

Vinyl Polymerization of Norbornene with Pyrazolyimine Nickel(II)/Methylaluminoxane Catalytic Systems

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ABSTRACT: The polymerization of norbornene (NBE) was investigated in the presence of two novel pyrazolyimine nickel complexes [2-(C₃HN₂Me₂-3,5){C(Ph)=[4-R₂C₆H₂(R₁)₂-2,6]}NiBr₂ (complex **1**, R₁ = ⁱPr and R₂ = H; complex **2**, R₁ = H and R₂ = NO₂)] activated by methylaluminoxane. The two catalytic systems showed high activity [up to 1.27 × 10⁶ g of polynorbornene (PNBE)/(mol of Ni h)] for NBE polymerization and provided PNBEs with high molecular weights (weight-average molecular weight ≤ 17.46 × 10⁵ g/mol) and narrow molecular weight distributions (ca. 2). The electron withdrawing of the nitro group in complex **2** could not enhance the catalytic activity for NBE polymerization; however, the mo-

lecular weights of the polymers were increased. The catalytic activity, molecular weight, and molecular weight distribution were influenced by the polymerization conditions, such as the polymerization temperature and Al/Ni molar ratios. The obtained PNBEs were characterized by means of ¹H-NMR and Fourier transform infrared spectroscopy techniques. The analysis results for PNBEs indicated that the NBE polymerization was a vinyl-type polymerization rather than a ring-opening metathesis polymerization. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3590–3595, 2008

Keywords: polyolefins; synthesis; catalysts

INTRODUCTION

It is well known that norbornene (NBE; i.e., bicyclo [2,2,1]hept-2-ene) can be polymerized in three different ways: ring-opening metathesis polymerization,^{1,2} cationic or radical polymerization,^{3–6} and vinyl (or addition) polymerization.^{7,8} Each polymerization mechanism leads to its own polymer type that is different in structure and properties from the other two. For vinyl addition polymerization, the bicyclic structure unit remains intact, and only the double bond of the π component is opened. Therefore, vinyl-type polynorbornene (PNBE), a special polymer with constrained rings in each unit, possesses interesting and unique properties such as high chemical resistance, good UV resistance, a low dielectric constant, a high glass-transition temperature, excellent transparency, a large refractive index, and low birefringence.^{9,10} Vinyl-type PNBE is more attractive for promoting homopolymerization and copolymerization with

ethylene. Many transition-metal complexes including titanium,^{11,12} zirconium,¹³ iron,¹⁴ nickel,^{15–25} palladium,^{26–30} and cobalt^{31–33} have been used as precursors for the vinyl polymerization of NBE. The resulting NBE polymers may be crystalline or amorphous, depending on the catalysts used.

To exploit fully the potential of this interesting class of polymers, designing new catalysts for the vinyl-polymerization and copolymerization of NBE is still a great challenge. This study addresses the synthesis of new nickel(II) complexes bearing pyrazolyimine chelating ligands and investigates their behavior for the vinyl-type polymerization of NBE after activation by methylaluminoxane (MAO).

EXPERIMENTAL

General procedures

All manipulations were performed under a nitrogen atmosphere with glovebox and Schlenk techniques. Extrapure-grade nitrogen was further purified before being fed into the reactor by passage through a DC-IB gas purification instrument (Milwaukee, WI). Toluene and hexane were refluxed over metallic sodium for 24 h, CH₂Cl₂ was refluxed over P₂O₅ for 8 h, and then they were distilled under a nitrogen atmosphere before use. 2,6-Diisopropylaniline and 3,5-dimethylpyrazole were purchased from Aldrich

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(St. Louis, MO). 2,6-Diisopropylaniline was distilled under reduced pressure before use. NBE (98%) was purchased from Aldrich Chemical Co.; it was purified and dried with potassium at 60°C for 12 h and was distilled under a nitrogen atmosphere, and then it was dissolved in toluene to make a 0.4 g/mL solution. The other reagents were purchased and used as received. ¹H-NMR spectra were recorded on a Varian Mercury-Plus 300-MHz NMR spectrometer at room temperature (RT) in CDCl₃ for ligands and in an *o*-dichlorobenzene solution for polymers with tetramethylsilane as an internal standard. IR spectra were recorded as KBr pellets on a PerkinElmer 1600 spectrometer (Waltham, MA). Gel permeation chromatography analyses of the molecular weights and molecular weight distributions (MWDs) of the polymers were performed on a Waters (Milford, MA) 2000 instrument with 1,2,4-trichlorobenzene as an eluent at 135°C and standard polystyrene as a reference.

Preparation

2-(C₃HN₂Me₂-3,5)[C(Ph)=N(C₆H₃ⁱPr₂-2,6)] (L1)

Benzoyl chloride (1.2 mL, 10.6 mmol) was added to a solution of 2,6-diisopropylaniline (2.0 mL, 10.6 mmol) in tetrahydrofuran (THF; 50 mL) and triethylamine (2.0 mL, 14.6 mmol). The reaction mixture was stirred for 12 h at RT. After the filtration of (C₂H₅)₃N·HCl and the evaporation of THF, a white solid {(C₆H₃ⁱPr₂-2,6)NH[(C₆H₅)C=O]} was obtained. Thionyl chloride (1.1 mL, 15.1 mmol) was added to amide (2.81 g, 10.0 mmol), and the reaction mixture was heated to reflux for 2 h. After the removal of the excess thionyl chloride under reduced pressure, toluene (50 mL), triethylamine (1.7 mL, 12.2 mmol), and 3,5-dimethylpyrazole (0.96 g, 10.0 mmol) were added to the reaction system. After the addition was completed, the mixture was heated to reflux for 12 h. (C₂H₅)₃N·HCl was removed by filtration, toluene was evaporated, and the resulting mixture was recrystallized from hexane to afford L1 as light yellow crystals in an 80.5% yield (2.89 g, 8.1 mmol).

Fast atom bombardment mass spectrometry (FABMS) *m/z*: 359, [M⁺]; 282, [M⁺ - Ph]; 264, [M⁺ - C₅H₇N₂]. ANAL. Calcd for C₂₄H₂₉N₃: C, 80.18%; H, 8.13%; N, 11.69%. Found: C, 79.96%; H, 8.12%; N, 11.53%. ¹H-NMR (300 MHz, CDCl₃, ppm, δ): 7.22–7.00 (m, 8H, Ar-H), 6.05 (s, 1H, Pz-H), 2.99–2.89 (m, 2H, CH), 2.61 (s, 3H, Pz-CH₃), 2.23 (s, 3H, Pz-CH₃), 1.13–1.11 (d, 6H, CH₃), 0.89–0.84 (d, 6H, CH₃).

2-(C₃HN₂Me₂-3,5)[C(Ph)=N(C₆H₄NO₂-4)] (L2)

L2 was prepared according to the method described for L1 with (C₆H₄NO₂-4)NH((C₆H₅)C=O) (3.63 g,

15.0 mmol) and 3,5-dimethylpyrazole (1.44 g, 15.0 mmol). The resulting mixture was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5/1) as an eluent, and recrystallization was attempted from ethanol to afford L2 as yellow crystals in a 62.3% yield (2.99 g, 9.4 mmol).

FABMS *m/z*: 320, [M⁺]; 243, [M⁺ - Ph]; 225, [M⁺ - C₅H₇N₂]. ANAL. Calcd for C₁₈H₁₆N₄O₂: C, 67.49%; H, 5.03%; N, 17.49%. Found: C, 67.38%; H, 5.05%; N, 17.46%. ¹H-NMR (300 MHz, CDCl₃, ppm, δ): 8.08–8.06 (m, 4H, Ar-H), 7.70–7.65 (m, 1H, Ar-H), 6.85–6.83 (m, 4H, Ar-H), 5.88 (s, 1H, Pz-H), 2.48 (s, 3H, Pz-CH₃), 1.89 (s, 3H, Pz-CH₃).

2-(C₃HN₂Me₂-3,5)[C(Ph)=N(R₂C₆H₃ⁱPr₂-2,6)]NiBr₂ (complex 1)

(DME)NiBr₂ (2.0 mmol) was added under a nitrogen atmosphere to 2.0 mmol of L1, which was dissolved in 40 mL of dry CH₂Cl₂. After the mixture was stirred at RT for 18 h, the resulting solution was concentrated, and then hexane was added to precipitate the product, which was washed with 20 mL of hexane and dried *in vacuo* to result in a purple powder with a 78.6% yield (0.91 g).

FABMS *m/z*: 498, [M⁺ - Br]; 418, [M - 2Br]²⁺; 264, [L1 - C₅H₇N₂]⁺. ANAL. Calcd for C₂₄H₂₉N₃NiBr₂: C, 49.87%; H, 5.06%; N, 7.27%. Found: C, 49.74%; H, 5.36%; N, 7.10%.

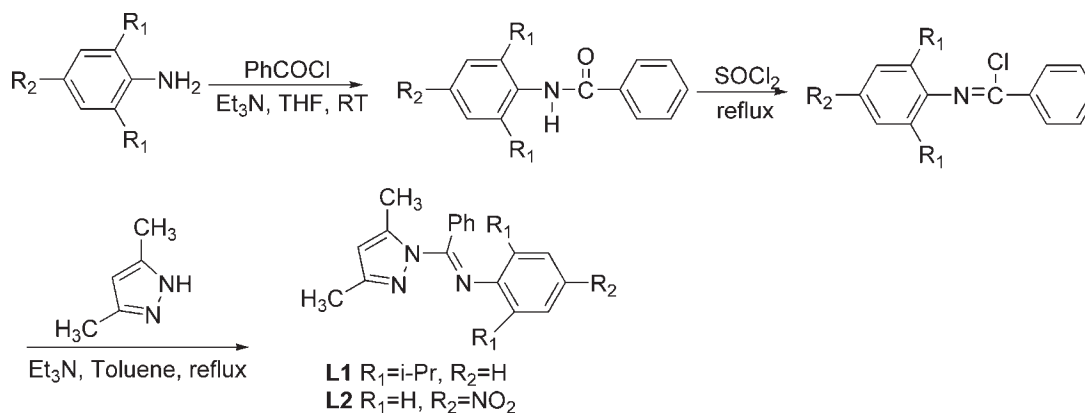
2-(C₃HN₂Me₂-3,5)[C(Ph)=N(C₆H₄NO₂-4)]NiBr₂ (complex 2)

(DME)NiBr₂ (2.0 mmol) was added under a nitrogen atmosphere to 2.0 mmol of L2, which was dissolved in 40 mL of dry CH₂Cl₂, and the mixture was stirred at RT for 18 h. Because of the poor solubility of complex 2 in CH₂Cl₂, the resulting solid was filtered, and the product was washed with 20 mL of CH₂Cl₂ and dried *in vacuo* to result in a purple powder with a 63.7% yield (0.69 g).

FABMS *m/z*: 459, [M⁺ - Br]; 379, [M - 2Br]²⁺; 225, [L2 - C₅H₇N₂]⁺. ANAL. Calcd for C₁₈H₁₆N₄O₂NiBr₂: C, 40.12%; H, 2.99%; N, 10.40%. Found: C, 40.19%; H, 3.22%; N, 9.84%.

NBE polymerization procedure

In a typical procedure, the appropriate MAO solid was added to a 50-mL flask, and then freshly distilled toluene and a solution of NBE dissolved in toluene (0.4 g/mL) were added via a syringe at the desired polymerization temperature. The resulting mixture was stirred for another 10 min, and the precursor catalyst solution in toluene was injected via a syringe. The polymerization was carried out for the desired time and then quenched with concentrated



Scheme 1 Synthesis of the pyrazolylimine ligands **L1** and **L2**.

HCl in ethanol (150 mL; 5 : 95 v/v HCl/ethanol). The precipitated polymer was collected and washed with ethanol and then dried overnight *in vacuo* at 50°C.

RESULTS AND DISCUSSION

Syntheses of pyrazolylimine ligands and nickel(II) complexes

Two phenyl-substituted pyrazolylimine ligands, **L1** and **L2**, were synthesized as shown in Scheme 1. In the first step, amide formation occurred rapidly at RT via the reaction of the corresponding substituted anilines and benzoyl chloride. In the second step, the intermediate benzimidoyl chlorides were prepared from the corresponding benzamides by a treatment with thionyl chloride. In the last step, the syntheses of pyrazolylimines were based on the reaction of benzimidoyl chlorides with 3,5-dimethylpyrazole in the presence of triethylamine. The pure pyrazolylimines could be obtained after purification in a yield of 80.5% for **L1** and in a yield of 62.3% for **L2**.

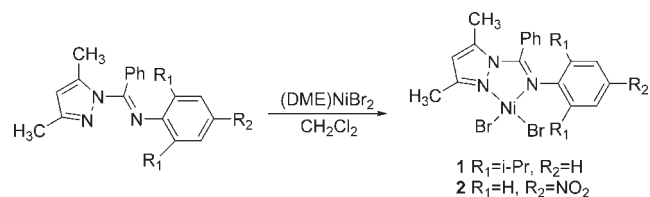
A general synthetic route for pyrazolylimine nickel(II) complexes **1** and **2** is shown in Scheme 2. Nickel dibromide complexes **1** and **2** were prepared under moderate conditions through the reaction of (DME)-NiBr₂ with 1.0 equiv of **L1** with a bulky 2,6-diisopropyl substituent or **L2** with an electron-withdrawing 4-nitro substituent on the *N*-phenyl ring in CH₂Cl₂ at RT with a yield of 78.6% for complex **1** and a yield of 63.7% for complex **2**.

NBE polymerization

When the pyrazolylimine complexes **1** and **2** were tested for ethylene polymerization, no polymeric products were obtained, probably because of chain termination. However, chain termination induced by β-H elimination is thermodynamically unfavorable

when NBE is used.³⁴ Therefore, we selected NBE as the monomer to verify the polymerization capability of this kind of novel nickel complex. Preliminary blank experiments were carried out with both of the pyrazolylimine nickel complexes in the absence of cocatalysts, and no polymer was obtained. Therefore, all the other experiments were carried out in the presence of MAO. Complexes **1** and **2**, activated by MAO, exhibited high catalytic activity for the vinyl polymerization of NBE. The PNBE was a white solid, and all polymers were soluble in chlorobenzene at RT; this implied that the PNBE had low stereoregularity.³⁵ The molecular weight and MWD of the PNBE was determined by gel permeation chromatography. The molecular weights of all PNBEs were between 10⁵ and 10⁶ g/mol, and the MWD was around 2.0. The resulting PNBEs were very stable up to about 400°C, as determined by thermogravimetric analysis under nitrogen. Moreover, according to the polymerization results, the yield, catalytic activity, molecular weight, and MWD depended significantly on the polymerization parameters, such as the polymerization temperature and Al/Ni molar ratio.

The polymerization temperature had a remarkable effect on the catalytic activity, molecular weight, and MWD of the obtained polymers. As shown in Table I, these catalytic systems displayed higher activity over a wide temperature range. Increasing the temperature was helpful in enhancing the yield and activity, but the activity decreased with a further



Scheme 2 Synthesis of the pyrazolylimine nickel complexes **1** and **2**.

TABLE I
Influence of the Temperature on NBE Polymerization with the 1/MAO and 2/MAO Catalytic Systems^a

| Entry | Complex | T_p (°C) | Yield (%) | Activity ^b | M_w^c | M_w/M_n |
|-------|---------|------------|-----------|-----------------------|---------|-----------|
| 1 | 1 | -20 | 13.8 | 4.41 | 17.46 | 1.93 |
| 2 | 1 | 0 | 35.4 | 11.33 | 14.10 | 1.96 |
| 3 | 1 | 20 | 26.5 | 8.48 | 8.98 | 1.99 |
| 4 | 1 | 40 | 20.6 | 6.59 | 4.31 | 2.02 |
| 5 | 2 | 20 | 5.6 | 1.79 | 11.02 | 1.39 |
| 6 | 2 | 40 | 13.3 | 4.26 | 10.17 | 1.51 |
| 7 | 2 | 60 | 23.5 | 7.52 | 9.54 | 1.56 |
| 8 | 2 | 80 | 16.8 | 5.38 | 8.11 | 1.86 |

M_w = weight-average molecular weight; M_n = number-average molecular weight; T_p = polymerization temperature.

^a Polymerization conditions: solvent, toluene; total volume = 16 mL; 3.0 μ mol of complex; 3.2 g of NBE; time = 20 min; Al/Ni = 600.

^b In units of 10^5 g of PNBE mol⁻¹ of Ni·h⁻¹.

^c In units of 10^5 g/mol.

increase in the temperature. This probably occurred because enhancing the temperature could accelerate the formation of active species and the rate of chain insertion and chain propagation. A further increase in the temperature could cause instability or decomposition of the active species. However, the molecular weight decreased significantly with the increase in the temperature all the while. In general, the rate of chain transfer is more sensitive to temperature than the rate of chain propagation, and at higher temperatures, chain transfer is predominant. Therefore, the molecular weight of PNBEs fell as the polymerization temperature increased. A molecular weight of 17.46×10^5 g/mol could be obtained at a reaction temperature of -20°C (entry 1 in Table I). At the same time, a higher temperature would lead to a broader weight distribution in terms of the existence of multichain transfers.

The pyrazolyimine nickel complex **2**, bearing a nitro group, displayed lower catalytic activity toward NBE polymerization [Table I; 20°C, 1.79×10^5 g

of PNBE/(mol of Ni h); 40°C, 4.26×10^5 g of PNBE/(mol of Ni h)] than the pyrazolyimine nickel complex **1** bearing diisopropyl groups [Table I; 20°C, 8.48×10^5 g of PNBE/(mol of Ni h); 40°C, 6.59×10^5 g of PNBE/(mol of Ni h)], and this indicated that the introduction of an electron-withdrawing group into the pyrazolyimine ligand could not increase the catalytic activity. This is different from neutral salicylaldimine nickel complexes bearing nitro groups, which markedly increase the catalytic activity for NBE polymerization.^{20,36} High catalytic activity means a fast rate of chain propagation, whereas fast chain propagation is often gone with a faster chain-transfer reaction.³⁷ This means that the molecular weights of the polymers obtained with complex **1** (Table I; 20°C, 8.98×10^5 g/mol; 40°C, 4.31×10^5 g/mol) were lower than those of the polymers obtained with complex **2** (Table I; 20°C, 11.02×10^5 g/mol; 40°C, 10.17×10^5 g/mol).

MAO was a highly active cocatalyst for the NBE polymerization catalyzed by these pyrazolyimine

TABLE II
Influence of the Al/Ni Molar Ratio on NBE Polymerization with the 1/MAO and 2/MAO Catalytic Systems^a

| Entry | Complex | Al/Ni | Yield (%) | Activity ^b | M_w^c | M_w/M_n |
|-------|---------|-------|-----------|-----------------------|---------|-----------|
| 1 | 1 | 600 | 35.4 | 11.33 | 14.10 | 1.96 |
| 2 | 1 | 800 | 39.7 | 12.70 | 12.11 | 2.32 |
| 3 | 1 | 1000 | 24.7 | 7.90 | 10.73 | 2.77 |
| 4 | 1 | 1200 | 22.8 | 7.30 | 8.64 | 2.99 |
| 5 | 2 | 600 | 23.5 | 7.52 | 9.54 | 1.56 |
| 6 | 2 | 800 | 24.7 | 7.90 | 9.04 | 1.65 |
| 7 | 2 | 1000 | 32.6 | 10.43 | 9.17 | 1.60 |
| 8 | 2 | 1200 | 26.8 | 8.58 | 6.95 | 2.05 |

M_w = weight-average molecular weight; M_n = number-average molecular weight; T_p = polymerization temperature.

^a Polymerization conditions: solvent, toluene; total volume = 16 mL; 3.0 μ mol of complex; 3.2 g of NBE; complex **1** T_p = 0°C; complex **2** T_p = 60°C; time = 20 min.

^b In units of 10^5 g of PNBE mol⁻¹ of Ni·h⁻¹.

^c In units of 10^5 g/mol.

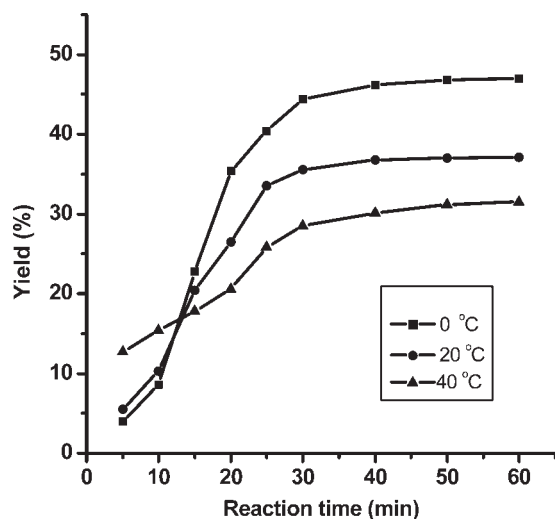


Figure 1 Kinetic study of the polymerization of NBE as catalyzed by the complex 1/MAO system at 0, 20, and 40 °C. Polymerization conditions: solvent, toluene; total volume = 16 mL; 3.0 μmol of complex 1; 3.2 g of NBE; and Al/Ni = 600.

nickel complexes. As shown in Table II, under the adopted polymerization conditions, NBE polymerizations are also dependent on the molar ratio of Al to Ni. The polymer yield and the catalytic activity increased with the Al/Ni molar ratio increasing and reached a maximum value of 1.27×10^6 g of PNBE/(mol of Ni h) at Al/Ni = 800 for complex 1/MAO and a maximum value of 1.04×10^6 g of PNBE/(mol of Ni h) at Al/Ni = 1000 for complex 2/MAO, and then they decreased with the MAO ratio further increasing. A suitable value of Al/Ni is required because MAO is necessary for the reaction of MAO with pyrazolylimine nickel complexes to produce sufficient active species for NBE polymerization and

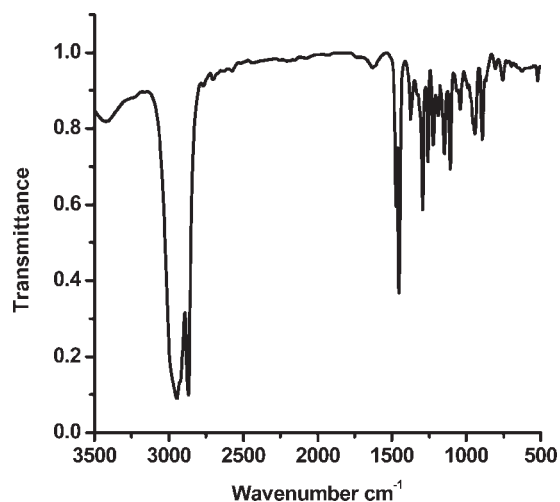


Figure 2 IR spectrum of PNBE obtained by the complex 1/MAO catalytic system (entry 2 in Table I).

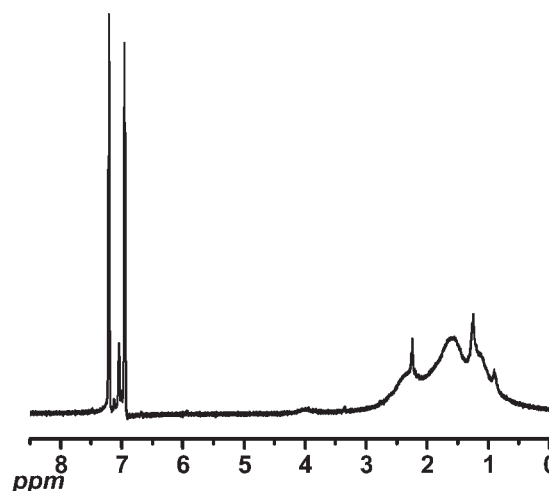


Figure 3 $^1\text{H-NMR}$ spectrum of PNBE in *o*-dichlorobenzene- d_4 prepared by the complex 1/MAO catalytic system (entry 3 in Table I).

is used to scavenge impurities. However, MAO is well known to act as a chain-transfer agent, so the higher Al/Ni ratio makes the catalyst activity and molecular weight of PNBE decrease.

The complex 1/MAO catalytic system was chosen for the kinetic study of NBE polymerization at 0, 20, and 40 °C. As shown in Figure 1, the polymer yields increased with the reaction time prolonged, and two distinct periods could be observed in the polymerization process. In the first period, about 5–25 min, the polymer yields increased rapidly. In the second period, the polymer yields increased very slightly and leveled off, probably because of the deactivation of active species. It is notable that the initial polymerization rate was slower at a low polymerization temperature than that at a high temperature; however, with the prolongation of the polymerization time, the polymer yield was higher at the low polymerization temperature. These results imply that the polymerization was initiated rapidly at the high temperature; however, the active species were unstable and easily deactivated at the high temperature.

A representative PNBE sample obtained from entry 2 in Table I was characterized with IR and $^1\text{H-NMR}$. The IR spectrum (Fig. 2) revealed the characteristic signal at about 941 cm^{-1} , which could be assigned to the ring system of bicyclo[2,2,1]heptane.³ The absence of absorption at $1620\text{--}1680\text{ cm}^{-1}$ and especially at 960 cm^{-1} in the IR spectrum also supported the vinyl polymerization of NBE.³⁸ The $^1\text{H-NMR}$ spectrum (Fig. 3) of the resulting PNBE indicated that all protons appeared at $\delta = 0\text{--}3$ ppm, and no proton signals were observed from 3.0 to 6.0 ppm; this usually indicates the ring-opening metathesis polymerization of NBE.¹³

CONCLUSIONS

Two pyrazolyimine nickel complexes were synthesized and used for NBE polymerization in the presence of MAO. These nickel complexes exhibited higher activities for NBE polymerization. The structural characterization of PNBE by $^1\text{H-NMR}$ and Fourier transform infrared spectroscopy indicated that the NBE polymerization was a vinyl-type polymerization. Under the appropriate conditions, the catalytic activity could be up to 1.27×10^6 g of PNBE/(mol of Ni h), and the molecular weight of PNBE was up to 17.46×10^5 g/mol. The electron withdrawing of the nitro group in complex **2** did not enhance the catalytic activity for NBE polymerization; however, the molecular weights of the polymers increased. The catalytic activity, molecular weight, and MWD could be controlled over a wide range by variations in the polymerization parameters.

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