Polymer Bulletin 18, 277–281 (1987)

Polymer Bulletin

Self-doped water-soluble conducting polymers

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Summary.

α –Terthienyl and pyrrole, substituted with alkylsulfonate side chains, can be polymerized electrochemically without the addition of a conduction salt. This gives rise to self-doped conducting polymers that are soluble in water in the doped state.

Introduction.

Soluble conducting polymers are searched for extensively (1). Poly(3-alkylsodiumsulfonate)thiophenes have recently been claimed to be soluble in water, both in the undoped and doped state (2). Although the concept of self-dope is disclosed with respect to the corresponding acid, there is in (2) no experimental evidence to support this idea. In a second paper of the same authors (3) still no conclusive demonstration is given that the materials studied are indeed self-doped. At most a partial self-dope is made probable, because the inclusion of another dopant from the solution is not unlikely.

In this paper we report on new polymers for which self-dope is proved beyond doubts and, moreover, they are soluble in water in the self-doped state. These polymers are obtained by electrochemical polymerization of alkylsulfonate substituted α-terthienyl and pyrrole, respectively, from solutions without any additional conduction salt. The aqueous solution of the substituted pyrrole is stable in the self-doped state.

Monomers.

Our approach to self-doped conducting polymers is based on monomers that are easier to polymerize electrochemically than thiophenes, *viz.* 3′-propylpotassiumsulfonate-2,2′-5′,5″-terthienyl and 3-butylsodiumsulfonate-pyrrole, further refered to as M3 and M6, respectively. The preparation of both monomers, which were unknown, is outlined in scheme 1. Starting with the alkylation of the well-known diketone M1 (4), followed by traditional functional group transformations, yielded the substituted α-terthienyl M3. The substituted pyrrole M6 was prepared from the *N* -protected pyrrole M4 by acylation, reduction and treatment with Na_2SO_3, followed by *N* -deprotection with base. Key experimental data characterizing the samples are summarized in Table 1. Both routes proved to be suitable for variations in the side-chains. A detailed account of the syntheses will be published elsewhere.

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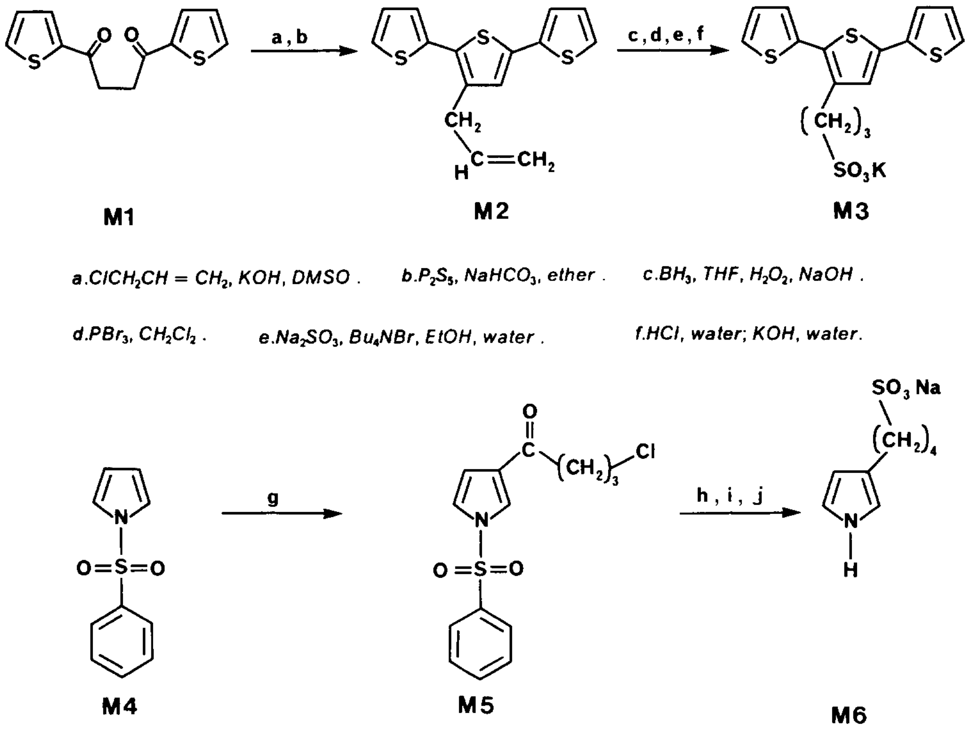

a. $ClCH_2CH = CH_2$, KOH, DMSO . *b.* P_2S_5, $NaHCO_3$, ether . *c.* BH_3, THF, H_2O_2, NaOH .

d. PBr_3, CH_2Cl_2 . *e.* Na_2SO_3, Bu_4NBr, EtOH, water . *f.* HCl, water; KOH, water.

g. $ClCO(CH_2)_3Cl$, $AlCl_3$. *h.* Zn(Hg), HCl . *i.* Na_2SO_3, Bu_4NBr, NaI, EtOH, water . *j.* NaOH .

Scheme 1. Outline of the synthesis of the monomers.

Table 1. Key experimental data of the monomers.

M3: (crystallized from H_2O),
^1H-NMR (D_2O) δ 7.3-6.8 (m,7H); 3.0-2.4 (m,4H); 2.3-1.8 (m,2H);
$^{13}C-NMR$ (DMSO – d6) δ 137.3; 134.2; 132.9; 132.5; 127.2; 126.1; 125.6; 124.6; 123.8; 123.1; 121.8; 48.9; 26.0; 23.8;
FTIR(KBr) 3535, 3390, 1205, 1180, 1060, 1050 cm^{-1} .

M6: (crystallized from ethanol),
^1H-NMR (D_2O) δ 6.6-6.4 (m,2H); 5.9 (m,1H); 2.9-2.6 (t,2H); 2.5-2.2 (t,2H); 1.7-1.4 (m,4H);
$^{13}C-NMR$ (D_2O – MeOH) δ 123.6 (s); 118.7 (d); 115.9 (d); 107.8 (d); 65.0 (t); 49.3 (t); 29.9 (t); 26.0 (t); 24.3 (t);
FTIR(KBr) 3520, 1205, 1050, 840, 708, 697 cm^{-1} .

The monomers M3 and M6 were both readily soluble in water and slightly soluble in acetonitrile. The oxidation potentials of saturated solutions of M3 and

M6 in acetonitrile were determined to be 0.85 *V SCE* and 0.7 *V SCE*, respectively. These values are somewhat lower than those of α -terthienyl , 1.0 *V SCE* (5) and pyrrole , 0.8 *V SCE* (6), respectively.

Polymers.

Polymers were prepared by electrochemical oxidation at 0.5 to 2 *V* above the oxidation potential from the solutions as such, that is without adding a conduction salt. In the case of acetonitrile solutions the monomer gradually dissolves during the reaction. Concurrently an acetonitrile- insoluble polymer is formed as a blue, changing into black, precipitate at the (*Pt* or ITO-glass) anode. The final solution is clear and colourless. The polymerization of M3 was carried out in a glove box ($[O_2] < 1$ ppm) to prevent sulfone formation (7). The precipitates on the anode dissolve readily in water. Only when the potential during the formation was very high the solutions were formed less eagerly or not at all. Probably then some crosslinking occurs. The polymers are also soluble in methanol.

The polymers P3 and P6 can also be prepared by continued electropolymerization of the solutions of the respective monomers in water. During this process, which is continued until the current has dropped to less than 5 per cent of its original value, the solution darkens and the electrodes remain blank.

Properties.

The anodic precipitates showed, after washing with acetonitrile, drying in vacuo for 5 hours and pressing into pellets, conductivities of 0.01 *S/cm* and 0.1 *S/cm* for the polymer of M3 (P3) and of M6 (P6), respectively. That these polymers are indeed self-doped follows conclusively from the absence of any other dopant during preparation and handling. In these first examples of conducting polymers in which self-dope is beyond any doubt, part of the sulfonate ions that are covalently attached to the polymeric backbone act as dopant and form "Zwitter-ions" having delocalized positive charges. The sulfonate ions not participating in the self-doping are neutralized by alkaline ions in the usual way (Fig. 1).

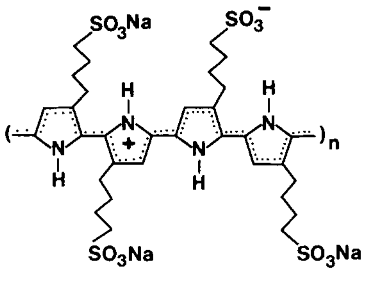

Fig. 1.Sketch of the self-doped conducting polymer P6.

The isolated polymers showed FTIR spectra in agreement with α – α coupled monomers (6,8). In fig. 2 the electronic spectra of solid films of P3 and P6, both prepared electrochemically on ITO-glass anodes, are compared with those of freshly prepared solutions of the very same samples. The spectra of the solutions in water clearly show low-energy humps that are characteristic of doped conjugated polymers (3,8,9).

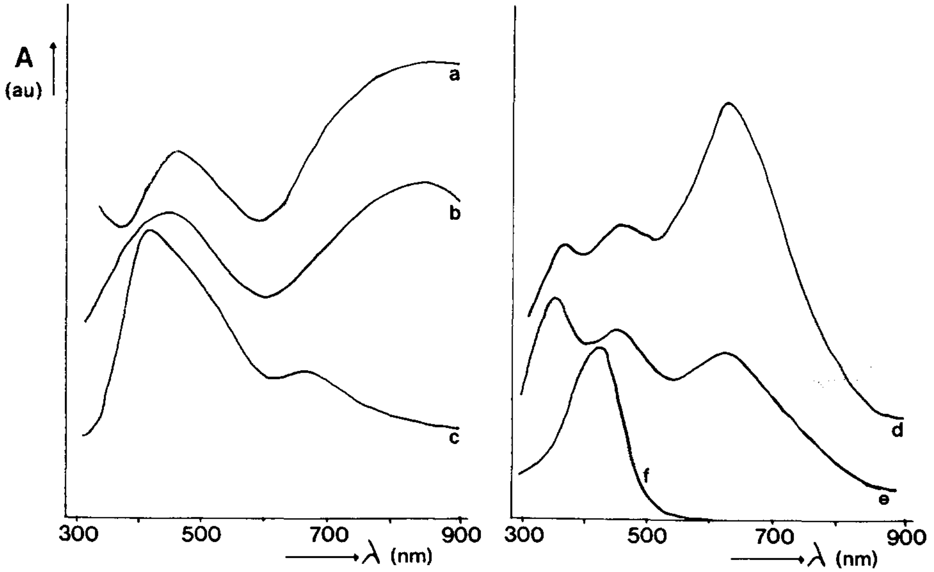

Fig. 2. Electronic spectra of the polymers P3 (right) and P6 (left).
a and d: solid films grown on ITO-glass electrodes in acetonitrile
b and e: water solutions obtained from these films.
c: film left after evaporation of water from solution of P6.
f: methanol solution of P3.

The degree of doping is probably somewhat smaller than that of the solid polymers. The spectrum of the methanol solution of P3 shows that the polymer has been dedoped while going into solution. The solution of P6 in water is stable (hardly any change in the UV-vis spectrum could be detected after one day), that of P3 in water changes gradually towards the undoped state. The difference in stability agrees with the known difference in stability for doped pyrrole- and thiophene-based conjugated polymers in general (6). The UV-vis spectra of solutions of polymers prepared directly by electrochemical polymerization in water correspond to slightly doped (P3) to medium doped (P6) polymers. Films obtained from the solutions by evaporating the water at about 70°C exhibited a low conductivity of about 0.01 *μS/cm*. Their UV-vis spectra (for P6 see fig.2) are similar to the spectra of samples that were dedoped by electrochemical means. Dedoped samples can be redoped electrochemically to conductivity values near to those of freshly prepared samples. Chemical redoping by treatment with iodine vapour gives similar conductivity values.

Conclusion.

Our investigations show the existence of self-doped conducting polymers that are soluble in water in the (partially) doped states. A proof of the self-dope is the absence of any other potential dopant during preparation and handling. Moreover, the self-doped polymer P6, poly(3-butylsulfonate-pyrrole), in which the negative charges are partly compensated by sodium ions, is even stable in aqueous solution.

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Accepted July 15, 1987 C