

Supporting Information

High-Temperature Living Copolymerization of Ethylene with Norbornene by Titanium Complexes Bearing Bidentate [O, P] Ligands

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Detailed Experimental procedures

General Procedures and Materials.

All manipulation of air- and/or moisture-sensitive compounds were carried out under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from MBraun solvent purification system (SPS). NMR data of the ligands were obtained on a Bruker 300 MHz spectrometer at ambient temperature with CDCl_3 as a solvent (dried by MS 4\AA). The ^{13}C NMR data of the copolymers were obtained on a Varian Unity-400 MHz spectrometer at 135 °C, with $o\text{-C}_6\text{D}_4\text{Cl}_2$ as a solvent. Elemental analyses were recorded on an elemental Vario EL spectrometer. The molecular weights and the polydispersity indexes of polymer samples were determined at 135 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three Plgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). The viscoelasticity test was performed on a Metravig Mak-04 Viscoanalyser at a rate of 3 °C/min.

The 2.5 M *n*-BuLi solution in hexane was purchased from Acros. Commercial titanium tetrachloride (TiCl_4) was distilled prior to use. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. Compounds **1a-c** were prepared according to former reported method.¹ The other reagents and solvents were commercially available.

Ligand and Complex Synthesis.

2-*tert*-butyl-6-diphenylphosphanyl-phenol (3a). To a solution of THP ether **1a** (11.7 g, 50 mmol) in hexane (60 mL) was added TMEDA (6.4 g, 55 mmol), *n*-BuLi (2.5 M in hexane) (22 mL, 55 mmol) at -10°C. The mixture was allowed to warm to room temperature and stirred for 12 h giving a yellow precipitate. The appropriate PPh₂Cl (12.1 g, 55 mmol) was added to the suspension dropwise at -10°C. The mixture was stirred at room temperature for additional 12 h. To the mixture was added water, and extracted with ether. The extract was evaporated under reduced pressure to give the crude product **2a**. Compound **2a** was then successively dissolved in THF (40 mL) and 5 M HCl added. The mixture was stirred at room temperature for 1 h. The product was neutralized with NaHCO₃ to pH = 7, and then extracted with ether. The organic phase was washed with water (2 × 50 ml), dried with Na₂SO₄, and concentrated to give the crude product. The crude product was chromatographed in a silica gel column to give compound **3a** as a white solid (9.8 g, 59% yield). ¹H NMR (CDCl₃): δ 1.41 (s, 9H, *t*-Bu), 6.82-6.86 (m, 2H, Ar-H), 7.25-7.26 (m, 1H, Ar-H), 7.34-7.38 (m, 10H, Ar-H). ¹³C NMR (CDCl₃): δ 30.1, 35.4, 120.9, 121.5, 129.0, 129.3, 129.5, 132.5, 133.7, 135.0, 136.5, 158.6 (d, J = 20.3 Hz). Anal. Calc. for C₂₂H₂₃OP: C, 79.02; H, 6.93. Found: C, 78.86; H, 6.87.

2,4-di-*tert*-butyl-6-diphenylphosphanyl-phenol (3b). Compound **3b** was prepared via the same procedure in 63% yield. ¹H NMR (CDCl₃): δ 1.15 (s, 9H, *t*-Bu), 1.41 (s, 9H, *t*-Bu), 6.78-6.81 (m, 1H, Ar-H), 6.86-6.88 (m, 1H, Ar-H), 7.32-7.36 (m, 10H, Ar-H). ¹³C NMR (CDCl₃): δ 30.1, 31.9, 34.8, 35.6, 120.4, 126.7, 129.0, 129.3, 129.5, 129.7, 133.9, 135.8, 142.7, 156.6 (d, J = 19.5 Hz). Anal. Calc. for C₂₆H₃₁OP: C, 79.97; H, 8.00. Found: C, 79.87; H, 8.05.

2-trimethylsilyl-6-diphenylphosphanyl-phenol (3c). Compound **3c** was prepared via the similar procedure in total yield 39%. ¹H NMR (CDCl₃): δ 0.31 (s, 9H, SiMe₃-H), 6.83-6.86 (m, 1H, Ar-H), 7.01-7.06 (m, 1H, Ar-H), 7.24-7.33 (m, 10H, Ar-H), 7.41-7.45 (m, 1H, Ar-H). ¹³C NMR (CDCl₃): δ 0.01, 120.2, 121.7, 126.6, 129.5, 129.8, 134.4, 136.0, 137.0, 138.3, 165.3 (d, J = 20.3 Hz). Anal. Calc. for C₂₁H₂₃OPSi: C, 71.97; H, 6.61. Found: C, 72.08; H, 6.57.

Bis(2-*tert*-butyl-6-diphenylphosphanyl-phenoxy)titanium dichloride (4a). To a stirred solution of compound **3a** (0.8 g, 2.4 mmol) in dried THF (30 mL) at -78 °C, a 2.5 M *n*-BuLi hexane solution (1 mL, 2.5 mmol) was added dropwise over 5 min. The mixture was allowed to warm to room temperature and stirred for 2.5 h. Then, the mixture was added dropwise to TiCl₄ (0.22g, 1.2

mmol) in dried THF (30 mL) at -78 °C with stirring over 30 min. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was then placed in a rotary evaporator to concentrate the reaction mixture under reduced pressure. The chilled solution placed in the freezer (-20 °C) and afforded complex **4a** (0.64 g) in 68% yield. ¹H NMR (CDCl₃): δ 1.07 (s, 9H, *t*-Bu), 1.54 (s, 9H, *t*-Bu), 6.51-6.60 (m, 1H, Ar-H), 6.65-7.78 (m, 2H, Ar-H), 6.81-7.03 (m, 7H, Ar-H), 7.08-7.21 (m, 3H, Ar-H), 7.30-7.53 (m, 11H, Ar-H), 7.71-7.83 (m, 2H, Ar-H). ¹³C NMR (CDCl₃): δ selected: 29.7, 30.0, 35.5. Anal. Calc. for C₄₄H₄₄Cl₂O₂P₂Ti: C, 67.27; H, 5.65. Found: C, 67.13; H, 5.59.

Bis(2,4-di-*tert*-butyl-6-diphenylphosphanyl-phenoxy)titanium dichloride (4b). Complex **4b** was prepared by the same procedure in 73% yield. ¹H NMR (CDCl₃): δ 1.07 (s, 9H, *t*-Bu), 1.13 (s, 9H, *t*-Bu), 1.31 (s, 9H, *t*-Bu), 1.53 (s, 9H, *t*-Bu), 6.49-6.53 (m, 1H, Ar-H), 6.65-6.82 (m, 4H, Ar-H), 6.85-7.96 (m, 4H, Ar-H), 7.02-7.33 (m, 9H, Ar-H), 7.35-7.46 (m, 4H, Ar-H), 7.74-7.87 (m, 2H, Ar-H). ¹³C NMR (CDCl₃): δ selected: 29.8, 30.1, 31.8, 32.0, 35.2, 35.6. Anal. Calc. for C₅₂H₆₀Cl₂O₂P₂Ti: C, 69.57; H, 6.74. Found: C, 69.70; H, 6.70.

Bis(2-trimethylsilyl-6-diphenylphosphanyl-phenoxy)titanium dichloride (4c). Complex **4c** was prepared by the same procedure in 75% yield. ¹H NMR (CDCl₃): δ 0.01 (s, 9H, SiMe₃-H), 0.45 (s, 9H, SiMe₃-H), 6.73-6.91 (m, 6H, Ar-H), 6.95-7.14 (m, 7H, Ar-H), 7.20-7.36 (m, 6H, Ar-H), 7.41-7.57 (m, 5H, Ar-H), 7.72-7.88 (m, 2H, Ar-H). ¹³C NMR (CDCl₃): δ selected: -0.16, 15.3, 23.8, 32.8. Anal. Calc. for C₄₂H₄₄Cl₂O₂P₂Si₂Ti: C, 61.69; H, 5.42. Found: C, 61.54; H, 5.38.

Procedure for Ethylene Polymerization.

The polymerization was carried out in a 150 mL Schlenk flask equipped with a mechanical stirrer. The flask was repeatedly evacuated and refilled with nitrogen, and finally filled with ethylene gas (atmospheric pressure) from a Schlenk line. Prescribed amount of toluene were added via a gastight syringe and the mixture was kept at a prescribed polymerization temperature. The polymerization was initiated by the addition of a heptane solution of MMAO and a toluene solution of the titanium complex into the reactor with vigorous stirring. Ethylene consumption was noted as a function of time from the gas burette. After prescribed time, ethanol containing 10% (v/v) hydrochloric acid was added to terminate the polymerization. The resulted polyethylenes were recovered by filtration, washed with ethanol, and dried in a vacuum oven at 60 °C.

Procedure for Copolymerization of Ethylene with Norbornene.

Copolymerization was carried out under atmospheric pressure using the same type equipment. The reactor was charged with the prescribed amount of toluene and norbornene, the ethylene gas feed was started followed by equilibration at prescribed polymerization temperature. The polymerization was initiated by the addition of a heptane solution of MMAO and a toluene solution of the titanium complex into the reactor with vigorous stirring. After prescribed time, ethanol containing 10% (v/v) hydrochloric acid was added to terminate the polymerization. Polymer purification and isolation was performed using the same method as the general procedure.

Procedure for Synthesis of Block Copolymer Poly(E-*co*-NB)₁-*b*-poly(E-*co*-NB)₂.

Copolymerization was carried out under atmospheric pressure using the same type equipment. The reactor was charged with the prescribed amount of toluene and norbornene (0.5 g), the ethylene gas feed was started followed by equilibration at 75 °C. The polymerization was initiated by the addition of a heptane solution of MMAO and a toluene solution of the titanium complex into the reactor with vigorous stirring. After 3 min, norbornene (5 g) was added to the mixture for another 3 min. The resulted mixture was then quenched with ethanol containing 10% (v/v) hydrochloric acid and the polymer was purified and isolated using the same method as the general procedure.

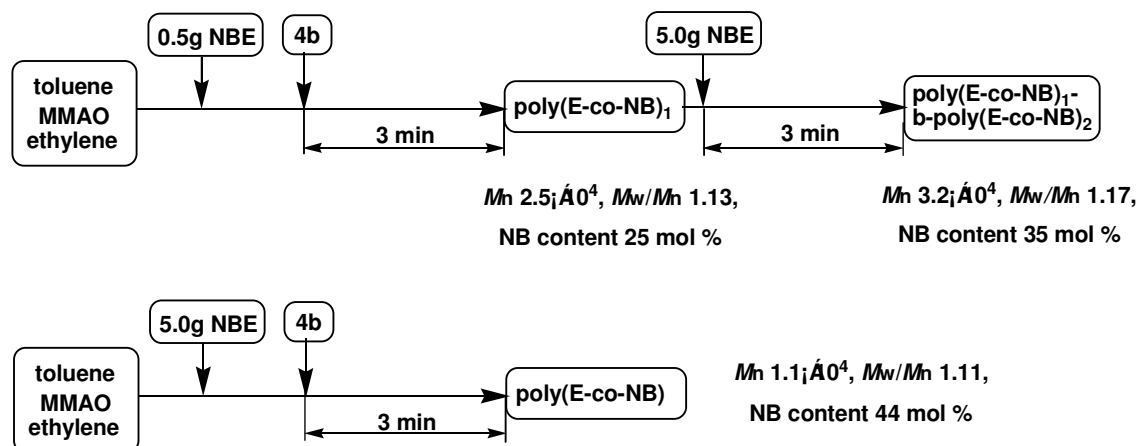


Figure 1. Procedure for poly(E-co-NB)₁-b-poly(E-co-NB)₂ synthesis.

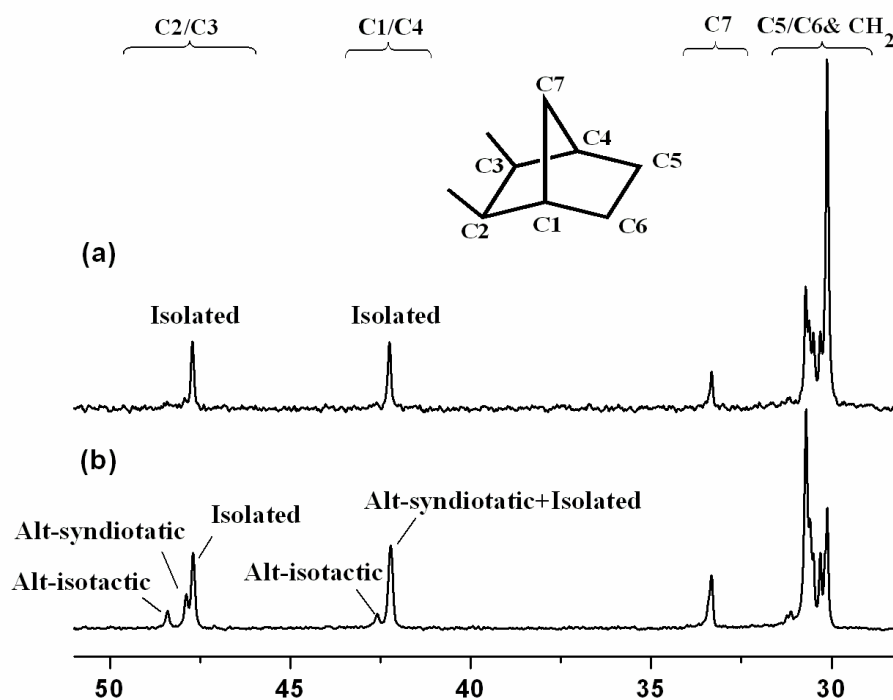


Figure 2. ¹³C NMR spectra (100 MHz, *o*-C₆D₄Cl₂, 135°C) of the typical E/NB copolymer samples obtained by catalyst **4b**: (a) NB content 10 mol %; (b) NB content 26 mol %.

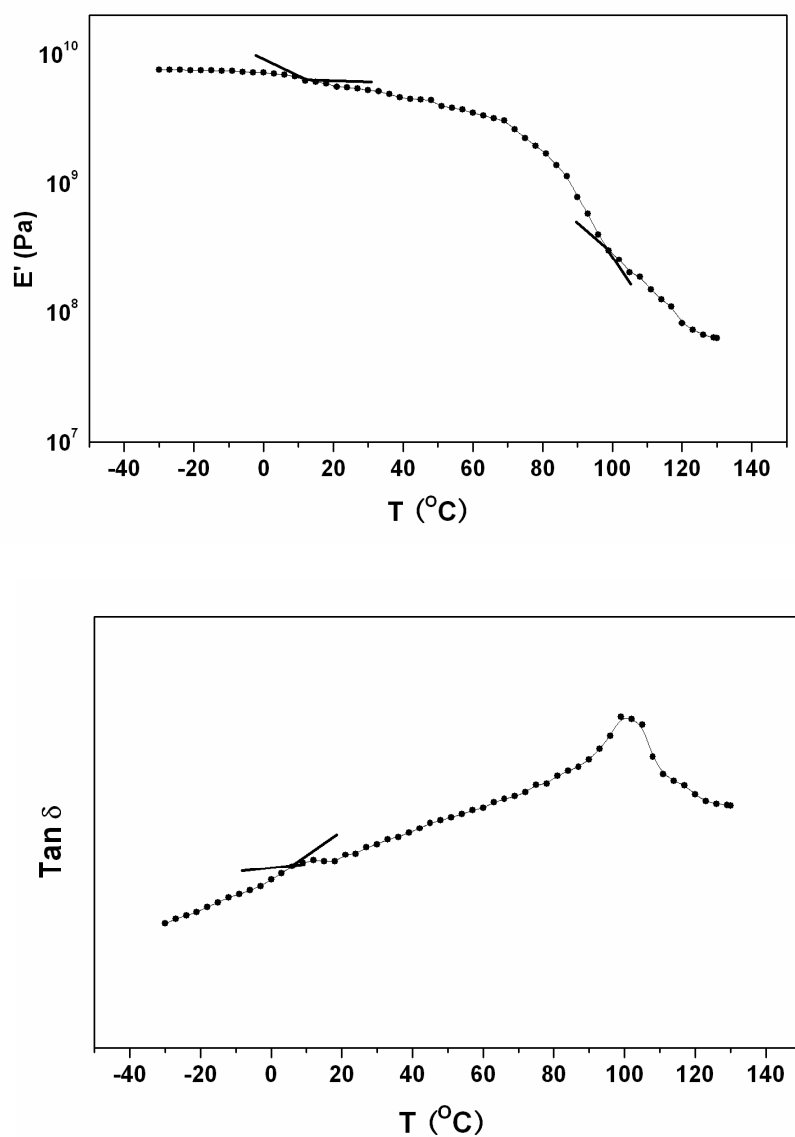


Figure 3. The charts for the viscoelasticity test of poly(E-co-NB)₁-b-poly(E-co-NB)₂.

Reference

- (1) He, L. P.; Liu, J. Y.; Pan, L.; Li, Y. S. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 7062-7073.