Metallocene-Mediated Olefin Polymerization with B−H Chain Transfer Agents: Synthesis of Chain-End Functionalized Polyolefins and Diblock Copolymers

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ABSTRACT: A systematic study of the scope and limitations of B−H chain transfer agents during metallocene-mediated olefin polymerization is discussed in this contribution. The polymerization procedures provide a convenient route to prepare chain-end functionalized polyolefins and polyolefin diblock copolymers containing both polyolefin and functional polymer blocks. With the proper choice of borane chain transfer agents, metallocene catalyst systems, and reaction conditions, the chemistry can be applied to a broad range of polyolefin homo- and copolymers, such as polyethylene, polypropylene, syndiotactic polystyrene, poly(ethylene-*co*-propylene), poly(ethylene-*co*-1-octene), and poly(ethylene-*co*-styrene). The molecular weight of the borane-terminated polyolefin is basically inversely proportional to the molar ratio of [borane]/[olefin]. In turn, the terminal borane group is very reactive, which can be quantitatively converted to various functional groups and also can be selectively oxidized to form a stable polymeric radical for living free radical polymerization of functional monomers. This process resembles a transformation reaction from metallocene polymerization to living free radical polymerization via the borane terminal group to produce functional polyolefin diblock copolymers, which are difficult to prepare using conventional initiaors.

Introduction

Ever since the discovery of Ziegler−Natta catalysts in the early 1950s, the functionalization of polyolefins has long been a scientifically interesting and technologically important subject.[1−4] The lack of functionality in polyolefins, resulting in poor compatibility with other materials, has been a major drawback in many applications, particularly those in which adhesion, dyeability, printability, or compatibility with other polymers is paramount. As an established technique,[5] the diblock copolymer structure is known to be the most effective compatibilizer for improving the interfacial interaction between two polymers. Usually, the incompatible polymer blends can be improved by adding a small quantity (as low as 1%) of suitable diblock copolymer, which alters the morphology of these blends as well as the interfacial adhesion between the two kinds of domains.

Unfortunately, the preparation of polyolefin diblock copolymers,[6] especially those containing functional groups, is very difficult. The extension of traditional sequential living polymerization processes[7] using Ziegler−Natta and metallocene catalysts has been very limited. In addition, the sensitivity of early transition metal active sites to functional groups further diminishes the possibility of finding a suitable catalyst. In the early 1990s, Yasuda[8] reported a new organolanthanide complex, $LnRCp^*_2$ ($Ln = Sm, Yb, Lu$; $R = H, CH_3$), that is capable of serving the dual functions of polymerizing both olefins and polar monomers, including methyl methacrylate (MMA), ϵ-caprolactone (CL), etc. The living olefin coordination polymerization takes place at ambient temperature. Upon addition of polar monomers, the polymerization process changes to other mechanisms, such as ring-opening or group-transfer mechanisms. Several polyolefin diblock copolymers were prepared with good control of copolymer structure and composition.

The in situ chain transfer reaction during the polymerization presents a very convenient route to introduce a reactive group to the polymer chain end. Ideally, this process does not require the change of reaction conditions, and the catalyst activity remains high during the regular polymerization. Marks[9] first showed that some organosilanes having Si−H group are effective chain transfer agents in metallocene-mediated polymerizations that result in silane-terminated polyolefins. Hessen[10] studied thiophene as a chain transfer agent in ethylene polymerization using a neutral yttrium catalyst system. In general, the polymerization showed low catalyst activity. Kim[11] also observed some chain transfer reaction in the copolymerization of ethylene and allylbenzene. Unfortunately, the polymers showed many terminal structures, which were associated with various modes of chain transfer reactions. Recently, we reported that 9-borabicyclononane (9-BBN) containing a B−H group is a very effective chain transfer agent in ethylene and styrene polymerization reactions to form borane-terminated polyethylene[12] and syndiotactic polystyrene,[13] respectively. We also observed a combined chain transfer agent, based on the mixture of a styreneic molecule and hydrogen,[14] during the metallocene-mediated propylene polymerization.

Our research interest in borane-containing polyolefins stems from its unique versatility in obtaining many

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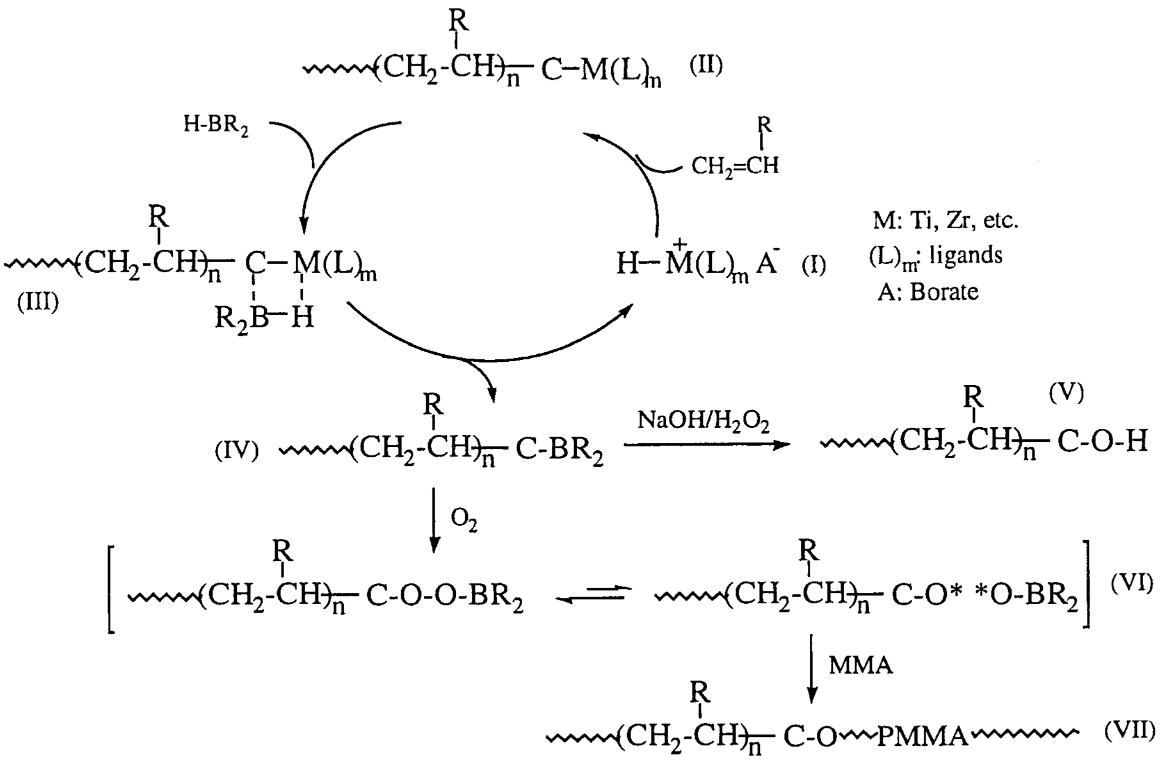
Scheme 1



desirable functional (polar) groups, such as hydroxy and anhydride groups, under mild reaction conditions.[15] In addition, some incorporated borane moieties can be selectively autoxidized by oxygen to form stable polymeric radicals for free radical polymerization of polar monomers.[16] In other words, the borane-terminated polyolefin will be a very useful intermediate for the preparation of chain-end functionalized polyolefins and polyolefin diblock copolymers containing both polyolefin and functional polymer segments. It is very desirable to expand this technology to a broad range of polyolefins, especially to the newly developed polyolefin copolymers by metallocene technology.[17]

Results and Discussion

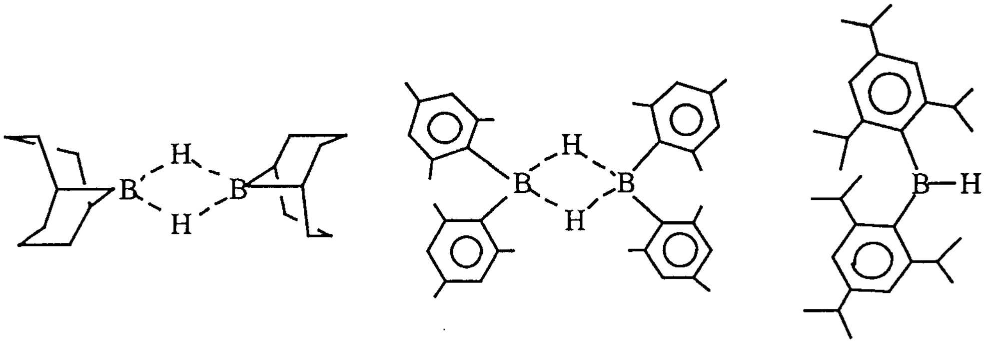
The scope and limitations in the preparation of borane-terminated polyolefins by in situ chain transfer reaction and the subsequent free radical chain extension to form functional polyolefin diblock copolymers containing both polyolefin and functional polymer segments are discussed in this paper. Scheme 1 illustrates the general chemistry that is centered on the in situ chain transfer reaction during metallocene-catalyzed α-olefin polymerization.

In the presence of a dialkylborane containing a B−H group, the metallocene-mediated propagating polyolefin chain (II) engages in a facile ligand exchange reaction between B−H and C−M (M: transition metal) bonds (III), due to the favorable acid−base interaction between the cationic (M) metal center and anionic (H) hydride. This ligand exchange reaction results in a borane-terminated polyolefin (IV) and a new active site (I) that can reinitiate the polymerization. Ideally, the chain transfer reaction should not change the overall catalyst activity, and each polymer will contain a terminal borane group with the polymer molecular weight inversely proportional to the molar ratio of [CT agent]/[α-olefin].

However, there are some potential potholes that can derail the catalytic cycle, namely hydroboration reaction[18] of the B−H to the α-olefin monomers and ligand exchange reaction between the B−H and the cocatalyst containing an Al−alkyl group. In addition, some other potential side reactions, such as an acid−base interaction[19] between borane and imido ligand in $[C_5Me_4(SiMe_2N^tBu)TiMe]^+$ catalyst—a good catalyst in the copolymerization reactions—may further limit the applicability of this reaction process to a broad range of polyolefin copolymers. To understand the scope and limitations, several borane chain transfer agents, metallocene catalysts, and olefin monomers were systematically investigated and discussed below.

Effects of Borane Chain Transfer Agents. Three dialkylborane chain transfer agents, including 9-borabicyclononane (9-BBN), dimesitylborane $(HB(Mes)_2)$, and bis(2,4,6-triisopropylphenyl)borane $(HB(Trip)_2)$ (illustrated in Chart 1), were investigated during the α-olefin polymerization reactions to understand the capability as chain transfer agents. As will be discussed later, both 9-BBN and $H\text{-}B(Mes)_2$ form stable dimers (via four-center bonding) in pure hydrocarbon solvents, while the $H\text{-}B(Trip)_2$ maintains monomeric structure due to steric hindrance. Table 1 compares the experimental results of three parallel ethylene polymerization sets using $[Cp^*_2ZrMe]^+[MeB(C_6F_5)_3]^-$ catalyst and 9-BBN, $HB(Mes)_2$), and $HB(Trip)_2$ chain transfer agents. To prevent the potential side reaction between dialkyborane and the cocatalyst containing an Al−alkyl group, perfluoroborates, such as $[MeB(C_6F_5)_3]^-$ and $[B(C_6F_5)_4]^-$ noncoordinated anion, were used. In comparison with the control reaction (without a chain transfer agent), the metallocene-mediated ethylene polymerization was clearly dependent on the borane chain transfer agents. Catalyst productivity only shows a small change in $HB(Mes)_2$ cases. However, a significant reduction was observed in 9-BBN cases, and no polymer

Chart 1



9-BBN dimer H-B(Mes)$_2$ dimer H-B(Trip)$_2$

Table 1. Comparison of Three Borane Chain Transfer Agents in $[Cp^*_2ZrMe]^+[MeB(C_6F_5)_3]^-$ Catalyzed Ethylene Polymerization[a]

run	chain transfer agent[b]	concn of borane (mM)	reaction time (min)	polymer yield (g)	M_n[c] ($\times 10^{-3}$)	M_w/M_n[c]
control	none	0.0	3	3.50	85.2	2.0
A-1	9-BBN	3.0	3	2.01	76.0	2.4
A-2	9-BBN	4.5	3	2.05	55.5	2.9
A-3	9-BBN	7.5	3	1.45	42.2	2.6
A-4	9-BBN	7.5	5	2.02	45.8	2.6
B-1	HB(Mes)$_2$	3.0	3	3.44	82.5	2.2
B-2	HB(Mes)$_2$	4.5	3	3.40	75.2	2.4
B-3	HB(Mes)$_2$	7.5	3	3.18	64.4	2.1
B-4	HB(Mes)$_2$	7.5	5	4.68	67.8	2.2
C-1	HB(Trip)$_2$	1.0	3	0		
C-2	HB(Trip)$_2$	3.0	3	0		

[a] Catalyst concentration = 0.3 mM; ethylene pressure = 1 atm; [ethylene] = 0.11 M; reaction temperature = 25 °C. [b] 9-BBN = 9-borabicyclononane; HB(Mes)$_2$ = dimesitylborane; HB(Trip)$_2$ = bis(2,4,6-triisopropylphenyl)borane. [c] By GPC in 1,2,4-trichlorobenzene vs polyethylene standards.

was formed in all HB(Trip)$_2$ cases. Overall, the catalyst activity decreases with the increase of both 9-BBN and HB(Mes)$_2$ chain transfer agents, indicating some competitive coordination at metallocene active sites between monomer and chain transfer agents. It is very interesting to witness completely opposite results between HB(Mes)$_2$ and HB(Trip)$_2$ chain transfer agents, despite both being diarylborane compounds with only a small difference in methyl and isopropyl substituents. The ^{11}B NMR spectra (shown in Figure 1) reveal the major difference between the two borane compounds in toluene solvent that was used in the polymerization reactions. The major chemical shift at 30 ppm (in Figure 1b) indicates a stable H-B(Mes)$_2$ dimer[20] formed in toluene, which is inactive to α-olefins. On the other hand, the single peak at 78 ppm in the H-B(Trip)$_2$ case (in Figure 1c) reveals a monomeric B−H structure that is very reactive to ethylene monomers. The hydroboration reaction of ethylene monomer by borane chain transfer agent certainly has negative effects on the polymerization. In addition, the coordination between the monomeric H-B(Trip)$_2$ and metallocene initiation site may also contribute to the inhibition of the polymerization process. Comparing 9-BBN and H-B(Mes)$_2$ in Figure 1a,b, a high field shift (~5 ppm) in diarylborane indicates the π-electron delocalization from aryl group to boron, which strengthens both aryl−B bonds and reduces the acidity of borane moiety. The later is expected to affect the chain transfer reaction between B−H and C−M moieties, illustrated in compound III.

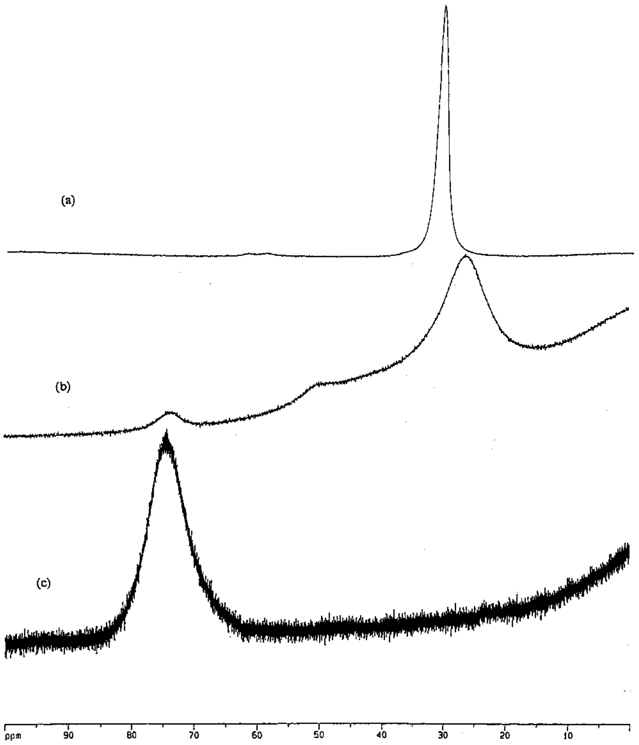


Figure 1. ^{11}B NMR spectra of (a) 9-borabicyclononane, (b) dimesitylborane, and (c) bis(2,4,6-triisopropylphenyl)borane in *d*-toluene (vs etherated BF$_3$).

Acomparative study was carried out by using 9-BBN and H-B(Mes)$_2$ chain transfer agents, respectively, during $[(Ind)_2ZrMe]^+[B(C_6F_5)_4]^-$ mediated ethylene polymerization. To maintain the constant [monomer]/[chain transfer agent] mole ratio, the reactions were carried out by rapid mixing and short reaction time. After a 3 min reaction time, the polymer solution was quenched with anhydrous/anaerobic MeOH, and the resulting borane-terminated polyethylene (PE-t-B) was washed with anhydrous/anaerobic THF to remove excess 9-BBN. Table 2 summarizes the experimental results. Figure 2 shows the GPC curves of several PE-t-B polymers using the H-B(Mes)$_2$ chain transfer agent. The effects of the chain transfer reaction are clearly revealed by the reduction of polymer molecular weight in the presence of both chain transfer agents. In general, the higher the concentration of borane chain transfer agent used, the lower the molecular weight of the resulting polyethylene obtained. The polymer molecular weight distribution is generally narrow, which is consistent with a single site polymerization process with a

Table 2. Comparison of Two Chain Transfer Agents 9-BBN and HB(Mes)$_2$ during [(Ind)$_2$ZrMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$ Mediated Ethylene Polymerization

run	catalyst[a]	borane (mM)	reaction time (min)	activity (kg of PE/(mol of catalyst atm h))		M_n[b] ($\times 10^{-3}$)	
				9-BBN	HB(Mes)$_2$	9-BBN	HB(Mes)$_2$
D-1	[(Ind)$_2$ZrMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$	0	3	3623		102.5	
D-2	[(Ind)$_2$ZrMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$	4.5	3	1853	3250	52.0	95.5
D-3	[(Ind)$_2$ZrMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$	7.5	3	1033	3027	40.0	65.7
D-4	[(Ind)$_2$ZrMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$	12.0	3	850	3011	19.5	37.5
D-5	[(Ind)$_2$ZrMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$	18.0	3	560	2087	14.0	24.5
D-6	[(Ind)$_2$ZrMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$	23.4	3	250	2065	8.5	18.2
D-7	[(Ind)$_2$ZrMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$	30.0	3	65	1657	5.2	15.6
D-8	[(Ind)$_2$ZrMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$	40.0	3		1356		10.0
D-9	[(Ind)$_2$ZrMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$	50.0	3		1211		8.5
D-10	[(Ind)$_2$ZrMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$	60.0	3		1011		5.1

[a] Ind = η^5-C$_9$H$_7$; catalyst concentration = 0.3 mM; ethylene pressure = 1 atm. [b] By GPC in 1,2,4-trichlorobenzene vs polyethylene standards.

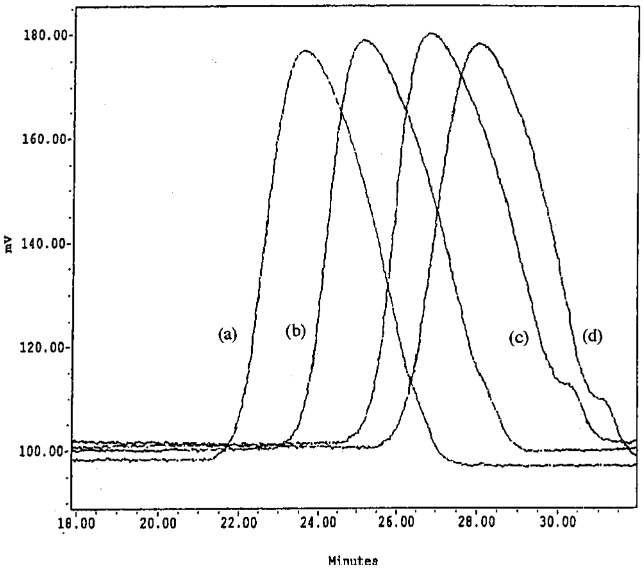


Figure 2. GPC curves of several dimesitylborane-terminated polyethylene (a) D-2, (b) D-3, (c) D-5, and (d) D-8 in Table 2 (solvent = trichlorobenzene; temperature = 135 °C).

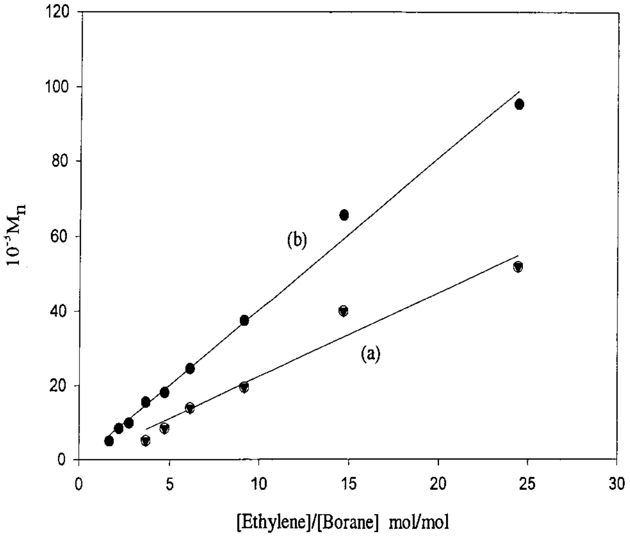
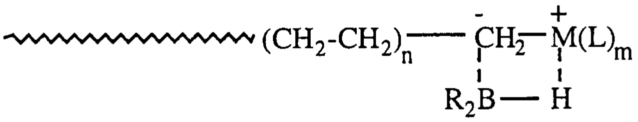


Figure 3. Plots of number-average molecular weight (M_n) of PE-t-B polymers vs the mole ratio of (a) [ethylene]/[9-BBN] and [ethylene]/[H-B(Mes)$_2$] in the feeds (runs in Table 2).

Chart 2



$$\sim\!\sim\!\sim (CH_2\text{-}CH_2)_n\text{—}\overset{-}{C}H_2\text{—}\overset{+}{M}(L)_m \quad R_2B\text{—}H$$

clean chain transfer reaction (no destructive termination due to borane chain transfer agent). Figure 3 shows the plot of polymer molecular weight (M_n) vs the mole ratios of [ethylene]/[9-BBN] and of [ethylene]/[H-B(Mes)$_2$], respectively, for the comparative runs in Table 2. The polymer molecular weight is almost linearly proportional to both molar ratio of [ethylene]/[9-BBN] and [ethylene]/[H-B(Mes)$_2$]. It is clear that the chain transfer reaction to dialkylborane molecule (with rate constant k_{tr}) is the dominant termination process and that it competes with the propagating reaction (with rate constant k_p). The degree of polymerization (X_n) follows a simple comparative equation $X_n = k_p$[olefin]/k_{tr}[dialkylborane] with the chain transfer constant $k_{tr}/k_p \sim 1/75$ and 1/137 for 9-BBN and H-B(Mes)$_2$, respectively. The cationic nature of the catalyst site, in combination with the stronger Lewis acidity of 9-BBN (observed in Figure 1), is reflected in its higher reactivity with 9-BBN than H-B(Mes)$_2$ during the chain transfer reactions, as illustrated in Chart 2. Both polymer molecular weight and catalyst activity sharply decrease with the increase of 9-BBN concentration. The chain transfer reaction did slow the polymerization process. On the other hand, H-B(Mes)$_2$ is a very suitable chain transfer agent allowing good control of polymer molecular weight and high catalyst activity. In addition, during oxidation, the resulting PE-t-B polymer containing a terminal C-B(Mes)$_2$ group selectively forms a stable polymeric radical [C—O* *O—B(Mes)$_2$] group[21] for chain extension with functional monomers. The results will be discussed later.

Effects of Metallocene Catalyst and Cocatalyst. It is very interesting to understand the effects of catalyst and cocatalyst to the B—H chain transfer reaction, especially the steric and electronic roles at active site on the rate of chain transfer reaction. On the basis of the previous results[22] in metallocene copolymerization reactions, it is logical to predict that the spatial opening may play important role in chain transfer reaction, especially involving a bulky chain transfer agent. Figure 4 (top) compares three linear plots of polymer molecular weight vs [ethylene]/[9-BBN] mole ratio, using two sandwiched metallocene catalysts, including [Cp*$_2$ZrMe]$^+$-[MeB(C$_6$F$_5$)$_3$]$^-$ and [(Ind)$_2$ZrMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$, and a constrained geometry [C$_5$Me$_4$(SiMe$_2$N^{t}Bu)TiMe]$^+$-[MeB(C$_6$F$_5$)$_3$]$^-$ catalyst. The first two active sites with small spatial opening show relatively low chain transfer

Table 3. Syndiospecific Polymerization[a] of Styrene in the Presence of 9-BBN Chain Transfer Agent by Using Cp*TiMe$_3$ Catalyst and B(C$_6$F$_5$)$_3$ and PBB[b] Cocatalysts

		activity (kg of s-PS/(mol of catalyst atm h))		M_w[c] ($\times 10^{-3}$)		syndiotacticity[d] of polymer (%)		T_m[e] (°C)	
run	9-BBN (μmol)	B(C$_6$F$_5$)$_3$	PBB	B(C$_6$F$_5$)$_3$	PBB	B(C$_6$F$_5$)$_3$	PBB	B(C$_6$F$_5$)$_3$	PBB
E-1	25	2600	5400	460	740	97.0	97.0	270	270
E-2	50	2800	5200	240	380	96.2	96.3	271	271
E-3	100	2600	5000	150	230	95.8	95.9	270	270
E-4	150	2200	4000	80	130	95.2	95.3	271	271
E-5	200	1600	3000	70	110	93.4	93.8	270	270
E-6	300	1000	2000	30	48	94.7	94.8	272	271
E-7	400	600	1000	15	29	95.0	95.1	270	270
E-8	500	200	400	10	21	93.2	93.3	270	270

[a] Styrene = 10 mL; catalyst concentration = 10 μmol; reaction time = 3 min. [b] PBB = tris(2,2′,2″-nonafluorobiphenyl)borane. [c] The molecular weight was determined from intrinsic viscosity in *o*-dichlorobenzene at 135 °C: $[\eta] = 1.38 \times 10^{-4} M_w^{0.7}$. [d] Determined by ^{13}C NMR. [e] Determined by DSC.

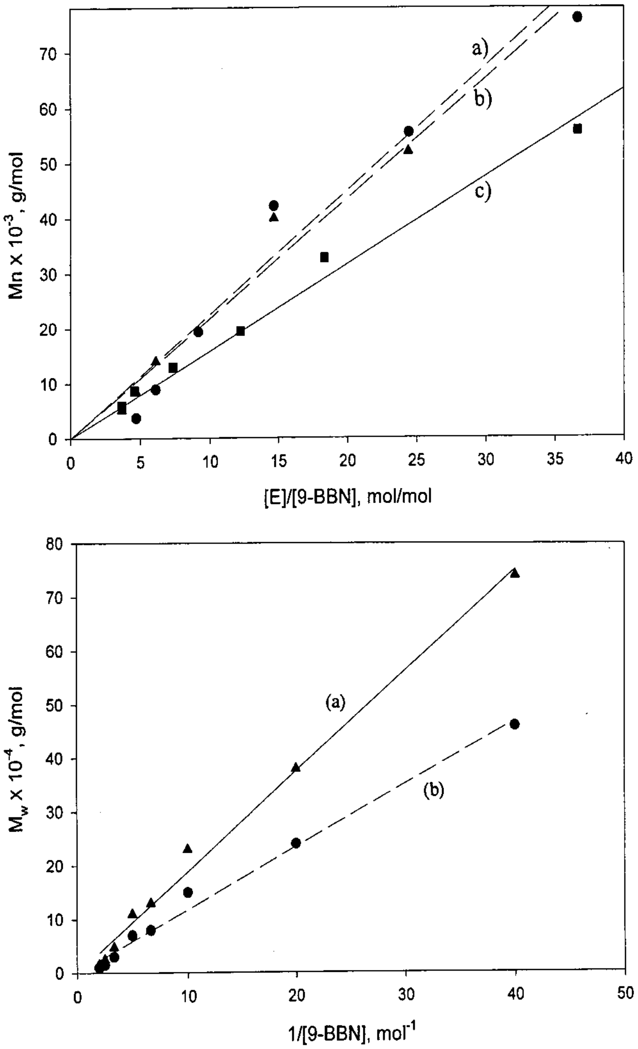


Figure 4. (top) Plots of number-average molecular weights (M_n) of PE-t-B polymers vs the mole ratio of [ethylene]/[9-BBN] by using (a) [Cp*$_2$ZrMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$, (b) [(Ind)$_2$ZrMe]$^+$-[MeB(C$_6$F$_5$)$_3$]$^-$, and (c) [C$_5$Me$_4$(SiMe$_2$N^{t}Bu)TiMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ catalysts. (bottom) Plots of molecular weights of s-PS-t-B polymers vs 1/[9-BBN] by using (a) [Cp*TiMe$_2$]$^+$[MePBB]$^-$ and (b) [Cp*TiMe$_2$]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ catalysts.

activities with $k_{tr}/k_p \sim 1/75$. On the other hand, the last one with an opened active site significantly exhibits higher chain transfer activity with $k_{tr}/k_p \sim 1/57$. The spatial opening at the active site does affect the chain transfer reaction; however, the electronic contribution is not clear.

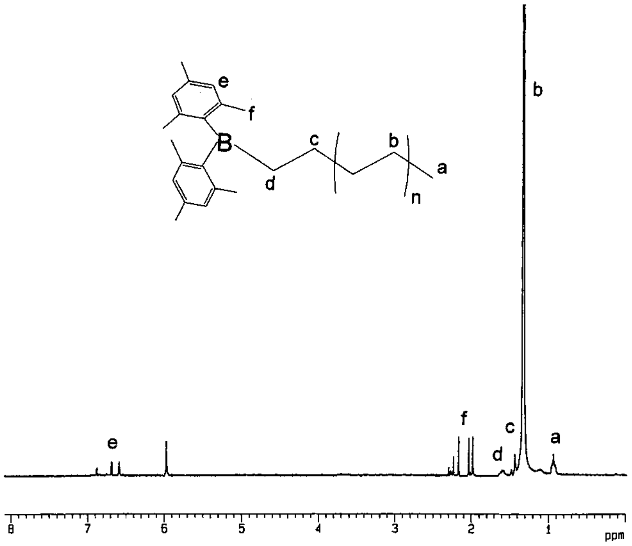


Figure 5. ^{1}H NMR spectrum of a PE-t-B(Mes)$_2$ sample (M_n = 5200 g/mol; M_w/M_n = 2.2), with an inset of chemical shift assignments (solvent = C$_2$D$_2$Cl$_4$; temperature = 110 °C).

Table 3 and Figure 4 (bottom) show several comparative syndiospecific styrene polymerizations in the presence of 9-BBN chain transfer agent by using a half-sandwich Cp*TiMe$_3$ catalyst and two different cocatalysts, including B(C$_6$F$_5$)$_3$ and a bulky tris(2,2′,2″-nonafluorobiphenyl)borane (PBB).[23] In general, the PBB system shows higher catalytic activity (about 2 times higher than the other) and lower chain transfer activity and almost no difference in syndiospecificities of the styrene insertions. The large (PBB−CH$_3$)$^-$ noncoordinated anion, located near the active half-sandwich titanocene cation, apparently does not block the active site from styrene monomer but does interfere the bulky 9-BBN dimer reacting with the propagating chain end.

Chain-End Analysis. End group structures at both polymer chain ends provide direct evidence for the chain transfer reaction. This analysis was greatly benefited by the low molecular weight polymers. Figure 5 shows the ^{1}H NMR spectrum of a PE-t-B(Mes)$_2$ sample (M_n = 5200 g/mol; M_w/M_n = 2.2), with an inset of chemical shift assignments.[24]

In addition to the major chemical shift at 1.30 ppm, corresponding to CH$_2$ in the PE backbone, there are several weak peaks associated with both polymer chain ends. The peak intensity ratio between C**H**$_3$ and ϕ-C**H**$_3$ indicates near 1:1 ratio of the two end groups. It is interesting to note that there is no detectable vinyl

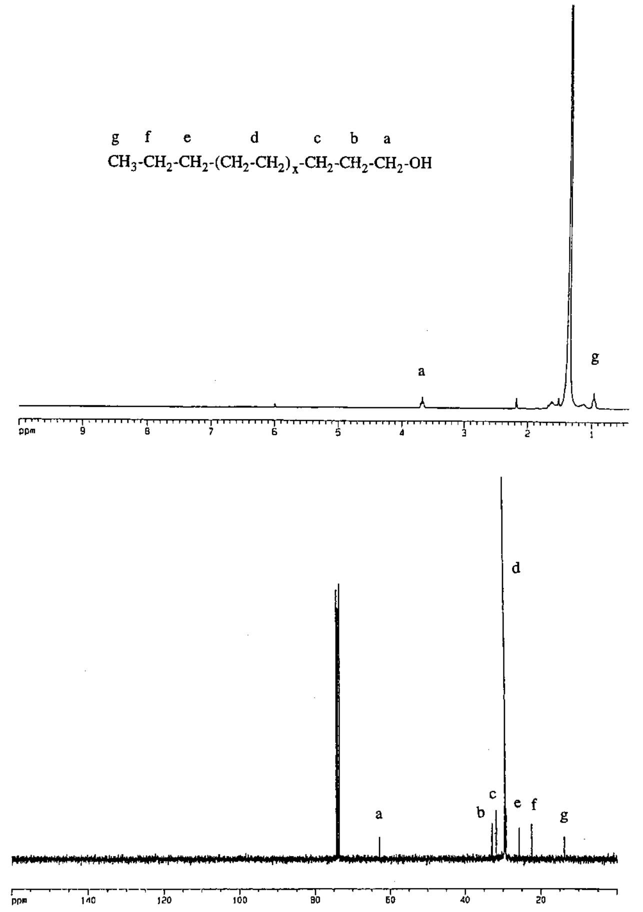


Figure 6. (top) ^{1}H and (bottom) ^{13}C NMR spectra of a hydroxy-terminated polyethylene, with an inset of chemical shift assignments (solvent = $C_2D_2Cl_4$; temperature = 110 °C).

group associated with the conventional chain transfer process (via β-H elimination).

The PE-t-B(Mes)$_2$ polymer was further oxidized by NaOH/H_2O_2 to form a hydroxy-terminated polyethylene (PE-t-OH). Figure 6 shows the ^{1}H and ^{13}C NMR spectra of the corresponding PE-t-OH.

In Figure 6a, the major chemical shift at 1.30 ppm (C**H**$_2$) is accompanied by several weak peaks at 0.97 ppm (chain end CH$_3$), 1.58 ppm ($-$C**H**$_2$CH$_2-$OH), 2.25 ppm ($-$O**H**), and 3.62 ppm ($-$**CH**$_2-$OH). The peak intensity ratio of O**H**:C**H**$_2-$O:C**H**$_3$ = 1:2:3 (±2%) indicates the exclusive production of hydroxy-terminated polyethylene. There is no detectable vinyl group associated with the β-H elimination. The same results were also observed in the ^{13}C NMR spectra with the chemical shifts corresponding to $-$C**H**$_2-$OH (δ 62.99) and chain end C**H**$_3$ (δ 13.85) groups. These findings strongly indicate the in situ chain transfer to H-B(Mes)$_2$ moiety during the catalytic polymerization of ethylene.

Similar experimental results were also observed in syndiotactic polystyrene (s-PS) by using borane chain transfer agents and $[Cp^*TiMe_2]^+[MeB(C_6F_5)_3]^-$ catalyst. Figure 7 compares the ^{1}H NMR spectra of a s-PS polymer and a dimesitylborane-terminated s-PS (s-PS-t-B(Mes)$_2$) having a molecular weight about 8000 g/mol. The inset shows the chemical shift assignments.[25]

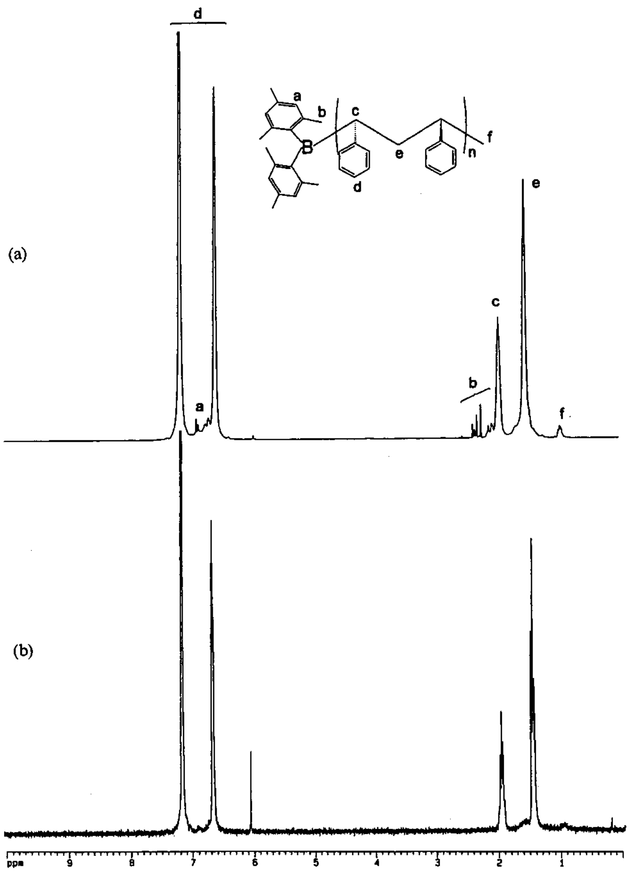


Figure 7. ^{1}H NMR spectra of (a) s-PS-t-B(Mes)$_2$ polymer (molecular weight 8000 g/mol) and (b) s-PS polymer, with an inset of chemical shift assignments.

In addition to the chemical shifts for s-PS polymer, the chemical shifts for both dimesitylborane and methyl end groups are clearly observed in Figure 7a. It is interesting to note that the borane chain transfer agents showed no effect on the stereospecific insertion of styrene monomers during the propagation processes. Both borane-terminated s-PS polymers appear to have similar melting temperatures with the corresponding unfunctionalized homopolymers.

Copolymerization Reactions. It is very important to broaden the scope of this chemistry to the copolymerization reactions. In addition to understanding the generality of B$-$H chain transfer reaction, the chemistry could provide a very valuable route to the functionalization of new polyolefin copolymers, such as metallocene$-$LLDPE[26] and ethylene/styrene[27] copolymers, which are becoming important commercial materials in new polyolefin applications.

In the ethylene copolymerization, the constrained geometry $[C_5Me_4(SiMe_2N^tBu)TiMe]^+$ catalyst with larger spatial opening at the catalytic site was a preferred choice, providing favorable copolymerization conditions for all ethylene copolymerization with many large size monomers, such as 1-propene, 1-butene, 1-octene,[26] styrene,[27] and *p*-methylstyrene.[22] In the B$-$H chain transfer reaction, it is very interesting to examine the effects of the potential acid$-$base interaction between borane and imido ligand in the $[C_5Me_4(SiMe_2N^tBu)TiMe]^+$ catalyst used to prepare borane-terminated polyolefin copolymers.

Table 4 summarizes the experimental results of two representative sets of ethylene/1-octene and ethylene/styrene copolymerization reactions by using the 9-BBN chain transfer agent and the $[C_5Me_4(SiMe_2N^tBu)TiMe]^+[MeB(C_6F_5)_3]^-$ complex. The copolymer molecular weight and composition were determined by GPC and ^{1}H NMR measurements.

Table 4. Summary of Ethylene/1-Octene and Ethylene/Styrene Copolymerization Reactions by Using $[C_5Me_4(SiMe_2N^tBu)TiMe]^+[MeB(C_6F_5)_3]^-$ Complex in the Presence of 9-BBN Chain Transfer Agent

	reaction condition[a]					copolymer structure		
run	time/temp (min/°C)	ethylene (atm)	comonomer/ (M)	9-BBN (mM)	catalyst activity (kg P/(mol Ti atm h))	comonomer[b] incorp (mol %)	M_n[c] (10^{-3})	M_w/M_n[c]
F-1	3/50	1	O/0.32	0	263	36.3	44.6	2.8
F-2	3/50	1	O/0.32	30	269	35.7	40.8	2.4
F-3	3/50	1	O/0.32	60	251	36.8	27.3	2.5
F-4	3/50	1	O/0.32	90	206	37.6	22.0	2.7
F-5	3/50	1	O/0.32	120	202	39.0	20.2	2.8
G-1	5/50	1	S/0.87	0	351	22.6	41.1	2.1
G-2	5/50	1	S/0.87	30	351	22.4	38.7	2.4
G-3	5/50	1	S/0.87	60	363	19.3	19.6	2.4
G-4	5/50	1	S/0.87	90	486	28.5	9.9	2.6
G-5	5/50	1	S/0.87	120	525	28.0	7.7	2.6

[a] Catalyst concentration = 3 mM; O = 1-octene; S = styrene; [ethylene] = 0.11 M; 20 mL of toluene; 50 °C. [b] By ^1H NMR. [c] By GPC in THF vs polystyrene standard.

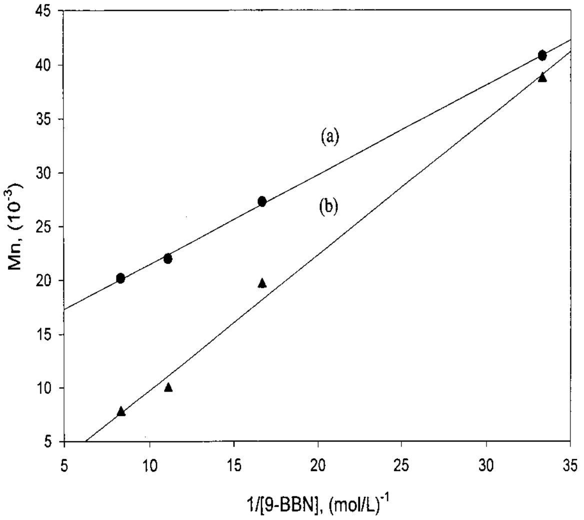


Figure 8. Plots of the molecular weight (M_n) of (a) EO-t-9-BBN and (b) ES-t-9-BBN copolymers vs 1/[9-BBN] (runs in Table 4).

In general, both resulting 9-BBN-terminated poly(ethylene-*co*-1-octene) (EO-t-9-BBN) and poly(ethylene-*co*-styrene) (ES-t-9-BBN) copolymers show similar trends—decreasing the polymer molecular weight with increasing B−H chain transfer agent—discussed in the homopolymerization reactions. Compared to the control runs (F-1 and G-1) (without 9-BBN chain transfer agent), the copolymerization reaction shows similar comonomer incorporation and catalyst activity with the presence of 9-BBN. There are no detected effects due to acid−base interaction between borane and imido ligand in the $[C_5Me_4(SiMe_2N^tBu)TiMe]^+[MeB(C_6F_5)_3]^-$ complex. A copolymer with very low molecular weight (few thousand) has been obtained, and the molecular weight distribution is generally narrow, which is consistent with single site polymerization processes. Figure 8 shows the plot of the molecular weight (M_n) of both EO-t-9-BBN and ES-t-9-BBN copolymers (in Table 4) vs 1/[9-BBN]. The linear relationship indicates the B−H chain transfer reaction (k_{tr}) as the dominant termination process and that it competes with the propagating reaction (k_p). The estimated chain transfer constants (k_{tr}/k_p), based on the combined monomer concentration, are 1/29 and 1/24 for EO-t-9-BBN and ES-t-9-BBN, respectively. Both of the chain transfer constants in the copolymerization reactions are significantly higher than that (1/75) of the correponding ethylene homopolymerization. The comonomers clearly slow the propagating process, especially in ethylene/styrene case. The cationic nature of the catalyst site is known to proceed 2,1-insertion[28] of styrene, which may result in a less active propagating site due to the interaction between the cationic Ti^+ center and the adjacent phenyl group at the polymer chain end.

The "slowdown" propagating chain end (after styrene insertion) increases the vulnerability to chain transfer reaction with 9-BBN. It is logical to predict the majority of the chain end structures will have a styrene unit right before the incorporation of borane terminal group. To increase the NMR sensitivity for determining the end group, the terminal borane group was converted to a hydroxy group. Figure 9 shows the ^{13}C (DEPT-135) NMR spectra of a hydroxy-terminated poly(ethylene-*co*-styrene) (ES-t-OH) that was converted from a ES-t-9-BBN polymer (sample G-4 in Table 3; styrene content = 28.5 mol %; M_n = 9900 g/mol; M_w/M_n = 2.6). The inset shows the chemical shift assignments.[27]

Along with all the expected chemical shifts, corresponding to the aliphatic and aromatic carbons in the polymer chain, there is only one chemical shift (at 51.36 ppm) corresponding to the end group $-\mathbf{C}(\phi)H-OH$. The results clearly explain the chain transfer mechanism in the copolymerization reactions.

Polyolefins Diblock Copolymers. As illustrated in eq 1, the ideal borane-terminated polyolefin (IV) can not only be converted to the hydroxy-terminated polyolefin (V), it can also be selectively transformed to a polymeric peroxide containing peroxylborane ($C-O-O-BR_2$) moiety (VI) by a simple oxygen autoxidation reaction. This peroxylborane is a reactive radical initiator[16] even at ambient temperature. The spontaneous homolytical cleavage of peroxide may take place by generating a reactive alkoxy radical ($C-O^*$) and a stable borinate radical ($^*O-BR_2$)[21] due to the back-donating of electron density to the empty p-orbital of boron. The alkoxyl radical then initiates the radical polymerization of functional (polar) monomers at ambient temperature. On the other hand, the dormant borinate radical serves as the end-capping agent to form a weak and reversible bond with the growing chain end during the polymerization. This process minimizes the undesirable chain transfer reaction and termination (coupling and disproportionation) reaction between the two growing chain ends. Overall, the process produces functional polyolefin diblock copolymers, and the nature and concentration of the functional groups in the polymer are basically determined by the functional monomers introduced during the chain extension reaction.

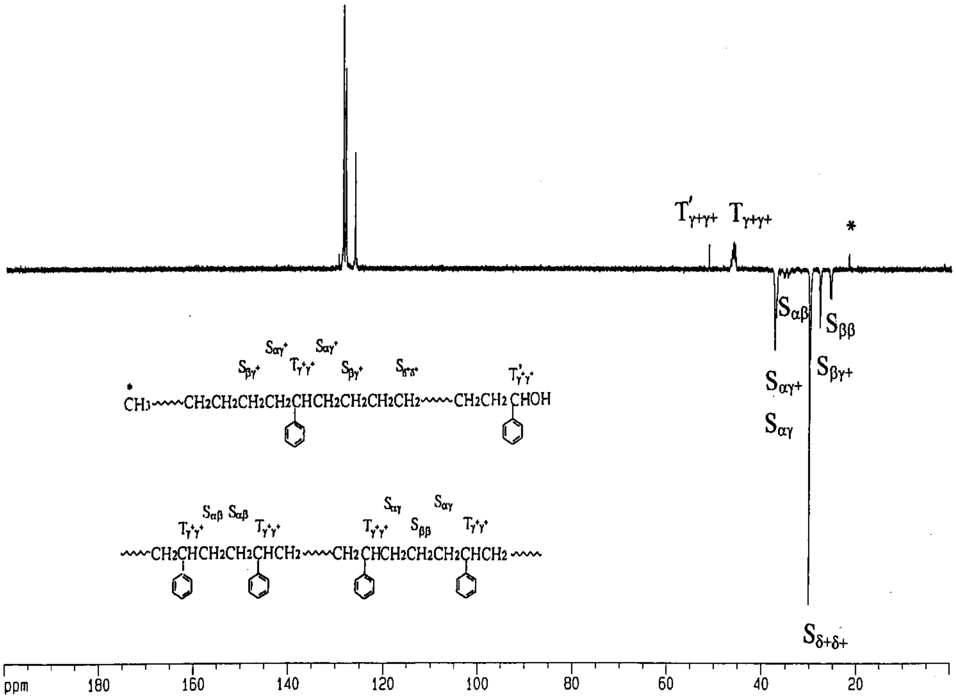


Figure 9. ^{13}C (DEPT-135) NMR spectrum of a hydroxy-terminated poly(ethylene-*co*-styrene), with an inset of chemical shift assignments.

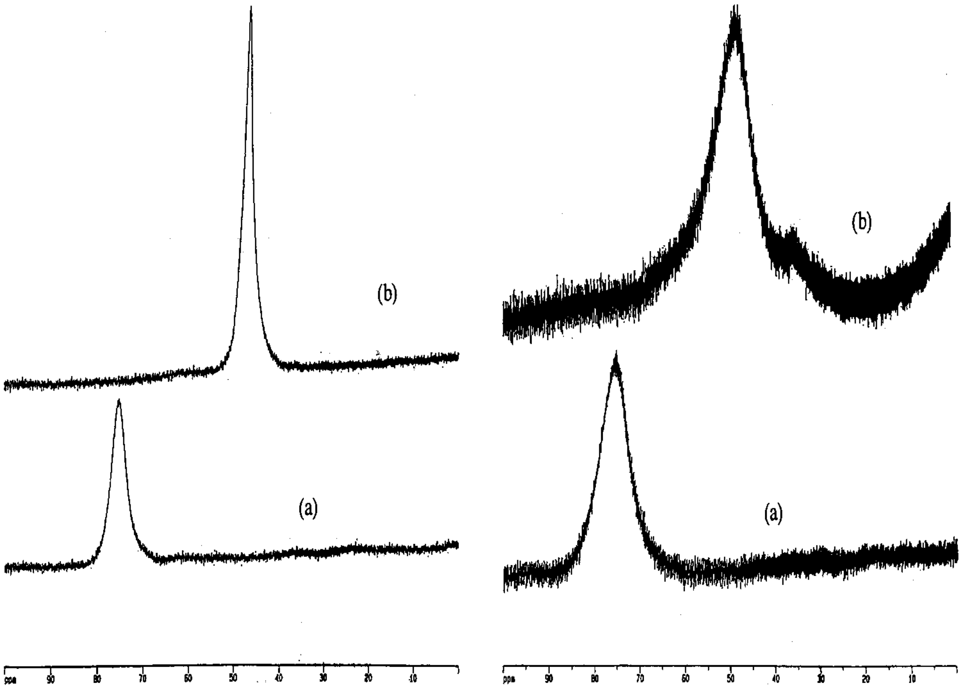


Figure 10. ^{11}B NMR spectra of (right) the PE-t-B(Mes)$_2$ sample before (a) and after (b) the oxidation reaction and (left) a control octyl-B(Mes)$_2$ sample before (a) and after (b) the oxidation reaction.

The key to efficiently forming diblock copolymer lies in the formation of polymer peroxylborane (C−O−O−BR$_2$) moiety (VI). Obviously, it is very important to have an asymmetrical C−BR$_2$ group (such as C-9-BBN and C-B(Mes)$_2$) in the polyolefin chain end (IV) that can engage in a selective oxygen insertion at the polymer C−B bond (instead of at the two other alkyl C−B bonds). In the following free radical chain extension, the polymeric peroxide (C−O−O−BR$_2$) produces polyolefin diblock copolymer, while the alkyl peroxide results in two homopolymers. It is very important to note that the asymmetrical C-B(Mes)$_2$ terminal groups show exceptionally good oxidation selectivity at the polymer C−B bond. Figure 10 compares the ^{11}B NMR spectra of the PE-t-B(Mes)$_2$ sample before and after the oxidation reaction, which were also compared parallelly with a control octyl-B(Mes)$_2$ sample.

The single chemical shift of C-B(Mes)$_2$ at 76 ppm (vs 88 ppm for alkyl-9-BBN)[18] in both polymer and small molecules indicates the strong π-electron delocalization around the B atom, which provides high bond order and good stability of the aryl−B bonds. Upon oxidation, both chemical shifts completely move to the higher field at 45 ppm, indicating a quantitative oxidation reaction to

Table 5. Summary of Polyethylene-*block*-poly(methyl methacrylate) Diblock Copolymers Prepared by Two Borane-Terminated PE Polymers

	reaction condition[a]							diblock copolymer		
run	T (°C)	PE-t-B (g)	O_2 (mL)	MMA (M)	reaction time (h)	yield (g)	MMA conv (%)	M_n[c]	M_w/M_n[b]	ethylene/MMA[c] (mol/mol)
			Starting PE-t-B Polymer I[b] with $M_n = 43\,000$ and $M_w/M_n = 2.2$							
H-1	25	5	1.4	1.87	2	6.12	5.3	48 000	2.3	100:3
H-2	25	5	1.4	1.87	6	6.78	9.5	62 000	2.4	100:13
H-3	25	5	1.4	1.87	12	8.74	20.0	76 000	2.0	100:22
H-4	25	5	1.4	1.87	24	10.24	28.0	98 000	2.3	100:36
			Starting PE-t-B Polymer II[b] with $M_n = 20\,000$ and $M_w/M_n = 2.7$							
I-1	25	3	1.9	1.87	6	3.98	10.5	49 000	2.1	100:43
I-2	25	3	1.9	1.87	12	6.56	19.0	63 000	2.4	100:62
I-3	25	3	1.9	1.87	24	8.05	27.0	91 000	2.0	100:102
I-4	25	6	3.8	1.87	6	8.80	31.0	66 000	2.2	100:66

[a] Total volume (MMA + benzene) = 50 mL. [b] Both M_n and M_w/M_n were determined by high-temperature GPC vs polyethylene standards. [c] Determined by ^{1}H NMR spectra.

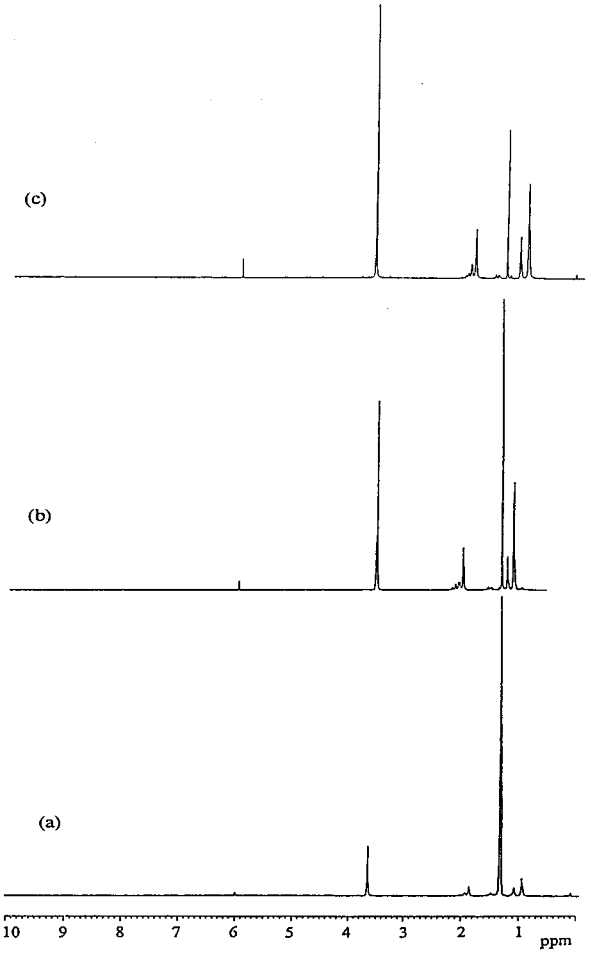


Figure 11. ^{1}H NMR spectra of three PE-*b*-PMMA copolymers, including (a) I-1, (b) I-2, and (c) I-3 shown in Table 5 (solvent = $C_2D_2Cl_4$; temperature = 110 °C).

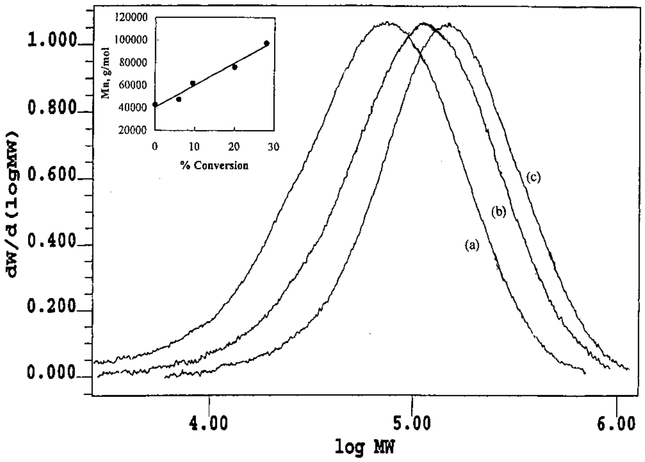


Figure 12. GPC curves of two PE-*b*-PMMA diblock copolymers (a) H-4 and (b) H-2 samples in Table 5 and (c) the starting PE-t-B polymer (M_n = 43 000 g/mol and M_w/M_n = 2.2).

produce C−O−O−B(Mes)$_2$ initiator. Because of the two strong aryl−B bonds, the oxidation reaction selectively takes place at the polymer C−B(Mes)$_2$ bond. Table 5 summarizes the experimental results of PE-*b*-PMMA copolymers that were started with two PE-t-B(Mes)$_2$ polymers having M_n = 43 000 and 20 000 g/mol, respectively. The resulting PE-*b*-PMMA reaction mixture was carefully fractionated by Soxhlet extraction using boiling THF for 24 h to remove any PMMA homopolymer. In the PE-t-B(Mes)$_2$ cases, almost no PMMA homopolymer was isolated. On the other hand, a very small amount (about 10%) of PMMA homopolymer[12] was usually observed by starting with a PE-t-9-BBN sample, which is due to the small level of nonselective oxygen oxidation reaction in the C-9-BBN group. Figure 11 shows the ^{1}H NMR spectra of three PE-*b*-PMMA copolymers that were sampled at different reaction times during the same chain extension process. The reaction was started by using a PE-t-B polymer with M_n = 20 000 g/mol and M_w/M_n = 2.7. The new peak at 3.58 ppm, corresponding to methoxyl groups (C**H**$_3$O) in PMMA, increased its intensity with the reaction time. Apparently, the PMMA segment in PE-*b*-PMMA grows with the reaction time, and high molecular weight diblock copolymer with up to 85 mol % of PMMA copolymer (Figure 11c) has been prepared. Considering there is only one terminal borane group in each PE chain, these experimental results imply a very effective chain extension process. Figure 12 compares the GPC curves of two PE-*b*-PMMA diblock copolymers and the starting PE-t-B polymer (M_n = 43 000 g/mol and M_w/M_n = 2.2). It is clear that the polymer continuously increased its molecular weight during the entire polymerization process. The polymer's molecular weight distribution was maintained at very constant and narrow levels (M_w/M_n = 2.0−2.4). The monochromatic increase of the copolymer molecular weight, with only a slight broadening in the molecular weight distribution and no detectable PE homopolymer, clearly points to the existence of a borane group at each PE chain end and a living radical polymerization of MMA in the chain extension process. The inset shows the linear plot of polymer molecular weight vs the monomer conversion and compares the results with a theoretical line based on the polymer molecular weight estimated from [grams of monomer consumed]/[moles of initiator]. A good match with the straight line through the origin strongly supports the presence of living polymerization in the reaction.

Experimental Details

Instrumentation and Materials. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 300 instrument. The molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) using a Waters 150 C with a refractive index (RI) detector and a set of u-Styragel HT columns of 10^6, 10^5, 10^4, and 10^3 pore sizes. The measurements were taken at 140 °C using 1,2,4-trichlorobenzene (TCB) as solvent and a mobile phase of 0.7 mL/min flow rate. Narrow molecular weight PS samples were used as standards for calibration.

All O_2- and moisture-sensitive manipulations were carried out inside an argon-filled Vacuum Atmosphere drybox. Toluene (Wiley Organics) was distilled over sodium naphthalide under argon. High-purity grade ethylene, propylene (MG Industries), methanol, methylaluminoxane (MAO) (Ethyl), 9-borabicyclononane, dimesitylborane, and bis(2,4,6-triisopropylphenyl)borane (Aldrich) were purchased and used as received. The metallocene catalysts, including $[Cp^*_2ZrMe]^+[MeB(C_6F_5)_3]^-$, $[Ind_2ZrMe]^+[MeB(C_6F_5)_3]^-$, $[C_5Me_4(SiMe_2N^tBu)TiMe]^+[MeB(C_6F_5)_3]^-$, and $[Cp^*TiMe_2]^+[MeB(C_6F_5)_3]^-$, were prepared according to the published procedures.[27,30,31]

Chain Transfer Reaction in Metallocene-Mediated Ethylene Polymerization. To a Parr 450 mL stainless autoclave equipped with a mechanical stirrer, 100 mL of anhydrous/anaerobic toluene and 7.5 mmol of 9-BBN were placed under argon flow. The reactor was then purged with ethylene gas (~1 atm) to saturate the solution at ambient temperature. About 0.3 mmol of $[Ind_2ZrMe]^+[MeB(C_6F_5)_3]^-$ catalyst in toluene solution was then syringed into the rapidly stirring ethylene/9-BBN solution under ethylene pressure to initiate the polymerization at 25 °C. Additional ethylene was fed continuously into the reactor to maintain a constant pressure of 1 atm during the whole course of the polymerization. After 3 min of reaction time, the polymer solution was quenched with anhydrous/anaerobic MeOH, and the resulting borane-terminated polyethylene (PE-t-B) was washed with anhydrous/anaerobic THF to remove excess 9-BBN and then dried at 50 °C in a high-vacuum line. About 1.9 g of borane-terminated polyethylene was obtained with the catalytic activity of 1267 kg of PE/(mol of catalyst atm h).

Oxidation Reaction of Borane-Terminated Polyethylene. About 2.0 g of PE-t-B(Mes)$_2$ ($M_n = 5200$ g/mol; $M_w/M_n = 2.2$) was placed in a suspension of 50 mL of dry, O_2-free THF in a drybox. The sealed reactor was moved out and purged with nitrogen gas. To the polymer slurry, a solution containing 0.4 g of NaOH in 2 mL of H_2O and 0.5 mL of MeOH purged by N_2 was added at room temperature, and then 1.6 mL of 30% oxygen-free H_2O_2 was added dropwise at 0 °C. The oxidation was performed at 40 °C for 6 h before being poured into 100 mL of MeOH. The resulting PE-t-OH solid was filtered and dried in vaccun oven at 50 °C for 8 h.

Synthesis of Poly(ethylene-*b*-methyl methacrylate) (PE-*b*-PMMA). In a glovebox with argon atmosphere, 9-BBN-terminated polyethylene (3 g; $M_n = 20\,000$ g/mol; $M_w/M_n = 2.7$), prepared by the procedure shown in example 1, was mixed with methyl methacrylate monomer (18.7 g) and 80 mL of anhydrous/anaerobic benzene solvent in a septum-capped 250 mL glass flask equipped with a high-vacuum stopcock and a magnetic stirring bar. The sealed flask was removed from the glovebox, and the free radical polymerization reaction was initiated by injecting a measured amount of O_2 (1.9 mL) into the reaction flask at room temperature. After a measured time interval (24 h), the polymerization reaction was terminated by adding 50 mL of methanol. The polymer was collected by filtration and then washed with methanol and THF, followed by drying under vacuum at 60 °C. The dried polymer was extracted with boiling THF to remove trace amounts of poly(methyl methacrylate) homopolymer. The insoluble fraction, but soluble in 1,1,2,2-tetrachloroethane and 1,2,4-trichlorobenzene at elevated temperatures, is PE-*b*-PMMA diblock copolymer (8.05 g). The diblock polymer was analyzed by ^{1}H NMR and GPC techniques. ^{1}H NMR spectra show the relative molar ratio between ethylene and MMA repeating units in each block is about 100:102, which is quite consistent with the GPC results showing the molecular weight of the diblock copolymer is $M_n = 91\,000$ g/mol.

Summary

The combination of borane (B−H) chain transfer reaction and selective oxidation of the terminal borane group provides a very versatile route to the preparation of functional polyolefin diblock copolymers containing polyolefin and functional polymer blocks. Under some specific reaction conditions, the chemistry is applicable to many metallocene catalysts and commercial polyolefins, including both homo- and copolymers. Dimesitylborane (HB(Mes)$_2$) seems to be a very suitable chain transfer agent, exhibiting high catalyst activity and good control of the polymer molecular weight during the metallocene-mediated olefin polymerization. The formed dimesitylborane-terminated polyolefin shows selective transformation of the borane terminal group to a living free radical initiator for polymerization of functional monomers. Overall, the process employs the best polymerization mechanisms (metallocene and living free radical) for preparing polyolefin and functional polymer blocks, respectively. The combined capability of these two polymerization mechanisms provides a broad composition range of diblock copolymers with relatively well-defined polymer structures.

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