

Enantioselective Chiral Poly(thiophenes)

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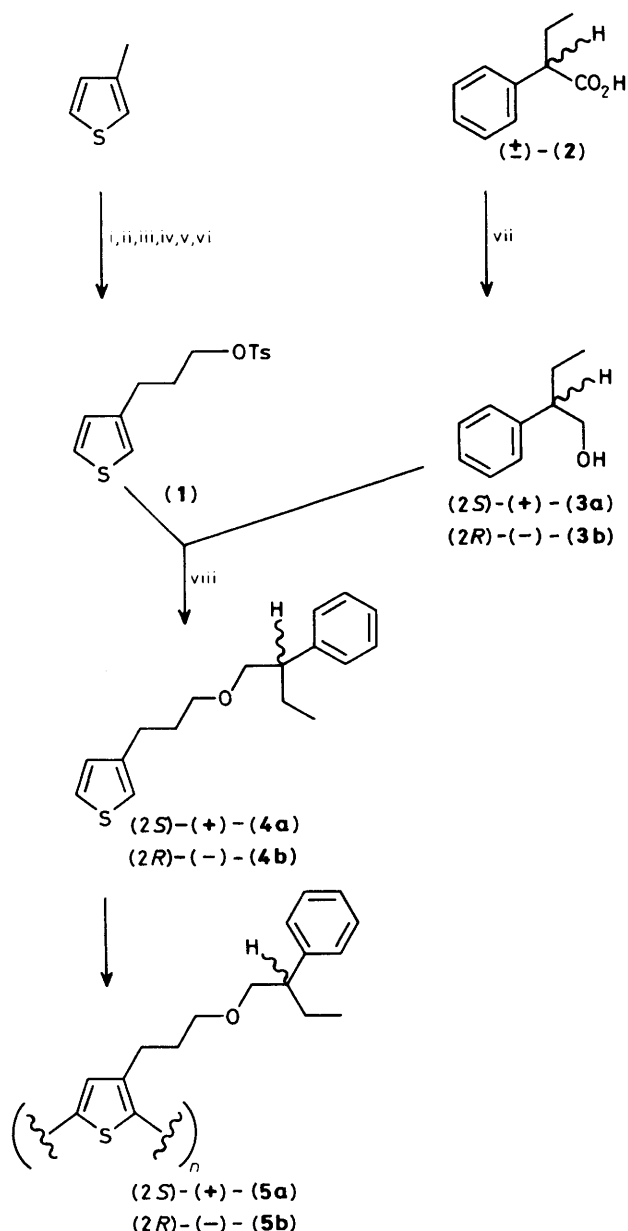
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Chiral poly(thiophenes) have been synthesized by electropolymerization; they exhibit high specific rotation, stability, and conductivity and can stereoselectively recognize chiral anions used as doping agents during voltammetric cycles.

During the last few years, considerable interest has been focused on the preparation of modified electrodes.¹ Among the many types of modified electrodes that have been prepared, chiral electrodes capable of performing stereoselective analysis and/or electrosynthesis appear to be an exciting

aspect.² The use of electrogenerated conducting polymers like poly(pyrrole) and poly(thiophene) derivatives present several advantages for the preparation of modified electrodes. Their electrochemical synthesis leads to direct grafting onto the electrode surface. Their high conductivity leads to fast and



Scheme 1. Reagents and conditions: i, *N*-bromosuccinimide, CCl_4 , benzoylperoxide; ii, diethyl malonate, NaH, tetrahydrofuran (THF); iii, NaOH, EtOH, $\text{H}^+/\text{H}_2\text{O}$; iv, 20 mm Hg, 200 °C; v, AlLiH_4 , THF; vi, toluene-*p*-sulphonylchloride, pyridine; vii, (*R*)-(-)- or (*S*)-(+)-1-phenylethylamine, then LiAlH_4 ; viii, THF, NaH, NBu_4Br , overall yield 60%.

efficient charge transfer and allows the preparation of electrodes of large surface to volume ratio and with maximum density of chiral active sites. Chiral poly(pyrroles) have been described previously by Salmon and Bidan,³ but the conductivity and stability of the polymers obtained are rather limited and their enantioselective properties have not been investigated. We have recently analysed the steric factors compatible with obtaining stable highly conducting poly(thiophenes).⁴ We now describe the synthesis of poly(thiophenes) having chiral functional groups and their properties as enantioselective electrodes.

In order to achieve stereoselectivity, the choice of the chiral structure is of major importance as only some are known to

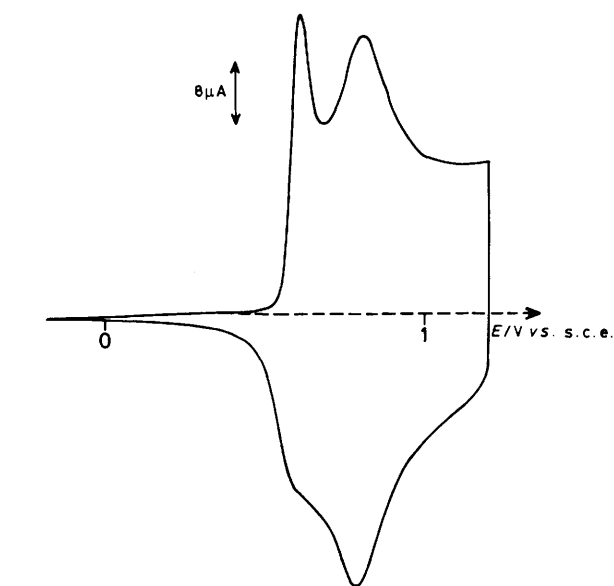


Figure 1. Cyclic voltammogram of chiral poly(thiophene) (5a); deposition charge 100 mC cm^{-2} , electrolyte LiClO_4 in MeCN (0.1 mol l^{-1}), scan 50 mV s^{-1} .

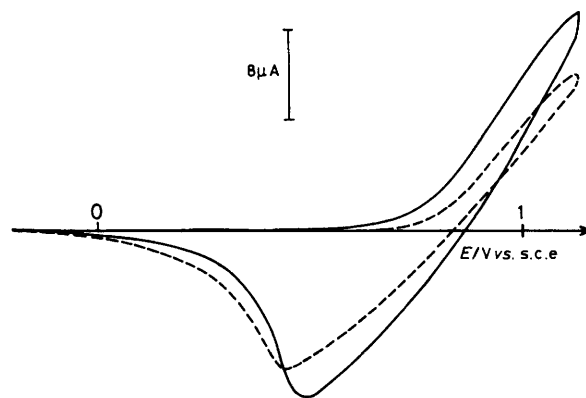


Figure 2. Cyclic voltammogram of chiral poly(thiophene) (5a) using chiral anions as doping agents; deposition charge 400 mC m^{-2} , electrolyte (+)- (—) and (-)- (---) 10-camphorsulphonic acid in MeCN (0.1 mol l^{-1}), scan 50 mV s^{-1} .

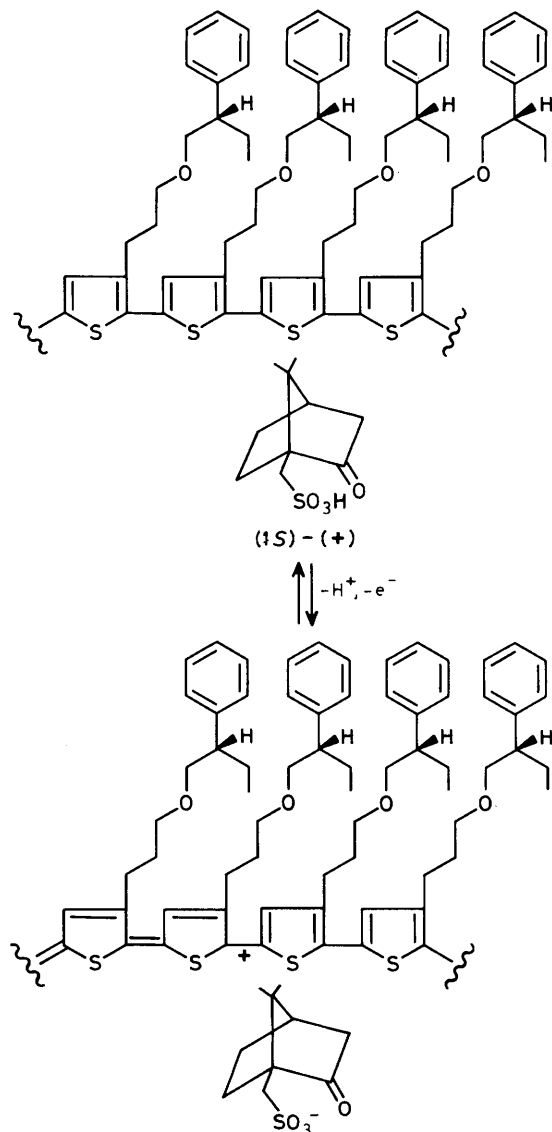
induce high diastereoselectivity during synthesis or resolution of chiral compounds. (\pm)-2-Phenylbutyric ('Horeau') acid (2) has been used for many years for enantiomeric excess (e.e.) determination of organic chiral compounds,⁵ so we used it as a building block for the synthesis of chiral thiophene monomers (4). Owing to the bulkiness of the groups bound to this chiral subunit, a linear propoxy chain was introduced as a spacer between the chiral and thiophene units to allow electropolymerization.⁶

The (*S*)-(+)- and (*R*)-(-)-2-phenylbutanols (3a) and (3b) were obtained by resolution of Horeau acid (2) using (*R*)-(-)- and (*S*)-(+)-1-phenylethylamine, respectively, and then reduction using AlLiH_4 . The 3-(3'-thienyl)propyl toluene-*p*-sulphonate (1) is obtained from 3-methylthiophene using a six-step procedure (Scheme 1).

The monomers were electropolymerized in a one-compartment three-electrode cell containing monomer (4) (0.2 mol l^{-1}) and NBu_4PF_6 (0.02 mol l^{-1}) in nitrobenzene. The electrosynthesis was performed at 5 °C under argon in

Table 1. Effect of structure of doping agent on doping level observed during cyclic voltammetry for poly(3-methylthiophene) and chiral poly(thiophenes) (**5a**) and (**5b**).

Polymer	LiClO ₄		(1 <i>S</i>)-(+)-10-Camphorsulphonic acid		(1 <i>R</i>)-(-)-10-Camphorsulphonic acid		(+)/(-)
	<i>Q</i> /mC cm ⁻²	Doping level/%	<i>Q</i> /mC cm ⁻²	Doping level/%	<i>Q</i> /mC cm ⁻²	Doping level/%	
PMeT	8.61	19	0.697	1.40	0.711	1.43	0.98
(5a)	7.38	3.75	1.87	0.95	1.23	0.62	1.53
(5b)	7.09	3.60	2.36	1.2	2.93	1.49	0.805

**Scheme 2**

galvanostatic conditions, applying a current density of 2 mA cm⁻². The anode was a platinum disk electrode of 0.07 cm² area for electrochemical characterization and an indium-tin oxide electrode (ITO) transparent for spectroscopy and conductivity measurements. An aluminium foil cathode was

used with a saturated calomel electrode (s.c.e.) as the reference electrode. The polymers (2*S*)(+) - and (2*R*)(-) - poly[3-(3'-thienyl)propyl 2-phenylbutyl ether] (**5a**) and (**5b**) were obtained as compact free standing films with conductivity ~1 S cm⁻¹ (measured by standard four probes technique). The u.v. spectra of the undoped polymers show an absorption maximum at 445 nm, indicating that the mean conjugation length of polymers (**5a**) and (**5b**) is close to that of poly(3-octadecylthiophene) previously synthesized.⁴

An undoped film of polymer (**5a**) shows a specific rotation $\alpha_D^{22} + 3000^\circ$ and polymer (**5b**) the opposite specific rotation $\alpha_D^{22} - 3000^\circ$. Such high values compared to the corresponding monomers [(**4a**) $\alpha_D^{22} + 21^\circ 5'$; (**4b**) $\alpha_D^{22} - 22^\circ 5'$ (2%, CHCl₃)] are consistent with a macromolecular asymmetry⁷ and a partial helical conformation as proposed for poly(3-alkylthiophenes).⁸

The high symmetry of cyclic voltammograms of the polymers (**5a**) and (**5b**) [Figure 1 shows that of (**5a**)] indicate electrochemical reversibility. These polymers exhibit high electrochemical stability under redox cycling and several tens of voltammetric cycles have been performed without any apparent loss of electroactivity. Previous studies have shown that the electrochemical behaviour of poly(pyrrole) and poly(thiophene) depends on the electrolyte used for the redox cycling and their ion sieving effects have been demonstrated.⁹ It was therefore interesting to examine the behaviour of our chiral poly(thiophene) electrodes using optically active anions as supporting electrolyte and doping agent. For this purpose, we compared the cyclic voltammograms recorded in acetonitrile containing 0.1 mol l⁻¹ (+)- and (-)-10-camphorsulphonic acid with polymers (**5a**) and (**5b**). Table 1 lists the charges exchanged upon reduction of the films and the corresponding doping levels. The results obtained under the same conditions with achiral poly(3-methylthiophene) (PMeT) are presented for comparison.

As shown by these results there is no difference in charge exchange by PMeT in (+)- or (-)-10-camphorsulphonic acid (Figure 2, Scheme 2). Conversely, the doping level of chiral polymer (**5a**) was 50% higher with (+)-compared to (-)-10-camphorsulphonic acid and a symmetrical response was obtained in the case of polymer (**5b**) (Table 1).

The oxidation of chiral polymers (**5a**) and (**5b**) using chiral anions as doping agent leads to the formation of two diastereoisomeric combinations which differ from both thermodynamic and kinetic points of view. The observed difference in oxidation rate (the rate of insertion of the chiral doping agent in the chiral polymeric matrix) is caused by the stereoselective recognition during the redox cycle. The electrochemical evaluation of enantioselectivity has already been reported in several papers,¹⁰ but the results were based on potentiometric methods. The results presented here represent, to our knowledge, the first example of amperometric evaluation of enantioselectivity. Stereoselective recog-

nitration of doping agents is of particular interest for the future development of these polymers as materials for enantioselective electrodes and membranes.

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