2054 © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***66****, 2054—2060(1993)* [Vol. 66, No. 7

Electropolymerization of Bis(4-cyano-1-pyridinio) Derivatives for the Preparation of Polyviologen Films on Electrodes

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(Received January 5, 1993)

Six bis(4-cyano-1-pyridinio) derivatives have been synthesized and deposited onto electrodes by cathodic electropolymerization ($E_{\mathrm{Red}}=-0.64$—-0.74 V vs. SCE) under basic conditions. The deposited films were constructed of polyviologens that showed characteristic electrochromisms with colorless or slightly yellow to blue- or red-violet. The derivative was reduced to 4-cyano-1,4-dihydro-4-pyridyl radicals, which were coupled successively to form a polyviologen film on the electrode with an elimination of cyanide ions. Characteristically, the polyviologen films deposited by this electropolymerization were insoluble in water and common organic solvents with a spontaneous cross-linking. Especially, a polyanion as a supporting electrolyte forced the polyviologen to form a polyelectrolyte complex in situ. The current efficiency of surface coverage with the polyanion electrolyte (23% in the typical case) was about four-times larger than those with monomeric anions.

Numerous investigations of viologen-modified electrodes and procedures for the modification of electrode surfaces, chemical modification techniques,[1,2] electropolymerizations of *N*-viologen-substituted pyrrole,[3,4] and polymer-coated techniques,[5] have been reported. The application of these viologen-modified electrodes have been proposed for electrocatalytic properties,[6—9] for electrochromic display devices,[10,11] and for organic electronic devices.[12,13]

Most of viologen derivatives have been synthesized from 4,4′-bipyridine and alkyl halides using the Menschutkin reaction.[14] In the same way, already-known polyviologens have been synthesized from 4,4′-bipyridyl and dihaloalkanes.[15] However there have been some reports that viologen cation radicals were observed in spectroscopic measurements of a chemical[16,17] or electrochemical[18—20] reduction of a 4-cyano-1-methylpyridinium salt. The reduced 4-cyano-1,4-dihydro-1-methyl-4-pyridyl radicals couple to form a viologen skeleton with the elimination of two cyanides, according to Scheme 1. In a similar way, Ageishi et al. reported that poly(trimethyleneviologen) was obtained by a chemical or electrochemical reduction of 1,3-bis(4-cyano-1-pyridinio)prpane dibromide.[21] Furthermore, Kitamura et al. reported that a viologen-crosslinked polymer was formed by a similar coupling of poly[{(4-cyano-1-pyridinio)methyl}stylene perchlorate].[22]

We herein wish to report that insoluble polyviologen films have been deposited on electrodes by the electroreduction of bis(4-cyano-1-pyrinio) derivatives. The present polyviologen films were insoluble in water and common organic solvents with spontaneous cross-linking, although already-known polyviologens are soluble in water.[15] Insolubility is a great advantage for the purpose of the above-mentioned applications, since the polymer used on the electrode must be insoluble. This procedure will involve a conventional method for the preparation of a polyviologen-modified electrode without an extra polymerization group. Using polyanion salts as supporting electrolytes, polyviologen-polyanion complexes were efficiently deposited by ionic crosslinkages.

Experimental

General Procedure. Proton NMR spectra were recorded in D_2O on a JEOLE FX-270 spectrometer. All chemical shifts were reported in parts per million (δ) down field from internal sodium 3-(trimethylsilyl)-1-propansulfonate (DSS). Cyclic voltammogram were recorded on a Nikko Keisoku DPGS-1 potentiogalvanostat and a Nikko Keisoku NFG-3 function generator. A saturated calomel electrode (SCE) was used as a reference electrode. For spectroelectrochemistry, a transparent indium-tin-oxide coated glass (ITO) electrode was used as a working electrode. The UV and visible spectra were recorded on a Shimadzu MPS-2000 spectrophotometer using a quartz cell. The thicknesses of the films were measured using a Tokyo Seimitsu 574A surface-texture meter.

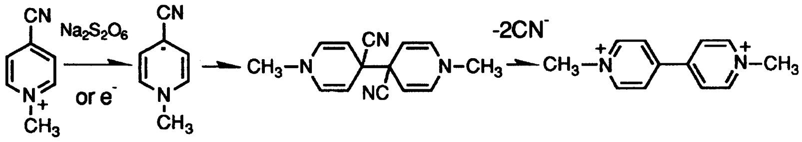
Materials. Bis(4-cyano-1-pyridinio) derivatives were synthesized with 4-cyanopyridine and α,α'-dibromo-*p*-xylene, α,α'-dibromo-*m*-xylene, α,α'-dibromo-*o*-xylene, 1,4-dibromobutane, 1,7-dibromoheptane, or 1,10-dibromodecane in acetonitrile. They were recrystallized from acetone.

α,α'-Bis(4-cyano-1-pyridino)-*p*-xylene Dibromide (1). Y=78%; ^{1}H NMR (D_2O) δ=6.02 (4H, s), 7.64 (4H, s), 8.53 (4H, d, J=7 Hz), 9.23 (4H, d, J=7 Hz). Found: C, 50.51; H, 3.40; Br, 33.58; N, 11.83%. Calcd for $C_{20}H_{16}Br_2N_4$: C, 50.87; H, 3.42; Br, 33.84; N, 11.87%.

α,α'-Bis(4-cyano-1-pyridino)-*m*-xylene Dibromide (2). Y=38%; ^{1}H NMR (D_2O) δ=5.99 (4H, s), 7.63 (3H, s), 7.69 (1H, s), 8.51 (4H, d, J=7 Hz), 9.21 (4H, d, J=7 Hz). Found: C, 50.81; H, 3.30; Br, 33.60; N, 11.88%. Calcd for $C_{20}H_{16}Br_2N_4$: C, 50.87; H, 3.42; Br, 33.84; N, 11.87%.

α,α'-Bis(4-cyano-1-pyridino)-*o*-xylene Dibromide (3). Y=80%; ^{1}H NMR (D_2O) δ=6.18 (4H, s), 7.34—7.74 (2H, m), 7.62—7.72 (2H, m), 8.56 (4H, d, J=7 Hz), 9.17 (4H, d, J=7 Hz). Found: C, 50.69; H, 3.38; Br, 33.68; N, 11.83%. Calcd for $C_{20}H_{16}Br_2N_4$: C, 50.87; H, 3.42; Br, 33.84; N, 11.87%.

1,4-Bis(4-cyano-1-pyridino)butane Dibromide (4). Y=78%; ^{1}H NMR (D_2O) δ=2.22 (4H, bs), 4.75 (4H, bs), 8.51 (4H, d, J=7 Hz), 9.19 (4H, d, J=7 Hz). Found: C, 45.16; H, 3.55; Br, 37.45; N, 13.21%. Calcd for $C_{16}H_{16}Br_2N_4$: C,



Scheme 1.

45.31; H, 3.80; Br, 37.68; N, 13.21%.

1, 7- Bis(4- cyano- 1- pyridino)heptane Dibromide (5). Y=76%; ^{1}HNMR (D_2O) δ=1.30—1.48 (6H, m), 1.98—2.13 (4H, m), 4.73 (4H, t, J=7 Hz), 8.49 (4H, d, J=7 Hz), 9.16 (4H, d, J=7 Hz). Found: C, 48.88; H, 4.66; Br, 34.30; N, 11.80%. Calcd for $C_{19}H_{22}Br_2N_4$: C, 48.95; H, 4.76; Br, 34.28; N, 12.02%.

1, 10- Bis(4- cyano- 1- pyridino)decane Dibromide (6). Y=63%; ^{1}HNMR (D_2O) δ=1.24—1.42 (12H, m), 1.98—2.12 (4H, m), 4.73 (4H, t, J=7 Hz), 8.50 (4H, d, J=7 Hz), 9.17 (4H, d, J=7 Hz). Found: C, 52.29; H, 5.61; Br, 31.44; N, 10.65%. Calcd for $C_{22}H_{28}Br_2N_4$: C, 51.99; H, 5.55; Br, 31.44; N, 10.82%.

The other chemicals were reagent-grade samples and were used without any further purification.

Results and Discussion

Preparation and Electropolymerization. Bis(4-cyano-1-pyridinio) derivatives **1**—**6** were synthesized from 4-cyanopyridine with dibromoalkanes (Chart 1). At first, the electrochemistry of these derivatives was investigated. For example, Fig. 1A shows continuous-cyclic voltammograms of **1** in a 0.1 mol dm^{-3} phosphate buffer at pH 7.4 using an ITO electrode. On the first scan, a very steep reduction peak at −0.64 V (vs. SCE), together with an oxidation peak at −0.52 V which showed minor tailing, were observed. A similar observation of the deposition and dissolution of *N*,*N*′-diheptyl-4,4′-bipyridinium dibromide was reported.[10] The reduction peak was independent of the scan rate, while the oxidation peak had a more anodic region and was broader at a lower scan rate. With a repetition of the scan, these reduction and oxidation peaks were decreased, while new reduction peaks at −0.43 and −0.90 V and oxidation peaks at −0.4 and −0.75 V appeared and then increased. The electrode showed an electrochromism from colorless (about 0 V) to blue-violet (λ_{max}=560 nm) at a more cathodic range than −0.4 V. A similar change of the cyclic voltammograms was reported by Kitamura et al. regarding the electro-

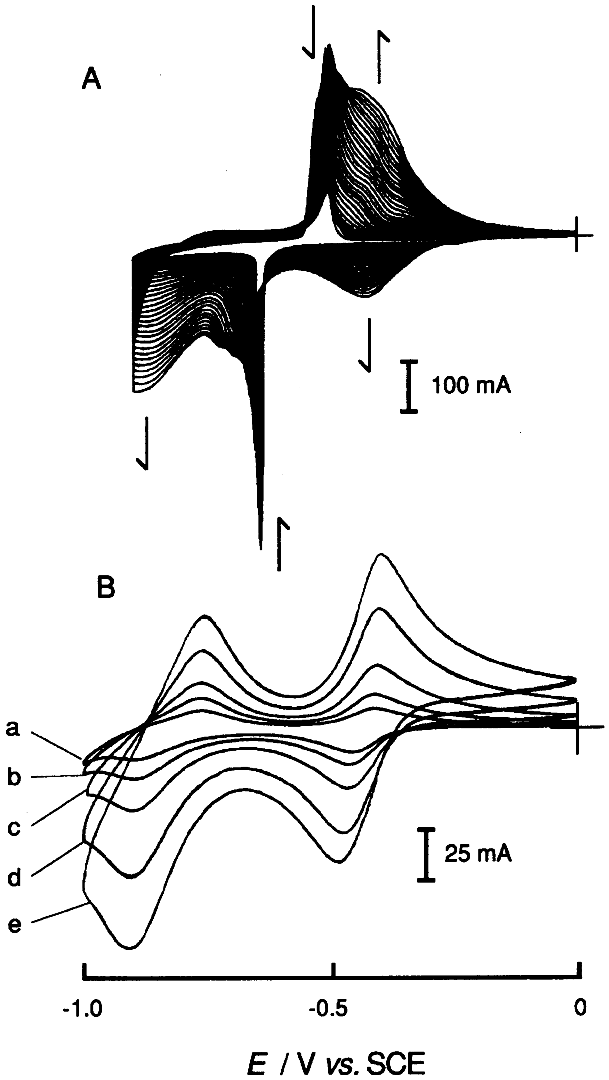


Fig. 1. (A) Cyclic voltammograms recorded continuously in a solution of 20 mmol dm^{-3} of **1** containing 0.1 mol dm^{-3} phosphate buffer at pH 7.4. The electrode potential was scanned at between 0 and −0.9 V vs. SCE at 100 mV s^{-1}. (B) Cyclic voltammograms of the polyviologen film on the ITO electrode recorded at different scan rates, 5 mV s^{-1} (a), 10 mV s^{-1} (b), 25 mV s^{-1} (c), 50 mV s^{-1} (d), 100 mV s^{-1} (e).

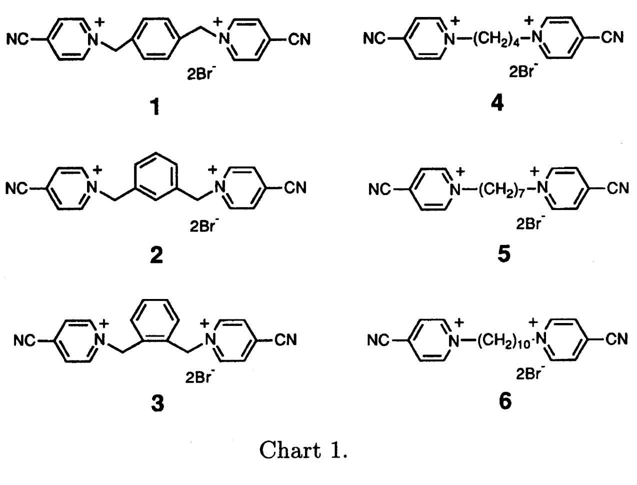


Chart 1.

chemical reduction of poly[{(4-cyano-1-pyridinio)methyl}stylene perchlorate].[22] They prepared an insoluble polymer crosslinked by viologen units that was formed by coupling of the 4-cyano-1-pyridinio groups along with an elimination of the cyanido ions.

After the measurement, a yellow film was deposited onto the electrode surface and the modified electrode was transferred, with through rinsing, to a clean electrolyte. The cyclic voltammograms of the film on the electrode in 0.1 mol dm^{-3} sodium sulfate showed two pairs of reversible redox waves whose half-wave potentials were obtained as $E^1_{1/2}=-0.44$ V and $E^2_{1/2}=-0.84$ V (Fig. 1B). Many viologen derivatives showed two pairs of redox waves whose half-wave potentials had almost the same values obtained here.[14] The cathodic and anodic peaks showed a small dependence on the scan rates and had half-widths greater than 90 mV. In addition, the peak currents were proportional to the square root of the scan rate ($\nu^{1/2}$). These results suggest that the film had no defects. Figure 2 shows the electrochromic absorption changes of the film. The characteristic two pairs of redox waves and the absorption changes showed that the film was constructed by a polyviologen. The polyviologen film on the electrode was insoluble in water and organic solvents, *N*,*N*-dimethylformamide (DMF), acetonitrile, acetone, and chloroform.

The cyclic voltammetries of other bis(4-cyano-1-pyridinio) derivatives, except for **3** and **6**, showed similar behaviors to that of **1**, and the polyviologen films were deposited by electropolymerization onto ITO electrodes. The potentials of the reduction and oxidation peaks of the bis(4-cyano-1-pyridinio) derivatives on the first cycle at $\nu=50$ mV s^{-1} are listed in Table 1, along with the half-wave potentials of the deposited polyviologen films.

The electrolyses of **3** and **6** formed less electrochemically active films than did the others. In the cyclic voltammograms, the reduction and oxidation peaks of **3** or **6** decreased along with a repetition; although new weak peaks of the viologen appeared, they didn't become larger. The surface coverage of the modified electrode of **3** or **6** was less than 2% of that of **1**. However, the electrolysis of **3**, a red species, instead of the blue-violet viologen cation radical, was observed on the electrode. On the other hand, in the case of **6**, no colored species was observed.

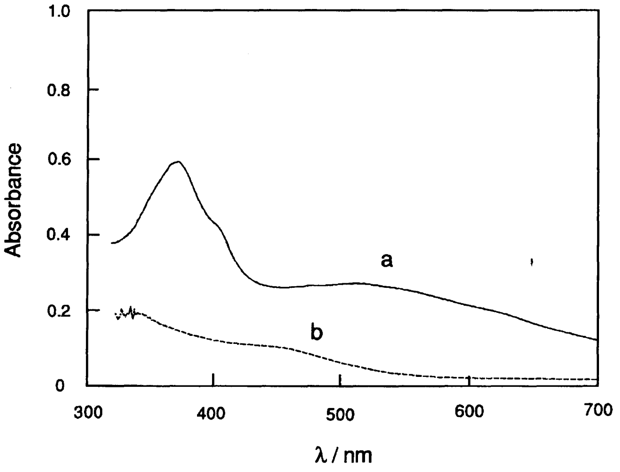


Fig. 2. Absorption spectra of the polyviologen film deposited from **1** on the ITO electrode at −0.8 V (a) and at 0 V (b) vs. SCE.

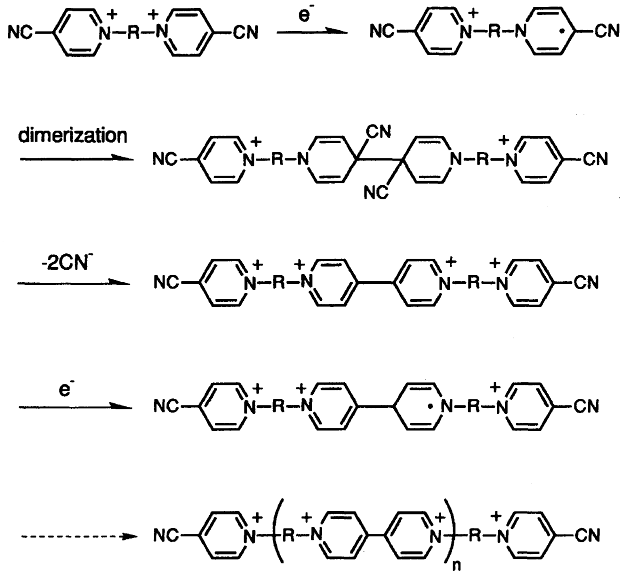
Table 1. Results of Cyclic Voltammetries of Bis(4-cyano-1-pyridinio) Derivatives and Deposited Polyviologen Films (V vs. SCE)

Derivative	Monomer[a)] E_{Pc}	Monomer[a)] E_{Pa}	Polyviologen film[b)] $E^1{}_{1/2}$	Polyviologen film[b)] $E^2{}_{1/2}$
1	−0.64	−0.54	−0.44	−0.84
2	−0.64	−0.53	−0.43	−0.78
3	−0.65	−0.45	−0.42	—[c)]
4	−0.74	−0.64	−0.53	−0.88
5	−0.72	−0.61	−0.49	−0.84
6	−0.68	−0.54	−0.49	—[c)]

a) All data are measured on first cycle in 0.1 mol dm^{-3} phosphate buffer (pH 7.4) at a sweep rate of 50 mV s^{-1}.
b) All data are measured in 0.1 mol dm^{-3} sodium sulfate.
c) Difficult to determine.

It was reported that 4-cyanopyridinium salt was reduced to the 4-cyano-1,4-dihydro-4-pyridyl radical (abb. to 4-cyano-4-pyridyl hereafter), followed by coupling to 4,4′-bipyridinium along with an elimination of cyanide ions.[16—20] Ageishi et al. proposed that both 4-cyano-1-pyridinio groups are reduced at the same time to form a 1,3-bis(4-cyano-1,4-dihydro-4-pyridyl)propane intermediate during the polymerization of 1,3-bis (4-cyano-1-pyridinio)propane dibromide. Although this proposal is applicable in the case of short alkylene chain derivatives, it dose not apply to the case of long alkylene-chain derivatives, such as **6**, whose polyviologen film dose not increase sufficiently. It is considered that the long alkylene chain of **6** depresses any electron transfer from the first viologen layer to the later 4-cyanopyridinium layer.[23] If a decamethylenebis(4-cyano-1,4-dihydro-4-pyridyl) intermediate is formed from **6** at first, the electron transfer is not depressed.

The most probable mechanism for the formation of the polyviologen from the bis(4-cyano-1-pyridinio) derivative is a successive coupling of the 4-cyano-4-pyridyl radical on the surface of the electrode as follows (Scheme 2): (1) One side of the 4-cyano-1-pyridinio group of the bis(4-cyano-1-pyridinio) derivative is reduced to a 4-cyano-4-pyridyl radical, and is then deposited onto the surface of the electrode while losing a charge. (2) The two 4-cyano-4-pyridyl radicals are couples to form the 1,1′,4,4′-tetrahydro-4,4′-bipyridyl derivative. (3) 4,4′-Bipyridinium dication is formed by the elimination of two cyanide ions. (4) The bipyridinium dication is instantly reduced to a cation radical,



Scheme 2.

such that its reduction potential is more anodical than that of the 4-cyano-1-pyridinio group. The viologen cation radical is therefor deposited onto the surface. (5) The same type coupling occurs at the other side of the 4-cyano-1-pyridinio group of the derivative. The successive coupling forms a viologen cation radical chain. After oxidation of the cation radicals, the polyviologen film is deposited onto the electrode.

According to this scheme, three electrons are required to form one viologen unit. The 4,4′-bipyridinium skeleton is formed chiefly by the coupling, since the most favorable site of radical formation in 4-cyanopyridyl is at the 4-position.[20,23,24] The insolubility of the present polyviologen film suggests an unknown cross-linked structure.

pH Effects on Electropolymerization. Figure 3 shows the pH effects in cyclic voltammograms of **1** on the first scans of the electrode potential in phosphate buffers (pH 8 prepared by an addition of sodium hydrogencarbonate) at 10 mV s^{-1}. Under basic conditions, the cathodic wave caused by the reduction of 4-cyanopyridinium cation to the 4-cyanopyridyl radical showed a steep peak at −0.64 V. On the other hand, that under acidic conditions showed major increases, which increased in a more anodic potential region under more acidic conditions, in spite of the peak top stayed at −0.64 V. This suggests that a pH-dependent side reaction occurred at a more anodic potential region than −0.64 V under acidic conditions. Moreover, after the electrolysis of **1** in 0.1 mol dm^{-3} hydrochloric acid, no electrochemically active film on the electrode was formed. Other bis(4-cyano-pyridinio) derivatives showed similar pH effects. Carelli and Cardinali reported that the reduction from the 4-cyano-1-methylpyridinium cation to 4-aminomethyl-1-methylpyridinium cation was favorable under acidic conditions at a more anodic potential region than that of the reduction to 4-cyano-1,4-dihydro-1-methyl-4-pyridyl radical.[18] In the present cases, the increases in acidic conditions were suspected to represent a similar reduction from the cyano to the aminomethyl group.

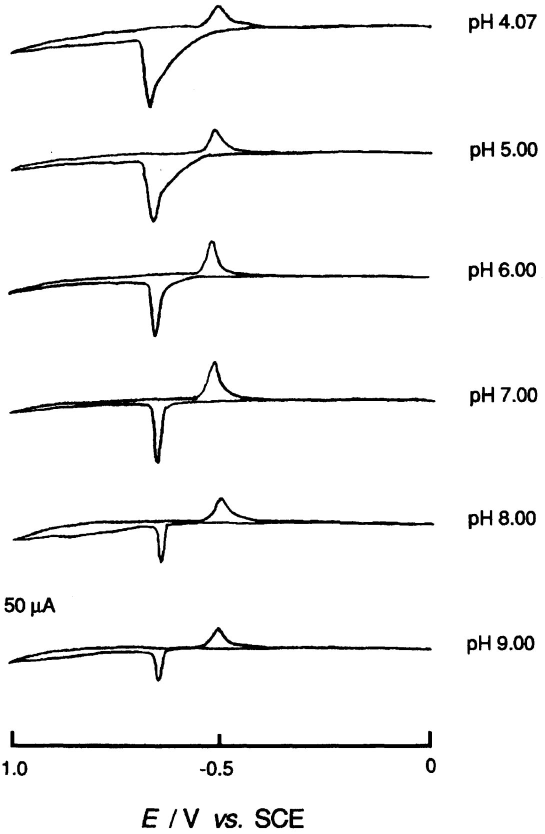


Fig. 3. pH effect on the first potential scanning of **1** from 0 V to −1 V vs. SCE at 10 mV s^{-1}.

Although electropolymerization requires basic conditions, the solution of bis(4-cyano-1-pyridinio) derivatives rapidly turned red under stronger basic conditions than pH 10; pH 7—10 is the favored for the preparation.

Preparation of Polyviologen-Polyanion Complex Films. The anions of the supporting electrolyte were incorporated into the deposited polyviologen film as counter anions. Figure 4 shows the surface coverages of the polyviologen films which were electropolymerized from **1** onto ITO electrodes at −0.8 V for 0.1 C cm^{-2} in solutions containing 0.1 mol dm^{-3} sodium chloride, sodium sulfate, sodium perchlorate, sodium tetrafluoroborate, or poly(ethylenesulfonic acid) potassium salt (PESK, calculated for potassium ethylenesulfonate) conditioned at pH 8 with sodium hydrogencarbonate. There was little difference in the surface coverage in the cases of monomeric anions. On the other hand, the surface coverage with polyanion (PESK) was about fourtimes larger than those with monomeric anions. Due to the low solubility of a polyviologen-polyanion complex in water[5,15] it is suggested that a polyviologen–polyethylenesulfonate (PV–PES) complex is formed on

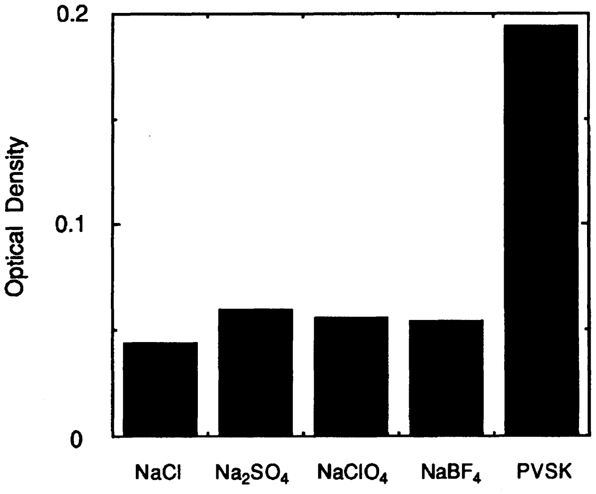


Fig. 4. Optical densities of the cation-radical states of the polyviologen films deposited from **1** using several supporting electrolyte on the ITO electrodes at −0.8 V vs. SCE.

the electrode in situ. The present PV–PES complex film was insoluble in water and organic solvents, DMF, acetonitrile, acetone, and chloroform. It was strong regarding scratching and ripping.

Figure 5 shows cyclic voltammograms of a PV–PES film prepared from **1**, recorded at several scan rates in 0.1 mol dm^{-3} potassium chloride. The cathodic and anodic peaks showed a larger dependence on the scan rates than that of a film prepared in a phosphate buffer (Fig. 1B); half-widths greater than 200 mV were observed. Those show the kinetic limitation of either a slow electron transfer or a slow ion transport of counter ions in the complexes. Considering that the peak current was proportional to the square root of the scan rate ($\nu^{1/2}$), the film had no defect and a dense structure.

Figure 6 shows the electrochromic absorption change of the PV–PES complex film. Before the reduction, the film was slightly yellow. After the reduction, the film showed the characteristic absorption assigned to the viologen cation radical dimer at λ_{max} 548 ($O.D.=0.91$) with a total charge of 0.015 C cm^{-2}. Since the surface coverage was estimated to be 1.55×10^{-7} mol cm^{-2} of viologen units by the charge, the current efficiency of the electropolymerization was calculated to be 23% by the above-mentioned three-electron scheme. This efficiency was almost of the same degree as that reported for the electropolymerization of 1-methyl-1′-(3-pyrrol-1-ylpropyl)-4,4′-bipyridinium tetrafluoroborate ($\Gamma=19\%$) by Bidan et al.[3]

The stability of the PV–PES complex film on ITO was provided by repeating the potential step between 0 and −0.8 V for 20 s. After 100 cycles, a 3.6% decrease in the optical density of the film at −0.8 V (viologen cation radical state) was observed. Most of the viologen cation radical salts show an *aging effect* caused by a crystallization of the cation radical salts.[10] Since the crystallized cation radical salts cannot be completely reoxidized, the color is unerasable. No *aging effect* was observed on the PV–PES complex film while repeating the potential step. Regarding the present polyviologen film, it is considered that the viologen units are so strongly fixed in the cross-linked structure that this depressed the *aging effect.* Akahoshi et al. reported a similar result regarding the spin coating film of poly[(xylene-α,α'-diyl)-substituted viologen]-polystyrenesulfonate.[5]

The electrochemical and spectroelectrochemical mea-

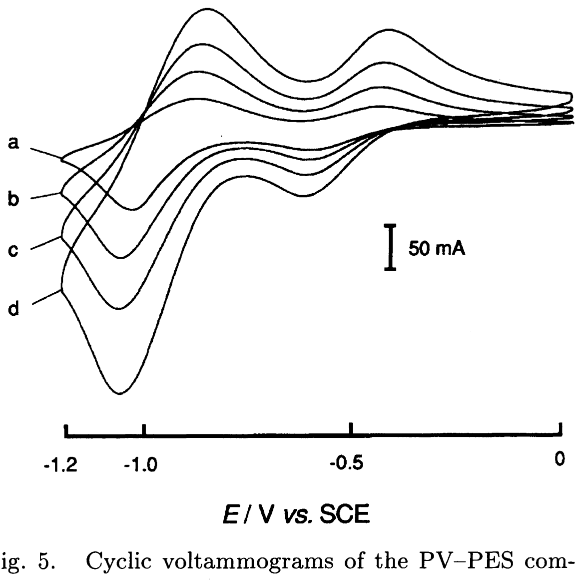


Fig. 5. Cyclic voltammograms of the PV–PES complex film deposited from **1** and PESK recorded at different scan rates, 10 mV s^{-1} (a), 25 mV s^{-1} (b), 50 mV s^{-1} (c), 100 mV s^{-1} (d).

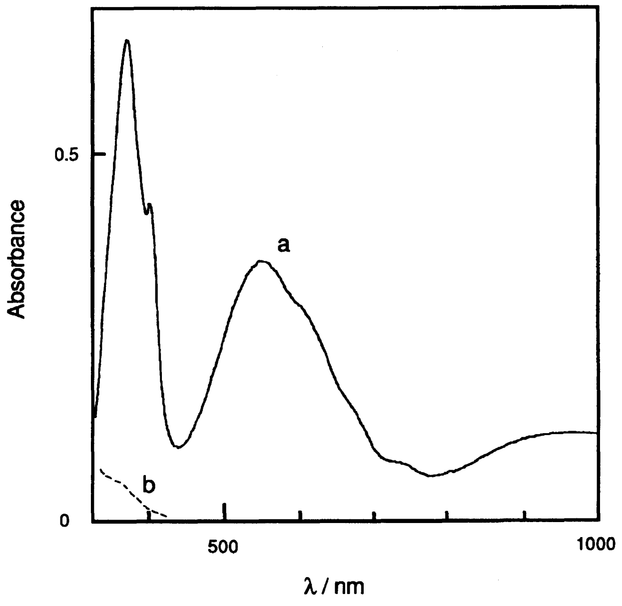


Fig. 6. Absorption spectra of the PV–PES complex film deposited from **1** and PESK at −0.8 V (a) and 0 V (b) vs. SCE.

Table 2. Results of Electrochemistry and Spectrolelctrochemistry of the Polyviologen–Polyethylenesulfonate Complex Films on ITO Electrodes

Derivative	$E^1{}_{1/2}$[a)] E/V	$E^2{}_{1/2}$[a)] E/V	$\lambda_{\max}$[b)] λ/nm	Thickness[c)] l/μm
1	−0.45	−0.91	970, 550, 380	0.7
2	−0.40	−0.92	960, 550, 380	0.6
3	—[d)]	—[d)]	950, 540, 375	<0.1
4	−0.55	−0.95	910, 552, 373	0.6
5	−0.52	−0.96	900, 543, 370	0.7
6	—[d)]	—[d)]	850, 540, 370	<0.1

a) All data measured in 0.1 mol dm^{-3} KCl. b) Of electrochromic absorptions at −0.8 V (SCE) in 0.1 mol dm^{-3} KCl. c) The films deposited by electropolymerizations for 0.15 C cm^{-2}. d) Difficult to determine.

surements of the PV–PES complex films deposited onto ITO electrodes from bis(4-cyano-1-pyridinio) derivatives are summarized in Table 2. They were deposited by potentiostatic electropolymerizations at −0.8 V for 0.15 C cm^{-2} with 0.01 mol dm^{-3} of solutions of bis(4-cyano-1-pyridinio) derivatives containing 0.1 mol dm^{-3} PESK (conditioned at pH 8). The deposited films of **1**,**2**,**4**, and **5** were either colorless or slightly yellow. They showed reversible two redox cycles as well as electrochromisms to blue-violet or red-violet. The surface coverages of **1**,**2**,**4**, and **5** seemed to be proportional to the total charge of the electropolymerization (Fig. 7). On the other hand, the surface coverates of **3** and **6** were saturated before 0.1 C cm^{-2}. These results were similar to the above-mentioned results using a phosphate buffer. The present PV–PES films deposited from **1**,**2**,**4**, and **5** onto the electrodes were insoluble in both water and common organic solvents, and showed good electrochromic properties.

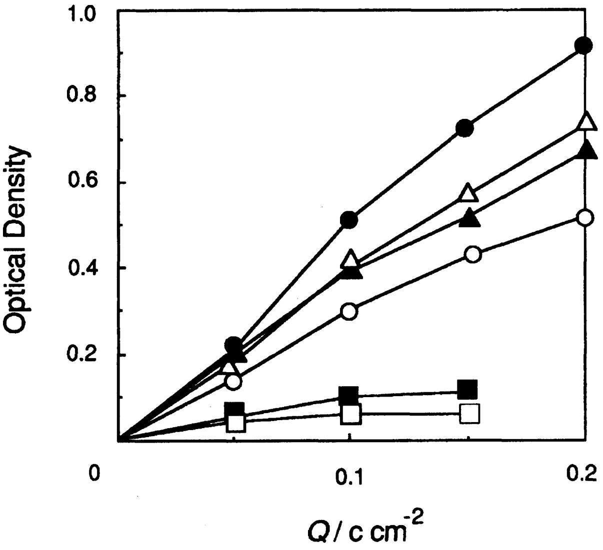


Fig. 7. Relationship between the surface coverege and the current of the electropolymerization for the PV–PES complex films, **1**: ●, **2**: ▲, **3**: ■, **4**: ○, **5**: △, and **6**: □.

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