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Efficient Addition Polymerization of Norbornene with Polar Norbornene Derivatives by Neutral Nickel(II) Catalysts

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Electronic Supplementary Information

Abstract A series of nickel complexes **4a**: [(2,6-*i*Pr₂C₆H₃)N=CHC₁₆H₁₂O]Ni(Me)(Py), **4b**: [(2,6-*i*Pr₂C₆H₂OCH₃)N=CHC₁₆H₁₂O]Ni(Me)(Py), **4c**: [(2,6-*i*Pr₂C₆H₂Cl)N=CHC₁₆H₁₂O]Ni(Me)(Py), and **4d**: [(2,6-*i*Pr₂C₆H₂CF₃)N=CHC₁₆H₁₂O]Ni(Me)(Py)} based on β -ketiminato ligands bearing various electron-donating or electron-withdrawing substituents on the *para*-position of the aniline group were synthesized and unambiguously characterized. The X-ray crystallographic analysis showed that complexes **4b** and **4d** adopted a near-square-planar geometry, and the anilines bearing a *para*-OMe or $-\text{CF}_3$ group were found to situate on the axial position of the metal center. All complexes exhibited high activities up to 1.25×10^7 – 1.35×10^7 g_{PNB}·mol_{Ni}⁻¹·h⁻¹ toward norbornene (NBE) addition polymerization (conversion > 91.2% in 2 min) under low loading of B(C₆F₅)₃ (B/Ni = 3) at 30 °C, affording polymers with high molecular weight up to 2.54×10^6 – 3.18×10^6 . Different levels of decrease in catalytic activities could be observed for all catalysts as the reaction temperature increased; **4d** bearing a strong electron-withdrawing $-\text{CF}_3$ group showed the highest activity at 70 °C, while others exhibited notable decrease in catalytic activity with the raise in reaction temperature. Complexes **4a**–**4d** showed remarkable tolerance to polar groups and could efficiently promote the copolymerization of NBE with its polar derivatives, including NBE bearing small acetate and hydroxyl group, as well as bulky oligomers, yielding copolymers with high functional NBE incorporations. Novel NBE copolymers with high functional comonomer incorporations and improved solubility were obtained in high yields.

Keywords Neutral nickel catalysts; Norbornene; Norbornene derivatives; Vinyl-type polymerization

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INTRODUCTION

Addition-type polynorbornene (PNBE) is a kind of promising material for manufacturing ion-exchange membranes,^[1,2] gas-separator,^[3,4] pervaporation membranes,^[5,6] and organic light-emitting diodes (OLEDs)^[7,8] because of its excellent thermal stability, chemical resistance, and optical properties. However, its poor solubility and mechanical brittleness result in the difficulties of processing. Introducing polar groups and long flexible side chains by direct copolymerization of norbornene (NBE) with comonomers was proved to be an efficient strategy to improve the solubility and the flowability of PNBE.^[7–13] Previous efforts pointed out that the efficient catalysts with high catalytic activity and outstanding polar group tolerance were indispensable for NBE copolymerization.^[14–17] For example, He and coworkers synthesized a series of Ni(II) and Pd(II) complexes with chi-

ral ligands, and found that these Pd(II) complexes showed high activity up to 4.8×10^8 g_{PNB}·mol_{Pd}⁻¹·h⁻¹ when being activated by aluminum compounds.^[18] It has also been well known that the steric hindrance and electronic effect of the ligand play very important roles in both catalytic performances and control of the microstructure of the resultant polymers.^[19–22] For example, Zheng and coworkers reported that the Pd(II) complexes with α -diamine ligands showed higher activities than the analogues with α -diimine ligands because of lower Lewis basicity of the sp³ hybridization of the electronic effect.^[23] Antonov and Carlini proved individually that the nickel complexes containing electron-withdrawing groups displayed high activities over 10^7 g_{PNB}·mol_{Ni}⁻¹·h⁻¹ toward norbornene polymerization.^[24,25] Sun and coworkers developed a series of palladium and nickel catalysts; good activities in norbornene-ethylene polymerization and high incorporation of ethylene could be achieved by tuning the electronic or steric effect of the ligands.^[26,27] However, while the vast majority of attentions have been paid to the catalytic capabilities of Ni(II) and Pd(II) com-

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plexes for the norbornene (co)polymerization, only few researchers have concerned with the issue of reducing the consumptions of cocatalysts.^[28,29] The residual alkyl aluminum in the obtained PNBE usually is difficult to remove and thus results in poor performances of polymers, while large consumption of $B(C_6F_5)_3$ will increase the producing cost of PNBE. Therefore, developing highly efficient catalysts for NBE (co)polymerization with no requirement of large amount of cocatalysts is highly desired. Previously, our group synthesized a novel nickel(II) catalyst bearing bulky group based on β -ketiminato ligands, which possessed unusual stability toward ethylene polymerization and entirely avoided bis-ligated deactivation.^[30] To further investigate the electronic effect of the catalytic properties of this catalyst, in this contribution, we synthesized a series of β -ketiminato nickel complexes by tuning the electronic effect of the anilines in ligand. In the presence of a small amount of $B(C_6F_5)_3$ ($B/Ni = 3$ or 6), these complexes showed high catalytic activities toward NBE (co)polymerization. Copolymerization of NBE with a series of functional NBE derivatives, including small polar group substituted NBEs and NBEs bearing polar oligomers, was also investigated.

EXPERIMENTAL

General Considerations

All air- and moisture-sensitive experimental manipulations were carried out under dry nitrogen atmosphere using standard Schlenk techniques or in an MBraun glovebox. All the solvents were purified from MBraun SPS system. NMR data of the complexes and polymers were collected by a Bruker 400 MHz spectrometer at ambient temperature or 120 °C. MALDI-TOF mass spectra were obtained on a Bruker Autoflex tof/tofIII mass spectrometer. Elemental analyses were performed on an elemental Vario EL spectrometer. The molecular weights and molecular weight distributions of polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three PLgel 10- μ m Mixed-B LS type columns. 1,2,4-Trichlorobenzene was used as the solvent at a flow rate of 1.0 mL·min⁻¹. The calibration was made by the polystyrene standard EasiCal PS-1(PL). $B(C_6F_5)_3$ was purchased from Aldrich Chemicals. NBE was purchased from Aldrich, dried over sodium, and distilled under N₂ atmosphere before use. 5-Norbornene-2-yl-acetate (NBA) and 5-norbornene-2-yl-methanol (NBM) were obtained from Acros and distilled under N₂ atmosphere before use.

Synthesis of Norbornene Derivatives

Synthesis of 5-norbornene-2-yl methyl dodecanoate (NMD)

Under N₂ atmosphere, NBM (12.4 g, 0.10 mol) was dissolved in trimethylamine (21 mL) in a 100 mL round flask and cooled to 0 °C. Dodecanoyl chloride (30 mL, 0.13 mol, 1.3 equiv.) was added dropwise by a constant pressure drop funnel. The reaction mixture was allowed to warm to room temperature, and stirred overnight. After reaction, the mixture was extracted with methylene dichloride (20 mL $\times$ 3) and concentrated by a rotary evaporator. 20.0 g of target compound was obtained by vacuum distillation at 195 °C

(yield, 65%). ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 6.20–5.88 (m, 2H, $-\text{CH}=\text{CH}-$), 3.90–3.60 (m, 2H, $-\text{OCH}_2-$), 2.80 (m, 2H, cyclo-H), 2.44–2.23 (m, 3H, $\text{O}=\text{CCH}_2-$, cyclo-H), 1.92–1.54 (m, 3H, $-\text{CH}_2-$, cyclo-H), 1.48–1.12 (m, 20H, $-\text{CH}_2-$, cyclo-H), 0.88 (t, $J = 6.8$ Hz, 3H, $-\text{CH}_3$). ¹³C-NMR (101 MHz, CDCl₃, δ , ppm): 173.71 ($\text{C}=\text{O}$), 137.45, 132.12 ($\text{C}=\text{C}$), 67.57 ($-\text{OCH}_2-$), 49.31, 44.90, 43.73, 42.17, 41.55 (cyclo-C), 37.88 ($\text{O}=\text{CCH}_2-$), 34.35, 31.89, 29.58, 29.46, 29.32, 29.26, 29.14, 28.93, 25.05, 22.66, 14.07 ($-\text{CH}_3$). Elemental Anal. Calcd. for C₂₀H₃₄O₂: C, 78.38; H, 11.18. Found: C, 78.06; H, 11.35.

Synthesis of 5-norbornene-2-yl methyl-polyol (NB-PPO)

Under N₂ atmosphere, NBM (6.4 g, 0.05 mol) was dissolved in ultra-dry tetrahydrofuran (25 mL) in a 100 mL round flask. NaH (1.5 g, 0.06 mol, 1.1 equiv.) was added slowly at 0 °C. After reaction for 24 h at room temperature, the reaction mixture was filtered through vacuum and the filtrate was transferred to a pressure bottle, simultaneously. Propylene oxide (36 mL, 0.51 mol, 10 equiv.) was slowly added into the pressure bottle, and the reaction mixture was stirred for 18 h at 80 °C. The pH value of reaction mixture was buffered close to 5–6 by hydrochloric acid. The reaction mixture was extracted with methylene dichloride (20 mL $\times$ 3), and concentrated by a rotary evaporator, yielding yellowish liquid of NB-PPO (25.0 g, 67.7%). ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 6.73–4.59 (m, 2H, $-\text{CH}=\text{CH}-$), 3.80 (m, 2H, $-\text{OCH}_2-$), 3.65–3.03 (m, 33H, $-\text{OCH}_2-$, $-\text{OCH}(\text{CH}_3)-$), 2.75 (m, 2H, cyclo-H), 2.22 (m, 2H, cyclo-H), 1.66 (m, 3H, cyc-H), 1.39–0.76 (m, 33H, CH₃). ¹³C-NMR (101 MHz, CDCl₃, δ , ppm): 136.98, 136.54 ($\text{C}=\text{C}$), 75.98 ($-\text{OCH}_2-$), 75.46–74.83 ($-\text{OCH}_2-$), 73.55–72.92 ($-\text{OCH}(\text{CH}_3)-$), 49.39, 44.94, 43.73, 41.83, 38.67, 29.33 (cyclo-C), 18.46–17.44 (CH₃), 16.94 (s, CH₃). Elemental Anal. Calcd. for C₃₈H₇₂O₁₁: C, 64.74; H, 10.29. Found: C, 64.82; H, 10.01. The structural analysis of the resulting NB-PPO with a relatively low M_n was performed by MALDI-TOF MS (Fig. S6 in electronic supplementary information, ESI), which exhibited molecular ion peaks corresponding to linear NB-PPO with NBM chain ends [$M_n = 124.08 + 57.08n + 23 (\text{Na}^+) \text{ or } 124.08 + 57.08n + 39 (\text{K}^+) \text{ g} \cdot \text{mol}^{-1}$].

Synthesis of Ligands

Synthesis of (2,6-*i*Pr₂C₆H₂OCH₃)N=CHC₁₆H₁₂OH (**3b**)

Under dry nitrogen atmosphere, potassium *tert*-butoxide (0.5 g, 4.5 mmol, 1.5 equiv.) was suspended in anhydrous diethyl ether (30 mL) in a 50 mL round flask and cooled to 0 °C. 8-Phenyl-1-tetralone (**1**) (0.7 g, 3.0 mmol) and ethyl formate (0.5 mL, 6.0 mmol, 2 equiv.) were added. After stirred for 30 min at 0 °C, the resulting suspension was warmed to room temperature and stirred overnight. The reaction mixture was separated by filtration and the filtrate was concentrated by a rotary evaporator. Formic acid in ethanol was added to the resulting mixture until pH < 7. The mixture was extracted with ethyl acetate and concentrated under vacuum. The resulting compound and 4-methoxy-2,6-diisopropylaniline (**2b**) (0.7 g, 3.1 mmol) were dissolved in toluene and stirred for 18 h, which was used directly for the preparation of ligand **3b**. Yield, 0.8 g (66%). ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 10.89 (d, $J = 12.2$ Hz, 1H, $-\text{OH}$), 7.73–

7.17 (m, 11H, Ar-H), 6.64 (s, 1H, N=CH-), 3.80 (s, 3H, -OCH₃), 3.14 (dt, $J = 13.7, 6.8$ Hz, 2H, *i*Pr-CH), 2.96–2.87 (m, 2H, -CH₂-), 2.63–2.55 (m, 2H, -CH₂-), 1.14 (d, $J = 6.9$ Hz, 12H, *i*Pr-CH₃). ¹³C-NMR (101 MHz, CDCl₃, δ , ppm): 187.38 (N=CH-), 158.56, 151.19, 146.90, 143.54, 143.39, 142.66, 134.22, 130.31, 130.10, 129.92, 128.51, 127.68, 127.02, 126.36, 108.74, 104.12, 55.15 (-OCH₃), 31.53 (*i*Pr-CH), 28.44 (-CH₂-), 27.58 (-CCH₂-), 23.63 (*i*Pr-CH₃). Elemental Anal. Calcd. for C₃₀H₃₃NO₂: C, 81.97; H, 7.57; N, 3.19. Found: C, 81.07; H, 7.25; N, 3.58.

Synthesis of (2,6-*i*Pr₂C₆H₂Cl)N=CHC₁₆H₁₂OH (**3c**)

A similar procedure was used as described for **3b**, except using 4-chloro-2,6-diisopropylaniline (**2c**) (0.7 g, 3.1 mmol) instead of **2b**. Ligand **3c** was obtained as yellow solids (0.9 g, 70%). ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 10.98 (d, $J = 10.0$ Hz, 1H, -OH), 7.41–7.06 (m, 11H, Ar-H), 6.64 (s, 1H, N=CH-), 3.22–3.05 (m, 2H, *i*Pr-CH), 2.97–2.86 (m, 2H, -CH₂-), 2.64–2.55 (m, 2H, -CH₂-), 1.14 (d, $J = 6.9$ Hz, 12H, *i*Pr-CH₃). ¹³C-NMR (101 MHz, CDCl₃, δ , ppm): 187.95 (N=CH-), 149.96, 147.12, 143.68, 143.40, 142.92, 135.46, 134.07, 132.98, 130.45, 128.59, 127.80, 127.26, 126.51, 124.00, 104.96, 31.53 (*i*Pr-CH), 28.48 (-CH₂-), 27.66 (-CH₂-), 23.60 (*i*Pr-CH₃). Elemental Anal. Calcd. for C₂₉H₃₀ClNO: C, 78.45; H, 6.81; N, 3.15. Found: C, 78.05; H, 6.29; N, 3.56.

Synthesis of (2,6-*i*Pr₂C₆H₂CF₃)N=CHC₁₆H₁₂OH (**3d**)

A similar procedure was used as described for **3b**, except using 4-(trifluoromethyl)-2,6-diisopropylaniline (**2d**) (0.8 g, 3.1 mmol) instead of **2b**. Ligand **3d** was obtained as yellow solids (0.7 g, 50%). ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 11.12 (s, 1H, -OH), 7.64–7.03 (m, 11H, Ar-H), 6.61 (s, 1H, N=CH-), 3.13 (dt, $J = 13.7, 6.9$ Hz, 2H, *i*Pr-CH), 2.90–2.82 (m, 2H, -CH₂-), 2.58–2.50 (m, 2H, -CH₂-), 1.11 (d, $J = 6.9$ Hz, 12H, *i*Pr-CH₃). ¹³C-NMR (101 MHz, CDCl₃, δ , ppm): 187.14 (N=CH-), 148.01, 144.32, 142.63, 142.23, 141.91, 138.93, 132.83, 129.47, 129.39, 127.49, 126.70, 126.12, 125.43, 119.73, 119.69, 104.39, 30.34 (*i*Pr-CH), 27.36 (-CH₂-), 26.55 (-CH₂-), 22.48 (*i*Pr-CH₃). Elemental Anal. Calcd. for C₃₀H₃₀F₃NO: C, 75.45; H, 6.33; N, 2.93. Found: C, 75.07; H, 6.22; N, 2.16.

Synthesis of Neutral Nickel Complexes

Synthesis of [(2,6-*i*Pr₂C₆H₂OCH₃)N=CHC₁₆H₁₂O]Ni(Me)(Py) (**4b**)

In an MBraun glovebox, [Py₂NiMe₂] (0.2 g, 1.3 equiv.) and ligand **3b** (0.3 g, 0.6 mmol) were dissolved in 20 mL of dry toluene in a 50 mL Schlenk bottle at room temperature. The color of the reaction solution gradually darkened. After stirred for 6 h, the resulting mixture was filtrated to remove nickel black. Pure target complex **4b** was obtained by recrystallization from toluene/hexane as orange-red solids (0.2 g, 62%). ¹H-NMR (400 MHz, C₆D₆, δ , ppm): 7.59–7.55 (m, 2H, *o*-H, Py), 7.04 (d, $J = 7.0$ Hz, 2H, Ar-H), 6.90–6.83 (m, 2H, Ar-H), 6.81–6.60 (m, 6H, Ar-H), 6.59 (s, 1H, N=CH-), 6.29 (t, $J = 7.6$ Hz, 1H, *p*-H, Py), 5.87 (t, $J = 7.5, 6.5$ Hz, 2H, *m*-H, Py), 4.15 (m, 2H, *i*Pr-CH), 3.18 (s, 3H, -OCH₃), 2.34 (m, 2H, -CH₂-), 2.12 (m, 2H, -CH₂-), 1.31 (d, $J = 6.9$ Hz, 6H, *i*Pr-CH₃), 1.00 (d, $J = 6.9$ Hz, 6H, *i*Pr-CH₃), -0.98 (s, 3H, Ni-CH₃). ¹³C-NMR (101 MHz, C₆D₆, δ ,

ppm): 169.35 (N=CH-), 160.67, 157.56, 151.47, 144.71, 143.91, 143.06, 142.19, 140.22, 134.29, 130.19, 128.93, 127.93, 127.69, 127.45, 126.27, 125.69, 122.68, 106.73, 54.46 (-OCH₃), 31.22, 26.80 (-CH₂-), 28.45 (*i*Pr-CH), 24.73, 23.11 (*i*Pr-CH₃), -6.26 (Ni-CH₃). Elemental Anal. Calcd. for C₃₆H₄₀N₂NiO₂: C, 73.24; H, 6.66; N, 4.74. Found: C, 73.07; H, 6.23; N, 4.99.

Synthesis of [(2,6-*i*Pr₂C₆H₂Cl)N=CHC₁₆H₁₂O]Ni(Me)(Py) (**4c**)

A similar procedure was used as described for **4b**, except using **3c** (0.3 g, 0.6 mmol) instead of **3b**. Complex **4c** was obtained as orange-red powder (0.3 g, 75%). ¹H-NMR (400 MHz, C₆D₆, δ , ppm): 7.81–7.78 (m, 2H, *o*-H, Py), 7.31–7.26 (m, 4H, Ar-H), 7.32–6.88 (m, 6H, Ar-H), 6.85 (s, 1H, N=CH-), 6.57 (t, $J = 7.7$ Hz, 1H, *p*-H, Py), 6.14 (t, $J = 7.6$ Hz, 2H, *m*-H, Py), 4.34 (m, 2H, *i*Pr-CH), 2.61 (m, 2H, -CH₂-), 2.37 (m, 2H, -CH₂-), 1.43 (d, $J = 6.9$ Hz, 6H, *i*Pr-CH₃), 1.14 (d, $J = 6.9$ Hz, 6H, *i*Pr-CH₃), -0.80 (s, 3H, Ni-CH₃). ¹³C-NMR (101 MHz, C₆D₆, δ , ppm): 170.01 (N=CH-), 159.78, 151.40, 149.75, 144.36, 143.77, 142.22, 140.30, 134.43, 130.78, 130.21, 128.86, 127.92, 127.68, 126.30, 125.74, 123.55, 122.75, 105.07, 31.12, 26.69 (-CH₂-), 28.21 (*i*Pr-CH), 24.49, 22.75 (*i*Pr-CH₃), -6.67 (Ni-CH₃). Elemental Anal. Calcd. for C₃₅H₃₇ClN₂NiO: C, 70.67; H, 6.10; N, 4.71; Found: C, 70.57; H, 6.22; N, 4.81.

Synthesis of [(2,6-*i*Pr₂C₆H₂CF₃)N=CHC₁₆H₁₂O]Ni(Me)(Py) (**4d**)

A similar procedure was used as described for **4b**, except using **3d** (0.3 g, 0.6 mmol) instead of **3b**. Complex **4d** was obtained as orange-red solids (0.2 g, 50%). ¹H-NMR (400 MHz, C₆D₆, δ , ppm): 7.79–7.75 (m, 2H, *o*-H, Py), 7.63 (s, 2H, Ar-H), 7.30–7.25 (m, 2H, Ar-H), 7.20–6.97 (m, 6H, Ar-H), 6.91 (m, 2H, Ar-H), 6.76 (s, 1H, N=CH-), 6.57 (t, $J = 7.6$ Hz, 1H, *p*-H, Py), 6.18–6.09 (t, $J = 7.6$ Hz, 2H, *m*-H, Py), 4.52–4.34 (m, 2H, *i*Pr-CH), 2.65–2.56 (m, 2H, -CH₂-), 2.36 (m, 2H, -CH₂-), 1.46 (d, $J = 6.9$ Hz, 6H, *i*Pr-CH₃), 1.14 (d, $J = 6.9$ Hz, 6H, *i*Pr-CH₃), -0.85 (s, 3H, Ni-CH₃). ¹³C-NMR (101 MHz, C₆D₆, δ , ppm): 170.36 (N=CH-), 159.15, 154.52, 151.23, 143.71, 143.53, 142.24, 140.34, 134.49, 130.21, 128.86, 127.92, 127.68, 127.43, 126.32, 125.77, 122.79, 120.35, 105.21, 31.14, 26.60 (-CH₂-), 28.04 (*i*Pr-CH), 24.19, 22.72 (*i*Pr-CH₃), -7.42 (Ni-CH₃). ¹⁹F-NMR (376 MHz, C₆D₆, δ , ppm): -61.32. Elemental Anal. Calcd. for C₃₆H₃₇F₃N₂NiO: C, 68.81; H, 5.77; N, 4.46; Found: C, 68.05; H, 5.56; N, 4.25.

Norbornene (Co)polymerization

Under nitrogen atmosphere, norbornene, catalyst, and B-(C₆F₅)₃ were separately dissolved in toluene. Norbornene, comonomers, and cocatalysts were added successively into a Schlenk flask with a mechanical stirrer by using dry syringes. The reaction condition was dependent on experimental requirements. The total volume of the reaction medium in toluene was fixed at 20 mL. The reaction was started by the addition of a fresh catalyst solution and stopped after required time, and 200 mL of ethanol was poured into reaction mixture. The solid polymer was filtered, washed with acetone several times, and dried at 60 °C for more than 10 h under vacuum.

Crystal Structure Determinations

The crystals of complexes **4b** and **4d** were manipulated in a glovebox. The intensity data were collected with the ω scan mode (186 K) on a Bruker Smart APEX diffractometer with a CCD detector using Mo K α radiation ($\lambda = 0.071$ nm). Lorentz, polarization factors were made for the intensity data, and absorption corrections were performed using the SADABS program. The crystal structures were solved using the SHELXTL program and refined using Olex2. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding mode along with corresponding parent carbons. Crystal data and processing parameters for **4b** and **4d** are summarized in Table S1 (in ESI).

RESULTS AND DISCUSSION

Synthesis and Characterization of the Neutral Nickel Complexes.

The synthetic pathway of neutral nickel complexes based on β -ketiminato ligands with electron-donating and electron-withdrawing substituents is shown in Scheme 1. Compound **1** was obtained by Suzuki coupling reaction of 8-bromo-1-tetralone and phenylboronic acid according to the literature methods.^[31,32] Compounds **2b**, **2c**, and **2d** were synthesized *via* known methods by using **2a** as the starting material.^[33–36] These compounds were not very stable and should be stored under nitrogen, away from light and placed at low temperatures. Ligands **3a–3d** were obtained by one-pot reaction of **1** with substituted 2,6-diisopropylaniline (**2a–2d**) at room temperature, and purified by recrystallization *via* known method for the preparation of **3a**.^[30] Nickel complexes **4a–4d** were finally obtained *via* reaction between excess fresh $\text{Py}_2\text{Ni}(\text{CH}_3)_2$ and corresponding ligands **3a–3d**.

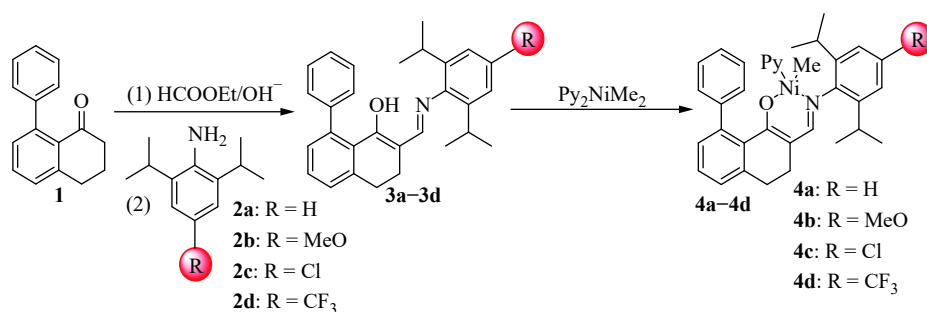
All complexes were characterized by ^1H -NMR spectroscopy. The NiCH_3 signals in ^1H -NMR spectra of the catalysts **4a–4d** were detected at -1.02 , -0.98 , -0.80 , and -0.85 ppm, respectively, suggesting that the pure complexes **4a–4d** have been successfully prepared. The resonance of proton of $i\text{Pr}-\text{CH}$ (Fig. 1) for **4a–4d** located at 4.17, 4.15, 4.34, and 4.41 ppm, respectively. Signals of $i\text{Pr}-\text{CH}$ of **4c** and **4d** shifted to downfield as the *para*-substituent electronegativity enhanced. The various electronic nature of the anilines in ligand is expected to play a role in catalytic properties.^[37,38]

To further confirm the structures of these complexes, single crystals of **4b** and **4d** suitable for X-ray crystallographic analysis were grown from toluene-hexane solutions.

Both complexes **4b** and **4d** exhibited near-square-planar coordination geometry around the Ni center and the aniline bearing a *para*-MeO— or $-\text{CF}_3$ situated at the axial position of the metal center. N1—C24 bond length in complex **4d** (1.439(4) Å) was slightly shorter than that in **4b** (1.456(2) Å). Meanwhile, the angle of N1—Ni—C23 in **4d** (92.67°) was smaller than that in **4b** (94.09°). The aniline bearing electron-withdrawing group ($-\text{CF}_3$) closer to the metal center might be owing to the electronic effect. As can be seen from Figs. 2 and 3, the bulky phenyl group (C1–C6) at the axial position of the catalysts provided a potential protection on the active species, which is expected to act as a sterically protective group to improve catalyst stability.^[30]

Homopolymerization of Norbornene

The β -ketiminato nickel complexes bearing substituents with variant electronegativity were separately investigated as catalysts for norbornene polymerization in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$. It was found that all the complexes exhibited excellent activity up to 1.25×10^7 – 1.35×10^7 $\text{g}_{\text{PNB}} \cdot \text{mol}_{\text{Ni}}^{-1} \cdot \text{h}^{-1}$ and produced high weight-average molecular weight (M_w up to 2.54×10^6 – 3.18×10^6) PNBEs, even at a low loading of $\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{B}/\text{Ni} = 3$, entries 1–4 in Table 1). Notably, complex **4c** bearing a Cl-substituted aniline in ligand exhibited the highest conversion of NBE monomer up to 98.5% within only 2 min at 30°C (entry 3 in Table 1). Most of the previously reported [N, O] type nickel systems required a large amount of alkyl aluminum (usually beyond 1000 of molar ratio) to form the active center and promote NBE polymerizations; however, in this research, the newly synthesized [N, O] type neutral nickel complex could be efficiently activated by very low dosage of $\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{B}/\text{Ni} = 3$). The polymerizations catalyzed by complexes **4a–4d** were further investigated at higher temperatures. As can be observed, activity decreased gradually with the reaction temperature elevated from 30°C through 50°C to 70°C , probably due to the catalyst decomposition similar to previous researches.^[26,39] At 30°C , catalysts with electron-withdrawing groups (**4c** and **4d**) showed slightly higher activity, while the catalysts bearing electron-donating group (**4b**) displayed the lowest activity. All catalysts yielded PNBEs with similarly high molecular weight (around 3×10^6). When the reaction temperature was elevated to 50°C , about a 30% decrease in activities can be observed, while the molecular weights were slightly decreased (entries 6–8). When the temperature was further enhanced to 70°C , the remarkable decrease in activity for **4a–4c** was observed, especially for **4a**, while **4d** still maintained



Scheme 1 Synthetic pathway to neutral nickel catalysts **4a–4d** based on β -Ketiminato ligands

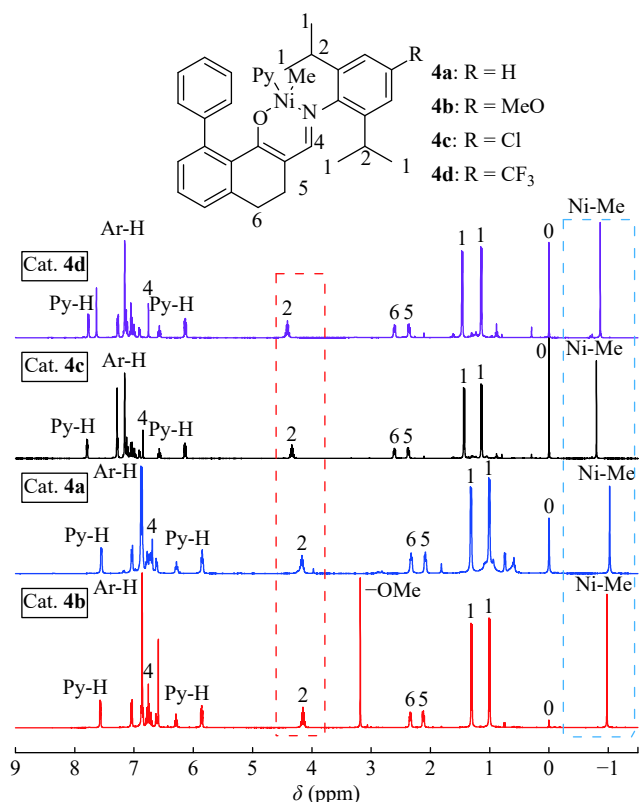


Fig. 1 Chemical shifts of *iPr*—CH of nickel complexes **4a–4d** in ^1H -NMR spectra

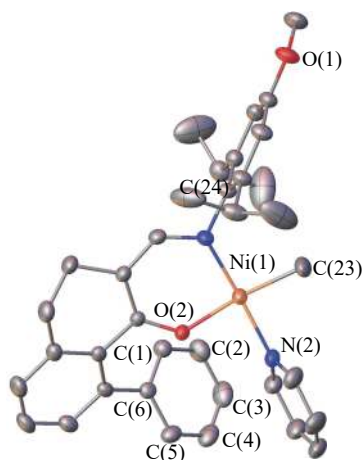


Fig. 2 ORTEP plot of complex **4b**. Ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)—O(1) 1.9153(11), Ni(1)—N(1) 1.8847(14), Ni(1)—N(2) 1.9130(16), Ni(1)—C(23) 1.928(2), N(1)—C(24) 1.456(2), O(1)—Ni(1)—N(1) 93.82(5), O(1)—Ni(1)—N(2) 85.39(5), N(2)—Ni(1)—C(23) 87.50(9), C(23)—Ni(1)—N(1) 94.09(9).

similarly high activity and gave PNBE with the highest molecular weight (entry 12 in Table 1). As previously discussed about the single crystalline structures, aniline bearing electron-withdrawing *para*-CF₃ group of **4d** was the closest to the metal center. Therefore, we propose that a secondary bond might be built between the metal center and the electron-withdrawing group, leading to the highest thermal stability of **4d**.

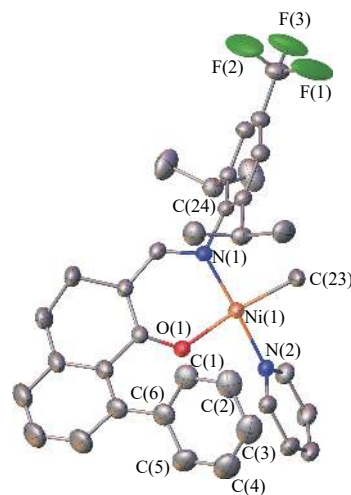


Fig. 3 ORTEP plot of complex **4d**. Ellipsoids are drawn at 30% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)—O(1) 1.922(2), Ni(1)—N(1) 1.883(3), Ni(1)—N(2) 1.914(3), Ni(1)—C(23) 1.957(3), N(1)—C(24) 1.439(4), O(1)—Ni(1)—N(1) 93.15(10), O(1)—Ni(1)—N(2) 85.86(10), N(2)—Ni(1)—C(23) 88.94(13), C(23)—Ni(1)—N(1) 92.67(13).

Copolymerization of NBE with Small-molecular Norbornene Derivatives

Since NBE is highly active in transition-metal-catalyzed polymerizations, it tends to be an effective method to produce functionalized PNBEs by copolymerizing NBE with its polar derivatives. Two NBE derivatives, 5-norbornene-2-yl-acetate (NBA) and 5-norbornene-2-yl-methanol (NBM), bearing pendent acetate and methanol group, respectively, were copolymerized with NBE under similar reactions with varying NBE/NBA ratio. Although all catalysts exhibited the highest catalytic activities in NBE homopolymerization at 30 °C, and the activities decreased with the increase in reaction temperature, the copolymerizations of NBE with polar NBE derivatives conducted at 30 °C yielded only a trace amount of polymers. To efficiently promote the copolymerization of NBE with polar monomers, higher reaction temperature (50 °C or 70 °C) was thus adopted in the copolymerization experiments. As observed in Table 2, runs 1–4, all Ni catalysts exhibited good catalytic capabilities toward the copolymerization with 5 mol% NBA as a comonomer at 50 °C. Complex **4c** showed the highest apparent conversion rate up to 97.0% and produced copolymers with the high molecular weight (M_w up to 1.24×10^6 , entry 3) in the copolymerization of NBE with NBA at 50 °C. We further enhanced the feeding amount of polar NBA to 10 mol%, but the apparent conversion rate decreased to 43.1% and the molecular weight of the copolymer decreased to 0.87×10^6 . Incorporation of NBA in the copolymers can be calculated by ^1H -NMR spectrum as shown in Fig. 4. The resonance presented at around 5 ppm was assigned to the marked proton of —CHOCOCH₃. As observed in Table 2, with the feedstock of NBA increased from 5 mol% to 10 mol%, the incorporation of NBA was increased from 4.93 mol% to 9.00 mol%.

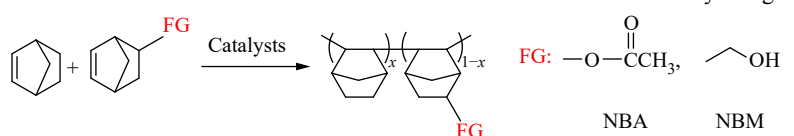
Entries 6–10 in Table 2 refer to the NBE/NBM copolymerization. All catalysts showed lower activities toward

Table 1 Polymerization of norbornene by using complexes **4a–4d**^a

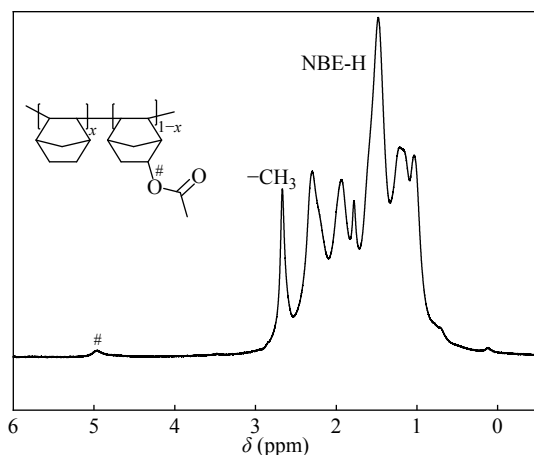
Entry	Cat.	Temp. (°C)	Yield (g)	Conversion (%)	Act. ^b	$M_w^c \times 10^{-6}$	PDI ^c
1	4a	30	1.28	93.4	12.8	2.54	1.80
2	4b	30	1.25	91.2	12.5	3.18	1.82
3	4c	30	1.35	98.5	13.5	2.97	1.90
4	4d	30	1.30	94.8	13.0	2.94	1.83
5	4a	50	0.84	61.2	8.40	2.70	1.78
6	4b	50	0.86	62.7	8.60	3.01	1.80
7	4c	50	0.91	66.4	9.10	2.09	1.77
8	4d	50	0.87	63.5	8.70	2.29	1.83
9	4a	70	0.25	18.3	2.50	0.94	1.57
10	4b	70	0.50	36.4	5.00	1.28	1.64
11	4c	70	0.46	33.5	4.60	1.40	1.67
12	4d	70	0.88	64.2	8.80	1.94	1.83

^a Polymerization conditions: 20 mL of toluene, 3 μ mol of catalyst, $B(C_6F_5)_3/Ni = 3$, 2 min, 14.5 mmol of total monomer; ^b In units of 10^6 g_{PNB}·mol_{Ni}⁻¹·h⁻¹; ^c Determined by GPC at 150 °C in 1,2,4-trichlorobenzene versus PS standards

Table 2 Copolymerization of norbornene with small-molecular norbornene derivatives by using complexes **4a–4d**^a

									
Entry	Cat.	[Comono.] (mol%)	Yield (g)	Conversion (%)			Incorp. ^b (mol%)	$M_w^c \times 10^{-6}$	PDI ^c
				Comono.	NBE	Total			
1	4a	NBA (5)	1.59	74.8	87.2	84.8	4.32	1.31	1.83
2	4b	NBA (5)	1.60	78.5	87.4	85.3	4.51	1.13	1.83
3	4c	NBA (5)	1.82	97.4	98.8	97.0	4.93	1.24	1.92
4	4d	NBA (5)	1.33	69.9	72.3	70.9	4.84	1.24	1.87
5	4c	NBA (10)	0.82	39.1	43.9	43.1	9.00	0.87	2.13
6	4a	NBM (5)	1.32	68.2	71.8	71.6	4.69	0.97	1.62
7	4b	NBM (5)	1.08	58.6	58.6	58.6	4.93	0.98	1.63
8	4c	NBM (5)	1.42	74.0	77.2	78.0	4.73	1.01	1.78
9	4d	NBM (5)	0.75	38.5	40.8	40.7	4.66	0.84	1.69
10	4c	NBM (10)	0.38	19.2	20.7	20.5	9.31	0.41	1.65

^a Polymerization conditions: 20 mL of toluene, 10 μ mol of catalyst, $B(C_6F_5)_3/Ni = 3$, 15 min, 50 °C, 19.0 mmol of total monomers; ^b Determined by ¹H-NMR spectroscopy at 120 °C; ^c Determined by GPC at 150 °C in 1,2,4-trichlorobenzene versus PS standards

**Fig. 4** ¹H-NMR spectrum of norbornene and NBA copolymers containing 4.32 mol% NBA (Table 2, entry 1)

NBE/NBM copolymerization compared with NBE/NBA copolymerization. Apparent conversion of the NBE/NBM monomers was decreased to only 40.7% for the copolymerization catalyzed by **4d**, while **4c** showed the highest apparent conversion rate of 78% under the same conditions. Increasing NBM loading ratio remarkably decreased the activity of

4c (entry 10 in Table 2), and apparent conversion of the NBE/NBM monomers was decreased to only 20.5%. The evident decrease in monomer conversions of above mentioned copolymerizations involving NBM could be ascribed to a higher polarity of hydroxyl groups, which made the Ni catalysts easily being deactivated. Although the monomer conversions were decreased compared to that of NBE homopolymerization, the incorporation of NBA or NBM maintained a considerable level (up to 9.00 mol% for NBA and 9.31 mol% for NBM, Table 2). Incorporation of NBM in the copolymers can be calculated by ¹H-NMR spectrum as shown in Fig. 5. The resonance signal presented at around 3.7 ppm was assigned to the marked proton of $-CH_2OH$.

Copolymerization of NBE with Macromolecular Norbornene Derivatives

Incorporating functional NBE derivatives bearing long side chains was expected to further overcome the brittleness and improve the solubility and mobility of NBEs at high temperature. Therefore, two macromolecular norbornene derivative based on NBM and NBA but with long alkane substituent (5-norbornene-2-yl methyl dodecanoate, NMD) or polyether chain (5-norbornene-2-yl methyl-polyol, NB-PPO) were synthesized and copolymerized with NBE. NMD was prepared by the one-step method through mixing dodecanoyl

chloride with NBM under appropriated conditions (details shown in experimental section), while NB-PPO was obtained by a two-step method through ring-opening polymerization of propylene oxide with sodium alkoxide as an initiator (see details in experimental section). When we conducted the copolymerization of NBE with NMD by using **4c** as catalyst and 3 folds of $B(C_6F_5)_3$ as an activator, the comonomer conversion was relatively low (74%), so a higher ratio of activators was adopted in the following copolymerizations ($B(C_6F_5)_3/Ni = 6$). All the Ni catalysts were separately used to promote the copolymerizations of norbornene with NMD and NB-PPO under optimized reaction conditions. At 50 °C, catalysts **4a** and **4b** exhibited similarly high monomer conversion beyond 97% in the presence of 6.0 equivalent of $B(C_6F_5)_3$, yielding NBE-NMD copolymers with similar NMD incorporation up to 9.30 mol% and 9.05 mol% (entries 1 and 2 in Table 3), respectively. On the contrary, catalysts **4c** and **4d**, bearing an electron-withdrawing group substituted aniline ligand displayed lower comonomer conversions (around 80%), and **4d** yielded copolymer copolymers with slightly

lower NMD incorporation (8.11 mol%). This observation might be originated from the steric effect of the long-chain substituents connected to the NBE ring of the polar macro-molecular which slowed down the coordination-insertion process.

In the case of NMD, the long aliphatic chain did not show negative influence on the NMD incorporation. As observed, the high NMD incorporation up to 35.5 mol% (Fig. 6) of copolymer could be achieved by increasing the feeding monomer ratio of NMD to 50% (entry 6 in Table 3).

Under the optimized reaction conditions, copolymerization of NBE with NB-PPO promoted by **4a–4d** gave only a trace amount of polymers, so we improved the polymerization by increasing the catalyst feed amount to 20 μ mol and extending the reaction time to 20 min at 70 °C. Nonetheless, the apparent conversions of copolymerization of NBE with NB-PPO by all catalysts were still lower than 41%. Besides, the NB-PPO incorporations (< 5 mol%, Fig. 7) in the copolymers and molecular weights were found to be much lower than those of NBE-NMD copolymers. The notably restrai-

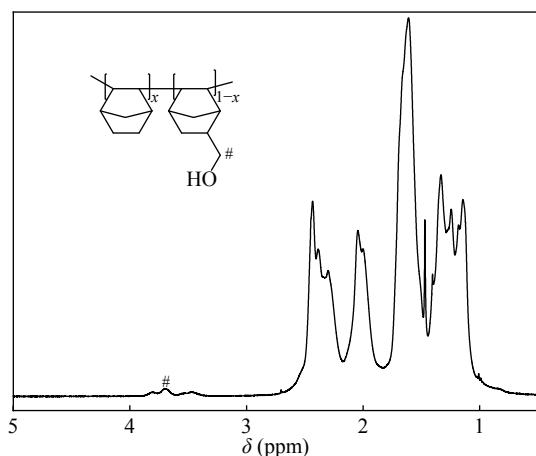


Fig. 5 ^1H -NMR spectrum of norbornene and NBM copolymers with NBM incorporation of 4.73 mol% (Table 2, entry 8)

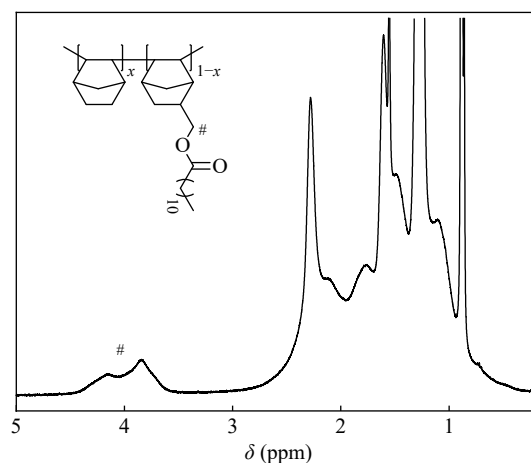


Fig. 6 ^1H -NMR spectrum of norbornene/NMD copolymer with NMD incorporation of 35.5 mol%

Table 3 Copolymerization of norbornene with norbornene derivatives containing long side chains by using complexes **4a–4d**^a

FG: NMDNB-PPO										
Entry	Cat.	[Comono.] (mol%)	Temp. (°C)	Yield (g)	Conversion (%)			Incorp. ^b (mol%)	<i>M</i> _w ^c × 10 ^{−6}	PDI ^c
					Comono.	NBE	Total			
1	4a	NMD (10)	50	1.11	90.6	98.2	97.4	9.30	1.31	2.18
2	4b	NMD (10)	50	1.12	89.4	99.8	98.2	9.05	0.94	1.92
3	4c	NMD (10)	50	0.95	81.2	82.7	83.3	9.83	1.41	2.64
4	4d	NMD (10)	50	0.90	65.5	82.5	78.9	8.11	1.68	2.27
5	4c	NMD (30)	50	1.25	66.4	97.0	79.6	22.7	1.65	2.50
6	4c	NMD (50)	50	1.01	42.3	76.8	50.6	35.5	0.62	1.55
7 ^d	4a	NB-PPO (10)	70	0.53	19.6	46.1	35.3	4.52	0.52	1.61
8 ^d	4b	NB-PPO (10)	70	0.55	20.6	47.7	36.7	4.58	0.52	1.64
9 ^d	4c	NB-PPO (10)	70	0.58	20.4	51.4	38.7	4.23	0.56	1.52
10 ^d	4d	NB-PPO (10)	70	0.62	21.0	55.5	41.4	4.04	0.61	1.79

ned monomer conversation as well as low molecular weight and NB-PPO incorporation might mainly be ascribed to partly deactivation of the catalyst by the polar polyether chain. It is worth mentioning that these polymers containing long alkane or polyether tails had significantly improved solubility compared to the NBE/NBA and NBE/NBM copolymers. The NBE/NMD copolymers, especially, were soluble in organic solvents such as trichloromethane, toluene, and dichloromethane at room temperature, while NBE/NBA and NBE/NBM copolymers could not be dissolved without heating. The representative DSC curves of copolymers are presented in Fig. S7 (in ESI).

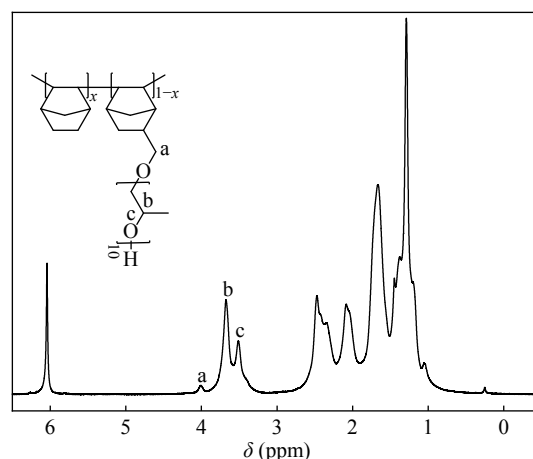


Fig. 7 ^1H -NMR spectrum of norbornene/NB-PPO copolymer with NB-PPO incorporation of 4.58 mol%

CONCLUSIONS

Nickel complexes **4a–4d** based on β -ketiminato ligands bearing various electron-donating or electron-withdrawing substituents on the *para*-position of the aniline group were synthesized. Their difference performances in addition polymerization of norbornene and copolymerization of norbornene with functional NBE bearing different polar groups or long polar/nonpolar sequences were investigated. Under mild conditions, all catalysts promoted NBE homopolymerization with high NBE conversion beyond 91.2% in 2 min, and produced polymers with high molecular weight up to 2.54×10^6 – 3.18×10^6 . In NBE homopolymerization, electronic effect only influenced catalytic activities slightly, while electron-withdrawing groups improved the stability of the catalysts markedly. Copolymerization of norbornene with functional norbornene derivatives bearing acetate or methanol group with tunable polar monomer incorporations could be easily obtained by using all Ni catalysts, with **4c** exhibiting the highest apparent monomer conversion. All complexes showed remarkable tolerance toward the pendent polar groups of NBE derivatives. For the first time, NBE copolymers containing long functional sequences were synthesized by direct copolymerization of NBE with elaborately designed macromolecular NBE monomers based on the small functional NBE derivatives. All these newly obtained functional PNBEs showed much improved solubility at room temperature.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2292-2>.

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REFERENCES

- Pierre, F.; Commarieu, B.; Tavares, A. C.; Claverie, J. High T_g sulfonated insertion polynorbornene ionomers prepared by catalytic insertion polymerization. *Polymer* **2016**, *86*, 91–97.
- Mandal, M.; Huang, G.; Kohl, P. A. Anionic multiblock copolymer membrane based on vinyl addition polymerization of norbornenes: Applications in anion-exchange membrane fuel cells. *J. Membr. Sci.* **2019**, *570*, 394–402.
- Chapala, P. P.; Bermeshev, M. V.; Starannikova, L. E.; Belov, N. A.; Ryzhikh, V. E.; Shantarovich, V. P.; Lakhtin, V. G.; Gavrilova, N. N.; Yampolskii, Y. P.; Finkelshtein, E. S. A novel, highly gas-permeable polymer representing a new class of silicon-containing polynorbornenes as efficient membrane materials. *Macromolecules* **2015**, *48*, 8055–8061.
- Maroon, C. R.; Townsend, J.; Gmernicki, K. R.; Harrigan, D. J.; Sundell, B. J.; Lawrence, J. A.; Mahurin, S. M.; Vogiatzis, K. D.; Long, B. K. Elimination of CO_2/N_2 langmuir sorption and promotion of “ N_2 -phobicity” within high- T_g glassy membranes. *Macromolecules* **2019**, *52*, 1589–1600.
- Kang, B. G.; Kim, D. G.; Register, R. A. Vinyl addition copolymers of norbornylnorbornene and hydroxyhexafluoroisopropylnorbornene for efficient recovery of *n*-butanol from dilute aqueous solution *via* pervaporation. *Macromolecules* **2018**, *51*, 3702–3710.
- Kim, D. G.; Takigawa, T.; Kashino, T.; Burtovyy, O.; Bell, A.; Register, R. A. Hydroxyhexafluoroisopropylnorbornene block and random copolymers *via* vinyl addition polymerization and their application as biobutanol pervaporation membranes. *Chem. Mater.* **2015**, *27*, 6791–6801.
- Park, J. H.; Koh, T. W.; Chung, J.; Park, S. H.; Eo, M.; Do, Y.; Yoo, S.; Lee, M. H. Polynorbornene copolymer with side-chain iridium(III) emitters and carbazole hosts: A single emissive layer material for highly efficient electrophosphorescent devices. *Macromolecules* **2013**, *46*, 674–682.
- Park, J. H.; Koh, T. W.; Do, Y.; Lee, M. H.; Yoo, S. Soluble polynorbornenes with pendant carbazole derivatives as host materials for highly efficient blue phosphorescent organic light-emitting diodes. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 2356–2365.
- Bermeshev, M. V.; Chapala, P. P. Addition polymerization of functionalized norbornenes as a powerful tool for assembling molecular moieties of new polymers with versatile properties. *Prog. Polym. Sci.* **2018**, *84*, 1–46.
- Blank, F.; Janiak, C. Metal catalysts for the vinyl/addition polymerization of norbornene. *Coord. Chem. Rev.* **2009**, *253*, 827–861.
- Chen, L.; Zhong, Z.; Chen, C.; He, X.; Chen, Y. N,O-chelating bidentate Ni (II) and Pd (II) complexes for copolymerization of norbornene and norbornene ester. *J. Organomet. Chem.* **2014**, *752*, 100–108.
- Kim, D. G.; Bell, A.; Register, R. A. Living vinyl addition polymerization of substituted norbornenes by a *t*-Bu₃P-ligated methylpalladium complex. *ACS Macro Lett.* **2015**, *4*, 327–330.
- Eo, M.; Lee, S.; Park, M. H.; Lee, M. H.; Yoo, S.; Do, Y.

- Vinyl-type polynorbornenes with pendant PCBM: A novel acceptor for organic solar cells. *Macromol. Rapid Commun.* **2012**, *33*, 1119–1125.
- 14 He, F.; Chen, Y.; He, X.; Chen, M.; Zhou, W.; Wu, Q. Copolymerization of norbornene and 5-norbornene-2-yl acetate using novel bis(β -ketonaphthylamino)Ni(II)/B(C₆F₅)₃/AlEt₃ catalytic system. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 3990–4000.
 - 15 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 centre nickel catalyst bearing bulky bis(α -diimine) ligand with strong electron-withdrawing groups. *Polym. Chem.* **2017**, *8*, 2390–2396.
 - 16 He, X.; Yang, Y.; Wang, S.; Han, Z.; Tu, G.; Zhang, F.; Huang, S.; Wang, Z.; Chen, D. Synthesis of bis-(benzocyclohexan-ketoimino) Ni(II) with different electron groups and their catalytic copolymerization of norbornene and polar norbornene. *RSC Adv.* **2017**, *7*, 48745–48753.
 - 17 Tian, J.; He, X.; Liu, J.; Deng, X.; Chen, D. Synthesis of well-defined C—C bridged Ni(II) complexes bearing β -ketoiminato-fluorene ligands by bifluorenyl in situ coupling and application for norbornene (co)polymerization. *RSC Adv.* **2015**, *5*, 61851–61860.
 - 18 He, J.; Liu, Z.; Du, G.; Fu, Y.; Zhang, S.; Li, X. Chiral palladium(II) and nickel(II) complexes C₂-symmetrical tridentate bis(oxazoline) ligands: Synthesis, characterization, and catalytic norbornene polymerization. *Organometallics* **2014**, *33*, 6103–6112.
 - 19 Chen, C. Designing catalysts for olefin polymerization and copolymerization: Beyond electronic and steric tuning. *Nat. Rev. Chem.* **2018**, *2*, 6–14.
 - 20 Tan, C.; Pang, W. M.; Chen, C. L. A phenol-containing α -diimine ligand for nickel- and palladium- catalyzed ethylene polymerization. *Chinese J. Polym. Sci.* **2019**, *37*, 974–980.
 - 21 Wang, F. Z.; Tian, S. S.; Li, R. P.; Li, W. M.; Chen, C. L. Ligand and steric effects on naphthyl- α -diimine nickel catalyzed α -olefin polymerization. *Chinese J. Polym. Sci.* **2018**, *36*, 157–162.
 - 22 Liao, H.; Gao, J.; Zhong, L.; Gao, H. Y.; Wu, Q. Regioselective polymerizations of α -olefins with an α -diamine nickel catalyst. *Chinese J. Polym. Sci.* **2019**, *37*, 959–965.
 - 23 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.
 - 24 Antonov, A. A.; Semikolenova, N. V.; Zakharov, V. A.; Zhang, W.; Wang, Y.; Sun, W. H.; Talsi, E. P.; Bryliakov, K. P. Vinyl polymerization of norbornene on nickel complexes with bis(imino)pyridine ligands containing electron-withdrawing groups. *Organometallics* **2012**, *31*, 1143–1149.
 - 25 Carlini, C.; Martinelli, M.; Galletti, A. M. R.; Sbrana, G. Vinyl polymerization of norbornene by bis(nitro-substituted-salicylaldehyde)nickel(II)/methylaluminoxane catalysts. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1514–1521.
 - 26 Zeng, Y.; Mahmood, Q.; Zhang, Q.; Liang, T.; Sun, W. H. Vinyl homo/copolymerization of norbornene and ethylene using sterically enhanced 1,2-bis(arylimino)acenaphthene-palladium precatalysts. *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 922–930.
 - 27 Zeng, Y.; Mahmood, Q.; Zhang, Q.; Liang, T.; Sun, W. H. Highly thermo-stable and electronically controlled palladium precatalysts for vinyl homo/co-polymerization of norbornene-ethylene. *Eur. Polym. J.* **2018**, *103*, 342–350.
 - 28 Zhang, Y.; Mu, H.; Li, Y.; Li, Y. Phosphine (oxide)-(thio) phenolate palladium complexes: Synthesis, characterization and (co)polymerization of norbornene. *Appl. Organomet. Chem.* **2018**, *32*, e4013.
 - 29 Zhang, Y. P.; Li, W.; Li, B. X.; Mu, H. L.; Li, Y. S. Well-defined phosphino-phenolate neutral nickel(II) catalysts for efficient (co)polymerization of norbornene and ethylene. *Dalton Trans.* **2015**, *44*, 7382–7394.
 - 30 Song, D. P.; Wang, Y. X.; Mu, H. L.; Li, B. X.; Li, Y. S. Observations and mechanistic insights on unusual stability of neutral nickel complexes with a sterically crowded metal center. *Organometallics* **2011**, *30*, 925–934.
 - 31 Nguyen, P.; Corpuz, E.; Heidelbaugh, M. T.; Chow, K.; Garst, E. M. A convenient synthesis of 7-halo-1-indanones and 8-halo-1-tetralones. *J. Org. Chem.* **2003**, *68*, 10195–10198.
 - 32 Gelat, F.; Richard, V.; Berger, O.; Montchamp, J. L. Development of a new family of chiral auxiliaries. *Org. Lett.* **2015**, *17*, 1819–1821.
 - 33 Elie, M.; Sguerra, F.; Di Meo, F.; Weber, M. D.; Marion, R.; Grimault, A.; Lohier, J. F.; Stallivieri, A.; Brosseau, A.; Pansu, R. B.; Renaud, J. L.; Linares, M.; Hamel, M.; Costa, R. D.; Gaillard, S. Designing NHC-copper(I) dipyrindylamine complexes for blue light-emitting electrochemical cells. *ACS Appl. Mater. Interfaces* **2016**, *8*, 14678–14691.
 - 34 Hospital, A.; Gibard, C.; Gaulier, C.; Nauton, L.; Thery, V.; El-Ghozzi, M.; Avignant, D.; Cisnetti, F.; Gautier, A. Access to functionalised silver(I) and gold(I) *N*-heterocyclic carbenes by [2 + 3] dipolar cycloadditions. *Dalton Trans.* **2012**, *41*, 6803–6812.
 - 35 Lane, T. K.; D'Souza, B. R.; Louie, J. Iron-catalyzed formation of 2-aminopyridines from diynes and cyanamides. *J. Org. Chem.* **2012**, *77*, 7555–7563.
 - 36 Lane, T. K.; Nguyen, M. H.; D'Souza, B. R.; Spahn, N. A.; Louie, J. The iron-catalyzed construction of 2-aminopyrimidines from alkynenitriles and cyanamides. *Chem. Commun.* **2013**, *49*, 7735–7737.
 - 37 Popeney, C.; Guan, Z. Ligand electronic effects on late transition metal polymerization catalysts. *Organometallics* **2005**, *24*, 1145–1155.
 - 38 Dai, S.; Sui, X.; Chen, C. Highly robust palladium(II) α -diimine catalysts for slow-chain-walking polymerization of ethylene and copolymerization with methyl acrylate. *Angew. Chem. Int. Ed.* **2015**, *54*, 9948–9953.
 - 39 Li, M.; Shu, X.; Cai, Z.; Eisen, M. S. Synthesis, structures, and norbornene polymerization behavior of neutral nickel(II) and palladium(II) complexes bearing aryloxide imidazolidin-2-imine ligands. *Organometallics* **2018**, *37*, 1172–1180.