# Mediated electron transfer reactions at electrodes coated with poly(viologen)s

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Electron and ion transport processes in microdomains of pendant-type poly(viologen)s were analysed by means of rotating disc voltammetry in aqueous media. Stability of poly(viologen)s on the electrode was improved by introducing long alkyl chains. Penetration or the diffusion of ions and the electron-propagation through the polymer layers were greatly affected by the type of supporting electrolyte and chain length of side alkyl groups. Indeed, almost no penetration of large anionic ions was observed in the case of pendant-type poly(viologen) possessing cetyl groups in a perchlorate supporting electrolyte. The electron-propagation through the polymer layers by the self-exchange reactions among redox-active viologen units seemed also to be slow, as the migration of the counter anion of poly(viologen) was limited inside the cationic domain. Similar behaviour was observed in the case of poly(viologen) coatings with ethyl pendant groups, but the electron-propagation was much slower in comparison with the former case. This difference could be attributed to the nature of cationic domains, since the polycations with long alkyl side chains might form a polymer micelle structure with a segregated hydrophobic domain and cationic channel for the electron-propagation.

**(Keywords: poly(viologen); poly(sodium styrenesulphonate); electron transfer reaction; cyclic voltammetry; rotating disc voltammetry; polymer coated electrode)**

## INTRODUCTION

The electrochemical properties of redox-active polymers have been extensively studied by means of voltammetry in order to realize a novel interfacial electrocatalytic system[1-15]. Poly(xylylviologen) has been known as one of the most common redox-active polymers with a reversible two step redox reaction[11-15], although its coatings on the electrode do not have sufficient stability due to their relatively high solubility in aqueous supporting electrolyte solutions. Basic knowledge on the formation of, and the characteristics of intermacromolecular complexes[16-22] has enabled the stabilization of these poly(viologen) coatings on the electrodes by complex formation with polyacids such as poly(sodium styrene sulphonate)[11,13-15], poly(L-glutamic acid) and poly(methacrylic acid)[23,24]. The insolubility and therefore the excellent stability of such intermacromolecular complexes have already been shown to be due to the strong ion paring forming entangled three-dimensional networks. However, intermacromolecular complex formation interferes with the electron-propagation process through the polymer coatings because of the lower mobility of counterions necessary for maintaining electro-neutrality of coatings[14,15]. The ion and electron transport processes through the polymer domain in the case of poly(alkylene viologen)s have been discussed previously[25]. Here, the effect of the primary structure of pendant-type poly(viologen)s on these transport processes was studied by means of stationary voltammetric analyses.

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## EXPERIMENTAL

### *Materials*

Pendant-type polyviologens such as 4,4′-bipyridine were mixed with equimolar amounts of ethyl bromide, octyl bromide or cetyl bromide in *N*,*N*′-dimethyl formamide and mixed gently at 60°C for 72 h. The precipitate formed was filtered with a glass filter and the filtrate evaporated. The precipitate was identified as dialkyl viologen by $^1$H-n.m.r. spectroscopy. The dried filtrate was dissolved in absolute methanol, poured slowly into dry acetone, and the precipitate formed was filtered and washed three times with dry acetone and dried *in vacuo*. The precipitate was identified as monoalkyl viologen by means of $^1$H-n.m.r. spectroscopy. The monoalkyl viologen was dissolved into *N*,*N*-dimethyl formamide and mixed with poly(*p*-chloromethyl styrene) average m.w. 40 000) and an excess of tetraethylammonium bromide to reduce the electrostatic repulsion which might suppress the degree of introduction of viologen units. The mixed solution was kept at 60°C for 72 h. and then slowly poured into aqueous saturated KBr solution to phase separate the pendant-type polyviologen and to exchange the counterions from $Cl^-$ to $Br^-$. The precipitate was dialysed for 72 h in pure water, filtered off and washed with distilled water several times and dried *in vacuo* at 60°C for 24 h. The pendant-type polyviologens having ethyl, octyl, and cetyl groups (PEV, POV and PCV) had 30, 41 and 38% viologen units respectively. PEV and PCV were used as pendant-type polyviologens because POV was not soluble in any organic solvents after complete drying.

The integral-type polyviologen poly(xylyl viologen) (PXV) was prepared in the same manner as described previously[12,16].

Poly(sodium styrene sulphonate) (PSS) was prepared by normal radical polymerization of a corresponding monomer in an aqueous medium at 60°C[20].

The low molecular weight viologen 4,4'-bipyridine was mixed with benzyl bromide equimolarly in *N,N*-dimethyl formamide and stirred gently for 72 h at 60°C. Monobenzyl viologen was purified in a similar manner and was then mixed with alkyl bromide in *N,N*-dimethyl formamide at 60°C for 72 h to prepare *N*-benzyl, *N'*-alkyl viologen. The main product was phase separated during the reaction. The filtered product was washed with dry acetone several times and dried *in vacuo*. The purity of the product was confirmed by means of $^1$H-n.m.r. spectroscopy. *N*-benzyl, *N'*-ethyl viologen and *N*-benzyl, *N'*-cetyl viologen were abbreviated as BEV and BCV respectively.

KCl and $NaClO_4$ were used as supporting electrolytes and a phosphate buffer (pH 7.0) was also used as supporting electrolyte solution in case of oxygen reduction. Potassium ferricyanide ($K_3Fe(CN)_6$) and molecular oxygen were used as substrates.

Bidistilled water was used after extended argon bubbling.

### *Methods*

The polyviologen modified pyrolytic graphite electrode was prepared by the same technique as reported previously[2,3,11-17].

The potentiostat, frequency generator and other apparatus employed were purchased from Nikko Keisoku Co., and cyclic voltammograms were recorded continuously with an *X–Y* recorder (Watanabe Sokki Co.). Potentials were measured with the SCE (standard calomel electrode) as the reference electrode.

Solutions were normally bubbled through with argon to expel oxygen.

**Table 1** Half-wave potential of viologens

| | $E_{1/2}$ (vs. SCE Volts) | |
|---|---|---|
| Viologen | First wave | Second wave |
| PXV | −0.42 | −0.85 |
| PXV–PSS | −0.51 | −1.00 |
| PEV | −0.45 | −0.90 |
| PCV | −0.38 | −0.69 |
| BEV | −0.45 | −0.62 |
| BCV | −0.37 | −0.72 |

**Table 2** Stability and electron transfer efficiency of polyviologens

| | $Q/Q_{ideal}\times 100$ (%) | | $\Delta E_p$ (mV) | |
|---|---|---|---|---|
| Polyviologen | A | B | A | B |
| PXV | –* | 36.6 | –* | 170 |
| PXV–PSS | 4.0 | 3.2 | 80 | 110 |
| PEV | 5.5 | 75.1 | 42 | 133 |
| PCV | 37.5 | 38.5 | 96 | 187 |

A: 0.2 M KCl, B: 0.2 M $NaClO_4$
* Did not reach constant (see Text)

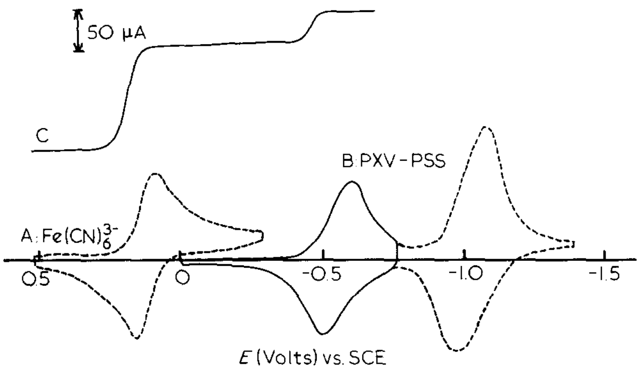

**Figure 1** Cyclic voltammograms (A), (B) and (C) rotating disc voltammogram of PXV–PSS complex coated graphite electrode in 0.2 M KCl aqueous solution containing 2 mM $K_3Fe(CN)_6$. Coated amount of PXV was $5.1\times10^{-8}$ unit mol cm$^{-2}$. Scan speed: (A), (B) 50 mV/s, (C) 5 mV/s. Rotating speed was 2500 rpm

## RESULTS AND DISCUSSION

### *Redox behaviour of poly(viologen)s*

The half-wave potentials of poly(viologen)s and those low molecular weight analogues employed in the present study are summarized in *Table 1*. The first half-wave potential of PCV had the most positive potential at −0.38 V vs. SCE. The half-wave potentials of poly(viologen)s are seen to be dependent on the primary structures or the inductive effect of quaternizing groups, as the low molecular weight analogues have essentially similar half-wave potentials.

The surface charges measured coulometrically are summarized in *Table 2*. They are less than the values expected from the amount applied on the electrode surface. Reasons for the smaller charges observed are (i) dissolving-out of coatings into the solution, (ii) too low space concentration of viologen units in order to complete the electron-propagation pathway, and (iii) very slow electron-exchange among viologen units possibly due to the slow migration of counterions. Since perchlorate anion forms a strong ion pair with PXV and insolubilizes the PXV coatings, the surface charges measured in 0.2 M $NaClO_4$ are much larger than those measured in 0.2 M KCl solution. Although the stability is also improved by the complex formation with poly(sodium styrene sulphonate) (PSS), the surface charges are only 4% of those expected from the applied amount probably due to reasons (ii) and (iii). The redox behaviour of PEV is very similar to that of PXV, but it gives the highest surface charges in perchlorate solution among poly(viologen)s listed in *Table 2*. PCV is essentially insoluble in aqueous supporting electrolyte solutions and its surface charges are independent of the type of counter anion.

### *Mediated electron-transfer reactions*

*PXV–PSS/Fe(CN)$_6^{3-}$ system.* The electron and ion transport processes of PXV–PSS coated electrodes were evaluated from rotating disc voltammetry in 2.0 mM $Fe(CN)_6^{3-}$ solution with 0.2 M KCl or $NaClO_4$ supporting electrolytes. As the first half-wave potential corresponded to the redox potential of $Fe(CN)_6^{3-}$, the first limiting current, $i_l$, was attributed to the reduction of ferricyanide, which penetrated through the polymer layers, at the electrode surface (*Figure 1*). In this case, $i_l$

could be expressed by the following equation[26],

$$i_l^{-1} = i_A^{-1} + i_S^{-1};$$
$$i_A = 0.2nFAC^b_{Fe}D_0^{2/3}\nu^{-1/6}\omega^{1/2};$$
$$i_S = nFA\kappa C^b_{Fe}D_S/\phi \qquad (1)$$

and therefore the Koutecky–Levich plot[27], $\omega^{-1/2}$ vs. $i_l^{-1}$, showed a linear relationship with the intercept of $i_S^{-1}$ and with the slope similar to that of bare electrode system (*Figure 2*). $C^b_{Fe}$, $D_0$, $\nu$, $\omega$, $\kappa$; $D_S$, and $\phi$ represent the bulk concentration of ferricyanide, diffusion coefficient of ferricyanide in bulk solution, kinematic viscosity of solution, electrode rotation speed, (polymer layer/solution) partition coefficient for ferricyanide, diffusion coefficient of ferricyanide in the polymer layers and polymer layer thickness, respectively, and other abbreviations are normal electrochemical parameters. The second limiting current with the half-wave potential at −0.40 V seemed to correspond to the mediated electron-transfer reaction

$$[\mathrm{PXV}^{+\cdot} \xrightarrow{e^-} \mathrm{Fe(CN)}_6^{3-}]$$

as the first redox potential of PXV units existed at −0.42 V. A similar Koutecky–Levich plot for $i_l + i_2$ (abbreviated by $i_t$) is also shown in *Figure 2*. Good linearity with slope the same as that for bare electrode system showed that the flux of electron-propagation through the PXV–PSS coatings was much larger than that for penetration of substrate or that of mediated electron-transfer reaction[26]. In this case, the kinetic situation was expressed by SR (according to Saveant's notation; Substrate penetration limited kinetics but chemical Reaction is also slow), and $i_t$ could be expressed by equation (2)[26], where $\Gamma_{PXV}$ and $k$ represent the cross-sectional concentration of PXV and heterogeneous cross-reactions are constant;

$$i_t^{-1} = i_A^{-1} + (i_S \cdot i_K)^{-1/2};\ i_K = nFA\kappa C^b_{Fe}\Gamma_{PXV} \cdot k \qquad (2)$$

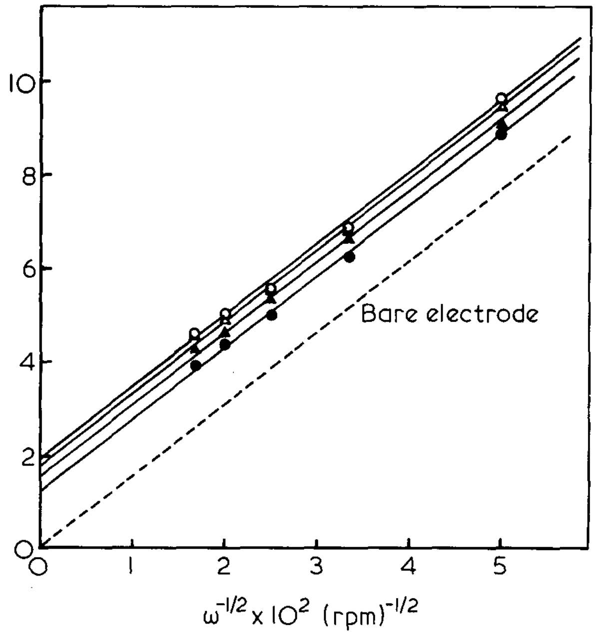

**Figure 2** Koutecky–Levich plot for the reduction of ferricyanide at a rotating graphite disk electrode coated with PXV–PSS complex. Coated amount of PXV was $5.1 \times 10^{-8}$ unit mol cm$^{-2}$. ○, ●: in 0.2 M KCl aqueous soln.; △, ▲: in 0.2 M NaCl$_4$ aqueous soln. Open points: $i_l$, Closed points: $i_l + i_2$

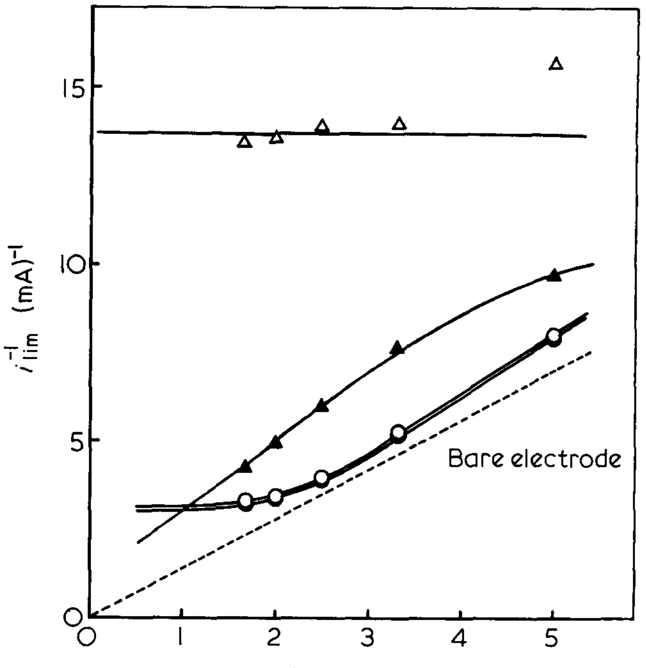

**Figure 3** Koutecky–Levich plot for the reduction of ferricyanide at a rotating graphite disk electrode coated with PEV. Coated amount of PEV was $5.1 \times 10^{-8}$ unit mol cm$^{-2}$. ○, ●: in 0.2 M KCl aqueous soln.; △, ▲: in 0.2 M NaCl$_4$ aqueous soln. Open points: $i_l$, Closed points: $i_l + i_2$

**Table 3** Kinetic data of PXV—PSS complex system

| Electrolyte | $i_S$ (mA cm$^{-2}$) | $(i_K \cdot i_S)^{1/2}$ (mA cm$^{-2}$) | $i_K$ (mA cm$^{-2}$) | $\kappa k$ (mol$^{-1}$.s$^{-1}$) |
|---|---|---|---|---|
| KCl | 3.13 | 4.43 | 6.29 | 5.4 x 10$^5$ |
| NaClO$_4$ | 3.35 | 3.83 | 4.37 | 3.8 x 10$^5$ |

$\Gamma_{PXV} = \Gamma_{PSS} = 5.1 \times 10^{-8}$ unit mol cm$^{-2}$
$C^b_{Fe(CN)_6^{3-}} = 2.0$ mM

As $i_S$ was already obtained from the Koutecky–Levich intercept for $i_l$, the $i_K$ and $\kappa k$ values were estimated (*Table 3*). The $\kappa k$ value was far smaller than expected, in spite of the large driving force of ~0.7 V and the reason for this is now under consideration.

*PEV or PCV/Fe(CN)$_6^{3-}$ systems.* The PEV/Fe(CN)$_6^{3-}$ system also showed two distinct waves similar to that of *Figure 1*. However, the first limiting current was not due only to the substrate penetration but also due to the self-exchange reaction between fixed ferricyanide ions and free ferricyanide ions, as those anions were spontaneously incorporated into PEV by the counterion exchange. In this case, $i_l$ might obey the reversible electrode reaction kinetics described by Saveant *et al.*[28]. The Koutecky–Levich plots for $i_l$ were non-linear for KCl solution and independent of rotation speed for measurements in NaClO$_4$ solution. These results indicate that the electron-propagation through the polymer layer was very slow and especially so for the latter case (in NaClO$_4$)

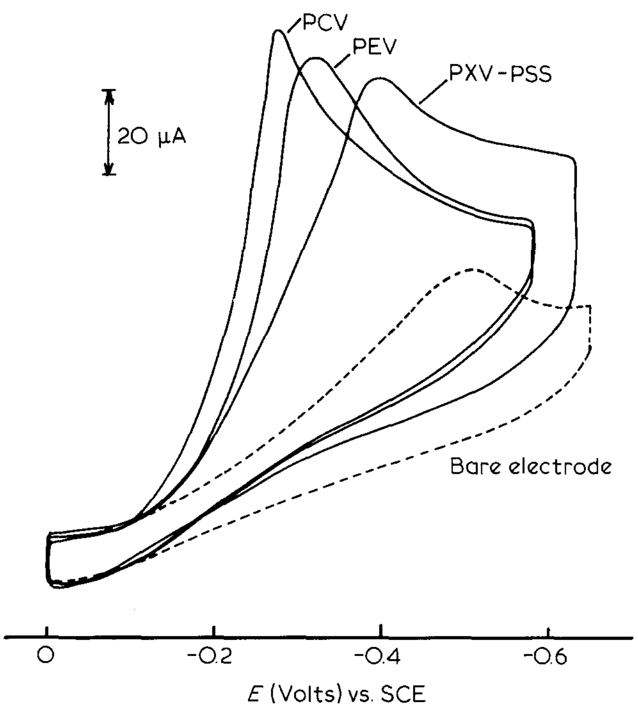

**Figure 4** Cyclic voltammograms for the reduction of oxygen molecules by the graphite electrode coated with polyviologens in oxygen saturated 0.2 M phosphate buffer solution (pH 7.0) at 25°C. Scan speed was 50 mV s$^{-1}$. Amount of polyviologens were 5.1 × 10$^{-8}$ unit mol cm$^{-2}$

where the kinetic situation seemed to be S + E (Substrate penetration and Electron-propagation are equally rate-determining steps). Poly(viologen)s usually became insoluble in aqueous perchlorate solutions and therefore the impervious films formed become inaccessable to ferricyanide penetration and perchlorate migration.

The Koutecky–Levich plots for $i_t$ were non-linear both in KCl and $NaClO_4$ solutions. This could also be caused by the slow electron-propagation through the polymer layers.

As for the PCV/$Fe(CN)_6^{3-}$ system, the results were very similar to those obtained for the PEV/$Fe(CN)_6^{3-}$ system.

### *Heterogeneous cross-reaction with molecular oxygen*

$PXV^+$ has been known to be one of the most potent catalysts for molecular oxygen reduction[29]. *Figure 4* illustrates the cyclic voltammograms recorded at poly(viologen)s coated electrodes in oxygen saturated 0.2 M phosphate buffer solution (pH 7.0). The much enhanced cathodic peak currents, the absence of return (anodic) waves and with peak potentials being more positive than those measured in oxygen free solution represent the rapid heterogeneous cross-reaction. From the slopes of the Tafel plots for the reduction of molecular oxygen, 85, 79 and 68 mV/decade were obtained for PXV–PSS, PEV and PCV coated electrodes, respectively. The slope for the PCV coated electrode was close to that calculated for one electron redox Nernstian, 59 mV/decade. This result suggests that the catalytic potency or the electron-transfer reaction rate of PCV was the highest of all.

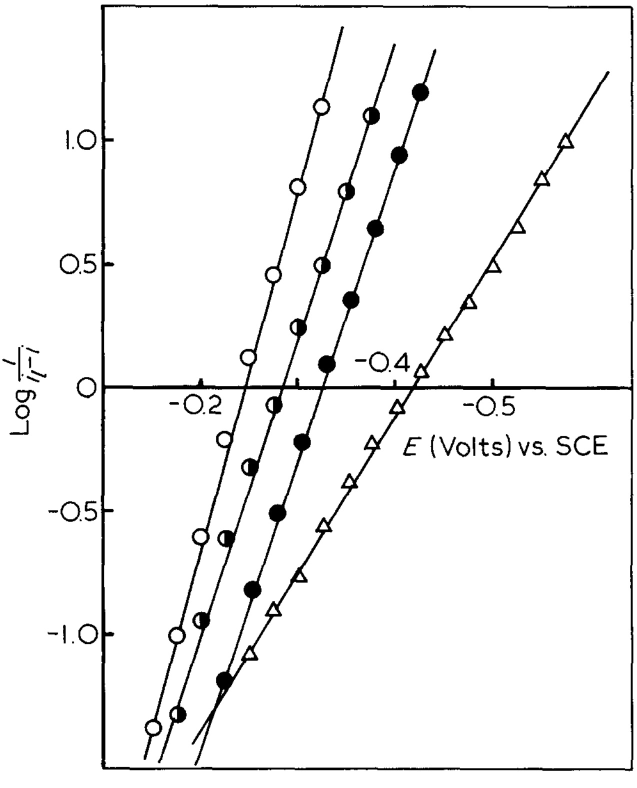

**Figure 5** Tafel plot for the reduction of oxygen molecules by the graphite electrode coated with polyviologens in oxygen saturated 0.2 M phosphate buffer solution at 25°C. Scan speed was 5 mV s$^{-1}$. Rotating speed was 400 rpm. Amount of polyviologens were 5.1 × 10$^{-8}$ unit mol cm$^{-2}$. ○: PCV; ◑: PEV; ●: PXV–PSS complex; △: bare electrode

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