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Photochemistry of Macromolecular Dyes in Aqueous Solutions

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PHOTOCHEMISTRY OF MACROMOLECULAR DYES IN AQUEOUS SOLUTIONS

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ABSTRACT

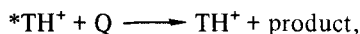
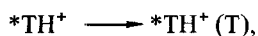
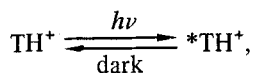
Thiazine and phenazine dyes are known to exhibit photoredox behavior in the excited states of these molecules. These dyes are covalently attached to macromolecules, and the photochemistry has been investigated in homogeneous solution and as thin films coated onto electrodes. Flash photolysis of the macromolecular thionine in the presence of quenchers shows reduction of the dye and the subsequent disproportionation of the reduced dye. In the case of macromolecular thionine, evidence for the formation of a complex between ferrous ion and thionine is observed in the flash photolysis experiments. Photoelectrochemical studies show a new type of behavior for the macromolecular dye films coated onto electrodes. Macromolecular thionine film coated onto platinum electrode makes the electrode a cathode on illumination of the electrode. Macromolecular phenosafranin dye films coated onto electrodes change the polarity of the illuminated electrode depending upon the nature of the macromolecule.

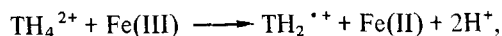
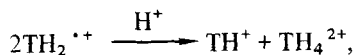
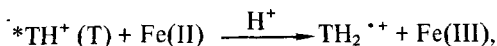
INTRODUCTION

In recent years there has been considerable interest in the properties of the ground and excited states of dyes [1, 2]. Photochemical reactions of different organic dye systems show electron transfer reactions from the excited states of molecules [3, 4]. Studies of the energy transfer processes in macromolecules throw light on the excited-state processes occurring in microheterogeneous systems [5]. The photochemistry of synthetic polymeric materials finds applications in photolithography, imaging, and topochemical polymerization reactions [6]. The electrochemistry of polymer-coated electrodes has been studied in several laboratories to understand electron transfer reactions mediated by the polymeric films [7-9]. The reactions of dye systems in the excited states are primarily studied in homogeneous solution. Many of the naturally occurring dyes, such as the flavones, porphyrins, and carotenoids, undergo reactions in biopolymer environments in natural systems. Only in recent years has attention been paid to the reactions of these molecules in micelles, monolayer systems, and colloidal solutions [10-12]. The present article deals with the photochemistry of polymer-bound thionine and phenosafranine, with particular reference to the electron-transfer processes induced by light on the macromolecular dye film electrodes.

PHOTOCHEMICAL PROCESSES OF MACROMOLECULAR THIAZINE DYES

Thionine is known to undergo an excited-state redox reaction when suitable reducing agents are present in the medium [13]. Although this reaction has been known for almost five decades [14], renewed interest in the photochemical reaction of thionine was generated for its possible application to convert visible light into galvanic potential. Several investigators [15-20] have studied the excited state reaction by flash photolysis methods, and the mechanism proposed for the photoredox reaction of thionine is summarized below:





where TH^+ = thionine

$\text{TH}_2^{*\cdot}$ = semithionine

TH_4^{2+} = leucothionine

T = triplet

The one-electron and two-electron reduced species of thionine have been generated by pulse radiolysis techniques [21], and the redox reactions observed subsequent to the primary photochemical reactions of thionine have been investigated.

In homogeneous solutions the thionine-iron(II) system shows a photogalvanic potential, and the dye is remarkably stable for a number of days on irradiation with visible light. However, the thermal reactions of semireduced thionine effectively compete with the electrode reaction in a photogalvanic cell, which makes it unsuitable for efficient energy-conversion processes [22]. Several attempts have been made to retard the rate of energy-wasting back thermal reactions by using a) totally illuminated thin-layer cells [23], b) derivatized thionine systems [24] to increase the solubility of the dye in aqueous solutions, or c) different types of electron donors [25]. In our laboratory we have synthesized a number of macromolecules [26] which are covalently bound with thionine and investigated the electrochemical and photochemical properties of the dye in homogeneous aqueous solution [27, 28] and at electrodes coated with films of macromolecular thionine. The macromolecular thionine systems investigated are shown in Fig. 1. The polymeric thionine systems synthesized are free of the monomeric thionine and stable for months in aqueous solution; no monomeric dye was detected in solution even after several months. Since the polymeric backbone is primarily a highly water-soluble polymer, the concentration of the dye could be varied over a wider range. A solution of the macromolecular thionine evaporated onto a glass plate or platinum electrode forms a film which is crosslinked and does not undergo dissolution in water.

The absorption spectra of the macromolecular thionine show a maximum around 600 nm, like the monomeric thionine. Polymeric thionine emits on excitation at 600 nm, and the absorption and emission spectra of the polymeric thionines are shown in Fig. 2. Ferrous and ferric ions

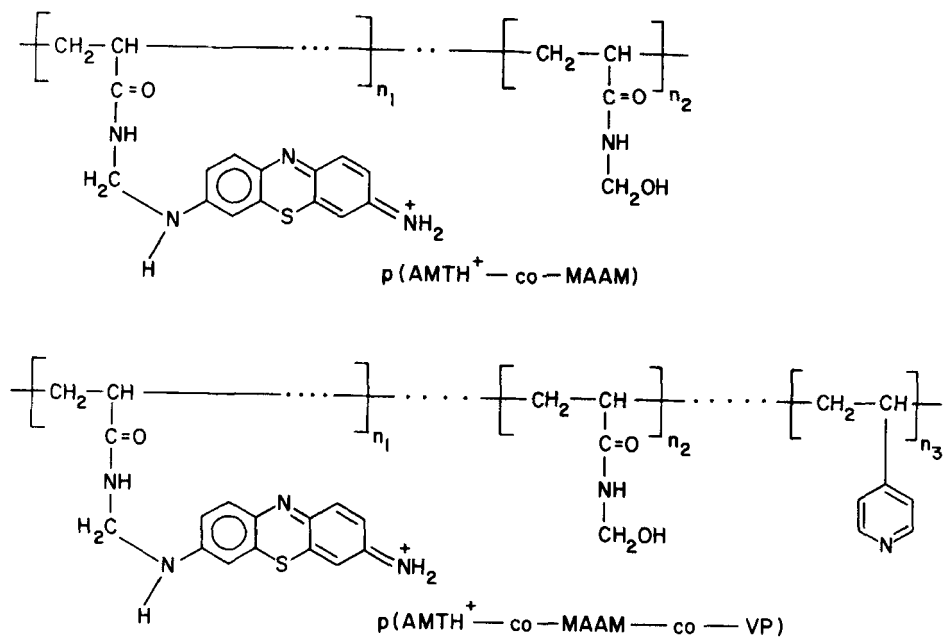


FIG. 1. Macromolecular thionine systems.

and complexes of Fe(II) and Fe(III) ions quench the emission from the excited state of macromolecular thionine. The Stern-Volmer constants for the quenching processes are given in Table 1. Flash photolysis of polymeric thionine dyes in the presence of ferrous ion in aqueous solution shows the transient polymeric semithionines, which disproportionate to give polymeric leucothionine and polymeric thionine. The rate constants for the decay of the monomeric and polymeric semithionines are given in Table 2. The rate constants for the disproportionation reaction of polymer-bound semithionine are two orders of magnitude less than that for monomeric semithionine. A fivefold increase in the concentration of macromolecular thionine does not change the rate constants for the disproportionation reaction as predicted [29]. It is therefore concluded that the disproportionation reaction occurs between semithionine dyes present on the same macromolecular chain. As the number of dye centers in a chain is increased, no appreciable change in the disproportionation rate constant is observed, indicating that the polymeric dye is in a coiled form and that the intrapolymer dye disproportiona-

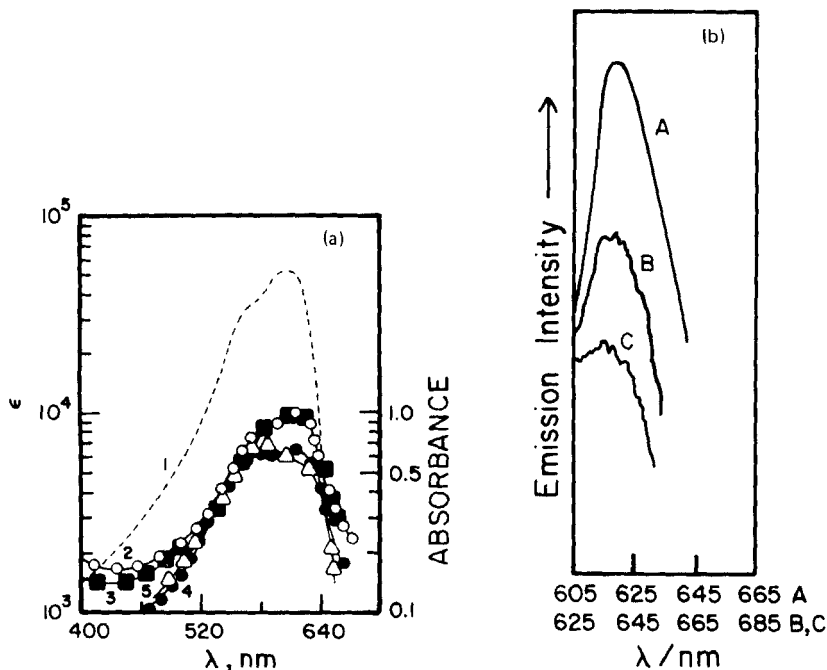


FIG. 2. Absorption (a) and emission (b) spectra of macromolecular thionine: (1) thionine; (2) P(AMTH⁺-co-MAAM), M/D = 96; (3) M/D = 33; (4) M/D = 16; (5) M/D = 12.

tion reaction is little affected by the variation of dye centers in the same chain.

The decay of the transient in the macromolecular thionines proceeds initially by first-order kinetics and subsequently by the equal-concentration second-order process. The excited state of macromolecular thionine forms the precursor complex with iron(II), and after the electron-transfer reaction, the successor complex dissociates to give semithionine and iron(III):

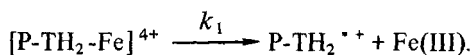
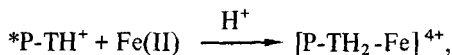


TABLE 1. Quenching of Fluorescence from Macromolecular Thionine^a by Ferrous and Ferric Ions

Dye	Monomer Dye	Stern-Volmer constant, K_{SV} , dm ³ /mol	
		Fe(II)	Fe(III)
Thionine		1.49	2.91
Thionine + P(MAAM) ^b		—	2.63
Thionine + P(MAAM- <i>co</i> -VP) ^c		—	2.34
A ^d	34.4	0.97	1.49
	42.2	0.97	1.70
	58.0	0.87	1.62
	119.0	0.84	1.69
B ^e		1.08	1.38

^a[Dye] = 6.8×10^{-6} mol/dm³. [H₂SO₄] = 0.05 mol/dm³.

^b[P(MAAM)] = 0.1 mol/dm³.

^c[P-(MAAM-*co*-VP)] = 0.1 mol/dm³.

^dA = Poly(*N*-acrylamidomethylthionine-*co*-methylolacrylamide).

^eB = Poly(*N*-acrylamidomethylthionine-*co*-methylolacrylamide-*co*-vinylpyridine).

Formation of such a complex between the semithionine and Fe(III) has been proposed [28] to explain the photoelectrochemical behavior of macromolecular thionine coated onto inert electrodes. The initial first-order decay reported for the macromolecular thionine is not observed for the monomeric thionine, presumably because the time scale for the disproportionation reaction monitored is not very different from that for the dissociation of the semithionine-iron(III) complex.

PHOTOELECTROCHEMISTRY OF MACROMOLECULAR THIONINE IN FILMS

Light-induced electron transport across thick films of macromolecular dyes is not known for many systems. In addition to the photoinduced potential,

TABLE 2. Decay of Macromolecular Semithionine^a

Dye	Monomer		$k_0, 10^{-2} \text{ s}^{-1}$
	Dye	$k, 10^{-7} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	
Thionine		293	—
Thionine + P(MAAM)		320	—
Thionine + P(MAAM-co-VP)		340	—
A ^b	200	1.3	3.74
B ^c	10	0.97	2.30
B	70	1.16	3.29
B	200	1.13	3.69

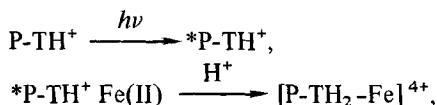
^aAbsorbance of the dye solution = 0.10 cm^{-1} , $[\text{H}_2\text{SO}_4] = 0.05 \text{ mol/dm}^3$, $[\text{Fe(II)}] = 10^{-2} \text{ mol/dm}^3$.

^bA = Poly(*N*-acrylamidomethylthionine-co-methylolacrylamide).

^cB = Poly(*N*-acrylamidomethylthionine-co-methylolacrylamide-co-vinylpyridine).

polymeric thionine films coated onto inert electrodes show a heterogeneous photoredox reaction not observed in homogeneous solution. In homogeneous solution the excited dye molecule oxidizes ferrous ion, and the resulting semithionine disproportionates to give the two-electron-reduced leucothionine. In homogeneous solution the electrode reaction is shown to involve leucothionine. In contrast, in polymeric films the disproportionation reaction is inhibited and the electrode reaction in the film involves a change in the polarity of the electrode in which thionine undergoes a redox reaction, as shown in Fig. 3. The electrode reactions occurring at the electrode coated with polymeric thionine and when the dye is present in the bulk solution at the uncoated platinum electrode are shown below.

Electrode Coated with Macromolecular Thionine



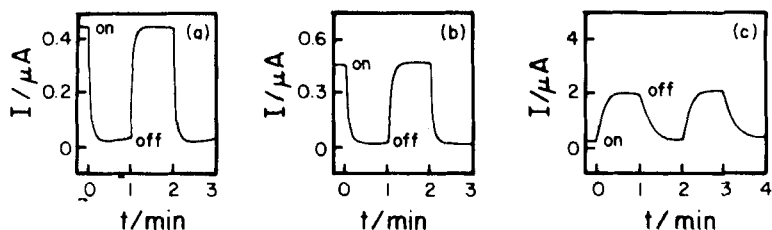
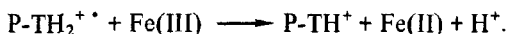
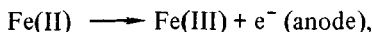
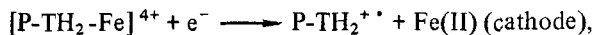
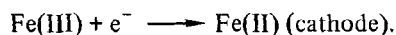
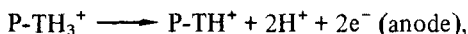
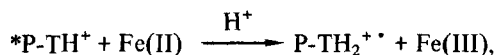


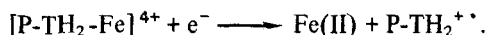
FIG. 3. Photocurrent for (a) iron-thionine system, (b) iron-polymer thionine system in homogeneous solution, and (c) iron-polymer thionine film for light "on" and "off" conditions.



Macromolecular Thionine Reaction in Homogeneous Solution



The species which is reduced at the polymer-dye electrode is proposed to be a complex between thionine and iron. The thionine-iron complex formed by the absorption of light is stabilized by the macromolecular structure and, at the electrode, this complex undergoes a one-electron reduction:



It thus seems that the macromolecular structure alters the nature of the photoelectrochemical reaction of polymeric thionine. The dye is present in the macromolecular-solvent environment as shown in Fig. 4. The macromolecule crosslinks at the electrode surface and forms a swollen film at the

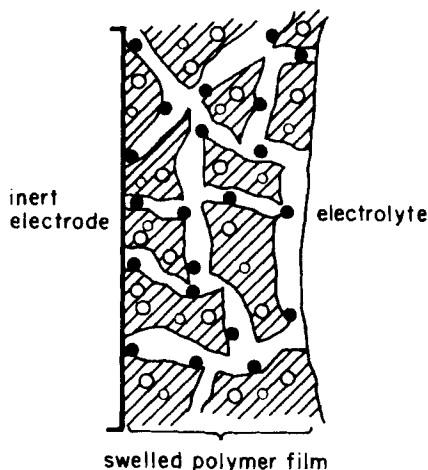


FIG. 4. Polymer-dye coated electrode system.

electrode, allowing free penetration of ions through the polymeric network. The macromolecular network plays an important role in the efficient charge injection at the thionine-polymer electrode. Studies on thionine dyes indicate that the redox behavior of the dye centers in the polymeric systems is similar to the monomeric dyes in homogeneous solution. However, electrodes coated with films of macromolecular thionine show somewhat different behavior depending upon the redox reaction occurring at the electrode, as shown in Table 3.

TABLE 3. Cyclic-Voltammetric Behavior at Coated and Uncoated Platinum Electrodes^a

Reaction	$E_{pc},^b$ mV	
	Uncoated	Coated
$\text{Fe(III)} + e^- \rightarrow \text{Fe(II)}$	0.37	0.26
$\text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{4-}$	0.14	0.00
$\text{Quinone} + 2e^- + 2\text{H}^+ \rightarrow \text{H}_2\text{Q}$	0.24	0.24

^a $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol/dm}^3$, potential sweep rate = $50 \text{ mV}\cdot\text{s}^{-1}$.

^bCathodic peak potential.

The cyclic voltammetric behavior of electrodes coated with polymeric thionine in the presence of ferrous ion reveals that the cathodic peak potential of the Fe(II)/Fe(III) couple shifts cathodically. Monomeric thionine shows similar behavior when coated onto inert electrodes. The cathodic peak of the $[\text{Fe}(\text{CN})_6^{4-}]/[\text{Fe}(\text{CN})_6^{3-}]$ couple also shifts negatively at the polymeric thionine electrode. This behavior is explained by the formation of a complex between the ferric ion and dye in the Fe(II)/Fe(III) case and by the formation of an ion pair between the ferrocyanide and thionine in the latter. The quinone system does not form an adduct with the polymeric thionine and, hence, its redox potential is not affected by the polymer electrode.

PHOTOCHEMICAL BEHAVIOR OF PHENOSAFRANINE DYE

Phenosafranine (3,7-diamino-5-phenylphenazium chloride) is known to undergo electron-transfer reaction in the excited state, as in the case of thionine. There have been reports [30, 31] on the use of the dye in photoelectrochemical cells. In these cells, illumination of the dye in aqueous solution in the presence of EDTA (ethylenediaminetetraacetic acid) produces a photopotential in a photogalvanic cell. In this case, EDTA is a sacrificial electron donor. The reactions involved in the photochemical reaction have been investigated for a derivative of phenosafranine, safranin-o (2,8-dimethyl-3,7-diamino-5-phenylphenazium chloride). Safranin-o exhibits three triplet species [32] in aqueous solution, and two semireduced species and the $\text{p}K_a$ values are similar to those for thionine. The order of reactivity of safranin-o triplet species toward EDTA is ${}^3\text{DH}_2^{2+} > {}^3\text{DH}_2^+ > {}^3\text{D}$; the scheme of photochemical reactions of phenosafranine is similar to that of thionine, except that EDTA is consumed in the photoredox reactions.

Phenosafranine has been linked covalently with the polymers poly(*N*-methylolacrylamide) [P(MAAM)] and poly(*N*-methylolacrylamide) [P(MAAM-*co*-VP)] (Fig. 5). The number of dye molecules attached to the macromolecule could be varied, and the macromolecular phenosafranine was purified from monomeric dye by repeated dissolving and reprecipitation. The polymeric dyes are stable in solution for months and do not undergo hydrolysis reactions. The absorption spectra of the monomeric and polymeric phenosafranine are shown in Fig. 6. The absorption spectra of poly(acrylamidomethylphenosafranine-*co*-methylolacrylamide) [P(AMPS-*co*-MAAM)] are similar to that of the monomeric dye, while poly(acrylamidomethylphenosafranine-*co*-methylolacrylamide-*co*-vinylpyridine) shows a visible absorption band slightly shifted toward the red. Fluorescence spectra of the monomeric and polymeric dye are shown in Fig. 7.

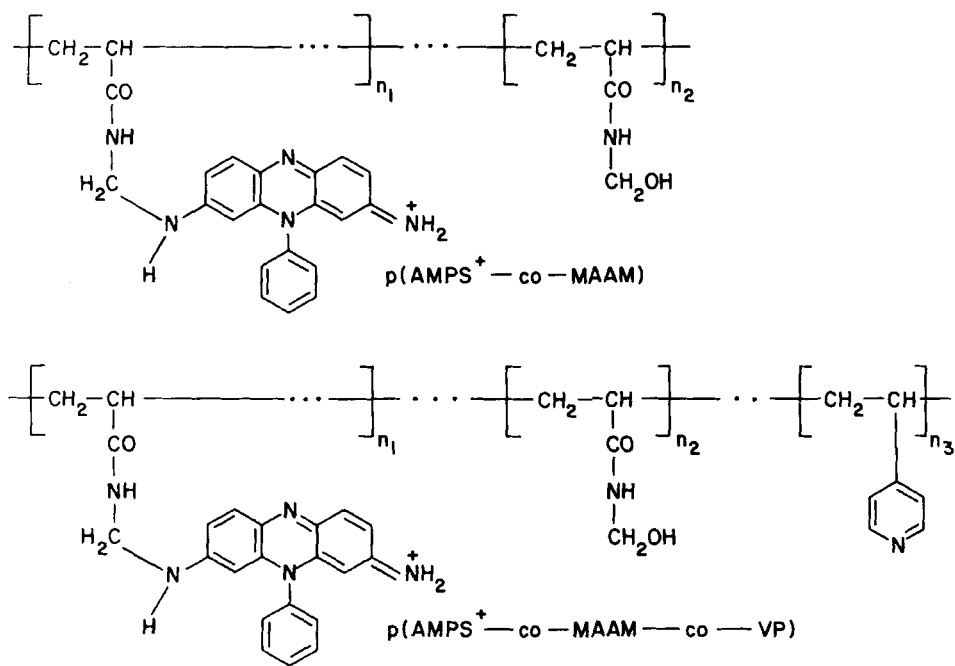
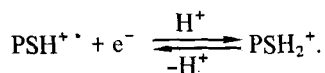
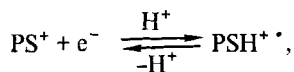


FIG. 5. Macromolecular phenosafranin systems.

Electrochemical properties of the monomeric and macromolecular phenosafranin dyes have been determined by obtaining the cyclic voltammograms shown in Fig. 8. Previous studies on phenazine dyes indicate the following redox reactions:



In cyclic voltammetric studies it was shown that the separation of peak potentials increases with an increase in the scan rate of the potential. It was also observed that, with an increase in the scan rate of the potential, the cathodic

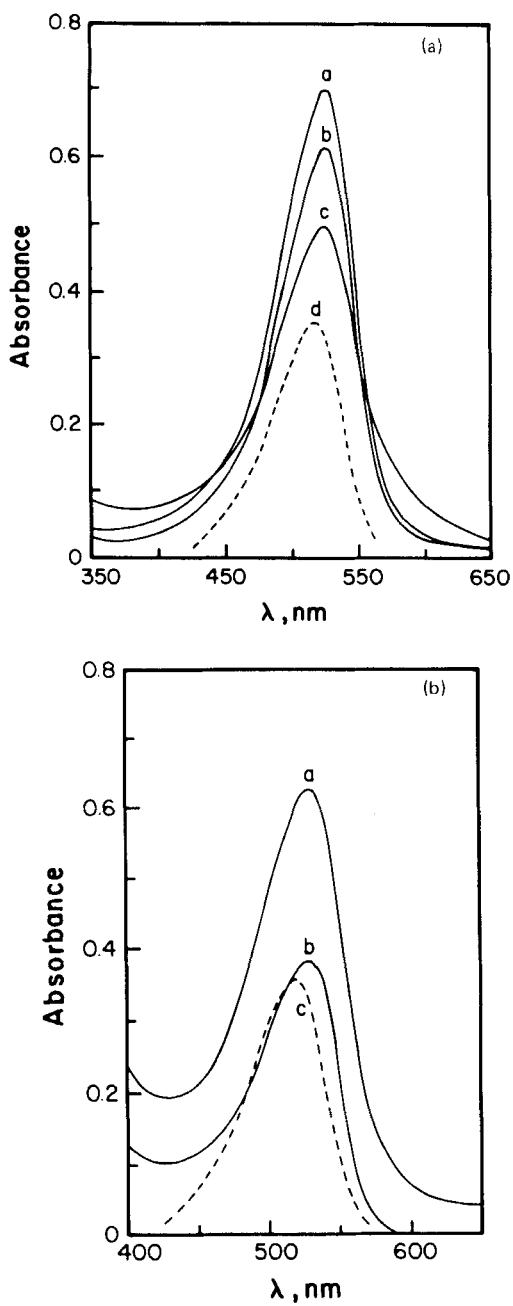


FIG. 6. Absorption spectra of phenosafranine polymers: (a) P(AMPS^+ -*co*-MAAM), (b) P(AMPS^+ -*co*-MAAM-*co*-VP).

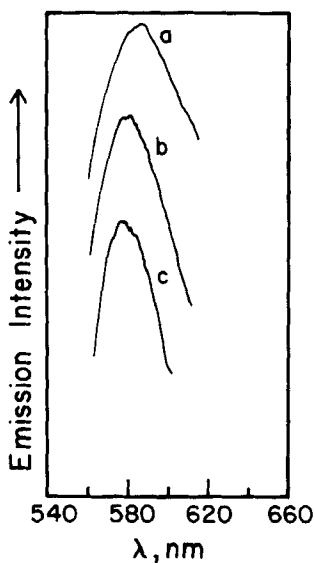


FIG. 7. Emission spectra of phenostrafarine polymers: (a) monomer, (b, c) polymer.

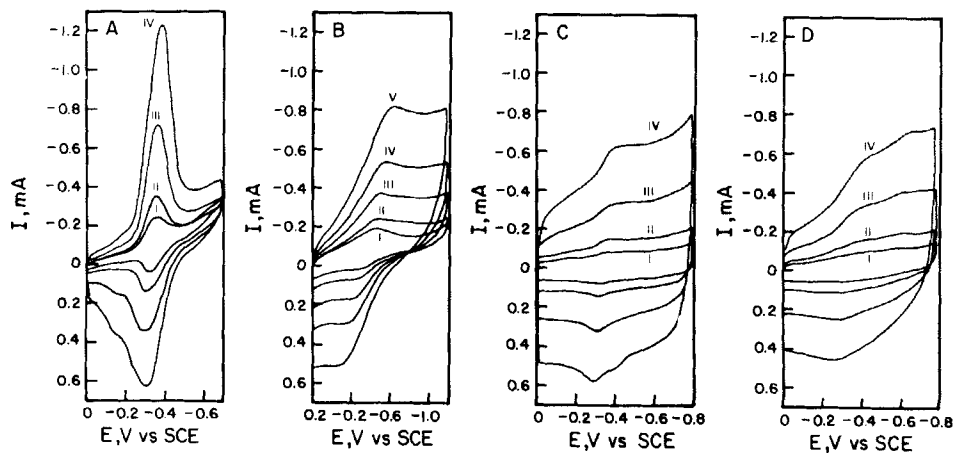


FIG. 8. Cyclic voltammograms of phenostrafarine: (A) monomer, (B) polymer in solution, (C, D) polymer coated on electrodes.

TABLE 4. Cyclic Voltammetric Data of Phenosafranine and Polymer-Bound Phenosafranine^a

A: PS ⁺ (present in solution)						
ν , mV/s	E_{pc} , V	E_{pa} , V	ΔE_p , mV		I_{pc} , μ A	
10	-0.36	-0.320	40		125	
20	-0.36	-0.315	45		220	
50	-0.37	-0.310	60		520	
100	-0.38	-0.305	75		970	
B: PS ⁺ (adsorbed on carbon)						
ν , mV/s	E_{pc} , V	E_{pa} , V	ΔE_p , mV			
10	-0.44	-0.32	120			
20	-0.46	-0.28	180			
50	-0.48	-0.24	240			
100	-0.54	-0.62	380			
200	-0.62	-0.10	520			
C: P(AMP ⁺ -co-MAAM) (coated on carbon), M/D = 41						
ν , mV/s	E_{pc}^1 , V	E_{pc}^2 , V	E_{pa}^1 , V	E_{pa}^2 , V	ΔE_p^1 , mV	ΔE_p^2 , mV
10	-0.35	-0.44	-0.33	-0.43	20	10
20	-0.35	-0.44	-0.32	-0.43	30	10
50	-0.36	-0.46	-0.31	-0.43	50	30
100	-0.38	-0.47	-0.30	-0.42	80	50
D: P(AMPS ⁺ -co-VP) (coated on carbon), M/D = 21						
ν , mV/s	E_{pc}^1 , V	E_{pc}^2 , V	E_{pa}^1 , V	E_{pa}^2 , V	ΔE_p^1 , mV	ΔE_p^2 , mV
10	-0.36	-0.60	-0.31	-0.56	50	40
20	-0.38	-0.61	-0.31	-0.56	70	50
50	-0.40	-0.63	-0.30	-0.54	100	90
100	-0.43	-0.66	-0.27	-0.53	160	130

^a[KCl] = 0.1 M. Potential range = +0.0 to -0.8 V. Solvent = 8:2 = CH₃CN:H₂O (v/v). Working electrode = carbon.

curve shifts to more negative potentials. In contrast to the monomeric dye, polymer-bound phenosafranine shows two anodic and two cathodic waves. The peaks are broader and the peak separation is larger for polymeric phenosafranine (Table 4). The reduction steps of the phenosafranine could be observed separately when the dye was bound to the macromolecule (Fig. 8). During the reduction of polymer-bound phenosafranine, protonation occurs, indicating that the process can be described in terms of an electron transfer-chemical reaction-electron transfer (ECE) mechanism.

CHARACTERISTICS OF SEMIPHENOSAFRANINE ATTACHED TO MACROMOLECULAR CHAINS

Phenosafranine dye, on flash photolysis in an aqueous solution containing EDTA, shows a transient which is identified as the one-electron reduced dye, semiphenosafranine. The absorption spectrum of the semiphenosafranine shows a maximum at 640 nm.

Macromolecular phenosafranine under identical conditions undergoes reduction on flash photolysis to produce a semireduced polymeric dye. The absorption spectra of macromolecular semiphenosafranine dyes are shown in Fig. 9. The absorption band maximum for the polymeric dye has shifted toward the red by 40 nm in the case of P(AMPS-*co*-MAAM-*co*-VP). The rate constant for the disproportionation of semiphenosafranine was found to be $2 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$. Macromolecular semiphenosafranine disproportionates with a rate constant of $5 \pm 3 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$. In the case of macromolecular thionine, a similar decrease in the disproportionation rate constants between the monomeric and macromolecular dye was observed. This difference is attributed to the difference in the diffusional rate between the monomeric and polymeric dye.

The polymer-bound dye P(AMPS⁺-*co*-MAAM-*co*-VP) does not give any transient on flash photolysis in the absence of EDTA whereas in the case of P(AMPS⁺-*co*-MAAM) a transient was observed on photoexcitation even in the absence of EDTA. The transient observed under similar conditions for the monomeric dye was suggested as a triplet. The presence of pyridine in the macromolecular chain brings about a different photochemical reaction in the absence of electron donors. As discussed below, the photoelectrochemical behavior of the dye depends on the nature of the macromolecule.

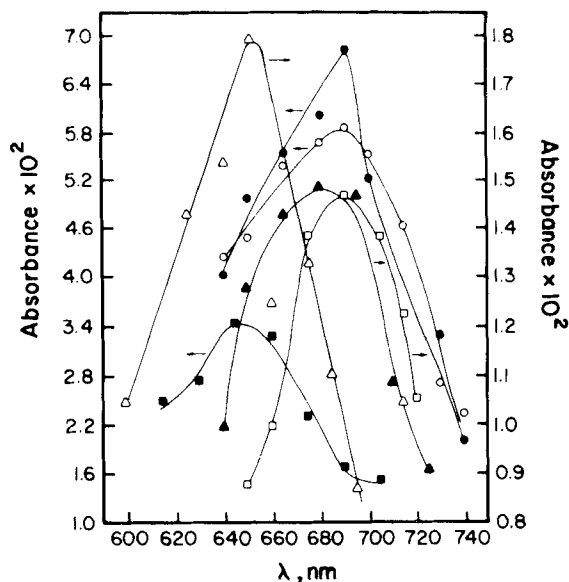


FIG. 9. Absorption spectra of semiphenosafranine formed from (Δ) phenosafranine and EDTA; (\blacksquare) phenosafranine only, (\bullet) P(AMPS⁺-co-MAAM), M/D = 16, with EDTA; (\circ) P(AMPS⁺-co-MAAM-co-VP) with EDTA; (\blacktriangle) P(AMPS⁺-co-MAAM), M/D = 16 without EDTA; (\square) P(AMPS⁺-co-MAAM), M/D = 41, with EDTA.

PHOTOELECTROCHEMICAL BEHAVIOR OF MACROMOLECULAR PHENOSAFRANINE DYE FILMS AS ELECTRODES [33]

The phenosafranine-EDTA system has been known to show appreciable photogalvanic potential. In the case of macromolecular phenosafranine dye, the polymeric dye was coated onto a platinum or carbon electrode by placing a solution of the macromolecular dye on the surface of the electrolytically cleaned inert electrode surface by blowing hot air over the surface. The polymer dye electrode, along with a plain platinum electrode or different macromolecular electrodes, was immersed in a cell containing 6:4 CH₃CN:H₂O (v/v) with potassium chloride or sodium perchlorate as the supporting electrolyte. The irradiation source was a tungsten lamp, and the current was monitored for the cell. The results are shown in Fig. 10. The current-voltage diagrams for the macromolecular dye-coated electrodes are shown in Figs. 11A and 11B.

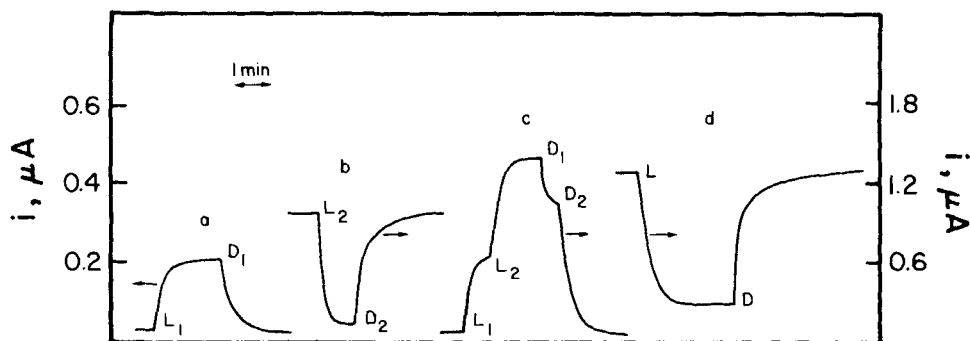


FIG. 10. (a) Photocurrent for P(AMPS⁺-*co*-MAAM)-coated electrode without EDTA. (b) Photocurrent for P(AMPS⁺-*co*-MAAM-*co*-VP)-coated electrode without EDTA. (c) Photocurrent for one of the electrodes coated with P(AMPS⁺-*co*-MAAM) and the other coated with P(AMPS⁺-*co*-MAAM-*co*-VP) coupled and kept in a two-compartment cell without EDTA. (d) Photocurrent for P(AMPS⁺-*co*-MAAM)-EDTA system. L₁: "Light on" condition for P(AMPS⁺-*co*-MAAM)-coated electrode. D₁: "Light off" condition for P(AMPS⁺-*co*-MAAM)-coated electrode. L₂: "Light on" condition for P(AMPS⁺-*co*-MAAM-*co*-VP)-coated electrode. D₂: "Light off" condition for P(AMPS⁺-*co*-MAAM-*co*-VP) coated electrode.

The current-potential curve of P(AMPS⁺-*co*-MAAM) coated onto carbon electrode shows that the photochemically produced semidye is easily oxidized at the carbon anode at a potential around -0.1 V vs SCE. The cyclic voltammetric data for P(AMPS⁺-*co*-MAAM) or P(AMPS⁺-*co*-MAAM-*co*-VP) coated onto carbon electrodes indicate the occurrence of a two-electron redox process which corresponds to the formation of semireduced dye at -0.54 V vs NHE and leuco dye at -0.69 V vs NHE.

PHOTOELECTROCHEMICAL REACTIONS AT MACROMOLECULE-BOUND PHENOSAFRANINE-COATED ELECTRODE: EXAMPLE OF A REGENERATIVE-TYPE WATER SPLITTING CELL

The electrode coated with P(AMPS⁺-*co*-MAAM) shows a photopotential in air-equilibrated solutions either in the single-compartment or in the two-compartment cell with the counterelectrode being uncoated platinum. Under the same conditions, an increase in the acid concentration leads to an increase

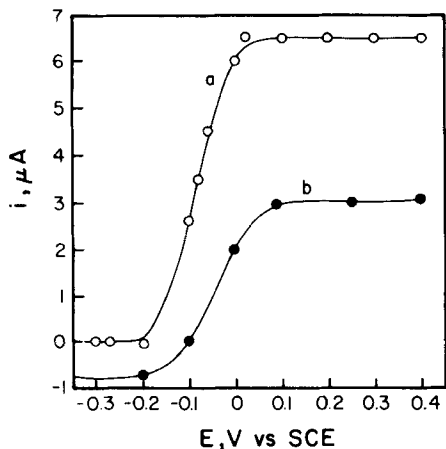


FIG. 11A. (a) Photocurrent plotted against applied voltage (vs SCE) across the working electrode-reference electrode for the $\text{P}(\text{AMPS}^+ \text{-co-MAAM})$ -coated electrode-EDTA system. (b) Photocurrent plotted against applied voltage (vs SCE) across the working electrode-reference electrode for the PS^+ -EDTA system.

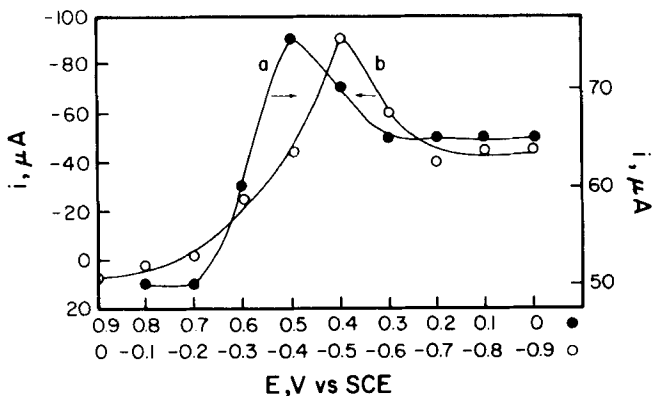


FIG. 11B. (a) Photocurrent plotted against applied voltage (vs SCE) across the working electrode-reference electrode for the $\text{P}(\text{AMPS}^+ \text{-co-MAAM-co-VP})$ -coated electrode without EDTA. (b) Photocurrent plotted against applied voltage (vs SCE) across the working electrode-reference electrode for the $\text{P}(\text{AMPS}^+ \text{-co-MAAM})$ -coated electrode without EDTA.

in the open-circuit photopotential and photocurrent. As far as the P(AMPS⁺-*co*-MAAM-*co*-VP) coated electrode is concerned, it shows the opposite polarity compared to an analogous cell with P(AMPS⁺-*co*-MAAM). In this case, however, in alkaline solution (pH ~10.0), an enhancement in the photocurrent and photopotential is observed. In experiments with two-compartment cells, where one of the electrodes is coated with P(AMPS⁺-*co*-MAAM) and the other coated with P(AMPS⁺-*co*-MAAM-*co*-VP) coupled and kept in different compartments connected by a salt bridge, the observed current is a sum of what was observed for the individual electrodes kept separately along with a plain platinum electrode in a single compartment cell. In this case both the electrodes were exposed to light.

The photoelectrochemical reactions are proposed to involve water and oxygen in the redox processes at the electrode. The photopotential depends upon the extent of oxygen present in the solution, which suggests that the electrode coated with macromolecular dye reduces oxygen to water at the cathode and oxidizes water to oxygen at the anode. The direction of the current is reversed depending upon the nature of the polymer-dye film.

INTERACTION BETWEEN CHROMOPHORES PRESENT IN THE MACROMOLECULAR CHAIN [34]

It is known that dyes in general aggregate to form oligomers. Investigations have been carried out with macromolecules which have both thionine and the ruthenium(II) polypyridyl complex in the same macromolecular chain. The absorption and emission spectral details are given in Table 5. Aggregation between thionine molecules is observed, and the equilibrium

TABLE 5. Polymer-Bound Thionine and Ruthenium(II) Complex

Polymer	M/D	λ_{abs} , nm	λ_{em} , nm	τ , ns
P(AmTH ⁺ - <i>co</i> -MAAM- <i>co</i> -VP)	70 ± 20	585, 615	640	
[Ru(bpy) ₂ (VP- <i>co</i> -AmTH ⁺ - <i>co</i> -MAAM) ₂ ²⁺]	70 ± 20	460, 635	660	20 ± 2
[Ru(bpy) ₂ (VP- <i>co</i> -MAAM) ₂ ²⁺]	—	460	610	34 ± 2

constant is known to be 4000 M^{-1} [35]. In the case of P(AmTH⁺-*co*-MAAM-*co*-VP), **1**, increased aggregation is observed when the number of dye counters increases in the macromolecule. When the ruthenium(II) complex is also present in the same chain, the intensity of the absorption feature due to aggregation is decreased. Emission spectral data for Polymers **1** and **2**, [Ru(bpy)₂VP-*co*-AmTH⁺-*co*-MAAM]₂²⁺, indicate that emission occurs from the thionine with a maximum at 640 nm on excitation at 610 nm, and emission from the ruthenium center is observed on excitation at 450 nm. When the M/D ratio of thionine in the macromolecule is <70, the emission intensity from the ruthenium center is found to decrease by an order of magnitude, while the intensity from the thionine-emitting state is not appreciably affected. When both thionine and the ruthenium(II) complex are bound to the same macromolecule, three effects are observed: 1) a shift of the absorption and emission spectra of thionine and not of the ruthenium(II) complex, 2) the lifetime of the polymer-bound ruthenium(II) complex is decreased by 50% compared to the macromolecular ruthenium(II) complex in the absence of thionine, and 3) there is a lack of aggregation between thionine centers.

The decrease in aggregation between the thionine centers in the presence of the ruthenium(II) complex in the macromolecule, when the thionine units are separated by an average of 70 monomer units, indicates a cooperative effect operating at fairly long distance. The effect is considerably reduced when the M/D ratio is 200. The quenching of the lifetime of the ruthenium(II) excited state by the thionine center operates only when the monomer-to-thionine ratio is below 70, and quenching is absent when the M/D ratio is 200. Thus the charge-transfer interaction between thionine and the ruthenium center in the macromolecular chain occurs within a distance of 30 ± 10 monomer units, which corresponds to a distance of $\sim 40 \text{ \AA}$. When the ruthenium(II) complex content in the chain is increased, no further change in the absorption/emission spectral properties of thionine or in the lifetime of the ruthenium(II) complex occurred.

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