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The anodic oxidation of poly(N-vinylcarbazole) films

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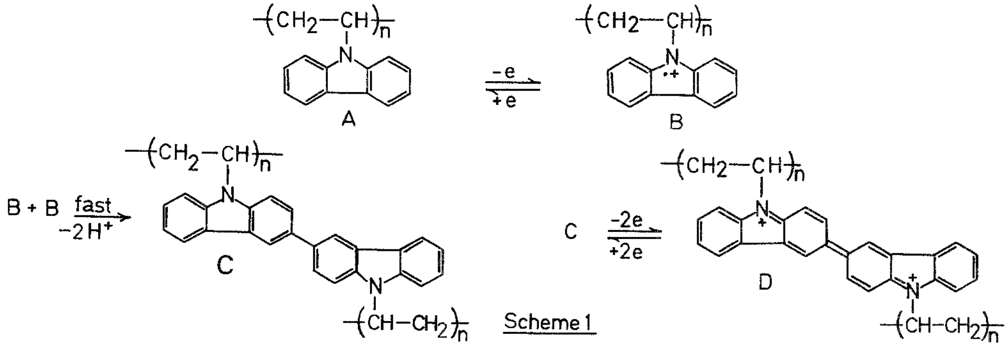
The electrochemical oxidation of thin coats of poly(*N*-vinylcarbazole) on platinum electrodes has been studied. The oxidation is shown to involve initially the cross-linking of the polymer chains through the oxidation of up to 50% of the carbazole moieties in the coat and the dimerization of the resulting pendant carbazole cation radicals. The resulting dimeric carbazole unit is more easily oxidized than the monomer and undergoes a further (reversible) two-electron oxidation. Theory is presented describing the shape of the current–voltage curves obtained, and this together with current transients obtained from potential-step experiments is used to confirm the mechanism and obtain a rate constant of $6 \times 10^{-3}\,M^{-1}\,s^{-1}$ for the dimerization of the carbazole cation radicals within the coat.

1. Introduction

The oxidation of poly(*N*-vinylcarbazole) (PVCz) has received attention both in the study of polymer-modified electrodes [1] and as part of the quest for useful organic metals and semiconductors. Recent work [2] has shown that the electrochemical oxidation of thin coats of PVCz on platinum electrodes produces material of a significantly higher level of conductivity (up to $6 \times 10^{-4}\,S\,cm^{-1}$) than can be obtained either by chemical oxidation, for example using tris-(*p*-bromophenyl)ammoniumyl hexachloroantimonate(V) [3], or through doping PVCz with, for example, iodine so as to produce a charge transfer complex [4]. Oxidized PVCz as a coat on an optically transparent electrode has also been suggested for use in electrochromic displays [5–8].

The purpose of the work described in this paper is the deduction of the chemical changes involved in the electrochemical oxidation of films of PVCz on platinum. It is suggested that the oxidation proceeds as shown in Scheme 1 and that the oxidation of C(→D) occurs at less positive potentials than are required for the oxidation of A(→B) and therefore that the overall reaction involves two electrons per pendant carbazole group oxidized. The current–voltage characteristics of such a scheme are deduced below and shown to be consistant with experiment. Current transients resulting from potential step experiments are also shown to confirm the mechanism. The latter enable the estimation of the switching times likely in any electrochromic device based on PVCz. A preliminary account of some of our results on this system has been published [9].



Scheme 1

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2. Theory

In this section we first consider the behaviour of the current–voltage curves displayed under linear sweep voltammetry by the system postulated in Scheme 1. Secondly, we examine the shape of transients obtained by stepping the potential from a value at which essentially no current flows to a value beyond to the conversion of A(→D).

We may summarize Scheme 1 as

$$\mathrm{A} \underset{+e}{\overset{-e}{\rightleftharpoons}} \mathrm{B} \quad E_1^0$$

$$2\mathrm{B} \xrightarrow{k} \mathrm{C}$$

$$\mathrm{C} \underset{+2e}{\overset{-2e}{\rightleftharpoons}} \mathrm{D} \quad E_2^0$$

where we assume $E_2^0 \ll E_1^0$ and that the kinetics of the chemical step are second-order (*vide infra*). In addition, both electrochemical steps are taken to be reversible.

If the polymer coat is sufficiently thin then, for a given electrode potential, E, we can apply the Nernst equation to the A/B couple throughout the coat:

$$[B] = [A] \exp(\theta) \tag{1}$$

where

$$\theta = (E - E_1^0)\frac{F}{RT} \tag{2}$$

and T = temperature, F = Faraday's constant, R = gas constant. In the particular case of interest to us, namely linear sweep voltammetry, E will vary linearly with time,

$$E = vt + E_{\mathrm{start}} \tag{3}$$

where t is time, v is the scan rate ($\mathrm{V\,s^{-1}}$) and E_{start} is the potential at the start of the sweep, taken to be before any appreciable current flows (i.e. $E_{\mathrm{start}} \ll E_1^0$).

Since the number of carbazole moieties on the coat must remain unchanged we can write

$$[A] + [B] + 2[D] = [A]_0 \tag{4}$$

where $[A]_0$ is the initial concentration of carbazole groups and the concentration of C is assumed close to zero since the second electrochemical step has been assumed to be heavily in favour of D. Under these conditions one D molecule is formed every time two B molecules undergo reaction, and we can write

$$\frac{\mathrm{d}[D]}{\mathrm{d}t} = k[B]^2 \tag{5}$$

From Equations 1, 4 and 5 we find that

$$\int_0^{[D]} \frac{\mathrm{d}[D]}{([A]_0 - 2[D])^2} = \int_0^t \frac{k}{(1 + e^{-\theta})^2}\,\mathrm{d}t \tag{6}$$

if we assume that the potential sweep is started at a potential corresponding to zero current flow. Solving the integrals we obtain

$$\frac{1}{2[A]_0} - \frac{1}{2([A]_0 - 2[D])} = \frac{kRT}{vF}\left[\ln\left(\frac{e^{-\theta_t}(1 + e^{-\theta_s})}{e^{-\theta_s}(1 + e^{-\theta_t})}\right) + \frac{1}{1 + e^{-\theta_t}} - \frac{1}{1 + e^{-\theta_s}}\right] \tag{7}$$

where

$$\theta_s = (E_{\mathrm{start}} - E_1^0)\frac{F}{RT} \tag{8}$$

and

$$\theta_t = (vt + E_{\text{start}} - E_1^0)\frac{F}{RT} \tag{9}$$

Solving Equations 1, 4 and 7 we see that

$$[B] = \frac{0.5}{(1 + e^{-\theta_t})}\left\{\frac{1}{2[A]_0} - \frac{kRT}{vF}\left[\frac{1}{1 + e^{-\theta_t}} - \frac{1}{1 + e^{-\theta_s}} + \ln\left(\frac{e^{-\theta_t}(1 + e^{-\theta_s})}{e^{-\theta_s}(1 + e^{-\theta_t})}\right)\right]\right\}^{-1} \tag{10}$$

Since the total charge, Q, passed by the coat at any time is given by

$$\frac{Q}{Fax} = [B] + 4[D] \tag{11}$$

where a is the area of the coat and x its thickness, we may write for the current I flowing

$$\frac{I}{Fax} = \frac{\mathrm{d}[B]}{\mathrm{d}t} + \frac{4\mathrm{d}[D]}{\mathrm{d}t} \tag{12}$$

Now from Equations 1 and 4 we find

$$[A]_0 = [B](1 + e^{-\theta_t}) + 2[D] \tag{13}$$

and so by differentiation

$$\frac{4\mathrm{d}[D]}{\mathrm{d}t} = 2[B]e^{-\theta_t}\frac{vF}{RT} - 2(1 + e^{-\theta_t})\frac{\mathrm{d}[B]}{\mathrm{d}t} \tag{14}$$

and hence finally

$$\frac{I}{Fax} = 2[B]\frac{vF}{RT}e^{-\theta_t} - (1 + 2e^{-\theta_t})\frac{\mathrm{d}[B]}{\mathrm{d}t} \tag{15}$$

where $[B]$ and $\mathrm{d}[B]/\mathrm{d}t$ may be found using Equation 10. A simple BASIC program was used to evaluate Equation 15 for a range of different values of k, v and $[A]_0$.

Fig. 1 shows typical theoretical current voltage curves for different scan rates for fixed values of k and $[A]_0$ obtained using Equation 15. Notice that Gaussian peaks typical of immobilized species undergoing reversible electrochemistry are obtained throughout. At extremely fast scan rates the behaviour is that expected of a one electron oxidation of an adsorbed species, whilst at extremely

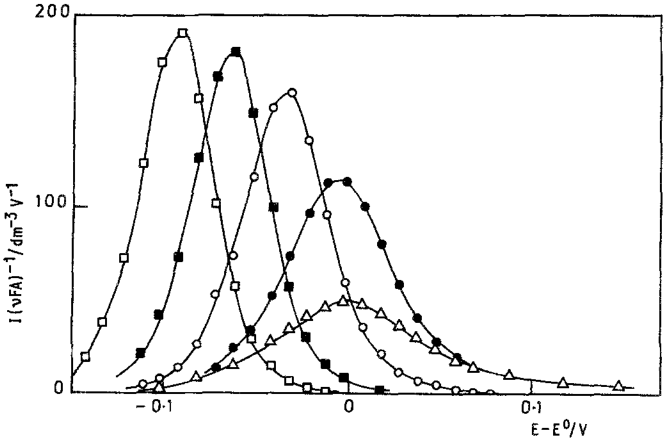


Fig. 1. Theoretical current–voltage curves calculated from Equation 15 assuming $[A]_0 = 5\,\text{mol dm}^{-3}$ and $k \equiv 10^{-2}\,\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$. The current values have been divided by scan rate. The different symbols relate to scan rates as follows: △, 10^{-1} V s^{-1}; ●, 10^{-3} V s^{-1}; ○, 10^{-4} V s^{-1}; ■, 10^{-5} V s^{-1}; □, 10^{-6} V s^{-1}.

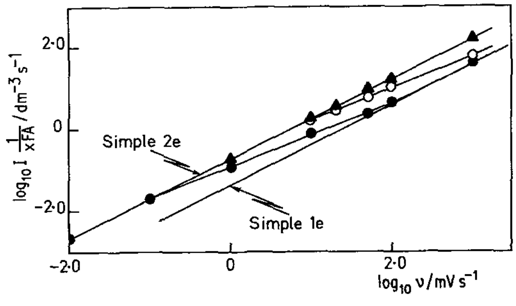


Fig. 2. Dependence of peak current on scan rate calculated assuming $[A]_0$ = 5 mol dm^{-3}; k = 10^2 M^{-1} s^{-1} (▲), 1 M^{-1} s^{-1} (○) and 10^{-2} M^{-1} s^{-1} (●).

slow scan rates the curves are those expected of a simple two electron oxidation of an immobilized species [10]. Thus at extremes of scan rate the peak width, ΔE, at half height is given by

$$\Delta E = 3.53 \frac{RT}{nF} \tag{16}$$

and the peak current, i_p, is

$$i_\mathrm{p}\ \alpha\ n^2 v$$

where $n = 1$ for a very fast scan and $n = 2$ for a very slow scan. The transition between the two extremes is governed by both $[A]_0$ and k. Fig. 2 shows the switchover of the peak current from one to two electron behaviour for different values of k at a fixed $[A]_0$. Likewise, Fig. 3 shows that the peak potential varies from being independent of scan rate (fast scans) to varying by 30 mV per decade (slow scans). Notice that a rate constant can only be obtained from experimental data (with peak current of rate potential) at scan rates corresponding to the switchover from one extreme to the other without knowledge of E_1^0.

We consider how the current transients obtained by stepping the potential from a value corresponding to essentially no current flow to a value beyond that necessary for the oxidation of A to D. Initially a very large current will flow, corresponding to the rapid conversion of A into B, followed by a current flow over a longer timescale governed by the rate at which B turns into C (and hence D). We can thus write

$$\frac{I}{Fax} = \delta(t = 0) + 2\frac{\mathrm{d}[D]}{\mathrm{d}t} \tag{17}$$

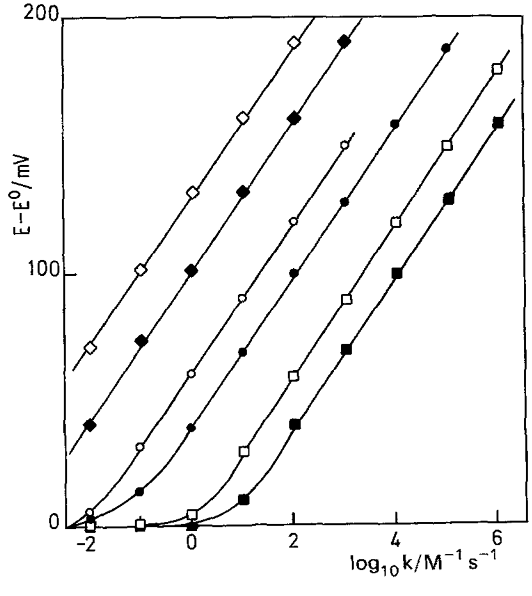


Fig. 3. Dependence of peak potential on scan rate and second-order rate constant calculated assuming $[A]$ = 5 mol dm^{-3}. The scan rates shown are: ◇, 10^{-2} V s^{-1}; ◆, 10^{-1} V s^{-1}; ○, 1 V s^{-1}; ●, 10 V s^{-1}; □, 10^2 V S^{-1}; and ■, 10^3 V s^{-1}.

where $\delta(t = 0)$ signifies the initial short burst of current due to the conversion of A into B. Using Equation 5, simple integration gives

$$\frac{I}{Fax} = \delta(t = 0) + 2k\left(\frac{1}{[A]_0^{-1} + kt}\right)^2 \tag{18}$$

It is apparent that the latter part of the transient may be analysed using the equation

$$I^{-1/2} = (2kFax)^{-1/2}\,([A]_0^{-1} + kt) \tag{19}$$

In particular a value for k may be readily found from the rate of the slope to the interrupt of a plot of $I^{-1/2}$ versus t if the initial concentration of carbazole moieties within the coat, $[A]_0$, may be estimated.

Subsequent potential step experiments will be different from the first in that the cross-linking of the polymer (B → C) is irreversible. Thus transients subsequent to the first will look at the rate of interconversion of C and D. This will be shown to occur on a shorter timescale than the initial transient and is experimentally, of course, the critical timescale that would operate in any practical electrochromic device which would undergo many potential cycles. The kinetics of this C → D charge transfer process within the coat should be described by a simple model in which the charge diffuses randomly among the different redox centres in the coat. The current is then given by [11]

$$\frac{I}{2Fa} = \frac{D_c[A]_0}{(\pi\tau)^{1/2}x}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2/\tau)\right] \tag{20}$$

where D_c is the diffusion coefficient, and $\tau = D_c t/x^2$.

3. Experimental details

3.1. *Preparation of polymer films*

Considerable effort was paid to obtaining stable, relatively even polymer films. The optimal procedure was found to involve evaporation of a small quantity of a solution of PVCz in toluene–cyclohexanone (1 : 1 by volume) from a platinum foil. Typically, 5 μl of a solution containing 5–7 mg PVCz in 5 ml solvent was placed onto a platinum foil ($\sim 7 \times 7$ mm) and the solvent removed *in vacuo*. The coat was then covered with a drop of acetonitrile and left to dry for about 10 min, warmed gently to 90° C and cooled prior to immersing in the electrolyte solution. In this way $\sim 5 \times 10^{-6}$ g of polymer was deposited on the electrode and we estimate the films produced to have a thickness of $\sim 10^{-7}$ m if the density of the deposited film is similar to that of the bulk polymer.

The pretreatment of the electrode by heating was found to be particularly crucial in producing stable polymer films. Dielectric relaxation studies [12] on high molecular weight PVCz have shown that a relaxation assigned to carbozole wagging motion occurs at $\sim 80°$ C. This may explain the need for warming the polymer to above this temperature in that the carbazoles units will be induced into taking up thermodynamically equilibrated positions.

3.2. *Chemicals*

Acetonitrile (Fisons' dried distilled) was refluxed with calcium hydride and then fractionally distilled. Tetrabutylammonium perchlorate (TBAP) (Fluka, purum) was recrystallized once from a mixture of ethanol and petroleum ether. $TBA^+BF_4^-$ and $TBA^+PF_6^-$ (Fluka, purum) were used as received. $TBA^+SbF_6^-$ was prepared by mixing a solution containing 4.2 g of $KSbF_6$ in acetone with a slight excess of TBAP. Precipitated potassium perchlorate was removed by filtration and water was added to the solution to produce an oil from which crystals were formed on scratching. These were recrystallized from an acetone ether mixture and dried under vaccum.

PVCz (Polysciences) was purified by repeated dissolution in dichloromethane followed by precipitation with methanol. Gas permeation chromatography (GPC) indicated a molecular weight, $\bar{M}_w \sim 7 \times 10^5$ (polystyrene equivalents).

3.3. *Techniques*

Electrochemical measurements were carried out using an Oxford Electrodes (Oxford, UK) potentiostat. Potential step experiments were recorded using a Data Labs DL910 (Mitcham, UK) transient recorder. Electrolysis was carried out in acetonitrile containing 0.1 mol dm^{-3} of the appropriate background electrolyte. Oxygen was removed by outgassing with nitrogen (pre-purified by passage over BTS catalyst) prior to electrolysis. A small quantity of alumina was added to the electrolyte solution in an attempt to remove any traces of water remaining. Voltages were measured relative to a silver/silver chloride reference electrode. ESR spectra were recorded on a Bruker ER 200 spectrometer using an *in situ* electolysis cell previously described [13].

4. Results and discussion

Fig. 4 shows a typical voltammogram obtained in acetonitrile containing 0.1 M TBAP as supporting electrolyte. A sharp, approximately Gaussian peak is seen at 1.35 V (versus Ag/AgCl) together with a much broader peak at 1.70 V. The shape of the first peak is concordant with the theory developed above for an immobilized species undergoing oxidation as described in Scheme 1. Consistent with this the peak current was found to vary directly with the scan rate (Fig. 5). The peak potential was also found to depend on scan rate as shown in Fig. 6. The line drawn has the slope expected from the theory given above for the limit of slow scan rates applied to Scheme 1. Reasonable agreement is seen.

Cyclic voltammograms in which the scan was reversed after the second peak (at +2.2 V) showed negligible current flowing on the reverse scan. However, on reversing the scan after the first peak and using a scan rate of 0.1 V s^{-1}, a current of about half of the forward current was seen. This led us to perform potential step experiments in which the electrode was stepped repeatedly between 0.6 and 1.25 V. Typical current transients are shown in Fig. 7. It was found that in the initial forward step a charge corresponding to ~0.85 electrons per mole of carbazole moiety was passed. However, as can be seen from Table 1, only half this number of electrons were transferred in subsequent steps. Any steps in either direction after the first oxidation step passed a charge corresponding to half the initial number of electrons passed. This can only be readily interpreted in terms of Scheme 1: in the initial oxidation A is converted into D (four electrons per molecule of D formed) whereas sub-

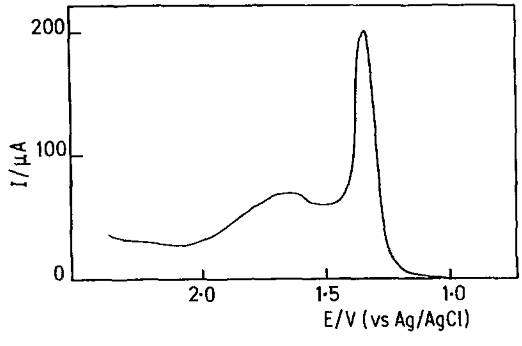


Fig. 4. A linear voltammogram of a PVCz coated platinum electrode.

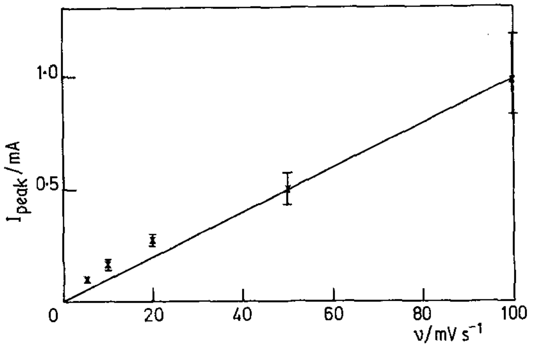


Fig. 5. Variation of peak current with scan rate.

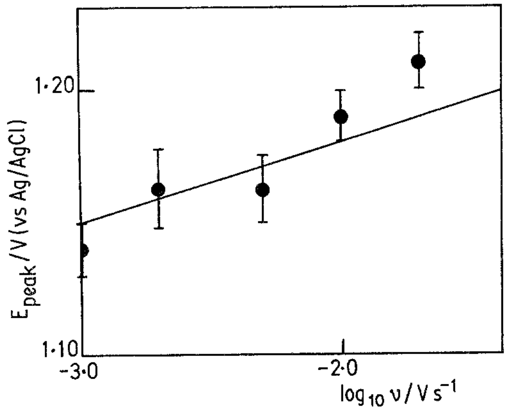


Fig. 6. The dependence of the peak potential on scan rate.

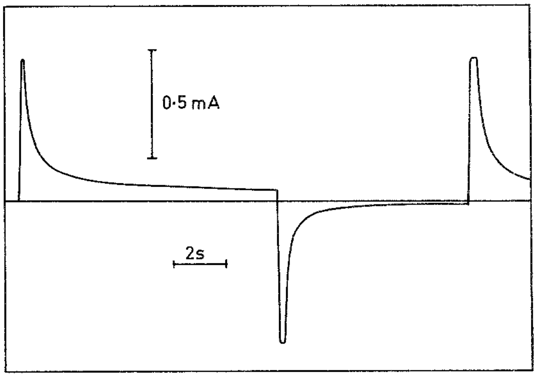


Fig. 7. Current transients obtained by pulsing the electrode between 0.6 and 1.25 V.

sequent steps will only involve the interconversion of C and D (two electrons) because of the irreversibility of the chemical step. The initial current transient occurs over a much longer timescale than the subsequent ones. This again is consistent with Scheme 1: the current response during the first step is controlled after an initial large current due to the conversion of A to B by the rate of dimerization of the cation radicals B whereas in subsequent steps the transient is governed by the rate of interconversion of C and D. The reaction of B to form C is reasonable since the dimerization of the cation radical of carbazole itself to form 3,3′-bicarbazolyl is a well established reaction [14].

ESR measurements showed that a symmetrical, broad (peak-to-peak line width, $\Delta H_{pp} \sim 3.8$ G), single line signal (see Fig. 8) could be observed in the polymer film produced by oxidation at 1.25 V. This would seem to contradict Scheme 1 which implies diamagnetic reaction products. However quantitative ESR measurements showed that the free radical was only a minor component of the film (3–10%). Thus, since radical products are not significant we suggest, on the basis of the charge passed during the oxidation, that the first peak in Fig. 4 corresponds to ~50% of the pendant carbazole groups undergoing oxidation as described in Scheme 1. The reason that not all the carbazole moieties undergo oxidation at 1.25 V is that the following chemical reaction causes the oxidation to occur at lower potentials than oxidation leading to carbazole cations in a unsuitable orientation for dimerization.

If the dimerization in the initial oxidizing potential step obeys second-order kinetics (Equation 5) then, as shown above, the transient should be described by Equation 19. Fig. 9 shows analysis of a typical transient according to this equation. For times greater than ~3 s an excellent straight line is obtained wich allows a mean value of $6.6 \times 10^{-3}\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ for the dimerization rate

Table 1. Charge (coulombs) passed during potential steps between 0.6 and 1.25 V (four separate experiments, average value given below)

Initial oxidative step	*First reductive step*	*Second oxidative step*
2.4×10^{-3}	0.8×10^{-3}	1.2×10^{-3}
2.8×10^{-3}	1.6×10^{-3}	1.1×10^{-3}
2.4×10^{-3}	1.1×10^{-3}	1.6×10^{-3}
2.4×10^{-3}	1.5×10^{-3}	1.4×10^{-3}
2.5×10^{-3}	1.25×10^{-3}	1.3×10^{-3}

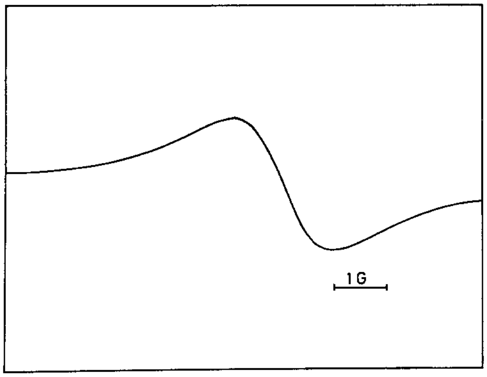


Fig. 8. ESR spectrum obtained from the oxidized polymer coat. The line is centred near $g \sim 2$ and the single broad line is that expected from a 'powder' spectrum of organic radicals.

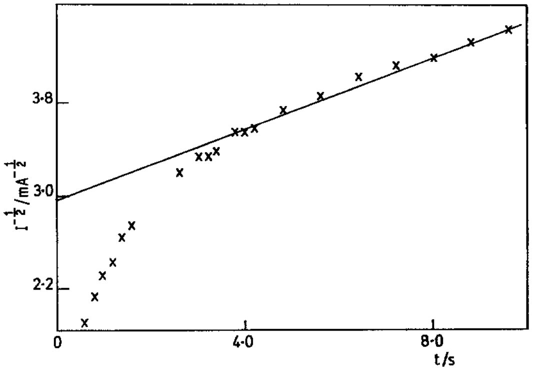


Fig. 9. Analysis of a typical current transient measured during the initial cross-linking of the σ film.

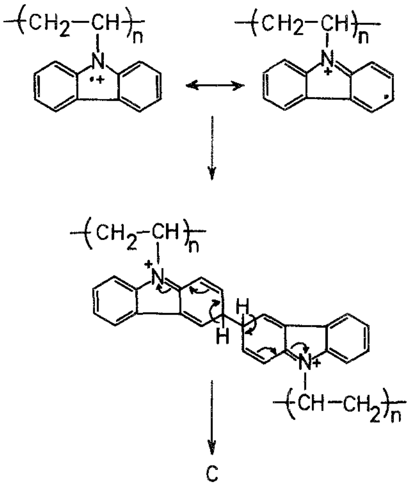
constant to be deduced it it is assumed that the film contains a concentration of carbazole units of $5 \times 10^{-3} \mathrm{mol\,cm^{-3}}$, i.e. assuming the film to have the same density as the bulk material. Table 2 shows rate constants thus calculated for five separate experiments. Also tabulated are values for the film thickness, x, deduced from the intercept of plots such as Fig. 9. Reasonable agreement is seen between different experiments implying that the films are reasonably reproducible. The deviation from linearity at short periods of time in Fig. 9 is due to a contribution to the current from the oxidation of A to B.

The above kinetic analysis indicates a second-order reaction between two cation radicals (B + B). This might be the result of a simple bimolecular step as in Scheme 2. However, an alternative mechanism involves a pre-equilibrium between A and B as shown in Scheme 3. Although we cannot distinguish between the two kinetic schemes it is clear that the rate determining step in either scheme involves two pendant groups coming together (either B + B as in Scheme 2 or B + E as in Scheme 3). This would suggest that the dimerization rate should be dependent on the molecular weight of the polymer. We have found such an effect in the anodic oxidation of films of the related material poly(*N*-vinyl-3-bromocarbazole) for which samples of differing molecular weight were available. This work will be reported separately [15].

We now consider the current transients obtained from potential steps after the film has become cross-linked. As explained in the theoretical section of this paper Equation 20 should be applicable. Fig. 10 shows a plot of current against $(\mathrm{time})^{-1/2}$. At short times (< 1 s) a good straight line is obtained as would be expected from semi-infinite diffusion theory. The deviation at longer times is due to the finite thickness of the coat and can be described by Equation 20. The dashed line shows behaviour calculated from this equation assuming a value for D_c/x^2 of $0.39\,\mathrm{s^{-1}}$. For a film thickness

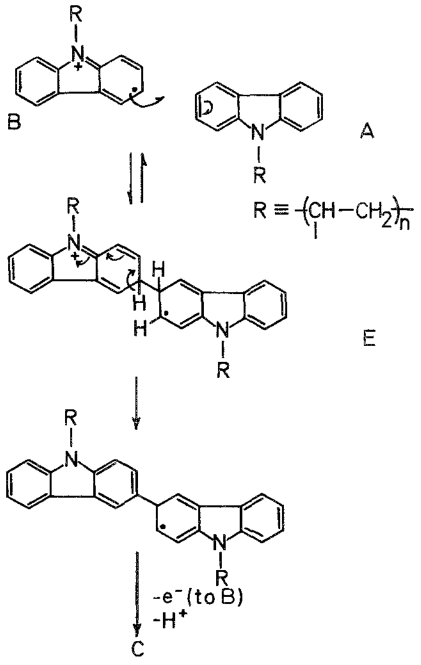
Table 2. Analysis of initial oxidative transients

Run	k *(mol^{-1} dm^3 s^{-1})*	*x (m)*
1	6.0×10^{-3}	7.8×10^{-8}
2	7.5×10^{-3}	7.9×10^{-8}
3	5.6×10^{-3}	1.6×10^{-7}
4	4.1×10^{-3}	2.2×10^{-7}
5	9.8×10^{-3}	2.1×10^{-7}
Average	6.6×10^{-3}	1.5×10^{-7}



Scheme 2

of 10^{-7} m this corresponds to a diffusion coefficient of 3.9×10^{-11} cm^2 s^{-1}. Similar studies by other workers [16] have found values for D_c, in other polymer systems, that range from less than 10^{-14} to 10^{-9} cm^2 s^{-1}. The diffusional process giving rise to our measured diffusion coefficient may be due either to electrons hopping between adjacent oxidized (B) and reduced (C) dimeric units or to charge compensating counter ion diffusion into the coat. We believe that the former explanation is correct since experiments with different background electrolytes (ClO_4^-, BF_4^-, PF_6^-, SbF_6^-) produced no significant changes in the transients seen in either oxidizing or reducing potential steps. This suggests that counter ion movement in the relatively open cross-linked film is rapid compared to charge



Scheme 3

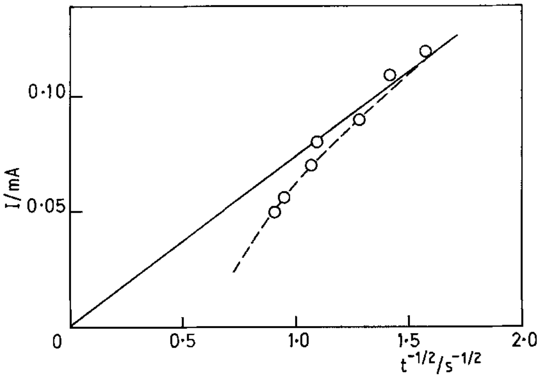
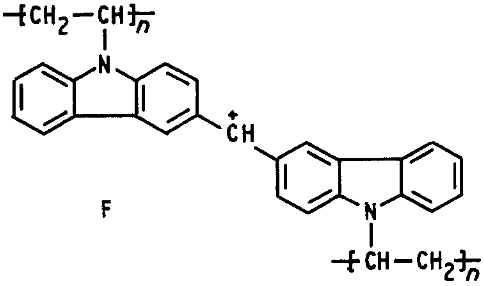


Fig. 10. Analysis of current transients obtained after the film has become cross-linked.

transfer between bicarbazolyl units. Rapid transport of counter ions in the film before cross-linking is implicit in the reversible character of the first peak in the linear sweep voltammogram. The oxidative transients are associated with a green colouring of the film which is bleached on reductive steps. This has led to PVCz being suggested as a possible electrochromic material [5–8]. Clearly from Fig. 7 the switching times of any devices would be of the order of seconds.

We consider now the second broad peak in the voltammogram in Fig. 4. During this wave the green product formed during the first wave is replaced by an intense blue colouration suggesting that the wave is due to the formation of the dicarbazoyl methyl cation (F) [17, 18]



F

where the $-\overset{+}{C}H-$ bridge has been derived from the solvent as has been observed by Partridge [19] during the chemical oxidation of PVCz. It was found once the polymer coat had been taken to potentials corresponding to the formation of the second oxidation peak that it was impossible to electrochemically reduce the polymer coat and the reversible electrochemical behaviour at 1.35 V was lost. It was found that the relative charge passed during the two waves was very sensitive to the method of preparation of the film: in coats made as described above and subjected to pre-swelling by acetonitrile and to warming at 90° C the intensity of the second wave was very low, whereas in unheated, non-swollen coats the second wave could entirely mask the first wave. Given the irreversible nature of the second wave this observation has importance for the fabrication of electrochromic devices based on PVCz.

5. Conclusions

In conclusion, we have shown the following.

1. Stable coats of high molecular weight PVCz can be coated onto platinum electrodes and reproducible electrochemical measurements made.
2. Oxidation at 1.35 V proceeds via the reaction mechanism in Scheme 1 and involves the oxidation of ~ 50% of the carbazole units. This degree of oxidation is substantially higher than has hitherto

been obtained by oxidation using chemical methods [3] where a value of a few per cent is typically the most that can be obtained. It is probable that this enhanced oxidation is the cause of the improved conductivity of electrochemically doped films [2].

3. The oxidation at 1.35 V can be reasonably modelled by an idealized scheme in which the oxidation is described by an EC_2E mechanism for an immobilized species. Reasonable agreement with most experimental parameters is observed with the exception of the peak width at half height which is rather greater than the value of 45 mV predicted theoretically. This is typical behaviour of polymer coats and can be attributed to activity effects [1].

4. Oxidation at ~1.7 V produces an irreversible transformation of the coat and involves the formation of F.

Acknowledgements

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