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Synthesis of Novel Substituted Poly(arylene−vinylene)s by the Palladium-Catalyzed Three-Component Coupling Polymerization

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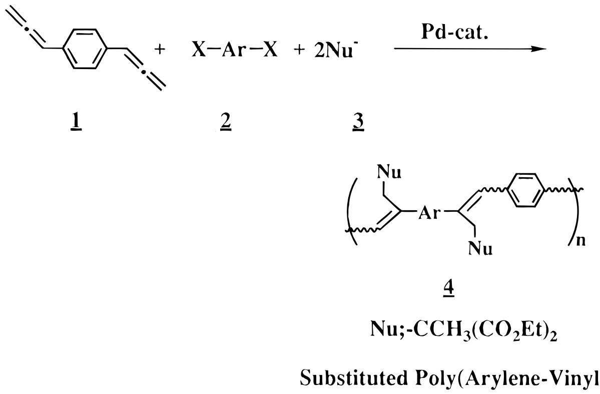
The characteristic properties of π-conjugated polymers allow them to be applied to electronic and optoelectronic devices such as rechargeable batteries and electroluminescent devices.[1] The palladium-catalyzed polymerization system represents one of many useful strategies for the preparation of these polymers. For instance, the application of the Suzuki coupling,[2] the Stille coupling,[3] and the Heck reaction[4] enables one to supply a variety of conjugated polymers, including polyarylenes and poly(arylene−vinylene)s. However, poor proccessability, functionality, and solubility of the resulting polymers have required the structural modification of monomers.

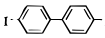
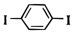
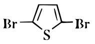
Recently, we have reported the three-component coupling polymerization of bis(allene), aryl dihalides, and nucleophiles by using a palladium catalyst to give highly functional polymers containing building blocks originating from three kinds of monomers in high yields.[5] In the coupling polymerization, the character of the nucleophiles affects the structures of the obtained polymers.[6] We report herein the three-component coupling polymerization of an aromatic allene *via* a π-allylpalladium complex[7] as a new convenient route to produce various poly(arylene−vinylene)s bearing functional groups with ordered sequences (Scheme 1).

Scheme 1



The three-component coupling polymerization of **1**, 4,4′-diiodobiphenyl (**2a**), and **3** was carried out at 80 °C for 3 h in 1,4-dioxane by using Pd(OAc)$_2$−4P(*o*-tolyl)$_3$ catalyst (3 mol %).[8] The poly(arylene−vinylene) bearing the nucleophilic part (i.e., diethyl methylmalonate moieties) in the side chain (**4a**) was obtained in 92% yield. The obtained white powdery polymer (**4a**) is soluble in common organic solvents and has a good film-forming character. The proposed structure of **4a** was confirmed to be an objective one by ^{1}H-NMR, ^{13}C-NMR, IR spectra, and elemental analysis.[9] The 10% weight loss and the glass transition temperatures (T_{d10} and T_g) of the polymer (**4a**) were observed at 323.6 and 64.8 °C, respectively. As summarized in Table 1, various aryl dihalides (**2a**−**c**) gave the corresponding poly(arylene−vinylene)s in high yields. In the case of 1,4-diiodobenzene (**2b**), a substituted poly(*p*-phenylene−vinylene)

Table 1. Polymerizations of 1, 3, and Various Dihalides (2a−c)[a]

Run	Aryl Dihalide	Yield(%)[b)]	$\overline{M}_n(\overline{M}_w/\overline{M}_n)$[c)]
1	 (2a)	92	19,400(1.94)
2	 (2b)	84	21,700(1.96)
3	 (2c)	67	15,000(1.97)

[a] Polymerizations were carried out at 80 °C for 3 h in 1,4-dioxane with 3 mol % of the palladium catalyst. [b] Isolated yields after precipitation with methanol and then with *n*-hexane. [c] GPC (THF, PSt, Std).

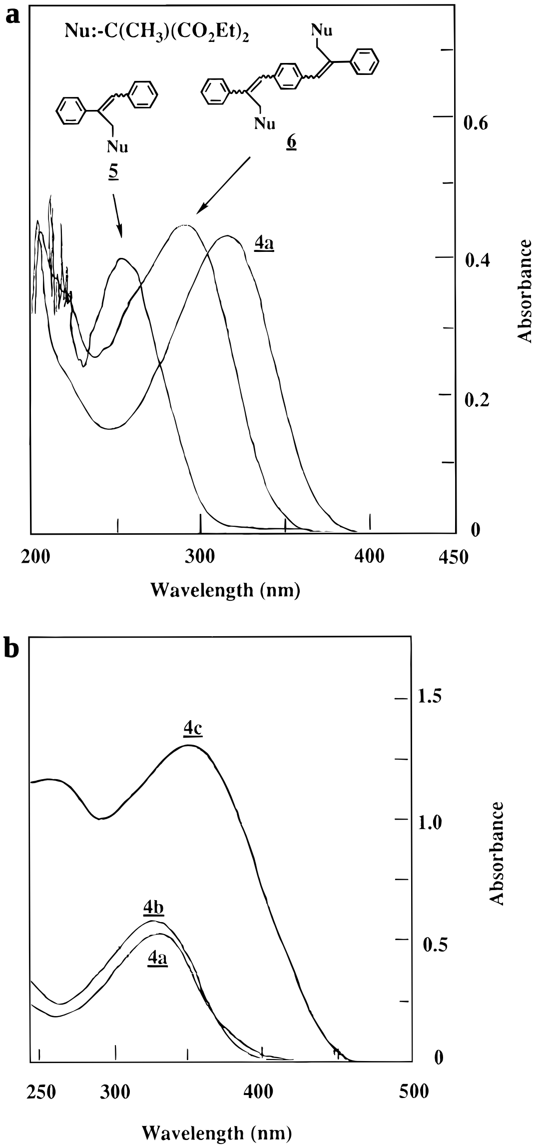


Figure 1. UV spectra of model compounds (**5** and **6**) and **4a** (a) and those of polymers (**4a**−**c**) (b) in 1,4-dioxane (c = 0.01 mmol/L).

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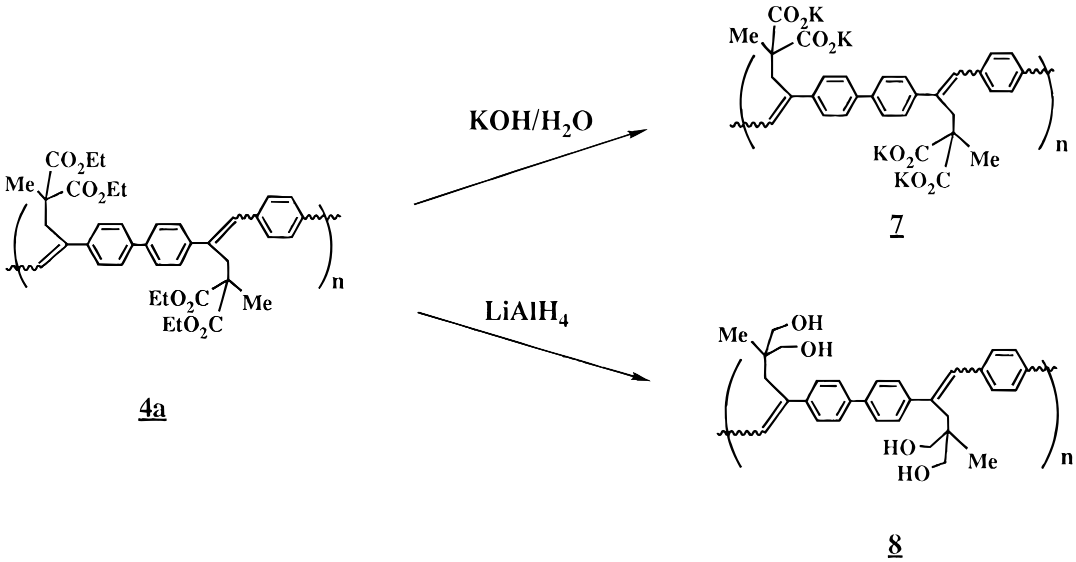
Scheme 2



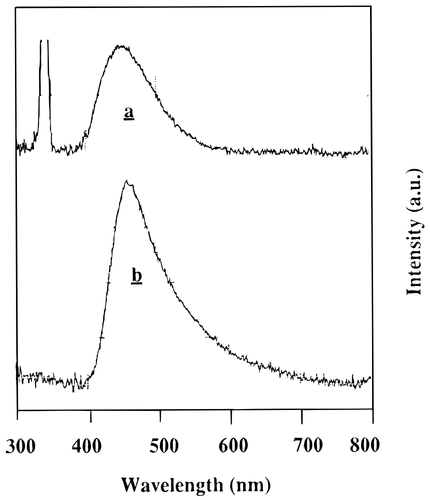


Figure 2. (a) PL spectrum of the polymer (**4a**). (b) EL spectrum of an ITO/polymer (**4a**)/Mg:Ag device.

(PPV) (**4b**) was obtained in 84% (M_n = 21 700, run 2). From 2,5-dibromothiophene (**2c**), a yellow-colored poly(heteroarylene–vinylene) (**4c**) was also obtained in 67% yield.

The ultraviolet spectra of the obtained polymers (**4a–c**) and those of the corresponding model compounds in 1,4-dioxane (c = 0.01 mmol/L) are shown in Figure 1. Compared with the absorption maximum (λ_{max}) of the model compounds (**5**, 260 nm, and **6**, 300 nm), those of the polymers appeared at higher wavelengths (e.g., **4a**, 325 nm, and **4c**, 352 nm).[10] The polymer (**4a**) is active for both photoluminescence (PL) and electroluminescence (EL) spectra (Figure 2). A blue green light was observed from the EL single-layer-type device (i.e., ITO/**4a**/Mg:Ag device) in a continuous dc mode with Mg:Ag negative. The result may indicate that the electron–hole recombination takes place in the polymer layer, resulting in excitation of the polymer. The ionic potential of the polymer was measured as 5.93 eV, and the LUMO was estimated to be 2.93 eV by the ionic potential and the UV spectrum. Accordingly, the polymer (**4a**) may be expected to be an electron transport polymer.[12]

To modify the properties of the polymer (**4a**), hydrolysis of diethyl methylmalonate moieties in **4a** was carried out under basic conditions to produce a water-soluble polymer (**7**) in quantitative yield.[13] Reduction of diethyl methylmalonate moieties in **4a** was also carried out with $LiAlH_4$ to give a polymer having diol moieties (**8**) in the side chain (Scheme 2).[14]

Since the present synthetic methodology is suitable to incorporate various three-membered building blocks into the polymer structures with ordered sequences simply by varying the appropriate monomers, design and synthesis of various functional substituted poly(arylene–vinylene)s are currently being investigated.

Supporting Information Available: Text giving synthetic details and figures showing spectral data (6 pages). Ordering information is given on any current masthead page.

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(8) To a test tube equipped with a magnetic stirrer chip were added tri-*o*-tolylphosphine (0.0182 g, 0.060 mmol), $Pd(OAc)_2$ (0.0034 g, 0.015 mmol), **2a** (0.203 g 0.5 mmol), **3** (0.392 g, 2.00 mmol), and 1,4-dioxane (1.1 mL), and the mixture was kept stirring at ambient temperature for 15 min under nitrogen. To the resulting solution, **1** (0.073 g, 0.50 mmol) in 1,4-dioxane (0.9 mL) was added and the tube was sealed

under reduced pressure. After the reaction at 80 °C for 3 h, the reaction mixture was precipitated with methanol and then with *n*-hexane. The precipitate was freeze-dried from benzene. **4a**: yield 92% (0.300 g, 0.460 mmol).

(9) **4a**: ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm) 0.95−1.24, 1.30−1.48 (−CH_3, 18H), 3.18, 3.24, 3.50, 3.59 (−C═C−CH_2−, 4H), 3.64−4.04 (−OCH_2−, br, 8H), 6.39, 6.52, 6.68, 6.78 (−C═CH−, 2H), 6.96, 7.10−7.70 (−C_6H_4−, 12H); ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm) 13.8, 19.6, 25.6, 34.1, 53.4, 61.1, 67.9, 126.4, 126.9, 127.9, 128.5, 128.8, 129.8, 133.3, 135.3, 136.1, 138.4, 139.4, 142.2, 171.7; IR (in CH_2Cl_2) 2984, 2940, 2905, 1730, 1604, 1495, 1447, 1379, 1296, 1240, 1194, 1107, 1022, 912, 860, 833, 733 cm^{-1}. Anal. Calcd for $C_{40}H_{44}O_8$: C, 73.53; H, 6.74. Found: C, 73.26; H, 6.89. The obtained polymer (**4a**) contained three isomeric units (i.e., *E*−*E*, *Z*−*Z*, and *E*−*Z*) and the isomeric ratio of **4a** was estimated as ca. 42:46:11.

(10) The $\lambda_{\mathrm{max,abs}}$ of PPV (all-trans) has been reported to be ca. 420 nm by the models of PPV (see ref 11). The obtained polymer (**4a**) had λ_{max} in shorter wavelength, probably due to the steric restriction caused by the side chain and the contamination of the *Z*-unit.

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(13) **7**: yield 100% (0.145 g, 0.37 mmol); ^{1}H-NMR (400 MHz, D_2O, δ, ppm) 0.90 (−CH_3, br, 6H), 3.33 (C═C−CH_2, br, 4H), 6.40−6.80 (C═CH−, br, 2H), 6.90−7.70 (−C_6H_4−, 12H); ^{13}C-NMR (100 MHz, D_2O, δ, ppm) 21.0, 21.7, 35.0, 57.1, 126.1, 126.9, 128.5, 129.0, 135.0, 135.3, 135.9, 138.2, 182.4; IR (KBr) 2926, 1562, 1414, 1342, 1044, 465 cm^{-1}.

(14) **8**: ^{1}H-NMR (400 MHz, DMSO-d_6, δ, ppm) 0.60 (−CH_3, br, 6H), 2.80−3.30 (C═C−CH_2−, C−CH_2−OH, br, 12H, *E* and *Z*), 4.32 (−OH, br, 4H), 6.40, 6.54, 6.70 (C═CH−, br, 4H), 6.92, 7.28, 7.53, 7.72 (−C_6H_4−, br, 12H); ^{13}C-NMR (100 MHz, DMSO-d_6, δ, ppm) 18.7, 32.0, 41.6, 66.0, 126.1, 126.5, 127.4, 128.9, 130.9, 136.1, 138.0, 140.9, 144.6; IR (KBr) 3376, 3027, 2930, 2874, 1601, 1495, 1464, 1395, 1262, 1115, 1036, 895, 830, 766, 698, 542 cm^{-1}.

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