Supporting Information

# Zirconocene-Catalyzed Stereoselective Cyclocopolymerization of 2-Methyl-1,5-Hexadiene with Propylene

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**Figure S1.** ^{1}H NMR spectrum of PP copolymers with model olefins 8-TMSO and 1,6-MOD.

**Figure S2.** ^{1}H NMR spectrum of a P(P-*co*-MHB) copolymer produced with constrained geometry catalyst **4**/MAO.

**Figure S3.** GPC trace of a P(P-*co*-MHB) copolymer produced with **1**/MAO.

**Figure S4.** GPC trace of a P(P-*co*-MHB) copolymer produced with **2**/MAO.

**Figure S5.** GPC trace of a P(P-*co*-MHB) copolymer produced with **3**/MAO.

**Figure S6.** DSC thermogram of a P(P-*co*-MHB) copolymer produced with **1**/MAO.

**Figure S7.** DSC thermogram of a P(P-*co*-MHB) copolymer produced with **2**/MAO.

**Figure S8.** DSC thermogram of a P(P-*co*-MHB) copolymer produced with **3**/MAO.

† Those two authors equally contributed to this work.

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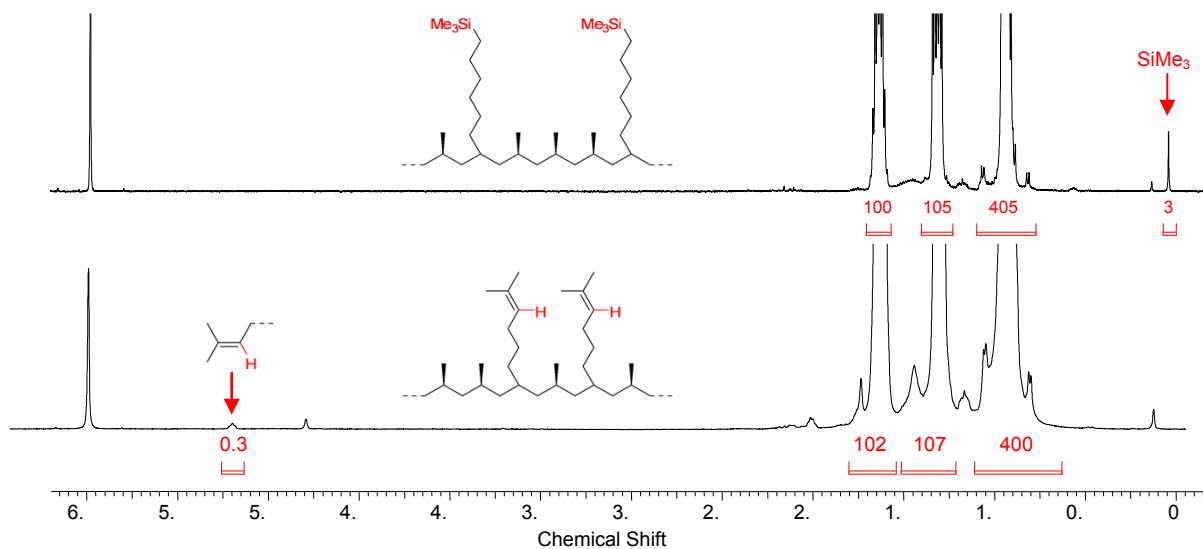
**Figure S1:** $^{1}$H NMR (398 K, C$_2$D$_2$Cl$_4$, 500 MHz) of PP copolymers with model olefins 8-TMSO (top spectrum) and 1,6-MOD (bottom spectrum) (Table 1, entries 15 and 16).



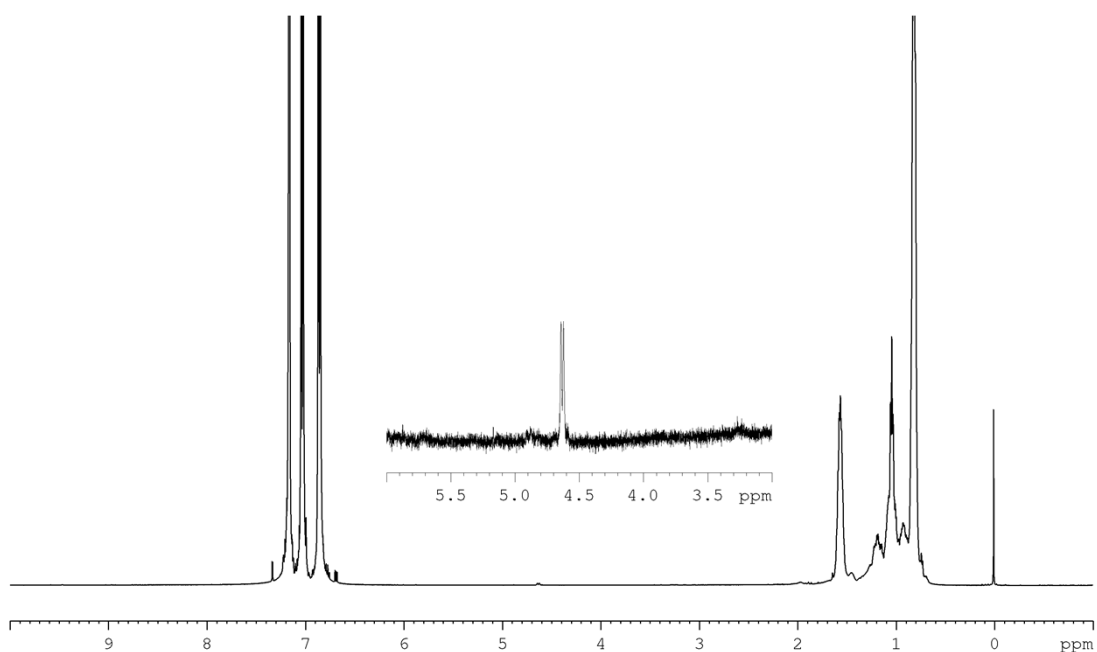**Figure S2:** $^{1}$H NMR (398 K, 1,2,4-trichlorobenzene/C$_6$D$_6$ (5:1), 500 MHz) of a P(P-*co*-MHB) copolymer produced with constrained geometry catalyst **4**/MAO (n$_{MHDi}$ = 12.0 mmol and [Ti] = 18.0 μmol.L$^{-1}$; Table 1, entry 13).

| Mn | 13278 |
|----|-------|
| Mw | 35402 |
| Mz | 72396 |
| D  | 2.7   |
| D' | 2     |

342039

**log M**

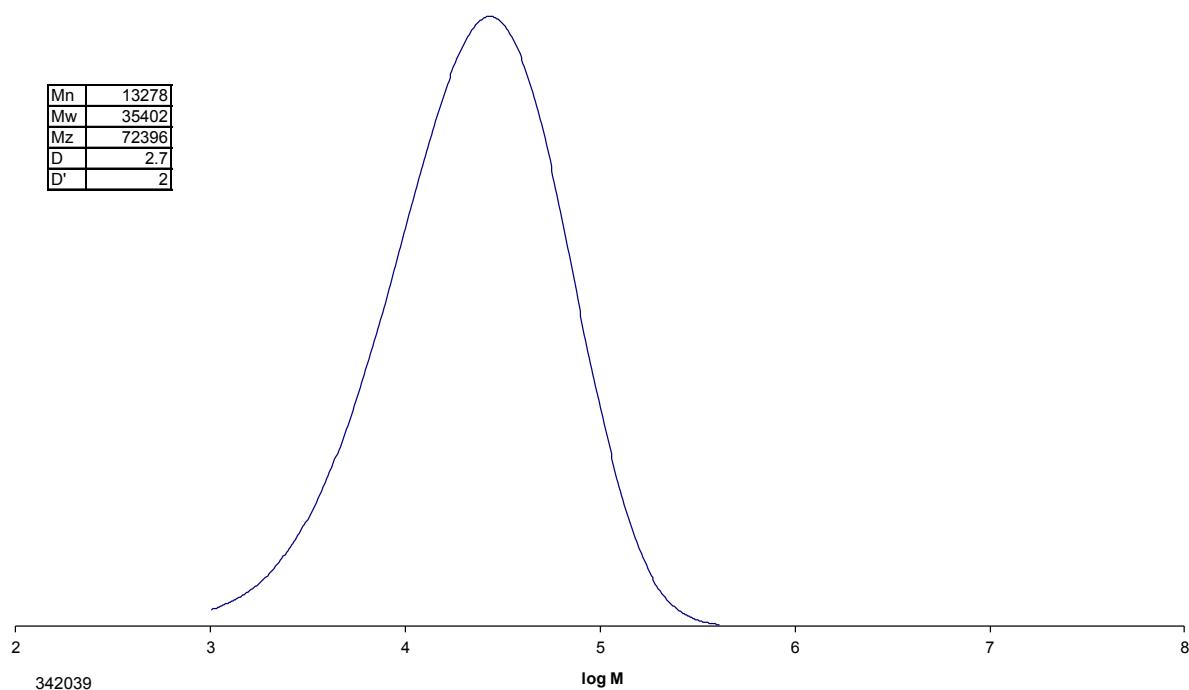**Figure S3:** GPC trace of a P(P-*co*-MHB) copolymer produced with **1**/MAO ($n_{MHDi}$ = 1.8 mmol and [Zr] = 3.8 µmol.L$^{-1}$; Table 1, entry 2).
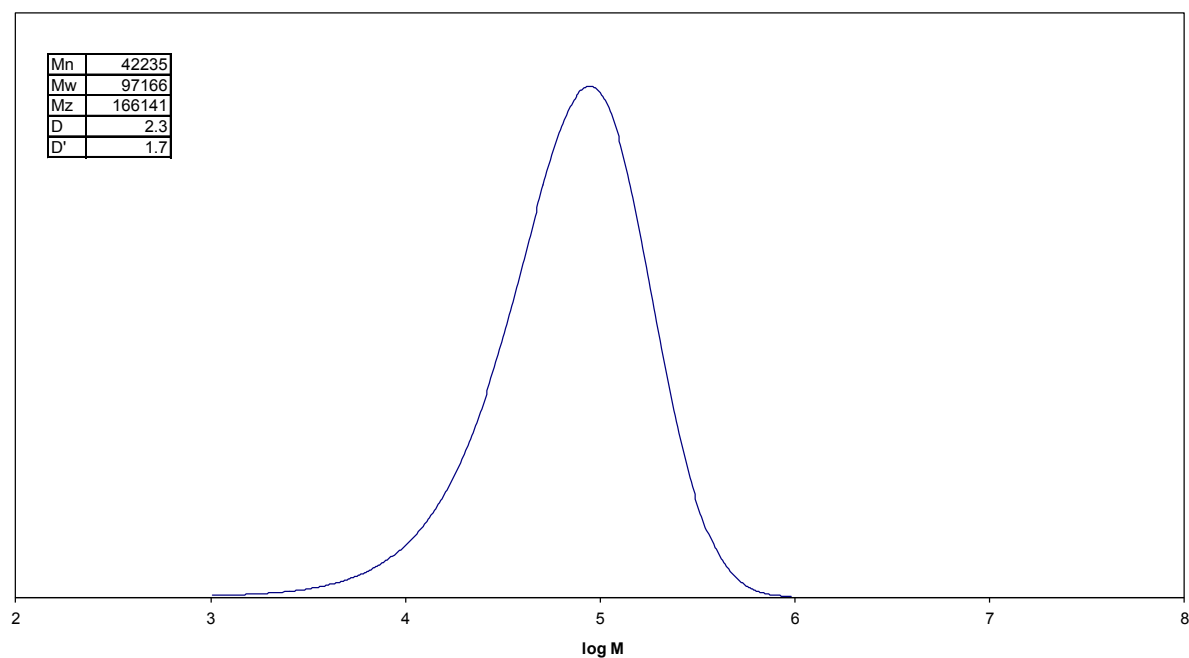


| Mn | 42235  |
|----|--------|
| Mw | 97166  |
| Mz | 166141 |
| D  | 2.3    |
| D' | 1.7    |

**log M**

**Figure S4:** GPC trace of a P(P-*co*-MHB) copolymer produced with **2**/MAO ($n_{MHDi}$ = 12.0 mmol and [Zr] = 11.0 µmol.L$^{-1}$; Table 1, entry 7).

| Mn | 54182 |
|----|-------|
| Mw | 117029 |
| Mz | 193548 |
| D  | 2.2 |
| D' | 1.7 |

609452

**log M**

**Figure S5**: GPC trace of a P(P-*co*-MHB) copolymer produced with **3**/MAO ($n_{MHDi}$ = 12.0 mmol and [Zr] = 9.3 µmol.L$^{-1}$; Table 1, entry 11).

Heat : -132.932 (J/g)
T : 121.45 and 93.22 (°C)
Peak Maximum : 112.731 (°C)

Heat : 112.781 (J/g)
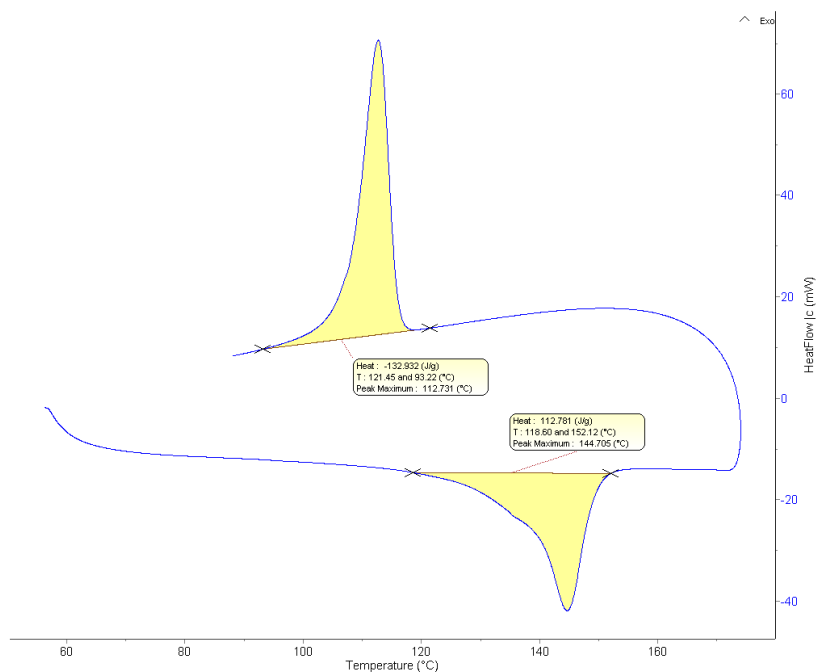T : 118.60 and 152.12 (°C)
Peak Maximum : 144.705 (°C)

HeatFlow Ic (mW)

Temperature (°C)

**Figure S6**: DSC thermogram of a P(P-*co*-MHB) copolymer produced by **1**/MAO ($n_{MHDi}$ = 1.8 mmol and [Zr] = 3.8 µmol.L$^{-1}$; Table 1, entry 3).
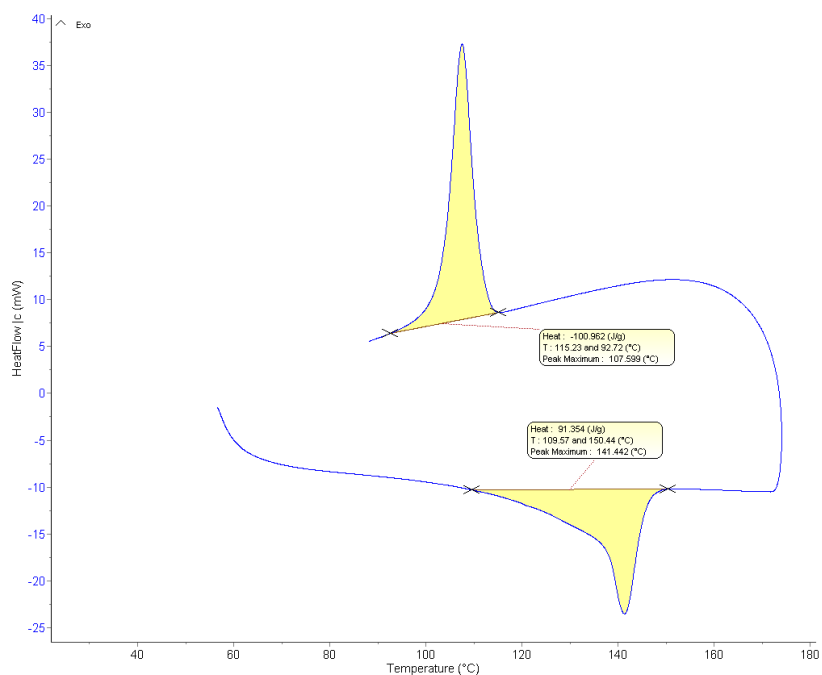
**Figure S7**: DSC thermogram of a P(P-*co*-MHB) copolymer produced by **2**/MAO ($n_{MHDi}$ = 12.0 mmol and [Zr] = 9.3 µmol.L$^{-1}$; Table 1, entry 8).



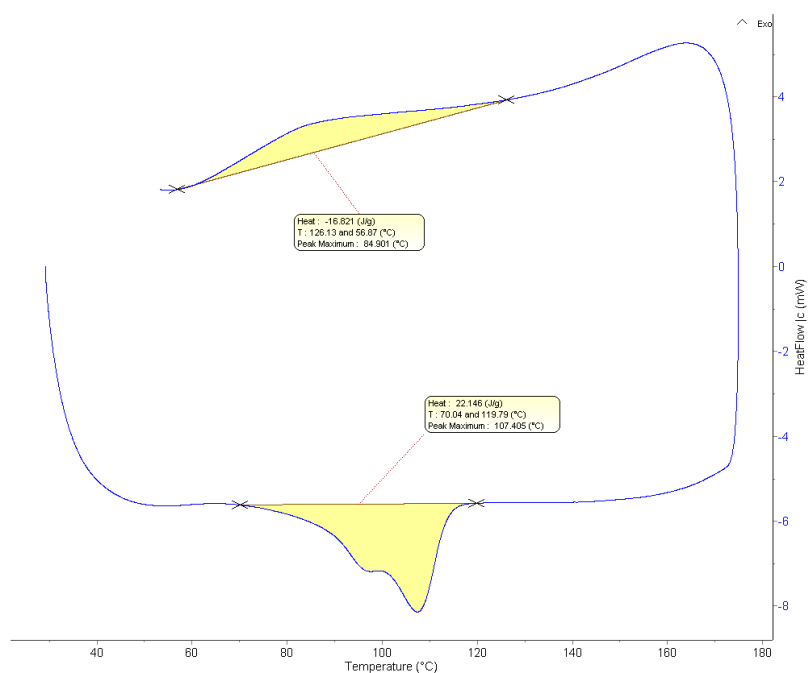**Figure S8**: DSC thermogram of a P(P-*co*-MHB) copolymer produced by **3**/MAO ($n_{MHDi}$ = 12.0 mmol and [Zr] = 9.3 µmol.L$^{-1}$; Table 1, entry 11).