Ring-Opening Metathesis Polymerization using Polyisobutylene Supported Grubbs Second-Generation Catalyst

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Experimental

Materials and Reagents

2,6-Dimethyl-4-(polyisobutyl)aniline **3**, N, N'-(Ethane-1,2-diylidene) bis(2,6-dimethyl-4-(polyisobutyl)aniline) **4** and 1,3-Bis(2,6-dimethyl-4-(polyisobutyl)phenyl)-4,5-dihydroimidazolium tetrafluoroborate **5**, were prepared according to literature procedure with modification.[1] Oxanorbornene imide **9** and monomers **10-21** were synthesized following reported procedure.[2] PIB (Glissopal 1000) was a gift from BASF. All other reagents were purchased from Sigma Aldrich. All reactions were carried out under argon using solvents and reagents as commercially supplied without further purification, unless otherwise stated. ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 spectrometer, using the residual solvent resonance of $CDCl_3$ or tetramethylsilane (TMS) as an internal reference and are given in ppm. Number-average (M_n) and weight average (M_w) were determined by GPC analyses, which were carried out using a Viscotek GPC Max VE 2001 instrument with a Viscotek TDA 302 triple array detector and Viscotek Org Guard column with three (in series) mixed medium columns (LT5000L) at 35 °C with a flow rate of 1.0 mL/min. A 12-point universal calibration curve was recorded using narrow polydispersity polystyrene standards. Flash chromatography (FC) was performed on silica gel (Merck Kieselgel 60 F254 230–400 mesh) unless otherwise indicated. Thin-layer chromatography was performed on Merck aluminum-backed plates precoated with silica (0.2 mm, 60 F254). ICP-MS data were obtained using a Perkin-Elmer ELAN DRCe instrument.

Synthesis:

Monomers **11–21** were synthesized according to our previously reported method.[1, 2]

PIB-supported 2nd generation Grubbs complex (6)

To a solution of 1,3-bis(2,6-dimethyl-4-(polyisobutyl)phenyl)-4,5-dihydroimidazolium tetrafluoroborate **5** (0.35 g, 0.15 mmol) in dry THF (1.7 mL) was added potassium t-butoxide (21 mg, 0.18 mmol) and the reaction mixture was stirred for 1h at room temperature in a glove box. A solution of $Cl_2Ru(CHPh)(PCy_3)_2$ (123 mg, 0.15 mmol) in dry toluene (1.7 mL) was added and the reaction mixture was heated at 85 °C overnight. The solvent was evaporated to dryness under vacuum. The crude residue was dissolved in toluene (10 mL) and the solution was filtrated through a celite pad and the filtrate was concentrated under vacuum. The brown oil was purified by column-chromatography on silica gel 60 using a 1:1 mixture of hexane and dichloromethane to afford a brownish-pink waxy oil (0.25 g, 60%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 19.05 (1H, s), 7.45 (m, 1H), 7.19 (s, 2H), 7.08 (s, 2H), 7.02 (bm, 4H), 3.87 (m, 1H), 3.70 (m, 4H), 2.61 (s, 6H), 2.12 (s, 6H), 0.72-1.74 (m, PIB-H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ: 305.90, 210.22, 163.83, 150.75, 143.19, 143.08, 141.70, 136.62, 135.86, 127.77, 126.87, 126.72, 126.62, 118.24, 38.09, 38.02, 37.71, 32.45, 32.20, 31.08, 30.98, 30.61, 18.76, 18.46; ^{31}P NMR (161.98 MHz, CD_2Cl_2) δ: 26.41.

Polymer Synthesis

General conditions for the kinetic study (Figures 3c).

Norbornene **M7** (0.1 mmol) in d_8-THF (0.25 mL) was place in a NMR tube, to that a solution of the Ru complex **G2** or **6** (1 mol%) in d*8*-THF (0.25 mL) was added and sealed. Conversion rates were measured by ^{1}H NMR at 25.0 °C (prethermostated probe) and spin rates of 20 Hz. The first spectrum was recorded after 6 min, and further spectra were recorded at 2 min intervals. Conversions were calculated from the integrals of the methylene hydrogen atoms of the polymers relative to those of the monomers (no other species were detected).

ICP-MS Digestion Procedure

The appropriate polymer and 4 mL of concentrated nitric acid was added to a glass vial. The mixture was heated to 110 °C until the entire sample was dissolved. The solution was then allowed to stand at room temperature. At this point, the concentrated acidic aqueous solution was diluted with distilled water, and the diluted sample solution was analyzed by ICP-MS.

General procedure for the ring-opening metathesis polymerization

Preparation of Polymer **P14**. In a glove box, the appropriate monomer 12 (50 mg, 0.226 mmol) and the PIB-supported complex **6** (1 mol%, 2.26 x 10^{-3} mmol) were weighed into a Schlenk flask and dissolved in anhydrous THF (2 mL) and the reaction was stirred for 1 h at room temperature. The polymerization was terminated by injecting 0.1 mL of ethyl vinyl ether and the solution was evaporated to dryness. The crude polymer was dissolved in 1 mL of CH_2Cl_2 and precipitated into hexane, collected, and then dried under vacuum to afford the polymer as a white solid. ^{1}H and ^{13}C NMR data was in agreement with previously reported work.

Polymer (P8)

^{1}H NMR (400 MHz, THF-d_8) δ: 5.26 (1H, br, *trans*), 5.09 (1H, br, *cis*), 3.48 (1H, br, *cis*), 2.35 (1H, br, *trans*), 1.70 (4H, br), 1.63 (1H, br), 0.91 (1H, br); ^{13}C NMR (100 MHz, THF-d_8) δ: 134.8, 134.1, 103, 44.7, 44.4, 43.2, 39.8, 39.6, 34.0, 33.9, 33.3, 33.2. Spectroscopic data matched previously reported data.[3]

- *When using PIB-supported complex **6***;
  Yield: 17 mg, 80%; GPC: M_n = 488,900 g/mol, M_w = 1.4 x 10^6 g/mol, PDI = 2.79; ICP: 3.45% Ru leaching. *cis:trans* ratio: 49:51

- *When using second-generation Grubbs catalyst **G2***;
  Yield: 41 mg, 81%; GPC: M_n = 456,400 g/mol, M_w = 1.3 x 10^6 g/mol, PDI = 2.85; ICP: 46.4% Ru leaching. *cis:trans ratio: 41:59*.

Polymer (P11)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.07 (1H, br, *trans*), 5.78 (1H, br, *cis*), 5.04 (1H, br, *cis*), 4.47 (1H, br, *trans*), 3.43 (2H, br), 3.32 (2H, br), 1.28 (2H, br), 0.90 (3H, br); *trans:cis* ratio:44:56; ^{13}C NMR (100 MHz, $CDCl_3$) δ:175.9, 131.3, 81.1, 50.5, 50.0, 41.1, 21.0, 11.3; Yield: 39.2 mg, 78%; GPC: M_n = 345,900 g/mol, M_w = 590,900 g/mol, PDI = 1.71; ICP: 2.09% Ru leaching.

Polymer (P12)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.07 (1H, br, *trans*), 5.78 (1H, br, *cis*), 5.02 (1H, br, *cis*), 4.46 (1H, br, *trans*), 4.04 (1H, br), 3.25 (2H, br), 1.92 (1H, br), 1.70 (1H, br), 1.34 (3H, br), 0.83 (3H, br); *trans:cis* ratio: 46:54; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176, 130.7, 81.3, 53.1, 52.0, 49.9, 25.8, 17.5, 11.2; Yield: 31.6 mg, 63%; GPC: M_n = 821,600 g/mol, M_w = 1.5 x 10^6 g/mol, PDI =1.83; ICP: 0.98% Ru leaching.

Polymer (P13)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.08 (1H, br, *trans*), 5.78 (1H, br, *cis*), 5.02 (1H, br, *cis*), 4.47 (1H, br, *trans*), 3.47 (2H, br), 3.30 (2H, br), 1.56 (2H, br), 1.31 (2H, br), 0.94 (3H, br), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.7, 131.0, 81.1, 53.3, 52.2, 38.8, 29.7, 20.0, 13.6.

- *When using PIB-supported complex **6***;
  Yield: 30 mg, 60%; GPC: M_n = 1.7 x 10^6 g/mol, M_w = 1.9 x 10^6 g/mol, PDI = 1.11; ICP: 1.82% Ru leaching. *trans:cis* ratio:44:54.

- *When using second-generation Grubbs catalyst **G2***;
  Yield: 35.4 mg, 71%; GPC: M_n = 125,500 g/mol, M_w = 294,300 g/mol, PDI = 2.34; ICP: 16.6% Ru leaching. *trans:cis* ratio:46:54.

Polymer (P14)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.08 (1H, br, *trans*), 5.79 (1H, br, *cis*), 5.03 (1H, br, *cis*), 4.46 (1H, br, *trans*), 3.45 (2H, br), 3.30 (2H, br), 1.63 (2H, br), 1.25 (10H, br), 0.87 (3H, br); *trans:cis* ratio:43:57; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.7, 131.2, 81.2, 53.4, 52.5, 39.2, 32.0, 29.7, 29.5, 27.9, 27.0, 22.8, 14.3; Yield: 40 mg, 80%; GPC: M_n = 737,600 g/mol, M_w = 1.48 x 10^6 g/mol, PDI = 2.0; ICP: 3.41% Ru leaching..

Polymer (P15)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.10 (1H, br, *trans*), 5.81(1H, br, *cis*), 5.05 (1H, br, *cis*), 4.48 (1H, br, *trans*), 3.49 (4H, br), 3.34 (2H, br), 1.87 (2H, br), 1.60 (2H, br), 1.49 (2H, br), 1.33 (2H, br); *trans:cis* ratio:44:56; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.0, 131.4, 81.2, 53.4, 52.3, 39.0, 33.9, 32.7, 27.8, 27.6, 26.1; Yield: 37 mg, 74%; GPC: M_n = 163,800 g/mol, M_w = 354,000 g/mol, PDI = 2.16; ICP: 6.1% Ru leaching.

References

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