The Novel Coupling of Two Mechanistically Distinct Polymerizations on a Single Metal Center: The Palladium Mediated Synthesis of Poly(Norbornene) - Poly(THF) Block Co-Polymers

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SUPPORTING INFORMATION

GENERAL PROCEDURES

^{1}H and ^{13}C-NMR were recorded on JEOL-270 or Varian Unity-500 spectrometers, while COSY and ^{13}C-decoupled ^{1}H-NMR spectra were obtained on the Varian Unity-500 spectrometer. MS was performed on a KRATOS MS 25RFA Mass Spectrometer in the direct inlet mode. Gel permeation chromatography was carried out using Waters 600E chromatograph equipped with Styragel HR 0.5, HR 2 and HR 4 columns in THF vs. polystyrene standards, and Waters 410 Differential Refractometer as detector.

Unless otherwise noted, all manipulations were carried out under an inert atmosphere in a Vacuum Atmosphere 553-2 drybox or by using standard Schlenk or vacuum line techniques. Diethyl ether and THF were distilled from sodium benzophenone under nitrogen. Pentane,

acetonitrile, methylene chloride and chloroform were distilled from CaH_2. Deuterated solvents were dried as their protonated analogues, but were vacuum-transferred from the drying agent and stored under nitrogen over 3_ molecular sieves.

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Liquids were freeze-pump-thawed three times to degas before use. 99% ^{13}CO was obtained from Cambridge Isotope Laboratories. (Bipy)Pd(CH_3)($NCCH_3$)$^+$ OTf$^-$ (**1**) was prepared by literature method.

SYNTHESIS AND SPECTROSCOPIC DATA ON 4 AND 6.

Synthesis of (bipy)Pd((C_7H_{10})CH_3)($NCCH_3$)$^+$ OTf$^-$ (4)

Norbornene (30 mg, 0.3 mmole) was added to a slurry of (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ (150 mg, 0.32 mmole) in a THF (15 mL) / acetonitrile (2 mL) mixture. After stirring for 45 minutes, the clear yellow solution was filtered through celite and concentrated to 3 mL under vacuum. Diethyl ether (8mL) was added. After decanting the solvents, a solid yellow product was collected and dried under vacuum (170 mg, 94% yield).

^{1}H-NMR (CD_2Cl_2): δ 8.63 (d, 2H), δ 8.22 (m, 4H), δ 7.73 (m, 2H), δ 2.63 (d, 1H), δ 2.56 (s, 3H), δ 2.24 (d, 1H), δ 1.93 (d, 1H), δ 1.74 (m, 2H), δ 1.60 (m, 1H), δ 1.21 (d, 3H), δ 1.20 (m, 4H). ^{13}C-NMR (CD_2Cl_2): δ 156.85, δ 152.11, δ 149.01, δ 148.93, δ 140.52, δ 140.01, δ 127.81, δ 127.11, δ 123.58, δ 122.61, δ 57.63, δ 45.96, δ 45.58, δ 45.23, δ 34.87, δ 30.21, δ 29.24, δ 21.87, δ 3.80. LR-MS (FAB-NBA) m/e: 371. Analysis calculated for $C_{21}H_{24}F_3N_3O_3PdS$: C, 44.89; H, 4.31; N, 7.48; found: C, 44.79; H, 4.08; N, 7.36.

Synthesis of (bipy)Pd((C_7H_{10})$_n$$CH_3$)($NCCH_3$)$^+$ OTf$^-$ (6)

Norbornene (376 mg, 4.0 mmole) was added to a slurry of (bipy)Pd(Me)(NCMe)$^+$ OTf$^-$ (45 mg, 0.1 mmole) in THF (5 mL). The resulting pale yellow solution was stirred for one and the

half hour at room temperature, forming a cloudy yellow solution. Acetonitrile (2mL) was added, and the solution further stirred for 2 hours. A clear yellow solution was obtained, and subsequently concentrated to 1 mL under vacuum. Pentane (3 mL) and diethyl ether (3 mL) were added to precipitate the product. After decanting the layer of solvents, the yellow solid was dried under vacuum (120 mg). Spectroscopic data showed a mixture of (bipy)Pd((C_7H_{10})$_n$$CH_3$)($NCCH_3$)$^+$ OTf^- (n = 7 to 12).

^{1}H-NMR (CD_2Cl_2): δ 8.58 (d, 2H), δ 8.22 (m, 4H), δ 7.67 (m, 2H), δ 3.22 (d, 1H), δ 2.82 (d, 1H), δ 0.60 - 2.40 (m, broad, 83H), δ 0.34 (t, 1H). ^{13}C-NMR (CD_2Cl_2): δ 156.9, δ 152.1, δ 148.7, δ 148.6, δ 140.5, δ 140.2, δ 135.2, δ 127.7, δ 126.6, δ 124.0, δ 122.9, δ 58.9, δ 50.0, δ 49.5, δ 48.9, δ 48.2, δ 47.9, δ 47.8, δ 47.3, δ 46.8, δ 46.7, δ 46.0, δ 45.9, δ 44.7, δ 42.7, δ 41.8, δ 40.4, δ 39.3, δ 39.0, δ 38.7, δ 38.5, δ 38.2, δ 38.0, δ 37.9, δ 37.7, δ 37.6, δ 37.5, δ 37.1, δ 36.8, δ 36.6, δ 36.2, δ 35.6, δ 32.8, δ 32.5, δ 32.3, δ 31.9, δ 31.7, δ 31.6, δ 31.5, δ 31.0, δ 30.1, δ 29.8, δ 29.6, δ 29.3, δ 29.0, δ 28.2, δ 24.4, δ 19.7. LR-MS (FAB-NBA) m/e: 935 (42.7), 1029 (13.3), 1123 (36.7), 1218 (8.9), 1311 (9.3), 1405 (2.3).

POLYMERIZATION PROCEDURES WITH 4 AND 6

Polymerization of THF with (bipy)Pd((C_7H_{10})Me)(NCMe)$^+$ OTf^- (4) in ^{13}CO

A slurry of (bipy)Pd((C_7H_{10})Me)(NCMe)$^+$ OTf^- (28 mg, 0.05 mmole) in THF (10.0 g) in a 25 ml reaction bomb was prepared in the box. The resulting cloudy yellow solution was then placed under 1 atm of ^{13}CO(g), followed by stirring at room temperature for 1 hour. The dark grey mixture was subsequently placed in heat bath (70°C) for twenty four hours. After cooling, the reaction solution was diluted with CH_2Cl_2, filtered through celite and solvent removed in vacuo. The polymer was re-dissolved in minimum amount of CH_2Cl_2, and precipitated by adding CH_3CN. The resulting white solid was dried under vacuum overnight (yield = 0.81 g).

^{1}H-NMR (270 MHz, $CDCl_3$): δ 3.96 (m, $CH_2O^{13}COC_7H_{10}CH_3$), δ 3.33 (s, OCH_2), δ 1.53 (s, OCH_2CH_2), δ 0.75 - 2.33 (m, $O^{13}COC_7H_{10}CH_3$); ^{13}C-NMR ($CDCl_3$): δ 174.1 ($CH_2O^{13}COC_7H_{10}$), δ 70.4 (OCH_2), δ 26.3 (OCH_2CH_2). GPC analysis: M_n = 27,200, M_w = 55,600.

Polymerization of THF with (bipy)Pd($(C_7H_{10})_nMe$)(NCMe)$^+$ OTf$^-$ (6) in ^{13}CO.

A slurry of (bipy)Pd($(C_7H_{10})_nMe$)(NCMe)$^+$ OTf$^-$ (n ~ 8) (60 mg, 0.05 mmole) in THF (10.0 g) was in a 25 ml reaction bomb was prepared in the box. The cloudy yellow solution was then placed under 1 atm of ^{13}CO(g), followed by stirring at room temperature for 1 hour. The mixture was subsequently placed in heat bath (70°C) for twenty four hours. After cooling, the reaction solution was diluted with CH_2Cl_2, filtered through celite and solvent removed in vacuo. The polymer product was re-dissolved in minimum amount of CH_2Cl_2, and precipitated by adding CH_3CN. The resulting white solid was dried under vacuum overnight (yield = 0.72 g).

^{1}H-NMR (270 MHz, $CDCl_3$): δ 4.02, δ 3.96 (m, $CH_2O^{13}CO(C_7H_{10})_nCH_3$), δ 3.38 (s, OCH_2), δ 1.58 (s, OCH_2CH_2), δ 0.78 - 2.50 (m, $O^{13}CO(C_7H_{10})_nCH_3$); ^{13}C-NMR ($CDCl_3$): δ 175.6, δ 175.4, δ 174.8, δ 174.5 (4 isomers, $CH_2O^{13}CO(C_7H_{10})_n$), δ 70.7 ($OCH_2$), δ 26.6 ($OCH_2CH_2$). GPC analysis: M_n = 41,000, M_w = 146,300.