

Chloromethylation of Bis(2-thienyl) Sulfide

L. K. Papernaya, E. N. Sukhomazova, E. P. Levanova,
G. F. Myachina, and E. N. Deryagina

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia

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Abstract—Chloromethylation of bis(2-thienyl) sulfide is accompanied by fast polycondensation of the primary chloromethylation product with the initial sulfide. The reaction gives a new polymer in which the thiophene rings are alternately separated by sulfur atoms and methylene groups. Fusion of the polymer with molecular sulfur gave new sulfur-enriched polymers whose specific electric conductivity is comparable with that of organic semiconductors.

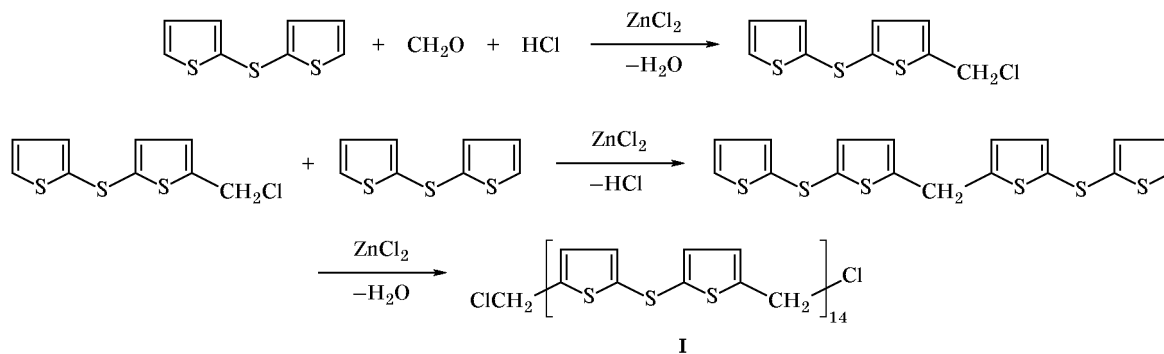
Thiophene and a series of its derivatives undergo chloromethylation by the action of formaldehyde or paraformaldehyde in concentrated hydrochloric acid in the presence of Lewis acids at reduced temperature [1, 2]. We made an attempt to obtain chloromethyl derivative of bis(2-thienyl) sulfide. However, this compound turned out to behave differently from the other thiophene derivatives under chloromethylation conditions. The reaction of bis(2-thienyl) sulfide with formaldehyde was carried out at 5–8°C in concentrated hydrochloric acid containing ZnCl₂ as catalyst with bubbling of hydrogen chloride through the mixture. As a result, a greyish pink solid material was obtained. An analogous light pink powder was isolated in the reaction performed at lower temperature, –4 to 0°C. At –10°C and in the absence of a catalyst, the reaction was not complete, and the conversion of bis(2-thienyl) sulfide was 67%. In this case we obtained 55% of thiophene-2-thiol due to

decomposition of the initial sulfide and a solid product which was analogous to those obtained in the preceding experiment. Insofar as this product is insoluble in boiling organic solvents, it is likely to have a polymeric structure. The calculation by the terminal chlorine atoms gave a molecular weight of 3114. The data of elemental analysis and molecular weight correspond to polymeric structure **I** shown in Scheme 1. The IR spectrum is also consistent with that structure.

Presumably, our failure to obtain mono- or bis-(chloromethyl) derivative originates from activation of position 2 in the thiophene ring. As a result, the primary chloromethylation product quickly reacts with initial bis(2-thienyl) sulfide to give a structure having a methylene bridge, and the process rapidly comes to completion via formation of the respective polymer.

We also tried to effect chloromethylation of bis-(2-thienyl) sulfide with paraformaldehyde, following

Scheme 1.

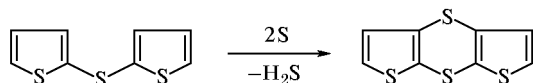


the procedure covered by patent [2] (at -5 to -10°C in the absence of a catalyst). However, neither polymer nor any other product was obtained under these conditions, which indicates that the polymeric product is formed by polycondensation of bis(2-thienyl) sulfide with its chloromethyl derivative.

Thus, chloromethylation of bis(2-thienyl) sulfide is accompanied by fast polycondensation of the primary chloromethylation product with the initial sulfide to give polymer **I** in which the thiophene rings are alternately separated by sulfur atoms and methylene groups. We failed to avoid the polycondensation process despite wide variation of the reaction conditions. Our results open new possibilities for synthesizing polymeric products by polycondensation of appropriate heterocyclic structures.

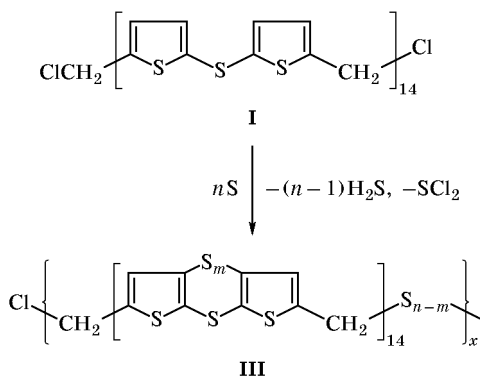
It is known that thermal reaction of bis(2-thienyl) sulfide with sulfur leads to dithieno[2,3-*b*:3',2'-*e*]-[1,4]dithiine. In this case, the thiophene rings are linked at the 3,3'-positions through a sulfur bridge (Scheme 2) [3]. Sulfurization of various polymers, including large-scale products, with elemental sulfur was reported [4, 5]. For example, sulfur-containing polymers with thiophene units were obtained from polyethylene and polystyrene.

Scheme 2.



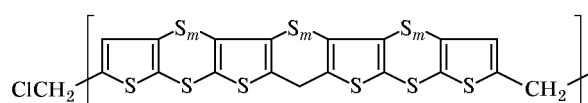
By fusion of polymer **I** with molecular sulfur at 135 – 140°C we obtained a new sulfur-rich polymer **II**. Removal of excess (unbound) sulfur from **II** by dissolving it in carbon disulfide gave polymer **III**. Presumably, polymer **I** reacts with sulfur in a way similar to bis(2-thienyl) sulfide [3], according to which the thiophene rings are linked at the 3,3'-posi-

Scheme 3.



tions through polysulfide chains. It is also possible that sulfur links polymer chains via replacement of the terminal chlorine atoms (Scheme 3). This follows from the reduced concentration of chlorine in polymeric product **III**.

In keeping with the data of elemental analysis and the difference between the molecular weights of compounds **I** and **III**, 6 sulfur atoms is added to each monomeric unit of **I**. The IR spectra of **I** and **III** are almost similar, indicating that the main polymer skeleton is conserved. However, the spectrum of **III** contains S–S absorption bands at 489 and 466 cm^{-1} , while the C–Cl absorption disappears. Probably, the following units are also present in the molecules of polymer **III**:



The isolated polymeric products are dark powders with a metal luster, which exhibit properties typical of high-resistance organic semiconductors. For instance, polymer **I** is characterized by a specific electric conductivity of $1.4 \times 10^{-11}\text{ S/cm}$. Polymer **II** (obtained by fusion of **I** with elemental sulfur; S 86.3%) shows a specific conductivity of $6.2 \times 10^{-15}\text{ S/cm}$. The sharp reduction in the conductivity is likely to result from the presence in **II** of some unreacted sulfur which is known as a dielectric ($\sigma \approx 10^{-17}\text{ S/cm}$). In fact, removal of unbound sulfur from polymer **II** gave product **III** which contains 67.2% of sulfur, and its specific conductivity is greater by three orders of magnitude ($6.4 \times 10^{-12}\text{ S/cm}$). Thus the specific electric conductivity of polymers **I** and **III** is comparable with that typical of organic semiconductors.

EXPERIMENTAL

The IR spectra were recorded on an IFS-25 instrument (Sample Scant : 250) from samples pelleted with KBr or prepared as films. Liquid reaction products were analyzed by GLC on an LKhM-80 chromatograph using a $2000 \times 3\text{-mm}$ column charged with 5% of XE-60 silicone on Chromaton N-AW-HMDS; carrier gas helium; linear oven temperature programming at a rate of 12 deg/min . The electric conductivity was measured with the aid of a VK-2-16 electrometric amplifier and an E6-13A teraohmmeter. Samples were prepared as pellets under a pressure of 400 kg/cm^{-2} (until constant electric resistance). Clamping copper electrodes were used in the measuring unit.

Chloromethylation of bis(2-thienyl) sulfide.

a. Bis(2-thienyl) sulfide, 9.8 g (0.05 mol), was cooled to 5–8°C, and 5.3 ml of concentrated hydrochloric acid, 3.5 ml of a 40% formaldehyde solution, and 0.3 g of ZnCl₂ were added. Dry hydrogen chloride was bubbled through the mixture at a high flow rate over a period of 5 h until a solid light green material was obtained. The solid product was washed with hot methanol, extracted with three portions of boiling water, and dried. The product lightened and turned greyish pink. Yield 9.7 g. IR spectrum, ν , cm⁻¹: 3080 (CH, thiophene); 2916, 2855 (CH₂); 1421, 1206, 1208, 1056 (CH, CH₂); 977 (CH, thiophene); 796, 699 (C–S); 419 (C–Cl). Found, %: C 50.00; H 3.70; Cl 2.28; S 42.13.

b. Dry hydrogen chloride was bubbled at –4 to 0°C through a mixture of 4.9 g (0.025 mol) of bis(2-thienyl) sulfide, 2.8 ml of concentrated hydrochloric acid, 2 ml of a 40% formaldehyde solution, and 0.2 g of ZnCl₂. After 2 h, the mixture turned lighter and thickened. By treatment with acetone, the colorless resinous material was converted into light pink grains which were filtered off, washed with several portions of water, and dried. Yield 5 g. The IR spectrum of the product was identical to that of a sample obtained as described in *a*.

c. A mixture of 9.8 g (0.05 mol) of bis(2-thienyl) sulfide, 3.5 ml of a 40% formaldehyde solution, and 5.3 ml of concentrated hydrochloric acid was cooled to –10°C, and hydrogen chloride was bubbled through the mixture under stirring over a period of 5 h. The greenish mixture was treated with a solution of sodium hydrogen carbonate, washed with water until neutral reaction, and extracted with ether. The extract was evaporated to give a dark liquid which, according to the GLC data, was a mixture of thiophene-2-thiol and initial bis(2-thienyl) sulfide at a ratio of 1:1. The conversion of bis(2-thienyl) sulfide was 67%, and the yield of thiophene-2-thiol, 3.2 g (55%). From the

aqueous phase a polymeric product separated which was identical to samples obtained in *a* and *b*.

d. Hydrogen chloride was bubbled over a period of 1 h through a mixture of 9.8 g (0.05 mol) of bis(2-thienyl) sulfide, 0.058 mol of paraformaldehyde, and 6.35 ml of concentrated hydrochloric acid, stirred at –10°C. The mixture was stirred for 3 h at –5 to –10°C, diluted with a 200-fold amount of water, and extracted with 3 portions of ether. The extract was dried and evaporated to isolate unreacted bis(2-thienyl) sulfide.

Fusion of polymer I with molecular sulfur.

Sulfur, 3 g, was heated to the melting point, and 1 g of powdered polymer I was added in small portions to the melt at 135–140°C. During the addition, the mixture gradually thickened and solidified to give a black powder. Yield of polymer II 3.83 g. Found, %: C 9.43; H 0.50; S 86.28.

A 1.3-g portion of polymer II was washed with carbon disulfide to a constant weight (to remove unbound sulfur). We thus obtained 0.56 g of polymer III. Found, %: C 26.95; H 2.15; Cl 0.60; S 65.24.

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