

Synthesis of thiophene-containing conjugated polymers from 2,5-thiophenebis(boronic ester)s by Suzuki polycondensation†

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High molecular weight thiophene-containing conjugated polymers were successfully synthesized by Suzuki polycondensation of aryl dibromides and 2,5-thiophenebis(boronic acid) derivatives by using a new thiophene-containing bulky phosphorous compound as the ligand for a zerovalent palladium catalyst.

Suzuki–Miyaura cross-coupling was first used by Schlüter *et al.* in 1988 to synthesize poly(*para*-phenylene)s,^{1–3} and Suzuki polycondensation (SPC) has become one of the most powerful methods for synthesizing conjugated polymers. This method has the advantages over alternative methods (including Kumada Corriu,⁴ Negishi⁵ and Stille⁶) of wide functional group tolerance, commercial availability of a large number of nontoxic, stable boronic acids, and ready separation of the boron-containing by-product from the desired compound. The synthesis of thiophene-containing conjugated polymers by SPC is successful only when aryl diboronic acids and 2,5-thiophene dihalides are used as starting materials. Because of the hydrolytic deboration of 2,5-thiophenebis(boronic acid pinacol ester) under standard Suzuki–Miyaura cross-coupling conditions,^{7a,8} most attempts to synthesize thiophene-containing conjugated polymers from electron-rich 2,5-thiophenebis(boronic acid pinacol ester) and aryl dibromides by SPC have failed to afford high molecular weight polymers,^{3,5,7} except for a report by Lu *et al.* of SPC of 2,5-thiophenebis(boronic acid pinacol ester)s and 2,7-dibromo-9,9-dioctyldibenzosilole using Pd(PPh₃)₄ as the catalyst precursor afforded high molecular weight polymers.⁹

Thiophene-containing conjugated polymers have attracted considerable attention because of their potential applications in optoelectronics, microelectronics, and chemical and biological sensors,¹⁰ and have been widely used to fabricate high

efficiency heterojunction polymer solar cells.¹¹ Our long term objective is to design and synthesize new narrow band thiophene-containing conjugated polymers for high efficiency polymer solar cells. We believe that it is of great importance to develop new effective palladium catalysts for the synthesis of thiophene-containing conjugated polymers from 2,5-thiophenebis(boronic acid pinacol ester) and aryl dihalides by SPC. In this communication, we report design and synthesis of a new thiophene-containing phosphorous compound **L1** (Chart 1), which was used as the ligand for a zerovalent palladium catalyst for SPC of 2,5-thiophenebis(boronic acid pinacol ester) and aryl dihalides. Using this new catalyst SPC proceeds very rapidly. High molar mass polymers can be easily obtained in about 1.5 h, hence the influence of hydrolytic deboration of 2,5-thiophenebis(boronic acid pinacol ester) on the polymerization can be minimized. To the best of our knowledge, this is the first report of SPC of 2,5-thiophenebis(boronic acid pinacol ester) and aryl dibromides to afford high molecular weight thiophene-containing conjugated polymers. This method should be of great interest for the synthesis of pharmaceutical and agrochemical compounds and natural products.⁸

As shown in Chart 1, two bulky phosphorous ligands (**L1** and **L2**) and two palladium complexes (Pd(PPh₃)₄ and Pd(PTh₃)₃)¹² were screened as the catalyst precursors for SPC of 2,5-thiophenebis(boronic ester)s and aryl dibromides. Pinacol esters of 2,5-thiophenebis(boronic acid) were used for the polycondensation because they are much more stable than the

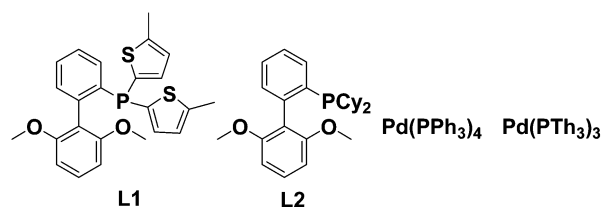


Chart 1 Chemical structures of phosphorous ligands and palladium catalysts used for SPC of 2,5-thiophenebis(boronic ester)s and aryl dibromides.

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corresponding boronic acids at elevated temperature. Bulky electron-rich ligands are more active than the commonly used palladium catalysts such as $\text{Pd}(\text{PPh}_3)_4$, since oxidative addition of an aryl halide to a palladium complex is much more facile when the complex has a bulky electron-rich ligand.¹³ It is worth noting that the bulky phosphorous ligand **L2** was first developed by Buchwald *et al.* for cross-coupling of aryl chlorides and aryl boronic pinacol esters.¹⁴ Because thienyl is more electron-rich than cyclohexyl, the replacement of two cyclohexyl groups on the phosphorous atom with two 2-methylthienyl substituents should lead to a more active and efficient catalyst which enhances the reaction rate. A high polymerization rate should minimize the influence of unwanted deboronation side reaction. The synthesis of the thienyl-containing bulky ligand **L1** is shown in Scheme S1.[†] The structure and high purity of **L1** were established by ^1H , ^{13}C and ^{31}P NMR spectroscopy and elemental analysis.

To test the performance of our new ligand **L1**, we chose first a moderately hindered substrate as a test case (Scheme 1). The reaction of 1,4-dibromo-2,5-dimethylbenzene with 2-thiopheneboronic ester gave 1,4-bis(thiophen-2-yl)-2,5-dimethylbenzene in 87% yield using 1% $\text{Pd}_2(\text{dba})_3/\text{L1}$ (Table 1, entry 4). The applicability of our new catalyst system is shown in Table 1, with eight different aryl and heteroaryl halides, which gave corresponding products in good to excellent yield. For example, electron-rich aryl halides (Table 1, entries 5 and 6; 90–93%) coupled as smoothly as electron deficient aryl halides (Table 1, entry 2; 93%). Compared with the catalysts $\text{Pd}_2(\text{dba})_3/\text{L2}$, $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pd}(\text{PTh}_3)_3$, ligand **L1** in the presence of $\text{Pd}_2(\text{dba})_3$ ($\text{Pd}/\text{L1} = 1/3$) generally gave higher yields in reactions

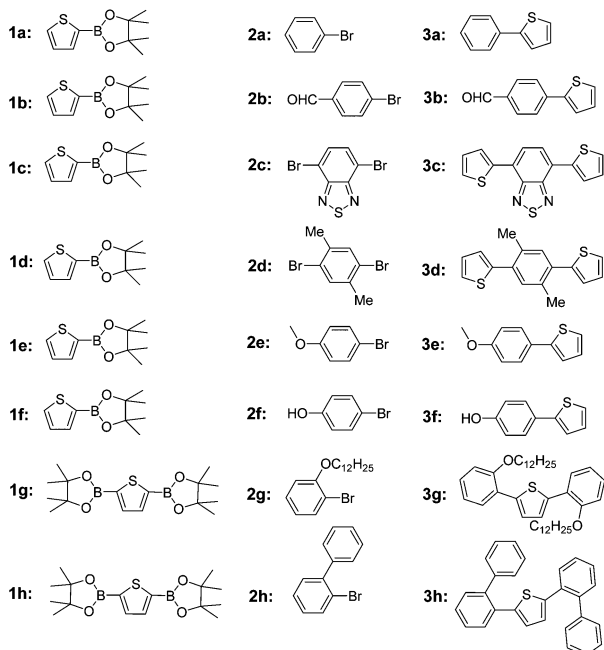
Table 1 Isolated yields of **3** by Suzuki–Miyaura cross-coupling of **1** and **2** with different catalysts^a

Entry	3	$\text{Pd}_2(\text{dba})_3 + \text{L1}$	$\text{Pd}_2(\text{dba})_3 + \text{L2}$	$\text{Pd}(\text{PPh}_3)_4$	$\text{Pd}(\text{PTh}_3)_3$
1	3a	94%	88%	84%	<1%
2	3b	93%	89%	84%	<1%
3	3c	95%	95%	78%	<1%
4	3d	87%	83%	67%	<1%
5	3e	90%	75%	72%	<1%
6	3f	93%	80%	87%	<1%
7	3g	87%	38%	—	—
8	3h	89%	28%	—	—

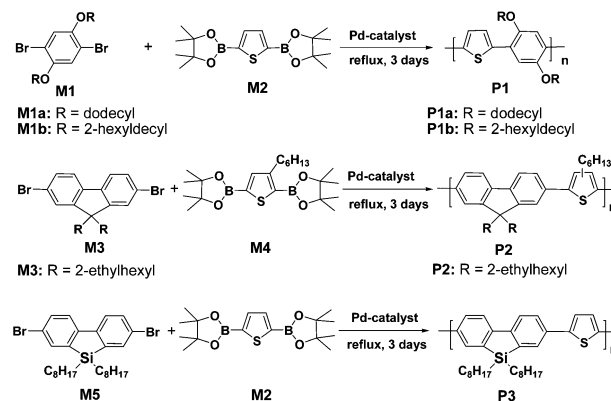
^a Reaction conditions: **1** (1 or 2 equiv.), **2** (1 or 2 equiv.), NaHCO_3 (15 equiv.), THF (16 mL), H_2O (4 mL), ≤ 1 mol% $\text{Pd}_2(\text{dba})_3/\text{L1}$, 1 mol% $\text{Pd}_2(\text{dba})_3/\text{L2}$, 1 mol% $\text{Pd}(\text{PPh}_3)_4$ or 1 mol% $\text{Pd}(\text{PTh}_3)_3$, and reflux for 40–48 h.

of aryl halides and 2-thiopheneboronic esters. For Suzuki–Miyaura cross-coupling of 2,5-thiophenebis(boronic acid pinacol ester)s and *ortho* substituted bromobenzenes, ligand **L1** gave the desired products in isolated yields of 87–89%; whereas under the same conditions ligand **L2** furnished the target products in isolated yields of only 28–38%.

The catalytic system based on ligand **L1** and $\text{Pd}_2(\text{dba})_3$ ($\text{Pd}/\text{L1} = 1/3$) was tested for SPC of 2,5-thiophenebis(boronic acid pinacol ester)s and aryl dibromides (Scheme 2). For comparison, Buchwald type ligand **L2** and $\text{Pd}_2(\text{dba})_3$ ($\text{Pd}/\text{L2} = 1/3$), $\text{Pd}(\text{PPh}_3)_4$, and $\text{Pd}(\text{PTh}_3)_3$ were also used as catalyst precursors for the same polymerization. SPC of 2,5-thiophenebis(boronic acid pinacol ester)s with 2,5-dialkoxy-1,4-dibromobenzene and 3-hexyl-2,5-thiophenebis(boronic acid pinacol ester) with 2,7-dibromo-9,9-bis(2-ethylhexyl)-9H-fluorene was carried out in a biphasic mixture of THF and aqueous NaHCO_3 with freshly prepared $\text{Pd}_2(\text{dba})_3/\text{L1}$, $\text{Pd}_2(\text{dba})_3/\text{L2}$, $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pd}(\text{PTh}_3)_3$ as the catalyst precursors. The polymerization results are summarized in Table 2. Using a typical palladium catalyst, $\text{Pd}(\text{PPh}_3)_4$, SPC of aryl dibromides (**M1a** and **M1b**) with thienylene-2,5-diboronic ester (**M2**) afforded only low molecular weight oligomers with M_w less than 2200 g mol^{-1} ; similar



Scheme 1 Suzuki–Miyaura cross-coupling of aryl bromides and thiophene-based boronic esters with different palladium catalyst precursors.



Scheme 2 SPC of aryl dibromides and 2,5-thiophenebis(boronic acid pinacol ester)s with different palladium catalyst precursors.

Table 2 Monomers, catalyst precursors, yield, weight average molecular weight (M_w), and polydispersity index (PDI)

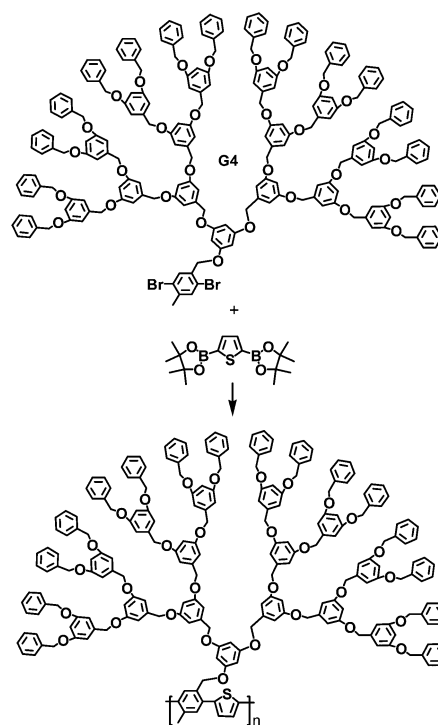
Polymers	Monomers	Catalyst	Yield (%)	M_w^a (g mol ⁻¹)	PDI
P1a	M1a + M2	Pd ₂ (dba) ₃ /L1	92	24 600 ^b	2.8
P1a	M1a + M2	Pd ₂ (dba) ₃ /L2	60	1000	1.2
P1a	M1a + M2	Pd(PPh ₃) ₄	61	2200	1.1
P1a	M1a + M2	Pd(PTh ₃) ₃	0		
P1b	M1b + M2	Pd ₂ (dba) ₃ /L1	89	17 000	1.8
P1b	M1b + M2	Pd ₂ (dba) ₃ /L2	75	1000	1.1
P1b	M1b + M2	Pd(PPh ₃) ₄	54	1700	1.3
P1b	M1b + M2	Pd(PTh ₃) ₃	0		
P2	M3 + M4	Pd ₂ (dba) ₃ /L1	98	94 000	4.9
P2	M3 + M4	Pd ₂ (dba) ₃ /L2	68	2500	1.3
P2	M3 + M4	Pd(PPh ₃) ₄	89	7000	1.7
P2	M3 + M4	Pd(PTh ₃) ₃	0		
P3	M5 + M2	Pd(PPh ₃) ₄	64	79 000	3.1
P3	M5 + M2	Pd ₂ (dba) ₃ /L1	69	62 000	2.8

^a Molecular weight determined by GPC with THF as the eluent, calibrated with polystyrene standards. ^b Molecular weight determined by GPC at 150 °C with 1,2,4-trichlorobenzene as the eluent, calibrated with polystyrene standards.

results have been reported in the literature.^{7a,15} SPC of **M3** and **M4** using Pd(PPh₃)₄ as the catalyst precursor afforded polymer **P2** with slightly improved molecular weight (M_w = 7000 g mol⁻¹). We previously demonstrated that Pd(PTh₃)₃ is an efficient catalyst for SPC of 2-(5-halo-4-hexyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Hence Pd(PTh₃)₃ was tested as a catalyst precursor for SPC of **M1a** with **M2**, **M1b** with **M2**, and **M3** with **M4**, respectively. In all three cases, no polymer was formed. The Buchwald type bulky ligand **L2** has been widely used together with zerovalent palladium (Pd₂(dba)₃) for Suzuki–Miyaura cross-coupling of chloroaromatics and aryl boronic acids or esters. It is worth mentioning that, surprisingly, in view of their versatility in cross-coupling reactions, there are few reports on the use of Buchwald type ligands for catalyzing SPC.¹⁴ Schlüter *et al.* first used these ligands for SPC of aryl dichlorides and aryl diboronic esters. SPC of 2,5-thiophenebis(boronic acid) s and aryl dibromides was also performed using a Buchwald type ligand and Pd₂(dba)₃ as the catalyst precursors.¹⁶ In all three cases, the polycondensation afforded only low molecular weight oligomers with M_w less than 2500 g mol⁻¹. SPC of **M1a** and **M2** with **L1** as the ligand for zerovalent palladium afforded high molecular weight polymer **P1a**. The polycondensation proceeded very rapidly and the polymer precipitated from the reaction mixture about 2 h after the reaction started. Polymer **P1a** was not soluble in THF even at elevated temperature, but was soluble in warm chloroform and 1,2,4-trichlorobenzene. The molecular weight of **P1a** was determined by GPC at 150 °C with 1,2,4-trichlorobenzene as the eluent, and calibration with polystyrene standards. The precipitation of polymer **P1a** from the reaction medium prevents the precipitated chains from polymerizing further to give high molecular weight polymers. And as a result polymer **P1a** showed a bimodal molecular weight distribution. To obtain polymers that were fully soluble in the reaction media we chose 2,7-dibromo-9,9-bis(2-ethylhexyl)-9H-fluorene (**M3**) and 3-hexyl-thienylene-2,5-diboronic ester (**M4**) as

monomers. SPC of **M3** and **M4** with Pd₂(dba)₃/L1 as the catalyst precursors afforded polymer **P2**, which was fully soluble in THF at room temperature. The GPC elution curve of **P2** showed a mono modal molecular weight distribution. **P2** had number average molecular weight 19 000 g mol⁻¹, weight average molecular weight 94 000 g mol⁻¹, number-average degree of polymerization (P_n) 34, and weight average degree of polymerization (P_w) 169. SPC of 2,5-thiophenebis(boronic acid pinacol ester)s (**M2**) and 2,7-dibromo-9,9-dioctyldibenzosilole (**M5**) was also tested using Pd(PPh₃)₄ or Pd₂(dba)₃/L1 as the catalyst precursors, and under both conditions high molecular weight polymers were obtained. The results are also summarized in Table 2.

We demonstrated previously that SPC can effectively cope with steric hindrance imparted by fourth generation dendritic monomers.¹⁷ Here, as shown in Scheme 3, SPC of a fourth generation dendritic dibromo monomer and 2,5-thiophenebis(boronic acid pinacol ester) was tested by using two bulky phosphorous compounds **L1** and **L2** as the ligands for zerovalent palladium catalysts. Fourth generation dendronized polymers with M_w 64 000 g mol⁻¹ and polydispersity index 1.8 were obtained using **L1** as the ligand. In the control experiment with **L2** as the ligand only low molecular weight (M_w = 3800 g mol⁻¹) oligomers were obtained. To more fully understand the polymerization process we investigated the polymerization kinetics. The variation of weight average molecular weight with polymerization time is shown in Fig. 1. It is clear that with **L1** as the ligand SPC proceeded very rapidly; M_w of the fourth generation dendronized polymer reached 29 000 g mol⁻¹ after 0.5 h

**Scheme 3** SPC of the fourth generation dendritic dibromo monomer and 2,5-thiophenebis(boronic acid pinacol ester) with Pd₂(dba)₃/L1 and Pd₂(dba)₃/L2, respectively, as the catalyst precursors.

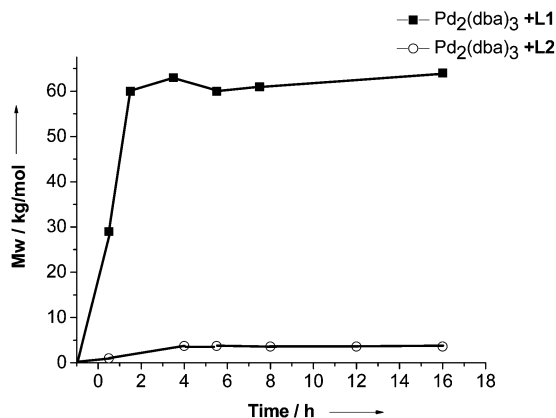


Fig. 1 M_w versus reaction time curves of the fourth generation dendritic polymer prepared by SPC from the dibromo monomer and 2,5-thiophenebis(boronic acid pinacol ester) using $\text{Pd}_2(\text{dba})_3/\text{L1}$ and $\text{Pd}_2(\text{dba})_3/\text{L2}$ as the catalyst precursors.

and 60 000 g mol^{-1} after 1.5 h. After 1.5 h, increase of reaction time did not cause increase of the molecular weight and no monomer can be detected from the reaction mixture, indicating a conversion of 100%. In the control experiment with L2 as the ligand, M_w reached only about 3800 g mol^{-1} . In standard SPC, at least 2 to 7 days were required to achieve high molecular weight polymers. Obtaining high molecular weight polymers from 2,5-thiophenebis(boronic acid pinacol ester)s by SPC is probably enabled by the extremely high polymerization rate. With the new ligand (L1), we were able to obtain high molecular weight polymers by using electron-rich 2,5-thiophenebis(boronic acid pinacol ester)s as monomers.

In summary, we report a new thiophene-containing bulky phosphorous ligand that can be used with $\text{Pd}_2(\text{dba})_3$ as a catalyst system for SPC of aryl dibromides and 2,5-thiophenebis(boronic acid pinacol ester)s. 2,5-Thiophenebis(boronic acid pinacol ester)s that have been considered not suitable for SPC with aryl dibromides because of deboronation under basic conditions were successfully polymerized with this thiophene-containing bulky ligand. The new catalytic system can enhance the SPC reaction rate and cope with steric hindrance imparted by the monomers. With the new ligand SPC proceeded very rapidly, and high molecular weight fourth generation dendronized polymers could be obtained in only 1.5 h.

Acknowledgements

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