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Preparation of Poly(2,5-selenophenediyl-vinylene) Film by Sulfonium Salt Method

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Soluble poly(2,5-selenophenediyl-methoxyethylene) was prepared by the reaction of (2,5-selenophenediyl dimethylene) bis(dimethylsulfonium bromide) with a base in a mixture of methanol and water. Its cast film was heated at 200 °C under nitrogen to obtain poly(2,5-selenophenediyl-vinylene) film.

Recently, many attempts have been made to prepare poly(arylene-vinylene) films because of the promising application in electrical and optical materials. Poly(2,5-thienylene-,$^{1-3)}$ furylene-,$^{4,5)}$ 1,4-phenylene-,$^{6-8)}$ and 2,6-disubstituted-1,4-phenylene-vinylene$^{9,10)}$) films were successfully prepared by so-called sulfonium salt method. (Arylene dimethylene)bis(dimethylsulfonium halide) was reacted with a base in an aqueous solution to obtain a soluble precursor polymer which was cast into film. It was heated under inert gas to yield poly(arylene-vinylene) film. Selenophene is a homologue of thiophene and is lower in oxidation potential than thiophene as shown in Fig. 1, indicating that selenophene is stronger in electron-donating character than thiophene. Thus, poly(2,5-selenophenediyl-vinylene) (**1**) is expected to be fully π-conjugated polymer with the higher electron density. In this letter was reported novel preparation of **1** by sulfonium salt method.

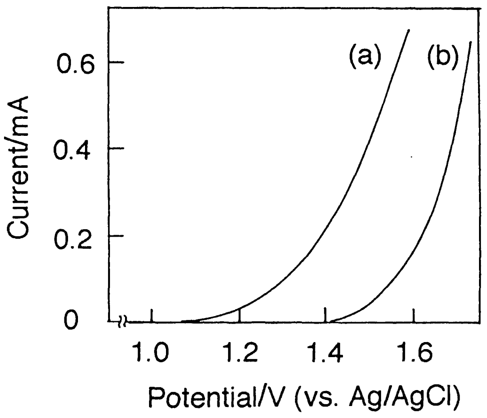
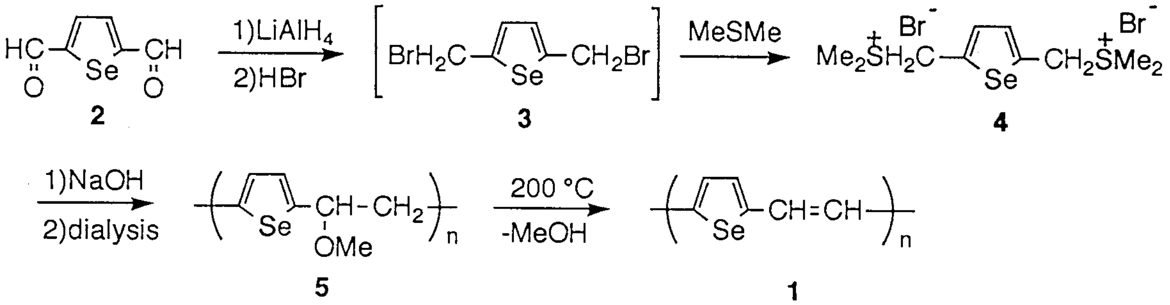


Fig. 1. i-V curves of (a) selenophene and (b) thiophene: solvent, CH_3CN containing $(Bu_4N)ClO_4$ (0.1 mol dm^{-3}); working electrode, glassy carbon; reference electrode, Ag/AgCl; scan rate, 100 mV s^{-1}.

Compound **1** was prepared according to Scheme 1.



Scheme 1.

A solution of selenophene-2,5-dicarbaldehyde[11](**2**) (1.0 g, 5.3 mmol) in 30 cm^3 of ether was added dropwise to the suspension of $LiAlH_4$ (0.2 g, 5.3 mmol) in 6 cm^3 of ether at room temperature. After their mixture was stirred for 1 h, excess hydrogen bromide gas was bubbled at -30 °C. The reaction mixture was washed with water and extracted twice with 15 cm^3 portion of ether. The combined ether extract was dried over anhydrous magnesium sulfate. When the solution was condensed under reduced pressure, 2,5-bis(bromomethyl)selenophene(**3**) was not able to be isolated as a pure compound, probably due to its ready decomposition. Therefore, without trying to isolate **3**, dimethyl sulfide (10 g, 160 mmol) was added into the ether extract and stirred for 24 h to obtain a white solid, which was recrystallized from acetic acid to give (2,5-selenophenediyl dimethylene) bis(dimethylsulfonium bromide)(**4**) (1.37 g, 58%) as white needles; mp 88.5 °C(decomp); IR(KBr) 1600, 1400, 1320 cm^{-1}; ^1H NMR(DMSO-d_6) δ 7.47(s, 2H), 5.11(s, 4H), 2.90(s, 12H); Anal. Found: C, 27.49; H, 4.27%. Calcd for $C_{10}H_{18}Br_2S_2Se$: C, 27.23; H, 4.11%.

The sulfonium salt **4** (1.32 g, 3.0 mmol) was dissolved in 10 cm^3 of a mixture of methanol and water (1:1 by volume) at -30 °C. A solution of sodium hydroxide (0.12 g, 3.0 mmol) in 1 cm^3 of water was added and stirred for 10 h. Then, the reaction mixture was placed in a dialysis cellulose tube (VISKING, Niplone Labware Co.) and immersed into a mixture of methanol and water (1:1 by volume) at 0 °C for 48 h to give 0.1 g of yellow powder which was dissolved in *N,N*-dimethylformamide (DMF). The resulting solution was cast on a glass plate and placed at room temperature under reduced pressure to give a tough orange film. It was soluble in DMF and tetrahydrofuran (THF) but insoluble in water. Its number-average molecular weight ($\overline{M}_n$) was measured to be 95,000 by gel permeation chromatography (GPC) using THF and standard polystyrenes as an eluent and references, respectively. Its IR spectrum as shown in Fig. 2a exhibits absorption peaks in the range of 2800 to 2900 cm^{-1} and at 1060 cm^{-1}, assigned to methyl and methylene groups and methoxy group, respectively. Anal.

Found: C, 44.88; H, 4.74%. Calcd for C_7H_8OSe: C, 44.94; H, 4.31%. It was concluded therefore that the film is composed of poly(2,5-selenophenediyl-methoxyethylene) (**5**).

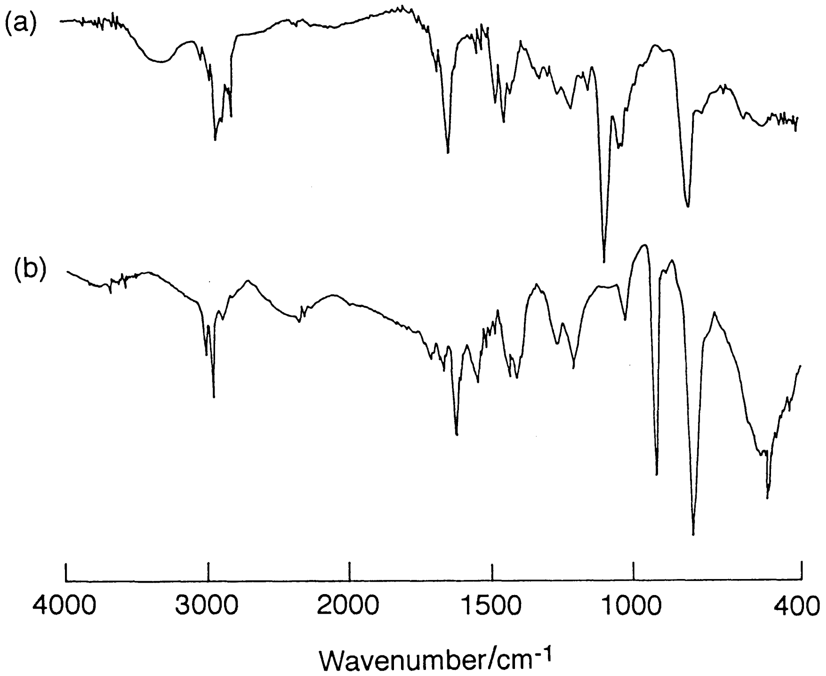


Fig. 2. IR spectra of (a) precursor polymer **5** and (b) product after heat treatment at 200 °C.

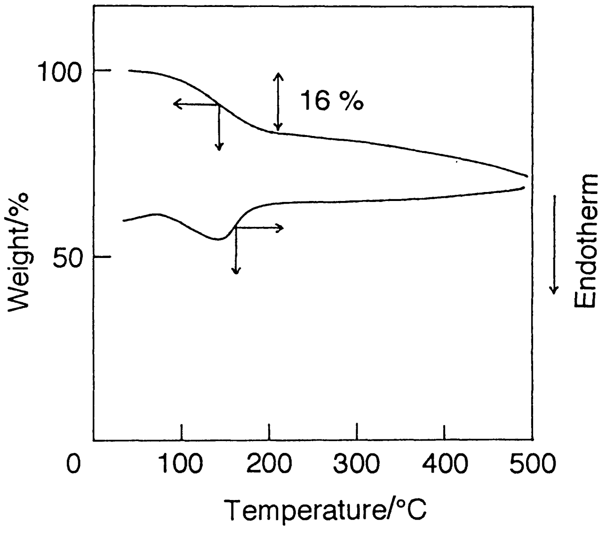


Fig. 3. TG-DTA curves of precursor polymer **5**: heating rate, 10 K min^{-1}.

TG-DTA curves of **5** are shown in Fig. 3. The sample endothermically decreased in weight by 16% in a temperature range of 80 to 150 °C. This weight loss almost corresponds to the calculated value of 17.1% based on the elimination of one molecule of methanol per the monomer unit.

A piece of film of **5** was kept at 200 °C under nitrogen for 1 h. The film changed in color from orange to black with metallic luster. Figure 2b shows IR spectrum of the heat-treated film which exhibits a peak at 912 cm^{-1} assigned to the C-H out-of-plane bending of a trans vinylene group instead of peaks in the range of 2800 to

2900 cm^{-1} and 1060 cm^{-1}. Anal. Found: C, 45.98; H, 2.94%. Calcd for C_6H_4Se: C, 46.48; H, 2.60%. It was concluded therefore that the film of **5** was subject to the complete elimination reaction of methanol under nitrogen at 200 °C to give the film of the fully π-conjugated polymer **1**.

The electroconductivity of the film of **1** was determined to be below 10^{-9} S cm^{-1} at room temperature but it increased to 330 S cm^{-1} when doped by I_2(0.2 mol monomer unit^{-1}). This value is higher than those of poly(2,5-thienylene-vinylene) film doped with I_2(200,1) 60,2) and 623) S cm^{-1}), probably corresponding to the higher electron-donating character of selenophene compared with thiophene.

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