

## The Modification of Electrodes with Poly(4-vinyl-4',4''-dibromotriphenylamine)

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The synthesis of the novel polymer poly(4-vinyl-4',4''-dibromotriphenylamine) is described along with the properties of modified electrodes based on this polymer which are shown to mediate the oxidation of carboxylate anions.

The uses of the cation radical of 4,4',4''-tribromo-triphenylamine (**1**) in bringing about a wide variety of homogeneous oxidations of organic compounds have been well documented,<sup>1</sup> including the oxidation of carboxylate anions.<sup>2</sup> A particular virtue is that the cation radical is electrochemically regenerable and may therefore be used in catalytic amounts. In this note we describe the synthesis of the related polymer, poly(4-vinyl-4',4''-dibromotriphenylamine) (**2**) and show that this, when coated onto platinum electrodes, may be electrochemically oxidised and the coat used to mediate electron transfer from carboxylate anions. Such electrodes may provide a more attractive means of performing the oxidations previously carried out with the cation radical of (**1**), since separation problems are avoided in a heterogeneous system, and given appropriate optimisation<sup>3</sup> catalytic efficiencies may be greater. Furthermore, since oxidation produces an intensely blue-coloured coat (of cation radicals), they may find application in electrochromic displays.

The polymer was synthesised in the following manner. The monomer 4-vinyl-4',4''-dibromotriphenylamine was obtained *via* a standard Wittig reaction on the corresponding aldehyde which, in turn, was obtained by bromination of 4-(diphenylamino)benzaldehyde. Bromination of the aldehyde requires carefully controlled conditions and full details will be presented elsewhere.<sup>4</sup> The polymer (**2**) was obtained in essentially quantitative yield by cationic polymerisation using tris-(*p*-bromophenyl)ammonium hexafluorophosphate ( $10^{-4}$  M) in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$ .

Stable polymer coats with good adhesion characteristics were prepared by evaporation of a small quantity of a solution of (**2**) from a platinum foil. In a typical experiment a solution (7.5  $\mu\text{l}$ ) containing 6 mg of (**2**) in  $\text{CH}_2\text{Cl}_2$  (5 ml) was coated onto a small piece of platinum foil (*ca.*  $4 \times 4$  mm). Solvent was allowed to evaporate off and the electrode left to dry. The electrode was then warmed to  $90^\circ\text{C}$  in an oven for about 30 min. Cyclic voltammograms were taken in acetonitrile containing tetra-*n*-butylammonium perchlorate ( $0.1 \text{ mol dm}^{-3}$ ) as background electrolyte. Figure 1 shows a typical voltammogram obtained at a scan rate of  $20 \text{ mV s}^{-1}$ . The initial anodic scan produces a voltammogram very different from the second and subsequent scans which are essentially identical (showing negligible desorption of the polymer in either its oxidised or reduced states) and display a sharp, approximately Gaussian peak at 1.18 V (*vs.* Ag/AgCl). The shape of this peak is indicative of an electrochemically reversible one-electron

oxidation of an immobilised species and Tafel analysis of the initial portion of the curve produces slopes close to 60 mV. Quantitative e.s.r. measurements showed that the coat was fully converted into cation radicals during the oxidation. The dependence of peak current on scan rate was found to change from direct to square root as the scan rate was increased, indicating that at higher scan rates the rate of charge transfer is

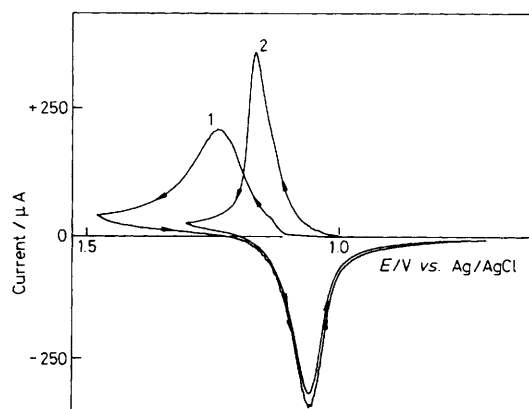


Figure 1. Cyclic voltammogram showing the first 2 potential cycles of a polymer-coated electrode in  $0.1 \text{ mol dm}^{-3}$  tetrabutylammonium perchlorate-acetonitrile. Scan rate:  $20 \text{ mV s}^{-1}$ .

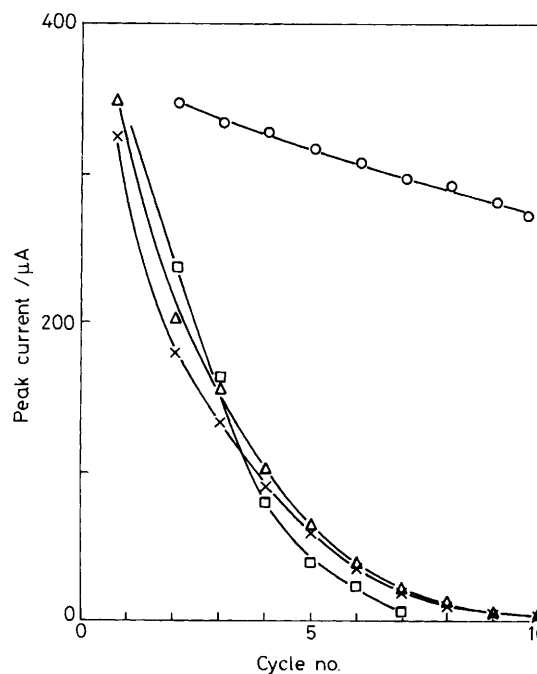
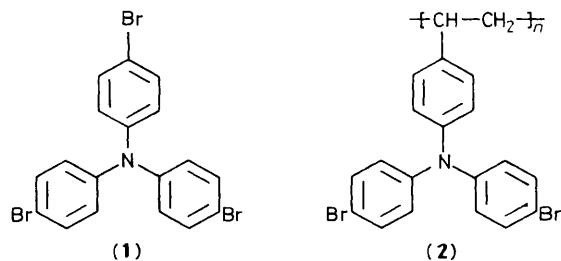
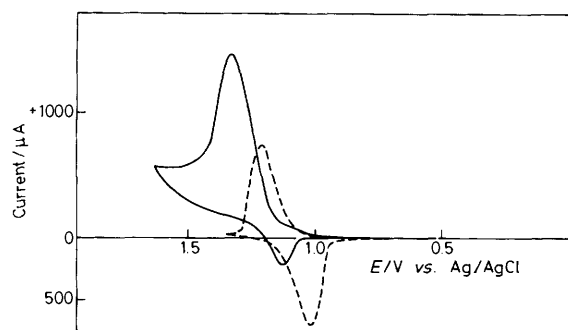


Figure 2. The stability of the coated electrodes to potential cycling in the presence of different anions:  $\circ$   $\text{ClO}_4^-$ ;  $\times$   $\text{PF}_6^-$ ;  $\square$   $\text{BF}_4^-$ ;  $\triangle$   $\text{SbF}_6^-$ .





**Figure 3.** Cyclic voltammogram in (a) the presence and (b) the absence of  $0.025 \text{ mol dm}^{-3}$  tetrabutylammonium acetate. Scan rate:  $50 \text{ mV s}^{-1}$ .

controlled by the rate of diffusion of counter-ions into the coat. It was found that the nature of the counter-ion produced a dramatic effect on the stability of the coats to potential cycling. If the anions  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ , or  $\text{SF}_6^-$  were used then essentially complete desorption of the coat occurred within 6 cycles whereas with  $\text{ClO}_4^-$  the coats were virtually indefinitely stable (Figure 2). This may point to an unusual degree of organisation within the polymer coat. In particular if the polymer adopts a helical conformation then 'stacking' of the pendant groups is possible and this would be especially sensitive to the nature of the anions.<sup>5</sup> The existence of a significant degree of ordering in the coat was further confirmed by differential scanning calorimetry measurements on the polymer which showed an appreciable endotherm superimposed on a glass transition ( $166^\circ\text{C}$ ) indicating some crystallinity in the polymer.

The electrocatalytic properties of the modified electrode were examined by studying the oxidation of carboxylate anions. The direct electron transfer from  $\text{RCO}_2^-$  to the electrode is a very slow process and considerable over-

potentials must be applied.<sup>6</sup> This results in working potentials close to that for the discharge of the solvent. The cation radical of (1) has been shown<sup>2</sup> to be an effective mediator for the oxidation of carboxylates. Figure 3 shows a cyclic voltammogram obtained in the presence of  $2.5 \times 10^{-2} \text{ mol dm}^{-3}$  tetrabutylammonium acetate. The anodic peak is enhanced compared to that obtained in the absence of acetate and the cathodic peak diminished; this is indicative of an electrocatalytic oxidation of the acetate ions. However, prolonged cycling showed a progressive reduction in the size of the anodic peak current indicating degradation of the coat, presumably by reaction with the methyl radicals produced as intermediates in the oxidation reaction. Nevertheless we believe that in the wide variety of cases<sup>1</sup> where the oxidation is 'clean,' modified electrodes based on (2) will find considerable application.

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## References

- 1 W. Schmidt and E. Steckhan, *Angew. Chem.*, 1978, **90**, 717; 1979, **91**, 850, 851; *J. Electroanal. Chem.*, 1979, **101**, 123; *Chem. Ber.*, 1980, **113**, 577; C. R. Jones, *J. Org. Chem.*, 1981, **46**, 3370; M. Ploten and E. Steckhan, *Tetrahedron Lett.*, 1980, **21**, 511; S. Dapperfield and E. Steckhan, *Angew. Chem.*, 1982, **94**, 785; D. J. Bellville, D. D. Wirth, and N. L. Bauld, *J. Am. Chem. Soc.*, 1981, **103**, 718; V. Yu. Atamayuk, V. G. Koshenko, and V. D. Pokhodenko, *Zh. Org. Khim.*, 1980, **16**, 1901; P. Martigny and J. Simonet, *J. Electroanal. Chem.*, 1980, **111**, 133; K. Hando and S. K. Handoo, *Indian J. Chem., Sect. B*, 1982, **21**, 270.
- 2 W. Schmidt and E. Steckhan, *J. Electroanal. Chem.*, 1978, **89**, 215.
- 3 W. J. Albery and A. R. Hillman, *J. Electroanal. Chem.*, 1984, **170**, 27.
- 4 A. Ledwith and I. I. Abu-Abdoun, to be published.
- 5 J. Kommandeur, *Nouv. J. Chim.*, 1985, **9**, 341.
- 6 O. Hammerich and V. D. Parker, *Adv. Phys. Org. Chem.*, 1984, **20**, 101.