

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

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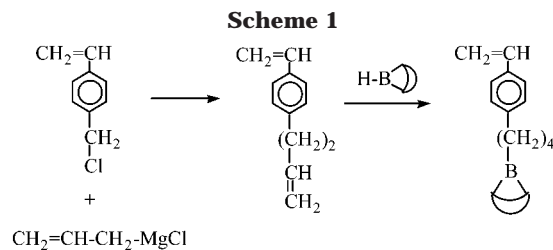
ABSTRACT: This paper discusses an effective route in the functionalization of s-PS polymer that involves the direct copolymerization of styrene with a borane-containing styrenic monomer, i.e., 4-[B-(*n*-butylene)-9-BBN]styrene (B-styrene). The reactivity ratios of the two comonomers are quite close, 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 ¹³C 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*-PMMA graft copolymers.

Introduction

One of the most important advances in metallocene technology is the preparation of syndiotactic polystyrene (s-PS)¹ that exhibits high melting point (~270 °C) and a relatively high crystallization rate that is several orders of magnitude² 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 >300 °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 °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 sulfonation³ and bromination⁴ of s-PS and hydroxylated s-PS⁵ prepared via poly(styrene-*co*-4-*tert*-butyldimethylsilyloxystyrene) 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,⁶ which was further engaged in the free radical chain extension with methyl methacrylate (MMA) to form s-PS-*b*-PMMA diblock copolymers.

Several years ago, we developed a very useful method to functionalize polyolefins, such as polyethylene (PE) and polypropylene (PP), which involved direct copolymerization⁷ of α -olefin and borane-containing α -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 reactions⁸ to prepare polyolefin graft copolymers, such as PP-*g*-PMMA and PE-*g*-PMMA. 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 α -olefin groups, this resulting asymmetrical diene was selectively monohydroborated by 9-BBN at the α -olefinic double bond in an anti-Markovnikov manner.

Both reaction steps are very effective and produce high yields. Figure 1 compares the ¹H 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

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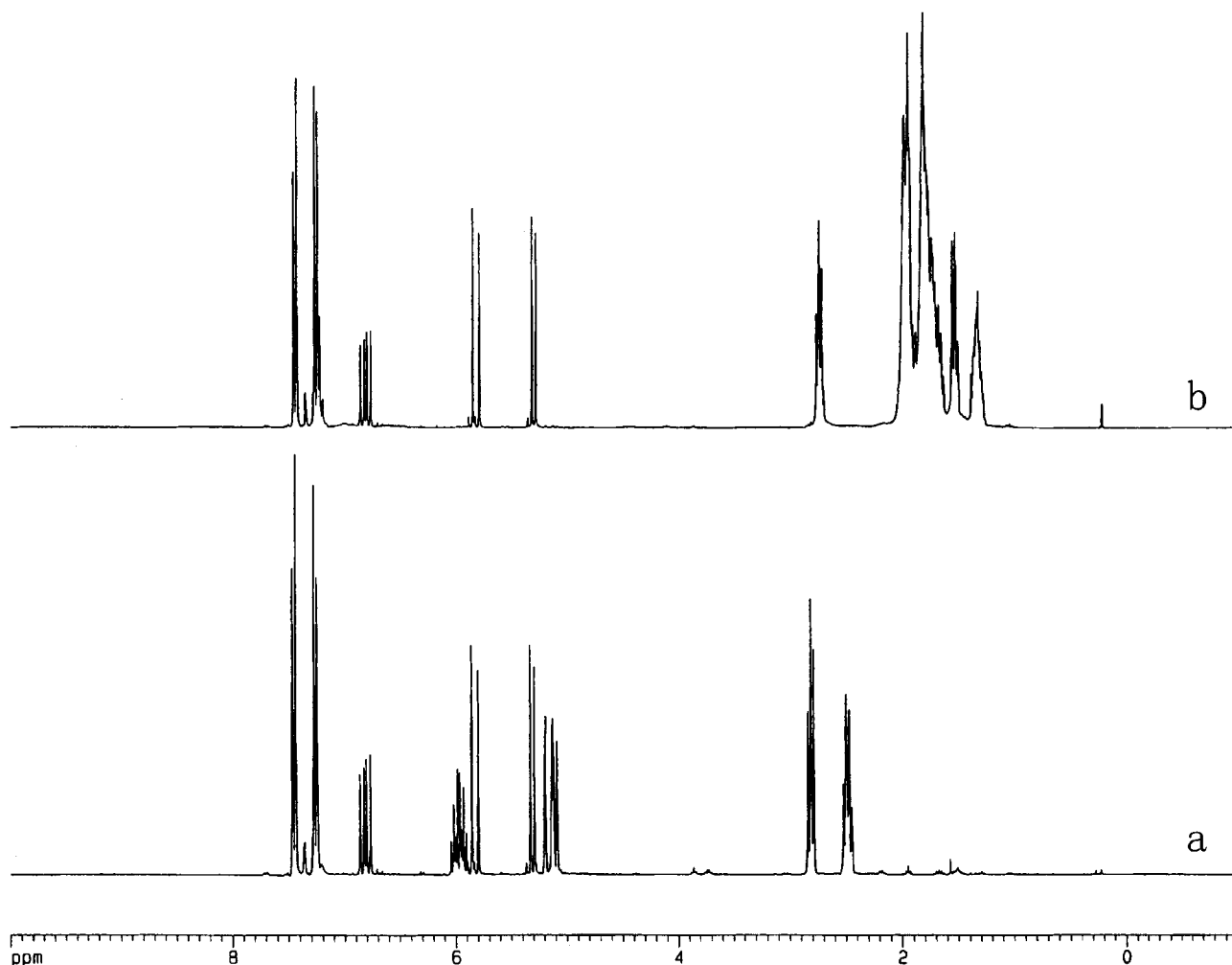


Figure 1. ^1H NMR spectra of (a) 4-(3-butenyl)styrene and (b) 4-[B-(*n*-butylene)-9-BBN]styrene (solvent: *d*-chloroform).

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

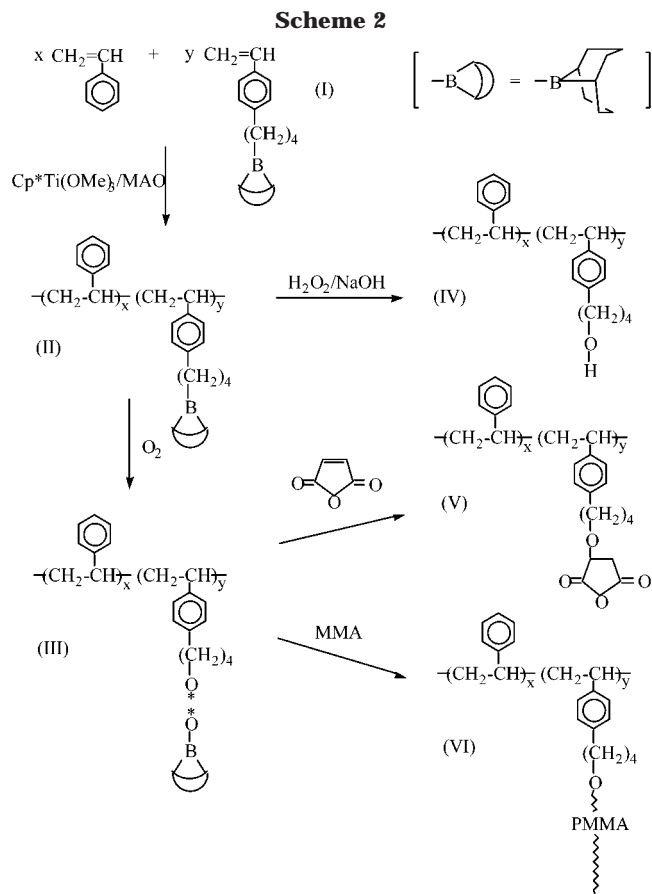
| run no. | catalyst | B-S in feed (mol %) | [S] (mol/L) | [B-S] (mol/L) | yield (g) | catalyst activity ^b | B-S content in copolymer (mol %) | $M_w \times 10^4$ (g/mol) | $M_n \times 10^4$ (g/mol) | PDI M_w/M_n |
|---------|--------------------------------------|---------------------|-------------|---------------|-----------|--------------------------------|----------------------------------|---------------------------|---------------------------|---------------|
| A-1 | $\text{Cp}^*\text{Ti}(\text{OMe})_3$ | 0 | 1.73 | 0 | 3.48 | 67.0 | 0 | 20.3 | 7.0 | 2.9 |
| A-2 | $\text{Cp}^*\text{Ti}(\text{OMe})_3$ | 0.63 | 1.73 | 0.011 | 4.44 | 85.1 | 1.0 | 21.5 | 8.0 | 2.7 |
| A-3 | $\text{Cp}^*\text{Ti}(\text{OMe})_3$ | 1.76 | 1.73 | 0.031 | 4.66 | 88.3 | 2.1 | 20.7 | 8.3 | 2.5 |
| A-4 | $\text{Cp}^*\text{Ti}(\text{OMe})_3$ | 2.59 | 1.73 | 0.046 | 5.13 | 96.2 | 3.0 | 15.5 | 6.7 | 2.3 |
| A-5 | $\text{Cp}^*\text{Ti}(\text{OMe})_3$ | 5.38 | 1.59 | 0.091 | 5.36 | 106.3 | 6.1 | 14.4 | 6.3 | 2.3 |
| A-6 | $\text{Cp}^*\text{Ti}(\text{OMe})_3$ | 7.16 | 2.14 | 0.165 | 6.73 | 97.3 | 8.4 | 12.7 | 5.5 | 2.3 |
| A-7 | $\text{Cp}^*\text{Ti}(\text{OMe})_3$ | 12.2 | 2.04 | 0.284 | 6.04 | 86.7 | 16.7 | 9.8 | 5.2 | 2.0 |
| A-8 | $\text{Cp}^*\text{Ti}(\text{OMe})_3$ | 24.3 | 1.13 | 0.363 | 2.98 | 66.7 | 32.2 | 5.3 | 2.8 | 2.0 |
| A-9 | $\text{Cp}^*\text{Ti}(\text{OMe})_3$ | 100 | 0 | 0.730 | 1.91 | 87.3 | 100 | | | |
| B-1 | CpTiCl_3 | 6.10 | 1.41 | 0.091 | 3.52 | 78.2 | 6.7 | | | |
| C-1 | Cp^*TiCl_3 | 6.10 | 1.41 | 0.091 | 2.98 | 66.2 | 5.4 | | | |

^a Polymerization conditions: [cat] = 100 $\mu\text{mol/L}$, Al/Ti = 2000, temperature = 50 $^\circ\text{C}$, time = 3 h, solvent = 40 mL of toluene. ^b In kg of polymer/mol Ti \cdot h \cdot mol/L.

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*-butene)-9-BBN]-

styrene (B-styrene) was carried out with conventional half-sandwich metallocene catalysts, including $\text{Cp}^*\text{Ti}(\text{OMe})_3/\text{MAO}$, $\text{Cp}^*\text{TiCl}_3/\text{MAO}$, and $\text{CpTiCl}_3/\text{MAO}$ complexes¹ that exhibit high syndiospecificity and good catalyst activity in styrene polymerization. The resulting borane-containing copolymers, poly(styrene-*co*-4-[B-(*n*-butylene)-9-BBN]styrene) (II), were completely soluble in tetrachloroethane at elevated temperature (110 $^\circ\text{C}$). Some copolymers with high B-styrene comonomer contents (>8.4 mol %) are soluble in toluene or THF at ambient temperature. ^{11}B NMR spectra of all copolymers show a single chemical shift at 87 ppm (vs



$\text{BF}_3 \cdot \text{OEt}_2$) corresponding to the pendant alky-9-BBN moieties.

Because of the oxygen sensitivity of the borane moiety, the borane-containing s-PS copolymers were usually oxidized by $\text{NaOH}/\text{H}_2\text{O}_2$ to form the correspond-

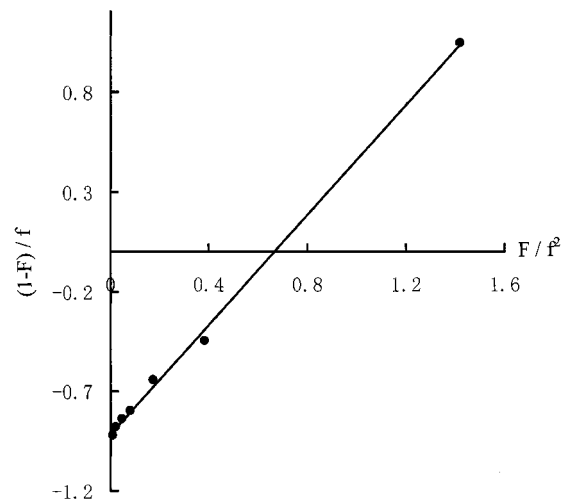


Figure 2. Fineman and Ross plots for copolymerization of styrene/B-styrene and the least-squares best-fit line ($f = [\text{styrene}]/[\text{B-styrene}]$ in feed and $F = d[\text{styrene}]/d[\text{B-styrene}]$ mole ratio in polymer).

ing 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/4-[B-(*n*-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

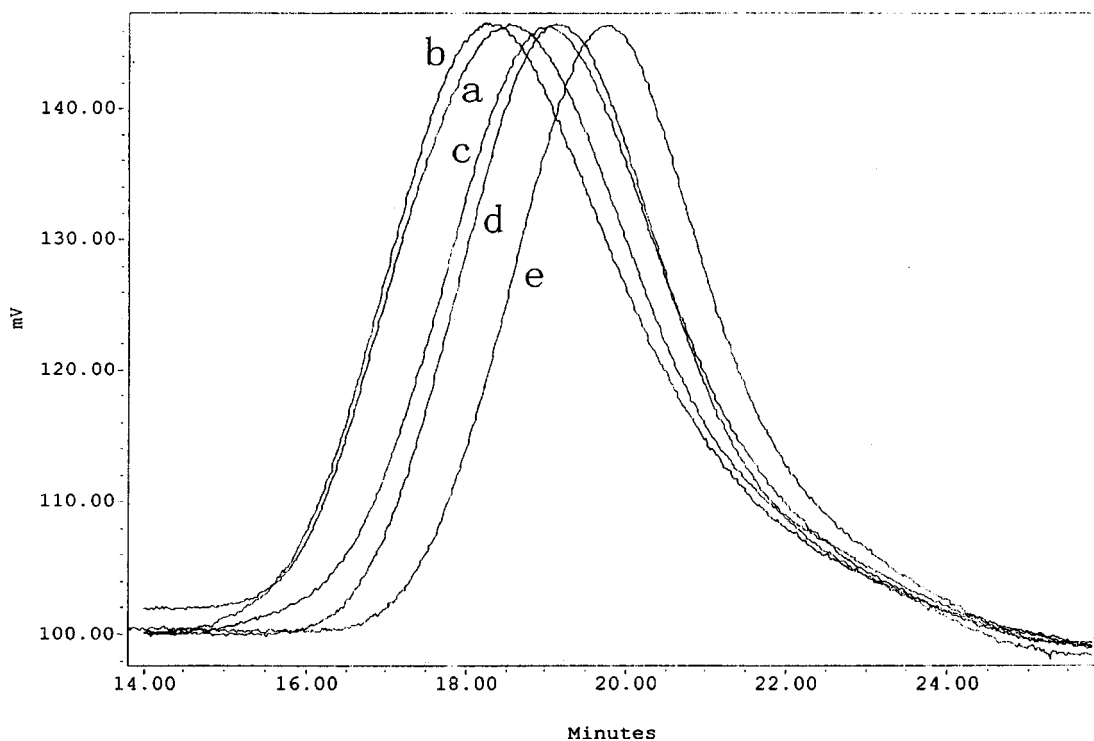


Figure 3. GPC curves of (a) s-PS homopolymer (A-1) and several styrene/B-styrene copolymers, including (b) A-2, (c) A-4, (d) A-5, and (e) A-7 in Table 1 (solvent: trichlorobenzene; temperature: 135 °C).

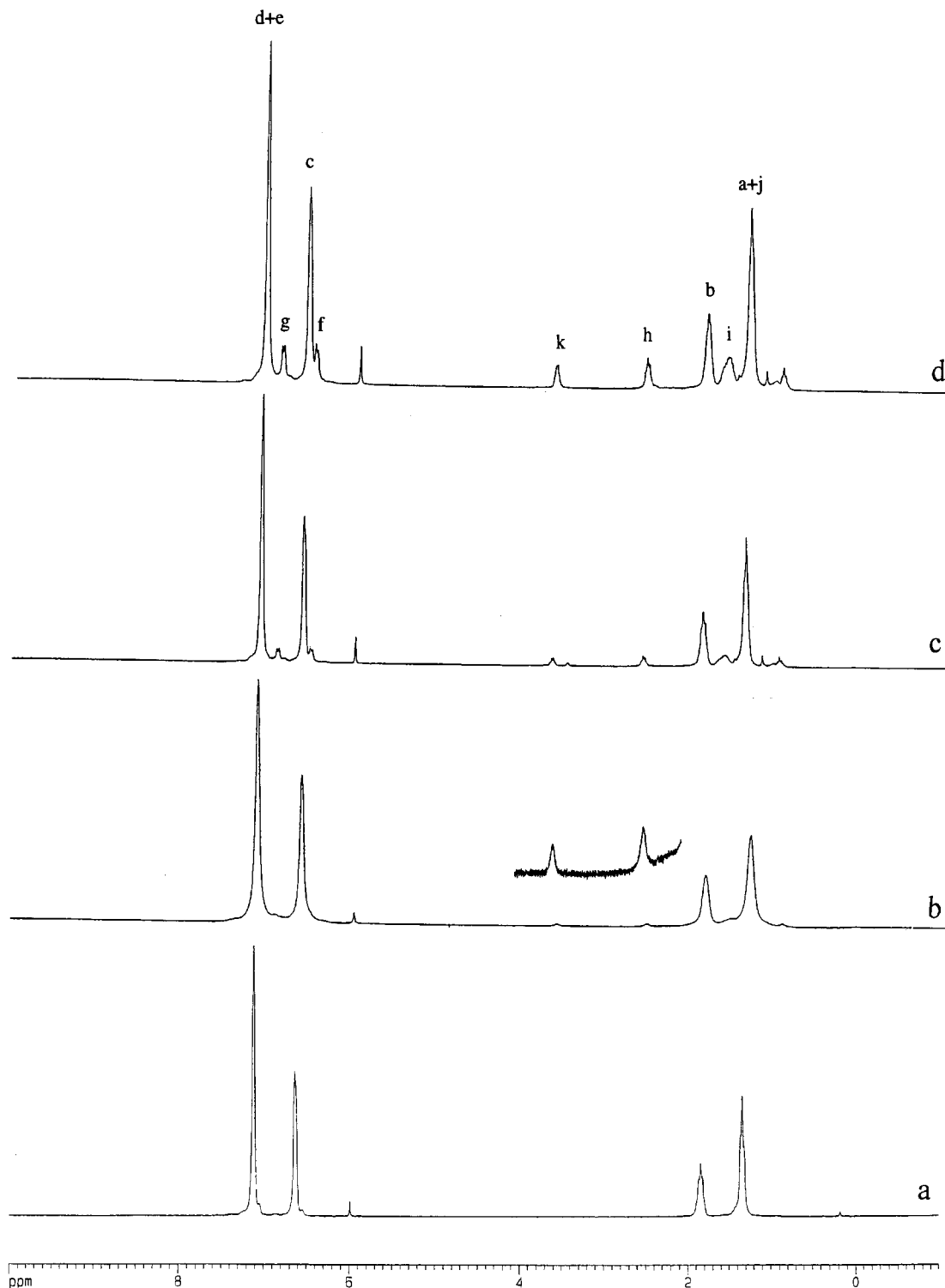


Figure 4. ^1H NMR spectra of (a) s-PS and three s-PS-OH copolymers, containing (b) 2.1, (c) 8.4, and (d) 16.7 mol % of OH groups (solvent: $\text{C}_2\text{D}_2\text{Cl}_4$; temperature: 110°C).

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.⁹ 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 $\text{Cp}^*\text{Ti}(\text{OMe})_3/\text{MAO}$ 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

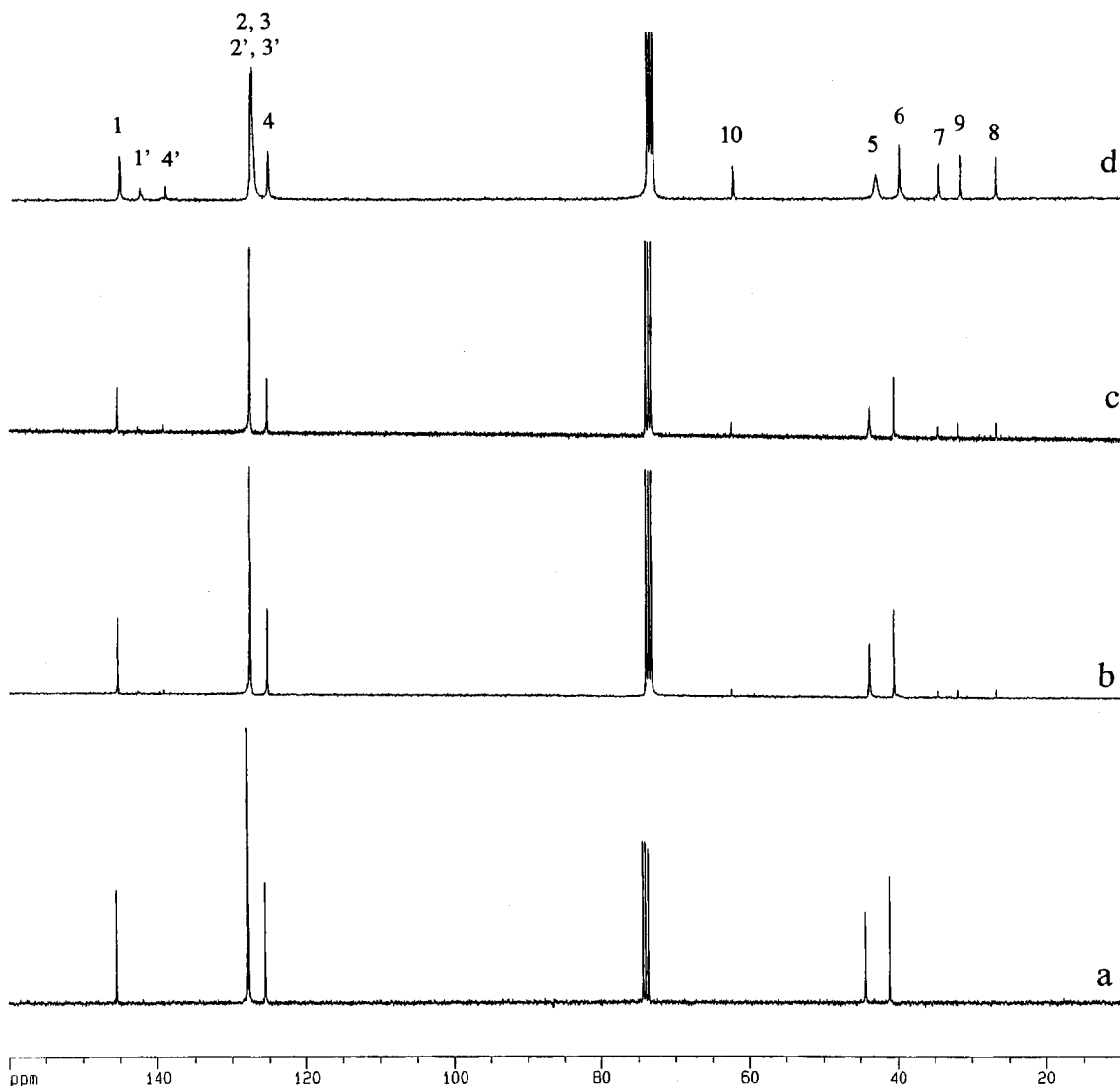


Figure 5. ^{13}C NMR spectra of (a) s-PS and three s-PS-OH copolymers, containing (b) 2.1, (c) 8.4, and (d) 16.7 mol % of OH groups (solvent: $\text{C}_2\text{D}_2\text{Cl}_4$; temperature: 110°C).

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).

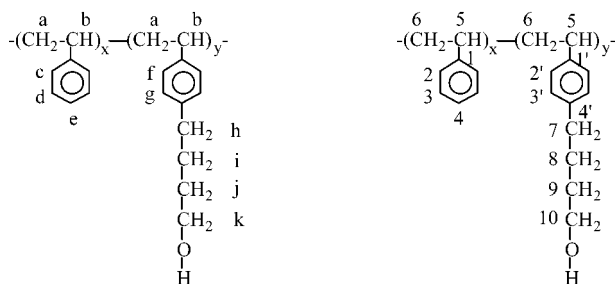
Figure 3 shows several GPC curves of the styrene/B-styrene copolymers (runs A-1, A-2, A-4, A-5, and A-7 in Table 1) prepared by the $\text{Cp}^*\text{Ti}(\text{OMe})_3/\text{MAO}$ complex. The narrow molecular weight distribution in all samples, with $\bar{M}_w/\bar{M}_n = 2-3$, implies that the polymerization follows a single-site reaction mechanism. In fact, the GPC curves show a slight reduction of molecular weight distribution in the copolymers, from $\bar{M}_w/\bar{M}_n = 2.9$ 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 $\text{Cp}^*\text{TiCl}_3/\text{MAO}$ and $\text{CpTiCl}_3/\text{MAO}$ 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 O_2 is excluded. In this study, the borane groups in the copolymers were oxidized by $\text{NaOH}/\text{H}_2\text{O}_2$ 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 ^{13}C 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 arrangement¹ 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-

Chart 1



droxylated comonomer units, there are two new aromatic proton (H_f and H_g) peaks at 6.50 and 6.92 ppm and two distinctive proton peaks at 2.55 and 3.68 ppm corresponding to the protons (H_h and H_k) adjacent to the aromatic ring ($-\text{CH}_2-\text{Ph}$) and the primary alcohol ($-\text{CH}_2-\text{OH}$) in the hydroxylated B-styrene units. The combination of integrated intensities at 3.68 and 7.15 ppm and the corresponding protons in each chemical shift provides the copolymer composition (see Chart 1).

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 resonance¹⁰ for the substituted aromatic C_1 carbon in phenyl groups at 145.3 shows that these polymers are highly syndiotactic. The same conclusion can be reached by considering two C_5 and C_6 aliphatic carbons 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 methylene carbon atom (C_{10}) in the $-\text{CH}_2-\text{OH}$ group. Overall, 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 groups¹¹ 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 (χ_c) of the copolymer are affected by the side chains. The higher the density of the side chain, the lower the T_m and χ_c . The detailed results of the melting point (T_m) and crystallinity (χ_c) of the copolymers are summarized in Table 2. The crystallinity (χ_c) of the copolymer was calculated from fusion enthalpy according to the following equation: $\chi_c = H_f/H_f^\circ \times 100$, where H_f and H_f° (53 J/g)¹² 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 $T_m = 250$ °C. In addition to its functionality, this s-PS-OH copolymer may also benefit from better processability at <300 °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

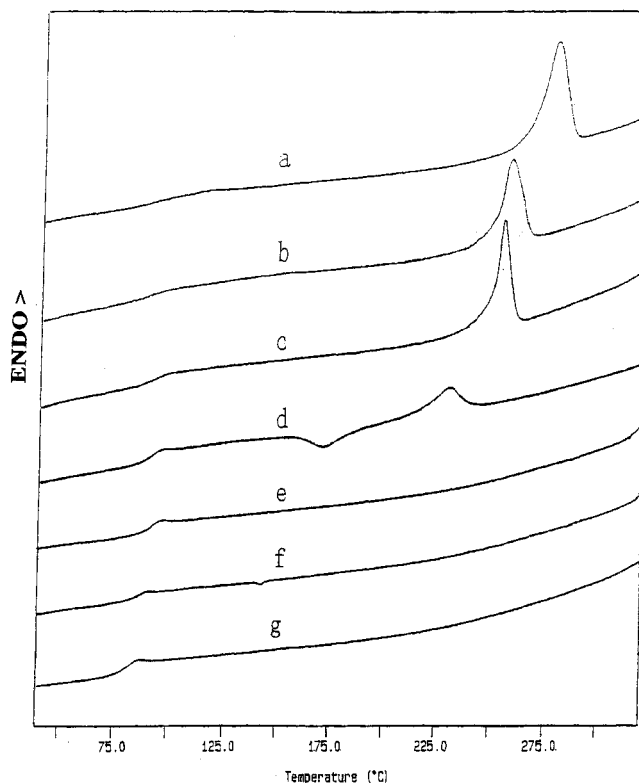


Figure 6. DSC curves of (a) s-PS homopolymer and several s-PS-OH copolymers, containing (b) 1.0, (c) 2.1, (d) 6.1, (e) 8.4, (f) 16.7, and (g) 32.2 mol % of OH groups.

(III) that are associated with "stable" borinate radicals.⁸ The polymeric radicals react in situ with maleic anhydride (MA) to produce maleic anhydride grafted s-PS (s-PS-*g*-MA) (V) 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 $\nu_{\text{C}=\text{O}}$ vibration modes between s-PS and three s-PS-*g*-MA copolymers with 1, 3, and 8 mol % MA contents, respectively.

After the MA graft reaction, several new absorption peaks were observed at 1860 and 1780 cm^{-1} corresponding to two $\nu_{\text{C}=\text{O}}$ vibrational stretching modes¹³ 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.

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*-PMMA (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 graft reaction, the product, isolated by filtration and washed with boiling MeOH, was then extracted with acetone in a Soxhlet apparatus for 24 h to remove PMMA homopolymer (<10%). 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*-

Table 2. A Summary of the Thermal Properties^a of Hydroxylated s-PS Copolymers

| entry | OH- content (mol %) | T_g (°C) | T_m (°C) | T_c^b (°C) | ΔH (J/g) | χ_c^c (%) |
|-------|---------------------|------------|-----------------|--------------|------------------|----------------|
| A-1 | 0 | 101.5 | 272.5 | 233.1 | 30.1 | 56.8 |
| A-2 | 1.0 | 97.6 | 263.0 | 226.9 | 26.8 | 50.5 |
| A-3 | 2.1 | 94.1 | 250.1 | 208.7 | 21.9 | 41.3 |
| A-4 | 3.0 | 93.1 | 247.2 | 197.7 | 20.2 | 38.1 |
| A-5 | 6.1 | 87.8 | 223.9 | ND | 16.6 | 31.3 |
| A-6 | 8.4 | 87.9 | ND ^d | ND | | |
| A-7 | 16.7 | 81.3 | ND | ND | | |
| A-8 | 32.2 | 79.8 | ND | ND | | |

^a Based on DSC measurement with heating and cooling rate of 20 °C/min. ^b Crystallization temperature. ^c Crystallinity. ^d ND = not detected.

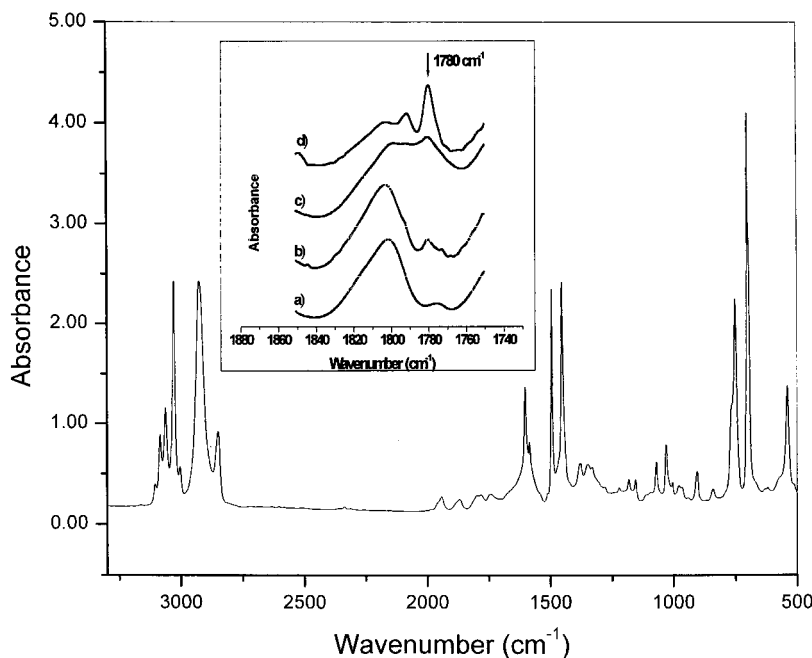


Figure 7. IR spectrum of a s-PS-*g*-MA copolymer containing 8 mol % of MA units. The inset compares the absorption region of $\nu_{C=O}$ vibration modes between (a) s-PS and three s-PS-*g*-MA copolymers with (b) 1, (c) 3, and (d) 8 mol % MA content.

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 ($\text{CH}_3\text{-O}$) in PMMA.

Experimental Details

Instrumentation and Materials. All room- and high-temperature ^1H 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. $\text{Cp}^*\text{Ti}(\text{OMe})_3$ (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]styrene. 4-[B-(*n*-butylene)-9-BBN]styrene 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)styrene 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)styrene 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-butenyl)styrene/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]styrene with 90% yield. The ^1H NMR spectrum (shown in Figure 1) confirms the molecular structure.

Copolymerization of Styrene and 4-[B-(*n*-butylene)-9-BBN]styrene. 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

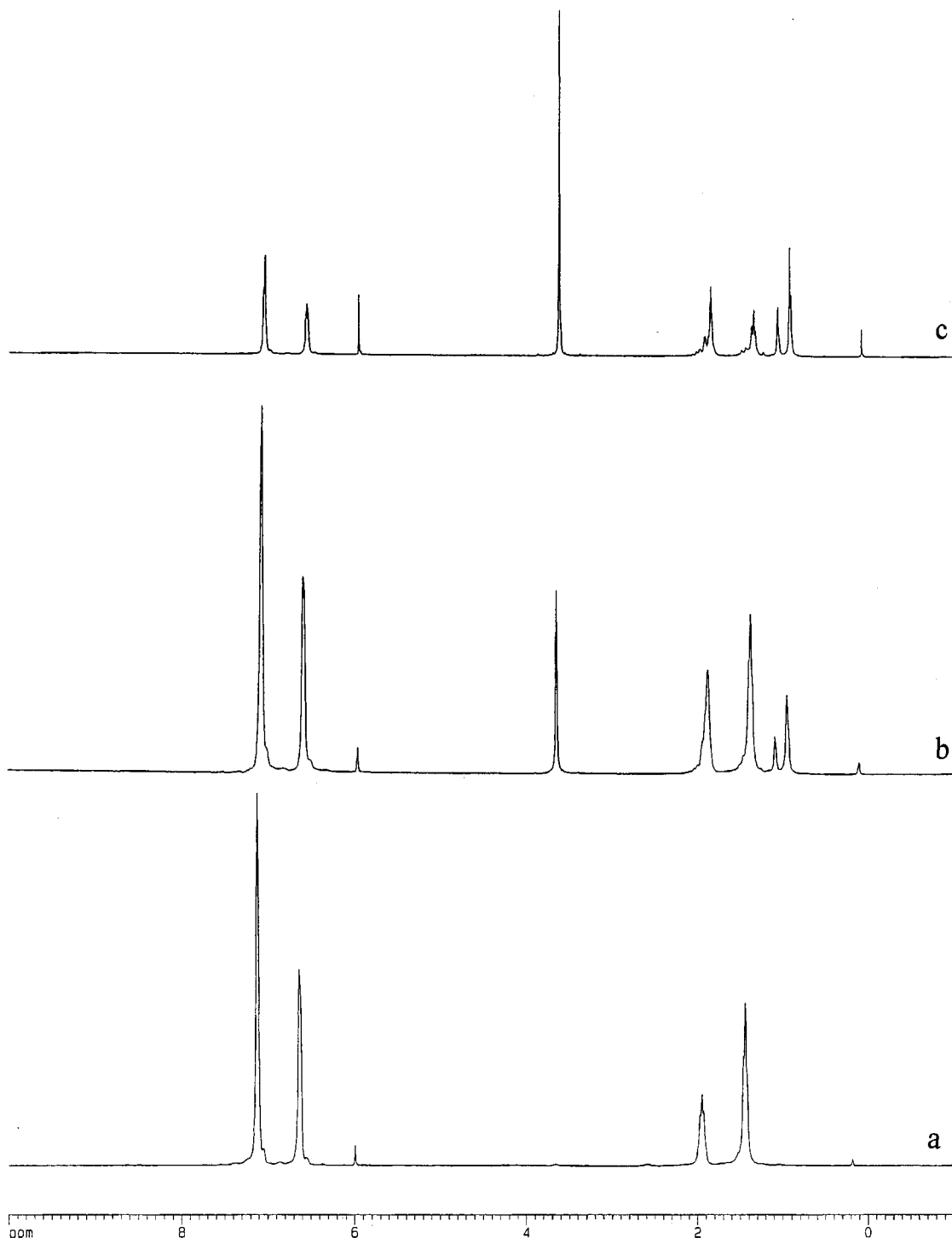


Figure 8. ^1H NMR spectra of (a) s-PS-OH containing 1 mol % OH units and two corresponding s-PS-*g*-PMMA graft copolymers with (b) 20 and (c) 59 mol % MMA contents.

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 $\text{Cp}^*\text{Ti}(\text{OMe})_3$ /toluene solution. The polymerization was carried out at 50 $^\circ\text{C}$ 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 $\text{NaOH}/\text{H}_2\text{O}_2$ solution ($\text{B}/\text{NaOH}/\text{H}_2\text{O}_2 = 1/2/3$) (0.06 g) and 5 mL of methanol at 0 $^\circ\text{C}$. The reaction mixture was warmed to 40 $^\circ\text{C}$ 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 $\text{B}(\text{OH})_3/\text{MeOH}$ 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 N_2 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

by precipitating the polymer mixture in 2-propanol. The maleated s-PS product (2.8 g) was isolated by filtration and purified by Soxhlet extraction with acetone for 24 h before drying the resulting polymer under vacuum.

The MA concentration in the polymer was estimated with the following equation: $\text{MA wt \%} = kA_{1780 \text{ cm}^{-1}}/d$, where d is the film thickness, $A_{1780 \text{ cm}^{-1}}$ is the peak absorbency, and k is the absorption constant for anhydride. The k constant is determined by calibration of the known compounds, assuming the absorption constant is independent of the incorporated MA structures.

Graft Reaction of s-PS with PMMA. In nitrogen atmosphere, 3 g of s-PS-B copolymer containing 1 mol % B-styrene units suspended in 30 mL of THF solvent was mixed with 6 g of MMA monomer in a septum-capped 250 mL flask equipped with a magnetic stirring bar. Under agitation, a stoichiometric quantity (15 mL) of oxygen (vs borane) was slowly added to the suspended polymer solution. The graft polymerization was allowed to proceed at room temperature for 12 h before exposing the solution to air. The suspended polymer solution was poured into 200 mL of acetone, then filtered, and washed with acetone several times. The isolated polymer was extracted with boiling THF to remove PMMA homopolymer. The insoluble fraction (soluble in 1,1,2,2-tetrachloroethane, 1,2,4-trichlorobenzene at elevated temperatures) is s-PS-*g*-PMMA graft copolymer (7.3 g). The ^1H NMR spectrum of the graft copolymer shown in Figure 8c indicates 59 mol % MMA content.

Conclusion

This paper has shown a facile route in the preparation of functional s-PS polymers and s-PS graft copolymers. 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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