Investigations of Chain Shuttling Olefin Polymerization Using Deuterium Labeling

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ABSTRACT: Chain shuttling among olefin polymerization catalysts with differing monomer responses has been developed for the preparation of block copolymers with enhanced performance. The chain shuttling agent (CSA) is usually a main group alkyl complex that is able to exchange polymeryl chains with the catalysts. We have performed a diverse yet complementary set of polymerization experiments using a hafnium pyridyl−amide catalyst (**1**) and Oct_3Al as CSA. Ethylene/1-hexene copolymerization experiments using different amounts of CSA were quenched with D_2O after varied reaction times. In ethylene homopolymerizations with fairly constant polymer yields, M_w/M_n is less than 2 and decreases monotonically with the addition of CSA, indicative of chain shuttling. However, less than half of the available Al sites are occupied by polymer chains. This indicates that chain shuttling (polymeryl−polymeryl exchange) is kinetically competitive with chain transfer (polymer−alkyl exchange) in this system. This approach also allows a more complete accounting of the fates of each polymeryl and alkyl chain by using multiple characterization techniques (GPC, GC, and ^{2}H NMR). The mass balance agreement among these techniques is excellent, which validates our techniques and our basic understanding of chain shuttling processes. The results indicate that chain transfer to aluminum is the dominant termination mechanism under these conditions. Furthermore, ^{2}H and ^{13}C NMR experiments indicate that chain transfer from **1** to Oct_3Al occurs significantly faster after an ethylene insertion than after a hexene insertion.

Introduction

Polyethylene is the world's cheapest and most ubiquitous synthetic polymer. Global sales volume for 2006 was about 60 billion pounds of HDPE and 40 billion pounds each of LLDPE and LDPE. While HDPE and LDPE are ethylene homopolymers with relatively narrowly defined product specifications, LLDPE's are copolymers of ethylene and higher α-olefin comonomers and have much more structural variation and complexity. One key control variable is the amount of comonomer, which determines the density and crystallinity of the polymer. The comonomer disrupts the crystallinity of the polyethylene and therefore changes the properties from hard, brittle, and crystalline at low comonomer content to soft, elastomeric, and amorphous at higher comonomer content.

Several research groups have sought to combine the desirable properties of both the soft and hard polymer types by conjoining them in the form of a block copolymer. Block copolymers are most often synthesized by using a living catalyst and changing the reactor composition during chain growth, a protocol that has long been employed for styrenic polymers. In fact, some groups have successfully employed living catalysts for synthesis of ethylene-based block copolymers.[1] However, living polymer chain growth is stoichiometrically limited by the polymerization catalysts, which generally require multistep syntheses for polyethylene. In addition, the reported batch or semibatch reactor conditions might suffer commercially from lower production rates and from the practical difficulty of quickly changing reactor composition to produce sharp block junctions. Researchers at Dow recently discovered a new approach to block copolymer synthesis called chain shuttling. The chain shuttling process uses a continuous reactor with constant monomer composition, which is enabled by using catalysts of differing monomer reactivity with a chain shuttling agent (CSA) that exchanges live polymer chains among active catalyst sites (Figure 1).[2] In this way, polymer chain production is not limited stoichiometrically by polymerization catalyst or CSA. Chain shuttling generates a new type of block copolymer architecture with demonstrably advantaged performance compared to random copolymers,[3] and Dow anticipates the commercialization of some of these olefin block copolymers (OBC's) under the tradename INFUSE (trademark of the Dow Chemical Company).

More recently, an alternative approach to living polymerization using continuous reactors in series and a catalyst/CSA system which also produces multiple polymer chains per catalyst was reported.[4] In this application, the CSA acts as a reservoir for growing polymer chains as they pass from a first reactor into a second reactor, which has different monomer concentrations than the first. In this way, the block copolymers are produced in a stoichiometric fashion relative to CSA, instead of the catalyst.

The key parameter for effective shuttling, the relative rate of shuttling to propagation, is expected to be determined by the [CSA]/[monomer] ratio. Thus, both of the aforementioned chain shuttling approaches are most effective under continuous reactor conditions at high monomer conversions.[2a] However, it is both simple and instructive to examine single-catalyst polymerization experiments using batch or semibatch reactors. Under these conditions, chain shuttling can narrow molecular weight distribution, approaching living polymerization behavior if shuttling is very fast.[2,5] In fact, batch reactor experiments, when carried out with minimal concentration changes (low monomer conversion), can be more desirable for fundamental investigations of chain transfer behavior, since the distribution of residence times in continuous reactors can complicate the analysis of molecular weight distributions.

The emerging role of chain transfer phenomena in the development of olefin block copolymer technology prompted us to undertake more detailed investigations of the underlying reaction steps. Specifically, a series of semibatch polymerization reactions using a known chain shuttling catalyst/CSA pair were conducted, systematically varying yield and CSA loading. Furthermore, quenching the polymerization with D_2O labels the chains that reside on the CSA (or catalyst), providing a measure

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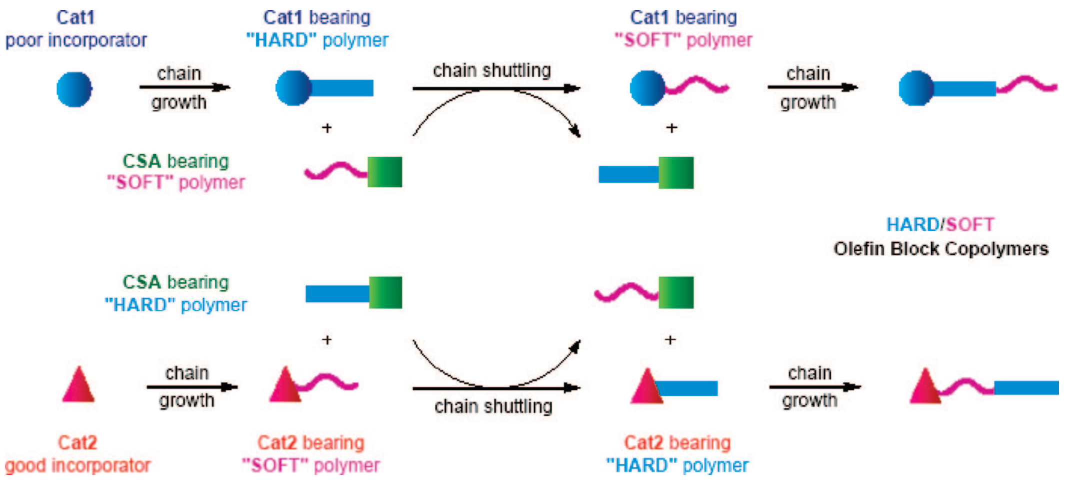

Figure 1. Schematic illustrating the chain shuttling process to produce hard/soft linear olefin block copolymers using chain shuttling polymerization.

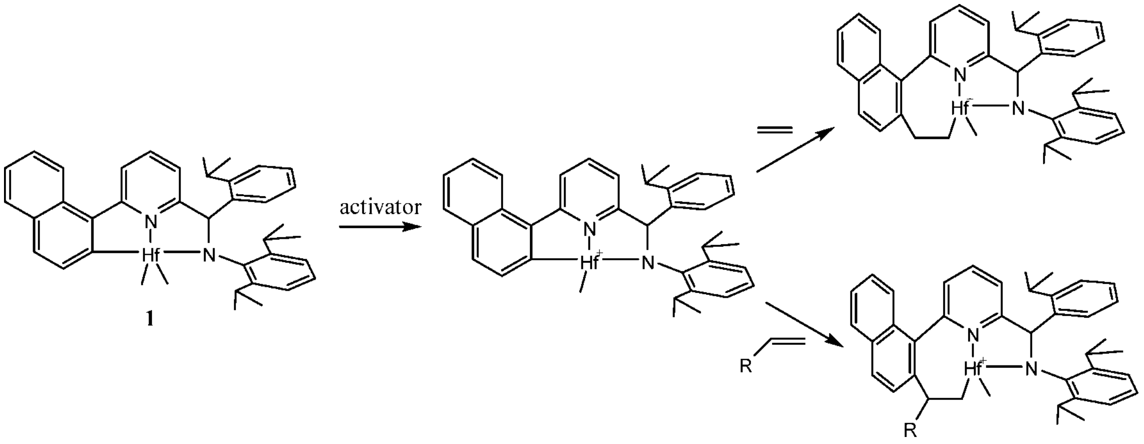

Figure 2. Structure and activation of **1** showing ligand modification by monomer, which generates multiple active species.

of the extent of chain transfer (i.e., the fraction of potential CSA sites bearing polymeryl chains). This ^{2}H label also allows for characterization of the polymer terminus using ^{2}H and ^{13}C NMR, providing information about the relative rate of chain transfer after insertion of ethylene relative to α-olefin. ^{2}H quench experiments have been used by Landis for active site counting and mechanistic elucidation in the absence of chain transfer agents,[6] and others have used ^{3}H quench experiments as mechanistic probes.[7]

Results and Discussion

These studies require a catalyst that undergoes fast chain transfer and chain shuttling reactions and is also able to incorporate α-olefins. The pyridyl-amide hafnium catalyst **1** (Figure 2) was selected to meet these requirements.[2,8] For the CSA, Oct_3Al was chosen because the relatively nonvolatile product of its reaction with D_2O, 1-*d*-octane, can be readily quantified by GC. This measurement in turn allows measurement of the overall distribution of chain types at the end of the reaction, and serves as an internal check for the validity of our measurements.

Effect of CSA Load on Polydispersity. We began our study with a relatively simple series of experiments using no α-olefin and varying levels of CSA (runs 1−5, Table 1). These ethylene homopolymerization runs are the most indicative test of chain shuttling as opposed to simple chain transfer, because chain shuttling generates polymer with a narrow molecular weight distribution whereas chain transfer broadens it.[9] It is especially difficult to generate narrow molecular weight distribution ethylene/α-olefin copolymers with **1**, because it is modified by monomer(s) during its activation to generate multiple catalysts with differing molecular weight capabilities (Figure 2).[6b] Thus, performing these initial experiments in the absence of comonomer reduces the possible number of catalysts generated. The polymer yields were also held relatively constant, using the same catalyst loading and similar polymerization times, in order to minimize the effects of monomer conversion on molecular weight distributions (vide infra). Using the highest CSA loading, polyethylene is generated with $M_w/M_n = 1.47$. This narrow distribution cannot be obtained by simple chain transfer and is a clear indicator of chain shuttling. Furthermore, the molecular weight and PDI both decrease markedly and monotonically as the CSA loading is increased. This progression results from a simple kinetic phenomenon: higher CSA concentrations provide more alkyl chains available for shuttling.

The number of polymer chains is easily calculated from the polymer yield and the M_n as determined by GPC.[10] Assuming that chain transfer to aluminum is the dominant chain termination mechanism, this number allows us to calculate a “CSA fill ratio”, which is simply the ratio of Al-bound polymer chains to initial aluminum alkyl groups[11] ($3 \times Oct_3Al + 1 \times$ MMAO). Interestingly, less than half of the available aluminum sites are filled in these experiments. Thus, the effects of chain shuttling are observed for this catalyst/CSA pair even prior to complete conversion of alkyls to polymeryls on the CSA. This implies

Table 1. Batch Polymerization Results for Polymerizations Performed at 80 °C with 100 psig C_2H_4 using 2.0 μmol of Catalyst 1 and 2.0 μmol of $[R_2NMeH][B(C_6F_5)_4]$

Run#	Oct_3Al (mmol)	MMAO (mmol)	1-hexene (g)	Time (min)	Polymer Yield (g)	Mn (GPC)	PDI (GPC)	Oct-D (mmol)[a]	poly-D (mmol)[b]	poly-D + Oct-D (mmol)	Al Sites[c]	CSA Fill Ratio[d] (^2H NMR)	Mn (^2H NMR)
1	0.25	0.1	0	3.6	5.9	15427	2.03	nd	nd	nd	0.85	0.45[e]	nd
2	0.5	0.1	0	4	5.2	8676	1.92	nd	nd	nd	1.6	0.37[e]	nd
3	1	0.1	0	3.5	6.1	4560	1.7	nd	nd	nd	3.1	0.43[e]	nd
4	2	0.1	0	4.2	6.4	2781	1.61	nd	nd	nd	6.1	0.38[e]	nd
5	4	0.1	0	5.2	5.1	1763	1.47	nd	nd	nd	12.1	0.24[e]	nd
6	0.25	0.1	40	3.2	11.4	33940	1.95	0.54	0.37	0.9	0.85	0.44	30811
7	0.5	0.1	40	3.3	10.8	15996	2.07	1.01	0.66	1.68	1.6	0.41	16364
8	1	0.1	40	3.3	9.5	6560	2.1	1.99	1.29	3.28	3.1	0.42	7364
9	2	0.1	40	4.1	9.1	3349	2.04	4.39	2.22	6.61	6.1	0.36	4099
10	4	0.1	40	4.7	7.7	1235	2.59	9.52	3.18	12.69	12.1	0.26	2421
11	8	0.1	40	5.5	6.8	794	2.25	21.54	4.38	25.92	24.1	0.18	1553
12	2	0.1	40	3.6	8.7	3454	1.97	nd	1.73	nd	6.1	0.28	5033
13	2	0.01	40	6.4	28.8	5139	1.96	nd	4.02	nd	6.01	0.67	7156
14	2	0.01	40	30	36.1	5849	1.92	nd	4.57	nd	6.01	0.76	7901
15	2	0.01	40	12.4	51	9710	2.07	nd	5.05	nd	6.01	0.84	10097

[a] Determined by GC integration relative to nonane internal standard. All samples were exclusively monodeuterated as determined by GC/MS. [b] Determined by ^2H NMR integration relative to C_6D_6 internal standard. [c] Total aluminum alkyl functionality (3 × Oct_3Al + 1 × MMAO). [d] Ratio of polymeryl chains to total aluminum alkyl functionality. [e] Determined using GPC.

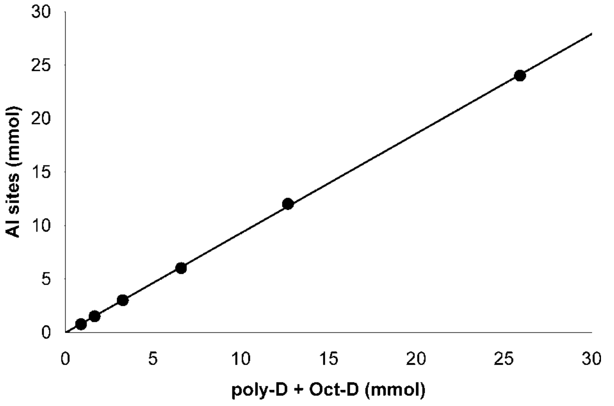

Figure 3. Mass Balance for Chain Shuttling Reaction. Amounts of ^2H-terminated polymer and 1-*d*-octane were determined by ^2H NMR and GC, respectively.

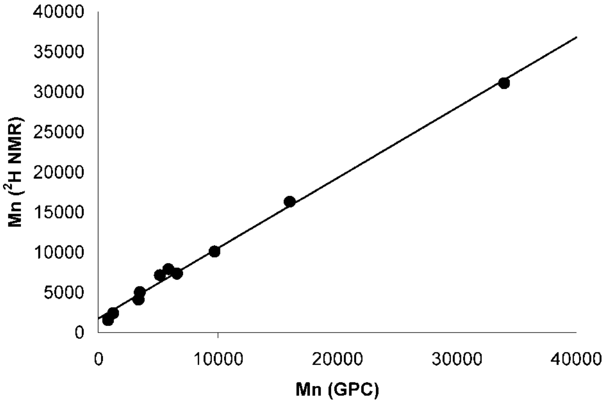

Figure 4. Comparison of M_n determined by GPC to M_n determined by ^2H NMR.

that Oct_3Al may be a good model for $(polymeryl)_3Al$, which can simplify mathematical analysis of the reaction kinetics.[12]

Chain Growth Mass Balance. The CSA provides a number of sites during the polymerization process that are occupied by either an alkyl from the original CSA or by a polymer chain. Higher monomer conversion (greater extent of polymerization) is expected to result in more polymeryl chains and fewer alkyl chains on the CSA. To demonstrate this process experimentally, we performed several copolymerization reactions using **1** and Oct_3Al (TOA). After a predetermined time the mixture was hydrolyzed by adding D_2O, which permitted the quantification of the number of Al-bound polymer chains and octyl groups at the time of the D_2O quench. The polymers typically contain 13−16 mol % hexene, so the contribution of natural abundance ^2H from methyl groups on side chains is expected to be very minor.[13] We also varied the CSA loading under copolymerization conditions, holding other variables constant. The results are tabulated in Table 1 (runs 6−15).

In Figure 3. we plot the observed total chains (polymer + octane) against the calculated number of aluminum sites in the reactor. The linear fit is remarkably good ($R^2 = 0.9998$), with a slope of 0.93 (theoretical = 1.00) and intercept of 0.046 (theoretical = 0.000). This excellent agreement validates our analytical methods and demonstrates mass balance consistent with our fundamental understanding of the chain shuttled polymerization reaction.

Predicted M_n. Assuming that there are no significant chain termination mechanisms (e.g., β-hydrogen elimination) other than transfer to CSA, ^2H NMR can be used to estimate M_n, which is simply the ratio of polymer yield to number of polymer chains. Shown in Table 1 are molecular weight data as predicted by this method compared to the values as measured by GPC, and illustrated graphically in Figure 4. The linear fit is excellent ($R^2 = 0.995$). The slope is 0.88 and the intercept is 1766. We interpret this excellent agreement as confirmation that chain transfer to aluminum is by far the most kinetically relevant termination mechanism for **1** under these conditions.

Chains/CSA. There is a clear relationship between CSA fill ratio and polymer yield (conversion), as shown in Figure 5. We plot only copolymers (runs 6−15) here since the homopolymers (runs 1−5) are generated using a different protocol. Also, the CSA fill ratio is calculated from the ^2H NMR integrations (rather than GPC) to minimize any complicating effects from other termination mechanisms. In fact, the data can be fit to a simple first-order (exponential) decay of [CSA]. However, the actual chain transfer constant cannot be derived from this fit since the active catalyst concentration changes during the experiment due to catalyst initiation and deactivation.

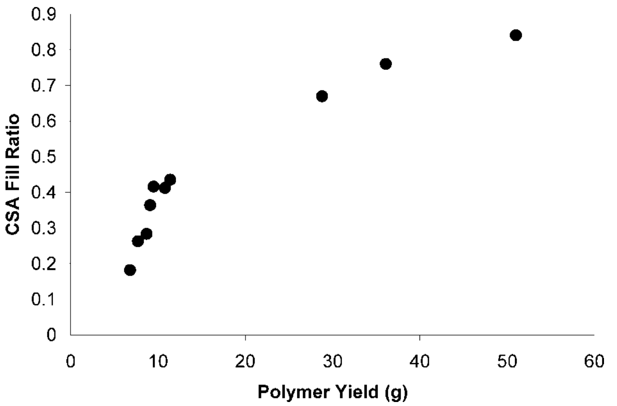

Figure 5. Relationship between CSA fill ratio and polymer yield. The CSA fill ratio is the fraction of Al sites bearing a polymer chain at the end of the polymerization.

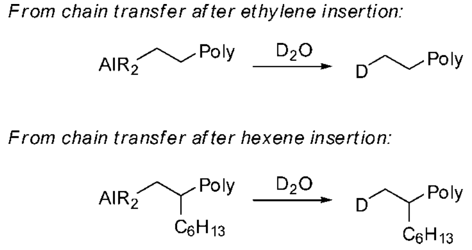

Figure 6. Polymer end group dependence on selectivity of chain transfer.

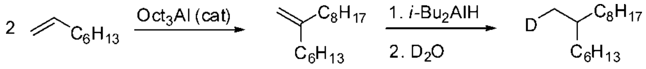

Figure 7. Synthesis of a Model for a Branched Chain End.

Selectivity of Chain Transfer in **1**. In ethylene/hexene copolymerization, it is possible for shuttling to occur either after an ethylene insertion or after a hexene insertion. Gibson et al. have observed exchange of linear alkyls to be faster than linear-for-branched exchange.[5b] However, Busico and Stevens have shown that chain shuttling rates in polypropylene, which requires exchange of isoalkyl groups, can be enhanced by using a polar solvent.[14] By quenching a polymerization reaction with D_2O, we are able to distinguish the polymer's terminal carbon in $^{13}C\{^1H\}$ NMR from the side chains because the signal displays coupling to the ^2H nucleus, allowing us to determine the nature of the last-inserted monomer prior to chain transfer (Figure 6).

In order to assign the end group type, model compounds were prepared. As a model for straight-chain end groups, d_1-octane was prepared by simply adding D_2O to Oct_3Al. To model the branched-chain end group, we synthesized $DCH_2CH(C_6H_{13})(C_8H_{17})$ in two steps, as shown in Figure 7.

The spectra in Figure 8 and Figure 9 unambiguously demonstrate that the polymer chain end carbon is not adjacent to a branch point. We therefore conclude that chain transfer occurs highly preferentially after ethylene insertions when catalyst **1** is used with Oct_3Al as CSA. This result is easily explained by simple steric arguments.

Conclusions

While chain transfer to aluminum has long been recognized as a prominent chain termination mechanism, the utility of chain shuttling for forming block copolymers has only recently been exploited.[2a] The experiments described here were performed to further our understanding of chain shuttling and to optimize our ability to design better polymers. We used semibatch reactor experiments with D_2O quench to elucidate some of the fundamental aspects of chain shuttling polymerization. In ethylene homopolymerization, chain shuttling leads to low M_w/M_n values that decrease at higher CSA loading, as predicted. The mass balance is very good and accounts for the fate of all aluminum-bound alkyl and polymeryl chains. Interestingly, the molecular weight narrowing effect of chain shuttling is apparent well prior to the exhaustive conversion of aluminum alkyls to polymeryl chains, implying that chain shuttling is kinetically competitive with chain transfer for this catalyst/CSA combination. A good correlation was found between monomer conversion (polymer yield) and CSA fill ratio, which is the fraction of aluminum valencies occupied by polymeryl chains. Furthermore, this work implies that chain transfer between **1** and trioctylaluminum during an ethylene-hexene polymerization occurs selectively after insertion of ethylene. This preference was expected from previous work, but this is the first observation of this effect via direct competition of two monomers.

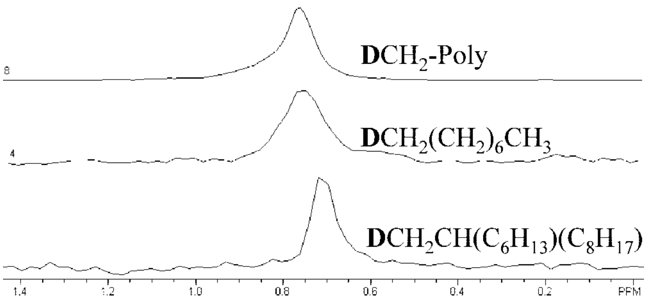

Figure 8. ^2H NMR for end-functionalized polymer, and for model compounds.

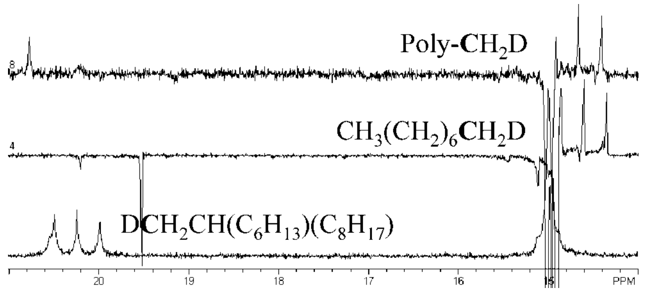

Figure 9. $^{13}C\{^1H\}$ NMR spectra for end-functionalized polymer and model compounds. The top two spectra were acquired using an APT pulse sequence to more clearly show the deuterated methyl peak.

Experimental Section

All NMR spectra were recorded on a Varian INOVA 300 MHz instrument, operating with a wide-bore probe, using 10-mm diameter tubes. GC measurements were performed using an HP5890 with a 20 m DB-1 column using standard calibration methods.

Batch Polymerization Runs. Polymerization reactions are performed using a one-liter stainless steel Parr reactor with a removable stainless steel liner. Temperature control is achieved using 50 psig steam and chilled water for heating and cooling, respectively. In a typical run, the reactor is dried by heating at >105 °C for 30 min under a nitrogen purge (500 sccm). All gases and solvents are dried and deoxygenated immediately prior to use. Hexane (600 mL) is charged to the reactor, and the reactor is briefly purged with nitrogen (200 sccm) while stirring. Then 1-hexene (40 mL, if required), nonane internal standard (0.6804 g), and trioctylaluminum (0.25 mmol) are sequentially charged by syringe. In a glovebox, catalyst **1**, $[R_2NMeH][B(C_6F_5)_4]$ ($R = C_{14}-C_{16}$ alkyl), and MMAO are combined and transferred to a length of $^1/_4$ in. stainless steel tubing capped on one end by a ball valve and connected on the other end via another ball valve to a 50-mL stainless steel sample cylinder containing toluene (5 mL). This catalyst injection assembly is attached to the reactor head and 200 psig nitrogen is applied to the sample cylinder. The reactor is then heated to 80 °C and pressurized to 125 psig (100 psig ethylene partial pressure). The catalyst is added by opening both ball valves. Ethylene pressure is maintained throughout the polymerization reaction. After the allotted reaction time, the polymerization is quenched by addition of D_2O (1.0 mL), maintaining rapid stirring. After cooling to near room temperature, the reactor is opened, and the polymer is collected and dried in a vacuum.

^{2}H NMR of Polymers. For ^{2}H NMR spectra, the polymer (ca. 200 mg, accurately weighed) is dissolved in 0.010 M C_6D_6 in tetrachloroethylene (3.00 mL). Spectra are acquired using a 90°pulse, and a preacquisition delay of 6.0 s. In a representative sample, T_1 values for the ^{2}H nuclei of C_6D_6 and ^{2}H-terminated polymer were found to be 1.08(9) and 0.32(3) s, respectively. The relative integrated intensities of the signals at δ 7.15 and 0.75 ppm were used to determine the number of chains in the polymer sample. A broad signal of low intensity at δ 0.76 was typically observed, assigned to natural abundance ^{2}H in the polymer.

^{13}C NMR of Polymers. Typically, after acquiring the ^{2}H spectrum, additional C_6D_6 (0.5 mL) was added to allow a deuterium lock during acquisition and chromium(III) tetramethylheptanedionate $Cr(TMHD)_3$ (0.16 mmol) was added to aid relaxation. Spectra were acquired using a 90° pulse, and a 4.0 s delay. Hexene incorporation was estimated by the integral ratio of the methyl quartet at δ 15.0 ppm to the other peaks at δ 40−22 ppm, and found to range from 13 to 16 mol % in the copolymer samples.

Synthesis of $DCH_2CH(C_6H_{13})(C_8H_{17})$. Using the classic Ziegler olefin dimerization process, 1-octene (5.0 mL, 36 mmol) was heated at reflux temperature with Oct_3Al (6 mol %) for 20 h. Quenching an aliquot with water indicated that most of the octene was consumed. To the cooled vial was then added $^iBu_2AlH$ (3.0 mL, 17 mmol) and the mixture was stirred at ambient temperature for 13 days. The resulting adduct was quenched while cooled in an ice−water bath with D_2O (1.1 mL), added at such a rate that the temperature of the solution/slurry never exceeded 30 °C. After the aqueous layer was removed, the hydrocarbon layer was stirred over sodium sulfate and filtered to yield a solution composed of two layers, with the upper layer having significantly more volume. The upper layer was analyzed by GC/MS, which showed that there was about 27% of the octene dimer left (but this would not affect our analysis). The major product was of molecular weight *m*/*e* 227 with no evidence of *m*/*e* 226, the expected molecular weight of the undeuterated product alkane.

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(9) Provided that the experiments are terminated at relatively low monomer conversion (see ref 12).

(10) ^{2}H NMR spectra were not measured for ethylene homopolymers due to poor polymer solubility.

(11) A small amount of MMAO was added as a scavenger in the catalyst activation (see Experimental Section).

(12) Arriola et al. submitted to *Macromolecules*.

(13) Consider the "worst case" scenario of $M_n = 35\,000$ for polymer with 16 mol % hexene. An average polymer chain has about 151 methyl groups, corresponding to 453 hydrogen atoms. With ^{2}H natural abundance of 0.015%, this corresponds to 0.07 ^{2}H atoms.

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