3-Dithiolthione-substituted Polythiophene and Its Redox Activities

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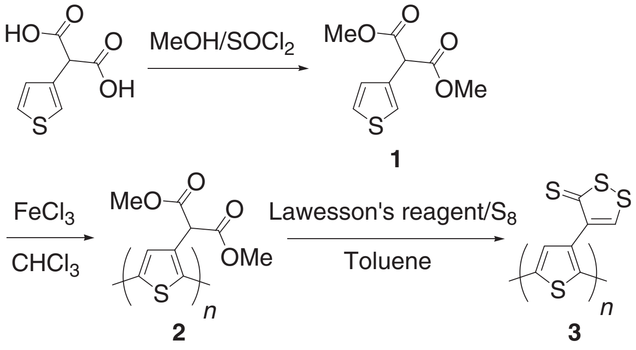
We synthesized 3-dithiolthione-substituted polythiophene, poly[3-(1′,2′-dithiol-3′-thione-4′-yl)thiophene], by cyclization reaction of poly[3-bis(methoxycaronyl)methyl thiophene]. Its redox behavior and electronic states showed that the oxidation of the polythiophene followed the oxidation of the dithiolthione ring to the radical cation of the dithiolthione ring.

π-Conjugated polymers with redox-active side groups are expected to have sophisticated properties, because the electronic states of the main chain are controlled by the presence of the side groups, and the redox response of the side groups would also change the electrochemical properties of the polymers.[1] For example, after the introduction of redox active groups to a π-conjugated polymer, the electrochemical capacity becomes higher than that of the precursor polymer, or the redox sites play a role in an improving electron conductivity.[2] 1,2-Dithiol-3-thione derivatives have attracted attention because they possess remarkable redox activity by virtue of the electron-delocalizing effect of the thiocarbonyl group, and have chemopretentive activities.[3] However, there have been no attempts to introduce the dithiolthione ring into a polymer to take advantage of its redox activity. We report on the synthesis of poly[3-(1′,2′-dithiol-3′-thione-4′-yl)thiophene] and its redox properties in this letter.

The synthetic route to poly[3-(1′,2′-dithiol-3′-thione-4′-yl) thiophene] **3** is summarized in Scheme 1.



Scheme 1.

Thionyl chloride (5 mmol) was dropped into cold methanol (5 mL) at 0 °C, and 3-thiophene malonic acid was added and stirred at rt for 3 h. After the removal of thionyl chloride and methanol, the residue was extracted with $CHCl_3$/water. The ester derivative **1** was obtained in a 99% yield. The oxidative polymerization of **1** was carried out in the presence of $FeCl_3$ (5 mmol) in a 100 mM $CHCl_3$ (10 mL) solution of **1** under N_2 at rt for 24 h. The resulting polymer was dissolved in $CHCl_3$ and purified by reprecipitation from methanol several times, yielding red-orange solid poly[3-bis(methoxycarbonyl)methylthiophene] **2** in a 23% yield.[4] To a toluene solution of the polymer **2** (1.0 mmol), Lawesson's reagent (2.4 mmol) and sulfur (2.0 mmol) were added and stirred at 115 °C for 6 h.[5] The resulting polymer dissolved in $CHCl_3$ and was purified by reprecipitation from methanol several times, yielding deep-red solid poly[3-(1′,2′-dithiol-3′-thione-4′-yl)thiophene] **3** in a 58% yield. The chemical structure of polymer **3** was identified by IR and ^{1}H NMR, and the conversion of the malonic acid ester to the dithiolthione ring was estimated as 70% from a ^{1}H NMR measurement.[6] The polymer **3** was very soluble in $CHCl_3$, DMF, and THF, insoluble in methanol and hexane at rt, and a GPC analysis showed $M_n = 4000$ and $M_w/M_n = 1.28$. The residual malonic acid ester of the resulting **3** was hydrolyzed and cross-linked with hexamethylenediamine to obtain gel materials, which could be utilized as composite electrodes.

To investigate the redox properties of **3**, **2** and 3-(1′,2′-dithiol-3′-thione-4′-yl)thiophene **4** as references,[7] cyclic voltammetry was employed. The cyclic voltammogram (CV) of the monomer **4** in MeCN revealed two oxidation waves (1.13, 1.53 V vs Ag/AgCl) in the first scan (Figure 1a). The oxidation wave at 1.13 V is assigned to the oxidation of the dithiolthione ring.[8] The oxidation wave at 1.53 V is assigned to the oxidation of the thiophene ring. However, there are no reduction waves that are corresponding to the oxidation waves. These results indicated that the dithiolthione ring was oxidized at first, and then a subsequent reaction occurred involving the oxidation of the thiophene ring. The oxidation wave at −0.19 V and the reduction wave at −1.25 V are assigned to the redox reactions between thiol and disulfide.[8]

The CV of **3** in DMF revealed two oxidation waves (1.26, 1.87 V vs Ag/AgCl) and two reduction waves (−0.22, 1.60 V) in several scans (Figure 1b, solid line). The oxidation wave at 1.26 V is assigned to the oxidation of the dithiolthione ring be-

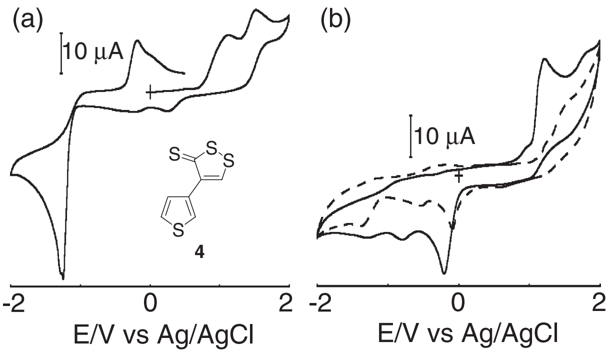


Figure 1. Cyclic voltammograms (a) **4** (10 mM in MeCN containing 0.1 M $TBABF_4$. Sweep rate: 100 mV/s), (b) **2** (dashed line) and **3** (solid line). (10 mM in DMF containing 0.1 M $TBABF_4$. Sweep rate: 100 mV/s).

cause **4** indicated the oxidation wave at 1.13 V and the precursor polymer **2** (Figure 1b, dashed line) showed no corresponding oxidation waves. The reduction wave at −0.22 V is assigned to the reduction of the oxidized dithiolthione ring, and the redox couple indicates the improvement of the electrochemical capacity of the polymer **3** comparing with the polymer **2** and the stability of **3** against potential sweep. The oxidation wave at 1.87 V and the reduction wave at 1.60 V are considered to belong to the redox reaction of the polythiophene main chain.

In order to trace the electronic states of the oxidized **3**, UV–vis spectroelectrochemical studies were carried out as shown in Figure 2. A π–π^* absorption band found at 472 nm before the oxidation changed over two potential intervals ((i)0–1.6 V and (ii)1.7–2.0 V vs Ag/AgCl). In the first range of potential, the absorbance of at 472 nm π–π^* band decreased with an accompanying increase of the absorbance at 726 nm, which is assigned to the oxidation of the dithiolthion ring by comparison with the CV of **3**. At the higher potential over 1.7 V, the $\lambda_{\max}$ of the π–π^* absorption was shifted to shorter wavelength by the oxidation of the polythiophene and the absorbance at 726 nm decreased.

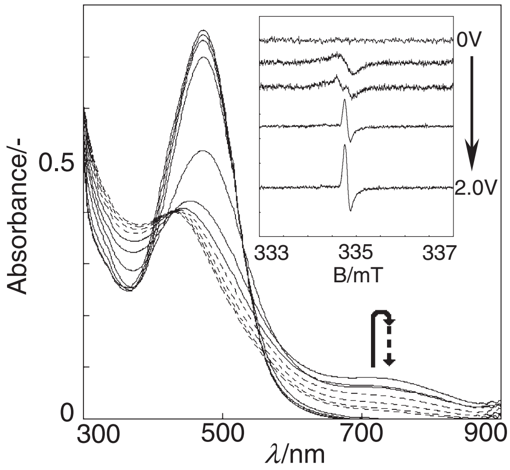


Figure 2. Absorption spectra of **3** [1 mM in DMF containing 0.1 M $TBABF_4$. Applied potential: solid line: 0, 1.0, 1.5, 1.6 V (5, 10, 15, and 40 min), dashed line: 1.7, 1.8, 1.9, 2.0 V] and ESR spectrum of oxidized **3** (10 mM in DMF containing 0.1 M $TBABF_4$. Applied potential: 0, 1.1, 1.5, 1.6, 2.0 V).

There was no increase of absorbance at 726 nm in the oxidation of **2** (data not shown). The ESR signal of **3** was also monitored with applying potential. There was no change of the ESR signal at 0–1.0 V, however, a broad signal at $g = 2.0019$ (line width: 0.34 mT) was detected at 1.1–1.4 V (Figure 2). It indicated that the cation radical appeared by the oxidation of the dithiolthione ring. The signal was split at 1.5 V and became sharp (line width: 0.12 mT) over 1.6 V. Therefore, we consider that the absorption band at 726 nm shown in Figure 2 would be associated with the dithiolthione radical affected by polythiophene radical.[9]

In conclusion, we found that 3-dithiolthione-substituted polythiophene **3** has reversible redox activity, and made the first observations of the radical cation of dithiolthione formed by the oxidation of the dithiolthione ring directly conjugated to a π-conjugated polymer such as polythiophene. The polymer **3** showed fluorescence at 569 nm ($\lambda_{\text{ex}} = 472$ nm). We are now investigating the conductivity and fluorescence of **3** in the form of a radical or cation at different potentials.

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4 ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33 (1H, m, Th–H), 4.92 (1H, m, Th–H), 3.80 (6H, m, –OCH_3). IR (NaCl, cm^{-1}): 2953 ($\nu_{\text{C-H}}$), 1738 ($\delta_{\text{C=O}}$). GPC ($CHCl_3$, polystylene standard): $M_n = 1350$, $M_w = 1440$ ($M_w/M_n = 1.1$).

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6 ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.84 (0.7H, m, vinyl–H), 6.98 (1H, m, Th–H), 3.80 (1.8H, m, –OCH_3). IR (NaCl, cm^{-1}): 2950 ($\nu_{\text{C-H}}$), 1739 ($\delta_{\text{C=O}}$), 1259 ($\delta_{\text{C=S}}$). GPC ($CHCl_3$, polystylene standard): $M_n = 3100$, $M_w = 4000$ ($M_w/M_n = 1.3$). The introduction ratio of the dithiolthione ring was calculated by comparing to the proton signal of thiophene ring.

7 ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.34 (1H, s, vinyl–H), 7.93 (1H, m, Th–H), 7.23 (2H, m, Th–H). ^{13}C NMR ($CDCl_3$): δ 212, 154, 143, 133, 127, 125, 124. IR (NaCl, cm^{-1}): 3052 ($\nu_{\text{C-H}}$), 1299 ($\delta_{\text{C=S}}$). MS: m/z 215 (M^+). The cyclization was performed with the same condition as that of the polymer **2**.

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