

Polymer-coated electrodes: cyclic voltammetry and chronoamperometry of non-ideal systems — the anodic oxidation of poly(4-vinyl-triphenylamine) films

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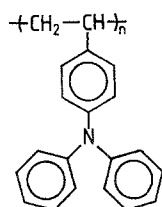
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Theory is presented for the interpretation of cyclic voltammetric and chronoamperometric measurements made on electrodes modified by being covered with an insoluble layer of a polymer containing electroactive pendant groups. It is assumed that the redox behaviour of the film is non-ideal and that the activity coefficients of the components of the redox couple can be reasonably modelled by regular solution theory. In this way non-ideal behaviour is interpreted in terms of a single 'interaction parameter'. It is found that a wide range of cyclic voltammograms for diverse polymer systems reported in the literature can be thus very satisfactorily described. We also report the synthesis of the novel polymer poly(4-vinyl-triphenylamine), PVTPA, and describe and interpret the behaviour of electrodes coated with this polymer during electro-oxidation in acetonitrile solution. Excellent agreement with the regular solution theory is found. Chronoamperometric data for the related polymer poly(4-vinyl-4',4''-dibromotriphenylamine) is also reported and found to give good agreement with the theory.

1. Introduction

The behaviour of electrodes modified by a diverse variety of polymers has been extensively investigated, both as part of the general quest for useful organic metals and semiconductors and, more specifically, in the search for effective electrocatalysts and for practical electrochromic materials [1]. In this paper we report the synthesis of the novel polymer poly(4-vinyl-triphenylamine), PVTPA,

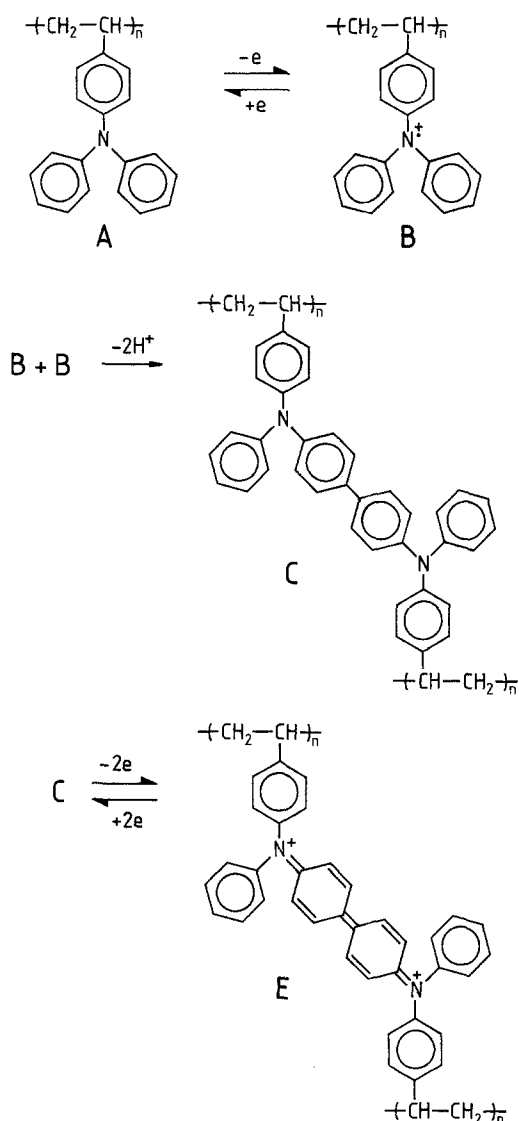


and describe and interpret the behaviour during the electro-oxidation of electrodes coated with the polymer. It is found that cyclic voltammetry and potential step chronoamperometry measurements on these electrodes cannot be interpreted on the basis of 'ideal' behaviour of the polymer coats. Accordingly we develop a theory, based on regular solution theory [2], to model the activity coefficients of the electroactive species and to allow the interpretation of the experimental data in

terms of a single interaction parameter. Excellent agreement between theory and experiment is found.

It will be shown that the electrochemical behaviour of PVTPA can be adequately explained by the processes shown in Scheme 1 from which it can be seen that the initial electron transfer produces the radical cation (B) of the pendant triphenylamine groups. These subsequently combine to form dimeric units (C) which are more readily oxidized than A and so undergo further electron transfer to form the 'quinonoid' structure (E). Overall the process involves two electrons per triphenylamine group. Potential steps subsequent to the initial oxidizing step involve the interconversion of C and E and take place on a different timescale to that of the first step. The current transients resulting from these steps enable the estimation of the switching times likely in any electrochromic device based on PVTPA. The stability conferred on the electrode coating by virtue of the cross-linking during the initial oxidation and the air-insensitivity of the electrode reaction suggests that the material may not be without practical application in such devices.

The tendency of the pendant cation radicals to dimerize within the coat mimics the solution phase behaviour of triphenylamine radical cations [3] which are known to couple with each other forming tetra-

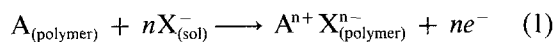


phenylbenzidine [4]. Tri-arylamines with blocked para positions conversely form stable cation radicals upon oxidation and we have shown previously [5] that this behaviour is preserved when the amines are attached to a polymer chain. Thus poly(4-vinyl-4',4''-dibromotriphenylamine) coated onto platinum electrodes can be fully converted into a coat of cation radicals by (reversible) oxidation at 1.18 V (vs Ag/AgCl) in acetonitrile [5]. Further chronoamperometric data relating to this system are presented here and shown to be consistent with our regular solution theory. The behaviour reported in this paper for both polymer systems allows further comparison to be made between cation radicals in solution and those immobilized in a polymer coat.

2. Theory

Consider an electrode coated with a polymer film, of thickness l , containing (immobilized) electroactive centres, A, which, on application of a suitably large oxidizing potential can be converted into the corresponding cations A^{n+} . Since the resulting oxidized film will be electro-neutral the oxidation must be

accompanied by the transport of charge compensating counter ions (X^-) from the solution phase into the coat and this process can be written,



We will consider the behaviour of the film when this process is brought about by both a potential step ('chronoamperometry') and by a potential sweep ('cyclic voltammetry'). In both cases it is assumed that A and A^{n+} form a regular solution in the polymer coat and so the activity coefficients of the two species are given by [2]

$$\ln \gamma_{A^{n+}} = (zw/kT)(1 - x_{A^{n+}})^2 \quad (2)$$

and

$$\ln \gamma_A = (zw/kT)(1 - x_A)^2 \quad (3)$$

where $x_{A^{n+}}$ is the mole fraction of A^{n+} in the coat, w is the interaction parameter and z the number of nearest neighbours around an A or A^{n+} .

2.1. Chronoamperometry

The current to the electrode can be thought of as causing the diffusion of cationic centres from site to site within the film as shown in Fig. 1. This is controlled by Fick's first law, which can be written as [6],

$$J_{A^{n+}} = -D_{id} \frac{d[A^{n+}]}{dx} \left\{ 1 + \frac{d \ln \gamma_{A^{n+}}}{d \ln [A^{n+}]} \right\} \quad (4)$$

where x is the distance measured normal to, and starting from the electrode surface, $\gamma_{A^{n+}}$ is the activity coefficient of A^{n+} and D_{id} is the diffusion coefficient which would be observed under 'ideal' conditions. If a potential step is applied to the film at time $t = 0$ so that all the A at the electrode surface is converted into A^{n+} then the relevant boundary conditions for Equation 2 are,

$$t = 0 \quad 0 < x < l \quad [A] = [A]^0 \quad [A^{n+}] = 0 \quad (5)$$

$$t > 0 \quad x = 0 \quad [A] = 0 \quad [A^{n+}] = [A]^0 \quad (6)$$

$$t > 0 \quad x = l \quad \frac{d[A]}{dx} = 0 \quad \frac{d[A^{n+}]}{dx} = 0 \quad (7)$$

The evolution of the oxidation of the coat is described by the following form of Fick's second law,

$$\frac{d[A^{n+}]}{dt} = - \frac{dJ_{A^{n+}}}{dx} \quad (8)$$

and substitution of Equation 4 into Equation 8 gives,

$$\begin{aligned} (1/D_{id}) \frac{d[A^{n+}]}{dt} = & \left\{ 1 + \frac{d \ln \gamma_{A^{n+}}}{d \ln [A^{n+}]} \right\} \frac{d^2[A^{n+}]}{dx^2} \\ & + \frac{d}{dx} \left\{ \frac{d \ln \gamma_{A^{n+}}}{d \ln [A^{n+}]} \right\} \frac{d[A^{n+}]}{dx} \end{aligned} \quad (9)$$

If we assume that the oxidation proceeds with no

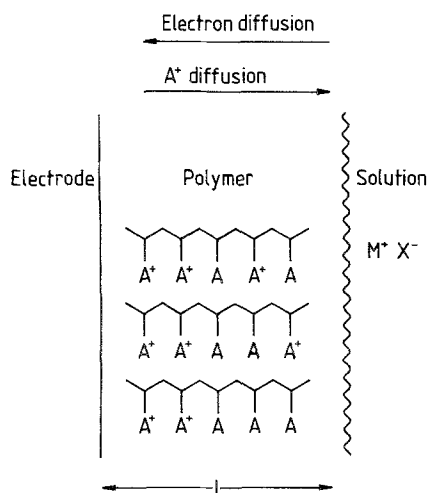


Fig. 1. A schematic representation of the diffusion of cationic centres from site to site within the film of electroactive polymer.

change of volume then

$$x_{A^{n+}} = [A^{n+}]/[A]^0 = a^+ \quad (10)$$

and substituting Equations 2 and 3 into Equation 9 it is found that,

$$(D_{id})^{-1} \frac{da^+}{dt} = \{1 - 2a^+Z(1 - a^+)\} \frac{d^2a^+}{dx^2} - \frac{2Z}{[A]^0} (1 - a^+) \frac{da^+}{dx} \quad (11)$$

where $Z = zw/kT$. Equation 11 is solved subject to the boundary conditions (Equations 5-7) using a simple finite-difference method. The interval $0 < x < 1$ is split into $N + 1$ grid points so that the interval between them is

$$x = 1/N \quad (12)$$

and small intervals of (real) time Δt are considered. We use $a_{j,m}^+$ to denote the value of a^+ at the j th grid

point ($1 < j < N + 1$) and at time, $t = m\Delta t$. We then write,

$$\frac{da^+}{dx_{j,m}} = \frac{(a_{j,m}^+ - a_{j-1,m}^+)}{(\Delta x)} \quad (13)$$

and

$$\frac{d^2a^+}{dx_{j,m}^2} = \frac{(a_{j+1,m}^+ - 2a_{j,m}^+ + a_{j-1,m}^+)}{(\Delta x)^2} \quad (14)$$

The transient behaviour is then computed using,

$$a_{j,m+1}^+ = a_{j,m}^+ + da_{j,m}^+ \quad (15)$$

where the increments are calculated from,

$$da_{j,m}^+ = D_{id} \Delta t \left\{ \{1 - 2a_{j,m}^+Z(1 - a_{j,m}^+)\} \times \frac{\{a_{j+1,m}^+ - 2a_{j,m}^+ + a_{j-1,m}^+\}}{(\Delta x)^2} - \frac{2Z}{[A]^0} (1 - a_{j,m}^+) \frac{\{a_{j,m}^+ - a_{j-1,m}^+\}}{(\Delta x)} \right\} \quad (16)$$

The boundary conditions 5, 6 and 7 take the following form in the computation,

$$\begin{aligned} m = 0 \quad 0 < x < 1 \quad a_{j,0}^+ &= 1, \quad 1 < j < N + 1 \\ m > 0 \quad j = 1 \quad a_{1,m}^+ &= 0 \\ m > 0 \quad j = N + 1 \quad a_{N,m}^+ &= a_{N+1,m}^+ \end{aligned} \quad (17)$$

and the transient current, I_m , is calculated from,

$$I_m = nFA_r D \frac{\{a_{2,m}^+ - a_{1,m}^+\} [A]^0}{(\Delta x)} \quad (18)$$

where F is the Faraday constant and A_r is the area of the electrode. In applying Equation 18 the question arises as to what particular value of D should be used. The basis of this problem can be understood by substituting Equation 2 into Equation 4 which results

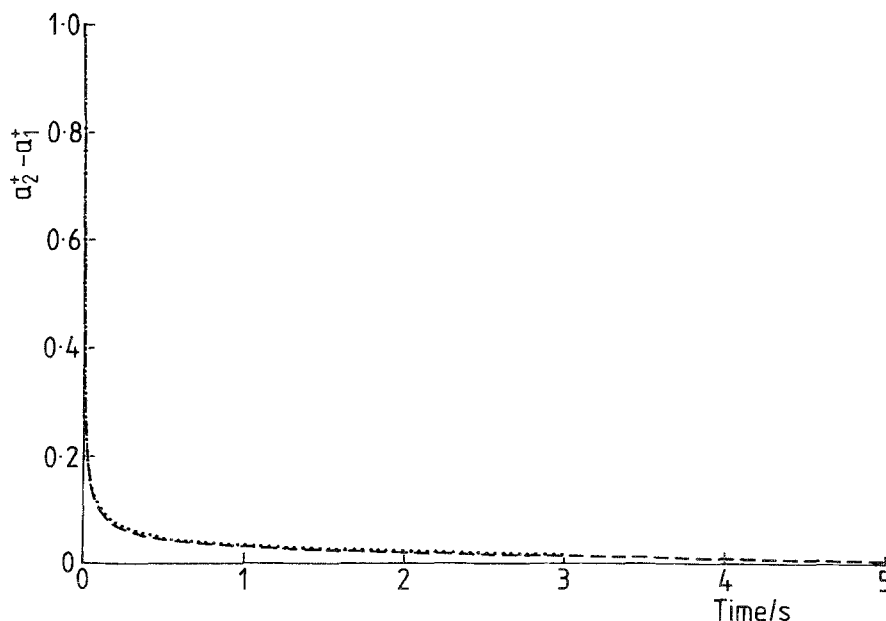


Fig. 2. A comparison of the numerically generated transient for $Z = 0$ (---) with that calculated from analytical theory via Equation 19 (···). Excellent agreement is evident.

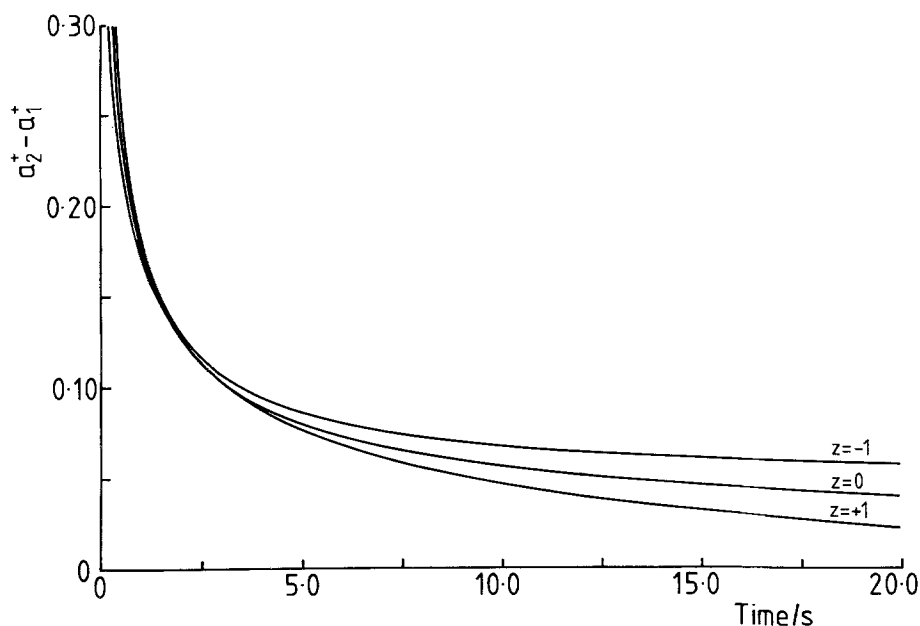


Fig. 3. Numerically generated transients for $Z = 0, 1.0, -1.0$. Positive values of Z correspond to repulsive interactions in the polymer coat, negative values to attractive interactions.

in,

$$J_{A^{n+}} = -D_{id} \{1 - 2Za^+(1 - a^+)\} \frac{d[A^{n+}]}{dx}$$

which clearly shows that repulsive ($Z > 0$) interactions diminish the rate of oxidation of the coat. In applying Equation 18 we take

$$D = D_{id} \{1 - 2Z\langle a^+ \rangle(1 - \langle a^+ \rangle)\}$$

where $\langle a^+ \rangle = 0.5(a_{1,m}^+ + a_{2,m}^+)$, i.e. we use the mean diffusion coefficient over the interval between the first two grid points (the approximation $D = D_{id}$ resulted in anomalies in the computation of the current at short times).

A FORTRAN program was written to deduce the form of the current transients as a function of D_{id} , $[A]^0$, l and Z . When $Z = 0$, i.e. when ideal con-

ditions prevail, an analytical solution is available for Equation 11 [7],

$$I = \frac{nFA_r D_{id} [A]^0}{l(\pi\tau)^{1/2}} \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2/\tau) \right\} \quad (19)$$

where $\tau = D_{id} t/l^2$. Figure 2 shows a comparison of our numerically generated transients with Equation 19 for $Z = 0$, $l = 7.2 \times 10^{-6}$ cm, $D = 7.2 \times 10^{-12}$ cm² s⁻¹, $\Delta t = 0.0001$ s and $[A]^0 = 2.3 \times 10^{-3}$ mol cm⁻³. Excellent agreement is evident and this was found to be the case for a wide range of other values for l , D and $[A]^0$ that were tested. Figures 3 and 4 show transients computed for various values of Z — both attractive ($Z < 0$) and repulsive ($Z > 0$). In these figures the data shown were generated with the following parameters: $l = 10^{-3}$ cm, $D = 10^{-9}$ cm² s⁻¹, $\Delta t =$

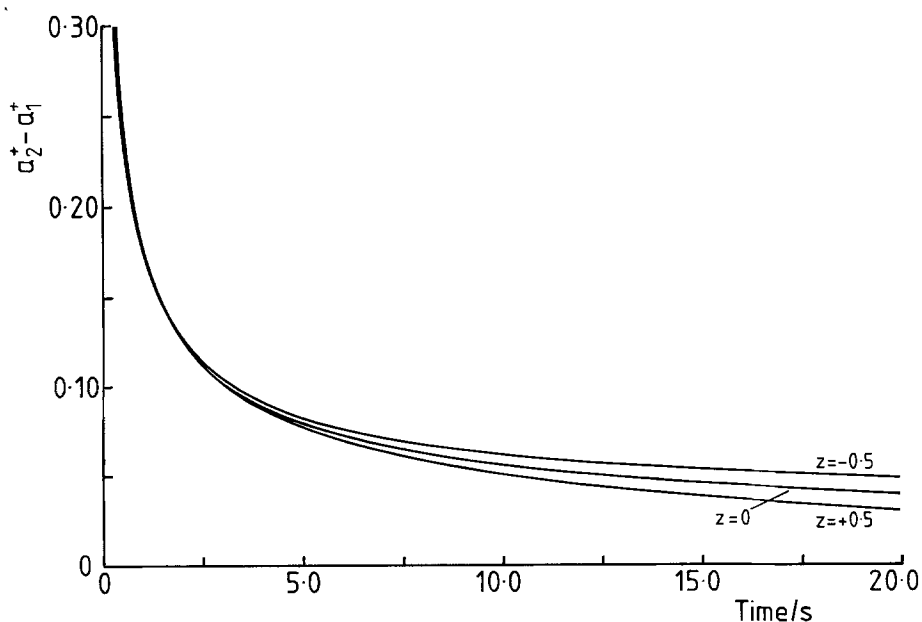


Fig. 4. Numerically generated transients for $Z = 0, 0.5, -0.5$.

0.0001 s and $[A]^0 = 2 \times 10^{-3} \text{ mol cm}^{-3}$. It can be seen that attractive interactions cause an enhanced current to flow at short times and so the oxidation of the coat takes place more rapidly than for an 'ideal' coat. The converse is true for repulsive interactions as predicted above. The amount of charge passed in the transients depicted in Figs 3 and 4 corresponds to the oxidation of only a small percentage ($< 10\%$) of the electroactive groups in the coat. At very long times the transients for the attractive cases were found to fall below those for the repulsive. This is because complete oxidation of the coat occurs sooner in the case of $Z < 0$.

2.2. Cyclic voltammetry

We again consider Reaction (1) and suppose that the electrode reaction is electrochemically reversible. Then writing a for $[A]/[A]^0$ and assuming that the potential is being scanned sufficiently slowly that the composition throughout the coat is controlled by the electrode potential, i.e. that the polymer coat behaves as a 'thin layer cell', we have from the Nernst equation,

$$\gamma_A a / \gamma_{A^+} a^+ = \exp(-\theta) \tag{20}$$

where

$$\theta = (nF/RT)(E - E^0), \tag{21}$$

E^0 being the standard electrode potential for the A/A^{n+} couple. Also

$$a + a^+ = 1 \tag{22}$$

If the initial electrode potential is sufficiently negative that all the pendant groups are effectively in the A form, then the amount of charge, Q , passed at any subsequent time is given by,

$$Q = nFA_r I [A]^0 a^+ \tag{23}$$

The current is therefore given by the following

$$I = \frac{dQ}{dt} = nFA_r I [A]^0 \frac{da^+}{dt} \tag{24}$$

Eliminating a from Equations 21 and 22 we find that,

$$a^+ = \{1 + (\gamma_{A^+}/\gamma_A) \exp(-\theta)\}^{-1} \tag{25}$$

Using Equations 2 and 3 it is readily shown that Equation 24 becomes

$$a^+ = \{1 + \exp(Z(1 - 2a^+)) \times \exp(-\theta)\}^{-1} = f(\theta) \tag{26}$$

The derivative in Equation 23 is now readily evaluated as

$$\frac{da^+}{dt} = f'(\theta)(nF/RT)v \tag{27}$$

where v is the rate at which the voltammogram is scanned ($V s^{-1}$) and $f'(\theta)$ is $df/d\theta$. From Equations 24 and 27 we see that the peak current is proportional to the scan rate and independent of activity effects, although the latter control the shape of the wave. In order to calculate the current as a function of potential the transcendental Equation 26 has to be solved. We proceed as follows. For a selected value of Z and a wide range of values of θ , we calculate $f(\theta)$ as a function of a^+ using Equation 26. Then it is found where this quantity is equal to a^+ and this gives the particular value of a^+ corresponding to those values of Z and θ . The current observed at any potential, θ , can then be deduced from Equations 26 and 27. Typical voltammograms are depicted in Fig. 5 for selected values of Z . Notice that attractive interaction parameters ($Z < 0$) cause a broadening of the voltammetric wave, whereas repulsive parameters induce a narrowing. For $Z = 0$ the expected behaviour of an 'ideal' immobilized surface-species [8] was found, i.e. a peak width, E , at half-height given by

$$E = 3.53 RT/nF \tag{28}$$

and a peak current,

$$i_p \propto n^2 v \tag{29}$$

Equation 28 predicts peak widths about 90 mV at room temperature.

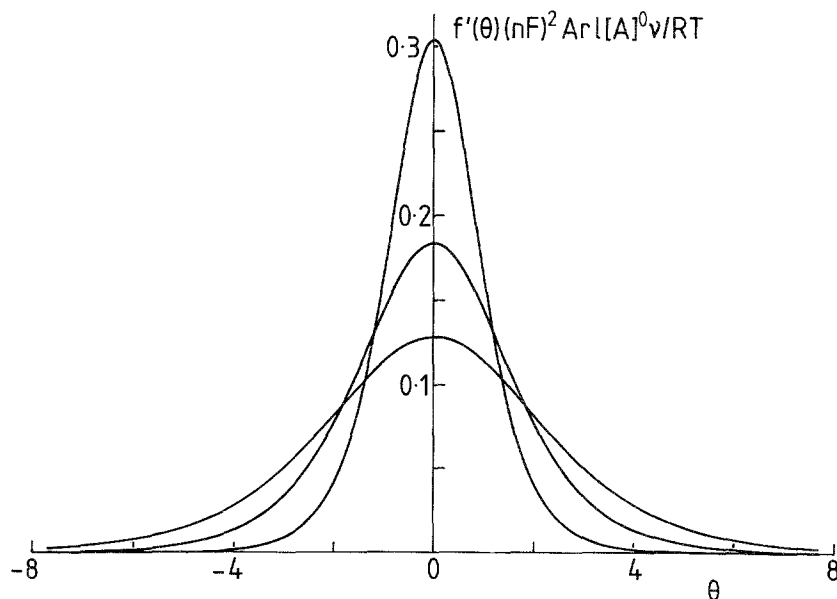


Fig. 5. Typical theoretical linear sweep voltammograms calculated for $Z = -1, 0$ and $+1$.

Table 1.

Polymer	Film preparation	n	Coverage ($10^{-9} \text{ mol cm}^{-2}$)	E_{FWHM} (mV)	Z	Ref.
$\{\text{CH}_2\text{CH}[\text{CONH}(\text{CH}_2)_2(3,4\text{-HOPh})]_{0.41}\text{-}[\text{CH}_2\text{CH}(\text{CO}_2\text{H})]_{0.59}\}_x$	DC	2	0.23	130.39	-5.5	[9]
$\{\{\text{CH}_2\text{CH}(\text{PhCH}_2\text{SCN})\}_{0.7}\text{-}[\text{CH}_2\text{CH}(\text{PhCH}_2\text{O}_2\text{CTTF})]_{0.3}\}_x$	SC	1	214	152.2	-4.4	[10]
$\{\text{CH}_2\text{PhCH}_2\text{-}4',4'\text{bipy}\}^{2+}\text{Cl}_2\}_x$	DE, EP	1	70	152.07	-3.2	[11]
$[\text{CH}_2\text{CH-(pNO}_2\text{-C}_6\text{H}_5)]_x$	DC	1	24.9*	138.85	-2.8	[12]
$\{\{\text{CH}_2\text{CH}(\text{PhCOAq})\}_{0.23}[\text{CH}_2\text{CH}(\text{Ph})]_{0.77}\}_x$	DE	1	1.39	97.93	-0.22	[13]
$\{\{\text{CH}_2\text{CH}(\text{FeCp}_2)\}\}_x$	EP, DC, DE	1	1.2	104.2	-0.40	[14]
$\{\{\text{CH}_2\text{N}(\text{COPhN}_2\text{Ph})\text{CH}_2\}_{0.23}\text{-}[\text{CH}_2\text{NHCH}_2]_{0.77}\}_x$	DC	1	0.45	88.1	+0.60	[15]

DC = dip coating; DE = droplet evaporation; SC = spin casting; EP = electrochemical precipitation; Ph = phenyl; TTF = tetra-thiofulvene; bipy = bipyridyl; Aq = anthraquinone; CP = cyclopentadienyl.

* Apparent no. moles (not coverage).

In order to test the general applicability of our cyclic voltammetry theory we have taken assorted cyclic voltammograms reported in the literature for a diversity of polymer-coated electrodes. These are tabulated in Table 1 together with the method of film preparation, the surface coverage (mol cm^{-2}) and the number of electrons exchanged per pendant group. In each case an excellent fit of the experimental data was found for some selected value of Z . The latter are also reported in Table 1. There is a large range of Z values ranging from the highly attractive to the slightly repulsive. We conclude that the above model is capable of successfully describing the experimentally determined cyclic voltammograms of a wide diversity of polymer-coated electrodes prepared in different ways with varying coverages of polymer.

3. Experimental details

3.1. Preparation of polymer films

PVTPA was synthesized by the following procedure which is to be reported more fully elsewhere [16]. The monomer 4-vinyl-triphenylamine was obtained via a standard Wittig reaction on the corresponding aldehyde which, in turn, was obtained from triphenylamine by reaction with phosphorous oxychloride/dimethylformamide. The polymer was obtained in good yield (35%) by free radical polymerization using AIBN (0.01%) in CH_2Cl_2 at 65°C (sealed tube and water bath) for 22 h. Electrode coatings were produced by evaporation of a small quantity of a solution of PVTPA in dichloromethane from a platinum flag ($4 \times 4 \text{ mm}$) which had previously been carefully polished. Typically $10 \mu\text{l}$ of a solution containing 5 mg of polymer in 5 ml of solvent was used. After evaporation the coat was then covered with a drop of acetonitrile and left to dry. The electrodes were then warmed in an oven for approximately 20 min. We have found previously with other polymer systems [17] that pretreatment of the electrode by heating is

beneficial in producing stable polymer films with reproducible characteristics.

3.2. Chemicals

Acetonitrile (Fison's dried distilled) was dried over 4 \AA molecular sieves before use. Tetrabutylammonium perchlorate (TBAP) (Fluka, purum) was recrystallized once from a mixture of ethanol/petroleum ether and dried in an oven.

3.3. Techniques

Electrochemical measurements were carried out using an Oxford Electrodes (Oxford, UK) potentiostat. Current transients arising from potential step experiments were recorded with a Gould digital storage oscilloscope (model 054000). Electrolysis was carried out in acetonitrile containing 0.1 mol dm^{-3} of TBAP as background electrolyte. Oxygen was removed by outgassing with dry nitrogen (pre-purified by passage over BTS catalyst) prior to electrolysis. Potentials were recorded relative to a saturated calomel electrode.

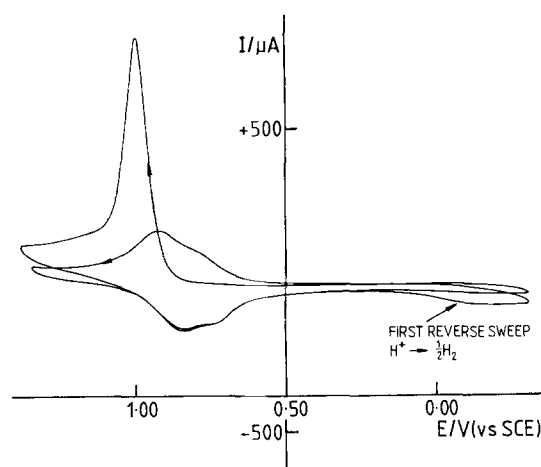


Fig. 6. A cyclic voltammogram for the oxidation of an electrode coated with PVTPA recorded at 100 mV s^{-1} .

Table 2. Charge (coulombs) passed during potential steps between 0.60 and 0.98 V (four separate experiments, slightly differing film thicknesses)

Initial oxidative transient	First reductive step
2.2×10^{-3}	1.1×10^{-3}
4.1×10^{-3}	1.9×10^{-3}
3.3×10^{-3}	1.7×10^{-3}
3.5×10^{-3}	2.0×10^{-3}

4. Results and discussion

Figure 6 shows a typical cyclic voltammogram relating to the oxidation of an electrode coated with PVTTPA recorded at 100 mV s^{-1} . It is apparent that the first cycle involves very different behaviour to that shown in subsequent cycles. In particular the amount of charge passed during the initial cycle may be seen to be approximately twice that passed during the following cycles. This was confirmed in a more quantitative manner by recording the current transients resulting from potential steps between $+0.60 \text{ V}$ and $+0.98 \text{ V}$. Typical transients are shown in Fig. 7. Integration of the transients gave the charge passed during the initial oxidative step and during subsequent oxidative and reductive steps. Representative data are shown in Table 2 from which one may conclude that twice the number of electrons are involved in the first step as compared to the second step. This observation is clearly consistent with the mechanism proposed in

Scheme 1. This suggested mechanism involves the production of protons during the first anodic scan. Evidence for the formation of these comes from the cathodic scan of the initial cyclic voltammogram of Fig. 6 which clearly reveals a reduction wave at about -0.1 V which can be reasonably ascribed to proton reduction [4].

Further evidence in favour of the proposed mechanism is provided by analysis of the shapes of the transients in Fig. 7. In the case of the initial oxidizing transient we have shown elsewhere [17] that if the rate-determining step in the mechanism is the (second order) dimerization of the pendant cation radicals (B-C) then

$$I/FA_r l = \delta(t=0) + 2k(kt + [A]_0^{-1})^{-2} \quad (30)$$

where $[A]_0$ is the initial concentration of triphenylamine moieties within the coat, A_r and l are the film area and thickness, respectively, and k is the rate constant for the dimerization reaction. The term $\delta(t=0)$ signifies the initial short burst of current due to the conversion of A into B.

Equation 30 suggests that analysis of the latter part of the transient should give a linear dependence of $I^{-1/2}$ on t . Figure 8 shows an initial oxidative transient treated in this way. The good straight line behaviour for sufficiently long times supports the choice of mechanism and allows the deduction that the rate constant for dimerization is $1.9 \text{ mol}^{-1} \cdot \text{dm}^3 \text{ s}^{-1}$, if one assumes a value of 3.7 M for $[A]_0$. It is interesting that the corresponding value for the oxidation of the polymer poly(*N*-vinylcarbazole), which reacts via a

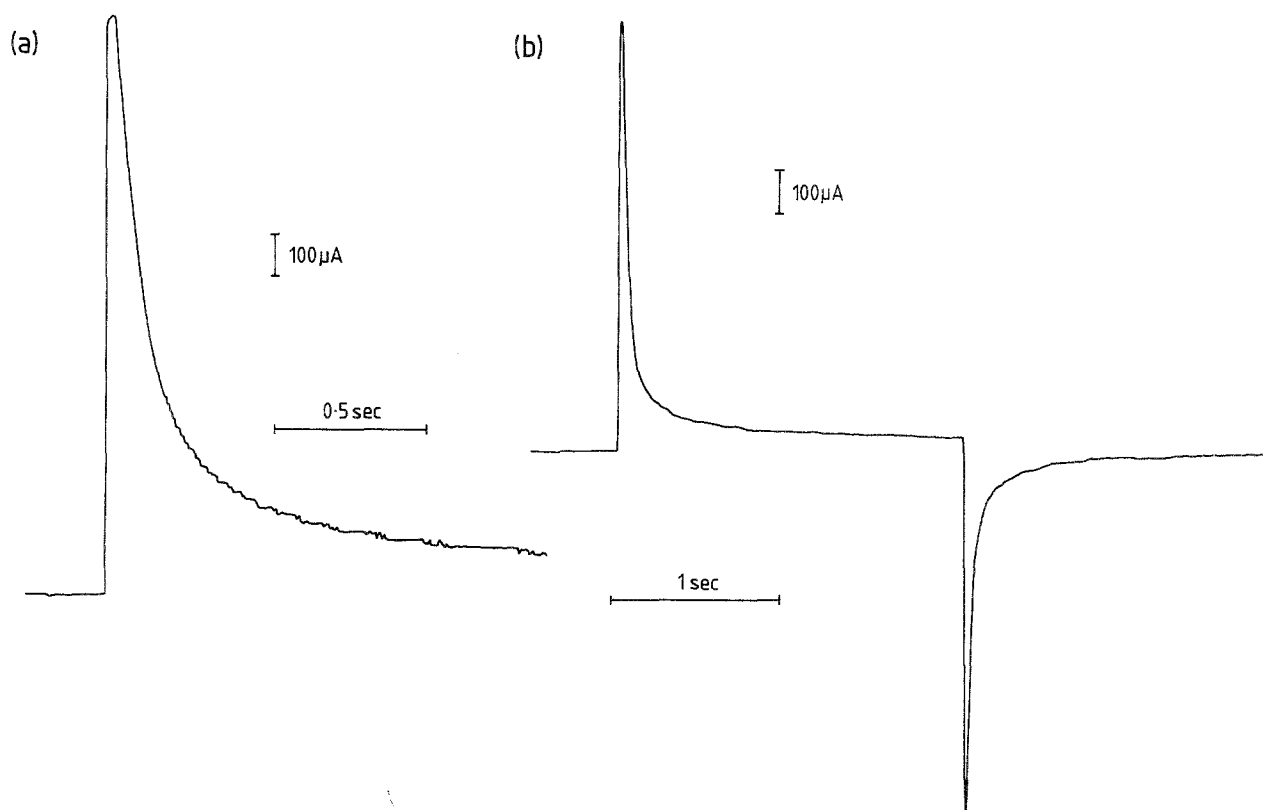


Fig. 7. Current-time transients obtained from potential-step experiments. (a) is the initial oxidative behaviour and corresponds to the conversion of A to E (Scheme 1); (b) is the subsequent oxidation and reduction behaviour and relates to the interconversion of C and E.

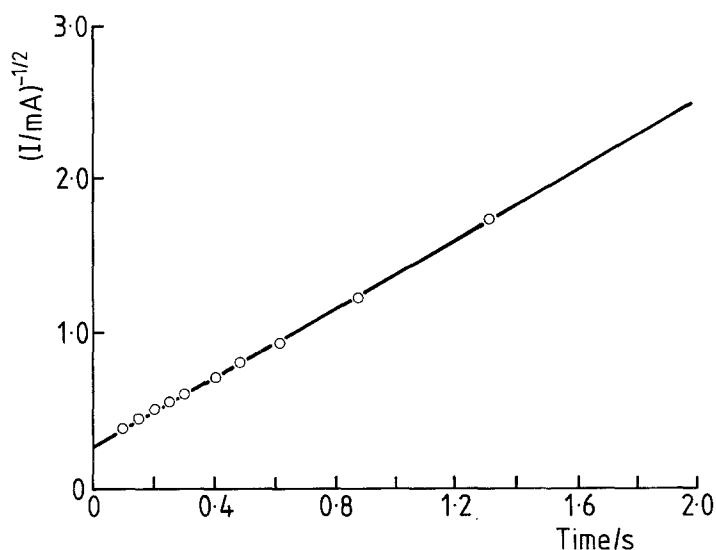


Fig. 8. Analysis of the initial transient shown in Fig. 7a in terms of Equation 30.

mechanism entirely analogous to that in Scheme 1, has been shown to be $6.6 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ [17]. In contrast the dimerization of triphenylamine radical cations in acetonitrile proceeds with a rate constant of $1 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ as compared to 9×10^7 for carbazole radical cations [18]. In general the homogeneous dimerization rate constant for the cation radicals of various substituted triphenylamines is 10^4 – 10^6 times slower than for the corresponding carbazole [3]. This has been attributed to electronic factors: in the amines the phenyl groups are twisted out of plane due to the interactions between hydrogen atoms *ortho* to nitrogen whereas in the carbazoles they are necessarily held planar and this is thought [3, 18] to lead to an increased efficiency of electronic transmission in the latter case. It is obvious that electronic factors are playing no kinetically limiting part in the process described by k for the polymer species where the amine reacts faster than the carbazole. It seems reasonable to ascribe the rate-determining behaviour to motions of the polymer chain bringing the pendant

groups together. We have shown [19] that for the substituted carbazole poly(3-bromo-*N*-vinylcarbazole) k is about $500 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and this material was thought, on the basis of dipole moment data, to be rather more flexible than poly(*N*-vinylcarbazole) which forms rod-like helices. Analogous comments might be made, on the basis of the work presented above, in the context of PVTTPA.

Returning to Fig. 7 we consider next the analysis of transients subsequent to the first oxidizing step. These transients simply look at the interconversion of C and D since the cross-linking of the polymer is irreversible. The subsequent transients occur on a shorter timescale than the initial transient and, of course, represent the critical timescale that would operate in any practical electrochromic device which would undergo many potential cycles. The transient in Fig. 7 cannot be described by the simple model in which the charge diffuses randomly among the different redox centres taken to behave ideally (Equation 19). Instead we apply the transient theory relating to regular solutions

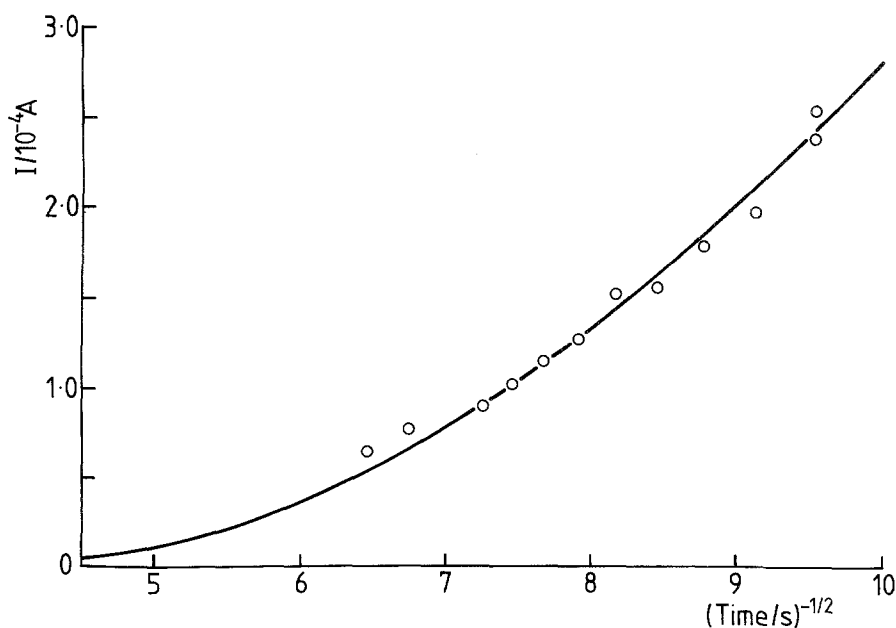


Fig. 9. Potential-step transients such as Fig. 7b are very well modelled by the regular solution theory with a value of $Z = -0.6$ (—).

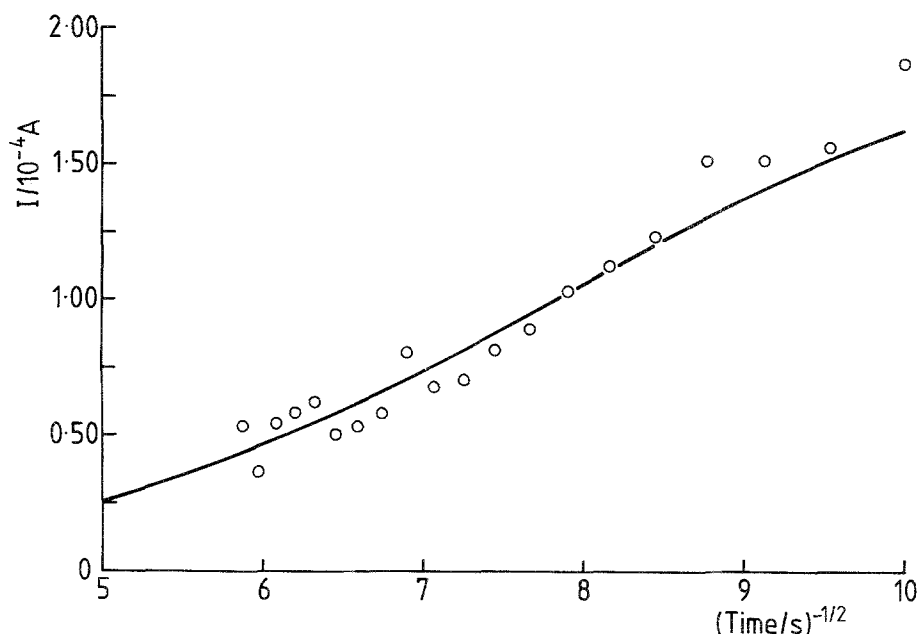


Fig. 10. Analysis of chronoamperometric data for electrodes coated with poly(4-vinyl-4',4''-dibromotriphenylamine) in terms of regular solution theory with $Z = -1.6$.

and described above. Figure 9 shows that the transients are well modelled for $Z = -0.6$. Good agreement between theory and experiment is apparent.

Consideration of the amount of charge passed during both the transients and the cyclic voltammograms suggests that only 30% ($\pm 5\%$) of the monomer units are involved in the cross-linking reaction, from which one may infer that some 70% of the original monomer units are left unchanged during the oxidation. This behaviour differs from that found for polymer-coated electrodes in which charge transfer leads to kinetically stable species, where complete conversion of the coat is invariably observed. The difference may be understood if it is recognized that the charge transfer during the oxidation of the coat leads to the release of protons not all of which are necessarily released from the polymer coat but may protonate the nitrogen atoms in the pendant triphenylamine groups which remain unoxidized. These groups would then be stabilized towards electro-oxidation. This effect may be compounded by the loss of chain mobility as cross-linking develops which may prevent the attainment of the correct relative orientations of groupings inductive to electron transfer. Evidence for the partial release of protons accompanying the dimerization is apparent from Fig. 6 in which the size of the H^+ reduction peak is significantly smaller than would be expected if all the protons formed during the initial cycle were available for reduction. Moreover the observation that only part of the electroactive groups become oxidized when there is a dimerization of the resulting cation radicals which releases protons has also been reported for other polymers containing potentially basic centres, both when electrochemically [17, 19] and chemically [20] oxidized. This retention of protons requires, of course, the influx of charge-compensating anions from the electrolyte solution.

The success of the theory presented above in

describing the transient data such as is shown in Fig. 7b encouraged us to examine whether it could be applied in other systems which are known to display non-ideal behaviour. In particular we have shown previously that poly(4-vinyl-4',4''-dibromotriphenylamine) [5] is such a system. We have analysed chronoamperometric data for the oxidation of electrodes coated with this polymer and, as shown in Fig. 10, have found them to be well modelled by regular solution theory with $Z = -1.6$.

In conclusion we can say that the regular solution theory presents a simple yet effective way of modelling both the cyclic voltammetry and the chronoamperometry behaviour of a diverse range of polymer systems in terms of a single interaction parameter.

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