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ORIGINAL ARTICLE

Polycondensation behavior between propargyl carbonates having a bulky ester group and bisphenols in the presence of Pd(0) catalyst: synthesis of exomethylene-containing polyethers

Hiroshi Nishino, Noriyuki Nishioka and Toshio Koizumi

Isopropyl and *tert*-butyl propargyl carbonates (1b and 1c) were investigated as monomers for Pd(0)-catalyzed polycondensation with bisphenols. These carbonates afforded high-molecular-weight polyethers compared with methyl propargyl carbonate (1a). The number-average molecular weight (M_n) values of the obtained polyethers increased in the order of methyl carbonate 1a < isopropyl carbonate 1b < *tert*-butyl carbonate 1c. Pd(0)-catalyzed condensation reaction of 1a–c with *p*-methoxyphenol was carried out as a model reaction. The yield of the desired model product increased with increasing bulkiness of the ester group of 1 (1a < 1b < 1c). *tert*-Butyl propargyl carbonate 1c was the most effective for Pd(0)-catalyzed polycondensation with bisphenols. The use of slightly excess 1c yielded higher-molecular-weight polyethers.
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Keywords: bisphenol; palladium catalyst; polycondensation; polyether; propargyl carbonate

INTRODUCTION

Palladium-catalyzed reactions of propargylic carbonates with nucleophiles attract much attention because of a useful method for the formation of heterocyclic compounds such as dihydrofurans, 1,4-benzodioxins and β-lactams in organic synthesis.[1–13] In these reactions, two consecutive nucleophilic attacks occur. A nucleophile attacks at the central carbon of the η^3-allenyl/propargyl intermediate generated by reaction of a propargylic carbonate with Pd(0) to yield a π-allylpalladium intermediate, which is successively attacked by a second nucleophile. This suggests that propargylic carbonates can be regarded as monomers for polycondensation with bifunctional nucleophiles. We have recently reported that a Pd(0)-catalyzed polycondensation of methyl propargyl carbonate (**1a**) with bifunctional oxygen nucleophiles such as bisphenols proceeded successfully to afford polyethers having exomethylene groups (Scheme 1).[14,15] Exomethylene-containing polymers are expected to undergo polymer reactions. The polycondensation was capable of proceeding under stoichiometrically imbalanced conditions because the propagating species always have two hydroxy groups at the polymer termini through two consecutive nucleophilic attacks. The polycondensation between bisphenols and an excess of **1a** yielded the corresponding polyethers with high molecular weights.

Although we found the successful Pd(0)-catalyzed polycondensation of **1a** with bisphenols, the number-average molecular weights (M_n) of the obtained polyethers were not high (M_n=1500–5000).[14,15] The model reaction of **1a** with *p*-hydroxyacetophenone suggested that the methanol liberated from **1a** caused termination reactions.[15] Three by-products formed by a reaction between **1a** and methanol were isolated in the model reaction. The formation of such by-products implies that methanol is nucleophilic enough to hinder polycondensation. Therefore, we anticipated that propargyl carbonates having a bulky alkyl ester group would yield polyethers with higher M_n as the bulky alcohols liberated are low nucleophilic. Isopropyl and *tert*-butyl propargyl carbonates (**1b** and **1c**) were prepared and their polymerization behaviors with bisphenols examined under palladium catalysis. In this paper, we report that propargyl carbonates **1b** and **1c** lead to formation of the corresponding polyethers with high molecular weights, compared with the polycondensation with **1a**.

EXPERIMENTAL PROCEDURE

Materials

All commercially available chemicals were used as received. Propargyl carbonate **1a** was synthesized by the reported method.[4] Tetrahydrofuran (THF) and ether were distilled from sodium/benzophenone ketyl under nitrogen before use. Pyridine was distilled over calcium hydride under nitrogen.

Measurement

Both ^{1}H nuclear magnetic resonance (NMR) (300 MHz) and ^{13}C NMR (75.5 MHz) spectra were recorded on Jeol-AL300 (Jeol, Tokyo, Japan) with $CDCl_3$ as the solvent. Chemical shifts are reported in p.p.m. (δ) with reference to Me_4Si or $CDCl_3$. Infrared (IR) spectra were recorded on Jasco FT-IR 460 Plus (Jasco, Tokyo, Japan). Gel-permeation chromatographic analyses were performed on a Tosoh HLC-8220 system (Tosoh, Tokyo, Japan) equipped with

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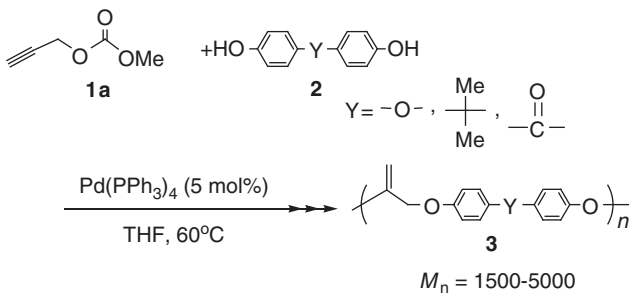


Scheme 1 Pd(0)-catalyzed polycondensation of **1a** with bisphenols **2**.

three columns (TSK gel, Super HM-M, Super HM-N and Super H3000), and THF was used as an eluent at 40 °C The GPC was calibrated with standard polystyrene samples. Elemental analyses were carried out using a Thermo-Finnigan Flash EA1112 CHN-O analyzer (Thermo-Finnigan, Milan, Italy).

Synthesis of Isopropyl Propargyl Carbonate 1b

To a solution of propargyl alcohol (9.7 g, 173 mmol) and dry pyridine (31 ml) in dry ether (150 ml), isopropyl chloroformate (25.6 g, 200 mmol) was added dropwise at 0 °C over 40 min under Ar. After being stirred at room temperature for 3 h, 1 M hydrochloric acid (30 ml) was added to the mixture at 0 °C. The ethereal layer was separated and the aqueous layer extracted with ether (30 ml×2). The combined ethereal layers were washed with saturated sodium chloride aqueous solution two times and dried over anhydrous magnesium sulfate. After filtration, the ethereal solution was evaporated to dryness and the residue distilled under reduced pressure to obtain **1b** (18.42 g, 75%): bp 98–99 °C/77 mm Hg; IR (neat): 3295, 2986, 2943, 1748, 1380, 1260, 1094, 962, 918 cm^{-1} ^{1}H NMR ($CDCl_3$): δ 1.31 (CH_3, d, J=6.34 Hz, 6H), 2.52 (CHC, t, J=2.4 Hz, 1H), 4.71 (CH_2, d, J=2.4 Hz, 2H), 4.91 (C**H**$(CH_3)_2$, sept, J=6.3 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 21.72 (CH_3), 54.86 (CH_2), 72.76 (CH), 75.43 (**C**HC), 77.15 (CH**C**), 154.00 (C=O). Anal. calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.37; H, 7.08.

Synthesis of *tert*-butyl propargyl carbonate 1c

This compound was synthesized according to the method reported by Haight *et al.*[16] To a solution of propargyl alcohol (12.43 g, 222 mmol) in dry THF (200 ml), 2.64 M *n*-butyl lithium *n*-hexane solution (84 ml, 222 mmol) was added dropwise at 0 °C over 30 min under Ar. After being stirred for 30 min, di-*tert*-butyl dicarbonate was added to the THF solution at 0 °C. The mixture was warmed to room temperature and stirred for 24 h. Distilled water (100 ml) was added slowly to the reaction mixture at 0 °C, and the solution was extracted with ether (100 ml×2). The combined ethereal layers were washed with saturated sodium chloride aqueous solution and dried over anhydrous magnesium sulfate. After filtration, the ethereal solution was evaporated to dryness. The residue was distilled under reduced pressure to obtain **1c** (28.95 g, 84%): bp 71–74 °C/18 mm Hg. IR (neat): 3294, 2985, 2941, 1750, 1371, 1280, 1255, 1160, 1097, 957, 856 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.50 (CH_3, s, 9H), 2.50 (CHC, t, J=2.4 Hz, 1H), 4.66 (CH_2, d, J=2.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 27.65 (CH_3), 54.27 (CH_2), 75.20 (**C**HC), 77.32 (CH**C**), 83.00 (**C**Me_3), 152.69 (C=O). Anal. calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.89; H, 7.78.

Pd(0)-catalyzed reaction of carbonate 1a with *p*-methoxyphenol: isolation of 6

A large-scale reaction was carried out to isolate by-product **6**. To a yellow solution of $Pd(PPh_3)_4$ (1.156 g, 1.0 mmol) in THF (55 ml), *p*-methoxyphenol (**4**; 4.964 g, 40 mmol) was added. A solution of methyl propargyl carbonate **1a** (2.282 g, 20 mmol) in THF (5 ml) was added to the mixture. After being stirred at 60 °C for 24 h under Ar, the reaction mixture was evaporated to dryness. The residue was subjected to flash column chromatography on silica gel (4:1 hexane/ethyl acetate) to yield the desire 1:2 product **5**[15](3.72 g, 61%) and by-product **6** (0.03 g, 1%).

5, ^{1}H NMR ($CDCl_3$): δ 3.74 (CH_3, s, 3H), 3.76 (CH_3, s, 3H), 4.11 (CH_2=C, d, J=2.1 Hz, 1H), 4.47 (CH_2=C, d, J=2.1 Hz, 1H), 4.57 (CH_2, s, 2H), 6.81–6.87 (ArH, m, 4H), 6.94–7.00 (ArH, m, 4H).

6, IR (neat): 3049, 2996, 1504, 1247, 1212, 1038, 964, 841 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.98 (CH_3, s, 3H), 3.79 (OCH_3, s, 3H), 3.81 (CH_2=C, s, 1H), 4.05 (CH_2=C, s, 1H), 6.86 (ArH, d, J=8.7 Hz, 2H), 7.12 (ArH, d, J=8.3 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 20.21 (CH_3), 55.57 (OCH_3), 87.58 (**C**H_2=C), 114.52 (Ar), 122.12 (Ar), 148.70, 156.13, 160.65. Anal. calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.48; H, 7.59.

Pd(0)-catalyzed polycondensation of carbonates 1 with bisphenols: a typical procedure

To an orange solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (in which dba is dibenzylideneacetone; 0.026 g, 0.025 mmol) and 1,1′-bis(diphenylphosphino)ferrocene (DPPF; 0.056 g, 0.1 mmol) in THF (2 ml) was added 4,4′-dihydroxydiphenyl ether (**2a**; 0.182 g, 0.9 mmol). To the mixture, a solution of propargyl carbonate **1c** (0.156 g, 1.0 mmol) in THF (1 ml) was added. After being stirred at 60 °C for 0.5 h under an Ar atmosphere, the reaction mixture was poured into methanol (100 ml) to precipitate the polymer (run 6 in Table 3). The resulting polymer was filtered off, washed with methanol and dried in vacuo (0.127 g, 59%) yielding polymer **3a**: IR (KBr): 3045, 2927, 2865, 1654, 1491, 1198, 830 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.22 (CH_2=C, d, J=6.0 Hz, 1H), 4.55 (CH_2=C, d, J=6.0 Hz, 1H), 4.62 (CH_2, s, 2H), 6.93–7.06 (ArH, m, 8H).

3b, IR (neat): 3060, 2925, 2869, 1654, 1597, 1221, 1161, 927, 851 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.57 (CH_2=C, s, 1H), 4.74 (CH_2, s, 2H), 4.85 (CH_2=C, 1H), 7.04–7.06 (ArH, m, 2H), 7.18–7.20 (ArH, m, 2H), 7.80–7.84 (ArH, m, 4H).

3c, IR (KBr): 3036, 2966, 2934, 2871, 1508, 1223, 1181, 828 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.64 (CH_3, br s, 6H), 4.25 (CH_2=C, s, 1H), 4.58 (CH_2 and CH_2=C, s, 3H), 6.85–6.97 (ArH, m, 4H), 7.12–7.19 (ArH, m, 4H).

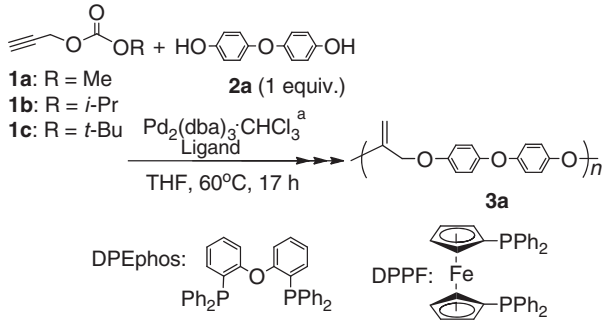
3d, IR (KBr): 3056, 2938, 2875, 1658, 1609, 1510, 1246, 1172, 968, 827 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.47 (CH_2=C, s, 1H), 4.64 (CH_2, s, 2H), 4.75 (CH_2=C, s, 1H), 6.92–6.96 (ArH, m, 2H), 7.05–7.09 (ArH, m, 2H), 7.30–7.38 (ArH, m, 4H). ^{13}C NMR ($CDCl_3$): δ 67.28, 94.01, 114.43, 119.54, 126.09, 129.10, 131.72, 155.68, 156.65, 158.47.

RESULTS AND DISCUSSION

Isopropyl carbonate **1b** was prepared by reaction of propargyl alcohol with isopropyl chloroformate in the presence of pyridine. *tert*-Butyl carbonate **1c** was synthesized from di-*tert*-butyl dicarbonate and propargyl alcohol. These carbonates were examined for polycondensation with 4,4′-dihydroxydiphenyl ether **2a** having an ether linkage in the presence of the palladium catalyst. The polymerization was carried out in THF at 60 °C for 17 h. Various phosphine ligands such as PPh_3, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane were used. Among them, DPPF and bis[(2-diphenylphosphino)phenyl]ether (DPEphos) were effective. Table 1 shows the results with DPPF and DPEphos. The effect of the alkyl ester moiety of **1a–c** on the polycondensation with **2a** appeared. As expected, the M_n value of polyether **3a**[15] increased with increasing bulkiness of the alkyl ester moiety. The molecular weight of **3a** was 2100 (run 1) in the polycondensation using methyl carbonate **1a** and DPPF as a ligand. Isopropyl carbonate **1b** afforded higher-molecular-weight **3a** than **1a** (Run 2). Polyether **3a** with the highest M_n was obtained from *tert*-butyl carbonate **1c** (M_n=5000; run 3). The polycondensation using DPEphos was similar to that using DPPF. The M_n value of **3a** increased in the order of **1a**<**1b**<**1c** (runs 4–6). *tert*-Butyl carbonate **1c** was found to be most effective for the formation of high-molecular-weight polyether **3a**. A monodentate phosphine ligand, PPh_3, also yielded polyether **3a** from **1a–c**, but the difference between the M_n values was not observed (ca. 3000). In this case, polydispersities were relatively large (M_w/M_n>3.0) compared with those of **3a** shown in Table 1.

Pd(0)-catalyzed condensation between **1a–c** and *p*-methoxyphenol (**4**) was conducted as a model reaction. The results are shown in Table 2. Methyl carbonate **1a** was treated with **4** in the presence of

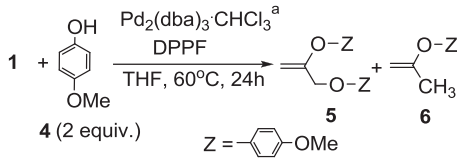
Table 1 Pd(0)-catalyzed polycondensation of carbonates 1 with 2[a]



Run	**1**	*Ligand*	*Yield (%)*[b]	M_n[c]	M_w/M_n[c]
1	**1a**	DPPF	50	2100	2.02
2	**1b**	DPPF	68	3900	2.54
3	**1c**	DPPF	62	5000	3.17
4	**1a**	DPEphos	44	3000	2.23
5	**1b**	DPEphos	67	3900	2.85
6	**1c**	DPEphos	52	4400	2.53

Abbreviations: DPEphos, bis[(2-diphenylphosphino)phenyl]ether; DPPF, 1,1′-bis(diphenylphosphino)ferrocene; GPC, gel-permeation chromatographic.
[a]2.5 mol%; Pd : *P*=1 : 4.
[b]Insoluble in MeOH.
[c]Estimated by GPC (PSt).

Table 2 Model reaction of 1 with *p*-methoxyphenol

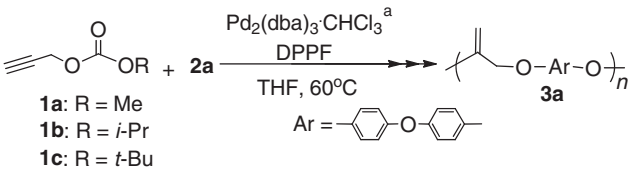


		Yield (%)[b]	
Run	**1**	**5**	**6**
1	**1a** (R=Me)	73	4
2	**1b** (R=*i*-Pr)	76	2
3	**1c** (R=t-Bu)	84	Trace

Abbreviation: NMR, nuclear magnetic resonance.
[a]2.5 mol%; Pd: *P*=1: 4.
[b]Yield was determined by ^{1}H NMR using nitromethane as an internal standard.

$Pd_2(dba)_3{\cdot}CHCl_3$/DPPF to yield the desired 1:2 product **5** (71%) and by-product **6** (4%). The yield of **5** increased with increasing bulkiness of the alkyl ester moiety. The reaction using **1c** yielded 84% of **5** (runs 1–3).[16,17] On the other hand, the yield of **6** decreased as bulkiness increased. By-product **6** seems to be obtained by reductive elimination of the hydride palladium intermediate generated by reaction of **1** with Pd(0).[15] It is known that a palladium alkoxide causes β-hydrogen elimination to afford a hydride palladium complex.[18,19] The formation of **6** was diminished by the use of **1c** (run 3) because β-hydrogen elimination of the palladium *tert*-butoxide generated from **1c** cannot take place. The large-scale reaction of **1a** with **4** was also carried out, but other by-products, except **6** could not be detected.

Table 3 Effects of feed ratio and time on the polycondensation of 1 with 2a



Run	**1**	*equiv. of* **2a**	*Time (h)*	*Yield (%)*[b]	M_n[c]	M_w/M_n[c]
1	**1a**	1.0	0.5	62	2900	2.33
2	**1b**	1.0	0.5	70	10 400	3.11
3	**1c**	1.0	0.5	72	13 500	2.68
4	**1a**	0.9	0.5	73	4100	2.88
5	**1b**	0.9	0.5	47	15 800	2.55
6	**1c**	0.9	0.5	59	16 100	2.49
7	**1c**	0.9	17	79	5200	2.34

Abbreviation: GPC, gel-permeation chromatographic.
[a]2.5 mol%; Pd : *P*=1: 4.
[b]Insoluble in MeOH.
[c]Estimated by GPC (PSt).

We next conducted polycondensation of **1a–c** with **2a** for a shorter time because longer reaction time causes a decrease in the M_n value of polyethers obtained from **1a** and bisphenols.[15] The results are shown in Table 3. A large increase in M_n was observed when polymerization with **1c** was conducted for 0.5 h (M_n=13 500; run 3), whereas methyl carbonate **1a** yielded a low molecular weight of **3a** (run 1). Polyether **3a** with high M_n was also formed from isopropyl carbonate **1b** (run 2).

A characteristic of the Pd(0)-catalyzed condensation between methyl carbonate **1a** and bisphenols is that the corresponding polyethers are formed efficiently even under stoichiometrically imbalanced conditions. This is because the propagating termini always have two nucleophilic sites.[20–25] We reported that the use of an excess of **1a** was required for formation of higher-molecular-weight polyethers because **1a** itself was slightly consumed by side reactions under the polymerization conditions.[14,15] Consequently, the consumption of **1a** interferes with polycondensation because of the existence of excess bisphenols when 1 equiv. of bisphenols toward **1a** was used. Therefore, polycondensation was next investigated using slightly excess **1a–c** toward **2a** (runs 4–6 in Table 3). When 0.9 equiv. of **2a** to **1c** was used, the molecular weight of **3a** increased from 13 500 to 16 100 (runs 3 and 6). The same trend was also observed in the polycondensation with **1b**. The M_n value was 15 800 (run 5). Methyl carbonate **1a** yielded the lowest M_n of **3a** (run 4). Prolonged reaction time (17 h) caused a decrease in the molecular weight (run 7). Thus, high-molecular-weight **3a** could be obtained when polycondensation using propargyl carbonates **1b** and **1c** was carried out for 0.5 h using 0.9 equiv. of **2a**.

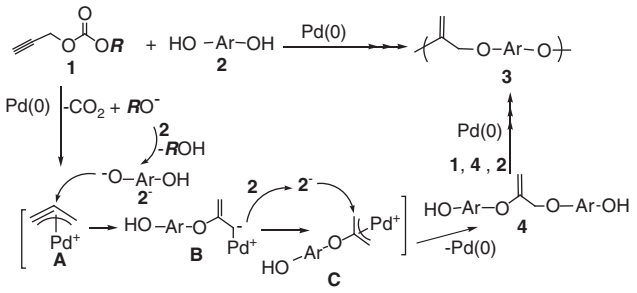
A plausible polymerization mechanism is shown in Scheme 2. Propargyl carbonate **1** reacts with Pd(0) to generate η^3-allenyl/propargyl intermediate **A**.[26–28] The central carbon of **A** is attacked by bisphenol **2** to produce intermediate **B** followed by protonation to yield η^3-allylpalladium intermediate **C**. A second **2** attacks intermediate **C** to afford **4**, which is equivalent to **2** and acts as a nucleophile.

Polyether **3a** with low M_n was formed in the polycondensation with methyl carbonate **1a**. It is possible that the methanol liberated from **1a** attacked intermediate **A** and/or **C** as a nucleophile during polymerization and interfered with the polycondensation.[15] We detected the

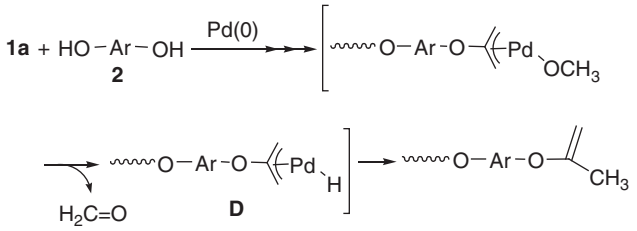
formation of **6** as a by-product in the model reaction; consequently, reductive elimination of hydride palladium intermediate **D** would also be a possible termination in the polycondensation with **1a** as shown in Scheme 3.

Polycondensation with 4,4′-dihydroxybenzophenone (**2b**) having a carbonyl group was next investigated using carbonates **1b** and **1c** to compare with the results with **2a** having an ether linkage. We already reported that polycondensation of methyl carbonate **1a** with 0.5 equiv. of **2b** was carried out in THF at 60 °C in the presence of benzenesulfonamide as an additive and $Pd(PPh_3)_4$ (5 mol%) to yield polyether **3b**[15] (M_n=3300). In this case, the resulting polyether **3b** was gradually decomposed under polymerization conditions. Polycondensation of *tert*-butyl carbonate **1c** with **2b** was conducted under the same conditions and produced **3b**, but the M_n value was rather low (M_n=2900). We explored the polymerization conditions and found that polycondensation with **1c** proceeded successfully in dioxane at 100 °C for 10 min. Table 4 summarizes the results with **1a–c** and **2b**. Isopropyl carbonate **1b** yielded the desired polymer **3b** in a good yield, but the molecular weight was about equal to that of **3b** from **1a** (runs 1 and 2). *tert*-Butyl carbonate **1c** was the most effective. The M_n value of **3b** reached 11 000 (run 3).

The relationship between the M_n value of **3b** and polymerization time was examined in the polycondensation using **1a** and **1c** under the same conditions of Table 4. Figure 1 shows the results. The molecular weight of **3b** reached a maximum after 10 min in each case. After 3 h, methyl carbonate **1a** yielded oligomeric **3b**, the M_n value of which was 400. Signals based on **3b** were observed in the ^{1}H NMR spectrum. In addition, a small signal due to the methoxy group was observed (3.62 p.p.m.). These results suggest that the methanol liberated from **1a** reacted with the resulting polymer **3b** under the polymerization conditions to afford the oligomeric product **3b**. We recently reported that the methoxylated product **8** was obtained in a good yield by the Pd(0)-catalyzed reaction of **1a** with *p*-hydroxyacetophenone (**7**) and methanol as shown in Scheme 4 (1).[29] Furthermore, we already found that model compound **9** obtained from **1a** and 2 equiv. of **7** reacted with the methoxide ion liberated from **1a** to produce **8** as shown in

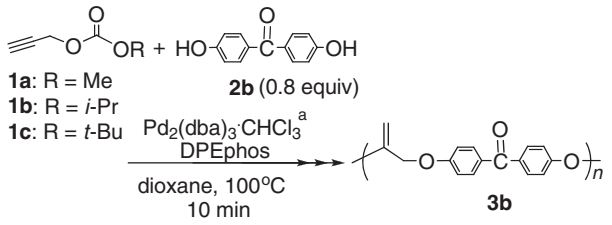


Scheme 2 Possible mechanism.



Scheme 3 Possible termination.

Table 4 Pd(0)-catalyzed polycondensation of 1 with 2b



Run	**1**	*Yield (%)*[b]	M_n[c]	M_w/M_n[c]
1	**1a**	69	4800	2.08
2	**1b**	69	4900	2.16
3	**1c**	72	11 000	2.03

Abbreviation: GPC, gel-permeation chromatographic.
[a]2.5 mol%; Pd : *P*=1: 4.
[b]Insoluble in MeOH.
[c]Estimated by GPC (PSt).

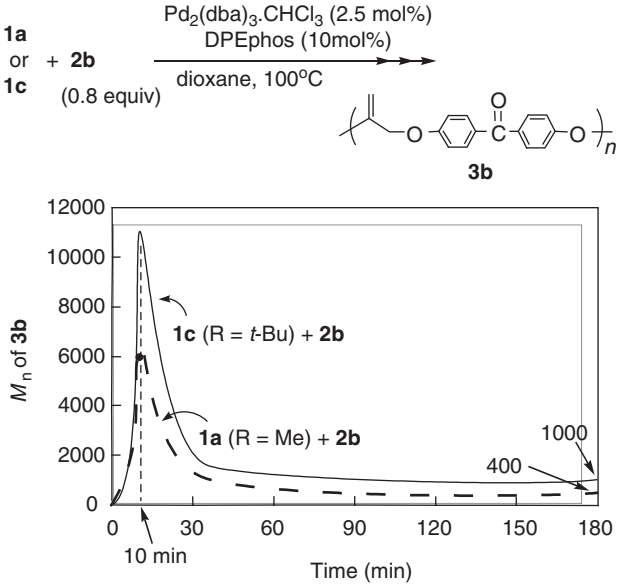
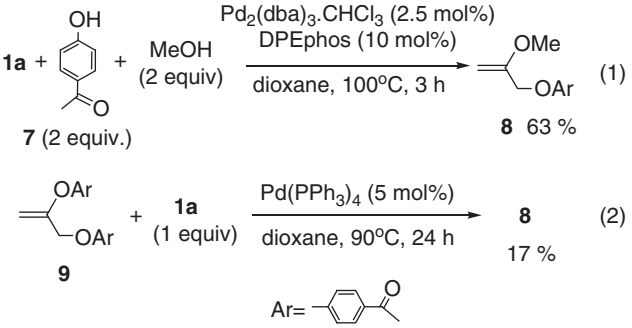


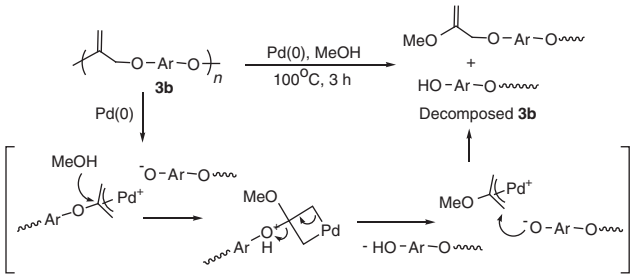
Figure 1 Plots of M_n of **3b** vs time.



Scheme 4 Formation of methoxylated product **8**.

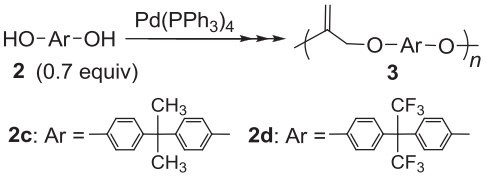
Scheme 5 (2).[15] Therefore, the sharp decrease in the M_n value would be caused by reaction between the resulting **3b** and the methanol liberated from **1a**. A plausible mechanism is shown in Scheme 5. Oxidative addition of polyether **3b** to Pd(0) generates a π-allylpalladium intermediate, subsequently in which the central carbon is attacked by the methanol. The resulting palladacyclobutane intermediate isomerizes to the methoxylated π-allylpalladium intermediate followed by reaction with the aryloxide liberated from **3b** to yield the decomposed **3b**. Organ reported a Pd(0)-catalyzed reaction of 1,2-dibromo-2-propene with phenol to afford 1,2-diphenoxy-2-propene and proposed a reaction mechanism similar to Scheme 5.[30] The presence of the vinyl carbon having an aryloxy group seems to cause the initial nucleophilic attack at the central carbon of the π-allylpalladium intermediate.

Polycondensation with *tert*-butyl carbonate **1c** also afforded oligomer **3b** after 3 h, but the molecular weight was high (M_n=1000) compared with that of **3b** from **1a**. No signal due to the *tert*-butoxy group was detected in the ^{1}H NMR spectrum. These results indicate that the *tert*-butanol liberated from **1c** did not react with the resulting polymer **3b**. Consequently, the decomposition of **3b** would be retarded. The observed decrease in M_n might be caused by reaction of **3b** with trace amounts of water because it is known that allyl carbonates react with water in the presence of the Pd(0) catalyst.[16, 17]



Scheme 5 Decomposition of **3b**.

Table 5 Pd(0)-catalyzed polycondensation of carbonates 1 with 2[a]



Run	**1** *(R)*	**2**	**3**	*Yield (%)*[b]	M_n[c]	M_w/M_n[c]
1	**1a** (Me)	**2c**	**3c**	74	4800	2.76
2	**1b** (*i*-Pr)	**2c**	**3c**	42	5000	2.77
3	**1c** (*t*-Bu)	**2c**	**3c**	47	5500	3.08
4	**1a** (Me)	**2d**	**3d**	56	11 000	1.64
5	**1b** (*i*-Pr)	**2d**	**3d**	49	11 400	1.96
6	**1c** (*t*-Bu)	**2d**	**3d**	59	13 000	2.05

Abbreviation: GPC, gel-permeation chromatographic.
[a]Conditions: **1**, 1.0 mmol; **2**, 0.7 mmol; $Pd(PPh_3)_4$, 50 μmol (5 mol%); THF 3.0 ml; 60 °C; 17 h.
[b]Insoluble in MeOH.
[c]Estimated by GPC (PSt).

To examine the difference in decomposition behavior between polyethers **3a** and **3b**, we conducted polycondensation using **1c** and 4,4′-dihydroxydiphenyl ether **2a** in dioxane at 100 °C in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ and DPPF. The M_n value of **3a** reached 16 000 after 5 min and decreased to 2800 after 3 h. These results show that polyether **3b** is decomposed easier than **3a**, probably due to the higher reactivity of **3b** toward the Pd(0) catalyst.

Bisphenol A (**2c**) and 4,4′-(hexafluoroisopropylidene)diphenol (**2d**) also afforded higher-molecular-weight polyethers **3c**[15] and **3d** in the polycondensation with *tert*-butyl carbonate **1c**. The results are shown in Table 5. Polycondensation was carried out at 60 °C for 17 h in the presence of $Pd(PPh_3)_4$. A monodentate ligand, PPh_3, was superior to DPPF and DPEphos as the ligand in this case. Prolonged reaction time (17 h) required to obtain high-molecular-weight polymers **3c** and **3d**, contrary to the polycondensation using **2a** and **2b**. In the polycondensation with **2c**, *tert*-butyl carbonate **1c** yielded higher-molecular-weight **3c**. The M_n values of the polyether **3c** obtained from **1a** and **1c** were 4800 and 5500, respectively (runs 1 and 3). Similarly, polycondensation of **1c** with **2d** produced high-molecular-weight polyether **3d** (M_n=13 000; run 6). Bisphenol **2d** having trifluoromethyl groups showed high reactivity and afforded **3d** with high M_n values compared with **2c**.

CONCLUSIONS

We investigated isopropyl and *tert*-butyl propargyl carbonates **1b** and **1c** for the Pd(0)-catalyzed polycondensation with bisphenols and found that propargyl carbonates having a bulky alkyl ester group could lead to the formation of polyethers **3** with high molecular weight. The M_n values of the obtained polyethers increased in the order of **1a** (methyl ester) < **1b** (isopropyl ester) < **1c** (*tert*-butyl ester). The results of the model reaction of **1a–c** with phenol **4** were consistent with those of the polycondensation. The yield of the model compound **5** increased in the order of **1a** < **1b** < **1c**. Polyether **3b** was decomposed easier than polyether **3a**.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

1 Tsuji, J. *Palladium Reagents and Catalysts, New Perspectives for the 21st Century* 543–563 (John Wiley: Chichester, UK, 2004).
2 Tsuji, J. & Mandai, T. Palladium-catalyzed reactions of propargylic compounds in organic synthesis. *Angew. Chem. Int. Ed. Engl.* **34,** 2589–2612 (1995).
3 Tsuji, J., Watanabe, H., Minami, I. & Shimizu, I. Novel palladium-catalyzed reactions of propargyl carbonates with carbonucleophiles under neutral conditions. *J. Am. Chem. Soc.* **107,** 2196–2198 (1985).
4 Minami, I., Yuhara, M., Watanabe, H. & Tsuji, J. A new furan annelation by the palladium-catalyzed reaction of 2-alkynyl carbonates or 2-(1-alkynyl)oxiranes with β-keto esters. *J. Organomet. Chem.* **334,** 225–242 (1987).
5 Labrosse, J. R., Lhoste, P. & Sinou, D. Palladium-catalyzed synthesis of 2,3-dihydro-2-ylidene-1,4-benzodioxins. *J. Org. Chem.* **66,** 6634–6642 (2001).
6 Dominczak, N., Damez, C., Rhers, B., Labrosse, J. R., Lhoste, P., Kryczka, B. & Sinou, D. Asymmetric palladium-catalyzed annulation of benzene-1,2-diol and racemic secondary propargylic carbonates bearing two different substituents. *Tetrahedron* **61,** 2589–2599 (2005).
7 Dominczak, N., Lhoste, P., Kryczka, B. & Sinou, D. Palladium-catalyzed heteroannulation of catechol with functionalized propargylic carbonates: influence of the functional group on the regioselectivity of the cyclization. *J. Mol. Cat. A Chem.* **264,** 110–118 (2007).
8 Uemura, K., Kawaguchi, T., Takayama, H., Nakamura, A. & Inoue, Y. Preparation of alkylidene cyclic carbonates via cyclization of propargylic carbonates. *J. Mol. Cat. A Chem.* **139,** 1–9 (1999).
9 Yoshida, M., Fujita, M., Ishii, T. & Ihara, M. A novel methodology for the synthesis of cyclic carbonates based on the palladium-catalyzed cascade reaction of 4-methoxycarbonyloxy-2-butyn-1-ols with phenols, involving a novel carbon dioxide elimination-fixation process. *J. Am. Chem. Soc.* **125,** 4874–4881 (2003).

10 Yoshida, M., Morishita, Y., Fujita, M. & Ihara, M. Palladium-catalyzed cyclization reactions of propargylic carbonates with nucleophiles: a methodology for the syntheses of substituted 2,3-dihydrofurans and benzofurans. *Tetrahedron* **61,** 4381–4393 (2005).
11 Yoshida, M., Higuchi, M. & Shishido, K. Highly diastereoselective synthesis of tetrahydrobenzofuranones by palladium-catalyzed reaction of propargylic carbonates with 2-substituted cyclohexane-1,3-diones. *Tetrahedron Lett.* **49,** 1678–1681 (2008).
12 Kozawa, Y. & Mori, M. Novel synthesis of carbapenam by intramolecular attack of lactams nitrogen toward η^1-allenyl and η^3-propargylpalladium complex. *J. Org. Chem.* **68,** 8068–8074 (2003).
13 Ren, Z. H., Guan, Z. H. & Liang, Y. M. Highly regioselective synthesis of benz[a]anthracene derivatives via a Pd-catalyzed tandem C-H activation/biscyclization reaction. *J. Org. Chem.* **74,** 3145–3147 (2009).
14 Koizumi, T., Sugie, K., Kiyonaga, O., Yamanaka, M. & Kawabata, S. Novel palladium – catalyzed polycondensation of propargyl carbonates and bisphenols: synthesis of polyethers having exomethylene groups. *Macromolecules* **37,** 9670–9672 (2004).
15 Takemura, T., Sugie, K., Nishino, H., Kawabata, S. & Koizumi, T. Pd(0)-catalyzed polycondensation of methyl propargyl carbonate and bisphenols under stoichiometrically imbalanced conditions. *J. Polym. Sci., Part A: Polym. Chem.* **46,** 2250–2261 (2008).
16 Haight, A. R., Stoner, E. J., Peterson, M. J. & Grover, V. K. General method for the palladium-catalyzed allylation of aliphatic alcohols. *J. Org. Chem.* **68,** 8092–8096 (2003).
17 Stoner, E. J., Peterson, M. J., Allen, M. S., DeMattei, J. A., Haight, A. R., , Leanna, M.R., Patel, S. R., Plata, D. J., Premchandran, R. H. & Rasmussen, M. Allylation of erythromycin derivatives: introduction of allyl substituents into highly hindered alcohols. *J. Org. Chem.* **68,** 8847–8852 (2003).
18 Wu, M. J., Wei, L. M., Lin, C. F., Leou, S. P. & Wei, L. L. Palladium-catalyzed reactions of aryl iodides with trimethylsilylacetylenes and disubstituted alkynes: the synthesis of diarylacetylenes and triarylethylenes. *Tetrahedron* **57,** 7839–7844 (2001).
19 Zask, A. & Helquist, P. Palladium hydrides in organic synthesis: reduction of aryl halides by sodium methoxide catalyzed by tetrakis(triphenylphosphine)palladium. *J. Org. Chem.* **43,** 1619–1620 (1978).
20 Nomura, N., Tsurugi, K. & Okada, M. Mechanistic rationale of a palladium-catalyzed allylic substitution polymerization: carbon-carbon bond-forming polycondensation out of stoichiometric control by cascade bidirectional allylation. *Angew. Chem. Int. Ed.* **40,** 1932–1935 (2001).
21 Tsurugi, K., Nomura, N. & Aoi, K. Palladium-catalyzed allylic substitution reaction: oxidative addition versus dissociation in an olefin-palladium(0)-complex. *Tetrahedron Lett.* **43,** 469–472 (2002).
22 Nomura, N., Tsurugi, K., Yoshida, N. & Okada, M. Palladium-catalyzed allylic substitution reaction in polymer synthesis. *Curr. Org. Synth.* **2,** 21–38 (2005).
23 Kihara, N., Komatsu, S., Takata, T. & Endo, T. Significance of stoichiometric imbalance in step polymerization via reactive intermediate. *Macromolecules* **32,** 4776–4783 (1999).
24 Iimori, H., Shibasaki, Y., Ando, S. & Ueda, M. Nonstoichiometric polycondensation I. synthesis of polythioether from dibromomethane and 4,4'-thiobisbenzenethiol. *Macromol. Symp.* **199,** 23–26 (2003).
25 Zhao, D. & Moore, J. S. Nucleationelongation polymerization under imbalanced stoichiometry. *J. Am. Chem. Soc.* **125,** 16294–9 (2003).
26 Su, C. C., Chen, J. T., Lee, G. H. & Wang, Y. Direct approach to palladium-mediated cycloaddition. First single-crystal structure and convenient synthesis of zwitterionic η^3-trimethylenemethane-palladium from nucleophilic addition of carbanions to an Allenyl complex. *J. Am. Chem. Soc.* **116,** 4999–5000 (1994).
27 Casey, C. P., Nash, J. R., Yi, C. S., Selmeczy, A. D., Chung, S., Powell, D. R. & Hayashi, R. K. Kinetic addition of nucleophiles to η^3-propargyl rhenium complexes occurs at the central carbon to produce rhenacylcyclobutenes. *J. Am. Chem. Soc.* **120,** 722–733 (1998).
28 Tsutsumi, K., Ogoshi, S., Nishiguchi, S. & Kurosawa, H. Synthesis, structure, and reactivity of neutral η^3-propargylpalladium complexes. *J. Am. Chem. Soc.* **120,** 1938–1939 (1998).
29 Nishioka, N. & Koizumi, T. Selective synthesis of functionalized allylic compounds by Pd(0)-catalyzed three-component reaction of methyl propargyl carbonate with phenols and nucleophiles. *Tetrahedron Lett.* **52,** 3662–3665 (2011).
30 Organ, M. G., Miller, M. & Konstantinou, Z. Mechanism of nucleophilic attack on 1- and 2-bromo(π-allyl)palladium complexes. *J. Am. Chem. Soc.* **120,** 9283–9290 (1998).