Water-Soluble Conducting Polymers

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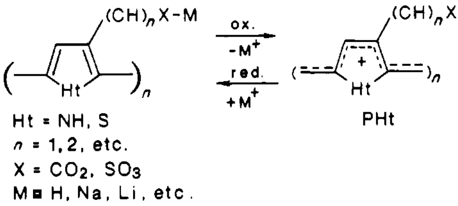
It has only been within the last few months that organic-solvent-soluble conducting polymers have been developed.[1] Previously, solubility in a mixture of arsenic trifluoride/pentafluoride was the singular path available to processability of conducting polymers.[2] In this paper we report our success in the preparation of two polymers which are soluble in water in the *doped and undoped states*!

Sodium poly(3-thiophene-β-ethanesulfonate) (P3-ETSNa, **1**) and sodium poly(3-(thiophene-δ-butanesulfonate) (P3-BTSNa, **2**) and their respective conjugate acids are water soluble. The latter are of interest because, upon oxidation, they can lose a proton concomitant with electron loss to produce self-doped polymers; i.e., doped polymers where the counterion is attached to the polymer via a covalent bond (cf. general Scheme I). The concept and applications of self-doped polymers are covered in a separate publication.[3]

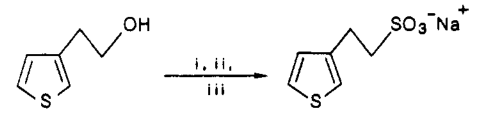
Only polymers where Ht = S, n = 2 and 4, and X = SO_3 are the subject of this paper. These were prepared by the usual electropolymerization of the 3-substituted thiophene monomers. The monomers were not reported in the literature but were obtained as depicted in the Schemes II and III.

In Schemes II and II the iodide exchange for mesylate can be avoided with careful ion-exchange chromatographic separation of sodium mesylate and excess sodium sulfite from the desired 3-ETSNa and 3-BTSNa in the reaction mixture. Attempts to polymerize the 3-ET sulfonic acid or its sodium salt failed.[4] We therefore polymerized the methyl esters first, followed by conversion to the polyelectrolyte via sodium iodide in acetone (the monomeric methyl esters were obtained from the sodium salts via the sulfonyl chlorides[5]). The methyl ester of P3-ETS was soluble in acetonitrile whereas the same ester of P3-BTS was only sparingly soluble in the same solvent. When freshly prepared methyl ester films were dipped in acetone containing an excess of sodium iodide, they rapidly dedoped (changed from blue-green to orange), dissolved, and slowly produced an orange precipitate. The latter was, depending on the starting polyester, either the P3-ETS's or P3-BTS's sodium salt (conversion occurred quantitatively in 24 h as determined by ir spectroscopy and elemental analysis), which was insoluble in acetone, DMF, NMP, and methanol but slightly soluble in Me_2SO and soluble in water. These salts could be cast as a film on various substrates, principally ITO glass (indium–tin oxide coated glass) and PVC. Later we discovered that the polymeric salts were also slightly soluble in Me_2SO. Evaporation of the aqueous polymer solutions yielded orange, tacky films which could be used for spectroscopic studies.[3]

Scheme I



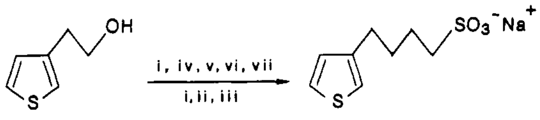
Scheme II[a]



3-ETSNa

[a] i, MsCl; ii, NaI; iii, Na_2SO_3/H_2O.

Scheme III[a]



3-BTSNa

[a] i, MsCl; ii, NaI; iii, Na_2SO_3/H_2O; iv, $CH_2(CO_2Et)_2$/NaH; v, KOH/EtOH; vi, Δ; vii, LAH.

Attempts to dehydrate the films under vacuum at 80 °C overnight failed. Thionyl chloride and concentrated sulfuric acid dehydrated the films, converting them from orange to blue-green. The dehydrated films of P3-ETSNa and P3-BTSNa were found to be sparingly soluble in sulfuric acid. Blue *polymer solutions* of P3-ETSNa (H?)[6] in concentrated sulfuric acid were found to be stable at room temperature for several days. Aqueous solutions of P3-EtSNa could also be doped with bromine or $NOPF_6$ to blue-green, *air unstable* solutions which would turn orange upon standing but could not be redoped due to decomposition (λ_{max} shifted to the blue by 55–85 nm with a long tail into the visible).

A freshly cast film of P3-ETSNa showed a conductivity between 10^{-7} and 10^{-2} S cm^{-1} (depending on relative humidity).[3] Bromine vapor caused the conductivity to rise[7] to $\sim$10 S cm^{-1}. This doping behavior was confirmed by in situ electronic spectroscopy during electrochemical doping.[3,7,8] The latter experiments showed that the band gap of methyl P3-ETS was larger than that of polythiophene by $\sim$0.5 eV whereas the band gap of methyl P3-BTS was the same as that of polythiophene. Cyclic voltammetry showed that the oxidation of *both* monomer esters occurred at approximately the same potential as in the case of thiophene. It is understandable that the oxidation potential of methyl 3-ETS should be somewhat higher than that of 3-methylthiophene (1.80 vs. 1.60 V) due to the inductive effect of the 2-(sulfonylmethyl)ethyl group but it is more difficult to believe that a sulfonylmethyl group located *at a distance of four carbon atoms* has qualitatively the same inductive effect. However, there are subtle effects; for example, doped methyl P3-BTS films are much more stable toward "spontaneous" dedoping in methanol than methyl P3-ETS films. The latter are dedoped within minutes of dipping in methanol at room temperature, whereas the former survive for at least 48 h under the same conditions.

Finally, "free standing" films of P3-ETSNa can be obtained by casting a coat on a PVC film and dissolving the latter in THF. The orange films thus obtained are relatively brittle (qualitatively the same as polythiophene or PITN).

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(4) The 3-BTSNa is polymerizable in 6 N HCl to give a blue solution which bleaches overnight.

(5) All precursors to the esters exhibited the expected spectroscopic properties as well as acceptable C, H, S elemental analyses. The 3-ETS methyl ester is a colorless solid, mp 27–28.5 °C. Anal. Calcd for $C_7H_{10}S_2O_3$: C, 40.76; H, 4.89; S, 31.08. Found: C, 40.90; H, 4.84; S, 30.92. IR (neat film, ν in cm^{-1}) 1355 s, 1165 s, 985 s, 780 w; UV–vis [λ_{max}, MeOH, nm (ϵ)] 234 (6 × 10^3); NMR ($CDCl_3$, δ ppm relative to Me_4Si) 7.42–7.22 (q, 1 H), 7.18–6.80 (m, 2 H), 3.85 (s, 3 H), 3.6–2.9 (m, 4 H). The 3-BTS methyl ester is a colorless oil. Anal. Calcd for $C_9H_{14}S_2O_3$: C, 46.13; H, 6.02; S, 27.36. Found: C, 45.97; H, 5.98; S, 27.28. IR (neat film, ν in cm^{-1}) 1350 s, 1160 s, 982 s, 770 w; UV–vis [λ_{max}, MeOH, nm (ϵ)] 220 (6.6 × 10^3); NMR ($CDCl_3$, δ ppm relative to Me_4Si) 7.33–7.13 (t, 1 H), 7.03–6.77 (d, 2 H), 3.83 (s, 3 H), 3.09 (t, 2 H), 2.67 (t, 2 H), 2.2–1.5 (m, 4 H).

(6) Preliminary experiments indicate that P3-ETSNa and P3-BTSNa are converted to P3-ETSH and P3-BTSH via ion-exchange chromatography.

(7) The color of the P3-ETSNa film with a σ of $\sim$5–10 S cm^{-1} was green, indicating that it was not fully doped. The fully doped, blue form is unstable as evidenced by in situ electronic spectroscopy experiments and visual inspection.

(8) Colaneri, N., unpublished results.

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Registry No. 3-ETSNa, 106681-66-7; 3-BTSNa, 106681-67-8; methyl 3-ETS, 106681-68-9; methyl 3-BTS, 106681-69-0; Br_2, 7726-95-6.

New Oligomeric Tungsten–Selenium Anions: Synthesis and Characterization by ^{77}Se NMR and X-ray Diffraction Techniques

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The synthesis, characterization, and chemistry of soluble transition-metal sulfides is an active area of research.[1] Particular emphasis has been directed toward Mo and W sulfides in connection with the modeling of biological systems[2] and with industrial catalytic processes.[3] The formation of many of the sulfides involves internal redox chemistry[4] and for this reason the reaction solutions often contain a number of different species that are difficult to characterize. The cation, solvent, and pH determine what can be isolated as a solid. We anticipated that because of the differing redox processes involved, the chemistry of the selenides would not parallel directly that of the sulfides. We also believed that NMR techniques (^{77}Se) would prove to be extremely valuable in the study of selenide solutions; no comparable probe exists for the sulfide solutions. Surprisingly, there are very few reports of soluble transition-metal selenides.[1,5] Here we report the syntheses and characterization of four new oligomeric anions in the W–Se system: $W_3Se_9^{2-}$, $W_2Se_9^{2-}$, and $W_2Se_{10}^{2-}$ (two isomers).

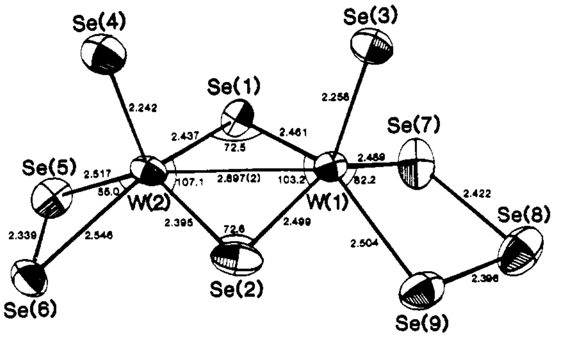

Figure 1. Structure of the $W_2Se_9^{2-}$ ion. Here and in Figures 2 and 3 the 50% probability ellipsoids are shown and the estimated standard deviations in the W–Se and Se–Se bond distances are 0.003–0.004 and 0.005–0.010 Å, respectively, and those in the bond angles are ~0.1°.

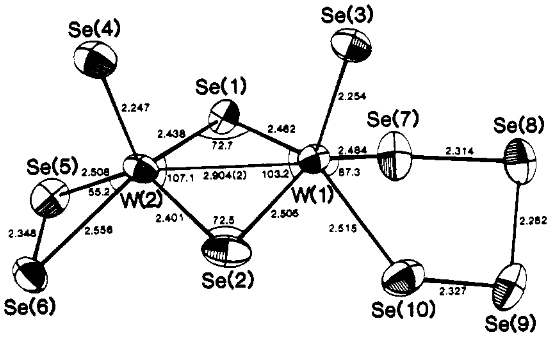

Figure 2. Structure of one isomer of the $W_2Se_{10}^{2-}$ ion.

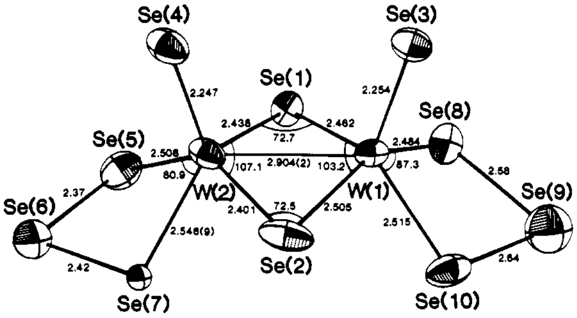

Figure 3. Structure of a second isomer of the $W_2Se_{10}^{2-}$ ion.

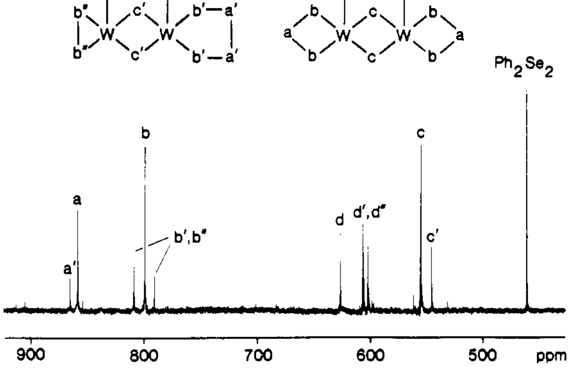

Figure 4. ^{77}Se NMR spectrum for the two $W_2Se_{10}^{2-}$ isomers of Figures 2 and 3 (DMF solvent). The spectrum is referenced relative to Me_2Se at 0 ppm. Ph_2Se_2/C_6D_6 was present as an external standard.

The $W_3S_9^{2-}$,[6] $W_3S_8^{2-}$,[7] and $W_4S_{12}^{2-}$ [8] ions have been isolated from acidified solutions of $[NH_4]_2[WS_4]$. Acidification of $[NH_4]_2[WSe_4]$ (0.10 g) with CH_3COOH (1.0 mL) in methanol (10 mL), followed by addition of $[PPh_4]Cl$ (0.20 g) in methanolic solution (2 mL), afforded $[PPh_4]_2[W_3Se_9]$ in 25% yield.[9] The ion closely resembles the analogous $W_3S_9^{2-}$ species. The W–W distances are approximately 0.06 Å longer than in the sulfide, while the W–Se distances are about 0.12 Å longer than the W–S distances. $[PPh_4]_2[W_3Se_9]$ may also be produced in 35% yield by heating $[NH_4]_2[WSe_4]$ (0.20 g) with $[PPh_4]Cl$ (0.15 g) in refluxing acetonitrile (10 mL) or by heating the same mixture in DMF (10 mL) to 85 °C for 0.5 h followed by addition of excess diethyl ether. When the supernatant solution was cooled to −15 °C for a period of 8 h red-black crystals of $[PPh_4]_2[W_2Se_9]/[PPh_4]_2[W_2Se_{10}]$ were obtained in 45% yield.[10] The $W_2Se_9^{2-}$ and

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(9) Crystal data for $[PPh_4]_2[W_3Se_9]/[PPh_4]_2[W_3Se_8O]$ (ratio 0.46/0.54). $C_{48}H_{40}O_{0.54}P_2Se_{8.46}W_3$, triclinic, C_i^1-$P\bar{1}$, $Z = 1$, $a = 9.085$ (5) Å, $b = 10.666$ (4) Å, $c = 13.407$ (3) Å, $\alpha = 87.22$ (2)°, $\beta = 86.30$ (3)°, $\gamma = 84.11$ (3)°. $V = 1288$ Å^3 at −150 °C, 9599 reflections measured out to 2θ(Mo Kα_1) = 50°, $R = 0.046$ on 2912 reflections having $F_o^2 > 3\sigma(F_o^2)$. The anions have crystallographically imposed symmetry $\bar{1}$ and are disordered at the central W–Se/O moiety. Similar contamination of S with O and disorder occur in the analogous sulfide.[6] ν(W–Se) = 325, 310 cm^{-1}; ν(W–O) = 962 cm^{-1}. It is thought that oxygen was incorporated from the acetic acid. Its presence was confirmed by Auger spectroscopy.

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