

## Borane Chain Transfer Agent in Metallocene-Mediated Olefin Polymerization. Synthesis of Borane-Terminated Polyethylene and Diblock Copolymers Containing Polyethylene and Polar Polymer

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Since the discovery of Ziegler–Natta catalysts in the early 50s, it has been a long scientific interest and technological important subject<sup>1–6</sup> to investigate the route to effectively incorporate functional (polar) groups into a polyolefin chain. Unfortunately, the common functionalization procedures are far from satisfactory and present many technological difficulties.<sup>7</sup>

The in situ chain transfer reaction to the molecule containing heteroatom during the transition metal coordination polymerization of  $\alpha$ -olefins presents a very convenient method of prepare polyolefins containing a terminal polar group. Recently, Mark et al.<sup>8</sup> reported that organosilanes having Si–H groups are effective chain transfer agents in metallocene-mediated polymerizations that result in silane-terminated polyolefins and copolymers.

In this paper, we report a new organoborane chain transfer agent containing a B–H group, such as a 9-borabicyclo[3.3.1]nonane (9-BBN) dimer, that can effectively engage chain transfer reactions during metallocene-catalyzed  $\alpha$ -olefin polymerizations. The research plan was formulated with several intriguing questions and objectives in mind. With the known reactivity of H–H and Si–H groups to many metallocene catalytic sites, it may be possible to extend the chain transfer reaction to the B–H group if we can prevent the hydroboration reaction of the B–H to the  $\alpha$ -olefin monomers. It is known that the borane compounds containing B–H groups usually form a stable dimer<sup>9</sup> (unreactive to olefins) in hexane and toluene solvents which are used in metallocene polymerizations, allowing the ligand exchange reaction to take place between B–H and M–C (M = transition metal).

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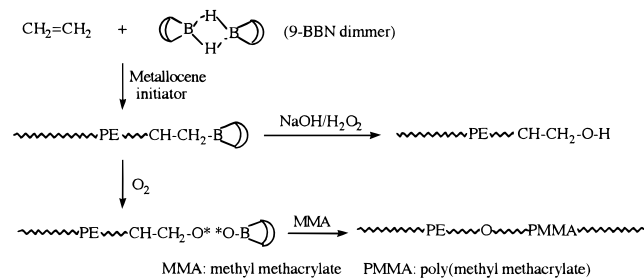
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On the other hand, the formed borane-terminated polyolefin will be a very versatile “intermediate”<sup>10</sup> that can be used to prepare various functional polymers and diblock copolymers, as illustrated in eq 1



In addition to the quantitative conversion of the terminal borane group to the hydroxy group, it can also be spontaneously transformed to a peroxide (B–O–O–C) moiety<sup>11</sup> for living free radical polymerization. Overall, the reaction process resembles a transformation reaction from metallocene coordination polymerization to living free radical polymerization via a borane group at the polymer chain end.

The metallocene catalysts,  $[\text{Cp}^*_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  and  $[\text{Cp}^*_2\text{ZrMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{H}_5, \eta^5\text{-Me}_5\text{C}_5$ ), were prepared as described in the literature.<sup>12</sup> Polymerization of ethylene was conducted in the presence of 9-BBN and toluene under anhydrous/anaerobic conditions. To maintain the constant comonomer feed ratio, the reactions were carried out by rapid mixing and short reaction time. After a 3 to 5 min reaction time (as summarized in Table 1), 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.

Some of the PE-t-B polymer was oxidized by NaOH/H<sub>2</sub>O<sub>2</sub> to form a hydroxy-terminated polymer (PE-t-OH). Most of the borane-terminated polymer was subjected to the oxidation reaction by oxygen in the presence of free radical polymerizable MMA monomers.

<sup>1</sup>H NMR spectrum of a low-molecular weight PE-t-OH ( $M_n = 3,700$  g/mole) shows a major chemical shift at 1.30 ppm, corresponding to  $\text{CH}_2$  in the PE backbone, which is accompanied by several weak peaks at 0.97 ppm (chain end  $\text{CH}_3$ ), 1.58 ppm ( $-\text{CH}_2\text{CH}_2-\text{OH}$ ), 2.25 ppm ( $-\text{OH}$ ), 3.62 ppm ( $-\text{CH}_2-\text{OH}$ ). The peak intensity ratio of  $\text{OH}:\text{CH}_2-\text{O}:\text{CH}_3 = 1:2:3$  ( $\pm 2\%$ ) indicates the exclusive production of hydroxy-terminated polyethylene. It is interesting to note that there is no detectable vinyl group associated with the conventional chain transfer process (via  $\beta$ -H elimination). The same results were also observed in the <sup>13</sup>C NMR spectra with the chemical shifts corresponding to  $-\text{CH}_2-\text{OH}$  ( $\delta$  62.99) and chain end  $\text{CH}_3$  ( $\delta$  13.85) groups. These findings strongly indicate the in situ chain transfer to 9-BBN moiety during the catalytic polymerization of ethylene.

The effects of the chain transfer reaction are further revealed by the reduction of polymer molecular weight in the presence of 9-BBN. The experimental results are summarized in Table 1. Figure 1 shows the plot of polymer molecular weight ( $M_n$ ) vs the mole ratio of ethylene/9-BBN for the comparative runs 1–8

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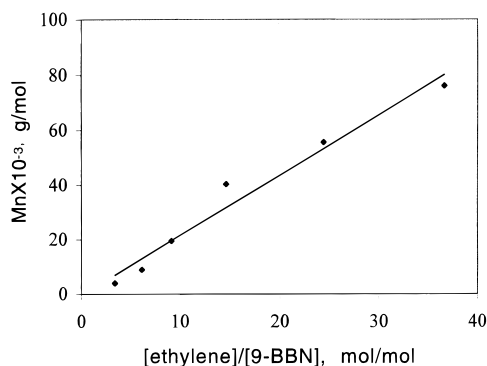
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**Table 1.** Metallocene-Activated Ethylene Polymerization in the Presence of 9-BBN as Chain Transfer Agent<sup>a</sup>

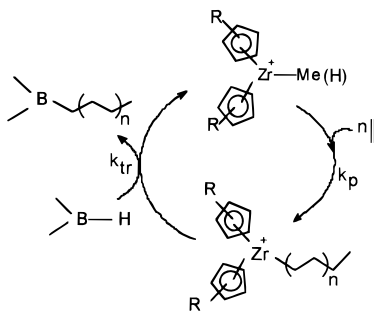
| run | catalyst  | 9-BBN (mM) | reaction time (min) | yield (g) | activity (kg of PE/mol of catalyst·atm·h) | $M_n^b$ ( $\times 10^{-3}$ ) | $M_w/M_n^b$ |
|-----|---|------------|---------------------|-----------|---|------------------------------|-------------|
| 1   | [Cp* <sub>2</sub> ZrMe] <sup>+</sup> [MeB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup>   | 0          | 3                   | 3.50      | 2333                                      | 85.2                         | 2.0         |
| 2   | [Cp* <sub>2</sub> ZrMe] <sup>+</sup> [MeB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup>   | 3.0        | 3                   | 2.01      | 1333                                      | 76.0                         | 2.4         |
| 3   | [Cp* <sub>2</sub> ZrMe] <sup>+</sup> [MeB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup>   | 4.5        | 3                   | 2.05      | 1366                                      | 55.5                         | 2.9         |
| 4   | [Cp* <sub>2</sub> ZrMe] <sup>+</sup> [MeB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup>   | 7.5        | 3                   | 1.45      | 1033                                      | 42.2                         | 2.6         |
| 5   | [Cp* <sub>2</sub> ZrMe] <sup>+</sup> [MeB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup>   | 7.5        | 5                   | 2.02      | 1333                                      | 45.8                         | 2.6         |
| 6   | [Cp* <sub>2</sub> ZrMe] <sup>+</sup> [MeB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup>   | 12.0       | 3                   | 1.20      | 800                                       | 19.4                         | 2.7         |
| 7   | [Cp* <sub>2</sub> ZrMe] <sup>+</sup> [MeB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup>   | 18.0       | 3                   | 0.75      | 500                                       | 8.9                          | 3.2         |
| 8   | [Cp* <sub>2</sub> ZrMe] <sup>+</sup> [MeB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup>   | 23.4       | 3                   | 0.25      | 167                                       | 3.7                          | 4.0         |
| 9   | [Cp* <sub>2</sub> ZrMe] <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>     | 4.5        | 3                   | 2.00      | 1333                                      | 59.4                         | 2.6         |
| 10  | [Cp* <sub>2</sub> ZrMe] <sup>+</sup> [B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>     | 7.5        | 3                   | 1.51      | 1000                                      | 46.2                         | 2.5         |
| 11  | [(Ind) <sub>2</sub> ZrMe] <sup>+</sup> [MeB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup> | 7.5        | 3                   | 1.90      | 1267                                      | 43.9                         | 2.3         |
| 12  | [Cp <sub>2</sub> ZrMe] <sup>+</sup> [MeB(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ] <sup>-</sup>    | 7.5        | 3                   | 2.50      | 1667                                      | 46.9                         | 2.1         |

<sup>a</sup> Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>, Cp\* =  $\eta^5$ -Me<sub>5</sub>C<sub>5</sub>, Ind =  $\eta^5$ -C<sub>9</sub>H<sub>7</sub>; catalyst concentration = 0.3 mM; ethylene pressure = 1 atm; [ethylene] = 0.11 M. <sup>b</sup> By GPC in 1,2,4-trichlorobenzene vs polystyrene standards.



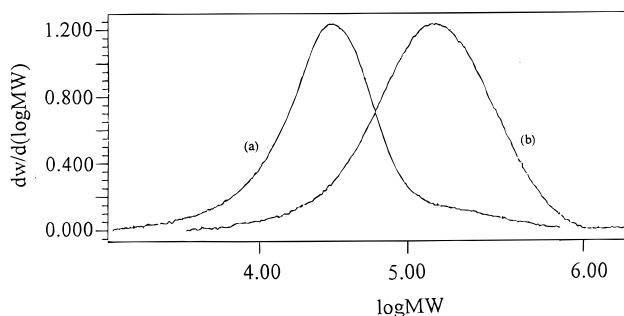
**Figure 1.** Plot of number average molecular weight ( $M_n$ ) of PE-t-B polymers vs the mole ratio of [ethylene]/[9-BBN] in the feed. (runs 2–8 in Table 1).

in Table 1. The polymer molecular weight is almost linearly proportional to the molar ratio of [ethylene]/[9-BBN]. It is clear 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  $k_p$ ) as illustrated below.



The degree of polymerization ( $X_n$ ) follows a simple comparative equation  $X_n = k_p[\text{olefin}]/k_{tr}[9\text{-BBN}]$  with a chain transfer constant  $k_{tr}/k_p \approx 1/75$ .

The existence of a borane group at the PE chain end is further supported by its chain extension reaction. As illustrated in eq 1, the borane-terminated PE was selectively oxidized and transformed to a stable polymeric radical for polymerization of methyl methacrylate. The resulting PE-*b*-PMMA reaction mixture was carefully fractionated by Soxhlet extraction using boiling THF to remove any PMMA homopolymer. (about 10%). The insoluble



**Figure 2.** The GPC curve comparison between (a) PE-t-B polymer ( $M_n = 19\,400$  and  $M_w = 38\,800$  g/mole) and (b) the corresponding PE-*b*-PMMA ( $M_n = 90\,300$  and  $M_w = 243\,800$  g/mole). (solvent: trichlorobenzene; temp.: 135 °C).

fraction, but soluble in 1,1,2,2-tetrachloroethane, 1,2,4-trichlorobenzene at elevated temperatures, is PE-*b*-PMMA diblock copolymer. <sup>1</sup>H NMR spectrum shows a new peak at 3.58 ppm, corresponding to methoxyl groups (CH<sub>3</sub>O) in PMMA, increased its intensity with the reaction time. Apparently, the PMMA segment in PE-*b*-PMMA grows with the reaction time, which implies the living free radical polymerization in this chain extension process. Figure 2 compares the GPC curves of a PE-*b*-PMMA diblock copolymer and the starting PE-t-B polymer. The polymer molecular weight increases several times from  $M_n = 19\,400$  to 90 300 g/mole, which is consistent with the <sup>1</sup>H NMR results of a near 1/1 of [PE]/[PMMA] mole ratio in the PE-*b*-PMMA copolymer. The monochromatic increase of the copolymer molecular weight, with only a slightly 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.

In summary, this research clearly demonstrates a new borane (B-H) in situ chain transfer reaction in metallocene-catalyzed olefin polymerization. The chemistry provides a convenient and efficient route to prepare borane-terminated polyolefins that are very valuable intermediates for preparing functionalized polyolefins with a polar end group or diblock copolymer containing a polyolefin and functional (polar) polymer segments.

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