The Electrochemical Oxidation of Poly(*N*-vinylcarbazole) Films

Frederick J. Davis, Harry Block, and Richard G. Compton*

Department of Inorganic, Physical and Industrial Chemistry, The University of Liverpool, P.O. Box 147, Donnan Laboratories, Grove Street, Liverpool L69 3BX, U.K.

The potentiostatic anodic oxidation of thin coats of poly(*N*-vinylcarbazole) on platinum electrodes, which produces electrically conductive polymers, is shown to involve cross-linking of the polymer chains through the oxidation of up to 50% of the carbazole moieties in the coat, followed by rapid dimerisation of the resulting pendant carbazole cation radicals; this, in turn, is followed by a further reversible 2-electron oxidation of the resulting dimeric carbazole entity.

It is well known that the chemical doping of poly(*N*-vinylcarbazole) (PVCz), for example by oxidation,[1] or by charge transfer complexation with iodine,[2] produces a useful semiconducting material. It has recently been shown[3] that the level of conductivity can be significantly enhanced (up to 6×10^{-4} S cm^{-1}) by employing electrochemical oxidation of PVCz in thin films coated onto a platinum electrode. Apart from the intrinsic interest in conducting polymers, oxidised PVCz finds specific application in electroluminescent devices[4,5] and, as coats on optically transparent electrodes, in electrochromic displays.[6—9] We report here the chemical changes involved in the electrochemical oxidation of films of PVCz on platinum.

Stable polymer coats with good adhesion characteristics were prepared by evaporation of a small quantity of a solution of PVCz from a platinum foil. In a typical experiment a solution (5 μl) containing PVCz (5—7 mg) in toluene–cyclohexanone (1 : 1 by volume; 5 ml) was coated onto a small piece of platinum foil (*ca.* 7 × 7 mm). The solvent was then removed *in vacuo*. This coat was then covered with a drop of acetonitrile and left to dry for about 10 min. The electrode was then warmed gently (to 90 °C) and cooled prior to immersing in the electrolyte solution. Cyclic voltammograms were taken in acetonitrile containing tetra-n-butylammonium perchlorate (0.1 mol dm^{-3}) as background electrolyte. Figure 1 shows a typical voltammogram which displays a sharp, approximately gaussian peak at 1.35 V (*vs.* Ag/AgCl) and a much broader peak at 1.7 V. The shape of the first peak is indicative of an electrochemically reversible oxidation of an immobilised species. Consistent with this, Tafel analysis of the initial portion of the curve produced slopes close to 60 mV/decade and peak current was found to vary directly with scan rate. On reversing the scan after the second peak (at +2.2 V) negligible current was observed on the return scan. However

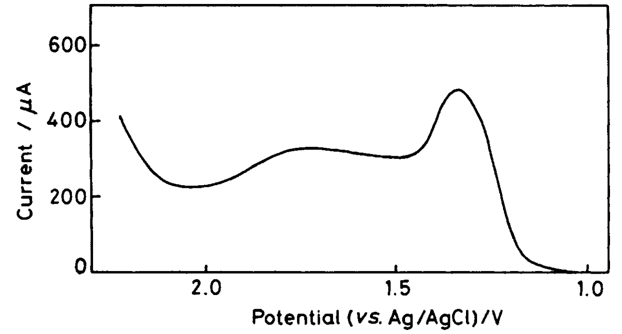
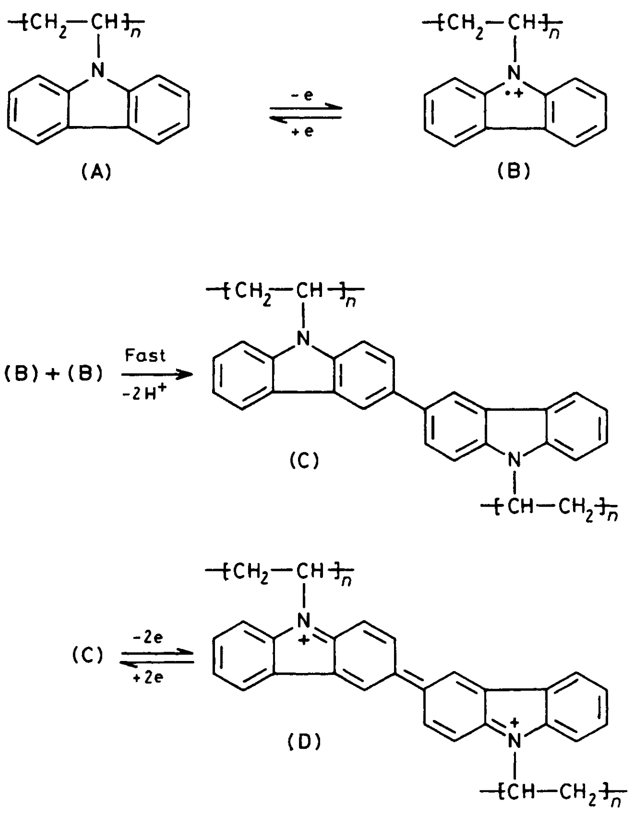


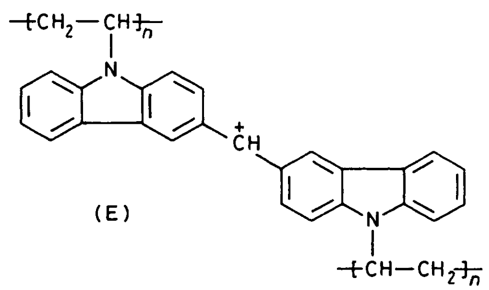
Figure 1. A linear sweep voltammogram for the oxidation of a PVCz coat. The scan rate employed was 50 mV s^{-1}.



Scheme 1

Table 1

Scan rate/mV s^{-1}	Peak potential/V (*vs.* Ag/AgCl) (Mean of several runs)
5	1.16
10	1.19
20	1.21
50	1.35
100	1.35



(E)

on reversing the scan after the first peak (at +1.3 V) a current of about 50% of the forward current was seen using a scan rate of 100 mV s^{-1}. Experiments in which the potential was stepped repeatedly between 0.6 and 1.25 V showed that in the initial forward step, a charge corresponding to 0.85 electrons per mol of carbazole moiety was passed. However on reversing the potential from 1.25 to 0.6 V only half this number of electrons were transferred. Any number of subsequent steps in either direction passed charges corresponding to half the initial number of electrons passed.

It is attractive to interpret these observations in terms of the simple formation of the carbazole cation radical [(B) in Scheme 1] and indeed, symmetrical e.s.r. signals (ΔH_{pp} *ca.* 3.8 G; 1 G = 10^{-4} T) were observed in films produced by oxidation at 1.25 V. However, quantitative e.s.r. measurements showed that the free radical was only a minor component of the film (*ca.* 10%) and it is well established[10] that the cation radical of the carbazole monomer very readily dimerises, producing a 3,3′-bicarbazolyl which is more easily oxidised than the parent carbazole. We therefore suggest that the first peak corresponds to *ca.* 50% of the pendant carbazole units undergoing oxidation [to (B)] followed by rapid dimerisation [to (C)] facilitated by fast charge migration and further oxidation [to (D)]. The reason that not all the carbazole moieties undergo oxidation at 1.2 V is that the following reaction causes the oxidation to occur at lower potentials than oxidation leading to carbazole cations in an unsuitable orientation for dimerisation. Consistent with this the potential of the first peak shows a systematic variation with scan rate not inconsistent with an ECE process (see Table 1). The potential experiments described above can be understood in terms of the formation of (D) from (A) on the initial step and the interconversion between (C) and (D) on subsequent steps.

During the second wave the green product formed during the first wave is replaced by an intense blue colouration which suggests that the wave is due to the formation of the dicarbazolylmethyl cation (E),[11,12] where the -$\overset{+}{C}$H- bridge has been derived from the solvent as has been observed by Partridge[4] from the chemical oxidation of PVCz. XPS and i.r. measurements show that both waves are associated with the uptake of ClO_4^- from solution. Experiments in which ClO_4^- in the background electrolyte was replaced by BF_4^- or PF_6^- produced no significant changes in the transients seen on stepping from 0.6 to 1.25 V. This suggests that counter ion movement in the film is rapid and thus is implicit in the reversible character of the first peak. Facile movement in the film is also clearly required by the fact that *ca.* 50% of the carbazole units become dimerised (either as cross-links or as intra-chain links). Thus this degree of oxidation is substantially higher than has hitherto been obtained by oxidation using chemical methods,[1] where a value of a few percent is typically the most that can be obtained, and it is probable that this enhanced oxidation is the cause of the observed improved conductivity of electrochemically doped films.

We thank M. Gower, R. Turner, and G. R. Sealy for preliminary measurements, Prof. A. Ledwith for useful discussions, and the S.E.R.C. for financial support.

Received, 19th April 1984; Com. 562

References

1 H. Block, M. A. Cowd, and S. M. Walker, *Polymer,* 1977, **18**, 781.
2 A. M. Hermann and A. Rembaum, *J. Polym. Sci., Polym. Symp.*, 1967, **17**, 107.
3 H. H. Kanega, Y. Shirota, and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, 1984, 158.
4 R. H. Partridge, *Polymer,* 1983, **24**, 733.
5 R. H. Partridge, *Polymer,* 1983, **24**, 739, 748, 755.
6 A. Desbene-Monvernay, P. C. Lacaze, and J. E. Dubois, *J. Electroanal. Chem.*, 1981, **129**, 229.
7 J. E. Dubois, A. Desbene-Monvernay, and P. C. Lacaze, *J. Electroanal. Chem.*, 1982, **132**, 177.
8 P. C. Lacaze, J. E. Duboise, A. Desbene-Monvernay, P. L. Desbene, J. J. Basselier, and D. Richard, *J. Electroanal. Chem.*, 1983, **147**, 107.
9 A. Desbene-Monvernay, P. C. Lacaze, J. E. Dubois, and P. L. Desbene, *J. Electroanal. Chem.*, 1983, **152**, 87.
10 J. F. Ambrose and R. F. Nelson, *J. Electrochem. Soc.*, 1968, **115**, 1159.
11 P. J. Bruck, *J. Org. Chem.*, 1970, **35**, 2222.
12 P. J. Bruck, A. K. Ledwith, and A. C. White, *J. Chem. Soc. B*, 1970, 205.

Electronically typeset and printed by Heffers Printers Ltd, Cambridge, England