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Articles

Highly Branched Polyethylene from Ethylene Alone via a Single Zirconium-Based Catalyst

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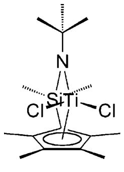
ABSTRACT: A single zirconium-based constrained geometry catalyst ($\mathrm{Me_2Si}(\eta^1\text{-}\mathrm{C_{29}H_{36}})(\eta^1\text{-N-}^t\mathrm{Bu})\mathrm{ZrCl_2}\cdot\mathrm{OEt_2}$/methylaluminoxane) has been employed to produce homopolymers of ethylene which contain degrees of branching unprecedented for early transition metal systems. A variable density of long branches is observed (10−50 branches per thousand carbon atoms) with strong dependences on both polymerization temperature and pressure. These branches are attributed to the exceptionally facile incorporation of long α-olefin macromonomers formed *in situ* via the usual β-hydride elimination of polymer chains. Additionally, a relatively constant low degree of ethyl branches is observed (∼5 branches per thousand carbon atoms) under all polymerization conditions; this is attributed to β-hydride transfer to monomer followed by immediate reinsertion of the coordinated olefin-terminated polymer into the formed metal−ethyl bond.

Introduction

Traditional heterogeneous and homogeneous catalyst systems are capable of producing highly linear high-density polyethylene (HDPE).[1] More recently developed late transition metal homogeneous catalyst systems are capable of producing hyperbranched low-density polyethylene (LDPE).[2] Early transition metal constrained geometry catalysts (CGCs), exemplified by the Dow titanium CGC $\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^1\text{-N-}^t\mathrm{Bu})\mathrm{TiCl_2}$ (**1**), are capable of incorporating α-olefins into copolymers with ethylene to produce linear low-density polyethylene (LLDPE) with well-defined branches.[3] LDPE and LLDPE are often desirable because they have unique processing properties related to their lower melting temperatures, smaller crystallite size, and lower melt viscosities. However, the high temperature and high-pressure free radical process used to produce LDPE commercially is energy-intensive. Additionally, the purified olefinic comonomers (typically 1-hexene or 1-octene) required to produce LLDPE are expensive compared to ethylene. Therefore, a method for obtaining branched polyethylene under relatively mild conditions from a pure ethylene feed is of great commercial interest.[4]



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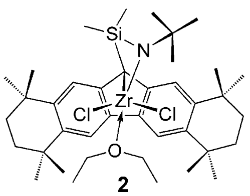

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Early reports of long-chain branching in ethylene homopolymerizations were based on work with **1**, and the patent on this catalyst is generally referenced as being the standard for the formation of long-chain branched polyethylene.[3] Branch formation by this catalyst is generally presumed to occur because of its ability to incorporate long-chain α-olefins, produced *in situ* via β-hydride elimination, an important chain termination mechanism.[5] Our group has recently reported the synthesis and characterization of a new, sterically expanded CGC, $\mathrm{Me_2Si}(\eta^1\text{-}\mathrm{C_{29}H_{36}})(\eta^1\text{-N-}^t\mathrm{Bu})\mathrm{ZrCl_2}\cdot\mathrm{OEt_2}$ (**2**) which, upon activation with methylaluminoxane (MAO), is capable of producing highly syndiotactic polypropylene, syndiotactic poly(4-methyl-1-pentene), and syndiotactic copolymers of propylene with higher α-olefins.[6] Remarkably, **2**/MAO is also found to be *more active* toward α-olefins than it is toward ethylene, greatly exceeding the activity of **1**/MAO for α-olefin homopolymerizations and certain copolymerizations (Figure 1).[6a]

With this unusual preference for α-olefins in mind, we set out to investigate the ability of **2**/MAO to produce branched polyethylene from ethylene alone. We supposed that if our catalyst produced any olefin-terminated oligomers or polymers via β-hydride elimination, these would behave as macromonomers and be rapidly incorporated into growing polymer chains. Long-chain branching in early transition metal homogeneous polymerization systems is typically less than 0.5 long-chain branches per 1000 carbon atoms (although most reports are for slurry rather than solution polymerizations).[7] One recent report employing a zirconium heteroscorpionate catalyst has shown as many as 10 long-chain branches per 1000 carbon atoms.[8] It is of interest to note that a $\mathrm{Cp^*TiCl_3}$ system has been reported by Pellecchia to give up to 50 butyl branches per 1000 carbon atoms, but the polydispersity indices (PDIs) of 5−15 suggest multisite behavior and branching dropped off sharply as polymerization temperature (T_p) deviated from 25 °C.[9]

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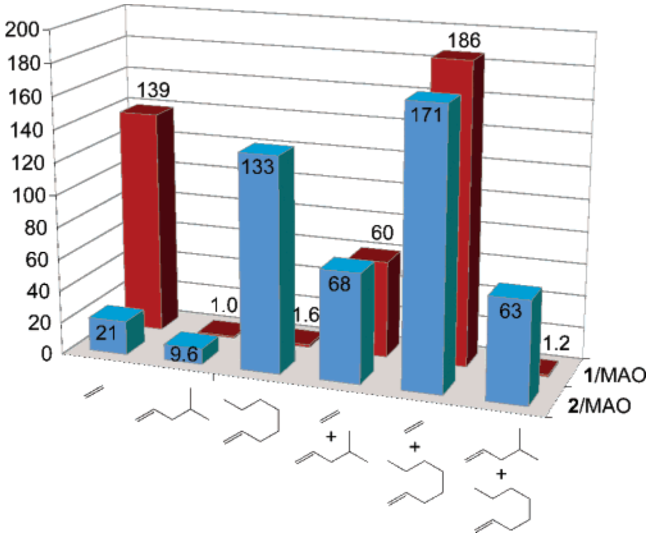


Figure 1. Relative homopolymerization and copolymerization activities for **1**/MAO and **2**/MAO in units of mass polymer/([monomer]·mol M·time).

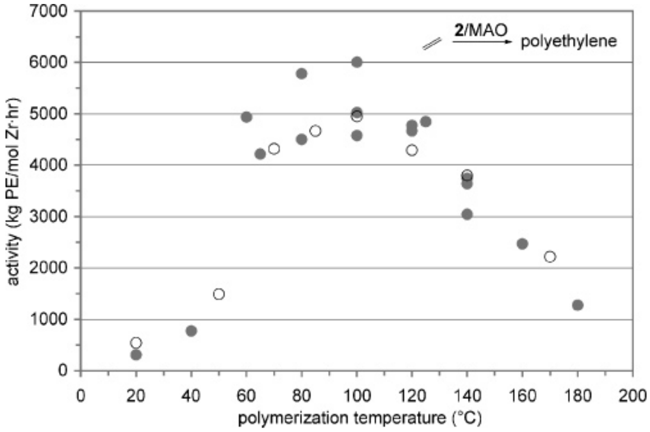
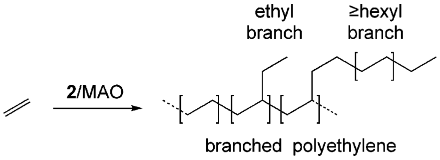


Figure 2. Ethylene polymerization activity of **2**/MAO as a function of temperature at 80 psi ethylene. Data points (○) from ref 6b are also included.

Results and Discussion

We have found that **2**/MAO is capable of producing polymers with many more branches, both long and short, than previously reported catalysts, with a strong dependence on polymerization conditions. In particular, as illustrated in Scheme 1, we found that all of the polyethylenes produced using **2**/MAO contained significant numbers of ethyl branches and long branches (≥hexyl), with some samples containing limited quantities of methyl, *n*-propyl, and *n*-amyl branches, and occasionally *n*-butyl branches. Similar polymers were reported by Bazan et al. using a mixture of *three* catalysts, each preactivated using a borane activator.[10] Even with the advantage of discrete oligomerization catalysts present, the Bazan system was reported to produce a maximum of two long-chain branches per 1000 carbon atoms, with more than twice as many butyl branches and up to 27 ethyl branches per 1000 carbon atoms. Sperber and Kaminsky subsequently reported a binary catalyst system capable of approximately two long-chain branches per 1000 carbon atoms.[11] In contrast to previous work, our single catalyst system is capable of producing over 50 long branches per 1000 carbon atoms with two to eight ethyl branches and minimal branches of other lengths (Table 1). For comparison, titanium CGC **1**/MAO (Table 1, entry 51) produced polyethylene with one ethyl and six long branches per 1000 carbon atoms only under rather favorable branching conditions of elevated polymerization temperature (145 °C) and reduced ethylene pressure (20 psi). Additionally, copolymerizations of ethylene with 1-butene and 1-hexene are provided in entries 52 and 53, confirming the affinity of **2**/MAO for α-olefins, as well as our ^{13}C NMR peak assignments.

Scheme 1. Generalized Branched Structure of Polyethylene Produced by 2/MAO from Ethylene Alone



Branching vs Polymerization Temperature. As shown in Figure 2, the ethylene polymerization activity of **2**/MAO at constant ethylene pressure (80 psi over toluene) increases with T_p up to about 100 °C, and then falls off slowly. Long branching (≥hexyl) generally increases with T_p from 60 °C up to 180 °C, as depicted in Figure 3. This increase was anticipated for two reasons: (1) At higher temperatures, increased net activity and enhanced relative rates of unimolecular β-hydride termination

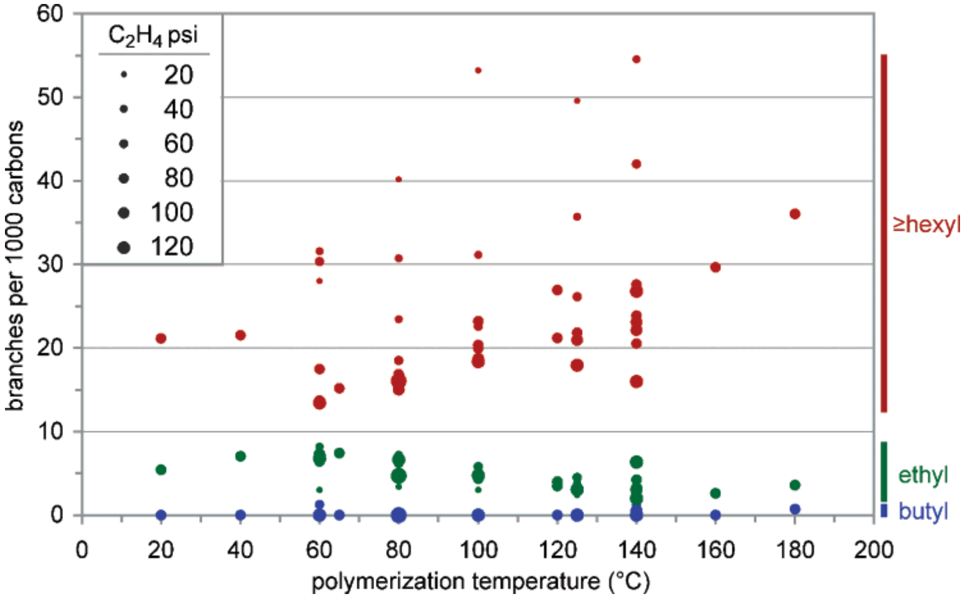


Figure 3. Butyl (blue), ethyl (green), and long (red) branches vs polymerization temperature for a variety of ethylene pressures.

Table 1. Ethylene Polymerization Results with 3.33 μmol 2 Activated with 1000 equiv of MAO in 25 mL Toluene

entry	T_p (°C)	$P_{ethylene}$ (psi)	time (min)	yield (g)	activity (kg/mol Zr•h)	$N_M{}^a$	$N_E{}^a$	$N_P{}^a$	$N_B{}^a$	$N_A{}^a$	$N_L{}^a$	$N_T{}^a$	T_m (°C)
1	20	80	10	0.17	310		5.4	1.5			21.2	28.1	
2	40	80	10	0.43	770		7.1				21.5	28.6	110.4
3	60	20	20	0.01	10		3.0				28.0	31.0	
4	60	40	15	0.21	250	0.7	8.2	1.4			31.6	40.5	
5	60	60	10	0.30	530	2.3	3.4		1.2		30.3	36.1	107.4
6	60	80	10	2.74	4940		6.4				17.5	23.9	112.7
7	60	100	10	2.85	5140		7.2				13.6	20.9	
8	60	120	10	2.62	4720		6.8	0.9			13.4	20.2	
9	65	80	5	1.17	4220		7.4	1.1			15.2	24.1	114.5
10	80	20	20	0.14	130	2.8	3.4				40.2	46.4	99.3
11	80	40	10	n.d.	n.d.	1.2	6.2	0.8		1.2	30.7	40.0	107.3
12	80	40	40	2.50	5710		7.2				23.5	30.7	
13	80	60	10	2.21	3980	1.9	6.2			0.8	18.5	27.4	
14	80	80	10	3.21	5780		5.0				16.9	21.9	113.2
15	80	80	10	2.50	4500		6.9				16.6	23.5	113.2
16	80	100	10	3.03	5460	1.0	6.7				15.0	23.2	
17	80	100	20	4.92	4440		6.6				15.9	22.5	
18	80	120	10	3.65	6580		6.6				16.1	22.7	
19	80	160	15	4.75	1130		4.7				16.1	20.8	
20	100	20	20	0.20	180	1.0	3.0	1.0		1.1	53.2	59.4	
21	100	40	10	0.98	1770	0.6	4.5			0.7	31.1	36.9	103.8
22	100	60	10	1.99	3590		5.8				22.6	28.4	
23	100	80	10	2.79	5030		4.4				20.0	24.3	
24	100	80	10	2.54	4580		5.0	0.6		4.0	20.3	30.0	101.2
25	100	80	5	1.67	6010	3.7	4.8			5.7	23.2	37.6	
26	100	100	5	2.69	9690	1.5	4.7				18.7	24.9	
27	100	120	5	3.04	10 950		4.7				18.4	23.1	
28	120	80	10	2.59	4670		4.0			0.8	26.9	31.7	110.3
29	120	80	10	2.65	4770		3.5				21.2	24.7	
30	125	20	60	0.38	110		2.4	1.8		8.5	49.6	62.6	
31	125	40	20	1.39	1250		3.7	1.5		2.5	35.7	43.4	98.4
32	125	60	10	1.62	2920		4.5				26.1	30.6	
33	125	80	10	2.69	4850		2.9				21.8	24.7	110.9
34	125	100	10	2.89	5210		3.2				21.0	24.2	
35	125	120	10	3.79	6830		3.1				17.9	21.0	
36	140	40	10	0.27	490	3.7	2.2	1.6		3.3	54.6	65.4	
37	140	60	10	1.03	1860		2.6	0.8	1.2	1.3	42.0	45.9	
38	140	80	10	2.08	3750		4.3				20.5	25.0	
39	140	80	10	1.69	3050		3.2				23.9	27.1	108.9
40	140	80	10	2.02	3640	1.6	2.7	0.6			27.6	32.5	105.5
41[b]	140	100	10	n.d.	n.d.		3.2				22.2	25.4	
42	140	100	10	2.55	4590		3.0		0.5	1.3	23.1	27.9	108.5
43	140	120	10	2.08	3750	2.6	2.0	1.3			26.8	32.7	
44	140	120	10	3.13	5640		6.4				16.0	22.3	112.1
45	160	80	10	1.37	2470	2.6	2.6	3.3		1.3	29.7	39.5	95.5
46	180	80	10	0.71	1280	2.8	3.6	6.3	0.7	1.4	36.0	50.9	
47[c]	65	80	5	1.03	3710		7.0	0.8			5.4	13.3	118.9
48[d]	65	80	5	1.07	3860		7.6				10.3	18.0	116.8
49[e]	65	80	5	0.78	2810		7.0			0.8	20.4	26.8	111.6
50[f]	65	80	5	0.35	1270	1.8	6.1				26.3	34.3	104.7
51[g]	145	20	15	0.11	110		1.0				5.8	6.9	
52[h]	80	120	5	3.53	12 730		36.3				12.4	35.1	
53[i]	80	120	5	3.40	12 250	12.8	5.0		15.4		13.5	36.6	

[a] Number of methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, longer, and total branches, expressed as branches per 1000 carbon atoms. [b] n.d. = not determined. [c] 250 equiv of MAO. [d] 500 equiv of MAO. [e] 2000 equiv of MAO. [f] 3000 equiv of MAO. [g] 4 μmol of **1**; 1000 equiv of MAO. [h] Spiked with 20 psi 1-butene, with a continuous feed of ethylene to give a total pressure of 120 psi. [i] Spiked with 0.5 mL of 1-hexene.

result in more chains (albeit of lower molecular weight) and therefore the concentration of macromonomers should be higher than at lower temperatures; (2) As temperatures increase, the catalyst should become less discriminating between small (ethylene) and large (macromonomer) substrates, allowing for enhanced incorporation of the typically less reactive macromonomer. Note that the greatest density of long branches is found for lower ethylene pressures because under these conditions (lower ethylene concentration), there is less ethylene present to compete with the macromonomers.

Short-chain branch density does not increase with temperature, suggesting a different mechanism of formation. In fact, the density of ethyl branches is found to decrease slightly with increasing polymerization temperature. This result is consistent with a mechanism proposed by Oliva in which β-hydride transfer to monomer occurs with the resultant macromonomer remaining coordinated to the metal center and immediately inserting into the metal-ethyl bond.[12] This mechanism—which is specific for ethyl branches—also explains the absence of butyl branches in the homopolymers, and has been observed in other CGC systems.[13] Only 4 of the 45 polymers in Figure 3 contained measurable amounts of butyl branches. *In situ* dimerization to 1-butene is an unlikely source of the ethyl branches because a greater response of their density to the polymerization conditions would be expected. Additionally, chain walking/isomerization mechanisms[14] can be ruled out by analysis of the polymers, which generally lack significant numbers of methyl and other odd-carbon branches.

Branching vs Ethylene Pressure. Figure 4 plots the same branch density data as Figure 3, but does so as a function of increasing ethylene pressure. We anticipated an increase in long branch density with lowered ethylene pressure as ethylene

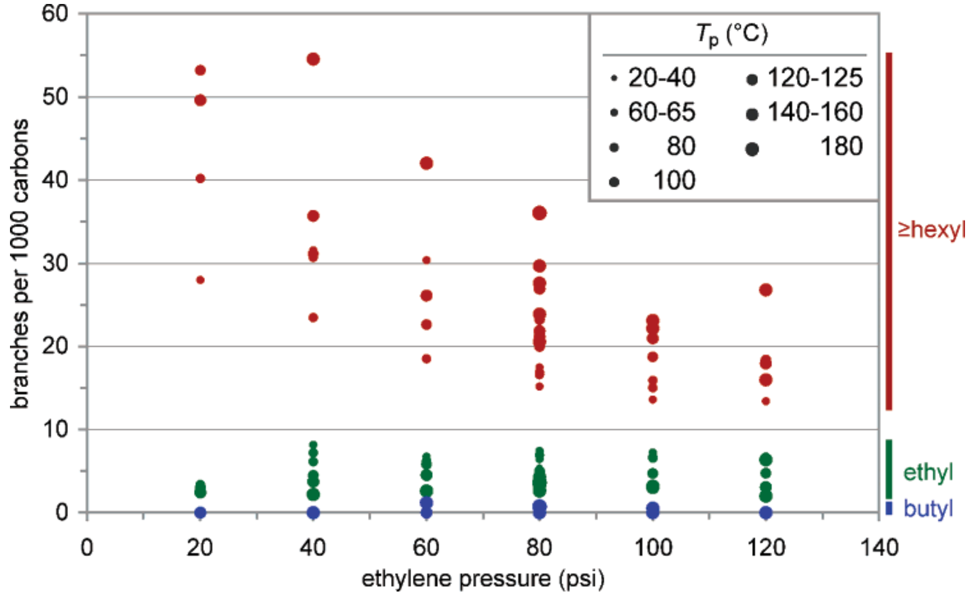


Figure 4. Butyl (blue), ethyl (green), and long (red) branches vs ethylene pressure for a variety of polymerization temperatures.

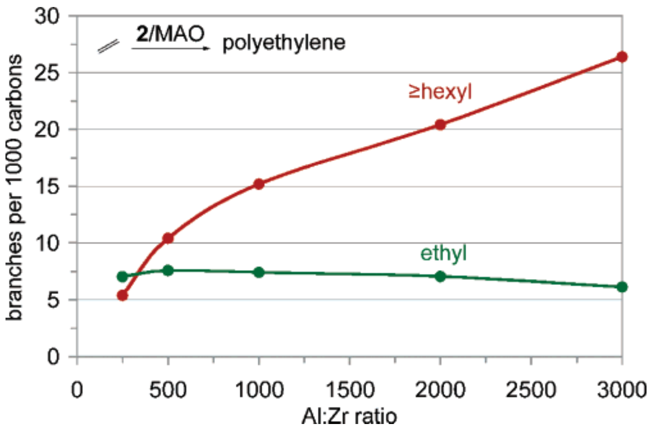


Figure 5. Ethyl (green) and long (red) branches vs the Al:Zr ratio for polymerizations conducted at 65 °C with 80 psi of ethylene.

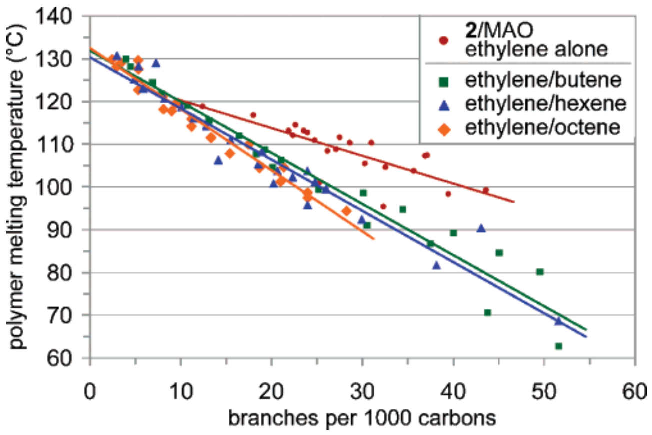


Figure 6. Polymer melting temperature vs branch density. The polyethylene homopolymers from **2**/MAO have depressed melting temperatures, but not as depressed as authentic samples of LLDPE.[15]

concentration decreased. This effect was observed, with a steeper dependence found for higher polymerization temperatures. Note that pressure control appears to be a better method than temperature control for introducing high densities (>50 branches per 1000 carbons) of long branches. Long branch density does not exceed 30 per 1000 carbons for ethylene pressures above 60 psi—except for the extreme example with $T_p = 180$ °C. Ethyl branch density appears to be rather invariant to ethylene pressure. This further implicates the Oliva mechanism for ethyl branch formation because both propagation (no ethyl branch) and β-hydride transfer to monomer followed by macromonomer reinsertion (ethyl branch introduction) are first order in ethylene; thus, the ratio of these two pathways is predicted to be insensitive to ethylene concentration.[12]

Branching vs the Al:Zr Ratio. In order to further characterize the system, polymerizations were conducted with various aluminum (from the MAO cocatalyst) to zirconium ratios. As the ratio of MAO to zirconium catalyst increased, the density of long branches increased proportionally (Figure 5). This behavior can be rationalized by considering that at higher Al:Zr ratios, the average zirconium electrophilicity is higher and the resultant catalyst is likely less discriminating between small and large substrates. This would explain an increased inclination for macromonomer incorporation and the corresponding increase in long branch density. There is effectively no dependence of the ethyl branch density on the Al:Zr ratio, further suggesting that ethyl branches are formed by a wholly independent pathway.

Table 2. Molecular Weight Data for Polyethylene Samples[a]

entry	M_n	M_w	M_w/M_n	N_L	average n in $-(CH_2)_n-$
12	2160	4630	2.15	23.5	18
14	1610	3420	2.13	16.9	23
17	2820	6580	2.33	15.9	27
18	1900	4370	2.30	16.1	25
19	2860	6780	2.38	16.1	27
31	810	2890	3.57	35.7	11
45	780	1340	1.73	29.7	17

[a] Entry numbers correspond to those of Table 1. Reported data are the average of two runs. Data for entries 31 and 45 are estimates due to chromatographic conditions.

Branching vs Polymer Melting Temperature. In an attempt to better quantify the length of the long branches, the melting temperatures of the ethylene homopolymers produced were compared to those of a series of linear low-density polyethylenes (LLDPEs) prepared by Mirabella and Crist.[15] We presumed that

Table 3. ^{13}C Peak Assignments[17]

peak no.	8	9	10	13	19	20	21	22	24	25	28	32	33
δ (ppm)	23.37	24.61	26.51	27.79	31.50	32.16	32.65	33.14	33.83	33.94	36.72	38.24	39.44
assignment	$2B_4$	1,5-$\beta'B_1$	$2B_2$	1,6-$\beta'B_1$	1,4-$\alpha'B_n$	$3B_n$, 1,4-$3B_n$	$3B_5$	brB_1, 1,5-brB_1, 1,6-brB_1	αB_2	$4B_4$	$3B_3$	1,4-brB_n	brB_2

any significant deviation of our polymers from the previously reported linear relationship would indicate that the branches in our polymer were significantly longer than the ethyl, butyl, and hexyl branches of the reported LLDPEs. Figure 6 compares the effect that branching has on polymer melting temperature. For our series of ethylene homopolymers prepared from **2**/MAO, the ethyl and long branches are combined to give the total branches per 1000. Compared to the ethylene/α-olefin copolymers[15] plotted in Figure 6, the homopolymers have considerably higher melting temperatures for a given branch density. This finding may suggest that many of the branches are long enough to participate in crystallites. This attribute would offset, partially, the disruption in crystallinity caused by the branch point itself and would lead to more crystallinity and higher melting temperatures than if the branches were assumed to have solely disruptive behavior.

Molecular Weight and Methylene Sequence Length Analysis. Gel permeation chromatography (GPC) analysis of several polymer samples suggests that the molecular weights of the polymers are too low for branches to be of rheological importance. Branches are not considered rheologically important if they are shorter than the entanglement length, generally taken as ~150 carbon atoms.[16] Thus, a polyethylene molecule having fewer than 450 carbon atoms (~6300 g/mol) does not contain a rheologically long branch. As shown in Table 2, GPC analysis indicates that the number-average molecular weights are below this threshold and therefore, the 10−50 "long" branches per 1000 carbon atoms consist statistically of rheologically insignificant branches of length C_6 < branch < C_{150}. In fact, our knowledge of the branch density suggests a narrower range than this. Considering the M_n of entry 18 (1900 g/mol), we calculate an average of 136 carbon atoms per macromolecule. The measured 16.1 long branches per 1000 carbon atoms (see Table 1) suggests that this sample averages 2.2 long branches per macromolecule. Thus, the average methylene sequence length ($-(CH_2)_n-$) is

$$n = [((M_n - 2)/14) - (N_L((M_n - 2)/14)/1000)] \div [(N_L((M_n - 2)/14)/1000) + (1 + (N_L((M_n - 2)/14)/1000))]$$

where the numerator is equal to the total number of methylene groups and the denominator tallies the average number of linear segments according to [no. of branches + (1 + no. of branch points)]. In the example of entry 18, $n = [(136) - (2.2)] \div [(2.2) + (1 + (2.2))] \approx 25$. The corresponding values of n for the other samples are listed in Table 2.

Conclusions

Homopolymers of ethylene were prepared under a variety of polymerization temperatures and ethylene pressures using the zirconium-based CGC **2** activated with MAO. Analysis of the polymer samples by ^{13}C NMR spectroscopy shows that the polymers *all* contain significant numbers of branches. The branches are found to be largely C_2 or $\geq C_6$, with low levels of C_1, C_3, and C_5 branches in some polymers and C_4 branches detectable in less than 10% of the samples. The density of ethyl branches was between 2 and 8 per 1000 carbons and was largely invariant to the polymerization conditions. The density of long branches ($\geq C_6$) was between 13 and 55 per 1000 carbons and responded in logical ways to the polymerization conditions. Polydispersity indices (M_w/M_n) near 2.0 were found, as expected from a single-site catalyst.

The branches are likely formed by a combination of two mechanisms. Ethyl branching can be explained by β-hydride transfer to monomer followed by immediate reinsertion of coordinated olefinic macromonomer. Longer branches, on the other hand, are formed by incorporation of free olefinic macromonomers into growing polymer chains—a generally unlikely process made feasible by the known proclivity of **2**/MAO toward α-olefins. Increased MAO:Zr ratios are found to induce additional long branches. Importantly, this single catalyst system offers a route for converting a pure ethylene feed into materials akin to LDPE or LLDPE, without the energetic requirements of a high pressure, high-temperature free radical reaction, or the expense and complications of α-olefins.

Experimental

Materials. Toluene was dried over elemental sodium and distilled under nitrogen into a Straus flask or filtered through an mBraun solvent filtration system, degassed and stored in a Straus flask until needed. Ethylene (polymerization grade) was obtained from Matheson and used following passage through a Matheson 6410 drying system equipped with an OXYSORB column. Precatalyst **2** was prepared as in reference 6a and stored as a 3.33 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.

Polymerizations. ***Caution!*** All polymerizations should be carried out in a fume hood behind a blast shield. Ethylene polymerizations 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 0.193 g of solid MAO (3.33 mmol, 1000 equiv) and 25 mL of toluene. Then 1.0 mL (3.33 μmol) of a 3.33 mM stock solution of **2** was drawn into a 5 mL Hamilton gastight syringe which was capped with a septum. The reactor was removed from the box to an oil bath at the desired temperature, pressurized with ethylene, and allowed to equilibrate for at least 10 min while stirring. After equilibration, the solution of **2** was injected and the solution immediately changed color from yellow to orange. The reaction was stopped by rapidly venting the reactor and pouring the polymerization solution into approximately 200 mL of 10% aqueous HCl in MeOH. This solution was stirred overnight to quench the MAO completely, and the polymer was collected by filtration, thrice rinsed with fresh methanol, and dried in vacuo.

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 16501.7 Hz, a pulse angle of 70°, and a recycle delay of 5.5 s to allow complete relaxation of the nuclei. 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 (Table 3).[17] Polymer melting temperatures were determined using a TA Instruments Q600 SDT differential scanning calorimeter under an argon purge at a heating rate of 10 °C/min from 25 to 180 °C. The melting temperature was taken as the maximum of the melting endotherm on the second heating cycle.

Peak numbers and carbon numbering xB_n follow the scheme outlined by Galland:[17] n gives the length (in carbon atoms) of the branch in question (1, 2, 3, 4, 5, or n for longer branches), with carbon atoms *x* numbered starting from the terminal methyl group; “br” refers to the backbone methine and Greek letters refer to the backbone methylene carbon atoms; and “1,4”, “1,5”, and “1,6” give the relative locations of closely spaced branches. 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; I_m refers to the normalized integral area under peak number *m*.

$$N_M = I_{22} - I_{13} - 2I_9$$

$$N_E = (I_{10} + I_{33})/2$$

$$N_P = I_{28}$$

$$N_B = I_8$$

$$N_A = I_{21}$$

$$N_L = I_{20} - (I_{19} + I_{32})/4$$

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Supporting Information Available: A scheme showing the basic reaction and structures, a table of polymerization results, and figures showing representative ^{13}C NMR spectra, DSC thermograms, and GPC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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