# Vinyl Polymerization of Norbornene with Dinuclear Diimine Nickel Dichloride/MAO

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**ABSTRACT:** Vinyl-addition polymerization of norbornene was accomplished by two novel dinuclear diimine nickel dichloride complexes in combination with methylaluminoxane (MAO). The activities were moderate. The catalyst structure, Al/Ni molar ratio, solvents, and polymerization temperature all affected the catalytic activities. The obtained polynorbornenes were characterized by ^{1}H-NMR, ^{13}C-NMR, FTIR, DSC, WAXD, and intrinsic viscosity measurements. The vinyl-addition polymers were amorphous but with a short-range order and high packing density. The polynorbornenes showed glass transition temperatures ($T_g$) above 240°C and decomposed above 400°C. The catalyst structure and polymerization conditions have effects on the molecular weight and the microstructure of the polymers. The nickel complex with bulkier substituents in the ligand produced polynorbornene with a higher packing density and higher regularity and, therefore, with higher $T_g$. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 3273–3278, 2003

**Key words:** addition polymerization; amorphous; catalysts

## INTRODUCTION

Norbornene can be polymerized by two basically different mechanisms (Fig. 1): ring-opening metathesis polymerization (ROMP)[1,2] and vinyl-addition polymerization,[2,3] as Janiak and Lassahn reviewed.[4] Polynorbornenes produced by ROMP catalysts are unsaturated, generally exhibit good solubility in a variety of solvents, and can be used as an elastomeric material for vibration and sound damping or a soaking material for oil spills. Vinyl-addition polynorbornenes are usually 2,3-addition saturated and show high chemical resistance and thermal stability and good optical properties.

Recently, much interest has paid to the copolymerization of norbornene and acyclic olefins (with or without functionalization) by vinyl addition so as to obtain materials with new microstructures and to improve their properties. The study of vinyl-addition homopolymerization of norbornene via new catalysts is still of interest. The vinyl-addition polymerization of norbornene can be completed by metal complexes based on titanium, zirconium, nickel, palladium, chromium, cobalt, and iron.[2–5] So far, catalyst selection for the vinyl-addition polymerization of norbornene is still a topic. Many nickel catalytic systems have been reported active for the polymerization of norbornene: $\pi$-allylnickel trifluoroacetate (HFA or HCA) with no cocatalyst,[6] nickel stearate,[7] Ni(acac)$_2$ (acac = acetylacetonate), Ni(2-ethylhexanote), (COD)$_2$Ni$^0$ (COD = cyclooctadiene),[8] BrNi(NPMe$_3$)]$_4$,[9] nickel(salen),[10] and [ArN=C(R)–C(R)=NAr]NiX$_2$ (X = Cl, Br)[5] with methylaluminoxane (MAO) as the cocatalyst. Besides MAO, B(C$_6$F$_5$)$_3$ has also been used as an activator for nickel-based catalytic systems.[11] Recently, novel dinuclear (monomeric-activated species in solution) diimine nickel dibromide or dichloride complexes combined with MAO have been described as catalytic systems for the polymerization of ethylene.[12,13] Polyethylenes have a high degree of short-chain branching. Whether the new nickel catalysts show activities for norbornene polymerization is of interest.

In this article, two novel dinuclear diimine nickel dichloride complexes: di-$\mu$-chlorodichlorobis{2,6-bisisopropyl-$N$-[1-(2-pyridinyl)ethylidene]ph-enylamine}dinickel(II) (complex I) and di-$\mu$-chlorodichlorobis{2,6-bismethyl-$N$-[1-(2-pyridinyl)ethylidene]phenylamine}dinickel(II) (complex II), were used for the polymerization of norbornene. Detailed studies on the effects of the polymerization condi-
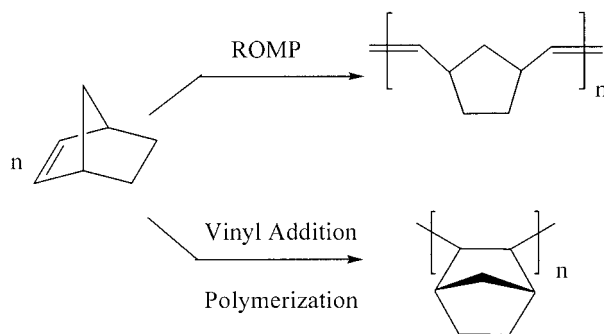
**Figure 1** Two polymerization mechanisms of norbornene.

tions on the activity, the molecular weight, as well as the polymer microstructure are presented.

## EXPERIMENTAL

All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques.

### Materials

Norbornene (from Acros) was distilled over sodium and then dissolved in dried toluene to give a 0.6 g/mL solution. Toluene (from the Beijing Chemical Co. Ltd., Beijing, China) was refluxed with sodium, while $CH_2Cl_2$, with $CaH_2$, was freshly distilled before use. MAO (purchased from the Albemarle Co., TX; 1.4$M$ in toluene) was used as received.

### Preparation of the catalysts

The complexes, di-$\mu$-chlorodichlorobis{2,6-bisisopropyl-$N$-[1-(2-pyridinyl)ethylidene]phenylamine}dinickel(II) (complex I) and di-$\mu$-chlorodichlorobis{2,6-bis- methyl-$N$-[1-(2-pyridinyl)ethylidene]phenylamine}dinickel(II) (complex II), shown in Figure 2, were prepared according to a similar procedure published by Köppl and Alt[12] and Timo et al.[13] For complex I, FAB MS: $m/z$: 746[M$^+$—2Cl], 373[1/2 M$^+$—Cl]. For complex II, FAB MS: $m/z$: 669[M$^+$—Cl], 634[M$^+$—2Cl], 317[1/2 M$^+$—Cl].

### Polymerization and analytical procedures

A 100-mL flask was filled with 5 mL of a norbornene solution (0.6 g/mL in toluene), toluene, MAO, and then the catalyst solution (2.440 $\mu$mol/2 mL in $CH_2Cl_2$). The total volume was 15 mL. After 1 h, the polymerization was quenched by the addition of a 10 vol % HCl/ethanol solution. The polymer was isolated, washed with water and ethanol, and then dried in a vacuum at 70°C to a constant weight.

Mass spectra were measured on a Kratos AEI MS-50 instrument using the fast atom bombardment (FAB) technology. FTIR spectra were recorded as KBr pellets

on a Perkin–Elmer 2000 spectrometer at a scanning rate of 0.2 cm$^{-1}$/s. $^1$H-NMR and $^{13}$C-NMR spectra were measured with a Bruker DMX-300 NMR spectrometer operating at 300 MHz in 1,2-dichlorobenzene-$d_4$. The glass transition temperatures of the polymers were determined by DSC with a Perkin–Elmer DSC-7 at a heating rate of 10°C/min. Wide-angle X-ray diffraction (WAXD) curves of the polymer powders were obtained using a RINT-2400 X-ray diffractometer, with monochromatic radiation at a wavelength of 1.54 Å. Scanning was performed with 2$\theta$ ranging from 3 to 60°. Viscosity measurements were carried out in 1,2,4-trichlorobenzene at 135°C using an Ubbelohde viscometer.

## RESULTS AND DISCUSSION

Compared to other nickel complexes in the literature, such as Ni(acac)$_2$ and Ni(2-ethylhexanote) [10$^6$ g PNB/(mol Ni h)],[8] the present nickel complexes I and II show moderate activity [10$^5$ g PNB/(mol Ni h)] for the polymerization of norbornene (Table I). There is no obvious precipitation in the solvents toluene/$CH_2Cl_2$ (5:1) during the polymerization, which is similar to the systems of Ni(acac)$_2$, Ni(2-ethylhexanote), and (COD)$_2$Ni$^0$/MAO, as reported.[8] As shown in Table I (runs 1–4), the activity varies slightly with the amount of MAO when the Al/Ni molar ratio is increased from 100 to 1600, so the small amount of MAO is enough to activate these catalysts without a significant loss in activity, as observed in ref. 8. The molecular weight, however, increases first and then decreases with increase of the Al/Ni molar ratio. The chain transfer promoted by MAO was as usual. In a comparison of runs 5–7, lower temperature has the
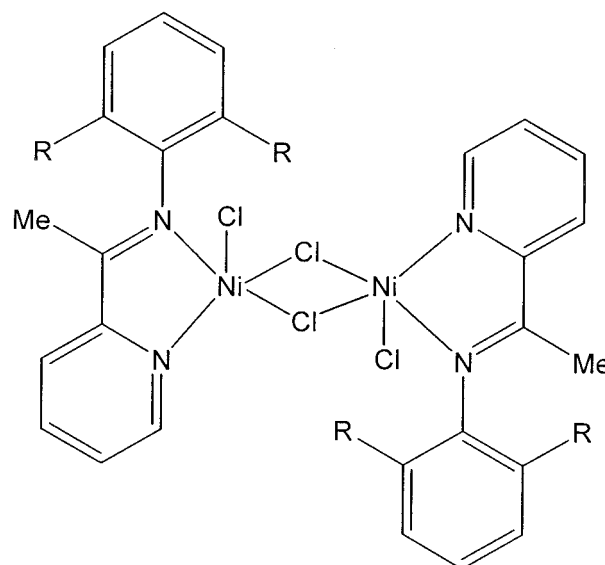


**Figure 2** Nickel complexes I and II that were used. R = isopropyl: complex I; R = methyl: complex II.

TABLE I
Polymerization Results of Norbornene by Nickel Complexes I and II

| Run no. | Catalyst | Al/Ni (mol/mol) | Solvents | $T$ (°C) | Yield (%) | Activity kg polymer/ (mol Ni h) | $[\eta]^a$ (dL/g) |
|---|---|---|---|---|---|---|---|
| 1 | I | 100 | Toluene/CH$_2$Cl$_2$ | 40 | 18.43 | 226.6 | 1.99 |
| 2 | I | 400 | Toluene/CH$_2$Cl$_2$ | 40 | 19.72 | 242.5 | 2.28 |
| 3 | I | 800 | Toluene/CH$_2$Cl$_2$ | 40 | 20.36 | 250.3 | 2.14 |
| 4 | I | 1600 | Toluene/CH$_2$Cl$_2$ | 40 | 21.06 | 258.9 | 1.56 |
| 5 | I | 400 | Toluene | 40 | 13.76 | 169.2 | 2.13 |
| 6 | I | 400 | Toluene | 60 | 9.71 | 119.4 | 1.51 |
| 7 | I | 400 | Toluene | 0 | 46.93 | 577.0 | 2.61 |
| 8 | II | 400 | Toluene/CH$_2$Cl$_2$ | 40 | 10.81 | 132.9 | 2.22 |

Polymerization conditions: monomer concentration [NBE] = 2.128 mol/L catalyst concentration [Ni]/2 = 8.170 × 10$^{-5}$ mol/L; polymerization time $t$ = 1 h. Except runs 5–7, toluene/CH$_2$Cl$_2$ = 5:1 (volume ratio).
$^a$ Intrinsic viscosity $[\eta]$ was determined in 1,2,4-trichlorobenzene at 135°C.

advantage of higher activity and higher molecular weight in these catalytic systems, which could be explained by the slower irreversible deactivation of activated species and less chain transfer, respectively, at lower temperature.

The polymerization medium also influences the activity and molecular weight. The better solubility in CH$_2$Cl$_2$ made the nickel complex dispersed enough in the medium and then activated enough, so the activity in the mixture of toluene and CH$_2$Cl$_2$ (5:1, volume ratio) (run 2) is higher than that in toluene only as the solvent (run 5). Under the same conditions, the yield by the complex I/MAO is higher than that by the complex II/MAO (runs 2 and 8). The bulkier substituents in the ligand of complex I are assumed to be favorable to stabilize the active center in comparison to the relatively small substituents in the ligand of complex II. Furthermore, the bulkier substituents could make the β-elimination of hydrogen[14] much more difficult, and, therefore, the molecular weight of the polymer produced by complex I, estimated as the intrinsic viscosity $[\eta]$, is higher than that of the polymer produced by complex II.

The microstructure of the obtained polynorbornene is characterized by $^1$H-NMR and $^{13}$C-NMR spectra. Seen from Figure 3, no resonances are displayed from 5.0–6.0 ppm in the $^1$H-NMR spectrum of the polynorbornene obtained by I/MAO, which usually indicates the presence of ROMP structures.[5] The $^{13}$C-NMR spectrum (Fig. 4) of the same sample shows the main four groups of resonances: (48.2, 47.4), (40.5–38.7, 37.6–36.6), (31.2, 31.1, 30.9), and (29.8, 29.6) ppm, attributed to the backbone carbon (1), bridgehead carbon (2), bridge carbon (3), and the vinyl-addition polymer structures of norbornene (4) , respectively.[15] The polynorbornene obtained by II/MAO has similar $^1$H-NMR and $^{13}$C-NMR spectra. Therefore, both the present nickel complexes produce vinyl-addition polynorbornenes.

FTIR spectra of polynorbornenes obtained by I/MAO catalytic systems with different Al/Ni molar ratios, shown in Figure 5, reveal the characteristic signals of polynorbornenes at about 941 cm$^{-1}$. There are no absorptions at 1620–1680 cm$^{-1}$, especially about 960 cm$^{-1}$, assigned to the *trans* form of double bonds, which are characteristic of the ROMP structure of polynorbornenes.[16] These absorption peaks about 941 cm$^{-1}$ could be assigned to the ring system of bicyclo[2.2.1]heptane, as Kennedy and Makowski noted.[17] The variation of the Al/Ni molar ratio has no effect on the FTIR signals of the polymers. The FTIR spectra of polynorbornenes generated by II/MAO are similar.

The polynorbornenes obtained are amorphous, which can be observed by WAXD, as shown in Figure 6. Two broad halos at $2\theta$ of 9°–11° (peak 1) and 18°–19° (peak 2) appear in the diagrams of the polymers generated under different polymerization conditions, which is similar to the results reported by Haselwender et al.[18] and Zhao et al.[19] According to their opinions, peak 1 can be regarded as a reflection of the interchain or intersegment distance of the polymer, while peak 2 can be regarded as a reflection of the intrachain distance. No traces of Bragg reflections, characteristic of crystalline regions, were revealed. The polynorbornene, therefore, is noncrystalline, but, similarly, the polymers are in a short-range order and in a condensate state. The interchain distance is given in ref. 20 as being equal to 1.22 times the Bragg distance:

$$d_{\text{interchain}} = 1.22 d_{\text{Bragg}} = 1.22\lambda/(2\sin\theta)$$

Figure 6 shows the values of $2\theta$ related to peak 1 of all compared polynorbornenes as well as the main compared conditions. Accordingly, the interchain distances of the polymers are 10.87 Å (run 6), 10.43 Å (run 5), 11.20 Å (run 7), 11.01 Å (run 1), 10.79 Å (run 2), and 10.43 Å (run 8). Only when the Al/Ni molar ratio increases to 1600 (run 4) for complex I is peak 1 obviously weakened and becomes a shoulder of the other peak, so the packing of the polymer is loose at a
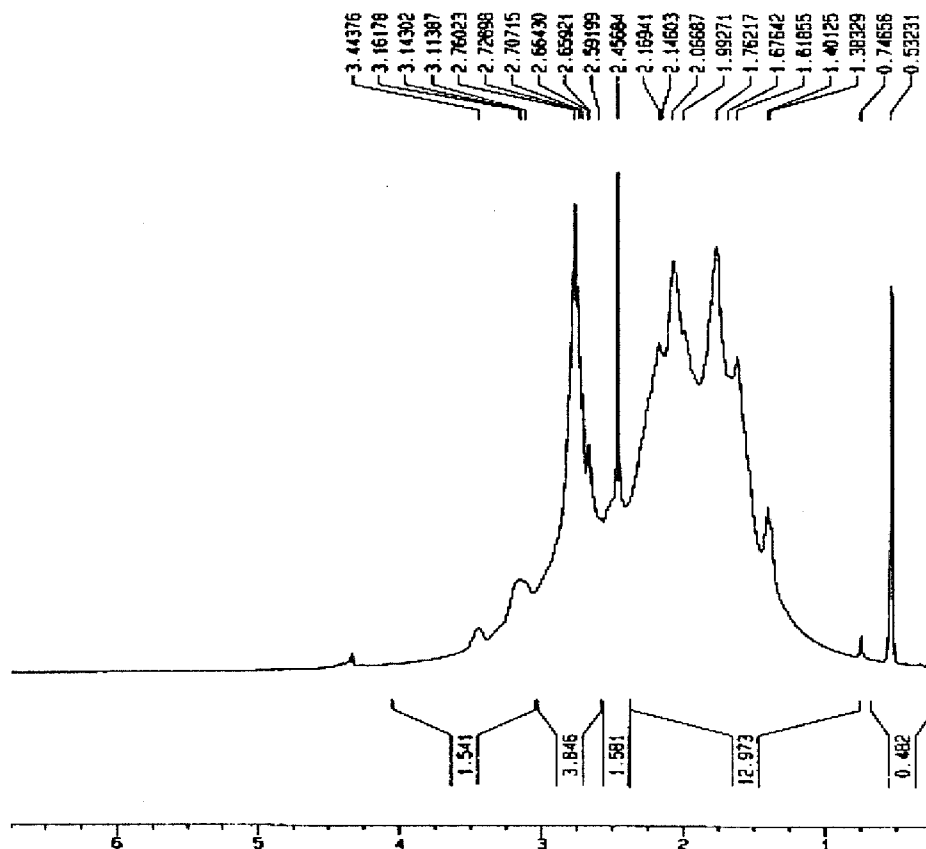
**Figure 3** ¹H-NMR spectrum of polynorbornene obtained by I/MAO.

higher Al/Ni molar ratio and the free volume increases. Except for run 4, the interchain distances of the polymers are similar but with a few differences: The interchain distance of the polymer forming at

40°C (run 5) is a little shorter than that of the polymer forming at a higher temperature (run 6) or at a lower temperature (run 7). We presume that the special structure or molecular weight was obtained at 40°C or the error from the analyzer led to the result. We will undertake further study on it. As can also be seen, the interchain distance of the polynorbornene obtained by
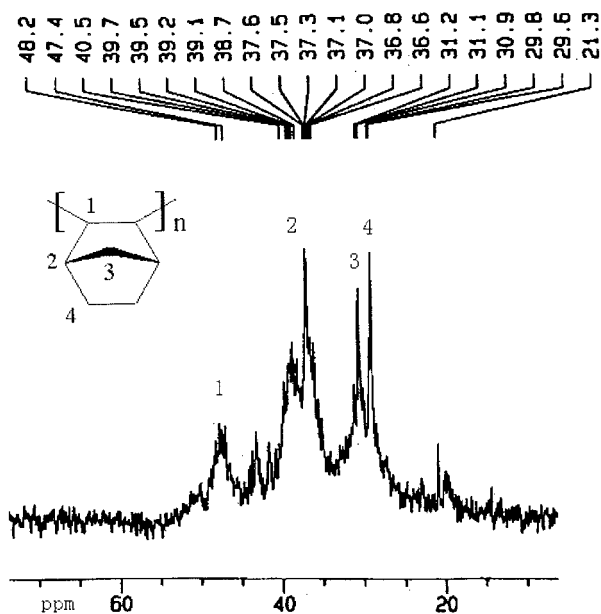


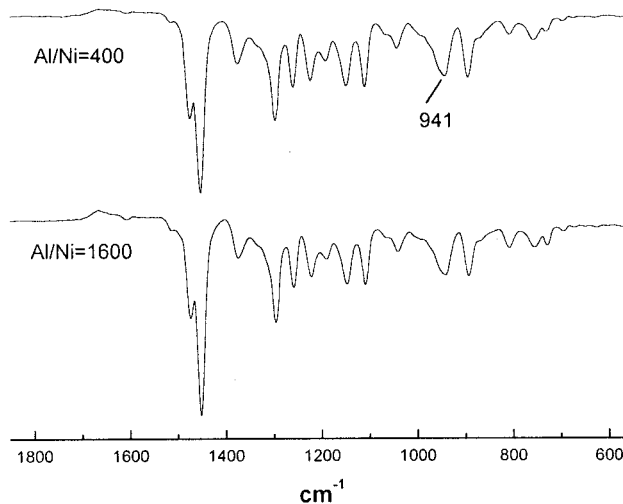**Figure 4** ¹³C-NMR spectrum of polynorbornene obtained by I/MAO.



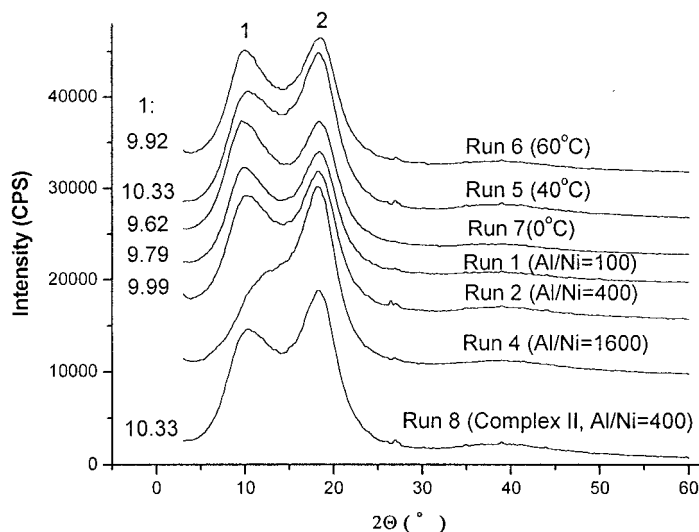**Figure 5** FTIR spectra of polynorbornenes obtained by I/MAO.

**Figure 6** WAXD diagrams of polynorbornenes obtained under different polymerization conditions.

II/MAO (run 8, 10.43Å) is shorter than that of the polymer obtained by I/MAO (run 2, 10.79 Å) and, therefore, the regularity or packing density is accordingly higher.

DSC analyses show that the glass transition temperatures ($T_g$) of the polynorbornenes forming appear above 240°C and the decomposition temperatures lie above 400°C, as shown in Figure 7. The amount of MAO has an evident effect on the $T_g$. When the Al/Ni molar ratio increases from 400 to 1600 (related to run 2 and run 4), the $T_g$ clearly decreases. In addition, there is some difference between the glass transition temperatures of the polynorbornenes obtained by nickel complexes I and II (runs 2 and 8). The higher packing density, as revealed in WAXD, will suppress the motions of the molecular segments, which, in turn, enhances the $T_g$ of the polymer obtained by II/MAO. In contrast, the lower packing density makes $T_g$ of the polymer obtained at Al/Ni = 1600 much lower than that of the polymer obtained at Al/Ni = 400.

## CONCLUSIONS

The vinyl-addition polymerization of norbornene was carried out with moderate activities by two kinds of dinuclear diimine nickel dichloride complexes combined with MAO. The obtained polynorbornenes were amorphous but with a short-range order and high packing density. The catalyst structure and polymerization conditions showed effects on the activities, the molecular weight, and the packing of the polymers. The polynorbornenes showed a $T_g$ above 240°C and decomposed above 400°C. The nickel complex with bulkier substituents in the ligand produced polynorbornene with a higher packing density and higher regularity and, therefore, with a higher $T_g$.
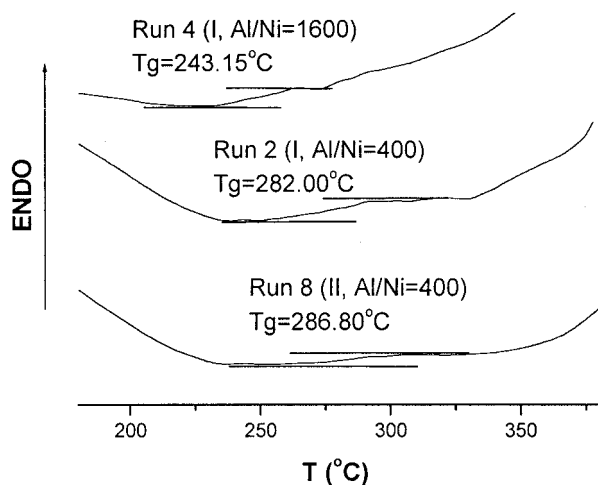
**Figure 7** DSC diagrams of polynorbornenes obtained by I or II/MAO.

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