**Supporting Information for:**

# Insertion/Isomerization Polymerization of 1,5-Hexadiene: Synthesis of Functional Propylene Copolymers and Block Copolymers

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## General Considerations

All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen using a Braun Labmaster drybox or standard Schlenk line techniques. Polymer $^{1}H$ spectra were recorded on a Varian Inova ($^{1}H$, 400 MHz) spectrometer and referenced versus residual non-deuterated solvent shifts. $^{13}C$ NMR spectra of the polymers were recorded on a Varian VXR-400 (100 MHz) spectrometer and referenced versus residual non-deuterated solvent shifts. The polymer samples were dissolved in $C_2D_2Cl_4$ in a 5 mm O.D. tube by heating to 120˚C in an oil bath.

Molecular weights ($M_n$ and $M_n$) and polydispersities ($M_w/M_n$) were determined by high temperature gel-permeation chromatography (GPC). All analyses were performed with a Waters Alliance 2000 liquid chromatograph equipped with a Waters DRI detector and a Jordi styrene-divinylbenzene linear mixed-bed column. The GPC columns were eluted with 1,2,4-trichlorobenzene (TCB) containing 0.1 wt % Irganox 1010 at 140°C at 1.0 mL/min and were calibrated using 23 monodisperse polystyrene standards. Polymer samples were typically placed in a 140˚C oven for 24 h to eliminate supermolecular aggregates prior to molecular weight measurements. DSC analyses were performed on a Seiko DSC 220C instrument using EXSTAR 6000 processing software. The measurements were made in crimped aluminum pans under nitrogen with a heating rate of 10 °C/min from -50 - 200 °C, and reported values originate from the second heating scan. The sample containing 96% propylene (Table 1, Entry 4) was annealed at 80°C for one hour to ensure sufficient time for crystallization.

**Materials**

Toluene was purified over columns of alumina and copper and degassed by freeze-pump-thaw cycles. Propylene (Matheson, polymer grade) was purified through a mixed bed column (R&D Separations, BOT-4). Methylaluminoxane (PMAO-IP, 12.9 *wt* % Al in toluene, Akzo Nobel) was concentrated in vacuo to dryness ($10^{-3}$ mm Hg) at 40˚C for 18 h to remove residual trimethylaluminum, providing a solid white powder. 1,5-Hexadiene was purchased from Aldrich, dried over activated 3Å molecular sieves, and distilled before use. **1** was synthesized according to a published procedure (Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134-5135). All other chemicals were commercial materials and were used as received.

**Polymer Synthesis**

**Polymerization of 1,5-Hexadiene using 1/MAO.** A Schlenk-type flask equipped with a magnetic stir bar was charged with a PMAO (0.29 g, 5.0 mmol), toluene (85 mL), and 1,5-hexadiene (11.0 g). The flask was equilibrated at 0 °C and **1** (0.018 g, 0.020 mmol, [Al]/[Ti] = 250) in toluene (4 mL) was added via gas-tite syringe. After 20 min, the reaction was carefully quenched with methanol/HCl and the polymer was precipitated in copious methanol/HCl, filtered, washed with methanol, and then dried *in vacuo* to constant weight (0.67 g, $M_n$ = 268,000, $M_w/M_n$ = 1.27).

**Hydrogentaion of Poly(1,5-Hexadiene).** For NMR studies, the unsaturated poly(1,5-hexadiene) was hydrogenated according to the procedure of Wu et al. (Wu, Z.; Benedicto, A. D.; Grubbs, R. H. *Macromolecules* **1993**, *26*, 4975-4977). In a slightly modified experiment, a toluene solution (10 mL) of the polymer (0.20 g, 0.90 mmol C=C) and *p*-toluenesulfonylhydrazide (*p*-$TsNHNH_2$) (1.36 g, 7.30 mmol) was heated at 80 °C. After 3 h, another 8 equiv. *p*-$TsNHNH_2$ (1.36 g, 7.30 mmol) was added and the slurry was stirred for 15 h. At this point, another 3 equiv. *p*-$TsNHNH_2$ (0.45 g, 2.4 mmol) was added and the mixture was again stirred at 80 °C for 10 h. The saturated polymer was then isolated by precipitation into copious methanol, filtered, and dried *in vacuo* to constant mass (0.18 g isolated yield).

**General Procedure for 1,5-Hexadiene/Propylene Copolymerization.** A 6 ounce Lab-Crest® pressure reaction vessel (Andrews Glass) equipped with a magnetic stir bar was first conditioned under dynamic vacuum and high temperature and then charged with PMAO (0.29 g,

5.0 mmol), toluene (85 mL), and 1,5-hexadiene (11.0 g). The reactor was the equilibrated at 0 °C, the atmosphere was exchanged with propylene three times, and the solution was saturated under propylene pressure. The catalyst **1** (0.018 g, 0.020 mmol, [Al]/[Ti] = 250) in toluene (4 mL) was then added via gas-tite syringe. After 4 h, the reactor was vented and the polymer was precipitated in methanol/HCl, filtered, washed with methanol, and then dried *in vacuo* to constant weight.

**Synthesis of Poly(propylene)-*block*-poly(propylene-*co*-1,5-Hexadiene).** A 6 ounce Lab-Crest® pressure reaction vessel (Andrews Glass) equipped with a magnetic stir bar was first conditioned under dynamic vacuum and high temperature and then charged with PMAO (0.29 g, 5.0 mmol), toluene (85 mL). The reactor was the equilibrated at 0 °C, the atmosphere was exchanged with propylene three times, and the solution was saturated under propylene pressure (10 psi). The catalyst **1** (0.018 g, 0.020 mmol, [Al]/[Ti] = 250) in toluene (4 mL) was then added via gas-tite syringe. After 4 h, a 5 mL sample of the polymerization medium was removed, quenched with methanol, and the polymer was filtered and dried *in vacuo* to constant weight ($M_n$ = 51,500, $M_w/M_n$ = 1.11). 1,5-Hexadiene (11.0 g) was then added to the reactor via gas-tite syringe. After another 2 h, the reactor was vented and the polymer was precipitated in methanol/HCl, filtered, washed with methanol, and then dried *in vacuo* to constant weight (0.98 g, $M_n$ = 93,300, $M_w/M_n$ = 1.11).

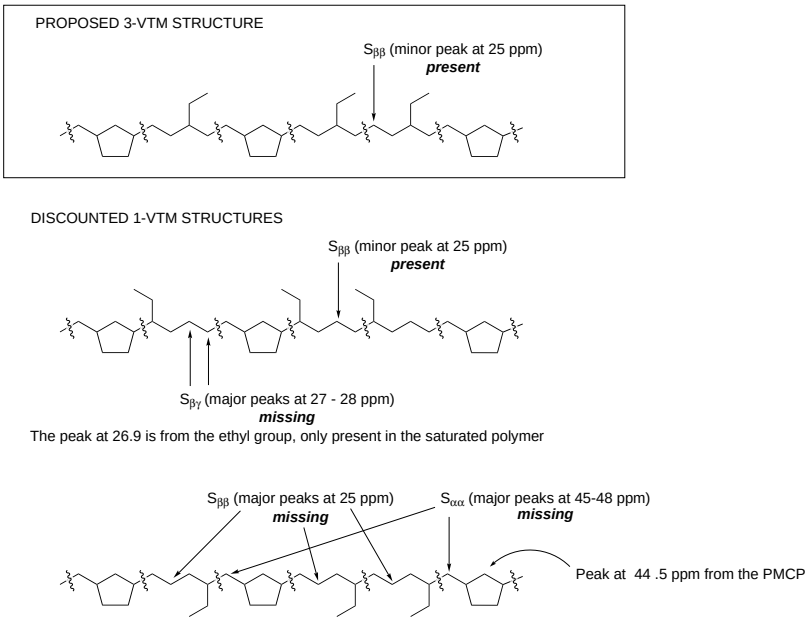


**Figure S1.** $^{1}H$ NMR spectrum (400 MHz, $C_2D_2Cl_4$, 80°C) of the 1,5-hexadiene polymer from **1**/MAO (Table 1, Entry 1).

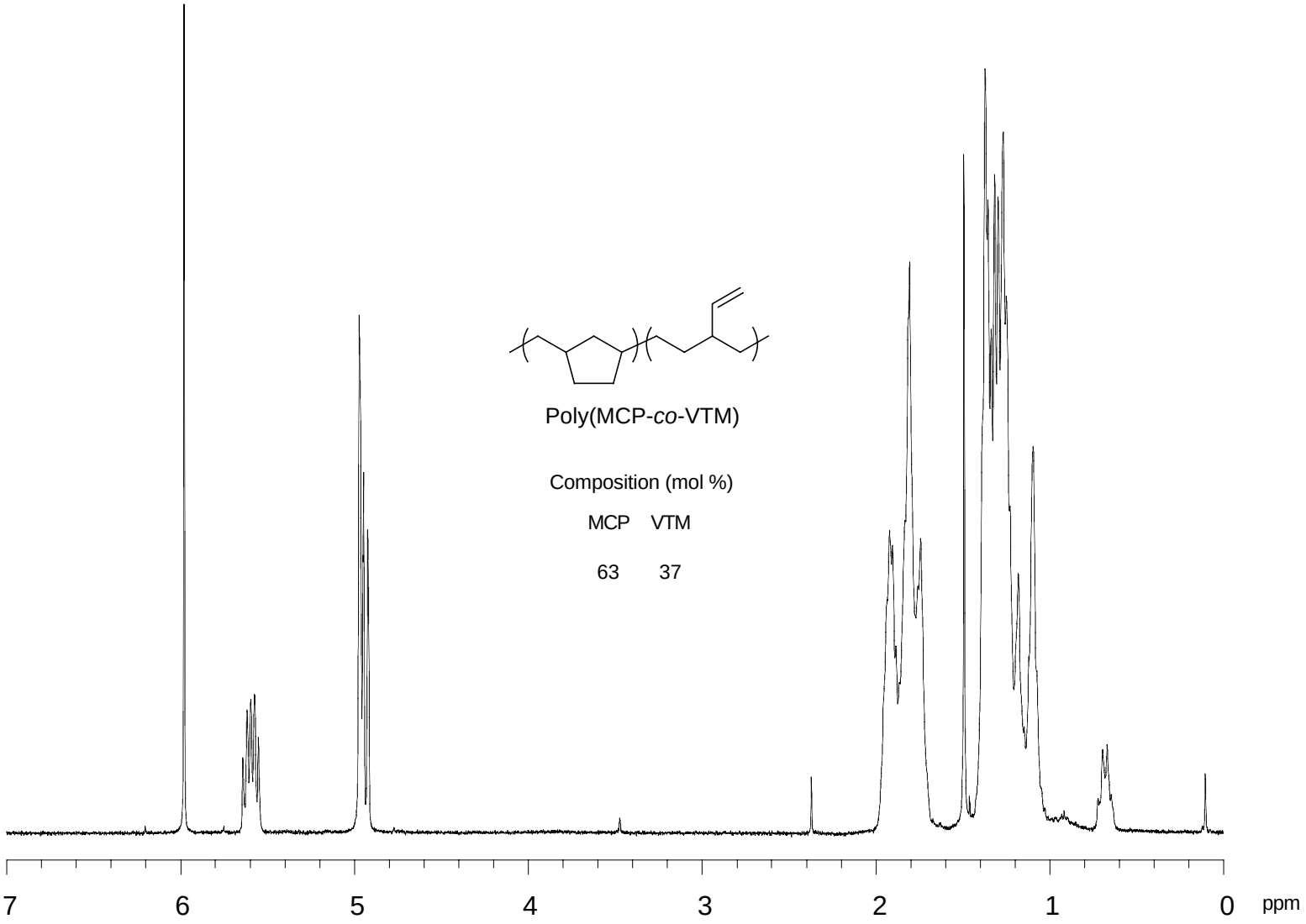


**Figure S2.** $^{13}C$ NMR spectrum (100 MHz, $C_2D_2Cl_4$, 90°C) of the 1,5-hexadiene polymer from **1**/MAO (Table 1, Entry 1).

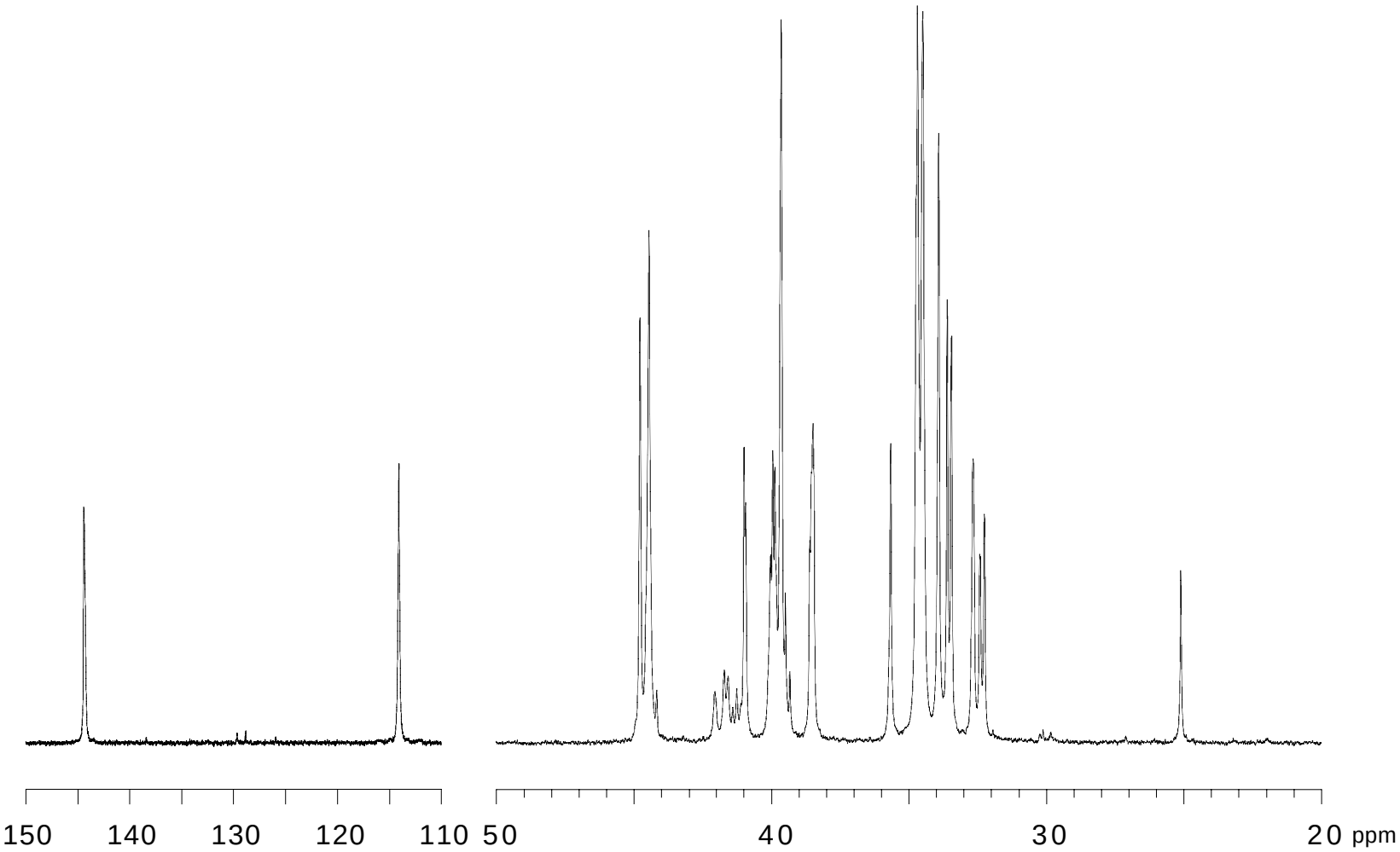


**Figure S3.** $^{13}C$ NMR spectrum (100 MHz, $C_2D_2Cl_4$, 90 °C) of the saturated hexadiene polymer from **1**/MAO and subsequent treatment with *p*-TsNHNH$_2$.

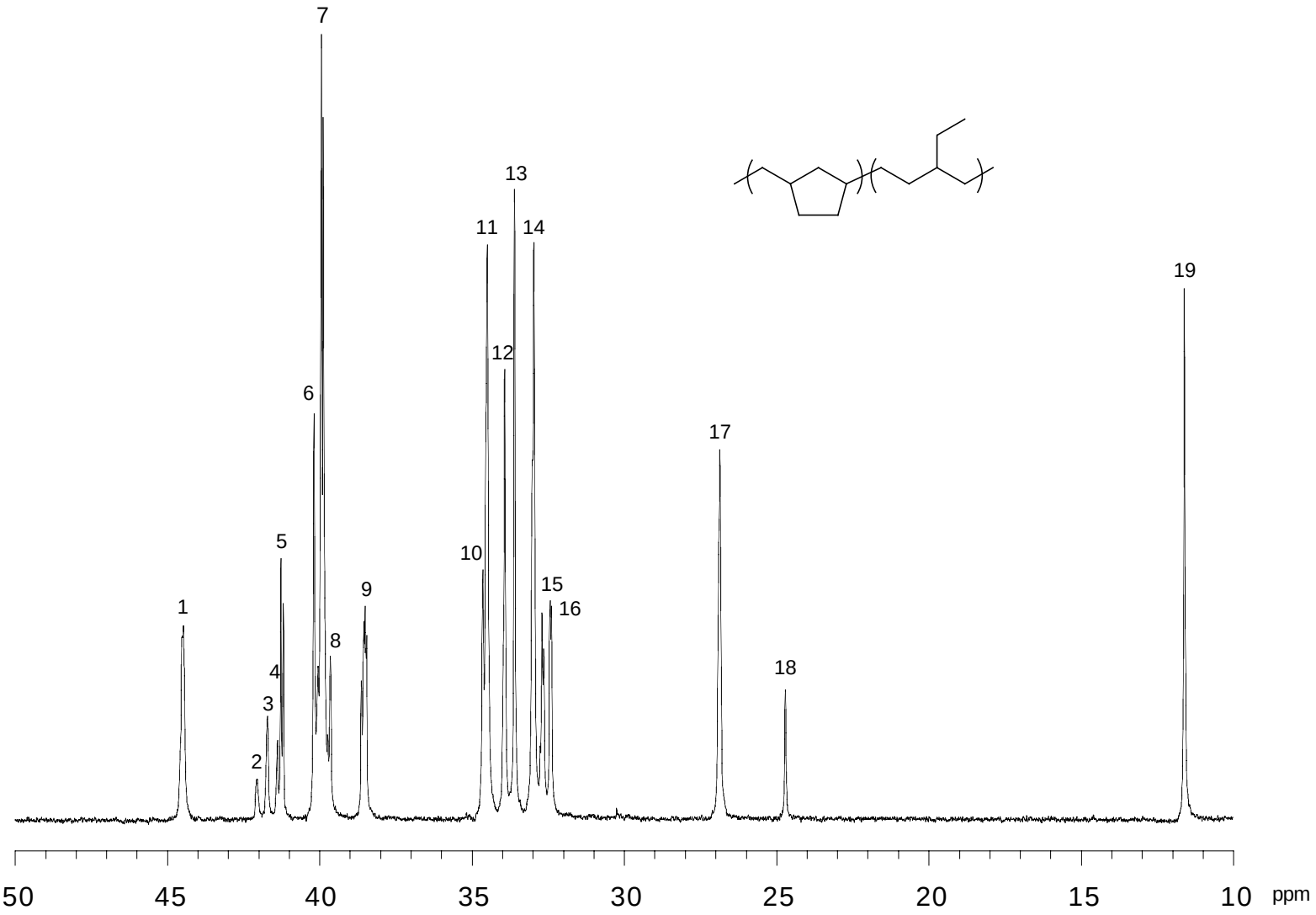


**Figure S4.** $^{13}C$ NMR spectrum (a) and DEPT spectrum (b) (100 MHz, $C_2D_2Cl_4$, 90 °C) of the saturated hexadiene polymer from **1**/MAO and subsequent treatment with *p*-$TsNHNH_2$.

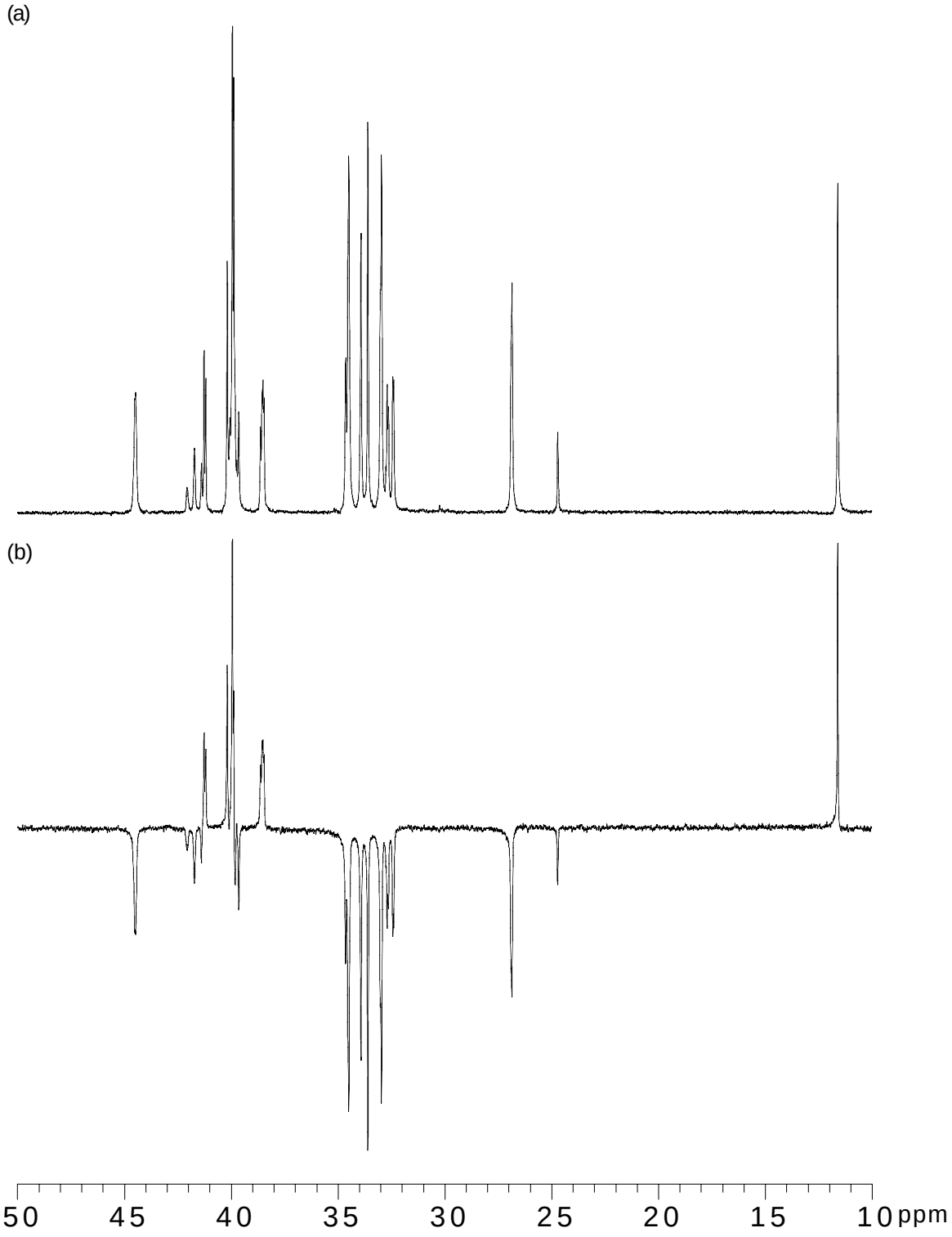
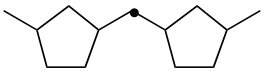
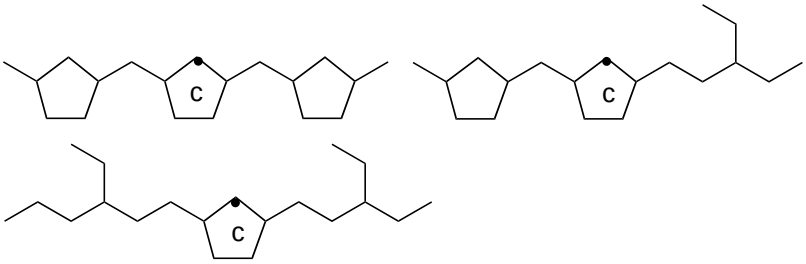
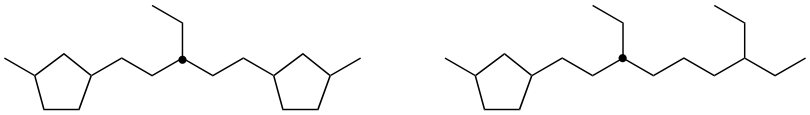
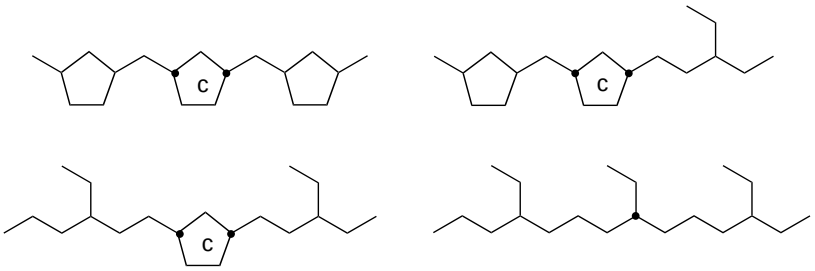
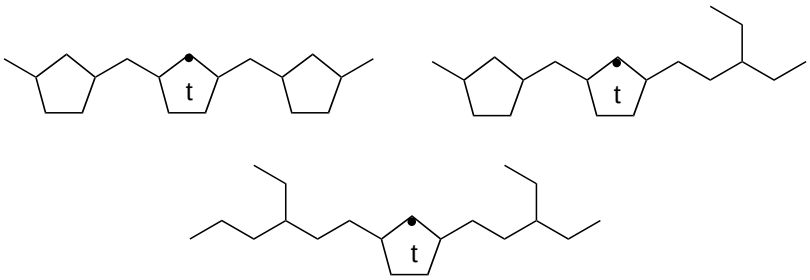
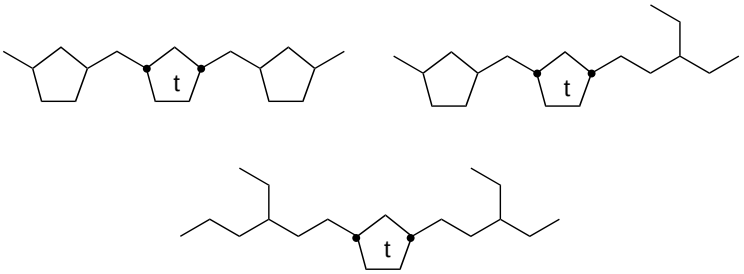
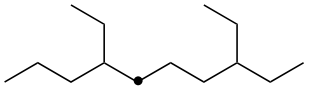
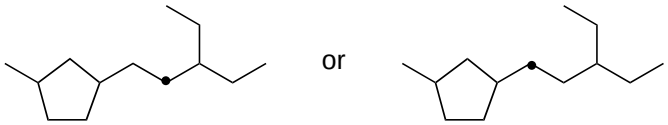
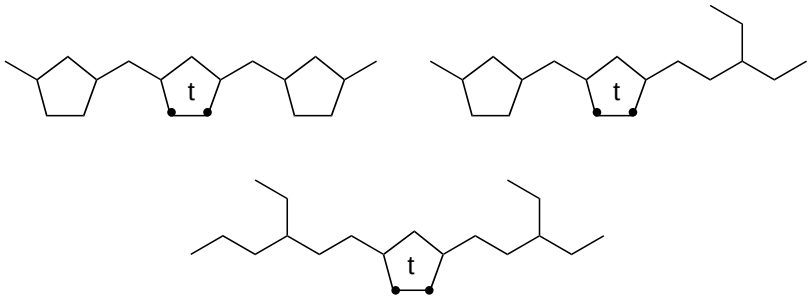
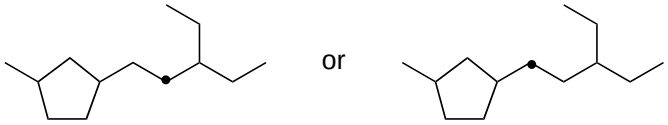
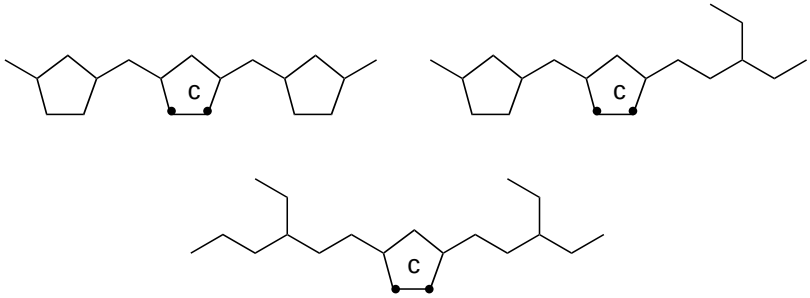
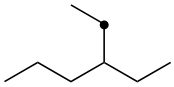
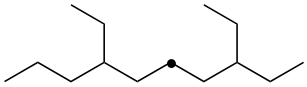
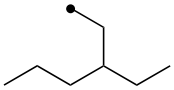


**Table S1.** Tentative $^{13}C$ NMR peak assignment for hexadiene polymers following hydrogenation of the pendant vinyl substituents.

| Peak | Shift, ppm | Microstructure and Assignment* | Carbon |
|---|---|---|---|
| 1 | 44.5 |  | $S_{\alpha\alpha}$ |
| 2 - 4 | 42.0 - 41.2 |   | $C_2$ |
| 5 | 41.2 |  | $T_{\gamma\gamma}$ $T_{\gamma\delta}$ |
| 6,7 | 40.1-39.8 |   | $C_{1.3}$ $T_{\delta\delta}$ |
| 8 | 39.8 - 39.6 |   | $C_2$ |
| 9 | 38.6 - 38.5 |   | $C_{1,3}$ + $T_{\delta\delta}$ |
| 10 | 34.6 |  | $S_{\alpha\gamma}$ |

| | | | |
|---|---|---|---|
| 11 | 34.5 |   | $S_{\alpha\beta}$ |
| 12, 13 | 33.9 - 33.6 |   | $C_{4,5}$ |
| 14 | 33.0 |   | $S_{\alpha\beta}$ |
| 15, 16 | 32.7 - 32.4 |   | $C_{4,5}$ |
| 17 | 26.9 |  | $CH_2CH_3$ |
| 18 | 24.7 |  | $S_{\beta\beta}$ |
| 19 | 11.6 |  | $CH_2CH_3$ |

c : *cis*-ring, t : *trans*-ring

*Assignments based on $^{13}C$ and DEPT spectra and related assignments for (a) ethylene/hexadiene copolymers (Choo, T. N.; Waymouth, R. M. *J. Am. Chem. Soc.* **2002**, *124*, 4188-4189), (b) ethylene/butene copolymers (Cheng, H. N. *Macromolecules* **1991**, *24*, 4813-4819), (c) ethylene/propylene copolymers (Wang, W. J.; Zhu, S. *Macromolecules* **2000**, *33*, 1157-1162 and references therein), and (d) poly(1,5-hexadiene) (Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953-4954).

**Figure S5.** $^{1}$H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 80 °C) of the propylene/hexadiene copolymer from **1**/MAO (Table 1, Entry 3).

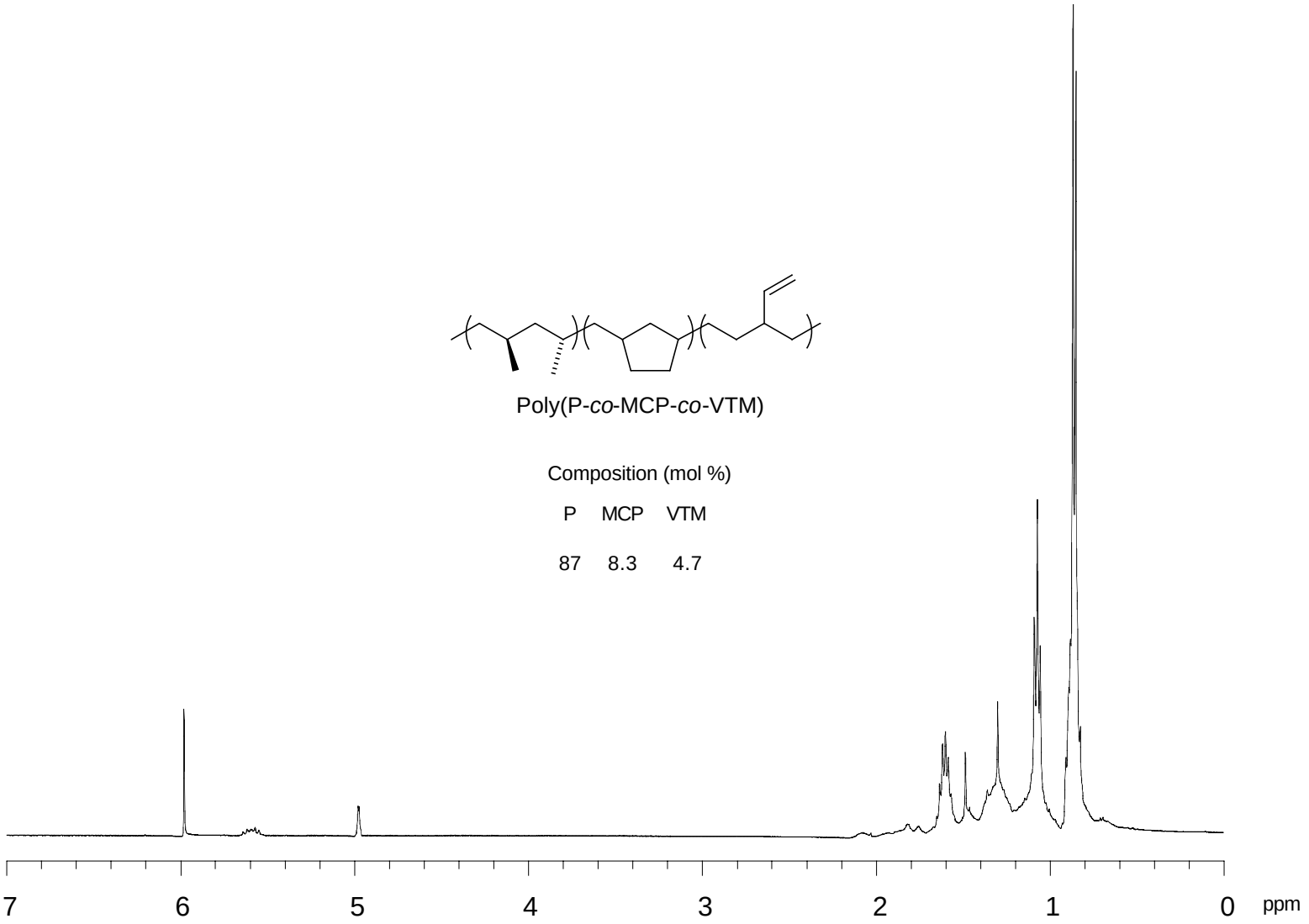


**Figure S6.** $^{13}C$ NMR spectrum (100 MHz, $C_2D_2Cl_4$, 90 °C) of the propylene/hexadiene copolymer from **1**/MAO (Table 1, Entry 4).

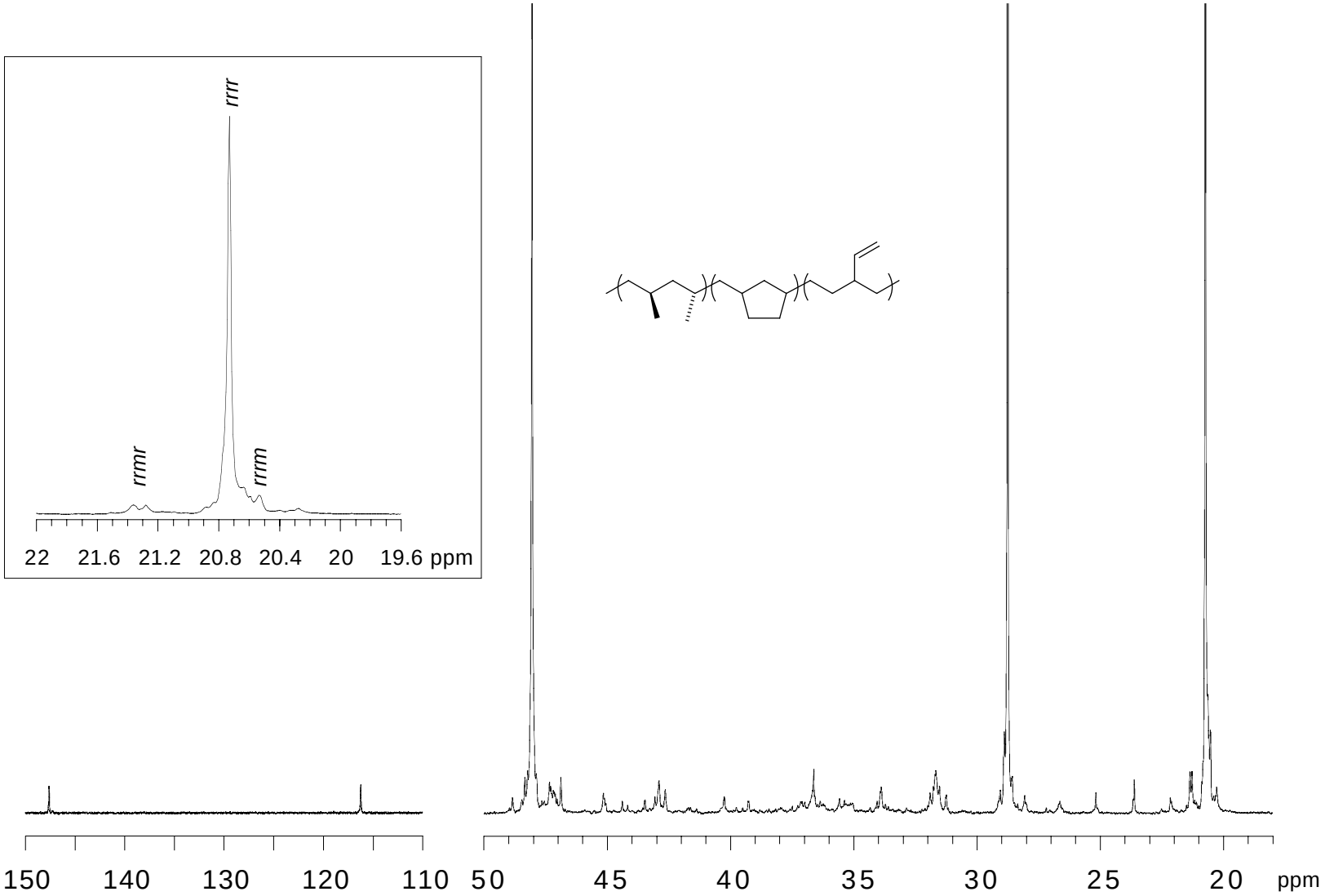


**Figure S7**. GPC data for the polypropylene-*block*-poly(propylene-*co*-hexadiene) copolymer.

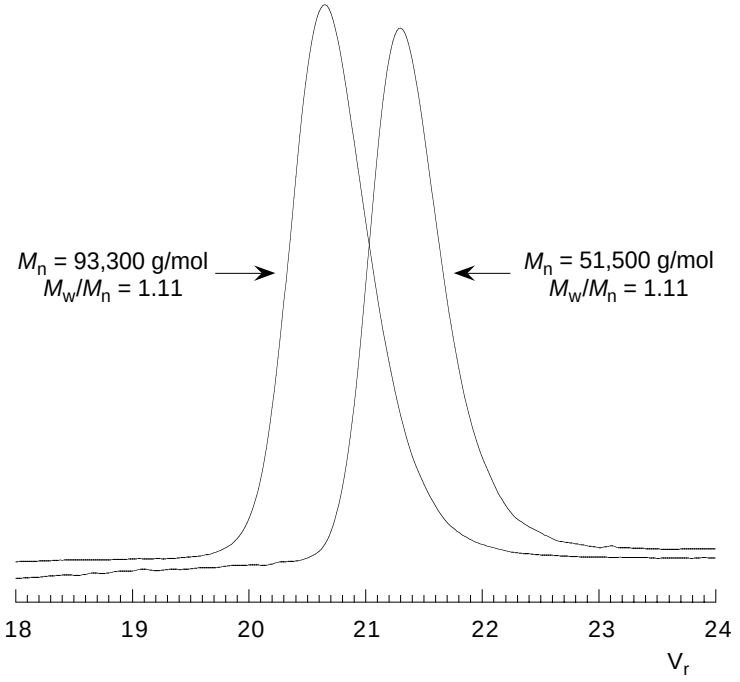



**Table S2.** DSC characterization of hexadiene polymers and hexadiene/propylene copolymers.

| Entry | Composition (mol %)[a] | | | $T_g$[b] | $T_m$[b] |
|---|---|---|---|---|---|
| | P | MCP | VTM | (°C) | (°C) |
| 1 | 0 | 63 | 37 | -19.3 | - |
| 2 | 100 | 0 | 0 | - | 146 |
| 3 | 87 | 8.3 | 4.7 | 2.8 | - |
| 4 | 96 | 1.5 | 2.5 | 0.6 | 93.2 |
| 5[c] | 100/93[d] | 0/4.3[d] | 0/2.7[d] | 2.6 | 137 |

[a] Calculated from the $^1$H NMR spectra. [b] Determined by DSC. [c] After reaction of **1**/MAO with propylene for 4 hours, 1,5-hexadiene was added and polymerization was conducted for another 2 hours. [d] Data for the initial polypropylene block and the final *syndio*-poly(propylene)-*block*-poly(propylene-*co*-hexadiene) diblock polymer.