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ORIGINAL PAPER

Highly active novel Ni-diimine pre-catalyst containing bis-ketimine ligand for the vinyl polymerization of norbornene

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Abstract Novel Nickel-diimine pre-catalyst (1NiBr$_2$) containing *N*,*N′*-bis(diphenylmethylene)-ethylenediamine ligand was able to quantitatively polymerize norbornene (NBE) into polynorbornene (PNBE) at 50 °C upon activation with methylaluminoxane (MAO). The monomer concentration governs the rate of reaction and the polymer characteristics. Thermal and spectral analysis revealed the polymerization pathway to occur via vinyl addition and not ring opening. The homopolymerization of 1-hexene or ethylene could not be achieved using 1NiBr$_2$/MAO catalyst system, but the presence of 1-hexene did not prevent the quantitative polymerization of NBE without 1-hexene incorporation. The characteristics of the polymers formed were found to be different in terms of solubility and molecular weight compared to those of the product generated by the homopolymerization of NBE in the absence of 1-hexene. Here 1-hexene acted as a chain transferring agent and control the molecular weight of PNBEs produced.

Keywords Vinyl addition · Polynorbornene · Diimine · Methylaluminoxane · Nickel · Single-site catalyst · Non-metallocene

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Dedicated to the late Prof. G. Sundararajan.

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Introduction

The synthesis of novel homogenous catalysts has been one of the most attractive topics of research in the field of olefin polymerization for the past three decades. The new generation group 4 metal catalysts for olefin polymerization, having non-metallocene ligands, have attracted the polyolefin researchers because of their possibility to produce tailor made polymers [1, 2]. Different group 4 metal complexes having alkoxides, aryloxides, amines, and imines were reported in the literature, which are capable of producing polymers in a controlled fashion [1–3]. Attention has been drawn toward the synthesis of diimine-based late transition metal catalysts after Brookhart and his coworkers used cationic Ni(II) and Pd(II) α-diimine-based system for the polymerization of olefins [4]. Subsequently Grubbs has reported the living polymerization of ethylene using phenoxy-imine based Ni(II) catalyst. These highly active, heteroatom-tolerant neutral late transition metal complexes produced high-molecular-weight polyethylene, polymerized functionalized olefins, and required no cocatalyst [5].

In general, cyclic olefins like norbornene (NBE) can be polymerized in three different ways, namely ring-opening metathesis polymerization (ROMP), cationic or radical polymerization, and vinyl-addition polymerization [6, 7]. Polynorbornene (PNBE) synthesized through ROMP consists of an unsaturated backbone and are freely soluble in various organic solvents at ambient temperature [8–11]. Cationic or radical polymerization of NBE produce PNBEs via 2,7-connectivity having low molecular weight [12–14]. Vinyl-addition polymerization of NBE produces completely saturated PNBEs that retain the bicyclic structure [6, 7]. Among the three different NBE polymerization pathways, vinyl-addition polymerization produce PNBEs with special properties such as high glass transition temperature (T_g), high thermal stability, low birefringence, excellent optical transparency, and good chemical resistance [15–19]. Vinyl-addition polymerization of the cyclic olefins (cyclobutene, cyclopentene, cyclooctene, norbornene, etc.) is possible by both metallocene and non-metallocene catalysts containing transition metals [6, 7, 20–34].

PNBE prepared by vinyl-addition polymerization find applications as a specialty polymer with high optical transparency, good mechanical strength, and heat resistance. The physical properties of PNBE, such as crystallinity, solubility, and T_g depend upon the polymerization conditions and the catalyst employed. The physical properties and the potential applications of these PNBEs also depend on its molar mass. In this paper, we discuss the synthesis of Ni-based diimine pre-catalyst and its catalytic activity toward NBE homo- and copolymerization; and the effect of chain transferring agent 1-hexene on produced PNBE's molecular weights eventually on its solubility.

Experimental section

Materials and general considerations

All reactions were carried out under dry and oxygen-free argon atmosphere using glove box or standard Schlenk techniques. Toluene and cyclohexane were distilled from sodium/benzophenone ketyl under argon prior to use. MAO was purchased as 10% (w/w) solution in toluene from Witco GmbH, Germany and was used after estimating the aluminum content. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using Bruker AV-400 spectrometer or Jeol GSX-400 spectrometer. ^{13}C NMR spectra of PNBEs were recorded with short pulse angle and long relaxation delay. Solid-state ^{13}C CPMAS NMR spectra of these PNBEs were acquired on a Bruker AV 400 spectrometer operating at 100 MHz, in zirconium rotor with a spinning rate of 7000 Hz and a total of 700 scans were collected. Molecular weights of the toluene soluble PNBEs were determined by Waters make gel permeation chromatography (GPC) instrument with Styragel columns (10^6, 10^5, and 10^3 Å columns connected in series) and a RI detector using toluene as eluent at a flow rate of 1.0 mL/min, with polystyrene standards as a reference. The Fourier transform infrared (FT–IR) spectra were recorded on Perkin-Elmer spectrum one FT–IR spectrometer model L120. Differential scanning calorimeter (DSC) measurements were done on a Stanton Redcrofts simultaneous thermal analyzer (781 series). Elemental analysis was carried out on a Perkin–Elmer 2400 model CHNS analyzer. Wide angle X-ray diffraction measurements for PNBE powders were performed using a Phillips X-ray diffractometer, with monochromatic radiation at a wavelength of 1.5426 Å.

Synthesis of *N*,*N*′-bis(diphenylmethylene)-ethylenediamine (BDPEDA) ligand (**1**)

The bis-ketimine ligand *N*,*N*′-bis(diphenylmethylene)-ethylenediimine (**1**) was synthesized as follows. Benzophenone (18.22 g, 0.1 mol) and ethylenediamine (3 g, 0.05 mol) were dissolved in 100 mL of toluene and refluxed for 48 h under acidic conditions. After completion of the reaction, the solvents were removed under reduced pressure. The resulting light yellow colored solid was dissolved in chloroform and washed with saturated $NaHCO_3$ solution (3 × 50 mL). The organic portions were dried over anhydrous Na_2SO_4 and evaporated to give white crystalline solids. This crude product was purified by column chromatography using hexane–ethyl acetate (90:10) mixture. The final yield is 58%. The resulting compound was re-crystallized from pentane to get white spongy crystals. The compound was characterized thoroughly by NMR, mass, and IR spectral techniques.

BDPEDA: Nature = white spongy crystalline solid; melting point = 117 °C; Mass: 388 (Parent ion peak), 368, 342, 279, 256, 243, 228, 213, 194, 196, 158, 149, 129, 116, 95, 91 (100% base peak), 69; IR (KBr, cm^{-1}): 1622 (C=N str). ^{1}H NMR (400 MHZ, $CDCl_3$): δ 7.1–7.6 ppm (m, 10 H, Ar), 3.7 ppm (s, 4H, CH_2–CH_2).

Preparation of nickel diimine catalyst $1NiBr_2$

General procedure for the synthesis of $1NiBr_2$ is as follows. Into a 100 mL flame-dried round bottomed flask, 2 g of diimine ligand **1** (7.73 mmol), 2.36 g of $NiBr_2$.DME (7.73 mmol), and 50 mL dichloromethane were charged and stirred at room temperature for 18 h. After completion of the reaction, dichloromethane was evaporated and diethyl ether was added. The resulting purple color precipitate was separated by removing diethyl ether through double tipped needle.

In order to get pure catalyst system, the above obtained purple color catalyst was dissolved in minimum amount of dichloromethane and re-precipitated in dry diethyl ether. The resulted purple color catalyst was dried under reduced pressure and stored in an inert atmosphere.

Elemental analysis, Calculated (%): C = 55.63, H = 4.00, N = 4.63; Found (%): C = 55.68, H = 4.09, and N = 4.61

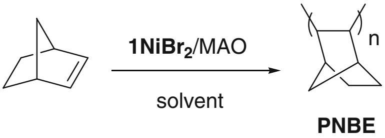
$$\text{EIMS}: m/z = 446\ (\text{M}^+ - 2\text{Br})$$

Polymerization of norbornene

Into a 100 mL flame-dried round bottom flask, 5 mg of pre-catalyst $1NiBr_2$, 2 g of norbornene, and 5 mL of cyclohexane or toluene were taken. Polymerization was initiated by adding appropriate amount of MAO to the above reaction mixture. The reaction mixture was stirred at desired temperature for the required time. The polymerization reaction was quenched by pouring this viscous mass into 100 mL of acidified methanol. The precipitated polymer was filtered, washed with methanol, and dried in vacuum at 80 °C for 24 h (Scheme 1)

Results and discussion

We have synthesized BDPEDA ligand diimine ligand *N*,*N'*-bis(diphenylmethylene)-ethylenediimine (**1**) by reacting benzophenone and ethylenediamine as shown in Scheme 2. This diimine ligand was complexed with (DME)$NiBr_2$ to produce a novel violet colored $1NiBr_2$ pre-catalyst (Scheme 2). Formation of the complex was confirmed by spectral and elemental analysis. NBE polymerization was carried out by using $1NiBr_2$ in combination with MAO under different reaction conditions by varying solvent, temperature, dilution, and Al/Ni ratio. Optimization of Al/Ni ratios was done in order to find the value that affords the highest catalytic activity and the value was found to be 100. It is thus very interesting to note that a quantitative conversion of NBE to PNBE could be achieved in 1 h by using Al/Ni ratio of 100. Usually, it is known from the literature that very high Al/metal ratios are required for better catalytic activity [35, 36]. Whereas, in this case, when the ratio was increased further, a decrease in the catalyst activity (Table 1) was observed, probably due to leaching of the metal from the ligand framework. In these polymerization reactions, we observed that the monomer concentration had a significant impact over the polymer productivity (Table 2). Quantitative yields were obtained when the reaction was carried out with a NBE concentration of 0.4 g/mL



Scheme 1 Homo-polymerization of norbornene

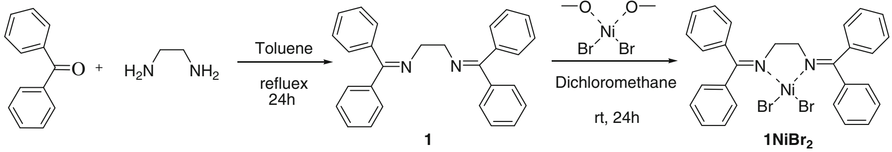
in toluene. When the NBE concentration was reduced to 0.2 g/mL then the yield dropped to 57.5%, on further reduction to 0.1 g/mL the yield dropped sharply as low as 6%. The decrease in catalyst activity with dilution is due to decrease in the concentration of both monomer and catalyst [29, 36, 37]. The charge separation between the contact ion-pair, i.e., the cationic Ni and anionic Al that formed upon activation of the Ni complex with MAO gets widened at higher dilution and thus the reactivity toward NBE becomes poor.

The polymerization reactions were carried out in toluene at two different temperatures namely 25 and 50 °C. The polymers obtained at 50 °C exhibits free solubility in cyclohexane and chlorobenzene and in toluene they were found soluble only at 70 °C. Upon changing the polymerization temperature to 25 °C, the polymer obtained did not dissolve in the above three solvents even after heating to 70 °C. The change in the solubility of the PNBE formed with respect to the polymerization temperature suggested structural changes in the polymers obtained. Upon changing the polymerization medium to cyclohexane the obtained PNBE exhibited an exactly opposite trend (in terms of solubility vs. polymerization temperature). Indeed the polymer sample obtained in cyclohexane at 25 °C showed free solubility in cyclohexane and chlorobenzene but were soluble in toluene only at above 70 °C, whereas the PNBE produced in cyclohexane at 50 °C did not dissolve in the above three solvents even after heating to 70 °C. Apparently, the solubility of the sample formed is an indication of their structural features such as stereo-regularity and molecular weight. Freely soluble PNBEs indicate lower stereo-regularity [32]. From this, it is clear that the polymer structural features depend upon polymerization temperature and the solvent employed.

Thus, it is observed that the molecular weight of these PNBEs vary to a large extent with temperature and solvent. When we have done the polymerization in cyclohexane solvent, temperature enhanced the rate of polymerization there fore favoring the propagation that lead to insoluble higher molecular weight polymers.

Effect of 1-hexene

This $1NiBr_2$/MAO catalyst did not show any activity toward 1-hexene homopolymerization (Table 3). When NBE polymerization was carried out with $1NiBr_2$/MAO in the presence of 1-hexene, the obtained polymer is freely soluble in cyclohexane, chlorobenzene, and toluene at room temperature. The spectral studies of the resultant polymer did not show any incorporation of 1-hexene thus confirm the absence of copolymer formation during this process [24]. Here the role of



Scheme 2 Synthesis of diimine-based nickel catalyst $1NiBr_2$

Table 1 Polymerization of NBE in toluene using $1NiBr_2$/MAO catalyst system

Run	Al/Ni ratio	Reaction temperature (°C)	Reaction period (h)	Yield (%)	Activity (kg PNBE/mol Ni/h)
1	10	25	72	3.0	0.1
2	10	50	20	7.8	1.0
3	50	50	20	28.5	3.6
4	100	50	0.5	52.7	264
5	100	50	1	99.1	248
6	200	50	1	71.5	178
7	300	50	1	67.8	170
8	400	50	1	64.0	160

Polymerization conditions: 2 g of NBE; 5 mg (8 μmol) of pre-catalyst, toluene = 5 mL

Table 2 Effect of dilution on polymerization

Run	Concentration of NBE (g/mL)	Yield (%)	Activity (kg PNBE/mol Ni/h)
9	0.4	89	222
10	0.2	57.5	144
11	0.1	6	15

Polymerization conditions: 2 g of NBE, 5 mg (8 μmol) of pre-catalyst; Al/Ni ratio 100; polymerization period 1 h, polymerization temperature = 25 °C, solvent = toluene

1-hexene is limited to the molecular weight of the sample favoring the transfer reaction [26].

Norbornene polymerization reactions were carried out with different amounts of 1-hexene. There was no drastic change in the activity up to 20 mol% of 1-hexene in the reaction mixture. Sharp decrease in the polymerization activity was observed upon increasing the 1-hexene content beyond 20 mol%. Polymerization reaction was not taken place when 1-hexene content exceeded 75 mol% in the reaction mixture. Due to these chain transfer reactions, molecular weight of these polymer samples were low and are soluble in different solvents at room temperature. The PNBEs formed under these conditions did not show any glass transition temperatures (T_g). As these polymers are freely soluble in toluene at room temperature, we determined their molecular weight using GPC. GPC traces are shown in Fig. 1.

Polymer characterization

These PNBEs prepared in the presence/absence of 1-hexene were characterized by spectral (NMR, IR) and thermal (DSC, Thermogravimetric analysis (TGA)) analysis. Figure 2 shows the ^{1}H NMR spectrum of PNBE and the absence of peaks around 5–6 ppm region suggests the absence of any ring opening polymerization. Figure 3 shows the ^{13}C NMR spectrum of PNBE produced. The ^{13}C NMR spectrum of PNBE showed signals at five different regions and the

Table 3 Effect of co-monomer (1-hexene) on NBE polymerization

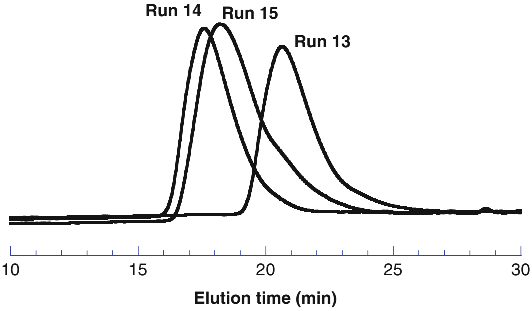
Run	1-hexene in mL/ (mol% to NBE)	Polymerization period (h)	Yield (%)	Activity[a]	M_n (PDI)[b]
12	–	1	89	222	n.d
13	0.01/(0.37)	1/2	76	380	32,230 (1.54)
14	0.01/(0.37)	1	80	200	38,000 (1.41)
15	0.01/(0.37)	4	92	58	36,970 (1.72)
16	0.1/(3.74)	1	79	197	30,250 (1.50)
17	0.25/(9.36)	1	77.5	194	27,200 (1.48)
18	0.5/(18.73)	1	72.5	181	21,200 (1.75)
19	0.75/(28.10)	1	47	117	n.d
20	1.0/(37.48)	5	38	19	9,450 (1.40)
21	1.5/(56.21)	5	10	5	4,500 (1.42)
22	2.0/(75)	5	No polymer	–	–
23	2.66(100)	24	No polymer	–	–

Polymerization conditions: 2 g of NBE, 5 mg (8 μmol) of pre-catalyst, Al/Ni ratio 100; toluene = 5 mL, polymerization temperature = 25 °C

[a] Catalyst activity in kg of PNBE/mol Ni/h

[b] M_n and PDI was calculated by GPC analysis using toluene as solvent at a flow rate of 1 mL/min, with polystyrene standards as a reference

Fig. 1 GPC overlay of PNBE in toluene synthesized by using 1NiTiCl_2/MAO in the presence of 1-hexene



absence of signals around 120–150 ppm corresponding to unsaturated carbons supported the formation of vinyl-addition polymers. The absence of signals between 20 and 24 ppm region indicates the exo-enchainment in the polymer [22]. The broadness of the signals in the ^{13}C NMR spectrum suggest that these polymers are stereo-irregular polymers. In IR spectrum of PNBE absorption peak at around 940 cm^{-1} can be assigned to bicyclic heptanes system and the absence of peaks at 1620–1680 and 960 cm^{-1} further confirmed the absence of any ROMP of NBE (see Figure S1 in ESI for IR spectrum of PNBE). We got similar NMR and IR spectra for different PNBEs (toluene soluble and insoluble) produced under different conditions by vinyl-addition polymerization. The solubility of these PNBE obtained depends on the reaction conditions.

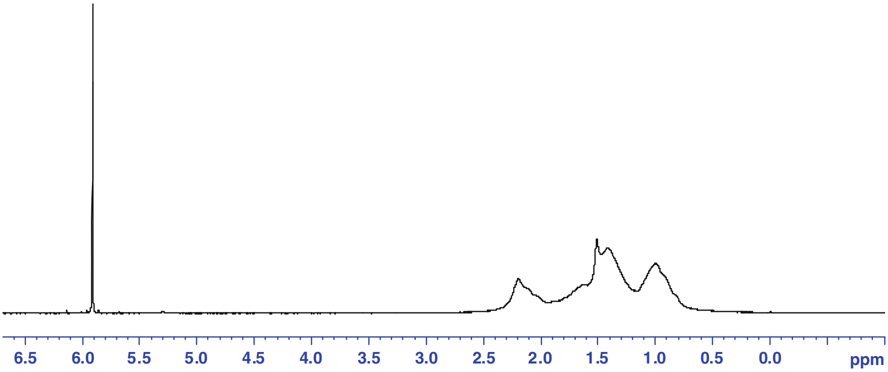


Fig. 2 ^{1} H NMR spectrum of PNBE

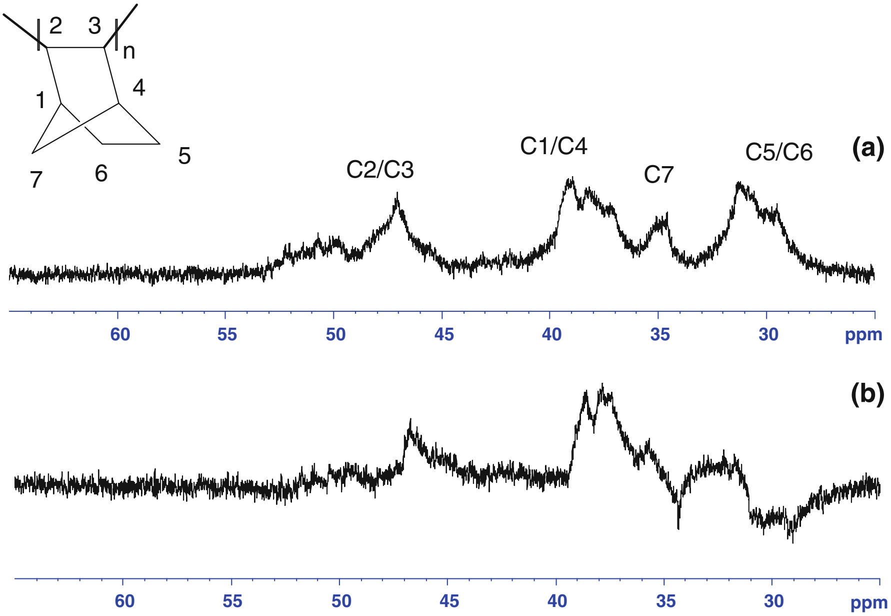


Fig. 3 **a** ^{13}C NMR spectrum of PNBE in $C_2D_2Cl_4$. **b** DEPT 135 ^{13}C NMR spectrum

Thermogravimetric analysis showed that all these polymers are stable up to 430 °C and beyond that they started decomposing (see Figure S2 in ESI). Glass transition temperature (T_g) for these PNBE samples were determined from DSC analysis. Polymers that exhibit free solubility in toluene at room temperature showed lower T_g value compared to polymers which did not have free solubility. For example, PNBE obtained in cyclohexane solvent at polymerization temperatures 25 and 50 °C had T_g values 161 and 180 °C (see Figure S3 in ESI), respectively. Ricci et al. [38] mentioned that T_g values could be affected by differences in stereo-regularity.

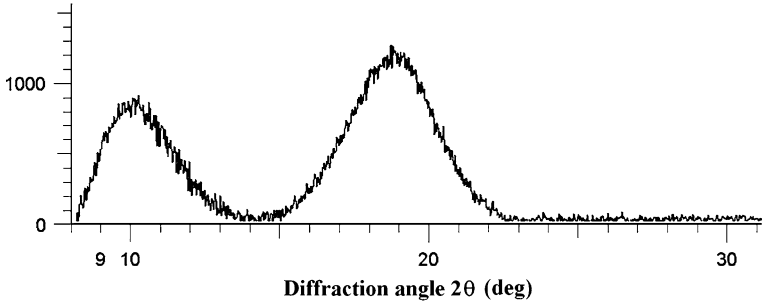


Fig. 4 X-ray diffraction pattern of PNBE

All the PNBE samples, irrespective of the polymerization conditions employed showed identical powder XRD patron. Figure 4 shows the Powder XRD spectrum of the PNBE. As seen in Fig. 4, there are two wide and weak signals at a diffraction angle $2\theta = 10°$ and 19° were observed, which are characteristic peaks for non-crystalline or lower crystalline PNBEs [35, 39, 40]. None of these polymers exhibit characteristic peak of crystallinity in DSC analysis. We believe that the PNBE obtained with this catalyst contains limited range of orderly segments.

Conclusions

The new Ni(II)-diimine pre-catalyst used in combination of MAO polymerized NBE in quantitative yields at 50 °C via vinyl addition at a Al/Ni ratio of 100. From NMR and IR spectral studies, we confirm that these PNBEs are free from polymers obtained through ring opening polymerization. The obtained PNBEs are amorphous in nature. The solubility of these PNBEs depends on the polymerization temperature and the solvent employed. The control over the molecular weights of PNBE was accomplished by introducing a chain transferring agent such as 1-hexene and the obtained polymers did not show any T_g. Here the role of 1-hexene is limited to controlling the molecular weight of the sample favoring the transfer reaction without any co-insertion.

Supporting information

In the electronic supporting information, IR, DSC, and TGA for PNBEs are given. This information is available online for free of cost.

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