added a solution of 471 mg (2.90 mmol) of iodine monochloride in 30 mL of carbon tetrachloride at 20 °C. After the reaction mixture was stirred for 2 h, it was poured into a large amount of ice–water and extracted with dichloromethane. The extract was washed with sodium thiosulfate solution and water, dried over sodium sulfate, and evaporated in vacuo to leave the mixture of **2a–e** and recovered **1** (the yields were determined by GLC analysis).

Compounds **2d** and **2e** were prepared by chlorination of **1** with sulfuryl chloride. Compound **2e** was obtained in small amount by preparative GLC.

2c: colorless prisms; ^{1}H NMR ($CDCl_3$) δ 0.68 (6 H, s), 2.6–2.9 (8 H, m), 7.06 (4 H, s); mass spectrum, m/e 396, 398 (M^+).

Compound **3** was obtained in 67% yield by recrystallization of the reaction mixture of run 4 from hexane. **3**: colorless prisms (hexane); mp 255–256 °C; IR (KBr) 3040, 2950, 1565, 1440, 1420, 1375, 1175, 890, 860, 830, 825, 800, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.62 (3 H, s), 1.04 (3 H, s), 2.60–3.04 (4 H, m), 3.18 (1 H, dd, J = 15 Hz, 5.5 Hz), 3.4 (1 H, dd, J = 15 Hz, 5.5 Hz), 5.40 (1 H, dd, J = 5.5 Hz, 2.5 Hz), 7.00–7.40 (4 H, m); mass spectrum, m/e 338, 340, 342, 344 (M^+). Anal. Calcd for $C_{18}H_{17}Cl_3$: C, 63.64; H, 5.04. Found: C, 63.69; H, 5.10.

Chlorination of 1 with Sulfuryl Chloride. To a solution of 273.6 mg (1.16 mmol) of **1** and 4 mL of sulfuryl chloride in 120 mL of carbon tetrachloride was added 1 mL of boron trifluoride–ether complex at room temperature. After the reaction mixture was refluxed for 12 h, it was cooled, poured into a large amount of ice–water, and extracted with dichloromethane. The extract was dried over sodium sulfate and evaporated in vacuo to give a mixture of **2d** and **2e** in 12% and 88% yields, respectively. (The yields were determined by GLC analyses.) The mixture was recrystallized from hexane to afford 31 mg (10%) of **2d** and 250 mg (70%) of **2e**.

2d: colorless prisms (MeOH); mp 201–202 °C; IR (KBr) 3040, 2930, 1560, 1370, 1250, 1010, 960, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.52 (3 H, s), 0.69 (3 H, s), 2.52–3.01 (8 H, m), 6.74–7.10 (5 H, m); mass spectrum, m/e 270, 272 (M^+). Anal. Calcd for $C_{18}H_{19}Cl$: C, 79.84; H, 7.07. Found: C, 79.10; H, 7.01.

2e: colorless prisms (hexane); mp 244–245 °C; IR (KBr) 3040, 2930, 1570, 1360, 1210, 1010, 950, 940 cm^{-1}; NMR ($CDCl_3$) δ 0.66 (6 H, s), 2.52–3.01 (8 H, m), 7.05 (4 H, s); mass spectrum, m/e 304, 306, 308 (M^+). Anal. Calcd for $C_{18}H_{18}Cl_2$: C, 70.83; H, 5.94. Found: C, 70.40; H, 5.81.

Reaction of 4 with Iodine Monochloride. To a solution of 1.20 g (10 mmol) of **4** in 50 mL of carbon tetrachloride was added a solution of 1.95 g (12 mmol) of iodine monochloride in 10 mL of carbon tetrachloride at 20 °C. After the reaction mixture was stirred for 6 h, it was poured into a large amount of ice, extracted with sodium thiosulfate solution and water, dried over sodium sulfate, and evaporated in vacuo to leave a residue that was distilled under reduced pressure to give 2.21 g (90%) of **5**.

5: colorless liquid; bp 80–82 °C (2 mm) [lit.[7] bp 144–145 °C (20 mm)].

Iodination of 4 with Iodine in the Presence of HIO_4/H_2SO_4. A mixture of 6.01 g (50 mmol) of **4**, 2.31 g (9.1 mmol) of $HIO_4{\cdot}2H_2O$, 5.1 g (20 mmol) of iodine, 25 mL of AcOH, 3 mL of H_2O, and 1 mL of concentrated H_2SO_4 was warmed at 65–70 °C for 12 h, was then cooled to room temperature, and extracted with dichloromethane. The extract was washed with sodium thiosulfate solution and water, dried over sodium sulfate, and evaporated in vacuo to leave a residue that was distilled under reduced pressure to give 8.61 g (70%) of **5**.

Reaction of 2b with Iodine Monochloride. Typical Procedure. To a solution of 96 mg (0.2 mmol) of **2b** in 40 mL of carbon tetrachloride was added a solution of 62.4 mg (1 mmol) of iodine monochloride in 4 mL of carbon tetrachloride at 20 °C. After the reaction mixture was stirred for 2 h, it was poured into a large amount of ice–water, extracted with sodium thiosulfate solution and water, dried over sodium sulfate, and evaporated in vacuo to leave a mixture of **2c** and **2e** and recovered **2b** in 60%, 32%, and 60% yields, respectively (the yields were determined by GLC analyses).

Reaction of 3 with *t*-BuOK. A solution of 100 mg (0.294 mmol) of **3** and 250 mg (2.23 mmol) of potassium *tert*-butoxide in 30 mL of *tert*-butyl alcohol was refluxed for 12 h under a nitrogen atmosphere. After the reaction mixture was cooled to room temperature, it was extracted with dichloromethane. The extract was washed with water, dried over sodium sulfate, and evaporated in vacuo to leave a residue, which on column chromatography (silica gel) with hexane as eluant afforded 80 mg (89.6%) of **6**: colorless prisms (MeOH); mp 223–224 °C; IR (KBr) 3040, 2920, 1555, 1430, 1175, 890, 850, 830, 775, 750, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (6 H, s), 2.40–2.90 (4 H, m), 6.53 (2 H, s), 6.81 (2 H, d, J = 2.5 Hz), 6.94 (2 H, d, J = 2.5 Hz); mass spectrum, m/e 302, 304, 306 (M^+). Anal. Calcd for $C_{18}H_{16}Cl_2$: C, 71.30; H, 5.32. Found: C, 71.06; H, 5.37.

Registry No. **1**, 51689-61-3; **2a**, 91239-66-6; **2b**, 91239-67-7; **2c**, 91239-68-8; **2d**, 91239-69-9; **2e**, 91239-70-2; **3**, 91239-71-3; **4**, 526-73-8; **5**, 41381-33-3; ICl, 7790-99-0; sulfuryl chloride, 7791-25-5.

---

[7] Suzuki, H.; Sugiyama, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 586.

Poly(isothianaphthene)

F. Wudl,* M. Kobayashi, and A. J. Heeger

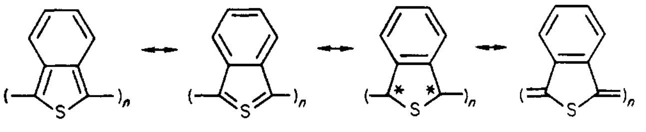
Institute for Polymers and Organic Solids, Department of Physics, University of California, Santa Barbara, California 93106

Received February 22, 1984

The title polymer was prepared by several different approaches. Electrochemical polymerization of isothianaphthene is strongly electrolyte dependent; nonnucleophilic anions produce poly(dihydroisothianaphthene), whereas nucleophilic anions (Br^-, Cl^-) allow formation of the title compound. The latter, either in a Brønsted acid ($HSO_4{\cdot}nH_2O$) doped form or chloride doped form is a better conductor than polythiophene by ca. 1 order of magnitude and about as good a conductor as poly(3-methylthiophene).

Within the rapidly expanding field of polymeric conductors,[1] the poly(heterocycles) have received attention because they are easily prepared in film form and are considerably more stable to atmospheric exposure than poly(acetylene) or poly(phenylene).[2] As an extension of our recent entry into the study of poly(thiophene),[3] we sought to prepare poly(isothianaphthene), a polymer of a

Scheme I[a]



1a 1b 1c 1d

[a] * = +, −, ·.

---

[1] Proceedings of the International Conference on the Physics and Chemistry of Polymeric Conductors, *J. Phys. Colloq.* (*Orsay, Fr.*) **1983**, *C-3*.

[2] For use in stabilizing a semiconductor surface, see: Noufi, R.; Frank, A. J.; Nozik, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 184 and references therein.

0022-3263/84/1949-3382$01.50/0

"nonclassical" thiophene.[4] We expected the title polymer (1) to exhibit higher stability (and perhaps conductivity) than poly(thiophene) because the resonance contributors 1c and 1d shown in Scheme I were expected to be important in the stabilization of open-shell species (1c) and delocalization along the backbone (1d) responsible for high electrical conductivity.

The analogous resonance structures (particularly the analogue of 1d) would not be expected to be as important contributors to the electronic structure of poly(thiophene) as they are in the case of 1 because of the overwhelming gain in stability resulting from incorporation of the 3,4 bond of thiophene into a benzene ring.

Of all the possible methods for the preparation of poly(thiophene), the two simplest are anodic polymerization of pure thiophene[5] and chemical coupling of 2,5-dihalothiophenes.[3,6] The former procedure provides improved materials if 2,2′-dithienyl is employed as starting material[7] and the electrolysis is carried out at relatively low applied voltages (≃3.5 V). From a practical point of view, the anodic polymerization is the more desirable; it is simple and the product appears in the form of a relatively tough, blue-black film. The chemically coupled product is of more academic interest since it is crystalline and its number-average molecular weight is known[3] but it is invariably produced in powder form.

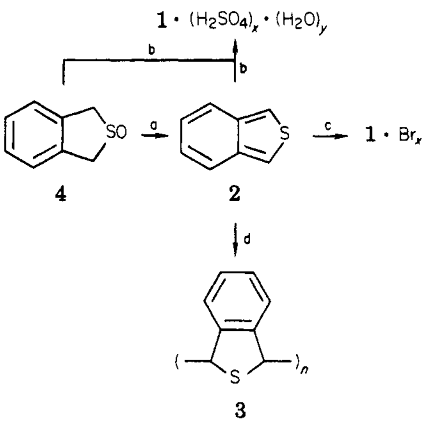
From the above, it is clear that the most desirable approach to 1 would be through the electrochemical coupling of isothianaphthene[8] (2). Moreover, we were not optimistic about the possible preparation of a dihaloisothianaphthene.[9]

In this publication we present procedures (electrochemical and chemical) for the preparation of the title compound. As will be shown below, electrochemical polymerization to yield the desired *unsaturated* polymer is possible only under very specific conditions.

Results and Discussion

When a freshly prepared sample of 2 was electrolyzed in the anode compartment of an H cell using Bu_4NClO_4 or Bu_4NBF_4 as supporting electrolyte and tin oxide coated glass (TOG) as anode, a copious amount of a *white precipitate* ("WP") filled the anode compartment. Upon careful observation it was discovered that the anode was first (instantanously) covered with a very thin blue film, and immediately thereafter formation of WP commenced. Appearance of WP was independent of electrode material, solvent, or temperature. Isolation, characterization (IR, elemental analyses), and chemical manipulation (see below) proved WP to be poly(dihydroisothianaphthene) (3).

Scheme II[a]



[a] a = Al_2O_3; b = H_2SO_4; c = LiBr, 1.5 V, CH_3CN; d = $LiBF_4$, 1.5 V, CH_3CN.

Table I. List of Compaction Conductivity of the Doped Polymer 1

compd	σ [S/cm][a]
$1 \cdot Cl_x$	1.2×10^{-1}
$1 \cdot (HSO_4)_{0.05} \cdot (H_2O)_{0.33}$	2.0×10^{-2}
$1 \cdot (AlCl_4)_x$	2.8×10^{-2}
$1 \cdot (TCNQ)_x$	1.5×10^{-2}
$1 \cdot (chloranil)_x$	1.3×10^{-2}
$1 \cdot Br_x$	4.0×10^{-1}

[a] Two-probe compaction measurement.

Why does thiophene produce partially oxidized ("doped") polymer films under the above conditions while isothianaphthene, after deposition of an extremely thin blue film (presumably doped 1), is transformed to WP? The only sensible explanation for this observation was that 1 was acting as an initiator of cationic polymerization of 2. In order to test this hypothesis we exposed freshly prepared solutions of 2 to the usual catalysts for cationic initiation (Brønsted and Lewis acids) and found that all polymerized isothianaphthene to different degrees. But by far the most interesting result was with sulfuric acid in methylene chloride. Under these conditions, 2 was converted to a blue-black powder form of 1 doped with hydrated sulfuric acid. Clearly the acid acted not only as catalyst but also as oxidizing agent. A reassuring "convergent" test for the above hypothesis was that the product of chloranil dehydrogenation of WP and the product of H_2SO_4 polymerization exhibited identical infrared spectra![10]

Since 2 is produced by dehydration of dihydroisothianaphthen *S*-oxide[8] (4), we reasoned that H_2SO_4 may convert 4 directly into $1 \cdot (H_2SO_4)_x \cdot (H_2O)_y$. Addition of solid 4 to 98% H_2SO_4 did in fact produce the desired partially doped 1 (cf. Scheme II below).

We could also show that even TCNQ could be used as a catalyst for cationic polymerization. Unfortunately the product did not exhibit higher conductivity than any of the other doped 1 compounds, indicating that the acceptor is probably not involved in the conductivity of the solid. Two reasons could be advanced for that observation, the acceptor molecules are probably not stacked in small crystalline regions and/or there is complete charge transfer.

---

[3] (a) Kobayashi, M.; Chen, J.; Chung, T.-C.; Moraes, F.; Heeger, A. J.; Wudl, F. *Synth,. Met.* **1984**, *9*, 77. (b) Chung, T.-C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Ref. B*, in press.

[4] Cava, M. P.; Lakshhmikantham, M. V. *Acc. Chem. Res.* **1975**, *8*, 139.

[5] (a) Diaz, A. *Chem. Scr.* **1981**, *17*, 145. (b) Tourillon, G., Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173. (c) Kossmehl, C.; Chalzithedoron, G. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 551. (d) Bargon, J.; Mohmand, S.; Waltman, R. J. *IBM J. Res. Dev.* **1983**, *27*, 330. (e) Kaneto, K.; Kohno, Y.; Yoshino, K.; Inuishi, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 382.

[6] (a) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett.* **1980**, *18*, 9. (b) Lin, J. W.-P.; Dudek, L. P. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2869.

[7] Druy, M. A.; Seymour, R. J. *J. Phys. Colloq. (Orsay, Fr.)* **1983**, *C-3*, 595.

[8] (a) Gladysz, J. A.; Wong, V. K.; Jick, B. S. *Tetrahedron* **1979**, *35*, 2239. (b) Cava, M. P.; Deana, A. A. *J. Am. Chem. Soc.* **1959**, *81*, 4266. (c) Cava, M. P.; Pollack, N. M.; Mammer, O. A.; Mitchell, M. J. *J. Org. Chem.* **1971**, *36*, 3932.

[9] Wudl, F.; Kruger, A. A.; Thomas, G. A. *Ann. N.Y. Acad. Sci.* **1978**, *313*, 79.

[10] (a) The only reasonable explanation for this observation is that the infrared spectra of doped poly(isothianaphthene) are dominated by the absorptions due to the conduction electrons and the absorptions due to intramolecular vibrations are weak features of the spectrum. (b) In the absence of additional control experiments, it is difficult to speculate about a specific mechanism to explain this electrolyte effect.

While the above result explained the nature of the process of formation of WP and allowed the discovery of a clean procedure for the chemical synthesis of 1, it still did not offer an entry to the electrochemical polymerization of 2. How could one prevent the catalysis for WP formation by "nascent" doped 1? We rationalized that if the reaction medium contained a species which was more nucleophilic than 2, the propagation step would be interrupted. A test experiment which involved addition of iodide to the anode compartment prior to electrolysis failed because iodide was simply oxidized under the electrolysis conditions. However, elctrolysis with LiBr, Bu_4NBr, or (better) Ph_4AsCl produced excellent films on platinum or TOG.[10]

While the results of physical measurements on 1 will be presented elsewhere,[11] preliminary results of conductivity measurements are collected in Table I. The band edge of 1 was estimated (from transmission through thin films at low doping levels) to be $\simeq$1 eV (1.1 μm). This is nearly 1 eV lower than that of polythiophene ($\simeq$2 eV, 620 nm).[3]

Summary and Conclusions

We have shown that the metastable isothianaphthene can be polymerized to well-characterizable highly conducting polymers by at least three different procedures; one of these involves the unusual electrochemical preparation of poly(dihydroisothianaphthene). As expected from examination of valence-bond structures (Scheme I), the title polymer is a better conductor than its relative poly(thiophene).

Experimental Section

1. Poly(dihydroisothianaphthene) (3). 1. A. Electrochemical Polymerization. The monomer 2 was prepared by the procedure described in the literature[8] and used directly after preparation. The polymer 3 was obtained by electrochemical oxidation of this monomer in a two-electrode, separate compartment cell. Platinum sheet was used as the anode, and oxidized graphite was used as the cathode. The clear colorless solution used for the polymerization contained 0.23 mol of 2 with 0.30 M electrolyte, Bu_4NPF_6, in acetonitrile. The acetonitrile (Mallinckrodt) was used directly without further purification. A series of 1.5-V batteries (U.C.C. Eveready) was used as the power supply.

All experiments were carried out under dry N_2. When 4.5 V was connected across this cell, a lot of white powder appeared near the anode instantly. The batteries were disconnected after 10 min. This white powder, polymer 3, was separated by suction filtration, washed with acetonitrile and diethyl ether, and dried under vacuum. The resulting solid was purified for elemental analysis by reprecipitation from THF–H_2O. Infrared spectrum (KBr, cm^{-1}) 3050, 3010, 2870, 1590, 1475, 1445, 1320, 1275, 1140, 1100, 1025, 940, 835, 745, 620, 530. Anal. Calcd for C_8H_6S: C, 71.60; H, 4.51; S, 23.89. Found: C, 71.27; H, 4.54; S, 23.96.

$LiBF_4$ and Bu_4NClO_4 can be used as the electrolyte for this reaction.

1. B. Chemical Cationic Polymerization. The monomer 2 (396 mg, 2.96 mmol) was dissolved in 10 mL of methylene chloride which was previously dried over P_2O_5. When 1 drop of methanesulfonic acid (Aldrich) was added to this solution, there was an instantaneous change in the reaction mixture from colorless to red. This color became violet after 90 min. After removal of methylene chloride by evaporation, the residue was dissolved in THF. And when this solution was poured into methanol, the polymer 3 precipitated from this solution. This was separated by centrifugation and dried under vacuum. The infrared spectrum was identical with that of polymer 3 mentioned above.

2. Doped Poly(isothianaphthene). 2. A. Electrochemical Polymerization. The polymerization procedure was essentially the same as that described above for the polymer 3. The most important point was the electrolyte. When lithium bromide (Aldrich) was used as the electrolyte, a blue film of the doped polymer 1 was grown on the anode (conducting glass) instantly after connecting a 1.5-V battery. Bu_4NBr and Ph_4AsCl can also be used as the electrolyte for this reaction. Infrared spectrum (KBr, cm^{-1}) 1580, 1445, 1370, 1250, 1215, 1180, 1130, 1040, 960, 865, 830, 730, 425. Anal. Calcd for $(C_8H_4S)Cl_{0.05}\cdot(H_2O)_{0.46}$: C, 67.55; H, 3.49; S, 22.54; Cl, 1.25. Found: C, 67.85; H, 3.06; S, 22.57; Cl, 1.32.

2. B. Chemical Cationic Oxidative Polymerization. 2. B. 1. Sulfuric Acid. Sulfuric acid (5 mL, Mallinckrodt) was added to the monomer 2 (396 mg, 2.96 mmol). The monomer color changed from white to reddish black instantly. When the reaction mixture was poured into 400 mL of methanol after overnight stirring, a brown powder, the doped polymer 1, precipitated from this solution. This was separated by centrifugation and extracted with methylene chloride and chlorobenzene by using a Soxhlet extraction apparatus, followed by drying under vacuum. This reaction can be also carried out with a suspension of sulfuric acid in methylene chloride.

The monomer 4 instead of 2 can be used. The polymerization procedure was the same as that mentioned above. Infrared spectrum (KBr, cm^{-1}) 1445, 1370, 1250, 1215, 1180, 1130, 1040, 865, 830, 730, 425. Anal. Calcd for $(C_8H_4S)\cdot(HSO_4)_{0.05}\cdot(H_2O)_{0.33}$: C, 67.19; H, 3.32; S, 23.54. Found: C, 67.26; H, 3.12; S, 23.59.

2. B. 2. Aluminum Chloride/Cupric Chloride. The monomer 2 (238 mg, 1.77 mmol) was dissolved in 5 mL of methylene chloride. Aluminum chloride (anhydrous) (Mallinckrodt) (118 mg, 0.89 mmol) was added to this solution. The reaction mixture color changed instantaneously to violet. Next, cupric chloride ($CuCl_2\cdot 2H_2O$) (Mallinckrodt) (152 mg, 0.89 mmol) was also used. Black precipitation from this mixture occured slowly. Methylene chloride was evaporated after overnight stirring. The residue, the doped polymer 1, was washed with methanol, methylene chloride and chlorobenzene with a Soxhlet extraction apparatus and dried under vaccum.

2. B. 3. TCNQ (7,7,8,8-Tetracyanoquinodimethane). The monomer 2 (238 mg, 1.77 mmol) was dissolved in 5 mL of methylene chloride. After a few milligrams of TCNQ (Aldrich) were added to this solution, its color changed to red very slowly. After overnight stirring this color became blueish black. Next, more TCNQ, which was double the molar quantity of the monomer 2, was added to this solution. This was heated up to 110 °C and this temperature was kept for 1 h. When this reaction mixture was poured into methanol, greenish black powder precipitated from this solution. This was washed with methanol and chlorobenzene by using a Soxhlet extraction apparatus, following by drying under vacuum.

2. C. From Polymer 3. The polymer 3, which was prepared by electrochemical polymerization, was dissolved in hot chlorobenzene. This was a light-brown solution. Tetrachloro-*p*-benzoquinone (Aldrich) was added to this solution. Immediately the solution color changed to dark green. A powder precipitated from this solution by cooling. This was separated by suction filtration, washed with methanol, and dried under vacuum. All materials which were mentioned in Section 2 showed identical infrared spectra.

Acknowledgment. We thank Showa Denko K. K. for support of this work.

Registry No. 1, 91201-87-5; 2 homopolymer, 91201-85-3; 3, 91201-86-4.

---

(11) Kobayashi, M.; Chen, J.; Colaneri, N.; Moraes, F.; Wudl, F.; Heeger, A. J., unpublished results.