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Palladium-catalyzed three-component coupling

Polymerization of diyne, aryl dihalide, and hydride

Nobuyuki Miyaki[1], **Ikuyoshi Tomita**[2], **Takeshi Endo**[1,*]

[1] Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226, Japan
[2] Department of Electronic Chemistry, Interdisziplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226, Japan

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Summary

The palladium-catalyzed three-component coupling reaction of acetylenes, aryl halides, and hydride and it's application to polymer synthesis are described. The coupling reaction of 1,2-diphenylacetylene, iodobenzene, and sodium diethyl benzylmalonate was carried out at 80 °C for 48 h in 1,4-dioxane with $Pd(OAc)_2$ / tri-*o*-tolylphosphine, from which triphenylethylene was obtained in 71 % isolated yield. The benzylic hydrogen of sodium diethyl benzylmalonate was supposed to be a hydride source in the present reaction by detecting diethyl benzalmalonate in the reaction system. Based on the results, the coupling polymerization of 1,2-bis(4-phenylethynylphenyl)ethane, 4,4'-diiodobiphenyl, and sodium diethyl benzylmalonate was carried out at 80 °C for 48 h to produce a polymer (M_n=8500, M_w/M_n=3.0) in high yield. Using various aryl dihalides, the corresponding polymers having trisubstituted ethylene units were also obtained in high yields.

Introduction

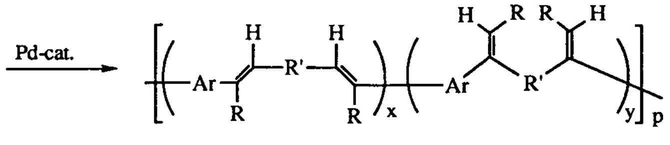
Step-growth polymerizations of monomers containing acetylene or allene moieties might be attractive for the synthesis of reactive or functional polymers containing unsaturated structures. Polymers possessing unsaturated units have been mostly produced by the polyaddition of diynes or bisallenes with monomers having heteroatoms (*e.g.*, O, S, Se, P, Sn, B, Si, *etc.*) by means of the carbon-heteroatom bond formation such as the hydrometallation, the radical, and the ionic addition reactions (1). The resulting polymers have been reported to reveal interesting functions such as liquid crystallinity, thermal stability, electroconductivity, and so on.

Previously, we have developed a unique coupling polycondensation concerning on allenes (*i.e.*, the palladium-catalyzed three-component coupling polymerizations of bisallenes, aryl dihalides, and nucleophiles), where three different building blocks can be incorporated into the polymer structure with ordered sequence at the same time (2).

While many step-growth polymerizations of acetylenes by the carbon-heteroatom bond formation have been reported, those by carbon-carbon bond formation processes (*i.e.*, the polymerization *via* hydroalkylation or hydroarylation) have been limited so far. To develop these polymerization methods, it is required to establish appropriate addition methods toward acetylenes (3). The hydroarylation reaction, for instance, has been reported by Cacchi *et al.*, in which the combination of aryl halides and formate anion is described to be effective for the production of the hydroarylated products in high yields. However, the reaction requires an excess amount of the aryl halide components due to the competitive reduction of the halide moieties (4).

Scheme 1

$R-\equiv-R'-\equiv-R + X-Ar-X + 2H^-$



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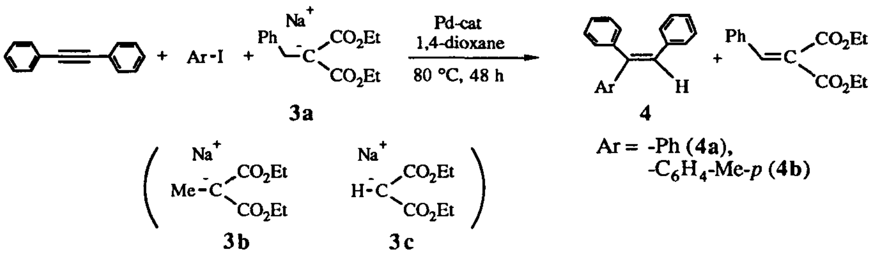
* Corresponding author

Herein, we would like to describe a new type of efficient palladium-catalyzed hydroarylation that can be carried out under the stoichiometric conditions of aryl halide components and it's application to the polymer synthesis (Scheme 1).

Results and Discussion

Model Reactions. The coupling reaction of 1,2-diphenylacetylene, iodobenzene, and sodium diethyl benzylmalonate (**3a**) was carried out at 80 °C for 24h in 1,4-dioxane in the presence of $Pd(OAc)_2$ / tri-*o*-tolylphosphine (4 equiv. to Pd) to give triphenylethylene (**4a**) in 71 % isolated yield as a result of the hydroarylation reaction toward 1,2-diphenylacetylene. Besides **4a**, diethyl benzalmalonete derived from sodium diethyl benzylmalonate was detected in the reaction products by the spectroscopic analyses (Scheme 2).

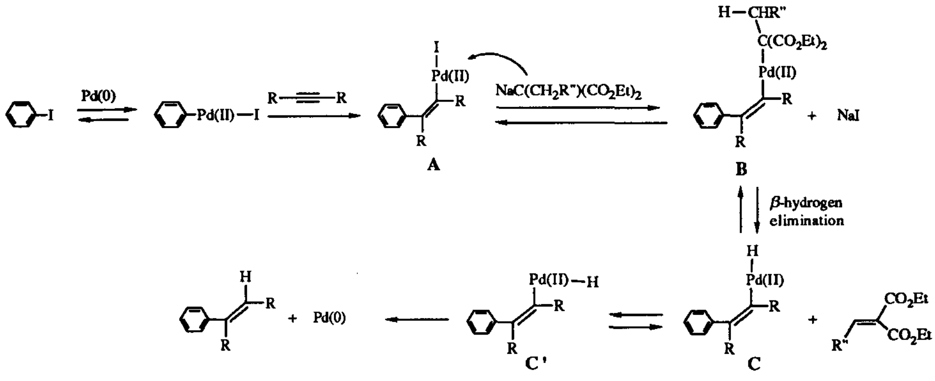
Scheme 2



In the case of sodium diethyl methylmalonate (**3b**), the product (**4a**) was obtained in 39 % yield (5). From sodium diethyl malonate (**3c**), however, **4a** could not be produced to recover the starting materials quantitatively. These results may indicate that the *β*-hydrogens of the sodium diethyl alkylmalonates are most probably a source of the hydride.

In order to get an information on the geometrical selectivity in the hydroarylation process, the coupling reaction of 1,2-diphenylacetylene, *p*-iodotoluene, and sodium diethyl benzylmalonate (**3a**) was carried out under similar conditions, from which a trisubstituted ethylene (**4b**) was obtained in 70 % isolated yield whose geometry was determined as the *cis*-adduct from the X-ray analysis.

Scheme 3. Plausible Reaction Mechanism



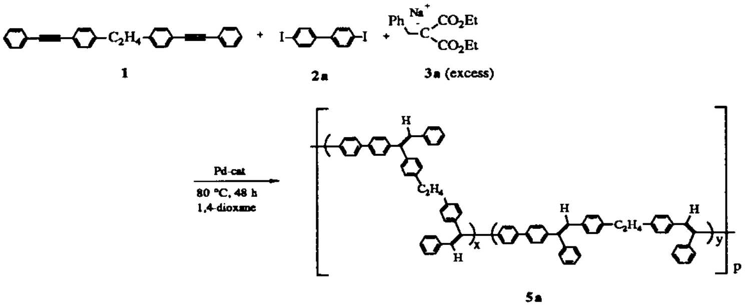
Although further attempts to clarify the mechanism have not been made yet, a plausible reaction mechanism is shown in Scheme 3. That is, the reaction may proceed by the initial oxidative addition of the aryl halide to the palladium (0) (6), the insertion of the acetylenes to give a vinylpalladium complex (A), and the transmetallation of sodium diethyl alkylmalonate to produce a trans-vinylpalladium complex having the diethyl alkylmalonate moieties (B) and sodium iodide. From the complex (**B**), the β-hydrogen elimination of the alkyl groups of the malonate moieties might occur to give a *trans*-vinylpalladium hydride complex (**C**) which isomerizes to a *cis*-vinylpalladium hydride complexes (**C'**) followed by the reductive elimination to give the olefin as a hydroarylation product (7).

The present coupling reaction is suitable for the hydroarylation polymerization, because the reaction yields the hydroarylation products in good yields under the stoichiometric conditions of the acetylene and the aryl halide.

Polymerizations. On the basis of these model reactions, the coupling polymerization of a bistolane (**1**), 4,4'-diiodobiphenyl (**2a**), and sodium diethyl benzylmalonate (**3a**) was carried out at 80 °C for 2 days in 1,4-dioxane in the presence of $Pd(OAc)_2$ / tri-*o*-tolylphosphine (7 equiv. to Pd). As a result, a pale yellow powdery polymer (**5a**) was obtained in 83 % yield by precipitation with methanol (Scheme 4) (8). The obtained polymer is soluble in organic solvents whose number average molecular weight (M_n) was estimated to be 8,500 by GPC measurement.

As shown in Figure 1, the ^{1}H-NMR spectrum supported the structure of the obtained polymer (**5a**). The benzylic and olefinic protons were observed at 2.4-3.1 ppm and 6.4-7.8 ppm, respectively, from which, however, it was difficult to determine the geometrical structure of **5a** (9). On the basis of the model reaction using *p*-iodotoluene (*vide supra*), **5a** should have specific *cis*-hydroarylated olefin units. The obtained polymer (**5a**) was supposed to be composed of two regioisomeric units, because the insertion of acetylene moieties may take place from both positions of acetylene moieties.

Scheme 4



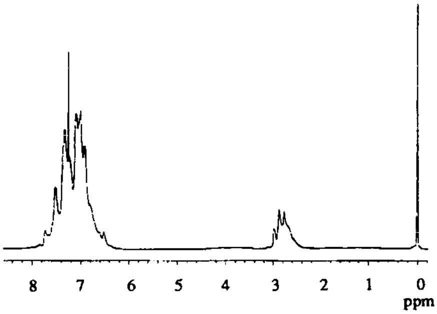
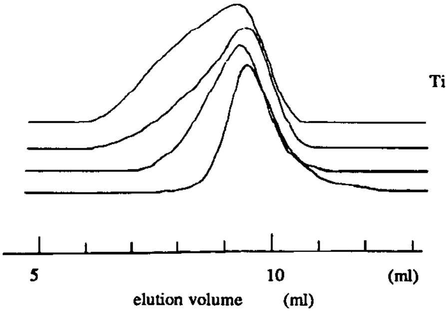


Figure 1. ^{1}H-NMR spectrum of **5a**.

The coupling polymerization of **1**, **2a**, and **3a** was carried out at 80 °C in 1,4-dioxane in the presence of the palladium catalyst and the molecular weight of the resulting polymer (**5a**) was monitored by GPC after designated reaction periods (Figure 2). From the result, the molecular weight of **5a** was found to keep increasing through the reaction for 48 h.



Time (h)	Yield(%)	$M_n(M_w/M_n)$
48	83	8500 (3.0)
24	86	6000 (3.0)
12	55	5200 (2.3)
6	22	1400 (3.8)

Figure 2. Time vs. M_n in the coupling polymerization of **1**, **2a**, and **3a**.

Table 1 Effect of feed ratio of **1** and **2a**.[a)]

Run	1:2a	Yield(%)[b)]	Gel Yield(%)	$M_n(M_w/M_n)$[c)]
1	1.0:0.7	60	23	11000(4.11)
2	1.0:0.9	36	60	6200(3.36)
3	1.0:1.0	85	0	8500(2.99)
4	1.0:1.1	92	0	9600(3.46)
5	1.0:1.3	87	0	3400(3.31)

a) Polymerization was carried out at 80°C for 2 days in 1,4-dioxane with 2.5mol% of $Pd(OAc)_2$-7(o-toly)$_3$P.
b) Precipitated with methanol and then with diethyl ether.
c) GPC (THF, PSt Std).

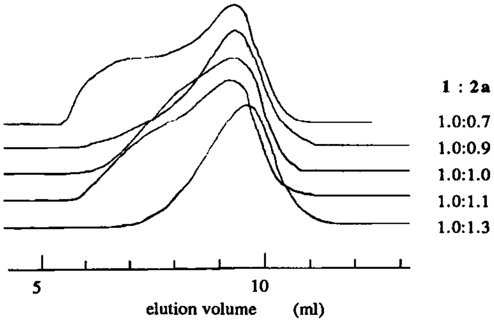


Figure 3. GPC traces of **5a** prepared under the various feed ratios of the monomers (**1**:**2a**).

The effect of the feed ratio of the diyne (**1**) to the aryl dihalide (**2a**) on the polymerization was likewise examined at 80°C for 2 days (Table 1 and Figure 3). Although, the stoichiometric concentration of monomers are suitable for general step-growth polymerizations to obtain polymers with higher molecular weights, a partial gelation was observed in the present system using an excess amount of the diyne which might indicate that any side reactions are involved in the present system (runs 1 and 2). In the presence of the excess diyne monomer, the polymer may tend to have acetylene moieties as the end groups which might undertake the multiple insertion by the palladium intermediate (10). In the case of the stoichiometric or a little excess amount of aryl dihalide, the gelation was not observed and the soluble polymer was obtained in high yield (runs 3 and 4). However, a large excess of aryl dihalide decreased the molecular weight as observed generally in the polycondensation (run 5).

The results on the polymerizations of **1**, **2a**, and **3a** under varied conditions are summarized in Table 2. In the presence of an excess of tri-*o*-tolylphosphine (7 equiv. relative to Pd), the polymer with high molecular weight was obtained in high yield (run 1), while the polymerization in the presence of 4 equiv. of tri-*o*-tolylphosphine produced partially an insoluble polymer (run 2). The polymerization did not proceed sufficiently by using $Pd(OAc)_2$ / 4 PPh_3, probably due to the stronger coordination of the ligand to the palladium (run 4). According to the solvent, *N,N*-dimethyl formamide (DMF) was not suitable for the polymerization, where oligomers (M_n = 1,580, M_w/M_n = 2.1) were obtained in 75 % yield (run 3).

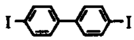
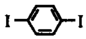
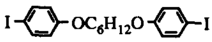
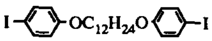
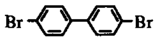
Table 2 Coupling polymerization of **1**, **2a**, and **3a** under various conditions.[a]

Run	Ligand	Solvent	Time (h)	Yield (%)[b]	$M_n(M_w/M_n)$[c]
1	$7(o\text{-toly})_3P$	1,4-dioxane	48	83	8500(3.0)
2	$4(o\text{-toly})_3P$	1,4-dioxane	48	62[d]	7300(5.4)
3	$4(o\text{-toly})_3P$	DMF	48	75	1580(2.1)
4	$4Ph_3P$	1,4-dioxane	72	60[e]	930(1.6)

a) Polymerization was carried out at 80°C in 1,4-dioxane with 2.5mol% of palladium catalysts.
b) Precipitated with methanol and then with diethyl ether.
c) GPC (THF, PSt Std).
d) The product ontained 11 % of a fraction insoluble in organic solvents.
e) Precipitated with methanol.

The coupling polymerization of **1** and **3a** was carried out by using various aryl dihalides (**2a**-**2e**) (Table 3). A polymer possessing triphenylethylene moieties (**5b**, M_n = 8,000, M_w/M_n = 2.2) was obtained by using 1,4-diiodobenzene (**2b**) in 77 % yield (run 2). From aryl diiodides linked by ether moieties (**2c** and **2d**), the corresponding polymers (**5c** and **5d**) were also obtained in high yields (runs 3 and 4). 4,4'-Dibromobiphenyl also produced the polymer having the identical structure to **5a** in 64 % yield (run 5).

Table 3
Polymerization of **1**, **3**, and Various Aryl Dihalides (**2a-e**).[a]

Run	X-Ar-X		Yield(%)[b]	$M_n(M_w/M_n)$[c]
1		(**2a**)	85	8500(3.0)
2		(**2b**)	77[d]	8000 (2.2)
3		(**2c**)	97	4600 (2.7)
4		(**2d**)	93	8200 (2.4)
5		(**2e**)	64	3600 (1.7)

a) Polymerization was carried out at 80°C for 48 h in 1,4-dioxane with 2.5mol% of $Pd(OAc)_2$-$7P(o\text{-tolyl})_3$.
b) Precipitated with methanol and then with *n*-hexane.
c) GPC (THF, PSt Std).
d) Precipitated with methanol and then with diethyl ether.

Thermal Properties. Thermogravimetric analyses (TGA) and differential scanning calorimetric (DSC) analyses were performed under nitrogen to estimate the thermal properties of the polymers (**5a** and **5d**) (Figure 4). The 10 % weight loss temperature (T_{d10}) of **5a** was observed at 413 °C and ca. 70 wt% of the residue remained after the heating at 500 °C. The glass transition temperature (T_g) of **5a** was observed at 184 °C, probably owing to the aliphatic part. In the case of **5d**, the weight loss started at ca. 300 °C (T_{d10} = 353 °C) and two T_g's were observed at 60 and 175 °C.

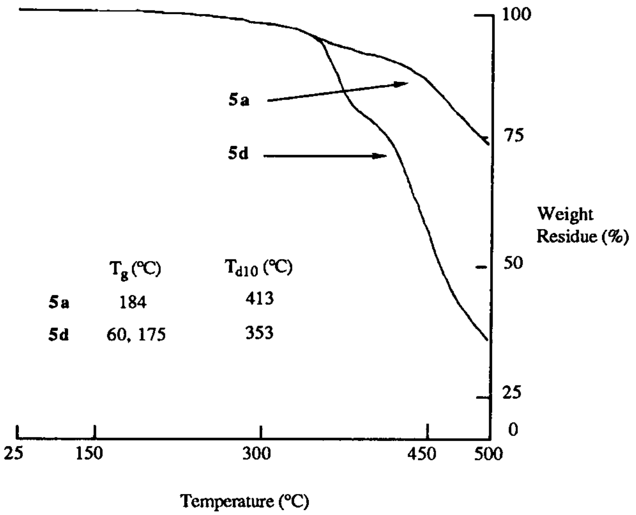


Figure 4. Thermogravimetric analyses of **5a** and **5d** under nitrogen.

Experimental

Instruments. IR spectra were obtained on a JASCO FT/IR-5300 spectrophotometer. ^{1}H-NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-EX90 (90MHz) or a JEOL JNM-GX400 (400 MHz) instrument. ^{13}C-NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-GX400 (100 MHz) instrument. Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh HLC-8020 (TSK gel G4000HXL, G3000HXL or G2500HXL, standard polystyrene samples, tetrahydrofuran as an eluent). Thermogravimetric analyses (TGA) were made on a Seiko TG/DTA220 instrument (10 °C / min.) under nitrogen stream. Differential scanning calorimetry (DSC) analyses were measured on a Seiko DSC220 instrument (10 °C / min.) under nitrogen stream.

Materials. Derivatives of sodium diethyl malonate (**3a**-**3c**) were prepared from sodium hydride and the corresponding diethyl malonate derivatives and then purified by washing successively with *n*-hexane. 4,4'-Diiodobiphenyl (**2a**) was purified by recrystallization from toluene. 1,4-Diiodobenzene (**2b**), 1,6-bis(4-iodophenoxy)hexane (**2c**), and 1,12-bis(4-iodophenoxy)dodecane (**2d**) were prepared as described (2a) and were purified by recrystallization from *n*-hexane. Tri-*o*-tolylphosphine was also purified by recrystallization from *n*-hexane. 1,4-Dioxane was dried over sodium and distilled under nitrogen. DMF was dried over calcium hydride and distilled under reduced pressure. Other reagents were used as received.

Synthesis of Monomer

Bistolane (1). To a mixture of 1,2-bis(4-iodophenyl)ethane (6.50 g, 15.0 mmol), palladium dichloride (0.0289 g, 0.170 mmol), copper (I) iodide (0.0152 g, 0.0800 mmol), triphenylphosphine (0.151 g, 0.575 mmol), and diethylamine (50 mL) was added ethynylbenzene (3.06 g, 60.0 mmol). The mixture was stirred at ambient temperature for 12 h. After removing diethylamine in *vacuo*, 50 mL of water was added to the remaining solid. The mixture was extracted with three 100 mL of portions of diethyl ether and the ethereal layer was dried over magnesium sulfate. After removing the solvent in *vacuo*, the residue was purified by recrystallization from chloroform. Yield: 47.7 % (2.74 g, 7.16 mmol). ^{1}H-NMR (δ, ppm) 2.93 (-CH_2-, s, 4H), 7.10-7.55 (C_6H_5, C_6H_4, 18H); ^{13}C-NMR (δ, ppm) 37.6, 89.0, 89.4, 120.9, 123.4, 128.1, 128.3, 128.6, 131.6, 141.7; IR (neat) 2921, 2855, 1593, 1509, 1439, 833, 754, 693, 550, 527 cm^{-1}.

Model Reaction

Coupling Reaction of 1,2-Diphenylacetylene, Iodobenzene, and Sodium Diethyl Benzylmalonate (3a). To a test tube equipped with a magnetic stirrer chip, were added 1,2-diphenylacetylene (0.178 g, 1.00 mmol), iodobenzene (0.204 g, 1.00 mmol), **3a** (0.544 g, 2.00 mmol), and 1,4-dioxane (1.00 mL). To the resulting mixture, a dioxane solution (1.00 mL) of tri-*o*-tolylphosphine (0.0304 g, 0.100 mmol) and palladium acetate (0.0056 g, 0.025 mmol) was added and the tube was sealed under reduced pressure. After the reaction at 80 °C for 24 h, the solvent was removed under reduced pressure. The residue was dissolved in diethyl ether, washed several times with water and dried over magnesium sulfate. After removing the solvent, the residue was purified by SiO_2 column chromatography (*n*-hexane) to give triphenylethylene (**4a**, 0.182 g, 71 %, 0.71 mmol). **4a**: MS (EI) m/z 256 (M^+) (4a).

Polymerization

Coupling Polymerization of Bistolane (1), 4,4'-Diiodobiphenyl (2a), and Sodium Diethyl Benzylmalonate (3a). To a test tube equipped with a magnetic stirrer chip, were added bistolane (0.0478 g, 0.125 mmol), 4,4'-diiodobiphenyl (0.0508 g, 0.125 mmol), **3a** (0.137 g, 0.500 mmol), and 1,4-dioxane (0.75 mL). To the resulting mixture, a dioxane solution (0.25 mL) of tri-*o*-tolylphosphine (0.0133 g, 0.0438 mmol) and palladium acetate (0.0014 g, 0.0062 mmol) was added and the tube was sealed under reduced pressure. After the reaction at 80 °C for 48 h, the solvent was evaporated under reduced pressure. The resulting residue was dissolved in THF (3 mL) and the solution was precipitated with methanol (50 mL). The polymer was dissolved again in chloroform (2 mL) and was reprecipitated with *n*-hexane (50 mL). **5a**: 80.2 % yield (0.0538 g, 0.100 mmol). ^{1}H-NMR (see, also Figure 1, δ, ppm) 2.40-3.00 (-CH_2-, 4H), 6.40-7.72 (-C=CH-, -C_6H_4-, -C_6H_5, 28H); ^{13}C-NMR (δ, ppm) 37.4, 126.7, 127.0, 127.4, 127.7, 127.9, 128.1, 128.2, 128.5, 128.7, 128.9, 129.5, 130.3, 130.4, 130.8, 130.9, 131.1, 137.5, 137.8, 139.6, 140.4, 141.4, 142.0, 142.5, 157.9; IR (neat) 3025, 2926, 2857, 1911, 1599, 1510, 1493, 1443, 1410, 1183, 1111, 1073, 1020, 1001, 909, 820, 733, 698 cm^{-1}.

Coupling Polymerization of Bistolane (1), Various Aryl Dihalides (2b-2d), and Sodium Diethyl Benzylmalonate (3a). The polymerizations were carried out similar to the case of **2a**, as mentioned above. The polymers (**5b**-**5d**) were isolated by precipitation with methanol followed by reprecipitation with diethyl ether.

5b: from **1** (0.0478 g, 0.125 mmol), **2b** (0.0413 g, 0.125 mmol) and **3a** (0.137 g, 0.500 mmol); Yield 76.8 % (0.0442 g, 0.0960 mmol); ^{1}H-NMR (δ, ppm) 2.40-2.95 (-CH_2-, 4H), 6.41-7.60 (-C=CH-, -C_6H_5, -C_6H_4-, 24H); ^{13}C-NMR (δ, ppm) 37.4, 125.5, 126.7, 127.2, 127.4, 127.9, 128.1, 128.2, 128.3, 128.7, 129.5, 130.3, 131.5, 135.8, 137.2, 137.4, 137.7, 140.4, 141.4, 142.1, 143.2, 151.5; IR (neat) 3023, 2926, 2855, 1599, 1510, 1443, 910, 826, 733, 698 cm^{-1}.

5c: from **1** (0.0478 g, 0.125 mmol), **2c** (0.0653 g, 0.125 mmol) and **3a** (0.137 g, 0.500 mmol); Yield 97.4 % (0.0794 g, 0.121 mmol); ^{1}H-NMR (δ, ppm) 1.18-1.86 (-CH_2-, 8H), 2.43-2.96 (-CH_2-, 4H), 3.72-4.00 (-OCH_2-,4H) 6.56-7.51 (-C=CH-, -C_6H_5, -C_6H_4-, 28H); ^{13}C-NMR (δ, ppm) 25.9, 29.1, 37.5, 67.9, 82.5, 114.1, 114.5, 116.9, 126.3, 127.2, 127.6, 127.7, 127.8, 128.1, 128.3, 128.6, 128.7, 129.4, 130.2, 130.3, 131.5, 136.0, 137.7, 138.1, 139.9, 140.7, 142.1, 158.8; IR (neat) 3023, 2926, 2857, 1605, 1510, 1487, 1470, 1443, 1283, 1244, 1177, 1113, 1022, 911, 828, 756, 733, 698 cm^{-1}.

5d: from **1** (0.0478 g, 0.125 mmol), **2d** (0.0758 g, 0.125 mmol) and **3a** (0.137 g, 0.500 mmol); Yield 93.1 % (0.0857 g, 0.116 mmol); ^{1}H-NMR (δ, ppm) 1.02-1.86 (-CH_2-, 20H), 2.50-2.96 (-CH_2-, 4H), 3.75-4.02 (-OCH_2-,4H) 6.51-7.51 (-C=CH-, -C_6H_5, -C_6H_4-, 28H);

^{13}C-NMR (δ, ppm) 26.0, 29.3, 37.5, 68.1, 82.3, 114.1, 114.5, 116.9, 126.3, 127.2, 127.7, 127.8, 128.1, 128.3, 128.6, 129.4, 130.2, 130.3, 131.5, 135.9, 137.7, 138.1, 140.7, 142.1, 158.9; IR (neat) 3023, 2927, 2855, 1605, 1510, 1487, 1470, 1443, 1283, 1224, 1177, 1111, 1028, 828, 756, 698 cm^{-1}.

5e: from **1** (0.0478 g, 0.125 mmol), **2e** (0.0390 g, 0.125 mmol) and **3a** (0.137 g, 0.500 mmol); Yield 63.6 % (0.0427 g, 0.080 mmol); ^{1}H-NMR (δ, ppm) 2.40-3.00 (-CH$_2$-, 4H), 6.40-7.72 (-C=CH-, -C$_6$H$_4$-, -C$_6$H$_5$, 28H); ^{13}C-NMR (δ, ppm) 37.4, 126.7, 127.0, 127.4, 127.7, 127.9, 128.1, 128.2, 128.5, 128.7, 128.9, 129.5, 130.3, 130.4, 130.8, 130.9, 131.1, 137.5, 137.8, 139.6, 140.4, 141.4, 142.0, 142.5, 157.9; IR (neat) 3025, 2926, 2857, 1911, 1599, 1510, 1493, 1443, 1410, 1183, 1111, 1073, 1020, 1001, 909, 820, 733, 698 cm^{-1}.

References and Notes

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5. In the case of the reaction with **3b**, the starting material (i.e., 1,2-diphenylethylene) was recovered in 61 % yield.
6. Trost BM (1977) Tetrahedron 33: 2615
7. For the review related to the mechanisms on the Pd-catalyzed reactions, see: (a) Ram S, Ehrenkaufer RE (1988) Synthesis 91 (b) Tsuji J, Shimizu I (1990) J Synth Org Chem Jpn 48: 1016
8. A white powdery polymer could be isolated when the polymer was purified further by HPLC. Thus, the pale yellow color observed for the polymer after precipitation is originated from any contaminants (e.g., the palladium catalyst).
9. The small peaks appeared at 6.5 ppm in the ^{1}H-NMR spectrum might be attributed to the protons in the diene unit produced by the double insertion of the acetylene moieties. From the detailed analysis of the minor products in the model reaction of 1,2-diphenylacetylene, *p*-iodotoluene, and sodium diethyl benzylmalonate (**3a**), as described above, 1-*p*-tolyl-1,2,3,4-tetraphenyl-1,3-butadiene (*i.e.*, a double insertion product of the acetylene to the arylpalladium species) was isolated in 19 % yield (based on 1,2-diphenylacetylene) beside the major product. Although this result indicates the presence of the branched unit in **5a** by means of the double insertion of the acetylene moieties, no gelation was observed unless the polymerization was carried out with an excess amount of the diyne.
10. The double insertion process was detected as a side reaction in the model experiment. See, ref. (8).