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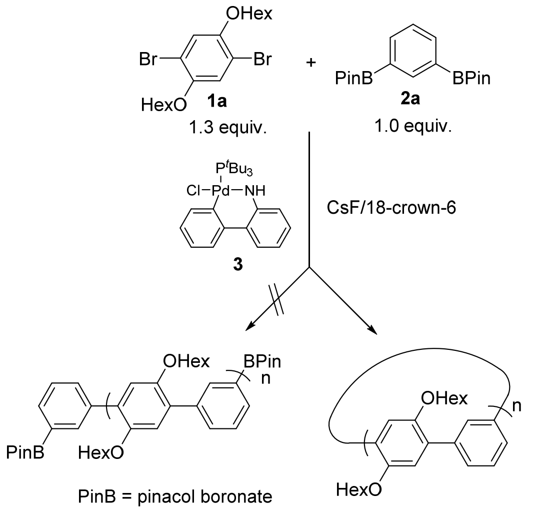
Unusual cyclic polymerization through Suzuki-Miyaura coupling of polyphenylene bearing diboronate at both ends with excess dibromophenylene

Hajime Sugita,[a] Masataka Nojima,[a] Yoshihiro Ohta[a] and Tsutomu Yokozawa[a]

Suzuki-Miyaura coupling polymerization of *p*-dibromophenylene and *m*-phenylenediboronic acid ester, as well as *m*-dibromophenylene and *p*-phenylenediboronic acid ester, and the combination of two *meta*-phenylene monomers, in the presence of *t*-Bu$_3$PPd(0) catalyst selectively afforded cyclic polyphenylenes through polyphenylene bearing boronate at both ends when excess dibromophenylene was used.

Cyclic oligophenylenes[1] were initially synthesized because of their structural interest,[2] but have recently attracted attention as bipolar charge carrier transport materials for organic light-emitting diodes (OLEDs).[3] They can be synthesized stepwise, or by one-step reaction followed by separation with HPLC or column chromatography. In polymer synthesis, cyclic oligophenylenes are obtained as by-products in the synthesis of high-molecular-weight linear polyphenylenes. For example, Sakamoto and coworkers conducted Suzuki-Miyaura polycondensation of *m*-bromophenylboronic acid ester by slow monomer addition to suppress cyclization.[4] From the opposite point of view, however, selective synthesis of cyclic polyphenylenes without formation of linear polymer has not been explored.

We recently reported that *t*-Bu$_3$PPd-catalyzed Suzuki-Miyaura condensation polymerization of dibromoarene and arylenediboronic acid ester affords high-molecular-weight π-conjugated polymers with boronate moieties at both ends, even if excess dibromoarene is used.[5] This unstoichiometric polycondensation behavior was attributed to intramolecular transfer of the Pd catalyst on dibromoarene. We subsequently attempted to synthesize poly[(*p*-phenylene)-*alt*-(*m*-phenylene)][6] by polymerization of excess *p*-dibromophenylene **1a** with *m*-phenylenediboronic acid ester **2a**; however, we found that the reaction afforded not polyphenylene with boronate chain ends, but cyclic polyphenylene[7] (Scheme 1). Here, we present details of this selective cyclic polymerization of dibromophenylene **1** and phenylenediboronic acid ester **2** in the presence of *t*-Bu$_3$PPd(0) catalyst under unstoichiometric conditions. This unstoichimetric cyclic polymerization is intriguing, because Kricheldorf and coworkers published a general overview of unstoichiometric polycondensation,[8] in which they claimed that telechelic oligomers or extremely high-molecular-weight polymers are obtained due to suppression of cyclization, in contrast to the case of stoichiometric polycondensation, which gave cyclic polymers in the final stage.[9] However, we show here that cyclic polymer is predominantly formed under unstoichiometric conditions, rather than stoichiometric conditions, contrary to Kricheldorf's view.



Scheme 1. Cyclic polyphenylene obtained by unstoichiometric Suzuki-Miyaura coupling polymerization of 1.3 equiv. of **1a** and 1.0 equiv. of **2a** in the presence of Pd catalyst **3** and CsF/18-crown-6.

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Electronic Supplementary Information (ESI) available: Detailed experiments, effect of excess amount of **1a**, polymerization with other catalysts, and attempts to synthesize cyclic polyphenylenes by using *ortho*-monomers (MALDI-TOF mass spectra). See DOI: 10.1039/x0xx00000x

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Suzuki-Miyaura coupling polymerization of 1.3 equiv. of **1a** and 1.0 equiv. of **2a** was first carried out in the presence of 5.0 mol% of *t*-Bu_3P-ligated Pd precatalyst **3**,[10] which generates *t*-$Bu_3PPd(0)$ with the assistance of base, and CsF/18-crown-6 as a base at room temperature for 24 h. The matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrum of the products (M_n = 5400, M_w/M_n = 1.69) surprisingly showed essentially one series of peaks due to cyclic poly[(*p*-phenylene)-*alt*-(*m*-phenylene)] (Fig. 1a).[11] The ^1H and ^{13}C NMR spectra showed only signals of repeat units (ESI). When equimolar **1a** and **2a** were polymerized under the same conditions, linear polyphenylenes with boronate at both ends (designated as PinBPh/BPin; PinB = pinacol boronate) and with a hydrogen at one end and BPin at the other (H/BPin) were formed, as well as cyclic polyphenylene (M_n = 4850, M_w/M_n = 1.51; Fig. 1b). On the other hand, when 1.4 equiv. of boronate monomer **2a** was used, boronate-terminal polyphenylene (M_n = 2090, M_w/M_n = 1.14) was selectively obtained (Fig. 1c). It should be noted that this polymerization protocol can selectively generate either linear polymer or cyclic polymer simply by changing the feed ratio of the two monomers. In general, cyclic polymer[12] is synthesized by using a cyclic initiator in chain-growth polymerization[13] or by cyclization of end-functionalized polymers at high dilution.[14]

Polymerization of **1a** and **2a** resulted in cyclic polymer even at high monomer concentration, and the molecular weight of the cyclic polymer increased up to M_n = 8540 with increasing concentration. The polydispersity approached 2.0 (Fig. 2). Therefore, the molecular weight of the cyclic polymer can be controlled to some extent by changing the monomer concentration. As for other Pd catalysts often used in Suzuki-Miyaura coupling polymerization, $(PPh_3)_4Pd$ afforded mainly linear oligomer. XPhos Pd(0),[15] generated from the corresponding precatalyst having the biphenylamino moiety with base, gave both cyclic polymer and linear polymers with several kinds of polymer ends (Fig. S2 and S3). Consequently, it turned out that *t*-$Bu_3PPd(0)$, which has high intramolecular transfer ability on aromatics, was the most appropriate catalyst for this unstoichiometric cyclic polymerization.

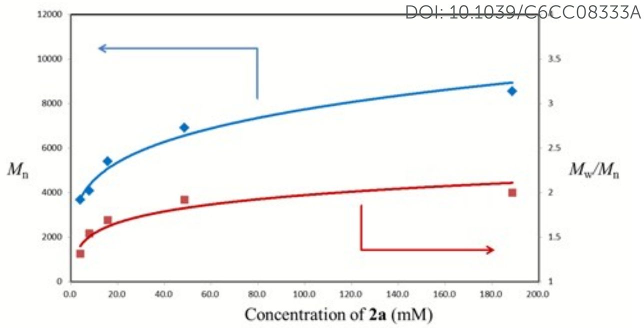

Fig. 2 M_n and M_w/M_n values of products as a function of monomer concentration ([**2a**]$_0$) in polymerization of 1.3 equiv. of **1a** and 1.0 equiv. of **2a** with 5.0 mol % of **3**, CsF (4 equiv.), and 18-crown-6 (8 equiv.) in THF and water (THF/water = 3.0/0.1, v/v) at rt for 24 h.

In order to investigate the cyclic polymerization mechanism, we followed the conversion of **2a** and changes of products with polymerization time (Fig. 3). The MALDI-TOF mass spectra indicated that linear polyphenylene with PinBPh/BPin ends was predominantly formed until the conversion reached 89% (1 h). This behavior was the same as in the case of unstoichiometric polymerization of excess *p*-dibromophenylene and 1.0 equiv. of *p*-phenylenediboronoc acid ester with **3**.[5] Cyclic polymer and polymer with H/BPin ends were observed at 97% conversion (3 h), and both peaks then increased until 100% conversion (5 h). After 24 h, the products converged to cyclic polymer. Since the H/BPin-ended polymer was converted to cyclic polymer, the hydrogen end was presumably formed by hydrolysis of a polymer-Pd-Br end during quenching with hydrochloric acid.

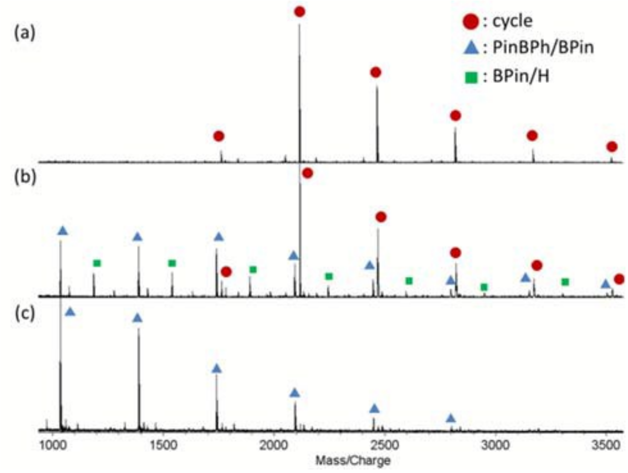

Fig. 1 MALDI-TOF mass spectra of the products obtained by the polymerization of **1a** and **2a** with 5.0 mol % of **3**, CsF (4 equiv.), and 18-crown-6 (8 equiv.) in THF ([**2a**]$_0$ = 16.6×10^{-3} M) and water (THF/water = 3.0/0.1, v/v) at rt for 24 h, followed by quenching with 1 M hydrochloric acid: monomer feed ratio of **1a**/**2a** is (a) 1.3/1.0, (b) 1.0/1.0, and (c) 1.0/1.4

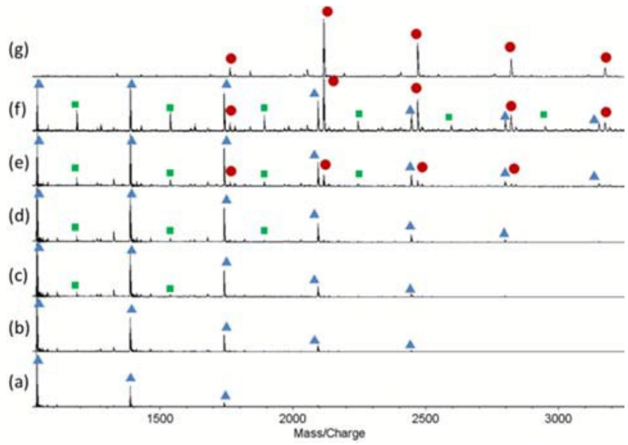

Fig. 3 Changes of products with polymerization time and conversion of **2a** in the polymerization of 1.3 equiv. of. **1a** and 1.0 equiv. of **2a** with 5.0 mol % of **3**, CsF (4 equiv.), and 18-crown-6 (8 equiv.) in THF ([**2a**]$_0$ = 16.6×10^{-3} M) and water (THF/water = 3.0/0.1, v/v) at rt: time, conversion of **2a**, and M_n are (a) 15 min, 72%, 1640; (b) 30 min, 83%, 1720; (c) 45 mim, 86%, 1810; (d) 1 h, 89%, 1940; (e) 3 h, 97%, 2770; (f) 5 h, 100%, 3790; (g) 24 h, 100%, 4920.

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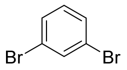
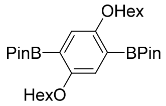
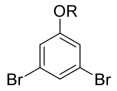
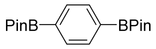
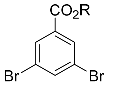
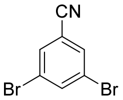
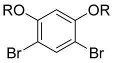
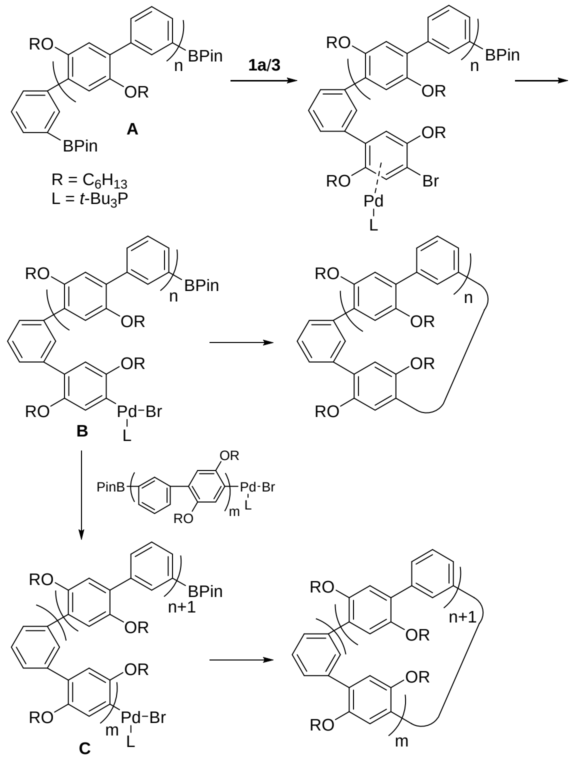
On the basis of the changes of products with polymerization time, we propose the following mechanism (Scheme 2). The coupling polymerization of **1a** and **2a** proceeded via intramolecular catalyst transfer on dibromo monomer **1a** to afford polyphenylene **A** with PinBPh/BPin ends until diboronate monomer **2a** was almost completely consumed. Excess **1a** reacted with the boronate chain end, followed by intramolecular oxidative addition to generate Br-Pd/BPin-ended polymer **B**. If polymer **B** has a favorable conformation for cyclization, the two chain ends would react to yield cyclic polymer. Cyclic polymer could be also formed by intramolecular reaction of the two chain ends of polymer **C** formed by intermolecular coupling reaction between polymer **B**s. However, the former cyclization would mainly take place, because the molecular weight of polymer was increased only slightly in the final stage of polymerization. Since this polymerization proceeds through the formation of boronate-terminal polymer **A**, excess **1a** should promote generation of cyclization precursor polymer **B** in the final stage. In addition, kink structure of *meta*-monomer is crucial for cyclic polymerization because the combination of *para*-monomers gave linear polymer with BPin at both ends.[5]

Unstoichiometric cyclic polymerization of other phenylene monomers was also examined under similar conditions (Table 1). The reverse combination of monomers, i.e., 1.3 equiv. of *m*-dibromophenylene **1b** and 1.0 equiv. of *p*-phenylenediboronic acid ester **2b**,[10] resulted in cyclic polymer with similar molecular weight (Entry 1). Cyclic polymerization through intramolecular catalyst transfer on dibromoarene **1** was not influenced by an electron-donating substituent (**1c**, Entry 2) or an electron-withdrawing substituent (**1d**, Entry 3) on **1**. Furthermore, polymerization of acceptor dibromophenylene **1e** and donor phenylenediboronic acid ester **2b** similarly afforded cyclic polymer (Entry 4), although the combination of acceptor dibromoarene and donor arylenediboronic acid ester resulted in low-molecular-weight polymer in the unstoichiometric Suzuki-Miyaura coupling polymerization that we previously reported.[5] Furthermore, we examined polymerization of *m*-dibromophenylene and *m*-phenylenedioronic acid ester. Cyclic polymer was not clearly detected by MALDI-TOF mass spectrometry in the polymerization of 1.3 equiv. of **1c** and 1.0 equiv. of **2a**, but the use of dialkoxy-substituted **1f** instead of **1c** resulted in cyclic polymer formation (Entry 5). When *o*-dibromophenylene and *o*-phenylenediboronic acid ester were used in any combination of monomers, linear polymer was mainly obtained, along with some cyclic oligomers (Fig. S9-S12).

Table 1. Cyclic polymerization of 1.3 equiv. of **1** and 1.0 equiv. of **2** with **3** and CsF/18-crown-6. [a]

Entry	1 [b]	2	Yield (%) [c]	M_n (M_w/M_n) [d]
1	 **1b**	 **2b**	83	5610 (1.86)
2	 R = 2-ethylhexyl **1c**	 **2c**	93	5030 (1.72)
3	 R = 2-ethylhexyl **1d**	**2c**	90	5320 (1.65)
4	 **1e**	**2b**	88	5600 (1.64)
5	 R = hexyl **1f**	**2a**	94	2580 (1.42)

[a] Polymerization of 1.3 equiv of **1** and 1.0 equiv .of **2** was carried out with 5.0 mol % of **3**, CsF (4 equiv), and 18-crown-6 (8 equiv) in THF ($[\mathbf{2}]_0 = 16.1\times10^{-3}$ M) and water (THF/water = 3/0.1, v/v) at rt for 24 h, followed by quenching with 1 M hydrochloric acid. [b] 1.3 equiv. [c] Isolated yield after preparative HPLC. [d] Estimated by GPC based on polystyrene standards (eluent: THF).



Scheme 2. Proposed mechanisms for cyclic polymerization of excess **1a** and 1.0 equiv. of **2a** with Pd catalyst

In conclusion, we have demonstrated that Suzuki-Miyaura coupling polymerization of *meta*/*para*- and *meta*/*meta* combinations of monomers in the presence of *t*-Bu$_3$PPd(0) catalyst, which has a high propensity for intramolecular π-face transfer, selectively affords cyclic polyphenylenes when excess

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dibromophenylene is used, in contrast to similar Suzuki-Miyaura coupling polymerization of the *para*/*para* combination of monomers, which results in linear high-molecular-weight polyphenylene with boronate moieties at both ends. This cyclic polymerization proceeded irrespective of monomer concentration, and the molecular weight of the cyclic polymer increased with increasing monomer concentration. MALDI-TOF mass spectra of the products obtained during polymerization of 1.3 equiv. of *p*-dibromophenylene **1a** and 1.0 equiv. of *m*-phenylenediboronic acid ester **2a** indicated that linear polyphenylene with boronate ends, formed until **2a** was almost completely consumed, would undergo cyclization by reaction of the boronate polymer ends with excess **1a** in the final stage. Since this cyclic polymerization is hardly influenced by electronic substituent effects on the monomers, it should be useful in the design and synthesis of many kinds of cyclic polyphenylenes for application to OLEDs. Extension of this unstoichiometric cyclic polymerization to other aromatics and applications to OLEDs are under investigation.

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