Synthesis and Electrochemical Properties of New Main Chain Type Polyquinones Constituted of Thiophene-Fused Benzoquinone and Transformation of the Polymers to a Dicyanoquinonediimine Type Polymer

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ABSTRACT: New main chain type polyquinones, poly(3,7-dialkylbenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione-2,6-diyl), P(2,6-Th₂Bq(diR)) (R = hexyl(Hex); octyl(Oct); dodecyl(Dod)), and poly(benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione-1,3-diyl), P(1,3-Th₂Bq), were prepared by organometallic polycondensation. P(2,6-Th₂Bq(diR)) was soluble in organic solvents such as chloroform and dichloromethane. P(1,3-Th₂Bq) is soluble in CF₃COOH, NMP, and DMI (1,3-dimethyl-2-imidazolidione). P(2,6-Th₂Bq(diHex)) received electrochemical two step reduction with peak reduction potentials (E_{pc}) of –1.18 V and –1.84 V vs. Ag⁺/Ag, respectively. This electrochemical reduction corresponds to Wurster type reduction characteristic of quinones. P(1,3-Th₂Bq) was also electrochemically active and its reduction took place at E_{pc} = –1.50 V and –1.74 V vs. Ag⁺/Ag. The film of P(1,3-Th₂Bq) changed its color from brown to blue (electrochromism) on the electrochemical reduction. Powder XRD patterns of P(2,6-Th₂Bq(diR))s indicated that they assumed an ordered structure; they showed an XRD peak in a low angle region (2θ (Cu- $K\alpha$) < 7°). The *d*-value of the peak increased linearly with increase in the number of the carbon of the R groups, suggesting that the *d*-value corresponded to a distance between the polymer main chains separated by the R groups and P(2,6-Th₂Bq(diR)) took a stacked structure in the solid. The quinone unit of P(2,6-Th₂Bq(diR))s was transformed to a strong electron withdrawing dicyanoquinonediimine (DCNQI) unit by reaction with bis(trimethylsilylcarbodiimide) (TMS–N = C = N–TMS); a high degree of transformation was observed by elemental analysis. A cast film of the obtained polymer underwent the electrochemical reduction with the first E_{pc} at a very high potential of –0.56 V vs. Ag⁺/Ag, reflecting the high electron-withdrawing properties of the DCNQI unit.

KEY WORDS π -Conjugated Polymer / Organometallic Polycondensation / Thiophene-Fused Benzoquinone / Electrochemical Response / Thiophene-Fused Dicyanoquinonediimine (DCNQI) /

There has been current interest in the synthesis of novel π -conjugated polymers as interesting and useful optical and electronic materials.¹ Among the π -conjugated polymers, those constituted of redox active recurring units have attracted attention due to their interesting electrochemical behavior. Quinones are known as typical redox active compounds and a number of papers have been published about redox behaviors of quinone and its derivatives.² In spite of their attractive properties, examples of polymers consisting of the quinone units are still limited.^{3,4} Peover and co-workers reported the preparation of meta-bonded poly(hydroquinone) and its electrochemical responses.^{3a} Arai and co-workers reported electrochemical synthesis of poly(mercapto-*p*-benzoquinone) and poly(mercapto-*p*-hydroquinone).^{3b} However, in these cases, the bonding modes of the monomeric units in the polymer chains are not controlled and their chemical properties have not been revealed well.

Previously, we reported preparation of polyanthraquinones and poly(*p*-benzoquinone) having

quinone units in the main-chain *via* organometallic polycondensations.⁴ The obtained polyquinones had well-defined structures and polyanthraquinones were soluble in organic solvents. Hodge and coworkers also reported preparation of another main-chain-type polyanthraquinone *via* similar organometallic polycondensation.⁵ The main-chain-type polyquinones are redox active and their usefulness as an electron carrying layer in organic electric devices (*e.g.*, EL device and organic transistor) is expected. In order to expand the scope of the main-chain-type polyquinones, we have prepared the following new two types of polyquinones, both being constituted of the thiophene-fused benzoquinones. π -Conjugated polymers composed of thiophene units show interesting chemical and physical properties including self-assembling property, and various thiophene-based π -conjugated polymers have been prepared.¹ Some of the polymers are now industrially used. Electronic and optical data of P(2,6-Th₂Bq(diR)) and P(1,3-Th₂Bq) are expected to give bases for better understanding of the thiophene-based polymers.

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Herein we report preparation of the above shown polymers and their electrochemical responses. The benzoquinone unit in P(2,6-Th₂Bq(diR))s can be converted into a highly electron accepting dicyanoquinonediimine (DCNQI)⁶ unit and electrochemical properties of the DCNQI polymer will also be reported.

EXPERIMENTAL

Measurements

IR spectra were recorded on a JASCO IR-810 spectrometer. NMR spectra were taken using a JEOL EX-400 or EX-90 spectrometer. X-Ray diffraction patterns were recorded on a Philips PS-1051 instrument. Microanalyses of C, H, and N were carried out with a Leco CHNS-932 or a Yanaco CHN CORDER MT-5. Analyses of halogen and sulfur were carried out on a Leco CHNS-932 (sulfur) or a Yanaco YS-10 (halogen). GPC analysis was carried out with a Shimadzu C-R7A equipped with an LC9A column using a CHCl₃ solution as an eluent or Tosoh HLC-8020 gel permeation chromatograph (polystyrene standards; eluent = DMF containing 0.01 M of LiBr). 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 solution of [NBu₄]PF₆ (0.10 M) under nitrogen. Density of the polymer samples were measured by sink and float tests using aqueous solutions of ZnCl₂.

Synthesis of 2,6-Dibromo-3,7-dihexyl-4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (2,6-Dibromo-Th₂Bq(diHex))

This monomer was prepared by modifying a literature method.⁷ A typical procedure is as follows. A mixture of 3-(dimethylaminocarbonyl)-4-hexyl-2,5-dibromothiophene (1.2 g, 3.3 mmol) with *n*-BuLi (3.3 mmol) in dry ether was stirred for 1 h at -78 °C and continuously for 12 h at room temperature. The reaction mixture was poured into 1 M HCl(aq) and extracted with ether for three times. Purification by column chromatography on SiO₂ with chloroform/hexane (1/1) gave a yellow solid. After recrystallization from hexane, yellow needles of 2,6-dibromo-3,7-dihexyl-4,8-

dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione, 2,6-dibromo-Th₂Bq(diHex), were obtained. Yield 33%. Mp 132 °C. ¹H NMR (CDCl₃, 400 MHz): δ 0.89 (t, 6 H), 1.30–1.55 (m, 16 H), 2.96 (t, 4 H). Anal. Calcd. for (C₂₂H₂₆Br₂O₂S₂): C, 48.8; H, 4.8; Br, 29.1; S, 11.4%. Found: C, 48.5; H, 4.9; Br, 29.4; S, 11.8%.

3,7-Dihexyl-4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione, Th₂Bq(diHex)

This monomeric model compound for the repeating unit, was prepared in an analogous way from 3-(dimethylaminocarbonyl)-4-hexylthiophene. Yield 34%. Mp 84 °C. ¹H NMR (CDCl₃, 400 MHz): δ 1.1 (t, 6 H), 1.30–1.89 (m, 16 H), 3.30 (t, 4 H), 7.30 (s, 2 H). Anal. Calcd. for (C₂₂H₂₈O₂S₂): C, 68.0; H, 7.3; S, 16.5%. Found: C, 67.6; H, 7.0; S, 16.3%.

Other dibromo monomers, 2,6-dibromo-Th₂Bq(diOct) (Yield = 48%) and 2,6-dibromo-Th₂Bq(diDod) (Yield = 26%) were prepared similarly. 2,6-Dibromo-Th₂Bq(diOct): Mp 117 °C. ¹H NMR (CDCl₃, 400 MHz): δ 0.89 (t, 6 H), 1.30–1.55 (m, 24 H), 2.96 (t, 4 H). Anal. Calcd. for (C₂₆H₃₄Br₂O₂S₂): C, 51.8; H, 5.7; Br, 26.5; S, 10.6%. Found: C, 52.2; H, 5.5; Br, 26.9; S, 10.8%. 2,6-Dibromo-Th₂Bq(diDod): Mp 100 °C. ¹H NMR (CDCl₃, 400 MHz): δ 0.88 (t, 6 H), 1.26–1.53 (m, 40 H), 2.95 (t, 4 H). Anal. Calcd. for (C₃₄H₅₀Br₂O₂S₂): C, 57.1; H, 7.1; Br, 22.4; S, 9.0%. Found: C, 57.2; H, 7.0; Br, 22.7; S, 8.9%.

Synthesis of 1,3-Dibromo-4,8-dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (1,3-dihydro-Th₂Bq)

This monomer was prepared by modifying a literature method.⁸ To a solution of AlCl₃ (0.53 g, 4.0 mmol) and CH₃NO₂ (0.24 g, 4.0 mmol) in dry 1,2-dichloroethene (5 mL) was added thiophene-3,4-dicarboxylic acid chloride (0.42 g, 2.0 mmol) in dry 1,2-dichloroethene (5 mL). The resulting solution was stirred for 15 min, and then 2,5-dibromothiophene (0.80 g, 3.0 mmol) was added. The red-brown mixture was stirred for 48 h at 60 °C. The reaction mixture was poured into 6 M HCl(aq) and extracted with chloroform for three times. The organic layer were washed with saturated NaHCO₃(aq) and dried with MgSO₄. Purification from column chromatography on Al₂O₃ with chloroform/hexane (1/1) gave a pale yellow solid. After recrystallization from chloroform/hexane, a pale yellow solid of 1,3-dibromo-4,8-dihydrobenzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione, 1,3-dibromo-Th₂Bq, was obtained. Yield 16%. ¹H NMR (CDCl₃, 400 MHz): δ 8.05 (s, 2 H). Anal. Calcd. for (C₁₀H₂Br₂O₂S₂): C, 31.8; H, 0.5; Br, 42.3; S, 17.0%. Found: C, 31.7; H, 0.5; Br, 42.4; S, 16.9%.

Ni(0) Promoted Dehalogenative Polycondensation

Preparation of the polymer was carried out by using a zerovalent nickel complex.⁹ A typical procedure is as follows. To a dark purple solution containing bis(1,5-cyclooctadiene)nickel(0), Ni(cod)₂, (0.30 g, 1.1 mmol) and 2,2'-bipyridyl, 2,2'-bpy, (0.17 g, 1.1 mmol) in dry DMF (15 mL) was added 2,6-dibromo-Th₂Bq(diHex) (0.38 g, 0.70 mmol). The dark brown mixture was stirred for 48 h at 60 °C. The reaction mixture was poured into 1 M HCl(aq), and the obtained brown powder was washed with 1 M HCl(aq), an aqueous solution of disodium EDTA for three times, distilled H₂O, and MeOH. Reprecipitation from a chloroform solution to hexane gave a light brown powder of poly(3,7-di-hexyl-4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione-2,6-diyl), P(2,6-Th₂Bq(diHex)). Yield 98%. ¹H NMR (CDCl₃, 400 MHz): δ 0.89–1.70 (22 H, –C₅H₁₁ of the hexyl group), 2.8–3.1 (4 H, methylene proton). Anal. Calcd. for (C₂₂H₂₆O₂S₂·0.5 H₂O)_n: C, 66.8; H, 6.9; S, 16.2%. Found: C, 66.5; H, 6.7; Br, 0.0; S, 16.5%. Other P(2,6-Th₂Bq(diR))s were prepared similarly. P(2,6-Th₂Bq) (R = H): Yield = 79%. ¹H NMR (DMSO-*d*₆, 400 MHz): δ 7.8 (2H of 3,7-positions). Anal. Calcd. for Br(C₁₀H₂O₂S₂·0.6 H₂O)₃Br: C, 42.5; H, 1.1; S, 22.7; Br, 18.9%. Found: C, 42.5; H, 1.2; S, 22.5; Br, 18.9%. P(2,6-Th₂Bq(diOct)) (R = *n*-C₈H₁₇): Yield = 89%. ¹H NMR (CDCl₃, 400 MHz): δ 0.89–1.70 (30 H, –C₇H₁₅ of octyl group), 2.8–3.1 (4 H, methylene proton). Anal. Calcd. for Br(C₂₆H₃₄O₂S₂)₃Br: C, 63.0; H, 6.9; S, 12.9; Br, 10.7%. Found: C, 62.9; H, 7.4; S, 12.1; Br, 10.0%. P(2,6-Th₂Bq(diDod)) (R = *n*-C₁₂H₂₅): Yield = 88%. ¹H NMR (CDCl₃, 400 MHz): δ 0.89–1.70 (46 H, –C₁₁H₂₃ of dodecyl group), 2.8–3.1 (4H of methylene proton). Anal. Calcd. for Br(C₃₄H₅₀O₂S₂)₃Br: C, 67.2; H, 8.3; S, 10.6; Br, 8.8%. Found: C, 67.3; H, 8.0; S, 11.1; Br, 8.0%.

Synthesis of P(1,3-Th₂Bq) was carried out analogously to yield a light brown powder. Yield 88%. ¹H NMR (CF₃CO₂D, 400 MHz): δ 8.55 (s, 2H). Anal. Calcd. for (C₁₀H₂O₂S₂)_n: C, 54.5; H, 1.8; S, 29.1%. Found: C, 54.2; H, 1.7; Br, 0.0; S, 26.6%.

Transformation of P(2,6-BqTh₂(diR)) to the Dicyanodenediimine Polymer

To a solution of P(2,6-Th₂Bq(diHex)) (106 mg) in dry toluene (10 mL) was added a toluene solutions of 1 M TiCl₄ (0.55 mmol), and the mixture was stirred for 24 h at 90 °C, similar to cases applied for low molecular weight quinones.¹⁰ The resulting mixture was poured into 1 M HCl(aq) and the product was extracted with chloroform. The organic layer was con-

centrated and poured into an excess amount of hexane to yield a black powder of the polymer containing DCNQI units. Yield, 60 mg. Anal. Calcd. for {(C₂₂H₂₆O₂S₂)_{0.1}(C₂₄H₂₆N₄S₂)_{0.9}·H₂O}: C, 63.8; H, 6.3; N, 11.3; S, 14.3%. Found: C, 64.0; H, 6.3; N, 11.4; S, 13.7%.

RESULTS AND DISCUSSION

Preparation

The monomer and its hydrogen terminated compound, Th₂Bq(diHex) (with H at the 2- and 6-positions instead of Br: monomeric model compound for the polymer), were prepared from the corresponding thiophene derivatives by modifying the previously reported method (Scheme 1).⁶

Scheme 1. Synthesis of monomer. The model compound without Br, Th₂Bq(diHex), was also prepared analogously.

1,3-Dibromo-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (1,3-dibromo-Th₂Bq) was prepared by Friedel-Crafts reaction with 3,4-thiophene carboxylic acid chloride and 2,5-dibromothiophene in the presence of AlCl₃ (Scheme 2).⁸

Scheme 2. Synthesis of 1,3-dibromo-Th₂Bq.

The previously reported organometallic polycondensation⁹ using the zero valent nickel complex (a mixture of Ni(cod)₂ and bpy) was applicable to the present cases, and the polycondensation in DMF at 60 °C for 48 h (Scheme 3) gave the corresponding polymers in good yield (79–98%).

Results of the organometallic polycondensation are summarized in Table I.

P(2,6-Th₂Bq) was insoluble in organic or aqueous solvents so far tested, however, P(2,6-Th₂Bq(diR)) containing long alkyl chains at the 3,7-positions were soluble in chloroform, dichloromethane, and toluene. P(1,3-Th₂Bq) was also soluble in organic solvents such as CF₃COOH, NMP (*N*-methyl-2-pyrrolidinone), and DMI (1,3-dimethyl-2-imidazolidinone). GPC

Ni(0)L_m: a mixture of bis(cyclooctadiene)nickel(0), Ni(cod)₂, and 2,2'-bipyridyl, bpy.

Scheme 3. Synthesis of polyquinones.

Table I. Results of the polymerization

run	Compound	Yield %	Color	$M_n \times 10^{-3}$ ^a	M_w/M_n
1	P(2,6-Th ₂ Bq)	79	dark brown	— ^b	—
2	P(2,6-Th ₂ Bq(diHex))	98	light brown	3.5 ^c	1.34
3	P(2,6-Th ₂ Bq(diOct))	89	light brown	2.5 ^c	1.20
4	P(2,6-Th ₂ Bq(diDod))	91	light brown	2.0 ^c	1.25
5	P(1,3-Th ₂ Bq)	88	light brown	6.5 ^d	1.31

^aGPC analysis (vs. polystyrene standards). ^bNot measured.

^cEluent = CHCl₃. ^dEluent = DMF.

analysis indicated that P(2,6-Th₂Bq(diHex)) (eluent = chloroform; vs. polystyrene standards) and DMF soluble part of P(1,3-Th₂Bq) (eluent = DMF vs. polystyrene standards) had number average molecular weights, M_n , of 3500 and 6500 with weight average molecular weights, M_w , of 4700 and 8500, respectively. P(2,6-Th₂Bq(diR)) having a longer alkyl side chain, -C₈H₁₇ or -C₁₂H₂₅, showed lower molecular weight as shown in Table I. The dihexyl monomer had sufficient solubility in the polymerization solvent, however, the dioctyl and didodecyl monomers had poor solubility in the solvent, and this may be the reason for the lower molecular weights of P(2,6-Th₂Bq(diOct)) and P(2,6-Th₂Bq(diDod)). The IR spectra of P(2,6-Th₂Bq(diHex)) and P(1,3-Th₂Bq) resembled those of their corresponding monomers, except for disappearance of a $\nu(\text{C-Br})$ absorption band at about 1100 cm⁻¹.¹¹ They showed absorption peak characteristic of carbonyl groups at about 1650 cm⁻¹, indicating that the C=O group remained intact, similar to cases of the previously reported synthesis of polyquinones.⁴

Figure 1 exhibits the ¹H NMR spectrum of P(2,6-Th₂Bq(diHex)) in CDCl₃ at room temperature; the peak area ratios agree with the structure of the polymer. Splitting of the α -CH₂ signal attached at the aromatic ring into two peaks at δ 2.8 and 3.0 is considered to

Figure 1. ¹H NMR spectrum of P(2,6-Th₂Bq(diHex)) in CDCl₃.

be due to the presence of *s-cis* and *s-trans* rotamers concerning the bond connecting the monomeric units and/or due to the terminal groups. Measurement of the ¹H NMR spectrum at 50 °C showed essentially the same splitting of the α -CH₂ signal, suggesting that the weaker peak at δ 3.0 originate from the terminal unit. However, if this is the case, the area of the peak at δ 3.0 suggests that not only the α -CH₂ group in the terminal unit but also that in the penultimate unit contribute to the peak at δ 3.0. Since P(2,6-Th₂Bq(diHex)) contained no Br (*cf.* experimental), the polymer is considered to be Ni-terminated, and the -polymer-Ni-terminal unit is considered to be converted into the H-terminated groups during the work-up including treatment with HCl, similar to poly(anthraquinone)s and poly(pyridine-2,5-diyl).^{4,9} The area of the signal assigned to the terminal-H and observed at δ 7.33 agrees with the M_n value or degree of polymerization of about 9 estimated from GPC analysis. Although the degree of polymerization is not large, optical and electrochemical data reveal basic properties of the polymer.

Figure 2. UV-vis spectra of (a) P(2,6-Th₂Bq(diHex)) and (b) Th₂Bq(diHex) in CHCl₃.

Optical Properties

Figure 2 shows UV-vis spectra of P(2,6-Th₂Bq(diHex)) and its monomeric compound, Th₂Bq(diHex), in chloroform. P(2,6-Th₂Bq(diHex)) exhibits a π - π^* absorption peak ($\epsilon = 9500 \text{ M}^{-1}\text{cm}^{-1}$; molarity is base on the monomeric unit) at 398 nm (Figure 2 (a)). The peak position of P(2,6-Th₂Bq(diHex)) is shifted to a longer wavelength by 20 nm from that of the monomeric compound (Figure 2 (b)). P(2,6-Th₂Bq(diOct)) and P(2,6-Th₂Bq(diDod)) gave the π - π^* absorption peaks at 396 and 393 nm, respectively, in chloroform.

P(1,3-Th₂Bq) showed a π - π^* absorption peak ($\epsilon = 8000 \text{ M}^{-1}\text{cm}^{-1}$) at 344 nm in NMP and its film cast from NMP gave broadened absorption peak at about 430 nm. In the film, the polymer may take a stacked structure which leads to face-to-face π - π interaction between the polymer chains, and this may be the origin of the red shift in the solid.

Electrochemical Properties

All the polymers were susceptible to electrochemical reduction. Table II summarized CV (cyclic voltammetry) data of the polymers. Figure 3 exhibits CV charts of P(2,6-Th₂Bq(diHex)) film laid on a Pt plate and of Th₂Bq(diHex) in a solution.

Quinone or polyquinone usually receives two-step electrochemical reductions, so-called Wurster type reductions from quinone to radical anion and from radical anion to dianion, respectively. As shown in Figure 3 (b), the monomeric compound Th₂Bq(diHex) also received two reductions and the electrochemical reduction is reasonably accounted for by the Wurster type reductions¹² as shown in Scheme 4.

P(2,6-Th₂Bq(diHex)) received the corresponding first and second reductions with E_{pc} of -1.14 and $-1.84 \text{ V vs. Ag}^+/\text{Ag}$, and the electrochemical reduction is accompanied by the color changes as shown in Figure 3 (a).

Scheme 4.

Table II. Peak reduction potentials of polymers^a

run	Compound	E_{pc}^1	E_{pc}^2
1	Th ₂ Bq	-1.05	-1.84
2	Th ₂ Bq(diHex)	-1.12	-2.10
3	P(2,6-Th ₂ Bq(diHex))	-1.14	-1.84
4	P(2,6-Th ₂ Bq(diOct))	-1.18	-1.84
5	P(2,6-Th ₂ Bq(diDod))	-1.15	-1.85
6	P(1,3-Th ₂ Bq)	-1.50	-1.74

^a E/V vs. Ag^+/Ag . Obtained with polymer film in an CH_3CN solution of $0.10 \text{ M} [\text{Bu}_4\text{N}]\text{PF}_6$.

Figure 3. (a) Cyclic voltammogram of P(2,6-Th₂Bq(diHex)) film cast on a Pt plate in an CH_3CN solution of $[\text{Bu}_4\text{N}]\text{PF}_6$ (0.10 M) and (b) Cyclic voltammogram of $8.0 \times 10^{-4} \text{ M}$ of Th₂Bq(diHex) in an CH_3CN solution of $[\text{Bu}_4\text{N}]\text{PF}_6$ (0.10 M). At 100 mVs^{-1} .

The first-step electrochemical reduction or n -doping of P(2,6-Th₂Bq(diHex)) proceeds at a higher potential by about 0.2 V than that of poly(anthraquinone-1,4-diyl)s ($E_{pc}^1 = -1.38 \text{ V vs. Ag}^+/\text{Ag}$).^{4a} This more facile electrochemical reduction of P(2,6-Th₂Bq(diHex)) is considered to be a reflection of higher first reduction potential of the monomeric model compound (Th₂Bq(diHex): $E_{pc} = -1.12 \text{ V vs. Ag}^+/\text{Ag}$) than that of anthraquinone ($E_{pc} = -1.30 \text{ V}$) by about 0.2 V . The electrochemically reduced polymer film became partly soluble in CH_3CN , and the smaller anodic n -dedoping peak at -1.02 V than cathodic n -doping peak at -1.14 V was attributed to loss of the polymer due to partially dissolution of the reduced polymer in the solu-

Figure 4. Electrochromism of a film of P(1,3-Th₂Bq) on an ITO glass electrode at various applied potentials vs. Ag⁺/Ag. The curve (a) shows UV-vis spectrum of the as-cast film of P(1,3-Th₂Bq). Applied potential: (b) -1.50, (c) -1.70, (d) -2.0 V vs. Ag⁺/Ag.

tion. Without the chemical reduction, the film of P(2,6-Th₂Bq(diHex)) was stable in CH₃CN and dissolution into CH₃CN was not observed. However, coloring of the solution due to dissolution of the *n*-doped P(2,6-Th₂Bq(diHex)) was observed after the electrochemical reduction. Because of loss of P(2,6-Th₂Bq(diHex)) by dissolution, repeated scanning gave smaller CV peaks.

P(1,3-Th₂Bq) showed similar two-step reduction. The CV curve of the polymer gives electrochemical reduction peaks, E_{pc} , at about -1.50 V and -1.74 V vs. Ag⁺/Ag, respectively. The polymer film was stable at the stage of the first reduction. However, after the second step reduction, the polymer was dissolved in the solution. The doping level of the polymer (stored negative charge/repeating unit) was estimated at 1.6 from the doping current obtained at the first CV cycle carried out beyond the second reduction. The first reduction was coupled with *n*-dedoping peak at -1.30 V. The second reduction did not show the *n*-dedoping due to the dissolution of the polymer. Reduction of the benzoquinone unit will give an anion radical of the benzoquinone unit and dianion of a hydroquinone unit.^{4d,8a,13} Formation of such reduced species will generate sulfur with a high valency for P(1,3-Th₂Bq).¹³ This will make the reduced state unstable and may be the reason for the irreversibility of the electrochemical process. The dopant, Bu₄N⁺, may have a strong affinity toward the *n*-doped polymer, possibly by coordination to S, and, if this is the case for P(1,3-Th₂Bq), it also accounts for the irreversibility, at least partly. The polymer showed electrochromism from brown to blue with electrochemically doping, and Figure 4 exhibits changes of UV-vis spectrum of the film of P(1,3-Th₂Bq) during electrochemical reduction. As describe above, the film of neu-

Figure 5. X-Ray diffraction patterns of P(2,6-Th₂Bq(diR)).

tral P(1,3-Th₂Bq) gave a broad peak at 430 nm at 0.0 V vs. Ag⁺/Ag. On application of the reduction potential, at -1.50 V, the polymer film showed decrease of the π - π^* absorption peak at 430 nm, and new absorption band(s) appeared in a longer wavelength (500–800 nm) region. By applying higher reduction potentials of -1.7 and -2.0 V, intensity of the new absorption band(s) increased.

Packing Structure

Figure 5 depicts powder XRD patterns of P(2,6-Th₂Bq(diR)). The XRD patterns show a sharp peak in a low angle region (2θ (Cu-Kα) < 7°), similar to XRD patterns of previously reported regioregular head-to-tail poly(3-alkylthiophene-2,5-diyl) HT-P3RT and head-to-head poly(4,4'-dialkyl-2,2'-bithiazole-5,5'-diyl) HH-P4RBTz.¹⁴ Main-chain-type poly(heterocycle)s with long alkyl side chains often give similar XRD peaks in the low angle region, and its corresponding d_1 -value has been assigned to a distance between the poly(heterocycle) main chains separated by the alkyl side chains.^{9,14}

Scheme 5. An end-to-end packing model of π -conjugated polymers with long side chains.

Figure 6. Relationship of d_1 -space and carbon number of alkyl side chain of P(2,6-Th₂Bq(diR)).

The d_1 -value given in Figure 5 increases with the length of the side alkyl chain, and plots of the d_1 -value vs. number of the carbon of alkyl side chain gives a linear line with a slope of 1.33 Å per number of carbon, as shown in Figure 6. The slope of the linear line is smaller than those (1.8–2.0 Å/carbon) observed with HT-P3RT and P4BTz, however, it is still larger than the unit height of alkyl chain (the $-\text{CH}_2-\text{CH}_2-$ distance).^{14d,15} These data suggests that the polymer take an ordered structure with an end-to-end type packing shown above (Scheme 5) rather than an interdigitation packing. The density of the alkyl chain (1 alkyl chain per about 8 Å of the repeating quinone unit) along the polymer chain is smaller than that (1 alkyl per about 4 Å) of HT-P3RT. Therefore, the alkyl side chain is considered to take a less stiff structure in the side space of the polymer main chain. This seems to account for the smaller slope of the straight line given in Figure 6 than those observed with HT-P3RT and HH-P4RBTz. The XRD pattern also exhibits 2nd ($d_1' = d_1/2$) and 3rd ($d_1'' = d_1/3$) peaks of the d_1 peak.

The peak at about $2\theta = 21.5^\circ$ ($d = 4.1$ Å) in Figure 5 is characteristic of polymers with long alkyl chains and usually assigned to packing distance between alkyl chains,¹⁴ although in the present case it may contain a contribution from face-to-face packing of the polymer planes. P(2,6-Th₂Bq(diHex)) gave a density of 1.41 g cm⁻³. If one assumes a layered packed structure of the polymer with an interlayer distance of about 4 Å which is normal for stacked π -conjugated polymers,¹³ and the repeating height of 8.0 Å, this assumption and the d_1 -value of 13 Å give a calculated density of $(386/6 \times 10^{23}) / (4 \times 8 \times 13.0 \times 10^{-24}) = 1.55$ g cm⁻³. Polymers usually give a lower observed density than a calculated density because of their containing amorphous parts, and the observed density with P(2,6-Th₂Bq(diHex)) is reasonable for the calculated density. P(2,6-Th₂Bq(diOct)) and P(2,6-Th₂Bq(diDod)) also showed density (1.36 and 1.28, respectively), which is reasonable for their calculated values (1.41 and 1.34, respectively). The intercept D (5.2 Å) of the

Figure 7. IR spectra of (a) P(2,6-Th₂Bq(diHex)) and (b) P(thiophene-fused DCNQI-2,6-diyl).

linear line in Figure 6 is considered to correspond to the thickness of the main chain.

Chemical Transformation

Dicyanoquinonediimine (DCNQI) and its derivatives are typical electron acceptors stronger than quinones and many studies have been carried out with these compounds.^{6,10} On this basis, we have carried out transformation reaction of the fused dithiophenebenzoquinone unit of P(2,6-Th₂Bq(diHex)) into the DCNQI unit by using bis(trimethylsilylcarbodiimide), (TMS-N=C=N-TMS) in the presence of the TiCl₄ (Scheme 5). Data from elemental analysis of the obtained black powder indicated that the quinone group of P(2,6-Th₂Bq(diHex)) was transformed into the DCNQI unit in about 90% degree. IR spectrum of the obtained polymer showed new absorption bands of $\nu(\text{C}\equiv\text{N})$ at 2156 cm⁻¹ and of $\nu(\text{C}=\text{N})$ at 1555 cm⁻¹, as exhibited in Figure 7. However, the peak of $\nu(\text{C}=\text{O})$ at about 1650 cm⁻¹ still remained. The obtained polymer was soluble in chloroform and toluene.

Scheme 6. Transformation to a DCNQI polymer.

The UV-vis spectrum of the obtained polymer, P(thiophene-fused DCNQI-2,6-diyl), showed absorption peak at about 440–470 nm in chloroform, which was shifted by about 70 nm to a longer wavelength compared with that of P(2,6-Th₂Bq(diHex)).

As shown in Figure 8, the CV chart of a cast film of P(thiophene-fused DCNQI-2,6-diyl) laid on a Pt plate shows two reduction peaks with E_{pc}^1 and E_{pc}^2 of -0.56 V and -1.06 V vs. Ag⁺/Ag, respectively. The first reduction peak locates near that (about -0.5 V vs.

Figure 8. CV chart of a film of P(thiophene-fused DCNQI-2,6-diyl) on a Pt plate in an CH_3CN solution of $[\text{Bu}_4\text{N}]\text{PF}_6$ (0.10 M) at 100 mVs^{-1} .

Ag^+/Ag of poly(*p*-benzoquinone).^{4d} The small peak at negative higher potential, (the peak at about E_{pc} value of $-1.51 \text{ V vs. Ag}^+/\text{Ag}$) may originate from the remaining quinone unit. According to the reduction, color of the film changed to black from dark brown. By the electrochemically reduction, the polymer film became partly soluble in the CV solvent (CH_3CN), and the smaller *n*-dedoping peaks at -0.42 and -0.80 V were attributed to loss of electrochemically reduced polymer into the solvent.

CONCLUSION

New main chain type polyquinones constituted of 4,8-dihydrobenzodithiophene-4,8-dione rings have been prepared. UV-vis spectrum of the polymers gave $\pi-\pi^*$ absorption at a longer wavelength than that of the corresponding monomers. The polymers showed two electrochemical reduction peaks and exhibited electrochromism. Transformation to DCNQI unit of P(2,6-Th₂Bq(diHex)) was achieved and the obtained polymer received more facile reduction than the precursor polyquinone. These polymers are expected to serve as *n*-type conducting materials in electronic and optical devices.

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In the P(1,3-Th₂Bq) system, anion radicals formed in the adjacent two repeating unit may undergo bond rearrangement to form a thiophene = thiophene type quinoide unit in the main chain. In this case, sulfur with the high valency is not generated.
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