

## Soluble, Conducting Polymers from 3-Substituted Thiophenes and Pyrroles

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The anodic electropolymerisation of long-chain 3-substituted pyrroles and thiophenes gives highly conducting polymeric materials, some of which are soluble in common organic solvents in the conducting state.

Electrochemical preparation of conducting polythiophene and polypyrrole films has attracted great attention.<sup>1</sup> These materials exhibit a range of remarkable solid-state properties and offer tremendous technological potential, *e.g.* in the fabrication of molecular electronic devices, solid-state 'batteries', and chemically modified electrodes and sensors. A limiting feature of the current generation of electroactive polymers is that they are frequently insoluble and intractable materials that do not possess the required (mechanical, air, or thermal) stability to merit commercial application.

Properties of thiophene and pyrrole derivatives substituted in the 3-position by methyl, ethyl, or methoxy groups have been extensively studied by several research groups,<sup>2</sup> but only recently have any derivatives bearing longer alkyl chains been reported, *viz.* poly(alkylthiophenes) (1).<sup>3</sup> We describe the preparation and electrochemical polymerisation of thiophene and pyrrole monomers containing a range of long-chain substituents attached at the 3-position. The polymers are flexible, highly conducting, and are typically stable up to 210 °C. A 5% loss in conductivity is observed on cycling three times between room temperature and 180 °C. Some of these new polymers are soluble in common organic solvents in

the conducting state, and reconstituted films which retain high conductivity can be cast from solution.

Thiophene monomers (2)–(4), containing ether linkages in the side-chain, and monomer (5) containing an amide linkage, have been obtained from 3-(bromomethyl)thiophene in one- and three-step procedures, respectively. Alkoxy-substituted thiophene (6) is prepared directly from 3-bromothiophene. Ketopyrrole derivatives (7) and (8) have been synthesised in a two-step procedure from 1-tosylpyrrole.† Details of electrochemical polymerisation of the monomers are given in Table

† All monomers gave satisfactory analytical and spectroscopic data. Compounds (2)–(4) were prepared from 3-(bromomethyl)thiophene by reaction with the sodium salt of the appropriate alcohol in refluxing CCl<sub>4</sub>. Compound (5) was prepared from 3-(bromomethyl)thiophene by sequential reactions: i, potassium phthalimide, 18-crown-6, dimethylformamide, 80 °C; ii, N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, refluxing EtOH; iii, appropriate acid chloride, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, –5 °C. Compound (6) was prepared from 3-bromothiophene and sodium methoxyethoxyethoxide, CuO<sub>2</sub>, KI, 110 °C. Compounds (7) and (8) were prepared from *N*-tosylpyrrole by sequential reactions; i, appropriate acid chloride, AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 20 °C; ii, 5 M NaOH, refluxing dioxane.

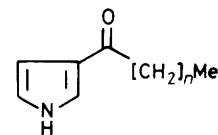
Table 1.

Compound <sup>a</sup>	Solvent	Anode	Concentration of monomer (molar)	Concentration of Bu <sub>4</sub> N <sup>+</sup> PF <sub>6</sub> <sup>-</sup> (molar)	Conductivity $\sigma_{r,t}$ <sup>b</sup> / S cm <sup>-1b</sup>
(2) <sub>n</sub> X	PhNO <sub>2</sub>	Pt	1.0 × 10 <sup>-1</sup>	3.0 × 10 <sup>-2</sup>	0.31 <sup>c</sup>
(3) <sub>n</sub> X	PhNO <sub>2</sub>	Pt	1.0 × 10 <sup>-1</sup>	3.7 × 10 <sup>-2</sup>	51 <sup>c</sup>
(4) <sub>n</sub> X	PhNO <sub>2</sub>	Pt	2.8 × 10 <sup>-1</sup>	3.1 × 10 <sup>-2</sup>	1050 <sup>d</sup>
(5) <sub>n</sub> X	PhNO <sub>2</sub> -CH <sub>2</sub> Cl <sub>2</sub>	Pt or ITO	2.0 × 10 <sup>-2</sup>	5.0 × 10 <sup>-2</sup>	200 <sup>d</sup>
(6) <sub>n</sub> X	CH <sub>2</sub> Cl <sub>2</sub>	ITO	5.2 × 10 <sup>-2</sup>	1.2 × 10 <sup>-2</sup>	0.05 <sup>c</sup>
(7) <sub>n</sub> X	MeCN-CH <sub>2</sub> Cl <sub>2</sub>	ITO	1.6 × 10 <sup>-2</sup>	2.6 × 10 <sup>-3</sup>	360 <sup>d</sup>
(8) <sub>n</sub> X	MeCN-CH <sub>2</sub> Cl <sub>2</sub>	ITO	4.8 × 10 <sup>-3</sup>	1.0 × 10 <sup>-3</sup>	10 <sup>d</sup>

<sup>a</sup> X = PF<sub>6</sub>. <sup>b</sup> r.t. = room temperature. <sup>c</sup> Two-probe measurement. <sup>d</sup> Four-probe measurement.

1. Polymerisation was carried out at 10°C under a nitrogen atmosphere in a one-compartment cell using tetrabutylammonium hexafluorophosphate as the electrolyte, and a platinum or indium-tin oxide (ITO) anode. The concentrations of monomer and electrolyte, and conductivity data for the polymers are given in Table 1. The optimum current density for electropolymerisation varies with the monomer between 1.0 and 2.5 mA cm<sup>-2</sup>.

D.c. conductivity measurements of the oxidised films were obtained either while the film was attached to the anode surface (using a two-probe technique with a mercury drop contact) or on a free-standing film that had been peeled off the anode (using a four-probe technique). High conductivity ( $\sigma > 10$  S cm<sup>-1</sup>) is obtained reproducibly for polymers in both the thiophene and pyrrole series, the highest value ( $\sigma$  1050 S cm<sup>-1</sup>) being for polythiophene (4). The conductivity values for many of the polymers (2)–(8) are significantly higher than those reported for polymers (1) ( $\sigma$  11–95 S cm<sup>-1</sup>).<sup>3</sup> Polymers (2)–(6) are typically stable up to 210°C.



(1)  $-(CH_2)_n Me$  [ $n = 5, 7, 11, 17, 19$ ]

(7)  $n = 10$

(2)  $-CH_2O Me$

(8)  $n = 16$

(3)  $-CH_2O[CH_2]_2O Me$

(4)  $-CH_2O[CH_2]_2O[CH_2]_2O Me$

(5)  $-CH_2NHC(O)[CH_2]_{10} Me$

(6)  $-O[CH_2]_2O[CH_2]_2O Me$

Polymers (1), in the insulating form, are reported to be soluble in common solvents.<sup>3</sup> More importantly polymer (4) is soluble in the conducting form. For example, slow evaporation of a solution of polymer (4) in a mixture of tetrahydrofuran–dichloromethane–trichloroethene (4 : 1 : 1) regenerates polymer (4) as a thin film (ca. 40  $\mu$ m thick) with reduced conductivity ( $\sigma_{r,t}$  0.3 S cm<sup>-1</sup>, four-probe measurement). This provides one of the first examples of an organic polymer that is solution processable in the conducting state.

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