



Highly active vinyl-polymerization of norbornene by [2-methyl-8-(diphenylphosphino)quinoline]nickel(II) dichloride/methylaluminoxane

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Abstract

Polymerization of norbornene has been promoted by a catalyst system composed of [2-methyl-8-(diphenylphosphino)quinoline]nickel dichloride and MAO. The catalytic system showed high activity (activity $< 1.70 \times 10^8$ g-PNB/mol-Ni h) for vinyl addition type polymerization. The resultant polynorbornenes possessed high molecular weight ($M_w < 2.08 \times 10^6$ g/mol) with wide molecular weight distribution ($M_w/M_n < 19.20$), and were soluble, showing no crystallinity in the solid state. The catalytic activity, molecular weight as well as polydispersity of the resultant polymer can be controlled over a wide range by varying the reaction parameters.

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Keywords: Vinyl polynorbornene; High activity; High molecular weight; Wide molecular weight distribution; Amorphous polymers

1. Introduction

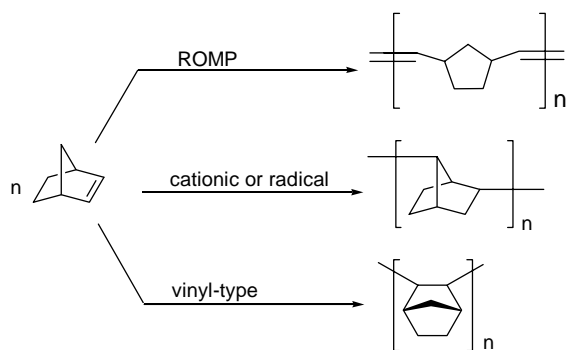
Norbornene and its derivatives are known to undergo three different modes of polymerization: ring-opening metathesis polymerization (ROMP), cationic or radical polymerization, and vinyl-polymerization (Scheme 1). Each route leads to its own polymer type which is different in structure and properties from the other two [1–3].

Since the first report in the 1950s by Andersen and Merklung [4], ring-opening metathesis polymerization has been well investigated. This type of polymerization can be performed by a variety of transition metal complexes with the high oxidation state [5–7], and

the polymers produced were commercialized widely by vulcanization or hydrogenation of double bonds in the polymer backbone [3]. The cationic and the radical polymerization of norbornene was first described in 1967 and the polymer obtained via this kind of route shows a 2,7-linkage and low molecular weights (molecular weight < 1000) at low yield because of rearrangements and transfer reactions [7].

The vinyl-polymerization of norbornene was firstly reported by Sartori et al. [8–10], and the polymers showed interesting properties since the bicyclic structure was retained in the main chain. The molecular dynamic simulations show that the vinyl polynorbornenes (PNB) displays a characteristic rigid random coil conformation, showing restricted rotation about the main chain. Based on their peculiar structural features, various interesting properties are expected for polynorbornenes. For example, these polymers

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Scheme 1. Schematic representations of norbornene polymerization.

possessed very high decomposition temperatures and exhibited improved thermal stability, excellent dielectric properties and high transparency. Therefore, they are attractive materials not only for microelectronics and optical applications, but also for other potential uses for packing and gas separation [11–14].

Polynorbornenes prepared by this type of polymerization were varied from amorphous to more stereo regular and crystalline, and this is dependent upon the catalytic system used. Various transition metal complexes such as nickel [15–19], cobalt [20], chromium [21], titanium [2], zirconium [22], iron [23] and palladium [24–29] have been known to be active for vinyl homo-polymerization of norbornene and other strained cyclic olefins. In general, these complexes are activated by methylaluminoxane (MAO) or cationic complexes with weakly coordinating counter ions like BF_4^- or PF_6^- (Ni, Pd). In order to fully exploit the potential of this interesting class of polymers, catalytic activities and control of molecular weight have to be improved as well as functionalizing PNB by using norbornene derivatives. Therefore, designing new catalysts for vinyl-polymerization of norbornene is still a challenge. Previously, we reported the synthesis of nickel(II) complexes [2-methyl-8-(diphenylphosphino)quinoline]nickel(II) dichloride (Fig. 1) and its activity for ethylene oligomerization [30]. The complex [2-methyl-8-(diphenylphosphino)quinoline]nickel(II) dichloride was extensively explored as catalysts for polymerization of cyclic olefins. Here, we report the systematical investigation of the activity of [2-methyl-8-(diphenylphosphino)quinoline]nickel(II)

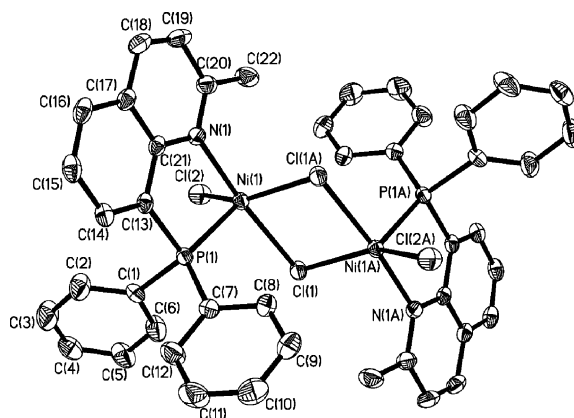


Fig. 1. Perspective view of nickel catalyst.

dichloride/MAO (methylaluminoxane) system for norbornene polymerization.

2. Experimental part

2.1. Materials

Toluene was dried over sodium metal and distilled under nitrogen. Methylaluminoxane was purchased from Albemarle as a 1.4 M of a toluene solution and used without further treating. [2-Methyl-8-(diphenylphosphino)quinoline]nickel(II) dichloride was synthesized and characterized according to the procedure reported in our previous work [30]. Norbornene (Acros) was purified by distillation over potassium and dissolved in toluene. All work involving air- and/or moisture-sensitive compounds was carried out under an atmosphere of nitrogen by using standard Schlenk and cannula techniques.

2.2. Measurements

NMR data for polynorbornene were obtained at ambient temperature on a JEOL AL-300 instrument using *o*-dichlorobenzene- d_4 as a solvent and were expressed in ppm using TMS as internal standard. IR spectra were recorded on a Perkin-Elmer system 2000 FT-IR spectrometer. Molecular weights were determined by a Waters Alliance GPCV 2000 system (USA) at 135 °C in 1,2,4-trichlorobenzene with narrow polystyrene as the distribution standards.

2.3. Typical polymerization procedure

Polymerizations were conducted in an oil bath (ice-water bath for 0 °C) to ensure a constant temperature. The polymerization mixture was stirred with a magnetic stirrer. Unless otherwise stated, the total reaction volume was 20 ml. This was achieved by variation of the amount of toluene if necessary. In a typical procedure (run 2 in Table 4) the catalyst (5 μmol , 10 μmol Ni) was dissolved in a Schlenk-type glass tube in 9.30 ml of dry, degassed toluene under nitrogen and a 6.40 ml solution of norbornene in dry, degassed toluene (7.80 M, 50 mmol of norbornene) was added via a syringe through a rubber septum. The polymerization was initiated by addition of a 1.4 M (10%) solution of methylaluminumoxane in toluene

(4.30 ml) via a syringe. After 10 min, the polymerization was terminated by pouring into 200 ml acidic ethanol (ethanol:HCl_{conc.} = 95:5). The polymer was isolated by filtration, washed three times with 30 ml ethanol, and dried in vacuum at 100 °C for 100 h. This gave white polynorbornene, which is soluble in chlorobenzene and some polar solvents. DSC investigation was failed, however, it showed no crystallinity in the solid state. Even different molecular weights were obtained by changing reaction conditions, same spectra were observed for those PNB. IR (KBr): 2947 (vs), 2869 (vs), 1474 (m), 1453 (s), 1375 (m), 1295 (m), 1258 (m), 1222 (m), 1147 (m), 1108 (m), 1041 (w), 942 (m), 892 (m), 727 (w), 694 (w), 519 (w) cm^{-1} . ^1H NMR (*o*-dichlorobenzene- d_4 , Fig. 2): δ = 0.87–2.28 (m, maxima at 0.87, 1.24, 1.59, 2.22).

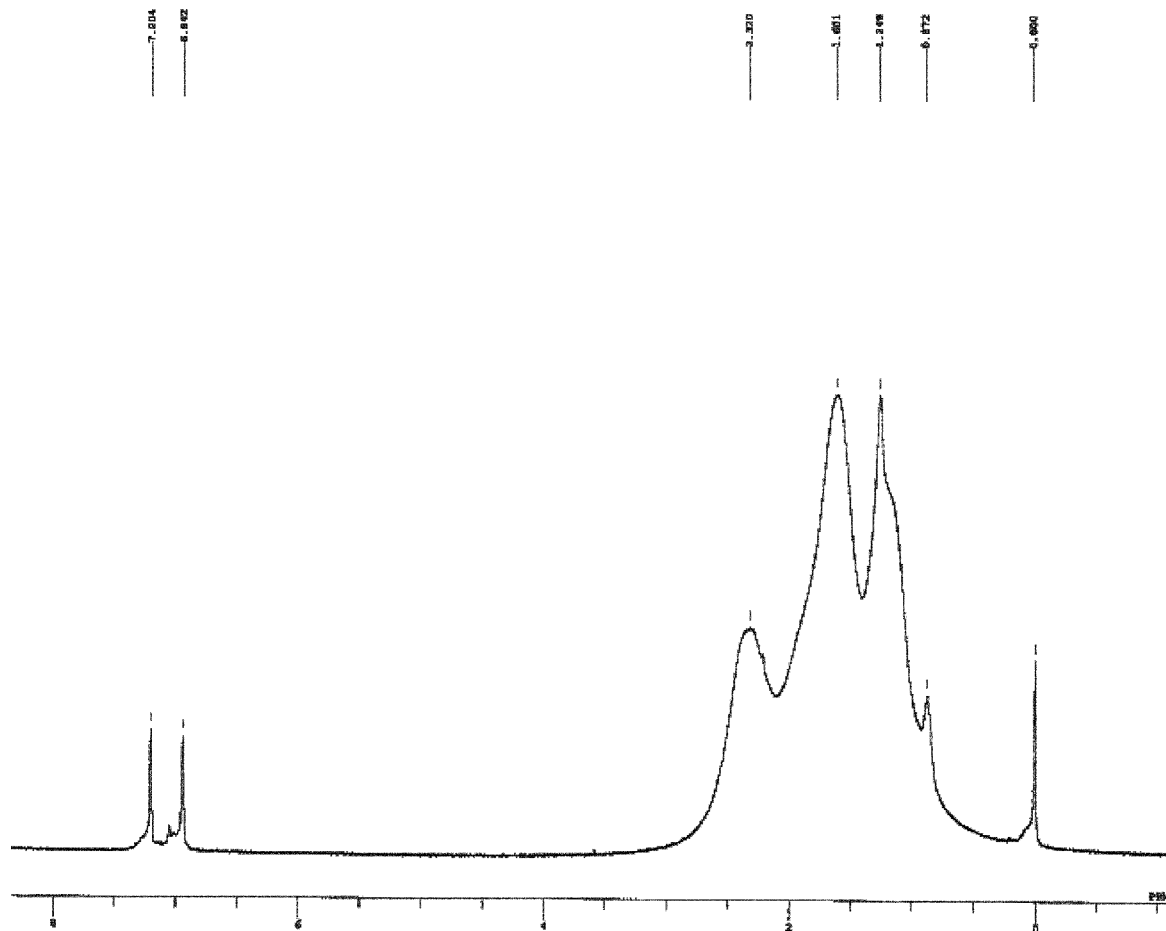


Fig. 2. ^1H NMR spectrum of polynorbornene.

^{13}C NMR (*o*-dichlorobenzene- d_4): $\delta = 30.35\text{--}48.92$ (m, maxima at 30.35, 32.55, 37.87, 48.55, 48.74).

3. Results and discussion

The active center was produced in situ in toluene solution by activating the nickel complex [2-methyl-8-(diphenylphosphino)quinoline]nickel(II) dichloride with cocatalyst methylaluminoxane. Although the dimeric structure of the nickel complex in the solid state was confirmed by X-ray single crystallography, the activated species are plausible monomers in the reaction solution [3,31]. Polymerization of norbornene in the presence of [2-methyl-8-(diphenylphosphino)quinoline]nickel(II) dichloride and MAO afforded polynorbornene. The IR and ^1H NMR spectra (Fig. 2) showed that the polymerization took place exclusively in a vinyl addition manner. The resultant polymers were soluble in chlorobenzene, suggesting that these polymers possessed low stereo regularity. Yield, molecular weight and molecular weight distribution of polymer, as well as the catalytic activity, depended significantly on the reaction parameters.

It was revealed that MAO was essential for this polymerization, and the catalytic activity was dependent upon the Al/Ni molar ratio as shown in Table 1 (1 mol catalyst = 2 mol Ni). The optimized Al/Ni molar ratio for the activity was 600 (run 3 in Table 1), and the activity decreased for both lower and higher molar ratios. GPC analyses showed that M_w value increased due to increase in the Al/Ni molar ratio.

As summarized in Table 2, the conversion were increased with increasing reaction time. Interestingly, an initiation period was observed; the activity after

Table 1
Influence of the MAO amount (Al/Ni)

Run	Al/Ni	Yield (%)	Activity ($\times 10^4$, g-PNB/mol-Ni h)	M_w (10^{-5} g/mol)	M_w/M_n
1	250	37.73	3.77	2.30	3.49
2	500	58.81	5.88	2.40	3.34
3	600	84.38	8.44	3.45	3.03
4	750	48.26	4.83	3.71	2.88
5	1000	46.73	4.67	4.24	3.59

Conditions: reaction volume, 20 ml; temperature, 25 °C; time, 1 h; nickel mole, 10 μmol ; M/Ni = 1062; MAO, prescribed milliliter.

Table 2
Influence of reaction time (*t*)

Run	<i>t</i> (min)	Yield (%)	Activity (g-PNB/mol-Ni h)
1	10	4.64	1.31×10^5
2	20	40.51	5.72×10^6
3	40	45.85	3.24×10^5
4	80	69.21	2.94×10^5
5	160	70.63	1.25×10^5

Conditions: reaction volume, 30 ml; Al/Ni = 600; nickel mole, 10 μmol ; M/Ni = 5000; temperature, 25 °C.

20 min was 5.72×10^6 g-PNB/mol-Ni h although the activity after 10 min was 1.31×10^5 g-PNB/mol-Ni h. The conversion was almost quantitative after 4 days, and the polymerization still took place by adding more norbornene into the reaction mixture. These results clearly indicated that the catalyst was still active after 4 days.

Effect of the monomer concentration (molar ratio of norbornene/catalyst (M/Ni)) was found to be very significant for the catalytic activity as well as for the molecular weight and polydispersity of resultant polynorbornene (Table 3). The high activity of 1.70×10^8 g-PNB/mol-Ni h and the M_w value of 20.78×10^5 with polydispersity index (PDI, M_w/M_n) of 19.20 were obtained when the polymerization was performed at the M/Ni ratio of 20,000:1 (run 6 in Table 3), whereas the activity of 8.44×10^4 g-PNB/mol-Ni h and the M_w value of 3.45×10^5 with PDI of 3.03 were obtained at the M/Ni ratio of 1062:1 (run 1 in Table 3). These phenomena demonstrated that the activity and molecular weight as well as the molecular weight distribution strongly depended upon the monomer concentration. Thus, regulating the M/Ni ratio provides an efficient

Table 3
Influence of the molar ratio of monomer:catalyst (M/Ni)

Run	M/Ni	Yield (%)	Activity (g-PNB/mol-Ni h)	M_w (10^{-5} g/mol)	M_w/M_n
1	1062	84.38	8.44×10^4	3.45	3.03
2	2000	65.52	1.37×10^5	5.42	3.22
3	2500	63.16	1.49×10^5	9.32	3.39
4	5000	55.38	7.82×10^5	17.74	7.04
5	10000	45.57	8.58×10^6	14.97	5.54
6	20000	37.64	1.70×10^8	20.78	19.20

Conditions: reaction volume, 20 ml; Al/Ni = 600; nickel mole, 10 μmol ; temperature, 25 °C; time: (1) 1 h, (2) 1 h, (3) 1 h, (4) 20 min, (5) 3 min, (6) 15 s.

Table 4
Influence of the reaction volume (*V*)

Run	<i>V</i> (ml)	Yield (%)	Activity (g-PNB/mol-Ni h)	M_w (10^{-5} g/mol)	M_w/M_n
1	10	55.96	3.16×10^6	13.19	6.44
2	20	54.42	1.54×10^6	11.26	4.77
3	40	17.34	4.90×10^5	14.47	3.92
4	80	5.19	1.47×10^5	5.34	2.51

Conditions: Al/Ni = 600; nickel mole, 10 μ mol; M/Ni = 5000; temperature, 25 °C; time: (1) 5 min, (2) 10 min, (3) 10 min, (4) 10 min.

way to control the M_w and M_w/M_n of polynorbornene. It is noteworthy that when the M/Ni ratio is over 5000:1, control of reaction temperature became critical due to the extreme exothermal reaction.

Changing the total volume of the catalytic system alters the concentration of both monomer and catalyst. Table 4 listed the result of enlarging the reaction volume through adding more toluene. The catalytic activities significantly decreased with increasing the reaction volume due to decrease in concentrations of both monomer and catalyst; moreover, the molecular weight dispersion decreased systematically.

The catalytic system showed good activities over a wide range (0–100 °C) of reaction temperature (Table 5), and it is clear that the M_w value was lower at higher temperature. Interestingly, the activities had a wavy relationship with the reaction temperature, which was reproducible when reaction parameters were carefully controlled. The plausible reason might be attributed to the configuration transformation of active center or the conversion of the propagating polymer chain configurations.

Moreover, the solvents have a great influence on the catalytic activities. With Al/Ni = 600 and M/Ni =

Table 5
Influence of reaction temperature (*T*)

Run	<i>T</i> (°C)	Yield (%)	Activity ($\times 10^4$, g-PNB/mol-Ni h)	M_w (10^{-5} g/mol)	M_w/M_n
1	0	67.07	6.71	3.73	2.79
2	25	84.38	8.44	3.45	3.03
3	50	47.98	4.80	2.52	3.06
4	75	66.93	6.69	2.63	2.45
5	100	80.25	8.03	2.24	3.67

Conditions: reaction volume, 20 ml; time, 1 h; Al/Ni = 600; nickel mole, 10 μ mol; M/Ni = 1062.

5000 at room temperature, the catalytic activity was 5.60×10^3 g-PNB/mol-Ni h in *n*-hexane and 7.82×10^5 g-PNB/mol-Ni h in toluene. A better catalytic activity of 2.70×10^7 g-PNB/mol-Ni h was observed in 1,2-dichloroethane, which is 35 times as high as the activity in toluene.

4. Conclusions

The [2-methyl-8-(diphenylphosphino)quinoline]nickel dichloride/MAO system showed high activity up to 1.70×10^8 g-PNB/mol-Ni h for the vinyl homopolymerization of norbornene. The catalytic activities, yields, molecular weights and molecular weight dispersions could be modified by adapting the reaction parameters. The polynorbornenes obtained were soluble in chlorobenzene at room temperature. Properly designed N–P nickel complexes could open new perspectives for further development of vinyl-type norbornene polymerization.

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