New Narrow-Bandgap Polymer Composed of Benzobis(1,2,5-thiadiazole) and Thiophenes

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Received October 27, 1994

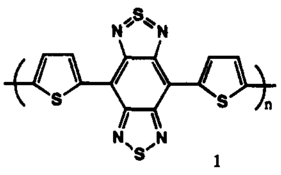
Recently much attention has been focused on development of narrow-bandgap polymers in the field of materials science since they are expected to show interesting physical properties such as intrinsic conductivities and good nonlinear optical properties.[1] Recent studies have shown that copolymerization of aromatic and *o*-quinoid heterocycles or alternation of donor and acceptor units is effective for lowering bandgaps.[2] In this context we have now designed a new narrow-bandgap polymer, **1**, where thiophene is an aromatic donor and benzobis(1,2,5-thiadiazole) is an *o*-quinoid type acceptor. This system seems to possess several advantages in having a narrow bandgap. First, the benzobis(thiadiazole) unit containing hypervalent sulfur atoms has a high electron affinity.[3] Second, a strong contribution of the quinoid form **1′** is expected since more stable classical 1,2,5-thiadiazole rings are generated in this form. Third, this system has no steric repulsion between the adjacent heterocyclic units, leading to a planar geometry. Fourth, the synthesis of the monomer units is relatively easy. Finally, strong interchain interactions may be caused by short intermolecular S•••N contacts which are often observed in 1,2,5-thiadiazole derivatives.[3,4] We have found that polymer **1** has a bandgap below 0.5 eV that is the lowest value in the reported heterocyclic polymers.[2b,5] The preparation and characterization of polymer **1**, the related polymer **2**, and their monomers are described here.

The monomer molecule 4,8-di(2-thienyl)benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]thiadiazole, **3b**, was prepared as follows. The coupling of bromide **4b**[6] with tributyl(2-thienyl)tin in the presence of catalytic $Pd(PPh_3)_2Cl_2$ in THF gave dithienyl derivative **4c** (mp 259–260 °C) in 65% yield. Reduction of **4c** with iron dust in acetic acid afforded diamine **4d** (mp 239–240 °C). Benzobis(thiadiazole) **3b** was obtained in 82% yield by reaction of **4d** with *N*-thionylaniline in pyridine at 80 °C. The novel heterocycle **3b** is thermally stable and was purified by sublimation (300 °C/0.05 Torr) to give blue needles (mp 334–336 °C). For comparison, 4,7-di(2-thienyl)benzo[*c*][1,2,5]thiadiazole, **4e** (mp 130–131 °C), was prepared by the coupling reaction of the corresponding dibromide **4f**[7] with tributyl(2-thienyl)tin.

Table 1. Absorption Maxima and Redox Potential of Monomers

monomer	λ_{max}/nm (log ϵ)^a	$E_{pa}{}^b$	$E_{pc}{}^b$	$\Delta E_{sum}{}^c$
3b	702 (4.23)	+0.95	−0.53	1.48
4e	445 (4.45)	+1.23	−1.22	2.45
5^d	618 (4.04)^e	+0.85	−0.93	1.78

^{a} In $CHCl_3$. ^{b} 0.1 mol dm^{-3} n-Bu_4NClO_4 in PhCN, Pt electrode, scan rate 100 mV s^{-1}, V vs SCE. ^{c} $\Delta E_{sum} = E_{pa} - E_{pc}$. ^{d} Reference 2c. ^{e} In CH_2Cl_2.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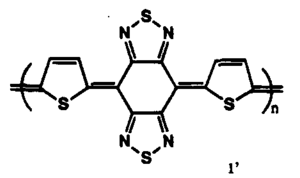
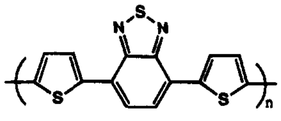

1′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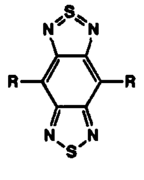
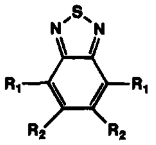
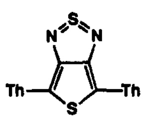

3a: R = H
3b: R = Th
3c: R = Ph
3d: R = Br

Th = 2-thienyl


4a: $R_1 = R_2 = H$
4b: $R_1 = Br$, $R_2 = NO_2$
4c: $R_1 = Th$, $R_2 = NO_2$
4d: $R_1 = Th$, $R_2 = NH_2$
4e: $R_1 = Th$, $R_2 = H$
4f: $R_1 = Br$, $R_2 = H$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The lowest energy absorption maxima of heterocycles **3b** and **4e** are listed in Table 1 along with that of terthiophene derivative **5**, which gives a polymer with a narrow bandgap of 0.9 eV.[2c] The absorption of **3b** is observed at a longer wavelength compared to that of **4e** and **5**, indicating that **3b** has a smaller HOMO–LUMO separation. It is also much red-shifted compared to that of diphenyl derivative **3c** (λ_{max} 558 nm),[3] suggesting that intramolecular charge transfer from the electron-donating thiophene part to the electron-withdrawing benzobis(thiadiazole) part takes place.

The cyclic voltammograms of **3b** and **4e** showed both an irreversible oxidation wave and a reversible reduction wave. The redox potentials are given in Table 1. The reduction potential of **3b** is as high as that of *p*-benzoquinone, indicating its high electron affinity. The difference between oxidation and reduction potentials is smaller in **3b** than in **4e** and **5**. This fact is consistent with the absorption data supporting the smaller HOMO–LUMO separation in **3b**. It should be noted that both oxidation and reduction take place more easily in **3b** than in **4e**. This is supported by the PM3 calculations showing that the energy level of the HOMO for **3a** (−8.73 eV) is higher than that for **4a** (−9.63 eV) and that the energy level of the LUMO for **3a** (−3.21 eV) is lower than that for **4a** (−1.81 eV).[8]

X-ray structural analysis of **3b** revealed that the molecule is planar (Figure 1).[9] Selected bond lengths are given in Figure 1. They are similar to those of dibromo derivative **3d**.[3] The S–N and C–N bonds of the thiadiazole rings are shorter and longer, respectively, than the corresponding bonds of usual 1,2,5-

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(8) Calculated by the PM3 method, MOPAC program. Steward, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221.

(9) Crystal data for **3b**: $C_{14}H_6N_4S_4$, fw 358.47, monoclinic, space group $P2_1/n$, $a = 17.393(8)$ Å, $b = 4.818(2)$ Å, $c = 8.345(4)$ Å, $\beta = 99.17(2)°$, $V = 690.3(6)$ Å^3, $Z = 2$, $\varrho_{calcd} = 1.72$ g cm^{-1}. The thiophene rings are statistically disordered by 180° rotation. Therefore, refinement was carried out with mixed atom scattering factors [X (75% S and 25% C) and Y (25% S and 75% C)]. The final R value is 0.063 for 1052 reflections with $|F_o| > 3\sigma|F_o|$.

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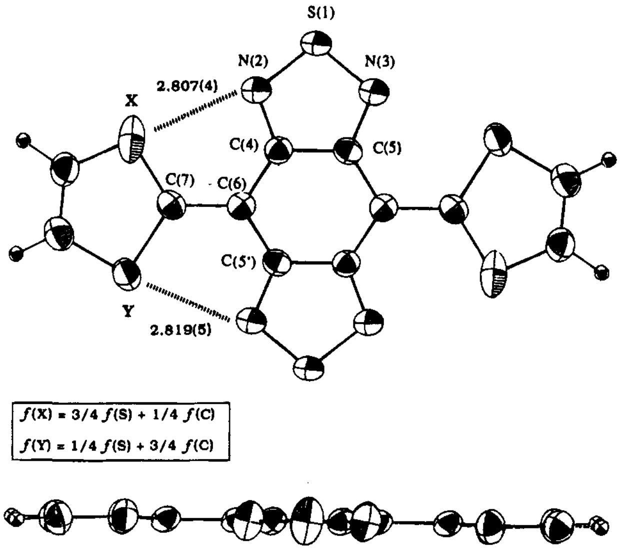

Figure 1. Molecular structure of **3b**. Selected bond lengths (Å): S(1)–N(2), 1.589(4); N(2)–C(4), 1.352(5); N(3)–C(5), 1.348(5); C(4)–C(5), 1.464(6); C(4)–C(6), 1.405(6); C(6)–C(5′), 1.405(5); C(6)–C(7), 1.471(6).

thiadiazoles.[10] Molecules **3b** are uniformly stacked along the *b* axis with an intermolecular distance of 3.42 Å. No significant interheteroatom contacts are observed in contrast to the case of **3d** forming a three-dimensional crystal by intermolecular interactions based on short heteroatom contacts.[3]

Heterocycles **3b** and **4e** gave electroactive polymers by an electrochemical method. Thus polymers **1** and **2** were grown on a Pt disk electrode and indium tin oxide (ITO) glass electrode by anodic oxidation.[11] The cyclic voltammogram of polymer **1** prepared from **3b** is shown in Figure 2. It shows both oxidation and reduction waves. The difference in the threshold potentials for p-doping and n-doping is very small and indicative of a very narrow bandgap. The electronic spectrum of ITO glass is shown in Figure 3.[12] The difference spectra as a function of p-doping support that the film is dedoped at 0.0 V. The optical bandgap can be estimated from the absorption edge of the dedoped film to be below 0.5 eV.[13] This extraordinarily narrow bandgap can be attributed to the high electron affinity and large quinoid contribution of the benzobis(thiadiazole) ring. The rigid planar geometry with short S⋯N contacts may also contribute to lowering the bandgap.[14] The electrical conductivities of compressed pellets of dedoped and I_2-doped polymers were 5.0 × 10^{-5} and 5.6 × 10^{-3} S cm^{-1}, respectively.[15]

On the other hand, the optical bandgap of polymer **2** derived from **4e** was found to be about 1.1 eV, which is higher than that of **1** but much lower than that of polythiophene (2.1 eV). Functionalized narrow-bandgap polymers might be prepared based on polymer **2** since substituents can be easily introduced into the benzothiadiazole skeleton. The more detailed characterization of narrow-bandgap polymers obtained here and preparation of related new polymers are now in progress.

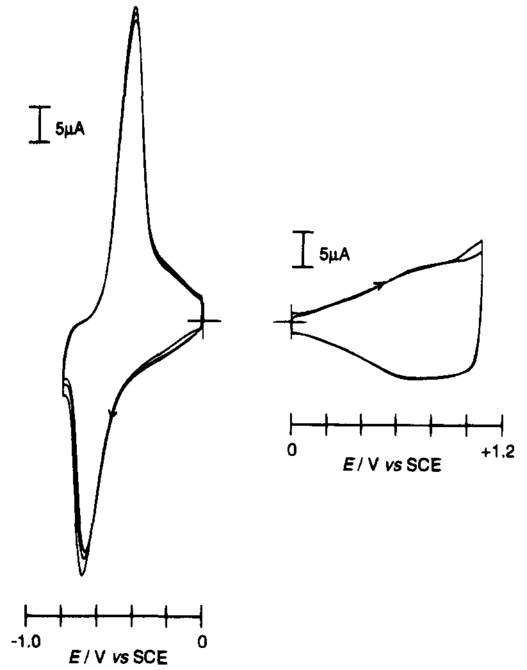

Figure 2. Cyclic voltammogram of polymer **1** measured on a Pt disk (scan rate 10 mV s^{-1}, in PhCN with 0.1 mol dm^{-3} n-Bu_4NBF_4).

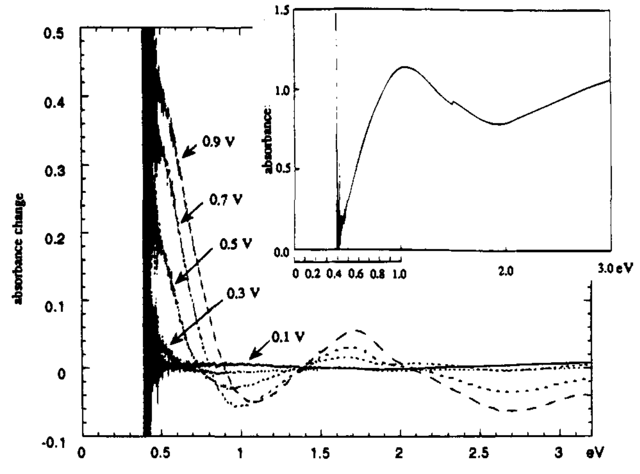

Figure 3. Electronic absorption spectrum of polymer **1** as a function of applied potential plotted as the difference from the polymer dedoped at 0.0 V. The insert shows the spectrum of the dedoped polymer.

Acknowledgment. This work was supported by Grant-in-Aid for Scientific Research on Priority Areas No. 06243105 from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Experimental details of the preparation of new compounds and X-ray structural analysis of **3e** containing tables of atomic coordinates, thermal parameters, bond lengths, and angles (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(11) The polymers were prepared by a potential sweep electrolysis (from 0.0 to 1.125 V vs SCE, scan rate 100 mV s^{-1}) in an argon-degassed solution of **3b** (10^{-3}–10^{-4} mol dm^{-3}) in PhCN containing 0.1 mol dm^{-3} n-Bu_4NBF_4.

(12) The polymer film grown on an ITO electrode was electrochemically dedoped or doped.

(13) The absorption edge cannot be determined accurately because of the intense absorption of the ITO electrode itself.

(14) Roncali et al. have recently reported that rigidification of the π-conjugated system leads to a reduction of the bandgap. Roncali, J.; Thobie-Gautier, C.; Elandaloussi, E. H.; Frère, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2249.

(15) The polymer for the conductivity measurement was prepared by a constant potential method at 1.1 V vs SCE using an ITO electrode in PhCN containing 0.1 mol dm^{-3} Bu_4NBF_4. It was dedoped by NH_3.