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Controlled Functionalization of Crystalline Polystyrenes via Activation of Aromatic C−H Bonds[†]

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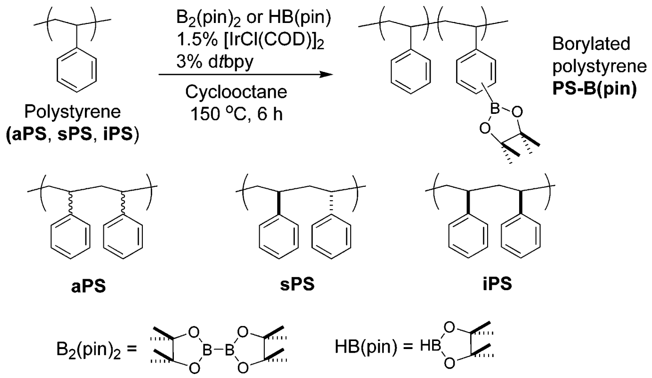
ABSTRACT: The iridium-catalyzed functionalization of the C−H bond of commercial polystyrenes with three types of tacticities (syndiotactic, isotactic, atactic) using boron reagents is reported. The boronate ester group in the polystyrene was further converted to hydroxy and arene via oxidation and Suzuki−Miyaura cross-coupling, respectively. These functionalizations proceeded without affecting the tacticity or chain length of the starting polymer, and the functional group concentration was easily controlled by changing the ratio of boron reagent to polymer repeating unit. The size and concentration of the functional group in the syndiotactic polystyrenes were found to have huge impacts on the thermal properties of the functionalized polymers. The incorporation of even a small amount (<5 mol %) of the bulky boronate ester group induced complete disappearance of crystallinity for the boryl-functionalized syndiotactic polystyrene. The high crystallinity and melting temperature of syndiotactic polystyrene were not significantly changed, however, until 10 mol % hydroxy group was incorporated into the polymer, presumably owing to the small size of hydroxy group.

Introduction

Polyolefins are the most ubiquitous commercial polymer in the world owing to their good chemical and physical properties, processability, and low production cost. The controlled introduction of specific functionality into nonpolar polyolefins can yield a new class of polymeric materials with enhanced abilities such as adhesion to polar surfaces, but the synthesis of such materials (i.e., functionalized polyolefins) remains an important challenge in polymer chemistry. Syndiotactic polystyrene (sPS) is a good example of a stereoregular polyolefin that needs further property improvement. sPS exhibits intriguing physical properties such as a high degree of crystallinity, high melting temperature (270 °C), polymorphic phase behavior, good chemical resistance, and good mechanical properties even at high temperature.[1] Despite these properties, however, sPS has drawbacks that must be overcome if it is to have wide commercial application. These drawbacks are (a) an excessively high melt-processing temperature (>300 °C) that is close to the polymer degradation temperature, (b) poor compatibility with polar materials owing to lack of functionality, and (c) poor impact strength. To address these problems, researchers have attempted to synthesize functionalized sPS either by introducing a second monomer into the copolymerization or by carrying out the postfunctionalization of sPS. Unfortunately, as with other transition metal−catalyzed stereospecific olefin polymerizations,[2] syndiospecific copolymerization of styrene with functionalized styrenes in the former approach generates polymers that have significantly lower molecular weights and/or lower yields compared with those afforded by the syndiospecific homopolymerization of styrene.[3,4]

Scheme 1. C−H Activation/Borylation of Polystyrene with Iridium Catalyst



Owing to significant progress in the development of homogeneous metallocene polymerization catalysts, a variety of polyolefins with differing tacticities and molecular weights can be conveniently accessed as starting materials. Thus, controlled postfunctionalization of such a diverse spectrum of polyolefins could be an attractive alternative approach for the synthesis of functionalized polymers with different microstructures and molecular weights.[5] Most polyolefin postfunctionalizations are based on a free radical−initiated reaction, however, which does not control the molecular weight of the polymer. Instead, competitive side reactions such as chain scission, chain transfer, and coupling reactions, which can alter the molecular weight and physical properties of the functionalized polymer, occur under the reaction conditions. Free radical modification of sPS can also reduce the tacticity at the benzylic position of the polymer.

Electrophilic aromatic substitution (e.g., sulfonation) has been commonly practiced to introduce a high percent of functional group to the aromatic ring of atactic polystyrene (aPS), an amorphous material that is readily soluble in a wide range of

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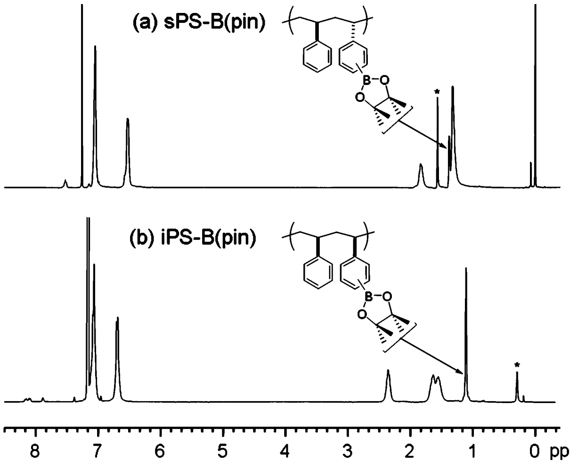


Figure 1. ^1H NMR spectra of borylated crystalline polystyrenes (delay time = 1 s; number of scans = 16. An asterisk indicates H_2O from deuterated NMR solvents): (a) sPS−B(pin) (Table 1, entry 4; 10 mg/mL $CDCl_3$); (b) iPS−B(pin) (Table 1, entry 9; 10 mg/mL C_6D_6).

solvents.[6] The high crystallinity of sPS induces very poor solubility in most organic solvents, however, which makes functionalization via homogeneous organic reaction very challenging. For example, electrophilic sulfonation of sPS in chlorinated solvents generates only 3−12 mol % sulfonated aromatic rings in sPS.[7−10] Studies of molecular weight properties from sPS postfunctionalization are even more rare. So far, only a handful of sPS postfunctionalizations using reactive carbon intermediates (free radical or carbocation) have been reported, mostly under heterogeneous conditions with limited success.[7−13] The homogeneous functionalization method would be the preferred route because heterogeneous methods afford less control of uniform functionalization, especially on a large scale.

Boron moiety in polymer can serve as a versatile intermediate for a diverse range of functionalized polymers, especially polyolefins.[14] Boron-containing polymers have been prepared via either the polymerization of boron−functionalized monomers or the postfunctionalization of boron precursor polymers. An early study of the direct borylation of aPS with haloboranes reported that a low degree of borylation and significant side reactions occurred under forcing conditions.[15] Although the boron moiety could be incorporated into the aromatic ring of the polystyrene resin via a multistep sequence of postfunctionalizations,[16] this method resulted in significant cross-linking when it was adopted for the preparation of soluble boron polymers. Recently reported soluble boron-functionalized polystyrene prepared from the silylated precursor polymer via silicon−boron exchange reaction, although not a catalytic process, is a notable example that maintains controlled molecular weight distribution and excellent chemo- and regioslectivity.[17,18]

Recently, transition metal−catalyzed C−H activation/functionalization has emerged as a new methodology in polyolefin functionalization.[19−24] Unlike traditional free radical−initiated polymer modification, this new method yields functionalized polyolefins with negligible changes in molecular weight properties compared to those of the starting polymers. Of special interest, the rhodium-catalyzed C−H borylation of saturated polyolefins generated a boron moiety in the side chain of polyolefins that could be converted to hydroxy and amine groups via simple organic reactions.[21−23] Some of these examples, however, rely on amorphous polyolefins with relatively low molecular weights as starting polymers and require the preparation of special metal catalysts.[19−21] When semicrystalline polyolefins are used for the postfunctionalization via activation of C−H bonds, their functionalization efficiencies, defined as the concentration of the functional group relative to the reagent added, were low.[22−24] Herein, we report a highly efficient, aromatic C−H bond activation/functionalization of high-molecular-weight polystyrenes with different tacticities [syndiotactic (sPS), atactic (aPS), isotactic (iPS)] using a commercially available iridium catalyst (Scheme 1). We have found that the iridium-catalyzed borylation of aromatic C−H bonds[25−29] can incorporate a high level of boronate ester group (up to 42 mol %) without disrupting the molecular weight distribution of the parent polymer. To our knowledge, this example is the first of crystalline polyolefin functionalization that provides a high degree of functionalization without any disruption in polymer chain length (i.e., there is complete absence of chain scission or coupling of polymer chains). Because the iridium-catalyzed arene C−H activation/borylation is known to occur only at the aromatic ring of arenes,[25−29] this functionalization would allow the generation of borylated polystyrenes of different tacticities in a single step. We also demonstrate herein that the aryl boronate ester group of sPS can serve as a versatile synthetic precursor for a range of functionalized sPS products.

Results and Discussion

To achieve effective functionalization of sPS under homogeneous conditions, we first examined appropriate solvents that could dissolve the crystalline polymer at a reasonable concentration. sPS is insoluble in most organic solvents except hydrocarbon and chlorinated solvents at elevated temperature. Thus, we selected two hydrocarbon solvents with high boiling points, cyclooctane and 1,3,5-triisopropylbenzene, and two chlorinated solvents, chloroform and carbon tetrachloride, for a solubility test of sPS. Observation of a mixture of sPS and solvent in a 1:6 molar ratio (sPS repeating unit to solvent) revealed a homogeneous solution under the following conditions: in cyclooctane at 150 °C, in 1,3,5-triisopropylbenzene at 200 °C, and in chloroform at 60 °C. sPS was insoluble in carbon tetrachloride even at its boiling temperature. Although sPS could be dissolved in chloroform, we discovered that the C−H borylation of cumene [$C_6H_5-CH(CH_3)_2$], a model small arene whose structure resembles that of the polystyrene repeating unit, was inactive in chloroform; thus we did not pursue it as a solvent for the C−H borylation of sPS. When different transition metal catalysts—$[IrCl(COD)]_2$/d*t*bpy (COD = 1,5-cyclooctadiene; d*t*bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), $[Ir(OMe)(COD)]_2$/d*t*bpy, $[IrCl(COE)_2]_2$/d*t*bpy (COE = cyclooctene), and Cp*Rh-(η^4-C_6Me_6)—were examined for the C−H borylation of cumene with bis(pinacolato)diboron ($B_2(pin)_2$) in cyclooctane (in a 1:6 molar ratio of cumene and solvent) at 150 °C, all iridium catalysts were much more reactive than the rhodium catalyst. Among the iridium catalysts, $[IrCl(COD)]_2$/d*t*bpy was slightly more effective than the two other catalysts. Thus, the experimental condition of $[IrCl(COD)]_2$ (3 mol % iridium) and d*t*bpy ligand (3 mol %) in cyclooctane solvent (in a 1:6 molar ratio of sPS repeating unit to solvent) at 150 °C was selected as the standard condition for the C−H borylation of sPS, which has a number-average molecular weight (M_n) of 127 kg/mol and a polydispersity index (PDI = M_w/M_n) of 2.64.

The iridium-catalyzed reaction of commercial polystyrenes (sPS, aPS, iPS) with pinacolborane (HB(pin)) or $B_2(pin)_2$ in cyclooctane produced the corresponding borylated polymers (PS−B(pin)) as shown in Scheme 1. ^1H NMR spectra of all PS−B(pin) gave rise to a distinctive new resonance at 1.20−1.35 ppm for the four methyl groups of pinacolboronate ester (B(pin)): 1.35 ppm for sPS−B(pin) in $CDCl_3$; 1.20 ppm for iPS−B(pin), sPS−B(pin), and aPS−B(pin) in C_6D_6 (see Figure

Table 1. Borylation of Crystalline Polystyrene (Syndiotactic [sPS] and Isotactic [iPS]) with Bis(pinacolato)diboron ($B_2(pin)_2$)[a]

					PS−B(pin)			
entry	PS	M_n[b]	PDI[b] (M_w/M_n)	$[B_2(pin)_2]$/[monomer]	M_n[b]	PDI[b] (M_w/M_n)	B(pin) (%)[c]	effic (%)[d]
1	sPS	127	2.64	0.03	132	2.37	2.5	42
2	sPS	127	2.64	0.05	116	2.74	5.9	59
3	sPS	127	2.64	0.07	116	2.53	9.9	71
4	sPS	127	2.64	0.1	90.0	2.50	16.4	82
5	sPS	127	2.64	0.2	124	2.40	23.6	59
6	sPS	127	2.64	0.4	97.0	2.55	34.2	43
7	sPS	127	2.64	0.8	*g*	*g*	41.1	26
8	sPS	127	2.64	1.2	*g*	*g*	42.1	18
9[e]	iPS	309	6.42	0.1	418	5.00	10.6	50
10[e]	sPS	127	2.64	0.1	*g*	*g*	13.7	69
11[f]	sPS	127	2.64	0.1	*g*	*g*	12.9	65

[a] B(pin) = pinacolboronate ester. PS = polystyrene. Unless otherwise specified, C−H borylation was conducted on 200−260 mg of polymer with 3 mol % of iridium and 3 mol % of ligand relative to $B_2(pin)_2$ in cyclooctane (in a 1:6 molar ratio of polystyrene repeating unit to solvent) at 150 °C for 6 h. sPS = syndiotactic polystyrene; iPS = isotactic polystyrene. [b] Number-average molecular weight (M_n) in kg/mol and polydispersity index (PDI) measured with high-temperature size-exclusion chromatography in 1,2,4-trichlorobenzene at 160 °C relative to polystyrene standards. [c] The mol % of B(pin) functionalized styrene unit calculated from the ^1H NMR spectrum. [d] Efficiency of functionalization (i.e., the percentage of functionalized styrene unit relative to boron atoms added). [e] Borylation conducted in cyclooctane in a 1:10 molar ratio of polystyrene repeating unit to solvent. [f] 0.5 mol % of iridium and 0.5 mol % of ligand were used. [g] Not measured.

Table 2. Borylation of Monodisperse Atactic Polystyrene (aPS) with Bis(pinacolato)diboron ($B_2(pin)_2$)[a]

					aPS−B(pin)			
entry	PS	M_n[b]	PDI[b] (M_w/M_n)	$[B_2(pin)_2]$/[monomer]	M_n[b]	PDI[b] (M_w/M_n)	B(pin) (%)[c]	effic (%)[d]
1	aPS	25.1	1.09	0.05	26.5	1.09	8.4	84
2	aPS	25.1	1.09	0.07	27.0	1.09	11.1	80
3	aPS	25.1	1.09	0.1	27.9	1.10	16.4	82
4	aPS	25.1	1.09	0.2	29.2	1.10	22.4	56
5	aPS	25.1	1.09	0.4	30.1	1.11	32.8	41
6	aPS	25.1	1.09	0.8	30.9	1.12	42.3	26
7	aPS	25.1	1.09	1.2	31.1	1.14	41.1	17
8	aPS	247	1.07	0.1	256	1.05	16.9	85

[a] B(pin) = pinacolboronate ester. PS = polystyrene. C−H Borylation was conducted on 200 mg of polymer with 3 mol % of iridium and 3 mol % of ligand relative to $B_2(pin)_2$ in cyclooctane (in a 1:6 molar ratio of polystyrene repeating unit to solvent) at 150 °C for 6 h. [b] Number-average molecular weight (M_n) in kg/mol and polydispersity index (PDI) measured with size exclusion chromatography in THF at 40 °C relative to polystyrene standards. [c] The mol % of B(pin) functionalized styrene unit calculated from the ^1H NMR spectrum. [d] Efficiency of functionalization (i.e., the percentage of functionalized styrene unit relative to boron atoms added).

1 and the Supporting Information). The two resonances from CH_2 and CH of the polystyrene main chain maintained a ratio of 2:1, confirming that the methylene and methine groups of polystyrene were intact during the borylation. The aryl−B(pin) moiety of the polymer showed new sharp resonances at 83.5 and 24.9 ppm in the ^{13}C NMR spectrum. ^{13}C NMR attached proton test (APT) and distortionless enhancement by polarization transfer (DEPT) spectroscopies of sPS−B(pin) confirmed that the two resonances corresponded to the methyl and the quaternary carbon atoms of the B(pin) structure. The ^{11}B NMR spectrum of sPS−B(pin) showed a broad peak at 27 ppm, which is consistent with the chemical shift of previously reported B(pin)-functionalized aPS homopolymer.[18]

The mol % of the borylated styrene repeating unit was calculated from the ^1H NMR spectrum by integrating the ratio of the methine proton of the polystyrene main chain and the methyl groups of B(pin). These results are summarized in Tables 1 and 2. Note that the efficiency of functionalization in Tables 1 and 2 is defined as the percentage of borylated styrene units relative to boron atoms added. Regardless of polymer tacticity, all polystyrenes could be efficiently functionalized with varying numbers of boryl groups. Except for the functionalizations of sPS with a very low ratio of added $B_2(pin)_2$ to monomer unit (ratios <0.1; Table 1, entries 1−3), both sPS and aPS generally showed decreased efficiency of functionalization as the added diboron amount was increased (Table 1, entries 4−8 for sPS; Table 2, entries 1−7 for aPS). The explanation for the sPS exceptions is unclear and needs further study. Although efficiency of C−H borylation steadily decreases as more $B_2(pin)_2$ is added to the styrene unit, up to 42 mol % of styrene repeating units of sPS and aPS can be easily borylated using 3 mol % of the commercially available iridium catalyst and the ligand using this method (Table 1, entry 7 for sPS; Table 2, entry 6 for aPS).

The effect of solubility on the efficiency of functionalization was observed in the case of iPS. Because of the extremely high molecular weight of iPS (M_n = 309 kg/mol, PDI = 6.42), homogeneous dissolution at 150 °C was achieved by adding more solvent (i.e., in a 1:10 molar ratio of iPS repeating unit to solvent). However, the solvent dilution induced a decrease in efficiency compared with that under the standard condition for sPS−B(pin) (Table 1, entries 4 and 9). Similarly, the borylation of sPS under the identical diluted condition also resulted in a slightly reduced efficiency compared with that under the standard condition (Table 1, entries 4 and 10). Unlike other transition metal−catalyzed polyolefin C−H functionalizations,[19−24] the iridium-catalyzed borylation of sPS was highly effective even at low catalyst loading (i.e., 0.5 mol % iridium catalyst loading for Table 1, entry 11).

The C−H borylation of cumene with $B_2(pin)_2$ under the standard condition of sPS functionalization produced sterically controlled statistical isomers of borylated cumene (e.g., a mixture of meta- and para-substituted isomers in an approximate ratio of 7:3; see Figure 2a for the ^1H NMR spectrum). These results agree with those from a related iridium-catalyzed C−H borylation.[29] Surprisingly, when we investigated the ratio of regioisomers of borylated polymer products based on the resonances at 7.50−8.50 ppm on the ^1H NMR spectrum of sPS−B(pin), we found the ratio of meta- and para-borylated polymers to be approximately 4:3. Although the ^1H NMR resonances of the two isomers in the region were unresolved in $CDCl_3$, the

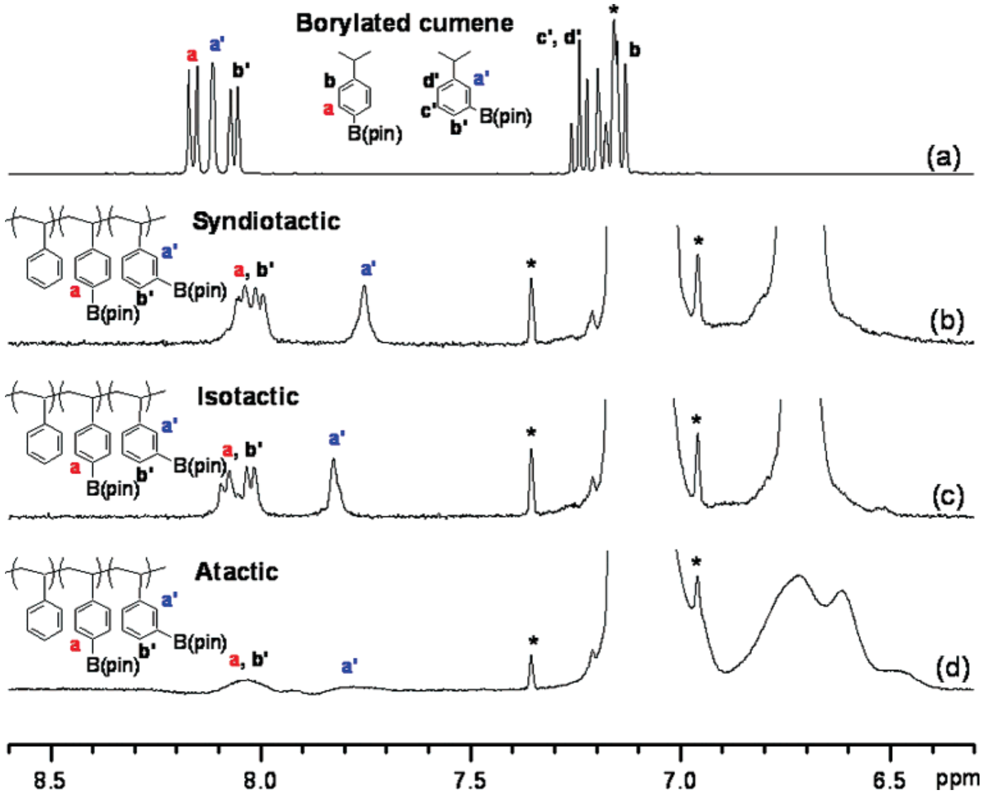


Figure 2. Expanded ^{1}H NMR spectra of (a) borylated cumene, (b) sPS−B(pin), (c) iPS−B(pin), and (d) aPS−B(pin) in C_6D_6. Asterisks show resonances from the deuterated NMR solvent.

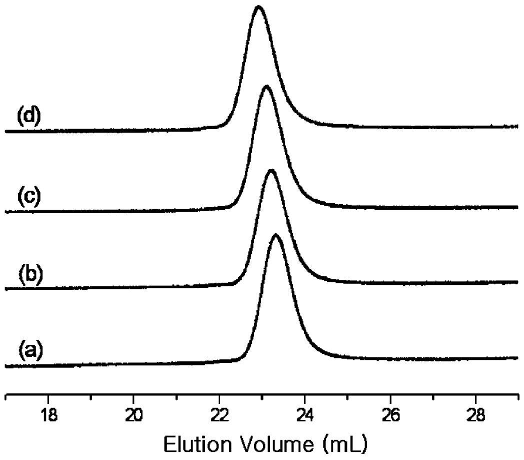


Figure 3. Size-exclusion chromatography [1 mg/mL THF at 40 °C] for (a) atactic polystyrene (aPS) [M_n = 25.1 kg/mol; PDI = 1.09]; (b) aPS−B(pin) [M_n = 26.5 kg/mol; PDI = 1.09] (Table 2, entry 1); (c) aPS−B(pin) [M_n = 27.8 kg/mol; PDI = 1.10] (Table 2, entry 3); and (d) aPS−B(pin) [M_n = 30.1 kg/mol; PDI = 1.11] (Table 2, entry 5). M_n relative to polystyrene standards.

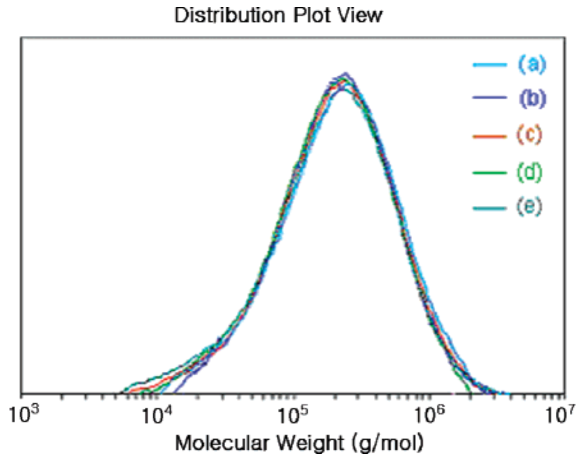


Figure 4. High-temperature size exclusion chromatography [1 mg/mL in 1,2,4-trichlorobenzene at 160 °C] for (a) syndiotactic polystyrene (sPS) [M_n = 127 kg/mol; PDI = 2.64]; (b) sPS−B(pin) [M_n = 132 kg/mol; PDI = 2.37] (Table 1, entry 1); (c) sPS−B(pin) [M_n = 116 kg/mol; PDI = 2.74] (Table 1, entry 2); (d) sPS−B(pin) [M_n = 116 kg/mol; PDI = 2.53] (Table 1, entry 3); and (e) sPS−B(pin) [M_n = 97.0 kg/mol; PDI = 2.55] (Table 1, entry 6). M_n relative to polystyrene standards.

^{1}H NMR spectra of both sPS−B(pin) and iPS−B(pin) in C_6D_6 showed distinctive peaks for their meta and para isomers (Figure 2b,c). The isomer ratio of aPS−B(pin) remained undetermined owing to the absence of stereoregularity in the polymer chain and the resulting broad resonances at 7.50−8.50 ppm region of the ^{1}H NMR spectrum (Figure 2d); however, we assume that it possesses a similar ratio of isomers. The higher percentage of para isomer in the borylated polystyrene compared with that of borylated cumene is believed to result from reduced steric accessibility of the iridium catalyst for the meta site of the polymer in the reaction medium. Because aromatic rings are attached to every other carbon of the polystyrene main chain, the available space for the active iridium catalyst to insert into the meta C−H bond of the aromatic rings in the polystyrene chain is much smaller compared with that in the C−H borylation of cumene.

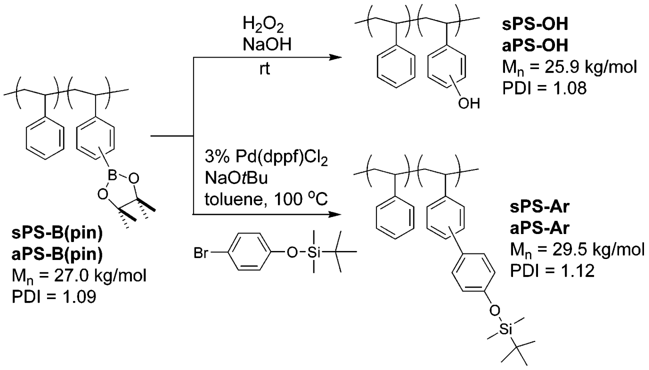
To investigate whether any changes in M_n and PDI occurred during the C−H activation process, we subjected two model aPS materials with narrow molecular weight distributions (M_n of 25.1 kg/mol with a PDI of 1.09, and M_n of 247 kg/mol with a PDI of 1.07) to the standard borylation condition. As shown both in entries 1−8 of Table 2 and in Figure 3, an increase in the ratio of $B_2(pin)_2$ to monomer resulted in an M_n increase owing to the incorporation of more B(pin) group into aPS−B(pin). All PDI values remained at ∼1.10, however, even with

Table 3. Borylation of Polystyrene (syndiotactic [sPS] and Atactic [aPS]) with Pinacolborane (HB(pin))[a]

entry	PS[b]	M_n[c]	PDI[c] (M_w/M_n)	[HB(pin)]/ [monomer]	PS−B(pin)			
					M_n[c]	PDI[c] (M_w/M_n)	B(pin) (%)[d]	effic (%)[e]
1	sPS	127[f]	2.64[f]	0.05	*g*	*g*	2.6	52
2	sPS	127[f]	2.64[f]	0.1	*g*	*g*	4.5	45
3	sPS	127[f]	2.64[f]	0.2	82.1[f]	2.65[f]	7.1	36
4	sPS	127[f]	2.64[f]	0.4	93.8[f]	2.38[f]	9.8	25
5	aPS	25.1	1.09	0.1	25.7	1.09	4.0	40
6	aPS	25.1	1.09	0.4	26.0	1.10	5.9	15
7	aPS	247	1.07	0.1	259	1.07	4.0	40
8	aPS	247	1.07	0.4	262	1.05	5.6	14

[a] B(pin) = pinacolboronate ester. Borylations were conducted with 200−260 mg of polymer with 3 mol % of iridium and 3 mol % of ligand relative to HB(pin) in cyclooctane (in a 1:6 molar ratio of polystyrene repeating unit to solvent) at 150 °C for 16 h. [b] PS = polystyrene. aPS [M_n = 25.1 kg/mol, PDI = 1.09; and M_n = 247 kg/mol, PDI = 1.07]; sPS [M_n = 127 kg/mol, PDI = 2.64]. [c] M_n in kg/mol and PDI measured with size exclusion chromatography in THF at 40 °C relative to polystyrene standards unless otherwise specified. [d] The mol % of B(pin)-functionalized styrene unit calculated from the ^{1}H NMR spectrum. [e] Efficiency of functionalization (i.e., the percentage of functionalized styrene unit relative to boron atoms added). [f] M_n in kg/mol and PDI measured with high-temperature size exclusion chromatography in 1,2,4-trichlorobenzene at 160 °C with polystyrene standards. [g] Not measured.

Scheme 2. Oxidation and Suzuki-Miyaura Coupling Reaction of Borylated Polymers (See Entries 1−6 of Table 1 for sPS−B(pin) and Entry 2 of Table 2 for aPS−B(pin))



the incorporation of 41 mol % of B(pin) group (Table 2, entry 7). These data clearly indicate that the iridium-catalyzed arene C−H activation process does not induce any deleterious side reactions leading to cleavage or coupling of polymer chains. Although the molecular weight data of sPS (Table 1, entries 1−6) and iPS (Table 1, entry 9) apparently show slight deviation from those of unfunctionalized crystalline polymers (i.e., M_n = 127 kg/mol, PDI = 2.64 for sPS; M_n = 309 kg/mol, PDI = 6.42 for iPS), these values may be due to the nature of the relatively broader molecular weight distributions of the polymers. When examined using high-temperature size exclusion chromatography (SEC) in 1,2,4-trichlorobenzene at 160 °C, their SEC traces did not show any sign of polymer chain degradation or coupling (Figure 4).

The iridium-catalyzed C−H borylation of polystyrene can also be accomplished with HB(pin) as the boron reagent (Table 3). Although the efficiency of functionalization with HB(pin) was lower than that with $B_2(pin)_2$, the borylation using various ratios of HB(pin) to styrene repeating unit produced 1−10 mol % B(pin)-functionalized sPS and aPS. Once again polymer chain lengths after the postfunctionalization were unchanged from those of the starting polymers.

To explore the possibility of introducing a polar group into nonpolar polystyrene, sPS−B(pin) (see Table 1, entries 1−6) and aPS−B(pin) (see Table 2, entry 2) were oxidized with NaOH/H_2O_2 in THF to give the corresponding hydroxylated polymers, sPS−OH and aPS−OH, respectively (Scheme 2). Although a hydroxy-functionalized sPS obtained via copolymerization with functionalized styrenes is known,[3] its molecular weight and concentration of hydroxy group were low (M_n = 9.2 kg/mol, 1.8 mol % OH group).[3] When a borane-functionalized styrene monomer containing long alkylene spacer between the borane group and the aromatic ring was used in syndiospecific polymerization with styrene, a higher concentration of hydroxy group could be incorporated into sPS after oxidation.[4] However, their molecular weights and degrees of crystallinity were significantly decreased compared with those of sPS homopolymer. In our study, the hydroxy group was directly incorporated into the aromatic ring of sPS. The hydroxy group of sPS−OH could be easily identified by a strong O−H stretching band at 3477 cm^{-1} in the IR spectrum (Figure S9 in the Supporting Information). The complete disappearance of resonances of the B(pin) group in the ^{13}C NMR spectrum of sPS−OH demonstrated successful oxidation in the polymer chain. Thus, the iridium-catalyzed borylation of aromatic C−H bonds and subsequent oxidation is a convenient method for introducing a hydroxy group directly into the aromatic ring of sPS.

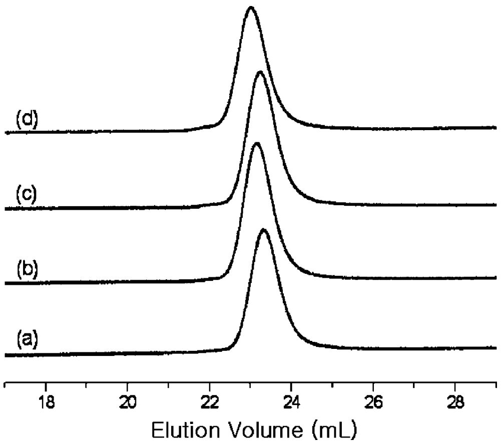


Figure 5. Size-exclusion chromatography [1 mg/mL THF at 40 °C] for (a) aPS [M_n = 25.1 kg/mol, PDI = 1.09], (b) aPS−B(pin) [M_n = 27.0 kg/mol, PDI = 1.09] (see Table 2, entry 2), and (c) aPS−OH [M_n = 25.9 kg/mol, PDI = 1.08] (see Scheme 2), (d) aPS−Ar [M_n = 29.5 kg/mol, PDI = 1.12] (see Scheme 2). M_n relative to polystyrene standards

The molecular weight changes from the borylation−oxidation sequence, which was studied in depth with model aPS, were negligible (Figure 5: aPS: M_n = 25.1 kg/mol, PDI = 1.09; aPS−B(pin): M_n = 27.0 kg/mol, PDI = 1.09; aPS−OH: M_n = 25.9 kg/mol, PDI = 1.08), highlighting the mildness of this protocol. The Suzuki−Miyaura cross-coupling reaction is one of the most powerful aryl C−C bond formation methods owing to its compatibility with a wide range of functional groups.[30] Because aryl pinacolboronate ester is an established versatile synthetic intermediate in Suzuki−Miyaura cross-coupling, the coupling reaction of the polymer B(pin) groups with function-

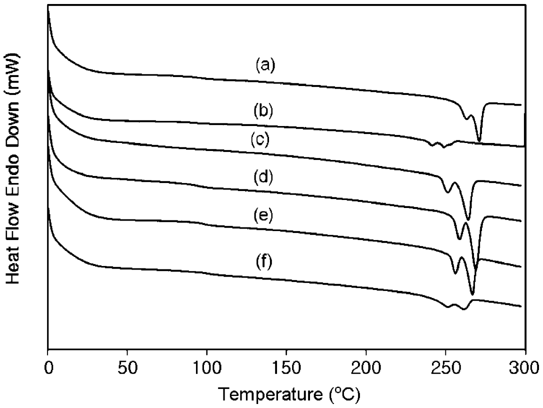


Figure 6. Differential scanning calorimetry scans of (a) syndiotactic polystyrene (sPS); (b) 2.5 mol % B(pin)-functionalized sPS−B(pin) (Table 1, entry 1); (c) 2.5 mol % OH-functionalized sPS−OH (from oxidation of entry 1 of Table 1); (d) 5.9 mol % OH-functionalized sPS−OH (from oxidation of entry 2 of Table 1); (e) 9.9 mol % OH-functionalized sPS−OH (from oxidation of entry 3 of Table 1); (f) 16.4 mol % OH-functionalized sPS−OH (from oxidation of entry 4 of Table 1).

alized aryl halide would allow installation of various functional groups at the polymer side chain. With 3 mol % of palladium catalyst, (4-bromophenoxy)-*tert*-butyldimethylsilane coupled with PS−B(pin) to form arene-functionalized polystyrenes (sPS−Ar and aPS−Ar in Scheme 2). The ^{1}H NMR spectra of the coupled products show the complete disappearance of B(pin) groups and the appearance of a *tert*-butyldimethylsilyl group with a similar concentration. The molecular weight distribution of the Suzuki coupling product, which was studied in depth with the model aPS, was again found to be unchanged from that of the precursor polymer (Figure 5: aPS−B(pin): M_n = 27.0 kg/mol, PDI = 1.09; aPS−Ar: M_n = 29.5 kg/mol, PDI = 1.12).

The thermal properties of unfunctionalized sPS, sPS−B(pin), and sPS−OH are displayed in Figure 6. sPS is known to possess a complex polymorphism. The most stable α and *β* crystalline forms have similar melting temperatures of approximately 270 °C, and their crystallization behaviors strongly depend on experimental conditions,[31−33] which may explain why the unfunctionalized sPS exhibits more than one melting transition in our study (Figure 6a). Although sPS has high crystallinity, the melting point and crystallinity of functionalized sPS were found to be strongly dependent on the size and concentration of the functional group on the polymer (Figure 6 and Table 4). For example, the sPS−B(pin) containing 5.9 mol % B(pin) group (Table 1, entry 2) lost crystallinity completely because the bulky B(pin) group disrupted crystallization. This observation is consistent with thermal behavior of lightly (i.e., <5 mol %) sulfonated sPS in which the melting point and degree of crystallinity decreased sharply as the concentration of sulfonic acid increased.[8] After oxidation, however, the corresponding sPS−OH recovered crystallinity because the smaller hydroxyl group did not interfere with the crystallization process as the bulky B(pin) group did. Even the sPS−OH with 9.9 mol % OH group (from oxidation of entry 3 of Table 1) preserved high crystallinity (36%), which was very close to the crystallinity of unfunctionalized sPS (40%), and showed a slightly lower melting point (267 °C) (Figure 6e and Table 4). Overall, the borylation−oxidation process can yield polar group−functionalized sPS that has a slightly lower melting point without causing degradation or cross-linking of the parent polymer.

Table 4. Thermal Properties of Syndiotactic Polystyrene (sPS) and Functionalized sPS[a]

polymer	functional group	T_g (°C)[b]	T_m (°C)[c]	ΔH$_f$ (J/g)[d]	crystallinity[e] (%)
sPS	none	99	271	21.1	40
sPS−B(pin)	2.5 mol % B(pin)	95	249	3.1	6
sPS−B(pin)	5.9 mol % B(pin)	109	*f*		
sPS−OH	2.5 mol % OH	*f*	264	19.5	37
sPS−OH	5.9 mol % OH	100	269	17.9	34
sPS−OH	9.9 mol % OH	104	267	19.2	36
sPS−OH	16.4 mol % OH	106	261	8.3	16
sPS−OH	23.6 mol % OH	118	260	0.9	2
sPS−OH	34.2 mol % OH	129	*f*		

[a] Differential scanning calorimetry (DSC) measurements conducted using heating/cooling rates of 10 °C/min. The OH mol % is based on the assumption of quantitative conversion of B(pin) group without formation of other deborylated byproducts. [b] Glass transition temperature in °C. [c] Melting point of polymer in °C. [d] Heat of fusion of polymer in J/g. [e] The percent of crystallinity based on the theoretical heat of fusion calculated for 100% crystalline sPS (i.e., ΔH$_f$° = 53.3 J/g; from reference 1). [f] Not detected.

Conclusion

Controlled functionalization of commercial polystyrenes with three types of tacticity—syndiotactic, isotactic, and atactic—was accomplished with the iridium-catalyzed activation/borylation of aromatic C−H bonds. The functionalization allowed the introduction of a boronate ester group (up to 42 mol %) without negatively affecting the polymer chain length or the tacticity of the starting polymer. The concentration of the boryl group can be easily controlled with as low as 0.5 mol % of catalyst loading by changing the ratio of boron reagent to monomer unit, and the boryl group in the polymer was further converted to other useful functional groups such as hydroxy and arene. The thermal behavior of sPS−OH indicated that the functionalized polymers containing up to 10 mol % of hydroxy group maintained high crystallinity with high melting temperature. This new method to install functional groups into crystalline polystyrenes will expand the application of these important polyolefins.

Experimental Section

General Comments. [IrCl(COD)]$_2$, d*t*bpy, HB(pin), hydrogen peroxide, tetrahydrofuran (THF), sodium hydroxide, and chloroform were reagent grade and used without further purification. B$_2$(pin)$_2$ was obtained from Frontier Scientific Co. and used after recrystallization from hexane. Cyclooctane was dried using sodium and benzophenone, distilled under reduced pressure, and stored in a nitrogen-filled glovebox. sPS (M_n = 127 kg/mol with PDI = 2.64) and two model aPS of narrow molecular distributions (M_n = 25.1 kg/mol with PDI = 1.09 and M_n = 247 kg/mol with PDI = 1.07) were obtained from LG Chem Ltd., Daejeon, South Korea, and Aldrich Chemical Co., respectively, and used as received. To improve the solubility of iPS (M_n = 309 kg/mol, PDI = 6.42, 90% isotactic from Aldrich Chemical Co.) in the borylation medium, the following procedure was performed. One gram of the polymer was placed in a two-neck round-bottom flask, and then the flask was evacuated and backfilled with nitrogen three times. 1,2-Dichlorobenzene (30 mL) was added to this flask and the mixture was refluxed at 180 °C under nitrogen for 30 min to dissolve all iPS. The solution was then cooled to 140 °C and poured into cold methanol (300 mL). The precipitate was filtered and dried under vacuum at 60 °C.

^{1}H NMR spectra were obtained using a 400 MHz Varian NMR spectrometer at room temperature and chemical shifts were referenced to TMS. The NMR samples were prepared by applying gentle heat to dissolve polymer in $CDCl_3$ (for sPS) or C_6D_6 (for sPS, aPS, and iPS). The ^{1}H NMR samples were prepared at a concentration of 10 mg/mL. The B(pin) mol % of PS−B(pin) was determined based on the relative area of −CH− in polystyrene main chain ($\delta = 1.81$ in $CDCl_3$; $\delta = 2.10-2.30$ in C_6D_6) to $-CH_3$ of B(pin) ($\delta = 1.35$ in $CDCl_3$; $\delta = 1.15-1.20$ in C_6D_6) in the spectra and provided in Tables 1−3. For molecular weight characterization of aPS materials, size exclusion chromatography (SEC) analysis was conducted using a VISCOTEK chromatograph equipped with three viscoGEL I Series columns and tetra detector array (UV/vis, low and right angle light scattering, refractive index, viscometer) at 40 °C. THF was the mobile phase and the flow rate was set at 1.0 mL/min. High-temperature size exclusion chromatography analysis for the molecular weight measurement of sPS and iPS was obtained using a Polymer Laboratory GPC-220 high-temperature size exclusion chromatography at 160 °C. 1,2,4-Trichlrobenzene was the mobile phase and the flow rate was set at 1.0 mL/min. Both instruments were calibrated using polystyrene standards. The differential scanning calorimetry (DSC) measurement was conducted on a Perkin-Elmer Pyris 6 DSC series under a nitrogen atmosphere. The polymer samples were heated to 300 °C, with a hold at 300 °C for 1 min in order to remove the influence of thermal history, cooled to 0 °C, held at 0 °C for 1 min, and then reheated to 300 °C, all at a rate of 10 °C/min. All DSC curves in Figure 6 were obtained from the second heating. The temperatures (T_g and T_m) and enthalpy (ΔH_f) were obtained after calibration with high-purity indium and zinc standards.

sPS: ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.30$ (2H, CH_2), 1.81 (1H, CH), 6.55 (2H, H_{arom}), 7.06 (3H, H_{arom}); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) $\delta = 40.54$ (CH), 43.84 (CH_2), 125.60 (C_6H_5−C4), 127.60 (C_6H_5−C2,6), 127.86 (C_6H_5−C3,5), 145.19 (C_6H_5−C1).

Preparation of sPS—B(pin) Using $B_2(pin)_2$ (Entry 4 of Table 1). In a nitrogen-filled glovebox, a mixture of sPS (260 mg, 2.50 mmol polystyrene repeating unit), $B_2(pin)_2$ (63.0 mg, 0.25 mmol), $[IrCl(COD)]_2$ (2.5 mg, 3 mol % iridium based on the amount of $B_2(pin)_2$), d*t*bpy (2.0 mg, 3 mol % based on the amount of $B_2(pin)_2$), and cyclooctane (1.68 g, 15.0 mmol) and a magnetic stirring bar were placed into a vial and capped with a Teflon-lined septum. The vial was removed from the glovebox and placed in an oil bath at 150 °C for 6 h. After cooling to room temperature, the mixture was diluted with chloroform (30 mL) and filtered through a short plug of silica to remove the catalyst. The filtrate was concentrated by rotary evaporator to ca. 5 mL, and cold methanol (25 mL) was added to precipitate the polymer. The dissolution and precipitation process was repeated one more time to ensure complete removal of any small molecules trapped in the polymer. The borylated polymer was filtered as a white solid and dried under vacuum at 60 °C (281 mg, 108% yield based on polymer weight): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.30$ (2H, CH_2), 1.35 (s, $BOCCH_3$), 1.80 (1H, CH), 6.54 (2H, H_{arom}), 7.05 (3H, H_{arom}), 7.56 (H_{arom} from C_6H_4−B(pin)); ^{1}H NMR (400 MHz, C_6D_6) $\delta = 1.15$ and 1.19 ($BOCCH_3$), 1.49 (2H, CH_2), 2.08 (1H, CH), 6.07 (2H, H_{arom}), 7.05 (3H, H_{arom}), 7.75 (H_{arom} from C_6H_4−B(pin)), 8.00 (H_{arom} from C_6H_4−B(pin)), 8.04 (H_{arom} from C_6H_4−B(pin)); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) $\delta = 24.88$ ($BOC\mathit{C}H_3$), 40.53 (CH), 43.83 (CH_2), 83.51 ($BO\mathit{C}CH_3$), 125.60 (C_6H_5−C4), 127.19 (C_{arom} from C_6H_4−B(pin)), 127.66 (C_6H_5−C2,6), 127.85 (C_6H_5−C3,5), 130.94 (C_{arom} from C_6H_4−B(pin)), 132.25 (C_{arom} from C_6H_4−B(pin)), 133.96 (C_{arom} from C_6H_4−B(pin)), 134.51 (C_{arom} from C_6H_4−B(pin)), 144.60 (C_{arom} from C_6H_4−B(pin)), 145.18 (C_6H_5−C1), 148.79 (C_{arom} from C_6H_4−B(pin)); ^{11}B NMR (128.26 MHz, $CDCl_3$) $\delta = 27.98$ (br).

Preparation of sPS—B(pin) Using HB(pin) (Entry 2 of Table 3). In a nitrogen-filled glovebox, a mixture of sPS (260 mg, 2.50 mmol polystyrene repeating unit), HB(pin) (32.0 mg, 0.25 mmol), $[IrCl(COD)]_2$ (2.5 mg, 3 mol % iridium based on the amount of HB(pin)), d*t*bpy (2.0 mg, 3 mol % based on the amount of HB(pin)), and cyclooctane (1.68 g, 15.0 mmol) and a magnetic stirring bar were placed into a vial and capped with a Teflon-lined septum. The vial was removed from the glovebox and placed in an oil bath at 150 °C for 16 h. After cooling to room temperature, the mixture was diluted with chloroform (30 mL) and filtered through a short plug of silica to remove the catalyst. The filtrate was concentrated by rotary evaporator to ca. 5 mL, and cold methanol (25 mL) was added to precipitate the polymer. The dissolution and precipitation process was repeated one more time to ensure complete removal of any small molecules trapped in the polymer. The borylated polymer was filtered as a white solid and dried under vacuum at 60 °C (255 mg, 98% yield based on polymer weight).

Preparation of sPS—OH. sPS−B(pin) (100 mg) (from entry 4 of Table 1) was dissolved in THF (100 mL) in a 250 mL flask by applying gentle heat and then cooled to room temperature. A mixture of aqueous 3M NaOH (1 mL) and 30% H_2O_2 (1 mL) was slowly added to the polymer solution at room temperature. The resulting solution was stirred at room temperature for 12 h. The solution was concentrated by rotary evaporator to ca. 5 mL, and a mixture of methanol and water (10 mL/40 mL) was added. The heterogeneous suspension was stirred for 20 min and filtered. The collected white solid was washed with water (3 × 10 mL) and then with methanol (3 × 5 mL). The solid was dried under vacuum at 60 °C (87 mg, 87% yield based on polymer weight from sPS−B(pin)): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.30$ (2H, CH_2), 1.80 (1H, CH), 6.54 (2H, H_{arom}), 7.05 (3H, H_{arom}); ^{13}C {^{1}H} NMR (100 MHz, 1,1,2,2-tetrachloroethane-d_2 at 70 °C) $\delta = 40.74$ (CH), 43.83 (CH_2), 112.42 (C_{arom} from C_6H_4−OH), 114.73 (C_{arom} from C_6H_4−OH), 120.09 (C_{arom} from C_6H_4−OH), 125.59 (C_6H_5−C4), 127.63 (C_6H_5−C2,6), 127.90 (C_6H_5−C3,5), 124.00−129.23 (multiple C_{arom} from C_6H_4−OH), 137.47 (C_{arom} from C_6H_4−OH), 145.16 (C_6H_5−C1), 147.23 (C_{arom} from C_6H_4−OH), 153.02 (HO-*p*-C_6H_4−C4), 154.86 (HO-*m*-C_6H_4−C3); FT-IR (film) $\nu = 3477$ cm^{-1} (O−H).

Preparation of sPS—Ar by Suzuki—Miyaura Cross-Coupling of sPS—B(pin) (from Entry 3 of Table 1). In a nitrogen glovebox, a mixture of sPS−B(pin) (50 mg, 0.043 mmol B(pin)), (4-bromophenoxy)-*tert*-butyldimethylsilane (62.0 mg, 0.215 mmol), dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) (1.1 mg, 3 mol % based on the amount of boron concentration in sPS−B(pin)), sodium *tert*-butoxide (12.4 mg, 0.129 mmol, 3 equiv to the amount of boron concentration in sPS−B(pin)), and toluene (1 mL) and a magnetic stirring bar were placed into a vial and capped with Teflon-lined septum. The vial was removed from the glovebox and placed in an oil bath at 100 °C for 22 h. After cooling, the mixture was diluted with chloroform (30 mL) and filtered through a short plug of silica. The filtrate was concentrated by rotary evaporator to ca. 5 mL, and cold methanol (25 mL) was added to precipitate the polymer. The dissolution and precipitation process was repeated one more time to ensure complete removal of any small molecules trapped in the polymer. The polymer product was filtered as a white solid and dried under vacuum at 60 °C (45 mg, 90% yield based on polymer weight from sPS−B(pin)): ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.24$ (s, $Si(C\mathit{H}_3)_2C(CH_3)_3$), 1.02 (s, $\mathrm{Si(CH_3)_2C(C}H\mathrm{_3)_3}$), 1.30 (2H, $\mathrm{CH_2}$), 1.80 (1H, CH), 6.54 ($\mathrm{H_{arom}}$), 7.06 ($\mathrm{H_{arom}}$); ^{13}C {^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$) $\delta = -4.35$ ($\mathrm{Si(}C\mathrm{H_3)_2C(CH_3)_3}$), 18.26 ($\mathrm{Si(CH_3)_2}C\mathrm{(CH_3)_3}$), 25.74 ($\mathrm{Si(CH_3)_2C(}C\mathrm{H_3)_3}$), 40.54 (CH), 43.84 ($\mathrm{CH_2}$), 120.16 ($\mathrm{C_c}$), 124.06 ($\mathrm{C_{arom}}$ from $\mathrm{C_6H_4{-}Ar}$), 125.59 ($\mathrm{C_6H_5{-}C4}$), 126.09 ($\mathrm{C_{arom}}$ from $\mathrm{C_6H_4{-}Ar}$), 127.67 ($\mathrm{C_6H_5{-}C2,6}$), 127.85 ($\mathrm{C_6H_5{-}C3,5}$), 128.00 ($\mathrm{C_b}$), 134.61 ($\mathrm{C_a}$), 145.19 ($\mathrm{C_6H_5{-}C1}$), 154.99 ($\mathrm{C_d}$).

aPS: ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$) $\delta = 1.60$ (br, 2H, $\mathrm{CH_2}$), 2.10 (br, 1H, CH), 6.41−6.88 (2H, $\mathrm{H_{arom}}$), 6.91−7.28 (3H, $\mathrm{H_{arom}}$); ^{13}C {^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$) $\delta = 40.74$ (CH), 41.3−47.2 ($\mathrm{CH_2}$), 126.02 ($\mathrm{C_6H_5{-}C4}$), 128.02 ($\mathrm{C_6H_5{-}C2,6}$), 128.34 ($\mathrm{C_6H_5{-}C3,5}$), 145.70 ($\mathrm{C_6H_5{-}C1}$).

Preparation of aPS—B(pin) Using $\mathbf{B_2(pin)_2}$. Borylated atactic polystyrene with different ratios of $\mathrm{B_2(pin)_2}$/monomer in Table 2 was prepared in a 200 mg scale (1.92 mmol polystyrene repeating unit) according to the procedure described for the preparation of sPS−B(pin) using $\mathrm{B_2(pin)_2}$: ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$) $\delta = 1.17$ (s, $\mathrm{BOCCH_3}$), 1.58 (br, 2H, $\mathrm{CH_2}$), 2.09 (br, 1H, CH), 6.41−6.88 (2H, $\mathrm{H_{arom}}$), 6.91−7.28 (3H, $\mathrm{H_{arom}}$), 8.03 (br, $\mathrm{H_{arom}}$ from $\mathrm{C_6H_4{-}B(pin)}$); ^{13}C {^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$) $\delta = 24.88$ ($\mathrm{BOC}C\mathrm{H_3}$), 40.34 (CH), 41.3−47.2 ($\mathrm{CH_2}$), 83.51 ($\mathrm{BO}C\mathrm{CH_3}$), 125.63 ($\mathrm{C_6H_5{-}C4}$), 127.63 ($\mathrm{C_6H_5{-}C2,6}$), 127.94 ($\mathrm{C_6H_5{-}C3,5}$), 131.02 ($\mathrm{C_{arom}}$ from $\mathrm{C_6H_4{-}B(pin)}$), 132.39 ($\mathrm{C_{arom}}$ from $\mathrm{C_6H_4{-}B(pin)}$), 134.66 ($\mathrm{C_{arom}}$ from $\mathrm{C_6H_4{-}B(pin)}$), 145.31 ($\mathrm{C_6H_5{-}C1}$); ^{11}B NMR (128.26 MHz, $\mathrm{CDCl_3}$) $\delta = 27.51$ (br).

Preparation of aPS—B(pin) Using HB(pin). Borylated atactic polystyrene with different ratios of HB(pin)/monomer in Table 3 was prepared in a 200 mg scale (1.92 mmol polystyrene repeating unit) according to the procedure described for preparation of sPS−B(pin) using HB(pin).

Preparation of aPS—OH. Hydroxylated atactic polystyrene was prepared in a 100 mg scale according to the procedure described for the preparation of sPS−OH: ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$ $\delta = 1.60$ (2H, $\mathrm{CH_2}$), 2.11 (1H, CH), 6.41−6.88 (2H, $\mathrm{H_{arom}}$), 6.91−7.28 (3H, $\mathrm{H_{arom}}$); ^{13}C {^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$) $\delta = 40.27$ (CH), 41.3−47.2 ($\mathrm{CH_2}$), 125.66 ($\mathrm{C_6H_5{-}C4}$), 127.68 ($\mathrm{C_6H_5{-}C2,6}$), 112.65 ($\mathrm{C_{arom}}$ from $\mathrm{C_6H_4{-}OH}$), 114.77 ($\mathrm{C_{arom}}$ from $\mathrm{C_6H_4{-}OH}$), 128.05 ($\mathrm{C_6H_5{-}C3,5}$), 129.20 ($\mathrm{C_{arom}}$ from $\mathrm{C_6H_4{-}OH}$), 145.16 ($\mathrm{C_6H_5{-}C1}$), 153.26 (HO-p-$\mathrm{C_6H_4{-}C4}$), 155.17 (HO-m-$\mathrm{C_6H_4{-}C3}$); FT-IR (film) $\nu = 3472\ \mathrm{cm^{-1}}$ (O−H).

Preparation of aPS—Ar by Suzuki—Miyaura Cross-Coupling of aPS—B(pin) (from Entry 2 of Table 2). Arene functionalized atactic polystyrene was prepared from aPS−B(pin) (50 mg, 0.043 mmol B(pin)) according to the procedure described for the preparation of sPS−Ar: ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$) $\delta = 0.19$ (s, $\mathrm{Si(C}H\mathrm{_3)_2C(CH_3)_3}$), 1.06 (s, $\mathrm{Si(CH_3)_2C(C}H\mathrm{_3)_3}$), 1.60 (2H, $\mathrm{CH_2}$), 2.11 (1H, CH), 6.41−6.88 ($\mathrm{H_{arom}}$), 6.91−7.28 ($\mathrm{H_{arom}}$); ^{13}C {^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$) $\delta = -4.32$ ($\mathrm{Si(}C\mathrm{H_3)_2C(CH_3)_3}$), 18.28 ($\mathrm{Si(CH_3)_2}C\mathrm{(CH_3)_3}$), 25.76 ($\mathrm{Si(CH_3)_2C(}C\mathrm{H_3)_3}$), 40.38 (CH), 41.3−47.2 ($\mathrm{CH_2}$), 120.19 ($\mathrm{C_c}$), 124.12 ($\mathrm{C_{arom}}$ from $\mathrm{C_6H_4{-}Ar}$), 125.65 ($\mathrm{C_6H_5{-}C4}$), 126.22 ($\mathrm{C_{arom}}$ from $\mathrm{C_6H_4{-}Ar}$), 127.64 ($\mathrm{C_6H_5{-}C2,6}$), 127.95 ($\mathrm{C_6H_5{-}C3,5}$), 134.61 ($\mathrm{C_a}$), 145.27 ($\mathrm{C_6H_5{-}C1}$), 155.01 ($\mathrm{C_d}$).

iPS: ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$) $\delta = 1.59$ and 1.65 (2H, $\mathrm{CH_2}$), 2.33 (1H, CH), 6.77 (2H, $\mathrm{H_{arom}}$), 7.08 (3H, $\mathrm{H_{arom}}$); ^{13}C {^{1}H} NMR spectrum could not be obtained due to lack of solubility of the polymer in $\mathrm{C_6D_6}$ or $\mathrm{CDCl_3}$.

Preparation of iPS—B(pin) Using $\mathbf{B_2(pin)_2}$ (Entry 9 of Table 1). In a nitrogen-filled glovebox, a mixture of iPS (200 mg, 1.92 mmol polystyrene repeating unit), $\mathrm{B_2(pin)_2}$ (48.3 mg, 0.192 mmol), $\mathrm{[IrCl(COD)]_2}$ (1.9 mg, 3 mol % iridium based on the amount of $\mathrm{B_2(pin)_2}$), d*t*bpy (1.5 mg, 3 mol % based on the amount of $\mathrm{B_2(pin)_2}$), and cyclooctane (2.15 g, 19.2 mmol) and a magnetic stirring bar were placed into a vial and capped with a Teflon-lined septum. The vial was removed from the glovebox and placed in an oil bath at 150 °C for 6 h. After cooling to room temperature, the mixture was diluted with chloroform (40 mL). (Because of high viscosity of the solution, filtration through silica was avoided). The solution was concentrated by rotary evaporator to ca. 5 mL, and cold methanol (25 mL) was added to precipitate the polymer. The dissolution and precipitation process was repeated one more time to ensure complete removal of any small molecules trapped in the polymer. The precipitated solid was filtered and dried under vacuum at 60 °C (203 mg, 102% yield based on polymer weight from iPS): ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$) $\delta = 1.16$ (s, $\mathrm{BOCCH_3}$), 1.59 and 1.65 (2H, $\mathrm{CH_2}$), 2.33 (1H, CH), 6.71 (2H, $\mathrm{H_{arom}}$), 7.06 (3H, $\mathrm{H_{arom}}$), 7.83 ($\mathrm{H_{arom}}$ from $\mathrm{C_6H_4{-}B(pin)}$), 8.03 ($\mathrm{H_{arom}}$ from $\mathrm{C_6H_4{-}B(pin)}$), 8.08 ($\mathrm{H_{arom}}$ from $\mathrm{C_6H_4{-}B(pin)}$); ^{13}C {^{1}H} NMR spectrum could not be obtained due to lack of solubility of the polymer in $\mathrm{C_6D_6}$ or $\mathrm{CDCl_3}$.

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Supporting Information Available: Figures showing NMR spectra (PS, PS−B(pin), PS−OH, PS−Ar) and IR spectra (PS−OH). This material is available free of charge via the Internet at http://pubs.acs.org.

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