Homogeneous Two-Component Polycondensation without Strict Stoichiometric Balance via the Tsuji–Trost Reaction. Remote Control of Two Reaction Sites by Catalysis

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Experimental:

All manipulations were conducted under a nitrogen atmosphere using standard Schlenk techniques. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian JEMINI-2000 spectrometer for ¹H (300 MHz) and ¹³C (75 MHz). IR spectra were obtained using a JASCO FT/IR-5MP spectrometer. Size exclusion chromatography (SEC) was conducted with a Tosoh SD-8020 system using Tosoh TSK-gel G2000H_{XL}, G3000H_{XL}, and G5000H_{XL} columns in chloroform at 40 °C (polystyrene standards). Gel filtration was conducted using Sephadex LH-60 gel in CHCl₃/MeOH (1/2) at 25 °C.

Materials:

Pd₂(dba)₃, dppb, and BSA were used as purchased from Aldrich, and BSA was stored under a nitrogen atmosphere. PPh₃ was purchased from Kanto Chemical Co. Inc., Japan. Dry solvents such as toluene, diethyl ether, and tetrahydrofuran (THF) were distilled from Na–benzophenone under N₂. Dichloromethane, DMF, DMI, and HMPA were distilled from calcium hydride. Those solvents were stored under a nitrogen atmosphere.

Remote Double Activation of Bifunctionality by Catalysis

General procedure for polymerization (Table 1, entry 2):

The orange solution of Pd₂(dba)₃ (4.7 mg, 5.1 μmol), dppb (4.2 mg, 9.8 μmol), and BSA (0.74 mL, 3.0 mmol) in CH₂Cl₂ (0.3 mL) and DMF (0.1 mL) was stirred for 10 min at room temperature. To the solution of **2** (276 mg, 0.75 mmol) and **6** (80 mg, 0.50 mmol) in CH₂Cl₂ (0.6 mL), the orange solution of the palladium catalyst was transferred using a cannula, and the reaction was stirred at 25 °C. Small amounts of crude samples from the reaction mixture were analyzed by ¹H NMR and SEC until the values of *M_n* reached the upper limits (2.5 days). At the completion of polymerization, 5 mL of 1 N HCl was added to the reaction mixture, and the stirring was continued for 30 min. The organic compounds were extracted with CHCl₃ (ca. 20 mL), and dried over MgSO₄. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by gel filtration to afford the analytically pure polymer (102 mg, 98%). *M_n* = 14,000, *M_w*/*M_n* = 1.6₂.

1. Scouting the electrophilic monomers for polycondensation out of stoichiometric control

Entry	Y	time, days	yield, ^a %	M_n^b	M_w/M_n	obtained DP_n
1	CH ₂	6.0 (2.0) ^c	— ^d	1,800 (1,800) ^c	1.4 ₁ (1.4 ₂) ^c	14 (14) ^c
2	OCMe ₂ O	1.0	— ^d	2,100	1.3 ₃	7.6
3	CHCO ₂ Et	1.0	— ^d	1,800	1.3 ₉	10
4	O	6.0 (2.5) ^c	96	11,000 (10,000) ^c	1.6 ₂ (1.6 ₆) ^c	78 (71) ^c

Reaction conditions: **6**, 5.0 mmol; Pd₂(dba)₃, 5.0 μmol; dppb, 10 μmol; BSA, 3.0 mmol; solvent CH₂Cl₂–DMI (9/1); temp., 25 °C; Crude samples from the reaction mixture were analyzed every 6–12 h or 1–2 days until the values of M_n reached the upper limits.

^a Isolated yield. ^b Estimated by SEC (polystyrene standards, CHCl₃). ^c By analysis of crude samples of the polymerization mixture in the process of polycondensation. ^d Not isolated.

2. Examination of the specific conditions for polycondensation out of stoichiometric control using monomer **5**

entry	ligand	solvent	5/6	M_n^a (obtained DP_n^a)
1	dppb	CH ₂ Cl ₂ –DMI (9/1)	1.5/1.0	11,000 (78)
2	dppb	CH₂Cl₂–DMF (9/1)	1.5/1.0	14,000 (99)
3 ^b	dppb	CH ₂ Cl ₂ –DMF (9/1)	1.0/1.5	800 (6)
4	dppcyh ^c	CH ₂ Cl ₂ –DMF (9/1)	1.5/1.0	9,600 (68)
5	2 PPh ₃	CH ₂ Cl ₂ –DMF (9/1)	1.5/1.0	— ^d
6	PPh ₃	CH ₂ Cl ₂ –DMF (9/1)	1.5/1.0	— ^d
7	2 PCy ^c	CH ₂ Cl ₂ –DMF (9/1)	1.5/1.0	— ^d

All reactions were carried out with 0.50 mmol of **6**, 3 mmol of BSA, and 5 μmol of Pd₂(dba)₃ and 10 μmol of the ligand (entries 1–4 and 6) or 20 μmol of the ligand (entries 5 and 7) in 1 mL of the solvent under N₂ at 25 °C unless otherwise noted. Reactions were monitored by SEC analysis of crude samples from the reaction mixture until M_n reached upper limits.

^a Estimated by SEC (polystyrene standards, CHCl₃). ^b An excess amount of **6** was applied (**2**, 0.50 mmol; **6**, 0.75 mmol). ^c See below. ^d Oligomers ($DP_n < 10$) were formed.

Spectroscopic data of the polymers in Table 1:

Poly{oxy[(2*E*,7*E*)-5,5-bis(ethoxycarbonyl)nona-2,7-dienylene]} (entries 1 and 2): ¹H NMR (300 MHz, CDCl₃) δ = 1.24 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃), 2.61 (d, *J* = 6.6 Hz, 2 H, CCH₂C), 3.86 (d, *J* = 5.7 Hz, 2 H, OCH₂CH=CH), 4.17 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂), 5.57 (m, 2 H, C=CH); ¹³C NMR (75 MHz, CDCl₃) δ = 14.02 (CO₂CH₂CH₃), 35.28 (CCH₂C), 57.40 (C(CO₂Et)₂), 61.22 (CO₂CH₂), 70.06 (OCH₂CH=CH), 127.44, 131.15 (olefin), 170.68 (C=O); IR (KBr, cm⁻¹) 2981, 2937, 2857, 1730, 1445, 1367, 1263, 1200, 1097, 1042, 975, 859. Anal. Calcd. for C₁₅H₂₂O₅: C, 63.81; H, 7.85. Found: C, 63.79; H, 7.72.

Poly{oxy[(2*E*,7*E*)-5,5-diacetoxynona-2,7-dienylene]} (entry 4): ¹H NMR (300 MHz, CDCl₃) δ = 2.10 (s, 3 H, C(O)CH₃), 2.64 (d, *J* = 6.9 Hz, 2 H, CCH₂C), 3.83 (d, *J* = 5.4 Hz, 2 H, OCH₂CH=CH), 5.37 (dt, *J* = 15.0 Hz, 7.5 Hz, 1 H, OCH₂CH=CH), 5.61 (dt, *J* = 15.3 Hz, 6.0 Hz, 1 H, OCH₂CH=CH); ¹³C NMR (75 MHz, CDCl₃) δ = 27.10 (C(O)CH₃), 33.44 (CCH₂C), 69.84, 70.27 (OCH₂CH=CH and C(CO₂Et)₂), 127.02, 131.17 (olefin), 205.71 (C=O); IR (KBr, cm⁻¹) 2924, 2853, 1698, 1436, 1360, 1261, 1177, 1103, 1045, 973, 802.

Poly{oxy[(*E*)-but-2-enylene](1,3-indandione-2,2-diyl)[(*E*)-but-2-enylene]} (entry 5): ¹H NMR (300 MHz, CDCl₃) δ = 2.24 (d, *J* = 7.5 Hz, 2 H, CCH₂C), 3.34 (d, *J* = 5.7 Hz, 2 H, OCH₂CH=CH), 5.08 (dt, *J* = 15.3 Hz, 7.5 Hz, 1 H, OCH₂CH=CH), 5.34 (dt, *J* = 15.3 Hz, 6.2 Hz, 1 H, OCH₂CH=CH), 7.79–7.93 (m, 2 H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ = 37.17 (CCH₂C), 58.19 (C(CO₂Et)₂), 68.90 (OCH₂CH=CH), 123.11, 126.33, 131.41, 135.86, 142.13 (benzene ring and olefin), 203.19 (C=O); IR (KBr, cm⁻¹) 3018, 2912, 2854, 1742, 1707, 1595, 1435, 1357, 1246, 1106, 1043, 975, 915, 729.

Poly{oxy[(2*E*,12*E*)-5,5,10,10-tetrakis(ethoxycarbonyl)tetradeca-2,12-dien-7-ynylene]} (entry 6): ¹H NMR (300 MHz, CDCl₃) δ = 1.24 (t, *J* = 7.0 Hz, 6 H, CH₃CH₂ x 2), 2.72 (br, 4 H, CH₂C(CO₂Et)₂CH₂), 3.85 (d, *J* = 5.7 Hz, 2 H, RCH=CHCH₂O), 4.18 (q, *J* = 7.1 Hz, 4 H, OCH₂Me), 5.47 (dt, *J* = 15.3, 7.5 Hz, 1 H, CH=C), 5.66 (dt, *J* = 15.0, 5.9 Hz, CH=C); ¹³C NMR (75 MHz, CDCl₃) δ = 13.93 (CH₃CH₂O), 22.72 (spC–CH₂), 34.76 (sp²C–CH₂C(CO₂Et)₂), 56.84 (C(CO₂Et)₂), 61.47 (OCH₂Me), 70.01 (C=CCH₂O), 77.73 (spC), 126.91, 131.58 (C=C), 169.77 (C=O); IR (KBr, cm⁻¹) 2981, 2360, 1733, 1277, 1203, 1096, 1067, 859.

Poly[(1*E*,3*E*)-6,6-bis(ethoxycarbonyl)hepta-1,3-dienylene] (major polymer of entries 7–9): ¹H NMR (300 MHz, CDCl₃) δ = 1.22 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃), 2.59 (d, *J* = 6.9 Hz, 2 H, CCH₂C), 4.16 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂), 5.00–6.37 (m, 2 H, C=CH); ¹³C NMR (75 MHz, CDCl₃) δ = 14.05 (CO₂CH₂CH₃), 35.95 (CCH₂C), 57.85 (C(CO₂Et)₂), 61.17 (CO₂CH₂), 126.65, 133.92 (olefin), 170.73 (C=O); IR (KBr, cm⁻¹) 2981, 2937, 1731, 1445, 1367, 1284, 1242, 1186, 1095, 992, 927, 859, 733.

Poly{(*p*-toluenesulfonylimino)[(2*E*,7*E*)-5,5-bis(ethoxycarbonyl)nona-2,7-dienylene]} (entry 11): ¹H NMR (300 MHz, CDCl₃) δ = 1.15 (t, *J* = 7.2 Hz, 6 H, CO₂CH₂CH₃), 2.54 (d, *J* = 5.7 Hz, 4 H, CCH₂C), 3.70 (br, 4 H, NCH₂), 4.08 (q, *J* = 7.2 Hz, 4 H, CO₂CH₂), 5.37 (m, 4 H, C=CHCH₂), 6.56–7.17 (m, 5 H, ArH); ¹³C NMR (75 MHz, CDCl₃) δ = 13.93 (CO₂CH₂CH₃), 35.10 (CCH₂C), 51.34 (NCH₂), 57.62 (C(CO₂Et)₂), 61.10 (CO₂CH₂), 112.52, 116.32, 125.74, 129.05, 130.38 (olefin and CH of benzene ring), 148.53 (NC of benzene ring), 170.74 (C=O); IR (KBr, cm⁻¹) 2981, 1730, 1599, 1506, 1366, 1266, 1196, 1096, 1036, 973, 748, 692.

Poly{1,2-phenylene[(1*E*,6*E*)-4,4-bis(ethoxycarbonyl)hepta-1,6-dienylene]} (entry 12): ¹H NMR (300 MHz, CDCl₃) δ = 1.14 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃), 2.76 (d, *J* = 6.9 Hz, 2 H, CCH₂C), 4.10 (q, *J* = 7.2 Hz, 2 H, CO₂CH₂), 5.89 (dt, *J* = 15.3 Hz, 7.7 Hz, 1 H, ArCH=CH), 6.60 (d, *J* = 15.3 Hz, 1 H, ArCH=CH), 7.15–7.20 (m, 1 H, Ar*H*), 7.31–7.35 (m, 1 H, Ar*H*); ¹³C NMR (75 MHz, CDCl₃) δ = 14.07 (CO₂CH₂CH₃), 36.74 (CCH₂C), 58.19 (C(CO₂Et)₂), 61.28 (CO₂CH₂), 126.55, 126.62, 127.58, 131.77, 135.23 (benzene ring and olefin), 170.74 (C=O); IR (KBr, cm⁻¹) 2980, 1728, 1444, 1367, 1263, 1198, 1096, 1032, 966, 911, 860, 748.