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Living and Block Copolymerization of Ethylene and α-Olefins Using Palladium(II)−α-Diimine Catalysts

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ABSTRACT: Living polymerizations of ethylene with palladium(II) diimine complexes coupled with use of a functionalized initiator and/or cleavage of the palladium−polymer bond with various reagents provides a protocol for synthesis of mono- and di-end-functionalized, branched, amorphous polyethylenes. The functional initiator used is the chelate complex $[(ArN{=}C(Me){-}C(Me){=}NAr)\overline{Pd(CH_2)_3C(O})OMe][(BAr'_4)]$ ($Ar = 2,6\text{-}(iPr)_2C_6H_3$) (**3**). The alkyl chain is cleaved by insertion of alkyl acrylates or methyl vinyl ketone, followed by cleavage with Et_3SiH to generate alkyl ester or methyl ketone end groups, respectively. Insertion of 5-hexen-1-ol, followed by chain running and β-elimination, results in formation of aldehyde end groups. Conditions for living polymerization of propylene, 1-hexene, and 1-octadecene have also been established. Rates of first monomer insertion and subsequent chain growth are shown to be a sensitive function of the palladium complex used for initiation and the nature and concentration of auxiliary nitrile ligands. Block copolymers of ethylene and 1-octadecene were prepared under living conditions. The copolymer microstructure differed depending on the order of introduction of the blocks.

Introduction

The key feature of living polymerization is that chain growth occurs without significant chain transfer or termination. Living polymerization techniques allow the synthesis of polymers with control of the average M_n and narrow molecular weight distributions as well as block copolymers and end-functionalized materials. Transition-metal-catalyzed polymerization of olefins in a living fashion via a coordination−insertion mechanism is frequently frustrated by facile chain transfer processes, especially β-elimination and chain transfer to aluminum activators. The past few years have witnessed a growing number of reports of transition metal catalysts which have achieved living polymerizations of ethylene and α-olefins.[1] In this regard, more progress has been reported for α-olefins than for ethylene.

Much of the groundwork in this area was laid by Doi who described living polymerization of propylene using derivatives of $V(acac)_3$ activated with aluminum alkyls.[2] These catalysts exhibit living character only at low temperatures (−78 °C) which favor a high ratio of the propagation rate to the chain transfer rate. Doi also showed that these systems could be used to prepare end-functionalized polypropylene[3] as well as polypropylene/polyethylene block and copolymers.[4] More recent examples of early metal catalysts which carry out living polymerizations of α-olefins at much higher temperatures have been reported by McConville (Ti),[5] Kim (Zr),[6] Schrock (Zr, Hf),[7] Sita (Zr),[8] Shino (Ti),[9] Fukui (Zr, Hf),[10] Kol (Zr, Ti),[11] Coates (Ti),[12] and Fujita (Ti).[13] Examples of early transition metal complexes which have been shown to polymerize ethylene in a living fashion include Mashima's $C_5Me_5M(butadiene)X_2/MAO$ (M = Nb, Ta) systems,[14] which operate at −20 °C, and Fujita's highly active bis(salicylaldiminato)titanium-based catalysts.[15]

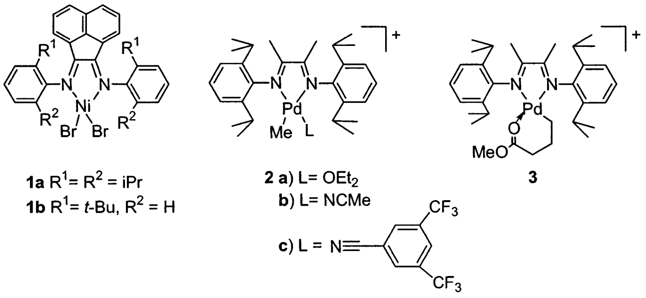

Figure 1. Ni and Pd α-diimine catalysts.

Our interests have centered on developing late metal catalysts for olefin polymerizations, and in connection with those studies we have probed the possible use of these systems for living polymerization. Attractive features of these late metal systems include production of polymers with quite different microstructures relative to early metal systems, compatibility with polar solvents and certain functionalized olefins, and facile incorporation of chain-end functionality. The first system examined, the cobalt(III) catalyst $[C_5Me_5P(OMe)_3CoCH_2CHR\text{-}\mu\text{-}H]^+$ (R = H, alkyl), polymerizes ethylene in a living fashion at 25 °C (M_w/M_n ∼1.1−1.2 up to M_n = 20 000) and, using functionalized initiators, produces end-capped polyethylene.[16]

More recently, our focus has shifted to Ni and Pd α-diimine catalysts. The Ni complexes **1a**,**b** (Figure 1) polymerize α-olefins in a living fashion at −10 °C in dilute monomer solutions.[17] High molecular weight polymers with quite narrow molecular weight distributions can be obtained (for example, polypropylene M_n = 161 000, M_w/M_n = 1.13; poly(1-hexene) M_n = 44 000, M_w/M_n = 1.09.) Block polymers of various α-olefins were also prepared and exhibit unusual properties since, due to a chain-straightening mechanism, long chain α-olefins such as 1-octadecene are crystalline in contrast to polypropylene and poly(1-hexene) which are amorphous materials.

The Pd α-diimine catalysts **2b** and **3** have been shown to carry out living polymerization of ethylene at 5 °C

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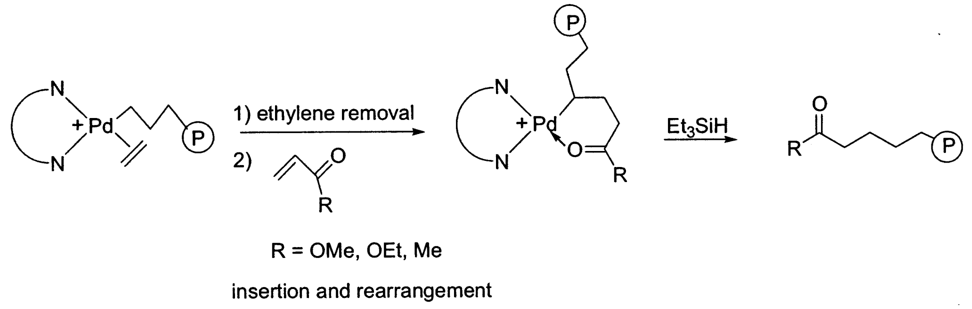
Scheme 1. End-capping of Polyethylene with Functionalized Olefins



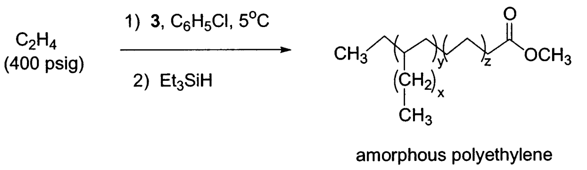
under 400 psi ethylene.[18] Quenching the polymerization reaction with silane, which cleaves the Pd–C bond to generate a saturated end group, proved to be critical in obtaining monomodal polymers with narrow molecular weight distributions. Without the silane quench, some chain coupling occurs which results in polymers with bimodal distributions. Amorphous, highly branched polyethylene (~100 branches per 1000 Cs) with M_n values greater than 100K and M_w/M_n's less than 1.1 could readily be prepared. This system was also used to prepare polyethylene macromonomers with functional end groups that were copolymerized with *n*-butyl acrylate via ATRP.[19]

In this manuscript, we describe extension of our studies of Pd α-diimine-catalyzed living polymerization of ethylene to include the following: (1) use of this catalyst system to prepare mono- and di-end-functionalized amorphous polyethylene; (2) demonstration of living polymerization of α-olefins; (3) preparation of 1-octadecene/ethylene diblock polymers with unusual microstructures.

Results and Discussion

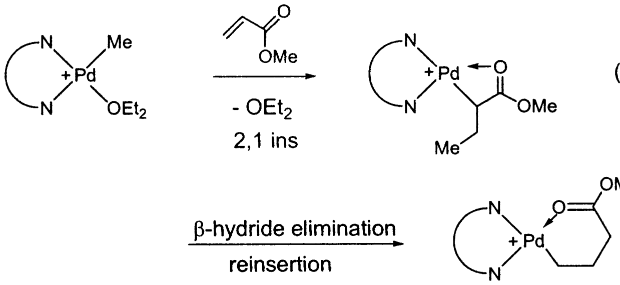
A. End-Capped Polyethylene. A number of methods have been previously described for end-functionalizing polyolefins prepared through a coordination/insertion mechanism. A common method involves cleavage of the metal–carbon bond with various reagents following chain growth. For example, in the Doi vanadium systems, cleavage of the vanadium–carbon bond with I_2 results in production of an iodo end group,[3a] reaction with CO/H$^+$ results in a terminal aldehyde,[3d] propylene oxide/H$^+$ yields predominantly a secondary alcohol,[3e] and styrene/H$^+$ provides an aryl end group.[3e] Numerous chain transfer agents have been used to end cap polymers and oligomers. The advantage of this method is that many chains per metal center can be generated but this high productivity comes at the expense of broader molecular weight distributions, typically about 2. Examples of molecules successfully used as chain transfer agents include silanes,[20] boranes,[21] thiophene,[22] and allyl alcohol.[23] A less common method of end-capping has been the use of functionalized initiators, which introduce a functional group at the start of the chain rather than after chain growth.[16]

As reported in our earlier communication, polymerization of ethylene with catalyst **2b** (Figure 1) followed by quenching with Et$_3$SiH results in a fully saturated, unfunctionalized, amorphous polyethyelene.[18] However, reaction of ethylene with the functionalized initiator generated from methyl acrylate insertion into the Pd–CH$_3$ bond of **2a** (the chelate complex **3**,[24] Figure 1) followed by silane quench yields saturated polyethylene end-functionalized with a methyl ester group as shown in eq 1.



(1)

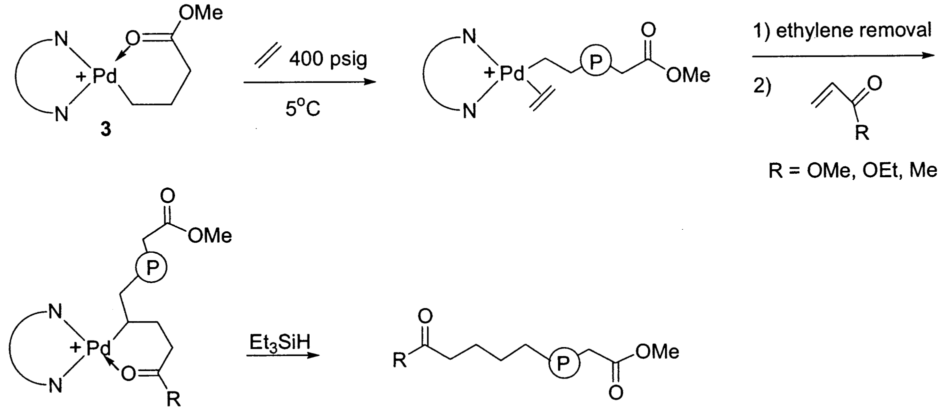
Taking advantage of the ability of alkyl acrylates to insert into a Pd–C bond and form chelates which do not exhibit further insertion chemistry with acrylates (as shown in eq 2), we have developed a method for end-capping the polymer following chain growth. This procedure is outlined in Scheme 1.



(2)

Ethylene was polymerized with catalyst **2c** for 1 h at 5 °C and 400 psi ethylene (high pressures are generally required to ensure rapid initiation.) After 1 h, all of the ethylene was purged from the reactor and 200 equiv of methyl acrylate were added. After 1 h, the time required for complete acrylate insertion, the catalyst was quenched by addition of Et$_3$SiH. A turnover frequency of 216/h was calculated on the basis on moles of catalyst employed per weight of polymer produced. The ^{1}H NMR spectrum of the isolated polymer showed the presence of the ester end group and was without olefinic resonances. The polymer prepared by this method was identical in all respects (including integral ratios and yield) to the material prepared from chelate initiator **3** (1 h, 5 °C, 400 psi ethylene) followed by silane quench which introduces the ester end cap at the beginning of the chain. Similar terminal end-capping procedures employing ethyl acrylate and methyl vinyl ketone produced polyethylene end-functionalized with ethyl ester and methyl vinyl ketone end groups, respectively. In the case of methyl vinyl ketone, longer times and higher temperatures (18 h, 25 °C) were used to ensure complete insertion.

Scheme 2. Synthesis of Telechelic Polyethylene



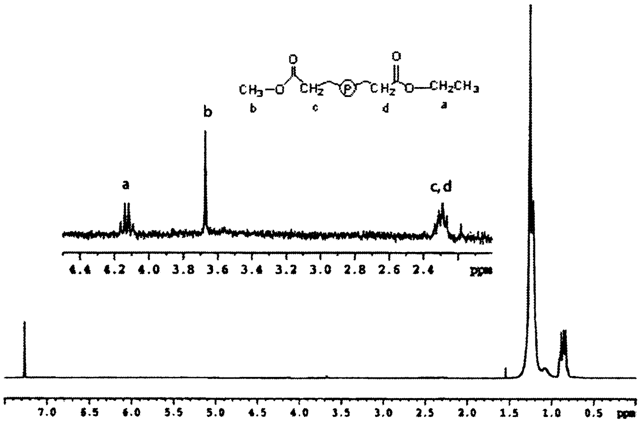


Figure 2. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C) of telechelic polyethylene end-capped with both a methyl ester and an ethyl ester end group. (The inset shows a blowup of the 4.5–2.0 ppm region to reveal end groups.)

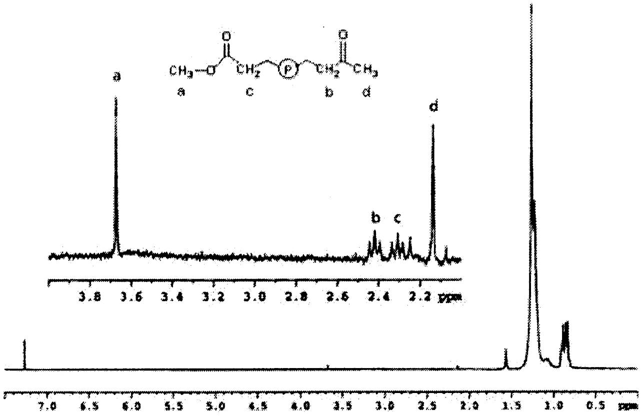
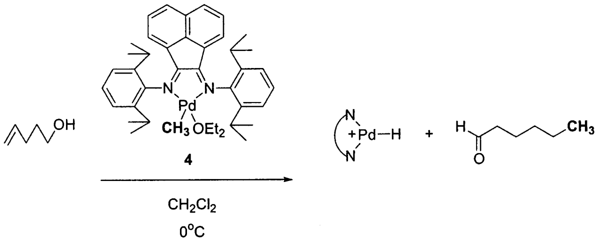


Figure 3. ^1H NMR ($CDCl_3$, 400 MHz, 25 °C) of telechelic polyethylene end capped with both a methyl ketone and a methyl ester end group. (The inset shows a blowup of the 4.0–2.0 ppm region to reveal end groups.)

By a combination of the functionalized initiator **3** and the end-capping procedure described above, difunctional (telechelic) polyethylene could be prepared. The general method is outlined in Scheme 2.

To prepare the polyethylene bearing one methyl ester and one ethyl ester group, the following procedure was used. Chelate complex **3** was exposed to ethylene for 1 h (5 °C, 400 psi) after which ethylene was purged from the solution and 200 equiv of ethyl acrylate were added. After 2 h, Et_3SiH was added, and the polymer was isolated in the usual way. The ^1H NMR spectrum of the polymer is shown in Figure 2. Again, no olefinic resonances are present, and the 3:2 integral ratio of the methyl group of the methyl ester at 3.68 ppm to the methylene quartet of the ethyl ester at 4.1 ppm indicates a molar ratio of ester groups of 1:1. This ratio firmly establishes that the introduction of the ester functional group following chain growth is highly efficient; otherwise, the molar ratio of ethyl ester to methyl ester would have been less than 1. Figure 3 shows the ^1H NMR spectrum of the telechelic polymer containing one methyl ester group and one methyl ketone group prepared from initiation with **3** and quenching with methyl vinyl ketone. Again, an integral ratio of functionalities of 1:1 is established.

One other telechelic technique was developed to end-cap polymers with an aldehyde group. In unpublished work,[25] we have shown that 4-penten-1-ol will insert into the Pd–CH_3 bond of **4** and, following Pd migration down the chain, the alkyl complex will undergo β-hydride elimination to yield an aldehyde (eq 3).

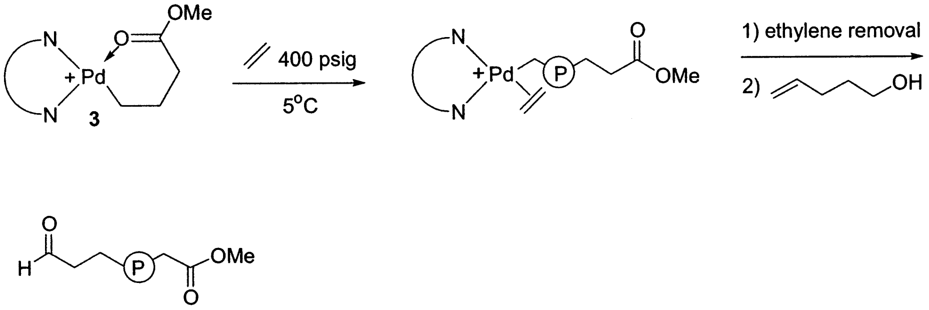


(3)

This reaction can be used to end-cap polyethylene following chain growth. The polymerization method using the chelate initiator **3** and quenching with 4-penten-1-ol is outlined in Scheme 3. The ^1H NMR spectrum of the polyethylene prepared using this procedure exhibits an aldehyde CH resonance at 9.78 ppm and a methyl ester resonance at 3.68 ppm in a 1:3 intensity ratio confirming successful quantitative end functionalization.

B. Living Propylene Polymerization. After ethylene was successfully polymerized in a living manner with the Pd(II) α-diimine catalysts, efforts turned to living polymerization of α-olefins. Initial attempts to polymerize propylene were carried out with the chelate catalyst **3**. The results obtained using 1 atm of propylene at 0 °C were inconsistent and often reflected very little catalyst activation for polymerization. To initiate propylene polymerization, the alkyl propylene complex must be generated through palladium chelate opening and propylene coordination. Since the bulkier propylene

Scheme 3. Synthesis of Telechelic Polyethylene with an Aldehyde End Cap



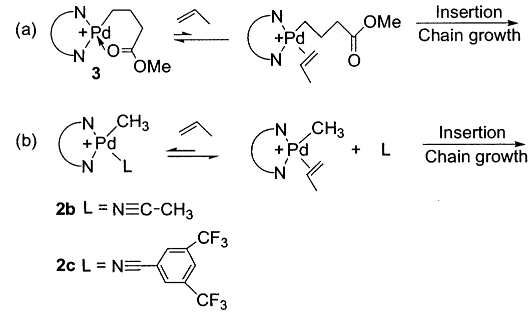


Figure 4. Initiation of propylene polymerization using Pd(II) α-diimine catalysts

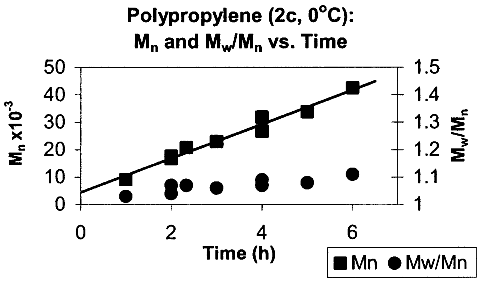


Figure 5. Plot of M_n and M_w/M_n as a function of reaction time for the polymerization of propylene (1 atm) [0 °C; catalyst **2c** (5×10^{-6} mol) in 20 mL of chlorobenzene; Et_3SiH quench].

has a lower binding affinity than ethylene and since the carbonyl oxygen of the chelate is fairly strongly bound to palladium, the propylene concentration at 1 atm is not sufficient to shift the equilibrium appreciably to the palladium propylene complex as shown in Figure 4a. Quantitative aspects of this equilibrium have been studied and support this contention.[24] This unfavorable equilibrium results in extremely slow initiation.

To circumvent the chelate problem, catalyst **2c** (Figure 1) which features the weakly bound, electron-deficient 3,5-bis(trifluoromethyl)benzonitrile ligand was employed. Using this ligand, the equilibrium shown in Figure 4b apparently lies sufficiently far to the right to provide an initiation rate comparable to the propagation rate since living behavior is observed. The results of polymerization of propylene in chlorobenzene at 0 °C under 1 atm of propylene are summarized in Figure 5. As with ethylene polymerizations, solutions are quenched with Et_3SiH prior to work up.

The plots in Figure 5 show a linear increase in polypropylene molecular weight with time accompanied by a narrow molecular weight distribution. The average turnover frequency based on the weight of polymer produced vs moles of catalyst employed at 0 °C in 20 mL of chlorobenzene under 1 atm of propylene (5×10^{-4} M in **2c**) was constant at approximately 100 turnovers per hour. At M_n values above ca. 40K, there was a broadening of the polypropylene molecular weight distribution accompanied by the appearance of a low molecular weight tail in the GPC traces, indicating catalyst decomposition. These systems are thus not as long-lived as the ethylene polymerization systems where polymers with M_n's of up to 200K can be achieved with molecular weight dispersities of less than 1.1.

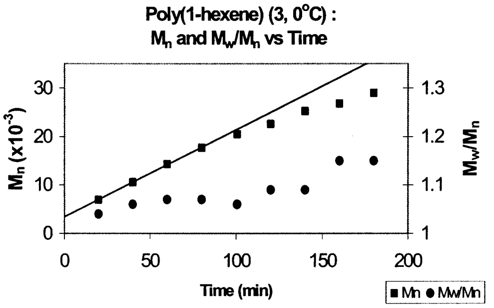
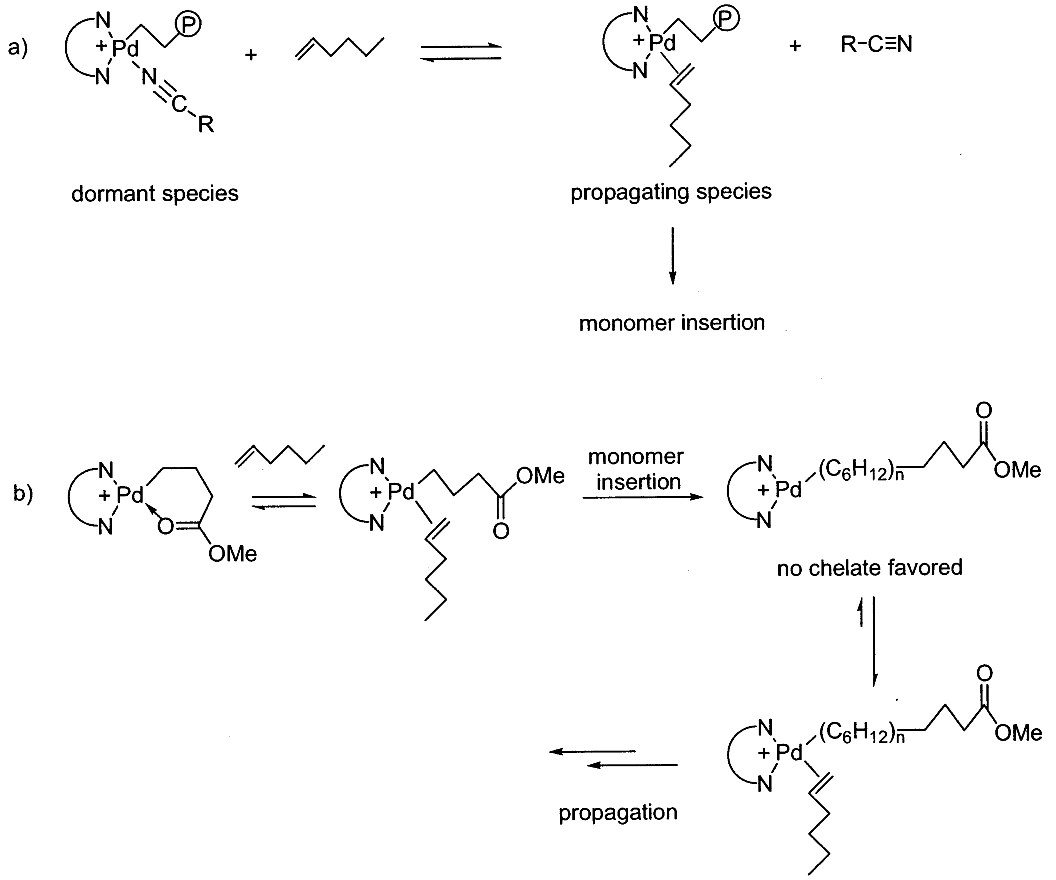


Figure 6. Plot of M_n and M_w/M_n as a function of reaction time for the polymerization of 1-hexene (0.8 M, 2 mL) [0 °C; catalyst **3** (15×10^{-6} mol) in chlorobenzene, 20 mL of total solution; Et_3SiH quench].

Just as nonliving behavior was exhibited in the ethylene polymerizations at room temperature, the molecular weight of propylene increased in a nonlinear fashion with time at 25 °C. A low molecular weight tail in the GPC traces of these polymers indicates that catalyst decomposition is taking place, preventing a living polymerization. As has been previously observed, the polypropylenes generated under living conditions exhibit branching numbers of ~253 branches per 1000 carbons. This low branching number is indicative of some chain straightening occurring via a 2,1-insertion followed by chain-walking of the Pd, which results in 1,3-enchainment of propylene.[26]

C. Living 1-Hexene Polymerization. The palladium chelate complex **3** was found to initiate polymerization of 1-hexene (0.8 M) at 0 °C at rates comparable to chain growth. The success of the chelate complex here is clearly due to high concentrations of 1-hexene which produce a significant equilibrium concentration of the (diimine)Pd(alkyl)(1-hexene)$^+$ complex, the species required for initiation. By taking aliquots of the polymerization solution and quenching with Et_3SiH, the M_n and molecular weight dispersity of the poly(1-hexene) could be monitored as a function of time. Results are presented graphically in Figure 6. M_n grows linearly with time in the early stages of polymerization (up to ca. 100 min) but then, the slope begins to decrease. The dispersity remains low (<1.08) through 100 min and then begins to increase, reaching 1.15 at a 3 h polymerization time. These results suggest that either some catalyst decay is occurring or that chain transfer is

Scheme 4. Competition of Nitrile and 1-Hexene for the Open Coordination Site at Pd

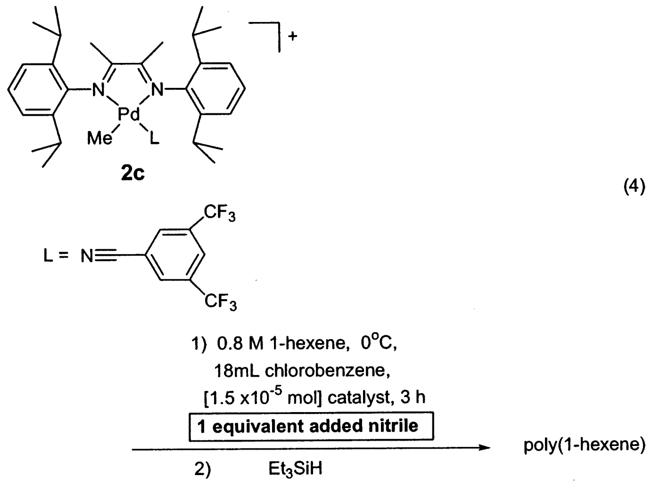


beginning to limit M_n and broaden the molecular weight distribution.

Catalysts **2b** and **2c** were also used to polymerize 1-hexene under the same reaction conditions. The polymers made with these catalysts showed nearly linear molecular weight growth over time with corresponding narrow molecular weight distributions over polymerization times of 3 h. The chelate catalyst **3** produces poly(1-hexene) with an M_n of 35 000 after 3 h, whereas the 3,5-bis(trifluoromethyl)benzonitrile ligated catalyst **2c** and the acetonitrile ligated catalyst, **2b**, yield lower molecular weight poly(1-hexene), 30 000 and 14 000, respectively. The lower molecular weights of the polymers made with nitrile catalysts are attributed to the ability of the nitrile to compete with 1-hexene for the open coordination site at palladium throughout the polymerization reaction as illustrated in Scheme 4a.

Under these conditions, some fraction of the Pd species exists as the dormant nitrile complex. As expected, the more basic, sterically less bulky acetonitrile ligand has a higher binding affinity than $(CF_3)_2C_6H_3$-CN and thus when catalyst **2b** is used, a greater fraction of the Pd species exists as the dormant nitrile complex leading to slower chain growth and a lower M_n of poly(1-hexene) after a given polymerization time. In the case of the chelate complex, following a relatively few monomer insertions, formation of a chelate will no longer be favorable and no other ligand is present to compete with 1-hexene for the vacant site. This feature is illustrated in Scheme 4b.

To further illustrate the effect of the equilibrium between dormant and active Pd complexes, polymerizations were carried out using catalyst **2c** in chlorobenzene and adding 1 equiv of various nitriles. The reaction protocol is outlined in eq 4.

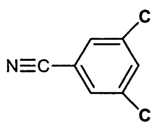
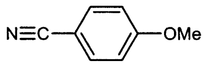


(4)

The results are summarized in Table 1. As expected, the M_n values and turnover frequencies decrease as a function of the coordinating ability of the nitrile. For the most basic nitrile, *p*-methoxybenzonitrile, the TOF falls to 19 TO per hour and the M_n falls to ca. 3300 relative to 234 TO/h and $M_n = 31\ 000$ for catalyst **2c** with no added nitrile.

The data in Table 1 illustrates two additional points. First, added nitrile ligands do not induce chain transfer as is evident from the very narrow molecular weight distributions observed, generally significantly less than 1.1. Second, the TOF's are not consistent with the M_n

Table 1. Polymerization of 1-Hexene by 2c with 1 equiv of Nitrile Added[a]

	Nitrile added	M_n ($\times10^{-3}$)[b]	M_w/M_n[b]	TOF (h^{-1})[c]
(1)	none	31	1.03	234
(2)		20	1.06	175
(3)	N≡C—Me	8.3	1.05	48
(4)		3.0	1.10	19

[a] Polymerizations at 0 °C; 3 h; 0.8 M 1-hexene (2 mL); catalyst **2c** (15×10^{-6} mol) in chlorobenzene; 20 mL total solution; 1 equiv of nitrile to catalyst added; Et_3SiH quench. [b] Molecular weight data determined by GPC vs polystyrene standards. [c] TOF (turnover frequency = "moles of monomer/moles of catalyst")

Table 2. Effect of 3,5-Bis(trifluoromethyl)benzonitrile Concentration on the Polymerization of 1-Hexene[a]

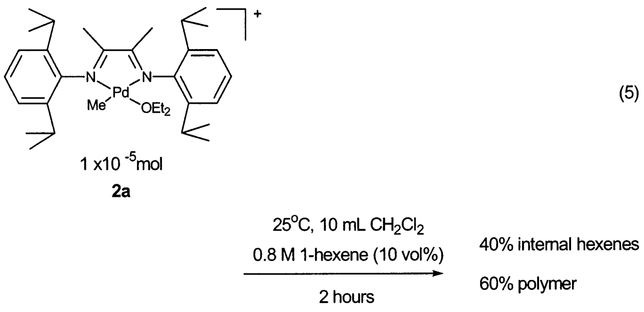
entry	added nitrile ($\times10^{-4}$ M)	M_n ($\times10^{-3}$)[b]	M_w/M_n[b]
1	0	31.0	1.03
2	2.5	24.4	1.05
3	5.0	23.4	1.04
4	7.5	19.7	1.06

[a] 1-hexene (0.8 M, 2 mL); 0 °C; 3 h; catalyst **2c**, (15×10^{-6} mol) in chlorobenzene for a total solution volume of 20 mL; Et_3SiH quench. [b] Molecular weight determined by GPC vs polystyrene standards.

values measured by GPC. For example, for entry 1, the TOF is 234/h which would lead to a M_n of 60 400 in a living polymerization [1-hexene (234/h × 3 h × 86 g/mol 1-hexene).] The measured M_n using polystyrene standards is 30 000. This molecular weight discrepancy can be attributed to the polystyrene standards used to calibrate the results. For the same M_n values, the hydrodynamic volume for a branched poly(1-hexene) in THF will differ from that of polystyrene in THF. Thus, the GPC data collected are useful for comparing relative molecular weights of branched poly(1-hexenes) but are not accurate for determining absolute molecular weights.

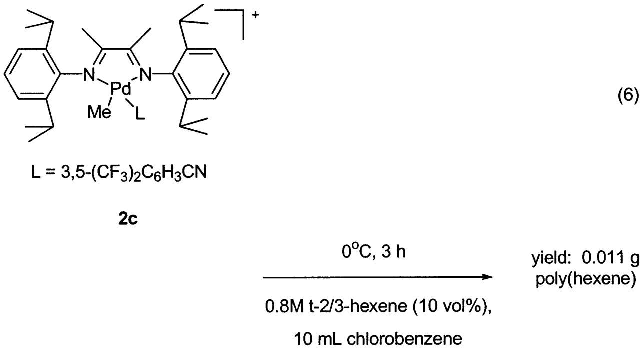
In the second experiment designed to establish a nitrile concentration dependence on the rate of polymerization, increasing numbers of equivalents of 3,5-bis(trifluoromethyl)benzonitrile were added to polymerizations of 1-hexene catalyzed by **2c**. The results in Table 2 show that as the concentration of 3,5-bis(trifluoromethyl)benzonitrile increases, the molecular weight of the polymer made over a 3 h time period decreases. The increased nitrile concentration shifts the equilibrium toward the dormant palladium-nitrile complex and thus decreases the rate of chain growth, resulting in lower M_n's (Scheme 4). Again, the molecular weight distribution is not affected by excess nitrile.

One final aspect of 1-hexene polymerization with the Pd(II) α-diimine systems was examined. Previous results[27] showed that at room temperature, using catalyst **2a**, isomerization of 1-hexene to internal hexenes is competitive with polymerization. A typical result is shown in eq 5.



(5)

Two questions were raised about the effect of isomerization in the Pd(II) α-diimine systems. First, could these catalysts polymerize the internal olefins, the products of isomerization? And second, was isomerization a factor at the lower temperatures used for the living polymerizations? As eq 6 illustrates, the polymerization of internal olefins (*trans*-2-hexene and *trans*-3-hexene) by the Pd(II) α-diimines does take place, but at a very slow rate, yielding only 11 mg of polymer in a 3 h run, well below the 296 mg of poly(1-hexene) obtained under the same conditions. The dramatic decrease in the rate of polymerization of internal hexenes is attributable to their increased steric bulk which leads to both decreased coordination and a slower rate of insertion. Given the very slow rate of polymerization of the internal hexenes, complete isomerization of 1-hexene would lead to a dramatically decreased rate of polymerization in the living systems.



(6)

A study similar to the one shown in eq 5, utilizing the reaction conditions that achieved living polymerization (0 °C, 0.8 M 1-hexene, **2c** (15×10^{-6} mol) in chlorobenzene, total solution volume 20 mL) was then undertaken in order to determine whether 1-hexene isomerization was occurring during the polymerization. Aliquots were removed from the polymerization solution at various times. The volatiles were separated from any polymer that had formed and then examined by GC to assess the ratios of hexene isomers. Figure 7 summarizes the data obtained over the course of the experiment. After 3 h polymerization at 0 °C, 71% of all hexenes in solution remained as 1-hexene, while 29% of the 1-hexene had been isomerized to internal olefins. The binding affinity of 2- and 3-hexenes is far less than that of 1-hexene, thus these isomers neither inhibit the binding and insertion of 1-hexene nor undergo insertion competitive with 1-hexene.

Under living conditions, the poly(1-hexene) is chain straightened as has been previously observed.[17,28] The branching in these polymers ranges from 75 to 85 branches per thousand carbons and, as observed in the ethylene polymerizations, the branching numbers at 0 °C are unaffected by catalyst or monomer concentration and are the same for catalysts **2a**−**c** and **3**.

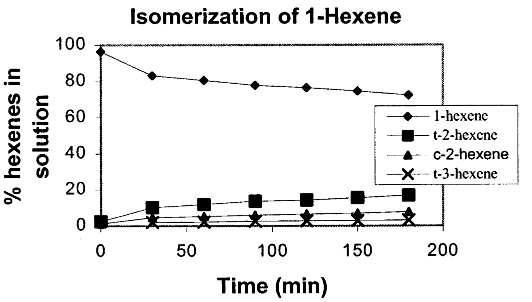


Figure 7. Distribution of hexenes in solution over time during polymerization (0 °C, 0.8 M 1-hexene, catalyst **2c** (15×10^{-6} mol) in chlorobenzene, determined by GC).

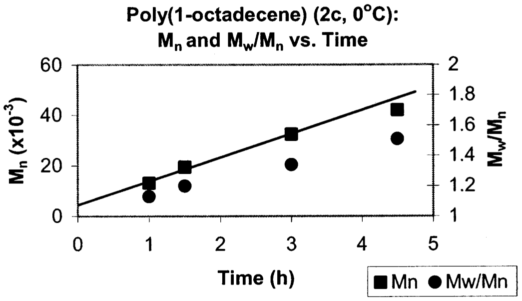
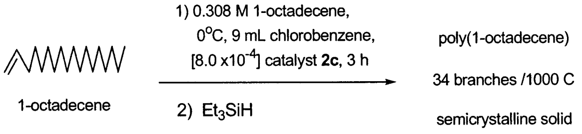


Figure 8. Plot of M_n and M_w/M_n as a function of reaction time for the polymerization of 1-octadecene (0.3 M, 1.0 mL) [0 °C; catalyst **2c** (8×10^{-6} mol) in chlorobenzene, 10 mL of total solution; Et_3SiH quench].

D. 1-Octadecene Polymerization. One of the attractive features of living polymerization is the ability to make block copolymers. Such polymers are of particular interest when the blocks have different physical properties. The polyethylene, polypropylene, and poly(1-hexene) made under living conditions with the Pd(II) α-diimine catalysts are all highly branched, amorphous polymers. Using the Pd(II) α-diimine catalysts for polymerization of very long chain α-olefins (e.g., 1-octadecene) leads to a semicrystalline polymer (T_m = 71.7 °C, 86.1 °C) as a result of lower branching numbers due to enchainment of the long chain α-olefin in 1,ω-"chain straightened" fashion.[29] Thus, it was of interest to screen a long chain α-olefin, 1-octadecene, for living polymerization with the intent of incorporating it in formation of a diblock α-olefin polymer.

1-Octadecene polymerizations were carried out using catalyst **2c** at low temperatures (0 °C) and monomer concentrations of 0.3 M, and were quenched in the usual way with Et_3SiH. The polymer produced was a solid, semicrystalline material containing a modest 34 branches per thousand carbons[30] (eq 7). Like the other α-olefins



(7)

polymerized by **2c**, the poly(1-octadecene) is chain straightened (from an anticipated 55−56 branches per thousand carbons).

A plot of M_n vs M_w/M_n for the polymerizations described in eq 7 is shown in Figure 8. While the M_n values clearly increase with polymerization time, the M_w/M_n values, in contrast to similar polymerizations with propylene and 1-hexene, broaden quite substantially over 4.5 h. For example, at 1 h, M_w/M_n = 1.13 while at 3 h the distribution has broadened to 1.34. Visual observation of the polymerization reveals that a white, flaky solid begins to precipitate from the cold chlorobenzene after approximately 1.5 h. We suggest this precipitation process is responsible for the broadening dispersities.

The turnover frequency at 0 °C for 1-octadecene is very low (9−12 TO/h) at this monomer concentration, and unfortunately, the turnover rate limits the molecular weight of the polymer that can be achieved. The turnover frequency does not decrease significantly over a $4^1/_2$ h polymerization time, indicating that the catalyst is not decomposing. This claim is also supported by a lack of a low molecular weight tail in the GPC traces as observed when decomposition of catalyst occurs during the polymerization of other monomers. Solubility of the polymer at low temperatures seems to be the only impediment to sustaining molecular weight distributions of <1.1. The growth in M_n with time and the lack of appreciable catalyst decay over 4 h implies that this monomer can be successfully used in the formation of block polymers, and these experiments are reported in the next section.

E. Block Copolymers. Given the differing properties of polyethylene vs poly(1-octadecene) it was of interest to attempt to prepare block copolymers. This section describes preparation of polyethylene-*b*-poly(1-octadecene) copolymers and, as will be illustrated, the microstructure of the block polymers differs substantially depending on the order of growth of the blocks from the palladium center.

1. Block Copolymer Synthesis. Careful attention to experimental protocol is necessary to ensure that each block of the diblock is a homopolymer block and not a copolymer block. In cases where ethylene is introduced as the first block, it is relatively easy to remove excess ethylene from the polymerization solution through a series of cycles involving application of vacuum to the reaction mixture followed by purging with argon at 0 °C. This process is described in detail in the Experimental Section. Control experiments have established that no chain transfer or termination occurs during this procedure and that all ethylene is removed prior to introduction of the 1-octadecene for growth of the second block.

In cases where the α-olefin block is grown first, the removal of excess monomer becomes more difficult since all of the 1-octadecene cannot be consumed during polymerization and the 1-octadecene is not sufficiently volatile to be removed under reduced pressure at low temperatures. A successful procedure was developed which involved running the 1-octadecene polymerization at 0−5 °C in concentrated solutions (0.353 M, 7 mL solution volume) then diluting these solutions to 100−150 mL followed by introduction of ethylene at 400 psi. Since the binding affinity of ethylene is so much greater than α-olefins,[28] under these conditions of dilute 1-octadecene and high ethylene pressure, only ethylene is incorporated. A control experiments was conducted in which ethylene was polymerized at 400 psi in the presence of 0.015 M 1-octadecene. The polyethylene produced had physical and spectral properties essentially identical to homopolyethylene indicating insignificant incorporation of 1-octadecene.

Table 3 summarizes the molecular weight data and branching numbers for a series of diblock polymers made using the above protocols. Examining the data in

Table 3. Polyethylene-*b*-poly(1-octadecene)[a] and Poly(1-octadecene)-*b*-polyethylene[b]

PE[c] (h)	C18[d] (h)	M_n[e] ($\times 10^{-3}$)	M_w/M_n[e]	branches/1000 C[f]	C-18[d] (h)	PE[c] (h)	M_n[e] ($\times 10^{-3}$)	M_w/M_n[e]	branches/1000 C[f]
2	1	30	1.10	64	1	2	18	1.15	43
2	2	34	1.18	59	2	2	25	1.06	74
2	3	50	1.22	53	3	2	23	1.10	66
1	2			55	2	1			75
2	2	34	1.18	59	2	2			74
3	2	46	1.17	58	2	3			67

[a] Catalyst **2c** (8×10^{-6} mol), ethylene (400 psig, 5−6 °C, 80 mL chlorobenzene); ethylene removal; 1-octadecene (10 mL in 10 mL chlorobenzene) added (0.32 M, 4 °C). [b] Catalyst **2c** (8×10^{-6} mol), 1-octadecene (0.7 mL, 0.32 M, 7.0 mL solution, 2 °C); ethylene (400 psig, 5−6 °C, 143 mL of chlorobenzene). [c] PE = polyethylene. [d] C-18 = poly(1-octadecene). [e] By GPC vs polystyrene standards ($k = 4.34 \times 10^{-4}$; $\alpha = 0.724$). [f] By ^{1}H NMR.

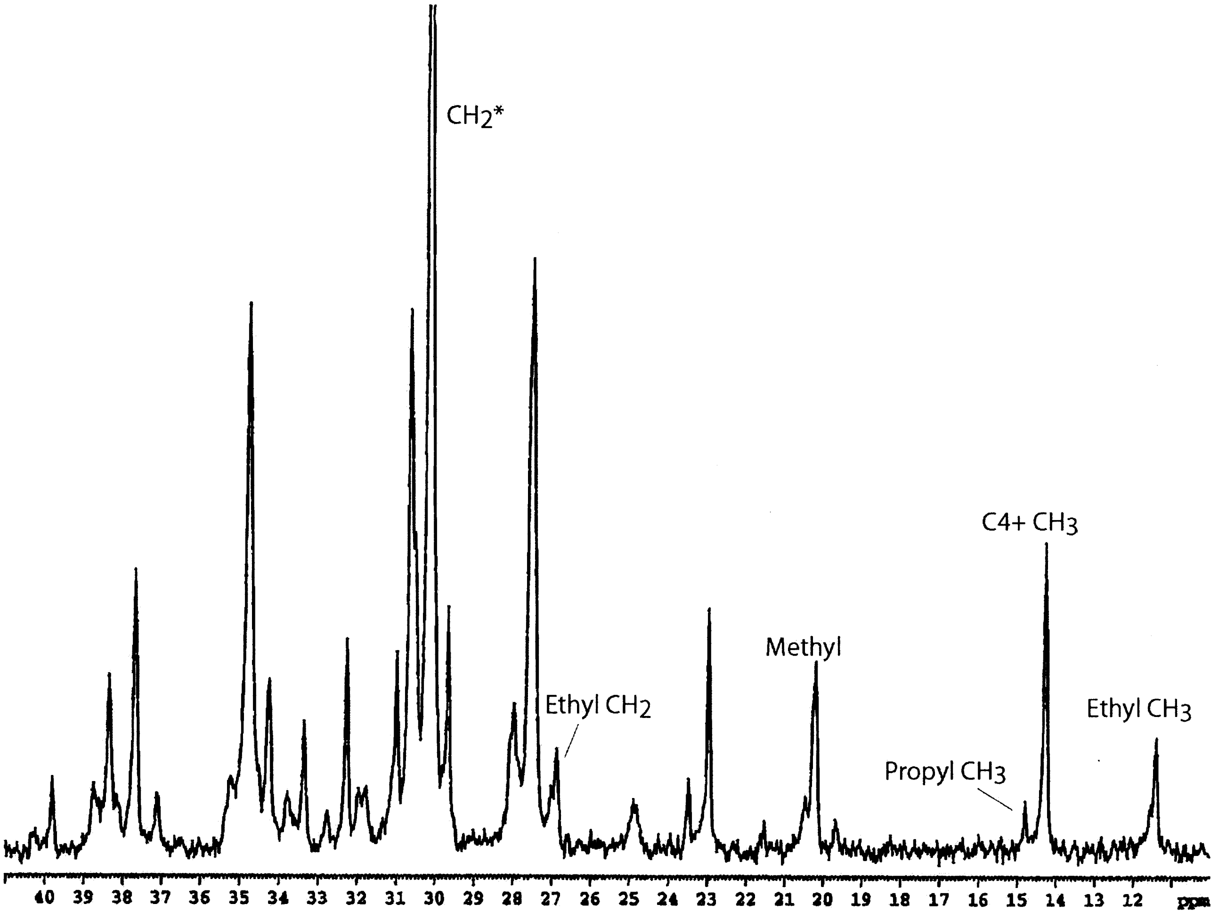


Figure 9. ^{13}C NMR (C_6D_5Br, 0.5 M $Cr(acac)_3$, 100 MHz, 120 °C) of polyethylene.

Table 3, the left half contains data on polyethylene (PE)-*b*-poly(1-octadecene) (C18) polymers in which the polyethylene block is made first, while the right half summarizes data for blocks grown in the reverse order. As shown in Table 3, all copolymers have fairly narrow molecular weight distributions (1.06−1.22) and the overall branching numbers of the copolymers (43−75) fall between the 90−110 branches per 1000 C of polyethylene and the 39−40 branches/1000 C of poly(1-octadecene.) The copolymers are clear, rubbery solids (as opposed to amorphous gels (polyethylene) or white solids (poly(1-octadecene)), with the stiffness of the material increasing with increasing 1-octadecene incorporation. Polymer molecular weights of the polyethylene-*b*-poly(1-octadecene) polymers increase with increasing polyethylene or poly(1-octadecene) block time. Contrary to this trend, the molecular weights of the poly(1-octadecene)-*b*-polyethylene copolymers increase from the one to 2 h polymerization time of 1-octadecene but do not increase beyond this point. The reason for the lower than anticipated polymer molecular weight is likely due to the precipitation of the polymer from the cold polymerization solution as observed in the homopolymerization of 1-octadecene.

2. Characterization of Block Copolymers by ^{13}C NMR Spectroscopy. The most intriguing feature of these block copolymers is that there are differences in microstructures as a function of the order of growth of the blocks, as indicated by ^{13}C NMR analysis and DSC data. To analyze these differences we first must consider the ^{13}C analyses of the homopolymers themselves. Resonances in the ^{13}C spectrum of the hyperbranched polyethylenes produced from Pd(II) α-diimine catalysts have been previously assigned, and it has been shown that branches can be quantitated by running spectra in deuterated bromobenzene at 120 °C, using $Cr(acac)_3$ as a T_1 relaxation agent and employing a 5 s delay time.[31,32] Figure 9 shows a typical ^{13}C spectrum of polyethylene with the key methyl resonance from methyl, ethyl, propyl, and butyl or longer (C_4^+) branches

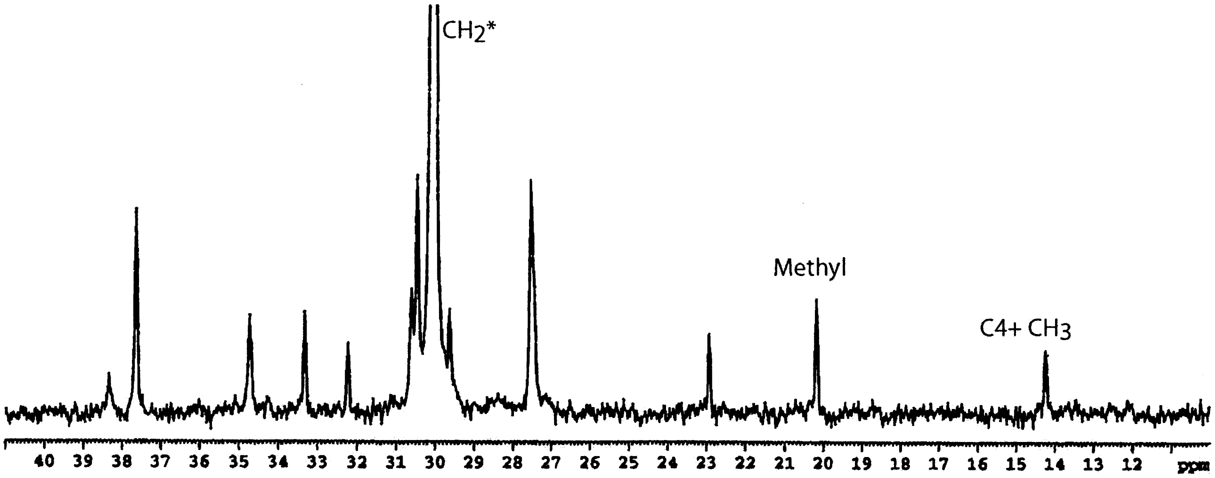


Figure 10. ^{13}C NMR (C_6D_5Br, 0.5 M $Cr(acac)_3$, 100 MHz, 120 °C) of poly(1-octadecene).

Table 4. Branches per 1000 C in Polyethylene-*b*-poly(1-octadecene) Copolymers[a]

	PE	PE(2) C18(1)	PE(2) C18(2)	PE(2) C18(3)	PE(3) C18(2)	C18
Me	28	25	24	27	25	16
Et	16	9.4	8.5	7.2	8.4	0
Pr	5.2	1.6	1.6	1.1	3.2	0
C_4^+	41	24	24	21	19	9

[a] By ^{13}C NMR (C_6D_5Br, 0.05 M $Cr(acac)_3$, 100 MHz, 120 °C) branches per 1000 C in polymer; Me = methyl; Et = ethyl; Pr = propyl; C_4^+ = butyl or longer chain; PE = polyethylene; C18 = poly(1-octadecene); PE(2)C18(3) = polyethylene (2 h)-*b*-poly(1-octadecene) (3 h).

Table 5. Branches per 1000 C in Poly(1-octadecene)-*b*-polyethylene Copolymers[a]

	PE	C18(1) PE (2)	C18(2) PE(2)	C18(3) PE(2)	C18(2) PE(3)	C18
Me	28	23	26	25	28	16
Et	16	14	13	11	13	0
Pr	5.2	3.3	5.1	3.6	5.4	0
C_4^+	41	30	26	28	36	9

[a] By ^{13}C NMR (C_6D_5Br, 0.05 M $Cr(acac)_3$, 100 MHz, 120 °C) branches per 1000 C in polymer; Me = methyl; Et = ethyl; Pr = propyl; C_4^+ = butyl or longer chain; PE = polyethylene; C18 = poly(1-octadecene); C18(3)PE(2) = poly(1-octadecene) (3 h)-*b*-polyethylene (2 h).

marked on the spectrum. The signal marked with an asterisk (∗) is due to CH_2 groups in the chain flanked by at least four methylene groups on each side.

The^{13}C spectra of poly(1-octadecene) is shown in Figure 10. As previously established, α-olefins insert only into primary Pd−carbon bonds and 1,2- and 2,1-insertions occur with about equal probability.[26] This feature, coupled with rapid chain running in the Pd−alkyl intermediates, results in "chain-straightened" polymers with fewer branches than expected. In the case of poly(1-octadecene), the polymer exhibits approximately 34−39 branches per 1000 carbons and only methyl and longer branches (most are no doubt C_{16} branches) occur. Even though palladium migrates down the chain following a 2,1-insertion, no insertion into secondary alkyl bonds occur and thus no propyl or ethyl branches are observed in these polymers (compare Figure 10 with Figure 9.)

Tables 4 and 5 summarize similar branching data for polyethylene/poly(1-octadecene) block polymers. The feature that is most diagnostic of the differences in microstructures as a function of the order of introduction of the blocks is the comparison of the ethyl and propyl branches per 1000 C's in block polymers which differ only in the order of block growth. While integration of the weak resonances of sparsely populated branches in the ^{13}C spectra can be imprecise, comparison of data in Tables 4 and 5 reveal a clear trend in these copolymers. The polymers in which the C-18 olefin is introduced second (Table 4) consistently exhibit lower fractions of ethyl and propyl branches compared to diblocks in which the C-18 olefin is made first (Table 5.) For example in comparing the P(C-18)(3 h)-*b*-PE(2 h) with the PE(2 h)-*b*-P(C-18)(3 h), the ethyl and propyl branching numbers decrease from 11 and 3.6, respectively, to 7.2 and 1.1. The ^{13}C NMR spectra of these polymers are shown in Figure 11. Similarly, comparing P(C-18)(2 h)-*b*-PE(3 h) with PE(3 h)-*b*-PC-18(2 h), branches decrease from 13 and 5.1 per thousand to 8.5 and 1.6, per thousand, respectively. These data clearly suggest that when 1-octadecene is introduced as the second block, ethyl and propyl branches are converted to other types of branches. A mechanistic rationale is proposed below.

3. Mechanistic Rationale. Previous mechanistic studies provide an explanation for the dependence of the microstructure of the diblock polymers on the order of block introduction. Mechanistic studies of polyethylene formation show that dissociation of ethylene from an alkyl ethylene complex (diimine)Pd(R)(ethylene)$^+$ (e.g., **5** in Scheme 5) at 25 °C is anywhere from 10 to 100 times faster than insertion, depending on the nature of R (the alkyl group) ($k_{dissoc} > k_{ins}$).[33] Furthermore, once dissociation occurs, Pd migration along the chain via 1,2-shifts takes place significantly faster than retrapping with ethylene ($k_{mig} > k_{trap}[=]$), (see Scheme 5) where obviously the trapping rate is dependent on ethylene concentration. Note also that we have established that metal migration through a tertiary center poses no barrier to chain walking. Thus, from the alkyl resting state (e.g., **5**), Pd migrates over tens to hundreds of carbons prior to insertion. Guan has shown that the overall architecture of the PE's produced depends on the ethylene pressure.[30,33] At low pressures, the polyethylene is hyperbranched with branches-on-branches while at higher pressures, the polyethylene is still highly branched, but the architecture is more linear and less hyperbranched with fewer branches-on-branches. This change in structure is a direct result of higher trapping rates of the alkyl complex at high ethylene pressures

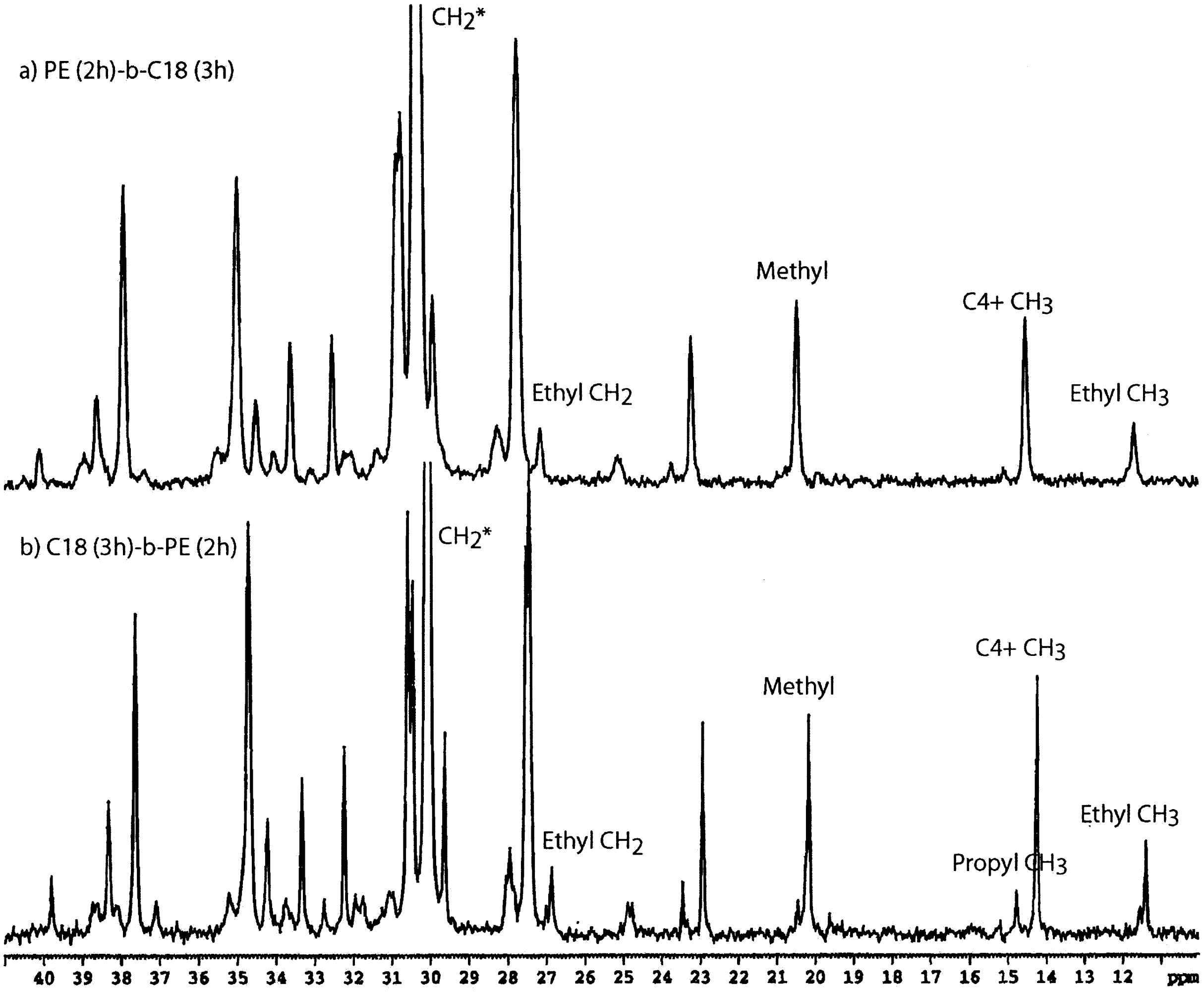
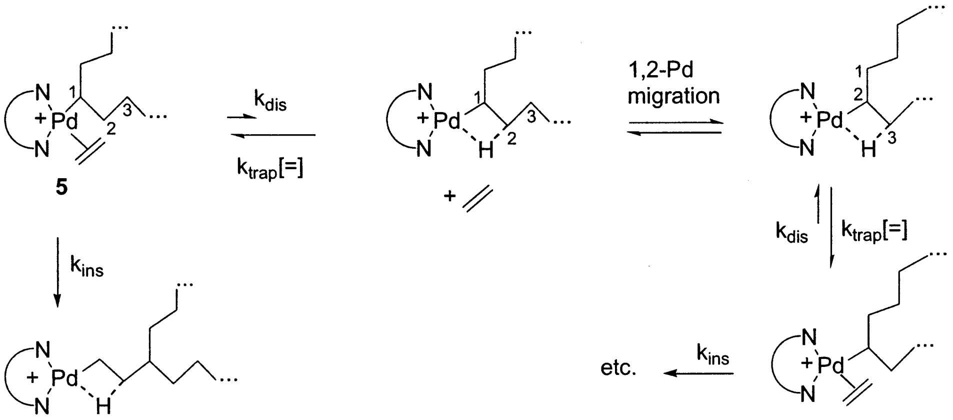


Figure 11. ^{13}C NMR (C_6D_5Br, 0.5 M Cr(acac)$_3$, 100 MHz, 120 °C): (a) polyethylene (2 h)-*b*-poly(1-octadecene) (3 h); (b) poly(1-octadecene) (3 h)-*b*-polyethylene (2 h).

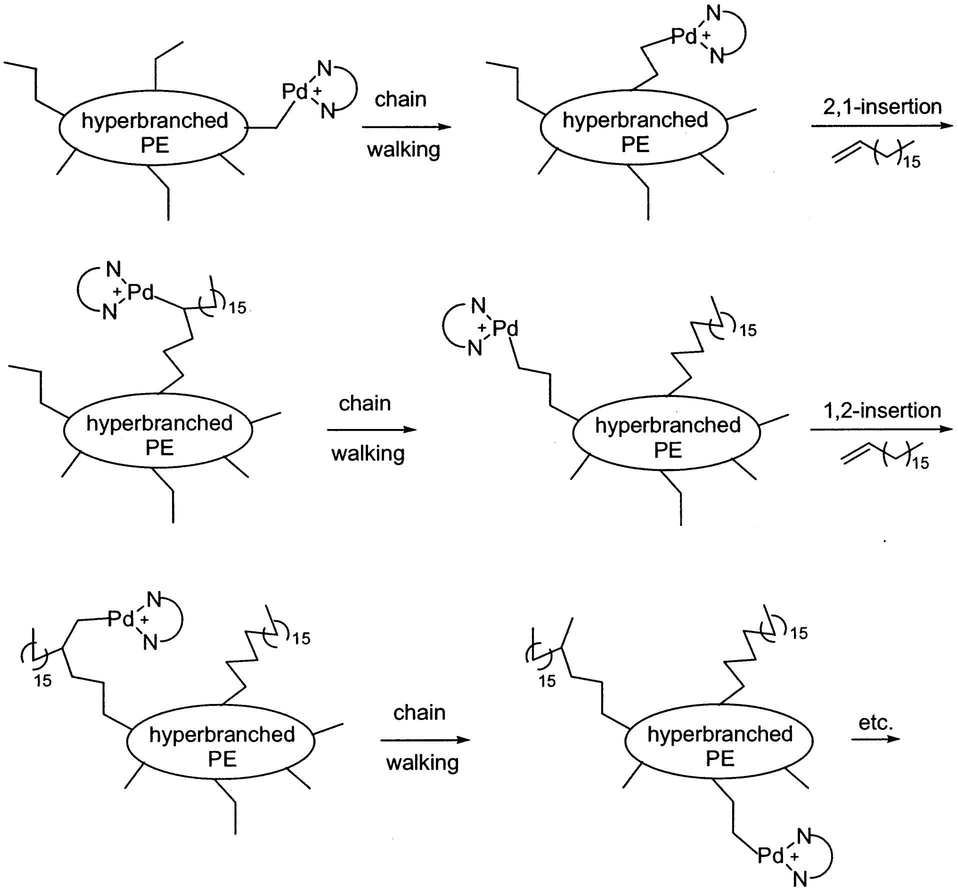
Scheme 5. Pd Chain-Walking during Ethylene Polymerization



and thus fewer 1,2-Pd migrations on average before insertion.

Consider how this picture will change when using an α-olefin monomer such as 1-octadecene in place of ethylene. Because of the increased bulk of the 1-octadecene relative to ethylene, the dissociation rate from an alkyl olefin complex will be faster while the trapping rate of a Pd alkyl complex will be slower relative to ethylene. Previous work has established that α-olefins do not insert into Pd secondary alkyl bonds which is a result of very low equilibrium concentrations of the Pd(α-olefin)(*sec*-alkyl)$^+$ complexes.[28b–d] Furthermore, α-olefin insertion into primary Pd–R bonds is somewhat slower than analogous ethylene insertions. Faster dissociation, slower trapping, and slower insertion into only primary Pd–R bonds, implies in this case that Pd will chain walk over far more carbons, probably 1000's of carbons, prior to α-olefin insertion. When insertion does occur, it will be into a Pd(*n*-alkyl)$^+$ bond. Thus, considering block polymer formation, if the initial block is hyperbranched polyethylene, then growth of an α-olefin block will occur from the ends of the branches of the hyperbranched polyethylene by virtue of the Pd chain walking extensively through the hyperbranched struc-

Scheme 6. Model for Growth of a Polyethylene-*b*-poly(1-octadecene) Copolymer.



ture prior to each insertion. In the case of 1-octadecene, insertion at the ends of ethyl branches will result in disappearance of the ethyl branch and formation of either a methyl branch following a 1,2-insertion or a long chain branch following a 2,1-insertion. Likewise, insertion at the end of a propyl branch will eliminate that branch and reduce the overall density of the branching in the polymer. Some typical possibilities are illustrated in Scheme 6. The net result of such a process is that the block polymer will form a "core" of polyethylene surrounded by a shell of 1-octadecene.

On the other hand, when the 1-octadecene block is grown first, it forms a polymer with methyl and C_{16} or longer branches. The high pressure of ethylene used to make the second block allows much less time for the palladium catalyst center to chain walk between insertions. This results in ethylene being added in a more linear fashion, working away from the first polymer block. These types of copolymers have branching data that correspond closely with what is expected from a mix of polyethylene and poly(1-octadecene). They appear to contain two distinct blocks, although some chain walking of the palladium into the first block while inserting ethylene may occur, and thus the blocks will not be "cleanly" separated.

The thermal data on the diblock polymers support the contention of differing microstructures depending on the order of monomer enchainments. All of the diblock polymers in which the poly(1-octadecene) was introduced first exhibit two high-temperature melting transitions (ca. 66 and 83 °C) and a broad low-temperature melt transition at ca −24 °C as shown in Figure 12. The diblock polymers in which polyethylene is made first show only two high melt transitions at 60 and 84 °C as shown in Figure 13. The two high-temperature melting transitions in both types of polymers are similar to those observed in the homo poly(1-octadecene) prepared from catalyst **2c** with $T_m = 67$ and 81 °C.

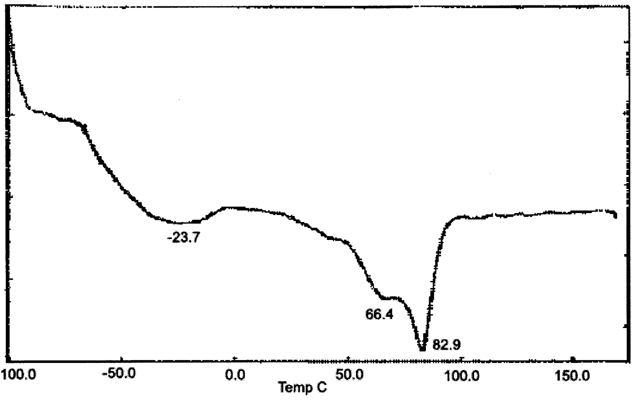


Figure 12. DSC trace of poly(1-octadecene) (2 h)-*b*-polyethylene (2 h).

For the block copolymer with the poly(1-octadecene) grown first, the two high melt transitions are attributed to the moderately linear main chain and the C16 side chains. The assignment of the −24 °C transition in the poly(octadecene)-*b*-polyethylene diblock materials is speculative at this point. As ethylene is enchained to form a second block, the catalyst walks back to some extent into the 1-octadecene block creating a few short branches on the primarily linear chain. As more ethylene is added, a block of highly branched PE with no T_m is grown. The "fuzzy" junction point between the two

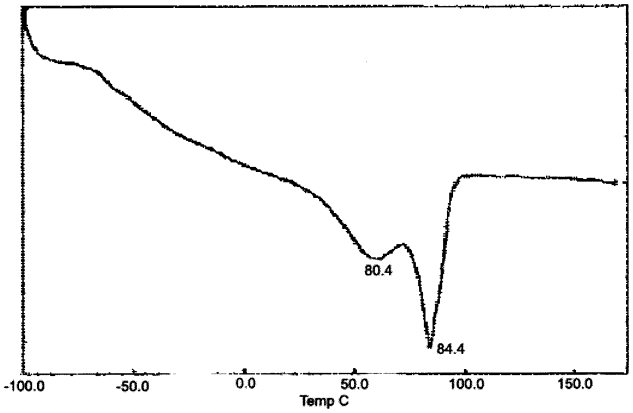


Figure 13. DSC trace of polyethylene (3 h)-*b*-poly(1-octadecene) (2 h).

blocks may account for the −24 °C T_m. Despite the lack of definitive assignment of this T_m, it is clear from the DSC traces in Figures 12 and 13 that the materials must possess somewhat different microstructures.

Experimental Section

General Methods. All manipulations of air and/or water sensitive compounds were performed using standard high vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF R3−11 catalyst (Chemalog) and 4 Å molecular sieves. Solid organometallic compounds were transferred in an argon-filled MBraun drybox. ^{1}H NMR spectra were recorded on a Bruker DRX400 or a Bruker AMX-300 spectrometer. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of TMS and were referenced to residual ^{1}H NMR and ^{13}C NMR signals of the deuterated solvents. ^{1}H NMR spectra of polyethylene, polypropylene, and poly(1-hexene) were taken at 25 °C in $CDCl_3$. ^{1}H NMR spectra of poly(1-octadecene) and ethylene/1-octadecene copolymers were taken at 120 °C in C_6D_5Br. ^{13}C spectra of polymers were taken as described below. GPC traces of polyethylene, polypropylene, and poly(1-hexene) were performed at UNC (35 °C, 1.0 mL/min) on a Waters Alliance HPLC Separations Module equipped with Waters Styragel HR2 (molecular weight range 500−200K), HR4 (molecular weight range 5K-600K), and HR5 (molecular weight range 50K-4M) columns all packed with 5 μm spherical particles in series and a Waters 2410 differential refractometer RI (refractive index) detector relative to polystyrene standards. Samples consisted of ∼1 mg of polymer in 1 mL of degassed THF. GPC traces of poly(1-octadecene) and ethylene/1-octadecene copolymers were performed at DuPont (Wilmington, DE) in 1,2,4-trichlorobenzene at 135 °C with a flow rate of 1.0 mL/min using a Waters HPLC 150C equipped with dual Shodex columns (Shodex AT-806MS columns with an exclusion limit of 20 000 000 Da.) A calibration curve was established with polystyrene standards and universal calibration was applied using Mark−Houwink constants for polyethylene ($k = 4.34 \times 10^{-4}$; $\alpha = 0.724$). Thermal analysis was preformed on a Seiko Instruments DSC220C differential scanning calorimeter. To standardize thermal measurements, every DSC sample was heated above the melting point of the polymer followed by rapid cooling and then data was collected at a heating rate of 10 °C/min (second heat). Isomerization of 1-hexene was analyzed on a Hewlett-Packard 5890 A gas chromatograph using a Supelco Petrocol DH 50.2 capillary column (50m, 0.20 i.d., 0.50 μm film thickness) and flame ionization detector.

Materials. Chlorobenzene (99.5+%, Aldrich) was dried over 4 Å molecular sieves and degassed with argon. Polymer grade ethylene and propylene were purchased from Matheson and used without further purification. Et_3SiH (97%), methyl acrylate (99%), ethyl acrylate (99%), methyl vinyl ketone (99%), 4-penten-1-ol (99%), and 1-octadecene (90%) were purchased from Aldrich and used as received. 1-Hexene (99+%) was purchased from Aldrich, dried over sodium, and distilled under argon before storing over sieves. Acetonitrile (99.5%), 3,5-bis(trifluoromethyl)benzonitrile (97%), and 4-methoxybenzonitrile (99%) were purchased from Aldrich and added as received to chlorobenzene to form a 0.1 M solutions that were degassed and stored over sieves. *cis*-2-Hexene (97%, Fluka), *trans*-2-hexene (97%, Lancaster), *cis*-3-hexene (95%, Fluka), and *trans*-3-hexene (99+%, Aldrich) were used as received for polymerization and as GC standards. The Pd(II) α-diimine complexes $[(Ar{-}N{=}C(Me){-}C(Me){=}N{-}Ar)Pd(Me)(NCMe)]^+BAr'_4{}^-$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$) (**2b**), $[(Ar{-}N{=}C(Me){-}C(Me){=}N{-}Ar)Pd(Me)(3,5\text{-}(CF_3)_2C_6H_3CN)]^+BAr'_4{}^-$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$) (**2c**), and $[(Ar{-}N{=}C(Me){-}C(Me){=}N{-}Ar)Pd((CH_2)_3C(O)OCH_3)]^+BAr'_4{}^-$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; Ar = 3,5-(C$_3$)$_2$C$_6$H$_3$) (**3**) were prepared according to the literature.[24]

Preparation of Ester End-Capped Polyethylene. A mechanically stirred 300 mL Parr reactor equipped with an electric heating mantle controlled by a thermocouple was heated overnight to 150 °C under vacuum and then cooled to 27 °C. The autoclave was pressurized to 100 psig ethylene and vented three times, then charged with 90 mL of chlorobenzene and sealed. Ethylene (100 psig) was added to the stirring solvent and released twice. The ethylene pressure was then raised to 400 psig. The Parr reactor was placed in an ice bath and the chlorobenzene polymerization solvent stirred under 400 psig ethylene until the system cooled to 5−6 °C. The ethylene pressure was vented and a solution of 0.0132 g (8.11×10^{-6} mol) of catalyst **2c** dissolved in 10 mL of chlorobenzene was transferred via cannula into the reactor. The system was pressurized to 400 psig ethylene to begin the polymerization. After the allotted polymerization time, ethylene was vented. Excess ethylene was then removed at 5 °C: vacuum was applied to the reactor for 3 min, the reactor was then backfilled with argon, and the polymerization solution was purged with argon for 3 min. The vacuum/backfill/purge cycle was repeated three times. Then, 200 equiv of methyl acrylate were added. The solution was stirred for 1 h. Finally, 0.2 mL of triethylsilane was added to quench the catalyst. The polymerization solution and two chlorobenzene rinses of the reactor were combined in a tared round-bottom flask from which all volatiles were removed via rotary evaporation. The light brown, highly viscous polymer was dissolved in hexanes and filtered through a plug of silica gel and alumina to remove the catalyst. The polymer was precipitated in methanol. ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C, δ 3.65 (s, 3H, CH_3OC(O)), 2.41 (t, 2H, CH$_3$OC(O)CH_2), 1.45−1.0 (polyethylene CH_2, CH), 0.8 (polyethylene CH_3). The ^{1}H integrals of the polymer showed ∼750 ethylene insertions per OMe end group. The number of insertions is in the range of insertions obtained while polymerizing ethylene with catalyst **3** under identical conditions with no end cap introduced.

Preparation of Telechelic Polyethylene. A procedure similar to that describred above using 0.0118 g (8.0×10^{-6} mol) of catalyst **3** dissolved in 10 mL of chlorobenzene to initiate the polymerization was used to polymerize ethylene. At the end of the polymerization time, the excess ethylene was vented and the reactor purged as described above. Then the functionalized monomer (methyl acrylate, ethyl acrylate, methyl vinyl ketone, or 4-penten-1-ol) (200 equiv) was added. The solution was stirred for the noted reaction time, allowing the system to warm to room temperature. Finally, 0.2 mL of triethylsilane was added to quench the catalyst except when 4-penten-1-ol was used as an end cap. The polymerization solution and two chlorobenzene rinses of the reactor were combined in a tared round-bottom flask from which all volatiles were removed via rotary evaporation. The light brown, highly viscous polymer was dissolved in hexanes and filtered through a plug of silica gel and alumina to remove the catalyst. The polymer was precipitated in methanol. ^{1}H NMR (CDCl$_3$, 300 MHz, 25 °C; polymer end-capped with a methyl ester group using methyl acrylate (1 h)): δ 3.65 (s, 3H, CH_3OC(O)), 2.41 (t, 2H, CH$_3$OC(O)CH_2), 1.45−1.0 (polyethylene CH_2, CH), 0.8 (polyethylene CH_3). The integrals of the polymer protons indicated ∼375 ethylene insertions per OMe group as expected based on the singly end-capped polyethylene chains. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C; polymer end-capped with an ethyl ester end group using ethyl acrylate (2 h)): δ 4.13 (q, 2H, $CH_3C\mathit{H}_2OC(O)$), 3.65 (s, 3H, $C\mathit{H}_3OC(O)$), 2.35 (m, 4H, $CH_3OC(O)C\mathit{H}_2$ and $CH_3CH_2OC(O)C\mathit{H}_2$), 1.45−1.0 (polyethylene $C\mathit{H}_2$, $C\mathit{H}$), 0.8 (polyethylene $C\mathit{H}_3$), ($C\mathit{H}_3CH_2OC(O)$) not visible. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C; polymer end-capped with a methyl ketone group using methyl vinyl ketone (overnight)): δ 3.65 (s, 3H, $C\mathit{H}_3OC(O)$), 2.41 (t, 2H, $CH_3OC(O)C\mathit{H}_2$), 2.31 (t, 2H, $CH_3C(O)C\mathit{H}_2$), 2.15 (s, 3H, $C\mathit{H}_3C(O)$), 1.45−1.0 (polyethylene $C\mathit{H}_2$, $C\mathit{H}$), 0.8 (polyethylene $C\mathit{H}_3$). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C; polymer end-capped with an aldehyde group using 4-penten-1-ol (3 h)): δ 9.78 (s, 1H, $\mathit{H}C(O)CH_2$), 3.65 (s, 3H, $C\mathit{H}_3OC(O)$), 2.41 (t, 2H, $CH_3OC(O)C\mathit{H}_2$), 2.30 (t, 2H, $HC(O)C\mathit{H}_2$), 1.45−1.0 (polyethylene $C\mathit{H}_2$, $C\mathit{H}$), 0.8 (polyethylene $C\mathit{H}_3$). The functionalities at the terminal end of the polymer chains integrated in a 1:1 molar ratio with the methyl ester introduced by initiation of the polymer chain with **3**.

General Polymerization of Propylene (1 atm). Catalyst **2c** (0.0065 g, 3.99×10^{-6} mol) was weighed into a flame-dried Schlenk flask in the drybox. Chlorobenzene (20 mL) was added to this flask to dissolve the catalyst, forming a bright orange-yellow solution. The polymerization solution was stirred in an ice bath at 0 °C for 30 min to cool to the polymerization temperature. Propylene (1 atm) was introduced to the flask to begin the polymerization by evacuating the flask and backfilling it with propylene three times. After the allotted polymerization time, triethylsilane (0.2 mL) was added to the polymerization to quench the catalyst. The polymerization solution and two rinses of the polymerization flask with chlorobenzene were combined in a tared flask and the solvent removed via rotary evaporation. The brown to orange, gooey polymer was dried overnight in vacuo. After weighing, hexanes were added to dissolve the polymer. The polymer solution was filtered through a plug of silica gel and alumina to remove the catalyst and the polymer precipitated in methanol. The methanol was decanted, the polymer washed in acetone and dried in a vacuum oven at ~60 °C overnight. Gel permeation chromatography (THF, 35 °C, polystyrene reference): (1 h) $M_n = 9000$, $M_w = 9500$, $M_w/M_n = 1.03$; (2 h) $M_n = 16\,800$, $M_w = 17\,400$, $M_w/M_n = 1.04$; (3 h) $M_n = 23\,000$, $M_w = 24\,300$, $M_w/M_n = 1.06$; (4 h) $M_n = 26\,800$, $M_w = 28\,700$, $M_w/M_n = 1.07$; (5 h) $M_n = 33\,900$, $M_w = 36\,700$, $M_w/M_n = 1.08$; (6 h) $M_n = 42\,400$, $M_w = 47\,200$, $M_w/M_n = 1.11$.

Aliquot Sampling of the Living Polymerization of 1-Hexene. Catalyst **2b**, **2c**, or **3** (1.5×10^{-5} mol) was weighed into a flame-dried Schlenk flask in a drybox. Chlorobenzene (10 mL) was added, dissolving the catalyst to form a light orange/yellow solution. 1-Hexene (15.0 mL) and chlorobenezne (125 mL) were added under argon to a second flame-dried Schlenk flask. The resulting solution of 1-hexene in chlorobenzene was stirred in an ice bath for 30 min to cool to the polymerization temperature. The catalyst solution was then cannulaed into the flask containing the 1-hexene solution to begin the polymerization. Every 20 min for 3 h, a 5.0 mL aliquot of the polymerization solution was removed and quenched by addition of 0.1 mL of triethylsilane. Solvent was removed from each aliquot via rotary evaporation, leaving a sticky brown polymer residue. Gel permeation chromatography (THF, 35 °C, polystyrene reference) was used to obtain the molecular weight and dispersity of each polymer aliquot.

Polymerization of 1-Hexene with Added Nitrile. Catalyst **2c** (1.5×10^{-5} mol) was weighed into a flame-dried Schlenk flask under argon in the drybox. Chlorobenzene (18 mL) was added to the flask to dissolve the catalyst. Any excess nitrile was added. The resulting solution was stirred in an ice bath for 30 min to cool it to the polymerization temperature. Polymerization was initiated upon addition of 2 mL of 1-hexene. After the 3 h polymerization time, 0.2 mL of triethylsilane was added to quench the catalyst. Solvent was then removed by rotory evaporation leaving a brown/orange sticky film of polymer. The polymer was dried overnight in vacuo and weighed to determine yield (accounting for the catalyst present). The polymer was then dissolved in hexanes, filtered through silica gel and alumina to remove the catalyst, and precipitated in methanol. The methanol was decanted and the polymer rinsed in acetone. Finally, the polymer was dried in a vacuum oven at 60 °C overnight. No added nitrile: 0.296 g of polymer; $M_n = 30\,700$, $M_w/M_n = 1.03$. 3,5-Bis(trifluoromethyl)benzonitrile (0.15 mL of a 0.1 M solution in chlorobenzene): 0.219 g of polymer; $M_n = 19{,}700$, $M_w/M_n = 1.06$. Acetonitrile (0.15 mL of a 0.1 M solution in chlorobenzene): 0.061 g of polymer; $M_n = 8300$, $M_w/M_n = 1.05$. 4-Methoxybenzonitrile (0.15 mL of a 0.1 M solution in chlorobenzene): 0.024 g of polymer; $M_n = 3000$, $M_w/M_n = 1.11$.

Polymerization of Internal Hexenes. Catalyst **1c** (0.0123 g, 7.56×10^{-6} mol) was weighed into a flame-dried Schlenk flask in the drybox. Chlorobenzene (9.0 mL) was added to the flask, dissolving the solid to form a yellow solution which was stirred in an ice bath for 30 min to cool to 0 °C. *trans*-2-Hexene (0.5 mL) and *trans*-3-hexene (0.5 mL) were combined in a vial. The hexenes were then added to the polymerization solution to begin the polymerization. After 3 h at 0 °C, the polymerization was quenched by adding 0.2 mL of Et_3SiH. The polymerization solution and two rinses of the polymer flask with chlorobenzene were combined in a tared flask and volatiles were removed via rotary evaporation. The final product was dried in vacuo and weighed to determine polymer yield. An ^{1}H NMR spectrum of the product showed traces of the catalyst as well as a very small amount of polymer.

Isomerization of 1-Hexene during Polymerization with 1c. Catalyst **1c** (0.0246 g, 1.5×10^{-5} mol) was weighed into a flame-dried Schlenk flask. Chlorobenzene (20 mL) was added, dissolving the catalyst to form a light orange-yellow solution. Benzene (0.125 mL) was also added as an internal standard. The catalyst solution was stirred in an ice bath for 30 min to cool it to the polymerization temperature. 1-Hexene (2.2 mL) was added to begin polymerization. Immediately, an aliquot (0.5 mL) was removed from the polymerization and quenched by adding 2−3 mL of acetone. Every 30 min for 3 h, an additional aliquot (0.5−1.0 mL) was removed and quenched by adding acetone (2−3 mL). Volatiles of the aliquot were vacuum transferred for analysis by GC. GC conditions: injector temperature 220 °C; detector temperature 250 °C; oven temperature program 30 °C/18 min; 20 °C/min ramp, 150 °C/25 min. Retention times for hexene isomers under analytical conditions used are as follows: 1-hexene, 14.45 min; *trans*-3-hexene, 15.75 min; *cis*-3-hexene, 15.82 min; *trans*-2-hexene, 16.14 min; *cis*-2-hexene, 17.15 min. The percentage of hexene isomer in solution was determined by taking its peak area and dividing by the sum of the areas of all hexene isomers present.

General Procedures for 1-Octadecene Polymerization. The catalyst **1c** (0.0065 g, 4×10^{-6} mol) was weighed into a flame-dried Schlenk flask under argon in a drybox. Chlorobenzene (1.5 mL) was added to the flask to dissolve the catalyst. A second flame-dried Schlenk flask was prepared with the desired amount of 1-octadecene and chlorobenzene to make a total of 8.5 mL. The 1-octadecene solution was stirred in an ice bath for 30 min to cool it to the polymerization temperature. The catalyst solution was vac-cannulaed into the flask containing the 1-octadecene solution to begin the polymerization. After the polymerization time (usually 1.5, 3, or 4.5 h), 0.2 mL of triethylsilane was added to quench the catalyst. The polymerization solution was poured into 150 mL of methanol and a white precipitate formed immediately. The solid was allowed to settle out and then collected on a Büchner funnel, rinsing copiously with hexanes and acetone to rid the polymer of any remaining monomer. The solid was collect and dried in a vacuum oven at 60 °C overnight. Gel permeation chromatography (1,2,4-trichlorobenzene, 135 °C, polystyrene standards, correction factors $k = 4.34 \times 10^{-4}$. $\alpha = 0.724$): (1 h) $M_n = 5600$, $M_w = 6300$, $M_w/M_n = 1.13$; (1.5 h) $M_n = 8200$, $M_w = 9900$, $M_w/M_n = 1.20$; (3 h) $M_n = 13\,600$, $M_w = 18\,000$, $M_w/M_n = 1.34$; (4.5 h) $M_n = 17\,600$, $M_w = 26\,500$, $M_w/M_n = 1.51$.

Control Experiments for Block Copolymerization. 1-Octadecene Polymerization after Ethylene Removal. This experiment was designed to determine the effectiveness of ethylene removal from the polymerization solution. Ethylene would be declared effectively removed if there was no change in 1-octadecene polymerization run after ethylene had been removed from solution as compared to a 1-octadecene polymerization run in solution where no ethylene was ever present.

A mechanically stirred 300 mL Parr reactor equipped with an electric heating mantle controlled by a thermocouple dipping into the reaction mixture was heated overnight to 150 °C under vacuum and then cooled to 27 °C. The reactor was pressurized to 100 psig of ethylene and vented three times. The reactor was then charged with 80 mL of chlorobenzene and sealed. Ethylene at 100 psig was added and released twice. Then, the reactor was pressurized to 400 psig and the solution cooled to 5−6 °C. Ethylene was vented, the reactor was placed under vacuum for 3 min, the reactor was back-filled with argon, and the polymerization solution was purged with argon for 3 min. The vacuum, backfill, and purge cycle was repeated three times.

Meanwhile catalyst (**2c**) (0.0129 g, 7.92×10^{-6} mol) was weighed into a flame-dried Schlenk flask in the drybox. Chlorobenzene (10.0 mL) was added to dissolve the catalyst, forming a bright yellow solution. A solution of 10.0 mL of chlorobenzene and 10.0 mL of 1-octadecene was also prepared in a flame-dried Schlenk flask. The monomer solution was stirred in an ice bath for 20 min in order to cool it to the polymerization temperature.

After the ethylene removal, the catalyst solution was added to the reactor via cannula. This addition was followed closely by the addition of the 1-octadecene solution to the reactor via cannula to begin the polymerization. The polymerization was carried out for 2 h and then quenched by adding 2.0 mL of triethylsilane. The polymerization solution and two chlorobenzene rinses of the reactor were poured into ∼300 mL of stirring methanol, immediately forming a white precipitate. The polymer was collected as a fluffy, light gray solid. The solid was washed with both methanol and acetone and dried in the vacuum oven. Polymer characterization was performed by ^{1}H NMR (400 MHz, C_6D_5Br, 120 °C). Poly(1-octadecene) run with no ethylene: 41 TO/h by polymer weight; DSC, $T_m = 67.1$ °C, 81.2 °C; by ^{1}H NMR 43 branches/1000 C. Poly(1-octadecene) after ethylene removal from chlorobenzene: 36 TO/h by polymer weight; DSC $T_m = 73.8$ °C, 85.3 °C; by ^{1}H NMR 39 branches/1000 C.

Polymerizing Ethylene in the Presence of Dilute 1-octadecene. The purpose of this experiment was to determine whether polyethylene made in the presence of diluted 1-octadecene was different from polyethylene made with no 1-octadecene present.

A mechanically stirred 300 mL Parr reactor equipped with an electric heating mantle controlled by a thermocouple was heated overnight to 150 °C under vacuum and then cooled to 27 °C. The autoclave was pressurized to 100 psig of ethylene and vented three times. The autoclave was then charged with 80 mL of chlorobenzene and sealed. Ethylene at 100 psig was added and released twice. Then, the reactor was pressurized to 400 psig and the solution cooled to 5−6 °C.

Meanwhile catalyst (**2c**) (0.0130 g, 8.0×10^{-6} mol) was weighed into a flame-dried Schlenk flask in the drybox. Chlorobenzene (10.0 mL) was added to dissolve the catalyst, forming a bright yellow solution.

Ethylene was vented from the reactor, and 0.1 mL of 1-octadecene was added followed by addition of the catalyst solution via cannula. The reactor was re-pressurized to 400 psig of ethylene and the polymerization begun. After 2 h of polymerization in 1-octadecene solution, the reactor was vented, and 0.2 mL of triethylsilane was added to quench the catalyst. The polymer was isolated using the procedure for poly(1-octadecene) workup described above. Polyethylene made in the absence of 1-octadecene as described in the literature:[18] 216 TO/h by weight; T_g −67 °C; 90−110 branches/1000 C. Polyethylene made in the presence of 0.034 M 1-octadecene: 270 TO/h; T_g −61 °C; 90 branches/1000 C.

General Procedure for Polyethylene-*b*-poly(1-octadecene). A mechanically stirred 300 mL Parr reactor equipped with an electric heating mantle controlled by a thermocouple dipping into the reaction mixture was heated overnight to 150 °C under vacuum and then cooled to 27 °C. The autoclave was pressurized to 100 psig of ethylene and vented three times. The autoclave was then charged with 75 mL of chlorobenzene and sealed. Ethylene to 100 psig was added and released twice. Then, the reactor was pressurized to 400 psig of ethylene and the solution cooled to 5−6 °C. The ethylene pressure was vented, and a solution of catalyst (**2c**) (0.013 g, 8×10^{-6} mol) weighed into a Schlenk tube under argon and dissolved in 5 mL of chlorobenzene was added to the reactor via cannula. The reactor was sealed and pressurized with ethylene to 400 psig. The reaction mixture was stirred under constant ethylene pressure for the given ethylene block time, after which time the ethylene pressure was vented.

Ethylene was removed: vacuum was applied to the reactor for 3 min, the reactor was back-filled with argon, and the polymerization solution was purged with argon for 3 min. The vacuum, backfill, and purge cycle was repeated three times. A solution of 1-octadecene (10 mL) in chlorobenzene (10.0 mL) that had been stirring in an ice bath was added to the reactor via cannula. The polymerization solution was stirred for the allotted block time. The catalyst was quenched by addition of 0.2 mL of triethylsilane. The polymerization solution and two rinses of the reactor with chlorobenzene were poured into 300 mL of stirring methanol. The polymer was collected via filtration, rinsed with methanol and acetone, and dried in a vacuum oven at 60 °C.

General Procedure for Poly(1-octadecene)-*b*-polyethylene. The catalyst (**2c**) (0.0130 g, 8×10^{-6} mol) was weighed into a flame-dried Schlenk flask under argon in the drybox. Chlorobenzene (1.0 mL) was added to the catalyst, dissolving the solid to form a bright yellow solution. 1-Octadecene (0.7 mL) and chlorobenzene (5.1 mL) were combined in a second flame-dried Schlenk flask and stirred in an ice bath to cool to the polymerization temperature. The catalyst solution was cannula transferred to the 1-octadecene solution to initiate polymerization of the first block.

Meanwhile, a mechanically stirred 300 mL Parr reactor equipped with an electric heating mantle controlled by a thermocouple dipping into the reaction mixture was heated to 150 °C under vacuum and then cooled to 27 °C. The autoclave was pressurized to 100 psig of ethylene and vented three times. The autoclave was then charged with 100 mL of chlorobenzene and sealed. Ethylene at 100 psig was added and released twice. Then, the reactor was pressurized to 400 psig of ethylene and the solution cooled to 5−6 °C. The reactor was vented after the noted 1-octadecene block time and the polymerization solution containing the poly(1-octadecene) block was added via cannula. The reactor was then pressurized to 400 psig of ethylene and the solution stirred for the allotted polyethylene block time. The polymerization was quenched by adding 0.2 mL of triethylsilane.

The polymerization solution and two chlorobenzene rinses of the reactor were poured into 300 mL of stirring methanol. The polymer was collected via filtration, washed with methanol and acetone and dried in the vacuum oven at 60 °C.

Polymer Characterization. The block copolymers were characterized by three methods. First GPC traces (as described above) were taken of the ethylene/1-octadecene block copolymers at DuPont. DSC traces of all polymers were obtained by heating polymer samples from 25 to 175 °C at 10 °/min and holding for 5 min. The samples were cooled to −100 °C at 10°/min and held for 15 min. The temperature was then raised at 10°/min to 175 °C to obtain the reported data. The T_g of most of the polymers was broad and tended to run into the T_m curves so they were not reported. Polymer T_m values are reported as the endothermic maximum. Finally, the polymers were characterized by ^{1}H and ^{13}C NMR spectroscopy. The ethylene/1-octadecene copolymers were characterized by ^{1}H NMR spectroscopy in C_6D_5Br at 120 °C (393 K). ^{13}C NMR (100 MHz) was carried out in C_6D_5Br containing 0.05 M $Cr(acac)_3$ at 120 °C (393 K) using a 90° pulse of 17.8 μs, a spectral width of 35 kHz, a relaxation delay of 5 s, an acquisition time of 0.64 s, and inverse gated decoupling to allow for integration.[31] ^{1}H

NMR spectroscopy was used to determine overall branching in the polymer, using the following formula:

$$\text{branches/1000 C} = \frac{\text{CH}_3\text{ integral}}{\text{total integral}} \times \frac{2}{3} \times 1000$$

^{13}C NMR was used to examine the types of branches in the polymers and block copolymers. Of the peaks identified in Figure 9, the CH_2* represents the methylenes in the middle of long, straight chains. Other carbons in the polymer chain such as the methine carbons at branch points and carbons in the main chain that are α-, β-, or γ- to a branch have been identified in the literature.[28c,d,31,34] The branches that were included in our polymer analysis all have peaks which are unique and easily separated from the other peaks in the spectrum to ensure more accurate integration. To calculate the number of methyl, ethyl, propyl, and C_4^+ branches, or the straight chain methylenes per 1000 carbons in the polymer chain, the integrals of all peaks from 10 to 42 ppm were summed. The integral of the peak representing the desired branch or methylene was then divided by the sum of all the carbons in the polymer chain and multiplied by 1000.

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