Synthesis of Wholly Aromatic Polymers Possessing Tetra-aryl-substituted Vinylene Units by Palladium-catalyzed Three-component Coupling Polymerization

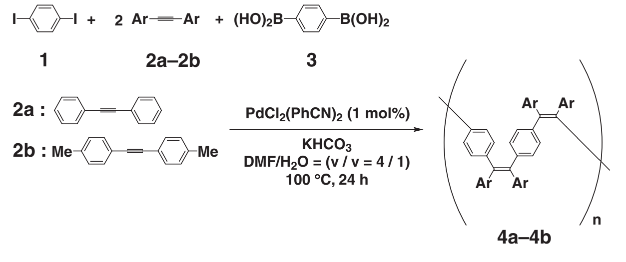
Kojiro Nakagawa and Ikuyoshi Tomita*
Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering,
Tokyo Institute of Technology, Nagatuta-cho 4259-G1-9, Midori-ku, Yokohama 226-8502

(Received January 25, 2007; CL-070092; E-mail: tomita@echem.titech.ac.jp)

The synthesis of novel wholly aromatic poly(arylenevinylene)s containing tetra-aryl-substituted olefin units in the main chain by the three-component coupling polymerization of aryl dihalides, aryl diboronic acids, and acetylene derivatives is described. For instance, a polymer ($M_n = 2600$, $M_w/M_n = 1.6$) was obtained in a 76% yield by the polymerization of 1,4-diiodobenzene, diphenylacetylene, and 1,4-phenylenediboronic acid in DMF/H_2O at 100 °C for 24 h in the presence of $PdCl_2(PhCN)_2$ (1 mol %) and $KHCO_3$. The obtained polymer is soluble in organic solvents such as $CHCl_3$, THF, and toluene, although it does not have any soft lateral segments.

Over the past few decades, a large number of studies on π-conjugated polymers have been carried out because of their characteristic properties.[1] For instance, poly(phenylenevinylene) (PPV) and its derivatives have been paid much attention in view of their potential applications in electroluminescence (EL) devices.[2] The transition metal-catalyzed polymerization systems based on homo- and cross-coupling processes represent one of the most useful strategies for the preparation of π-conjugated polymers, including PPV derivatives.[3] In these cases, however, the structural design of monomers is essentially important to overcome the poor processability and solubility of the resulting polymers. We have been working on the development and applications of three-component coupling polymerization systems in which highly functionalized polymers having well-defined sequence are accessible from simple monomers.[4] For instance, the palladium-catalyzed three-component coupling polymerization of aromatic bisallenes, aryl dihalides, and nucleophiles gives PPV derivatives possessing functional groups originated from the nucleophilic components on each vinylene unit.[4a–4d] The properties such as the solubility of the PPV derivatives can be tuned by the nature of the functional substituents.

Herein, we would like to report a new palladium-catalyzed three-component coupling polymerization of 1,4-diiodobenzene (**1**), internal alkynes (**2a** and **2b**), and 1,4-phenylenediboronic acid (**3**) as a novel synthetic method of a new class of PPV derivatives containing tetra-aryl-substituted olefin units in the main chain (Scheme 1).



Scheme 1. Synthesis of wholly aromatic polymers possessing tetra-aryl-substituted vinylene units.

On the basis of the palladium-catalyzed ternary coupling reaction of aryl halides, internal alkynes, and arylboronic acids,[5] the polymerization of **1**, **2a**, and **3** was carried out in DMF/H_2O (v/v = 4/1) at 100 °C for 24 h in the presence of $PdCl_2(PhCN)_2$ (1 mol %) and $KHCO_3$ (2 equiv.). After the reaction, a polymer **4a** was isolated by the precipitation with methanol as a yellow powder in a 76% yield.[6] In sharp contrast to the poor solubility of the unsubstituted PPV ($(–C_6H_4–CH{=}CH–)_n$), it was of fortunate that the obtained polymer **4a** exhibits good solubility in common organic solvents such as THF, $CHCl_3$, and toluene, although **4a** does not possess any soft lateral substituents. The number average molecular weight (M_n) of the polymer was estimated to be 2600 from the GPC measurement. Under the examined conditions, the polymer **4a** precipitated out during the polymerization, which might be the reason for the lower molecular weight of the polymer.

Also, a polymer having methyl substitutents (**4b**, $M_n = 2800$, $M_w/M_n = 1.5$) was obtained by the polymerization using di-*p*-tolylacetylene (**2b**) as an internal alkyne. The ^1H NMR spectrum of **4b** was informative to estimate the composition of the polymer. As shown in Figure 1, peaks for $–C_6H_4–$ and $–CH_3$ were observed, whose integral ratio (24:12) was in good agreement with that expected from the objective structure. Therefore, **4b** was confirmed to be composed of the objective tetra-aryl ethylene units. If the reaction of iodobenzene (0.5 mmol), diphenylacetylene (1.5 mmol), and phenylboronic acid (0.5 mmol) was carried out under the analogous conditions, the Suzuki–Miyaura coupling product, biphenyl was not detected in the reaction mixture. In this case, tetraphenylethylene (**5**) was isolated in a 74% yield by SiO_2 column chromatography (eluent: hexane). This result further supported that the polymers have the objective structure units.

As shown in Figures 2 and 3, the UV–vis absorption maximum (λ_{max}) of **4a** in a $CHCl_3$ solution appeared at slightly longer wavelength (330 nm) in comparison with that of a model compound, tetraphenylethylene (**5**, $\lambda_{max} = 310$ nm). A yellow transparent thin film with a thickness of about 20 µm was prepared by coating the polymer **4a** on glass substrate from a $CHCl_3$

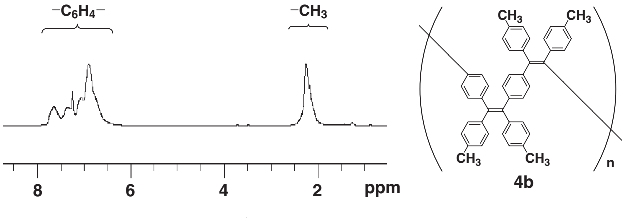


Figure 1. ^1H NMR spectrum of **4b**.

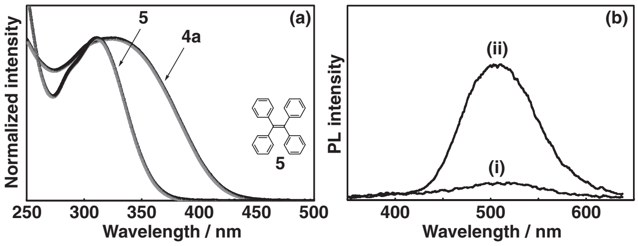


Figure 2. (**a**) UV–vis absorption spectra of **4a** and **5** in $CHCl_3$. (**b**) Photoluminescence spectra of **4a** ($c = 12.5$ mg/L, excited at 330 nm) in $CHCl_3$ (i) and in a mixed solvent of $CHCl_3$/MeOH (v/v = 30/70) (ii).

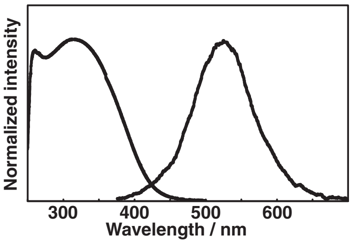


Figure 3. UV–vis absorption and photoluminescence (excited at 330 nm) spectra of **4a** in the film.

solution. The UV–vis absorption spectrum of the film was almost identical to that measured in a dilute $CHCl_3$ solution. Upon irradiation of UV–vis light, this film emits green light (λ_{em}, max = 525 nm), although only very weak fluorescence could be detected in a dilute $CHCl_3$ solution. However, it is of note that the corresponding emission was observable in a solution of a mixed solvent containing a considerable amount of poor solvent (e.g., $CHCl_3$/MeOH mixed solvent, v/v = 30/70) although **4a** could be dissolved completely under the examined conditions (Figures 2 and 3). By increasing the content of the poor solvent, the interaction between the polymer chains becomes much stronger than that in a solution without poor solvents. We assume that the fluorescence observed in the film and in the presence of poor solvents is due to the suppression of the twisting vibration of the aromatic rings in **4a**.[7]

In summary, a new class of wholly aromatic polymers having PPV backbone and the aryl substituents on the vinylene units was obtained by the palladium-catalyzed three-component coupling polymerization of 1,4-diiodobenzene, internal alkynes, and 1,4-phenylenediboronic acid. On the basis of the present polymerization method, a variety of fully substituted poly(aryl-enevinylene)s are expected to be produced by the simple monomer design. Thus, the synthesis and properties of a series of polymers are currently being investigated.

References and Notes

1 a) T. Ito, H. Shirakawa, S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11. b) A. F. Diaz, K. K. Kanazawa, G. P. Gardini, *J. Chem. Soc., Chem. Commun.* **1979**, *14*, 635. c) T. Yamamoto, K. Sanechika, A. Yamamoto, *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 9. d) L. W. Schacklette, R. R. Chance, D. M. Ivory, G. G. Miller, R. H. Baughman, *Synth. Met.* **1980**, *1*, 307. e) I. Murase, T. Ohnishi, T. Noguchi, M. Hirooka, *Polym. Commun.* **1979**, *20*, 1441.

2 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, *347*, 539.

3 a) A. Greiner, W. Heitz, *Makromol. Chem., Rapid Commun.* **1988**, *9*, 581. b) G. M. Farinola, F. Babudri, F. Naso, Y. Dubistky, A. Zaopo, F. D'Amore, S. M. Pietralunga, *Synth. Met.* **2003**, *137*, 1473.

4 a) N. Miyaki, I. Tomita, J. Kido, T. Endo, *Macromolecules* **1996**, *29*, 6685. b) N. Miyaki, I. Tomita, T. Endo, *Chem. Lett.* **1997**, 685. c) S. Kannoo, T. Saruhashi, S. Ishibe, K. Nakagawa, I. Tomita, *Polym. Bull.* **2006**, *57*, 843. d) N. Miyaki, I. Tomita, T. Endo, *Macromolecules* **1997**, *30*, 4504. e) N. Miyaki, I. Tomita, T. Endo, *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2097. f) N. Miyaki, I. Tomita, T. Endo, *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1211. g) S. Ishibe, I. Tomita, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3403.

5 C. Zhou, R. C. Larock, *J. Org. Chem.* **2005**, *70*, 3765.

6 A typical experimental procedure for the synthesis of **4a** is given as follows: to a test tube equipped with a magnetic stirrer chip were added **1** (0.082 g, 0.25 mmol), **2a** (0.267 g, 1.5 mmol), **3** (0.041 g, 0.25 mmol), $KHCO_3$ (0.050 g, 0.50 mmol), DMF (4 mL), and H_2O (1 mL). The mixture was stirred at 100 °C for 10 min. Then, a DMF solution of $PdCl_2(PhCN)_2$ (0.025 M, 0.20 mL, 0.0050 mmol) was added and the mixture was stirred at 100 °C for 24 h. After pouring into brine (10 mL), the aqueous phase was extracted three times with $CHCl_3$ (5 mL each). After drying over magnesium sulfate, the organic solution was concentrated and was precipitated into a large excess amount of methanol to give **4a** in a 76% yield (0.096 g). ^{1}H NMR (300 MHz, $CDCl_3$, δ) 6.19–8.04 ($-C_6H_5$ and $-C_6H_4-$, 28H). ^{13}C NMR (75 MHz, $CDCl_3$, δ) 126.0, 126.5, 127.2, 127.7, 130.8, 131.3, 131.8, 138.4, 139.4, 140.7, 142.1, 142.8, 143.7. IR (neat, cm^{-1}) 3056, 3027, 1803, 1665, 1597, 1491, 1443, 1400, 1345, 1275, 1181, 1111, 1074, 1030, 1005, 976, 909, 810, 733, 698. **4b**: from **1** (0.082 g, 0.25 mmol), **2b** (0.309 g, 1.5 mmol), and **3** (0.041 g, 0.25 mmol); Yield 82% (0.115 g); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.72–2.40 ($-CH_3$, 12H), 6.53–7.82 ($-C_6H_4-$, 24H). ^{13}C NMR (75 MHz, $CDCl_3$, δ) 21.2, 125.9, 127.2, 131.3, 131.9, 136.0, 138.2, 139.3, 139.6, 140.2, 140.9, 142.3, 143.3. IR (neat, cm^{-1}) 3025, 2992, 2920, 2866, 1905, 1794, 1655, 1607, 1508, 1487, 1449, 1404, 1273, 1182, 1113, 1020, 1005, 965, 909, 816, 768, 733.

7 The similar fluorescent behavior has also been reported in the cases of **5** and a polymer having analogous fully substituted vinylene structure. See Refs. 8 and 9.

8 a) S. Sharafy, K. A. Muszkat, *J. Am. Chem. Soc.* **1971**, *93*, 4119. b) P. F. Barbara, S. D. Rand, P. M. Rentzepis, *J. Am. Chem. Soc.* **1981**, *103*, 2156. c) W. Schuddeboom, S. A. Jonker, J. M. Warman, M. P. de Haas, M. J. W. Vermeulen, W. F. Jager, B. de Lange, B. L. Feringa, R. W. Fessenden, *J. Am. Chem. Soc.* **1993**, *115*, 3286.

9 D. M. Johansson, M. Theander, O. Inganäs, M. R. Anderson, *Synth. Met.* **2000**, *113*, 293.

Published on the web (Advance View) April 14, 2007; doi:10.1246/cl.2007.638