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New π -conjugated polymers constituted of dialkoxybenzodithiophene units: synthesis and electronic properties

Kouichi Shiraishi, Takakazu Yamamoto*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan Received 19 September 2001; received in revised form 22 February 2002; accepted 2 April 2002

Abstract

New stable and conductive polymers constituted of a new fused thiophene unit, 4,8-dialkoxybenzodithiophene, and related copolymers with thiophene were prepared by organometallic polycondensation in high yields. They showed electrical conductivity of 10^{-2} -5 S cm⁻¹ on doping with iodine. Homopolymers were prepared by Ni-promoted dehalogenation polycondensation, and their molecular structures were confirmed by data from IR spectroscopy and elemental analysis. They were partly soluble in organic solvents, and the soluble part gave number average molecular weights, M_n , of 3000–3600 with M_w/M_n value (M_w = weight average molecular weight) of 1.1–2.4 in the GPC analysis; the M_n value corresponds to a degree of polymerization of about eight. Alternative copolymers consisting of the 4,8-dimethox-ybenzodithiophene and thiophene units were synthesized by a Pd catalyzed polycondensation.

Soluble organic model compounds for the homopolymer and copolymers were synthesized via analogous organometallic coupling reaction, and optical and electrochemical properties of the model compounds were compared with those of the polymers. UV–VIS spectrum of the oligomeric model compounds showed a large bathochromic shift by >50 nm from the monomeric compound. The p-doping of the polymers was reversible, and the iodine-doped polymers were neutralized by hydrazine. Packing structures of the polymers are discussed based on their XRD patterns and density.

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1. Introduction

Active investigations have been carried out for polythiophenes [1–5], and modification of polythiophene by introducing various substituents has been made. For example, poly(3,4-ethylenedioxythiophene), PEDOTh, is attracting attention due to its industrial usefulness [6–12]. The electron-donating ethylenedioxy group in PEDOTh



seems to stabilize the p-doped conducting state.

We now report preparation and properties of a new class of π -conjugated polythiophene derivatives, which is constituted of a new fused-thiophene unit with electron-donating alkoxy substituents, 4,8-dialkoxybenzodithiophene unit.



Polythiophenes having fused ring structure (e.g. polyisothianaphthene and polynaphthothiophene [13–15]) have also been attracting attention. Oligomeric model compounds of the new polymers have also been prepared for better understanding of the new polymers.

2. Experimental

2.1. Syntheses of monomers **1a–1d** and a monobrominated product of 4,8-dimethoxybenzodithiophene

4,8-Dimethoxybenzo[1,2-*b*:4,5-*b*']dithiophene, Benz-(OMe)₂Th₂ was prepared according to the literature [16]; $\lambda_{\text{max}} = 350 \text{ nm}$ in CHCl₃. Its analogues were prepared analogously. Bromination of these compounds with Br₂ in

^{*} Corresponding author. Tel.: +81-45-924-5220; fax: +81-45-924-5276. *E-mail address:* tyamamot@res.titech.ac.jp (T. Yamamoto).

CHCl₃ gave the corresponding dibromo compounds, monomers 1a-1d, in good yields. For example, reaction of $Benz(OMe)_2Th_2$ (0.45 g, 1.8 mmol) with Br_2 (0.64 g, 4.0 mmol) in 15 ml of CHCl₃ for 2 h at r.t. gave monomer **1a.** After purification by column chromatography on SiO_2 (eluent = $CHCl_3$), 2,6-dibromo-4,8-dimethoxybenzo[1,2b:4,5-b']dithiophene (monomer 1a) was isolated as white needles; Yield = 67%. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.47$ (s, 2H), 4.06 (s, 6H). Anal. Found: C, 35.1; H, 1.8; S, 15.4; Br, 39.5%. Calcd. for C₁₂H₈Br₂O₂S₂: C, 35.3; H, 2.0; S, 15.7; Br, 39.2%. Addition of an equimolar amount of Br₂ in a CHCl₃ solution of Benz(OMe)₂Th₂ gave monobrominated Benz(OMe)₂Th₂, which was purified analogously. Other monomers, 1b-1d, were synthesized analogously. **1b**: ¹H NMR (400 MHz, CDCl₃): $\delta = 4.0$ (s, 6H), 2.6 (s, 6H). Anal. Found: C, 38.4; H, 2.7; S, 14.7; Br, 36.3%. Calcd. for C₁₄H₁₂Br₂O₂S₂: C, 38.6; H, 2.8; S, 14.7; Br, 36.3%. **1c**: ¹H NMR (400 MHz, CDCl₃): $\delta = 7.4$ (s, 2H), 4.2 (s, 4H), 1.8 (m, 4H), 1.4–1.5 (m, 12H), 0.9 (t, 6H). Anal. Found: C, 48.0; H, 5.0; S, 11.5; Br, 29.1%. Calcd. for C₂₂H₂₈Br₂O₂S₂: C, 48.2; H, 5.2; S, 11.7; Br, 29.1%. 1d: ¹H NMR (400 MHz, CDCl₃): $\delta = 4.0$ (s, 6H), 2.9 (t, 4H), 1.7–1.3 (m, 16H), 0.9 (t, 6H). Anal. Found: C, 50.3; H, 5.5; S, 11.0; Br, 27.8%. Calcd. for C₂₄H₃₂Br₂O₂S₂: C, 50.0; H, 5.6; S, 11.1; Br, 27.7%.

2.2. Homopolymerization using Ni(0) complex

A mixture of **1a** (0.41 g, 1.0 mmol), Ni(cod)₂ (bis(1,5cyclooctadiene)nickel(0)) (0.36 g, 1.3 mmol), bpy (2,2'bipyridyl) (0.20 g, 1.3 mmol), and 1,5-cyclooctadiene (0.14 g, 1.3 mmol) in dry DMF (15 ml) was stirred for 24 h at 60 °C. The obtained powder was washed with 1 M HCl for three times, aqueous solutions of EDTA for three times, distilled water, and MeOH. Poly(4,8-dimethoxybenzo[1,2-b:4,5-b']dithiophene-2,6-diyl), **2a**: Yield=95%. Anal. Found: C, 55.9; H, 3.0; S, 24.3; Br, 2.6%. Calcd. for H(C₁₂H₈O₂S₂)₁₀Br: C, 56.2; H, 3.2; S, 25.0; Br, 3.1%. **2b**: Yield = 82%. Anal. Found: C, 60.0; H, 4.6; S, 22.7; Br, 0.0%. Calcd. for $(C_{14}H_{12}O_2S_2^{\bullet}0.2H_2O)_n$: C, 60.1; H, 4.5; S, 22.9%. 2c: Yield = 95%. Anal. Found: C, 68.0; H, 7.3; S, 16.5; Br, 0.0%. Calcd. for (C₂₂H₂₈O₂S₂)_n: C, 67.2; H, 7.3; S, 16.7%. 2d: Yield = 98%. Anal. Found: C, 67.8; H, 7.7; S, 14.8; Br, 0.0%. Calcd. for $(C_{24}H_{32}O_2S_2 \circ 0.5H_2O)_n$: C, 67.7; H, 7.9%; S, 15.1%.

2.3. Copolymerization by Stille coupling

Copolymers, **4a**, **4b**, and **4c**, were prepared by utilizing Stille coupling reaction. To 2,5-bis(trimethylstannyl)thiophene or 5,5'-bis(trimethylstannyl)-2,2'-dithiophene and Pd(PPh₃)₄ (5 mol%) in dry toluene were added **1a** or **1c**, and the reaction mixture was stirred for 48 h at 90 °C. The resulting red powder was washed with an aqueous KF solution for three times, 1 M HCl for three times, and MeOH for three times. Poly(4,8-dimethoxybenzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl-*alt*-thiophene-2,5-diyl), **4a**: Yield=97%. Anal. Found: C, 58.5; H, 3.7; S, 24.3; Br, 1.8%. Calcd. for $(C_{16}H_{10}O_2S_3)_n$: C, 58.2; H, 3.1; S, 29.1%. **4b**: Yield = 93%. Anal. Found: C, 56.0; H, 3.4; S, 26.4; Br, 1.1%. Calcd. for Br($C_{20}H_{12}O_2S_4 \cdot 0.6H_2O)_{12}$ H: C, 55.7; H, 3.1; S, 29.7; Br, 1.5%. **4c**: Yield = 91%. Anal. Found: C, 65.8; H, 6.7; S, 20.4; Br, 0.7%. Calcd. for Br($C_{26}H_{30}O_2S_3)_{20}$ H: C, 65.7; H, 6.4; S, 20.3; Br, 0.8%.

2.4. Synthesis of model compounds 5a, 5b, and 5c

Similar organometallic coupling reaction were applied for synthesis of model compounds, **5a**, **5b**, and **5c**. For **5a**, monobrominated compound of Benz(OMe)₂Th₂ (0.22 g, 0.67 mmol) was added to a mixture of Ni(cod)₂ (0.22 g, 8.0 mmol) and 2,2'-bipyridyl (0.12 g, 8.0 mmol) in 10 ml of DMF and the mixture was stirred for 24 h at 60 °C. The obtained solution was washed with 1 M HCl, and the product was extracted with CHCl₃. Drying up the CHCl₃ solution gave a yellow solid, and purification by column chromatography on SiO₂ (eluent = CHCl₃) and recrystalization from CHCl₃/hexane gave yellow needles of **5a**; Yield = 67%. ¹H NMR (400 MHz, CDCl₃): δ = 7.7 (s, 2H), 7.5 (d, 2H), 7.4 (d, 2H), 4.2 (d, 12H). Anal. Found: C, 57.8; H, 3.6; S, 25.6%. Calcd. for C₂₄H₁₈O₄S₄: C, 57.8; H, 3.6; S 25.7%.

Similarly, a mixture of the monobrominated compound of Benz(OMe)₂Th₂ (1.90 g, 5.8 mmol) and 2,5-bis(trimethylstannyl)thiophene (1.23 g, 3.0 mmol) in the presence of a catalytic amount of Pd(PPh₃)₄ (0.17 g, 5 mol%) in toluene was stirred for 24 h at 90 °C. The reaction mixture was washed with 1 M HCl and extract with CHCl₃. The yellow product obtained after drying up the CHCl₃ solutions was purified by column chromatography on SiO₂ (eluent = CHCl₃), and recrystallization from CHCl₃/hexane gave yellow fine needles of **5b**; Yield = 56%. ¹H NMR (400 MHz, CDCl₃): δ = 7.6 (s, 2H), 7.5 (d, 2H), 7.4 (d, 2H), 7.3 (s, 2H), 4.2 (d, 12H). Anal. Found: C, 58.0; H, 3.8; S, 27.4%. Calcd. for C₂₈H₂₀O₄S₅: C, 57.9; H, 3.5; S, 27.6%.

The oligomer **5c** was prepared by Grignard coupling reaction between a Grignard reagent prepared from 2-bromothiophene (0.33 g, 2.0 mmol) and Mg and **1a** (0.41 g, 1.0 mmol) in the presence of a catalytic amount of NiCl₂(dppp) (dppp = 1, 3-bis(diphenylphosphino)propane) (0.03 g, 5 mol%) in 15 ml of THF for 12 h at 60 °C. The resulting solution was poured into 1 M HCl and the product was extracted with CHCl₃. The product obtained after drying up the CHCl₃ solution was purified by column chromatography (on SiO₂ eluent = CHCl₃), and recrystallization from CHCl₃/hexane gave yellow needles of **5c**; Yield = 39%. ¹H NMR (400 MHz, CDCl₃): δ = 7.5 (s, 2H), 7.3 (m, 4H), 7.1 (m, 2H), 4.1 (s, 6H). Anal. Found: C, 57.9; H, 3.7; S, 30.8. Calcd. for C₂₀H₁₄O₂S₄: C, 57.9; H, 3.4; S, 30.9%.

2.5. Analyses

NMR and IR spectra were recorded on a JEOL EX-400 spectrometer and a JASCO IR-810 spectrometer, respectively.

GPC analysis was carried out with a Tosoh HLC 8210 analysis equipped with polystyrene gel columns (TSK gel G2500, G4000, and G5000), (eluent = a DMF solution of LiBr (0.01 M)) or Shimadzu LC-6A system (eluent = CHCl₃). UV–VIS spectra were measured with a Shimadzu UV-3100PC spectrometer. Cyclic voltammograms were obtained with a Hokuto Denko HA-501 galvano/potentiostat and a Hokuto Denko HB-104 function generator using an CH₃CN or CH₃CN/CH₂Cl₂ solution of [NBu₄]PF₆ (0.10 M) at 100 mVs⁻¹. MALDI TOF mass analyses were performed using a Thermo Quest LASERMAT 2000 and/or a Hewlett Packard G 2025A, both equipped with a 337 nm nitrogen laser. As the matrix we used 1,8,9-trihydroxy-anthracene (dithranol). Analytes were dissolved in DMF and added on the matrices with a syringe. A typical analyte-matrix ratio was 1:500. For more detailed information on the sample preparation, see literature [17]. Density of polymers were measured by sink and float tests using aqueous solutions of ZnCl₂.

3. Results and discussion

3.1. Homopolymers

The dialkoxybenzodithiophene type compounds such as $Benz(OMe)_2Th_2$ (R¹ = CH₃, R² = H in Eq. (1) [16]) were easily synthesized by reactions of p-Tos-OR¹

reddish brown powders, and 2b and 2d as brown powders. Data from elemental analysis agreed with their structures. Some of the polymers seemed to contain water, which was difficult to be removed even under heating under vacuum, and the absence or low contents of Br indicated that the polymerization proceeded well. The raw products are considered to have Ni-terminated ends (-polymer-NiL_m) and the polymer ends are considered to be converted into H-terminated ends (-polymer-H) during the work-up in acidic condition [3–5].

The IR spectrum of 2a shows v(C–O–C) absorption peaks at 1207 and 1048 cm^{-1} as shown in Fig. 1(b). Other polymers show analogous IR spectra.

The obtained polymers did not have good solubility in usually used organic and aqueous solvents, even for 2d which had hexyl substituents at 3,7-position and methoxy substituents at 4,8-position. The polymers were only partially soluble in CHCl₃. Since the CHCl₃-soluble part and CHCl₃-insoluble part showed the same IR spectrum, both the parts are considered to have the same molecular structure and a fraction with lower molecular weights is considered to be dissolved in CHCl₃.

GPC analysis of the CHCl₃-soluble part (about 5%) of 2c indicated that it had a number average molecular weight $(M_{\rm n})$ of 3000 with a $M_{\rm w}/M_{\rm n}$ value $(M_{\rm w} = {\rm weight average})$ molecular weight) of 1.1, and those of 2d (about 10%) had a

(1)

(2)



 $(p-CH_3C_6H_4SO_2-OR^1; R^1 = CH_3, n-C_6H_{13})$ with thiophene-fused benzoquinones. Bromination of dialkoxybenzodithiophenes with Br₂ proceeded quantitatively to yield monomers 1a-1d.

The dehalogenative polycondensation of the monomer with a zerovalent nickel complex $Ni(0)L_m$ [3-5] gave the polymers in high yields. 2a and 2c were obtained as



(zerovalent nickel complex: a mixture of Ni(cod)₂ and bpy)

monomer 1a - 1d **1a**: $R^1 = CH_3$, $R^2 = H$ **1b**: $R^1 = CH_3$, $R^2 = CH_3$ 1c: $R^1 = n - C_6 H_{13}$, $R^2 = H$ 1d: $R^1 = CH_3$, $R^2 = n - C_6 H_{13}$





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 $M_{\rm n}$ of 3600 with a $M_{\rm w}/M_{\rm n}$ value of 2.4 (eluent = CHCl₃, versus polystyrene standards). The M_n values of 2c and 2dcorrespond to a degree of polymerization of about eight. Although similar dehalogenative polycondensations often give π -conjugated polymers with higher molecular weights [1,3,4], limited solubility of 2c and 2d seems to prevent formation of polymers with high molecular weights; the



Fig. 1. IR spectra of (a) Benz(OMe)₂Th₂; (b) 2a, and (c) 4a.

insoluble part of the polymer, however, is considered to have a higher molecular weights as described in Section 2.

MALDI TOF mass spectrum [17] of **2a** exhibited peaks of molecules with n = 5-13 in a mass range of 1300–3300, whereas that of **2b** showed peaks with n = 7-10 in a range of 1900–2800. The mass difference between the peaks agreed with the mass of the repeating unit. Molecules with lower *n* values may be more sensitive for the MALDI TOF mass analysis due to their easier vaporization.

3.2. Copolymers

The following copolymers with thiophene or bithiophene spacing unit were prepared by the copolycondensation. The thiophene and bithiophene are expected to



relax the steric repulsion between the bulky dialkoxybenzodithiophene units and increase the coplanarity of the polymer.

Fig. 1(c) shows IR spectrum of 4a. The $v_{asym}(C-O-C)$ and $v_{sym}(C-O-C)$ peaks are observed at 1200 and 1067 cm⁻¹, respectively. Peaks in a range of 1300–1500 cm⁻¹ are assigned to skeletal vibrations of thiophene [18] and benzodithiophene unit. 4b gives an analogous IR spectrum.

The 4a was only partly (about 5%) soluble in DMF, and insoluble in other solvents; a fraction with lower molecular weights is considered to be dissolved in DMF. The soluble part of 4a gave M_n and M_w of 2900 and 3200 in GPC analysis (eluent DMF, versus polystyrene standards), and this $M_{\rm n}$ value corresponds to the *n* value of about nine. The limited solubility of 4a also seems to prevent further elongation of the polymer chain, although the insoluble part of 4a is considered to have a higher molecular weight. 4b was insoluble in solvent. Its MALDI TOF mass spectrum showed peaks in a range of 2700 through 3900 (n = 6-9). We have carried out similar polycondensation between 1c and 3a with expectations that the obtained copolymer had higher solubility due to the hexyloxy groups. However, only about 10% of the copolymer was soluble in CHCl₃, toluene, and THF, and GPC analysis of the soluble part gave M_n and M_w of 1400 and 2100, respectively.

Although molecular weights of the homopolymers and copolymers are not so high, they are still considered to give basic optical, electrical, and electrochemical properties of π -conjugated polymers consisting of the dialkoxybenzodithiophene unit. Basic properties of π -conjugated polyaryrenes usually become essentially unchanged when their degree of polymerization reaches about 10 (e.g. for polypyridine [19]) and PEDOT which is the most widely used polythiophene is considered to have a molecular weight of about 3000 [20].

The basic chemical and physical properties of the homopolymers and copolymers are described in Section 3.3.

3.3. Optical data

The homopolymers **2a** and **2c**, which have no substituents at 3,7-positions (cf. Eq. (2)) are reddish brown, whereas **2b** and **2d** with alkyl substituents at the 3,7-positions are brown. The CHCl₃-soluble parts of **2a**, **2b**, **2c**, and **2d** showed π - π * absorption peaks at 422, 375, 448, 370 nm, respectively in CHCl₃. The copolymers **4a** and **4b** with the thiophene or bithiophene spacing unit are deeply colored red. The DMF soluble parts of **4a** and **4b** exhibited peaks at 466 and 466 nm, respectively. These results suggest the presence of an extended π -conjugation system along the polymer chain in **2a**, **2c**, **4a**, and **4b**.

Fig. 2(a) compares the UV–VIS data of the CHCl₃ soluble parts of **2c** and **2d**. **2c** exhibited λ_{max} at 448 nm, whereas **2d** at a much shorter wavelength of 370 nm, in consistent with the steric repulsion originated from the R² (hexyl) group in **2d**. However, the hexyl group at the center positions (4- and 8-positions) does not seem to interfere with the formation of expanded π -conjugation system, as in **2c**. Comparison of the above described UV–VIS data of **2a** and **2b** also shows similar steric effect of the R^2 group.

2d gave only a minor shift from λ_{max} of Benz(OMe)₂Th₂ at 350 nm, which is shown in Fig. 2(b). The soluble part of **4a** showed a large bathochromic shift from its monomeric compounds (Benz(OMe)₂Th₂: 350 nm; thiophene: 231 nm in chloroform) as expected, and gave a peak at 466 nm. The UV–VIS peak of the copolymer between





1c and **3a** in CHCl₃ (470 nm) shifted by 23 nm to a longer wavelength in cast film, suggesting formation of a stacked structure [1,3] in the film.

For better understanding of the optical data and electrochemical response of the polymers, we synthesized the oligomeric model compounds, as described below and in Section 2.

The UV–VIS peak of the monomeric compound Benz-(OMe)₂Th₂ at 350 nm (cf. Fig. 2b) shifted by 57 nm to a longer wavelength in the dimeric compound **5a** ($\lambda_{max} =$ 407 nm in CHCl₃; cf. Fig. 2(b)). The **5b** ($\lambda_{max} =$ 412) and **5c** ($\lambda_{max} =$ 422) also showed a π – π * absorption peak at a longer wavelength than Benz(OMe)₂Th₂, supporting a view



Fig. 2. (a) UV–VIS spectra of 2c (—) and 2d (- - -) in CHCl₃, and (b) $Benz(OMe)_2Th_2$ (—) and 5a (- - -) in CHCl₃.

that formation of an expanded π -conjugated system is possible between the monomeric units without the substituent at the 3,7-position.

3.4. Electrochemical doping

Electrochemical responses of model oligomeric compounds were examined by cyclic voltammetry (CV) in solutions, which were compared with those of some polymer films. CV curves of Benz(OMe)₂Th₂ and **5a** gave reversible CV response in a oxidative region; however no reduction (n-doping) peak was observed. The chart (a) in Fig. 3 exhibits



Fig. 3. Cyclic voltammogarms of (a) $Benz(OMe)_2Th_2$; (b) **5a**; (c) **2a**, and (d) **4a**. Curves (a) and (b) were obtained in an CH₃CN/CH₂Cl₂ solution of [BuN₄]PF₆ (0.10 M), whereas curves (c) and (d) were obtained with a dispersion film cast on a Pt plate, in an CH₃CN solution of [BuN₄]PF₆ (0.10 M), at 50 mVs⁻¹.

CV curve of Benz(OMe)₂Th₂, which gives oxidation peaks at 0.56 and 0.86 V versus Ag^+/Ag , respectively. The chart (b) in Fig. 3 shows CV curve of **5a**, where the first step oxidation peak is splitted into two peaks by 140 mV, supporting the presence of electronic interaction between the two units. Conceivable oxidative polymerization of Benz(OMe)₂Th₂ and **5a** does not seem to proceed since formation of polymeric film on the Pt electrode was not observed.

Casting of suspended CHCl₃ solutions of the polymers on a Pt plate gave thin layers of dispersed polymer powder. Traces (c) and (d) in Fig. 3 exhibit CV curves of 2a and 4a which show E_{pa} at 0.75 and 0.66 versus Ag⁺/Ag, respectively. Polymers 2a-2d gave a shoulder peak at about 0.9 V versus Ag⁺/Ag. For all polymers, no dedoping peak was observed as shown in Fig. 3, indicating that the oxidized (or p-doped) state of the polymers was stable. When the dopant has a strong affinity toward electrochemically doped π conjugated polymers [21,22] or when it is difficult for the dopant to come out from the doped polymer film due to hardness to diffuse in the doped polymer film [23], dedoping of the doped polymer film becomes difficult and the electrochemical doping becomes irreversible. For the present case, the irreversibility presumably arises from strong interaction of the p-doped polymer with the p-dopant (PF_6^{-}) through coordination of the p-dopant with the $-OR^1$ group(s) and sulfur. Since the p-dedoping did not take place, repeated scan gave no observable peak.

The irreversible anodic peaks in Fig. 3(c) and (d) may be associated with electrochemical oxidative polymerization of oligomeric **2a** and **4a**, respectively. However, the major part of the anodic peak is not considered to originate from the electrochemical oxidative polymerization. If such electrochemical oxidative polymerization constitutes the major part of the anodic peak, the repeated scanning will show peaks of p-doping and p-dedoping of the formed polymer, which usually appear near the potential required for the electrochemical oxidative polymerization [2]. The repeated scanning did not show such peaks, and, as described above the electrochemical doping of polymers sometimes becomes irreversible due to various reasons [21–23].

3.5. Chemical doping

The polymers underwent p-doping with vapor iodine and absorbed about 0.2 g of iodine for 1 g of the homopolymer (**2a** and **2b**), 0.4–0.5 g of iodine for 1 g of the copolymer (**4a** and **4b**). The iodine doping brought about a shift of the aromatic ring vibration peak to a lower frequency, and the new peaks of p-doped thiophene appeared at about 1300 through 1500 cm⁻¹ in the IR spectrum as shown in Fig. 4(a), similar to the case of p-doped polythiophenes [9,18]. The p-doping also led to severe weakening of the aliphatic v(C–H) peaks. Such weakening of the v(C–H) peaks has been reported also observed p-doped poly(3-alkylthiophene) [20,21,24]. In the case of



Fig. 4. IR spectra of (a) I₂-doped 2a; (b) dedoped 2a (after treatment of N₂H₄•H₂O), and (c) I₂-doped 4a.

the p-doping of **4a** and **4b** with I_2 , all the IR peaks were broadened, as shown in Fig. 4(c). For all of the polymers, the iodine doping was reversible, and treatment of the iodinedoped sample with N_2H_4 recovered the original polymer as judged from the IR spectroscopy, which is exhibited by chart (b) in Fig. 4 for the dedoping of **2a**.

The non-doped polymers were insulators. However, the black powdery iodine adducts of the polymers were conductive with electrical conductivity of 4.5×10^{-2} , 2.2×10^{-4} , 1, 5, and 1 S cm⁻¹ for 2a, 2b, 4a, 4b, and the copolymer between 1c and 3a, respectively, at room temperature as measured with their compressed powders. Polymers 2c and 2d with the long alkoxy or alkyl groups also received p-doping with iodine. However, they easily lost iodine under reduced pressure to about 0.01 g of iodine per 1.0 g of the polymer, presumably due to the prevention of the interaction between the cation center in the polymer chain and $I_{\rm m}^{-}$ by the long alkoxy substituent. These lightly doped polymers showed electrical conductivity of an order of 10^{-6} S cm⁻¹. p-Doping by another dopant such as FeCl₃ gave p-doped adducts, which showed comparable electrical conductivity. FeCl₃ is a stronger oxidant than iodine, and even 2c which showed only a weak interaction with iodine due to the long alkoxyl chain, gave a black p-doped powder with FeCl₃, and the p-doped sample showed electrical conductivity of 2.0×10^{-3} S cm⁻¹ order.

Fig. 5(a) shows Arrhenius plots of $\ln \sigma$ versus T^{-1} of iodine doped **4b** in a temperature range from 205 to 315 K. From the linear line, an activation energy of 0.04 eV was evaluated. At lower temperatures (28–95 K), the temperature

dependence of the conductivity gives a roughly linear line when plotted according to a variable range hopping (VRH) model, as depicted in Fig. 5(b).

3.6. Packing structure

Powder X-ray diffraction patterns (Fig. 6) of 2a and 2b shows 3 obvious peaks indicating that they take ordered structures in the solid. The peaks of **2a** at d = 3.6 and 8.0 Å are tentatively assigned to a face-to-face packing distance between the polymer planes and a distance between the main chains separated by the methoxy groups, respectively. Recently analogous assignments have been given for XRD peaks of 3-substituted polythiophenes [25,26]. The longer distance of d = 4.2 Å observed with **2b** may be due to the presence of the methyl at the 3,7-position. 2a had density of 1.56 g cm^{-3} and less-well packed **2b** gave density of 1.23 g cm^{-3} . XRD patterns of copolymers 4a and 4b showed peaks at d = 3.7 and 8.5 Å for 4a, and d = 3.6and 7.6 Å for 4b, respectively. The distance of 3.7 Å for 4a seems also assignable to the face-to-face packing distance between the polymer planes, and the distance of 8.5 Å to the distance between chains separated by the OMe group. 4a and **4b** showed density of 1.46 and 1.59 g cm⁻³, respectively. **4a** seems to have a repeating height of 11.5–12.0 Å along the polymer chain as estimayed from the CPK molecular model. Use of repeating height of 11.5 Å gives a calculated density of $(330/6.02 \times 10^{23})/(3.7 \times 8.5 \times 11.5 \times 10^{-24})$ $= 1.51 \text{ gcm}^{-3}$, which roughly agrees with the observed value.



Fig. 5. (a) Arrhenius plots of electrical conductivity (σ) of iodine-doped **4b** in a temperature range from 205 to 315 K; (b) plots of s of iodine-doped **4b** vs. T^(-1/4) in a lower temperature range (28–95 K).



Fig. 6. XRD patterns of 2a and 2b.

4. Conclusion

New thiophene-based polymers constituted of 4,8-dialkoxybenzodithiophene unit were prepared by organometallic polycondensation. Structures of the obtained polymers were confirmed by IR, GPC, MALDI TOF mass, and elemental analysis. UV–VIS data revealed formation of extended π -conjugation system along the polymer chain. Copolymers with thiophene or bithiophene showed strong interaction with iodine, and the obtained p-doped samples showed electrical conductivity of an order of 10° S cm⁻¹. The polymers consisting of the 4,8-dimethoxybenzodithiophene units form ordered structures in the solid.

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