

# Highly Efficient Incorporation of Functional Groups into Aromatic Main-Chain Polymer Using Iridium-Catalyzed C–H Activation and Suzuki–Miyaura Reaction

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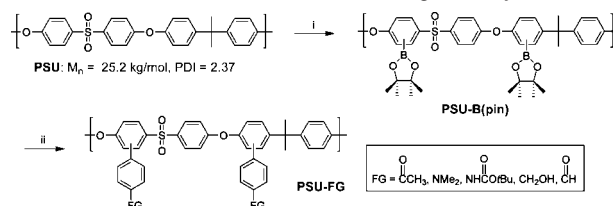
Aromatic main-chain polymers constitute a majority of engineering thermoplastics because they have excellent chemical and thermal stability and mechanical strength. The introduction of functional groups into the aromatic main-chain polymer would allow the creation of high-performance materials with specific function and durability and a wider scope of potential applications. For example, functionalized polysulfones have been actively investigated as membrane materials for liquid and gas separation<sup>1</sup> and fuel cells.<sup>2</sup>

The introduction of functionality into polysulfone can occur via copolymerization with a functionalized comonomer or postfunctionalization of the polymer. In the former approach, the reduced reactivity of the comonomer during condensation polymerization generally resulted in low-molecular-weight polymers.<sup>3</sup> In addition, some functionalities would be incompatible with the polymerization conditions because the nucleophilic aromatic substitution polymerization is generally conducted at elevated temperature (>150 °C) for an extended period of time (>12 h). In the latter approach, several modifications of polysulfone using sulfonation,<sup>4a</sup> bromination,<sup>4b</sup> chloromethylation,<sup>4c</sup> amidoalkylation,<sup>4d</sup> and lithiation<sup>4e</sup> have been developed, but most of them require careful selections of reaction condition and reagent to avoid undesirable side reactions such as cross-linking and chain scission, which can alter the molecular weight and reduce the favorable properties of polysulfone. Hence, alternative mild methods to introduce functionality to polysulfone are highly desired.

We describe herein a controlled, efficient conversion of the C–H bonds of the aromatic ring of polysulfone into desired functional groups using a combination of iridium-catalyzed activation/borylation of the aromatic C–H bond<sup>5</sup> and Suzuki–Miyaura cross-coupling reaction.<sup>6</sup> The major advantage of this postfunctionalization process is that various functional groups with specific concentrations can be incorporated into the aromatic ring of the polymer main chain under mild conditions.

The iridium-catalyzed reaction of a commercial polysulfone [PSU:  $M_n = 25.2$  kg/mol; PDI ( $M_w/M_n$ ) = 2.37] with different molar ratios of bis(pinacolato)diboron [ $B_2(\text{pin})_2$ ] to polymer repeating unit in THF yielded the corresponding pinacolboronate-functionalized polymer [PSU-B(pin)] (Scheme 1). <sup>1</sup>H NMR spectra of all PSU-B(pin) showed distinctive new resonances at 1.0–1.2 ppm for the four methyl groups of pinacolboronate ester [B(pin)] (Figure S3, Supporting Information). The <sup>13</sup>C NMR spectrum of PSU-B(pin) exhibited two distinct resonances at 24 and 84 ppm, corresponding to the four methyl groups and the quaternary carbon of the B(pin) group, respectively (Figure S4, Supporting Information). The <sup>11</sup>B NMR spectrum also displayed a broad peak at ~30 ppm, which was in good agreement with the chemical shift of the B(pin)-functionalized polystyrene<sup>7</sup>

## Scheme 1. Functionalization of Aromatic Rings of Polysulfone<sup>a</sup>



<sup>a</sup> Reagents and conditions: (i)  $B_2(\text{pin})_2$ , 1.5%  $[\text{IrCl}(\text{COD})]_2$ , 3% *dtbpy*, THF, 80 °C, 12 h. (ii) *p*-Br- $C_6H_4$ -FG, 3%  $\text{Pd}(\text{PPh}_3)_4$ , 3 equiv of  $K_2CO_3$ , THF/ $H_2O$  (10:1), 80 °C, 6 h.

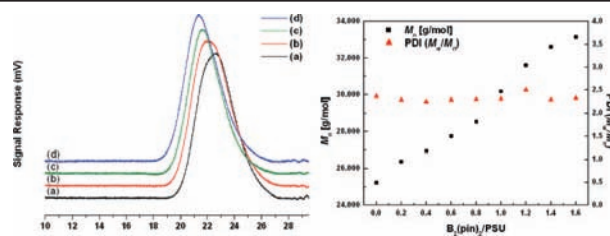
**Table 1.** Iridium-Catalyzed C–H Borylation of Polysulfone

entry	ratio <sup>a</sup>	B(pin) (%) <sup>b</sup>	effic. (%) <sup>c</sup>	$M_n^d$	PDI	IV <sup>e</sup>
1	0.2	14	34	26.4	2.29	0.77
2	0.4	46	57	26.9	2.25	0.79
3	0.6	73	61	27.7	2.29	0.86
4	0.8	108	68	28.5	2.30	0.89
5	1.0	138	69	30.2	2.31	0.93
6	1.2	176	74	31.6	2.50	1.01
7	1.4	196	70	32.6	2.30	1.02
8	1.6	224	70	33.1	2.33	1.05

<sup>a</sup> Initial ratio of  $B_2(\text{pin})_2$  to PSU repeating unit. <sup>b</sup> The mol% of B(pin) attached to PSU based on <sup>1</sup>H NMR spectra. <sup>c</sup> Efficiency (%) of C–H borylation: the amount of B(pin) attached to the polymer divided by the amount of boron atom added. <sup>d</sup> Number-average molecular weight reported in kg/mol. PSU has  $M_n$  of 25.2 kg/mol and PDI of 2.37. <sup>e</sup> Intrinsic viscosity measured using an Ubbelohde viscometer at 30 °C with a polymer concentration of 0.5 g/dL in chloroform (PSU has IV of 0.60 dL/g).

(Figure S5, Supporting Information). The iridium-catalyzed borylation substitutes only the aromatic C–H bonds of arene<sup>5</sup> and polystyrene.<sup>8</sup> Thus, the mol% of the attached B(pin) group per PSU repeating unit was calculated by comparing the proton resonance integrals of the isopropylidene group in the polymer main chain (at 1.69 ppm) and the four methyl groups of the B(pin). The mol% of B(pin) attached to the polymer varied in proportion to the amount of  $B_2(\text{pin})_2$  added (Table 1). The efficiency of C–H borylation, defined as the amount of B(pin) attached to the polymer divided by the amount of boron atom added, was 60–70% in most cases, allowing the degree of borylation to be conveniently controlled using stoichiometric tuning of the amount of  $B_2(\text{pin})_2$  added.

PSU has four different aromatic C–H bonds in the repeating unit, two in the aryl sulfone unit and two in the bisphenol A unit. Thus the C–H borylation of PSU can, in principle, generate a mixture of four different regioisomers of B(pin)-functionalized polymer. The <sup>1</sup>H NMR spectrum of 46% PSU-B(pin) (Table 1, entry 2) showed two proton resonances of the B(pin) group at 1.03 and 1.23 ppm, with an integral ratio of 1.0:5.6. PSU-B(pin)



**Figure 1.** (Left) Size exclusion chromatography of (a) PSU; (b) 46% PSU-B(pin) (Table 1, entry 2); (c) 176% PSU-B(pin) (Table 1, entry 6); (d) 224% PSU-B(pin) (Table 1, entry 8). (Right) Evolutions of  $M_n$  and PDI vs the amount of  $\text{B}_2(\text{pin})_2$  added relative to PSU.

with higher than 100% B(pin) concentration showed an additional minor resonance of B(pin) group at 1.11 ppm (Figure S3, Supporting Information). These results indirectly indicate the formation of multiple regioisomers with an unequal population. Although these results need further study, we speculate that the aromatic ring in the aryl sulfone repeating unit is borylated preferably owing to the favored electronic effect.<sup>5a</sup>

To investigate whether undesirable side reactions that could affect the molecular weight of the polymer have occurred during the C–H activation process, we measured the  $M_n$  and PDI of PSU-B(pin) using size exclusion chromatography. As shown in Table 1 and Figure 1, an increase in the ratio of  $\text{B}_2(\text{pin})_2$  to the polymer resulted in an increased  $M_n$  of PSU-B(pin) owing to the incorporation of more of the B(pin) moiety into the polymer chain and the corresponding hydrodynamic volume increase. All PDIs, however, remained consistently at  $\sim 2.30$  even with the incorporation of 224% B(pin) (Table 1, entry 8), suggesting a complete absence of cleavage or cross-linking of the polymer chains. A gradual increase in molecular weights owing to the attachment of more B(pin) groups was also reflected in the intrinsic viscosity measurement of PSU-(Bpin) (see Table 1).

Because aryl pinacolboronate is an effective substrate in the Suzuki–Miyaura cross-coupling reaction, by which various functional groups can be introduced via biaryl C–C bond formation, PSU-B(pin) can serve as a fruitful precursor for the generation of PSUs containing a diverse range of functional groups.<sup>9</sup> To explore this possibility, we took PSU-B(pin) with two different mol% values (46% of entry 2 and 176% of entry 6 in Table 1) and coupled them with aryl bromides containing ketone, amine, Boc-protected amine, hydroxy, and aldehyde using 3%  $\text{Pd}(\text{PPh}_3)_4$  catalyst (Scheme 1). The  $^1\text{H}$  NMR analysis of the polymer products from the Suzuki–Miyaura reaction (PSU-FG) revealed that the proton resonances of the B(pin) moiety disappeared completely, and a new set of resonances from the functionality (FG in Scheme 1) appeared with almost identical concentrations (Table 2; Figure S6, Supporting Information).

Similar to the results of PSU-B(pin), the molecular weight properties ( $M_n$ , PDI, intrinsic viscosity) of PSU-FG were essentially unchanged from those of the precursor polymers, indicating that no polymer chain scission or cross-linking occurred (see Table 2; Figure S7, Supporting Information).

In summary, we have demonstrated a new synthetic method for the introduction of functional groups into polysulfone using a combination of an iridium-catalyzed C–H activation/borylation and the Suzuki–Miyaura reaction. The concentration of attached B(pin) groups was controlled simply by adjusting the stoichiometry of the diboron reagent in the borylation. Subsequent cross-coupling with aryl bromide yielded PSU-FG containing a

**Table 2.** Suzuki–Miyaura Cross-Coupling Reactions of PSU-B(pin)

entry	FG	FG (%) <sup>c</sup>	$M_n$ <sup>d</sup>	PDI	IV <sup>e</sup>
1 <sup>a</sup>	COCH <sub>3</sub>	47	26.1	2.35	0.77
2 <sup>b</sup>		194	32.3	2.27	1.01
3 <sup>a</sup>	NMe <sub>2</sub>	48	33.9	2.41	0.76
4 <sup>b</sup>		171	47.4	2.72	1.01
5 <sup>a</sup>	NHBoc <sup>f</sup>	46	26.6	2.24	0.74
6 <sup>b</sup>		177	33.7	2.58	1.00
7 <sup>a</sup>	CH <sub>2</sub> OH	46	34.5	2.59	0.89
8 <sup>b</sup>		172	43.6	2.40	0.91 <sup>g</sup>
9 <sup>a</sup>	CHO	47	34.4	2.88	0.76
10 <sup>b</sup>		177	42.9	2.62	1.00

<sup>a</sup> From 46% borylated PSU-B(pin) (Table 1, entry 2). <sup>b</sup> From 176% borylated PSU-B(pin) (Table 1, entry 6). <sup>c</sup> The mol% of FG attached to PSU based on  $^1\text{H}$  NMR spectra. <sup>d</sup> Number-average molecular weight reported in kg/mol. <sup>e</sup> Intrinsic viscosity measured using an Ubbelohde viscometer at 30 °C with a polymer concentration of 0.5 g/dL in chloroform. <sup>f</sup> Boc = *tert*-butoxycarbonyl. <sup>g</sup> Measured in DMAc at 30 °C.

specific level of the desired functional group. Throughout the process this new PSU postfunctionalization proceeded without negatively affecting the polymer chain length. This highly efficient and mild postfunctionalization method allows the convenient preparation of a new family of functionalized polysulfones, which can ultimately find broader applications as new high-performance engineering plastic materials.

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**Supporting Information Available:** Experimental procedures,  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$  NMR, IR spectra, and SEC results of PSU-FG. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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