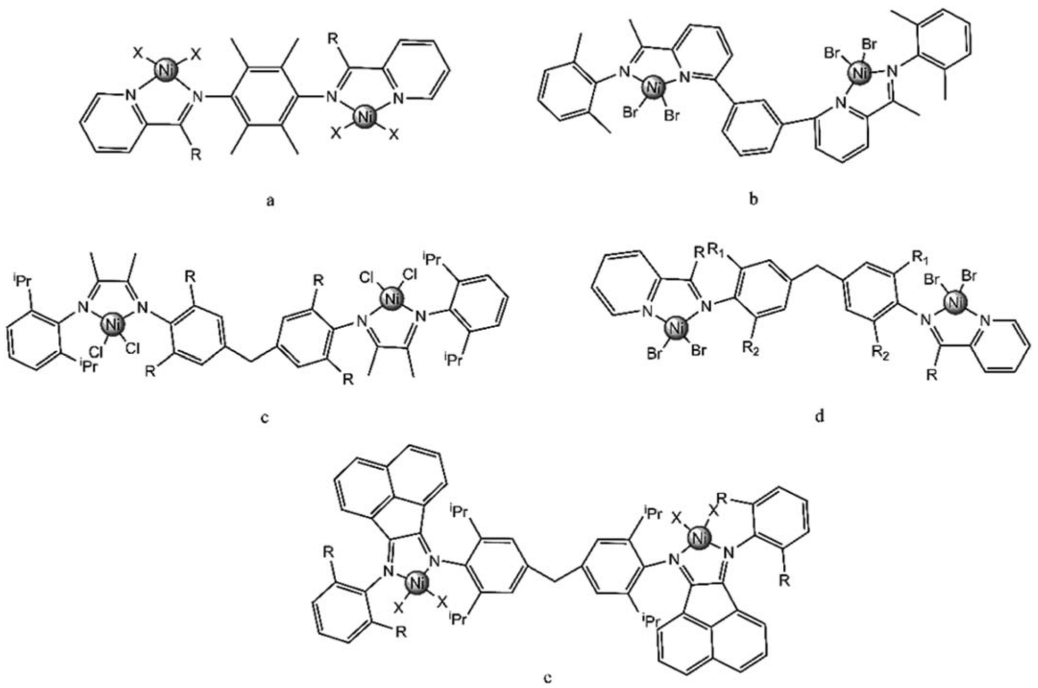


SCHEME 1 Some Reported Binuclear Diimine Ni(II)-Based Complexes.

and are useful to predict the best and the most stable configuration of the complexes.[49–53]

In this study, a novel series of homometallic Ni (II)-based binuclear catalysts (BNC$_n$ $n = 1$–4) with different structures and a mononuclear catalyst (MNC$_4$) were synthesized. These catalysts are used for polymerization of ethylene. Catalysts behavior and properties of the produced polymers were studied including dinuclearity effect such as synergistic and asymmetric structure in higher catalytic activity, higher PE molecular weight, branching, and broadening of MWD in comparison to the mononuclear analogous. Theoretical study on the structures of the catalysts was investigated and compared with practical results.

EXPERIMENTAL

Materials

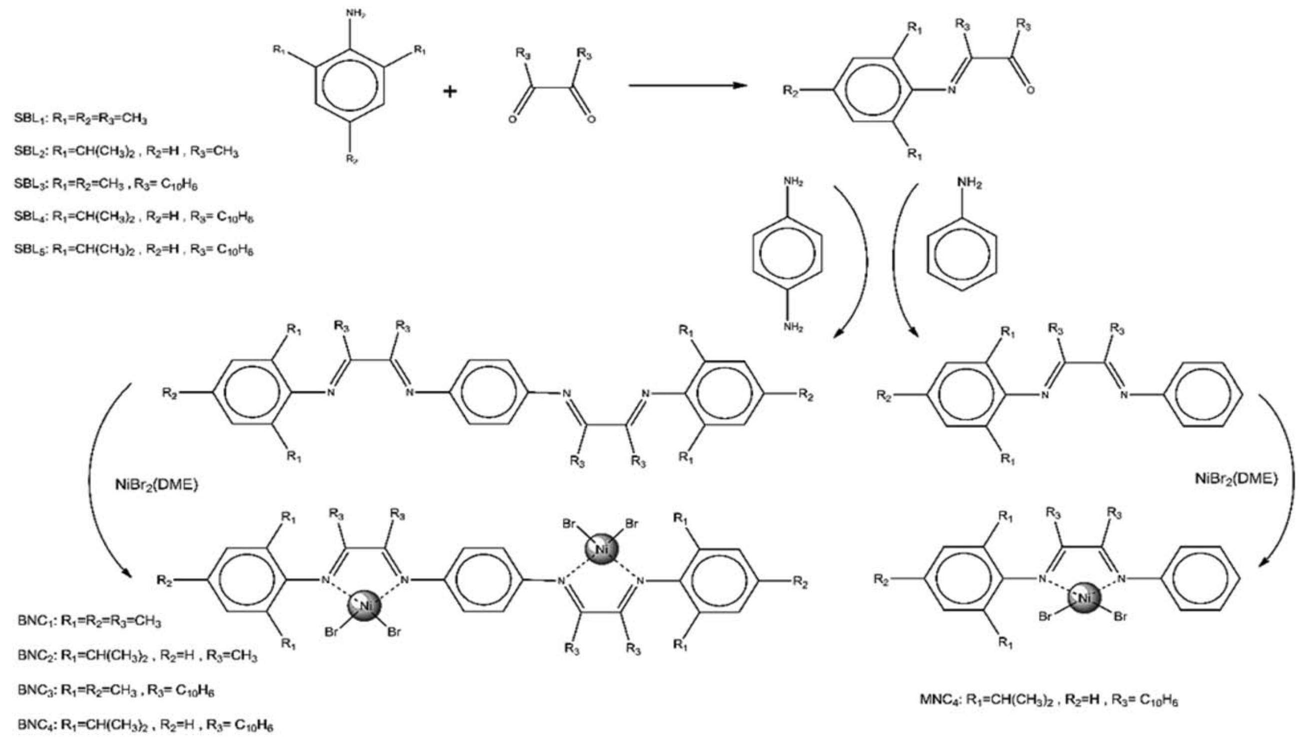
All manipulations of air and/or water sensitive compounds were conducted under argon or nitrogen atmosphere using the standard Schlenk techniques. All the solvents were purified before use. Toluene (purity 99.9%) (Iran, Petrochemical) was purified over sodium wire/benzophenone and used as polymerization media. Dichloromethane (purity 96%) (Sigma Aldrich Chemicals, Germany) and Methanol (Merck Chemical) was purified over calcium hydride powder and distilled before use in complex and ligand synthesis as solvent. Polymerization grade ethylene gas (purity 99.9%) (Iran, Petrochemical) was purified by passing through activated 4Å/13X molecular sieves column. Aniline, 2,4,6-trimethyl aniline, 2,6-diisopropyl aniline, 2,3-butanedione, 1,4-phenylene diamine, acenaphthoquinone, nickel (II) bromide ethylene glycol dimethyl ether complex [(DME) NiBr$_2$] (purity 97%) and diethyl ether (purity 99.5%) were supplied by Merck Chemical (Darmstadt, Germany) and used in synthesis of ligands and catalysts. Decaline (decahydronaphthalene) (purity 97%), chlorobenzene, and calcium hydride were purchased from Sigma Aldrich Chemicals (Steinheim, Germany). Triisobutylaluminum (purity 93%) was supplied by Sigma Aldrich Chemicals (Steinheim, Germany) which was used in synthesis of MAO according to the literature.[54]

Polymerization Procedure of Ethylene

The low-pressure polymerization process was carried out in a round-bottom flask which was equipped with Schlenk system, ethylene inlet, and magnetic stirrer, while the high-pressure process (more than 2 bars) was carried out using a 1-L Buchi bmd 300-type stainless steel reactor.

Characterization

^{1}H NMR, ^{13}C NMR, FTIR, and mass spectrums were recorded using Bruker AVANCE III-300, Thermo Nicolet AVATAR 370 and Varian CH-7A spectrometers, respectively. Elemental analysis was performed on a Thermo Finnigan Flash 1112EA microanalyzer. Total spectra of all new compounds are provided in the Supporting Information. The viscosity average molecular weight (M_v) of polymer samples was determined according to the literature.[55] Intrinsic viscosity [ŋ] was measured in decaline at 133 ± 1 °C using an Ubbelohde viscometer. M_v values were calculated according to Mark-Houwink equation, $\eta = KM_v^\alpha$ ($\alpha = 0.7$, $K = 6.2 \times 10^{-4}$). Differential scanning calorimetry (DSC) instrument (Mettler Toledo DSC822) with a rate of 10 °C/min instrument was used for polymer characterization. SEM images and GPC curve were resulted using LEO VP 1450 and Agilent PL-GPC220 instruments, respectively.



SCHEME 2 Synthesis Procedure of Ligands and Catalysts.

Synthesis of Ligands and Catalysts

The procedure of ligands (SBL_n $n = 1–5$) and complexes (BNC_n $n = 1–4$, MNC_4) synthesis are depicted in Scheme 2.

Synthesis of SBL_1 *{2,4,6-trimethyl-C_6H_2-N = C(CH_3)-(CH_3)C = N-C_6H_4-N = C(CH_3)-(CH_3)C = N-2,4,6-trimethyl-C_6H_2}*

To a stirred solution of diacetyl (5.3 mmol) and dichloromethane (15 mL) in a round-bottom flask which was placed in an ice bath, 2,4,6-trimethylaniline (5 mmol) was added dropwise in the presence of the catalytic amount of formic acid. The solution was stirred for 24 h. The ice bath was removed and a solution of 1,4-diaminophenyl (2.8 mmol) in dichloromethane (5 mL) was added dropwise. The mixture was stirred for another 24 h at room temperature. In both steps of the ligand synthesis, the reaction progress and consumption of the reactant was checked using TLC technique. The solid precipitate was washed with cold methanol several times, and the product was purified via column chromatography [10% ethyl acetate (EA)/*n*-hexane-silica gel]. The solvent was evaporated to afford the product with 60% yield.

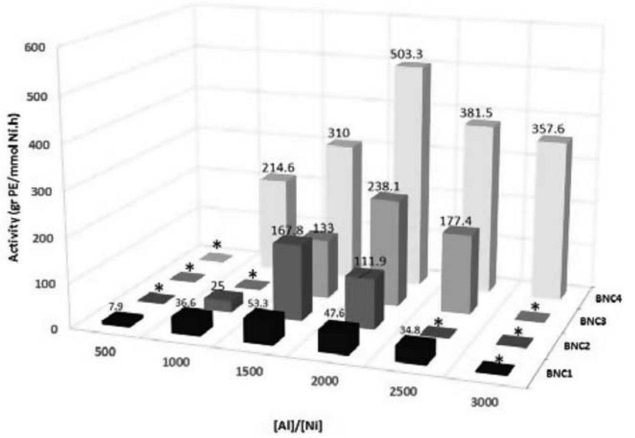


FIGURE 1 Clustered chart of BNC_n $n = 1–4$; activity versus [Al]/[Ni], polymerization condition: monomer pressure 1.5 bar, polymerization time 1 h, polymerization temperature 26 °C, mmol $BNC_n = 4.2 \times 10^{-3}$ mmol, *trace.

^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.2 (12H, s), 1.3 (6H, s), 2.1 (12H, s), 7.2 (4H, d), 7.3 (4H, s). ^{13}C NMR (300 MHz, $CDCl_3$, selected resonances, δ, ppm): 15.6, 16.4 (CH_3-C = N), 168.2 (C = N), 18.1, 18.6 (CH_3-Ar), 168.5 (C = N). MS (EI, *m/z*): 478 [M^+, 100%]. Anal. Calcd. for $C_{32}H_{38}N_4$: C, 80.3; H, 8.0; N, 11.7. Found: C, 80.5; H, 7.9; N, 11.5. FTIR (KBr, cm^{-1}): 1289 cm^{-1} (-C-N-), 1636 cm^{-1} (-C = N-).

Synthesis of SBL_2 *{2,6-diisopropyl-C_6H_2-N = C(CH_3)-(CH_3)C = N-C_6H_4-N = C(CH_3)-(CH_3)C = N-2,6-diisopropyl-C_6H_2}*

The preparation of ligand SBL_2 was similar to the method used for SBL_1 with 64% yield.

^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.2 (24H, d), 2.2 (12H, s), 2.8 (4H, q), 6.9 (4H, d), 7.2 (2H, t), 7.3 (4H, d). ^{13}C NMR (300 MHz, $CDCl_3$, selected resonances δ, ppm): 15.7, 16.6 (CH_3-C = N), 168.1 (C = N), 22.7, 23.2 ($CH(CH_3)_2$), 28.3, 28.5 ($CH(Me)_2$), 168.3 (C = N). MS (EI, *m/z*): 562 [M^+, 100%]. Anal. Calcd. for $C_{38}H_{50}N_4$: C, 81.0; H, 9.0; N, 10.0. Found: C,

TABLE 1 Properties of the Resulted PE Using BNC$_n$ $n = 1–4$

Entry	Catalyst	Melting Point (°C)	ΔH melt (Cal/g)	Crystallinity (%)	$M_v \times 10^{-4}$ (g/mol)	Amount of Vinyl (in 1000 C)	Degree of Branching (in 1000 C)
1	BNC$_1$	108.6	30.7	44.7	4.86	49.9	44
2	BNC$_2$	110.7	41.5	68.1	5.12	35.7	33
3	BNC$_3$	117.2	20.0	29.1	5.04	31.6	55
4	BNC$_4$	123.0	17.0	24.7	5.63	9.1	78

[a] Polymerization condition: [Al]/[Ni] = 1500/1, monomer pressure 1.5 bar, polymerization time 1 h, polymerization temperature 26 °C, mmol BNC$_n$ = 4.2×10^{-3} mmol.

81.3; H, 8.8; N, 9.7. FTIR (KBr, cm^{-1}): 1207 cm^{-1} (-C-N-), 1637 cm^{-1} (-C = N-).

Synthesis of SBL$_3$ *{2,4,6-trimethyl-C$_6$H$_2$-N = C-(C$_{10}$H$_6$)-C = N-C$_6$H$_4$-N = C-(C$_{10}$H$_6$)-C = N-2,4,6-trimethyl-C$_6$H$_2$}*

The preparation of ligand SBL$_3$ was similar to the method used for SBL$_1$ with 59% yield.

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 2.2 (12H, d), 2.4 (6H, s), 6.8 (4H, d), 7 (4H, s), 7.3 (4H, d), 7.4 (4H, t), 7.9 (4H, d). ^{13}C NMR (300 MHz, CDCl$_3$, selected resonances δ, ppm): 160.5 (C = N), 18.9, 19.2 (CH$_3$-Ar), 160.9 (C = N). MS (EI, *m*/*z*): 672 [M+, 100%]. Anal. Calcd. for $C_{48}H_{38}N_4$: C, 85.9; H, 5.7; N, 8.8. Found: C, 85.7; H, 5.3; N, 8.8. FTIR (KBr, cm^{-1}): 1274 cm^{-1} (-C-N-), 1646 cm^{-1} (-C = N-).

Synthesis of SBL$_4$ *{2,6-diisopropyl-C$_6$H$_2$-N = C-(C$_{10}$H$_6$)-C = N-C$_6$H$_4$-N = C-(C$_{10}$H$_6$)-C = N-2,6-diisopropyl-C$_6$H$_2$}*

The preparation of ligand SBL$_4$ was similar to the method used for SBL$_1$ with 64% yield.

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 1.2 (24H, d), 2.8 (4H, q), 2.1 (6H, s), 6.7 (4H, d), 7.3 (4H, d), 7.4 (2H, t), 7.9 (4H, t), 8.1 (4H, d), 8.3 (4H, d). ^{13}C NMR (300 MHz, CDCl$_3$, selected resonances δ, ppm): 161.3 (C = N), 24.3, 23.3 (CH(CH$_3$)$_2$), 29.4, 29.7 (CH(Me)$_2$), 160.8 (C = N). MS (EI, *m*/*z*): 756 [M+, 100%]. Anal. Calcd. for $C_{54}H_{50}N_4$: C, 85.9; H, 6.7; N, 7.4. Found: C, 85.8; H, 6.4; N, 7.1. FTIR (KBr, cm^{-1}): 1274 cm^{-1} (-C-N-), 1646 cm^{-1} (-C = N-).

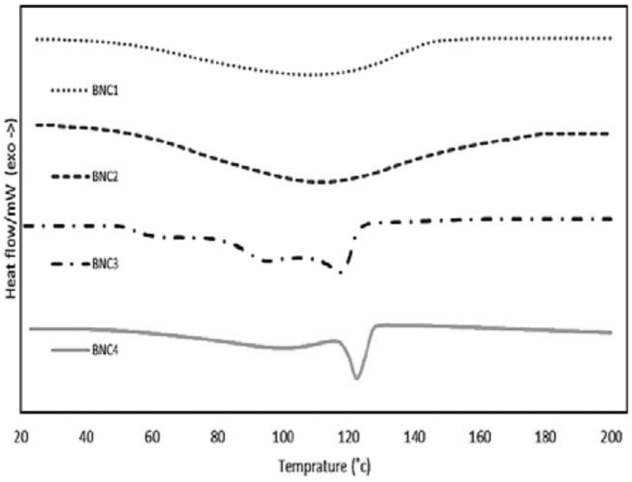


FIGURE 2 DSC thermograms of the resulted PE using the BNC$_n$ ($n = 1–4$), polymerization condition: as mentioned in Table 1.

Synthesis of SBL$_5$ *{2,6-diisopropyl-C$_6$H$_2$-N = C-(C$_{10}$H$_6$)-C = N-C$_6$H$_5$}*

To the first step obtained product of ligand synthesis, a solution of aniline (5 mmol) in 10 mL dichloromethane was added in the presence of formic acid as catalyst. The mixture was stirred for 24 h at room temperature. In both steps of the ligand synthesis, the reaction progress and consumption of the reactant was checked using TLC technique. The solid precipitate was washed with cold methanol several times and the product was purified via column chromatography [5% ethyl acetate (EA)/*n*-hexane-silica gel]. The solvent was evaporated to afford the product with 53% yield.

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 1.2 (12H, d), 2.7 (2H, q), 6.8 (2H, d), 6.9 (1H, t), 7.1 (2H, d), 7.2 (2H, t), 7.4 (1H, t), 7.7 (2H, t), 8.2 (2H, d), 8.3 (2H, d). ^{13}C NMR (300 MHz, CDCl$_3$, selected resonances δ, ppm): 161.1 (C = N), 24.9, 23.7 (CH(CH$_3$)$_2$), 29.1, 29.6 (CH(Me)$_2$), 160.6 (C = N). MS (EI, *m*/*z*): 416 [M+, 100%]. Anal. Calcd. for $C_{54}H_{50}N_4$: C, 86.5; H, 6.8; N, 6.7. Found: C, 86.1; H, 6.6; N, 6.7. FTIR (KBr, cm^{-1}): 1276 cm^{-1} (-C-N-), 1647 cm^{-1} (-C = N-).

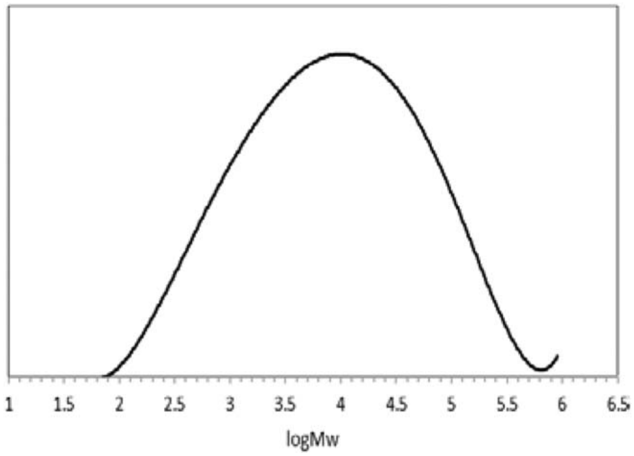
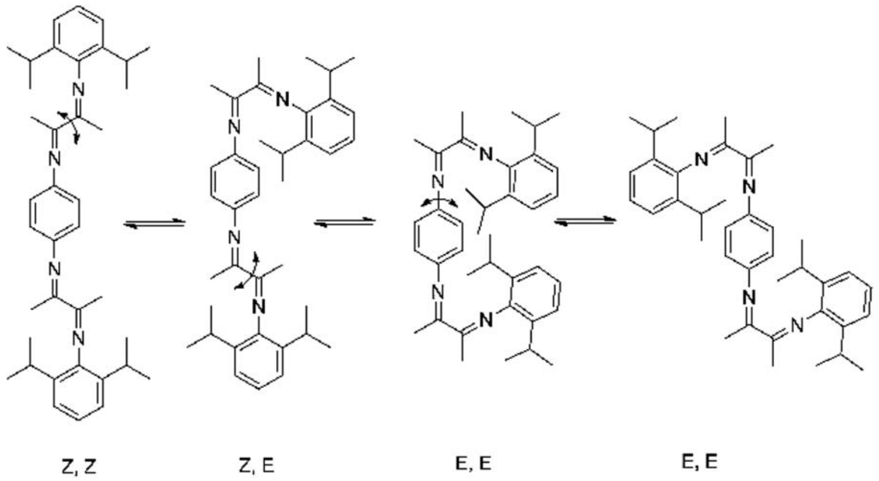


FIGURE 3 GPC curves of PE samples produced using BNC$_4$ catalyst.

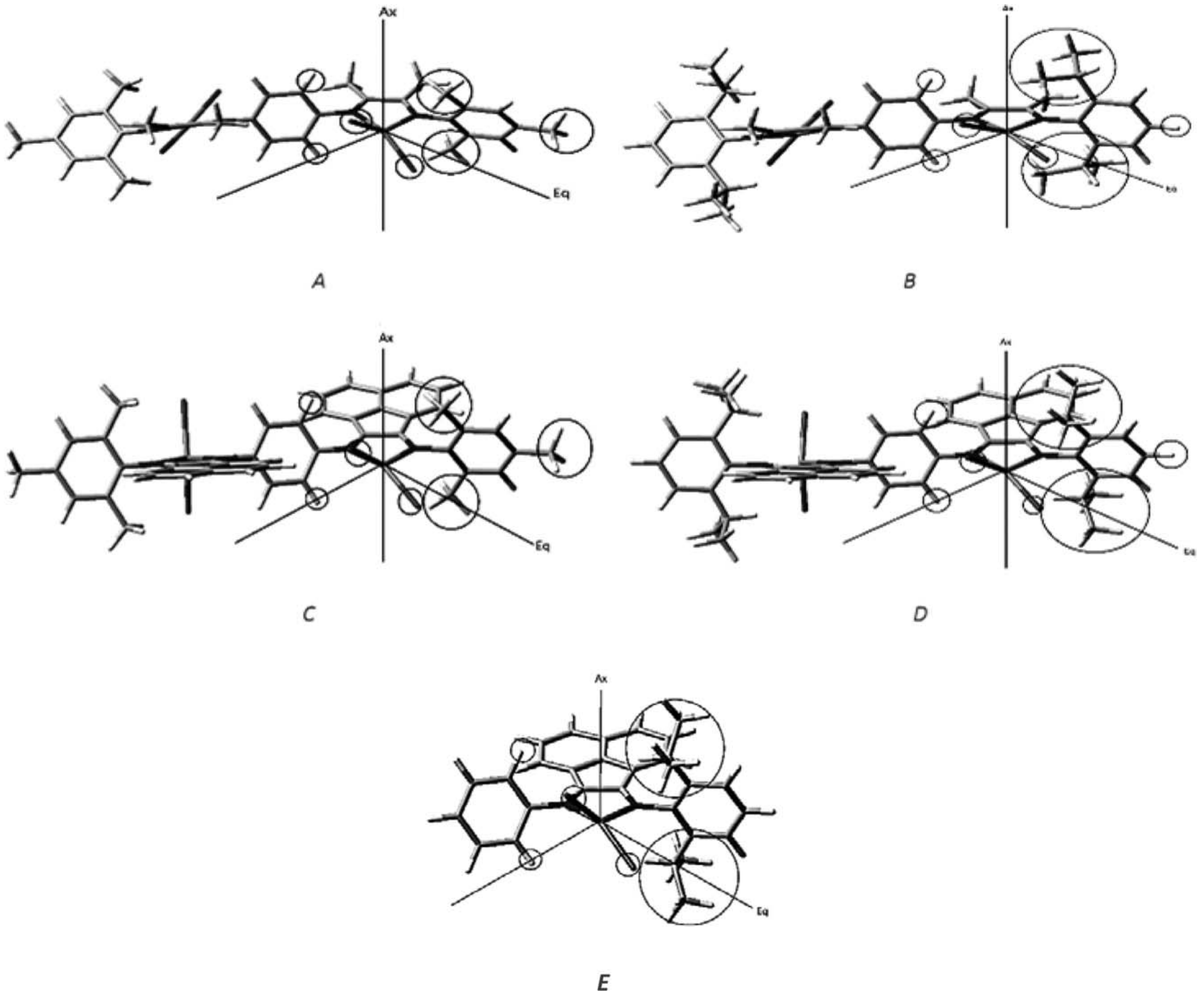
TABLE 2 Selected Bond Distances (A˚), Bonding Angle (°), Planes Angle, Dipole Moment, Band Gap, Mullikan Charge, Thermal and Free Energy of the BNC$_n$ $n = 1$–4 and MNC$_4$ Catalysts

Parameters	BNC$_1$	BNC$_2$	BNC$_3$	BNC$_4$	MNC$_4$
Ni—Br$_1$[a]	2.40	2.41	2.41	2.42	2.42
Ni—Br$_2$[b]	2.44	2.44	2.41	2.41	2.40
Ni—N$_1$[c]	2.03	2.03	2.33	2.34	2.05
Ni—N$_2$[d]	2.01	2.01	1.94	1.94	2.04
C=N	1.27	1.27	1.26	1.26	1.27
Ni—C$_1$[e]	4.31	4.28	4.25	4.25	4.21
Ni—C$_2$[f]	3.35	3.48	4.22	4.27	3.62
Ni—H$_1$[g]	3.39	3.40	3.71	3.64	4.16
Ni—H$_2$[h]	3.09	3.08	3.70	3.76	3.38
Br$_1$—Ni—Br$_2$	104.23	103.66	141.85	137.91	105.65
N—Ni—N	79.6	79.3	81.2	80.9	81.13
Ni—N—C (P$_s$[i])	121.27	120.86	130.43	131.33	124.36
Ni—N—C (P$_i$[j])	120.41	120.58	119.88	119.71	122.43
P$_{s1}$-P$_i$[k]	37.52	26.49	10.14	1.97	31.23
P$_{s2}$-P$_i$[l]	38.51	5.43	3.24	20.18	–
P$_{s1}$-P$_{s2}$	58.19	41.88	24.74	78.95	–
P$_{E1}$-P$_{E2}$[m]	145.6	166.63	172.59	173.46	–
Dipole moment (Debye)	8.30	8.35	8.47	8.61	18.04
Band gap (eV)	0.31	0.31	0.34	0.31	0.30
Charge of Mulliken on M	0.94	0.98	0.99	1.00	0.94
	0.95	0.96	0.98	0.96	–
Sum of electronic and thermal energies (e.u.)	−14,742.97	−14,976.85	−15,348.58	−15,582.48	−7906.49
Sum of electronic and thermal free energies (e.u.)	−14,743.10	−14,977.00	−15,348.73	−15,582.64	−7906.58

[a] Br$_1$: bromine atoms in front.
[b] Br$_2$: bromine atoms in behind.
[c] N$_1$: nitrogen atoms connected to the side aryl ring.
[d] N$_2$: nitrogen atoms connected to the middle aryl ring.
[e] C$_1$: carbon atom on *ortho*-position of side aryl ring (in front).
[f] C$_2$: carbon atom on *ortho*-position of side aryl ring (in behind).
[g] H$_1$: hydrogen atom on *ortho*-position of middle aryl ring (in front).
[h] H$_2$: hydrogen atom on *ortho*-position of middle aryl ring (in behind).
[i] P$_{s1}$: plane of the side aryl ring (right).
[j] P$_{s2}$: plane of the side aryl ring (left),
[k] P$_i$: plane of the middle aryl ring.
[l] P$_{E1}$: plane of the diimine (right).
[m] P$_{E1}$: plane of the diimine (left).



SCHEME 3 Example of Conformers SBL$_2$ Through Rotation Around C–N and C–C Bonds.



SCHEME 4 Optimized Structure of Catalysts; BNC_1 (A), BNC_2 (B), BNC_3 (C), BNC_4 (D), MNC_4 (E).

Synthesis of BNC_1 Catalyst

The procedure of catalyst synthesis was conducted under atmosphere of argon using the standard Schlenk techniques.

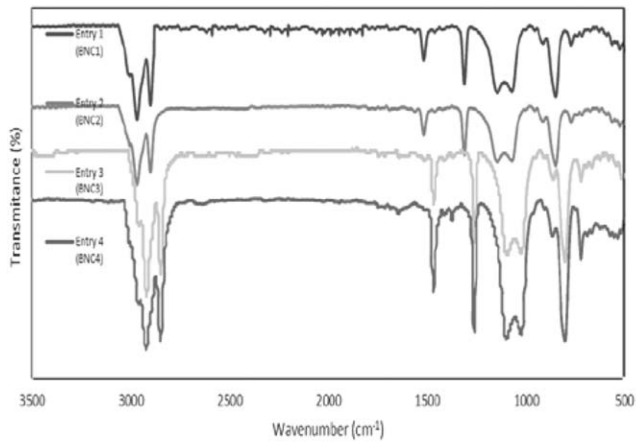
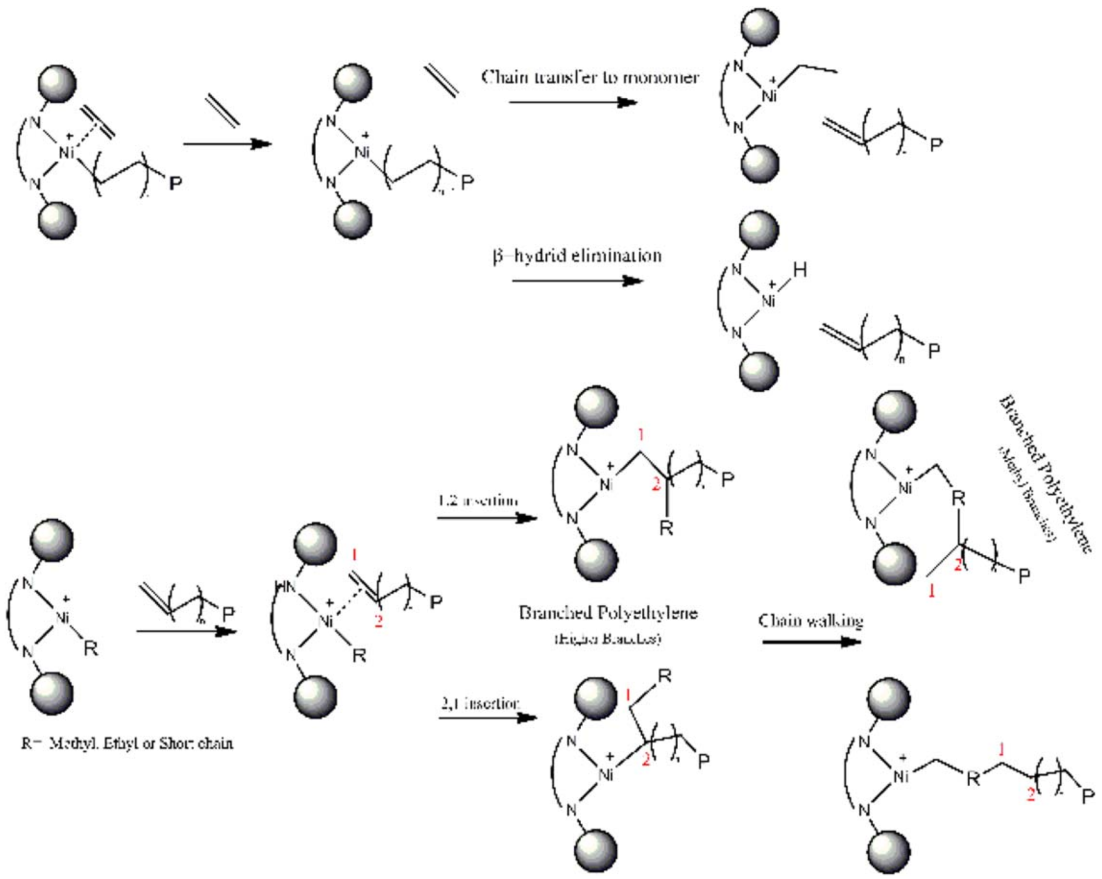


FIGURE 4 FTIR spectrums of the resulted PE using the BNC_n $n = 1–4$ catalysts.

Into a solution of dimethoxyethanenickel dibromide (DME) $NiBr_2$ (0.14 mmol) in dichloromethane (10 mL), a solution of Ligand SBL_1 (0.062 mmol) in dichloromethane (5 mL) was added dropwise. The mixture was stirred for 24 h at room temperature. The precipitation product was filtered and washed with Et_2O for several times. The solid product was collected after solvent evaporation. FTIR (KBr, cm^{-1}): the imine signal was shifted to weak field as it coordinated to the Ni atom; 1623 cm^{-1} (-C = N-). Anal. Calcd. for $C_{32}H_{38}Br_4N_4Ni_2$: C, 42.0; H, 4.2; N, 6.1. Found: C, 41.7; H, 4.0; N, 5.6.

Synthesis of BNC_2 Catalyst

The same method was employed for synthesis of BNC_2 as described in Synthesis of SBL_3 *{2,4,6-trimethyl-C_6H_2-N=C-($C_{10}H_6$)-C=N-C_6H_4-N=C-($C_{10}H_6$)-C=N-2,4,6-trimethyl-C_6H_2}* section. FTIR (KBr, cm^{-1}): the imine signal was shifted to weak field as it coordinated to the Ni atom; 1620 cm^{-1} (-C = N-). Anal. Calcd. for $C_{38}H_{50}Br_4N_4Ni_2$: C, 45.6; H, 5.0; N, 5.6. Found: C, 45.1; H, 4.6; N, 5.3.



SCHEME 5 A redrawn mechanistic route for catalytic polymerization, propagation versus β-H elimination, and chain branching.[75] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Synthesis of BNC_3 Catalyst

The same method was employed for synthesis BNC_3 as described in Synthesis of SBL_3 *{2,4,6-trimethyl-C_6H_2-N=C-($C_{10}H_6$)-C=N-C_6H_4-N=C-($C_{10}H_6$)-C=N-2,4,6-trimethyl-C_6H_2}* section. FTIR (KBr, cm^{-1}): the imine signal was shifted to weak field as it coordinated to the Ni atom; 1624 cm^{-1} (-C = N-). Anal. Calcd. for $C_{48}H_{38}Br_4N_4Ni_2$: C, 52.0; H, 3.5; N, 5.1. Found: C, 51.4; H, 3.3; N, 4.7.

TABLE 3 Polymerization of Ethylene Using the Catalyst BNC_4

Run	Time (min)	Temperature (°C)	Yield (g)	Activity (g PE/ mmol Ni h)
1	60	26	2.1	503.3
2	60	42	2.6	619.9
3	60	53	1.4	333.8
4	60	64	0.9	214.6
5	5	26	0.2	572.2
6	20	42	1.5	1,073.0
7	40	42	2.1	751.1
8	80	42	2.8	500.7

Polymerization condition: [Al]/[Ni]=2000/1, monomer pressure 1.5 bar, mmol $BNC_n = 4.2 \times 10^{-3}$ mmol.

Synthesis of BNC_4 Catalyst

The same method was employed for synthesis BNC_4 as described in Synthesis of SBL_3 *{2,4,6-trimethyl-C_6H_2-N=C-($C_{10}H_6$)-C=N-C_6H_4-N=C-($C_{10}H_6$)-C=N-2,4,6-trimethyl-C_6H_2}* section. FTIR (KBr, cm^{-1}): the imine signal was shifted to weak field as it coordinated to the Ni atom; 1623 cm^{-1} (-C = N-). Anal. Calcd. for $C_{54}H_{50}Br_4N_4Ni_2$: C, 54.4; H, 4.2; N, 4.7. Found: C, 53.8; H, 4.0; N, 4.3.

Synthesis of MNC_4 Catalyst

The same method was employed for synthesis BNC_4 as described in Synthesis of SBL_3 *{2,4,6-trimethyl-C_6H_2-N=C-($C_{10}H_6$)-C=N-C_6H_4-N=C-($C_{10}H_6$)-C=N-2,4,6-trimethyl-C_6H_2}* section. FTIR (KBr, cm^{-1}): the imine signal was shifted to weak field as it coordinated to the Ni atom; 1625 cm^{-1} (-C = N-). Anal. Calcd. for $C_{54}H_{50}Br_4N_4Ni_2$: C, 55.7; H, 4.4; N, 4.4. Found: C, 54.8; H, 4.3; N, 4.2.

RESULTS AND DISCUSSION

To investigate the effect of structure especially ortho substituent of the side aryl rings and adjacent group of diimines on the catalyst behavior, ethylene polymerizations were carried out using catalysts BNC_n $n = 1$–4 (Fig. 1) and MNC_4.

MAO was used as cocatalyst. Initial investigation showed that the catalyst BNC_4 have the highest activity among the

TABLE 4 Polymerization of Ethylene Using the Catalyst BNC_4

Run	Pressure (bar)	Yield (g)	Activity (g PE/ mmol Ni h)	Melting Point (°C)	ΔH_{melt} (Cal/g)	Crystallinity (%)	Amount of Vinyl (in 1000 C)	Branching (in 1000 C)
1	0.75	1.1	262.3	107.3	15.6	22.6	12.5	81
2	1.5	2.6	619.9	123.0	17.0	24.7	9.1	78
3	3	3.1	739.2	134.7	28.4	41.3	3.0	13
4	4.5	4.5	1073.0	128.0	30.7	44.6	7.6	11

Polymerization condition: [Al]/[Ni] = 2000/1, monomer pressure 1.5 bar, polymerization time 1 h, polymerization temperature 26 °C, mmol BNC_4= 4.2×10^{-3} mmol.

four prepared binuclear catalysts that was 503.3 (g PE/ mmol Ni h) in studied range. While correspond mononuclear BNC_4 catalyst (MNC_4) illustrated no activity in ethylene polymerization, Catalysts BNC_1, BNC_2, and BNC_3 were capable to polymerize ethylene with moderate activities (Fig. 1). Higher activity of BNC_4 denoted to the synergistic effect of dinuclearity and bulky group presence in comparison to no activity of MNC_4.

Polymer Characterizations

Thermal Properties

PE with the highest melting point was obtained using BNC_4 catalyst (123 °C) which showed the highest M_v as well, while the highest crystallinity (68.1%) was belong to the polymer obtained using BNC_2 catalyst (Table 1). The broad peaks in DSC of the polymers obtained using BNC_1, BNC_2 catalysts, and shoulders in BNC_3 and BNC_4 catalysts are related to the various crystallinity areas in the PE (Fig. 2). This area is resulted due to the polymerization in presence of the Ni (II) diimine-based catalysts that produced branched PE and binuclear type of these catalysts that increases this effect. To clarify, the broadening transition has been attributed to a sequence of melting followed by recrystallization steps of less ordered domains with the variable degrees of chain branching.[56,57]

Catalysts Structure and Polymer Properties

GPC analysis of the polymer obtained by BNC_4 catalyst (Fig. 3) showed a broad distribution of molecular weight with PDI= 17.8 ($M_w = 33{,}632.7$, $M_n = 1894.0$) which can attribute to difference in electronic environment around each active center.

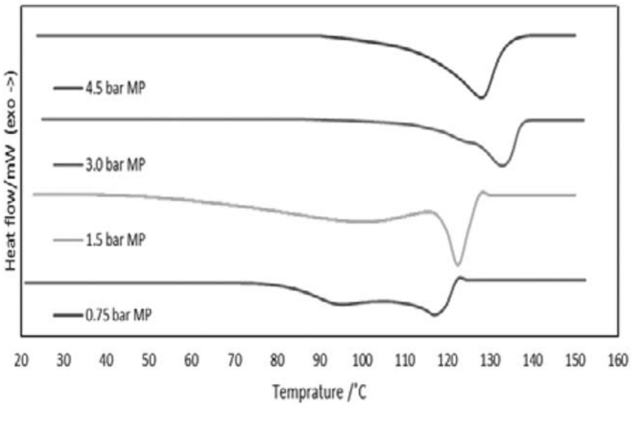


FIGURE 5 DSC thermograms of produced PE using BNC_4, polymerization condition as mentioned in Table 4.

Theoretical study on the optimized structures (Scheme 4) showed that there are more than one kind of active species during the polymerization such as the presence of an asymmetric centers which have impact on polymerization behaviors of the catalysts.[25,39,58,59] Furthermore, a suggested mechanism for the cooperative effect between the active centers can be considered as olefin or comonomer trapping occurred.[7,33] The highest viscosity average molecular weight was belong to the polymer obtained using BNC_4 catalyst. The behavior may have attributed to the presence substituents of aryl rings and adjacent diimine groups, which affect β-hydrogen elimination and any chain transfer reactions. Scheme 4 demonstrates *ortho*-positions with circles which bulky diisopropyl substituents (B,D) blocks the axial coordination sites.[38,60,61] Also bromine atoms in equatorial axis position that shown in Scheme 4 which generate a center for polymerization. *Para* substituents are characterized which have influence on the catalyst activity, molecular weights and extent of branching of polymer. The presence of methyl group instead of hydrogen can cause decreasing in activities and the average molecular weights of polymers.[62–64] Absence of the substituents in one side of MNC_4, which has less electronic and steric effects around the metal center, can cause decreasing in activity (E). In contrast, binuclears are more active than MNC_4 because of dinuclearity synergistic influence and more steric and electronic effects. Theoretical study of structure of the complexes confirmed obtained results from practical view of point (Table 2 and Scheme 4). Hartree-Fock (hf) method with 6–31g** basis set (by Gaussian 09W) was used to build up the structure and calculate the parameters. Computation performed by considering the possible conformers like foldamers (Scheme 3) and the most stable ligand structure after nickel coordination.[22,45,65] Results are depicted in the Scheme 4 and Table 2 including optimized structures, bond distances, bond angels, dipole moments, band gaps, Mullikan charges, sum of thermal, free and electronic energies. As it demonstrates that structure of the complexes have effects on the position of the atoms and the parameters, hindering and electronic impact of the bulky substituents are obvious in the Scheme 4 which axis blocked and electron withdrawing in retarding

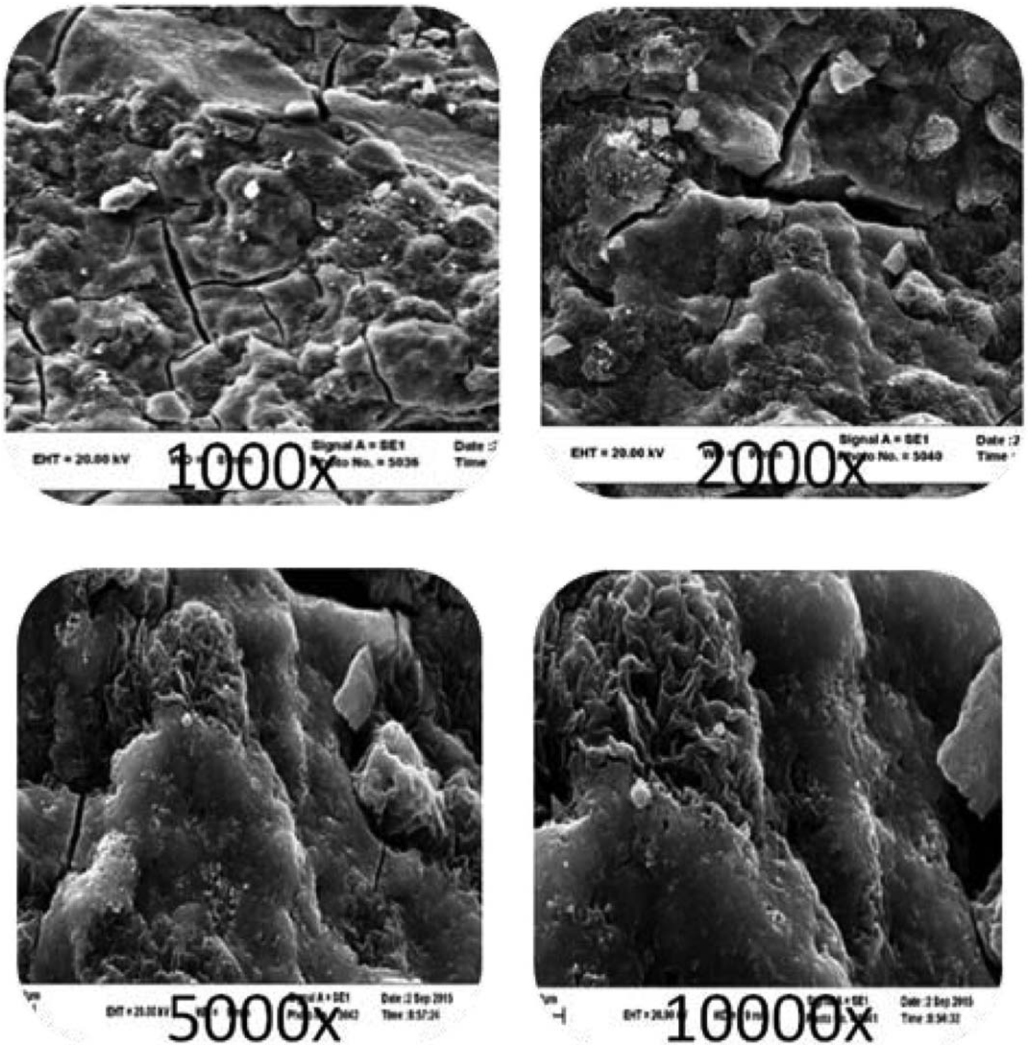


FIGURE 6 SEM images of the PE in low pressure (1.5 bar).

β-hydrogen elimination and the olefin trapping can cause to increasing of the activity and the average molecular weight.

Branching and Unsaturation Contents

As infrared spectrum of polymers illustrate in Figure 4, bands at 1377–83 cm^{-1} which assigned to the branching content by comparison to quantity of CH_3-end in HDPE (by subtracting a reference spectrum of HDPE).[66,67] To calculation vinyl amount in the PE, bands in the regions of 908 and 2019 cm^{-1} belong to vinyl and CH_2 groups were considered, respectively.[68] Unsaturation content in first sample (Entry 1) that was obtained using the catalyst BNC_1 is the highest one; 49.9 which shows more β-H elimination reaction (Scheme 5). Lower electronic effects of substituents on the ortho-position and adjacent diimine group which can cause to dissociation of the chain along with vinyl-end. In contrast, the highest degree of branching obtained by BNC_4 catalyst with more steric bulk and the highest hindering and electronic effects which can cause to reinsertion of micromonomer and produced PE with higher branches. Scheme 5 shows a predicted mechanism of propagation, β-hydride elimination, and branching.

Depending on the catalyst structure, the termination of chain growth occurred via β-H elimination, chain transfer to the monomer, or chain transfer to the cocatalyst and branching are due to reinsertion of vinyl-end chains (macro monomers) so called chain-walking mechanism allowing the growing center to migrate along the polymer chain.[69–74] As stated before, influence of structures and ligands on the polymerization behaviors of complexes are depicted using these circle signs.

Effect of Polymerization Conditions

Due to the high catalytic activity of the catalyst BNC_4, further studies have been focused on this catalyst. The effect of polymerization temperature and kinetics study of polymerization on the catalyst behavior (Table 3) confirmed the fact that polymerization temperature can enhance the catalyst performance through increasing in the kinetic energy of

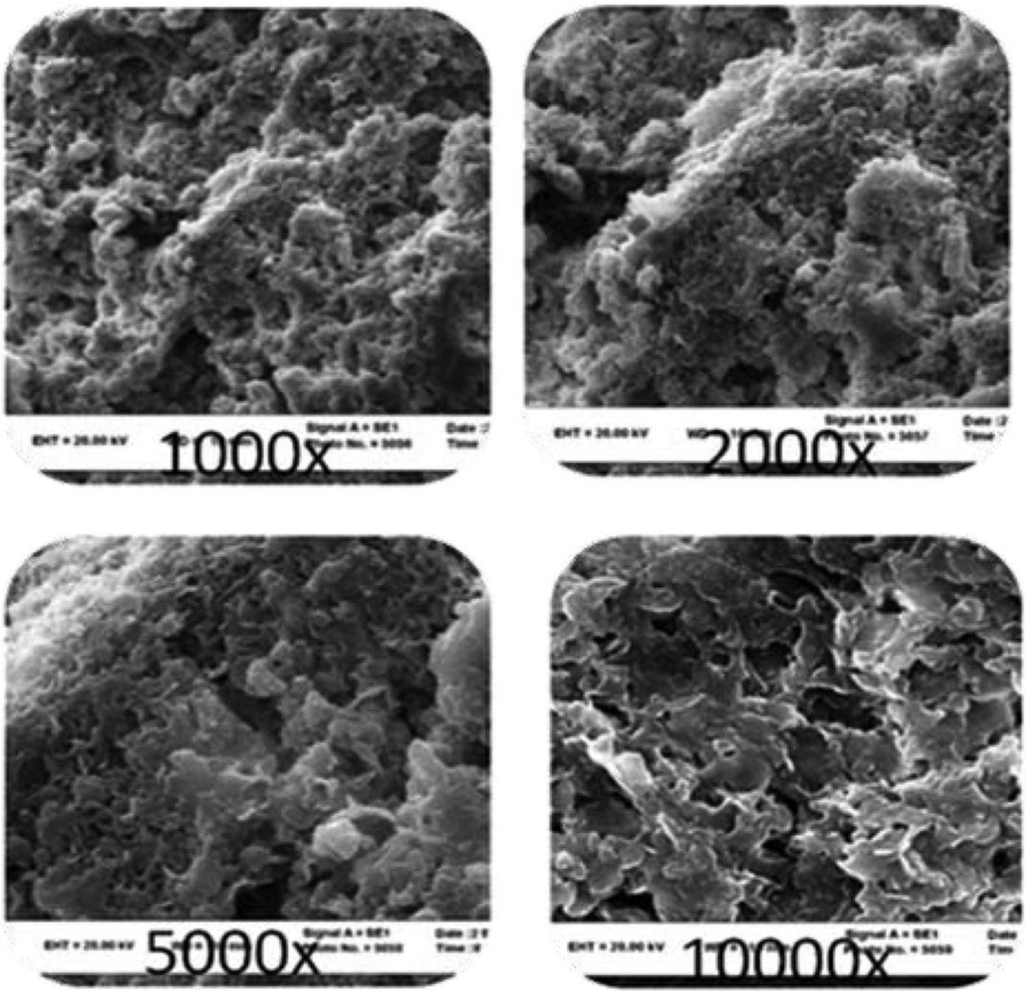


FIGURE 7 SEM images of the PE in high pressure (4.5 bar).

molecules which facilitates transfer of the monomer to the catalytic active centers and increasing alkylation reaction of metal centers (until 42 °C).[71] Polymerization temperature higher than 42 °C can cause irreversible deactivation of the active centers (chemical effect) and the reducing of solubility of monomer in solvent as a physical function to reduce activity of the catalyst.[72] Polymerization of ethylene in higher temperatures meanwhile (53 and 64 °C) yielded a rubber-like amorphous PE. Furthermore, the highest polymerization activity was obtained after 20 min of polymerization. Afterward, degradation and deactivation of active centers and encapsulation of the centers by the polymer chain to the metal which inhibit of insertion of monomer can cause to decreasing in catalyst activity.[52,60,61]

As monomer pressure increased, activity of the catalyst BNC_4 enhanced (Table 4) due to high concentration of the monomer close to the catalyst active centers which led to increasing of olefin trapping and reduction of branching extent.[61,74] The non-linear relationship between monomer pressure and activity was reported in the literatures.[75,76] In studied range, a promoting in catalyst productivity was obtained as monomer pressure increased, however, based on some literatures higher pressure can cause reverse effect on catalyst activity.[41,72,77] DSC thermograms obtained from catalyst BNC_4 (Fig. 5) indicated some uniformity in the crystallinity of obtained polymer. Study of the PE morphology in low and high pressure showed a uniformity in the morphology of the polymer meanwhile polymerization activity increased for catalyst BNC_4 (Figs. 6 and 7).

CONCLUSIONS

Synthesis, characterization, practical and theoretical study on structures and polymerization behaviors of a novel series of bi-nuclear (BNC_n, $n = 1–4$) and a mononuclear (MNC_4) Ni(II)-based catalysts in ethylene polymerization were presented. The BNC_4 catalyst showed the highest activity among the binuclear catalysts and its analogues mononuclear complex. Polymer architectures and catalyst activities were depending on the structures of the catalysts such that presence of bulky *ortho*-substituents on the side aryl rings and adjacent diimine groups led to promoting the catalysts productivity, increasing the viscosity average molecular weights, degree of branching in obtained polymers and also theoretical study confirmed these practical results. Furthermore, GPC and DSC analyses of resulted PEs in presence of BNC_4 catalyst illustrated a broad MWD due to cooperative effect of centers and a peak along with a shoulder in melting of crystallinity area in DSC thermograms. Increasing in monomer pressure led to more PE yield, uniformity, and regularity chain growth, which confirmed by DSC thermogram and caused a uniformity in SEM images.

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