


Article

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

Lixin Cao ¹, Mingyuan Li ^{2,*} and Zhengguo Cai ^{1,*} 

¹ State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

² Department of Chemistry, Guangdong Technion—Israel Institute of Technology, Shantou 515063, China

* Correspondence: mingyuan.li@gtit.edu.cn (M.L.); caizg@dhu.edu.cn (Z.C.)

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.

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



Citation: Cao, L.; Li, M.; Cai, Z. Copolymerization of Norbornene and Methyl Acrylate by Nickel Catalyst Bearing 2-(Diarylphosphino)-*N*-phenylbenzenamine Ligands. *Catalysts* **2023**, *13*, 311. <https://doi.org/10.3390/catal13020311>

Academic Editors: Victorio Cadierno and Raffaella Mancuso

Received: 3 January 2023

Revised: 20 January 2023

Accepted: 21 January 2023

Published: 31 January 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

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 α -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 α -diimine (I) [14–16], $[N,O]$ -type β -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.

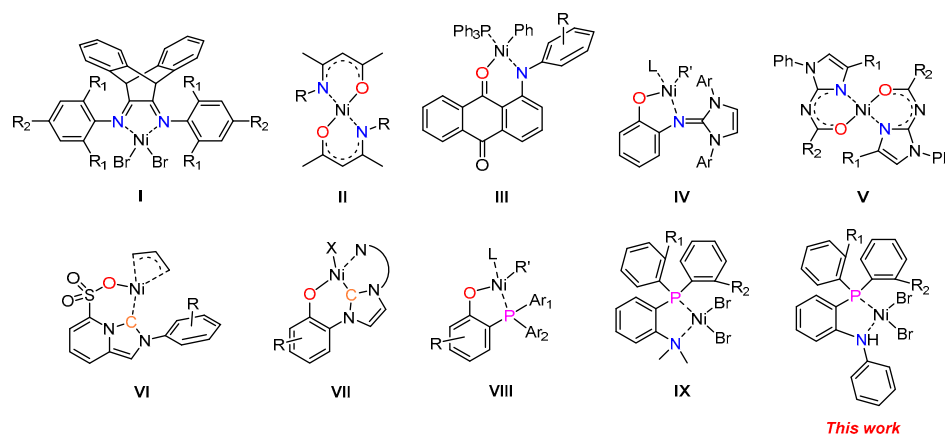
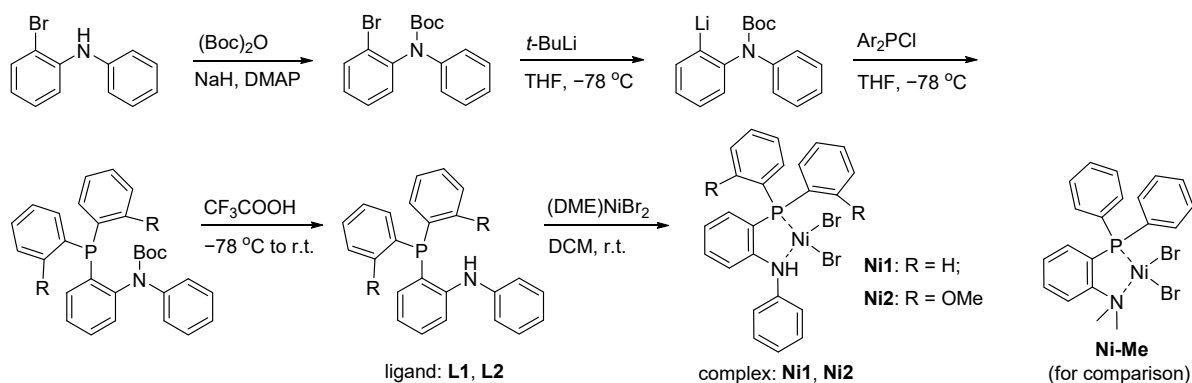


Chart 1. Reported nickel catalysts for norbornene copolymerization with polar monomers (R, R₁ and R₂ stand for different aryl and/or alkyl groups).

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)₂O 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 (Ar₂PCl), the target ligands **L1** and **L2** can be obtained by removing the Boc protective group from compound **4** with CF₃COOH. The treatment of each ligand with the nickel precursor (DME)NiBr₂ in DCM will give the expected nickel complexes **Ni1** (95%) and **Ni2** (93%) in excellent yields. The ligands **L1** and **L2** were characterized by ¹H, ¹³C, and ³¹P 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**.

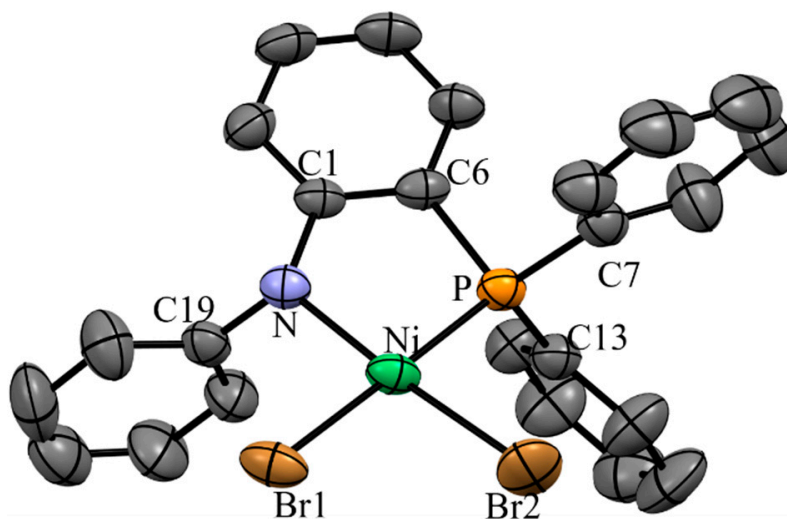


Figure 1. Oak Ridge thermal ellipsoid plot (ORTEP) representation of complex **Ni1** (50% thermal ellipsoids). Hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): Ni1–P1 2.1375(13), Ni1–N1 1.973(4), Ni1–Br1 2.3625(8), Ni1–Br2 2.2979(8), N1–Ni1–P1 87.87(11), Br1–Ni1–Br2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

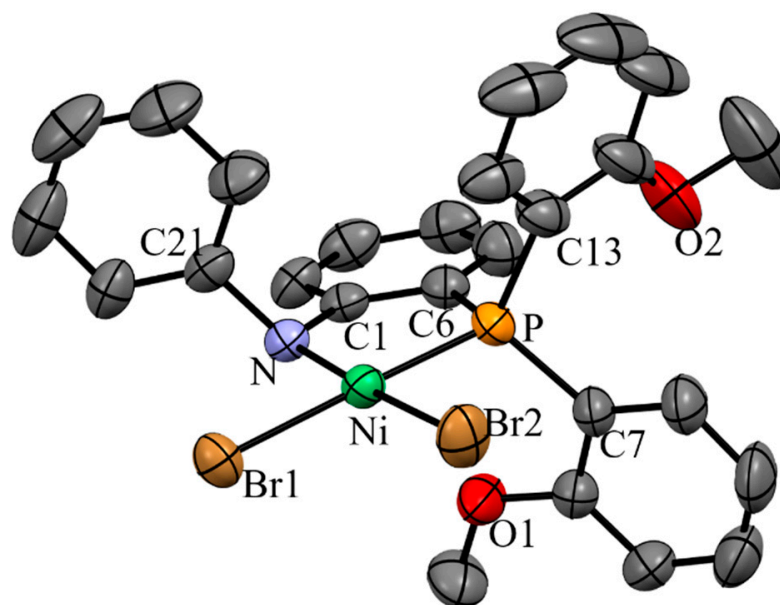


Figure 2. ORTEP representation of complex **Ni2** (50% thermal ellipsoids). Hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): Ni1–P1 2.1480(14), Ni1–N1 1.961(4), Ni1–Br1 2.3745(6), Ni1–Br2 2.3132(7), N1–Ni1–P1 87.69(10), Br1–Ni1–Br2 93.37(2).

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**.

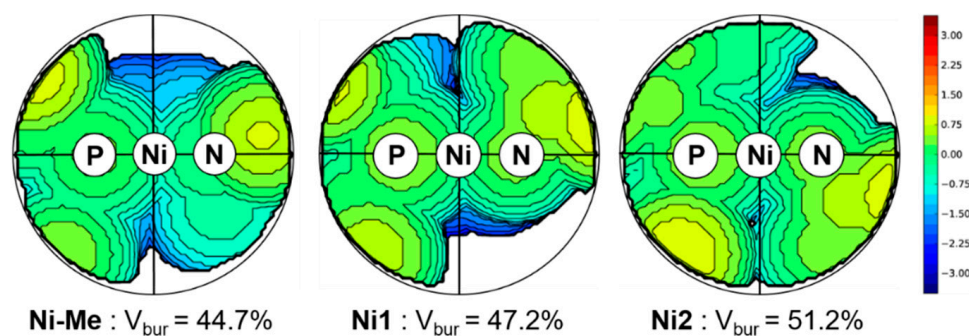


Figure 3. Topographic steric maps of different nickel complexes.

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 ^a.

Entry	Catalyst	T (°C)	Al/Ni	Yield (g)	Act. ^b (10^6)	M _n ^c (10^5)	PDI ^c
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 ^d	Ni-Me	80	1000	0.30	1.20	2.07	1.72

^a Polymerization conditions: Ni complexes, 2 μmol; cocatalyst, MAO; time = 5 min; V_{total} (toluene) = 10 mL; NB = 20 mmol (1.883 g). ^b Activity in unit of $\text{g mol}^{-1} \text{ h}^{-1}$. ^c GPC data in 1,2,4-trichlorobenzene at 150 °C with polystyrene standards, M_n in units of g mol^{-1} . ^d Data from literature [22].

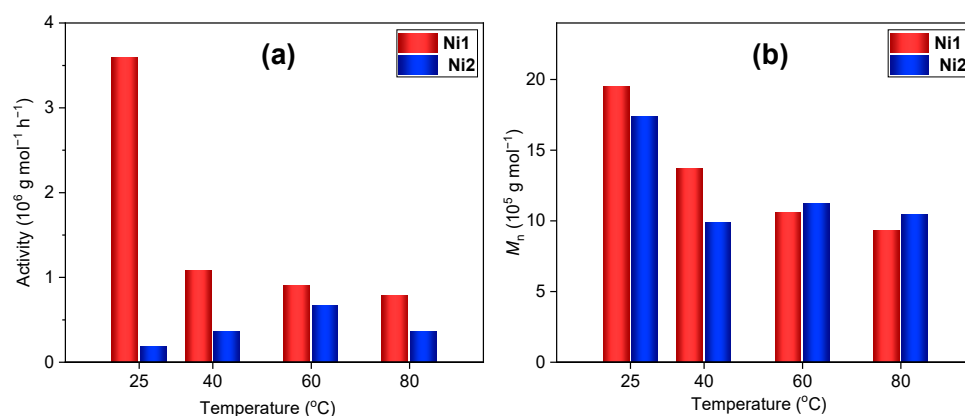


Figure 4. Comparison of (a) activity and (b) molecular weight M_n of Ni1 and Ni2 systems at different temperatures.

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_n ($9.27 \times 10^5 \text{ g mol}^{-1}$ for Ni1 and $10.4 \times 10^5 \text{ g mol}^{-1}$ for Ni2 at 80 °C) than that of Ni-Me ($2.07 \times 10^5 \text{ g mol}^{-1}$ at 80 °C). In other words, the introduction of a large steric hindrance around the metal center in these [N,P]-based phosphinobenzene nickel complexes can effectively increase the molecular weight of the polymer, which is consistent with reported results [24–27]. The monomer insertion rate (R_i) and chain termination rate (R_t) were calculated according to the references reported by Eisen et al. [28,29]. At 80 °C, the Ph-substituted Ni1 has a R_i value of 16.57 mmol/h and a R_t value of 1.68 μmol, while Ni2 has a lower R_i value of 7.65 mmol/h and an R_t value of

0.69 μmol (entries 9 and 13). In contrast, the previously reported **Ni-Me** exhibited a much higher R_t value of 5.80 μmol to produce low-molecular-weight polynorbornene (entry 14).

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 $T_g > 400$ °C).

Table 2. Copolymerization of norbornene with MA by nickel complexes ^a.

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

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

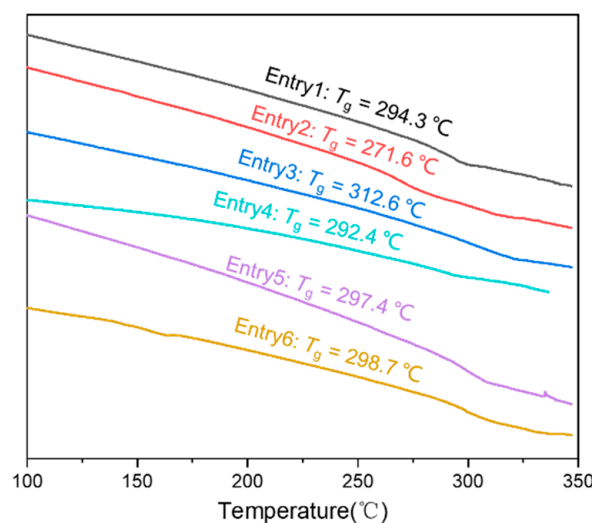


Figure 5. DSC curves of NB/MA copolymers obtained by Ni1 and Ni2.

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 ($CDCl_3$, d: 7.26, {77.16} ppm; DMSO, d: 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 $10\text{ }^\circ\text{C}/\text{min}$ from $40\text{ }^\circ\text{C}$ to $150\text{ }^\circ\text{C}$. 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 μ 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 μ mol or 5 μ 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 Ka 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 Boc₂O (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 NaHCO₃ aqueous solution was then added to the mixture, which was extracted with CH₂Cl₂ (3 \times 10 mL). The organic layers were collected and dried with anhydrous Na₂SO₄, 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. ¹H NMR (600 MHz, Chloroform-*d*) δ 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(CH₃)₃).

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 CF₃COOH (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. ¹H NMR (600 MHz, Chloroform-*d*) δ 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). ¹³C NMR (151 MHz,

Chloroform-*d*) δ 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}P NMR (243 MHz, Chloroform-*d*) δ -19.30. MALDI-TOF-MS (*m/z*): calcd for $\text{C}_{24}\text{H}_{20}\text{NP}$ 353.133, found 352.049 $[\text{M} - \text{H}]^-$.

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. ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 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-CH₃). ^{31}P NMR (243 MHz, $\text{DMSO-}d_6$) δ -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 $[\text{M} - \text{H}]^-$.

3.9. Synthesis of [2-(Diphenylphosphino)-*N*-phenylbenzenamine]NiBr₂ Complex Ni1

(DME)NiBr₂ (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_2Cl_2 /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 $[\text{M} - 2\text{Br}]^{2+}$.

3.10. Synthesis of [2-(di-(2'-methoxyphenyl)phosphino)-*N*-phenylbenzenamine]NiBr₂ 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 $[\text{M} - 2\text{Br}]^{2+}$.

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 S1–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: ^1H and ^{13}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.

Funding: This work was supported by the Fundamental Research Funds for the Central Universities (2232020A-05), National Natural Science Foundation of China (22071023, 22101056), and Program of Shanghai Academic/Technology Research Leader (22XD1400100).

Data Availability Statement: The data presented in this study are available in this article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Huo, P.; Liu, W.; He, X.; Mei, G. Vinylic Copolymerization of Norbornene and Higher 1-Alkene with Three-Dimensional Geometry Binickel Catalyst. *J. Polym. Res.* **2015**, *22*, 194. [CrossRef]
2. Sun, W.; Yang, H.; Li, Z.; Li, Y. Vinyl Polymerization of Norbornene with Neutral Salicylaldiminato Nickel(II) Complexes. *Organometallics* **2003**, *22*, 3678–3683. [CrossRef]
3. Ma, R.; Hou, Y.; Gao, J.; Bao, F. Recent Progress in the Vinylic Polymerization and Copolymerization of Norbornene Catalyzed by Transition Metal Catalysts. *Polym. Rev.* **2009**, *49*, 249–287. [CrossRef]
4. Zhao, W.; Nomura, K. Copolymerizations of Norbornene and Tetracyclododecene with α -Olefins by Half-Titanocene Catalysts: Efficient Synthesis of Highly Transparent, Thermal Resistance Polymers. *Macromolecules* **2016**, *49*, 59–70. [CrossRef]
5. Marconi, R.; Boggioni, L.; Ravasio, A.; Colo, F.D.; Tritto, I.; Stehling, U.M. Terpolymerization of Linear and Alicyclic α -Olefins with Norbornene and Ethylene by *ansa*-Metallocene Catalysts. *Macromolecules* **2011**, *44*, 795–804. [CrossRef]
6. Wang, X.; Dong, B.; Yang, Q.; Liu, H.; Hu, Y.; Zhang, X. Boosting the Thermal Stability of α -Diimine Palladium Complexes in Norbornene Polymerization from Construction of Intraligand Hydrogen Bonding and Simultaneous Increasing Axial/Equatorial Bulkiness. *Inorg. Chem.* **2021**, *60*, 2347–2361. [CrossRef]
7. Li, Y.; Zhang, H.; Xiao, R.; Cai, Z. Bis(*N*-acylated imidazolin-2-imine) nickel catalyzed norbornene copolymerization with methyl acrylate. *Polym. Chem.* **2020**, *11*, 5542–5547. [CrossRef]
8. Li, M.; Cai, Z.; Eisen, M.S. Neutral Nickel(II) Complexes Bearing Aryloxy Imidazolin-2-imine Ligands for Efficient Copolymerization of Norbornene and Polar Monomers. *Organometallics* **2018**, *37*, 4753–4762. [CrossRef]
9. Zheng, T.; Liao, H.; Gao, J.; Zhong, L.; Gao, H.; Wu, Q. Synthesis and Characterization of α -Diamine Palladium Complexes and Insight Into Hybridization Effects of Nitrogen Donor Atoms on Norbornene (Co)Polymerizations. *Polym. Chem.* **2018**, *9*, 3088–3097. [CrossRef]
10. Yang, D.; Dong, J.; Wang, B. Homo- and Copolymerization of Norbornene with Tridentate Nickel Complexes Bearing *o*-Aryloxy-*N*-Heterocyclic Carbene Ligands. *Dalton Trans.* **2018**, *47*, 180–189. [CrossRef]
11. Dang, L.; Guo, J.; Song, H.; Liu, B.; Wang, B. Synthesis, Structures, and Norbornene Polymerization Behavior of C(sp³), *N*-Chelated Palladacycles Bearing *o*-Aryloxy-*N*-Heterocyclic Carbene Ligands. *Dalton Trans.* **2014**, *43*, 17177–17183. [CrossRef] [PubMed]
12. Hong, M.; Cui, L.; Liu, S.; Li, Y. Synthesis of Novel Cyclic Olefin Copolymer (COC) with High Performance via Effective Copolymerization of Ethylene with Bulky Cyclic Olefin. *Macromolecules* **2012**, *45*, 5397–5402. [CrossRef]
13. Cheng, H.; Wang, H.; Li, Y.; Hu, Y.; Zhang, X.; Cai, Z. Structurally Simple Dinuclear Nickel Catalyzed Olefin Copolymerization with Polar Monomers. *J. Catal.* **2018**, *368*, 291–297. [CrossRef]
14. He, X.; Deng, Y.; Jiang, X.; Wang, Z.; Yang, Y.; Han, Z.; Chen, D. Copolymerization of Norbornene and Butyl Methacrylate at Elevated Temperatures by a Single Center Nickel Catalyst Bearing Bulky Bis(α -Diimine) Ligand with Strong Electron-Withdrawing Groups. *Polym. Chem.* **2017**, *8*, 2390–2396. [CrossRef]
15. Huo, P.; Li, J.; Liu, W.; Mei, G.; He, X. A Highly Active and Thermally Stable 6,13-Dihydro-6,13-Ethanopentacene-15,16-Diimine Nickel(II) Complex as Catalyst for Norbornene Polymerization. *RSC Adv.* **2017**, *7*, 51858–51863. [CrossRef]
16. Wu, J.; Deng, B.; Hou, J.; Huang, X.; Tang, H.; Wang, K. Thermal-Stable Asymmetric α -Diimine Nickel(II) Catalysts: Synthesis, Characterization, and Its Norbornene (Co)Polymerization Behavior. *Appl. Organomet Chem.* **2022**, *36*, e6712. [CrossRef]
17. Xing, Y.; He, X.; Chen, Y.; Nie, H.; Wu, Q. Copolymerization of Norbornene and *n*-Butyl Methacrylate Catalyzed by Bis-(β -Ketoamino)Nickel(II)/ B(C₆F₅)₃ Catalytic System. *Polym. Bull.* **2011**, *66*, 1149–1161. [CrossRef]
18. Chae, C.; Park, J.W.; Ho, L.N.T.; Kim, M.; Kim, E.C.; Lee, W.; Park, S.; Kim, D.; Jung, H.; Kim, Y.S. Bis(β -ketoimino)nickel(II) Complexes for Random Copolymerization of Norbornene and Methyl 5-Norbornene-2-carboxylate with Controlled Ester Group Incorporation. *Macromolecules* **2022**, *55*, 7049–7058. [CrossRef]
19. Dong, J.; Yang, D.; Wang, B. Homo- and Copolymerization of Norbornene with Allyl Palladium and Nickel Complexes Bearing Imidazo[1,5-*a*]pyridine Sulfonate Ligands. *Eur. J. Inorg. Chem.* **2021**, *45*, 4661–4668. [CrossRef]
20. Zhang, Y.; Li, W.; Li, B.; Mu, H.; Li, Y. Well-Defined Phosphino-Phenolate Neutral Nickel(II) Catalysts for Efficient (Co)Polymerization of Norbornene and Ethylene. *Dalton Trans.* **2015**, *44*, 7382–7394. [CrossRef]
21. Cao, L.; Cai, Z.; Li, M. Phosphinobenzenamine Nickel Catalyzed Efficient Copolymerization of Methyl Acrylate with Ethylene and Norbornene. *Macromolecules* **2022**, *55*, 3513–3521. [CrossRef]
22. Cao, L.; Cai, Z.; Li, M. Synthesis and Characterization of Phosphinobenzenamine Palladium Complexes and Their Application in Ethylene Polymerization and Copolymerization with Polar Monomers. *Organometallics* **2022**, *41*, 3538–3545. [CrossRef]
23. Falivene, L.; Cavallo, L.; Talarico, G. Buried Volume Analysis for Propene Polymerization Catalysis Promoted by Group 4 Metals: A Tool for Molecular Mass Prediction. *ACS Catal.* **2015**, *5*, 6815–6822. [CrossRef]

24. Dai, S.; Sui, X.; Chen, C. Direct Synthesis of Functionalized High-Molecular-Weight Polyethylene by Copolymerization of Ethylene with Polar Monomers. *Angew. Chem. Int. Ed.* **2016**, *54*, 13281–13285. [[CrossRef](#)]
25. Na, Y.; Dai, S.; Chen, C. Direct Synthesis of Polar-functionalized Linear Low-density Polyethylene (LLDPE) and Low-density Polyethylene (LDPE). *Macromolecules* **2018**, *51*, 4040–4048. [[CrossRef](#)]
26. Ota, Y.; Ito, S.; Munakata, K.; Kuroda, J.; Okumura, Y.; Nozaki, K. Quantification of the Steric Influence of Alkylphosphine-Sulfonate Ligands on Polymerization, Leading to High-Molecular-Weight Copolymers of Ethylene and Polar Monomers. *J. Am. Chem. Soc.* **2014**, *136*, 11898–11901. [[CrossRef](#)]
27. Zhang, Y.; Mu, H.; Pan, L.; Wang, X.; Li, Y. Robust Bulky [P,O] Neutral Nickel Catalysts for Copolymerization of Ethylene with Polar Vinyl Monomers. *ACS Catal.* **2018**, *8*, 5963–5976. [[CrossRef](#)]
28. Elkin, T.; Kulkarni, N.V.; Tumanskii, B.; Botoshansky, M.; Shimon, L.J.W.; Eisen, M.S. Synthesis and Structure of Group 4 Symmetric Amidinate Complexes and Their Reactivity in the Polymerization of α -Olefins. *Organometallics* **2013**, *32*, 6337–6352. [[CrossRef](#)]
29. Kulkarni, N.V.; Elkin, T.; Tumaniskii, B.; Botoshansky, M.; Shimon, L.J.W.; Eisen, M.S. Asymmetric Bis(formamidinate) Group 4 Complexes: Synthesis, Structure and Their Reactivity in the Polymerization of α -Olefins. *Organometallics* **2014**, *33*, 3119–3136. [[CrossRef](#)]
30. Zeng, Y.; Mahmood, Q.; Liang, T.; Sun, W.H. (Co-)polymerization of methylacrylate with NBE/1-hexene by (8-arylimino-5,6,7-trihydroquinoly)(methyl)palladium chlorides: An approaching mechanism and the polymeric microstructures. *New J. Chem.* **2017**, *41*, 3653–3660. [[CrossRef](#)]
31. Zeng, Y.; Mahmood, Q.; Liang, T.; Sun, W.H. Geometry Constrained N-(5,6,7-Trihydroquinolin-8-ylidene)arylamino-palladium Dichloride Complexes: Catalytic Behavior toward Methyl Acrylate (MA), Methyl Acrylate-co-Norbornene (MA-co-NB) Polymerization and Heck Coupling. *Molecules* **2016**, *21*, 1686. [[CrossRef](#)] [[PubMed](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.