Supporting Information

Longstanding Living Polymerization of Ethylene: Substituent Effect on Bridging Carbon of 2-Pyridinemethanamine Nickel Catalysts†

Shaobo Zai,[a,b] Fengshou Liu,[a] Haiyang Gao,*[a] Cong Li,[a] Guiyu Zhou,[a] Shan Cheng,[a] Lihua Guo,[a] Ling Zhang,[a] Fangming Zhu,[a] Qing Wu*[a.b]

a. DSAPM Lab, School of Chemistry and Chemical Engineering, Sun Yat-Sen (Zhongshan) University, Guangzhou, 510275, China.

b. PCFM Lab, OFCM Institute, Sun Yat-Sen (Zhongshan) University, Guangzhou, 510275, China.

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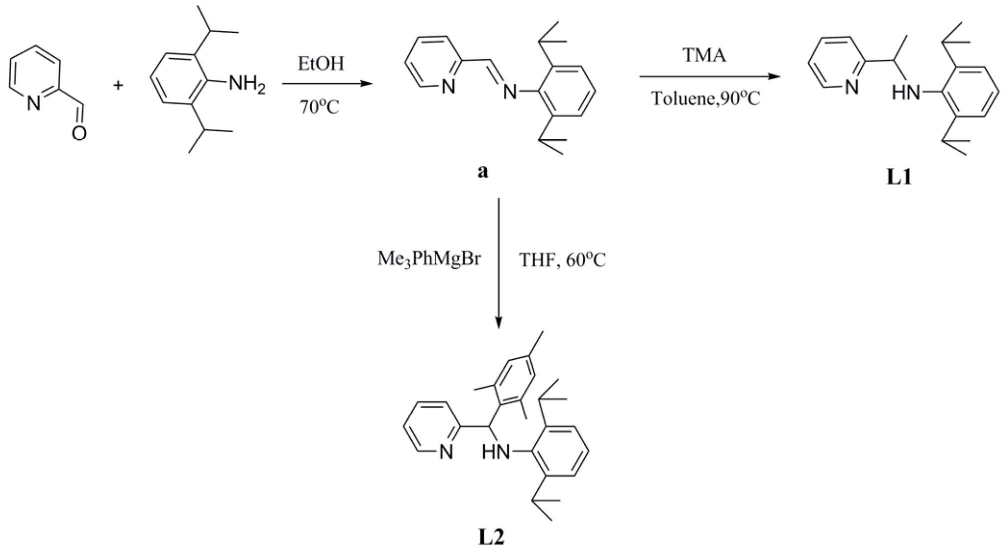
All manipulations of air- and/or moisture-sensitive compounds were performed under a dry and purified nitrogen atmosphere by means of standard Schlenk techniques.

Materials

Trimethylaluminum (TMA) (1M, hexane) was purchased from Aldrich Chemical. 2-Pyridinecarboxaldehyde (99%), 2-bromomesitylene (98%), 2,6-diisopropylaniline (98%), bromobenzene (98%) were purchased from Alfa Aesar and used without further purification. MAO was prepared by the hydrolysis of trimethylaluminum with $Al_2(SO4)_3 \cdot 18H_2O$ in toluene with the H_2O/Al molar ratio of 1.3:1. Solvents were purified by standard procedures. Polymerization-grade ethylene and extra-pure-grade nitrogen were further purified before feeding into the reactor by passing them through a DC-IB gas purification instrument.

NMR spectra of the ligands were carried out on a Varian Inova instrument (300 MHz) at room temperature in a $CDCl_3$ solution using tetramethylsilane as a reference. NMR spectra of polymer solutions (15 wt %) were performed on a Varian Inova instrument (500 MHz) at 120 °C with *o*-dichlorobenzene-*d* as the solvent. Elemental analyses were performed on a Vario EL microanalyzer. Differential scanning calorimetry (DSC) analysis was conducted with a Perkin-Elmer DSC-7 system in a heating rate of 10 °C/min and was recorded at second heating curves. The molecular weight and the polydispersity of he polymer samples were determinded at 135 °C by Waters-2000 based on standard linear polyethylene as the reference with 1,2,4-trichlorobenzene as the solvent at a flow rate of 1.0 mL/min. The X-ray diffraction data of single crystals were obtained with the ω-2θ scan mode on a Bruker SMART 1000 CCD diffractiometer with graphite-monochromated Mo Kα radiation (λ= 0.71073) at 173 K. The structure was solved using direct methods, and further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Synthesis of Ligands



2, 6-Diisopropyl-N-(pyridin-2-ylmethylene)aniline **(a)**[1]

2-Pyridinecarboxaldehyde (3.21 g, 30 mmol) was dissolved in 50 mL anhydrous ethanol and

2,6-diisopropylaniline (5.31 g, 30 mmol) was added. This mixture was refluxed under N_2 for 5 h. After filtration and removal of the volatiles under reduced pressure, 2,6-diisopropyl-N-(pyridin-2-ylmethylene)aniline was isolated as brown oil. Recrystallization from hexane afforded yellow crystal. Yield: 6.1 g (72%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.61 (d, 1H, pyridyl α-H), 7.50 (s, 1H, N=C*H*), 7.68-7.05(m, 6H, pyridyl and phenyl protons), 3.34 (m, 2H, C*H*(CH_3)$_2$), 1.27 (dd, 12H, CH(C*H*$_3$)$_2$).

2,6-Diisopropyl-N-(1-(pyridin-2-yl)ethyl)aniline (**L1**)

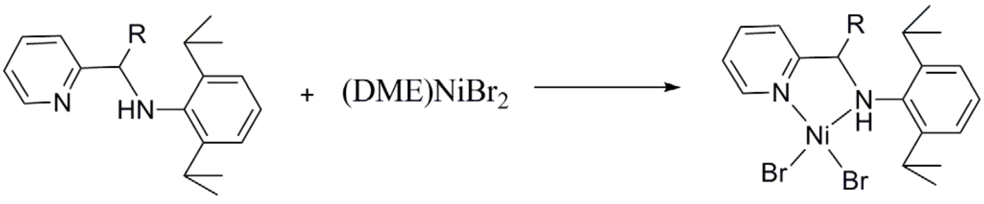
Trimethylaluminum (TMA) (12 mmol) was added slowly into a solution of 2,6-diisopropyl-N-(pyridin-2-ylmethylene)aniline(a) (2.66 g, 10 mmol) in 50 mL toluene. The mixture was refluxed under N_2 for 5 h. The mixture was quenched with 1N NaOH solution in an ice bath. The organic layer was washed twice with brine, dried, filtered and removed of solvent under reduced pressure. Recrystallization from hexane afforded white crystal. Yield 2.54 g (90%).^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.61 (d, 1H, pyridyl α-H), 7.55-7.02(m, 6H, pyridyl and phenyl protons), 4.18 (s, 1H, C*H*-NH), 4.06 (s, 1H, CH-N*H*), 3.23 (m, 2H, C*H*(CH_3)$_2$), 1.52 (s, 3H, C*H*$_3$), 1.24, 1.08 (dd, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 163.39, 149.70, 142.29, 141.80, 136.36, 123.59, 123.31, 122.24, 122.00, 61.24, 27.98, 24.60, 22.11. Anal. Calcd for $C_{19}H_{26}N_2$: C, 80.80; H, 9.28; N, 9.92%. Found: C, 80.61; H, 9.16; N, 10.09%。

2, 6-Diisopropyl-N-(mesityl(pyridin-2-yl)methyl)aniline (**L2**)

2,6-diisopropyl-N-(pyridin-2-ylmethylene)aniline(a) (2.68 g, 10 mmol) was added slowly into a dry round bottom flask which was charged with a solution of Grignard reagent, mesitylmagnesium bromide (10 mmol), in 50 mL THF. After refluxed under N_2 for 12 h, the mixture was quenched with 1N NH_4Cl solution. The organic layer was washed twice with brine, dried, filtered and removed of solvent under reduced pressure. Recrystallization from hexane afforded white crystal. Yield: 3.1 g (80%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.60 (d, 1H, pyridyl α-H), 7.57-6.71 (m, 8H, pyridyl and phenyl protons), 5.43 (s, 1H, C*H*-NH), 4.75 (s, 1H, CH-N*H*), 3.04 (m, 2H, C*H*(CH_3)$_2$), 2.20 (s, 3H, C*H*$_3$), 1.86 (s, 6H, C*H*$_3$), 1.08 , 0.83 (dd, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 162.92, 148.59, 145.19, 143.64, 137.44, 136.69, 136.36, 130.07, 124.66, 123.44, 121.51, 121.39, 65.21, 27.91, 24.76, 24.15, 21.20, 20.68. Elemental Anal. Calc. for $C_{27}H_{34}N_2$: C, 83.89; H, 8.87; N, 7.25. Found: C, 83.97; H, 8.88; N, 7.09%.

General Procedure for the Synthesis of Complexes



L1:R=Me
L2:R=Me_3Ph

1:R=Me
2:R=Me_3Ph

A solution of ligand and (DME)$NiBr_2$ in 30 mL CH_2Cl_2 was stirred under N_2 for 12 h. After filtration, the solution was evaporated to little volume in vacuum, and 20 mL n-hexane was added. The mixture was stirred and filtered, and then the residual solid was washed with n-hexane. Drying in vacuum produced the desired nickel complexes.

[2,6-Diisopropyl-N-(1-(pyridin-2-yl)ethyl)aniline]NiBr$_2$ (**1**)

Complex **1** prepared with **L1** (0.282 g, 1mmol) and (DME)$NiBr_2$ (0.308g, 1 mmol), was obtained as orange solid in yield 0.526 g (75.8%). Elemental Anal. Calc. for $C_{27}H_{34}N_2NiBr_2$: C, 45.56; H, 5.23; N, 5.59. Found: C, 45.72; H, 4.95; N, 5.23%. EI-MS (m/z): 420, 421, 422[M-Br]$^+$, 281[M-$NiBr_2$]$^+$.

[2,6-Diisopropyl-N-(mesityl(pyridin-2-yl)methyl)aniline]NiBr$_2$ (**2**)

Complex **2** prepared with **L2** (0.386 g, 1mmol) and (DME)$NiBr_2$ (0.308g, 1 mmol), was obtained as light brown solid in yield 0.526 g (75.8%). Elemental Anal. Calc. for $C_{27}H_{34}N_2NiBr_2$: C, 53.59; H, 5.66; N, 4.63. Found: C, 53.89; H, 5.72; N, 4.42%. EI-MS (m/z): 524, 525, 526[M-Br]$^+$, 385[M-$NiBr_2$]$^+$.

General Procedure for Ethylene Polymerization

The sealed glass reactor for ethylene polymerization was heated to 100 °C under vacuum for 1 h, and then cooled to room temperature. Ethylene gas was added and vacuumed twice, and then the reactor was charged with toluene and cocatalyst (MAO, $AlEt_2Cl$ or $AlEt_3$). The reactor was pressurized to the desired reaction pressure and the solution was stirred at the desired reaction temperature for 30 min. A solution of the appropriate amount of nickel complexes in CH_2Cl_2 was added to the reaction system via syringe. The total volume of solution in the reactor was kept 40 mL. The mixture was stirred under constant ethylene pressure for the desired reaction time. After that, ethanol (5 mL) was added to terminate the reaction. And the reaction mixture was added to acidified ethanol (20 mL concentrated HCl in 500 mL of ethanol). Solid polyethylene was obtained by filtration, washed with ethanol, and dried at 40 °C for 24 h in vacuum.

Living Ethylene Polymerization Using Catalyst 2/MAO (-10°C, 1.2 atm)

The sealed glass reactor for ethylene polymerization was heated to 100 °C under vacuum for 1 h, and then cooled to room temperature. Ethylene was added and vacuumed twice. Then, the reactor was charged with toluene and cocatalyst MAO (16 mmol). The reactor was pressurized to the desired reaction pressure and the solution was stirred at -10 °C for 30 min. A solution of catalyst **2**(20 μmol) in CH_2Cl_2 was added to the reaction mixture via syringe. The total volume of solution in the reactor was 40 mL. The mixture was stirred under constant ethylene pressure (1.2 atm) for the desired reaction time. After that, ethanol (2 mL) was added to terminate the reaction. And the reaction mixture was added to acidified ethanol (20 mL concentrated HCl in 500 mL of ethanol). Solid polyethylene was obtained by filtration, washed with ethanol, and dried at 40 °C for 24 h in vacuum.

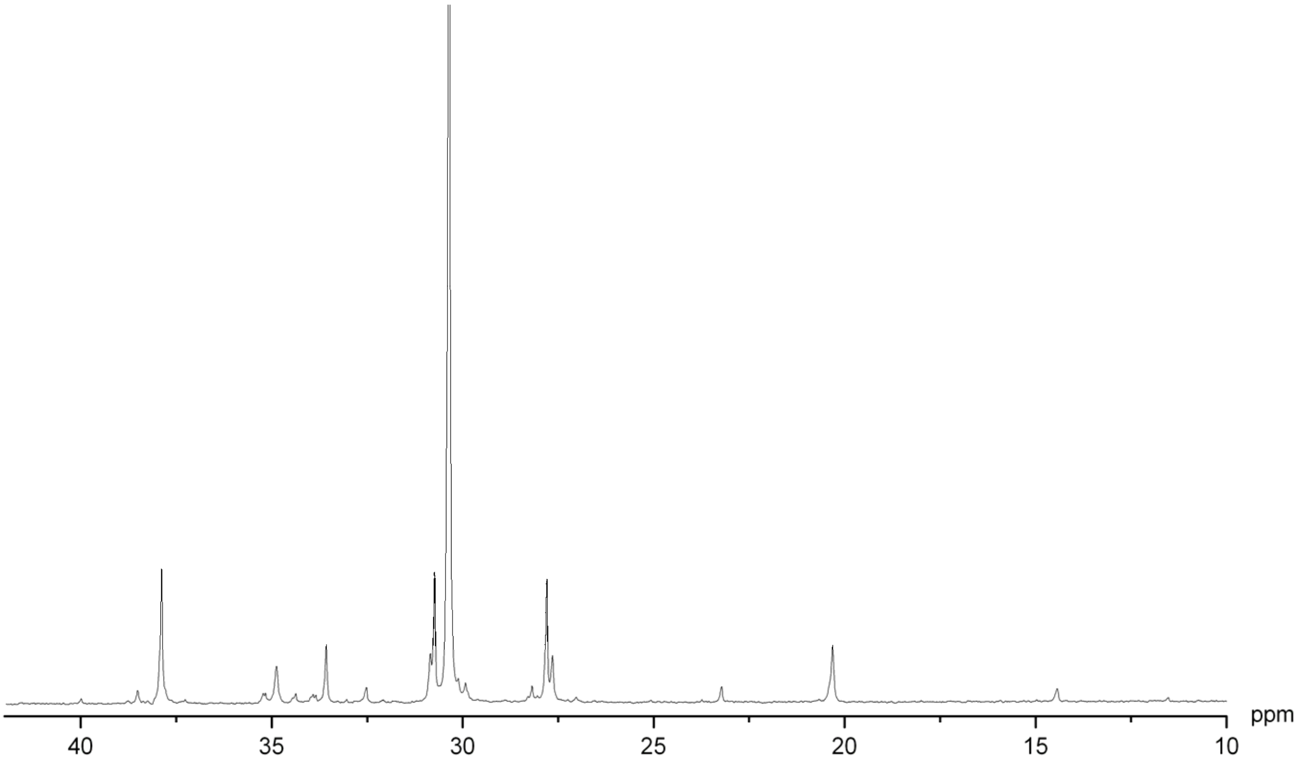


Figure S1.^{13}C NMR spectrum of polyethylene (0.5h, -10^{o}C, 1.2atm ethylene, catalyst **2**/MAO) in *o*-dichlorobenzene-*d*, 125 MHz, 120 °C.

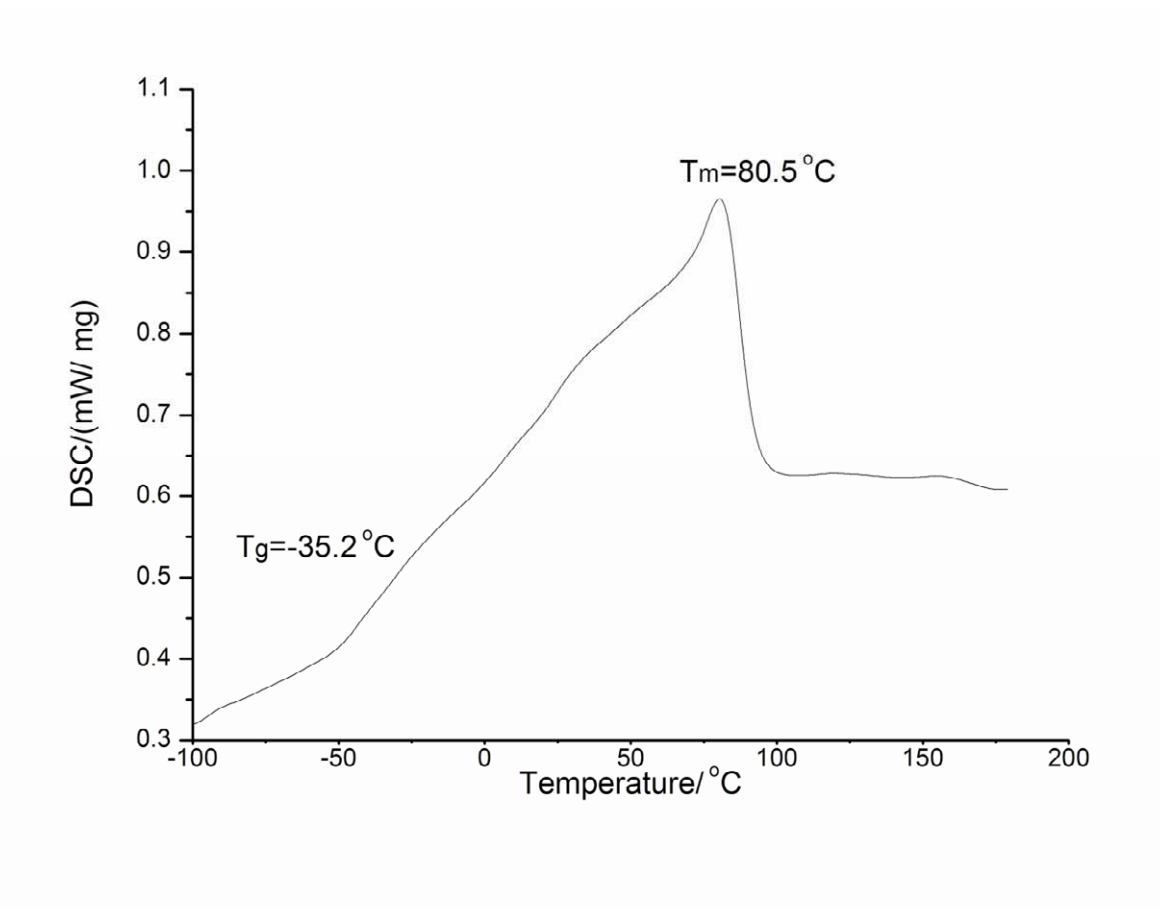


Figure S2. DSC spectrum of polyethylene (1h, -10^{o}C, 1.2atm ethylene, catalyst **2**/MAO)

Postpolymerization Using Catalyst 2/MAO (-10 °C, 1.2 atm)[2]

The sealed glass reactor for ethylene polymerization was heated 1 h to 100 °C under vacuum, then cooled to room temperature. Ethylene was added and vacuumed twice. Then, the reactor was charged with toluene and cocatalyst MAO (16 mmol). The reactor was pressurized to the desired reaction pressure and the solution was stirred at -10 °C for 30 min. A solution of catalyst **2** (20 μmol) in CH_2Cl_2 was added to the reaction mixture via syringe. The total volume of solution in the reactor was 40 mL. The mixture was stirred under 1.2 atm ethylene pressure for 1h. Then, the ethylene gas feed was stopped. N_2 was charged and vented for 3 times. The toluene was kept under N_2 for 10 h. Then, N_2 was vented and ethylene gas was charged to restart polymerization. Aliquots of the polymerization solution were removed via syringe at the desired time. (Aliquot 1, 0.5h total polymerization) $M_n = 0.89 \times 10^4$, $M_w = 1.08 \times 10^4$, $M_w/M_n = 1.21$; (aliquot 2, 1h total polymerization) $M_n = 1.71 \times 10^4$, $M_w = 1.98 \times 10^4$, $M_w/M_n = 1.16$; (aliquot 3, 1.5h total polymerization) $M_n = 3.01 \times 10^4$, $M_w = 3.63 \times 10^4$, $M_w/M_n = 1.21$; (aliquot 4, 2h total polymerization) $M_n = 3.76 \times 10^4$, $M_w = 4.62 \times 10^4$, $M_w/M_n = 1.23$; (aliquot 5, 2.5h total polymerization) $M_n = 4.54 \times 10^4$, $M_w = 5.53 \times 10^4$, $M_w/M_n = 1.22$.

Synthesis of block Polymer

The sealed glass reactor for ethylene polymerization was heated 1 h to 100 °C under vacuum, and then cooled to room temperature. Ethylene was added and vacuumed twice. Then, the reactor was charged with toluene and cocatalyst MAO (16 mmol). The reactor was pressurized to the desired reaction pressure and the solution was stirred at -10 °C for 30 min. A solution of catalyst **2** (20 μmol) in CH_2Cl_2 was added to the reaction mixture via syringe. The total volume of solution in the reactor was 40 mL. The mixture was stirred under constant ethylene pressure (1.2 atm) for 0.5h. Then, the ethylene gas feed was stopped. N_2 was charged and vented for 3 times. 5 mL hexene was added by syringe, and the mixture was stirred for 5 h. After that, ethanol (2 mL) was added to terminate the reaction. And the reaction mixture was added to acidified ethanol (20 mL concentrated HCl in 500 mL of ethanol). Solid polyethylene was obtained by filtration, washed with ethanol, and dried at 40 °C for 24 h in vacuum.

Table S1. Synthesis of Diblock Polymer

	t_1(h)[a]	Hex.(mL)	t_2(h)[b]	Yield(g)	M_n($\times10^4$)	PDI	T_g(°C)	Branches[c] /1000C
PE	0.5	0	0	0.170	0.89	1.22	-37.9	69
PE-*b*-PH	0.5	5	5	0.542	2.14	1.18	-49.2	77

Polymerization Conditions: catalyst 2×10^{-5} mol, 800 equiv. MAO, ethylene pressure 1.2 atm. [a] ethylene polymerization time. [b] hexene polymerization time. [c] Total branching was determined by ^{1}H NMR spectroscopy.

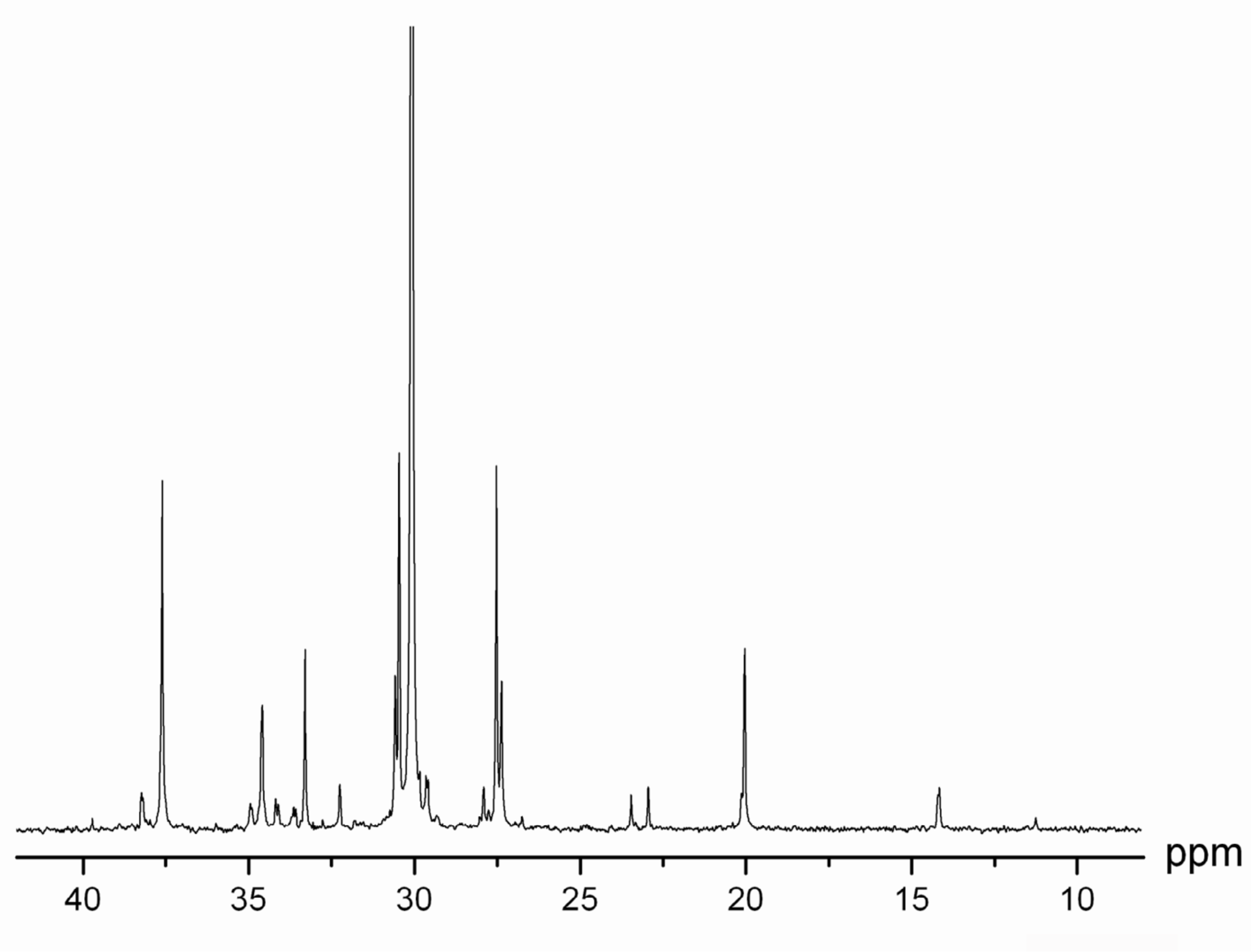


Figure S3. ^{13}C NMR spectrum of the PE-*b*-PH diblock polymer in *o*-dichlorobenzene-*d*, 125 MHz, 120 °C.

Table S2. Crystal data and structure refinement for complexes 1 and 2·H$_2$O

Ni complexes	**1**	**2·H$_2$O**
Empirical formula	C39 H54 Br4 Cl2 N4 Ni2	C28 H38 Br2 Cl2 N2 Ni O
Formula weight (g/mol)	1086.82	708.03

Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	monoclinic, P2(1)/c	monoclinic, P2(1)/c
Unit cell dimensions (Å or deg.)	a = 18.4583(17), alpha = 90, b = 15.3616(14), beta = 92.154(2) , c = 15.5084(14), gamma = 90	a = 13.4346(13), alpha = 90 b = 13.4926(13), beta = 105.588(2) , c = 17.6159(17), gamma = 90
Volume (Å^3)	4394.3(7)	3075.7(5)
Z, Calculated density(mg.m^{-3})	4, 1.643	4, 1.529
Absorption coefficient(mm^{-1})	4.648	3.426
F(000)	2184	1440
Crystal size (mm)	0.5 ×0.4 × 0.2	0.4 × 0.3× 0.3
Theta range for data collection(deg.)	1.73 to 27.00	1.93 to 27.06
Limiting indices	-22<=h<=23, -19<=k<=19, -19<=l<=12	-16<=h<=17, -17<=k<=16, -22<=l<=9
Reflections collected / unique	29190 / 9553 [R(int) = 0.0443]	15490 / 6637 [R(int) = 0.0358]
Completeness to theta = 26.10	99.7 %	97.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.3953 and 0.1128	0.4263and 0.3411
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9553 / 0 / 478	6637 / 0 / 329
Goodness-of-fit on F^2	1.021	0.878
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0769	R1 = 0.0371, wR2 = 0.1064
R indices (all data)	R1 = 0.0688, wR2 = 0.0921	R1 = 0.0680, wR2 = 0.1341
Largest diff. peak and hole (e.Å^{-3})	0.931 and -0.901	0.871 and -0.678

References

[1]Laine TV, Piironen U, Lappalainen K, Klinga M, Aitola E, Leskela M. *J. Organomet. Chem.* 2000, **606**, 112-24.

[2] M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* 2002, **124**, 3327–3336.