π-Conjugated Poly(dithiafulvene) by Cycloaddition Polymerization of Aldothioketene with Its Alkynethiol Tautomer. Polymerization, Optical Properties, and Electrochemical Analysis

Kensuke Naka,* Takashi Uemura, and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

Received March 1, 1999; Revised Manuscript Received May 4, 1999

ABSTRACT: π-Conjugated polymers (**2**) having electron-donating dithiafulvene units in the main chain were prepared by the addition reaction of aldothioketenes derived from π-conjugated diynes (1,4-diethynylbenzene, 4,4′-diethynylbiphenyl, 2,7-diethynylfluorene, and 1,3-diethynylbenzene) with their alkynethiol tautomers. The structures of the polymers were supported by IR and ^{1}H NMR spectra and by elemental analyses. The obtained polymers were soluble in DMSO and DMF and partially soluble in acetone and methanol. The absorption peak due to the $\pi-\pi^*$ transition of **2a** (prepared from 1,4-diethynylbenzene) was largely bathochromic shifted in comparison with that of 2-benzylidene-4-phenyl-1,3-dithiole (**3**) as a model compound. This red shift is ascribed to an effective expansion of the π-conjugation system in **2a**. In the case of **2d** (prepared from 1,3-diethynylbenzene), the absorption maximum was same as that of **3**. This result was caused by the fact that the π-conjugation is not expanded through 1,3-disubstituted benzene. The cyclic voltammograms show that an anodic shift and a broadening of the oxidation peak for the dithiafulvene unit for **2a** was observed compared with that of **3**. Before doping, **2a** exhibits an electrical conductivity of 3×10^{-7} S cm^{-1} as measured on a cast film from 1,3-dimethyl-2-imidazolidinone. Oxidation with iodine raised the electrical conductivity to 1×10^{-3} S cm^{-1}.

Introduction

Derivatives of dithiafulvene, including tetrathiafulvalenes (TTF), act as electron donors and form stable charge-transfer complexes and radical ion salts with a wide range of organic and inorganic acceptor species.[1] These molecules are components of organic metals. Since the first polymer containing a TTF moiety was prepared via a polycoupling process,[2] several attempts to incorporate such donor molecules into a polymeric framework have been carried out.[3−7] Polymers containing dithiafulvene units were prepared by polymerization of vinyl derivatives[4a] or polycondensation of substituted dithiafulvenes with diacid chlorides, *p*-phenylene diisocyanate, and terephthalaldehyde.[4b]

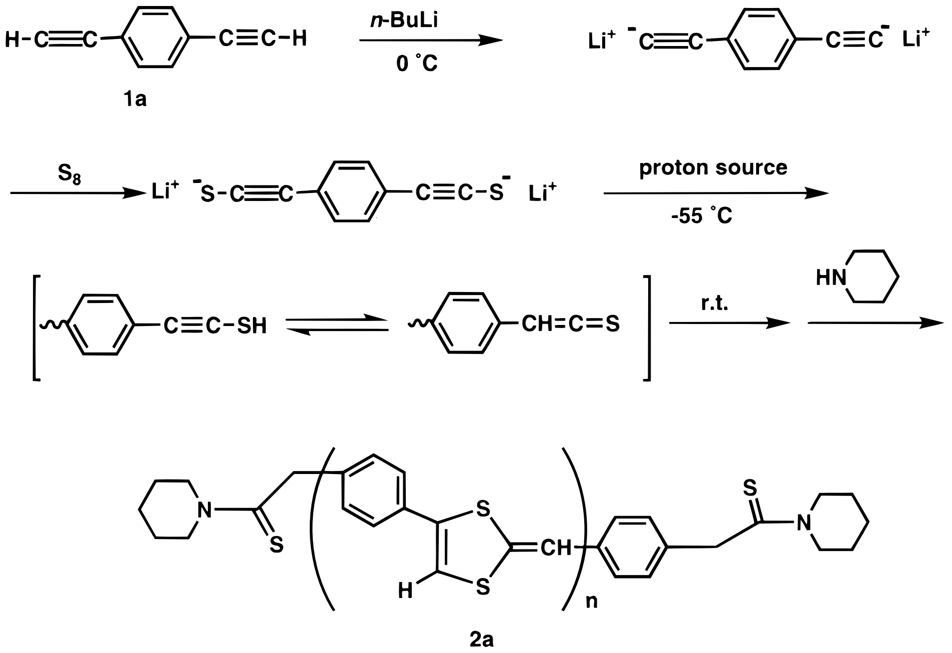
In a π-conjugated polymer having derivatives of dithiafulvene, not only the processability of charge-transfer salts can be improved but also the dimensionality of the conduction process can be increased in the doped state, due to the electron mobility along the polymer backbone via π-conjugation, as well as along the stacking direction via π-orbital overlap.[1c,8] Examples of polymers containing dithiafulvene derivatives in the π-conjugated main chain have been limited, however. Müllen et al. have prepared a fully conjugated structure by inserting a TTF moiety in the conjugated backbone.[5] Yamamoto et al. reported a preparation of soluble π-conjugated polymers containing TTF units in the π-conjugated main chain by Pd-promoted polycondensations.[6] Recently, we reported initial studies on a synthesis of a new π-conjugated polymer having an electron-donating dithiafulvene unit in the main chain by a cycloaddition polymerization of an aldothioketene derived from aromatic diyne monomers with their alkynethiol tautomers.[7] Among numerous preparation methods, thioketenes can be derived from alkynyl thiolates.[9] Alkynyl thiolates can be regarded as aldothioketene anions, and are accessible via addition of sulfur to acetylide anions. Protonation of alkynyl thiolates yields the thiols which tautomerize to aldothioketenes. The usual result of the reaction between aldothioketenes and their alkynethiol tautomer is the formation of dithiafulvenes.[10] Thioketenes are highly reactive and short-lived species similar to their ketene analogues.[11] The chemistry of ketenes has been developed since the beginning of this century and ketenes and bisketenes can be used as the monomer in several different types of polymerizations.[12] Although understanding of the reactions of thioketenes has been highly improved within last several decades, the direct use of thioketenes in polymer synthesis has been very limited to date. In this paper, we report the synthesis and properties of π-conjugated polymers having electron-donating dithiafulvene units in the main chain.

Results and Discussion

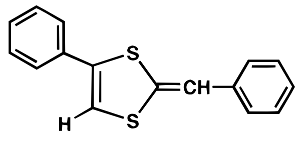
The cycloaddition polymerization of the aldothioketene derived from 1,4-diethynylbenzene was carried out as follows (Scheme 1). After a Et_2O solution of 1,4-diethynylbenzene (**1a**) was treated with *n*-butyllithium, sulfur powder was added to the solution. Protonation of the resulting alkynyl thiolate was performed by adding an equimolar amount of water to the mixture at −55 °C. The temperature of the mixture was allowed to rise to room temperature and the reaction mixture was stirred for 3 h to effect polymerization. Finally, piperidine was added to the mixture to quench terminal thioketenes. The mixture was then poured into a large quantity of Et_2O. The precipitate was washed with Et_2O several times to remove unreacted piperidine, followed by washing with water to remove inorganic salts. After drying under reduced pressure, an orange polymer (**2a**) was obtained in 76% yield. Polymer **2a** was soluble in DMSO and DMF, and partially soluble in acetone and methanol. Polymer **2a** was dissolved in DMSO and was

10.1021/ma990303h CCC: $18.00

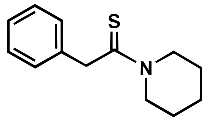
Scheme 1



subjected to GPC measurement. The number-average molecular weight (M_n) and the molecular weight distribution (MWD) of the polymer were $M_n = 11\,000$ and $M_w/M_n = 1.22$, respectively.



3



4

The structure of **2a** was confirmed by IR and ^{1}H NMR spectroscopies compared with those of model compounds. 2-Benzylidene-4-phenyl-1,3-dithiole (**3**),[10a] which was quantitatively obtained by the treatment of lithium 2-phenylethynethiolate with water in Et_2O, was used as a model compound for dithiafulvene unit. An almost quantitative model compound for the terminal thioamide (**4**) was also obtained from lithium 2-phenylethynethiolate with an excess of piperidine. The reaction between a thioketene and a secondary amine is a very efficient process and appears to be quantitative.[9b,c,11] The IR spectrum of polymer **2a** showed a strong peak at 1578 cm^{-1} due to a C=C vibration of the dithiafulvene unit. The IR spectrum also showed peaks at 1502 and 1256 cm^{-1} which were assigned to the terminal thioamide group. The ^{1}H NMR spectrum of **2a** was similar to that of the model compounds. In the ^{1}H NMR spectrum of **2a** (Figure 1c), a broad peak for the benzylidene proton appeared at 6.7 ppm, along with a broad peak for the 1,3-dithiole ring proton at 7.2 ppm. In the ^{1}H NMR spectrum of **4** (Figure 1b), two triplets (4.28 and 3.57 ppm) assigned to N$-$CH$_2-$ appeared due to hindered rotation around the C$-$N bond.[10b,c] The peak at 4.35 ppm was assigned to Ph$-$CH$_2-$C(=S)$-$N in **4**. The ^{1}H NMR spectrum of **2a** also shows two broad peaks at 4.2 and 3.6 ppm attributed to the terminal thioamide moiety. Comparison of the intensities of the absorptions of the dithiafulvene protons in the repeating unit with those of the absorptions of the terminal thioamide protons resulted in the estimation of number-average degree of polymerization (DP) as 26 ($M_n = 5440$). This value should be more reliable than that from GPC data.

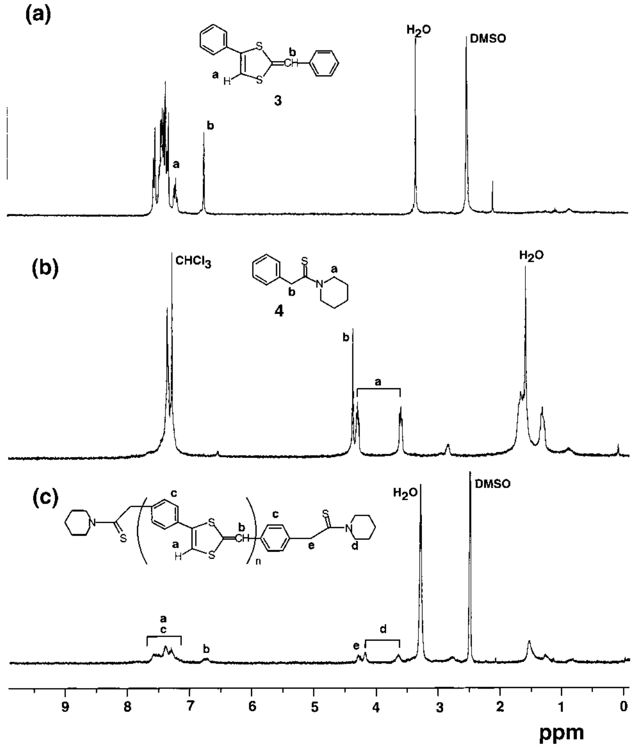
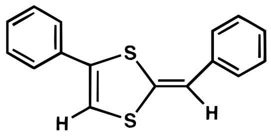
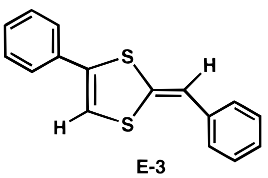


Figure 1. ^{1}H NMR spectra of (a) **3** in $(CD_3)_2SO$, (b), **4** in $CDCl_3$, and (c) **2a** in $(CD_3)_2SO$.



Z-3



E-3

Although the ^{13}C NMR spectrum of the polymer **2a** was not clearly obtained due to its low solubility, peaks

Table 1. Synthesis of Poly(dithiafulvene)

entry	proton source	solvent	polymerization time (h)	yield (%)	M_n[c]
1	H_2O	Et_2O	3	76	5440
2	H_2O	THF	3	33	1980
3	H_2O	toluene	3	10	1640
4	H_2O	Et_2O	6	74	4680
5	H_2O[a]	Et_2O	48	no[b]	
6	*t*-BuBr	Et_2O	48	no[b]	

[a] An excess amount of H_2O was added. [b] No polymeric product was obtained. [c] Determined from ^1H NMR.

around 113 ppm assigned to Ph−*CH*=C< and S−*CH*=C(Ph)−S of the dithiafulvene unit can be recognized. The ^{13}C NMR spectrum of the model compound **3** shows a major peak at 114.00 ppm and a minor peak at 113.55 ppm. The former and the later peaks are assigned to Ph−CH= in the Z and the E isomers of **3**, respectively.[13] Comparison of the peak areas shows that **3** was a mixture of *Z* (94%) and *E* isomers (6%). This observation indicated that a major structure of the repeating unit for the polymer **2a** might be a *Z* configuration.

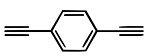
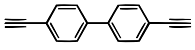
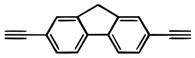
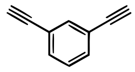
The results of the polymerization conducted under various conditions are summarized in Table 1. Further polymerization time for 6 h in Et_2O did not increase the molecular weight of the polymer (entries 1 and 4). The use of other solvents such as THF and toluene also decreased both the molecular weight and the yield of the polymers (entries 2 and 3). In preparation of thioamides from alkynyl thiolates and secondary amines, it was reported that favorable results were obtained when *tert*-butyl bromide was used as a proton donor.[9b] However, entry 6 shows that ideal polymerization did not proceed even after 48 h when *tert*-butyl bromide was used instead of water in this system. Although the model compound **3** was obtained in good yield after addition of a large amount of water to the alkynyl thiolate solution,[10a] adding an excess amount of water did not produce the polymeric product (entry 5). The polymerization could be inhibited by addition reaction of water to thioketene.

Thermogravimetric analysis (TGA) was recorded for **2a** under nitrogen. The small weight loss of the polymer started at 250 °C. Subsequently, a rapid weight loss began at about 430 °C and was completed at 540 °C. This relatively high thermal stability suggests the potential utility of the present materials in electronic devices.

The results of the polymerization with various diyne monomers are summarized in Table 2. In every case, the corresponding polymers were obtained in good yields. The relatively low molecular weights of **2b** and **2c** are probably due to the low solubility of the polymer products. The structures of the polymers were supported by IR and ^1H NMR spectra and elemental analyses.

The UV−vis absorption spectral data for the diluted acetonitrile solutions of **2a**−**d** are also shown in Table 2. Figure 2 shows the spectrum of **2a**, in which the peak due to the π−π^* transition of the polymers was observed at 398 nm. The value was largely bathochromic shifted in comparison with that of the model compound **3**. This red shift is ascribed to an effective expansion of the π-conjugation system in **2a**. The smaller bathochromic shift of **2b** from the λ_{max} of **3**, compared with the bathochromic shifts observed with **2a** and **2c**, was due to a steric distortion of the biphenyl moiety. In the case of **2d**, the absorption maximum was same as that of **3**. This result was caused by the fact that the π-conjugation is not expanded through 1,3-disubstituted benzene.

Table 2. Synthesis of Poly(dithiafulvene)s Using Various Aromatic Diynes[a]

diynes	polymer	yield (%) [b]	M_n [c]	UV λ_{max} (nm) [d]
	**2a**	76	5440	398
	**2b**	55	1830	379
	**2c**	66	2810	401
	**2d**	54	3980	359

[a] Polymerizations were carried out in Et_2O at room temperature for 3 h. [b] Isolated yields after washing with water. [c] Determined from ^1H NMR. [d] Absorption spectra were recorded in diluted acetonitrile solutions at room temperature.

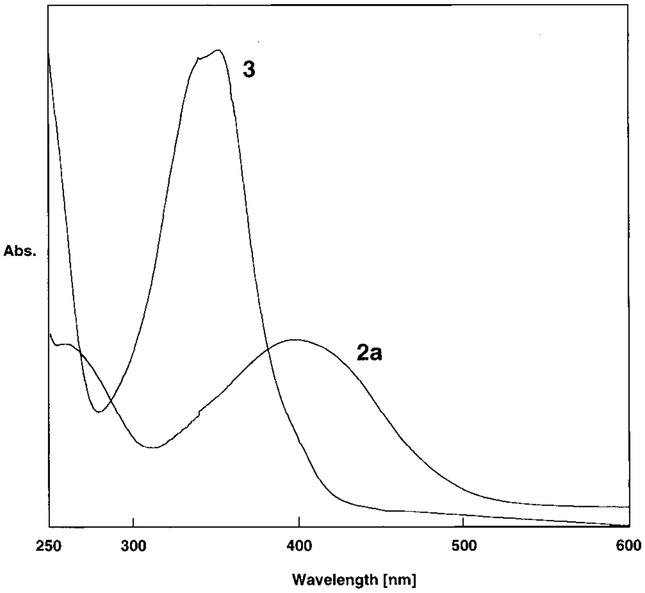


Figure 2. UV−vis spectra of **2a** and **3** in acetonitrile.

To elucidate the redox properties of the polymer, cyclic voltammetry measurements were carried out. As shown in Figure 3b, the cast film of **2a** gave a single-broad oxidation peak at about 0.61 V vs Ag/Ag$^+$. 2-Benzylidene-4-phenyl-1,3-dithiole (**3**) as a model compound for **2** showed a single oxidation peak at 0.40 V vs Ag/Ag$^+$ (Figure 3a). An anodic shift of the oxidation potential for the dithiafulvene unit in **2a** was observed compared with that of **3**. It clearly indicated that the dithiafulvene unit incorporated in the π-conjugated system caused a stabilization against oxidation.

In cyclic voltammograms of simple one-electron reversible redox reactions, the potential difference ($\Delta E_{p/2}$) between the oxidation peak (E_{ap}) and the half-peak potential ($E_{p/2}$) was 56.5 mV. The first oxidation peak of the model compound **3** gives potential difference ($\Delta E_{p/2}$) of 55 mV, whereas that of polymer **2a** gives 295 mV. An apparent broad oxidation peak for **2a** compared with that of **3** suggested the interaction between dithiafulvene units along the π-conjugated polymer main chain. Such an anodic shift and broadening of the peak have been reported for several electrochemically active π-conjugated polymers.[14]

The cast film of **2b**−**d** also gave single oxidation peaks. Oxidation potentials (E_{pa}) and half-peak poten-

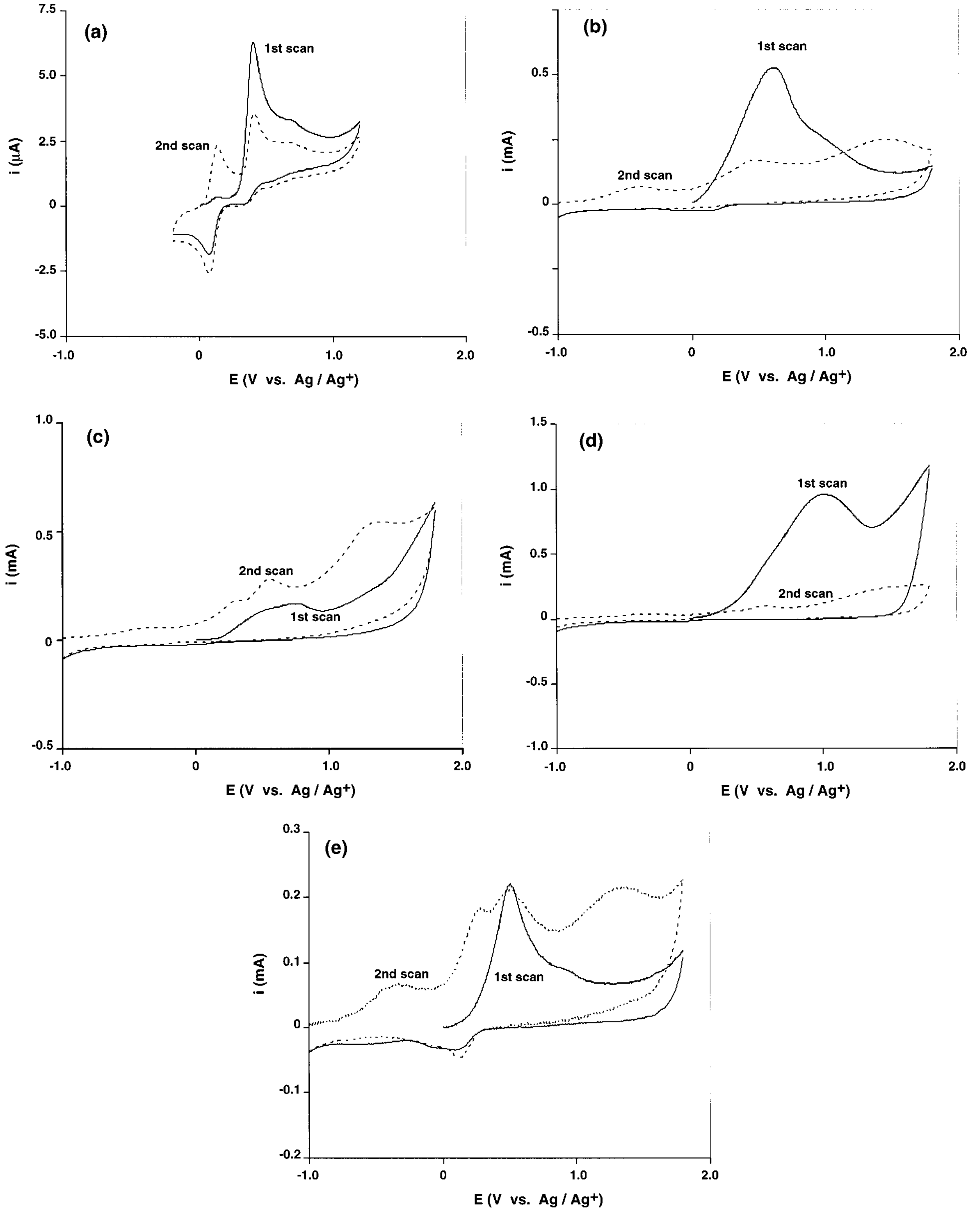


Figure 3. Cyclic voltammograms of (a) **3**, (b) **2a**, (c) **2b**, (d) **2c**, and (e) **2d**, measured in CH_3CN solution of 0.1 M $[NEt_4]BF_4$ at 300 mV s^{-1}.

tials ($E_{p/2}$) of the polymers are summarized in Table 3. The oxidation peaks of **2b** and **2c** were largely anodic shifted and broadened in comparison with that of **3**. The fairly higher oxidation potential of **2c** compared with that of **2b** was due to a plane configuration of the fluorene unit. As shown in Figure 3e, the oxidation peak of **2d** was contrasted with those of **2a**−**c**. The peak potential defference and the degree of broadening of **2d** are small, suggesting that the electron exchange between dithiafulvene units through 1,3-disubstituted benzene was not effective.

As shown in Figure 3a, during the reverse cathodic scan, a reversible wave appears at a less positive potential of the irreversible oxidation peak ($E_{ap} = 0.40$ V). This new redox system was due to a dimer product of the dithiafulvene. In the literature, oxidative dimerization of dithiafulvenes has been known to form tetrathiafulvalenes (TTF) vinylogues.[15] In cyclic volta-

Table 3. Oxidation Potentials and Half-Peak Potentials of Poly(dithiafulvene)s[a]

polymer	E_{pa} (V)	$E_{p/2}$ (V)	$\Delta E_{p/2}$ (V)[b]
2a	0.610	0.315	0.295
2b	0.755	0.350	0.405
2c	1.005	0.597	0.408
2d	0.504	0.315	0.136
model compound **3**	0.402	0.347	0.055

[a] Measured in a CH_3CN solution of 0.1 M $[NEt_4]BF_4$ at 300 mV s^{-1}. [b] Potential difference between oxidation peak (E_{ap}) and half-peak potential ($E_{p/2}$).

mmograms of **2a** and **2d**, reversible redox peaks were appeared after the irreversible oxidation peaks were scanned. These results show that the oxidation of the polymers led to an inter- and/or an intramolecular dimerization of the dithiafulvene unit.

Before doping, **2a** exhibits an electrical conductivity of 3×10^{-7} S cm^{-1} as measured on a cast film from 1,3-dimethyl-2-imidazolidinone. Oxidation with iodine raised the electrical conductivity of 1×10^{-3} S cm^{-1}, 4 orders of magnitude greater than the undoped polymer.

Experimental Section

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Solvents were dried and distilled under N_2. 4,4′-Diethynylbiphenyl, 2,7-diethynylfluorene, and 1,3-diethynylbenzene were synthesized according to the literature.[16]

Measurements. ^1H NMR and IR spectra were recorded on a JEOL JNM-EX270 spectrometer and a Perkin-Elmer 1600 spectrometer, respectively. UV−vis spectra were obtained on a JASCO V-530 spectrophotometer. Thermogravimetric analysis (TGA) was performed on a Shimadzu DT-30 instrument (10 °C/min). Gel permeation chromatography was carried out on Shodex K-803 plus K-804 columns by using DMSO as an eluent at 50 °C after calibration with standard poly(8-oxa-6-azabicyclo[3.2.1]octan-7-one) samples. For cyclic voltammetry studies, thin polymer films were deposited on a indium−tin−oxide (ITO) coated glass electrode by casting from a DMSO solution. The electrodes were dried under vacuum. Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley model 236 source measure unit. The polymer film (thickness = about 7.6 μm) was prepared by dropping 5 wt % 1,3-dimethyl-2-imidazolidinone/THF (1/1, w/w) solution onto glass plates equipped with gold electrodes, followed by drying at 50 °C for 1 h and 120 °C for 0.5 h. I_2 doping was carried out by contacting the polymer film with gaseous I_2 under vacuum.

Polymerization. A typical experimental procedure is as follows. To a solution of 1,4-diethynylbenzene (126 mg, 1.00 mmol) in Et_2O (1.0 mL) was added a 1.6 M solution of *n*-butyllithium in hexane (1.25 mL, 2.00 mmol) at 0 °C. After the mixture was stirred for 0.5 h, the sulfur powder (64 mg, 2.00 mmol) was added to the solution. The reaction mixture was stirred for 2 h and then cooled at −55 °C, and water (36 mg) was carefully added. The temperature of the mixture was allowed to rise at room temperature, and the reaction mixture was stirred for 3 h. Finally, to the mixture was added piperidine (0.3 mL), and the reaction mixture was stirred for 0.5 h. The mixture was then poured into a large quantity of Et_2O. The obtained precipitate was washed with Et_2O several times to remove unreacted piperidine, followed by washing with water to remove inorganic salts. After the product was dried under reduced pressure, an orange-colored polymer was obtained.

2a. Yield: 153 mg (76%). ^1H NMR (δ, ppm): 1.2−1.6 (CH_2 of piperidine unit), 3.6 ($N{-}CH_2$ of piperidine unit), 4.2 ($N{-}CH_2$ of piperidine unit), 4.3 ($CH_2C({=}S)N{<}$), 6.7 ($>C{=}CH{-}Ph$), 7.1−7.7 (aromatic and 1,3-dithiole ring protons). IR (KBr, cm^{-1}): 2928, 1578, 1540, 1502, 1493, 1290, 1256. Anal. Calcd: C, 63.07; H, 4.10; N, 1.44; S, 31.39. Found: C, 63.09; H, 4.45; N, 1.50; S, 30.96.

2b. ^1H NMR (δ, ppm): 1.2−1.6 (CH_2 of piperidine unit), 3.6 ($N{-}CH_2$ of piperidine unit), 4.2 ($N{-}CH_2$ of piperidine unit and $CH_2C({=}S)N{<}$), 6.8 ($>C{=}CH{-}Ph$), 7.1 (1,3-dithiole ring proton), 7.2−7.8 (aromatic). IR (KBr, cm^{-1}): 2918, 1578, 1534, 1500, 1491, 1247. Anal. Calcd: C, 72.05; H, 4.67; N, 1.47; S, 21.96. Found: C, 72.82; H, 4.39; N, 1.42; S, 20.97.

2c. ^1H NMR (δ, ppm): 1.3−1.7 (CH_2 of piperidine unit), 3.4 ($N{-}CH_2$ of piperidine unit), 4.0 (CH_2 of fluorene unit), 4.2 ($N{-}CH_2$ of piperidine unit and $CH_2C({=}S)N{<}$), 6.8 ($>C{=}CH{-}Ph$), 7.2−8.1 (aromatic and 1,3-dithiole ring protons). IR (KBr, cm^{-1}): 2934, 1567, 1558, 1504, 1479, 1283, 1259. Anal. Calcd: C, 73.14; H, 4.17. Found: C, 74.97; H, 4.30.

2d. ^1H NMR (δ, ppm): 1.1−1.6 (CH_2 of piperidine unit), 3.6 ($N{-}CH_2$ of piperidine unit), 4.2 ($N{-}CH_2$ of piperidine unit and $CH_2C({=}S)N{<}$), 6.7 ($>C{=}CH{-}Ph$), 6.9−7.6 (aromatic and 1,3-dithiole ring protons). IR (KBr, cm^{-1}): 2929, 1574, 1548, 1501, 1480, 1254. Anal. Calcd: C, 63.45; H, 3.61; N, 0.72; S, 32.26. Found: C, 63.69; H, 3.30; N, 1.04; S, 31.96.

2-Benzylidene-4-phenyl-1,3-dithiole (3). The model compound **3** was prepared according to ref 10a. Mp: 204−205 °C (lit.[4a] mp 197−199 °C). IR (KBr): 1578, 1556, 1484 cm^{-1}. ^1H NMR (270 MHz, $(CD_3)_2SO$): δ 6,73 ($>C{=}CH{-}Ph$, s, 1H), 7.19 (1,3-dithiole ring proton, m, 1H), 7.30−7.55 (aromatic, m, 10H). ^{13}C NMR (270 MHz, $CDCl_3$): δ 112.17, 114.00, 125.98, 126.56, 127.03, 128.50, 128.61, 128.72, 132.99, 134.59, 135.56, 137.11.

1-(2-Phenyl-1-thioxoethyl)-piperidine (4). To a solution of piperidine (2.5 mL, 25 mmol) in Et_2O (1 mL) was added 1.56 mL of 1.6 M solution in hexane of *n*-butyllithium (2.50 mmol) at −30 °C. Phenylacetylene (255 mg, 2.50 mmol) was added to the reaction mixture. The temperature of the mixture was allowed to rise to 80 °C. The sulfur powder (80 mg, 2.50 mmol) was added, the mixture was stirred for 2 h, and then 1 N HCl (5 mL) was added. The brown organic layer was separated, and the aqueous phase was extracted with Et_2O. The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated to give the product; yield 100%. Mp: 69−70 °C (lit.[9] mp 71−72 °C). ^1H NMR ($CDCl_3$): δ 1.30 (CH_2, m, 2H), 1.65 (CH_2, m, 4H), 3.57 ($N{-}CH_2$, t, 2H), 4.28 ($N{-}CH_2$, t, 2H), 4.35 ($CH_2C({=}S)N{<}$, s, 2H), 7.33 (aromatic, m, 5H). IR (KBr): 1500, 1458, 1289, 1260 cm^{-1}.

Acknowledgment. We would like to thank Prof. M. Okada and Dr. K. Aoi (Nagoya University) for providing the GPC data. We would like to thank Dr. A. Yamamoto and Dr. M. Fukushima of Shin-Etsu Chemical Co. for providing the electrical conductivity data.

References and Notes

(1) For recent reviews, see: (a) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 335. (b) Hansen, T. K.; Becher, J. *Adv. Mater.* **1993**, *5*, 288. (c) Roncali, J. *J. Mater. Chem.* **1997**, *7*, 2307.
(2) Ueno, Y.; Masuyama, Y.; Okawara, M. *Chem. Lett.* **1975**, 603.
(3) Pittman, C. U., Jr.; Liang, Y.-F.; Ueda, M. *Macromolecules* **1979**, *12*, 541.
(4) (a) Mulvaney, J. E.; Chang, D. M. *Macromolecules* **1980**, *13*, 240. (b) Mulvaney, J. E.; Figueroa, F. R.; Evans, S. B.; Osorio, F. V. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 971.
(5) Frenzel, S.; Arndt, S.; Gregorious, M. R.; Müllen, K. *J. Mater. Chem.* **1995**, *5*, 1529.
(6) Yamamoto, T.; Shimizu, T. *J. Mater. Chem.* **1997**, *7*, 1967.
(7) Naka, K.; Uemura, T.; Chujo, Y. *Macromolecules* **1998**, *31*, 7570.
(8) Adam, M.; Müllen, K. *Adv. Mater.* **1994**, *6*, 439.
(9) (a) Schuijl, P. J. W.; Brandsma, L.; Arens, J. F. *Rec. Trav. Chim. Pays-Bas* **1966**, *85*, 889. (b) Schuijl, P. J. W.; Brandsma, L. *Rec. Trav. Chim. Pays-Bas* **1968**, *87*, 38. (c) Sukhai, R. S.; de Jong, R.; Brandsma, L. *Synthesis* **1977**, 888.
(10) (a) Raap, R. *Can. J. Chem.* **1968**, *46*, 2251. (b) Sukhai, R. S.; de Jong, R.; Verkruijsse, H. D.; Brandsma, L. *Rec. Trav. Chim. Pays-Bas* **1981**, *100*, 368. (c) Harris, S. J.; Walton, D. R. M. *J. Organomet. Chem.* **1977**, *127*, C1.

(11) Schaumann, E. *Tetrahedron* **1988**, *44*, 1827.
(12) Zarras, P.; Vogl, O. *Prog. Polym. Sci.* **1991**, *16*, 173.
(13) Timm, U.; Merkle, U.; Meier, H. *Chem. Ber.* **1980**, *113*, 2519.
(14) (a) Yamamoto, T.; Morikita, T.; Maruyama, T.; Kubota, K.; Katada, M. *Macromolecules*, **1997**, *30*, 5390. (b) Yamamoto, T.; Maruyama, T.; Zhou, Z.-H.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832.
(15) (a) Hapiot, P.; Lorcy, D.; Tallec, A.; Carlier, R.; Robert, A. *J. Phys. Chem.* **1996**, *100*, 14823. (b) Fourmigué, M.; Boubekeur, K.; Nelson, C.; Batail, P. *J. Am. Chem. Soc.* **1993**, *115*, 3752.
(16) For syntheses of diyne monomers, see: Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112 and references therein.

MA990303H