Synthesis of Chain End Functional Isotactic Polypropylene by the Combination of Metallocene/MAO Catalyst and Organoborane Chain Transfer Agent

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ABSTRACT: This paper discusses a simple and effective route to prepare chain end functionalized PP and PP diblock copolymers, with high molecular weight and high purity. The reaction scheme involves a versatile "intermediate" of borane-terminated isotactic polypropylene (PP-t-B), which was prepared under a specific reaction condition, involving an iso-specific metallocene catalyst, purified MAO activator (without TMA), 9-borabicyclononane (9-BBN) dimmer chain transfer agent, and ambient reaction temperature. During the propylene polymerization mediated by the *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO catalyst system, the PP propagating chain end (C−Zr active site) engages in a selective ligand exchange reaction with a B−H group in the 9-BBN dimmer. Evidently, the side reaction between the 9-BBN dimmer and the purified MAO is very slow at <35 °C, so that the normal polymerization-chain transfer reaction mechanism can effectively take place to form the PP-t-B polymer. The polymer molecular weight is inversely proportional to the molar ratio of [9-BBN]/[propylene] with a chain transfer constant (k_{tr}/k_p) of 1/65. Despite the high molecular weight and heterogeneous reaction conditions, the terminal borane group in PP-t-B is quantitatively interconverted to the OH group under a mild ionic oxidation reaction condition. It is also selectively auto-oxidized by oxygen to form a control radical macroinitiator that affords the chain extension with methymethacrylate monomers to form PP-*b*-PMMA diblock copolymers.

Introduction

The functionalization of polyolefin[1−3] has been a long scientific interest and technological important research subject since the discovery of high density polyethylene (HDPE) and isotactic polypropylene (PP) about a half-century ago. The constant interest is obviously due to the commercial importance of polyolefin and the strong desire to improve its poor interactive properties. The hydrophobicity and low surface energy of polyolefin has limited its applications, especially in the areas of coating, blends, and composites, in which adhesion and comparability are paramount. Among polyolefins, PP is the most desirable, but also most difficult, of the functionalization approaches. In direct polymerization, only few stereospecific early transition metal catalysts can be used in the preparation of PP, which are normally poisoned by functional groups. On the other hand, i-PP has been one of the polymers most resistant to chemical modification. In many cases, the reaction involves serious side reactions, such as degradation of the PP polymer chain.[1]

Isotactic polypropylene having a terminal functional group[4,5] is a very attractive material that possesses an unperturbed isotactic chain structure with high melting temperature and high crystallinity. The terminal functional group with good mobility and reactivity can provide PP with the needed interactive properties, especially promoting adhesion to the substrates, forming graft and block copolymers, and reactive blending. Unfortunately, the chemistry to prepare chain end functionalized PP is very limited. The common approach of living polymerization methods, using a living initiator bearing a functional group[6,7] or a control termination (functionalization) reaction[8,9] of the living polymer chain end, can not be applied to the PP case. There are only a few transition metal coordination catalysts that exhibit living polymerization behavior, and most of them are limited to the preparation of polyethylene and poly(1-hexene) cases.[10−14]

More recently, there has been an increasing interest in control chain transfer reactions using a specific external chain transfer agent during the Ziegler−Natta (metallocene) mediated α-olefin polymerization to prepare various chain end functionalized polyolefin (including PE, PP, s-PS, EP, etc.). The potential benefits are high catalyst activity, good control of polymer molecular weight, a selected chain end structure by the chain transfer agent, and the same reaction process as that of regular propylene polymerization. Several reported chain transfer agents include borane,[15−17] silane,[18−20] styrene/H_2,[21−23] ally compounds,[24,25] and so on, which show some success and limitations. Most of them exhibit good activity in polyethylene and polystyrene cases, but show much less success in the polypropylene case due to the very limited selection of iso-specific catalyst systems and the too small special opening at the active sites for big chain transfer agents, as well as catalyst poison.

Organoborane compounds containing B−H group could be the ideal chain transfer agents in metallocene-mediated polymerization to form polyolefin containing a terminal borane group. There are many benefits: Lewis acidity compatible with the cationic active site (no catalyst poison); favorable electronic interaction with the active site (M−C) in the selective chain transfer reaction; and the resulting versatile terminal borane group for functionalization and graft reactions. A few years ago,[15−17] we investigated various B−H containing chain transfer agents during metallocene-mediated ethylene and styrene homo- and copolymerization reactions. To prevent the potential side reaction between the B−H group and the Al-alkyl (Al−C) activator group, a pure perfluoroborate activator, such as $[MeB(C_6F_5)_3]^-$ and $[B(C_6F_5)_4]^-$ noncoordinated anion, was used to yield PE and PS polymers with a terminal functional group and some diblock copolymers. However, the iso-specific polymerization of propylene is limited to only a few steric specific catalyst systems, such as *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$, with

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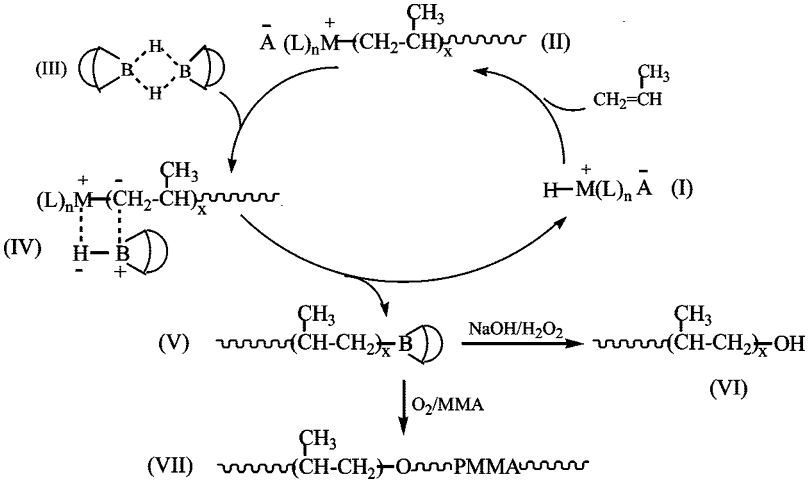
Scheme 1



a limited special opening for coordination. In addition, most of the iso-specific catalyst systems with only perfluoroborate activators show very poor catalyst activity toward propylene polymerization. In other words, to extend the organoborane chain transfer reaction we have to overcome some Al−C groups that have to be present during the propylene polymerization.

Experimental Section

Instrumentation and Materials. All solution ^{1}H and ^{11}B NMR spectra were recorded on a Bruker AM 300 instrument in 1,1,2,2-tetrachloroethane-d_2 or benzene-d_6 solvent at certain temperature. The molecular weight and 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 from the series. The measurements were taken at 140 °C using 1,2,4-trichlorobenzene (TCB) as a solvent and mobile phase with a 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 dry box. Toluene (Wiley Organics) was distilled over CaH_2 under argon. High purity grade propylene (MG Industries), methanol, and 9-borabicyclononane (9-BBN) dimmer (Aldrich) were purchased and used as received. Methylaluminoxane (MAO; ethyl) was purified by vacuum-pumping to remove trimethylaluminium (TMA) at 70−80 °C for 6 h. The *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$ catalyst was prepared by the published procedures.[26]

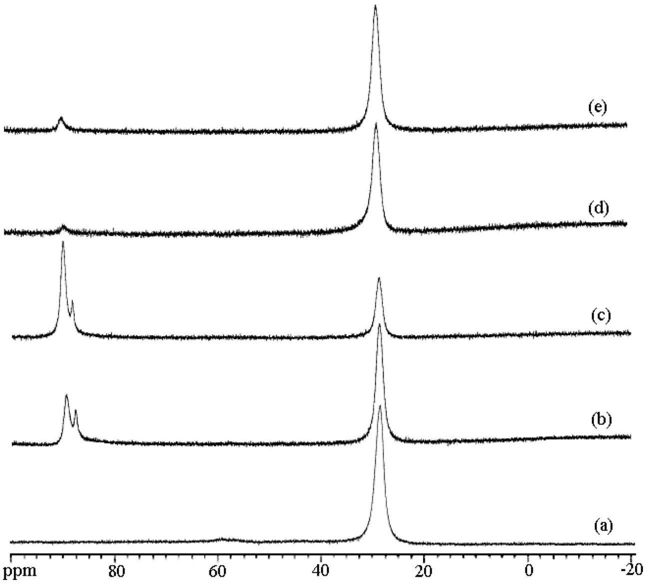


Figure 1. ^{11}B NMR spectra comparison of (a) 9-BBN dimmer and the reaction adducts between 9-BBN dimmer and commercial MAO (containing TMA; b) run 1 and (c) run 2, and between 9-BBN dimmer and the purified MAO (without TMA; d) run 3 and (e) run 4 in Table 1.

Table 1. Summary of the Reactions between 9-BBN Dimmer and MAO Activator

run	9-BBN/MAO (mole ratio)	temperature (°C)	time (min)	conversion[c] (%)
1	2:3[a]	20	15	28.0
2	2:3[a]	20	60	61.1
3	2:3[b]	20	15	1.5
4	2:3[b]	20	60	5.6
5	2:3[b]	35	15	10.3
6	2:3[b]	35	60	36.3
7	2:3[b]	50	15	33.3
8	2:3[b]	50	60	94.1

[a] Commercial MAO (containing TMA). [b] Purified MAO (without TMA). [c] Mole % of 9-BBN converted to CH_3-9-BBN.

Propylene Polymerization/Chain Transfer Reaction. In a typical metallocene-mediated propylene polymerization, a specific amount of borane chain transfer agent and 95 mL of toluene solvent were injected into a 250 mL flask, which had been vacuumed and filled with propylene gas. Propylene was continuously fed to keep a constant pressure at 1 atm throughout the entire polymerization process. About 2 mL (1×10^{-6} mol) of *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph)_2ZrCl_2$ and 3 mL (3×10^{-6} mol) of purified MAO were injected into the mixed solution to initiate the polymerization. Temperature and propylene pressure were kept constant. After 4 min, the reaction was quenched by hydrochloride acidified methanol, which converts the borane terminal group to hydrogen. The polymer was washed by methanol and dried in a vacuum oven at 60 °C for 10 h.

Oxidation Reaction. After polymerization, the resulting borane-terminated PP (PP-t-B) in toluene solution was quenched by tetrahydrofuran (THF), and the PP-t-B polymer was precipitated and washed by THF a few times. All these procedures were carried out in a dry box under an inert gas atmosphere. The polymer was then mixed with THF in a flask protected by N_2, before adding excessive NaOH and H_2O_2 at 0 °C for carrying out the borane oxidation reaction. The reaction temperature was elevated to 50 °C and kept for 10 h. Finally, the resulting hydroxy group terminated PP (PP-t-OH) was filtered and washed with boiling methanol and dried in a vacuum oven at 60 °C for 10 h.

Chain Extending Reaction. In a 100 mL flask equipped with a magnetic stirrer, about 1 g of the resulting PP-t-B polymer (powders) was dispersed in 20 mL of THF and 20 mL of methylmethacrylate (MMA) solution, protected by a N_2 atmosphere. About 0.2 mL of O_2 was added into the reactor in three increments with a 6 h interval between two increments. The reaction was carried

Table 2. Summary of Metallocene-Mediated Propylene Polymerization[a] Using 9-BBN Dimmer and Me-B-9-BBN as the Chain Transfer Agents

run	Cat./MAO (μmol/mmol)	borane[b] (mmol)	T_p[c] (°C)	yield (g)	activity (10^7g/mol·h)	M_v[d] (kg/mol)	M_n[e] (kg/mol)	PDI[e]
A-1	1/3	0	20	1.56	2.34	1110	536	2.3
A-2	1/3	9-BBN (0.2)	20	1.48	2.22	986	546	2.9
A-3	1/3	9-BBN (0.4)	20	1.51	2.26	749	355	3.8
A-4	1/3	9-BBN (0.8)	20	0.97	1.46	548	299	3.4
A-5	1/3	9-BBN (1.2)	20	0.45	0.69	411	169	3.1
A-6	1/3	9-BBN (2.0)	20	0.17	0.26	385	89	3.6
B-1	1/3	0	35	2.11	3.17	486		
B-2	1/3	9-BBN (0.1)	35	1.95	2.93	461		
B-3	1/3	9-BBN (0.2)	35	1.21	1.82	396		
B-4	1/3	9-BBN (0.4)	35	2.25	3.38	345		
B-5	1/3	9-BBN (0.6)	35	1.65	2.48	301		
B-6	1/3	9-BBN (0.8)	35	1.23	1.85	275		
B-7	1/3	9-BBN (1.2)	35	0.57	0.85	277		
B-8	1/3	9-BBN (2.0)	35	0.15	0.21	263		
C-1	1/3	Me-9-BBN (0.1)	35	1.89	2.84	453		
C-2	1/3	Me-9-BBN (0.4)	35	2.01	3.02	472		
C-3	1/3	Me-9-BBN (0.8)	35	1.78	2.67	469		
C-4	1/3	Me-9-BBN (2.0)	35	1.45	2.18	489		

[a] Polymerization conditions are *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph)_2ZrCl_2$ and MAO without TMA, 100 mL of toluene solution, propylene pressure is 1 atm, and polymerization time is 4 min. [b] 9-BBN dimmer was used as a chain transfer agent in sets A and B, and Me-B-9-BBN was used in set C. [c] T_p is polymerization temperature. [d] M_v is average viscosity molecular weight measured by viscositicmeter. [e] M_n and polydispersity index (PDI = M_w/M_n) measured by GPC.

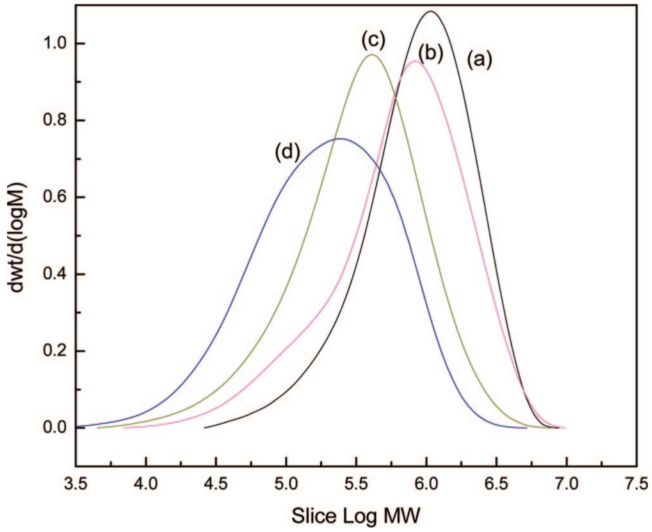


Figure 2. GPC curves of several PP-t-B polymers prepared by using 9-BBN dimmer as the chain transfer agent with various concentration, (a) run A-1, (b) run A-4, (c) run A-5, (d) run A-6 in Table 2 (solvent, trichlorobenzene; temp, 135 °C).

out at 50 °C. The resulting PP-*b*-PMMA diblock polymer was precipitated and washed by methanol. To quantify the amount of PMMA homopolymer, the polymer was dissolved in xylene and then precipitated in boiling THF. The obtained polymer was washed with acetone and placed in a vacuum oven at 60 °C for 10 h.

Results and Discussion

Clearly, the first task of this study is to identify the suitable reaction condition, with which we can carry out the metallocene-mediated propylene polymerization without encountering the ligand exchange reaction between Al−C (promoter) and B−H (chain transfer agent). The dimmer form of the B−H groups, existing in nonpolar hydrocarbon solvents, also prevents its hydroboration activity toward α-olefin monomers. As illustrated in Scheme 1, if all these side reactions could be avoided, the propagating polypropylene chain (II) should engage in a ligand exchange reaction between B−H (III) and C−M (M: transition metal) bonds, with the favorable acid−base interaction (IV). The selective chain transfer reaction results in a borane-terminated polypropylene (V) and a new active site (I) that can reinitiate the propylene polymerization.

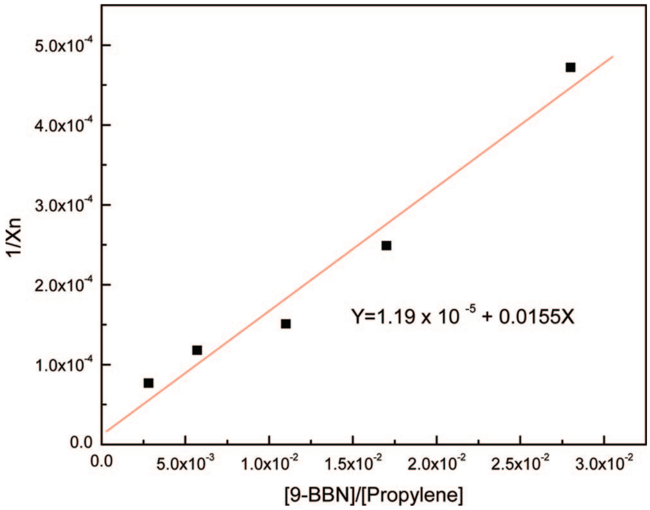


Figure 3. Plot of 1/Xn vs [9-BBN]/[propylene] mole ratios (Xn: degree of polymerization for the PP-t-B polymers in set A of Table 2).

Ideally, the chain transfer reaction shows no change in catalyst activity, and each polypropylene chain (PP-t-B) produced contains a terminal borane group that is versatile in the subsequent functionalization reactions. If this chain transfer reaction is the only termination process, the PP-t-B polymer molecular weight should be inversely proportional to the molar ratio of [CT agent]/[propylene]. It is also interesting to explore other organoborane chain transfer agents in the preparation of PP-t-B polymers, especially the ones containing only simple and stable B−C moieties that exhibit no side reactions associated with B−H moieties. Therefore, several organoboranes, including methyl-9-BBN and triethylborane containing only B−C moieties, were also examined under various reaction conditions using the same common iso-specific *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO catalyst system.

Reactions between Borane Chain Transfer Agent and Aluminum Activator. Figure 1 shows the in situ monitored ^{11}B NMR spectra of the reaction adducts between 9-BBN dimmer and alumimumoxane (MAO) activator at 20 °C for 15 and 60 min, respectively. One set in Figure 1b,c is for the reaction adducts using commercial MAO that is known to contain some trimethylaluminium (TMA). The other set of

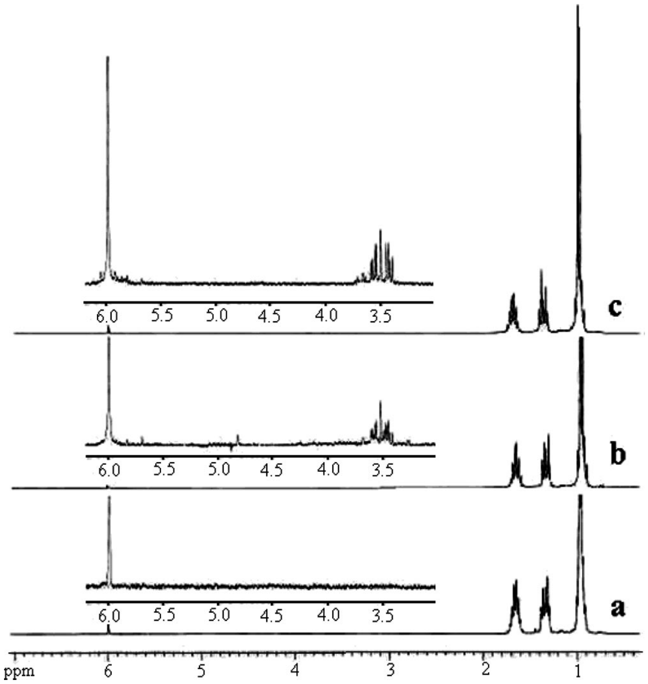


Figure 4. ^{1}H NMR spectra of three PP-t-OH samples: (a) runs A-1, (b) A-3, and (c) A-5 in Table 2 (solvent, $C_2D_2Cl_4$; temp, 110 °C).

Figure 1d,e compares similar reactions using the purified MAO (without TMA). There are only two chemical shifts at 30 and 90 ppm, corresponding to the starting 9-BBN dimmer and the ligand exchange product of methyl-9-BBN, respectively. Their peak intensity ratio represents the mole ratio between two species. Table 1 summarizes the experimental results under various comparative reaction conditions.

What is rather intriguing is that the commercial MAO (containing TMA) shows a facile methyl ligand exchange reaction with B−H in 9-BBN dimmer, even at ambient temperature. On the other hand, the same reaction in the purified MAO (without TMA) is extremely slow. The results imply that the Al−CH_3 group in TMA is much more reactive toward the B−H group than that of MAO. However, temperature is also a big factor with higher activation energy in the exchange reaction. Only about 1.5% of 9-BBN is consumed in 15 min at 20 °C (run 3), but it is almost completely consumed when the temperature is elevated to 50 °C for 1 h (run 8). It is a pleasantly surprise to observe no detectable B-OR and borane/aluminum coordinated species. The strong Al−O bond may prevent the ligand exchange reaction between B−H in 9-BBN dimmer and Al−OCH_3 in MAO. There is also no detectable ligand exchange reaction between trialkylborane (i.e., methyl-9-BBN and triethylborane) and MAO or TMA. The detailed experimental results are provided in the Supporting Information. The small atomic size of B with slightly bigger size CH_3 and C_2H_5 ligands dramatically reduces its ability to form four center bonding "intermediates" in the ligand exchange reaction.

Propylene Polymerization Using Boranes as the Chain Transfer Agents. Based on the understanding of the reaction kinetics between 9-BBN dimmer and MAO and/or TMA, the polymerization of propylene was mediated by *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph)_2ZrCl_2$/MAO catalyst system with the purified MAO (with complete removal of TMA). The polymerization temperature was controlled between 20 and 35 °C, so that the reaction of 9-BBN dimmer and MAO was very minimal. To keep the constant concentration of propylene and the chain transfer agent in the batch reaction, polymerizations were carried out under a high stirring ration and a short reaction time. After a four-minute reaction time, the polymer solution was quenched by THF. The resulting borane-terminated polypropylene (PP-t-B) polymer was either treated with HCl to form H-terminated PP (PP) for molecular weight measurements or oxidized by NaOH/H_2O_2 to form the hydroxy-terminated polypropylene (PP-t-OH; VI). Table 2 summarizes the experimental results of propylene polymerization with 9-BBN dimmer and Me-B-9-BBN as the chain transfer agents. Figure 2 compares the GPC curves of several PP-t-H polymers (runs in set A of Table 2).

The effects of the chain transfer reaction are clearly revealed by the reduction of polymer molecular weight in the presence of 9-BBN dimmer, but not in the case of Me-B-9-BBN. Basically, the higher the concentration of the 9-BBN chain transfer agent used, the lower the molecular weight of the resulting polypropylene obtained. The polymer molecular weight distribution maintains relatively narrow, which is consistent with the single site polymerization with the selective chain transfer reaction. The catalyst activity was also depressed in the presence of 9-BBN, which may reflect the competitive coordination at the propagating metallocene active sites (II) between monomer and chain transfer agent. Apparently, the ligand exchange in the chain transfer reaction complex (IV) is a relatively slow process comparing with the rate of propagation reaction, which slows down the overall polymerization rate. Both comparative sets A and B show the reduction of catalyst activity proportional to the 9-BBN concentration.

There is almost no change in the PP molecular weight and catalyst activity (runs C-1 to C-4) with the increase of Me-B-9-BBN concentration. In this *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO catalyst system, the propagating active site fails to engage a chain transfer reaction with the B−CH_3 moiety, which must be due to the steric effect, associated with its confined space opening at the active site. In fact, some CGC-metallocene catalysts with constained ligand geometry and open active sites show facile chain transfer reactions with Me-B-9-BBN during ethylene polymerization. The results will be reported in the near future.

Figure 3 shows the plot of 1/Xn (Xn: degree of polymerization for PP-t-B polymers) versus the mole ratio of [9-BBN]/[propylene] for the comparative A runs in Table 2. The 1/Xn data is almost linearly proportional to the molar ratio of [9-BBN]/[propylene]. This indicates that the chain transfer reaction to 9-BBN (with rate constant k_{tr}) is the dominant termination process, which competes with the propagating reaction (with rate constant k_p). A simple comparative eq $1/X_n = k_{tr}[9\text{-BBN}]/k_p[\text{propylene}]$ indicates a chain transfer constant $k_{tr}/k_p \sim 1/65$.

PP-t-B Chain End Functionalization and Chain Extension. The borane chain transfer reaction and the purity of the resulting PP-t-B polymers were further revealed by the chain end functionalization and chain extension reactions. Figure 4 compares the ^{1}H NMR spectra of two PP-t-OH polymers (VI) formed by the oxidation reaction of the corresponding PP-t-B polymers (runs A-3 and A-5) using NaOH/H_2O_2 reagent and a pure PP polymer (run A-1). In addition to three major chemical shifts between 0.9 and 1.8 ppm, corresponding to **CH**$_3$, **CH**$_2$, and **CH** in the PP backbone, Figure 4b,c shows an additional weak chemical shift centered at 3.5 ppm (-**CH**$_2$-OH, -**CH**(CH_3)-OH), indicating the existence of a terminal OH group with multiple species. There is no detectable vinyl group associated with the conventional chain transfer process (via *β*-H elimination). Due to high polymer molecular weight, it is difficult to quantitatively estimate the purity of the terminal functional group. The chain extension from the PP-t-B polymer will provide much better information about this.

One major advantage of the PP-t-B polymer is its ability to carry out a control radical chain extension reaction under a mild

Table 3. Summary[a] of PP-*b*-PMMA Copolymers Prepared by PP-t-B Polymers

run	temp (°C)	PP-t-B[b] (g)	O_2 (mL)	MMA (mL)	time (h)	yield (g)	MMA incorporation[c] (mol %)
D-1	50	1	0.2	20	24	1.2	7.4
D-2	50	1	0.2	20	24	1.3	11.6
D-3	50	1	0.2	20	48	1.8	24.1

[a] THF (20 mL) used as solvent. [b] PP-t-B (run A-3) was used in run D-1 and PP-t-B (run A-5) was used in runs D-2 and D-3. [c] Calculated by ^1H NMR spectra.

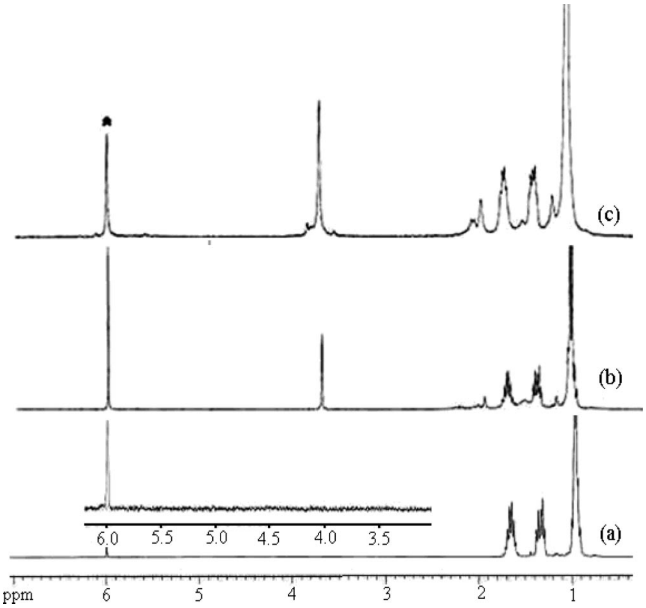


Figure 5. ^1H NMR spectra of (a) PP-t-OH and (b) PP-*b*-PMMA samples (solvent, $C_2D_2Cl_4$; temp, 110 °C).

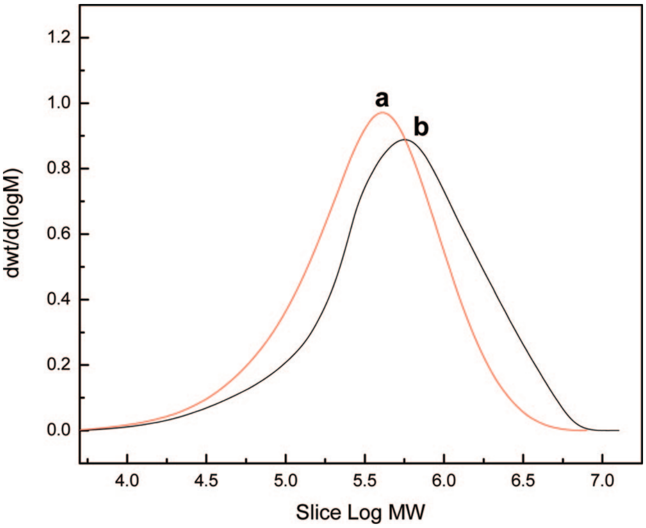


Figure 6. GPC curve comparison between (a) PP-t-B (run A-5 in Table 2; $M_n = 169 \times 10^3$ g/mol; $M_w/M_n = 3.1$) and PP-*b*-PMMA diblock copolymer (run D-3 in Table 3) containing 24.1 mol % [MMA] content (solvent, trichlorobenzene; temp, 135 °C).

reaction condition, which forms a broad range of functional PP diblock copolymers, containing a PP block and a functional polymer block. This experimental result also provides strong evidence in determining the existence of a terminal borane group in the PP-t-B polymer. Table 3 summarizes the experimental conditions and results for three PP-b-PMMA diblock copolymers (VII). The run D-1 copolymer was prepared from the PP-t-B polymer (run A-3 in Table 2): $M_n = 355 \times 10^3$ g/mol; $M_w/M_n = 3.8$. Runs D-2 and D-3 copolymers started with the PP-t-B polymer (run A-5): $M_n = 169 \times 10^3$ g/mol; $M_w/M_n = 3.1$. They are all polymers with very high molecular weight, and the chain extension reactions were carried out in heterogeneous condition by dispersing PP-t-B powders in the solution with the presence of MMA monomers. The spontaneous O_2-oxidation of the terminal borane group forms a stable polymeric radical for control radical polymerization. The resulting PP-*b*-PMMA reaction mixture was carefully fractionated by Soxlet extraction, using boiling THF to remove any PMMA homopolymer. In most cases, only a very small amount (about 10%) of PMMA homopolymer was observed, which may be initiated by the radical in a bicyclic ring, instead of a polymeric radical, due to the nonselective oxidation reaction of alkyl-9-BBN. The insoluble fraction, but soluble in 1,1,2,2-tetrachloroethane and 1,2,4-trichlorobenzene at elevated temperatures, is the PP-*b*-PMMA diblock copolymer. Figure 5 compares the ^1H NMR spectra of two PP-*b*-PMMA polymers (runs D-2 and D-3) with a control PP homopolymer. The new peak at 3.58 ppm, corresponding to methoxyl groups ($C\mathbf{H}_3O$) in PMMA, increased its intensity with the reaction time. Evidently, the PMMA segment in PP-*b*-PMMA grows with the reaction time, which implies the control radical polymerization in this chain extension process.

Figure 6 compares the GPC curves of a PP-*b*-PMMA diblock copolymer (run D-3) containing 24.1 mol % [MMA] content and the starting PP-t-B polymer (run A-5): $M_n = 169 \times 10^3$ g/mol; $M_w/M_n = 3.1$. Despite high molecular weight and high crystallinity of the PP-t-B polymer, the polymer continuously increased in its molecular weight during the entire polymerization process. The polymer's molecular weight distribution was maintained at very constant. The monochromatic increase of the copolymer molecular weight, without a detectable PP homopolymer, clearly points to the high purity of the starting PP-t-B polymer and effective chain extension reaction even under heterogeneous conditions.

Conclusion

Both chain end functionalized PP and PP diblock copolymer are two of the most desirable functional polymer structures but also the most challenging ones in polymer synthesis, especially having high molecular weight. The versatile PP-t-B provides a valuable "intermediate" for preparing both polymer structures; however, it has not been directly synthesized. This research identifies the suitable reaction condition that can prevent side reactions during *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$/MAO mediated propylene polymerization and an in situ B−H chain transfer reaction, with 9-BBN dimmer as the chain transfer agent. This chemistry affords a convenient and efficient route to prepare borane-terminated PP (PP-t-B) polymers with controlled polymer molecular weight, relatively narrow molecular weight distribution, and high purity. The resulting PP-t-B polymers were quantitatively interconverted to PP-t-OH polymer and chain-extended to PP-*b*-PMMA diblock copolymer. Despite high molecular weight, extremely low borane concentration, and heterogeneous reaction condition, both reactions show to be effective, even under mild reaction conditions.

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Supporting Information Available: Preparation of methyl-9-BBN and its ^{11}B NMR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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