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Studies on the photoelectrochemical properties of thionine dye covalently bound to poly(acrylamidoglycolic acid)

K. Viswanathan [a], P. Natarajan [a,b,*]

[a] *Department of Inorganic Chemistry, University of Madras, Madras-600 025, India*
[b] *Central Salt and Marine Chemicals Research Institute, Bhavnagar-364 002, India*

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Abstract

Thionine dye, TH^+, covalently attached to a macromolecule, poly(acrylamidoglycolic acid) (P(AGA)), was prepared. Flash photolysis of the macromolecule-bound thionine, P(AGA)–TH^+, in the presence of Fe(II) ions shows that the absorption spectrum of polymer-bound semithionine radical is not significantly changed from that of monomeric semithionine. The rate constant for the disproportionation reaction of polymer-bound semithionine is significantly decreased compared with that of unbound semithionine. Cyclic voltammetric studies show that the electron transfer processes occurring at the electrode are less reversible for P(AGA)–TH^+ in homogeneous solution than for P(AGA)–TH^+ coated onto an electrode as a thin film. For P(AGA)–TH^+ coated onto an electrode or an electrode immersed in P(AGA)–TH^+ in homogeneous solution, cathodic behaviour is observed at the illuminated electrode, indicating a change in the polarity of the electrode in comparison with the reaction observed at a platinum electrode with thionine and iron(II) present in homogeneous solution. Stabilization of the charge-separated thionine–iron(II) complex by the polymer network seems to be an important factor for efficient charge transfer at the electrode.

Keywords: Photoelectrochemical properties; Thionine; Macromolecule; Poly(acrylamidoglycolic acid)

1. Introduction

In recent years, there has been considerable interest in the study of photochemical reactions in microheterogeneous environments, such as micelles, monolayers, vesicles and polymers, to enhance the charge separation of the photochemically generated products [1]. We are interested in the synthesis of polymers containing thiazine and phenazine dyes and porphyrin systems and the investigation of their photochemical and photoelectrochemical behaviour [2]. We have reported previously that, when poly(methylolacrylamide)-bound thionine (P(MAAM)–TH^+) is coated onto an electrode, the charge-separated thionine–iron complex is stabilized by the macromolecular network. The polarity of the electrode coated with polymer-bound dye is reversed in comparison with that observed for the iron(II)–thionine system in homogeneous aqueous solution [2a]. In homogeneous solutions, flash photolysis of polymeric thionine in the presence of ferrous ions leads to a considerably reduced disproportionation rate constant of semithionine (produced by the reaction of the excited polymeric dye with ferrous ions) when thionine is bound to the macromolecule [2b]. In this paper, we report the flash photolysis and electrochemical and photoelectrochemical properties of thionine dye covalently bound to poly(acrylamidoglycolic acid) (P(AGA)–TH^+) and the effect of the macromolecular environment on the charge transfer at the electrode.

2. Experimental details

Thionine (7-amino-3H-phenothiazin-3-iminium chloride) was obtained as thionine acetate (Fluka) and purified by standard methods [3]. Poly(acrylamidoglycolic acid) (P(AGA)) was prepared by polymerizing acrylamidoglycolic acid (Aldrich) in water under a stream of nitrogen at 60 °C using potassium peroxydisulphate ($K_2S_2O_8$) as the initiator [4]. Thionine was condensed with P(AGA) by the following procedure [5]. Purified thionine was added to an aqueous solution of the polymer in the desired molar ratio and the mixture was kept at 90 °C in a water bath for 5 h. Hydroquinone was added to this mixture to prevent cross-linking of the polymer. The uncondensed thionine was removed by dialysing the solution (cellulose tubing

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[*] Corresponding author.

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(Sigma); molecular weight cut-off, 12 000) for several days against distilled water. Dialysis was stopped when the solvent outside the membrane showed no absorption at 600 nm, where thionine has a molar absorptivity of 5.29×10^4 dm^3 mol^{-1} cm^{-1}. The concentration of thionine bound to the macromolecule was estimated by titrating ferrous ammonium sulphate in orthophosphoric acid against polymer-bound thionine solution [2a]. A known volume of original polymer–dye solution was evaporated to dryness and the weight of the residue was taken as the amount of polymer–dye complex present in the original solution. The number of dye units bound to a polymer chain (consisting of a given number of monomer units (the m/d ratio)) was determined from the amounts of polymer and dye present per unit volume of solution.

Flash photolysis experiments were carried out using an Applied Photophysics model KN-020 flash kinetic spectrophotometer. The details of the experimental set-up are given elsewhere [2b]. The absorption spectra of semithionine and polymer-bound semithionine were obtained as follows. Dilute solutions of thionine or polymer-bound thionine (absorbance, 0.066 cm^{-1} at 600 nm) in 1.58×10^{-3} mol dm^{-3} H_2SO_4 containing 0.01 mol dm^{-3} iron(II) were irradiated with a flash energy of 200 J. The monitoring beam was first passed through a filter solution of thionine to prevent steady photolysis of thionine in the reaction mixture. The outer jacket of the sample cell contained 0.5 mol dm^{-3} iron(II) sulphate solution to prevent the absorption of light by iron(II) in the reaction mixture. The absorbance of semithionine in the 700–800 nm region, where the absorption by thionine and polymer-bound thionine is negligible, was monitored. The transient absorption spectrum of the semithionine species was obtained by recording the absorbances at different monitoring wavelengths with a delay of 0.5 ms after the flash. A plot of $1/\Delta A$ vs. time resulted in straight lines, indicating that the decay of the transient species follows second-order kinetics. The slope of the plot gives $k_d/\epsilon l$ where k_d is the disproportionation rate constant, ϵ is the molar absorptivity of semithionine and l is the path length of the flash cell. The molar absorptivity of semithionine ($\epsilon_{750} = 1.33 \times 10^4$ dm^3 mol^{-1} s^{-1}) [6] was used to calculate the rate constant.

The electrochemical data were obtained using PAR modules: 173 potentiostat/galvanostat, 175 universal programmer and 174 A polarographic analyser. A PAR 303 cell system, consisting of a glassy carbon working electrode (0.017 cm^2), a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE), was used. All the electrochemical studies were made after purging purified dinitrogen gas through the experimental solutions. The photovoltaic effect of the polymer–dye-coated electrode was studied using a single-compartment cell consisting of a 1 cm^2 platinum electrode coated with polymer-bound thionine and a bare 1 cm^2 platinum electrode. The distance between the electrodes was maintained at 5 ± 1 mm. Polymer-bound thionine was coated onto the platinum electrode by placing a known concentration of the polymer-bound dye on the surface of the electrolytically cleaned and dried platinum electrode and drying this at 90 °C in vacuum. The evaporation of the solvent left an insoluble stable film behind on the electrode surface. The photovoltaic effect of the electrode coated with polymer-bound thionine was studied by keeping the electrodes in 0.5×10^{-2} mol dm^{-3} sulphuric acid and 10^{-2} mol dm^{-3} ferrous solution. The solution was deaerated for 30 min by the passage of oxygen-free dinitrogen gas. The photovoltaic effect of the polymer-bound dye in homogeneous solution was studied using a two-compartment cell, consisting of two 1 cm^2 platinum electrodes interconnected by a salt bridge, with one of the electrodes masked from the light. A known concentration of polymer-bound dye containing 0.5×10^{-2} mol dm^{-3} sulphuric acid and 10^{-2} mol dm^{-3} ferrous solution was placed in both compartments and deaerated for 30 min in oxygen-free dinitrogen gas. To study the effect of the hydrogen ion concentration on the photovoltage, the pH of the solution was varied using sulphuric acid. The irradiation source used was a 300 W tungsten lamp.

3. Results

The absorption spectra of the transients were obtained following flash photolysis of polymer-bound thionine with various m/d ratios; the results are shown in Fig. 1. The disproportionation rate constants (k_d) for unbound and polymer-bound semithionine are given in Table 1.

Typical cyclic voltammograms of unbound thionine, P(AGA)-TH^+ in homogeneous solution and P(AGA)-TH^+ coated onto a glassy carbon electrode as a thin film in 0.5 mol dm^{-3} H_2SO_4 medium are shown in Figs. 2(A)–2(C); plots of I_{pc} vs. $(\nu)^{1/2}$ for unbound thionine and P(AGA)-TH^+ coated onto the electrode were found to be

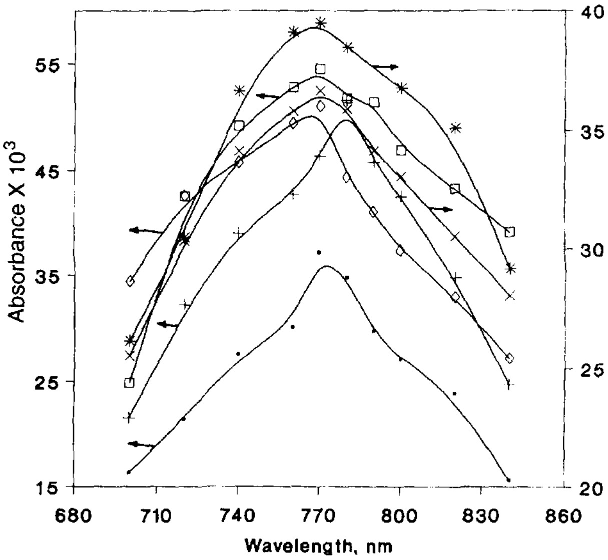

Fig. 1. Absorption spectra of semithionine formed from: ◇, unbound thionine; □, P(AGA)-TH^+, m/d = 259; +, P(AGA)-TH^+, m/d = 310; *, P(AGA)-TH^+, m/d = 542; □, P(AGA)-TH^+, m/d = 865; ×, P(AGA)-TH^+, m/d = 1330. pH 2.5, $[Fe^{2+}] = 1 \times 10^{-2}$ mol dm^{-3}.

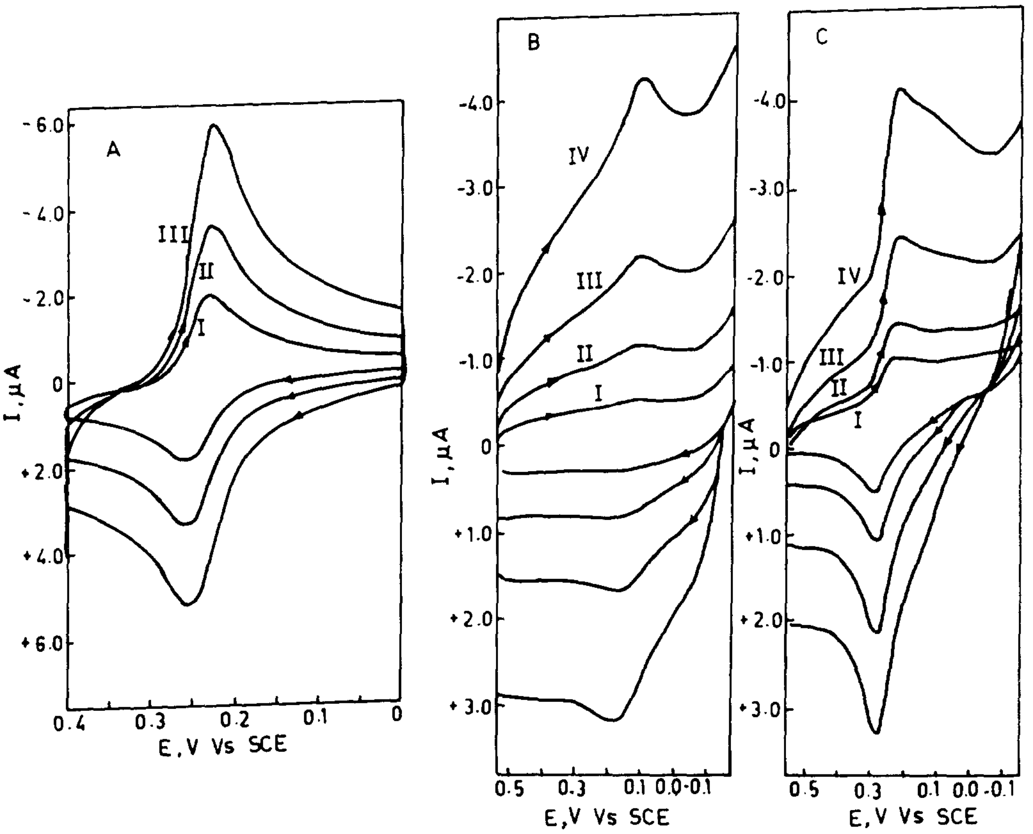

Fig. 2. Typical cyclic voltammograms for unbound thionine (A), P(AGA)–TH$^+$ in homogeneous solution (B) and P(AGA)–TH$^+$ coated onto glassy carbon electrode (C). Potential scan rates (mV s^{-1}) are as follows: (I) 20; (II) 50; (III) 100; (IV) 200. [H_2SO_4] = 0.5 mol dm^{-3}.

linear. The cathodic peak potential (E_{pc}), anodic peak potential (E_{pa}), separation of the peak potentials (ΔE_p) and cathodic peak current (I_{pc}) at various scan rates for P(AGA)–TH$^+$ in homogeneous solution and P(AGA)–TH$^+$ coated onto a glassy carbon electrode as a thin film are given in Tables 2 and 3 respectively. The concentration of thionine in P(AGA)–TH$^+$ was maintained constant in all cases; a plot of E_{pc} vs. the m/d ratio for P(AGA)–TH$^+$ in homogeneous solution is shown in Fig. 3.

Typical plots of the photocurrent vs. time of irradiation for unbound thionine, polymer-bound thionine in homogeneous solution and polymer-bound thionine coated onto the electrode are shown in Figs. 4(A)–4(C). The open circuit photopotential (ΔE_{oc}) and short circuit photocurrent (I_{sc}) for P(AGA)–TH$^+$ in homogeneous solution and for P(AGA)–TH$^+$ coated onto the electrode with different m/d ratios at different pH values are given in Table 4. The photocurrents measured in the photoelectrochemical cell with P(AGA)–TH$^+$ in homogeneous solution and P(AGA)–TH$^+$ coated onto the platinum electrode, immersed in a solution containing ferrous ions at different applied potentials with respect to SCE, are shown in Fig. 5.

Table 1

Disproportionation rate constants (k_d) for unbound semithionine and semithionine bound to P(AGA) with different m/d ratios. [Fe^{2+}] = 1×10^{-2} mol dm^{-3}, pH 2.5

Sample	m/d ratio	$k_d \times 10^8$ ($M^{-1} s^{-1}$)
Unbound tionine	–	31.8
P(AGA)–TH$^+$	259	2.46
P(AGA)–TH$^+$	310	2.42
P(AGA)–TH$^+$	542	2.01
P(AGA)–TH$^+$	865	3.66
P(AGA)–TH$^+$	1330	1.20

4. Discussion

4.1. Absorption spectrum of semithionine attached to macromolecular chains

The photoreaction of excited thionine and ferrous ion in acid solution involves electron transfer from ferrous ion to thionine in the triplet state [7]. In this work, flash photolysis studies of iron(II)–thionine and iron(II)–macromolecule-bound thionine (P(AGA)–TH$^+$) were carried out to investigate the effect of the polymer backbone on the properties of the semithionine radical. The absorption spectrum of the free semithionine radical shows an absorption maximum at 770 nm (Fig. 1) as reported previously [7a,b]. The absorption spectrum of semithionine radicals produced on flash irradia-

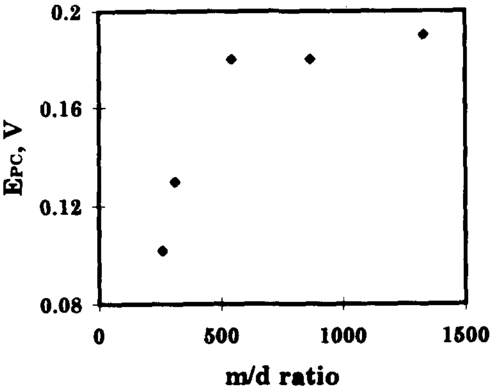

Fig. 3. Plot of cathodic peak potential (E_{pc}) at potential scan rate of 50 mV s^{-1} vs. m/d ratio for P(AGA)–TH^+ in homogeneous solution.

tion of P(AGA)–TH^+ in the presence of ferrous ions shows an absorption maximum around 770 nm (Fig. 1), suggesting that the absorption spectrum of the semithionine radical is not significantly influenced by its covalent linkage to the macromolecule. A similar observation in the case of poly(methylolacrylamide)-bound thionine has also been reported [2b].

4.2. Kinetics of decay of polymer-bound semithionine

The decay process of the semithionine radical, produced by electron transfer from ferrous ion to triplet thionine on flash excitation, is represented by the following equations

$$TH^+ \xrightarrow{h\nu} {}^*TH^+ \tag{1}$$

$$^*TH^+ + Fe^{II} \overset{H^+}{\rightleftharpoons} TH_2^{\bullet +} + Fe^{III} \tag{2}$$

$$2TH_2^{\bullet +} \overset{H^+}{\rightleftharpoons} TH^+ + TH_4^{2+} \tag{3}$$

$$TH_4^{2+} + Fe^{III} \xrightarrow{k_d} TH_2^{\bullet +} + Fe^{II} + 2H^+ \tag{4}$$

where TH^+ is thionine, $TH_2^{\bullet +}$ is semithionine and TH_4^{2+} is leucothionine. The rate constant k_d of disproportionation of semithionine (Eq. (3)) determined from this study (3.18×10^9 M^{-1} s^{-1}) agrees with the value reported by Hatchard and Parker [8] ($k_d = 2.4 \times 10^9$ M^{-1} s^{-1}). Re-oxidation of semithionine by ferric ions (Eq. (2)) is a relatively slow process [8] (rate constant, 7×10^7 M^{-1} s^{-1} [9]) compared with the rate constant for the disproportionation reaction (k_d). It has also been reported that, even at high concentrations of ferric ions (10^{-3} M), the decay of semithionine follows second-order kinetics [9]. The above observations clearly suggest that the decay of semithionine is predominantly due to the disproportionation reaction (Eq. (3)).

In the case of polymer-bound thionine, P(AGA)–TH^+, the decay of the transient, followed by the flash photolysis experiment, exhibits second-order kinetics as observed in the case of monomeric thionine (Table 1). The disproportiona-

Table 2
Cyclic voltammetric data of unbound thionine and P(AGA)–TH^+ in homogeneous solution. Working electrode, glassy carbon; reference electrode, SCE; supporting electrolyte, 0.5 mol dm^{-3} H_2SO_4

Sample	ν (mV s^{-1})	E_{pc} (V)	E_{pa} (V)	ΔE (mV)	I_{pc} (μA)
Unbound thionine	100	0.26	0.295	35	1.84
	50	0.26	0.295	35	1.28
	20	0.265	0.295	30	0.80
	10	0.265	0.295	30	0.60
P(AGA)–TH^+ m/d = 259	100	0.091	0.251	160	0.36
	50	0.102	0.251	150	0.20
	20	0.123	0.251	128	0.14
	10	0.123	0.251	128	0.08
P(AGA)–TH^+ m/d = 310	100	0.12	0.25	130	0.24
	50	0.13	0.25	120	0.16
	20	0.16	0.25	90	0.1
	10	0.17	0.25	80	0.06
P(AGA)–TH^+ m/d = 542	200	0.17	0.24	70	0.36
	100	0.17	0.23	60	0.16
	50	0.18	0.22	40	0.08
	20	0.19	0.22	30	0.04
P(AGA)–TH^+ m/d = 865	200	0.175	0.23	55	0.296
	100	0.18	0.23	50	0.144
	50	0.18	0.22	40	0.072
	20	0.19	0.22	30	0.032
P(AGA)–TH^+ m/d = 1330	200	0.17	0.26	90	0.12
	100	0.19	0.25	60	0.08
	50	0.19	0.24	50	0.06
	20	0.2	0.23	30	0.04

Table 3
Cyclic voltammetric data of P(AGA)–TH$^+$ coated onto a glassy carbon electrode. Reference electrode, SCE; supporting electrolyte, 0.5 mol dm^{-3} H_2SO_4

Sample	ν (mV s^{-1})	E_{pc} (v)	E_{pa} (V)	ΔE (mV)	I_{pc} (μA)
P(AGA)–TH$^+$ m/d = 259	100	0.24	0.30	60	1.8
	50	0.25	0.30	50	1.24
	20	0.25	0.30	50	0.75
	10	0.26	0.30	40	0.52
P(AGA)–TH$^+$ m/d = 310	100	0.22	0.28	60	1.6
	50	0.22	0.28	60	1.16
	20	0.22	0.28	60	0.72
	10	0.23	0.28	50	0.5
P(AGA)–TH$^+$ m/d = 542	100	0.22	0.28	60	1.06
	50	0.22	0.28	60	0.76
	20	0.23	0.28	50	0.48
	10	0.24	0.28	40	0.34
P(AGA)–TH$^+$ m/d = 865	100	0.13	0.28	150	0.20
	50	0.16	0.28	120	0.14
	20	0.22	0.28	60	0.09
	10	0.23	0.28	50	0.06
P(AGA)–TH$^+$ (m/d = 1330)	100	0.18	0.27	100	0.12
	50	0.20	0.27	80	0.09
	20	0.21	0.27	70	0.06
	10	0.22	0.27	60	0.04

tion rate constant (k_d) for polymer-bound semithionine (produced on flash excitation of P(AGA)–TH$^+$) is one order of magnitude less than that of monomeric thionine (Table 1). Thus the incorporation of thionine into the polymer chain increases the lifetime of the semithionine radical. The rate constant for an encounter-controlled reaction between two macromolecular systems is expected to be lower than that of a reaction occurring between two micromolecular systems. Thus the observed difference between the rate constants is due to the difference between the diffusion rates of monomeric semithionine and polymeric semithionine. It has been shown that, in sodium dodecyl sulphate micelles [10] and macromolecular media [11], the rate constant for the disproportionation reaction of semithionine decreases relative to that for monomeric thionine; for semithionine bound to P(MAAM) and its copolymers, the rate constant decreases by two orders of magnitude [2b]. When a macromolecule containing a pendant aromatic chromophore is dissolved in water, the hydrophobic groups interact with each other to form hydrophobic microdomains and charged segments of the polymer surround these microdomains providing a micellar structure [12]. P(MAAM)–TH$^+$ is expected to be more extensively coiled than P(AGA)–TH$^+$ due to the absence of ionic groups in the polymer chain. It is known that the polymer coil protects the buried chromophore from quenchers which, in turn, reduces the disproportionation rate. In a related study on the fluorescence lifetime of P(AGA)–TH$^+$ and P(MAAM)–TH$^+$, we have found that the dye molecules reside in two different environments; some in a hydrophobic environment where the chromophore is buried inside the polymer coil, and some in a hydrophilic environment where the chromophore is located in the solvent pool. When the con-

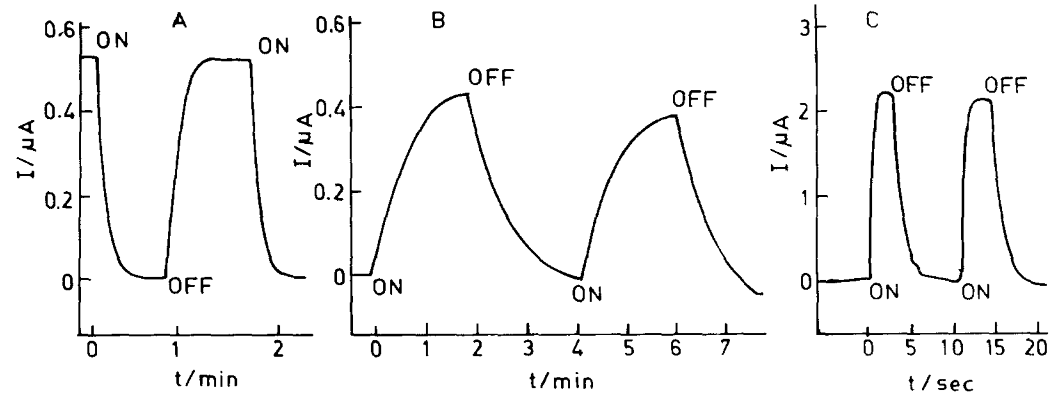

Fig. 4. Photocurrent for iron–thionine system (A), iron–P(AGA)–TH$^+$ in homogeneous solution (B) and iron–P(AGA)–TH$^+$- coated electrode (C) for "light on" and "light off" conditions.

formation of the polymer coil changes from an extended structure to a more extensively coiled form, the proportion of dye molecules buried inside the polymer coil increases [13]. It has also been shown that the proportion of dye molecules residing in the hydrophobic environment (buried chromophore) is greater for P(MAAM)–TH$^+$ than P(AGA)–TH$^+$ [13]. Thus the disproportionation rate constant for P(MAAM)–TH$^+$ is slower than that for P(AGA)–TH$^+$ as a larger number of dye molecules are buried in the polymer coil. When the m/d ratio of polymer-bound thionine (P(AGA)–TH$^+$) increases (loading of the dye decreases), the disproportionation rate constant k_d decreases (Table 1). It is known that the proportion of hydrophobic chromophores present in the interior of the polymer coil (less polar environment) increases as the loading decreases, since the hydrophobic chromophore prefers a less polar environment [14].

4.3. Electrochemical behaviour of polymer-bound thionine in homogeneous solution and electrodes coated with polymer-bound thionine

Cyclic voltammograms for unbound thionine in 0.5 mol dm^{-3} H_2SO_4 medium at a glassy carbon electrode indicate a simple two-electron transfer process occurring at $E_{1/2} = 0.28$ V (vs. SCE) with $\Delta E_p = 30$ mV (Fig. 2(a)). Hall et al. [15] have studied the electrochemical behaviour of thionine in protic solvents and concluded that an electron transfer–electron transfer-type (E–E) mechanism is involved in the reduction process.

In the case of P(AGA)–TH$^+$ in homogeneous solution, the cathodic peak shifts to more negative potential and the peaks are broadened with a large peak separation when compared with unbound thionine (Fig. 2(b) and Table 2); this indicates that the redox processes occurring at the electrode are less reversible in the case of P(AGA)–TH$^+$ in homogeneous solution when compared with those of unbound thionine. When thionine is added to an aqueous solution of P(AGA), there is no marked change in its redox behaviour, which indicates that the change observed in the redox behaviour of thionine in P(AGA)–TH$^+$ is due to the covalent linkage of the dye to the macromolecule. The sequential electrochemical reduction process of thionine to leucothionine

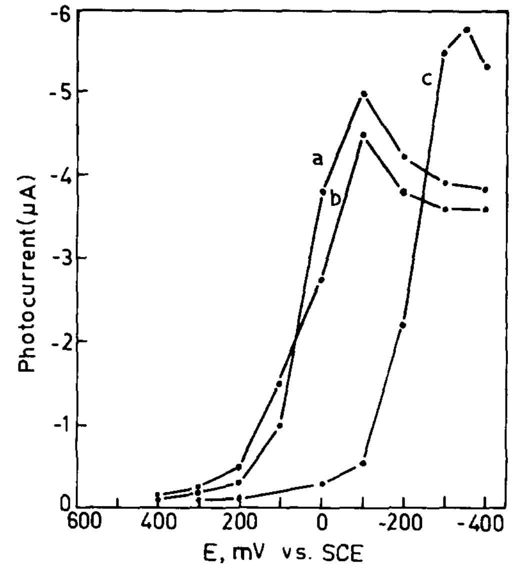

Fig. 5. Photocurrent vs. applied voltage curve for P(MAAM)–TH$^+$-coated electrode + iron system (a), P(AGA)–TH$^+$-coated electrode + iron system (b) and P(AGA)–TH$^+$ in homogeneous solution + iron system (c). [Fe^{2+}] = 1×10^{-2} mol dm^{-3}, [H_2SO_4] = 0.5×10^{-2} mol dm^{-3}.

Table 4
Open circuit photopotential (ΔE_{oc}) and short circuit photocurrent (I_{sc}) for polymer-bound tionine (P(AGA)–TH$^+$) in homogeneous solution and coated on the electrode as a thin film with different m/d ratios and at different pH values. [Fe^{2+}] = 1×10^{-2} mol dm^{-3}

Sample	m/d	pH	ΔE (mV)	I_{sc} (μA)
P(AGA)–TH$^+$ in homogeneous solution	259	2.0	5.7	–
		1.5	12.3	–
		1.0	15.4	–
P(AGA)–TH$^+$ in homogeneous solution	542	2.0	3.6	–
		1.5	8.8	–
		1.0	11.4	–
P(AGA)I–TH$^+$ in homogeneous solution	865	2.0	1.9	–
		1.5	4.5	–
		1.0	9.6	–
P(AGA)–TH$^+$ thin film	259	2.0	23.2	1.9
		1.5	18.0	2.0
		1.0	11.6	2.2
P(AGA)–TH$^+$ thin film	542	2.0	12.4	1.5
		1.5	8.8	1.7
		1.0	5.2	1.7
P(AGA)–TH$^+$ thin film	865	2.0	9.7	1.2
		1.5	7.5	1.5
		1.0	6.8	1.6

(i.e. $TH^+ \rightarrow TH_2^{\bullet +}$ and $TH_2^{\bullet +} \rightarrow TH_4^{2+}$) cannot be observed separately in the case of P(AGA)–TH^+, similar to other polymer-bound thionine systems [2c]. When the m/d ratio of P(AGA)–TH^+ is decreased (loading of the dye increases), the shift in the cathodic peak potential E_{pc} increases (Fig. 3). This indicates that aggregation of the dye molecules takes place with decreasing m/d ratio [2c]. For unbound thionine, it has been reported that there is a cathodic shift of the redox potential when the concentration of thionine is increased. This cathodic shift of the redox potential was attributed to increasing aggregation between the dye molecules [16].

An electron transfer mechanism for the reduction of polymer-bound thionine can be ascertained from the $I_{pc}/(\nu)^{1/2}$ ratios at different scan rates (ν). The variation of $I_{pc}/(\nu)^{1/2}$ as a function of the scan rate can be used to distinguish between the ECE (chemical reaction coupled between two electron transfer processes) and EE (two successive one-electron transfer processes) mechanisms [17]. When the protonation of the intermediate is the limiting step (ECE type), the ratio $I_{pc}/(\nu)^{1/2}$ should decrease with increasing scan rate (ν). However, the ratio $I_{pc}/(\nu)^{1/2}$ of P(AGA)–TH^+ in homogeneous solution and P(AGA)–TH^+ coated onto an electrode as a thin film indicates a reverse trend, showing that the heterogeneous reduction process proceeds by an EE mechanism coupled with a fast protonation reaction and not by an ECE mechanism. Interestingly, the cathodic peak current (I_{pc}) for P(AGA)–TH^+ in homogeneous solution decreases as the loading of the dye in the polymer decreases (Table 2). This observation explains how the surrounding medium can affect the redox properties of thionine. When the number of monomer units for a given number of dye units in the polymer increases, the peak current decreases, indicating that a smaller number of dye molecules are available for reduction as the number of dye molecules accessible to the electrode is decreased. As indicated by earlier studies on the fluorescence lifetime of the dye, when the loading of the dye is decreased in P(AGA)–TH^+, a larger number of dye molecules are found to reside in the interior of the polymer coil [13]. As a consequence, the decrease in the cathodic peak current (I_{pc}) with increasing m/d ratio in P(AGA)–TH^+ dissolved in aqueous solution can be attributed to the increase in the amount of "buried" dye molecules (which are relatively less accessible to the electrode).

The redox behaviour of P(AGA)–TH^+ coated onto the electrode is more reversible than that of P(AGA)–TH^+ in homogeneous solution (Fig. 2(c) and Table 3). The ΔE_p value for the P(AGA)–TH^+-coated electrode is larger than the theoretical value of 0 mV as observed for many polymer films. For the P(AGA)–TH^+- coated electrode, I_{pc} increases linearly with the square root of the scan rate. It should be noted that, for P(AGA)–TH^+-coated electrodes, when the m/d ratio of P(AGA)–TH^+ is increased (i.e. loading of the dye decreases), the cathodic peak current (I_{pc}) decreases as observed for P(AGA)–TH^+ in homogeneous solution.

4.4. *Photoelectrochemical properties of macromolecule-bound thionine dye*

The iron–thionine photogalvanic cell has been investigated extensively [18]. One-electron reduction of excited thionine by ferrous ion is known to produce semithionine, which disproportionates in homogeneous solution. The redox reaction occurring at the electrode when the dye is present in the bulk solution is illustrated in Eqs. (5)–(9)

$$TH^+ \xrightarrow{h\nu} {}^*TH^+ \quad (5)$$

$$^*TH^+ + Fe^{II} \xrightarrow{H^+} TH_2^{\bullet +} + Fe^{III} \quad (6)$$

$$2TH_2^{\bullet +} \xrightarrow{H^+} TH_4^{2+} + TH^+ \quad (7)$$

$$TH_4^{2+} \longrightarrow TH^+ + 3H^+ + 2e^- \text{ (illuminated electrode)} \quad (8)$$

$$2Fe^{III} + 2e^- \longrightarrow 2Fe^{II} \text{ (dark electrode)} \quad (9)$$

One of the requirements for the efficient conversion of light energy to electrical energy is that the illuminated electrode must discriminate between the photogenerated leucothionine (TH_4^{2+}) and Fe^{3+}. In other words, some selectivity in the electrode behaviour is essential for an efficient photogalvanic cell. Albery and Archer [19] have reported that differential electrode kinetics at the electrodes can be used to discriminate between the products; modification of the electrodes is another approach. Electrodes modified with thionine coatings or polypyrrole are known to discriminate between photogenerated leucothionine and ferric ions [20]. Electrodes modified with P(MAAM)-bound thionine were also reported to discriminate between leucothionine and ferric ions [2a].

For P(AGA)–TH^+ in homogeneous solution and P(AGA)–TH^+-coated electrodes, a change in polarity of the electrodes and hence a change in the direction of the current flow is noted compared with unbound thionine in homogeneous solution (Fig. 4). The illuminated electrode functions as a cathode, suggesting that at the uncoated electrode or dark electrode ferrous ion is oxidized to ferric ion. The species which is reduced at the illuminated electrode is presumed to be a complex between thionine and iron. A similar behaviour is shown by P(MAAM)–TH^+-coated electrodes where disproportionation of semithionine does not occur [2a]. Thus the nature of the polymer backbone is suggested to be responsible for the stabilization of the iron–thionine complex formed on irradiation with visible light. The reactions occurring at the electrode when P(AGA)–TH^+ is present in the bulk solution or when a P(AGA)–TH^+-coated electrode is used are given in Eqs. (10)–(14)

$$P\text{–}TH^+ \xrightarrow{h\nu} {}^*P\text{–}TH^+ \quad (10)$$

$$^*P\text{–}TH^+ + Fe^{II} \xrightarrow{H^+} [P\text{–}TH_2\text{–}Fe]^{4+} \quad (11)$$

$$[P\text{–}TH_2\text{–}Fe]^{4+} + e^- \longrightarrow P\text{–}TH_2^{\bullet +} + Fe^{II} \text{ (cathode)} \quad (12)$$

$$Fe^{II} \longrightarrow Fe^{III} + e^- \text{ (anode)} \quad (13)$$

$$P\text{–}TH_2^{\bullet +} + Fe^{III} \longrightarrow P\text{–}TH^+ + Fe^{II} + H^+ \quad (14)$$

The open circuit photopotential (ΔE_{oc}) and short circuit photocurrent (I_{sc}) for P(AGA)–TH$^+$ in homogeneous solution and P(AGA)–TH$^+$ coated onto the electrode decrease as the m/d ratio increases (Table 4). As the number of monomer units in the polymer chain increases for a given number of dye centres present, the polymer segments prevent the dye from approaching the electrode. The photocurrent generation and decay for P(AGA)–TH$^+$ in homogeneous solution are slow compared with those of P(AGA)–TH$^+$ coated onto the electrode and unbound thionine (Fig. 4). As the diffusion of the photochemically produced complex [P–TH$_2$–Fe]$^{4+}$ is hindered by the polymer network, the generation and decay of the photocurrent are very slow. Under identical conditions, an increase in the acid concentration leads to an increase in the photocurrent, as the formation of the polymer-bound thionine–iron complex is enhanced by a decrease in the pH of the solution.

The reaction at the illuminated electrode for P(AGA)–TH$^+$ in homogeneous solution and P(AGA)–TH$^+$ coated onto the electrode was ascertained from the applied voltage vs. photocurrent curves (Fig. 5). Even at a positive potential of +0.4 V, where there is a tendency for the polymer-bound dye to be in the oxidized state, the direction of current flow is opposite to that of the iron(II)–thionine system for P(AGA)–TH$^+$ in homogeneous solution and P(AGA)–TH$^+$ coated onto the electrode. P(MAAM)–TH$^+$-coated electrodes also exhibit a similar behaviour [2e]. It is suggested that the polymer-bound semithionine and ferric ion are produced photochemically and ferric ion forms a complex with polymer-bound semithionine. At the illuminated electrode, oxidation of the [P–TH$_2$–Fe]$^{4+}$ complex is much slower than reduction. As the applied potential is shifted from positive to negative, the photocurrents increase, indicating that the reduction of the complex at the electrode is favoured. When the applied potential is shifted to more negative values (−0.1 V for the P(AGA)–TH$^+$-coated electrode and −0.3 V for P(AGA)–TH$^+$ in homogeneous solution), the thionine in the polymer is reduced by the electrode to leucothionine, which cannot react with ferrous ions, causing a decrease in the photocurrent. It can be concluded from the plot of the photocurrent vs. the applied voltage that the reduction of the dye centre by the electrode is more favourable for P(AGA)–TH$^+$-coated electrodes than P(AGA)–TH$^+$ in homogeneous solution.

5. Conclusions

The absorption spectrum of polymer-bound semithionine radicals shows a maximum around 770 nm similar to that of unbound semithionine. The decay of the polymer-bound semithionine radical follows second-order kinetics as observed for unbound thionine; the rate constant for the disproportionation process of the polymer-bound semithionine radical is one order of magnitude less than that of monomeric semithionine.

The electron transfer process occurring at the electrode is less reversible in the case of P(AGA)–TH$^+$ in homogeneous solution compared with unbound thionine. The electron transfer process for P(AGA)–TH$^+$-coated electrodes is diffusion controlled and more reversible than that of P(AGA)–TH$^+$ in homogeneous solution. The peak current (I_p) decreases with an increase in the m/d ratio of P(AGA)–TH$^+$ in homogeneous solution and P(AGA)–TH$^+$-coated electrodes, demonstrating the protection of the dye centres by the macromolecular environment.

Modification of the electrode by coating with P(AGA)–TH$^+$ improves the efficiency of the photogalvanic cell. In the case of P(AGA)–TH$^+$ in homogeneous solution and P(AGA)–TH$^+$-coated electrodes, in addition to the photoinduced current, a polarity change in the photopotential, and hence a change in current flow, is noted. The nature of the polymer backbone is responsible for the observed results.

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