

Living copolymerization of ethylene with 4-methyl-1-pentene by α -diimine Ni(II)/Et₂AlCl catalyst: synthesis of diblock copolymers via sequential monomer addition

Supplementary Materials

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General Considerations and Materials. Manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk-line techniques. Toluene (Fluka, > 99.5% pure) was refluxed over Na for ca. 8 h and then distilled and stored over molecular sieves under nitrogen. Diethylaluminium chloride (Et₂AlCl) (Fluka) was used as received. Nickel(II) complex [ArN=C(CH₃)-(CH₃)C=NAr]NiBr₂ (Ar = 2,6-(iPr)₂C₆H₃) was synthesized according to the experimental procedures previously reported in literature.[reference 3a in the manuscript, L. K. Johnson, C. M. Killian and M. Brookhart, *JACS* **1995**, 117, 6414] 4-Methyl-1-pentene (4M1P) (Aldrich, ≥ 99% pure) was refluxed over CaH₂ for about 2 hours, then distilled trap-to trap and, finally, stored under dry nitrogen and kept at -20°C. 1-Hexene (Hex) (Aldrich, ≥ 99% pure) was refluxed over CaH₂ for about 2 hours, then distilled trap-to trap and, finally, stored under dry nitrogen and kept at -20°C. Ethylene was purified flowing through BTS catalysts, molecular sieves, and CaCl₂. Deuterated solvent for NMR measurements (C₂D₂Cl₄) (Cambridge Isotope Laboratories, Inc.) was used as received.

Synthesis of the nickel(II) complex.

Synthesis of [(2,6-(iPr)₂C₆H₃)N=C(CH₃)-(CH₃)C=N(2,6-(iPr)₂C₆H₃)] diimine ligand.

A 250 mL flask was charged with 2,6-diisopropylaniline (15.96 g, 90 mmol) and 80 mL of methanol. Formic acid was then added (few drops) to obtain a yellow solution. While stirring, a methanol solution (80 mL) of 2,3-butanedione (3.875 g, 45 mmol) was added drop by drop, and the reaction was stirred at room temperature for 2 hours until it was noticed the formation of a yellow precipitate. Then it was filtered and dried under vacuum to give 15.40 g of a yellow solid (84%).

FT-IR (nujol): 1640 cm⁻¹ $\nu_{(C=N)}$. C: 82,86% (83,11%); H: 9,97% (9,96%); N: 6,94% (6,92%).

Synthesis of [(2,6-(*i*Pr)₂C₆H₃)N=C(CH₃)-(CH₃)C=N(2,6-(*i*Pr)₂C₆H₃)]NiBr₂ (Ni-1) complex.

487.7 mg (1.58 mmol) of (DME)NiBr₂ and 687 mg (1.70 mmol) of [(2,6-(*i*Pr)₂C₆H₃)N=C(CH₃)-(CH₃)C=N(2,6-(*i*Pr)₂C₆H₃)] were combined as solids in a flame-dried 100 mL round-bottom Schlenk. Methylene chloride (30 mL) was added to the solid mixture and the reaction was stirred at room temperature for 20 hours. The solvent was removed in vacuo to give a red/brown solid which was then washed with freshly distilled pentane (3×15 mL). The product was isolated as a brown powder (Yield = 920.3 mg).

Polymerization Procedure. The polymerization experiments were carried out in a 25 mL round-bottomed Schlenk flask containing a stirring bar. The polymerization reactor was first dried by heating at 80°C and then vacuum was applied for 1h at 40°C.

Ethylene Polymerization [Table 1 in the manuscript, (run 1)].

The reactor vessel was charged with toluene and brought to the desired polymerization temperature. Et₂AlCl was added, the solution was degassed and saturated with ethylene under vigorous stirring for 10 min. The polymerization was started by adding a solution of the nickel compound under continuous flow of ethylene ($P_E \approx 1.01$ bar). Polymerizations were stopped with methanol containing a small amount of hydrochloric acid; the precipitated polymers were collected by filtration, repeatedly washed with fresh methanol, and then dried in vacuum at room temperature to constant weight.

4-Methyl-1-Pentene (4M1P) Polymerization.

4M1P polymerization was carried out as follows: toluene and the monomer were transferred into the reactor vessel; the solution was brought to the desired polymerization temperature, then Et₂AlCl and the nickel compound were added in the order. Polymerization was stopped as reported above.

Polymerization Conditions: toluene, total volume, 16 mL; 4M1P, 2 g; Ni-1, 10 μmol; Al/Ni molar ratio, 200; temperature, 0°C; time, 1 h.

Polymerization Result: monomer conversion, 5%.

1-Hexene Polymerization.

1-Hexene (1-Hex) polymerization was carried out as follows: toluene and the monomer were transferred into the reactor vessel; the solution was brought to the desired polymerization temperature, then Et₂AlCl and the nickel compound were added in the order. Polymerization was stopped as reported above.

Polymerization Conditions: toluene, total volume, 16 mL; 1-Hex, 2 g; Ni-1, 10 μmol ; Al/Ni molar ratio, 200; temperature, 0°C; time, 2 h.

Polymerization Results: monomer conversion, 25%; $T_g = -56$ °C; $M_n = 69000$ g/mol, $M_w/M_n = 1.21$.

Ethylene/4-methyl-1-pentene Copolymerization (Table 1, run 2–7).

The reactor vessel was charged with 4M1P and toluene and the solution was brought to the desired polymerization temperature. Et_2AlCl was added, the solution was degassed and saturated with ethylene under vigorous stirring for 10 min. The polymerization was started by adding a toluene solution of the nickel compound under continuous flow of ethylene. Polymerizations were stopped as reported above.

Synthesis of poly(E-co-4M1P)-block-poly(1-Hex) [Table 2 in the manuscript, (run 8–10)].

The reactor vessel was charged with 4M1P and toluene and the solution was brought to the desired polymerization temperature. Et_2AlCl was added, the solution was degassed and saturated with ethylene under vigorous stirring for 10 min. The polymerization was started by adding a toluene solution of the nickel compound (2 mg/mL) under continuous flow of ethylene ($P_E \approx 1.01$ bar). Subsequently, ethylene was removed under vacuo for 3 min and 1-hexene was added. After the specified time, reported in Table 2 in the manuscript, the polymerizations were stopped as reported above.

Polymer Characterization.

For ^{13}C NMR, about 100 mg of copolymer was dissolved in $\text{C}_2\text{D}_2\text{Cl}_4$ in a 10 mm tube. HDMS (hexamethyldisiloxane) was used as internal chemical shift reference. The spectra were recorded on a Bruker NMR AVANCE 400 Spectrometer operating at 100.58 MHz (13C) in the PFT mode working at 103 °C. The applied conditions were the following: 10 mm probe, 90° pulse angle; 64 K data points; acquisition time 5.56 s; relaxation delay 20 s; 3–4K transient. Proton broad-band decoupling was achieved with a 1D sequence using *bi_waltz_16_32* power-gated decoupling.

Differential scanning calorimetry (DSC) scans were carried out on a Perkin-Elmer Pyris 1 instrument. Typically, ca. 10 mg of polymer were analyzed in each run, with a scan speed of 20 °C/min under a nitrogen atmosphere. T_g was recorded during a second thermal cycle.

The molecular weight averages (M_n) and the molecular weight distribution (M_w/M_n) were obtained by a high temperature Waters GPCV2000 size exclusion chromatography (SEC) system using two online detectors: a differential viscometer and a refractometer. The experimental conditions consisted of three PL Gel Olexis columns, *o*-DCB as the mobile phase, 0.8 mL/min flow rate, and

145°C temperature. The calibration of the SEC system was constructed using eighteen narrow M_w/M_n polystyrene standards with molar weights ranging from 162 to 5.6×10^6 g/mol. For SEC analysis, about 12 mg of polymer was dissolved in 5 mL of *o*-DCB with 0.05% of BHT as antioxidant.

Copolymers Composition.

The poly(E-*co*-4M1P)s composition was determined by ^{13}C NMR analysis in $\text{C}_2\text{D}_2\text{Cl}_4$. The comonomer 4M1P content in copolymers was calculated by the following equations:

$$4\text{M1P (mol\%)} = \frac{[4\text{M1P}]}{[4\text{M1P}] + [\text{E}]} \times 100 = \frac{\bar{I}_Y}{\bar{I}_Y + \bar{I}_E} \times 100 \quad (1)$$

where I_Y indicates the area of the signal of the methylene carbon atom of the comonomer at 42.50 ppm.

$$\bar{I}_E = \frac{1}{2} I_E \quad (2)$$

where I_E is the area of the $\text{S}_{\delta\delta}$ methylene peak at 27.73 ppm.