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# FULL PAPER



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# Mono- and binuclear nickel catalysts for 1-hexene polymerization

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Saeid Ahmadjo, Department of Catalysis, Iran Polymer and Petrochemical Institute (IPPI), PO Box 14965/115, Tehran, Iran. Email: s.ahmadjo@ippi.ac.ir Polymerization of 1-hexene was carried out using a mononuclear (MN) catalyst and two binuclear (BN<sub>1</sub> and BN<sub>2</sub>)  $\alpha$ -diimine Ni-based catalysts synthesized under controlled conditions. Ethylaluminium sesquichloride (EASC) was used as an efficient activator under various polymerization conditions. The highly active BN<sub>2</sub> catalyst (2372 g poly(1-hexene) (PH) mmol<sup>-1</sup> cat) in comparison to BN<sub>1</sub> (920 g PH mmol<sup>-1</sup> cat) and the MN catalyst (819 g PH mmol<sup>-1</sup> cat) resulted in the highest viscosity-average molecular weight  $(M_v)$  of polymer. Moreover, the molecular weight distribution (MWD) of PH obtained using BN<sub>2</sub>/EASC was slightly broader than those obtained using BN<sub>1</sub> and MN (2.46 for BN<sub>2</sub> versus 2.30 and 1.96 for BN<sub>1</sub> and MN, respectively). These results, along with the highest extent of chain walking for BN2, were attributed to steric, nuclearity and electronic effects of the catalyst structures which could control the catalyst behaviour. Differential scanning calorimetry showed that the glass transition temperatures of polymers were in the range - 58 to -81 °C, and broad melting peaks below and above 0 °C were also observed. In addition, longer  $\alpha$ -olefins (1-octene and 1-decene) were polymerized and characterized, for which higher yield, conversion and molecular weight were observed with a narrower MWD. The polymerization parameters such as polymerization time and polymerization temperature showed a significant influence on the productivity of the catalysts and  $M_v$  of samples.

#### **KEYWORDS**

binuclear, chain walking, cooperative effect, late transition metal, poly(1-hexene)

# **1** | **INTRODUCTION**

Today, it is known that polyolefins play a significant role in human life. The production of these polymers, particularly highly branched polyolefins, is growing progressively.<sup>[1–3]</sup> For many applications, polyethylene, polypropylene and poly( $\alpha$ -olefin)s with long-chain branches have significant features. For instance, poly(1-hexene) and poly(1-octene) depending on their molecular weight and due to their mechanical, thermal and chemical strengths, low toxicity, appropriate fatigue properties, good resistance to plasticizer migration and low cost have numerous applications as lubricants, adhesives, waxes and oils, primers, drag-reducing agents used in oil pipe-lines, electrical insulators, etc.<sup>[4–8]</sup>

There are some reports on the polymerization of 1hexene using various types of catalysts.<sup>[9–17]</sup> In this regard, for example, the microstructure of poly(1-hexene) obtained using  $\alpha$ -diimine nickel catalysts was investigated by Sivaram and co-workers,<sup>[14]</sup> and a polymer structure with methyl, butyl and long-chain branches was demonstrated. Moreover, Nakata et al. reported the synthesis of poly(1-hexene) with a narrow molecular weight distribution (MWD) and high stereospecific index (95%) using Hf-based metallocene/methylaluminoxane catalytic system.<sup>[15]</sup> Our group has reported recently on highmolecular-weight poly(1-hexene) and its use in oil pipelines as a drag-reducing agent.<sup>[8,16]</sup> Study of the backbone of ligands of amine-imine nickel catalysts<sup>[16]</sup> indicated that steric hindrance led to selectivity of 1,2-insertion along with chain walking, causing the production of amorphous poly(1-hexene), while a less crowded structure on the backbone with 2,1-insertion resulted in polyethylene.<sup>[17]</sup> Furthermore, semicrystalline in comparison to mononuclear catalysts, the cooperative effect of binuclear palladium catalysts in polymerization of 1-hexene led to a low branching density level which could be attributed to higher chain walking ability (straightening of chain).<sup>[18,19]</sup> Contrary to mononuclear catalysts, the cooperative effect of multinuclear catalysts in olefin polymerization has a significant influence on the catalyst activity and microstructural features of the resulting polymer such as branching density, tacticity, molecular weight and unsaturation chain reinsertion.<sup>[20-24]</sup> The distance between the centres and the steric hindrance around the active sites are two main factors controlling the cooperative effect.<sup>[25–27]</sup> Moreover. the presence of aromatic bridges in binuclear catalysts leads to increasing thermal stability, and steric and electronic effects.<sup>[25-29]</sup> Marks and co-workers reported that binuclear complexes bearing rigid structure and proximate centres lead to higher productivities and methyl branch selectivity than their mononuclear analogues.<sup>[25]</sup> The results, which were confirmed by one- and twodimensional NMR observations, secondary agostic interaction, binding of monomer to the adjacent Ni centre and increasing high local concentration of monomer, could be attributed to the presence of the second metal centre, which, in turn, increased the chain walking.<sup>[24-30]</sup> Chen and co-workers also claimed a lower branching density for binuclear catalysts compared to mononuclear catalysts, which could be explained by the interaction of β-hydrogen and the second metal centre through the cooperative effect, which, in turn, increased the chain walking.<sup>[31]</sup> The effect of catalyst structure and reaction conditions on the chain walking mechanism was investigated by Guo et al.<sup>[32-34]</sup> For late transition metal catalysts based on nickel and palladium, before the second insertion of monomer, the reaction mechanism includes β-hydrogen elimination and an isomerization process.<sup>[32]</sup> The symmetry in the chelating ligand structure, steric hindrance and polymerization conditions such as temperature, pressure and monomer

concentration have an influence on the polymer microstructure.<sup>[35–46]</sup>

In continuation of previous work,<sup>[44]</sup> in the study reported here we synthesized and characterized a new binuclear catalyst and its mononuclear analogue and employed them in the polymerization of 1-hexene. The behaviour of the catalysts and the physical properties of the polymers such as average molecular weight, MWD, branching density and branching distribution as well as their thermal properties were investigated. The influences of catalyst structure, cooperative effect and polymerization conditions (monomer length, temperature, time and concentration of co-catalyst) on the polymer properties were also investigated.

# 2 | EXPERIMENTAL

# 2.1 | Materials

All manipulations of air-/water-sensitive compounds were conducted under Ar/N2 atmosphere using the standard Schlenk technique. All solvents were purified prior to use. Toluene from Iran Petrochemical Co. (99.9%) was purified over sodium wire/benzophenone, and used as polymerization medium. Dichloromethane (96%, Sigma-Aldrich Chemicals, Germany) and methanol (Merck Chemical Co.) as solvents were purified over calcium hydride powder and distilled prior to use in the synthesis of complex and ligand. Xylene was purchased from Merck Chemical Co. 1-Hexene, 1-ocetene and 1decene monomers were supplied by Mehr Petrochemical Company (Iran). 2,6-Diisopropylaniline, butanedione, 2,3,5,6-tetramethyphenyldiamine, acenaphthoquinone, nickel(II) bromide ethylene glycol dimethyl ether complex ((DME)NiBr<sub>2</sub>; 97%) and diethyl ether (99.5%) were supplied by Merck Chemical Co. (Darmstadt, Germany) and used in the synthesis of ligands and catalysts. Ethylaluminium sesquichloride (EASC; 97% purity) was supplied by Sigma-Aldrich Chemicals (Steinheim, Germany).

# 2.2 | Polymerization Procedure

The polymerization of 1-hexene, performed in a roundbottom flask, was carried out using a Schlenk system before and during the injections. It should be noted that 1-hexane monomer was purified prior to use. The monomer (10 ml) was injected to the flask containing 6 ml of solvent (toluene), and then the desired amounts of cocatalyst and catalyst were introduced into the flask. The poly(1-hexene) produced was precipitated and purified using acidic methanol (5%).

# 2.3 | Characterization

<sup>1</sup>H NMR, <sup>13</sup>C NMR and Fourier transform infrared (FT-IR) spectra were obtained using Bruker AC-300 and Thermo Nicolet AVATAR 370 spectrometers. Elemental and mass spectral analyses were performed with a Thermo Finnigan Flash 1112EA microanalyser and a Varian CH-7A spectrometer. The branching density and branching distribution of poly(1-hexene) were calculated according to the literature.<sup>[13,33,34]</sup> The insertion of 1-hexene monomer, which can be accomplished by 1,2- or 2,1-insertion, was calculated according to equation (1)<sup>[17,47]</sup>:

$$\%2, 1 = 166.7 - \frac{Br}{166.7} \tag{1}$$

where *Br* is the total branching density. For poly(1-octene) and poly(1-decene), the theoretical value (166.7) could be replaced by 125 and 100, respectively.

Moreover, the 1, $\omega$ -enchainment was calculated using the following equation<sup>[47]</sup>:

$$\%1, \omega = 1000 - \frac{aB}{1000} + 2B \tag{2}$$

where *a* is the number of pendant monomers chains and *B* is the overall branches. Intrinsic viscosity,  $\eta$ , was measured in toluene at room temperature using an Ubbelohde viscometer. Viscosity-average molecular weight ( $M_v$ ) values were calculated according to the Mark–Houwink equation<sup>[48,49]</sup>:

$$\eta = K M_{\rm v}^a \tag{3}$$

where the coefficients  $\alpha$  and *K* are 0.69 and 2.28 × 10<sup>-2</sup> ml g<sup>-1</sup>, respectively. Gel permeation chromatography (GPC) was conducted with an Agilent 1100 instrument using tetrahydrofuran as eluent, a refractive index detector at maximum temperature of 45 °C and a column with a diameter of 0.25 mm. Differential

scanning calorimetry (DSC) thermograms were recorded with a PerkinElmer DSC Q100 instrument.

#### 2.4 | Preparation of Ligands and Catalysts

The ligands (SL, SL<sub>1</sub> and SL<sub>2</sub>) and complexes (MN, BN<sub>1</sub> and BN<sub>2</sub>) were synthesized according to the procedure presented in Scheme 1. Experimental details including <sup>1</sup>H NMR, <sup>13</sup>CNMR, FT-IR and mass spectra and elemental analyses of ligands (SL, SL<sub>1</sub> and SL<sub>2</sub>) and complexes (MN, BN<sub>1</sub> and BN<sub>2</sub>) are provided in the supporting information.

#### 2.4.1 | Ligand SL

The procedure used was that according to Khoshsefat *et al.*<sup>[44]</sup> Yield 91%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 1.0 (12H, d), 1.3 (12H, d), 3.1 (4H, sep), 6.8 (2H, d) 7.4 (6H, m), 7.7 (2H, t), 8.3 (2H, d). MS (EI, *m/z*): 500 [M<sup>+</sup>, 100%]. Anal. Calcd for C<sub>36</sub>H<sub>40</sub>N<sub>2</sub> (%): C, 86.35; H, 8.05; N, 5.59. Found (%): C, 86.18; H, 7.98; N, 5.65. FT-IR (KBr, cm<sup>-1</sup>): 1271 (-C=N-), 1626 (-C=N-).

### 2.4.2 | Ligand SL<sub>1</sub>

The procedure used was that according to Khoshsefat *et al.*<sup>[44]</sup> Yield 72%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 1.1 (12H, d), 1.3 (12H, d), 2.3 (12H, s), 2.4 (12H, s), 3.1 (4H, sep), 7.1 (4H, d), 7.3 (2H, t). MS (EI, *m/z*): 618 [M<sup>+</sup>, 100%]. Anal. Calcd for C<sub>42</sub>H<sub>58</sub>N<sub>4</sub> (%): C, 81.5; H, 9.4; N, 9.1. Found (%): C, 80.9; H, 9.1; N, 9.5. FT-IR (KBr, cm<sup>-1</sup>): 1275 (-C-N-), 1644 (-C=N-).

#### 2.4.3 | Ligand SL<sub>2</sub>

The procedure used was that according to Khoshsefat *et al.*<sup>[44]</sup> Yield 67%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 1.0 (12H, d), 1.3 (12H, d), 2.2 (12H, s), 3.1 (4H, sep), 6.7 (4H, d), 7.3 (8H, t), 7.9 (4H, t), 8.2 (2H, d). MS (EI, *m/z*): 810 [M<sup>+</sup>, 100%]. Anal. Calcd for



SCHEME 1 Synthesis procedure for ligands and catalysts

ganometallic

 $C_{58}H_{58}N_4$  (%): C, 85.89; H, 7.21; N, 6.91. Found (%): C, 85.90; H, 7.09; N, 6.98. FT-IR (KBr, cm<sup>-1</sup>): 1279 (--C-N-), 1657 --C=N-).

#### 2.4.4 | Complex MN

The procedure used was that according to Khoshsefat *et al.*<sup>[44]</sup> FT-IR (KBr, cm<sup>-1</sup>): the imine signal was shifted to weak field as it coordinated to the Ni atom; 1625 (-C=N-). Anal. Calcd for C<sub>36</sub>H<sub>40</sub>Br<sub>2</sub>N<sub>2</sub>Ni (%): C, 60.12; H, 5.61; N, 3.89. Found (%): C, 59.89; H, 5.54; N, 3.91.

### 2.4.5 | Complex BN<sub>1</sub>

The procedure used was that according to Khoshsefat *et al.*<sup>[44]</sup> FT-IR (KBr, cm<sup>-1</sup>): the imine signal was shifted to weak field as it coordinated to the Ni atom; 1643 (—C=N—). Anal. Calcd for  $C_{42}H_{58}Br_4N_4Ni_2$  (%): C, 47,8; H, 5.5; N, 5.3. Found (%): C, 47.1; H, 5.3; N, 5.1.

# 2.4.6 | Complex BN<sub>2</sub>

The procedure used was that according to Khoshsefat *et al.*<sup>[44]</sup> FT-IR (KBr, cm<sup>-1</sup>): the imine signal was shifted to weak field as it coordinated to the Ni atom; 1652 (-C=N-). Anal. Calcd for C<sub>58</sub>H<sub>58</sub>Br<sub>4</sub>N<sub>4</sub>Ni<sub>2</sub> (%): C, 55.81; H, 4.68; N, 4.49. Found (%): C, 55.64; H, 4.21; N, 4.06.

## **3 | RESULTS AND DISCUSSION**

To study the catalyst structure, the polymerizations of 1-hexene were carried out using mono- and binuclear catalysts at different concentrations of EASC as co-catalyst (Table 1). As is evident from Table 1, an increase of the [AlNi] molar ratio leads to high value of conversion and productivity to an optimum value. The catalyst productivity, then, decreased due to the formation of inactive species of complexes.<sup>[50]</sup> The best [AlNi] molar ratios were 1000, 2000 and 1500 for the BN<sub>2</sub>, BN<sub>1</sub> and MN catalysts, respectively. Moreover, polymerization of higher  $\alpha$ -olefins (1-ocetene and 1-decene) was carried out at [AlNi] = 1000. The greater conversion of 1-octene than 1-decene is presumably for steric, diffusion and solubility reasons.<sup>[51]</sup>

The mechanism proposed for the higher level of enchainment followed by each insertion facilitated through the synergistic effect of adjacent second centre and optimum bulkiness is depicted in Scheme 2.<sup>[52]</sup> The represented Ni…X interaction suggested for the catalyst/co-catalyst complex formation is the same as that explained for methylaluminoxane or borate activation route.<sup>[53–55]</sup> Binuclear catalysts in most cases have shown the highest catalyst productivities and stabilities or even higher polymer molecular weights than their mononuclear analogues.<sup>[28,50,56,57]</sup> Similar behaviours were observed for the catalysts. For example, in comparison to catalyst BN<sub>1</sub>, catalyst BN<sub>2</sub> showed the highest

**TABLE 1** Results of  $\alpha$ -olefin polymerization using BN<sub>1</sub>, BN<sub>2</sub> and MN for various [AlNi] ratios<sup>a</sup>

| Entry | Catalyst                     | [AlNi] | Yield (g) | Conv. (%) | Productivity<br>(g mmol <sup>-1</sup> cat) | $M_{ m v}$<br>(× 10 <sup>5</sup> g mol <sup>-1</sup> ) |
|-------|------------------------------|--------|-----------|-----------|--|--|
| 1     | $BN_2$                       | 600    | 3.12      | 46.35     | 1248                                       | 5.92   |
| 2     | $BN_2$                       | 1000   | 5.93      | 88.11     | 2372                                       | 8.61   |
| 3     | BN <sub>2</sub>              | 1500   | 2.42      | 35.95     | 968  | 5.26   |
| 4     | BN <sub>2</sub>              | 2000   | 2.09      | 31.05     | 836  | 4.50   |
| 5     | BN2 <sup>b</sup>             | 1000   | 6.82      | 94.32     | 2719                                       | 10.65  |
| 6     | BN <sub>2</sub> <sup>c</sup> | 1000   | 6.41      | 86.15     | 2560                                       | 12.78  |
| 7     | $BN_1$                       | 1000   | 1.38      | 20.51     | 552  | 3.30   |
| 8     | $BN_1$                       | 1500   | 1.65      | 24.52     | 660  | 2.82   |
| 9     | $BN_1$                       | 2000   | 2.30      | 34.17     | 920  | 3.15   |
| 10    | $BN_1$                       | 2500   | 2.22      | 32.98     | 888  | 4.80   |
| 11    | MN                           | 600    | 1.75      | 26.02     | 700  | 3.21   |
| 12    | MN                           | 1500   | 2.18      | 32.39     | 871  | 1.15   |
| 13    | MN                           | 2000   | 2.05      | 30.46     | 819  | 1.94   |

 $a[catalyst] = 2.5 \times 10^{-3}$  mmol; polymerization temperature, 25 °C; polymerization time until gelation; 6 cm<sup>3</sup> of toluene used as solvent.

<sup>b</sup>Monomer: 1-octene.

<sup>c</sup>Monomer: 1-decene.



SCHEME 2 Brief proposed mechanism for facilitated insertions and enchainments

productivity and led to a higher molecular weight poly(1-hexene). The presence of acenaphthene group on C-C bond through the increasing of steric hindrance caused the reduction of N-Ni-N bond angle and blocking of axial sites by isopropyl groups. Moreover, the electron-withdrawing nature of the substituent and electron deficiency on the metal centre can cause an increase in the catalyst productivity. On the other hand, the steric effect on the catalyst backbone leads to a decrease of the chain transfer reactions and an increase of the molecular weight of the resulting polymer.<sup>[44,50,58-62]</sup> The synergistic effect of the structure and centres and high local monomer concentration around the active site of BN2 in comparison to MN led to higher catalyst productivity. This effect also caused the higher molecular weight of poly(1-hexene) as shown in Scheme 2. The productivity of both MN and BN<sub>1</sub> catalysts is affected by the backbone structure, while that of BN<sub>2</sub> increased due to the synergistic effect of the two metal centres.<sup>[26,49,50,63-65]</sup>

As evident from Table 2 and shown in Figure 1, the MWDs of the poly(1-hexene)s obtained using binuclear catalysts  $BN_1$  (2.30) and  $BN_2$  (2.46) are slightly broader than that of the poly(1-hexene)s obtained using MN (1.96). This can be attributed to the electronic effect around the metal centre of catalyst.<sup>[66]</sup> Sampson et al. also reported broader MWDs with multi-modal distributions

**TABLE 2** GPC results of obtained  $poly(\alpha$ -olefin) samples<sup>a</sup>

| Entry | $M_{\rm n}~(	imes~10^5~{ m g~mol^{-1}})$ | $M_{ m w}$ (× 10 <sup>5</sup> g mol <sup>-1</sup> ) | MWD  |
|-------|--|---|------|
| 2     | 1.99                                     | 4.9   | 2.46 |
| 5     | 4.69                                     | 7.03  | 1.50 |
| 6     | 5.49                                     | 7.65  | 1.39 |
| 9     | 0.88                                     | 2.08  | 2.30 |
| 12    | 0.95                                     | 1.87  | 1.96 |

<sup>a</sup>Polymerization conditions as Table 1.

for all polymers obtained using bimetallic zirconium catalysts compared to those obtained by monometallic catalysts.<sup>[11]</sup> It also can be suggested that the polymerization kinetics of bi- and multinuclear catalysts is complex and different from that of mononuclear catalysts.

Polymerization of 1-octene and 1-decene in the presence of BN<sub>2</sub> showed higher molecular weight and narrower MWD. By increasing the monomer length, as the insertion and enchainment can be much slower in comparison to short monomer and also higher electron density provided by the longer monomer, the chain transfer reaction can be suppressed and thereby molecular weights increased and MWD decreased.

Poly(1-hexene) microstructure (entries 2, 9 and 12 of Table 1) was investigated using <sup>1</sup>H NMR, <sup>13</sup>C NMR and FT-IR analyses (Figures S19-S27). Moreover, <sup>13</sup>C NMR spectra of poly(1-octene) and poly(1-decene) (entries 5 and 6) are included in the supporting information (Figures S28 and S29). The chemical shift values observed for the carbons of poly(1-hexene) are in agreement with those of other reports.<sup>[10,14,16,45,51]</sup> The signals observed in the region of 14 ppm are assigned to the methyl carbons of butyl or longer chain branches. Signals of  $(\omega$ -1)CH<sub>2</sub> carbons of the branches appear at 22.5–23.2 ppm.<sup>[14,16]</sup> Most of the carbon signals arising from a long branch appear near 30.00 ppm.<sup>[45]</sup> The lowfield peaks in the region 33.7-34.7 ppm can be a result of polymer tacticity, whereas the peak at 33.7 ppm maybe assigned to isotactic poly(1-hexene).<sup>[10,16]</sup> The peak observed at 37 ppm is related to the CH carbons associated with the branches in the polymer.<sup>[14,16]</sup> The poly(1-hexene) produced with catalyst BN<sub>2</sub> has lower branching density than that produced with catalyst BN<sub>1</sub> (Table 3). Similar behaviours were reported by Chen and co-workers.[45]

This observation may for two reasons: first, the electronic effect of acenaphthene group on the backbone that leads to fewer chain transfer reactions; and second, the



FIGURE 1 GPC curves of poly( $\alpha$ -olefin) s produced using BN<sub>1</sub>, BN<sub>2</sub> and MN catalysts

stronger synergistic effect resulted from chain walking.<sup>[11,26,45,67,68]</sup> Also, the poly (1-hexene) obtained in the presence of binuclear catalysts showed less chain branching than that obtained in the presence of mononuclear catalyst (MN). This result can be explained by the optimum bulkiness and synergistic effect owing to the presence of a second metal centre and plausible agostic interaction between the polymer chain and second centre, along with the greater chain walking (Scheme 2).<sup>[65,69,70]</sup>

The catalysts that have steric hindrance may favour 1,2-insertion due to sterically encumbered  $\alpha$ -olefins and repulsion with the substituents of the ligand. This trend is observed for the mononuclear catalyst bearing bulky substituents in the polymerization of 1-hexene, while for the binuclear catalysts, the 2,1-insertion ratio of monomer is greater. The rotation of N and N-aryl bonds in the binuclear complexes is possibly due to efficient agostic interaction which can stabilize the  $\pi$ -complex species.<sup>[18,71-73]</sup> Moreover, polymerization of 1-octene and 1-decene using the BN<sub>2</sub> catalyst showed the

monomer length is important in regard to high level of agostic interaction and distance between the centres.

Moreover, the steric repulsion between the inserted monomer and the substituents, backbone and bridge can control the rate-determining step of propagation, causing a specific insertion. The higher steric hindrance and stronger synergistic effect of  $BN_2$  is the reason for the greater extent of 2,1-insertion (Table 3).<sup>[18]</sup> In addition, re-enchainment for the binuclear catalysts is higher than that for the mononuclear analogue, leading to greater chain walking. This is owing to the electronic interaction between the metal centres and olefin oligomer/polymer chains.<sup>[24,65]</sup>

Chain walking is distinguished with the branching density, as the polymer chain contains butyl branches indicating less chain walking, whereas methyl and longchain branches ( $>C_4$ ) suggest greater chain walking. More chain walking for BN<sub>2</sub> in comparison to MN is attributed to the synergistic effect due to optimum bulkiness and presence of a second metal centre.<sup>[53,58]</sup> Moreover, the presence of acenaphthene group in BN<sub>2</sub> and

| Entry | BD <sup>b</sup> | BD <sup>c</sup> | Ме<br>(%) <sup>с</sup> | Et<br>(%) <sup>c</sup> | Pro<br>(%) <sup>c</sup> | Bu<br>(%) <sup>c</sup> | Long<br>(%) <sup>c,d</sup> | 1,2-ins.<br>(%) <sup>b</sup> | 2,1-ins.<br>(%) <sup>b</sup> | 2,6-en.<br>(%) <sup>b</sup> | 1,6-en.<br>(%) <sup>b</sup> | T <sub>g</sub><br>(°C) <sup>e</sup> |
|-------|-----------------|-----------------|------------------------|------------------------|-------------------------|------------------------|----------------------------|------------------------------|------------------------------|-----------------------------|-----------------------------|-------------------------------------|
| 2     | 115             | 113             | 29.7                   | 0                      | 2.2                     | 59.2                   | 8.9                        | 67.8                         | 32.2                         | 39.6                        | 44.7                        | -62.1                               |
| 9     | 117             | 116             | 19.0                   | 1.7                    | 3.2                     | 69.5                   | 6.6                        | 69.6                         | 30.4                         | 35.0                        | 43.5                        | -63.9                               |
| 12    | 136             | 131             | 26.8                   | 2.7                    | 1.8                     | 63.5                   | 5.2                        | 78.6                         | 21.4                         | 40.2                        | 37.7                        | -81.2                               |

**TABLE 3** Branching density and distributions of poly(1-hexene) samples (entries 2, 9 and 12 of Table 1)<sup>a</sup>

<sup>a</sup>Polymerization conditions as Table 1.

<sup>b</sup>Determined by <sup>1</sup>H NMR.

<sup>c</sup>Determined by <sup>13</sup>C NMR.

<sup>d</sup>Longer than C<sub>4</sub>.

<sup>e</sup>Determined by DSC.

the electronic effects lead to greater chain walking for  $BN_2$  than for  $BN_1$ , causing greater content of methyl and long branches (>C<sub>4</sub>) (Table 3).<sup>[14,18,74]</sup>

The FT-IR band at 723 cm<sup>-1</sup> representing butyl branches can confirm the NMR data. The stronger band in the region 723–725 cm<sup>-1</sup> for BN<sub>1</sub> and MN in comparison to BN<sub>2</sub> shows greater extent of butyl in microstructure.<sup>[16]</sup>

The broad melting points obtained when using the binuclear catalysts can be observed in the DSC thermograms of the samples shown in Figure S30 (supporting information). These thermal properties can be attributed to the sequence of melting points followed by recrystallization steps of less ordered domains with the variable degrees of chain straightening and branching.<sup>[18,75,76]</sup> The higher glass transition temperature of the poly(1hexene) obtained using catalyst BN<sub>2</sub> also confirmed this claim in relation to chain mobility.<sup>[77]</sup> Greater diversity and density in branching could lead to high chain mobility. For higher  $\alpha$ -olefins, higher linearity led to higher glass transition, melting area and melting point (Table 4). As a result, the affinity of binuclear catalysts for 1,2-insertion was increased by longer monomer length.

For the BN<sub>2</sub> catalyst, the effects of polymerization parameters were investigated at the optimum [AlNi] molar ratio. Polymerization of 1-hexene using BN<sub>2</sub> in the presence of EASC showed that EASC is an efficient activator leading to high catalyst productivity. The results are probably due to high alkylating and acid strength, causing more activation of metal centres.<sup>[41,64]</sup> Furthermore, the polymerization temperature can affect the activity of the catalyst. To clarify, a higher polymerization temperature improved the catalyst performance up to 25 °C (room temperature) (Figure 2a) through increasing the kinetic energy of 1-hexene, which facilitates the transfer of the monomer to the catalytic active centres and increases the alkylation reaction of metal centres. Irreversible deactivation of the active centres and reduction of monomer solubility at higher polymerization temperature lead to a reduction of the catalyst productivity.<sup>[71,78]</sup> For the MN catalyst, a same trend was observed; however, at 60 °C the mononuclear catalyst was almost



**FIGURE 2** 1-Hexene polymerization with  $BN_2$  catalyst under various conditions: (a) polymerization temperature; (b) polymerization time. Polymerization conditions: [catalyst] =  $2.5 \times 10^{-3}$  mmol, Al/Ni = 1000, 6 cm<sup>3</sup> of toluene as solvent with a time of 12 h (a) and at 25 °C (b)

inactive. This can be attributed to the high thermal stability of the binuclear catalyst.

The highest polymerization productivity was obtained after 12 h of reaction (Figure 2b), the conversion increasing with time. Degradation and deactivation of active centres and increasing viscosity of polymerization media inhibited the insertion of monomer and decreased the catalyst productivity.<sup>[79]</sup>

**TABLE 4**Microstructural and thermal properties of poly(1-octene) and poly(1-decene) samples<sup>a</sup>

| Entry | BD<br>(per 1000 C) <sup>b</sup> | Me<br>(%) | Et<br>(%) | Pr<br>(%) | Bu<br>(%) | ≥C <sub>6</sub><br>(%) | 1,2-<br>(%) | 2,1-<br>(%) | 1,ω<br>(%) | Т <sub>g</sub><br>(°С) <sup>с</sup> | Δ <i>H</i><br>(J g <sup>-1</sup> ) <sup>c</sup> | T <sub>m</sub><br>(°C) <sup>c</sup> |
|-------|---------------------------------|-----------|-----------|-----------|-----------|------------------------|-------------|-------------|------------|-------------------------------------|---|-------------------------------------|
| 5     | 88.2                            | 23.5      | 0         | 0.3       | 0         | 76.2                   | 70.5        | 29.5        | 40.0       | -59.6                               | 23.5  | 12.7                                |
| 6     | 80.3                            | 13.4      | 0         | 0.1       | 0         | 86.5                   | 80.3        | 19.7        | 30.8       | -58.3                               | 31.7  | 24.1                                |

<sup>a</sup>Polymerization condition as Table 1.

<sup>b</sup>Determined by <sup>13</sup>C NMR.

<sup>c</sup>Determined by DSC.

8 of 9 WILEY Organometallic Chemistry

# 4 | CONCLUSIONS

A mononuclear and two new binuclear *α*-diimine Nibased catalysts were prepared, characterized and used in polymerization of 1-hexene. Catalyst BN<sub>2</sub> showed the highest catalyst productivity which resulted in higher molecular weight and broader MWD of polymers in comparison to BN<sub>1</sub> and MN catalysts. The synergistic effect between the centres due to high local concentration of monomer at active-centre environment, efficient steric hindrance and electronic effects through optimum bulkiness are the reasons of these observations. These are also the reasons suggested for the pronounced chain walking of catalyst BN<sub>2</sub> due to higher methyl branch contents. The glass transition temperatures of the samples in relation to the microstructures were in the range -58 to -81 °C, and broadening the melting peaks showed that chain walking led to chain straightening and methyl branching, which, in turn, decreased the chain mobility. Polymerization of longer  $\alpha$ -olefins led to higher productivity and conversion. This result was along with higher molecular weight and narrow MWD. Lower branching densities and higher melting point and broader melting area were the further observations. Moreover, polymerization at higher temperature revealed the thermal stability of binuclear catalysts in comparison to the mononuclear analogue. Longer polymerization times, however, caused a higher catalyst productivity and  $M_{\rm v}$ .

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LEY Organometallic 9 of 9 Chemistry