Investigation of Catalyst-Transfer Condensation Polymerization for Synthesis of Poly(*p*-phenylenevinylene)

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ABSTRACT: Kumada-Tamao coupling polymerization of 1,4-dia-Ikoxy-2-bromo-5-(2-chloromagnesiovinyl)benzene (1) and 1,4dialkoxy-2-(2-bromovinyl)-5-chloromagnesiobenzene (2) with a Ni catalyst and Suzuki-Miyaura coupling polymerization of 2-{2-[(2,5-dialkoxy-4-iodophenyl)]vinyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3), its bromo counterpart 4, and 2,5-dialkoxy-4-(2bromovinyl)phenylboronic acid (5) with a Pd initiator were investigated under catalyst-transfer condensation polymerization conditions for the synthesis of well-defined poly(p-phenylenevinylene) (PPV). The Kumada-Tamao polymerization of vinyl Grignard-type monomer 1 with Ni(dppp)Cl₂ at room temperature did not proceed, whereas aryl Grignard-type monomer 2 afforded oligomers of low molecular weight. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra of the polymer obtained from 2 implied that the Grignard end group reacted with tetrahydrofuran to terminate polymerization. On the other hand, Suzuki-Miyaura polymeriza-

INTRODUCTION π -Conjugated polymers have received much attention because of their applications in electronic devices, including thin film transistors,¹ organic light-emitting diodes (OLEDs),² and photovoltaic cells.³ Many π -conjugated polymers have been conventionally synthesized by step-growth polymerization; however, it is difficult to control the molecular weight and to obtain polymers with low polydispersity using this method.⁴ However, development of chain-growth condensation polymerization with a transition metal catalyst has made it possible to synthesize well-defined π -conjugated polymers.^{5,6} We have proposed that this polymerization involves intramolecular catalyst transfer on the polymer backbone.⁶ Ni-catalyzed Kumada-Tamao catalyst-transfer condensation polymerization (Ni-CTCP) affords well-defined poly(alkylthiophene)s,⁷ polyfluorenes (PFs),⁸ polyphenylenes (PPPs),⁹ poly(*N*-alkylpyrrole)s,¹⁰ and poly(2-alkoxypyridine-3,5-diyl),¹¹ and block copolymers consisting of these π -conjugated polymers can also be obtained in one pot. Furtion of vinyl boronic acid ester type monomers **3** and **4** and phenylboronic acid type monomer **5** with a Pd initiator and aqueous KOH at -20 °C to room temperature yielded the corresponding PPV with high molecular weight within a few minutes. However, the molecular weight distribution was broad, and MALDI-TOF mass spectra showed the peaks of polymers bearing no initiator unit at the chain end, as well as those of polymers with the initiator unit. These results indicated that intermolecular chain transfer of the Pd catalyst occurred. Dehalogenation and disproportionation of the growing end also took place as side reactions. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *00*, 000–000

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thermore, Pd-catalyzed Suzuki-Miyaura CTCP (Pd-CTCP) also affords well-defined PF,¹² PPP,¹³ and poly(3-hexylthiophene) (P3HT).¹⁴ Recently, well-defined π -conjugated alternating copolymers¹⁵ and poly(*p*-phenylene ethynylene)¹⁶ have been synthesized by means of CTCP of biaryl and teraryl monomers and a phenylacetylene monomer, respectively.

Among π -conjugated polymers, poly(*p*-phenylenevinylene) (PPV) has been intensively investigated, especially for application to OLEDs.² Yu and Turner first succeeded in controlled synthesis of PPV by ring-opening metathesis polymerization of cyclophane monomers.¹⁷ Junkers and coworkers¹⁸ conducted controlled anionic and radical polymerization of quinodimethanes containing a sulfinyl group, followed by thermal elimination to obtain well-defined PPV. Furthermore, Galvin and coworkers¹⁹ obtained well-defined oligomers by means of stepwise synthesis, and they found that OLED devices made from PPV with narrow polydispersity showed better external quantum efficiency when

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SCHEME 1 Monomer design of phenylenevinylene-type monomers **1–5**.

compared with PPV with broad polydispersity. However, these polymerization methods are generally unsuitable for synthesizing π -conjugated block copolymers containing PPV. If PPV could be synthesized by means of CTCP, it would be easy to obtain well-defined π -conjugated block copolymers of PPV and other π -conjugated polymers such as P3HT, opening an entry into a new class of π -conjugated materials.

Mastrorilli and coworkers²⁰ conducted Suzuki/Heck copolymerization of dibromofluorene and potassium vinyl trifluoroborate for the synthesis of poly(fluorenylene vinylene), and they observed that the polymerization proceeded in a chaingrowth polymerization manner until the middle stage, whereas the formed oligomers were coupled in a stepgrowth polymerization manner in the final stage. In the current work, we studied whether CTCP could be applied for the synthesis of well-defined PPV in a more straightforward way: polymerization of phenylenevinylene monomers. Thus, we examined Ni-catalyzed Kumada-Tamao coupling polymerization of 1 and 2 and Pd-catalyzed Suzuki-Miyaura coupling polymerization of 3-5 (Scheme 1).

Monomers 1, 3, and 4 have metallated vinyl and halophenylene moieties, whereas monomers 2 and 5 have metallated phenylene and halovinyl moieties. van der Boom and coworkers demonstrated that the reaction of Ni(PEt₃)₄ with a bromostilbene derivative resulted in selective η^2 -C=C coordination, which was kinetically preferable at low temperature, followed by intramolecular "ring walking" of the metal center and intramolecular aryl-bromide bond activation, which was thermodynamically preferable when the temperature was raised. This result was also supported by density functional theory calculations.²¹

Therefore, we expected that the CTCP of 1-5 would proceed via transfer of the catalyst on both benzene rings and carbon-carbon double bonds. However, this would be challenging, because intramolecular transfer of the catalyst would need to be carried out at the same temperature as the polymerization, in contrast to the above two-step reaction.

EXPERIMENTAL

General

 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra were obtained on JEOL ECA-500 and ECA-600 spectrometers. The internal standard for ¹H NMR spectra in CDCl₃ was tetramethylsilane (0.00 ppm), and the internal standard for ¹³C NMR spectra in CDCl₃ was the midpoint of CDCl₃ (77.0 ppm). All melting points were measured with a Yanagimoto hot-stage melting point apparatus without correction. Column chromatography was performed on silica gel (Kieselgel 60, 230-400 mesh; Merck) with a specified solvent. Commercially available dehydrated tetrahydrofuran (THF, stabilizer-free; Kanto), dehydrated diethyl ether (Kanto), dehydrated dichloromethane (Kanto), and dehydrated N,N-dimethylformamide (DMF) (Wako) were used as dry solvents. Isopropylmagnesium chloride (ⁱPrMgCl; 2.0 M solution in THF and 2.0 M solution in diethyl ether; Aldrich) were used as received. 2,5-Bis((2-ethylhexyl)oxy)-4-bromobenzaldehyde (8),²² 2,5bis((2-ethylhexyl)oxy)-4-iodobenzaldehyde (9),²³ 1,4-bis((2ethylhexyl)oxy)-2,5-diiodobenzene (**11**),²⁴ 1-bromo-2,5-bis((2-ethylhexyl)oxy)-4-iodobenzene (**12**),²⁴ ^tBu₃PPd(Ph)Br (6),²⁵ and ${}^{t}Bu_{3}PPd(o-tolyl)Br$ (7)²⁶ were prepared according to the cited literature. The $M_{\rm n}$ and $M_{\rm w}/M_{\rm n}$ values of polymers were measured on a Tosoh HLC-8020 gel permeation chromatography unit (eluent, THF; calibration, polystyrene standards) with two TSK-gel columns ($2 \times$ Multipore H_{XL}-M). Matrix-assisted laser desorption ionization time-offlight (MALDI-TOF) mass spectra were recorded on a Shimadzu/Kratos AXIMA-CFR plus in the reflectron ion mode by use of a laser ($\lambda = 337$ nm). Dithranol (1,8dihydroxy-9[10H]-anthracenone) was used as the matrix for the MALDI-TOF mass measurements.

Synthesis of 1-Bromo-2,5-bis[(2-ethylhexyl)oxy]-4-(2-iodovinyl)benzene (1')

A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. Chromium dichloride (3.700 g, 30.11 mmol) was placed in the flask, and the atmosphere in the flask was replaced with argon. A solution of 8 (2.207 g, 5.00 mmol) and iodoform (3.938 g, 10.12 mmol) in THF (10.0 mL) was added at 0 °C, and the mixture was stirred at 0 °C for 2 h. The reaction was quenched with saturated aqueous NaHCO₃, and the mixture was then poured into 250 mL of ethyl acetate and filtered through Celite. The filtrate was extracted with ethyl acetate, and the combined organic layers were washed with aqueous Na₂S₂O₃ and brine and dried over MgSO₄. The solvent was removed under reduced pressure in a rotary evaporator, and the residue was purified by means of column chromatography (SiO₂ and hexane) to afford a mixture of geometric isomers (E/Z = 56/44) of **1**' as a slightly yellow oil (1.788 g, 75%).

¹H NMR (500 MHz, CDCl₃): $\delta = 7.58$ (d, J = 14.9 Hz, 1 H), 7.49 (s, 1 H), 7.36 (d, J = 8.6 Hz, 1 H), 7.06 (s, 1 H), 7.05 (s, 1 H), 6.94 (d, J = 14.9 Hz, 1 H), 6.79 (s, 1 H), 6.56 (d, J = 8.6Hz, 1 H), 3.93–3.78 (m, 4 H), 1.72–1.67 (m, 2 H), 1.60–1.20

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(m, 16 H), 0.98–0.82 (m, 12 H); ¹³C NMR (126 MHz, CDCl₃): $\delta = 188.9$, 155.9, 150.0, 124.2, 121.1, 118.3, 110.3, 72.1, 72.7, 39.4, 39.3, 30.5, 30.4, 29.03, 28.99, 23.93, 23.87, 22.99, 22.96, 14.05, 14.03, 11.1.

Synthesis of 1-(2,2-Dibromovinyl)-2,5-bis[(2ethylhexyl)oxy]-4-iodobenzene (10)

A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. Iodobenzaldehyde 9 (0.243 g, 0.50 mmol) and triphenylphosphine (0.276 g, 1.05 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry dichloromethane (1.1 mL) was added into the flask via a syringe, and the mixture was stirred at -10 °C. A solution of carbon tetrabromide (0.187 g. 0.57 mmol) in dry dichloromethane (1.1 mL) was added dropwise at -10 °C over about 90 min with stirring under dry nitrogen. Stirring was continued at -10 °C for 6 h, and then the reaction was quenched with saturated aqueous NaHCO₃. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous MgSO₄, and concentrated in vacuo. The residue was purified by means of column chromatography (SiO₂, hexane) to afford **10** as a slightly yellow oil (0.216 g, 67%).

¹H NMR (500 MHz, CDCl₃): $\delta = 10.42$ (s, 1 H), 7.31 (s, 1 H), 7.24 (s, 1 H), 3.93–3.89 (m, 4 H), 1.79–1.74 (m, 2 H), 1.58–1.24 (m, 16 H), 0.96–0.87 (m, 12 H); ¹³C NMR (126 MHz, CDCl₃): $\delta = 188.9$, 155.9, 150.0, 124.2, 121.1, 118.3, 110.3, 72.1, 72.7, 39.4, 39.3, 30.5, 30.4, 29.03, 28.99, 23.93, 23.87, 22.99, 22.96, 14.05, 14.03, 11.1.

Synthesis of (*E*)-1-(2-Bromovinyl)-2,5-bis[(2ethylhexyl)oxy]-4-iodobenzene (2')

A Schlenk flask was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. The obtained **10** (0.139 g, 0.22 mmol) and diethyl phosphite (0.102 g, 7.40 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Distilled triethylamine (0.4 mL) was added via a syringe, and the mixture was stirred at 80 °C for 8 h. The reaction was quenched with 1 M HCl, and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous MgSO₄, and concentrated *in vacuo*. The residue was purified by means of column chromatography (SiO₂ and hexane) to afford **2**', including a trace of geometric isomer as a slightly yellow oil (0.110 g, 90%).

¹H NMR (500 MHz, CDCl₃): $\delta = 10.42$ (s, 1 H), 7.31 (s, 1 H), 7.24 (s, 1 H), 3.93–3.89 (m, 4 H), 1.79–1.74 (m, 2 H), 1.58–1.24 (m, 16 H), 0.96–0.87 (m, 12 H); ¹³C NMR (126 MHz, CDCl₃): $\delta = 188.9$, 155.9, 150.0, 124.2, 121.1, 118.3, 110.3, 72.1, 72.7, 39.4, 39.3, 30.5, 30.4, 29.03, 28.99, 23.93, 23.87, 22.99, 22.96, 14.05, 14.03, 11.1.

Synthesis of 2,5-Bis[(2-ethylhexyl)oxy]-4-iodo-1-(2-trimethylsilylethynyl)benzene (13)

A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure and then cooled to

room temperature under an argon atmosphere. Diiodobenzene **11** (46.14 g, 78.73 mmol), dichlorobis(triphenylphosphine)palladium (2.79 g, 3.97 mmol), and copper(I) iodide were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry DMF (220 mL), distilled triethylamine (19 mL), and trimethylsilylacetylene (13.5 mL, 93.50 mmol) were added into the flask via a syringe, and the mixture was stirred at room temperature for 24 h. The reaction was quenched with saturated aqueous NH₄Cl, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with water, dried over anhydrous MgSO₄, and concentrated *in vacuo*. The residue was purified by means of column chromatography (SiO₂ and hexane) to afford **13** as a yellow oil (14.19 g, 32%).

¹H NMR (600 MHz, CDCl₃): δ = 7.24 (s, 1 H), 6.82 (s, 1 H), 3.86–3.78 (m, 4 H), 1.75–1.70 (m, 2 H), 1.60–1.26 (m, 17 H), 0.97–0.87 (m, 13 H), 0.24 (s, 9 H); ¹³C NMR (150 MHz, CDCl₃): δ = 155.0, 151.7, 123.3, 115.8, 113.2, 100.8, 99.2, 87.6, 72.1, 71.9, 39.6, 39.4, 30.51, 30.46, 29.1, 29.0, 23.95, 23.86, 23.1, 23.0, 14.1, 11.3, 11.2, 0.08.

Synthesis of 4-Bromo-2,5-bis[(2-ethylhexyl)oxy]-1-(2-trimethylsilylethynyl)benzene (14)

The desired **14** (0.153 g, 0.45 mmol) was obtained in 90% yield from **12** (0.270 g, 0.50 mmol) in a similar manner to that described for the synthesis of **13** from **11**.

¹H NMR (500 MHz, CDCl₃): δ = 7.03 (s, 1 H), 6.93 (s, 1 H), 3.87–3.79 (m, 4 H), 1.76–1.71 (m, 2 H), 1.62–1.23 (m, 21 H), 0.99–0.83 (m, 13 H), 0.24 (s, 9 H); ¹³C NMR (126 MHz, CDCl₃): δ = 154.9, 149.3, 117.54, 117.47, 113.5, 112.2, 100.6, 99.0, 72.3, 71.9, 39.6, 39.4, 30.5, 29.1, 29.0, 23.87, 23.86, 23.1, 23.0, 14.10, 14.08, 11.3, 11.1.

Synthesis of 1,4-Bis[(2-ethylhexyl)oxy]-2-ethynyl-5iodobenzene (15)

Tetrabutylammonium fluoride (1.0 M solution in THF, 51.5 mL, 51.5 mmol) was added to a solution of **13** (26.03 g, 46.77 mmol) in THF (400 mL) at room temperature, and the whole mixture was stirred at room temperature for 14 h. Then, ethyl acetate was added, and the mixture was washed with water and saturated aqueous NH₄Cl, dried over anhydrous MgSO₄, and concentrated *in vacuo*. The residue was purified by means of column chromatography (SiO₂, hexane) to afford **15** as a reddish brown oil (20.64 g, 94%).

¹H NMR (600 MHz, CDCl₃): δ = 7.28 (s, 1 H), 6.85 (s, 1 H), 3.84 (d, *J* = 6.2 Hz, 2 H), 3.82 (d, *J* = 6.2 Hz, 2 H), 3.27 (s, 1 H), 1.74 (m, *J* = 6.2 Hz, 2 H), 1.59–1.27 (m, 16 H), 0.95–0.87 (m, 12 H); ¹³C NMR (150 MHz, CDCl₃): δ = 155.1, 151.7, 123.6, 116.2, 112.2, 88.0, 81.7, 79.7, 72.3, 72.1, 39.40, 39.35, 30.5, 30.4, 29.03, 29.01, 23.9, 23.8, 23.01, 23.00, 14.08, 14.05, 11.2, 11.1.

Synthesis of 1,4-Bis[(2-ethylhexyl)oxy]-2-ethynyl-5bromobenzene (16)

The desired **16** (0.124 g, 0.28 mmol) was obtained in 95% yield from **14** (0.270 g, 0.50 mmol) in a similar manner to that described for the synthesis of **15** from **13**.



¹H NMR (500 MHz, CDCl₃): δ = 7.07 (s, 1 H), 6.96 (s, 1 H), 3.85–3.80 (m, 4 H), 3.83 (s, 1 H), 1.78–1.72 (m, 2 H), 1.58– 1.25 (m, 17 H), 0.97–0.85 (m, 12 H); ¹³C NMR (126 MHz, CDCl₃): δ = 154.9, 149.4, 118.0, 117.8, 113.9, 111.2, 81.5, 79.5, 72.32, 72.26, 39.4, 39.3, 30.4, 29.0, 23.86, 23.84, 23.0, 14.0, 11.1.

Synthesis of (*E*)-2-{2-[(2,5-Bis((2-ethylhexyl)oxy)-4-iodophenyl)]vinyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3)

A Schlenk flask was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. To a solution of diisopinocampheylborane (4.95 mmol), prepared from BH₃-SMe₂ (0.47 mL, 4.95 mmol) and α -pinene (1.387 g, 10.18 mmol) in THF (2.5 mL), a solution of 15 (3.637 g, 7.51 mmol) in THF (3.7 mL) was added at -35 °C. The mixture was stirred for 6.5 h at 0 °C, and a solution of acetaldehyde (3.0 mL, 53.12 mmol) in THF (2.5 mL) was added. This mixture was refluxed for 12 h, cooled to room temperature, and concentrated in vacuo. After the addition of a solution of pinacol (0.779 g, 6.59 mmol) in THF (2.0 mL), the reaction mixture was stirred for 13 h at room temperature and concentrated in vacuo. The resulting residue was purified by means of column chromatography (SiO₂, hexane/triethylamine/ethyl acetate = 50/1/1) to afford (*E*)-3 as a brownish-red oil (0.253 g, 55%).

¹H NMR (600 MHz, CDCl₃): δ = 7.69 (d, *J* = 18.5 Hz, 1 H), 7.24 (s, 1 H), 6.98 (s, 1 H), 6.14 (d, *J* = 18.5 Hz, 1 H), 3.84– 3.60 (m, 4 H), 1.79–1.71 (m, 2 H), 1.62–1.18 (m, 37 H), 0.99–0.84 (m, 16 H); ¹³C NMR (150 MHz, CDCl₃): δ = 152.2, 151.6, 143.6, 127.8, 123.9, 109.6, 87.4, 83.2, 72.3, 72.1, 39.43, 39.41, 30.6, 30.5, 29.04, 29.03, 27.8, 23.99, 23.94, 23.06, 22.98, 14.09, 14.08, 11.2.

Synthesis of (*E*)-2-{2-[4-Bromo-(2,5-bis((2ethylhexyl)oxy)phenyl)]vinyl}-4,4,5,5-tetramethyl-1,3,2dioxaborolane (4)

The desired 4 (1.462 g, 2.63 mmol) was obtained in 35% yield from **16** (3.274 g, 7.50 mmol) in a similar manner to that described for the synthesis of **3** from **15**.

¹H NMR (500 MHz, CDCl₃): $\delta = 7.69$ (d, J = 18.6 Hz, 1 H), 7.09 (s, 1 H), 7.06 (s, 1 H), 6.13 (d, J = 18.6 Hz, 1 H), 3.86– 3.60 (m, 4 H), 1.81–1.72 (m, 2 H), 1.59–1.19 (m, 28 H), 0.99–0.84 (m, 12 H); ¹³C NMR (126 MHz, CDCl₃): $\delta = 151.3$, 149.8, 143.4, 126.8, 117.9, 113.2, 111.2, 83.2, 77.2, 773, 77.2, 39.40, 39.35, 30.6, 30.5, 29.6, 29.0, 24.83, 24.79, 24.0, 23.9, 23.03, 22.98, 14.08, 11.16, 11.12.

Synthesis of (*E*)-4-(2-Bromovinyl)-2,5-bis[(2ethylhexyl)oxy]phenylboronic Acid (5)

A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. Bromoviny-liodobenzene 2' (2.716 g, 4.80 mmol) was placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (24 mL) was added to the flask via a syringe, and the mixture was stirred at 0 °C. ⁱPrMgCl (2.0 M

solution in THF, 2.4 mL, 4.8 mmol) was added via a syringe, and stirring was continued at 0 °C for 2 h. A solution of triisopropyl borate (1.825 g, 9.70 mmol) in dry THF (12 mL) was added via a syringe at -78 °C. After 2 h, the reaction mixture was warmed to room temperature and stirred for an additional 1.5 h. Then, the reaction was quenched with 1 M HCl, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with saturated aqueous NaHCO₃ and brine, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residue was recrystallized from hexane to give (*E*)-**5** as a white solid (1.413 g, 61%): mp 80.5–83.0 °C.

¹H NMR (600 MHz, CDCl₃): δ = 7.33 (s, 1 H), 7.31 (d, J = 14.0 Hz, 1H), 7.02 (d, J = 14.0 Hz, 1H), 6.79 (s, 1 H), 5.80 (s, 2H), 3.94–3.90 (m, 4 H), 1.78–1.72 (m, 2 H), 1.56–1.27 (m, 16 H), 0.97–0.88 (m, 12 H); ¹³C NMR (150 MHz, CDCl₃): δ = 158.1, 150.5, 133.1, 128.3, 119.7, 110.0, 109.4, 71.4, 71.2, 39.54, 39.50, 30.73, 30.66, 29.08, 29.02, 24.10, 24.07, 23.01, 22.94, 14.05, 14.01, 11.16, 11.09.

General Procedure for Kumada-Tamao Coupling Polymerization

All glass apparatus were dried prior to use. Addition of reagents to a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask equipped with a three-way stopcock containing lithium chloride (0.2 mmol) was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. Monomer precursor $\mathbf{1}'$ or 2' (0.2 mmol) was placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (1.0 mL) was added to the flask via a syringe, and the mixture was stirred at 0 °C. ⁱPrMgCl (2.0 M solution in THF, 0.1 mL, 0.2 mmol) was added via a syringe, and stirring was continued. A suspension of Ni catalyst (0.010 mmol, 5.0 mol %) in dry THF (1.0 mL) was added via a syringe, and stirring was continued at room temperature. After 24-60 h, 5 M hydrochloric acid was added. The mixture was extracted with chloroform, and the organic layer was washed with water, dried over anhydrous MgSO₄, and concentrated under reduced pressure to give PPV.

General Procedure for Suzuki-Miyaura Coupling Polymerization

All glass apparatus were dried prior to use. Addition of reagents into a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. Monomer **3**, **4**, or **5** (0.1 mmol), base (0.45 mmol), and dried 18-crown-6 (0.8 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (7.5 mL) and distilled water (0.5 mL) were added to the flask via a syringe, and the mixture was degassed with



SCHEME 2 Synthesis of monomer precursors 1'-2' and monomers 3-5.

argon. This mixture was added to a solution of **6** or **7** (0.005 mmol, 5.0 mol %) in dry THF (5.0 mL, degassed with argon), via a cannula, and the reaction mixture was stirred at room temperature. After 24–170 h, 1 M hydrochloric acid was added. The mixture was extracted with chloroform, and the organic layer was washed with water, dried over anhydrous MgSO₄, and concentrated under reduced pressure to give PPV.

RESULTS AND DISCUSSION

Synthesis of Monomer Precursors and Monomers

For a comprehensive study of CTCP leading to PPV, we prepared monomer precursors 1' and 2' for Ni-CTCP and monomers **3–5** for Pd-CTCP according to Scheme 2.

The iodine atom in $\mathbf{1}'$ and $\mathbf{2}'$ was expected to undergo selective Grignard-halogen exchange reaction to generate Grignard monomers containing bromine atom in a similar manner to that in which bromothiophene Grignard monomers were generated from bromoiodothiophenes in Ni-CTCP.^{7(a-d)} To increase the solubility of PPV, 2-ethylhexyloxy groups were

introduced into all the monomers. Iodovinyl bromobenzene 1' was synthesized by the reaction of **8**, which was obtained according to the reported method,²² with $CrCl_2$ and iodoform.²⁷ The obtained 1' is a mixture of trans and cis forms, which could not be separated, and thus, this mixture was used for polymerization. Bromovinyl iodobenzene 2' was prepared from 4-iodobenzaldehyde 9.²³ Wittig-type reaction of **9** with CBr₄ afforded dibromovinyl compound **10**, which was then subjected to reaction with diethyl phosphite in trie-thylamine, affording 2' with high (*E*) selectivity.²⁸

In contrast to Grignard-type monomers, boronic acid or boronic acid ester monomers are generally stable in air and can be isolated. Vinyl boronic acid ester monomers **3** and **4** were prepared by introduction of an ethynyl group into **11** and **12**,²⁴ followed by hydroboration of the ethynyl group.²⁹ Phenylboronic acid monomer **5** was obtained by selective boration of iodine of **2**' via iodo-Grignard exchange reaction.

Kumada-Tamao Coupling Polymerization of 1 and 2

When the same π -conjugated polymers are synthesized via Ni-CTCP and via Pd-CTCP, Ni-CTCP generally affords



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SCHEME 3 Polymerization of 1 and 2 for the synthesis of PPV.

polymers with lower polydispersity and higher molecular weight. For example, P3HT obtained with Ni-CTCP and with Pd-CTCP showed $M_{\rm n} = 17,200,$ $M_{\rm w}/M_{\rm n} = 1.26$ and $M_{\rm n} = 10,900, M_{\rm w}/M_{\rm n} = 1.56$, respectively.^{7(c),14} To understand the reason for these results, Nakamura and coworkers³⁰ investigated kinetic isotope effects in oxidative addition of haloarenes to Ni and Pd(0) catalyst and carried out theoretical calculations, and they concluded that the key irreversible processes are π -complexation with the Ni catalyst and oxidative addition to the Pd catalyst following π -complexation, respectively. In other words, once a Ni/haloarene π -complex forms, it does not dissociate and proceeds quickly to the oxidative addition step in an intramolecular manner. On the other hand, the Pd catalyst can dissociate from the Pd/haloarene π -complex. These results account for the better control in Ni-CTCP. Accordingly, Grignard-type phenylenevinylene monomers 1 and 2 were first polymerized under Ni-CTCP conditions (Scheme 3). To our knowledge, there is no previous report of PPV synthesis even by means of conventional Ni-catalyzed Kumada-Tamao coupling polycondensation.

Monomer precursor $\mathbf{1}'$ was converted to Grignard monomer $\mathbf{1}$ by treatment with 1 equiv of ^{*i*}PrMgCl in THF at room temperature for 3 h (conversion of $\mathbf{1}' = 90\%$). It was confirmed by means of ¹H NMR and GC analysis that the iodine at the C=C of $\mathbf{1}'$ was exclusively converted to a chloromagnesio group. Polymerization of $\mathbf{1}$ was then carried out by the addition of Ni(dppp)Cl₂, which is suitable for the synthesis of well-defined P3HT, to the reaction mixture; however, polymerization of $\mathbf{1}$ did not proceed. In the initiation step of Ni-CTCP, Ni(dppp)Cl₂ reacts with 2 equiv of monomers, and reductive elimination occurs with concomitant generation of a Ni(0) complex, which is inserted into the intramolecular C—Br bond. In the case of 1, however, diene was formed by initiation. This would strongly coordinate to the Ni catalyst, which might be responsible for inhibiting polymerization (Scheme 4).

To support this speculation, model reaction of phenylmagnesium bromide and 4-bromotoluene was carried out in the presence of 5 mol % of Ni(dppp)Cl₂ and (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene as a diene, resulting in no progress of the reaction (Supporting Information Fig. S1). In addition, it has been reported that Kumada-Tamao coupling reaction of vinyl Grignard reagents exhibits relatively low reactivity.³¹

We next examined polymerization of aryl Grignard monomer 2. Precursor 2' was converted to 2 by treatment with 1 equiv of ⁱPrMgCl in THF at 0 °C (conversion of 2' = 100%). Polymerization of 2 was then carried out by the addition of Ni(dppp)Cl₂ to the reaction mixture at room temperature to afford an oligomer ($M_n = 1990$, $M_w/M_n = 1.37$; Table 1, Entry 1). In an attempt to obtain high-molecular-weight PPV, the polymerization was conducted with several Ni catalysts having different ligands; however, oligomers of similar molecular weight were obtained (Table 1, Entries 2–5).

These results implied that termination reactions occur in this polymerization. Accordingly, the polymer end groups were analyzed by means of MALDI-TOF mass spectrometry using dithranol (1,8-dihydroxy-9[10H]-anthracenone) as a matrix. The spectrum of polymer obtained with Ni(dppp)Cl₂ showed several series of peaks (Fig. 1). The major peaks can be assigned to polymer in which one end group is THF and the other is a bromine atom (designated as THF/Br). It has already been reported that electron-rich aryl Grignard reagents react with THF through a radical pathway.³² Peaks due to THF/H-ended polymers were also observed. There were also two other series of minor peaks assignable to Br/Br- and Br/H-ended polymers, as well as a number of peaks that could not be assigned. If Ni-CTCP proceeds, the propagating end group should be PPV-Ni-Br, which cannot react with THF. Therefore, the THF-ended polymer was presumably generated by reaction of THF with Grignard-ended polymer formed through a conventional step-growth polymerization mechanism.



SCHEME 4 Proposed initiation reaction mechanism of 1 with Ni catalyst.

Entry	Solvent	Catalyst	Time (h)	Temperature (°C)	$M_{\rm n}~(M_{\rm w}/M_{\rm n})^{\rm b}$
1	THF	Ni(dppp)Cl ₂	60	Room temperature	1,990 (1.37)
2	THF	Ni(dppf)Cl ₂	24	Room temperature	1,850 (1.35)
3	THF	Ni(dppe)Cl ₂	24	Room temperature	2,140 (1.34)
4	THF	Ni(PPh ₃)Cl ₂	24	Room temperature	2,050 (1.40)
5	THF	Ni(dppp)Cl ₂	24	70	1,670 (1.25)
6	Et ₂ O	Ni(dppp)Cl ₂	24	Room temperature	1,860 (1.56)

standards (eluent: THF).

TABLE 1 Polymerization of 2 with various catalysts^a

^a Polymerization of **2** ($[\mathbf{2}]_0 = 0.1$ M) was carried out by the treatment of **2**' with 1.0 equiv of ⁱPrMgCl in the presence of LiCl, followed by the addition of 5.0 mol % of catalyst.

The polymerization was also carried out in diethyl ether instead of THF; however, similar oligomers were obtained (Entry 6). The MALDI-TOF mass spectrum did not show peaks of polymer ends reacted with diethyl ether (see Supporting Information Fig. S2); however, multiple unknown series of peaks were observed. Consequently, we concluded that elementary Kumada-Tamao coupling reaction using Ni-CTCP was not suitable for the synthesis of PPV.

Suzuki-Miyaura Coupling Polymerization of 3 and 4

Pd-CTCP proceeds under less basic conditions when compared with Ni-CTCP, and stable arylpalladium(II) halide complex can be used as an externally added initiator.¹² Moreover, Pd-catalyzed cross-coupling polymerization is more common for the synthesis of PPV than Ni-catalyzed polymerization,³³ and Suzuki-Miyaura coupling polymerization with a conventional Pd catalyst is often used.³⁴ Accordingly, we next examined Pd-CTCP for the synthesis of well-defined PPV. The polymerization of vinylboronic acid ester monomers **3** and **4** is described in this section, and the polymerization of phenyleneboronic acid monomer **5** in the following section (Scheme 5).

Polymerization of **3** with a Pd initiator **6** $([3]_0/[6]_0 = 20)$ was first carried out in the presence of CsF/18-crown-6 in THF containing a small amount of water at room temperature, in a similar manner to the case of Pd-CTCP for the synthesis of well-defined PPP¹³ and P3HT.¹⁴ However, the polymerization was considerably slower than Pd-CTCP leading to PPP and P3HT, and 3 remained even after 6 days, resulting in the formation of oligomer (Table 2, Entry 1). The polymerization of **3** was then carried out at 60 °C or with higher monomer concentration (from 8.33 imes 10⁻³ M to 2.50 \times 10⁻² M); however, high-molecular-weight polymer was not obtained (Table 2, Entries 2 and 3). The MALDI-TOF mass spectra of the obtained oligomer (Table 2, Entry 2) showed two series of peaks: one is oligomer with a phenyl group from the Pd initiator 6 at one end, and the other is oligomer with boronic acid pinacol ester or boronic acid group, formed by hydrolysis of the ester, at one end (Supporting Information Fig. S3). This result indicated that Pd-CTCP proceeded concomitantly with intermolecular transfer of the catalyst (chain transfer).

^b Estimated by gel permeation chromatography based on polystyrene

We next examined various bases. Common bases for Suzuki-Miyaura coupling reaction, such as K_2CO_3 , K_3PO_4 , and KOH,



FIGURE 1 MALDI-TOF mass spectra of products obtained by the polymerization of **2** with 5.0 mol % of Ni(dppp)Cl₂ in THF ([**2**]₀ = 0.1 M) at room temperature for 60 h (M_n = 1990, M_w / M_n = 1.37). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 5 Polymerization of 3-5 for the synthesis of PPV.

Entry	Monomer	Base	Temperature (°C)	Time	$M_{\rm n}~(M_{\rm w}/M_{\rm n})$
1 ^a	3	CsF/18-crown-6	Room temperature	144 h	2,630 (2.91) ^o
2 ^a	3	CsF/18-crown-6	60	144 h	2,630 (4.53) ⁶
3 ^b	3	CsF/18-crown-6	Room temperature	24 h	3,410 (2.61) ^o
4 ^b	3	K ₂ CO ₃	Room temperature	128 h	1,120 (1.06) ^o
5 ^b	3	K ₃ PO ₄	Room temperature	126 h	1,160 (1.08) ^o
6 ^b	3	КОН	Room temperature	79 h	2,400 (1.73) ^o
7 ^b	3	KOH/18-crown-6	Room temperature	5 min	5,940 (2.00)
8 ^b	3	KOH/18-crown-6	0	5 min	6,320 (2.06)
9 ^b	3	KOH/18-crown-6	-20	30 min	9,580 (2.26)
10 ^b	4	KOH/18-crown-6	Room temperature	5 min	6,410 (2.68)
11 ^b	4	KOH/18-crown-6	-20	30 min	9,450 (2.59)

TABLE 2 Polymerization of 3 or 4 with 5.0 mol % of 6 and various bases

^a $[\mathbf{3}]_0 = 8.33 \times 10^{-3}$ M.

 $^{\rm b}$ [3 or 4] $_{\rm 0}\,{=}\,2.50\,{\times}\,10^{-2}$ M.

did not work well, and monomer remained (Table 2, Entries 4–6). However, when KOH was used in combination with 18crown-6, the polymerization became dramatically fast, and monomer **3** was consumed within 5 min. The molecular weight was increased, but the molecular weight distribution was broad (Table 2, Entry 7). Anticipating that polymerization would be better controlled at low temperature, we conducted polymerization at 0 and -20 °C. The polymerization at 0 °C was still fast, being completed within 5 min, but the polydispersity was broad (Table 2, Entry 8). The polymerization proceeded even at -20 °C, and the M_n reached about 9600. Unfortunately, however, the polydispersity was more than 2.0 (Table 2, Entry 9).

To see how the polymerization proceeded, the end groups of the PPV obtained at -20 °C for 5 min and 30 min were analyzed by MALDI-TOF mass spectrometry (Fig. 2).

^c Monomer remained.

In the spectrum of PPV obtained at 5 min, two major series of peaks corresponding to polymer with a phenyl group at one end and an iodine atom at the other (Ph/I) and to Ph/ H-ended polymer were observed. Several other minor series of peaks were assigned to polymers ended with (boronic acid ester)/H or I, B(OH)₂/H or I, and H/H, which would not have been initiated by the Pd complex 6. In the polymerization for 30 min, the polymer ends surprisingly became almost uniform as Ph/H. These results implied that the polymerization of **3** was initiated by the Pd catalyst **6** and proceeded with intermolecular transfer of the Pd catalyst to afford boron-ended polymer. In the final stage, the boronended polymer reacted with Ph/I-ended polymer, followed by deiodination of the polymer end group to yield PPV with Ph/H. Deiodination in Pd-catalyzed Suzuki-Miyaura coupling polymerization has been reported by Janssen and coworkers.35



FIGURE 2 MALDI-TOF mass spectra of products obtained by the polymerization of **3** in the presence of KOH/18-crown-6 and 5.0 mol % of **6** in THF ([**3**]₀ = 2.50 × 10⁻² M) and water at -20 °C for (a) 5 min (M_n = 4360, M_w/M_n = 2.03) and (b) 30 min (M_n = 9580, M_w/M_n = 2.26).

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Moreover, the polymerization of **3** was carried out with bis[tris(tert-butyl)phosphine]palladium(0) instead of **6** under similar conditions. This Pd catalyst would not introduce a terminal group, such as the phenyl group in the case of **6**, but would afford polymer with boron/I ends during polymerization, which should result in higher molecular weight polymer via coupling reaction between these polymers. However, the molecular weight and molecular weight distribution were similar to those in the case of the polymerization with **6** (Fig. 3). Furthermore, not iodine but hydrogen atom was present at one end of the obtained polymer. These results suggested that the molecular weight and molecular weight distribution in the polymerization of **3** with **6** were governed by deiodination.

Expecting that dehalogenation of bromine would be suppressed, when compared with iodine, we next attempted the polymerization of bromo monomer **4** instead of iodo monomer **3**. The polymerization of **4** was still fast: **4** was consumed within 5 min at room temperature and within 30 min at -20 °C (Table 2, Entries 10 and 11). The obtained polymers showed similar molecular weight and polydispersity. The MALDI-TOF mass spectra showed major Ph/Br peaks and minor Ph/H, Bpin (boronic acid ester)/Br, and B(OH)₂/Br peaks in the middle stage and uniform Ph/H peaks in the final stage (Supporting Information Fig. S4). Consequently, it turned out that dehalogenation was not suppressed under this condition even when the halogen atom in the monomer was changed from iodine to bromine.

Suzuki-Miyaura Coupling Polymerization of 5

The polymerization of **3** and **4** required a stronger base, KOH, contrary to the case of Pd-CTCP with CsF for the synthesis of PPP¹³ and P3HT,¹⁴ and we considered that the strong base might induce dehalogenation. The low reactivity of **3** with CsF was presumably due to the low reactivity of



FIGURE 3 Gel permeation chromatography profiles of PPV obtained by the polymerization of **3** in the presence of KOH/18-crown-6 and 5.0 mol % of **6** or bis[tri(*tert*-butylphosphine)]palladium(0) in THF ([**3**]₀ = 2.50 × 10⁻² M) and water at room temperature: (1) **6** for 5 min (M_n = 5940, M_w/M_n = 2.00) and (2) bis[tri(*tert*-butylphosphine)]palladium(0) for 5 min (M_n = 6320, M_w/M_n = 2.01).

vinylborane, analogously with the low reactivity of vinyl Grignard reagent in Kumada-Tamao coupling reaction.³¹ On the other hand, monomer 5 bearing the boronic acid group on the benzene ring is expected to undergo polymerization with CsF, because the monomer leading to well-defined PPP with CsF has the same phenylboronic acid moiety.¹³ In the polymerization of 5, ${}^{t}Bu_{3}PPd(o-tolyl)Br$ (7) was used as an initiator instead of 6, as the phenyl group, which is introduced at the polymer end group from 6, and bromine is sometimes difficult to distinguish in MALDI-TOF mass spectra due to the similar molecular weights of the phenyl group and bromine atom. Thus, polymerization of 5 was carried out with the Pd initiator 7 in the presence of CsF/18-crown-6 at room temperature in a similar manner to the case of polymerization of 3 and 4. Contrary to our expectation, however, the polymerization was slow, and 5 remained even after a week. When KOH/18-crown-6 was used, the polymerization was completed within 2.5 min to yield high-molecular-weight PPV with a broad molecular weight distribution (Table 3). The different reactivity of 5 from the PPP monomer can presumably be accounted for by the different electron density of the benzene ring conjugated with a carbon-carbon double bond at the para position.

The MALDI-TOF mass spectra of PPV obtained by the use of CsF/18-crown-6 as a base showed tolyl/tolyl, tolyl/Br, tolyl/ H, H/Br, and H/H peaks (Fig. 4). As described above, polymers with tolyl/Br and tolyl/H ends would be obtained by initiation with the Pd initiator 7, and polymers with H/Br and H/H ends would be formed by intermolecular transfer of the Pd catalyst to monomer. The tolyl/tolyl-ended polymer is unique to the polymerization of 1-5 and can be accounted for by disproportion of tolyl-ended PPV-Pd(II)Br to PdBr₂ and (tolyl-ended PPV)₂Pd(II), affording PPV with tolyl/tolyl ends via reductive elimination (Scheme 6). The tendency for occurrence of disproportionation in the polymerization of monomer 5, in contrast to monomers 3 and **4**, can presumably be attributed to π -electron coordination of C=C adjacent to the Pd-Br end to the Pd in another C=C-Pd-Br end (Scheme 6). This disproportionation was supported by model reaction of (E)-(2-bromovinyl)benzene and Pd(P^tBu₃)₂, yielding (1E,3E)- 1,4-diphenylbuta-1,3-diene via disproportionation of PhCH=CH-Pd(P^tBu₃)-Br complex (Supporting Information).

Such disproportionation was also observed in the synthesis of poly[2-(dioxalkyl)pyridine-3,6-diyl] in Ni- and Pd-CTCP under similar conditions, owing to coordination of pyridine nitrogen adjacent to the carbon-M-Br (M = Ni or Pd) end to the M in another pyridine-M-Br end.²⁶ Consequently, it turns out that disproportionation of the vinylene-Pd-Br propagating end is liable to occur in Suzuki-Miyaura coupling polymerization of **5**. The MALDI-TOF mass spectrum of the polymer obtained with KOH/18-crown-6 did not show a bromine atom end, indicating that debromination also occurred when strong base was used (Supporting Information Fig. S5).



Entry	Base	Temperature	Time	$M_{\rm n}~(M_{\rm w}/M_{\rm n})$
1	CsF/18-crown-6	Room temperature	170 h	1,700 (2.16) ^a
2	KOH/18-crown-6	Room temperature	2.5 min	9,870 (3.75)

^a Monomer remained.



FIGURE 4 MALDI-TOF mass spectra of PPV obtained by the polymerization of **5** in the presence of CsF/18-crown-6 and 5.0 mol % of **7** in THF ([**5**]₀ = 8.33×10^{-3} M) and water at room temperature for 170 h ($M_n = 1700$, $M_w/M_n = 2.16$): (a) whole spectrum and (b) magnification of the spectrum between m/z = 2150-2550.

CONCLUSIONS

The feasibility of Ni-CTCP (Kumada-Tamao coupling polymerization) and Pd-CTCP (Suzuki-Miyaura coupling polymerization) for the synthesis of well-defined PPV was investigated. In Ni-CTCP, vinyl Grignard type monomer **1** did not undergo polymerization, whereas aryl Grignard type monomer **2** afforded oligomers with low molecular weight. The MALDI-TOF mass spectra indicated that the Grignard end group reacted with THF as a reaction solvent to terminate polymerization. In Pd-CTCP, vinyl boronic acid ester type monomers **3** and **4** and phenylboronic acid type monomer **5** underwent very fast polymerization in the presence of KOH/18-crown-6 to afford high-molecular-weight PPV with a broad molecular weight distribution. The MALDI-TOF mass spectra of the polymers obtained from **3** and **4** indicated that polymerization was accompanied with intermolecular chain transfer of



SCHEME 6 Proposed polymerization mechanism of 5 with 7.

the Pd catalyst and dehalogenation of the polymer terminal halogen. In the case of polymerization of **5**, disproportionation of the polymer-Pd-Br complex took place, probably due to π -electron coordination of the carbon-carbon double bond (C=C) adjacent to the Pd-Br end to the Pd in another C=CPd-Br end. Therefore, controlled synthesis of PPV by means of Pd-CTCP turned out to be difficult, even though high-molecular-weight PPV was obtained. We are now investigating the reason why intermolecular transfer of the catalyst occurs in the polymerization of monomers containing C=C, and we are also examining other coupling polymerization methods for the synthesis of well-defined PPV.

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