Synthesis of 3-Alkynyl-2,5-dibromothiophene and 3,3′-Dialkynyl-5,5′-dibromo-2,2′-bithiophene as the Starting Compounds for π-Conjugated Polymer

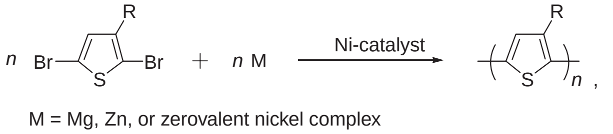
Takao Sato, Hisashi Kokubo, Hiroki Fukumoto, and Takakazu Yamamoto*

Chemical Resources Laboratory,
Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226-8503

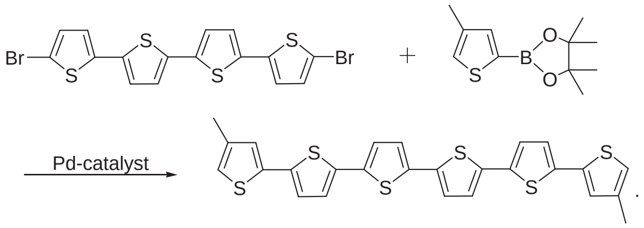
Received December 10, 2004; E-mail: tyamamot@res.titech.ac.jp

3-Alkynyl-2,5-dibromothiophene **2** and 3,3′-dialkynyl-5,5′-dibromo-2,2′-bithiophene have been prepared. Pd-catalyzed polycondensation between **2** and 2,2′-*p*-[2,5-bis(dodecyloxy)-1,4-phenylene]bis(5,5-dimethyl-1,3,2-dioxaborinane) gave a novel soluble red π-conjugated polymer.

π-Conjugated polythiophenes and oligothiophenes have been at the center of considerable scientific interest.[1–4] They have often been prepared via organometallic C–C coupling of the corresponding dihalogenated thiophenes, for example.



(1)[1–3]



(2)[5]

Consequently, dihalothiophenes are important starting compounds and syntheses of various dihalothiophenes have been carried out.[1–5] Herein we report syntheses of the following new dihalothiophenes (Chart 1 and Scheme 1[7–10]) and a new thiophene-based π-conjugated polymer.

Only one example of 2,5-dihalothiophene with such an acetylenic substituent at the β-position of thiophene has been reported, to our knowledge.[6] The compound **1** was synthesized via coupling[7,8] of 3-bromothiophene with 1-dodecyne. **3** was prepared analogously from 3,3′-dibromo-2,2′-bithiophene.[9,10] **1** and **3** were brominated by using butyllithium and CF_2BrCF_2Br.[11] **1** and **2** were characterized by IR, NMR, and high-resolution mass spectroscopy (HRMS), whereas **3** and **4** were characterized by IR, NMR, and elemental analysis. **1** and **2** were not stable and turned black after were left for about 5 days under air and at room temperature. However, they can be stored for more than 10 months under Ar at −20 °C without light.

2 exhibited UV–vis absorption peaks at a longer wavelength than its alkyl analogue (Chart 2). **2** and **4** gave new π-conjugated polymers via organometallic C–C couplings. For example, the following Pd-catalyzed polymerization gave red **Polymer-1** in 96.3% yield.

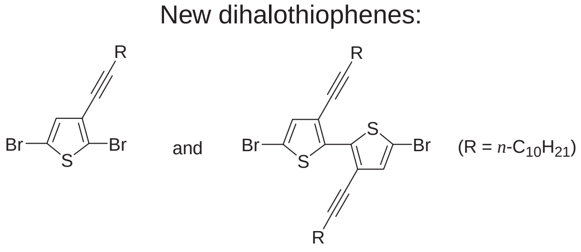
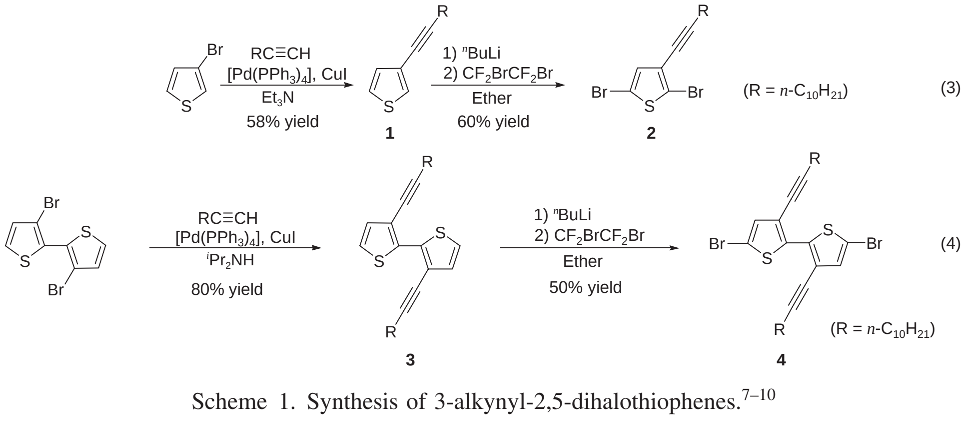


Chart 1.



Scheme 1. Synthesis of 3-alkynyl-2,5-dihalothiophenes.[7–10]

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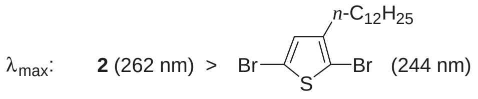
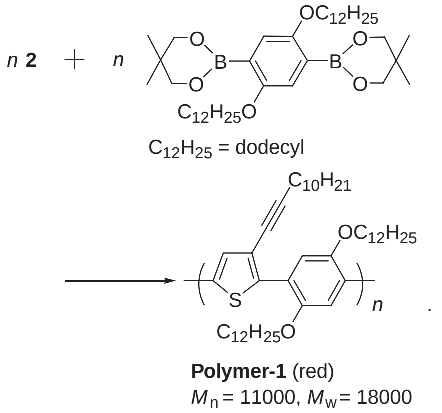


Chart 2.



(5)

Gel permeation chromatography indicated that **Polymer-1** had a number average molecular weight (M_n) of 11000 and a weight average molecular weight (M_w) of 18000, respectively.

Figures 1 and 2 exhibit the IR and the ^{1}H NMR spectra of **Polymer-1**. The IR peak of **2** at 995 cm^{-1} assigned to ν(C–Br) disappears after the polymerization. The ν(C≡C) peak of **2** shows a small shift to a lower frequency in **Polymer-1**, and the intensity of the ν(C≡C) peak is weakened, similar to the case of poly[3-(phenylethynyl)thiophene-2,5-diyl].[6]

The previously reported poly[3-(phenylethynyl)thiophene-2,5-diyl],[6] was insoluble. However, **Polymer-1** is soluble in organic solvents, and its ^{1}H NMR spectrum depicted in Fig. 2 agrees with the molecular structure.

Figure 3 shows UV–vis spectra of **Polymer-1**. The λ_{max} position (445 nm) observed in chloroform locates at a longer wavelength than those of related polymers, revealing the presence of a larger effective π-conjugation system (Chart 3).

A cast film shows a large shift of the absorption band to a longer wavelength, as depicted in Fig. 3. Such a large bathochromic shift is sometimes observed with π-conjugated polymers when they form supramolecules by stacking in the solid,[2,3,14] and the UV–vis data suggest formation of such a stacked structure in the solid. **Polymer-2** did not show such a large bathochromic shift in the solid (the inset of Fig. 3). The newly synthesized **2** and **4** are expected to serve as starting materials of new thiophene-based materials.

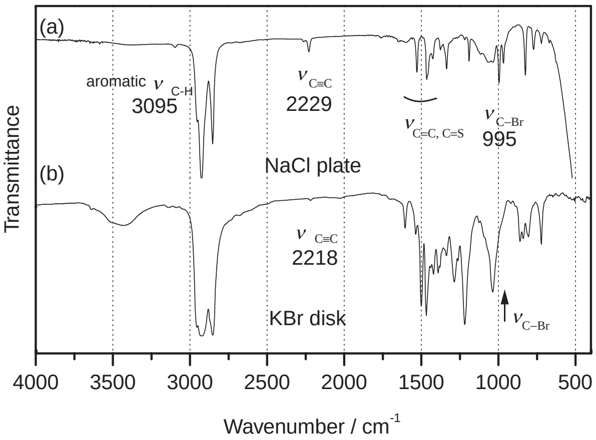


Fig. 1. IR spectra of (a) **2** and (b) **Polymer-1**.

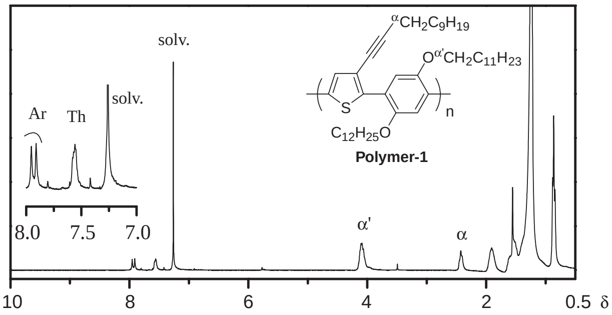


Fig. 2. ^{1}H NMR spectrum of **Polymer-1** in $CDCl_3$.

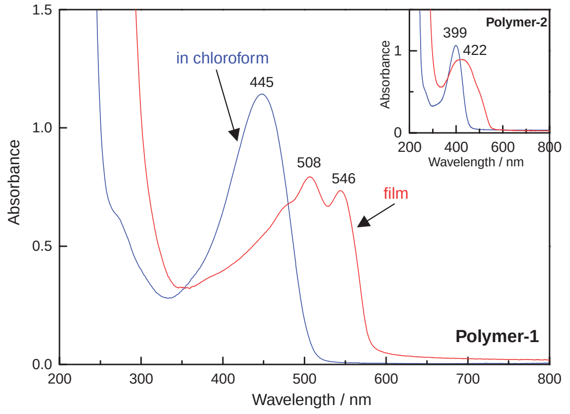


Fig. 3. UV–vis spectra of **Polymer-1**. The inset shows UV–vis spectra of **Polymer-2** in chloroform (blue line) and in the solid (red line).

Experimental

Materials. [Pd(PPh$_3$)$_4$],[15] 2,5-dibromo-3-dodecylthiophene,[16] and 2,2′-*p*-[2,5-bis(dodecyloxy)-1,4-phenylene]bis(5,5-dimethyl-1,3,2-dioxaborinane)[17] were prepared according to the literature.

Synthesis of 1. To a mixture of 3-bromothiophene (11.4 g, 70 mmol), Et_3N (150 cm^3), [Pd(PPh$_3$)$_4$] (3.23 g, 2.80 mmol), and CuI (0.53 g, 2.80 mmol) was added 1-dodecyne (14.0 g, 84 mmol); the mixture was next stirred for 8 h at 60 °C. An aqueous solution of NH_4Cl was added, and the product was extracted with chloroform (3 times). The extract was washed with an aqueous solution of NH_4Cl and dried over $MgSO_4$. After removal of the solvent, the black oil was subjected to column chromatography on SiO_2 (eluent = hexane). Removal of the eluent under vacuum gave a colorless oil of **1** (10.2 g, 58.4% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, 1H, $J = 2.9$, 1.0 Hz), 7.22 (dd, 1H, $J = 5.0$, 2.9 Hz), 7.07 (dd, 1H, $J = 5.0$, 1.0 Hz), 2.37 (t, 2H, $J = 7.1$ Hz), 1.63–1.50 (m, 2H), 1.48–1.27 (m, 14H), 0.88 (t, 3H, $J = 6.7$ Hz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 129.99, 127.44, 124.92, 122.99, 89.95, 75.49, 31.90, 29.58, 29.53, 29.32, 29.16, 28.93, 28.72, 22.68, 19.38, 14.12. HRMS (FAB): Found: 248.1604; calcd for $C_{16}H_{24}S$, 248.1599.

Synthesis of 2. An ether (100 cm^3) solution of **1** (3.92 g, 15.8 mmol) was added to a hexane solution of butyllithium (79 mmol)

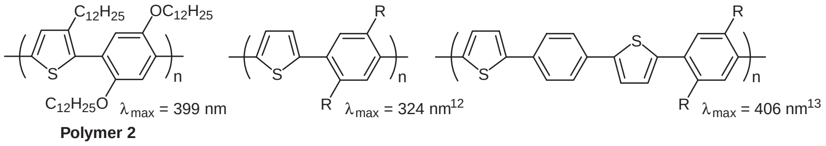


Chart 3.

at -40 °C. After the mixture was stirred for 5 h at room temperature (r.t.), an ether (40 cm^3) solution of CF_2BrCF_2Br (22.6 g, 86.9 mmol) was added at -40 °C for 0.5 h. To this mixture, an aqueous solution of $Na_2S_2O_3$ was added, and the product was extracted with chloroform (3 times). The extract was washed with brine, and dried over $MgSO_4$. After removal of the solvent, the black oil was treated with SiO_2 column chromatography (eluent = hexane). Removal of hexane under vacuum gave a yellow oil of **2** (3.85 g, 60.0% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (s, 1H), 2.41 (t, 2H, $J = 6.9$ Hz), 1.64–1.50 (m, 2H), 1.50–1.27 (m, 14H), 0.88 (t, 3H, $J = 6.7$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 132.21, 125.74, 114.54, 110.40, 95.34, 73.37, 38.46, 31.91, 29.80, 29.58, 29.53, 29.33, 29.11, 22.69, 19.47, 14.14. HRMS (FAB): Found: 403.9821; calcd for $C_{16}H_{22}Br_2S$, 403.9809.

Synthesis of 3. To mixture of 3,3′-dibromo-2,2′-bithiophene (13.0 g, 40.1 mmol), $[Pd(PPh_3)_4]$ (4.64 g, 4.02 mmol), CuI (0.76 g, 3.99 mmol), toluene (200 cm^3), and diisopropylamine (200 cm^3) was added 1-dodecyne (16.7 g, 100 mmol), and the mixture was stirred for 24 h at 135 °C. Work-up similar to that applied for isolation of **1** gave a yellow solid of **3** (15.9 g, 79.6% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, 2H, $J = 5.1$ Hz), 7.01 (d, 2H, $J = 5.1$ Hz), 2.48 (t, 4H, $J = 7.1$ Hz), 1.69–1.60 (m, 4H), 1.51–1.27 (m, 28H), 0.88 (t, 6H, $J = 6.7$ Hz). Anal. Found: C, 77.88; H, 9.44; S, 12.65%. Calcd for $C_{32}H_{46}S_2$: C, 77.67; H, 9.37; S, 12.96%.

Synthesis of 4. An ether (50 cm^3) solution of **3** (9.90 g, 20.0 mmol) was added to a hexane solution of butyllithium (80.0 mmol) at -40 °C. Work-up similar to that applied for isolation of **2** gave a yellow solid of **4** (6.50 g, 49.8% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (s, 2H), 2.49 (t, 4H, $J = 7.0$ Hz), 1.70–1.60 (m, 4H), 1.52–1.27 (m, 28H), 0.88 (t, 6H, $J = 6.7$ Hz). Anal. Found: C, 58.66; H, 6.73; S, 9.57; Br, 24.21%. Calcd for $C_{32}H_{44}Br_2S_2$: C, 58.29; H, 6.80; S, 9.83; Br, 24.49%.

Synthesis of Polymer-1. A mixture of **2** (0.162 g, 0.40 mmol), 2,2′-*p*-[2,5-bis(dodecyloxy)-1,4-phenylene]bis(5,5-dimethyl-1,3,2-dioxaborinane) (0.268 g, 0.40 mmol), $[Pd(PPh_3)_4]$ (0.02 g, 0.02 mmol), and 10 cm^3 of anhydrous THF was stirred for about 0.5 h at r.t.. After addition of an aqueous solution of K_2CO_3 (1.20 mmol; purged with argon), the mixture was stirred for 36 h at 80 °C. After cooling to r.t., the reaction mixture was poured into an excess amount of methanol. The precipitate was collected by filtration, washed with methanol twice, and dried under vacuum to obtain red **Polymer-1** (0.333 g, 96.3% yield). Anal. Found: C, 78.75; H, 10.16; Br, 0; S, 4.35%. Calcd for $(C_{46}H_{74}O_2S)_n$: C, 79.94; H, 10.79; S, 4.64%. The discrepancy between the found and calculated values may be due to high thermal stability of the polymer, contamination with a small amount of the catalyst or methanol, and/or the terminal unit; for example, if the boronic ester has lower reactivity than **2**, calculated values for $(HO)_2B$–$C_{30}H_{52}O_2$–$(C_{46}H_{74}O_2S)_{14}$–$B(OH)_2$ are: C, 79.41; H, 10.79; S, 4.42%; $M_n = 10900$.

Synthesis of Polymer-2. A mixture of 2,2′-*p*-[2,5-bis(dodecyloxy)-1,4-phenylene]bis(5,5-dimethyl-1,3,2-dioxaborinane) (0.356 g, 0.51 mmol), $[Pd(PPh_3)_4]$ (0.03 g, 0.03 mmol), and 25 cm^3 of anhydrous THF, 2,5-dibromo-3-dodecylthiophene (0.209 g, 0.51 mmol) was stirred for 0.5 h at r.t. Work-up similar to that applied for isolation of **Polymer-1** gave red **Polymer-2** (0.312 g, 87.9% yield). Anal. Found: C, 76.72; H, 10.48; Br, 0.91; S, 4.32%. Calcd for $(C_{46}H_{78}O_2S \cdot 0.5H_2O)_n$: C, 78.46; H, 11.31; S, 4.55%. **Polymer-2** showed M_n of 6500 in GPC analysis.

Supporting Information

Figs. S1 and S2 show ^{1}H and $^{13}C\{^1H\}$ NMR spectra of the compounds **1** and **2**, receptivity in PDF format. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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