

Highly Conducting Water-Soluble Polythiophene Derivatives

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Water-soluble sodium poly(2-(3-thienyloxy)ethanesulfonate) and sodium poly(2-(4-methyl-3-thienyloxy)ethanesulfonate) have been synthesized. The sulfonic acid form of these new polymers has revealed a self-acid-doping reaction that leads to stable, highly conducting (0.5–5 S/cm) materials together with low absorption in the visible range. This process is reversible, and upon deprotonation, the insulating and dark polymers are recovered. The high doping and conductivity levels seem to be related to the relatively low oxidation potentials (0.44–0.50 V vs Ag/AgCl) of these polymers, which allows an almost complete (reversible) oxidation reaction in air (oxygen), catalyzed by the presence of the sulfonic acid moiety.

Introduction

Significant progress has been recently obtained through the development of processable and conducting polymers.¹ The addition of side chains not only allows an easier processing of some electroactive polymers but can also modulate the electronic properties of the conjugated main chain. For instance, it has been reported that the introduction of strong electron-donating alkoxy side chains decreases the oxidation potential of the resulting polymers, giving a better stability for the oxidized (and conducting) state.^{2–13} Moreover, the presence of alkoxy side chains decreases the steric hindrance in the vicinity of the main chain, affording highly conjugated conformational structures. However, it has been found that the presence of flexible side chains and different counterions can significantly alter the stability of the doped (conducting) state.^{14,15} For instance, it is believed that repulsive interactions between the flexible side chains and the counterions are responsible for the poor stability of some of these conducting polymers, particularly at high temperatures. A partial solution to this problem could be the attachment of ionic (e.g., sulfonate moieties) side chains, which

allows the possibility of forming counterions covalently linked to the conjugated backbone (combined to good solubility in water), leading to the concept of self-doped conducting polymers.^{16–18} It is worth noting that an external redox reaction must be done onto the conjugated polymer to obtain the oxidized (conducting) state, but this process does not involve the introduction of any counterions during the doping process. Different studies on poly(ω -(3-thienyl)alkanesulfonate)s have also revealed that the preparation of the acidic form (involving a sulfonic acid functionality) of these polymers is accompanied by a partial doping (oxidation) without the use of any external oxidizing agent,^{19,20} this partial doping leading to conductivity levels of ca. 10^{-2} – 10^{-1} S/cm. To distinguish these two types of self-doping, the latter type was designated as self-acid-doping.²⁰ In this study, we wish to report some new developments in the field of conducting polymers by presenting the synthesis and characterization of new water-soluble sodium poly(2-(3-thienyloxy)ethanesulfonate) and sodium poly(2-(4-methyl-3-thienyloxy)ethanesulfonate). These new polymers should be particularly interesting for the development of almost colorless, stable, water-processable, antistatic coatings.

Experimental Section

Materials. 3-Methoxy-4-methylthiophene:¹¹ 22.3 g of 3-bromo-4-methylthiophene⁵ is added to a mixture of 80 mL of sodium methoxide (25% in methanol), 30 mL of NMP, and 11 g of CuBr. The mixture is refluxed for 3 days and after cooling, is filtrated and washed with water. The compound was extracted several times with diethyl ether. The organic phase is dried with magnesium sulfate and then evaporated. The resulting oil is purified by chromatography on a silica gel column with hexanes as eluent, yield 90%. ¹H NMR (CDCl₃, ppm) 6.75 (1H, d); 6.08 (1H, d); 3.72 (3H, s); 2.04 (3H, s). ¹³C NMR (CDCl₃, ppm) 156.74; 128.53; 119.81; 95.35 56.79; 12.33.

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3-(2-Bromo)ethoxy-4-methylthiophene.²¹ 4.2 g of 3-methoxy-4-methylthiophene is added to a mixture of 40 mL of toluene, 8.2 g of 2-bromo-1-ethanol (Aldrich), and 500 mg of NaHSO₄. The resulting mixture is heated until the produced methanol is distilled off, and the temperature raises to 110 °C. The product is cooled and washed several times with water and, subsequently, extracted with diethyl ether. The organic phase is dried with magnesium sulfate and then evaporated. The product was purified by column chromatography using silica gel and hexanes, yield 65%. ¹H NMR (CDCl₃, ppm) 6.83 (1H, d); 6.18 (1H, d); 4.25 (2H, t); 3.63 (2H, t); 2.11 (3H, s). ¹³C NMR (CDCl₃, ppm) 155.06; 129.18; 120.33; 97.23; 69.65; 29.20; 12.71.

Sodium 2-(4-methyl-3-thienyloxy)ethanesulfonate.²² 2.5 g of 3-(2-bromo)ethoxy-4-methylthiophene in 20 mL of acetone is added to a mixture of 1.5 g of Na₂SO₃ in 20 mL of water. The mixture is refluxed for 3 days. After cooling, the unreacted product is extracted with diethyl ether. The aqueous phase is then evaporated, giving a white crystalline powder. The desired product is recrystallized in a mixture of water/ethanol (1:1) at -10 °C, yield 60%. MP: 228 °C. ¹H NMR (D₂O, ppm) 7.01 (1H, d); 6.51 (1H, d); 4.38 (2H, t); 3.39 (2H, t); 2.08 (3H, s). ¹³C NMR (D₂O, ppm) 155.52; 130.13; 121.41; 98.92; 68.57; 50.91; 28.85; 11.83.

3-(2-Bromo)ethoxythiophene. Using a procedure similar to that described above, 5.00 g of 3-methoxythiophene (Aldrich) was solubilized with 11.00 g of 2-bromo-1-ethanol in 20 mL of toluene, and then 2.00 g of NaHSO₄ was added in one portion. The mixture was heated, and methanol was distilled off. The solution was cooled and washed with water and diethyl ether. The organic phase was dried with magnesium sulfate. After evaporation, a brown liquid was obtained which was purified by column chromatography on silica gel using a mixture of CCl₄ and CHCl₃ (9:1) as the eluent. An oil was recovered which was further purified by recrystallization in methanol. White crystals were then obtained with a yield of 67%, MP: 46 °C. ¹H NMR (CDCl₃, ppm) 7.18 (1H, m); 6.78 (1H, m); 6.28 (1H, m); 4.27 (2H, t); 3.63 (2H, t). ¹³C NMR (CDCl₃, ppm) 156.54; 124.79; 119.16; 98.12; 69.65; 28.62.

Sodium 2-(3-thienyloxy)ethanesulfonate. To a solution of 0.48 g of Na₂SO₃ in 5.00 mL of water was added a solution of 527 mg of 3-(2-bromo)ethoxythiophene dissolved in 10 mL of acetone. The mixture was allowed to reflux for 48 h. The solution was then cooled and washed with diethyl ether. The aqueous phase was separated and evaporated under reduced pressure. The crude product was dissolved in water, and few drops of ethanol was then added to induce the precipitation of the inorganic salt. The suspension was filtered and evaporated. A white crystal was obtained with a yield of 37%. This product decomposes over 290 °C before melting. ¹H NMR (D₂O, ppm) 7.46 (1H, m); 6.96 (1H, m); 6.70 (1H, m); 4.50 (2H, t); 3.47 (2H, t). ¹³C NMR (D₂O, ppm) 156.96; 126.50; 120.11; 100.25; 66.25; 50.92.

Polymers. For instance, 1.2 g of sodium 2-(4-methyl-3-thienyloxy)ethanesulfonate and 3.0 g of dry FeCl₃ are mixed in 30 mL of chloroform and stirred for 24 h at room temperature. The mixture is poured in 500 mL of methanol where few drops of anhydrous hydrazine have been added. After this treatment, the polymer is put in 500 mL of a 1 M NaOH methanolic solution. The precipitate is filtered and a dark powder is obtained (yield 50–60%). All polymer samples have been prepared using a similar procedure. Aqueous solutions of the sodium salt polymers have been passed through a cation (H⁺) exchange resin (Dowex HCR-W2) column to get the sulfonic acid form of the polymers.

Physical Methods. Cyclic voltammetry measurements were obtained with an EG&G potentiostat/galvanostat (Model 273). Ag/AgCl reference electrode and platinum counter and working electrodes were used. Polymers were cast on platinum electrodes from an aqueous solution. Electrochemical measurements were performed at 20 mV/s using an electrolyte made of 0.1 M tetrabutylammonium hexafluorophosphate

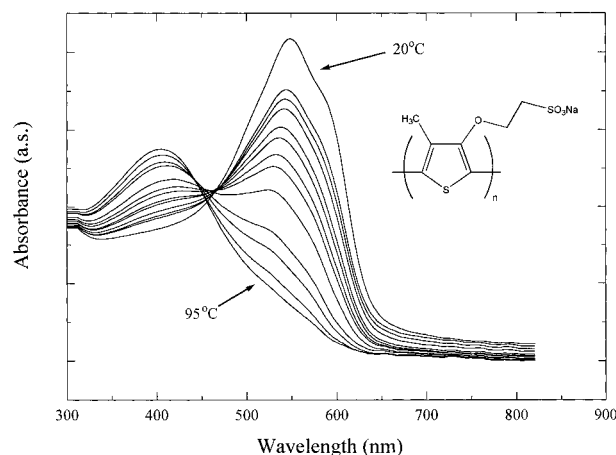


Figure 1. Temperature-dependent UV–visible absorption spectra of sodium poly(2-(4-methyl-3-thienyloxy)ethanesulfonate) in water, upon heating.

(Aldrich) dissolved in a mixture of acetonitrile and water (95:5 v/v). Absorption spectra were obtained with a Hewlett-Packard diode array UV–visible spectrophotometer (Model 8452A). 1-Cm quartz cells were used for solution measurements while solid-state experiments were performed with cast polymer films on quartz lamella. Temperature-dependent optical measurements were obtained by using a temperature control unit ranging from 25 to 250 °C with a maximum error of ±2 °C. Size-exclusion chromatography (SEC) measurements were carried out in water (0.1% LiCl) at 45 °C, with a Waters differential refractometer (model 410) equipped with Ultrahydrogel columns. Calibration was performed with monodisperse poly(ethylene glycol) standards (Waters).

Results and Discussion

Following a synthetic procedure described in a recent publication,²² sodium 2-(4-methyl-3-thienyloxy)ethanesulfonate was easily synthesized in three steps from 3-bromo-4-methylthiophene. Similarly, sodium 2-(3-thienyloxy)ethanesulfonate was prepared from 3-methoxythiophene. These monomers were then polymerized with iron trichloride in chloroform.^{5,22} SEC measurements revealed a number-average molecular weight of ca. 6000–8000 for both polymers with a polydispersity index of ca. 1.2. All resulting polymers showed a good solubility in water giving, at room temperature, a purple solution for sodium poly(2-(4-methyl-3-thienyloxy)ethanesulfonate) (Figure 1) and a dark blue solution for sodium poly(2-(3-thienyloxy)ethanesulfonate) (Figure 2). As reported for other poly(3-alkoxy-4-methylthiophene)s,^{5,23,24} sodium poly(2-(4-methyl-3-thienyloxy)ethanesulfonate) is thermochromic, exhibiting a purple-to-yellow color transition related to a rod-to-coil transition of the conjugated backbone. The rodlike, highly conjugated form is believed to be associated with intermolecular and intramolecular (through chain folding) π -stacks while, upon heating, side-chain disordering disrupts these assemblies to yield nonplanar (less conjugated) polymer chains.^{23–26} From theoretical calculations,²⁶ it seems that without strong attractive interchain interactions, poly(3-alkoxy-4-methylthio-

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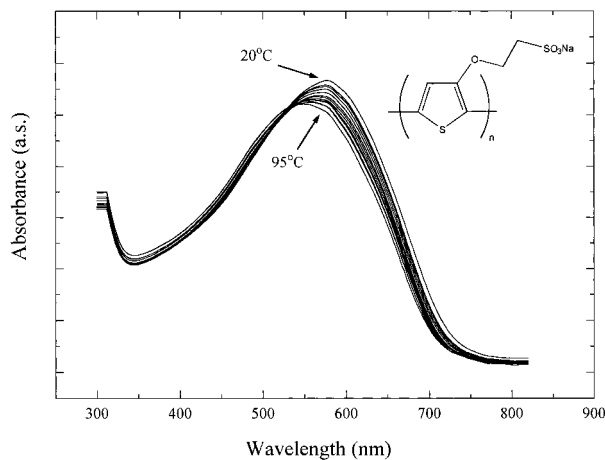


Figure 2. Temperature-dependent UV-visible absorption spectra of sodium poly(2-(3-thienyloxy)ethanesulfonate) in water, upon heating.

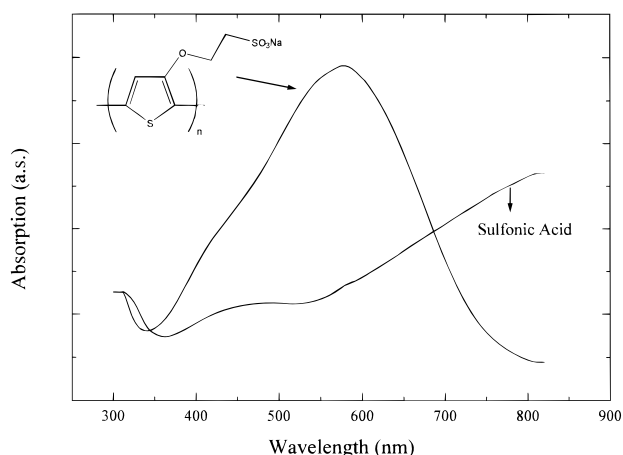


Figure 3. UV-visible absorption spectra of sodium poly(2-(3-thienyloxy)ethanesulfonate) and poly(2-(3-thienyloxy)ethanesulfonic acid) in water, at room temperature.

phene)s cannot adopt a coplanar and fully conjugated form. In contrast, due to an absence of sterically demanding side chains (i.e., the methyl group in the 4-position),^{23,26} sodium poly(2-(3-thienyloxy)ethanesulfonate) does not show a strong modification of its absorption spectrum upon heating, this polymer keeping a highly conjugated form in both aggregated and "isolated" forms. In the solid state, these polymers show essentially the same optical spectra as those reported, at room temperature, in water and exhibit an electrical conductivity lower than 10^{-6} S/cm, as measured on dry pressed pellets by the four-probe method.

Dissolved in water, these polymers were also passed through an ion-exchange resin column, leading to the sulfonic acid form. Dramatic color changes occurred upon protonation. For instance, the absorption maximum (580 nm) of sodium poly(2-(3-thienyloxy)ethanesulfonate) (Figure 3) decreases strongly while a new absorption band appears around 800 nm upon protonation, characteristic of a polythiophene doped (oxidized) state.^{19,20} The exact nature of the oxidized polymers and of the counterions is difficult to identify, but it is clear that an oxidation of the polythiophenes accompanies the protonation reaction. As mentioned above, a similar effect was previously reported for poly(ω -(3-thienyl)alkanesulfonic acid)s.^{15,16} Similarly, the absorption maximum centered around 550 nm for

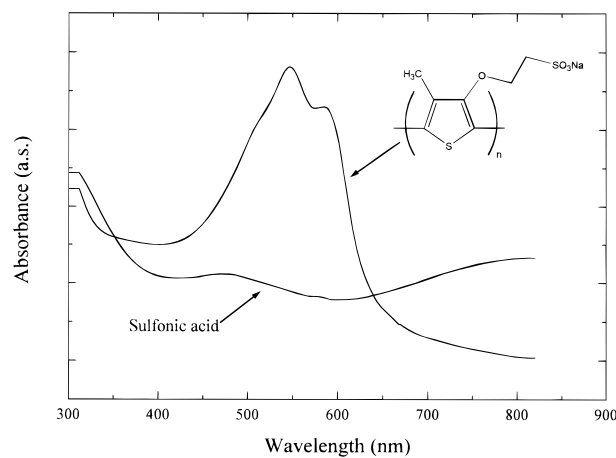


Figure 4. UV-visible absorption spectra of sodium poly(2-(4-methyl-3-thienyloxy)ethanesulfonate) and poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) in water, at room temperature.

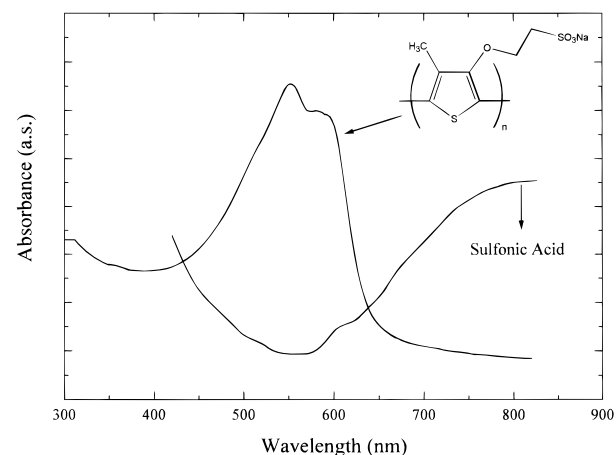


Figure 5. UV-visible absorption spectra of sodium poly(2-(4-methyl-3-thienyloxy)ethanesulfonate) and poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) in the solid state, at room temperature.

sodium poly(2-(4-methyl-3-thienyloxy)ethanesulfonate) (Figure 4) disappears almost completely in the acidic form together with the formation of a weak absorption band around 800 nm. This protonation reaction induces therefore a strong color change from dark purple to pale blue-gray. Cast films show almost the same optical features as the polymer solutions (Figure 5). Moreover, this transformation is reversible since the addition of NaOH aqueous solution to the protonated polymers induce the reverse color changes (Figure 6). All these reversible optical processes could be then useful as optical sensors.

The acid form of these polymers have been then freeze-dried to remove the water, and electrical conductivities have been measured by the four-probe method at room temperature. Stable electronic conductivities have been obtained for all polymers although the level of conductivity was found to be dependent upon the nature of the substituents. For instance, the conductivity of poly(2-(3-thienyloxy)ethanesulfonic acid) is found to be 0.5 S/cm and that of poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) is 5 S/cm. The nature of the doping mechanism is not yet established but this phenomenon can be related to that one reported by Han and Elsenbaumer where it has been shown that a

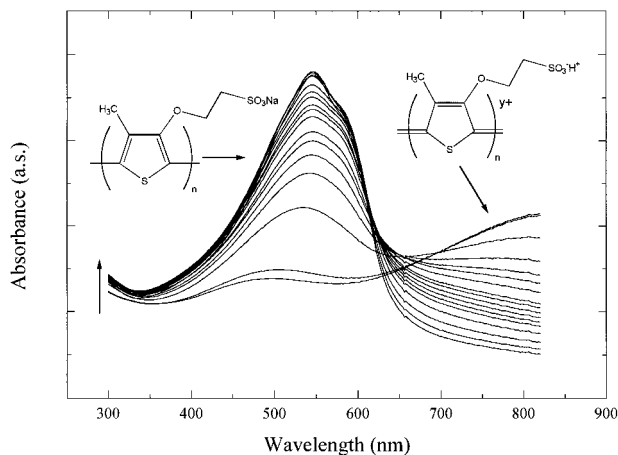


Figure 6. UV-visible absorption spectrum of an aqueous solution of poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid) upon addition of NaOH, at room temperature.

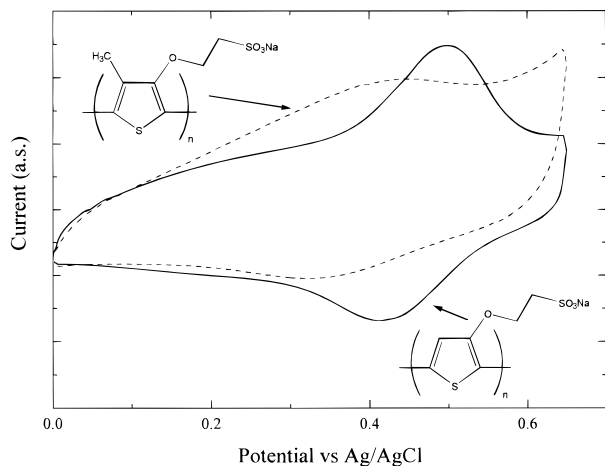


Figure 7. Cyclic voltammograms of sodium poly(2-(3-thienyloxy)ethanesulfonate) and sodium poly(2-(4-methyl-3-thienyloxy)ethanesulfonate), at 20 mV/s vs Ag/AgCl.

reaction (a contact) between some conjugated polymers and non-oxidative strong protonic acids can lead to a doping reaction and to high electrical conductivities.^{27,28} These authors have explained these results by a protonation of the conjugated polymers from an external protonic source that leads to the formation of different charge carriers (radical cations and dications).²⁷ A different mechanism could also explain these features and would involve an acid-catalyzed photooxidation reaction involving aromatic moieties and oxygen.²⁹ However, from all these results, it is clear that the presence of a strong protonic acid, oxygen (air), and a

conjugated backbone can lead to conducting (doped) polymers.

As mentioned in the Introduction, similar but weaker electrical properties were reported for poly(ω -(3-thienyl)alkanesulfonic acid)s,^{19,20} and the higher doping and conductivity levels found for these alkoxy-substituted polythiophenes can be partly related to their lower oxidation potentials. The oxidation potential of sodium poly(ω -(3-thienyl)alkanesulfonate)s are ca. +0.8 V vs Ag/AgCl³⁰ compared to ca. 0.5 vs Ag/AgCl for sodium poly(2-(3-thienyloxy)ethanesulfonate) and ca. 0.44 V vs Ag/AgCl for sodium poly(2-(4-methyl-3-thienyloxy)ethanesulfonate) (Figure 7). Therefore, with the combination of oxygen and a strong protonic acid, different self-acid-doped polythiophenes can be obtained, where the oxidation and conductivity levels seem to be related to the oxidation potential of the polymers. It is worth noting that the presence of a strong acid is important since recent report on the synthesis and characterization of poly(thiophene-3-propionic acid) does not mention any conducting properties for this material.²⁵ All these results could be therefore related to a pH-dependent oxidation by oxygen of conjugated polymers, but it is evident that more extensive characterization should be performed to get a clear picture of the mechanisms involved in these reversible doping processes.

Conclusion

From all these results, it seems that water-soluble and nearly colorless, highly conducting polymers can be obtained through the precise molecular design of the starting monomers. Electrical conductivities up to 5 S/cm have been obtained with poly(2-(4-methyl-3-thienyloxy)ethanesulfonic acid), which should be useful for the development of antistatic coatings and EMI shielding. For instance, all investigated polymers show an excellent stability in the acid (doped) state with no decrease of the electrical conductivity as a function of time. Finally, it is believed that this self-acid-doping approach based on low-oxidation potential conjugated polymers bearing strong protonic acids can be developed for other classes of conjugated polymers such as poly(3,4-cycloalkoxythiophene)s^{8,9} and poly(3-alkylpyrroles)³¹ and should lead to various processable, stable, and highly conducting materials.

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