Functionalized Syndiotactic Polystyrene Polymers Prepared by the Combination of Metallocene Catalyst and Borane Comonomer

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ABSTRACT: This paper discusses an effective route in the functionalization of s-PS polymer that involves the direct copolymerization of styrene with a borane-containing styrenic monomer, i.e., 4-[B-(n-butylene)]-9-BBN styrene (B-styrene). The reactivity ratios of the two comonomers are quite close, with $r_1 = 0.9$ for styrene and $r_2 = 1.2$ for B-styrene in the Cp$^*$Ti(OMe)$_3$/MAO catalyst system. A broad composition range of syndiotactic poly(styrene-co-B-styrene) copolymers has been prepared with narrow molecular weight and composition distributions. The random copolymer structure was further evidenced by DSC and $^{13}$C NMR analyses. With increasing B-styrene concentration, the copolymers show a systematic decrease in glass transition temperature, melting point, crystallization temperature, and crystallinity. At above 8.4 mol % B-styrene content, the crystallinity of the copolymer completely disappears. In turn, the borane groups in the copolymer are very versatile and can be quantitatively converted to other functional groups, such as hydroxy and anhydride groups, or transformed to free radical initiators for in situ free radical graft polymerization to prepare s-PS-g-P(MMA) graft copolymers.

Introduction

One of the most important advances in metallocene technology is the preparation of syndiotactic polystyrene (s-PS) that exhibits high melting point ($\sim 270^\circ$C) and a relatively high crystallization rate that is several orders of magnitude faster than that in isotactic polystyrene (i-PS). s-PS is a novel engineering plastic made from an inexpensive commodity monomer.

Despite its unique properties, s-PS polymer also has several drawbacks that pose serious concerns in many commercial applications. Because of a high melting point, the required melt processing temperature at $\sim 300^\circ$C (near the polymer decomposition temperature) causes a major problem in polymer processability. A modified s-PS polymer with a slightly reduced melting point (to about 250 $^\circ$C) would be a very desirable material. In addition, s-PS polymer has poor impact strength and low surface energy, similar to traditional atactic polystyrene prepared by free radical and anionic processes. So far, there are only a few reports discussing the modification of s-PS polymer, including sulfonation and bromination of s-PS and hydroxylated s-PS prepared via poly(styrene-co-tet­butylidimethylsilyloxy styrene) precursor. Recently, Xu and Chung also reported a new method using dialkylborane containing a $B-H$ group as a chain transfer agent during metallocene-mediated styrene polymerization to form borane-terminated syndiotactic polystyrene, which was further engaged in the free radical chain extension with methyl methacrylate (MMA) to form s-PS-b-P(MMA) diblock copolymers.

Several years ago, we developed a very useful method to functionalize polyolefins, such as polyethylene (PE) and polypropylene (PP), which involved direct copolymerization of $\alpha$-olefin and borane-containing $\alpha$-olefin by Ziegler–Natta and metallocene catalysts. Because of the excellent stability of borane moieties to catalysts and the good solubility of trialkylborane in hydrocarbon media, a broad range of borane-containing polyolefin copolymers with uniform molecular structure were prepared without sacrificing catalyst activity. In addition, the incorporated borane groups in the polyolefin copolymers are very versatile and can be effectively interconverted to various functional groups under mild reaction conditions and also transferred to polymeric radicals for graft reactions to prepare polyolefin graft copolymers, such as PP-g-P(MMA) and PE-g-P(MMA). We extended this borane monomer approach to s-PS to prepare functionalized s-PS polymers and s-PS graft copolymers that not only contain desirable functional groups but also have lower melting temperatures with improved processability.

Results and Discussion

Borane-Containing Monomer. As illustrated in Scheme 1, a new borane-containing monomer of 4-[B-(n-butylene)]-9-BBN styrene was prepared by a two-step reaction. After completing a coupling reaction between allylmagnesium chloride and vinyl benzyl chloride to form 4-[3-butenyl]styrene, containing a styrenic olefin and an $\alpha$-olefin groups, this resulting asymmetrical diene was selectively monohydroborated by 9-BBN at the $\alpha$-olefinic double bond in an anti-Markovnikov manner.

Both reaction steps are very effective and produce high yields. Figure 1 compares the $^{1}$H NMR spectra of 4-[B-(n-butylene)]-9-BBN styrene (B-styrene) and 4-[3-butenyl]styrene. After hydroboration reaction by a stoichiometric amount of 9-BBN, all the chemical shifts at...
2.44 - 2.58, 5.05 - 5.22, and 5.88 - 6.10 ppm (corresponding to the three type protons in \(-\text{CH}_2-\text{CH}==\text{CH}_2\) group) completely disappear. On the other hand, the chemical shifts at 5.30 - 5.37, 5.80 - 5.88, and 6.75 - 6.95 ppm (for the three methylene and methine protons in styrenic olefin) are unchanged. The big difference in hydroboration reactivities between the two double bonds toward 9-BBN provides an effective route to the preparation of B-styrene monomer (I) without forming an undesirable dihydroborated product.

**Copolymerization of Styrene with 4-[B-(n-butylene)-9-BBN]styrene.** As illustrated in Scheme 2, the copolymerization of styrene and 4-[B-(n-butylene)-9-BBN]-

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**Table 1. Copolymerization of Styrene (S) and 4-[B-(n-butylene)-9-BBN]styrene (B-S) with Syndiospecific Titanocene/MAO Catalysts**

<table>
<thead>
<tr>
<th>run no.</th>
<th>catalyst</th>
<th>B-S in feed (mol %)</th>
<th>[S] (mol/L)</th>
<th>[B-S] (mol/L)</th>
<th>yield (g)</th>
<th>[B-S] content in copolymer (mol %)</th>
<th>(M_w \times 10^4) (g/mol)</th>
<th>(M_n \times 10^4) (g/mol)</th>
<th>PDI (M_w/M_n)</th>
</tr>
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<tbody>
<tr>
<td>A-1</td>
<td>Cp*Ti(OMe)_3</td>
<td>0</td>
<td>1.73</td>
<td>0</td>
<td>3.48</td>
<td>67.0</td>
<td>20.3</td>
<td>7.0</td>
<td>2.9</td>
</tr>
<tr>
<td>A-2</td>
<td>Cp*Ti(OMe)_3</td>
<td>0.63</td>
<td>1.73</td>
<td>0.011</td>
<td>4.44</td>
<td>85.1</td>
<td>21.5</td>
<td>8.0</td>
<td>2.7</td>
</tr>
<tr>
<td>A-3</td>
<td>Cp*Ti(OMe)_3</td>
<td>1.76</td>
<td>1.73</td>
<td>0.031</td>
<td>4.66</td>
<td>88.3</td>
<td>20.7</td>
<td>8.3</td>
<td>2.5</td>
</tr>
<tr>
<td>A-4</td>
<td>Cp*Ti(OMe)_3</td>
<td>2.59</td>
<td>1.73</td>
<td>0.046</td>
<td>5.13</td>
<td>96.2</td>
<td>15.5</td>
<td>6.7</td>
<td>2.3</td>
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<tr>
<td>A-5</td>
<td>Cp*Ti(OMe)_3</td>
<td>5.38</td>
<td>1.59</td>
<td>0.091</td>
<td>5.36</td>
<td>106.3</td>
<td>14.4</td>
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</tr>
<tr>
<td>A-6</td>
<td>Cp*Ti(OMe)_3</td>
<td>7.16</td>
<td>2.14</td>
<td>0.165</td>
<td>6.73</td>
<td>97.3</td>
<td>12.7</td>
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<td>2.3</td>
</tr>
<tr>
<td>A-7</td>
<td>Cp*Ti(OMe)_3</td>
<td>12.2</td>
<td>2.04</td>
<td>0.284</td>
<td>6.04</td>
<td>86.7</td>
<td>9.8</td>
<td>5.2</td>
<td>2.0</td>
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<tr>
<td>A-8</td>
<td>Cp*Ti(OMe)_3</td>
<td>24.3</td>
<td>1.13</td>
<td>0.363</td>
<td>2.98</td>
<td>66.7</td>
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<tr>
<td>A-9</td>
<td>Cp*Ti(OMe)_3</td>
<td>100</td>
<td>0</td>
<td>0.730</td>
<td>1.91</td>
<td>87.3</td>
<td>100</td>
<td>0.7</td>
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<tr>
<td>B-1</td>
<td>CpTiCl_3</td>
<td>6.10</td>
<td>1.41</td>
<td>0.091</td>
<td>3.52</td>
<td>78.2</td>
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<tr>
<td>C-1</td>
<td>CpTiCl_3</td>
<td>6.10</td>
<td>1.41</td>
<td>0.091</td>
<td>2.98</td>
<td>66.2</td>
<td>66.2</td>
<td>5.4</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Polymerization conditions: [cat] = 100 µmol /L, Al/Ti = 2000, temperature = 50 °C, time = 3 h, solvent = 40 mL of toluene. \(^b\) In kg of polymer/mol Ti-h-mol/L.

![Figure 1. 1H NMR spectra of (a) 4-(3-butenyl)styrene and (b) 4-[B-(n-butylene)-9-BBN]styrene (solvent: d-chloroform).](image-url)
Because of the oxygen sensitivity of the borane moiety, the borane-containing s-PS copolymers were usually oxidized by NaOH/H2O2 to form the corresponding stable hydroxy-containing s-PS copolymers (s-PS-OH) for analysis. As will be discussed later, all of the transformation reactions were quantitative even in heterogeneous conditions. Table 1 summarizes the results of styrene/B-[(-butylene)-9-BBN]styrene copolymerization reactions under various reaction conditions.

In general, both monomers show similar reactivity. The para-substituted borane group exhibits almost no effect on the monomer incorporation, which also indicates the unique advantages of trialkylborane moiety with excellent stability to the transition-metal catalysts and good solubility in hydrocarbon reaction media. The copolymer composition is basically controlled by the comonomer feed ratio, and we have prepared a whole composition range of styrene/B-styrene copolymers. In
general, the catalyst efficiency in the copolymerization reaction increases somewhat compared to that of homopolymerization. The better diffusibility of monomers in the copolymer structures (due to lower crystallinity) may help provide better polymerization conditions.

The best way to investigate a copolymerization is to measure the reactivity ratio of the comonomers. A series of experiments were carried out by varying the monomer feed ratio and comparing the resulting polymer compositions at low conversion (<10%). The reactivity ratios of styrene \((r_1 = k_{11}/k_{12})\) and B-styrene \((r_2 = k_{22}/k_{21})\) are estimated by the Fineman and Ross method. Figure 2 shows the plot \((1 - F)/f vs F/f^2\) and the least-squares best-fit line, where \(f = [\text{styrene}]/[\text{B-styrene}]\) in feed and \(F = d[\text{styrene}]/d[\text{B-styrene}]\) mole ratio in polymer. The slope is \(r_2\), and the extrapolation to \(F/f^2 = 0\) gives \(-r_1\). We obtain \(r_1 = 0.9\), \(r_2 = 1.2\), and \(r_1 r_2 = 1.08\) for styrene/B-styrene copolymerization by a \(\text{Cp}^*\text{Ti(OMe)}_3/\text{MAO}\) catalyst.

With \(r_1\) and \(r_2\) near 1, this styrene/B-styrene copolymerization reaction is close to an ideal case. The copolymer obtained shall have a narrow composition

Figure 4. \(^1\text{H}\) NMR spectra of (a) s-PS and three s-PS–OH copolymers, containing (b) 2.1, (c) 8.4, and (d) 16.7 mol % of OH groups (solvent: \(\text{C}_2\text{D}_2\text{Cl}_4\); temperature: 110 °C).
distribution, and its composition shall be proportional to the monomer feed ratio, which are consistent with the DSC results (discussed later) and the experimental results shown in Table 1 (even with relatively long reaction time and high monomer conversion).

Figure 3 shows several GPC curves of the styrene/B-styrene copolymers (runs A-1, A-2, A-4, A-5, and A-7 in Table 1) prepared by the Cp*Ti(OMe)3/MAO complex. The narrow molecular weight distribution in all samples, with \( M_w/M_n = 2-3 \), implies that the polymerization follows a single-site reaction mechanism. In fact, the GPC curves show a slight reduction of molecular weight distribution in the copolymers, from \( M_w/M_n = 2.9 \) in s-PS to 2.0 in styrene/B-styrene copolymers containing 32.2 mol % of B-styrene. Similar narrow molecular distributions were also observed in the copolymers prepared by Cp*TiCl3/MAO and CpTiCl3/MAO complexes. The greater diffusibility of monomers in the copolymer structures (due to lower crystallinity) may also help provide the constant polymerization environment. In general, the copolymers exhibit high molecular weights that gradually decrease as the B-styrene content increases. However, they still maintain relatively high molecular weight (\( M_w = 53 \times 10^3 \) and \( M_n = 28 \times 10^3 \) g/mol), even in the copolymer containing a very high concentration (32.2 mol %) of B-styrene units.

**Functionalized s-PS Polymers.** The borane-containing copolymers are stable for long periods of time (6 months in a drybox) or at elevated temperatures (110 °C during NMR measurement) as long as O2 is excluded. In this study, the borane groups in the copolymers were oxidized by NaOH/H2O2 reagents at 40 °C for 3 h. The borane groups were completely converted to the corresponding hydroxy groups even under the heterogeneous conditions. The quantitative conversion under mild reaction conditions may be attributed to the combination of high reactivity and high surface area of borane groups in semicrystalline microstructure. Figures 4 and 5 compare the 1H and 13C NMR spectra of s-PS and three s-PS-OH copolymers containing 2.0, 8.4, and 16.0 mol % of OH groups, respectively.

In Figure 4, there are two aliphatic proton (H_a and H_b) peaks at 1.32 and 1.85 ppm and two sharp aromatic proton (H_c and H_d-e) peaks at 6.68 and 7.15 ppm present in all compositions, indicating a high syndiotactic arrangement of styrene units in all of the polymers. The borane group in the B-styrene comonomer did not interfere with the syndiotactic incorporation of styrene in the polymerization reaction. With increasing hy-
The melting point (A-3, A-5, A-6, A-7, and A-8 in Table 2). As expected, both the mono (A-1) and several s-PS prepared with other catalyst systems. 

The stereostructure of the polymer was further examined by $^{13}$C NMR. As shown in Figure 5, all peaks are sharp and assigned to the corresponding carbon atoms in the polymer structures (shown in the inset). According to the literature, the presence of a single resonance for the substituted aromatic $C_1$ carbon in the polymer backbone. Two sharp resonances at 44.5 and 41.0 ppm correspond to the methine $C_5$ and methylene $C_6$ in a highly stereoregular environment. In addition, a new resonance at 63.2 ppm corresponds to the methine $C_5$ and methylene $C_6$ in a highly stereoregular environment. In addition, a new resonance at 63.2 ppm corresponds to the methine carbon atom ($C_{11}$) in the -CH$_2$-OH group. The sharp resonances in the copolymers resembles that of syndiotactic polystyrene and are very different from several reported atactic polystyrene derivatives containing chloro and methoxy groups prepared with other catalyst systems.

Figure 6 compares the DSC curves of s-PS homopolymer (A-1) and several s-PS-OH copolymers (runs A-2, A-3, A-5, A-6, A-7, and A-8 in Table 2). As expected, both the melting point ($T_m$) and crystallinity ($\chi_c$) of the copolymer are affected by the side chains. The higher the density of the side chain, the lower the $T_m$ and $\chi_c$. The detailed results of the melting point ($T_m$) and crystallinity ($\chi_c$) of the copolymers are summarized in Table 2. The crystallinity ($\chi_c$) of the copolymer was calculated from fusion enthalpy according to the following equation: 

\[ \chi_c = \frac{H_m}{H_m^0} \times 100, \]

where $H_m$ and $H_m^0$ (53 J/g$^2$) are the fusion enthalpies of the copolymer and the s-PS homopolymer, respectively. Sample A-3, with an average of 1 side chain per 50 styrene units, still possesses $>40\%$ crystallinity with a sharp melting peak at $T_m = 250 ^\circ C$. In addition to its functionality, this s-PS-OH copolymer may also benefit from better processability at $<300 ^\circ C$. The melting peak in the copolymer completely disappears at $>8.4$ mol $\%$ of B-styrene concentration. Only a single $T_g$ was observed throughout the whole composition range, and the $T_g$ systematically decreases with increasing side-chain density. All of the experimental results indicate that the copolymer microstructure is homogeneous and that the copolymer morphology becomes completely amorphous with more than 8.4 mol $\%$ of B-styrene units.

As illustrated in eq 2, the pending borane groups were selectively oxidized by oxygen to form polymeric radicals that are associated with "stable" borinate radicals. The polymeric radicals react in situ with maleic anhydride (MA) to produce maleic anhydride grafted s-PS (s-PS-g-MA) with a single MA unit in each side chain. Figure 7 shows the IR spectrum of a s-PS-g-MA copolymer containing 8 mol $\%$ of MA units, and the inset compares the absorption region of the $\nu_{C=O}$ vibration modes between s-PS and three s-PS-g-MA copolymers. The $\nu_{C=O}$ absorption intensity and sample thickness.

Figure 6. DSC curves of (a) s-PS homopolymer and several s-PS-OH copolymers, containing (b) 1.0, (c) 2.1, (d) 6.1, (e) 8.4, (f) 16.7, and (g) 32.2 mol $\%$ of OH groups.

s-PS Graft Copolymers. The pending stable polymeric radicals associated with dormant borinate radicals in the s-PS copolymer (III) are very useful in the preparation of s-PS graft copolymers. In the presence of MMA monomers, the free radical graft polymerization results in s-PS-g-PDMA (VI) graft copolymers. The molecular weight of the incorporated PMMA side chain is proportional to the MMA monomers used, and the graft density is governed by the incorporated borane content. After the MA graft reaction, several new absorption peaks were observed at 1860 and 1780 cm$^{-1}$ corresponding to two $\nu_{C=O}$ vibrational stretching modes in succinic anhydride. A high concentration of MA groups has been incorporated in the s-PS copolymers that is similar to that of the incorporated borane units. The concentration of incorporated MA units was calculated by a standard industrial method (discussed in the Experimental Section), which is based on the IR carbonyl group absorption intensity and sample thickness.

Figure 8 compares the $^1H$ NMR spectra of a starting styrene/B-styrene copolymer containing 1 mol $\%$ B-styrene units (after hydroxylation) and two corresponding s-PS-g-
PMMA graft copolymers with 20 and 59 mol % MMA contents, respectively. In addition to the major peaks at 1.32, 1.85, 6.65, and 7.15 ppm for the protons in s-PS backbone, the distinctive peak at 3.58 ppm corresponds to methoxyl groups (CH$_3$O) in PMMA.

**Experimental Details**

**Instrumentation and Materials.** All room- and high-temperature $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM-300 spectrometer. Fourier transform infrared spectroscopy was performed on a Bio-Rad instrument using polymer thin film. The molecular weight was determined using a Waters 150C that was operated at 135 °C. The columns used were mStyragel HT of 10$^6$, 10$^5$, 10$^4$, and 10$^3$ Å. A flow rate of 0.7 mL/min was used, and the mobile phase was trichlorobenzene. Narrow molecular weight distribution polystyrene samples were used as standards. Differential scanning calorimetry (DSC) was measured (with a heating rate of 20 °C/min) on a Perkin-Elmer DSC-7, TAC-7 instrument controller.

All O$_2$- and moisture-sensitive manipulations were performed inside an argon-filled drybox equipped with a dry train. Cp*Ti(OMe)$_3$ (95%), Cp*TiCl$_3$ (97%), CpTiCl$_3$ (97%), MAO (10 wt % in toluene), and allylmagnesium chloride (2.0 M in THF) were purchased from Aldrich and used without further purification. 9-BBN (0.5 M in THF) from Callery Chemical Co. was used as received. Styrene (>99%) and vinylbenzyl chloride (90%) from Aldrich were dried over CaH$_2$ before distillation. CP grade toluene was deoxygenated by argon purge before refluxing for 48 h and then distilled over sodium.

**Synthesis of 4-[B-(n-butylene)-9-BBN]styrrene.** 4-[B-(n-butylene)-9-BBN]styrrene monomer was prepared by a two-step reaction process. The first step of the coupling reaction between allylmagnesium chloride and vinylbenzyl chloride was carried out in a 1000 mL flask equipped with a magnetic stirring bar and inert atmosphere. In the flask, 200 mL of allylmagnesium chloride/THF solution (2 M) was diluted with 150 mL of THF, and then 50 mL of 4-vinylbenzyl chloride (0.35 mol) diluted with 50 mL of THF was added dropwise with stirring and cooling to maintain the reaction temperature at 0 °C. The reaction mixture was slowly warmed to room temperature and maintained at room temperature for another 2 h before adding 100 mL of water to destroy the excess allylmagnesium chloride. The solution was then poured into 500 mL of water, and the organic layer was separated and dried over anhydrous sodium sulfate. After removing the THF solvent, about 46 g of the resulting 4-(3-butenyl)styrrene was distilled over calcium hydride under reduced pressure (about 25 Torr) at 60 °C with about 83% yield.

The selective mono-hydroboration of 4-(3-butenyl)styrrene by 9-BBN (0.3 mol) was carried out in THF (300 mL) at room temperature. An equal amount (600 mL) of 9-BBN (0.5 M in THF) was added dropwise into 4-(3-but enyl)styrrene/THF solution over a period of 4 h. After another 1/2 h of stirring at room temperature, the THF solvent was vacuum-removed. The reaction mixture was subjected to vacuum distillation (5 Torr) at 110 °C to obtain about 70 g of 4-[B-(n-butylene)-9-BBN]styrrene with 90% yield. The $^1$H NMR spectrum (shown in Figure 1) confirms the molecular structure.

**Copolymerization of Styrene and 4-[B-(n-butylene)-9-BBN]styrrene.** The copolymerization reactions were carried out in an argon-filled drybox. In a typical reaction (run 3 in Table 1), 20 mL of styrene and 0.86 g of B-styrene were mixed with 100 mL of anhydrous toluene in a 250 mL flask under a...
nitrogen atmosphere. 11 mL of MAO (10 wt % in toluene) was added with stirring. The copolymerization reaction was started by adding 1 mL (10 μmol) of Cp*Ti(OMe)₃/toluene solution. The polymerization was carried out at 50 °C for 3 h before terminating with 100 mL of IPA. The precipitated copolymer was isolated and washed with IPA and dried under vacuum to yield 4.66 g of polymer solid.

Hydroxylation Reaction. Under a nitrogen atmosphere, the powder form of styrene/B-styrene copolymer (3 g) containing 2.1 mol % B-styrene was suspended in 50 mL of THF solvent in a 200 mL flask equipped with a mechanical stirrer. Oxidation reaction was carried out by adding NaOH/H₂O₂ solution (B/NaOH/H₂O₂ = 1/2/3) (0.06 g) and 5 mL of methanol at 0 °C. The reaction mixture was warmed to 40 °C for 4 h. The polymer was isolated by precipitation in MeOH. The polymer was refluxed in MeOH for 1 h before removing residual boric acid by distillation of the B(OH)₃/MeOH azeotrope. The polymer was isolated by filtration and dried under vacuum to obtain 2.7 g of hydroxylated s-PS copolymer. The ¹H NMR spectrum shown in Figure 4a indicates a quantitative conversion of borane to hydroxy groups.

Maleic Anhydride Reaction. In a 150 mL flask equipped with a stirrer and N₂ atmosphere, 3 g of styrene/B-styrene copolymer containing 3.0 mol % of B-styrene was suspended in 50 mL of THF along with 5 g of maleic anhydride. Under stirring, a stoichiometric quantity of oxygen (vs borane) was slowly added to the suspended polymer solution at ambient temperature. After 2 h, the maleation reaction was terminated.
The chemistry involves a new 4-[B-(n-butylene)-9-BBN]-styrene (B-styrene) comonomer and half-sandwich metallocene catalysts. The reactivity ratios near to 1 in the two monomers allow the preparation of a broad composition range of s-PS copolymers with narrow molecular weight and composition distributions. The pending borane groups in the copolymer not only provide the desirable functional groups, such as hydroxy and anhydride, but also reduce the melting temperature of s-PS to the manageable processing temperature and still maintain high crystallinity. In addition, the pending borane groups were also transformed to stable radicals for graft-from polymerization to prepare s-PS-g-PMMA graft copolymers.

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### References and Notes


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