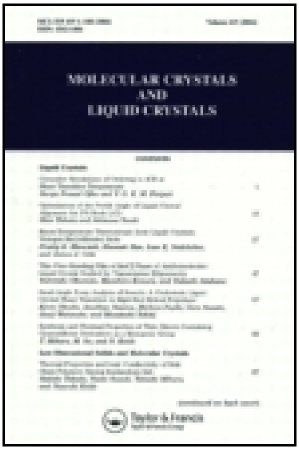

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Polyradicals: Synthetic Strategies and Characterization

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POLYRADICALS: SYNTHETIC STRATEGIES AND CHARACTERIZATION

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Abstract Synthetic routes to polyradicals are briefly reviewed; in addition the synthesis and electrochemical characterization of a novel 2,2,6,6-tetramethylpiperidinyloxy-1-pyrrylacetate(I) (or, TEMPO-1-pyrrylacetate) are reported. Rather than forming a conducting polymer deposit, this monomer coats the electrode with a passivating monolayer, which is electroactive at the nitroxide potential (+0.93 V vs $Ag^{+/0}$). The cyclic voltammetry of the surface-confined nitroxide not only exhibits typical monolayer behaviour (calculated coverage 0.5 nmol cm^{-2}), but also unusual spikes caused by trapped charge.

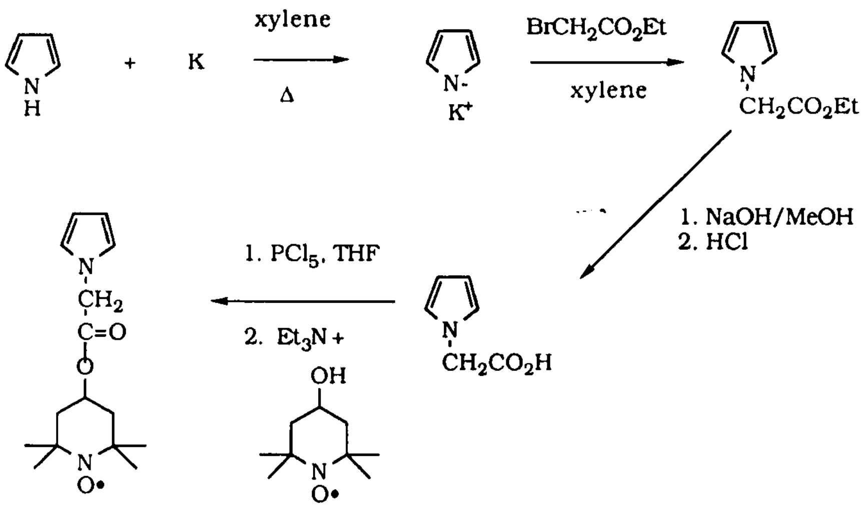
INTRODUCTION

Polyradicals may be readily prepared by attaching stable free radical groups (or free radical precursors) to conventional monomers, e.g. the tetramethyl piperidine-N-oxide

(TEMPO) derivative of acrylic acid.[1] These polymers electrocatalyse reactions when used as electrode coatings.[1] If, however, the nitroxide group is introduced into the backbone of a conducting polymer, e.g. by oxidizing poly(N-hydroxypyrrole),[2,3] then the conductivity is dramatically reduced and the polymer is unstable. Similar results are observed for poly(-N-hydroxyaniline).[4] Thus we sought to attach radical groups such as TEMPO or precursors such as quinones and bipyridines to a pyrrole or thiophene monomer. If the radical group can be brought into conjugation with the conducting polymer backbone then unusual magnetic and catalytic properties may result.[5]

Thiophene derivatives are less common because of synthetic difficulties in derivatizing at the 3-position. The most common method utilizes 3-(bromoalkyl) and 3-(hydroxyalkyl) thiophene[6] precursors; in this way thiophenes coupled to bipyridine[7] and quinone[8,9] groups have been prepared. Recently, we have developed a new synthetic strategy based on 3-(1-hexenyl)thiophene, which may be functionalised in a variety of ways.[10] Many previous workers have reported routes to pyrroles derivatized with nitroxides,[11] quinones,[12] bipyridines[13] and viologens.[14] Usually, the radical group is attached via facile alkylation of the pyrrole nitrogen, but this leads to a relatively low conductivity polymer. Here we report the preparation and electrochemistry of a pyrrole-TEMPO derivative according to the scheme below.

Scheme: Synthesis of I



SYNTHESIS

2,2,6,6-tetramethylpiperidinyloxy-1-pyrrylacetate(I) (Scheme)

To pyrrylacetic acid[15] (0.37g; 2.9 mmol) in THF (20 cm^3) is added a solution of PCl_5 (0.61g; 2.9 mmol) in THF (20 cm^3). The solution is refluxed for 2 h, then evaporated to dryness in high vacuum, solubilized in THF (30 cm^3) and added dropwise at 0°C to a solution of 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxide (0.5g; 2.9 mmol) and Et_3N (1.5g; 14.8 mmol) in THF (30 cm^3). Once the addition is complete, the mixture is stirred at room temperature for 15 h. The mixture is then hydrolyzed with H_2O (0.5 cm^3), evaporated to dryness, and CH_2Cl_2(50 cm^3) is added. Finally the solution is filtered to eliminate Et_3NHCl, dried over $MgSO_4$ and evaporated to dryness in high vacuum to give 0.7 g of an orange oil. (Yield 85%).

ELECTROCHEMISTRY

The cyclic voltammogram (c.v.) of the monomer (I) displays the typical nitroxide reversible 1-electron oxidation at +0.78 V vs $Ag^{0/+}$ and an irreversible oxidation due to the pyrrole ring at E_p^a +1.56 V (Fig. 1).

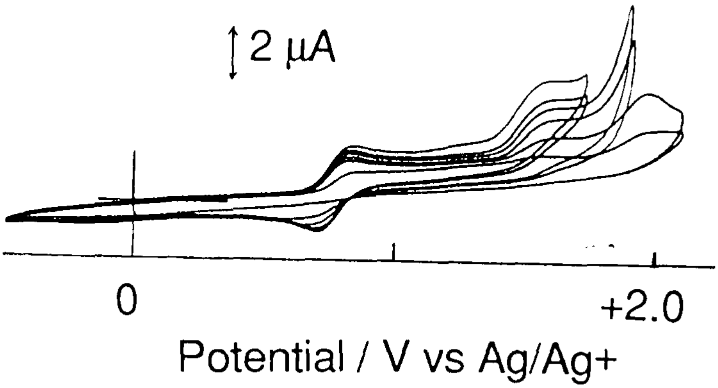


FIGURE 1 C. V. (200 mVs^{-1}) of **I** (5 mM) in MeCN/0.1M TBAT. Pt (0.002 cm^2). Cycles #1-2, 3-4, and 5-6 have anodic limits (resp.):+1.7, +1.9 and +2.1 V vs $Ag^{+/0}$.

The pyrrole oxidation occurs at a higher potential than pyrrole itself due to electrostatic interactions with the oxoammonium group ($>N=O^+$) of the TEMPO moiety. Continuous cycling to successively higher potential leads only to a reduced overall current, suggesting that the oxidized compound forms an insulating (passivating) layer on the electrode surface. There is only a plateau-like feature at +0.8V due to oxidation of dissolved I either occurring at the layer/electrolyte or at the layer/electrode interface. After rinsing the electrode and transferring it to monomer-free MeCN we observe (at a much more sensitive current scale) a reversible redox process due to the nitroxide group at $E^{0'}$ +0.93 V (ΔE_p= 20 mV at 25 mVs^{-1}) as shown in Fig. 2(a).

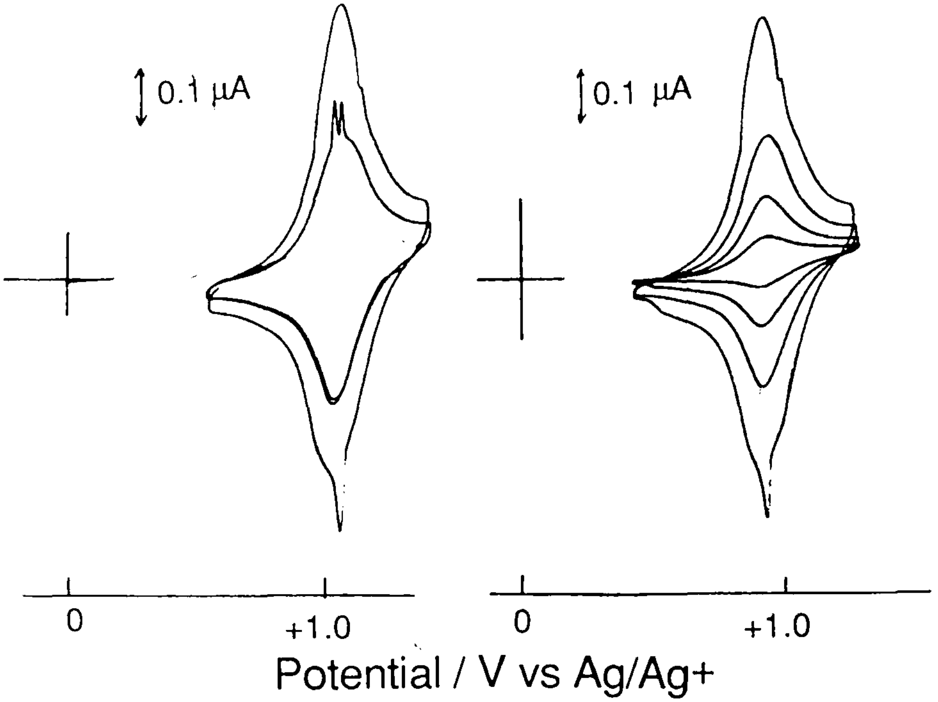


FIGURE 2 (a) C. V. (100, 200 mVs^{-1}) of a monolayer coating of I in MeCN/0.1 M TBAT. (b) Scan rates 25, 50, 100, 200 mVs^{-1}.

The peak separation and linear scan-rate dependence (Fig. 2(b)) confirm that the redox process is surface-confined. However, the very low amount of charge passed during the oxidation is consistent with monolayer coverage (0.5 nmol cm^{-2}). Finally, it is interesting to note the unusual spikes in c.v.s recorded at high scan rates, e.g. the spike at ca +1.0 V on the cathodic scan at 200 mVs^{-1} in both Fig 2 (a) and (b). We believe that these spikes are caused by the sudden discharge of redox active groups (such as short pyrrole segments isolated from the electrode) at potentials removed from their equilibrium potential, sometimes called "charge-trapping" peaks. Thus charge from the pyrrole segments may be ferried to the electrode via the nitroxide groups. Similar phenomena have been suggested for use in data storage devices in molecular electronics. Alternatively, the spikes may be due to the difficult ingress and egress of ions into the compact monolayer.

CONCLUSIONS

The new pyrrole-TEMPO monomer (I) is oxidized at Pt electrodes in MeCN to from a monolayer coating on the electrode surface which has the ability to trap charge.

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REFERENCES

1. F. MacCorquodale, J. A. Crayston, J. C. Walton and D. J. Worsfold, Tetrahedron Letters, 31, 771 (1990).
2. J. A. Crayston, C. Kakouris and J. C. Walton, Synth. Metals, 48, 65 (1992).
3. J. A. Crayston, C. Kakouris and J. C. Walton, Mag. Res. Chem., 30, 77-80 (1992).
4. J. A. Crayston, C. Kakouris and J. C. Walton, in preparation.
5. C. Alexander, W. J. Feast, R. H. Friend and L. H. Sutcliffe, J. Mater. Chem., 2, 459 (1992), and references therein.
6. P. Bauerle and K.–U. Gaudl, Synth. Metals, 41-43, 3037(1991).
7. R. Mirrazaei, D. Parker and H. S. Munro, Synth. Metals, 30, 265 (1989).
8. J. Grimshaw and S. D. Perera, J. Electroanal. Chem., 278, 287 (1990).
9. J. A. Crayston, A. Iraqi, and J. C. Walton, manuscript in preparation.
10. See for example: A. Iraqi, M. Watkinson, J. A. Crayston and D. J. Cole-Hamilton, J. C. S. Chem. Commun. 1991, 1767.
11. (a) S. Cosnier, A. Deronzier and A. Llobet, J. Electroanal. chem., 280, 213 (1990). (b) For a recent review of pyrrole derivatives see D. Curran, J. Grimshaw and S. D. Perera, Chem. Soc. Rev., 20, 391 (1991).
12. (a) P. Audebert and G. Bidan, J. Electroanal. Chem., 238, 183 (1987). (b) P. Audebert, G. Bidan and M. Lapkowski, J. Electroanal.Chem., 219, 165 (1987). (c) A. B. Kon, J. S. Foos and T. L. Rose, Chem. Mats. 4, 416 (1992).
13. (a) S. Cosnier, A. Deronzier and J. C. Moutet, J. Electroanal. Chem., 193, 193 (1985); (b) J. G. Eaves, H. S. Munro and D. Parker, Inorg. Chem., 26, 644 (1987).
14. (a) C. F. Shu and M. S. Wrighton, Am. Chem. Soc. Symp. Ser. 378, 408 (1988). (b) P. Bauerle and K.–U. Gaudl, Adv. Mats, 2, 185 (1990).
15. G. R. Clemo and G. R. Ramage, J. Chem. Soc., 1931, 49.