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**Supplementary Material for:**

**Polymers with Linked Macrocyclic Rings in the Main Chain. Zirconocene  
Coupling of 1,8-Cyclotetradecadiyne.**

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Air sensitive compounds were manipulated under an inert atmosphere of nitrogen using standard Schlenk techniques. Dry, oxygen-free solvents were employed in the syntheses of **2**, **4** and **5**. NMR spectra were recorded on a Varian Bruker AMX (400 MHz) spectrometer. Molecular weights were determined by gel permeation chromatography (gpc; Waters Company; Detector: Differential Refractometer R401; Waters 501 HPLC Pump; Waters 745 Data Module) with THF as the eluting solvent and polystyrene standards. Thermal analyses were performed on a DuPont 951 Thermogravimetric Analyzer attached to a 910 DSC cell base. Zirconocene dichloride was obtained from Strem Chemicals, Inc., and used as received. The *n*-butyllithium solution was obtained from Aldrich.

**Polymer 2:** A 100-mL round bottom flask was charged with  $\text{Cp}_2\text{ZrCl}_2$  (0.49 g, 1.7 mmol), 1,8-cyclotetradecadiyne (0.30 g, 1.6 mmol), and 5.0 mL of THF. The flask was cooled to  $-78\text{ }^\circ\text{C}$  and then 1.6 M *n*-butyllithium (2.1 mL, 3.4 mmol) was added dropwise. The flask was allowed to warm to room temperature, and stirring was continued for 48 h. An orange gel formed, which was only slightly soluble in THF. All the volatile materials were removed in vacuo to give 0.79 g of orange powder as the crude product. It contains **2** and ca. 2 equiv of LiCl.  $^1\text{H}$  NMR (benzene- $d_6$ , 400 MHz):  $\delta$  6.05 (s, 10 H,  $\text{C}_5\text{H}_5$ ), 2.35 (b, 4 H), 1.75 (b, 16 H).  $M_n = 2000$ ,  $M_w = 4000$  (for soluble portion). Anal. Calcd for  $\text{C}_{24}\text{H}_{30}\text{Cl}_2\text{Li}_2\text{Zr}$ : C, 58.29; H, 6.11. Found: C, 56.52; H, 6.25.

**Polymer 3:** A 100-mL round bottom flask was charged with **2**·2LiCl (0.30 g, 0.61 mmol) and 10 mL of THF. Then, 6.0 M of aqueous HCl solution (5.0 mL) was added to the flask and the resulting mixture was stirred for 2 h at room temperature. The reaction mixture was added dropwise to a vigorously stirred methanol solution (100 mL). The resulting white precipitate was collected to afford 0.10 g (86%) of **3**.  $^1\text{H}$  NMR (benzene- $d_6$ , 400 MHz):  $\delta$  5.60 (s, 1 H), 5.58 (s, 1 H), 2.29 (s, 4 H), 2.16 (s, 4 H), 1.44 (s, 12 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ , 100.6 MHz):  $\delta$  C=CH: 142.68, 142.34; C=CH: 127.18, 126.90; CH<sub>2</sub>: 29.08, 28.71, 28.30, 28.19, 27.98, 27.89, 27.79, 27.73, 27.57, 27.44, 27.21.  $M_n$  = 6500,  $M_w$  = 29,000. Anal. Calcd for C<sub>14</sub>H<sub>22</sub>: C, 88.35; H, 11.65. Found: C, 88.02; H, 11.99.

**Polymer 4:** A 100-mL round bottom flask was charged with **2**·2LiCl (0.30 g, 0.61 mmol) and 10 mL of THF. Then, 0.16 g (1.2 mmol) of S<sub>2</sub>Cl<sub>2</sub> was added dropwise to the flask, and the resulting mixture was stirred for 2 h at room temperature. This mixture was then added to a stirred quantity (100 mL) of methanol. The resulting white precipitate was collected, dissolved in THF, and reprecipitated with methanol to afford 0.070 g (52%) of **4**, along with a substantial amount of an insoluble polymer (ca.40 %).  $^1\text{H}$  NMR (benzene- $d_6$ , 400 MHz):  $\delta$  2.65 (s, 4 H), 2.50 (s, 4 H), 1.74 (s, 4 H), 1.57 (s, 4 H), 1.37 (s, 4 H).  $M_n$  = 4000,  $M_w$  = 9100. Anal. Calcd for C<sub>14</sub>H<sub>20</sub>S<sub>2</sub>: C, 70.18; H, 8.41; S, 21.41. Found: C, 69.78; H, 8.66; S, 22.15. Heating this sample to 210 °C under vacuum for 72 h removed the additional equiv of sulfur. Anal. Calcd for C<sub>14</sub>H<sub>20</sub>S: C, 76.35; H, 9.15. Found: C, 76.53; H, 8.34.

**Polymer 5:** A 100-mL thick-walled glass reactor was charged with **3** (0.080 g, 0.42 mmol), 5 mL of THF, and (Ph<sub>3</sub>P)<sub>3</sub>RhCl (0.005 g, 0.005 mmol). The flask was cooled with liquid nitrogen, and then charged with hydrogen (1 atm). The reaction mixture was warmed to ambient temperature, stirred for 48 h, and then added dropwise to a vigorously stirred methanol solution (100 mL). The resulting white precipitate was collected to give 0.070 g (87%) of **5**.  $^1\text{H}$  NMR (benzene- $d_6$ , 400 MHz):  $\delta$  2.19 (b, 6 H), 1.50 (b, 20 H).  $M_n$  = 7000,  $M_w$  = 56,000. Anal. Calcd for C<sub>14</sub>H<sub>26</sub>: C, 86.52; H, 13.48. Found: C, 86.50; H, 11.46.