# Palladium Catalyzed C-C Coupling for Synthesis of π-Conjugated Polymers Composed of Arylene and Ethynylene Units

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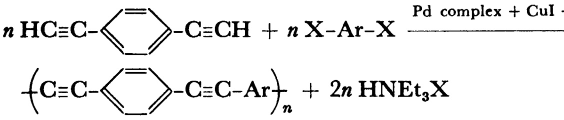
Palladium compounds such as $Pd(PPh_3)_4$ and $Pd(OAc)_2$ catalyze polycondensation between dihalo aromatic compounds, X-Ar-X (Ar=*p*-phenylene, 2,5-thiophenediyl, 9,10-anthracenediyl, 2,6-pyridinediyl, *p*-benzenedicarbonyl, *p*-xylene-α,α′-diyl), and acetylenic compounds ($p$-$C_6H_4(C\equiv CH)_2$ or $p$-$C_6H_4(C\equiv CMgBr)_2$). The polymers obtained have high thermal stabilities and most of them show fluorescence. One of the polymers is converted into semiconductors by doping with electron acceptors.

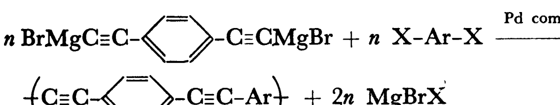
Preparation of π-conjugated polymers and studying their electric conducting properties are the subject of recent interest.[1–5] We have reported preparation of several π-conjugated, thermostable polymers such as poly(thienylene),[6] poly(phenylene),[7] and poly(1,1′-ferrocenediyl),[8] which are converted into semiconductors on doping with electron acceptors. We now report two new methods for preparation of π-conjugated polymers composed of arylene and ethynylene units.

Method I.



(1)

Method II.



(2)

Both the methods utilize Pd-catalyzed C–C coupling reactions. The basic reaction for Method I,

$$RC\equiv CH + R'X + Et_2NH \xrightarrow{\text{Pd complex}} RC\equiv CR' + Et_2NH_2X \qquad (3)$$

was developed by Hagihara and his coworkers.[9] They utilized a similar reaction to synthesize Pt-, Pd-, or Ni-containing polyynes.[10] The basic reaction for Method II,

$$RhC\equiv CMgBr + PhI \xrightarrow{\text{Pd complex}} PhC\equiv CPh + MgBrI \qquad (4)$$

was developed by Sekiya and Ishikawa.[11] Polymers containing C≡C bonds in their main chains have been recently prepared by several research groups.[10,12,13] A part of results given in this paper was reported elsewhere.[14]

## Results and Discussion

We first examined applicability of the Pd-catalyzed coupling reactions (3) and (4), which have been mainly developed for monohaloaromatic compounds, to condensation of two acetylene units with dihaloaromatic compounds (Eqs. 5 and 6).

$$X\text{-}Ar\text{-}X + 2PhC\equiv CH \xrightarrow{\text{Pd}} PhC\equiv C\text{-}Ar\text{-}C\equiv CPh \qquad (5)$$

$$X\text{-}Ar\text{-}X + 2PhC\equiv CMgBr \xrightarrow{\text{Pd}} PhC\equiv C\text{-}Ar\text{-}C\equiv CPh \qquad (6)$$

As shown in Table 1, $Pd(PPh_3)_4$ and $Pd(OAc)_2$ serve as good catalysts for the coupling reactions between dihaloaromatic compounds and the acetylenic compounds when used with an appropriate co-catalyst and/or base, whereas $PdCl_2$, $FeCl_2$, $FeCl_3$, $NiCl_2$, and $NiCl_2(bpy)$ were not effective for the C-C coupling reaction. Use of pyridine, instead of $NEt_3$, did not give the product, either. The products were characterized by elemental analysis and IR spectroscopy. The products, except for 1,4-bis(phenylethynylcarbonyl)benzene obtained in Nos. 2 and 3, fluoresce by visible light strongly when irradiated by UV light. Fluorescence of 9,10-bis(phenylethynyl)anthracene (product in No. 1) pre-

TABLE 1. Pd-CATALYZED COUPLING REACTIONS BETWEEN X-Ar-X AND PhC≡CH (A) OR PhC≡CMgBr (B)

| No. | Acetylenic compound[a)] | X-Ar-X[b)] | Catalyst[c)] | Base | Solvent | Temp °C | Time h | Yield[d)] % | Product[e)] Color | Product[e)] Fluorescence |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | A (2) | $C_{14}H_8Br_2$ | $Pd(PPh_3)_4+2\,CuI$ | $NEt_3$ | None | 89 | 3 | 100 | Brown | Green |
| 2 | A (2) | $C_6H_4(COCl)_2$ | $Pd(PPh_3)_4$ | $NEt_3$ | None | 89 | 0.1 | 92 | White | None |
| 3 | A (2) | $C_6H_4(COCl)_2$ | $Pd(OAc)_2+2\,PPh_3$ | $NEt_3$ | None | 89 | 0.1 | 85 | | |
| 4 | A (2) | $C_6H_4I_2$ | $Pd(PPh_3)_4+2\,CuI$ | $NEt_3$ | None | 89 | 0.05 | 100 | White | Bluish purple |
| 5 | B (4) | $C_6H_4Br_2$ | $Pd(OAc)_2+2\,PPh_3$ | None | THF | 66 | 2 | 92 | | |
| 6 | B (2) | $C_6H_4Br_2$ | $Pd(OAc)_2+2\,PPh_3$ | None | THF | 66 | 3 | 79 | | |
| 7 | B (2) | $C_6H_4I_2$ | $Pd(OAc)_2+2\,PPh_3$ | None | THF | 66 | 2 | 73 | | |
| 8 | B (2) | $C_4H_2SBr_2$ | $Pd(OAc)_2+2\,PPh_3$ | None | THF | 66 | 2 | 76 | Yellow | Bluish purple |

a) Molar ratios to X-Ar-X are given in the parentheses. b) $C_{14}H_8Br_2$=9,10-Dibromoanthracene. $C_6H_4(COCl)_2$=*p*-Benzenedicarbonyl dichloride. $C_6H_4X_2$=*p*-Dihalobenzene. $C_4H_2SBr_2$=2,5-Dibromothiophene. c) About 1 mol% of the Pd catalyst per mol of X-Ar-X was added. d) Yield of $(PhC\equiv C)_2Ar$ based on X-Ar-X. e) Color and fluorescing color of the product are shown.

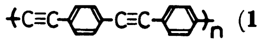
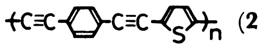
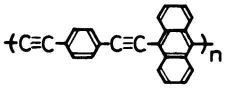
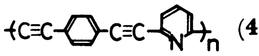
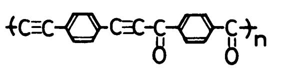
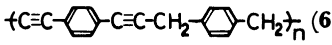
TABLE 2. Pd-CATALYZED POLYCONDENSATION BETWEEN X-Ar-X AND $p$-$C_6H_4(C{\equiv}CH)_2$ (A) OR $p$-$C_6H_4(C{\equiv}CMgBr)_2$ (B)

| Run | X-Ar-X[b] | Catalyst | Time / h | Yield[c] / % | Polymer obtained |
|---|---|---|---|---|---|
| Route I: Diacetylenic compound = A[a] | | | | | |
| 1 | $C_6H_4Br_2$ | $Pd(PPh_3)_4 + 2\ CuI$ | 2 | 79 | **1** |
| 2 | $C_6H_4I_2$ | $Pd(PPh_3)_4 + 2\ CuI$ | 2 | 97 | **1** |
| 3 | $C_4H_2SBr_2$ | $Pd(PPh_3)_4 + 2\ CuI$ | 2 | 84 | **2** |
| 4 | $C_{14}H_8Br_2$ | $Pd(PPh_3)_4 + 2\ CuI$ | 2 | 93 | **3** |
| 5 | $C_5H_3NBr_2$ | $Pd(PPh_3)_4 + 2\ CuI$ | 2 | 95 | **4** |
| 6 | $C_6H_4(COCl)_2$ | $Pd(PPh_3)_4 + 2\ CuI$ | 3 | 64 | **5** |
| Route II: Diacetylenic compound = B[d] | | | | | |
| 7 | $C_6H_4I_2$ | $Pd(PPh_3)_4$ | 2 | 97 | **1** |
| 8 | $C_4H_2SBr_2$ | $Pd(OAc)_2 + 2\ PPh_3$ | 3 | 82 | **2** |
| 9 | $C_6H_4(CH_2Cl)_2$ | $Pd(OAc)_2 + 2\ PPh_3$ | 3 | 72 | **6** |

a) Excess $NEt_3$ was added. In toluene under reflux. Amount of Pd catalyst = 0.01 mol per mol of X-Ar-X. b) $C_5H_3NBr_2$ = 2,6-Dibromopyridine. $C_6H_4(CH_2Cl)_2$ = $p$-Bis(chloromethyl)benzene. c) Yield based on the weight of carbon in the polymer (calculated from the weight and carbon content of polymer). Yield after removing toluene extractable fraction (see Experimental). d) In THF under reflux. Amount of Pd catalyst = 0.01 per mol of X-Ar-X.

pared through an independent reaction route have been extensively studied.[15] Recently Marvel and his coworkers reported preparation of 1,4-bis(phenylethynyl)benzene by a similar Pd-catalyzed coupling reaction.[16] 1,4-Bis(phenylethynylcarbonyl)benzene and 2,5-bis(phenylethynyl)thiophene prepared in Nos. 2 (or 3) and 8, respectively, are new compounds.

Based on the results shown in Table 1, we have carried out the polycondensation expressed by Eqs. 1 and 2. Table 2 shows the results. The repeating units of the new polymers thus obtained are shown below.

| | Color | Fluorescence |
|---|---|---|
|  (1) | Yellow | Bluish purple |
|  (2) | Yellow | Bluish purple |
|  (3) | Red | Green |
|  (4) | Light yellow | Purple |
|  (5) | White | None |
|  (6) | Yellow | Purple |

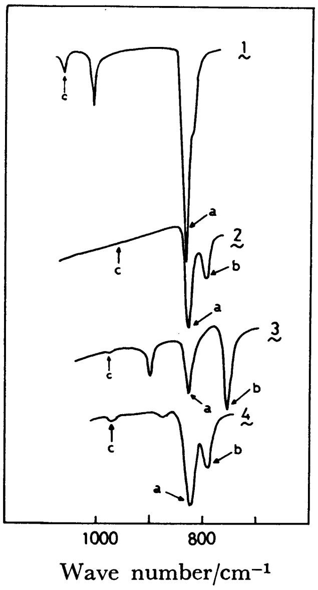


Fig. 1. IR spectra (in the range of 1100—700 cm$^{-1}$) of **1**—**4** obtained in Runs 1, 3, 4, and 5 (Table 2). Arrows a, b, and c show δ(C–H) of $p$-phenylene unit, δ(C–H) of other arylene unit, and position of ν(C–Br) of the terminal –Ar–Br group, respectively.

As shown in Table 2, yields of polymers attained by using Method I and Method II are comparable. Since Method II requires precaution to remove water from the reaction system, we consider that Method I is suprior to Method II in preparing the polymers.

The polymers, except for **5**, show strong fluorescence when irradiated by UV light. The polymers have low solubility in solvents. TGA curves of **1**, **2**, and **3** indicate that these polymers have high thermal stabilities. Degradation of these polymers starts at about 380 °C under $N_2$, and the TGA curves show residual weight of 70—85% at 800 °C. IR spectra of **1**—**6** are consistent with the structures described above, showing ν(C≡C) bands at about 2200 cm$^{-1}$, δ(C–H) of the phenylene unit at 830—835 cm$^{-1}$, and δ (C–H) of other arylene units, Ar, (*e.g.*, *cf.* Fig. 1). The IR spectrum of **5** shows a strong ν(C=O) band at 1630 cm$^{-1}$. IR spectra of **1**, **4**, and **6** show weak ν(C-halogen) bands of terminal groups of the polymers but ν(C–H) of terminal –C≡CH group is not observable in the IR spectra.[17] Since the ν(C–H) absorption band of –C≡CH generally has an absorption coefficient comparable to that of the ν(C-halogen) absorption band, the IR data indicate that most of terminal groups of the polymers are consisted of the halogenated group, –Ar–X. The low solubility of the polymers prevented measuring molecular weights of the polymers by usual methods. However, if we assume that the both polymer ends have halogen, the molecular weights of the polymers are calculated from their halogen contents. The molecular weights of **1**, **2**, **3**, and **4** prepared by Method I thus calculated are 1400(Run 1)—1690(Run 2), 4000, 1760, 1550, respectively. Polymers **1** and **2** prepared by Method II have comparable molecular weights to those of **1** and **2** prepared by Method I. Deposition of the polymers from the polymerization solvent seems to prevent further elongation of the polymer chain by the polycondensation. The molecular weight of some polymers can be roughly estimated also by comparing the strength of $\nu$(C–halogen) absorption band with that of $\delta$(C–H) of the phenylene and arylene unit in IR spectra of the polymers. The molecular weights thus estimated roughly agree with the molecular weights calculated from the halogen content. Powder X-ray diffraction patterns of the polymers show sharp diffraction bands, indicating high crystallinity of the polymers.

Polymers **1**—**6** are insulators having electric conductivity ($\sigma$) of below $10^{-12}$ S cm$^{-1}$. Polymers **1**, **2**, and **4** showed no apparent interaction with $I_2$, whereas **3** and **5** showed interaction with $I_2$ (gas). Polymer **3** showed electric conductivity of $\sigma=4\times10^{-5}$ S cm$^{-1}$ after exposure to vapor of $I_2$ for 18 h at room temperature, but the iodine adduct of **5** (iodine: 24 wt% per **5**) remained as an insulator. Polymer **3** showed certain electric conductivity ($\sigma=6.6\times10^{-8}$ S cm$^{-1}$ at 247 K) after exposure to vapor of $AsF_5$, whereas it did not interact with tetracyanoethylene and tetracyanoquinodimethane as proved by no change in IR spectrum after dipping **3** in solutions of these electron acceptors.

## Experimental

*Materials, Analysis, and Manipulation.* $Pd(PPh_3)_4$ was prepared according to literature.[18] $Pd(OAc)_2$, CuI, $PPh_3$, $NEt_3$, and crystalline dihaloaromatic compounds were used as purchased from Tokyo Kasei Kogyo Co., Ltd. or Kanto Chemical Co., Inc. 2,5-Dibromothiophene was recrystallized from hexane at 78 °C. $PhC\equiv CMgBr$ was prepared *in situ* by a reaction of $PhC\equiv CH$ with EtMgBr in a 1:1 ratio. 1,4-Diethynylbenzene was prepared according to literature,[19] and purified by sublimation: mp 96 °C (lit, 96.5 °C). Solvents were dried over $CaH_2$ or Na, distilled under $N_2$, and stored under $N_2$. Microanalysis of C, H, and N was performed with a Yanagimoto CHN Autocorder MT-2, and that of halogen with a Yazawa halogen analyzer. IR spectra were recorded on a Hitachi 295 spectrometer. Thermogravimetric analysis was performed with a Shimadzu thermoanalyzer DT-30. Powder X-ray diffraction patterns were obtained with Phillips PW-1051. Electric conductivity was measured wth a Takeda Riken TR-8651 electrometer. The powdery polymer–electron acceptor adduct was molded into a pellet (diameter=1.3 cm) by pressing it at 600 kg/cm$^2$. From the pellet a bar was obtained by cutting off other parts of the pellet and the electric conductivity was measured with the bar using the four-point method. Reactions listed in Tables 1 and 2 were carried out under nitrogen or argon by using Schlenk type tubes.

*Coupling Reactions between X–R–X and $PhC\equiv CH$ or $PhC\equiv CMgBr$ (cf. Table 1).*

*No. 1*: $Pd(PPh_3)_4$ (36 mg, 0.031 mmol) and CuI (12 mg, 0.062 mmol) were added to a mixture of 9,10-dibromoanthracene (1.06 g, 3.15 mmol), $PhC\equiv CH$ (0.645 g, 6.32 mmol), and $NEt_3$ (1.6 cm$^3$, 15 mmol). The reaction mixture was stirred for 3 h under reflux. Then, it was poured into an excess amount of methanol after cooling to room temperature. The light precipitate was collected by filtration and recrystallized to yield 0.72 g (1.9 mmol) of known 9,10-bis(phenylethynyl)anthracene.[15] Condensation of the methanol solution gave another crop (9.59 g, 1.3 mmol) of 9,10-bis(phenylethynyl)anthracene. Found: C, 95.4; H, 4.6%. Calcd for $C_{30}H_{18}$: C, 95.2; H, 4.8%.

Nos. 2—4 were carried out analogously. $p$-$(PhC\equiv CCO)_2C_6H_4$ was characterized by IR and elemental analysis. Found: C, 86.2; H, 4.2%. Calcd for $C_{24}H_{14}O_2$: C, 86.2; H, 4.2; mp 185 °C. IR(KBr): 2200s, 1640s, 1320m, 1205m, 1030m, 750s, 695m, 680m. 1,4-bis(phenylethynyl)benzene was characterized by IR and mp, 182 °C (lit,[19] 180—183 °C).

*No. 5*: A THF (11 cm$^3$) solution of $C_2H_5MgBr$ (13.6 mmol) was added to a THF solution of $PhC\equiv CH$ (1.39 g, 13.6 mmol) at room temperature, and the mixture was stirred for 2 h. To this mixture were added 0.80 g (3.4 mmol) of $p$-dibromobenzene, 10 mg of $Pd(OAc)_2$ and 34 mg of $PPh_3$. After the reaction mixture was stirred for 2 h under reflux, it was cooled to room temperature. Excess of dil. aqueous HCl solution was added to the reaction mixture. Extraction of the product with benzene, drying the benzene solution with $MgSO_4$, purification by column chromatography ($Al_2O_3$, benzene), and evaporation of benzene gave crystals of 1,4-bis(phenylethynyl)benzene: yield=0.87 g (92%), after recrystallization from toluene. Reactions shown by Nos. 6 and 7 were carried out analogously.

*No. 8*: A THF (14 cm$^3$) solution of $C_2H_5MgBr$ (24.2 mmol) was added to 2.48 g (24.2 mmol) of phenylacetylene. After stirring for 1.5 h at room temperature, 2,5-dibromothiophene (2.93 g, 12 mmol), $Pd(OAc)_2$ (39 mg, 0.12 mmol), and $PPh_3$ (100 mg, 0.24 mmol) were added to the reaction mixture. After stirring the reaction mixture for 2 h under reflux, it was cooled to room temperature. An excess amount of dil aqueous HCl solution was added to the reaction mixture. Extraction of the product with benzene, drying the benzene solution with $MgSO_4$, purification by the column chromatography, and recrystallization from methanol gave 2.61 g (76%) of brown 2,5-bis(phenylethynyl)thiophene, which was characterized by IR and elemental analysis; mp 85 °C. Found, 83.8; H, 4.3; S, 10.7%. Calcd. for $C_{20}H_{12}S$: C, 84.5; H, 4.3; S, 11.3%. IR(KBr disk): 1590m, 1480m, 1440m, 800s, 750s, and 680s.

*Polycondensation (cf. Table 2).* *Run 1*: $Pd(PPh_3)_4$ (27 mg, 0.023 mmol) and CuI (8 mg, 0.04 mmol) were added to a mixture of $p$-diethynylbenzene (300 mg, 2.38 mmol), $p$-dibromobenzene (562 mg, 2.38 mmol), and $NEt_3$ (2 cm$^3$) in toluene (39 cm$^3$). After stirring for 2 h under reflux, the reaction mixture was poured into excess methyl alcohol. The precipitate obtained was separated by filtration, washed repeatedly with methyl alcohol, and dried under vacuum to obtain 510 mg of **1**. After removing a toluene-soluble fraction of **1** by extraction with hot toluene using a Soxhlet extractor, the yellow solid was dried under vacuum to yield 0.43 g of **1**. Found: C, 83.5; H, 3.7; Br, 11.4%. From the toluene extract we obtained 80 mg of low molecular weight **1**. Polymerization in Run 2 was carried out analogously.

*Run 3*: $Pd(PPh_3)_4$ (45 mg, 0.039 mmol) and CuI (15 mg, 0.080 mmol) were added to a mixture of $p$-diethynylbenzene (514 mg, 4.07 mmol), 2,5-dibromothiophene (985 mg, 4.07 mmol), and $NEt_3$ (3 cm$^3$) in toluene (50 cm$^3$). After stirring for 2 h under reflux, the polymer obtained was treated as in the case of Run 1 to obtain 810 mg of crude **2**, from which 710 mg of toluene-unextractable **2** was obtained. Found: C, 80.2; H, 2.9; Br, 4.0%.

*Runs 4—6* were carried out analogously. Analytical data of **3**, **4**, and **5** are as follows. **3**: Found: C, 87.3; H, 3.8; Br, 9.1%. **4**: C, 80.7; H, 3.2; N, 6.1; Br, 10.3%. **5**:C, 77.4; H, 3.7; Br, 4.4%.

*Run 7*: When a THF (9.2 cm$^3$) solution of $C_2H_5MgBr$

(15.6 mmol) was added into a Schlenk tube containing 986 mg (7.82 mmol) of 1,4-diethynylbenzene at room temperature, vigorous evolution of ethane was observed. After addition of 7 cm$^3$ of THF and stirring the reaction mixture for 5 h at room temperature, 2.58 g (7.82 mmol) of *p*-diiodobenzene in 5 cm$^3$ of THF, 18 mg (0.080 mmol) of Pd(OAc)$_2$, and 42 mg (9.16 mmol) of PPh$_3$ were added. This reaction mixture was stirred for 2 h under reflux. After cooling to room temperature, the reaction mixture was poured into an HCl–methyl alcohol mixture (150 cm$^3$). This light yellow precipitate was collected by filtration, washed with methyl alcohol, and dried under vacuum to obtain 920 mg of crude **1**. Removing a toluene-soluble fraction (by Soxhlet technique) gave 800 mg of **1**. Found: C, 80.4; H, 3.0; I, 15.7%.

*Runs 8 and 9* were carried out analogously. **6**: C, 90.9; H, 4.7; Br, 1.2%.

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17) The IR spectra of toluene-extractable, low molecular weight fractions obtained during work-up of the polymers (see Experimental), show stronger $\nu$(C–halogen) bands. However, the $\nu$(C–H) band of the $-\mathrm{C{\equiv}CH}$ group is not observable or very weak.

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