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First Observation of an Intramolecular Charge-Transfer Complexation and Electron Relay between the Viologen and Ester Groups in a New Polymer System

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ABSTRACT: A viologen copolymer obtained by radical copolymerization of a new viologen monomer containing a vinyl pyridinium structure with methyl methacrylate exhibited a visible absorption at an unusually high wavelength (λ_{max} ca. 700 nm) in organic solvents. The copolymer in turn showed an efficient electron transfer ascertained by its cyclic voltammogram and IR spectrum. Such behavior was not observed in the copolymer with a spacer between the viologen structure and the main chain or a model compound. Thus, these new observations were suggested to be attained by intramolecular charge-transfer complexation and electron catch and relay between the pendant viologen and ester groups directly linked to the main chain and situated very closely.

Introduction

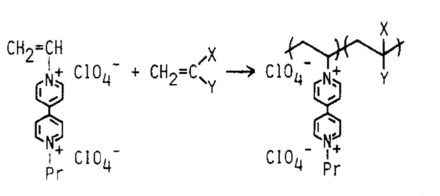
Electron-transport systems in biological cells are governed by the effective electron relay between conjugated redox enzymes such as flavoproteins and NAD-containing enzymes. Much attention has been paid to viologens as mediators for the electron-transfer process mimicking biological systems.[1] Smith et al.[2] have demonstrated the unidirectional electron transfer in the electrode-bound viologen–quinone assembly. We have reported an electron transport in the synthetic polymeric membranes mediated by the pendant viologen[3] and lipoamide groups.[4]

Recently, we synthesized a new viologen monomer, vinyl viologen, with a vinyl group directly linked to the pyridinium nitrogen.[5] We also observed the selective formation of dimeric and monomeric viologen cation radicals in its homopolymer and copolymer with dimethyl acrylamide derived by the strong interaction between the adjacent functional groups.[5]

In this study, we describe unusual intramolecular charge-transfer complexation and electron relay between the pendant viologen and ester groups in the copolymer of vinyl viologen with methyl methacrylate.

Results and Discussion

Radical copolymerization of vinyl viologen, 1-propyl-1′-vinyl-4,4′-bipyridinium diperchlorate (ViV^{2+}),[5] with methyl methacrylate (MMA) or acrylonitrile (AN) was carried out in γ-butyrolactone in the presence of azobis(isobutyronitrile) (AIBN) as an initiator at 80 °C for 24 h to obtain powdery copolymers 1 or 2, respectively (eq 1). For comparison, 1-propyl-1′-(vinylbenzyl)-4,4′-bipyridinium diperchlorate ($ViBzV^{2+}$) was copolymerized with MMA under the similar conditions as above to give copolymer 3 with a benzyl group as a spacer between a polymer main chain and the viologen structure. The representative results are shown in Table I.



(1)

ViV^{2+}

1: $X = CH_3$, $Y = CO_2CH_3$
2: $X = H$, $Y = CN$

Table I
Radical Copolymerization of Viologen Monomers with MMA and AN[a]

V^{2+} monomer (mol % in feed)	comonomer	copolymer (yield, %)	elem anal of nitrogen, %	content of V^{2+},[c] mol %
ViV^{2+} (10)	MMA	**1a** (28)	1.37	5.8
ViV^{2+} (15)	MMA	**1b** (20)	2.02	9.4
ViV^{2+} (20)	MMA	**1c** (13)	3.07	17.0
ViV^{2+} (25)	MMA	**1d** (11)	4.72	37.3
ViV^{2+} (5)	AN	**2a** (43)	19.92	5.7
ViV^{2+} (15)	AN	**2b** (29)	15.21	13.9
$ViBzV^{2+}$ (3)	MMA	**3a** (18)[b]	0.64	2.5
$ViBzV^{2+}$ (20)	MMA	**3b** (10)[b]	2.87	17.9

[a] Run as 30 M. 3 M solutions in γ-butyrolactone with 2 mol % of AIBN at 80 °C for 24 h. Polymers precipitated with MeOH. [b] Run as 3 M solutions at 60 °C for 20 h. [c] Estimated by elemental analysis of nitrogen.

A dimethyl sulfoxide (DMSO) solution of copolymer **1b** showed a visible absorption at an abnormally high wavelength (λ_{max} 700 nm, ϵ 3787) as shown in Figure 1. By addition of perchloric acid to this solution, the visible absorption disappeared completely. When aqueous sodium dithionite ($Na_2S_2O_4$) was added to the DMSO solution of copolymer **1b**, the new absorption was observed around 600 nm corresponding to the mixture of viologen cation radical and its dimer (Figure 1). On the contrary, copolymer **3b** or the mixture of propyl viologen and ethyl acetate showed no visible absorption in DMSO. These results suggest that an intramolecular charge-transfer complex was formed between the viologen and ester groups in copolymer **1b**. By protonation of the ester groups or reduction of the viologen group, charge-transfer interaction would be broken. Charge-transfer complexation of viologen molecules with their counteranions,[6] cysteine, and other acids[7] have been reported to show electronic spectra around 300–600 nm. Observations of a charge-transfer spectrum on copolymer **1b** at such a high wavelength indicated a strong interaction of ester groups with the viologen structures. This interaction might be derived by the direct linking of both groups to the polymer main chain to result in the situation of both groups very closely.

Cyclic voltammograms of these copolymers, dissolved in *N*,*N*-dimethylformamide (DMF) and cast on a gold electrode with the quantity of the viologen unit adjusted to 1.0×10^{-4} mmol, were measured in 0.2 M KCl-Tris buffer of pH 7.5 with a scan rate of 1×10^2 mV/s. Copolymer **3b** (V^{2+}, 17.9 mol %) showed two typical successive redox waves at redox potentials ($E_{1/2}$) of −0.45 (peak separation: ΔE_p, 40 mV) and −0.84 V corresponding to the formation of a viologen cation radical (one-electron re-

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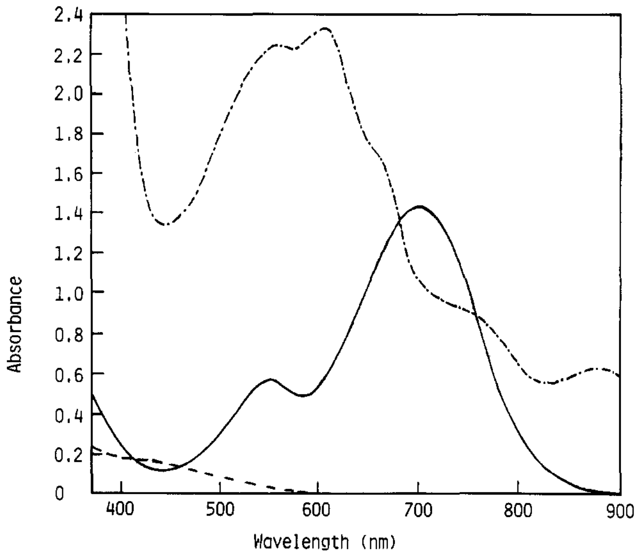


Figure 1. Electronic spectra of copolymers **1b** and **3b** in DMSO with the concentration of 4.4×10^{-4} M: (—) copolymer **1b**; (- - -) copolymer **3b**; (–•–) copolymer **1b** reduced with aqueous $Na_2S_2O_4$.

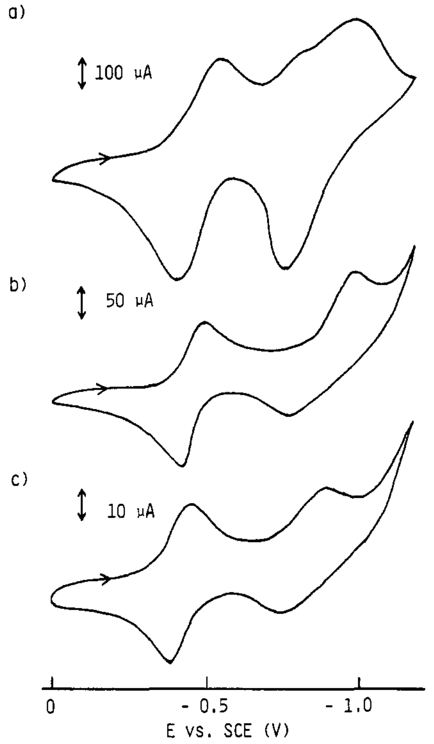


Figure 2. Cyclic voltammograms of copolymers **1c**, **2b**, and **3b** in 0.2 M KCl-Tris buffer (pH 7.5) with a scan rate of 1×10^2 mV/s, where the amount of viologen units cast on a gold electrode (0.28 cm^{-1}) was adjusted to 1.0×10^{-4} mmol: (a) copolymer **1c**; (b) copolymer **3b**; (c) copolymer **2b**.

duction) and its quinoid form (two-electron reduction) as shown in Figure 2b. Copolymer **1c** (V^{2+}, 17.0 mol %) showed two successive redox waves at more negative potentials of −0.48 (ΔE_p, 120 mV) and −0.88 V with much higher peak currents than those of copolymer **3b**. Enhanced redox currents and a wider ΔE_p for the first redox wave in copolymer **1c** suggested a strong interaction between the viologen and ester groups in the copolymer as also observed in its spectroscopic behavior mentioned above. These results indicated that the usual reduction of viologen groups on the surface of an electrode was followed by the successive electron relay with other functional groups in the copolymer. A cyclic voltammogram of copolymer **2b** also showed two typical successive waves at more positive potentials of −0.41 (ΔE_p, 60 mV) and −0.81 V.

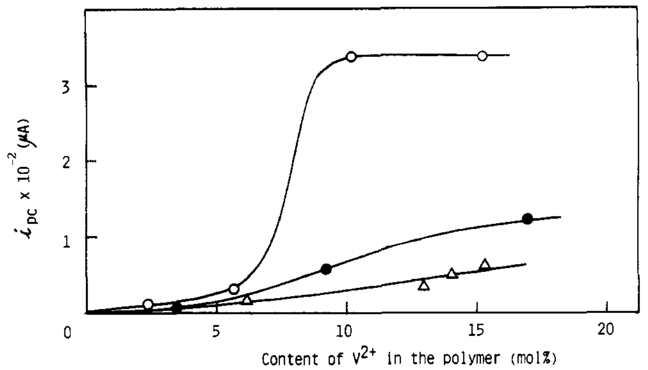


Figure 3. Dependence of i_{pc} on the content of the viologen structure in copolymers **1**–**3** measured in 0.2 M KCl-Tris buffer (pH 7.5) with a scan rate of 1×10^2 mV/s, where the amount of viologen units cast on a gold electrode (0.28 cm^{-1}) was adjusted to 1.0×10^{-4} mmol: (○) copolymer **1**; (△) copolymer **2**; (●) copolymer **3**.

The peak current (i_{pc}) of copolymer **1** at one-electron reduction was compared with those of copolymers **2** and **3**. Figure 3 the effect of the content of the viologen unit in copolymers on i_{pc} measured at a scan rate of 1×10^2 mV/s. In each case, the quantity of the viologen unit cast on an electrode was again adjusted to 1.0×10^{-4} mmol. By increasing the viologen content in the copolymer, i_{pc} increased gradually in cases of copolymers **2** and **3**, which might be due to the increase in the hydrophilicity of these copolymers by increasing the content of viologen unit in the copolymers. On the other hand, i_{pc} of copolymer **1** increased dramatically at the viologen content above 9 mol % and reached near the maximum value at this content. This suggested that viologen and other species (an equivalent amount of ester groups) in the copolymer susceptible for the reduction at this potential were effectively reduced. Whereas viologen units in other copolymers as solid membranes might be reduced only partly.

Thus, in the viologen-containing copolymers, copolymer **1** showed an unusually effective electron transfer compared to the other copolymers even with the content of viologen around 9 mol %. This might be caused by the electron catch and relay between the viologen and the ester groups activated as electron acceptors via charge transfer to the neighboring viologen groups even in the solid state. Around 9 mol %, viologen groups and the activated ester groups were considered to be well contacted to submit electron catch and relay, and then the i_{pc} reached to the maximum and at this content almost all viologen groups and presumably equimolar amount of ester groups were reduced in the same extent with the copolymer of the higher content of viologen unit. Thus the i_{pc} increase to a plateau would be observed. The cyano group was ineffective for an electron relay with the viologen group due to its poor electron-accepting character.

In the IR spectrum of copolymer **1d** with the viologen content of 37.3 mol %, a strong absorption band was observed at 1728 cm^{-1} based on the ester group. When copolymer **1d** was reduced with $Na_2S_2O_4$, the absorption (1728 cm^{-1}) of carbonyl band disappeared considerably and shifted to a lower wavenumber (Figure 4) and appeared reversibly by air oxidation. On the other hand, copolymers **2** and **3** and a model compound, 1-propyl-1′-(3-ethoxycarbonyl)propyl-4,4′-bipyridinium diperchlorate, were reduced in the same way; the decrease of the IR absorption was not observed.

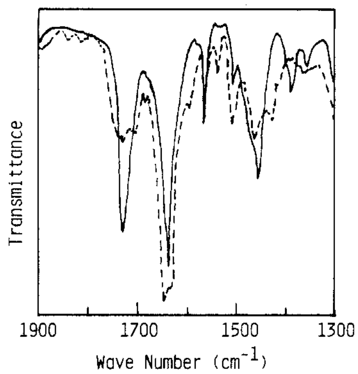
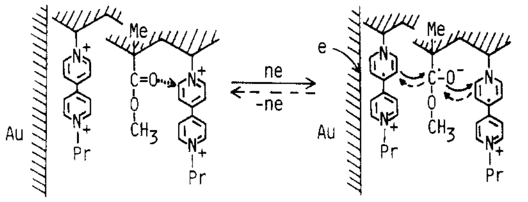


Figure 4. Change in IR absorption of copolymer **1d** (V^{2+}, 37 mol %) by aqueous $Na_2S_2O_4$ reduction: (—) untreated copolymer; (- - -) reduced form.

Scheme I



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These results further supported the electron-relay mechanism between the pendant viologen and ester groups activated by the close proximity in copolymer 1 to result in the high i_{pc} in its cyclic voltammogram as proposed in Scheme I.

We have demonstrated in this work that by designing a new viologen monomer, the unusual functional group assembly has been brought in its copolymer with MMA, and the intramolecular charge-transfer complexation and electron catch and relay have been observed for the first time between the viologen and the neighboring ester groups in the copolymer by the cooperative intramolecular interaction. These findings are attractive in view of molecular designing as well as expectation for new developments on the well-investigated viologens.

Experimental Section

Materials. 1-Propyl-1′-vinyl-4,4′-bipyridinium diperchlorate (ViV^{2+}) was prepared as described previously.[5] 1-Propyl-1′-(vinylbenzyl)-4,4′-bipyridinium diperchlorate ($ViBzV^{2+}$) was prepared by the exchange of counteranion with addition of sodium perchlorate to the methanolic solution of the corresponding dibromide salts[8] and recrystallized with ethanol (mp 72–73 °C). Other comonomers and chemicals used for this study were purified by the usual procedures.

Copolymerization. ViV^{2+} (127.6 mg, 0.3 mmol) and MMA (170.2 mg, 1.7 mmol) were dissolved in γ-butyrolactone (0.066 mL) and copolymerized with azobis(isobutyronitrile) (AIBN) (2 mol %) at 80 °C for 24 h after degassed and sealed in a polymerization tube. A product was precipitated with MeOH and purified by reprecipitation from DMF with MeOH to give a slightly blue powdery copolymer **1b** in 20% yield. The content of ViV^{2+} in the copolymer was estimated to be 9.4 mol % by the elemental analysis of nitrogen. Copolymerization of ViV^{2+} with AN was carried out by the same procedure as above. Copolymerization of $ViBzV^{2+}$ with MMA was carried out at 60 °C for 20 h with a monomer concentration of $^1/_{10}$-fold.

Spectral Measurements. The electronic spectra of copolymers were measured with a Hitachi 200-10 spectrophotometer by dissolving the copolymers in DMSO (3.8×10^{-4} M).

KBr disks of reduced copolymers for IR measurements were prepared as follows. Copolymers were suspended in MeOH, reduced with aqueous $Na_2S_2O_4$, dried well in vacuo, mixed with a KBr powder previously dried well and stocked under an argon atmosphere, and then pressed. Reduction and preparation of the KBr disk of copolymers were carried out under an argon atmosphere. The KBr disk of the reduced copolymer was oxidized by dry air until the blue color disappeared. IR spectra of these KBr disks were recorded on a Jasco FT/IR-3 spectrometer.

Cyclic Voltammetry. Copolymers were dissolved in DMF, cast on a gold inlay electrode (0.28 cm^2), and dried at 60 °C for 1 h to give gold electrodes coated with transparent polymeric membranes. The cyclic voltammograms of these copolymer membranes were measured with a Hokuto Denko potentiostat PS-1000 and a function generator HB-104 by use of a platinum spiral as the counterelectrode in 0.2 M KCl-Tris buffer (pH 7.5) bubbled with argon gas. All potentials were recorded against a saturated calomel electrode. The redox potential, $E_{1/2}$, was calculated as the average of the cathodic and the anodic peak potentials, and peak separation, ΔE_p, was the difference of these peak potentials.

Registry No. 1, 121988-33-8; **2**, 108317-26-6.

References and Notes

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