## **Supplementary Information For:**

# Ping-Pong Polymerization by Allylation and Hydroformylation for Alternating Vinyl Alcohol/Vinyl Monomer Copolymers

Shingo Ito,\* Masaki Noguchi, and Kyoko Nozaki\*

Department of Chemistry and Biotechnology, Graduate School of Engineering The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

#### **Experimental Section**

**General**: All manipulations were carried out using standard Schlenk techniques under argon purified by passing through a hot column packed with BASF catalyst R3-11. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Analytical thin-layer chromatography was performed using glass plates pre-coated with silica gel impregnated with a fluorescent indicator (Merck, #1.15685.0001). TLC plates were visualized by immersion in an acidic staining solution of *p*-anisaldehyde followed by heating on a hot plate. Silica gel column chromatography was performed as described by Still et al.,(1), employing silica gel 60N (spherical, neutral) purchased from Kanto Chemical Co. Inc. (Kanto). Reversed-phase column chromatography was performed with Chromatorex ODS DM1020T (Fuji Silysia Chemical, Ltd., 100-200 mesh).

**Instrumentation.** NMR spectra were recorded on JEOL JNM-ECP500 (<sup>1</sup>H: 500 MHz, <sup>13</sup>C: 126 MHz with digital resolution of 0.239, 0.960 Hz, respectively) or JEOL JNM-ECS400 (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 101 MHz with digital resolution of 0.0913, 0.767 Hz, respectively) NMR spectrometers. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8400 spectrometer or JASCO FT-IR-6100 equipped with an attenuated total reflection (ATR). Size-exclusion chromatography (SEC) analyses were carried out using two columns (Shodex KF-804 L) using tetrahydrofuran (THF) as an eluent at 40 °C. The molecular weight was calibrated against standard polystyrene samples. Mass spectra (MS) are taken with an ESI (Electron

Spray Ionization) method on a JEOL JMS-T100LP mass spectrometer and with an MALDI (Matrix-Assisted Laser Desorption/Ionization) method on a JEOL JMS-S3000 SpiralTOF mass spectrometer. Differential scanning calorimetry (DSC) measurements of polymers were performed on a Seiko DSC 7020 analyzer at a heating and cooling rate of 10 °C/min. The reported  $T_g$  values were determined from the second cooling scan. Thermogravimetric (TG) analyses were performed on a Seiko EXSTAR 6000 TG/DTA 6200 analyzer at a heating rate of 10 °C/min. X-ray diffraction (XRD) analyses were performed on a Anton Parr SAXSess mc<sup>2</sup> instrument. Elemental analysis was performed by the Microanalytical Laboratory, Department of Chemistry, Graduate School of Science, The University of Tokyo.

**Materials.** Anhydrous THF, and toluene were purchased from Kanto and purified by the method of Pangborn *et al.*(2) Syngas (H<sub>2</sub>/CO = 1/1) was purchased from Takachiho Chemical Industrial Co. and used as received. The following compounds were purchased from commercial suppliers and used as received: Rh(acac)(CO)<sub>2</sub> (Aldrich), PPh<sub>3</sub> (Kanto), 2-naphthaldehyde (Tokyo Chemical Industry, Co. Ltd. (TCI)), *t*-BuOK (Wako Pure Chemical Industries, Ltd.), 3-methylbut-1-ene (TCI), (*E*)-1-phenyl-1-propene (TCI), BuLi (hexane solution, Kanto), triisopropyl borate (TCI), (*L*)-(+)-dimethyl tartrate (TCI), and (*L*)-(+)-diisopropyl tartrate (TCI). The following compounds were prepared according to literature procedures: (*E*)-2-(but-2-en-1-yl)-1,3,2-dioxaborolane (**2**),(3) (*E*)-2-(but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*E*:*Z* = ~9:1) (**1**),(*4*), diisopropyl (4*R*,5*R*)-2-[(*E*)-but-2-en-1-yl]-1,3,2-dioxaborolane (*E*:*Z* = ~9:1) (**3**),(5) 9,9-dimethyl-4,5-bis(diphenyl-phosphino)xanthene (Xantphos).(6)

## Preparation of Diisopropyl (4*R*,5*R*)-2-(3-phenylprop-2-en-1-yl)-1,3,2-dioxaborolane-4,5dicarboxylate (4)



To a mixture of *t*-BuOK (5.61 g, 50 mmol) and (*E*)-1-phenylprop-1-ene (6.49 mL, 50 mL) in THF (50 mL), BuLi (a 2.76-M solution in hexane, 18.1 mL, 50 mmol) was added and the reaction mixture was stirred at -78 °C overnight. After addition of triisopropyl borate (11.5 mL, 50 mmol) at -78 °C, and the mixture was stirred at -78 °C for 3 h and then was warmed to 0 °C. The reaction was quenched with aqueous HCl (1 M) solution (50 mL) and aqueous NH<sub>4</sub>Cl saturated solution (50 mL). After stirring at room temperature for 1h, the organic layer

was separated and the aqueous layer was extracted with Et<sub>2</sub>O (50 mL×4). The combined extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated in vacuo to *ca*. 30 mL. The crude mixture was dissolved in Et<sub>2</sub>O (50 mL) and treated with (*L*)-(+)-diisopropyl tartrate (10.4 mL, 50 mmol) and MgSO<sub>4</sub>. The mixture was stirred at room temperature overnight and then was concentrated in vacuo to *ca*. 20 mL. The titled compound (*E*:*Z* = >9:1) was used as a mixture with (*L*)-(+)-diisopropyl tartrate in toluene after titration by <sup>1</sup>H NMR analysis using bromoform as an internal standard; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.33 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.30 (dt, *J* = 15.8, 7.7 Hz, 1H), 5.12 (sept, *J* = 6.2 Hz, 2H), 4.80 (s, 2H), 2.08 (d, *J* = 7.3 Hz, 2H), 1.29 (d, *J* = 6.4 Hz, 12H).

Preparation of Dimethyl (4*R*,5*R*)-2-(3-methylbut-2-en-1-yl)-1,3,2-dioxaborolane-4,5dicarboxylate (5)



In an 80-mL Schlenk tube containing THF (10 mL) was condensed 3-methylbut-1-ene (15 mL) at -78 °C. The solution was transferred to another 500 mL three-necked flask placed with t-BuOK (5.61 g, 50 mmol) in THF (65 mL). To the resulting mixture was added BuLi (a 2.66-M solution in hexane, 18.8 mL, 50 mmol), and the reaction mixture was stirred at -78 °C overnight. After addition of triisopropyl borate (11.5 mL, 50 mmol) at -78 °C, the mixture was stirred at -78 °C for 2 h and then was warmed to 0 °C. The reaction was guenched with aqueous HCl solution (1 M, 50 mL) and aqueous NH<sub>4</sub>Cl saturated solution (50 mL). After stirring at room temperature for 1 h, the organic layer was separated and the aqueous layer was extracted with  $Et_2O$  (50 mL  $\times$  4). The combined extracts were dried over  $Na_2SO_4$ , filtrated, and concentrated in vacuo to ca. 30 mL. The crude mixture was dissolved in Et<sub>2</sub>O (50 mL) and treated with (L)-(+)-dimethyl tartrate (8.94 g, 50 mmol) and molecular sieves 3A. The mixture was stirred overnight at room temperature and then concentrated in vacuo to ca. 20 mL. The titled compound was used as a mixture with (L)-(+)-dimethyl tartrate in toluene after titration by <sup>1</sup>H NMR analysis using bromoform as an internal standard; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  5.26–5.19 (m, 1H), 4.89 (s, 2H), 3.82 (s, 6H), 1.79 (t, J = 7.1 Hz, 2H), 1.69 (s, 3H), 1.60 (s, 3H).

#### Synthesis of Model Compounds

To acquire more information on the reaction mechanism and the polymer characterization, step-wise hydroformylation and allylboration reactions were performed to synthesize oligo(vinyl alcohol-*alt*-propylene) **9** as a model compound (Scheme S1). Starting from an essentially single diastereomeric silyl ether **6**, successive one-pot hydroformylation and allylboration reactions at 100 °C followed by silylation afforded bis(silyl ether) 7 as a mixture of two diastereomers (dr = ca. 1.2:1). Considering that allylboration generally proceeds in a highly diastereoselective manner, this diastereoselectivity would be attributed to *like* and *unlike* relationships of neighboring anti units (See Figure S10 for detail). Further one-pot hydroformylation/allylboration reactions were performed to afford one-unit elongated oligomer **8** in 54% yield. Final desilylation led to the formation of triol **9**, which exhibited <sup>1</sup>H and <sup>13</sup>C NMR spectra (Figures S4–S6) similar to those of the polymers obtained by the present ping-pong polymerization.

**Scheme S1.** Step-wise synthesis of oligo(vinyl alcohol-*alt*-vinyl monomer)s by hydroformylation and allylboration.



Conditions: a) **1** (1.2 equiv), Et<sub>2</sub>O, rt, 24 h; b) *t*-BuMe<sub>2</sub>SiOTf (1.5 equiv), 2,6-lutidine (2.0 equiv), CH<sub>2</sub>Cl<sub>2</sub>, rt, 1.5–2 h; c) Rh(acac)(CO)<sub>2</sub> (0.5 mol%), Xantphos (1.0 mol%), H<sub>2</sub>/CO (1.5/1.5 MPa), toluene, 100 °C, 15 h. d) **1** (1.2–1.4 equiv), toluene, 100 °C, 15 h. e) Bu<sub>4</sub>NF (excess), THF, 50 °C, 18 h.

#### Synthesis of 3-Methyloct-1-en-4-yl tert-butyldimethylsilyl ether (6)



To a solution of 1-pentanal (10.0 mmol, 1.1 mL) in Et<sub>2</sub>O (10 mL) in a 20-mL Schlenk tube was added (*E*)-2-(but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-di-oxaborolane (1, 2.18 g, 12.0 mmol) at room temperature, and the reaction mixture was stirred for 24 h. The mixture was concentrated in vacuo, passed through a short pad of silica gel, and evaporated to dryness. To the crude product was added CH<sub>2</sub>Cl<sub>2</sub> (10 mL) 2,6-lutidine (2.3 mL, 20.0 mmol) and t-BuMe<sub>2</sub>SiOTf (3.5 mL, 15.0 mmol), and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with aqueous NH<sub>4</sub>Cl saturated solution (20 mL). The organic layer was separated and the aqueous layer was extracted with  $CH_2Cl_2$  (20 mL×3). The combined extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated in vacuo. Purification by silica gel column chromatography (hexane/EtOAc = 95/5) afforded 6 (8.4) mmol, 84%) as a mixture with (t-BuMe<sub>2</sub>Si)<sub>2</sub>O (ca. 2.0 mmol); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 5.78 (ddd, J = 18.7, 8.9, 6.8 Hz, 1H, H2), 5.01–4.96 (m, 2H, H1), 3.53 (td, J = 6.0, 3.9 Hz, 1H, H4), 2.34–2.24 (m, 1H, H3), 1.42–1.15 (m, 6H, H5, H6, and H7), 0.99 (d, J = 6.9 Hz, 3H, H9), 0.89 (s, 9H, H11), 0.88 (t, J = 7.1 Hz, 3H, H8), 0.03 (s, 6H, H12); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ 141.1 (C2), 114.1 (C1), 75.8 (C4), 43.1 (C3), 33.2 (C5), 27.9 (C6), 25.9 (3C, C11), 22.8 (C7), 18.1 (C10), 15.4 (C9), 14.2 (C8), -4.3 (C12), -4.5 (C12').

#### Synthesis of 8-[(tert-Butyldimethylsilyl)oxy)]-3,7-dimethyldodec-1-en-4-ol (10)



To a 50-mL autoclave containing Rh(acac)(CO)<sub>2</sub> (10.3 mg, 0.040 mmol) and Xantphos (46.3 mg, 0.080 mmol) were transferred toluene (8.0 mL) and **6** (8.4 mmol, a mixture with *ca*. 2.0 mmol of (*t*-BuMe<sub>2</sub>Si)<sub>2</sub>O) under argon atmosphere. After being charged with H<sub>2</sub>/CO (1.5/1.5 MPa), the autoclave was stirred at 100 °C for 15 h. After cooling to room temperature, (*E*)-2- (but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-di-oxaborolane (**1**, 2.06 g, 11.4 mmol) was added at room temperature and the reaction mixture was stirred at 100 °C for 15 h. After cooling to room temperature to room temperature, the mixture was concentrated in vacuo. Purification by silica gel column

chromatography (hexane/EtOAc = 10/1) afforded **10** (1.35 g, 4.1 mmol, 49% in 2 steps) as a mixture of two diastereomers (dr = *ca*. 1.2:1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  5.81–5.69 (m, 1H, H2), 5.17–5.05 (m, 2H, H1), 3.57–3.45 (m, 1H, H8), 3.41–3.32 (m, 1H, H4), 2.32–2.15 (m, 1H, H3), 1.68–1.15 (m, 11H, H5, H6, H7, H9, H10, and H11), 1.04 (d, *J* = 6.6 Hz, *ca*. 1.6H, H13), 1.03 (d, *J* = 6.9 Hz, *ca*. 1.4H, H13), 0.88 (s, 9H, H16), 0.95–0.80 (m, 6H, H12 and H14), 0.02 (br s, 6H, H17); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz):  $\delta$  [140.3, 140.2] (C2), [116.4, 116.4] (C1), [76.1, 75.9] (C8), [75.2, 74.8] (C4), [44.0, 44.0] (C3), [38.6, 38.5] (C7), [32.3, 32.2] (C5), [31.8, 31.7] (C9), [28.6, 28.3] (C6), [28.1, 28.0] (C10), 25.9 (3C, C16), 22.9 (C11), 18.1 (C15), [16.4, 16.3] (C13), [14.6, 14.5] (C14), 14.2 (C12), [-4.4, -4.4] (C17) (Multiple signals in brackets are derived from diastereomers).

Synthesis of 9-(But-3-en-2-yl)-5-butyl-2,2,3,3,6,11,11,12,12-nonamethyl-4,10-dioxa-3,11disilatridecane (7)



To a solution of **10** (1.35 g, 4.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4.0 mL) was added 2,6-lutidine (0.96 mL, 8.2 mmol) and *t*-BuMe<sub>2</sub>SiOTf (1.4 mL, 6.1 mmol), and the reaction mixture was stirred at room temperature for 1.5 h. The reaction was quenched with and aqueous NH<sub>4</sub>Cl saturated solution (20 mL). The organic layer was separated and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL × 3). The combined extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated in vacuo. Purification by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) afforded **7** (3.6 mmol, 89%, *ca*. 0.25 mmol of (*t*-BuMe<sub>2</sub>Si)<sub>2</sub>O was contaminated) as a mixture of two diastereomers (dr = *ca*. 1.2:1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  5.85–5.74 (m, 1H, H2), 5.05–4.93 (m, 2H, H1), 3.57–3.44 (m, 2H, H4 and H8), 2.33–2.24 (m, 1H, H3), 1.58–1.04 (m, 11H, H5, H6, H7, H9, H10, and H11), 1.00 (d, *J* = 6.9 Hz, 3H, H13), 0.89 (s, 9H, H16 or H19), 0.88 (s, 9H, H16 or H19), 0.90–0.80 (3H, H12, not clearly observed due to overlap of signals), 0.83 (d, *J* = 6.9 Hz, 3H, H14), 0.04–0.01 (m, 6H, H17 and H20); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz):  $\delta$  [141.1, 141.0] (C2), [114.3, 114.2] (C1), [76.2 76.1] (C4 or C8), [75.9, 75.9] (C4 or C8), 43.0 (C3), [38.8, 38.4] (C7), [31.9, 31.8] (C5 or C9), 31.7 (C5 or C9), [28.3, 28.2] (C6 or C10), 28.1 (C6 or C10), 25.9 (6C, C16 and C19), [22.9, 22.9] (C11), 18.1 (2C, C15 and C18),

[15.6, 15.5] (C13 or C14), [14.9, 14.6] (C13 or C14), 14.2 (C12), [-4.3, -4.3, -4.4, -4.4, -4.5, -4.5] (4C, C17 and C20) (Multiple signals in brackets are derived from diastereomers).

#### Synthesis of 8,12-Bis[(tert-butyldimethylsilyl)oxy]-3,7,11-trimethylhexadec-1-en-4-ol (8)



To a 50-mL autoclave containing Rh(acac)(CO)<sub>2</sub> (5.2 mg, 0.020 mmol) and Xantphos (23.2 mg 0.040 mmol) were transferred toluene (4.0 mL) and 7 (3.6 mmol, a mixture with ca. 0.25 mmol of (t-BuMe<sub>2</sub>Si)<sub>2</sub>O) under argon atmosphere. After being charged with H<sub>2</sub>/CO (1.5/1.5 MPa), the autoclave was stirred at 100 °C for 15 h. After cooling to room temperature, (E)-2-(but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-di-oxaborolane (1, 0.79 g, 4.36 mmol) was added and was stirred at 100 °C for 15 h. After cooling to room temperature, the mixture was concentrated in vacuo. Purification by silica gel column chromatography (hexane) afforded 8 (2.0 mmol, 54 %, 2 steps) as a mixture of mainly four diastereomers; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 5.82–5.70 (m, 1H, H2), 5.17–5.05 (m, 2H, H1), 3.57–3.42 (m, 2H, H8 and H12), 3.41-3.32 (m, 1H, H4), 2.30-2.12 (m, 1H, H3), 1.68-1.12 (m, 16H, H6, H7, H8, H11, H12, H13, H16, H17, and H18), 1.06–1.01 (m, 3H, H17), 0.95–0.82 (m, 6H, HH18, H19, and H20), 0.88 (s, 18H, H21 and H24), 0.03 (br s, 12H, H22 and H25); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): δ [140.6, 140.5] (C2), [116.7, 116.7] (C1), [76.9, 76.9, 76.8, 76.7, 76.5, 76.2, 76.2] (2C, C8 or C12), [75.5, 75.1, 75.1] (C4), [44.4, 44.4, 44.3, 44.2] (C3), [39.2, 39.0] (C7 or C11), [39.0, 38.9, 38.8, 38.7] (C7 or C11), [32.7, 32.6, 32.6, 32.6] (C9 or C13), [32.1, 32.0] (C9 or C13), [30.8, 30.7, 30.6, 30.6] (C5), [29.0, 28.9, 28.8, 28.6, 28.6, 28.5, 28.5] (3.5C, C6, C10, C14, and C15), 26.2 (6C, C21 and C24), [25.1, 25.1] (0.5C, one of C6, C10, C14, and C15), [23.2, 23.2] (C15), 18.5 (2C, C20 and C23), [16.7, 16.6] (C17, C18, or C19), 15.2, 15.2, 15.0, 15.0] (C17, C18, or C19), [14.9, 14.8, 14.8, 14.8] (C17, C18, or C19), 14.5 (C16), [-4.0, -4.0, -4.1, -4.1] (4C, C22 and C25) (Multiple signals in brackets are derived from diastereomers).

#### Synthesis of 3,7,11-Trimethylhexadec-1-ene-4,8,12-triol (9)



To a solution of **8** (2.0 mmol) in THF (10 mL) was added tetrabutylammonium fluoride (a 1.0 M solution in THF, excess), and the reaction mixture was stirred at 50 °C for 18 h. The mixture was concentrated in vacuo and purified by silica gel column chromatography (hexane/EtOAc = 1/2) to afford triol **9** (1.2 mmol, 60%) as a mixture of diastereomers; <sup>1</sup>H NMR (CD<sub>3</sub>OD, 500 MHz):  $\delta$  5.90–5.72 (m, 1H, H2), 5.08–4.95 (m, 2H, H1), 3.58–3.18 (m, 3H, H4, H8, and H12), 2.31–2.12 (m, 1H, H3), 1.78–1.20 (m, 16H, H5, H6, H7, H9, H10, H11, H13, H14, and H15), 0.98 (br d, *J* = 6.9 Hz, 3H, H17), 0.96–0.85 (m, 9H, H16, H18, and H19); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 101 MHz):  $\delta$  [141.7, 141.5] (C2), [115.3, 115.2] (C1), [77.0, 76.4, 76.3, 75.9] (3C, C4, C8 and C12), [45.0, 44.8] (C3), [40.4, 40.2, 40.0, 39.9, 39.8] (2C, C7 and C11), [33.8, 33.7] (C5, C9, or C13), [33.2, 33.1, 32.7] (C5, C9, or C13), [32.1, 32.0, 31.7] (C5, C9, or C13), [29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 29.2] (3C, C6, C10, and C14), 23.8 (C15), [17.0, 16.8] (C17 or C18 or C19), [16.2, 16.1, 16.0, 15.9, 15.8] (2C, C17 or C18 or C19), 14.6 (C16) (Multiple signals in brackets are derived from diastereomers).

#### General Procedure for the Ping-Pong Polymerization (entries 1–6 in Table (S)1)

To a 50-mL autoclave containing Rh(acac)(CO)<sub>2</sub> (5.2 mg, 0.020 mmol) and Xantphos (23.2 mg, 0.040 mmol) were transferred toluene (4.0 mL) and allylic boronate (10.0 mmol) under argon atmosphere. After being charged with H<sub>2</sub>/CO (1.5/1.5 MPa), the autoclave was stirred at 100 °C for 24 h. After cooling to room temperature, the volatile matters were removed under vacuum. The copolymer was hydrolyzed with NaOH in H<sub>2</sub>O/THF under reflux conditions. Then, the organic layer was separated, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and evaporated to dryness. The polymer was further purified by reversed-phase column chromatography for DSC, XRD, and elemental analyses.

#### General Procedure for the Ping-Pong Polymerization (entries S1–S12 in Table S1)

To a 50-mL autoclave containing  $Rh(acac)(CO)_2$  (0.02–0.05 mmol), Xantphos (0.04–0.10 mmol), and 2-naphthaldehyde (0.10 mmol) were transferred solvent (toluene or THF; 4.0–10.0 mL) and allylic boronate (4.0 mmol or 10.0 mmol) under argon atmosphere. After being charged with H<sub>2</sub>/CO (1.5/1.5 MPa), the autoclave was stirred at 80–100 °C for 3 h–7 d. After

cooling to room temperature, the volatile matters were removed under vacuum. The copolymer was hydrolyzed with NaOH in  $H_2O/THF$  under reflux conditions. Then, the organic layer was separated, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and evaporated to dryness. The polymer was analyzed by <sup>1</sup>H and <sup>13</sup>C NMR and SEC analyses.

#### **Elemental Analysis**

Elemental analysis was performed for the polymer obtained in entry 3 of Table (S)1: Found C, 69.35; H, 11.42. Although the calculated values for the polymer depend on its chain ends and molecular weights, two major species detected by MALDI-TOF-MS analysis (red and blue structures in Scheme S12; n (degree of polymerization) = 25-35) are within the range of C 69.7–70.3; H, 11.5–11.7.

#### **Determination of Molecular Weights**

Molecular weights of the obtained polymers were determined by size-exclusion chromatography using standard polystyrenes. In order to confirm the accuracy of the obtained values, the molecular weight of a standard poly(vinyl alcohol) sample ( $M_n = 4,200$ ,  $M_w = 7,200$ ,  $M_n/M_w = 1.7$ ) were also measured, and the value was found to be  $M_n = 4,600$ ,  $M_w = 7,900$ ,  $M_n/M_w = 1.7$ ).



Scheme S2. Plausible mechanism of the ping-pong polymerization.

Scheme S3. Possible mechanism for termination of the ping-pong polymerization.





#### Table S1. Ping-Pong Polymerization by Allylation/Hydroformylation<sup>a</sup>

entry	ArCHO (mmol)	allylic boronate (mmol)	ligand	Rh/L (mmol/mmol)	solvent (mL)	temp (°C)	time (h)	conversion (%) <sup>b</sup>	yield (g) <sup>c</sup>	yield (%)	M <sub>n</sub> (/10 <sup>3</sup> ) <sup>d</sup>	$M_{\rm w}/M_{\rm n}^{d}$
1		<b>1</b> (10.0)	Xantphos	0.02/0.04	toluene (4)	100	24	84	(0.83) <sup>e</sup>		1.7	1.2
2		<b>2</b> (10.0)	Xantphos	0.02/0.04	toluene (4)	100	24	f	0.25	29	2.0	1.5
3		<b>3</b> (10.0)	Xantphos	0.02/0.04	toluene (4)	100	24	100	0.84	100	2.4	1.3
4	0.1	<b>3</b> (10.0)	Xantphos	0.02/0.04	toluene (4)	100	24	100	0.82	95	2.3	1.4
S1	0.1	<b>3</b> (4.0)	Xantphos	0.02/0.04	toluene (4)	100	24	100	0.27	78	2.3	1.3
S2	0.1	<b>3</b> (10.0)	Xantphos	0.02/0.04	toluene (10)	100	24	27				
S3	0.1	<b>3</b> (10.0)	Xantphos	0.02/0.04	toluene (10)	100	7d	100	0.84	98	2.2	1.5
S4	0.1	<b>3</b> (10.0)	Xantphos	0.05/0.10	toluene (10)	100	24	100	0.68	78	2.3	1.3
<b>S</b> 5	0.1	<b>3</b> (10.0)	Xantphos	0.02/0.04	toluene (4)	80	7d	100	0.84	98	2.4	1.3
S6	0.1	<b>3</b> (10.0)	Xantphos	0.02/0.04	THF (4)	100	24	88	0.79	92	2.0	1.2
S7	0.1	<b>3</b> (10.0)	A4N3	0.02/0.04	toluene (4)	100	24	100	0.68	69	1.0	1.8
S8	0.1	<b>3</b> (10.0)	$PPh_3$	0.02/0.04	toluene (4)	100	24	100	0.84	72	1.4	1.5
S9	0.1	<b>3</b> (10.0)	Xantphos	0.02/0.04	toluene (4)	100	3	4				—
S10	0.1	<b>3</b> (10.0)	Xantphos	0.02/0.04	toluene (4)	100	5	23	0.25	(29)	0.6	1.7
S11	0.1	<b>3</b> (10.0)	Xantphos	0.02/0.04	toluene (4)	100	10	64	0.49	57	1.5	1.3
S12	0.1	<b>3</b> (10.0)	Xantphos	0.02/0.04	toluene (4)	100	15	89	0.69	80	1.8	1.4
 5 <sup>g</sup>	0.1	<b>4</b> (10.0)	Xantphos	0.02/0.04	toluene (4)	100	24	100	0.53	36	1.6	1.5
$6^g$	0.1	<b>5</b> (10.0)	Xantphos	0.02/0.04	toluene (4)	100	24	93	0.75	70	0.8	

<sup>*a*</sup> The reaction of 2-naphthaldehyde and allylic boronate **1–5** was performed with Rh(acac)(CO)<sub>2</sub> and a ligand under H<sub>2</sub>/CO (1.5/1.5 MPa) pressure in a 50-mL autoclave unless otherwise noted. Entry numbers 1–6 correspond to the entries 1–6 in Table 1 in the main manuscript; Xantphos = 4,5-bis(diphenylphosphino)-9,9dimethylxanthene; A4N3 = tetra(1-naphthyl) [3,3',5,5'-tetra-*tert*-butyl-6,6'-dimethyl-(1,1'-biphenyl)-2,2'-diyl] bis(phosphite). <sup>*b*</sup> Conversion of allyic boronates determined by <sup>1</sup>H NMR analysis. <sup>*c*</sup> Yield of polymer after hydrolysis. <sup>*d*</sup> Molecular weight determined by SEC analysis using polystyrene as an internal standard. <sup>*e*</sup> The product was contaminated by pinacol. <sup>*f*</sup> Conversion could not be determined due to the insolubility of the crude polymer. <sup>*g*</sup> Allylic boronate was generated in situ and used without isolation.

#### Note 1:

In entry S2, where the conversion of crotylboronate **3** ( $E:Z = \sim 9:1$ ) was 27%, the E:Z ratio of the recovered **3** was found to be unchanged ( $E:Z = \sim 9:1$ ). We have not observed any significant *E* to *Z* isomerization of boronates during polymerization.

#### Note 2:

The plot of conversions of allyl boronate **3** against reaction time of the ping-pongpolymerization in the presence of an aldehyde initiator is shown in Figure S1 (entry 4 and S9– S12 in Table S1). Because the rate of the present polymerization depends on the relationship of allyboration and hydroformylation, the plot did not exhibit linear correlation but a curved line. The slow rate in the early stage of the polymerization corresponds to hydroformylation of boronate monomers to increase the concentration of aldehydes in the reaction system.



**Figure S1.** Time course of the ping-pong polymerization. Conversions of allyl boronate **3** were determined by <sup>1</sup>H NMR analyses.

#### Control Experiments: Crotylboration at 100 °C.



To a solution of crotyl boronate **3** (263  $\mu$ L) in toluene (2.0 mL) was added 3-phenylpropanal (623 mg, 2.09 mmol) at 100 °C, and the reaction mixture was stirred at that temperature for 1.5 h. After cooling to room temperature, the mixture was treated with THF (20 mL) and

aqueous NaOH solution (1N, 20 mL), and then refluxed for 20 h. The mixture was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and evaporated to dryness. Purification by silica gel column chromatography afforded 4-methyl-1-phenylhex-5-en-3-ol as colorless oil (247 mg, 65%). The *anti/syn* ratio was estimated by <sup>1</sup>H and <sup>13</sup>C NMR analyses to be 90/10.

#### **Differential Scanning Calorimetry (DSC)**

The glass transition temperatures ( $T_g$ ) of the copolymers derived from **3** and **4** were found to be 53 and 76 °C, respectively (Figures S15 and S21). The former value is consistent with those of statistical ethylene/vinyl alcohol copolymers (37–55 °C)(7) and poly(ethylene-*alt*vinyl alcohol) (45–52 °C).(7,8,9,10) No clear melting temperature ( $T_m$ ) was observed in either case. In general, ethylene/vinyl alcohol copolymers exhibit clear melting temperatures regardless of ethylene/vinyl alcohol ratios, because the hydrogen bonding strongly contribute to crystallization. Therefore it is suggested that methyl and phenyl substituents in the main chain inhibit intermolecular interaction between polymer chains and lower the crystallinity. Another possible reason is lower molecular weights of the obtained copolymers, which may not be enough high to exhibit polymer property.

#### Thermogravimetric Analysis (TGA)

TGA analyses of the copolymers derived from **3** and **4** showed an onset to decomposition at 357 and 354 °C, respectively, which corresponds to the decomposition of the main chain (Figures S16 and S22). In both cases, no weight loss attributed to dehydration was observed. The thermal stability of these polymers is higher than PVA homopolymer.(7,8) and comparable to other structurally-related ethylene/vinyl alcohol copolymers.(*11*)

#### X-Ray Diffraction (XRD)

XRD analyses of the polymers showed no sharp signals corresponding to crystalline domains (Figures S17 and S23).

Ta	ble	<b>S2.</b>	Thermal	Anal	lysis	Data <sup><i>a</i></sup>
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entry	polymer	τ <sub>g</sub> (°C) <sup>a</sup>	τ <sub>m</sub> (°C) <sup>a</sup>	τ <sub>d</sub> (°C) <sup>b</sup>	ref.
1	poly(propylene- <i>alt</i> -VA) derived from <b>3</b>	53	c	357	This work
2	poly(styrene- <i>alt</i> -VA) derived from <b>4</b>	76	c	354	This work
3	poly(ethylene- <i>alt</i> -VA) by Aldol GTP followed by hydrogenation	52	140	d	7
4	poly(ethylene- <i>alt</i> -VA) by ROMP followed by hydroboration/oxidation	49	114	d	9
5	poly(ethylene- <i>alt</i> -VA) by ROMP followed by oxidation	45	d	>400	10

<sup>*a*</sup> Determined by differential scanning calorimetry (DSC). <sup>*b*</sup> Determined by thermogravimetric analysis (TGA). <sup>*c*</sup> Not observed. <sup>*d*</sup> Not mentioned.

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## Dimethyl (4R,5R)-2-(3-phenylprop-2-en-1-yl)-1,3,2-dioxaborolane-4,5-dicarboxylate



Figure S2. <sup>1</sup>H NMR spectrum of crude cinnamyl boronate (4) (CDCl<sub>3</sub>, 500 MHz).

## Diisopropyl (4R,5R)-2-(3-phenylprop-2-en-1-yl)-1,3,2-dioxaborolane-4,5-dicarboxylate



Figure S3. <sup>1</sup>H NMR spectrum of the crude prenyl boronate (5) (CDCl<sub>3</sub>, 500 MHz).

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## 3,7,11-Trimethylhexadec-1-ene-4,8,12-triol (9)



Figure S4. <sup>1</sup>H NMR spectrum of triol 9 (CD<sub>3</sub>OD, 500 MHz).



Figure S5. <sup>13</sup>C NMR spectrum of triol 9 (CD<sub>3</sub>OD, 101 MHz).



Figure S6. <sup>13</sup>C NMR spectrum (10–80 ppm region) of triol 9 with assignments of the observed signals (CD<sub>3</sub>OD, 101 MHz).

## Polymer synthesized from (*E*)-crotyl boronate (entry 4 in Table 1)

Data File : C:¥EZChrom Elite¥Enterprise¥Projects¥Default¥Data¥Noguchi¥64-03-100-1.dat Method File: C:¥EZChrom Elite¥Enterprise¥Projects¥Default¥Method¥noguchi¥0X26THF-2.met System Date : 2011/01/07 15:40:08 2011/06/04 15:46:20 GPC System 1(THF)



Analysis	Start(min)	ш	14. 279
Analysis	End (min)		19. 704
	Mw Mn Mz+1 Mw/Mn Mp Mz/Mw Mz+1/Mw	пппппп	3357 2244 5614 11429 1.496 2958 1.672 3.405

Figure S7. SEC chart of the polymer obtained in entry 4 in Table 1.

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Figure S8. <sup>1</sup>H NMR spectrum of the polymer obtained in entry 4 in Table 1 (DMSO-*d*<sub>6</sub>, 500 MHz).



Figure S9. <sup>13</sup>C NMR spectrum of the polymer obtained in entry 4 in Table 1 (CD<sub>3</sub>OD, 101 MHz).

#### Note 2:

One possible explanation for the four peaks of *a* (CH) in Figure S9 is that they are attributed to four *like* and *unlike* relationships of the neighboring units as shown in Figure S10.



Figure S10. Possible interpretations for the quadripartite peak of *a* (CH) in the <sup>13</sup>C NMR spectrum.

**Note 3:** <sup>13</sup>C NMR analyses of some model compounds as shown below.



**Figure S11.** <sup>13</sup>C NMR data of the model compounds measured in CD<sub>3</sub>OD. Chemical shift values in parentheses are data measured in CDCl<sub>3</sub>. Chemical shift values in brackets are data in reference 14, but there is no mention about solvent used for the analyses.

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**Figure S12.** MALDI-TOF-MS spectrum of the polymer obtained by the ping-pong polymerization in the ABSENCE of 2-naphthaldehyde (entry 4 in Table 1).



**Figure S13.** MALDI-TOF-MS spectrum of the polymer obtained by the ping-pong polymerization in the PRESENCE of 2-naphthaldehyde (entry 3 in Table 1).



Figure S14. IR spectrum of the polymer obtained in entry 4 in Table 1



Figure S15. DSC chart of the polymer obtained in entry 4 in Table 1.



Figure S16. TG chart of the polymer obtained in entry 4 in Table 1.



Figure S17. WXRD chart of the polymer obtained in entry 4 in Table 1.

## Polymer Synthesized from (E)-Cinnamyl Boronate (Entry 5 in Table 1)



Analysis	Start(min)	Ξ	15. 991
Analysis	End (min)		20. 144
	Mw Mn Mz+1 Mw/Mn Mp Mz/Mw Mz+1/Mw		2049 1291 3004 4084 1.588 1997 1.466 1.993

Figure S18. SEC chart of the polymer obtained in entry 5 in Table 1.

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**Figure S19.** <sup>1</sup>H NMR spectrum of the polymer obtained in entry 5 in Table 1 (DMSO-*d*<sub>6</sub>, 500 MHz).



Figure S20. <sup>13</sup>C NMR spectrum of the polymer obtained in entry 5 in Table 1 (DMSO-*d*<sub>6</sub>, 101 MHz).





Figure S21. DSC chart of the polymer obtained in entry 5 in Table 1.



Figure S22. TG chart of the polymer obtained in entry 5 in Table 1.



Figure S23. WXRD chart of the polymer obtained in entry 5 in Table 1.

## Polymer Synthesized from Prenyl Boronate (Entry 6 in Table 1)

Data File : C:¥EZChrom Elite¥Enterprise¥Projects¥Default¥Data¥Noguchi¥64-03-110.dat Elite¥Enterpris Method File: C:¥EZChrom Elite¥Enterpris¥Projects¥Default¥Method¥noguchi¥0X26THF-2.met System Date : 2011/01/24 21:13:03 2011/06/04 15:48:12 GPC System 1(THF)



Analysis	Start(min)	н	16. 958
Analysis	End (min)		20. 099
	Mw Mn Mz+1 Mw/Mn Mp Mz/Mw Mz+1/Mw		1250 1000 1530 1840 1.250 1216 1.225 1.472

Figure S24. SEC chart of the polymer obtained in entry 6 in Table 1.



Figure S25. <sup>1</sup>H NMR spectrum of the polymer obtained in entry 6 in Table 1 (CD<sub>3</sub>OD, 500 MHz).



Figure S26. <sup>13</sup>C NMR spectrum of the polymer obtained in entry 6 in Table 1 (CD<sub>3</sub>OD, 101 MHz).





Figure S27. ESI-MS spectrum of the polymer obtained in entry 6 in Table 1.



Figure S28. Assignments of the observed ESI-MS signals in Figure S27.