Electrochemical Synthesis of a Copolymer of Thiophene and Pyrrole: Poly(thienylpyrrole)

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Electrolytic polymerization of 2,2′-thienylpyrrole gave tough violet films having good electrical conductivities and electrochemical response.

Electrolytic polymerization is one method of preparing a thin film of conductive polymer. Polymerization of heterocycles has been extensively studied by this method, polypyrrole (PP) and polythiophene (PT) receiving great attention.[1] It seemed interesting to attempt to synthesize a copolymer of pyrrole and thiophene which would modify the properties of PP or PT. However, electro-copolymerization of thiophene and pyrrole is difficult because of the large difference in their oxidation potentials. Recently Ingnäs *et al.* used a terthiophene starting monomer, the oxidation potential of which is roughly the same as that of pyrrole.[2] Moreover, the copolymerization using two different monomers might afford a random copolymer which

Table 1. Electropolymerisation of thienylpyrrole in various solvents.

Entry	Solvent	Concentration (M)		Current density ($mA\,cm^{-2}$)	Conductivity[a] ($S\,cm^{-1}$)	Dopant/TP[b]
		TP	Bu_4NHSO_4			
1	MeCN	0.03	0.1	6	0.082	0.20
2	PC[c]	,,	,,	0.75	0.72	0.29
3	$PhNO_2$	0.05	,,	2	0.65	0.32
4	,,	0.1	,,	3	1.10	0.38
5	,,	0.03	,,	1	3.30	0.44

[a] Measured using the four probe technique. [b] Calculated from elemental analysis data. [c] PC propylene carbonate.

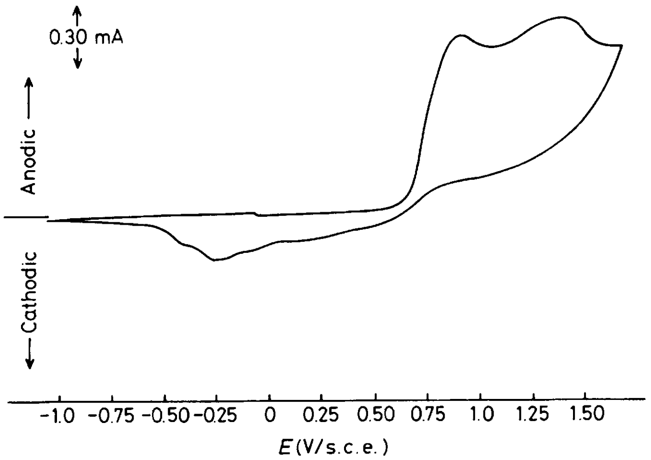
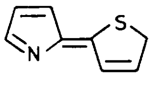
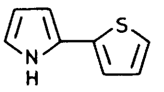


Figure 1. Cyclic voltammogram of 2,2′-thienylpyrrole (4 mM) in 0.1 M Bu_4NHSO_4–MeCN, sweep rate 20 mV s^{-1}. S.c.e. = saturated calomel electrode.



(A)



(B)

is inferior to the homopolymers in terms of conductivity. This paper reports the first synthesis of the copolymer, poly(thienylpyrrole) (PTP), electrochemically polymerized using 2,2′-thienylpyrrole (TP) as the starting monomer.

TP was synthesized by 1,5-dipolar cyclization of the imidoyl chloride of 2-thienoylallylamide according to a published method.[3] The cyclic voltammogram of TP is shown in Figure 1. This shows two anodic peaks, one of which corresponds to the formation of the cation radical and the other to that of the dication. This is in contrast with the behaviour of the individual heterocycles which are thought to be unstable because of repulsion of the dipositive charge. The ground-state energies for two forms of thienylpyrrole (A) and (B) were calculated by estimating the energy gap between the two forms.† The result yielded an energy gap of 0.926 eV, which suggests dication formation is possible.

We prepared PTP films under the following conditions: the two-compartment electrolytic cell was equipped with an indium tin oxide conducting glass or platinum anode and a platinum cathode. TP was purified by sublimation, and stored under an argon atmosphere. Solvents were dried over 4 Å molecular sieve and tetrabutylammonium hydrogensulphate was used without further purification. Results are shown in Table 1. It is clear that the polymer could be synthesized with various levels of dopant concentration, and that conductivities increased on increasing the doping level. Film with a violet lustre was obtained with high conductivity (up to 3.3 S cm^{-1}). PP and PT doped with the same dopant have been reported to have conductivities of 0.3 and 0.1 S cm^{-1}, respectively,[4,5] indicating that PTP is 10—30 times more conducting than the individual heterocycles.

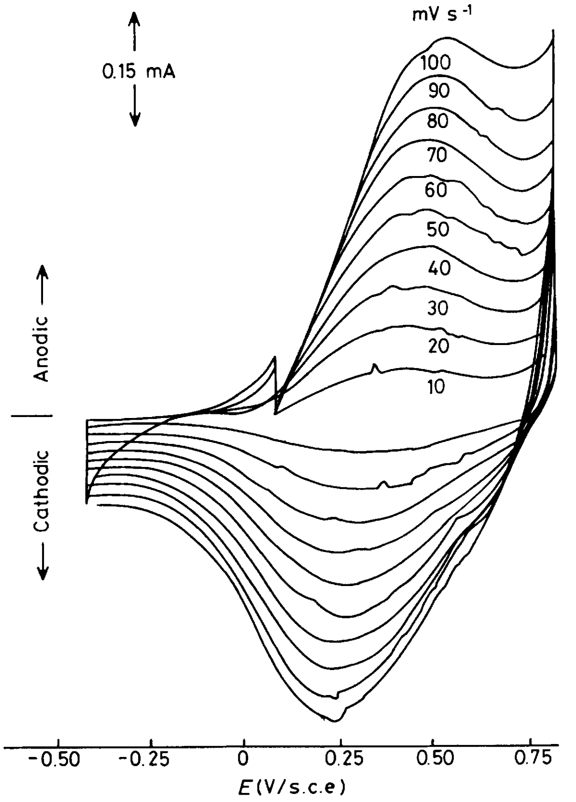


Figure 2. Cyclic voltammogram of poly(thienylpyrrole) film in 0.1 M Bu_4NHSO_4–MeCN.

A violet–blue film of PTP (1000 Å) was grown on a platinum surface by passing 60 mC cm^{-2} of charge in nitrobenzene. As seen in Figure 2, the cyclic voltammogram of this film shows good reversibility in acetonitrile containing 0.1 M Bu_4NHSO_4. The anodic potential (0.50 V *vs.* s.c.e.) is smaller than the oxidation potential of water (1.2 V) and the cathodic potential (0.25 V) is larger than the reduction potential of oxygen (−0.2 V). The oxidation and reduction of this film could be cycled repeatedly without decomposition. The film was orange in the neutral form.

Figure 3 shows the u.v.–visible absorption spectrum of an

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† Calculation using Quantum Chemistry Program Exchange 391, IBM Version, program translated by Charles M. Cook.

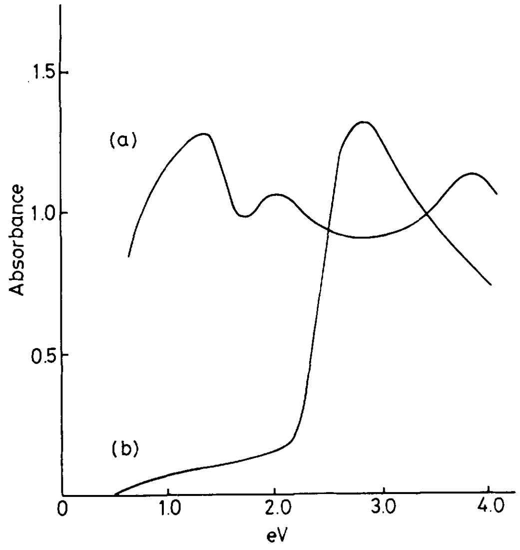

Figure 3. Optical absorption spectrum of poly(thienylpyrrole) films; (a) as-grown and (b) neutral film.

as-grown and neutral film. The neutral film shows a π–π^* absorption at 2.8 eV, which is intermediate between the values for PP (3.2 eV) and PT (2.6 eV). The as-grown film exhibited two mid-gap absorptions at 1.4 and 2.1 eV below a fundamental absorption edge of 2.2 eV, which can be explained in terms of the formation of bipolarons.

In conclusion electropolymerization of thienylpyrrole affords an alternative copolymer of pyrrole and thiophene. Poly(thienylpyrrole) is unique in the sense that it has a higher conductivity than the homopolymers, PT or PP, which is contrary to expectation.

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References

1 A. F. Diaz, K. K. Kanzazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, 1979, 635; G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, 1982, **135**, 173; K. Kaneto, Y. Kohno, K. Yoshino, and Y. Inuishi, *J. Chem. Soc., Chem. Commun.*, 1983, 382.
2 O. Ingnäs, B. Liedberg, and W. Chang-Ru, *Synth. Met.*, 1985, **11**, 239.
3 N. Engel and W. Steglich, *Angew. Chem.*, 1978, **90**, 719.
4 M. Salmon, A. F. Diaz, A. J. Logan, M. Krounbi, and J. Bargon, *Mol. Cryst. Liq. Cryst.*, 1982, **83**, 26.
5 R. J. Waltman, J. Bargon, and A. F. Diaz., *J. Phys. Chem.*, 1983, **87**, 1459.