A Facile Preparation of a Self-doped Conducting Polymer

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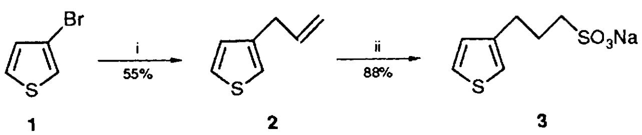
A self-doped conducting polymer having alkanesulphonic acid groups on polythiophene has been directly synthesized from sodium 3-(3-thienyl)propanesulphonate **3** by chemical polymerization with $FeCl_3$ in an aqueous medium; the resulting acid form of this polymer after work-up shows highly self-doped behaviour both in water and as a solid film and has a high molecular weight distribution.

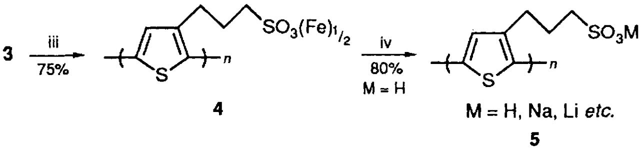
Since self-doped conducting polymers were first reported by Wudl and coworkers,[1] many analogous compounds[2] have been synthesized as water-soluble conducting polymers. The self-doping mechanism of these polymers was simply explained in terms of the potential counterions being covalently bound to the polymer chain and the charge injected into the π-electron system of the polymer being compensated by proton (or Li^+, Na^+, *etc.*) migration, leaving behind the oppositely charged counterion.[3] These conducting materials are soluble in water in both doped and undoped states.

More recently, we succeeded in preparing directly the self-doped polymer **5** from the monomeric sodium 3-(3-thienyl)propanesulphonate **3** by chemical polymerization using $FeCl_3$ as an oxidant in an aqueous reaction medium. This simple polymerization method is much shorter than those previously reported.[4] Although the chemical polymerization of thiophene derivatives in chloroform with an oxidant such as $FeCl_3$ is well known,[5] a similar polymerization procedure applied to compound **3** did not yield the expected polymer, because the monomer **3** did not fully dissolve in the organic solvent. Therefore, we tried to polymerize it in an aqueous reaction medium with $FeCl_3$. We failed to obtain a useful polymer by electrochemical polymerization of the monomer **3** in either methanol or water, only low molecular weight compounds being obtained.

Monomer synthesis



Chemical polymerization



Scheme 1 *Reagents and conditions*: i, BuLi, Et_2O, −73 °C, then allyl bromide, 2 h, −73 °C; ii, $NaHSO_3$, azoisobutyronitrile in $MeOH–H_2O$, 5 h, 80 °C; iii, $FeCl_3$ in H_2O, room temp.; iv, NaOH, then ion exchange resin

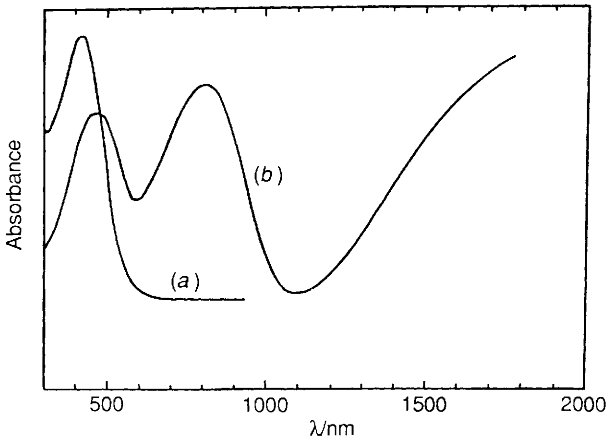


Fig. 1 UV–VIS and near-IR absorption spectra of self-doped conducting polymers: (*a*) is neutral **5** (M = Na) in water; (*b*) cast film of self-doped **5** (M = H) (acid form)

The monomeric sulphonate **3** was prepared in two steps from the commercially available 3-bromothiophene **1** in high total yield (48%) (Scheme 1).† It was polymerized to give the expected self-doped polymer by the above facile oxidative polymerization process, using an aqueous solution of $FeCl_3$ (1.76 mol dm^{-3}) and the monomer (0.44 mol dm^{-3}). The intermediate polymer **4** was estimated to have the stoichiometry $(thienylsulphonate)_2Fe$; it was insoluble in water. On treatment with alkali, it formed a soluble polymer, poly[sodium 3-(3-thienyl)propanesulphonate] **5**. In order to form the acid form (self-doped state) of the polymer, a red solution of **5** (undoped state) was passed through an ion-exchange resin column (H^+ type), according to the literature.[1] On complete conversion into the proton (acid) form, the aqueous polymer solution showed extremely highly doped behaviour in the UV–VIS and near-IR absorption spectrum, as shown in Fig. 1. We found that the Cl^-, Fe^{2+} or Fe^{3+} and Na^+ ions in the solution were completely removed (elemental analysis); the self-doped behaviour depended upon the degree of conversion into the proton form in the aqueous polymer solution.

Cast films of **5** (acid form) are deep greenish brown, and have a conductivity in the dry state of about 0.1 S cm^{-1} (intrinsically self-doped, without any other dopants such as Cl^-) by four-probe measurements. The molecular weight distribution of the polymer was measured by gel permeation chromatography (Shodex Ionpak S801-3 columns) and related to the standard pullulan (polysaccharide, Shodex standard P82; 0.1 mol dm^{-3} NaOH +0.1 mmol dm^{-3} Na_2SO_4 aqueous eluent); the average degree of polymerization of **5** was estimated to be ≈440 ($M_w \approx 1 \times 10^5$). This degree of polymerization is high enough for a flexible free-standing film to be cast. Cyclic voltammetric studies typically gave excellent electrochemical behaviour, showing a quick redox response without domination by the diffusive rate-determining process of the counter anion (as dopant), as shown in Fig. 2. Electrochromic devices using such self-doped polymers as electroactive materials may be able to achieve a quick response, high quality contrast and stable long lifetime under the given electrochemical conditions.

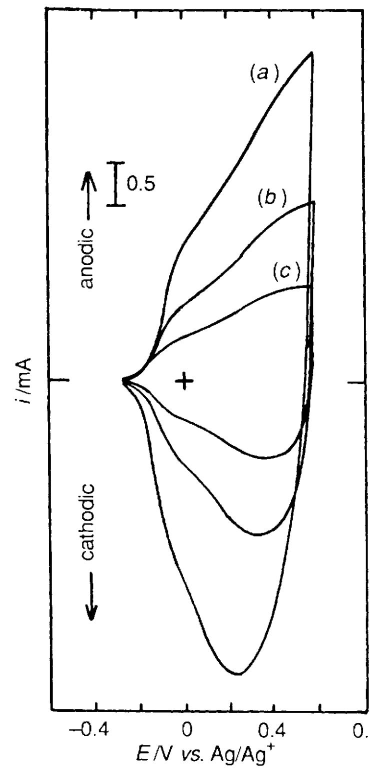


Fig. 2 Electrochemical behaviour of a cast film of **5** at several scan rates in acidic electrolyte solution, 0.5 mol dm^{-3} HBF_4 (6% H_2O)–acetonitrile where the working electrode was a 3100 Å thick film of 5 (M = H) cast on ITO (indium-tin oxide), the counter electrode was a Pt mesh and the reference electrode was Ag/Ag^+. Cyclic voltammograms were obtained at (*a*) 200, (*b*) 100 and (*c*) 50 mV s^{-1}, respectively.

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† The monomer **3** forms colourless planes, dec. >300 °C, and gave satisfactory elemental analyses; IR (KBr), ν/cm^{-1} 3576m, 3524m, 3092m, 2968m, 2944m, 1628s, 1206s, 1166s, 1058s and 776s; UV–VIS (H_2O), λ_{max}/nm (ε) 233 (5.18×10^3); NMR (D_2O, δ rel. to sodium 3-trimethylsilylpropanesulphonate) 2.00 (2H, tt, *J* 7.8 Hz), 2.75 (2H, t, *J* 7.8 Hz), 2.89 (2H, t, *J* 7.8 Hz), 7.00 (2H, d, *J* 4.8 Hz), 7.07 (2H, d, *J* 3.6 Hz) and 7.36 (1H, dd, *J* 4.8 and 3.6 Hz). The intermediate polymer **4** is black [Found: C, 30.2; H, 3.65; Cl, 3.3; Fe 12.6; S, 22.5 $(C_7H_7S_2O_3)_n(H_2O)_{1.8}Fe_{0.50}(FeCl_2)_{0.14}$ requires C, 29.9; H, 3.8; Cl, 3.5; Fe, 12.7; S, 22.8%].

For the acid-formed polymer **5**: Found: C, 41.0; H, 4.25; S, 31.15; Cl, <0.1; Na, <0.001; Fe, <0.01. $(C_7H_8S_2O_3)_n$ requires C, 41.2; H, 3.95; S, 31.4%.