Electrochemical and Chemical Doping Behavior of Bithiophene–Bithiazole Copolymer

Syun-ichi Otsuka, Hiroki Fukumoto, and Takakazu Yamamoto*

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

Received September 28, 2007; E-mail: tyamamot@res.titech.ac.jp

An alternating copolymer of 4,4′-dialkyl-2,2′-bithiazole (alkyl = tridecyl) and 2,2′-bithiophene receives electrochemical p-doping and n-doping with a peak current anode potential (E_{pa}) and a peak current cathode potential (E_{pc}) of 0.69 and −2.13 V vs. Ag^+/Ag, respectively. The copolymer undergoes chemical p-doping with $NOBF_4$. X-ray diffraction (XRD) data of the p-doped copolymer indicate that the π-stacking distance of the copolymer is shortened from 3.62 to 3.52 Å after the p-doping. Location of the BF_4^- dopant in the p-doped copolymer is discussed.

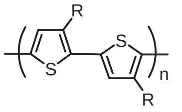
π-Conjugated polythiophene and thiophene copolymers are important materials for polymer-based electronic and optical devices,[1] and some of the polymers have been adopted in industry.[2] Their electrochemical and chemical doping has been attracting interest, and the effects of their molecular structures on their electrochemical and chemical properties have been discussed. Recently, self-assembly of thiophene-based π-conjugated polymers is also attracting interest.[3–5] Head-to-tail type poly(3-alkylthiophene), HT-P3RTh, is a typical example of such π-stacking polymers (Chart 1).

They are considered to self-assemble to form a π-stacked structure assisted by side alkyl chain aggregation.[3] However, the solid structure of π-conjugated polymers obtained after doping has not been explored much.

Previously, we reported synthesis of the following alternating copolymer of 4,4′-dialkyl-2,2′-bithiazole and 2,2′-bithiophene and strong self-assembly of the copolymer, **Copoly-1**, in solid (Scheme 1).[6] Because of the presence of electron-donating thiophene units and electron-accepting thiazole units as well as its strong self-assembling behavior, doping behavior of the copolymer and changes of packing structure of the copolymer after doping are considered to be interesting.

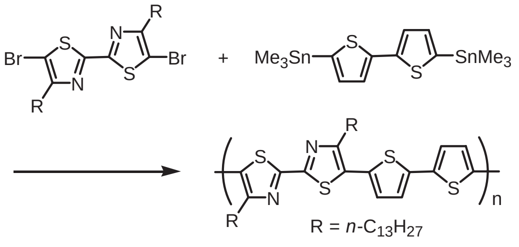
We herein report electrochemical and chemical doping behavior of the copolymer, **Copoly-1**, and structural changes of the copolymer caused by the doping.

Results and Discussion



head-to-tail type poly(3-alkylthiophene)
HT-P3RTh

Chart 1.



R = n-$C_{13}H_{27}$
Copoly-1

Scheme 1.

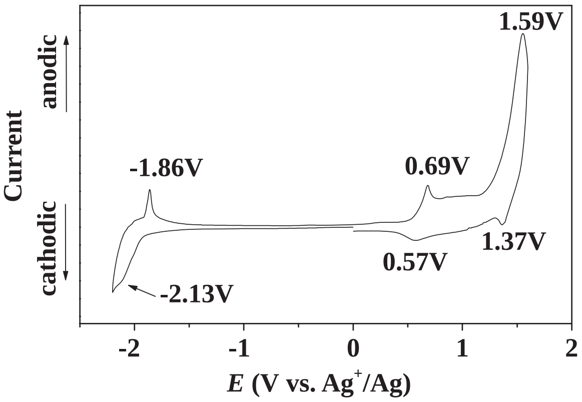
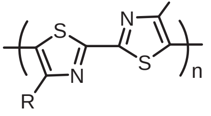


Figure 1. Cyclic voltammogram of **Copoly-1** film on a Pt plate. In an CH_3CN solution of $[N(n\text{-}C_4H_9)_4]BF_4$ (0.10 M) with a scanning rate of $50\,mV\,s^{-1}$.



PRBTz

Chart 2.

Figure 1 shows a cyclic voltammogram of a cast film of **Copoly-1**. As shown in Figure 1, the electrochemical p-doping (or oxidation) and n-doping (or reduction) of **Copoly-1** take place with peak current potentials of $E_{pa} = 0.69$ V and $E_{pc} = -2.13$ V vs. Ag^+/Ag, respectively. The cyclic voltammogram is reproducible for more than 5 times when scanned between −2.2 and 1.6 V vs. Ag^+/Ag.

Because a homopolymer of 4-alkylthiazole, poly(4,4′-dialkyl-2,2′-dithiazole-5,5′-diyl) **PRBTz** (Chart 2), is inert to electrochemical oxidation due to the electron-deficient nature of the thiazole unit,[7] the electrochemical oxidation of **Copoly-1** is considered to occur mainly at the bithiophene unit. The E_{pa} is comparable to that of polythiophene at about 0.6 V vs. Ag^+/Ag.[1] On the other hand, the electrochemical n-doping is considered to occur mainly in the bithiazole unit. The E_{pc} is comparable to that of **PRBTz** at about −2.2 V vs. Ag^+/Ag.[7] The CV data reveal that **Copoly-1** is electrochemically active both in the oxidation and in the reduction. Figure 2

Published on the web April 10, 2008; doi:10.1246/bcsj.81.536

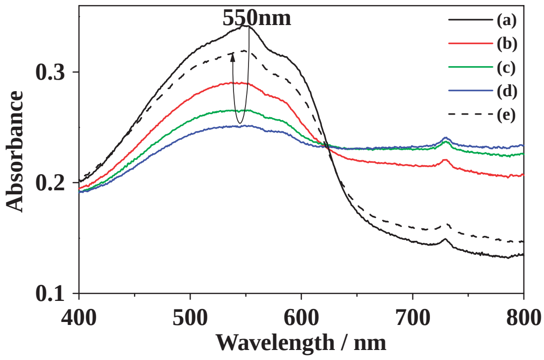
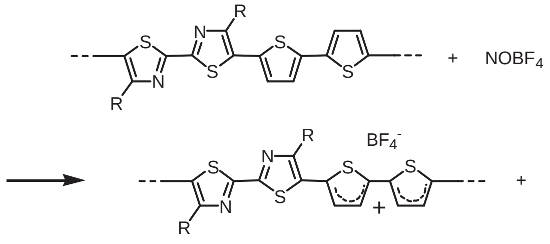


Figure 2. Changes of UV–vis spectrum of **Copoly-1** film on an ITO glass electrode. In an CH_3CN solution of $[N(n\text{-}C_4H_9)_4]BF_4$ (0.10 M). (a): Original film. (b): p-Doped at 0.80 V vs. Ag^+/Ag. (c): p-Doped at 1.0 V vs. Ag^+/Ag. (d): p-Doped at 1.2 V vs. Ag^+/Ag. (e): After de-doping the (d) sample at −0.20 V vs. Ag^+/Ag.



Scheme 2.

shows changes of the UV–vis spectrum of a **Copoly-1** film during electrochemical p-doping.

The absorption peak at 550 nm of the original **Copoly-1** is decreased by the p-doping and absorption in the longer wavelength region increases, suggesting the formation of a polaronic and/or bipolaronic state in the π-conjugated polymer.[1] Detailed examination of the UV–vis spectrum in the region longer than 850 nm was not possible due to the presence of an absorption band of CH_3CN at about 900 nm. When a reverse potential is applied, the UV–vis spectrum essentially returns to the original UV–vis spectrum as shown in Figure 2e.

Copoly-1 also undergoes p-doping chemically by using $NOBF_4$ as the oxidizing reagent (Scheme 2). The p-doping is considered to occur mainly at the bithiophene unit, however, the positive charge in p-doped **Copoly-1** is considered to be delocalized along the polymer chain. Chemical p-doping of π-conjugated oligomers and polymers with $NOBF_4$ has been reported.[8] When a **Copoly-1** film on a quartz glass plate was dipped in an CH_3CN solution of $NOBF_4$, the dark purple film turned to black, and X-ray photoelectron spectroscopy (XPS) and data from elemental analysis indicated the p-doping level (BF_4^- dopant/the thiophene unit) was about 0.4.[9]

As previously reported, **Copoly-1** in its cast film on a quartz glass plate assumes an ordered molecularly assembled structure with the alkyl side chains oriented toward the surface of the substrate.[6]

Figure 3 compares XRD diffraction patterns of **Copoly-1** and its $NOBF_4$-oxidized sample in a powder state and in the film. As shown in Figure 3a, **Copoly-1** gives rise to XRD peaks at $d_1(m) = 18.2\,\text{Å}/m$ ($m = 1$–3) and $d_2 = 3.62\,\text{Å}$. A peak at about $2\theta = 20°$ in Figure 3a is considered to correspond to a side-to-side distance of packed side alkyl chains. The d_1 is considered to correspond to the distance between the π-conjugated polymer chains separated by the tridecyl side chains (cf. Charts 3 and 4), and d_2 is considered to correspond to the face-to-face π-stacking distance between the π-conjugated **Copoly-1** planes,[6] similarly to the case of HT-P3RTh.[3,4a,4c] The cast film of **Copoly-1** gives only the $d_1'(m) = 19.2\,\text{Å}/m$ ($m = 1$–3) peaks as shown in Figure 3b, and the d_2 peak is not observed. This is taken as an indication of ordering of **Copoly-1** (cf. Chart 3) on the surface of the quartz glass plate,[6] similarly to the case of film HT-P3RTh on substrates.[4] The elongation of d_1 in the powder sample to d_1' in the cast film is considered to be due to a change of tilting angle of the alkyl side chain toward the polymer main chain in the cast film.

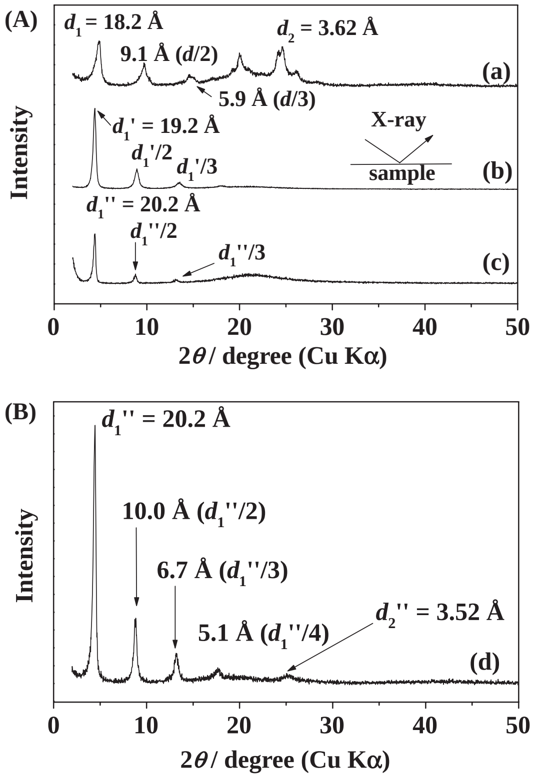


Figure 3. (A): XRD patterns of (a) powdery **Copoly-1**, (b) cast film of **Coploy-1** on a quartz glass plate, and (c) cast film of **Copoly-1** after $NOBF_4$ oxidation. (B): When the sample (c) is peeled off from the quartz plate and crushed, it gives the powder XRD pattern (d). The XRD pattern was measured in reflection mode.

When the **Copoly-1** film is p-doped with $NOBF_4$, the $d_1'(m) = 19.2\,\text{Å}/m$ peaks are shifted to $d_1''(m) = 20.2\,\text{Å}/m$ ($m = 1$–3) as shown in Figure 3c, indicating that the d_1' distance becomes longer by p-doping. When the p-doped film was peeled off from the quartz glass plate and crushed, the sample gave peaks at $d_1''(m) = 20.2\,\text{Å}/m$ ($m = 1$–4) and $d_2'' = 3.52\,\text{Å}$ as shown in Figure 3d, indicating that the π-stacking distance becomes shorter after p-doping. These data suggest that the dopant BF_4^- is located near the end of the alkyl side chain.

HT-P3RTh[1c] and a copolymer of isothianaphthene with *p*-

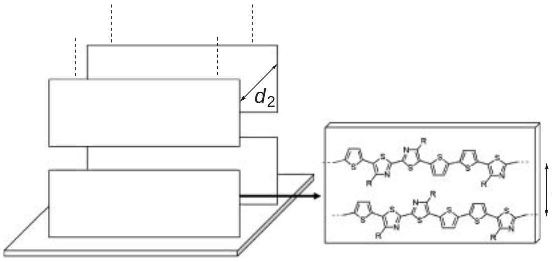


Chart 3. Alignment of **Copoly-1** on the substrate.

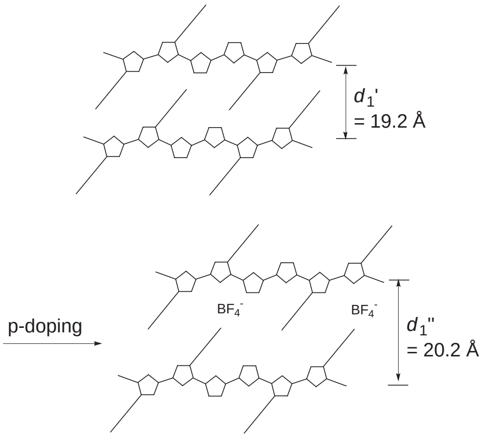


Chart 4. Elongation of the distance between the polymer main chains.

dialkoxybenzene[8c] also show similar elongation of the distance between the π-conjugated main chains (d_1) by electrochemical and chemical p-doping. p-Doping of **Copoly-1** causes shortening of the π-stacking distance, suggesting that the π-stacking force becomes stronger after p-doping. Similar shortening of the π-stacking distance by p-doping has been reported for HT-P3RTh[1c] and poly(3,4-ethylenedioxythiophene),[10] and the present results, together with the previously reported results, reveal a general trend that the p-doping causes (1) elongation of the distance between the π-conjugated main chain separated by the long side chains and (2) shortening of the π-stacking distance of π-conjugated polymers. $NOBF_4$ doping of powdery **Copoly-1** gave analogous XRD results.

Experimental

Copoly-1 with a number average molecular weight of 8600 and a weight average molecular weight of 26000 was prepared as previously reported.[6]

Cyclic voltammetry was carried out using a Hokuto Denko HSV-100 potentiostat. An *o*-dichlorobenzene solution of **Copoly-1** at 130 °C was cast on a Pt plate ($1 \times 1\,cm^2$). The film was dried and annealed at 130 °C for 1 h under air. This film on the Pt plate, a Pt plate ($1 \times 2\,cm^2$), and Ag^+/Ag were used as the working, counter, and reference electrodes, respectively. The measurement was carried out in an CH_3CN solution of $[N(n\text{-}C_4H_9)_4]BF_4$ (0.10 M) under N_2 at room temperature. Spectro-electrochemical behavior was investigated using a cast film. The cast film was prepared on ITO-coated glass substrates. UV–vis absorption spectra of **Copoly-1** were measured at various applied potentials between 0 and +1.2 V vs. Ag^+/Ag. UV–vis spectra were recorded on a Shimadzu UV-3100PC spectrometer.

Powder and film X-ray diffraction (XRD) data were obtained with a RINT 2100Ultima$^+$/PC diffractometer. An *o*-dichlorobenzene solution of **Copoly-1** at 130 °C was cast on quartz substrates and annealed at 130 °C for 1 h.

Reactions of **Copoly-1** with $NOBF_4$ were carried out by dipping the polymer powder and cast film into an CH_3CN solution of $NOBF_4$ (0.10 M) for 15 min. XPS data were obtained with a Perkin-Elmer ESCA5400MC.

References

1 a) D. Fichou, *Handbook of Oligo- and Polythiophenes*, Wiley-VCH, Weinheim, **1999**. b) H. S. Nalwa, *Handbook of Organic Conductive Molecules and Polymers*, Wiley, Chichester, **1997**. c) T. Yamamoto, H. Kokubo, *Electrochim. Acta* **2005**, *50*, 1453.

2 a) F. Jonas, G. Heywang, *Electrochim. Acta* **1994**, *39*, 1345. b) H. Tomozawa, Y. Saida, Y. Ikenoue, F. Murai, Y. Suzuki, T. Tawa, Y. Ohta, *J. Photopolym. Sci. Technol.* **1996**, *4*, 707. c) F. Wudl, M. Kobayashi, A. J. Heeger, *Org. Chem.* **1984**, *49*, 3382.

3 a) R. D. McCullough, S. Tristram-Nagle, S. P. Williams, R. D. Lowe, M. Jayaraman, *J. Am. Chem. Soc.* **1993**, *115*, 4910. b) T. Yamamoto, D. Komarudin, M. Arai, B.-L. Lee, H. Suganuma, N. Asakawa, Y. Inoue, K. Kubota, S. Sasaki, T. Fukuda, H. Matsuda, *J. Am. Chem. Soc.* **1998**, *120*, 2047.

4 a) H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Boss, J. H. Spiering, R. A. Janssen, E. W. Meijer, P. W. Herwig, D. M. Leeuw, *Nature* **1999**, *401*, 685. b) I. MaCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee, M. F. Toney, *Nat. Mater.* **2006**, *5*, 328. c) Z. Bao, A. Dodabalapur, A. J. Lovinger, *Appl. Phys. Lett.* **1996**, *69*, 4108.

5 H. Kishida, K. Hirota, T. Wakabayashi, H. Okamoto, H. Kokubo, T. Yamamoto, *Appl. Phys. Lett.* **2005**, *87*, 121902.

6 T. Yamamoto, S.-I. Otsuka, K. Namekawa, H. Fukumoto, I. Yamaguchi, T. Fukuda, N. Asakawa, T. Yamanobe, T. Shiono, Z. Cai, *Polymer* **2006**, *47*, 6038.

7 T. Yamamoto, H. Suganuma, T. Maruyama, T. Inoue, Y. Muramatsu, M. Arai, D. Komarudin, N. Ooba, S. Tomaru, S. Sasaki, K. Kubota, *Chem. Mater.* **1997**, *9*, 1217.

8 a) J. Cao, M. D. Curtis, *Chem. Mater.* **2003**, *15*, 4424. b) A. Kumagai, H. Fukumoto, T. Yamamoto, *J. Phys. Chem. B* **2007**, *111*, 8020. c) T. Yamamoto, H. Ootsuka, T. Iijima, *Macromol. Rapid Commun.* **2007**, *28*, 1786.

9 XPS data indicated a F/S atomic ratio of about 1.0. Because the XPS peak of F and S are broadened, the F/S ratio is considered to be in a range of about 1.0 ± 0.2. Data from elemental analysis: Found: C, 62.16; H, 8.08; N, 4.08; S, 15.97; Br, 1.13%. Calcd. for $(C_{40}H_{58}N_2S_4 \cdot 0.8BF_4)_n$: C, 62.44; H, 7.60; N, 3.64; S, 16.67%. The discrepancy between the calculated and observed values is considered to be, at least partly, due to high thermal stability of the polymer.

10 Y. Lei, H. Oohata, S.-I. Kuroda, S. Sasaki, T. Yamamoto, *Synth. Met.* **2005**, *149*, 211.