

SYNTHESIS AND PROPERTIES OF POLYMERIC BIS (ETHYLENEDITHIO)- TETRATHIAFULVALENES*

ZHAO Weiguo (赵卫国) and SHEN Yongjia (沈永嘉)**

(*Institute of Fine Chemicals, East China University of Science and Technology,
Shanghai 200237, China*)

LI Yongfang (李永舫) and YANG Jing (杨静)

(*Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences,
Beijing 100080, China*)

Abstract A polymer containing bis(ethylenedithio)-tetrathiafulvalene moiety was synthesized and its electrochemical properties were studied by cyclic voltammetry. The charge transfer complexes of the polymer with TCNQ and I_2 were obtained by chemical oxidation in dichlorobenzene. All of them are semi-conductors. A film of the polymer was obtained by casting. Its conductivity, after oxidation with iodine, is $2.24 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ and its conducting state is stable in air.

Keywords Tetrathiafulvalene; Charge-transfer-complex; Conducting polymer

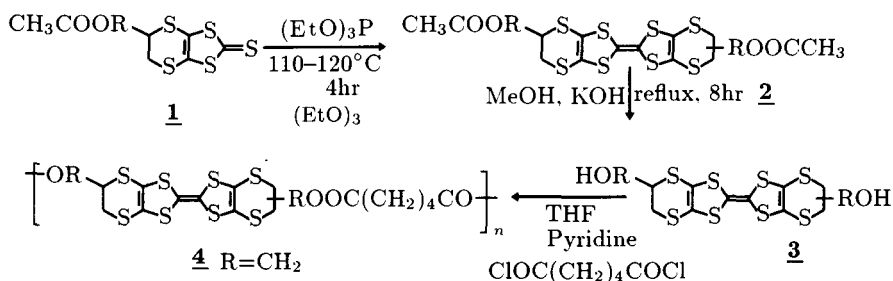
INTRODUCTION

There is considerable scientific and technological interest in the design, synthesis and characterization of organic materials that possess unusual solid-state properties. Of particular interest are organic charge-transfer (CT) complexes, especially in tetrathiafulvalene (TTF) and its derivatives. They can be used as a material for molecular electronic devices. It has been found that the molecular scale electronic and optical components may have potential use in next generation computer and sensors^[1,2]. So the preparation of such molecular scale components is a challenge to all the scientists in this field. Even if the conducting CT-complexes of tetrathiafulvalene and its derivatives have relatively higher conductivity and more stable conducting state, their processability is disappointing because of their crystal

* This work is supported by the National Natural Science Foundation of China (No. 29574156) and the Foundation of the Open Laboratory of Organic Solids, Chinese Academy of Sciences

** To whom correspondence should be addressed

structures^[3,4]. Though the systems containing TTF in the polymer backbone were considered too constrained to allow for the formation of stacked structure, which was found in the conducting CT-salts of TTF and its derivatives, the polymerization is probably one of the practical ways so that the processability of the CT-complexes may be improved^[5,6]. Therefore, some works have been done to synthesize functional TTF derivatives to be used as building blocks of the macrocyclic TTF or polymeric TTF^[7,8]. Here we report a polymer containing bis-ethylenedithio-tetrathiafulvalene (BEDT-TTF) moiety, which possesses conductivity after oxidation with tetracyano-p-quinodimethane (TCNQ) and iodine (I₂). The structure and synthetic route of the polymer are shown as follows:



EXPERIMENTAL

Acetoxymethylene substituted 4,5-ethylenedithio-1,3-dithiole-2-thione 1

The general method for the synthesis as described in Ref. [9] was used.

Bis-acetoxymethylene substituted 4,5-ethylenedithio-TTF 2

Thione 1 (3.0 g, 0.01 mol) was dissolved in freshly distilled triethylphosphite (20 mL) under argon atmosphere and heated to 110~120°C with stirring for 4 h; the solution became orange. Triethylphosphite was removed under reduced pressure and the residue was separated by elution chromatography on silica gel with petroleum ether (60~90°C): ethyl acetate =2:1 v/v. 0.9 g (3.4 mmol) of solid, 2, with orange color was obtained, in a yield of 34%, the m. p of which is 90~91°C, ¹H NMR (CDCl₃) δ: 2.05 (s, 6H), 3.18 (m, 4H), 3.85 (m, 2H), 4.30 (d, 4H); MS (EI) m/z: 528 (M⁺, 100%), 428 (52%), 308 (28%), 265 (20%); elemental analysis (Found): C, 36.66; H, 3.08; C₁₆H₁₆O₄S₈, calcd.: C, 36.36; H, 3.03%.

Bis-hydroxymethylene substituted 4,5-ethylenedithio-TTF 3

Bis-acetoxymethylene substituted 4,5-ethylenedithio-TTF 2 (1 g, 1.9 mmol) was dissolved in a mixture of chloroform (20 mL) and methanol (60 mL), potassium hy-

dioxide (0.85 g, 15 mmol) was added and the solution was heated to reflux for 8 h. Solvent was removed by evaporation and water (100 mL) was then added and solid was filtered, washed with sufficient amount of water and small amount of methanol. 0.8 g (1.8 mmol) of solid, **3**, with light yellow color was obtained, in a yield of 94%, the m.p. of which is 168~169°C. ^1H NMR (CD_3COCD_3) δ : 3.40 (*m*, 2H), 3.68 (*m*, 4H), 3.76 (*m*, 4H); EI-Mass *m/z*: 444 (M^+ , 17%), 386 (17%), 243 (28%), 178 (100%); elemental analysis (Found): C, 32.93; H, 2.88; $\text{C}_{12}\text{H}_{12}\text{O}_2\text{S}_8$, calcd.: C, 32.46; H, 2.70%.

Synthesis of polymer 4

Bis-hydroxylmethylene substitute 4,5-ethylenedithio-TTF **3** (4.848 g, 10.9 mmol) was placed in a dried three-necked flask equipped with a magnetic stirring bar and a pressure-equalizing dropping funnel which was fitted with a dry tube filled with anhydrous calcium chloride. Tetrahydrofuran (THF) dried with sodium (60 ml) and pyridine dried with calcium hydride (20 mL) were added to the flask and the mixture was cooled in an ice bath. The system was maintained in a dry argon stream. Adipic chloride (2.0 g, 10.9 mmol, prepared according to Ref. [10]) in dried THF (10 mL) was added dropwise to the cold diol solution. Then, the mixture was stirred at room temperature for 4 h, then heated to reflux for 2 h, some solid emerged. The polymer was precipitated by methanol (250 mL), filtered, washed with methanol. The solid was dissolved in *N*-methylpyrrolidone, filtered off undissolved material, and methanol was then added to precipitate the polymer, filtered, washed with methanol, dried under vacuum. 5.5 g (9.3 mmol) of solid, **4**, with brownish red color was obtained in a yield of 85%.

RESULTS AND DISCUSSION

The polymer **4** is completely soluble in *N*-methylpyrrolidone, *N*, *N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) at room temperature and in dichlorobenzene, nitrobenzene on heating. It is only partially soluble in methylenechloride, chloroform, acetone, ethyl acetate and THF and insoluble in benzene, toluene, hexane, methanol and ethanol. We were unable to obtain representative molecular weight by gel permeation chromatography (GPC) since the polymer was partially soluble in THF.

Absorption spectra

The polymer **4** exhibits three absorption peaks (265, 323, 347 nm in DMF) in the UV region and a weak absorption peak (473 nm) in the visible region, which is

similar to that of the monomer 3 (265, 324, 345, and 474 nm in DMF). The polymer 4 oxidized by iodine (polymer: I₂=4:1) shows a weak absorption peak at 583 nm and a strong absorption peak at 950 nm, which is similar to that of the monomer 3 oxidized by iodine. Therefore, we can conclude that the existence of BEDT-TTF moiety in the polymer renders the properties of polymer 4 should be identical to the monomer 3. The polymer 4 could be considered as a good donor because it can be easily oxidized by iodine.

The IR spectra are also in agreement with the structure fo polymer 4. An ester carbonyl absorption appears at 1730 cm⁻¹. The absorption at 1140 cm⁻¹ indicates the existence of ether group. The spectra exhibit bands at 1010, 900 and 770 cm⁻¹, which are the characteristic bands of bis-substituted BEDT-TTF moiety and the band at 2840~2940 cm⁻¹ is assigned as the absorption of methylene group. A weak absorption at 3420 cm⁻¹ results probably from the terminal hydroxyl group which means the polymer ended with the diol.

Redox properties of the polymer

The solution redox properties of the polymer 4 was studied by cyclic voltammetry. It shows two oxidation peaks. The relevant data of the polymer and the monomer together with BEDT-TTF are tabulated in Table 1. It is evident that the first oxidation potential of polymer 4 is a slightly higher than that of the monomer 3, presumably, it is the effect of electron withdrawal of the ester group.

Table 1 Oxidation potentials of the compounds (2, 3, 4 and BEDT-TTF) in THF

Compd.	$E_1^{1/2}$ (V)	$E_2^{1/2}$ (V)	$\Delta E^{1/2}$ (V)
BEDT-TTF	0.54	0.96	0.42
<u>2</u>	0.53	0.92	0.39
<u>3</u>	0.47	0.87	0.40
<u>4</u>	0.55	0.86	0.31

Conditions: Pt electrode, 25°C, under argon, Bu₄NPF₆ 0.1M in THF, SCE as the reference electrode, scan rate 5 mV s⁻¹

Charge transfer complexes of the polymer 4

The charge transfer complexes of the polymer 4 with TCNQ and I₂ were obtained by heating 4 with TCNQ and I₂ in dichlorobenzene, respectively. Dark solids were separated by filtration and washed with methylene chloride. The conductivities (σ) of the compacting powder measured by the two-probe contact, are shown in Table 2. They are semiconductors. The conductivities of polymer 4 with TCNQ and I₂ are similar to that of the charge transfer complex of the monomer 3 with TCNQ.

Table 2 The compacting powder conductivity (σ) of the charge-transfer complexes of compounds (**3** and **4**) with TCNQ or iodine

Compd.	σ (S·cm ⁻¹)
3 +TCNQ	8.65×10^{-6}
4 +TCNQ	4.86×10^{-6}
4 +I ₂	4.24×10^{-6}

Casting film

The polymer **4** was dissolved in a mixture composed of equal volume mixture of DMF and THF and casted into a film with KW-4 Spreadmeter. No polymer film will be formed, if a single solvent was used, because either the evaporation rate is low or the solubility of polymer **4** in THF is low. The thickness of the film formed is 100~1000 nm and its conductivity is 3.36×10^{-15} S·cm⁻¹. After oxidation with iodine, the film's conductivity is 2.24×10^{-6} S·cm⁻¹ and its conducting state was still maintains in air after 10 d.

REFERENCES

- [1] Ariram, A., "Molecular Electronics-Science and Technology", United Engineering Trustees Inc., New York, **1989**
- [2] Lehn, J.M., *Angew. Chem. Int. Ed. (Engl.)*, **1990**, 29, 1304
- [3] Fox, M.A., Pan, H.L., *J. Org. Chem.*, **1994**, 59, 6519
- [4] Pittman, Jr. C.U., Ueda, M., Liang, Y.F., *J. Org. Chem.*, **1979**, 44, 3639
- [5] Pittman, Jr. C.U., Liang, Y.F., Ueda, M., *Macromolecules*, **1979**, 12, 355
- [6] Green, D.C., Allen, R.W., *J. Chem. Soc. Chem. Commun.*, **1978**, 832
- [7] Blanchard, P., Duguay, G., Coussean, J., Salle, M., Jubault, M., Gorgues, A., Boubekeur, K., Batail, P., *Syn. Mat.*, **1993**, 55~57, 2113
- [8] Bryce, M.R., Cooke, G., Dhindsa, A.S., Lorcay, D., Moore, A.J., Pelty, M.C., Hursthouse, M.R., *J. Chem. Soc. Chem. Commun.*, **1990**, 816
- [9] Adam, M., Fanghaenel, E., Muellen, K., Shen, Y.-J., Wegner, R., *Syn. Mat.*, **1994**, 66, 275
- [10] Podkoscielny, W., Rudz, W., *J. Appl. Polym. Sci.*, **1994**, 53, 815