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A Novel Electroactive Polyelectrolyte with Alternating Seleno- and Selenoniophenylene Units

Kenji Miyatake, Tadahiro Ishikawa, and Eishun Tsuchida*

Department of Polymer Chemistry, Advanced Research Institute for Science and Engineering, Waseda University, Tokyo 169-8555, Japan

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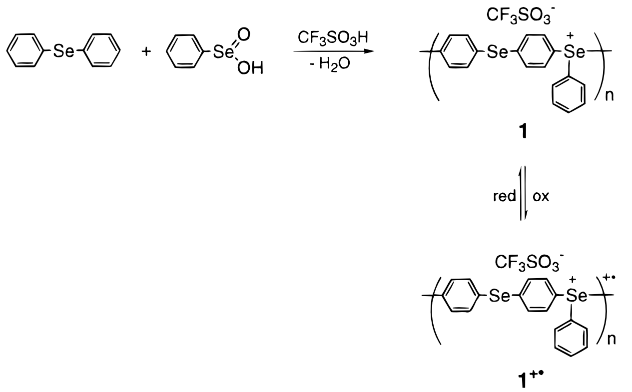
Poly(phenylselenonio-1,4-phenyleneseleno-1,4-phenylene triflate) (**1**) containing selenoether and phenylselenonio groups was prepared by the polycondensation of diphenyl selenide and benzeneseleninic acid in triflic acid. The polymerization also proceeds for diphenyl ether and diphenyl sulfide to give the corresponding poly(aryleneselenonium triflate)s, **2** and **3**. Polymer **1** is thermally stable to 320 °C with melting at 170 °C. The polymer shows reversible redox waves at 0.70 V (vs Ag/AgCl) and semiconductivity of 5×10^{-6} S cm^{-1} when doped with $FeCl_3$.

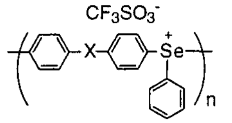
Recent studies of aromatic polymers have been devoted to developing extended π-conjugation for electronic and photonic applications as well as for the fundamental understanding of their band structures and inherent electron densities.[1] Chalcogen-containing polyaromatics such as poly(phenylene oxide)[2] and poly(phenylene sulfide)[3] are themselves important engineering plastics and show high electric conductivity when doped with I_2 or AsF_5.[4] Although the formation of chalcogenium salts has been suggested to be responsible for the extended conjugation through the overlapping of aromatic π-orbitals with the vacant d-orbital of the chalcogen atom,[5] the chemical and physical properties of chalcogenium-including polyaromatics are still not clear. The selenium analogue should be potentially suitable as a backbone for electroactive polymers because of the increased metallic character and the filled 3d orbitals of the selenium atom. Poly(phenylene selenide),[6] poly(selenophene),[7] and poly(selenophene vinylene)[8] have been reported to show electroactivity or electric conductivity or both. We hypothesized that if a phenylene polymer containing selenoether and selenonio bonds was produced, the combination of the redox activity of the selenoether and the hyperconjugation of the arylselenonio groups would produce a novel class of electroactive organic materials. We describe herein our successful preparation of a soluble polyelectrolyte composed of alternating seleno- and selenoniophenylene units, of which the electro- and photoproperties are investigated.

In a recent study, we reported that the superacidified reaction of aromatics with sulfinate derivatives leads to the formation of mono- and polysulfonium compounds.[9,10] The reaction proceeds well for seleninic acid to give the corresponding selenonium derivatives. The title compound [poly(phenylselenonio-1,4-phenyleneseleno-1,4-phenylene triflate), **1**] was prepared by the polycondensation of diphenyl selenide and benzeneseleninic acid as shown in Scheme 1.[11] The polycondensation proceeds in triflic acid under atmospheric conditions to give a brown powdered polymer in 59% yield.

Scheme 1. Synthesis and Redox Reaction of 1



Diphenyl ether and diphenyl sulfide could also be polymerized with benzeneseleninic acid to give the corresponding polyaryleneselenonium salts in 75% [poly(phenylselenonio-1,4-phenyleneoxy-1,4-phenylene triflate), **2**][12] and 72% [poly(phenylselenonio-1,4-phenylenethio-1,4-phenylene triflate), **3**][13] yields, respectively.



X=O (**2**)
S (**3**)

1 is soluble in polar organic solvents such as methanol, acetone, acetonitrile, and DMF. A homogeneous and transparent film can be prepared by casting the solution. The structure of the polymers was confirmed by IR, ^{1}H, and ^{13}C NMR spectra and elemental analysis. The eight signals at 128.3, 132.3, 132.4, 132.8, 133.4, 134.4, 134.6, and 135.9 ppm are assigned to the phenylselenonio-1,4-phenyleneseleno-1,4-phenylene unit in the ^{13}C NMR spectrum of **1** that provides good support for the linear structure of the polymer. In the ^{1}H NMR spectrum, minor multiplet peaks are observed at 7.28−7.43 ppm beside the major peaks of phenylene protons at 7.74−7.89 ppm. The minor peaks are assigned to the end selenophenyl groups of the polymer chain. The degree of polymerization (*n*) could be estimated to be 18 from the integration ration of the peaks.

The viscosity curve (η_{sp}/c vs c, c = concentration) of **1** in CH_3CN solution is strongly concave-upward, which is typical for polyelectrolytes. The inherent viscosity [η] could be estimated to be 0.04 using Fuoss's equation.[14] Differential scanning calorimetric (DSC) analysis shows that the polymer is semicrystalline with a melting temperature of 170 °C. It is stable in the melted state up to a temperature as high as 320 °C under nitrogen without any decomposition or chemical reaction. The triphenylselenonio groups in **1** are inactive to nucleophiles and could not be converted to diphenylseleno groups even by treating with refluxing NaOH aqueous solution or pyridine.

The redox nature of **1** was first examined in acetonitrile solution containing 0.1 M $TBABF_4$. The anodic cyclic voltammogram showed a reversible pair of waves at 0.70 V, 0.25 V lower than that of the irreversible oxidation peak of diphenyl selenide (0.95 V) (Figure 1a, b). This indicates that the $1^{\bullet+}$ formed is stable in the

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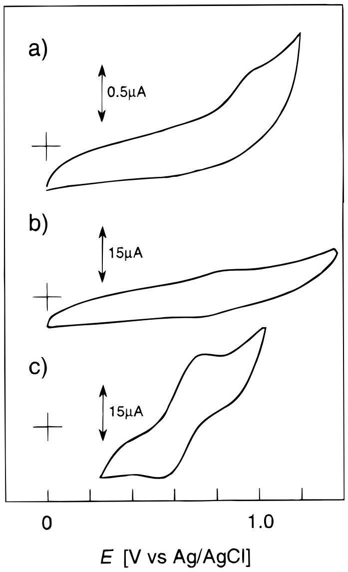

Figure 1. Cyclic voltammograms of (a) diphenyl selenide (0.2 mM) in CH_3CN and 0.1 M $TBABF_4$, (b) **1** (0.5 mM) in CH_3CN and 0.1 M $TBABF_4$, and (c) **1** deposited on a graphite carbon electrode in H_2O and 0.1 M NH_4PF_6.

solution, whereas that of diphenyl selenide is not. The reversible redox wave could be distinctly observed at 0.65 V for the polymer film coated on a graphite carbon electrode in aqueous solution containing 0.1 M NH_4PF_6 (Figure 1c). The film could undergo at least several hundred cycles from 0.2 to 0.9 V with no change in the shape of the voltammetric features even without removing all of the oxygen from the system. In contrast to this reversible redox process, another oxidation wave observed at 1.8 V is chemically irreversible, indicating that the formed polycation is not stable and undergoes a chemical reaction. For **2** and **3**, a reversible redox peak could not be confirmed, but only the irreversible oxidation peak was observed at 1.2 and 1.6 V, respectively.

The optical absorption of **1** in methanol is characterized by a broad absorption at 298 nm tailing to 375 nm. It shows bathochromic shifts compared to the corresponding monomeric compounds, diphenyl selenide (λ_{max} = 235 and 255 nm) and triphenylselenonium chloride (λ_{max} = 258, 265, and 272 nm) (Figure 2a), suggesting an extension of the π-delocalization of the polymer. Still, the relatively large band gap might be due to the steric distortion of the main chain by the bulky phenyl side group. The presence of positive charges along the backbone can also be expected to produce a localization of π-electrons and thus to increase the band gap. **1** has a strong blue fluorescence. The photoluminescence spectrum from methanol solution showed a maximum at 400 nm when excited at 300 nm. As shown in Figure 2b, **1** gives stronger photoluminescence in methanol than in acetone. The photoluminescence occurs at the onset of the $\pi-\pi^*$ absorption band as usually observed for π-conjugated polymers.

Preliminary electrical conductivity measurements were carried out on the film by the four-point method with direct current. The pristine polymer film is insulating and shows conductivity lower than 10^{-10} S cm^{-1}. Although **1** is a cation-containing material, p-type doping (oxidative doping) is possible. The film doped with $FeCl_3$ shows a conductivity of 5×10^{-6} S cm^{-1}. The black-colored doped film retains its flexibility and conductivity after several days under an N_2 atmosphere.

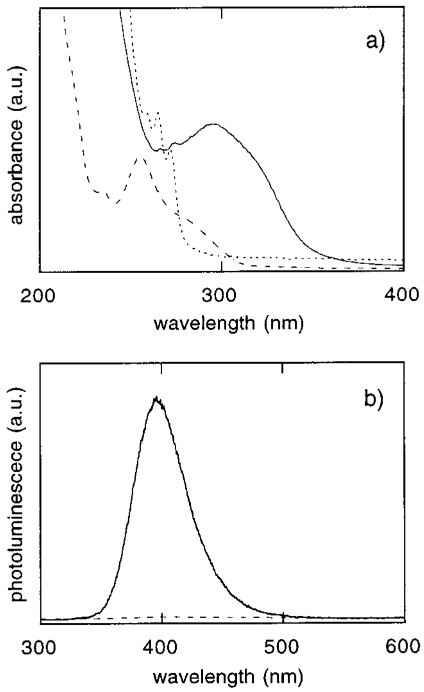

Figure 2. (a) UV/vis spectra of **1** (—), triphenylselenonium chloride (···), and diphenyl selenide (- - -) in methanol. (b) Emission spectra of **1** in methanol (—) and in acetone (- - -) excited at 300 nm.

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(11) The typical procedure is as follows. To a solution of diphenyl selenide (4 mmol) in triflic acid (5 mL), benzeneseleninic acid (4 mmol) was slowly added over a period of 10 min at 0 °C. The mixture was then stirred for 24 h at room temperature. The color of the reaction mixture gradually changed from pale yellow to navy with time. After the reaction, the mixture was poured into water (200 mL) to precipitate a brown powder. The precipitate was washed

with diethyl ether and then dried to obtain poly(phenylselenonio-1,4-phenyleneseleno-1,4-phenylene triflate) (**1**) in 59% yield. ^{1}H NMR (500 MHz, acetone-d_6, ppm): 7.28−7.43 (m, 0.42H, Ar), 7.74−7.89 (m, 13H, Ar). ^{13}C NMR (125 MHz, acetone-d_6, ppm) 118.3, 120.8, 123.4, 125.9 (CF_3), 128.3, 132.3, 132.4, 132.8, 133.4, 134.4, 134.6, 135.9 (Ar). IR (KBr, cm^{-1}): 3082, 1478, 1446, 1256, 1158, 1029, 811, 745, 638. Anal. Calcd for ($C_{19}H_{13}F_3O_3SSe_2$): C, 42.55; H, 2.44; Se, 29.45. Found: C, 42.91; H, 2.60; Se, 29.27.

(12) **Poly(phenylselenonio-1,4-phenyleneoxy-1,4-phenylene triflate) (2).** ^{1}H NMR (500 MHz, acetone-d_6, ppm): 7.34−7.37 (m, 0.70H, Ar), 7.46 − 7.90 (m, 13H, Ar). ^{13}C NMR (125 MHz, acetone-d_6, ppm): 118.3, 120.8, 123.4, 125.9 (CF_3), 122.8, 129.0, 132.2, 132.4, 134.3, 134.9, 154.2, 160.1 (Ar). IR (KBr, cm^{-1}): 3092, 1488, 1446, 1256, 1168, 1029, 870, 830, 743, 637. Anal. Calcd for ($C_{19}H_{13}F_3O_4SSe$): C, 48.21; H, 2.77; Se, 16.68. Found: C, 48.50; H, 2.69; Se, 16.43.

(13) **Poly(phenylselenonio-1,4-phenylenethio-1,4-phenylene triflate) (3).** ^{1}H NMR (500 MHz, acetone-d_6, ppm): 7.35−7.46 (m, 0.34H, Ar), 7.75−8.20 (m, 13H, Ar). ^{13}C NMR (125 MHz, acetone-d_6, ppm): 118.3, 120.8, 123.4, 125.9 (CF_3), 130.9, 132.0, 132.5, 132.6, 132.7, 133.0, 133.3, 136.0 (Ar). IR (KBr, cm^{-1}): 3083, 1475, 1447, 1258, 1157, 1029, 816, 755, 638. Anal. Calcd for ($C_{19}H_{13}F_3O_3S_2Se$): C, 46.63; H, 2.68; Se, 16.13. Found: C, 47.01; H, 3.04; Se, 15.80.

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