Facile Preparation of High Molecular Weight, Highly Conductive Poly(2,5-furylene vinylene)

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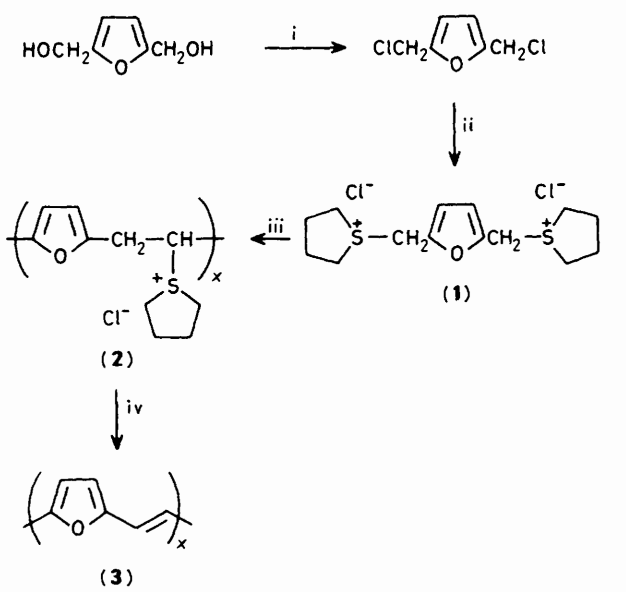
High molecular weight, freestanding films of poly(2,5-furylene vinylene) (PFV) are readily prepared *via* a water soluble precursor polymer, are electrochemically reversibly donor and acceptor dopable, and reach conductivities as high as 36 S/cm on acceptor doping.

The processibility of high molecular weight conducting polymers has been achieved recently by the development of soluble precursor polymers for polyacetylene,[1] polyphenylene,[2] poly(*p*-phenylene vinylene)[3,4] (PPV), and poly(thienylene vinylene)(PTV).[5] In each case, a two stage route was used to first produce a high molecular weight, soluble, non-conjugated precursor polymer that could be easily solution cast into films, followed by thermal conversion to the final conjugated polymer. Recently, we reported the facile preparation and oxidative behaviour of high molecular weight, environmentally stable poly(2,5-thienylene vinylene).[5] This polymer appears to be extensively conjugated and has a lower ionization potential than the parent directly linked aromatic polymer, polythiophene (PT). Furthermore, the chemical potential of heavily doped PTV is some 0.3 to 0.5 eV lower than heavily doped polythiophene, which greatly improves the environmental stability of the highly conductive form.

Given the simplicity of preparation of PPV and PTV *via* the quinodimethane route,[3,4,5] and the ease of synthesis of the starting monomers, we chose to investigate the applicability of this route to the general preparation of other poly(heteroarylene vinylenes).

Kossmehl *et al.*[6] reported the synthesis of poly(2,5-furylene vinylene) (PFV), (**3**) using a condensation reaction. Only low molecular weight intractable polymers were formed which



Scheme 1. *Reagents and conditions:* i, $SOCl_2$–$CHCl_3$–pyridine; ii, tetrahydrothiophene (excess)–MeOH, room temp.; iii, OH^- (aq., 1 equiv.), 0 °C, argon; iv, heat to 60 °C; then to 150 °C under reduced pressure.

reached low conductivities on doping (10^{-3}—10^{-2} S/cm). The conductive properties of the directly linked furan polymer, poly(2,5-furandiyl), have been reported only for electrochemically prepared polymer.[8] Thus, little information is available to assess the worthiness of the furan nucleus as a building-block for conductive polymers.

We now report the facile synthesis of high molecular weight, freestanding films of PFV by a similar route to that used to prepare PTV (see Scheme 1). 2,5-Bis(tetrahydrothiophenium methyl) furan chloride (**1**)† was dissolved in water, and one equivalent of alkali was added at 0 °C under argon. In just a few seconds a viscous solution of the polyelectrolyte (**2**) formed. After dialysis against water, a cast film of the polyelectrolyte was first gradually warmed to 60 °C then subjected to final heat treatment at 150 °C under reduced pressure to yield PFV. The resulting polymer had a golden lustrous colour, identical to that of PTV. I.r.: (film; cm^{-1}) 3001w, 3060w, 1710m, 1580m, 1380m, 1280s, 1250s, 1030s, 935s, 785.‡ Almost complete elimination of tetrahydrothiophene and HCl occurred to give the highly conjugated polymer as evidenced by the elemental analysis for sulphur (0.62%). The elimination of HCl and tetrahydrothiophene (or dimethylsulphide) occurred less readily from the precursor of PFV than from that of PTV. Compared to the precursor of PTV, handling and casting of the PFV precursor polyelectrolyte into films and coatings were easily accomplished around 0 °C. Random copolymers of PFV and PTV were smoothly prepared from a mixture of (**1**) and the thiophene analogue. Copolymer properties were found to be intermediate between PFV and PTV. In sharp contrast to polyacetylene, films of PFV after air exposure for extended periods (months at room temperature) appeared unchanged, remained flexible, and attained high conductivities on acceptor doping.

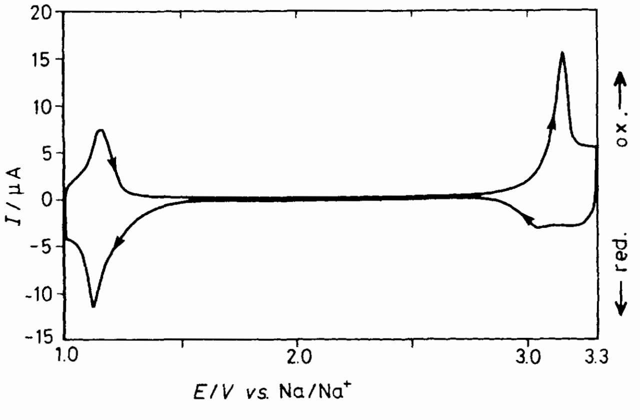


Figure 1. Cyclic voltammogram of a 5 μm poly(2,5-furylene vinylene) film *versus* a sodium counter and reference electrode in 1 M $NaPF_6$/dimethoxyethane. S = 0.1 mV/s.

Table 1. Conductivities of doped poly(2,5-furylene vinylene) films.

Dopant	Conductivity/S/cm
I_2	36
$FeCl_3$	25
Electrochemical (PF_6^-)	4
Air	10^{-4}

A remarkably rapid conductivity increase was observed on exposure of 10—15 μm thick films of (**3**) to different oxidizing dopants (Table 1). Conductivities as high as 36 S/cm were measured on the doped polymer; average values were around 20 S/cm. Undoped films exhibited a strong e.s.r. signal (*g*-factor 2.0021) and exhibited low levels of conductivity ($\sim 10^{-7}$ to 10^{-6} S/cm) much like *trans*-polyacetylene.[9] Air exposure caused a significant rise in conductivity which saturated at 10^{-4} to 10^{-3} S/cm. Absorption maxima for the thin undoped PFV film were observed at 633 and 530 nm. The absorption edge at 700 nm equates to an optical band gap of 1.76 eV, which is in close agreement with band gap determined electrochemically (*vide infra*), and slightly larger than that of *trans*-polyacetylene (1.4 eV).[10]

The cyclic voltammetric behaviour of PFV was studied using a three-electrode cell in which the working electrode consisted of a 5 μm film of PFV embedded in platinum gauze. The counter and reference electrodes were both sodium metal and the electrolyte used was 1 M $NaPF_6$–dimethoxyethane (DME). Clean oxidation and reduction waves for PFV were observed in this electrolyte for both p- and n-type doping (Figure 1). The oxidation peak for p-type doping occurred at 3.15 V *vs.* Na/Na^+ and the reduction peak for n-type doping occurred at 1.1 V *vs.* Na/Na^+. From the onset potentials, that is, the potential where the polymer starts to oxidize (3.0 V *vs.* Na/Na^+) and to reduce (1.25 V *vs.* Na/Na^+), the bandgap of PFV was determined to be about 1.75 V. After the initial 'break-in' oxidation and reduction cycle, subsequent cycles occurred with over 90% coulombic efficiency up to the 25 mol% doping level for both p-type doping and n-type doping of PFV. Reversible n-type doping was observed only at potentials above 0.9 V *vs.* Na/Na^+; below 0.9 V, charge passed freely but was not totally recoverable. This inefficiency may result from chemical degradation or metallation of the polymer backbone.

Owing to the weak resonance energy in the furan ring (16 kcal/mol; 1 cal = 4.184 J),[11] the electronic properties of PFV

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† Prepared by converting furan-2,5-dimethanol to 2,5-bis(chloromethyl) furan (m.p. 27—28 °C) with thionyl chloride in chloroform–pyridine, followed by treatment with excess tetrahydrothiophene in methanol at room temperature.

‡ Satisfactory C and H analyses were obtained for PFV (**3**).

in many respects resemble those expected for polyacetylene substituted with electron donating substituents. As anticipated, the onset potentials for p- and n-type doping are cathodically shifted (occur at lower potential) by 0.3 and 0.6 eV, respectively, from those of polyacetylene. Like polyacetylene, PFV is slightly doped by exposure to air (oxygen), but, as a consequence of hetroatom substitution and/or the existence of (weak) aromatic rings, both the undoped and acceptor-doped forms of PFV appear to be air stable while those of polyacetylene are not.

Received, 23rd February 1987; Com. 243

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