

Tandem Catalyst System for Linear Low-Density Polyethylene with Short and Long Branching

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ABSTRACT: A zirconium-based polymerization catalyst, $\text{Me}_2\text{Si}(\eta^1\text{-C}_{29}\text{H}_{36})(\eta^1\text{-N-}i\text{Bu})\text{ZrCl}_2 \cdot \text{OEt}_2$ (**1**), and a chromium-based oligomerization catalyst, $[(^i\text{BuSCH}_2\text{CH}_2)_2\text{NH}]\text{CrCl}_3$ (**2**), in combination with methylaluminoxane (MAO), constitute a novel tandem catalyst system for converting ethylene alone to linear low-density polyethylene with short and long branches. Independent reactions demonstrated that **1**/MAO converts ethylene to polyethylene with ethyl and long ($\geq 6\text{C}$) branches while **2**/MAO converts ethylene to 1-hexene and 1-octene. Under certain reaction conditions (80 °C, 120 psi ethylene), **2**/MAO produces 1-hexene and 1-octene from ethylene with 80–85% selectivity for 1-hexene and minimal production of polymer. Polymerization of ethylene by **1**/MAO in the presence of **2**/MAO yields polyethylene with 14–44 total branches per 1000 carbon atoms, with 4–16 of those branches arising from incorporation of 1-hexene. The fraction of branches arising from 1-hexene varies from 12 to 54%, depending on the relative amounts of **1**, **2**, and MAO present, as well as on the pressure of ethylene and the prepolymerization time. By adjusting the polymerization conditions, the branching characteristics of polyethylene could be varied in a controlled manner.

Introduction

We recently reported that a constrained geometry catalyst (CGC) developed in our group, $\text{Me}_2\text{Si}(\eta^1\text{-C}_{29}\text{H}_{36})(\eta^1\text{-N-}i\text{Bu})\text{ZrCl}_2 \cdot \text{OEt}_2$ (**1**),^{1,2} is capable of homopolymerizing ethylene to yield polymers with microstructures similar to that of linear low-density polyethylene (LLDPE).³ In combination with MAO (methylaluminoxane), the branching characteristics from **1** tend toward about 5 ethyl branches per 1000 carbon atoms and 10–50 long branches (those containing six or more carbon atoms) per 1000 carbon atoms. While the degree of long branching in this system can be varied by modifying polymerization conditions, the degree of ethyl branching—apparently arising from a separate mechanism⁴—is relatively static. Short branches (SB) and long branches (LB) impact the mechanical and processing properties of branched polyethylene in different ways, depending on their length.⁵ With a desire to better control the SB content in SB/LB LLDPE, we sought a tandem catalyst system⁶ that combined a highly selective oligomerization catalyst with **1**. The unusually high affinity of **1**/MAO for α -olefins¹ would ensure, we surmised, that a large fraction of the oligomers would be incorporated into a polymer chain.

Binary and ternary catalyst systems have been shown to be effective in producing polyethylenes with modified microstructures.⁷ We required an oligomerization catalyst that produces a narrow distribution of α -olefins, exhibits a low propensity for polymer production, and operates compatibly with our MAO-activated system. To this end, we chose the chromium complex $[(^i\text{BuSCH}_2\text{CH}_2)_2\text{NH}]\text{CrCl}_3$ (**2**) (Figure 1).^{8,9} With MAO cocatalyst, this ethylene oligomerization catalyst was shown by McGuinness et al. to give only 1.1 wt % polymer with an overall 98.4% selectivity for 1-hexene.⁸ The binary catalyst

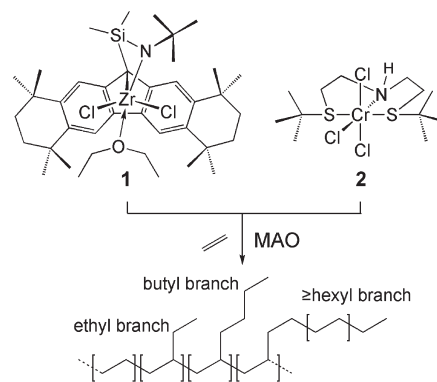


Figure 1. Tandem catalyst system consisting of polymerization catalyst **1** and oligomerization catalyst **2** for producing branched polyethylene. Ethyl and long branches are inherently produced by **1**/MAO, while butyl branches result from incorporation of 1-hexene produced *in situ* by **2**/MAO.

polymerization system of **1**/MAO/ethylene possesses many independently variable parameters, and without high-throughput equipment, it would be impossible to thoroughly explore all polymerization conditions. Nonetheless, we report herein polymerization results under a variety of conditions that effectively control the extent of butyl branching (attributable to **2**) while maintaining the ethyl and long branches (attributable to **1**) at relatively constant levels.

Results and Discussion

Orthogonal Branching Selectivity from 1 and 2. Catalyst **2** is reported to be highly selective for the production of 1-hexene under somewhat high ethylene pressure and moderate reaction temperature,⁸ conditions under which catalyst **1** produces polyethylene with fewer long branches. While

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Table 1. Ethylene Oligomerization Results with 2/MAO^a

entry	T_p (°C)	time (min)	Al/Cr	polymer (g, mass %)	1-hexene (g, mass %) ^b	1-octene (g, mass %) ^b	[1-hexene]/[1-octene]	TOF ^c
1	80	5	500	n.d.	0.25, 85.9	0.04, 14.1	6.10	25 370
2	80	5	500	0.18, 35.1	0.28, 54.7	0.05, 10.2	5.37	43 670
3	80	5	1000	0.01, 0.1	10.27, 50.9	9.89, 49.0	1.04	1 728 000
4	80	5	100	0.22, 93.9	~0	0.01, 6.1	very small	19 800
5	80	30	300	n.d.	0.921, n.d.	~0, ~0	very large	13 160
6	80	30	300	n.d.	1.13, 79.6	0.29, 20.4	3.90	20 270

^aOligomerization conditions: 5 μ mol of **2**; 120 psi ethylene; 25 mL of toluene; n.d. = not determined and not included in the mass % calculation. ^bAs determined by gas chromatography analysis vs neohexene. ^cTurnover frequency in units of mol (ethylene) mol (Cr)⁻¹ h⁻¹.

Table 2. Ethylene Polymerization Results with Tandem Catalyst System 1 and 2, Activated with MAO^a

entry	2:1 (μ mol)	P_E (psi)	volume (mL)	Al/Zr	t_0 (min)	t_p (min)	yield (g)	activity ^b	N_E^c	N_B^c	N_L^c	N_{total}	M_w	M_n	T_m (°C)
7	2.5:3.33	120	25	1000	0	5	1.84	6610	3.8	6.1	19.3	29.2	2280	1030	106
8	2.5:3.33	120	50	1000	0	10	2.05	3690	7.0	8.4	16.6	32.0	2780	1400	106
9	5.0:3.33	120	50	1000	0	5	0.85	3070	5.0	11.0	21.3	37.3	114900	1040	98
10	1.25:3.33	120	50	1000	0	10	3.18	5720	7.8	5.9	15.3	29.0	3450	1500	108
11	2.5:3.33	120	50	500	0	10	2.29	4130	6.5	9.8	10.0	26.3	8820	1430	103
12	2.5:3.33	120	50	2000	0	10	2.82	5090	5.5	5.1	21.8	32.4	1810	870	105
13	2.5:3.33	80	50	1000	0	10	1.15	2070	6.3	7.4	27.1	40.8	1470	780	103
14	2.5:3.33	120	50	1000	1	10	2.77	5000	6.4	3.7	12.7	22.8	3290	1470	107
15	2.5:3.33	120	50	1000	3	10	3.11	5610	5.9	3.8	21.3	31.0	3220	1450	108
16	2.5:3.33	120	50	1000	5	10	2.82	5070	4.8	7.4	22.1	34.3	3520	1540	105
17	5.0:3.33	120	50	500	0	5	0.49	1750	2.6	11.1	29.8	43.5	89700	1930	107
18	5.0:3.33	120	50	500	0	10	1.94	3490	8.3	15.6	4.9	28.8	22500	1810	99
19 ^d	5.0:6.66	320	400	500	0	120	7.71	580	3.9	5.3	4.9	14.1	n.d.	n.d.	n.d.

^aPolymerization conditions: 80 °C; toluene; injection of **1** t_0 minutes after injection of **2**; t_p = total polymerization time with **1** present. ^bIn units of kg of polymer/(mol of Zr·h). ^cNumber of ethyl, butyl, and long (≥ 6 C) branches, per 1000 carbon atoms. ^d T_p = 95 °C.

1/MAO produces ethyl and long branches in ethylene homopolymerizations, essentially no butyl branches—which would result from incorporation of 1-hexene—are observed. The orthogonal selectivity of **1** vs **2** greatly simplifies the diagnosis of this tandem catalyst system. Additionally, catalyst **2** requires only a modest amount of MAO activator, and any MAO in the system must naturally be shared between the oligomerization and the polymerization catalysts. Although decreased Al/Zr quotients result in somewhat decreased branching for **1**, this sacrifice is compensated by the butyl branching that results from the oligomerization activity of **2**.

Oligomerization Catalyst 2 Alone. Initial tests of catalyst **2**/MAO/ethylene in our hands resulted in more polymer and 1-octene production than described in the literature report.⁸ For example, entry 2 of Table 1 (T_p = 80 °C, Al/Cr = 500) shows that 35% of the recovered mass is polymer, and entry 3 of Table 1 (T_p = 80 °C, Al/Cr = 1000) shows that 1-hexene and 1-octene are produced with equal selectivity. These discrepancies were attributed to the reduced ethylene pressure used for our reactions; we employed 120 psi while the superior 1-hexene selectivity was obtained with 580 psi (40 bar) of ethylene. Nonetheless, acceptable 1-hexene selectivity could be obtained under certain conditions (e.g., entries 5 and 6, T_p = 80 °C, Al/Cr = 300).

Tandem Catalysis with 1 and 2. Initial tandem polymerizations showed that catalysts **1** and **2** were, as predicted, compatible with each other and resulted in polymerization activities resembling those for the homopolymerization of ethylene by **1** alone under similar conditions. As shown in Table 2, butyl branching was observed to be from 3.7 to 15.6 branches per 1000 carbon atoms, which equates to approximately 2.2–9.4 wt % 1-hexene incorporation. Table 2 also reveals that decreasing the amount of MAO resulted in decreased long branching and a concomitant increase in butyl branching. For example, as the Al/Zr quotient decreased from 2000 to 1000 to 500, the number of long branches per 1000 carbon atoms, N_L , decreased from 21.8 to 16.6 to 10.0, while N_B (butyl branches per 1000 carbon atoms) increased

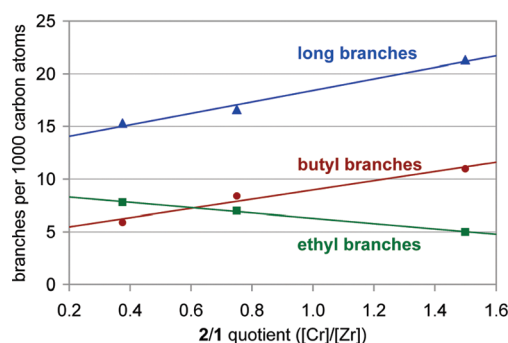


Figure 2. Butyl and long (≥ 6 C) branch densities increase as the quotient **2/1** is increased. In contrast, ethyl branch density is found to decrease slightly (Table 2, entries 8–10).

from 5.1 to 8.4 to 9.8 (runs 12, 8, and 11, respectively). These trends comport with the known inclination of **1** to make fewer long branches as Al/Zr decreases³ and the improved 1-hexene selectivity of **2** with modest amounts of MAO present (see Table 1).

As anticipated, butyl branching was proportional to the quotient of **2/1**, suggesting increased 1-hexene production from **2** relative to polymerization activity of **1** (Figure 2). Long branching also increased proportionally to the quotient of **2/1**, possibly because of an increase in 1-octene production by **2**. The 1-octene thereby consumed results in n -hexyl branching that contributes to the long branch content because linear branches with ≥ 6 C are indistinguishable.

Figure 3 illustrates the dependence of branching on the prepolymerization time, which is defined by the time that **2** is allowed to oligomerize prior to the addition of **1** to commence polymerization. These data are somewhat scattered, and clear trends are not apparent. An initial assumption might have been that butyl branching should increase with increased prepolymerization times, during which **2** is creating 1-hexene. However, this is not supported by the data.

An alternative explanation is that *all* the 1-hexene produced by **2** is ultimately incorporated because of the known affinity of **1** for α -olefins.^{1a} Thus, net butyl branching simply depends on the amount of 1-hexene that **2** produces in 10, 11, 13, or 15 min divided by the total amount of polymer that **1** is able to produce during the 10 min following its injection—which amounts to 2.05, 2.77, 3.11, and 2.82 g for entries 8, 14, 15, and 16, respectively. These yields are somewhat similar, but the lowest yield (2.05 g, entry 8) does correspond to the highest degree of butyl branching ($N_B = 8.4$).

Decreasing the ethylene pressure from 120 to 80 psi (Table 2, entry 13 vs entry 8) resulted in a slight drop in butyl branching (N_B from 8.4 to 7.4), but a significant increase in long branching (N_L from 16.6 to 27.1). Although **1** may consume all of the 1-hexene produced by **2**, less 1-hexene is generally made at reduced ethylene pressures,⁸ that would explain a slight drop in N_B . However, long branches should increase with reduced ethylene pressure because any macromonomeric α -olefins present can more effectively compete with ethylene, which is present at lower concentrations. Additionally, at lower ethylene pressures, catalyst **2** produces increased quantities of 1-octene (*vide supra*), which results in hexyl branches that contribute to N_L .

Polymerization at increased ethylene pressure and longer polymerization time (320 psi, 120 min, Table 2, entry 19) yielded polymer with a comparatively linear structure, considering the known propensity of catalyst **1** for making branched polyethylene. With $N_E = 3.9$, $N_B = 5.3$, $N_L = 4.9$, and $N_{\text{total}} = 14.1$ branches per 1000 carbons, this is the lowest level of long branching ever observed for **1**; the previous record was obtained with **1** alone and 250 equiv of MAO at 65 °C and 80 psi of ethylene: $N_E = 7.0$, $N_B = 0.8$, $N_L = 5.4$, and $N_{\text{total}} = 13.2$ branches per 1000 carbons.³ The low level of branching can be attributed to two factors. First, catalyst **1** is known to produce polyethylene with fewer long branches as

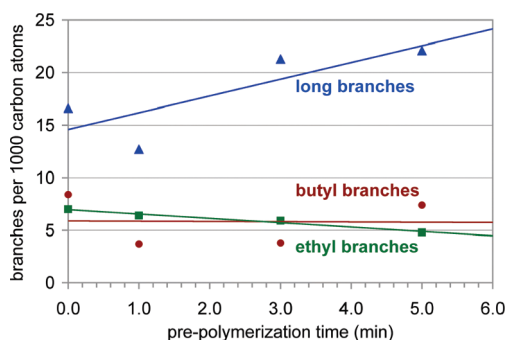


Figure 3. Extent of branching after various prepolymerization times—during which **2** oligomerizes alone—depends on several different factors, including the net yield of polymer (Table 2, entries 8, 14–16).

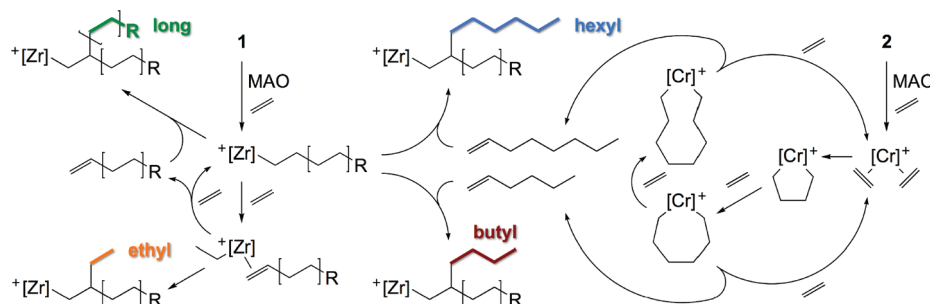


Figure 4. Proposed mechanism for the formation of branched polyethylene with short (ethyl, butyl, hexyl) and long branches from zirconium polymerization catalyst **1**, chromium oligomerization catalyst **2**, and ethylene alone.

ethylene pressure is increased, and entry 19 (Table 2) represents the highest reported ethylene polymerization pressure for **1**/MAO. Second, the increased ethylene pressure results in an increased ethylene concentration in solution, augmenting the rate of ethylene enchainment with respect to the rate of 1-hexene enchainment. Also, this relative rate is magnified because of the greater dilution of this polymerization (400 mL of toluene) compared to the other entries of Table 2 (50 mL of toluene), resulting in an even lower 1-hexene concentration at any given time.

The high degree of branching measured for these polymers translates into fairly low melting temperatures, as measured by differential scanning calorimetry (DSC). The observed melting temperatures of $T_m = 98$ – 108 °C are generally lower than those found for the polymers obtained without oligomerization catalyst **2**, which have $T_m = 96$ – 119 °C.³ According to the literature, purely linear polyethylenes of comparable molecular weight melt still higher at 124.5 °C (for $M_n = 1586$ with $M_w/M_n = 1.11$).¹⁰ Additionally, these primary melting endotherms are very broad and are typically accompanied by smaller, secondary endotherms at higher temperatures ($T_m = 118$ – 123 °C, see the Supporting Information), which likely correspond to the polyethylene byproduct demonstrably produced by the chromium species **2** alone (see Table 1). Such higher melting endotherms do not appear when zirconium catalyst **1** is used independently.³ Evidence for this byproduct is also found by gel permeation chromatography (GPC) analysis. A small amount of higher molecular weight material can sometimes (Table 2, entries 9, 11, 17, and 18) be identified in the GPC trace (see the Supporting Information), leading to a substantial broadening of the polydispersity index. When this high molecular weight material is absent, PDI values range from 1.9 to 2.3. The principal polyethylene products have fairly low molecular weight according to GPC ($M_n = 780$ – 1930), but it is possible that the high degree of branching gives artificially low molecular weight values versus linear polystyrene standards.¹¹

A proposed mechanism can be assembled that accounts for the observed branching. Figure 4 depicts the interplay of catalyst **1**, catalyst **2**, and ethylene alone that results in ethyl, butyl, hexyl, and long branches in an otherwise linear polyethylene chain. The zirconium polymerization catalyst **1** is inherently capable of producing ethyl and long branches,³ while the chromium oligomerization catalyst **2** supplies 1-hexene and 1-octene that become butyl and hexyl branches, respectively.

It should be noted that the archetypical CGC catalyst, $\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^1\text{-N-}^t\text{Bu})\text{TiCl}_2$ (/MAO), generally does not exhibit definitive incorporation of macromonomers (no long branches) for copolymerizations of ethylene with 4-methyl-1-pentene or with 1-octene,^{1a} conditions which

mirror those of 2/1/MAO. However, homopolymerization of ethylene with $\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(\eta^1\text{-N-}^i\text{Bu})\text{TiCl}_2/\text{MAO}$ can yield a relatively low “long” branch content (5.8 branches/1000 carbons), but a very high polymerization temperature of 145 °C is required.³

Conclusions

A tandem catalyst system has been developed in which a zirconium-based polymerization catalyst $\text{Me}_2\text{Si}(\eta^1\text{-C}_{29}\text{H}_{36})(\eta^1\text{-N-}^i\text{Bu})\text{ZrCl}_2\cdot\text{OEt}_2$ (**1**) and a chromium-based oligomerization catalyst $[(^i\text{BuSCH}_2\text{CH}_2)_2\text{NH}]\text{CrCl}_3$ (**2**), activated with methylaluminoxane (MAO), cooperate to produce highly branched polyethylene from ethylene alone. Both catalysts are efficiently activated by 500–1000 equiv of MAO and operate under the same reaction conditions, but they assume complementary catalytic roles: 1/MAO displays an inherent ability to form ethyl and long ($\geq 6\text{C}$) branches, while 2/MAO produces 1-hexene and 1-octene *in situ* that lead to butyl and hexyl branches, respectively. Thus, the incorporation of 1-hexene—the principal oligomer produced by catalyst **2**—was independently controllable and afforded polyethylene with 3.7–15.6 butyl branches per 1000 carbon atoms, with a total branch content of 14.1–43.5 branches per 1000 carbon atoms. The net 1-hexene content equates to 2.2–9.4 wt %. These changes were effected almost exclusively by modifying the 1:2:MAO ratios, and further variation was possible by modulating the ethylene pressure or increasing the prepolymerization time, during which **2** operates alone. Presumably, additional control over the polymer microstructure can be achieved by varying other reaction conditions—such as polymerization temperature—or by employing alternative oligomerization catalysts.

Experimental Section

Materials. Toluene was dried over elemental sodium and distilled under nitrogen into a Straus flask. Ethylene (polymerization grade) was obtained from Matheson and used following passage through a Matheson 6410 drying system equipped with an OXYSORB column. Precatalyst **1** was prepared as in ref 1a and stored as a 3.33 mM toluene stock solution in a volumetric flask in the glovebox. Precatalyst **2** was prepared as in ref 8 and stored as a 5.0 mM toluene stock solution in a volumetric flask in the glovebox. MAO (Albemarle, 30 wt % in toluene) was dried at 70 °C under high vacuum for 3 days and stored as a solid in the glovebox. A 1.0 M stock solution of MAO in toluene was prepared and stored in the glovebox in a volumetric flask.

Oligomerizations. CAUTION: All oligomerizations should be carried out in a fume hood behind a blast shield. Ethylene oligomerizations were performed in an 85 mL glass Lab-Crest (Andrews Glass Co.) cylindrical polymerization vessel equipped with a 2.5 in. octagonal stir bar. In the glovebox, the reactor was charged with the appropriate amounts of MAO stock solution and toluene, and 1.0 mL (5.0 μmol) of 5.0 mM stock solution of **2** was drawn into a Hamilton gastight syringe and capped with a septum. The reactor was removed from the box to an oil bath at 80 °C, purged with ethylene for 5 min, and equilibrated for 5 min with 120 psi of ethylene, after which the catalyst was injected. After the desired oligomerization time was reached, the reaction was vented and quenched with 3 mL of 10% aqueous HCl in MeOH (no acidic methanol was added in runs 4 and 5). The reaction mixture was poured into 100 mL of saturated aqueous sodium bicarbonate, and 1.0 mL of neohexene was added. The mixture was stirred for more than 3 h, after which the polymer was collected by filtration and the organic layer isolated and dried over CaCl_2 , and 0.5 μL was analyzed by gas chromatography. The relative areas of the neohexene, 1-hexene, and 1-octene peaks were used to determine the mass of the oligomers that were produced, after corrections according to a Beer's law plot. The polymer was rinsed with fresh methanol and dried *in vacuo*.

Polymerizations. CAUTION: All polymerizations should be carried out in a fume hood behind a blast shield. Ethylene polymerizations were performed in either an 85 mL glass Lab-Crest (Andrews Glass Co.) cylindrical polymerization vessel equipped with a 2.5 in. octagonal stir bar or in a 600 mL glass Parr reaction vessel. In a typical polymerization, the reactor was charged with 0.193 g of MAO and 50 mL of toluene in the glovebox. Then 1.0 mL (3.33 μmol) of the stock solution of **1** and 0.5 mL (2.5 μmol) of the stock solution of **2** were mixed thoroughly and drawn up into a Hamilton gastight syringe, which was capped with a septum. The sealed reactor was placed in an oil bath at 80 °C and purged with ethylene for 3 min and then pressurized to 120 psi with ethylene. After an additional 7 min of stirring in the oil bath, the catalyst solution was injected. After the desired polymerization time, the reaction was rapidly vented and then poured into ~200 mL of 10% aqueous HCl in MeOH. After stirring overnight in acidic methanol, the polymer was collected by filtration, thrice rinsed with fresh methanol, and dried *in vacuo*.

Some polymerizations were quenched as described in the oligomerization procedure. For polymerizations having a prepolymerization period, two gastight syringes were used to inject the solutions of **2** and **1** at separate times. For the higher pressure polymerization in the Parr reactor (entry 19 in Table 2), MAO, toluene, and catalyst solutions were combined in the reactor, which was equilibrated in an oil bath at 95 °C for 2.5 h. The polymerization was initiated by pressurizing with 320 psi of ethylene and terminated by venting the reactor and adding acidic methanol.

Polymer Analysis. Polymer samples for ^{13}C NMR characterization were prepared by dissolving ~100 mg of polymer in ~1.5 mL of 1,1,2,2-tetrachloroethane- d_2 . Spectra were obtained on an Inova 300 NMR spectrometer observing at 75.4 MHz with at least 1500 transients collected at 100 °C using a pulse width of 16 501.7 Hz, a pulse angle of 70°, and a recycle delay of 5.5 s to allow complete relaxation of the nuclei.¹² Chemical shifts were referenced to the main chain “ $\delta^+\delta^+$ ” polyethylene peak at 30.0 ppm; peak assignments and branch density formulas followed those of Galland et al.¹³ The formulas used for calculating branch densities were slightly modified from those of Galland due to the lack of baseline separation between peaks 24 and 25 in our spectra. This approach is fully described in ref 3 and its Supporting Information. Polymer melting temperatures were determined using a TA Instruments Q1000 differential scanning calorimeter (DSC) under a nitrogen purge at a heating rate of 10 °C/min from 0 to 150 °C. The melting temperature was taken as the maximum of the melting endotherm on the second heating cycle. Polymer molecular weights were determined using a Waters 150C gel permeation chromatograph (GPC) with a Tosoh TSKgelGMH6-HT GPC column using *o*-dichlorobenzene as the solvent and an elution temperature of 140 °C; polystyrene standards were employed.

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Supporting Information Available: Polymerization results, representative ^{13}C NMR spectra, GPC traces, and DSC thermograms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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