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Vinyl polymerization of norbornene by nickel(II) complexes bearing β-diketiminate ligands

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Norbornene polymerizations were carried out using nickel(II) bromide complexes $CH\{C(R)NAr\}_2NiBr$ (1, $R = CH_3$, $Ar = 2,6\text{-}^iPr_2C_6H_3$; 2, $R = CH_3$, $Ar = 2,6\text{-}Me_2C_6H_3$; 3, $R = CF_3$, $Ar = 2,6\text{-}^iPr_2C_6H_3$; 4, $R = CF_3$, $Ar = 2,6\text{-}Me_2C_6H_3$) in the presence of methylaluminoxane. Compound 3 is the most active norbornene polymerization catalyst of all the nickel complexes tested. The activity of theses catalysts increases with increases in steric bulk of the substituents on the aryl rings. The electronic nature of the ligand backbone also affects the activity. The resulting polynorbornenes are vinyl type by IR and NMR analyses. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: nickel complexe; β-diketiminate ligand; norbornene polymerization; MAO

INTRODUCTION

Norbornene (bicycle[2,2,1]hept-2-ene) has been used as a monomer for homo- and co-polymerization to prepare new types of polyolefin materials over recent decades.[1,2] The high level of interest in polymer materials of norbornene has led to a variety of new transition metal catalysts. Norbornene can be polymerized via three different mechanisms (Scheme 1): ring-opening metathesis polymerization (ROMP),[3,4] cationic or radical polymerization[5–8] and vinyl (or addition) polymerization.[9–11] Each pathway has led to polymers with different structures and properties. Of these three processes, ROMP has been most widely investigated, since it generates polymers with unsaturated backbones and high solubility in a wide range of organic solvents.[3,4] Cationic and radical polymerization result in low molecular weight oligomeric materials with 2,7-connectivity.[5–8] Polynorbornenes via vinyl addition polymerization are popular polymer materials and possesses special properties, such as high thermal stability, high glass transition temperatures, excellent optical transparency and low birefringence because of the saturated carbon's constrained nature.[1,2,12]

Many transition metal complexes, including titanium,[13,14] zirconium,[15,16] iron,[17] nickel,[18–20] palladium[21,22] and cobalt,[23] can catalyze the vinyl polymerization of norbornene. Previously we reported that nickel(II) complexes bearing anilido-imine ligands[24,25] and nickel(II), copper(II) and cobalt (II) complexes of β-ketoamine ligands[26–29] effect vinyl polymerization of norbornene. The bis(β-ketoamino)nickel(II) complexes can catalyze copolymerization of norbornene with polar monomers.[27] In this paper, we report the behavior of norbornene polymerization by nickel(II) complexes with β-diketiminate ligands in the presence of methylaluminoxane (MAO). Complexes with different sunstituents on the ligands backbone and different *ortho*-aryl substituents at nitrogen thus allowed us to investigate the effects of sterics and electronic properties of the ligand environment on norbornene polymerization.

RESULTS AND DISCUSSION

Synthesis and characterization of nickel(II) complexes

Figure 1 shows the structures of the nickel complexes employed in this study. The synthesis and characterization of

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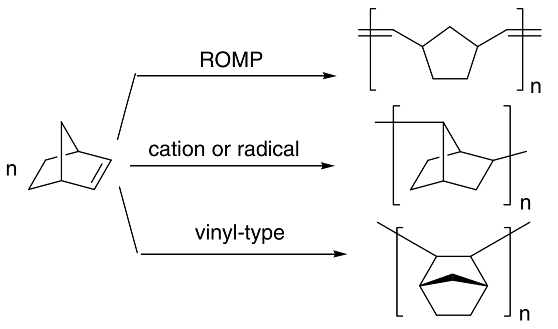


Scheme 1. Schematic representation of the three different types of polymerization for norbornene.

β-diketiminate ligands **L1**,**L2** and their nickel complexes **1**, **2**,[30] as well as the fluorinated β-diketiminate ligands **L3**,**L4** and their nickel complexes **3**, **4**[31] have been reported previously.

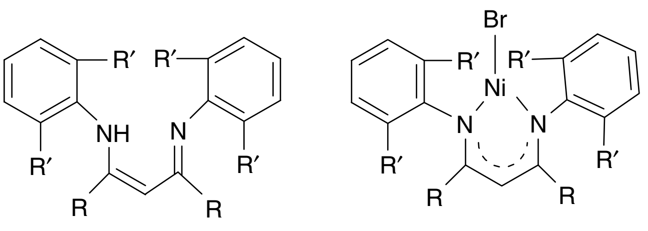
Norbornene polymerization behavior

The polymerization of norbornene catalyzed by **1**–**4** was investigated in the presence of MAO at 60 °C and an Al : Ni ratio of 1500. The result are listed in Table 1.

Under the same polymerization conditions, the highest activity of 1.43×10^6 g polynorbornene (PNB) mol^{-1} Ni h^{-1} was obtained using the **3**–MAO system (Table 1). It is clear from the data that the fluorinated backbone complexes **3** and **4** form more active catalysts than the nonfluorinated backbone analog. This trend may be understood in light of the relative rate of monomer insertion. The electron withdrawing substituents (CF_3) on the ligand backbone have been shown to have pronounced electronic effects on the metal center.[32] The higher activities of **3** and **4** than nonfluorinated analogs can be attributed to stronger electronic deficiencies of the active centers, consequently favoring the coordination of the monomer on the active centers. While the nature of the backbone substituents of the complexes influences the conversion of monomer to polymer, it not seems to dramatically affect the molecular weight M_w or distribution (M_w/M_n) of the obtained polynorbornenes (Table 1).

Compared with the electronic effect, the influence of steric bulk of the substituents on the aryl rings on the activity of norbornene polymerization is more significant (Table 1). Complex **1** with bulky *ortho*-aryl substituents at nitrogen exhibits more than four times the activity of **2;** complex **3** has about double the activity of **4**. These results suggest that the high of norbornene polymerization activity is obtained from catalysts with bulkier *ortho*-aryl substituents at nitrogen in these catalytic systems. However, the molecular weights of polynorbornenes are almost independent of the catalyst structure. GPC molecular weights (M_w) of polymers obtained from four catalytic systems are very high, almost 1.5×10^6 g mol^{-1}, indicating that chain transfer (β-H elimination) is limited using these catalytic systems.

The effect of Al : Ni ratio on norbornene polymerization by complexes **3** at 60 °C was investigated, and the results are summarized in Table 2. Variation of the Al : Ni ratio in the range 500–2500 showed considerable effect of the amount of MAO on polymer yield and molecular weight. The lowest polymer yield and molecular weight of polynorbornene was achieved at an Al : Ni ratio of 500, suggesting that the precatalyst was not fully activated by MAO. However, when the Al : Ni ratio increased to 1000, higher polymer yields and molecular weights were obtained. Significant increases in polymer yield to 54% were observed by increasing the Al : Ni ratio to 1500. Nevertheless, further increases in the Al : Ni ratio to 2000 decreased the polymer yield as well as the molecular weight. Considering that solid MAO usually contains reduced $AlMe_3$ ($\geq 5\%$), the relatively low molecular weight in high Al : Ni ratio may be attributed to chain transfer to $AlMe_3$. This result is in accord with our previous experiments.[24,25,33]



L1- L4

$R = CH_3$, $R' = {}^iPr$ **1**
$R = CH_3$, $R' = Me$ **2**
$R = CF_3$, $R' = {}^iPr$ **3**
$R = CF_3$, $R' = Me$ **4**

Figure 1. Structure of β-diketiminate ligands **L1**–**L4** and nickel(II) complexes **1**–**4** used for polymerization of norbornene.

Table 1. Effect of the complex structure on norbornene polymerization[a]

Complex	Temperature (°C)	Al : Ni	Yield (%)	Activity[b]	M_w[c]	M_w/M_n
1	60	1500	45	1.2	12.3	2.00
2	60	1500	11	0.3	11.9	2.05
3	60	1500	54	1.4	12.1	1.94
4	60	1500	29	0.8	11.6	2.01

[a] Polymerization conditions: solvent, toluene; total volume, 30 ml; complex, 3 µmol; norbornene, 4 g; reaction time, 30 min. [b] 10^6 g PNB mol^{-1} Ni h^{-1}. [c] 10^5 g mol^{-1}.

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Table 2. Effect of Al : Ni ratio on norbornene polymerization[a]

Temperature (°C)	Al : Ni	Yield (%)	Activity[b]	M_w[c]	M_w/M_n
60	500	4	0.1	8.26	2.00
60	1000	39	1.0	9.83	1.90
60	1500	54	1.4	12.1	1.94
60	2000	42	1.1	11.2	1.98
60	2500	38	1.0	10.0	2.03

[a] Polymerization conditions: solvent, toluene; total volume, 30 ml; complex **3**, 3 μmol; norbornene, 4 g; reaction time, 30 min. [b] 10^6 g PNB mol^{-1} Ni h^{-1}. [c] 10^5 g mol^{-1}.

The reaction temperature also dramatically affects catalytic behavior. Almost linear increases in the polymer yield vs temperatures were obtained for **3**–MAO system (Table 3). However, molecular weights of the obtained polynorbornene decreased exceedingly with increasing temperature, molecular weight distributions (M_w/M_n) broadened accordingly (Table 3). Similar results were obtained for norbornene polymerization with the **1, 2** and **4**–MAO systems. In our previous studies of norbornene polymerization with nickel complexes of anilido-imine ligands,[25] bimodal distributions of polynorbornene were observed at higher temperatures. However, the molecular weight distributions of the polynorbornene are narrow for these catalytic systems, and no bimodal distribution was detected even at 90 °C for **3**–MAO (Table 3), indicating that a single active species was involved all through polymerizations.

Characteristics of obtained polynorbornene

All polynorbornenes obtained from these catalytic systems are soluble in cyclohexane and chlorobenzene at room temperature, which indicates low stereoregularity. Indeed, analysis by wide-angle X-ray diffractometry showed no indication of crystallinity. GPC showed a polynorbornene with high molecular weights (M_w) and narrow molecular weight distributions (M_w/M_n in the range 1.90–2.23). Differential scanning calorimeter (DSC) studies did not give endotherms heating to 400 °C, and the thermogravimetry analyzer (TGA) scans suggested that the polynorbornenes are stable to 450 °C.

Table 3. Effect of the reaction temperature on norbornene polymerization[a]

Temperature (°C)	Al : Ni	Yield (%)	Activity[b]	M_w[c]	M_w/M_n
10	1500	14	0.4	15.62	1.90
30	1500	25	0.7	13.81	1.92
60	1500	54	1.4	12.13	1.94
70	1500	56	1.5	9.25	2.08
90	1500	66	1.8	6.57	2.23

[a] Polymerization conditions: solvent, toluene; total volume, 30 ml; complex **3**, 3 μmol; norbornene, 4 g; reaction time, 30 min. [b] 10^6 g PNB mol^{-1} Ni h^{-1}. [c] 10^5 g mol^{-1}.

The microstructure of polynorbornene was characterized by NMR and IR. All polynorbornene obtained from these catalytic systems gave similar spectroscopic characteristics, e.g. for the ^{1}H NMR spectra of polynorbornene, no proton signals are detected from 6.0 to 3.0 ppm, which are usually observed for ROMP of norbornene.[34] The ^{13}C NMR of polynorbornene obtained from **3**–MAO at 60 °C (Fig. 2) showed no carbon signals at about 130–150 ppm (carbon peaks of double bond in olefin). The upfield carbon peaks between 55 and 28 ppm are easily assignable: 53.0–47.0 ppm are C_2 and C_3, 40.0–38.0 ppm are C_1 and C_4, 37.5–35.0 ppm are C_7 and 32.0–29.5 ppm are C_5 and C_6.[35] In IR spectra of polynorbornene, the absorption at about 941 cm^{-1} was assigned to the bicycle^{2,2,1} heptane system.[36] The absence of absorption at 1620–1680 cm^{-1} and at about 960 cm^{-1} also supports vinyl polymerization of norbornene.[37]

Mechanistic consideration

The NMR and IR analyses of polynorbornenes produced by nickel complexes bearing β-diketiminate ligands show no ROMP but only 2,3-addition. Also, the high molecular weights of polynorbornene (from 10^5 to 10^6 g mol^{-1}) are not typical of cationic or radical polymerization, which usually exhibit low molecular weights and low yields because of rearrangement and chain transfer reactions.[36,38] We can conclude that the norbornene polymerization with these catalytic systems occurs via a vinyl addition coordination mechanism.

The proposed mechanism for norbornene polymerization with nickel complexes of β-diketiminate ligands is given. At the initiation step, nickel complexes activated with MAO produce the active species LNi-CH_3. The norbornene monomer occupies the coordination site, and the norbornene will insert the Ni–carbon bond by *cis-exo* insertion if a new monomer is ready to complex. The repetition of coordination-insertion steps leads to polymer chain growth (Fig. 3). In the vinyl polymerization of norbornene, chain termination

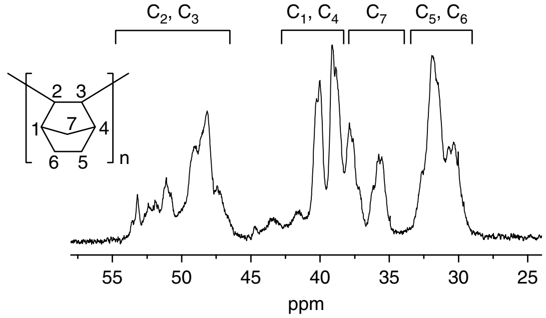

Figure 2. ^{13}C NMR spectrum of polynorbornene obtained from **3**–MAO system.

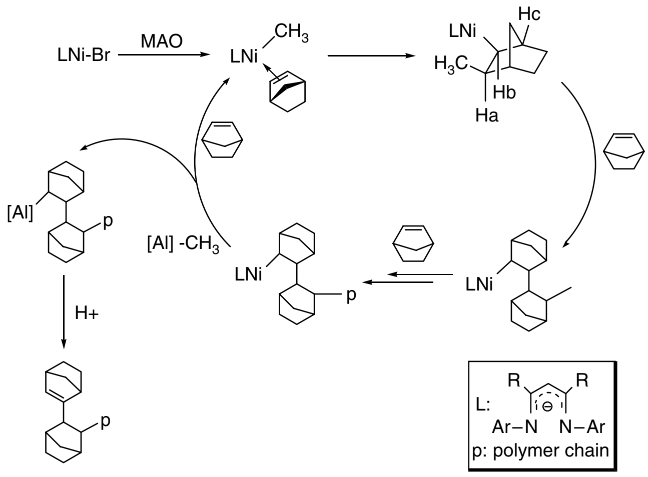

Figure 3. Proposed mechanism for vinyl polymerization of nornornene promoted by nickel complex bearing β-diketiminate ligand.

via β-hydrogen elimination is prohibited because the β-hydrogen (H_a) is at the *endo* position of the norbornene unit and elimination of H_c would result in a bridgehead double carbon bond, violating Bredt's rule.[39] Chain transfer to a monomer should also be prohibited because of sterically hindered propagation of the chain end and the norbornene monomer. Given the fact that MAO contains reduced $AlMe_3$, the chain transfer to $AlMe_3$ will be inevitable. This has been proved by our experimental results.

CONCLUSIONS

Norbornene polymerization was examined with nickel(II) complexes of β-diketiminate ligands in the presence of MAO. We found that the steric bulk of the substituents on the aryl rings have a pronounced effect on norbornene polymerization rates. Ligands have electron withdrawing substituents increased catalytic activity. The activity of the catalysts increases with increasing Al : Ni molar ratio first, and then decreases due to the chain transfer to $AlMe_3$. With an increase in the reaction temperature, the catalytic activities for norbornene polymerization increase obviously. However, broad molecular weight distributions were observed. All polynorbornenes obtained have high molecular weights and good solubility in ordinary solvents, such as cyclohexane, chlorobenzene and *o*-dichlorobenzene. The obtained polynorbornenes are vinyl-type by NMR and IR analysis.

EXPERIMENTAL

Materials

All manipulations that are air- and/or moisture-sensitive were performed under a dry, deoxygenated nitrogen atmosphere using standard high vacuum or Schlenk techniques. Toluene was obtained from Guangzhou Chemical Reagent Company of China, and used freshly distilled under nitrogen from sodium/benzophenone. Norbornene (bicycle^{2,2,1}hept-2-ene) was purchased from Fluka and purified by distillation over potassium and used as a solution in toluene. Dry, solid MAO was prepared according to literature procedures.[29]

NMR analyses

All ^1H NMR spectra were recorded on Mercury-plus 300 MHz NMR at room temperature in o-Cl_2-C_6D_4 solution. Chemical shifts were reported in ppm and referenced to tetramethylsilane (TMS). All ^{13}C NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer in a 5 : 1 mixture of o-Cl_2-C_6H_4 and o-Cl_2-C_6D_4 (3.0 ml) at 110 °C. A spectral width of 27 000 Hz, a pulse width of 4.0 ms, an acquisition time of 1.0 s and no relaxation delay were used for each spectrum. Chemical shifts were referenced to o-Cl_2-C_6D_4 (127.3 ppm).

IR analyses

All IR spectra were recorded on a Nicolet/Nexus 670 FT-IR spectrometer with resolution $\pm 0.09\ cm^{-1}$ in the region $400-4000\ cm^{-1}$ using KBr disks.

Gel permeation chromatography

All GPC were determined using a Waters Breeze gel permeation chromatography; the column was set at 40 °C and chlorobenzene was employed as a solvent at a flow rate of $1.00\ ml\ min^{-1}$. The system was calibrated using polystyrene stands.

Procedure for norbornene polymerization

Norbornene polymerization was carried out in a 50 ml glass vessel. The appropriate solid MAO was added to the flask, and then 10 ml of a toluene solution of norbornene ($0.4\ g\ ml^{-1}$, 42.5 mmol) was added via syringe. Toluene (19 ml) and 1 ml nickel complex (3.0 μmol) of toluene solution were syringed into the well-stirred solution. The reaction system was continuously stirred for an appropriate period at the polymerization temperature. The reaction was quenched by adding HCl–ethanol solution. The polymer was filtered, washed with ethanol several times, and dried at 60 °C in vacuum to a constant weight. ^1H NMR (*ortho*-dichlorobenzene-d_4, 500 MHz): δ_H, ppm: 0.86–2.71 (m, maxima at 1.2, 1.6, 2.3). ^{13}C NMR (*ortho*-dichlorobenzene-d_4, 500 MHz): δ_C, ppm: 55.0–28.0 (m, maxima at 52.8, 50.7, 47.8, 39.6, 38.7, 37.5, 35.4, 31.5, 29.6). IR (KBr): 2943, 2869, 1477, 1450, 1260, 1220, 1190, 1152, 1109, 1043, 941, 893 cm^{-1}.

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