

## Article

# Copolymerization of Norbornene and Methyl Acrylate by Nickel Catalyst Bearing 2-(Diarylphosphino)-*N*-phenylbenzenamine Ligands

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**Abstract:** The synthesis of polar functionalized cyclic olefin copolymers (COCs) from the coordination copolymerization of norbornene (NB) and polar monomers catalyzed by late transition metal catalysts has been a recent research hotspot. However, few catalysts have achieved efficient copolymerization with commercial vinyl-type polar monomers, such as methyl acrylate (MA). In this contribution, nickel complexes bearing 2-(diarylphosphino)-*N*-phenylbenzenamine ligands were synthesized and applied as pre-catalysts to catalyze the (co)polymerization of norbornene. Upon the activation of methylaluminoxane (MAO), these nickel catalysts were active for norbornene polymerization with the highest activity achieved being  $3.6 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$  and the highest number average molecular weight ( $M_n$ ) of polynorbornene (PNB) reaching  $27.4 \times 10^5 \text{ g mol}^{-1}$ . Moreover, these nickel catalysts also promoted the copolymerization of norbornene and MA to furnish high-molecular-weight NB/MA copolymers ( $M_n$  up to  $6.20 \times 10^4 \text{ g mol}^{-1}$ ) with reasonable MA contents (3.07–5.90 mol%). The molecular weight of PNB and NB/MA copolymers obtained by the present nickel catalysts are remarkably higher than those of the (co)polymers from our previous reported dimethyl substituted phosphinobenzenamine nickel catalyst, suggesting significant progress in this field.

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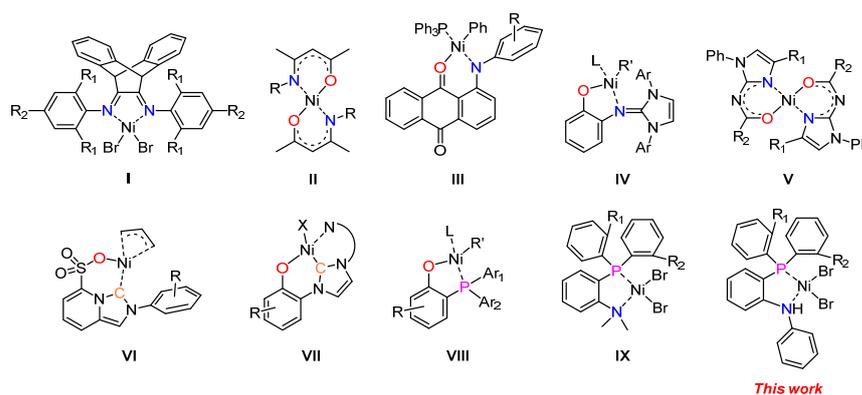
**Keywords:** phosphinobenzenamine nickel catalyst; norbornene; methyl acrylate; coordination copolymerization; polar functionalized cyclic olefin copolymer

## 1. Introduction

Polynorbornene (PNB) is known to be synthesized from norbornene (NB) by three catalytic methods: ring-opening metathesis polymerization (ROMP), cationic/radical polymerization, and vinyl-type addition polymerization [1–4]. The coordination polymerization of norbornene through its olefin double bond is a powerful catalytic approach since it not only furnishes saturated PNB products, which exhibit interesting and unique properties such as high transparency, excellent thermal stability, high chemical resistance, and good UV resistance, but also largely regulates the polymer microstructures and properties through an appropriate choice of catalyst. Ziegler–Natta catalysts, metallocene catalysts, early transition metal based non-metallocene catalysts, and late transition metal catalysts have been used to catalyze norbornene polymerization [1–11]. However, the non-polar polymer chain of PNB also brings several deficiencies such as poor solubility, mechanical brittleness, and low compatibility. In order to achieve further improvements in the properties, cyclic olefin copolymers (COCs) were developed through the coordination copolymerization of NB with various 1-alkenes such as ethylene, propylene, higher  $\alpha$ -olefins, and also polar monomers. In general, early transition metal catalysts play a dominant role in the preparation of non-polar COCs with precisely controlled

microstructures [4,5,12], while the late transition metal catalysts with lower oxygen affinities are more effective in the copolymerization using polar monomers [7–9,13].

Nickel catalysts have been widely used in the copolymerization of NB with polar monomers due to their flexible initiation process, high activity, good stability, and low cost. Most importantly, nickel catalysts exhibit high catalytic activity and good tolerance toward a wide scope of polar monomers; hence, it is a promising candidate to synthesize polar functionalized COCs from commercially available polar monomers, such as methyl acrylate (MA). As shown in Chart 1, nickel catalysts bearing the familiar  $[N,N]$ -type  $\alpha$ -diimine (**I**) [14–16],  $[N,O]$ -type  $\beta$ -ketoamine (**II**) [17,18], aniline-anthraquinone (**III**) [13], imidazolidin-2-imine (**IV** and **V**) [7,8] and  $N$ -heterocyclic carbene ligands (**VI** and **VII**) [10, 19], as well as  $[P,O]$ -type phosphino-phenolate ligands (**VIII**) [20] have been reported for the (co)polymerization of NB and polar monomers. However, very few of these nickel catalysts achieved the effective copolymerization of NB and a commercial MA monomer. We preconceive that a novel ligand platform, which is clearly distinguished from traditional catalyst skeletons, will provide potential catalysts with enhanced catalytic performance. Therefore, a series of  $[N,P]$ -based phosphinobenzenamine ligands (**IX**) were developed in our very recent work. Their nickel and palladium catalysts exhibited good catalytic performance toward olefin copolymerization with polar monomers including MA [21, 22]. In this contribution, substituents on the N atom of  $[N,P]$ -based phosphinobenzenamine ligands were further modified to achieve larger steric hindrance around the metal center in the nickel complexes, and the catalytic behaviors of these nickel catalysts in NB polymerization and copolymerization with MA were investigated.

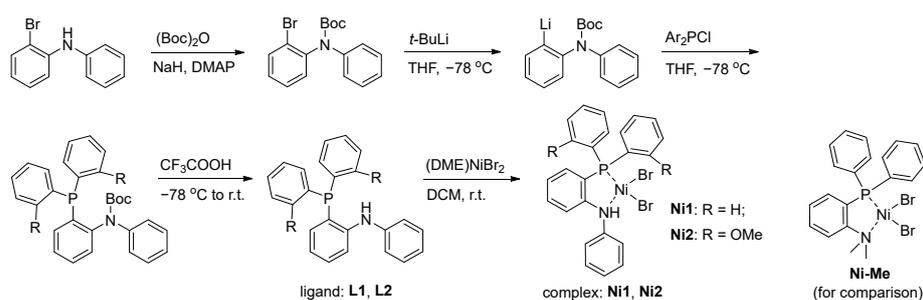


**Chart 1.** Reported nickel catalysts for norbornene copolymerization with polar monomers (R, R<sub>1</sub> and R<sub>2</sub> stand for different aryl and/or alkyl groups).

## 2. Results and Discussion

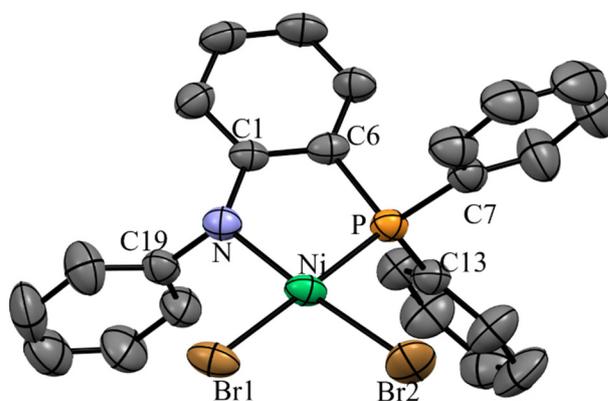
### 2.1. Synthesis of Ligands and Nickel Complexes

Scheme 1 shows the procedures for synthesis of ligands and nickel complexes. In the beginning, 2-bromodiphenylamine (**1**) was reacted with (Boc)<sub>2</sub>O in the presence of NaH and DMAP in THF to provide a pre-treated intermediate compound **2**, which was then transformed to its lithium salt (**3**) through the treatment with *t*-BuLi at  $-78$  °C. Following the reaction of **3** with substituted diphenyl-phosphinous chloride (Ar<sub>2</sub>PCl), the target ligands **L1** and **L2** can be obtained by removing the Boc protective group from compound **4** with CF<sub>3</sub>COOH. The treatment of each ligand with the nickel precursor (DME)NiBr<sub>2</sub> in DCM will give the expected nickel complexes **Ni1** (95%) and **Ni2** (93%) in excellent yields. The ligands **L1** and **L2** were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra and MALDI-TOF-MS analysis, and the nickel complexes **Ni1** and **Ni2** were confirmed using MALDI-TOF-MS analysis, elemental analysis, and single crystal X-ray diffraction analysis, respectively. All of the characterization results confirmed the successful synthesis of the target products. Moreover, the molecular structure of the reported phosphinobenzenamine nickel complex **Ni-Me** was also given for comparison [21].

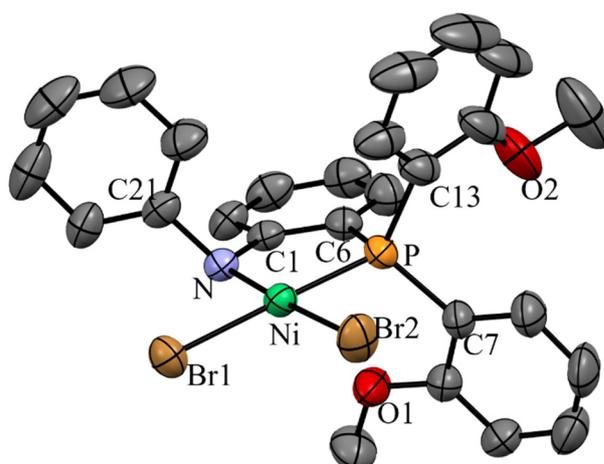


**Scheme 1.** Synthesis of 2-(diarylphosphino)-*N*-phenylbenzenamine ligands and nickel complexes.

The molecular structures of **Ni1** and **Ni2** in Figures 1 and 2 revealed that the nickel center presented nearly square-planar geometry, in which the N, P, Br1, and Br2 atoms served as four vertices of the plane and the nickel atom was located in the center with a very short displacement distance (0.015 Å for **Ni1** and 0.022 Å for **Ni2**) from the plane. The nickel atom formed a folded five-membered chelate ring with the ligand, and the dihedral angle between the plane consisting of N, C1, C6, and P atoms and the plane consisting of N, Ni, and P atoms was 171.54° (for **Ni1**) and 171.68° (for **Ni2**), respectively. The two nickel complexes **Ni1** and **Ni2** also exhibited structural differences with our previously reported complex **Ni-Me** [21], since the latter displayed a distorted tetrahedral geometry of the nickel center and thus had a smaller dihedral angle (145.11°) between the two planes. Another significant difference is the bond length. Although **Ni1** and **Ni-Me** have the same diphenylphosphine substituent, the introduction of a phenyl group on the N atom in **Ni1** afforded it a much shorter Ni–N bond length (1.973 Å) than that of **Ni-Me** (2.228 Å), suggesting the phenyl substituted *N*-donor in complex **Ni1** is stronger than the dimethyl substituted *N*-donor in complex **Ni-Me**.

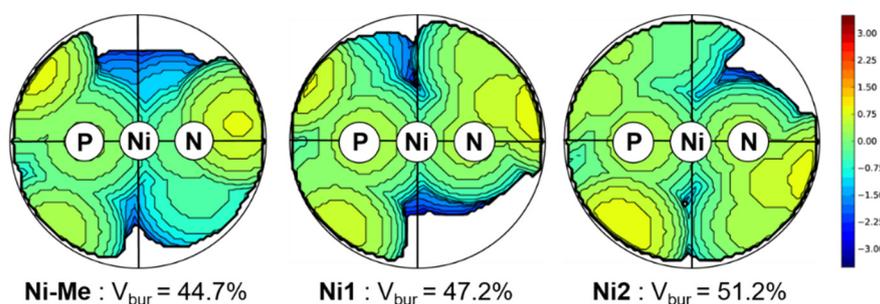


**Figure 1.** Oak Ridge thermal ellipsoid plot (ORTEP) representation of complex **Ni1** (50% thermal ellipsoids). Hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): Ni1–P1 2.1375(13), Ni1–N1 1.973(4), Ni1–Br1 2.3625(8), Ni1–Br2 2.2979(8), N1–Ni1–P1 87.87(11), Br1–Ni1–Br2 93.08(3).



**Figure 2.** ORTEP representation of complex **Ni2** (50% thermal ellipsoids). Hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): Ni1–P1 2.1480(14), Ni1–N1 1.961(4), Ni1–Br1 2.3745(6), Ni1–Br2 2.3132(7), N1–Ni1–P1 87.69(10), Br1–Ni1–Br2 93.37(2).

The steric hindrance around the nickel center in different complexes was visualized and quantified through the comparison of steric maps which was calculated using the SambVca 2.1 program (Figure 3) [23]. The buried volume percentage ( $V_{bur}$ ) value of the central nickel was effectively increased when the dimethyl substituted N group in the complex **Ni-Me** (44.7%) was replaced with a phenyl group in the complex **Ni1** (47.2%). The  $V_{bur}$  value was able to be further increased to 51.2% with the installation of a methoxy group on the aryl-phosphine moiety in complex **Ni2**.



**Figure 3.** Topographic steric maps of different nickel complexes.

## 2.2. Norbornene Polymerization

Norbornene homopolymerization was firstly investigated and the results are shown in Table 1. **Ni1** was selected as a representative pre-catalyst to find out the optimal parameters. Upon activation of MAO, **Ni1** was active for norbornene polymerization and the Al/Ni ratio significantly influenced the activity and also the molecular weight of the obtained polymers. When the Al/Ni ratio was increased from 200 to 2000, the activity of **Ni1** firstly increased from  $0.3 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$  to  $3.6 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$  (Al/Ni = 1000), and then slightly decreased to  $2.82 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$  (entries 1–5). The increased Al/Ni ratio is of help to improve the molecular weight of the polymer, and the highest molecular weight  $M_n$  was obtained at  $27.4 \times 10^5 \text{ g mol}^{-1}$  when an Al/Ni ratio of 2000 was used (entry 5). The influence of temperature on the polymerizations was also investigated at a constant Al/Ni ratio of 1000. With the temperature increased from 0 to 80 °C, the highest activity and the highest molecular weight of **Ni1** were both obtained at 25 °C (entries 3 and 6–9). With the temperature increased from 25 to 60 °C, the activity of **Ni2** increased from 0.18 to  $0.66 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$ , and then decreased to  $0.36 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$  at 80 °C (entries 10–13). Although the molecular weights of obtained polymers have subtle differences, **Ni2** exhibited much lower activity than **Ni1** under the same temperature (Figure 4), suggesting that the

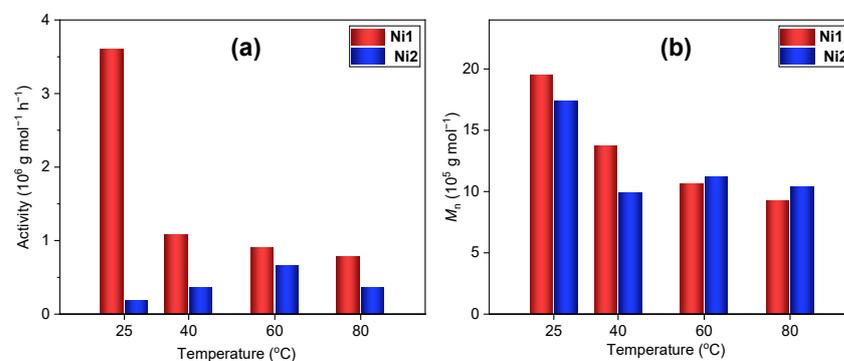
introduction of an electron-donating OMe substituent on the phosphine ligand may reduce the electropositivity of the nickel atom and weaken the coordination effect of monomers to the metal.

**Table 1.** Polymerization of norbornene by nickel complexes<sup>a</sup>.

Entry	Catalyst	T (°C)	Al/Ni	Yield (g)	Act. <sup>b</sup> (10 <sup>6</sup> )	M <sub>n</sub> <sup>c</sup> (10 <sup>5</sup> )	PDI <sup>c</sup>
1	Ni1	25	200	0.05	0.30	11.1	2.36
2	Ni1	25	500	0.05	0.30	10.6	2.40
3	Ni1	25	1000	0.60	3.60	19.5	2.21
4	Ni1	25	1500	0.50	3.00	22.3	2.57
5	Ni1	25	2000	0.47	2.82	27.4	2.23
6	Ni1	0	1000	0.23	1.38	13.6	2.79
7	Ni1	40	1000	0.18	1.08	13.7	2.68
8	Ni1	60	1000	0.15	0.90	10.6	2.58
9	Ni1	80	1000	0.13	0.78	9.27	2.49
10	Ni2	25	1000	0.03	0.18	17.4	2.50
11	Ni2	40	1000	0.06	0.36	9.88	2.99
12	Ni2	60	1000	0.11	0.66	11.2	3.03
13	Ni2	80	1000	0.06	0.36	10.4	2.62
14 <sup>d</sup>	Ni-Me	80	1000	0.30	1.20	2.07	1.72

<sup>a</sup> Polymerization conditions: Ni complexes, 2 μmol; cocatalyst, MAO; time = 5 min; V<sub>total</sub> (toluene) = 10 mL; NB = 20 mmol (1.883 g). <sup>b</sup> Activity in unit of g mol<sup>-1</sup> h<sup>-1</sup>. <sup>c</sup> GPC data in 1,2,4-trichlorobenzene at 150 °C with polystyrene standards, M<sub>n</sub> in units of g mol<sup>-1</sup>. <sup>d</sup> Data from literature [22].

Compared to the norbornene polymerization catalyzed by complex **Ni-Me** which has dimethyl substituents on the *N*-atom (entry 14), both of the Ph-substituted **Ni1** and **Ni2** exhibited higher molecular weight M<sub>n</sub> (9.27 × 10<sup>5</sup> g mol<sup>-1</sup> for **Ni1** and 10.4 × 10<sup>5</sup> g mol<sup>-1</sup> for **Ni2** at 80 °C) than that of **Ni-Me** (2.07 × 10<sup>5</sup> g mol<sup>-1</sup> at 80 °C). In other words, the introduction of a large steric hindrance around the metal center in these [N,P]-based phosphino-benzenamine nickel complexes can effectively increase the molecular weight of the polymer, which is consistent with reported results [24–27]. The monomer insertion rate (R<sub>i</sub>) and chain termination rate (R<sub>t</sub>) were calculated according to the references reported by Eisen et al. [28,29]. At 80 °C, the Ph-substituted **Ni1** has a R<sub>i</sub> value of 16.57 mmol/h and a R<sub>t</sub> value of 1.68 μmol, while **Ni2** has a lower R<sub>i</sub> value of 7.65 mmol/h and an R<sub>t</sub> value of 0.69 μmol (entries 9 and 13). In contrast, the previously reported **Ni-Me** exhibited a much higher R<sub>t</sub> value of 5.80 μmol to produce low-molecular-weight polynorbornene (entry 14).



**Figure 4.** Comparison of (a) activity and (b) molecular weight M<sub>n</sub> of **Ni1** and **Ni2** systems at different temperatures.

### 2.3. Norbornene Copolymerization

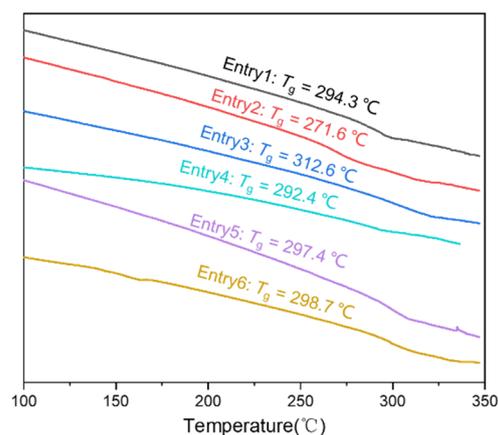
The copolymerization results of norbornene and MA catalyzed by **Ni1** and **Ni2** are listed in Table 2. It is consistent with most of the previous reports that the addition of polar monomers will reduce the activity due to the poisoning effect of polar functional groups. However, all of the copolymerization activities were maintained at a  $10^4 \text{ g mol}^{-1} \text{ h}^{-1}$  order of magnitude, suggesting the good tolerance of the two nickel complexes. When 2 mmol MA was used in feed, the highest activity **Ni1** achieved was  $5.80 \times 10^4 \text{ g mol}^{-1} \text{ h}^{-1}$  to produce NB/MA copolymers with a molecular weight  $M_n$  of  $2.44 \times 10^4 \text{ g mol}^{-1}$  and an MA incorporation of 3.53 mol% (entry 1). When the MA in feed was increased to 4 mmol, the activity and molecular weight were reduced, accompanied by an increase in the MA incorporation to 5.90 mol% (entry 2). Keeping the high MA dosage at 4 mmol, the increased Al/Ni ratio did not give any improvement either in the activity, the molecular weight, or the MA incorporation (entry 3). At the temperature of 20 °C and with the 2 mmol MA in feed, the activity of **Ni2** was still lower than **Ni1**. The activity of **Ni2** increased from 0.94 to  $2.20 \times 10^4 \text{ g mol}^{-1} \text{ h}^{-1}$  and then decreased to  $2.0 \times 10^4 \text{ g mol}^{-1} \text{ h}^{-1}$  with the temperature increase from 20 to 60 °C, accompanied by decreased molecular weight and MA incorporation (entries 4–6). The OMe substituted **Ni2** produced copolymers with higher molecular weights than the polymers obtained by **Ni1**. In fact, all of the NB/MA copolymers obtained by the present Ph-substituted nickel catalysts exhibited higher molecular weights than those of the dimethyl substituted **Ni-Me**, although the latter gave higher activity (entries 7 and 8). The obtained NB/MA copolymers were characterized using DSC analysis with the temperature increased from 40 to 350 °C, and the NB/MA copolymer exhibited lower  $T_g$  values (271.6–312.6 °C, Figure 5) compared to NB homopolymers (usually  $T_g > 400 \text{ °C}$ ).

**Table 2.** Copolymerization of norbornene with MA by nickel complexes<sup>a</sup>.

Entry	Cat.	<i>T</i> (°C)	MA (mmol)	Yield (mg)	Act. <sup>b</sup> (10 <sup>4</sup> )	$M_n^c$ (10 <sup>4</sup> )	PDI <sup>c</sup>	Incorp <sup>d</sup> (mol %)	$T_g^e$ (°C)
1	<b>Ni1</b>	20	2	145.0	5.80	2.44	2.37	3.53	294.3
2	<b>Ni1</b>	20	4	77.3	3.09	2.27	2.01	5.90	271.6
3 <sup>f</sup>	<b>Ni1</b>	20	4	66.5	2.66	2.48	2.60	5.32	312.6
4	<b>Ni2</b>	20	2	47.0	0.94	6.20	2.45	4.16	292.4
5	<b>Ni2</b>	40	2	110.0	2.20	3.05	2.90	3.11	297.4
6	<b>Ni2</b>	60	2	100.0	2.00	2.88	4.65	3.07	298.7
7 <sup>g</sup>	<b>Ni-Me</b>	40	2	94.0	37.6	0.74	1.86	6.18	329.0
8 <sup>g</sup>	<b>Ni-Me</b>	40	4	70.0	28.0	0.72	1.43	6.47	327.0

<sup>a</sup> Polymerization conditions: Ni complexes, 5 μmol; Al/Ni = 200; time = 30 min for **Ni1**, time = 60 min for **Ni2**;  $V_{\text{total}}$  (toluene) = 6 mL; NB = 20 mmol (1.883 g). <sup>b</sup> Activity in units of  $\text{g mol}^{-1} \text{ h}^{-1}$ . <sup>c</sup> GPC data in 1,2,4-trichlorobenzene at 150 °C with polystyrene standards,  $M_n$  in units of  $\text{g mol}^{-1}$ . <sup>d</sup> Incorporation of MA in the copolymer determined by <sup>1</sup>H NMR spectroscopy. <sup>e</sup> Determined by DSC. <sup>f</sup> Al/Ni = 500. <sup>g</sup> Data from literature [22].

It should be noted that palladium catalysts bearing [N,N]-type ligands have been reported to produce NB/MA copolymers with a high MA incorporation, up to 82 mol% [30,31], while few nickel catalysts have achieved the copolymerization of norbornene and MA. The bis(*N*-acylated imidazolin-2-imine) nickel catalyst can promote the copolymerization of norbornene and MA with a similar activity and molecular weight to the present nickel catalyst to produce copolymers with a much lower MA incorporation (1.13–2.54 mol%).



**Figure 5.** DSC curves of NB/MA copolymers obtained by Ni1 and Ni2.

### 3. Experimental Section

#### 3.1. General Conditions

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware (SYNTHWARE, Beijing, China) or J-Young Teflon valve-sealed NMR tubes (SYNTHWARE, Beijing, China) on a dual manifold Schlenk line (SYNTHWARE, Beijing, China) interfaced to a high vacuum ( $10^{-5}$  Torr) line, or in a nitrogen-filled Innovative Technologies glovebox (Oldham, UK) with a medium-capacity recirculator (1–2 ppm of  $O_2$ ).

#### 3.2. Materials

Norbornene, methyl acrylate and  $CaH_2$  were purchased from J&K scientific (Beijing, China). MAO was purchased from Methyl Technology Co., Ltd (Wuhan, China). Dichloromethane, tetrahydrofuran, diethyl ether, toluene, and *n*-hexane were purchased from Lingfeng Chemical Reagent Co., Ltd (Shanghai, China). Other reagents were purchased from local suppliers (Shanghai, China).

Nitrogen (Chenggong Gas Industry Co., Ltd, Shanghai, China) was purified by passage through a  $MnO$  oxygen-removal column and a Davison 4 Å molecular sieve column. Dichloromethane, tetrahydrofuran, diethyl ether, toluene, and *n*-hexane were purified using a PS-MD-5 (Innovative Technology, Oldham, UK) solvent purification system. Norbornene was dissolved in dry toluene and stirred with  $CaH_2$  for 24 h, then the solution was distilled under reduced pressure. Methyl acrylate (MA) was dried with  $CaH_2$  overnight and then freshly distilled before use. All the other reagents were purchased and used as received.

#### 3.3. Measurements

NMR spectra were recorded on a Bruker-600 (Bruker, Fällanden, Switzerland) spectrometer using  $CDCl_3$  and DMSO as solvent, and the central peak of the solvent was used as an internal reference ( $CDCl_3$ ,  $\delta$ : 7.26, {77.16} ppm; DMSO,  $\delta$ : 2.50, {39.52} ppm). Elemental analyses were performed with the Vario ELIII elemental analyzers manufactured by Elementar Analysensysteme GmbH (Hanau, Germany). Differential scanning calorimetry (DSC) analyses were performed on a TA Differential Scanning Calorimeter Q2000 (TA Instruments, New Castle, DE, USA) and the DSC curves of the samples were recorded under a nitrogen atmosphere at a heating rate of 10 °C/min from 40 to 150 °C. Molecular weight and molecular weight distribution of the polymers obtained were determined using a polymer laboratory PL GPC-220 (Polymer Laboratories, Varian, Palo Alto, CA, USA) equipped with a triple-detection array consisting of a differential refractive index (DRI) detector, a two-angle light scattering (LS) detector at a laser wavelength of 658 nm, and a four-bridge capillary viscosity detector. This system included one guard column (PL#

1110–1120) and two 30 cm columns (PLgel 10  $\mu$ m MIXED-B 7.5  $\times$  300 mm). Polymer characterization was carried out at 150 °C with 1,2,4-trichlorobenzene as eluent and calibrated by polystyrene standards.

### 3.4. Norbornene (Co)Polymerization

Norbornene (co)polymerization was performed in a 50 mL flask equipped with a magnetic stirrer and carried out using the following methods. At first, the flask was charged with norbornene (20 mmol, 1.883 g), MA (2 mmol, 0.172 g or 4 mmol, 0.344 g, for copolymerization), and toluene under nitrogen. The cocatalyst MAO (Al/Ni ratio of 200–2000) was also injected into the flask prior to the nickel catalyst. After the mixture was kept at the desired temperature for 10 min, (co)polymerization was initiated by the introduction of the nickel complexes (2  $\mu$ mol or 5  $\mu$ mol) in toluene into the flask via syringe, and the reaction was started. The desired time later, the (co)polymerization was terminated by the addition of 10% HCl in ethanol. The precipitated polymer was washed with ethanol and water and dried at 60 °C in a vacuum to a constant weight. For all the (co)polymerization procedures, the reaction volume in total was constant, which can be achieved by variation in the added toluene when necessary.

### 3.5. Crystal Structure Determinations

The single crystals were mounted under a nitrogen atmosphere at low temperature, and data collection was conducted on a Bruker APEX2 diffractometer (Bruker, Fällanden, Switzerland) using graphite monochromated with Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The SMART program package was used to determine the unit cell parameters. The absorption correction was applied using the SADABS (Version 2.03) program. All structures were solved by direct methods and refined on F2 by full-matrix least-squares techniques with anisotropic thermal parameters for nonhydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation. Calculations were carried out using the SHELXS-97 (Sheldrick, 2015), SHELXL-2014 (Sheldrick, 2015), or Olex2 (Version 1.5) program. Crystallographic data are summarized in Tables S1 and S2, and in CIF files, and checks are provided in the Supplementary Materials.

### 3.6. Synthesis of *Tert-Butyl N-(2-bromophenyl)-N-phenylcarbamate*

A solution of Boc<sub>2</sub>O (11 mmol, 1.1 eq.) in THF (5 mL) was added to a solution of 2-bromo-*N*-phenylaniline (10 mmol, 1.0 eq.) in THF (50 mL) along with a catalytic amount of DMAP (0.25 mmol, 0.025 eq.) and 10 mmol of NaH (1.0 eq.). The reaction mixture was refluxed at 100 °C for 12 h. A saturated NaHCO<sub>3</sub> aqueous solution was then added to the mixture, which was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  10 mL). The organic layers were collected and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure. The product was dissolved with hexane and recrystallized to afford the desired product (85.7% yield) as a white solid. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  7.65 (m, 1H, Ar-CH), 7.34–7.27 (m, 6H, Ar-CH), 7.16 (m, 1H, Ar-CH), 7.12 (m, 1H, Ar-CH), 1.44 (s, 9H, CH(CH<sub>3</sub>)<sub>3</sub>).

### 3.7. Synthesis of 2-(diphenylphosphino)-*N*-phenylbenzenamine Ligand L1

A solution of *t*-BuLi (1.1 eq.) was added dropwise by syringe to the THF solution of *tert*-butyl *N*-(2-bromophenyl)-*N*-phenylcarbamate (1.0 eq.) at –78 °C and the mixture was stirred for 2 h. Subsequently, the solution of chlorodiphenyl phosphine (1.1 eq.) in THF (5 mL) was added to the reaction mixture, and the reaction continued for 6 h at room temperature. Thereafter, the reaction system was again reduced to –78 °C and CF<sub>3</sub>COOH (20.0 eq.) was added and stirred for 7 h. The solvent was evaporated at a reduced pressure and the product was washed with methanol to afford the desired product (80.0% yield) as a white solid. <sup>1</sup>H NMR (600 MHz, Chloroform-*d*)  $\delta$  7.40–7.34 (m, 10H, Ar-CH), 7.32 (m, 1H, Ar-CH), 7.28–7.24 (m, 1H, Ar-CH), 7.24–7.20 (m, 2H, Ar-CH), 6.98–6.95 (m, 2H, Ar-CH),

6.91 (m, 2H, Ar-CH), 6.87–6.84 (m, 1H, Ar-CH), 6.33 (s, 1H, NH).  $^{13}\text{C}$  NMR (151 MHz, Chloroform-*d*)  $\delta$  146.89, 142.86, 135.31, 134.77, 133.88, 130.27, 129.32, 129.17, 128.87, 124.39, 121.59, 121.23, 119.11, 116.82.  $^{31}\text{P}$  NMR (243 MHz, Chloroform-*d*)  $\delta$  -19.30. MALDI-TOF-MS (*m/z*): calcd for  $\text{C}_{24}\text{H}_{20}\text{NP}$  353.133, found 352.049 [M - H] $^-$ .

### 3.8. Synthesis of 2-(di-(2'-methoxyphenyl)phosphino)-N-phenylbenzenamine Ligand L2

Ligand **L2** was synthesized in a similar way to ligand **L1**, in which the chlorodiphenyl phosphine was replaced by chloro-di-(2-methoxyphenyl) phosphine.  $^1\text{H}$  NMR (600 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.34 (m, 2H, Ar-CH), 7.32–7.26 (m, 1H, Ar-CH), 7.23–7.16 (m, 2H, Ar-CH), 7.13 (m, 2H, Ar-CH), 7.02 (m, 2H, Ar-CH), 6.90 (m, 2H, Ar-CH), 6.87 (m, 2H, Ar-CH), 6.74 (m, 1H, Ar-CH), 6.68 (m, 1H, Ar-CH), 6.60 (m, 2H, Ar-CH), 3.67 (s, 6H, O-CH<sub>3</sub>).  $^{31}\text{P}$  NMR (243 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  -38.17. MALDI-TOF-MS (*m/z*): calcd for  $\text{C}_{26}\text{H}_{24}\text{NO}_2\text{P}$  413.154, found 412.030 [M - H] $^-$ .

### 3.9. Synthesis of [2-(Diphenylphosphino)-N-phenylbenzenamine]NiBr<sub>2</sub> Complex Ni1

(DME)NiBr<sub>2</sub> (5 mmol, 1.0 eq.) and ligand **L1** (5 mmol, 1.0 eq.) were dissolved in dichloromethane and reacted at room temperature for 12 h. Then, the solvent was removed under a vacuum and the product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Hexane to obtain purple crystals (yield: 95%). Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{Br}_2\text{NNiP}$ : C, 50.40; H, 3.53; N, 2.45; Found: C, 50.13; H, 3.21; N, 2.32. MALDI-TOF-MS (*m/z*): calcd for  $\text{C}_{24}\text{H}_{20}\text{Br}_2\text{NNiP}$  568.905, found 410.999 [M - 2 Br] $^{2+}$ .

### 3.10. Synthesis of [2-(di-(2'-methoxyphenyl)phosphino)-N-phenylbenzenamine]NiBr<sub>2</sub> Complex Ni2

Ni2 was synthesized in a similar way to **Ni1**, in which **L1** was replaced by **L2**. Complex **Ni2** was isolated as a purple crystal (yield: 93%). Anal. Calcd for  $\text{C}_{26}\text{H}_{24}\text{Br}_2\text{NNiO}_2\text{P}$ : C, 49.42; H, 3.83; N, 2.22; Found: C, 49.38; H, 3.71; N, 2.12. MALDI-TOF-MS (*m/z*): calcd for  $\text{C}_{26}\text{H}_{24}\text{Br}_2\text{NNiO}_2\text{P}$  628.926, found 470.995 [M - 2 Br] $^{2+}$ .

## 4. Conclusions

2-(Diarylphosphino)-N-phenylbenzenamine nickel complexes were synthesized and characterized. In the presence of MAO, these nickel catalysts are active for norbornene polymerization to produce high-molecular-weight PNB. **Ni2** bearing an electron-donating OMe substituent on the ligand exhibited lower activity than the nonsubstituted catalyst **Ni1**. These nickel catalysts also exhibited good tolerance toward polar groups and promoted the copolymerization of norbornene and an MA monomer to generate an NB/MA copolymer with moderate activity, high molecular weight, and reasonable MA incorporations. Compared to the previously reported dimethyl-substituted nickel catalyst **Ni-Me**, the installation of a Ph group on the N atom of a phosphinobenzenamine ligand enabled their nickel catalyst to produce PNB and NB/MA copolymers with significantly increased molecular weights.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13020311/s1>, Table S1: Crystal data and structure refinement for complexes **Ni1** and **Ni2**; Table S2: Crystal data and structure refinement for complexes **L2**; Table S3–S6: NMR spectrum of **L1** and **L2**; Figure S7: ORTEP representation of ligand **L2**; Table S8–S11: MALDI-TOF-MS spectrum of **L1**, **L2**, **Ni1** and **Ni2**; Table S12–S18:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of copolymers; Table S19–S36: GPC data of the polymers; Table S37–S41: DSC curves of the copolymers.

**Author Contributions:** L.C. performed overall experimental work. M.L. constructed the experimental protocols and participated in the analysis of structural data. The setting up of the experimental protocols as well as the interpretation of the obtained results were performed under the supervision of Z.C. All authors tried their best to contribute effectively to perform and analyze this

experimental work. They all participated to the writing of the present manuscript. All authors have read and agreed to the published version of the manuscript.

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