Supporting Information

Enhancing Chain Initiation Efficiency in the Cationic Allyl-Nickel Catalyzed (Co)Polymerization of Ethylene and Methyl Acrylate

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1. Experimental Section

1.1. General Considerations

All manipulations, unless otherwise mentioned, were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Deuterated solvents used for NMR spectroscopy were dried and distilled prior to use. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker AscendTm 400 MHz spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ¹H and ¹³C NMR spectra were referenced to tetramethylsilane, while the ³¹P NMR spectra were referenced to an external 85% H₃PO₄ solution. X-ray diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) radiation at room temperature. Elemental analyses were performed by the Analytical Center of the University of Science and Technology of China. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of the (co)polymers at 150 °C were performed on a high temperature chromatograph, PL-GPC 220 instrument equipped with a triple detection array, including a differential refractive index (RI) detector, a two-angle light scattering (LS) detector, and a four-bridge capillary viscometer. The system was calibrated with a polystyrene standard and chromatograms were corrected for linear polyethylene through universal calibration using the Mark–Houwink parameters of Rudin: K = 1.75 $\times 10^{-2}$ cm³/g and R = 0.67 for polystyrene, and K = 5.90 $\times 10^{-2}$ cm³/g and R = 0.69 for polyethylene. Differential scanning calorimetry (DSC) was performed by a DSC Q20 from TA Instruments. Samples were quickly heated to 150 °C and kept for 5 min to remove thermal history, then cooled to 40 °C at a rate of 10 K/min, and finally reheated to 150 °C at the same rate under a nitrogen flow (50 mL/min). The maximum point endotherm (heating scan) were taken as the melting temperature (T_m) . Toluene, *n*hexane, CDCl₃ and CH₂Cl₂ were purified over 4 Å molecular sieves. All the other reagents were used as received from commercial sources. All diphosphazane monoxide

(PNPO) ligands L1–L3 and their nickel complexes Ni1′–Ni3′ were synthesized according to reported procedures (Chen, M.; Chen, C. L. *Angew. Chem. Int. Ed.* 2018, *57*, 3094–3098).

1.2. Preparation of Nickel Complexes Ni1-Ni3



Preparation of Ni1. A mixture of **L1** (268 mg, 0.5 mmol), [methallylNiCl]₂ (74 mg, 0.25 mmol), and NaBAr^F₄ (443 mg, 0.5 mmol) in 15 mL DCM was stirred at room temperature for 12 h. The resulting mixture was filtrated and evaporated. The resulting solid was recrystallized from DCM and hexane solution to give **Ni1** as a bright yellow solid (651 mg, 86%). ¹H NMR (CDCl₃, 400 MHz): δ 7.85–7.66 (m, 9H), 7.65–7.33 (m, 15H), 7.13–6.82 (m, 9H), 6.24 (br, 2H), 5.59 (br, 1H), 3.67 (s, 6H, *-OMe*), 2.05 (s, 3H, Ally-*Me*). ¹³C NMR (100 MHz, CDCl₃): δ 163.0 (s), 162.5 (s), 162.0 (s), 161.5 (s), 160.9 (d, *J*_{PC} = 7.0 Hz), 135.5 (s), 135.3 (s), 134.9 (d, *J*_{PC} = 2.0 Hz), 132.6 (d, *J*_{PC} = 10.0 Hz), 131.3 (s), 129.8 (s), 129.6 (d, *J*_{PC} = 7.0 Hz), 129.4 (s), 129.3 (s), 129.1 (s), 129.0 (br), 126.4 (s), 125.04, 123.7 (s), 121.7 (d, *J*_{PC} = 9.0 Hz), 121.0 (s), 118.0 (br), 114.3 (s), 112.1 (d, *J*_{PC} = 4.0 Hz), 55.9 (s, *-OMe*), 23.8 (s). ³¹P NMR (CDCl₃, 162 MHz): δ 73.8 (d, *J*_{PP} = 68.0 Hz), 61.1 (d, *J*_{PP} = 68.0 Hz). Anal. Calcd for C₆₈H₄₈BF₂₄NNiO₃P₂: C, 53.93; H, 3.19; N, 0.92; Found: C, 53.91; H, 3.20; N, 0.89.



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Preparation of Ni2. Smilar procedure was employed except **L2** (268 mg, 0.5 mmol) was used. **Ni2** was obtained as a bright yellow solid (636 mg, 80%). ¹H NMR (CDCl₃, 400 MHz): δ 7.78–7.56 (m, 10H), 7.52 (d, J = 7.1 Hz, 1H), 7.50–7.38 (m, 9H), 7.28–7.19 (m, 4H), 7.15–6.98 (m, 6H), 6.94–6.78 (m, 4H), 6.52–6.32 (m, 4H), 4.00 (s, 1H), 3.47 (s, 3H, *-OMe*), 3.25 (s, 3H, *-OMe*), 2.06 (d, J = 6.0 Hz, 1H), 1.53 (s, 3H, Allyl-*Me*), 1.39 (s, 1H), 0.88 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 163.1 (s), 162.6 (s), 162.1 (s), 161.6 (s), 160.34, 159.7 (s), 159.0 (s), 142.9 (d, *J*_{PC}= 25.0 Hz), 135.9 (s), 135.4 (s), 135.1 (br), 134.7 (dd, *J*_{PC}=9.0, 3.0 Hz), 133.8 (s), 133.5 (d, *J*_{PC}=10.0 Hz), 132.7 (s), 131.8 (d, *J*_{PC}=6.0 Hz), 131.7 (s), 131.5 (s), 131.1 (s), 131.0 (s), 130.0 (s), 129.8 (br), 129.7 (br), 129.5 (br), 129.2 (d, *J*_{PC}=13.0 Hz), 127.1 (d, *J*_{PC}=6.0 Hz), 126.5 (s), 123.8 (s), 121.1(s), 118.1 (t, *J*_{PC}=3.0 Hz), 108.0 (s), 106.3 (s), 58.0 (s, *OMe*), 56.2 (s, *OMe*), 50.1 (s), 23.5 (s). ³¹P NMR (CDCl₃, 162 MHz): δ 78.2 (d, *J*_{PP}=61.2 Hz), 53.3 (d, *J*_{PP}=61.2 Hz). Anal. Calcd for C₇₄H₅₂BF₂₄NNiO₃P₂: C, 55.88; H, 3.30; N, 0.88; Found: C, 55.90; H, 3.28; N, 0.86.



Preparation of Ni3. Similar procedure was employed except **L3** (272 mg, 0.5 mmol) was used. **Ni3** was obtained as a bright yellow solid (664 mg, 82%).¹H NMR (CDCl₃, 400 MHz): δ 7.80–7.69 (m, 11H), 7.65–7.47 (m, 9H), 7.43–7.30 (m, 6H), 7.30–7.27 (m, 1H), 7.20–7.05 (m, 3H), 6.99–6.87 (m, 1H), 6.68–6.56 (m, 4H), 6.54–6.40 (m, 2H), 4.12 (s, 1H), 3.67 (s, 3H, Ar-*OMe*), 3.61 (s, 3H, Ph-*OMe*), 3.35 (s, 3H, Ar-*OMe*), 2.19 (s, 1H), 1.68 (s, 3H, Allyl-*Me*), 1.51 (s, 1H), 0.97 (s, 1H). ³¹P NMR (CDCl₃, 162 MHz): δ 78.0 (d, J_{PP} = 64.6 Hz), 53.3 (d, J_{PP} = 64.6 Hz). Anal. Calcd for C₇₅H₅₄BF₂₄NNiO₄P₂: C, 55.58; H, 3.36; N, 0.86; Found: C, 55.61; H, 3.38; N, 0.84.

1.3. Procedure for Ethylene Polymerization

In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with 18 mL toluene and a magnetic stir bar in the glovebox. The pressure vessel was connected to a high-pressure line and the solution was degassed. The vessel was warmed to the desired temperatures using an oil bath and allowed to equilibrate for 15 minutes. Then, the catalyst solution in CH_2Cl_2 (2.4 µmol, 2 mL) was injected into the polymerization system with a syringe. With rapid stirring, the vessel was pressurized and maintained at desired ethylene pressure. After the desired amount of polymerization time, the pressure vessel was vented and the reaction was quenched by addition of acidic methanol (5%). The polymers obtained were filtered from solution, washed with methanol, and dried at 50 °C for 24 h in a vacuum oven to constant weight.

1.4. Procedure for Ethylene and MA Copolymerization

In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with toluene and and co-monomer ([MA] =1.0 M) to total volume of 20 mL in a glovebox. The pressure vessel was connected to a high-pressure line and the solution was degassed. The vessel was warmed to 80 °C using an oil bath and allowed to equilibrate for 15 min. The metal complex (20 μ mol) in CH₂Cl₂ (2 mL) was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized with ethylene, which was maintained at desired ethylene pressure. After 3 h, the pressure vessel was vented and the copolymer was precipitated in acidified methanol (methanol/HCl = 50/1) and dried at 50 °C for 24 h under vacuum. The copolymers obtained were filtered from solution, washed with methanol, and dried at 50 °C for 24 h in a vacuum oven to constant weight.

2. NMR Spectra of Nickel Complexes Ni1–Ni3



Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃) of Ni1.



Figure S2.³¹P NMR spectrum (162 MHz, CDCl₃) of Ni1.



Figure S3.¹³C NMR spectrum (100 MHz, CDCl₃) of Ni1.



Figure S4. ¹H NMR spectrum (400 MHz, CDCl₃) of Ni2.



Figure S5.³¹P NMR spectrum (162 MHz, CDCl₃) of Ni2.



Figure S6.¹³C NMR spectrum (100 MHz, CDCl₃) of Ni2.



Figure S7. ¹H NMR spectrum (400 MHz, CDCl₃) of Ni3.



Figure S8. ³¹P NMR spectrum (162 MHz, CDCl₃) of Ni3.

3. NMR Spectra of the Polyethylenes and E-MA Copolymers



Figure S9. ¹H NMR spectrum of the polyethylene (400 MHz, in $C_2D_2Cl_4$ at 120 °C, Table 1, entry 3).



Figure S10. ¹³C NMR spectrum of the polyethylene (100 MHz, in $C_2D_2Cl_4$ at 120 °C, Table 1, entry 3).



Figure S11. ¹H NMR spectrum of the polyethylene (400 MHz, in $C_2D_2Cl_4$ at 120 °C, Table 2, entry 2).



Figure S12. ¹H NMR spectrum of the polyethylene (400 MHz, in $C_2D_2Cl_4$ at 120 °C, Table 2, entry 3).



Figure S13. ¹H NMR spectrum of the polyethylene (400 MHz, in $C_2D_2Cl_4$ at 120 °C, Table 2, entry 4).



Figure S14. ¹H NMR spectrum of the polyethylene (400 MHz, in $C_2D_2Cl_4$ at 120 °C, Table 2, entry 5).



Figure S15. ¹H NMR spectrum of the polyethylene (400 MHz, in $C_2D_2Cl_4$ at 120 °C, Table 2, entry 6).



Figure S16. ¹H NMR spectrum of the polyethylene (400 MHz, in $C_2D_2Cl_4$ at 120 °C, Table 2, entry 7).



Figure S17. ¹H NMR spectrum of the polyethylene (400 MHz, in $C_2D_2Cl_4$ at 120 °C, Table 2, entry 8).

4. GPC Curves of the (Co)Polymers



Figure S18. GPC trace of the polymer (Table 2, entry 3).



Figure S19. GPC trace of the polymer (Table 2, entry 5).



Figure S20. GPC trace of the polymer (Table 2, entry 6).



Figure S21. GPC trace of the polymer (Table 2, entry 10).



Figure S22. GPC trace of the polymer (Table 2, entry 17).



Figure S23. GPC trace of the polymer (Table 2, entry 20).



Figure S24. GPC trace of the polymer (Table 2, entry 21).



Figure S25. GPC trace of the copolymer (Table 2, entry 1).



Figure S26. GPC trace of the copolymer (Table 2, entry 2).



Figure S27. GPC trace of the copolymer (Table 2, entry 3).



Figure S28. GPC trace of the copolymer (Table 2, entry 5).



Figure S29. GPC trace of the copolymer (Table 2, entry 6).



Figure S30. GPC trace of the copolymer (Table 2, entry 7).



Figure S31. GPC trace of the copolymer (Table 2, entry 8).

5. DSC Data of the (Co)Polymers



Figure S32. DSC data of the PE obtained by Ni1 (Table 1, entry 3).



Figure S33. DSC data of the PE obtained by Ni1 (Table 1, entry 6).



Figure S34. DSC data of the PE obtained by Ni1' (Table 1, entry 9).



Figure S35. DSC data of the PE obtained by Ni2 (Table 1, entry 14).



Figure S36. DSC data of the PE obtained by Ni3 (Table 1, entry 18).



Figure S37. DSC data of the PE obtained by Ni3 (Table 1, entry 20).



Figure S38. DSC data of the E-MA copolymer obtained by Ni1 (Table 2, entry 1).



Figure S39. DSC data of the E-MA copolymer obtained by Ni1' (Table 2, entry 2).



Figure S40. DSC data of the E-MA copolymer obtained by Ni1 (Table 2, entry 3).



Figure S41. DSC data of the E-MA copolymer obtained by Ni1' (Table 2, entry 4).



Figure S42. DSC data of the E-MA copolymer obtained by Ni1 (Table 2, entry 5).



Figure S43. DSC data of the E-MA copolymer obtained by Ni1' (Table 2, entry 6).



Figure S44. DSC data of the E-MA copolymer obtained by Ni2 (Table 2, entry 7).



Figure S45. DSC data of the E-MA copolymer obtained by Ni3 (Table 2, entry 8).

6. X-Ray Crystallography



Figure S46. Molecular structure of Ni1'.



Figure S47. Molecular structure of Ni1.



Figure S48. Molecular structure of Ni3.

Table S1. Crystal data and structure refinement for Ni1'.		
Identification code	Ni1′	
CCDC	196663	
Empirical formula	C ₆₇ H ₄₆ BF ₂₄ NNiO ₃ P ₂	
Formula weight	1500.51	
Temperature/K	298(2)	
Crystal system	Triclinic	
Space group	P-1	
a/Å	13.0660(12)	
b/Å	21.6641(19)	
c/Å	26.133(2)	
α/°	70.2000(10)	
β/°	82.633(2)	
γ/°	80.897(2)	
Volume/Å ³	6850.2(11)	
Z	4	
$\rho_{calc}g/cm^3$	1.455	
µ/mm ⁻¹	0.441	
F(000)	3032	
Crystal size/mm ³	$0.40 \times 0.35 \times 0.20$	
Radiation	MoKa (λ = 0.71073)	
20 range for data collection/°	4.44 to 50.04	
Index ranges	$-13 \le h \le 15, -25 \le k \le 22, -29 \le l \le 31$	
Reflections collected	34776	
Independent reflections	23783 [$R_{int} = 0.0488, R_{sigma} = 0.1035$]	
Data/restraints/parameters	23783/0/2225	
Goodness-of-fit on F ²	1.065	
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.1216, wR_2 = 0.3684$	
Final R indexes [all data]	$R_1 = 0.1980, wR_2 = 0.4023$	

Identification code	Nil
CCDC	1966480
Empirical formula	C ₆₈ H ₄₈ BF ₂₄ NNiO ₃ P ₂
Formula weight	1514.53
Temperature/K	298(2)
Crystal system	Tetragonal
Space group	I4(1)/a
a/Å	19.4324(18)
b/Å	19.4324(18)
c/Å	73.736(5)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å ³	27844(4)
Z	16
$\rho_{cale}g/cm^3$	1.445
µ/mm ⁻¹	0.435
F(000)	12256
Crystal size/mm ³	0.45 imes 0.43 imes 0.35
Radiation	MoKa ($\lambda = 0.71073$)
2 Θ range for data collection/°	4.40 to 50.04
Index ranges	$-18 \le h \le 23, -23 \le k \le 23, -87 \le l \le 68$
Reflections collected	70597
Independent reflections	12284 [$R_{int} = 0.1367, R_{sigma} = 0.0967$]
Data/restraints/parameters	12284/0/1126
Goodness-of-fit on F ²	1.062
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.06\overline{45}, WR_2 = 0.1552$
Final R indexes [all data]	$R_1 = 0.1768, wR_2 = 0.2047$

Table S2. Crystal data and structure refinement for Ni1.

Identification code	Ni3
CCDC	1966482
Empirical formula	C ₇₅ H ₅₄ BF ₂₄ NNiO ₄ P ₂
Formula weight	1620.65
Temperature/K	298(2)
Crystal system	Triclinic
Space group	P-1
a/Å	20.0110(18)
b/Å	20.3249(19)
c/Å	21.903(2)
α/°	66.4730(10)
β/°	63.6770(10)
γ/°	83.938(2)
Volume/Å ³	7293.3(12)
Z	4
$ ho_{calc}g/cm^3$	1.476
µ/mm ⁻¹	0.421
F(000)	3288
Crystal size/mm ³	0.40 imes 0.27 imes 0.16
Radiation	MoKa ($\lambda = 0.71073$)
2 Θ range for data collection/°	4.36 to 50.04
Index ranges	$-23 \le h \le 23, -22 \le k \le 24, -23 \le l \le 26$
Reflections collected	37382
Independent reflections	25346 [$R_{int} = 0.0440, R_{sigma} = 0.1282$]
Data/restraints/parameters	25346/0/2391
Goodness-of-fit on F ²	1.034
Final R indexes $[I \ge 2\sigma (I)]$	$R_1 = 0.0548, wR_2 = 0.0815$
Final R indexes [all data]	$R_1 = 0.16\overline{05}, wR_2 = 0.0930$

Table S3. Crystal data and structure refinement for Ni3.