# Photophysical and Photoelectrochemical Behavior of Poly[styrene-*co*-3-(acrylamido)-6-aminoacridine]

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ABSTRACT: Photochemically and photoelectrochemically active copolymer poly[styrene-*co*-3-(acrylamido)-6-aminoacridine] (PS-AA) has been synthesized. The absorption properties of this copolymer (PS–AA) are dependent on the acidity of the medium as it can exist in neutral and singly and doubly protonated forms in solution. The excited singlet and triplet state properties of PS–AA are very similar at different acidities, indicating thereby the singly protonated species is the only dominant species that is responsible for excited-state emission. The fluorescence and triplet quantum yields are 0.16 ± 0.03 and 0.22 ± 0.06, respectively. The feasibility of employing these polymer films as photosensitive electrode materials has been demonstrated. A photon-to-photocurrent conversion efficiency (IPCE) of <1% has been observed with a PS–AA-coated nanocrystalline $SnO_2$ film.

## 1. Introduction

Photoactive polymers have important applications in photolithography, xerography, photocuring of paints and resins, and solar energy conversion systems.[1] These photoactive polymers can be synthesized either by covalently linking photoactive guest molecules to the backbone of a polymer or by copolymerizing a suitable acrylic or vinylic derivative of the photoactive molecule. The copolymerization strategy is, however, more appropriate since this enables us to tailor make the polymer of required property by suitable choice of comonomers and their compositions.

The use of polymer-bound photosensitizers to enhance the efficiency of photoinduced electron transfer and charge separation is an area that has attracted considerable attention due to its relevance in solar energy conversion.[2–7] For example, it has been shown that the hydrophobic environment of Nafion polymer plays an important role in enhancing the yields of the photoinduced electron-transfer process and retarding the rate of the back-electron-transfer process.[8] Such polymers are also important for extending the photoresponse of semiconductor electrodes used in photoelectrochemical cells.[6,7] Various aspects of photochemical processes in polymers have been presented in recent reviews.[1,9–11]

3,6-Diaminoacridine (proflavine) has been extensively studied as a sensitizer for light-induced hydrogen evolution from water.[12,13] Proflavine has also been utilized for selective binding to polynucleotides,[14] as well as for laser-selective photodamage of synthetic polynucleotides.[15] The excited-state proton-transfer mechanism of proflavine in aqueous[16,17] as well as micellar solutions[13] has also been studied in detail.

In the present work, the monomer, 3-(acrylamido)-6-aminoacridine, was synthesized from proflavine and copolymerized with styrene. The resultant copolymer (PS–AA) was observed to exist in an acid concentration dependent equilibrium between the neutral and singly and doubly protonated forms, in solution. The excited singlet and triplet state properties of the different forms have been investigated by fluorescence and transient absorption spectroscopy. Attempts have also been made to evaluate the photoelectrochemical behavior of PS–AA.

## 2. Experimental Section

**2.1. General Methods.** NMR spectra were recorded on a JEOL EX-90 NMR spectrometer. IR spectra were recorded using a Perkin-Elmer 882 instrument. HPLC analyses were carried out using a Shimadzu LC-6AD instrument, employing a CLC–ODS analytical column. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN instrument. Neutral proflavine was prepared from proflavine hydrochloride by neutralizing with a dilute $NH_4OH$ solution.

**2.2. Synthesis of 3-(Acrylamido)-6-aminoacridine.** To a stirred solution of acryloyl chloride (0.4 mL, 4.8 mmol) in THF was added dropwise in an argon atmosphere a solution of neutral proflavin (1 g, 4.8 mmol) in THF. The precipitated product was dissolved in water and neutralized with dilute $NH_4OH$. HPLC analysis of this mixture showed a 30% yield of the monomer.

The neutralized product mixture was chromatographed over alumina using a mixture (19:1) of ethyl acetate and methanol to give a product of 96% purity. Being sensitive to air and heat, further purification of this compound was not attempted. $^1H$ NMR ($CD_3OD/CDCl_3$): $\delta$ 5.8–6.5 (3H, m, vinylic), 7.1–8.5 (7H, m, aromatic). $^{13}C$ NMR ($CD_3OD/CDCl_3$): $\delta$ 166.8, 152.5, 150.4, 142.0, 137.8, 132.7, 131.2, 130.6, 129.0, 123.4, 122.9, 121.6, 120.2, 115.6, 104.3. IR spectrum (KBr): $\nu_{max}$ 3420, 3338, 3236, 1678 (C=O), 1619 $cm^{-1}$. UV spectrum ($\lambda_{max}$, nm): ($CH_3OH$ and $CF_3CO_2H$ (30 mM)) 455 ($\epsilon$, 19 700 $M^{-1}$ $cm^{-1}$), 393 (15 700 $M^{-1}$ $cm^{-1}$), 290 (32 600 $M^{-1}$ $cm^{-1}$); ($CH_3OH$ and $(C_2H_5)_3N$ (18 mM)) 378 (14 500 $M^{-1}$ $cm^{-1}$), 284 (45 000 $M^{-1}$ $cm^{-1}$).

**2.3. Synthesis of the Copolymer.** An argon-degassed solution of 3-(acrylamido)-6-aminoacridine (300 mg, 1.1. mmol) and styrene (9 g, 87 mmol) in DMF, containing 50 mg of azobis(isobutyronitrile) (AIBN) was heated at 70 °C for 13 h. The polymer formed was diluted with DMF, and the solution was poured into an excess of methanol, filtered, and dried. The polymer was purified by dissolving it in chloroform and reprecipitating with methanol. This procedure was repeated three times to give 6.3 g (68%) of the copolymer. IR spectrum (KBr): $\nu_{max}$ 3088, 3033, 2929, 2856, 1680 (C=O), 1605, 1496, 1454 $cm^{-1}$. $^1H$ NMR ($CDCl_3$): 1.2–2.3 (3H, br), 6.2–7.5 (5H, br). The polymer composition was determined by nitrogen analysis (0.23%) which gave 1 mol % of the aminoacridine moiety.

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**2.4. Molecular Weight Determination.** The number-average molecular weight ($\bar{M}_n$) of the copolymer was determined to be 19 000 by gel permeation chromatography on a Shimadzu LC-8A instrument equipped with a refractive index detector and Shimpac 802, 804, and 80M columns connected in series, using THF as the eluent. Calibration was done using standard polystyrene samples.

**2.5. Thermogravimetric Analysis.** The polymer was subjected to a thermal degradation study on a DuPont thermogravimetric analyzer Model 951, attached to a Thermal Analyst 2000 system at a heating rate of 10 °C/min from 30 to 800 °C under a nitrogen flow of 40 mL/min. This polymer was found to be thermally stable up to 370 °C.

**2.6. Absorption and Emission Spectroscopy.** Absorption spectra were recorded on a Shimadzu 2100 spectrophotometer. Fluorescence spectra were measured using a SPEX-F112X fluorimeter. Quantum yields of fluorescence were measured by the relative method using optically matched dilute solutions. Proflavine having a quantum yield of fluorescence of 0.34 in aqueous solutions at pH 4 was used as reference.[18] The quantum yields of fluorescence were calculated using the expression (1), where $\Phi_s$ and $\Phi_r$ are quantum

$$\Phi_s = \Phi_r(A_s n_s^2)/(A_r n_r^2) \qquad (1)$$

yields of fluorescence of the sample and reference, respectively. $A_s$ and $A_r$ are the areas of fluorescence peaks of the sample and reference, respectively, and $n_s$ and $n_r$, the refractive indices of the sample and reference solvents, respectively.

**2.7. Laser Flash Photolysis Studies.** The transient absorption measurements were carried out with the Spectra Physics Nd:YAG laser, operated at the third harmonic (20 ns pulse width, 70 mJ/pulse). The time-dependent optical density changes at different wavelengths were monitored using the Applied Photophysics LKS-50 time-resolved spectrometer. The quantum yield measurements were carried out with 355 nm laser pulse (6 ns pulse width, 4 mJ/pulse) from a Quanta-Ray CDR-1 ND:YAG system in a right angle excitation geometry. The photomultiplier output was digitized with a Tektronix 7912 AD programmable digitizer.[19]

**2.8. Preparation of Semiconductor Particulate Films.** A small aliquot (usually 0.2–0.3 mL) of the $SnO_2$ colloidal suspension (1%) was applied to a conducting surface of 0.8 × 5 cm$^2$ of OTE (optically transparent electrode, Donnelly Corp., Holland, MI) and was dried in air on a warm plate. The semiconductor colloid-coated glass plate was then annealed at 673 K for 1 h. The typical thickness of the semiconductor particulate film was ~1 $\mu$m. Absorption spectra were recorded using a Perkin-Elmer 3840 diode array spectrophotometer.

**2.9. Electrochemical and Photoelectrochemical Measurements.** These measurements were carried out with a standard three-compartment cell consisting of a Pt wire gauze counter electrode. All photoelectrochemical measurements were carried out in 0.1 M LiI in acetonitrile. Photocurrent measurements were carried out with a Kiethley Model 617 programmable electrometer. A collimated light beam from a 150-W xenon lamp was used for excitation of the dye-modified electrode. A Bausch and Lomb high-intensity grating monochromator was introduced into the path of the excitation beam for selecting the wavelength.

## 3. Results and Discussion

**3.1. Synthesis of the Monomer and the Copolymer.** The monomer 3-(acrylamido)-6-aminoacridine (**3**) was synthesized from 3,6-diaminoacridine (proflavine) (**1**) through its reaction with acryloyl chloride (**2**) (Scheme 1). The monomer **3** upon copolymerization with styrene, using azobis(isobutyronitrile) (AIBN) as initiator, forms the copolymer, PS–AA (**4**). The copolymer **4** bearing a low mole fraction of aminoacridine moiety was purified by several reprecipitations from methanol. The purified copolymer was characterized by IR, UV, and NMR spectroscopy (see the Experimental Section for spectral characteristics). The copolymer composition was determined by elemental nitrogen analysis which indicated the incorporation of 1 mol % of the aminoacridine moiety.

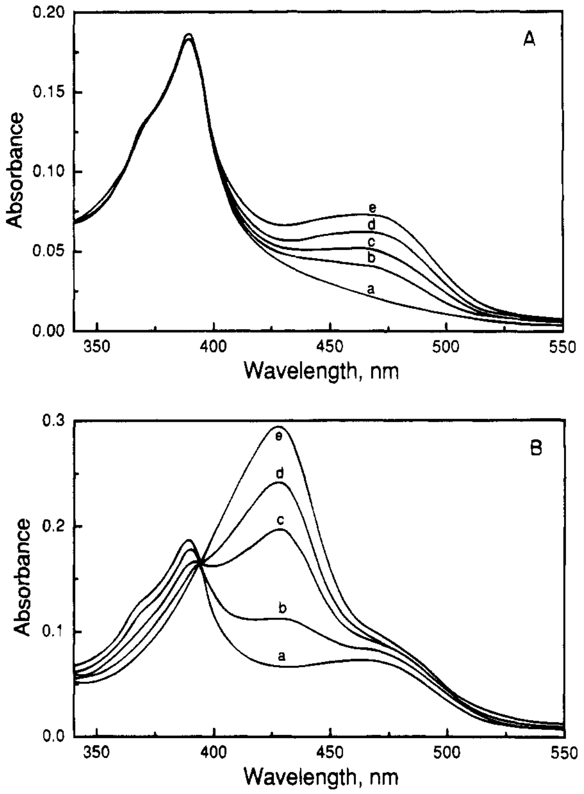
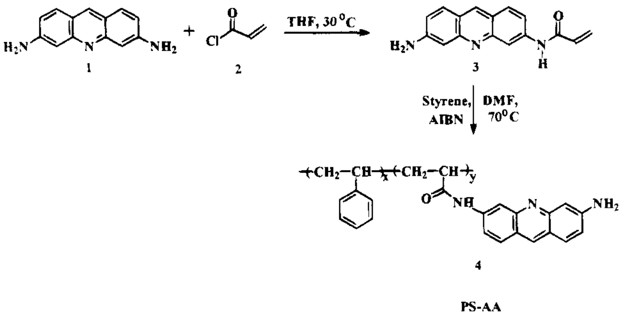


**Figure 1.** (A) Change in the absorption spectrum of the copolymer with increasing concentration of trifluoroacetic acid (TFA) in DMF. [TFA]: (a) 0; (b) 9.1 × 10$^{-5}$; (c) 10.6 × 10$^{-5}$; (d) 11.7 × 10$^{-5}$; (e) 13.0 × 10$^{-5}$ M. (B) Change in the absorption spectrum of the copolymer in DMF, with increasing concentration of trifluoroacetic acid (TFA). [TFA]: (a) 13.0 × 10$^{-5}$; (b) 14.3 × 10$^{-5}$; (c) 18.1 × 10$^{-5}$; (d) 26.0 × 10$^{-5}$; (e) 90.9 × 10$^{-5}$ M.

**Scheme 1**



**3.2. Absorption Spectra.** The absorption spectrum of the neutral form of PS–AA in DMF (Figure 1A, curve a) shows a maximum around 390 nm and a broad shoulder around 410–420 nm. This band is similar to the absorption band of neutral proflavine and is typical of the $\pi$–$\pi^*$ transition of the acridine chromophore. Upon addition of trifluoroacetic acid to this solution, a new band appears at around 470 nm, whereas the band centered around 390 nm remains unchanged (Figure 1A). This species may be assigned as the singly protonated form of the copolymer (PS–AAH$^+$). It has been shown that protonation of proflavine results in the disappearance of the 394 nm band and the formation of a band with a maximum around 444 nm due to the preferential protonation of the intracyclic nitrogen.[13,17] By analogy, the first protonation for PS–AA should occur at the intracyclic nitrogen. The long-wavelength transition observed for PS–AAH$^+$ can be assigned to the

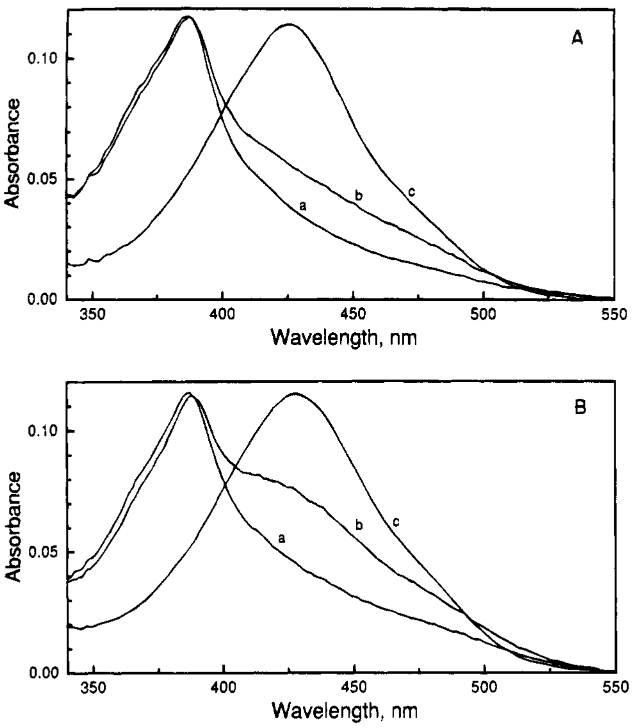


**Figure 2.** (A) Absorption spectra of the copolymer in chloroform: (a) neutral form, (b) singly protonated form, and (c) doubly protonated form. (B) Absorption spectra of the copolymer in toluene: (a) neutral form, (b) singly protonated form, and (c) doubly protonated form.

intramolecular charge-transfer transition, where charge transfer occurs from the amino group toward the electron-poor acridinium moiety. This transition is similar to that observed in the protonated form of proflavine[17] and also in some 9-(aminophenyl)acridinium derivatives.[20]

Continued addition of trifluoroacetic acid leads to a decrease in absorption around 390 nm, and this is accompanied by the formation of a new band around 435 nm (Figure 1B, curve e). An isosbestic point at 395 nm and a shoulder at 470 nm are also observed. The spectrum observed under these conditions is assigned to the doubly protonated form, PS−$AAH_2^{2+}$. The second protonation is likely to occur at the amino group of the aminoacridine moiety. Under similar conditions, the doubly protonated form of proflavine was not observed. In aqueous solution, the p$K_a$ corresponding to the protonation equilibrium of this group in proflavine is reported to be 0.5.[16] The protonation of the amino group in PS−$AAH_2^{2+}$ would prevent the intramolecular charge-transfer process. The band at 435 nm is typical of acridinium chromophores.[20,21] The shoulder at 470 nm on the absorption band may be attributed to residual amounts of PS−$AAH^+$.

The absorption spectra of the neutral and protonated forms in chloroform and toluene are shown in parts A and B of Figure 2, respectively. Although the absorption spectra of PS−AA and PS−$AAH_2^{2+}$ are relatively independent of the nature of the solvent, the absorption spectrum of PS−$AAH^+$ shows a blue shift in the long-wavelength band. The blue shift in these less polar solvents supports the view that the long-wavelength band for PS−$AAH^+$ arises from intramolecular charge-transfer transitions.

**3.3. Emission Spectra.** The emission spectra of DMF solutions of PS−AA, PS−$AAH^+$, and PS−$AAH_2^{2+}$, recorded upon excitation at 460 nm, are shown in Figure 3. The emission spectra of all these species show a broad band with the maxima centered around 510−520 nm, although the absorption maxima of PS−AA and PS−$AAH_2^{2+}$ are considerably blue shifted compared to that of PS−$AAH^+$. The anomalous Stokes' shifts for PS−AA and PS−$AAH_2^{2+}$ suggest that the fluorescence emissions for these species do not take place directly from their excited states. The excitation spectra, recorded for different species (Figure 4), are very similar to the absorption spectra of the corresponding species. This indicates that the emission does not arise from any trace amounts of the singly protonated PS−$AAH^+$ which might be present in these solutions.

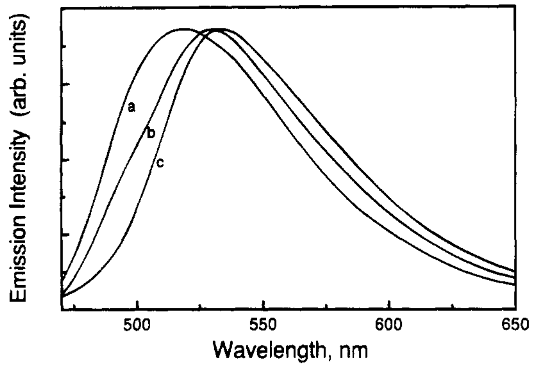


**Figure 3.** Emission spectra of the copolymer in DMF ($\lambda_{ex}$ = 460 nm): (a) neutral form, (b) singly protonated form, and (c) doubly protonated form.

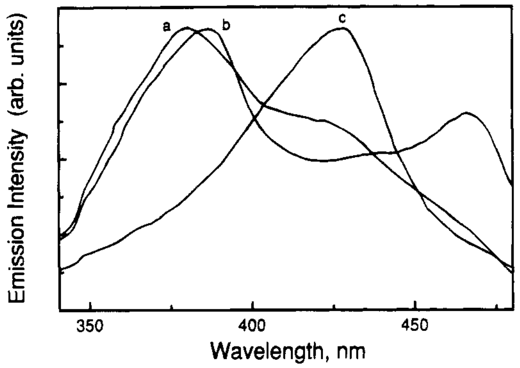


**Figure 4.** Excitation spectra in DMF ($\lambda_{max}$ = 490 nm): (a) neutral form, (b) singly protonated form, and (c) doubly protonated form.

The anomalous Stokes' shifts observed for PS−AA and PS−$AAH_2^{2+}$ can be understood on the basis of excited-state proton-transfer mechanisms. Upon excitation of PS−AA, the singlet excited state can pick up a proton from the solvent, due to its increased basicity, and emission from PS−$AAH^{+*}$ is observed. Similar enhancement in the basicity of the intracyclic nitrogen has been reported for proflavine.[13,17] Excitation of the doubly protonated form, PS−$AAH_2^{2+}$, also yields an emission spectrum, which is very similar to that of the singly protonated form. Earlier studies on 2-naphthylamine[22] and amino acridines[23] have indicated that the p$K_a$ of the amino group in the excited state can be much lower than that in the ground state. A mechanism for the excited-state proton-transfer processes is shown in Scheme 2.

The slight red shift in the emission maxima observed with increasing degree of protonation is attributed to the stabilizing effect of the trifluoroacetic acid anion which is associated within the solvent sphere of the aminoacridine moiety, thus affecting the dielectric effect of the surrounding medium.

**Table 1. Absorption and Emission Data for the Neutral and Protonated Forms of the Copolymer (PS−AA, PS−AAH$^+$, PS−AAH$_2$$^{2+}$)**

| | PS−AA | | | PS−AAH$^+$ | | | PS−AAH$_2$$^{2+}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| solvent | $\lambda_{max}^{abs}$ (nm) | $\lambda_{max}^{em}$ (nm) | $\Phi_f$ (±0.03) | $\lambda_{max}^{abs}$ (nm) | $\lambda_{max}^{em}$ (nm) | $\Phi_f$ (±0.03) | $\lambda_{max}^{abs}$ (nm) | $\lambda_{max}^{em}$ (nm) | $\Phi_f$ (±0.03) |
| toluene | 385 | 487 | 0.16 | 385 | 510 | 0.15 | 430 | 533 | 0.19 |
| chloroform | 385 | 496 | 0.16 | 385 | 514 | 0.16 | 425 | 526 | 0.16 |
| DMF | 390 | 513 | 0.18 | 390, 470 | 524 | 0.14 | 430 | 533 | 0.13 |

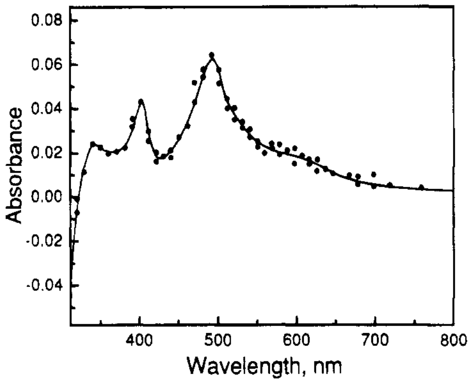


**Figure 5.** Transient absorption spectrum, recorded immediately following the laser pulse (355 nm) excitation, of PS−AA in DMF.

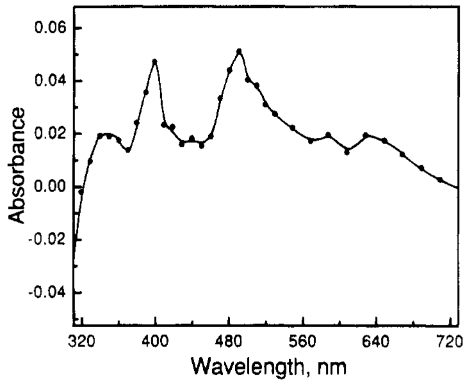
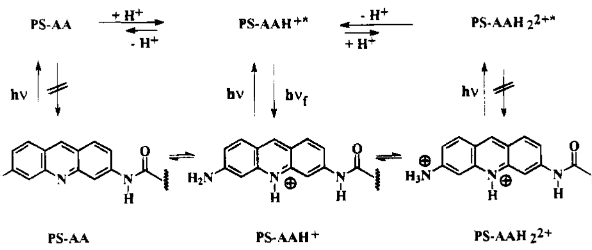


**Figure 6.** Transient absorption spectrum, recorded immediately following the laser pulse (355 nm) excitation, of PS−AAH$^+$ in DMF.

**Scheme 2**



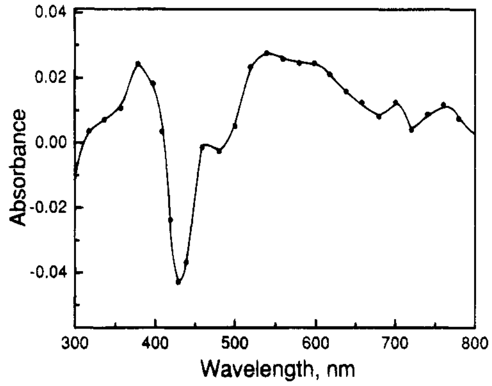


**Figure 7.** Transient absorption spectrum, recorded immediately following the laser pulse (355 nm) excitation, of PS−AAH$_2$$^{2+}$ in DMF.

The emission and excitation spectra of the various forms recorded in toluene and chloroform were similar to those observed in DMF, and these results are summarized in Table 1.

**3.4. Triplet Excited-State Properties.** In order to characterize the excited triplet of this photoactive polymer, nanosecond laser flash photolysis experiments were carried out at different concentrations of trifluoroacetic acid. The transient absorption spectra recorded upon excitation of PS−AA, PS−AAH$^+$, and PS−AAH$_2$$^{2+}$ with a 355 nm laser pulse are shown in Figures 5−7. The transient absorption observed with direct excitation of various protonated forms of PS−AA is attributed to the formation of the triplet excited state. The transient spectra recorded with excitation of PS−AA and PS−AAH$^+$ are very similar. The transient spectrum obtained with PS−AAH$_2$$^{2+}$ excitation shows a bleaching in the wavelength region 400−450 nm. This bleaching mainly arises from the depletion of the ground-state PS−AAH$_2$$^{2+}$ which has a strong absorption in this region. However, the transient absorptions below 400 nm and above 480 nm are very similar. These observations indicate that the triplet excited state generated from the excitation of three different protonated forms of PS−AA has similar absorption characteristics. Therefore, one can conclude that the transient species observed in Figures 5−7 arise from the common triplet excited state, $^3$PS−AAH$^{+*}$, similar to the common emitting singlet excited state, $^1$PS−AAH$^{+*}$, observed in fluorescence studies.

The assignment of the transients in Figures 5−7 to the triplet excited state is further confirmed by energy transfer to lower lying triplets of oxygen and $\beta$-carotene. In deaerated DMF solutions the triplet excited state is long-lived, with lifetimes ranging from 130 to 220 $\mu$s. Upon exposing the solution to air, the lifetime of this transient is significantly decreased. The pseudo-first-order rate constant for the triplet decay shows a linear dependence on the oxygen concentration. The oxygen-quenching rate constant for the triplet of PS−AA* was found to be $0.57 \times 10^9$ M$^{-1}$ s$^{-1}$.[24] Similarly, energy transfer from triplet excited polymer to $\beta$-carotene was confirmed from the formation of a $\beta$-carotene triplet excited state with an absorption maximum at 520 nm (eq 2).

$$^3\text{PS-AAH}^{+*} + \beta\text{-carotene} \rightarrow \text{PS-AAH}^+ + {}^3\beta\text{-carotene}^* \quad (2)$$

The transient absorption profile at 520 nm shown in Figure 8 (trace b) indicates the formation of a $\beta$-carotene triplet. The bimolecular rate constant for the energy transfer to $\beta$-carotene (eq 2) was determined to be $8.8 \times 10^9$ M$^{-1}$ s$^{-1}$. Upon changing the acidity of the medium, the quenching rate constant changed little.

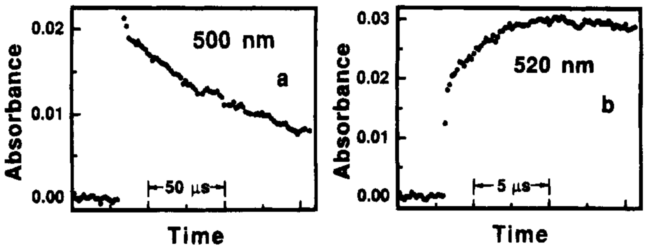


**Figure 8.** Absorption–time profiles of transients recorded with 355 nm laser pulse excitation of PS–AA in a laser flash photolysis experiments. (a) Decay of $^3$PS–AAH$^{+*}$ at 500 nm in a deaerated DMF solution. (b) The formation of $^3\beta$-carotene* at 520 nm (eq 2) in a DMF solution containing PS–AAH$^+$.

**Table 2. Properties of the Triplet Excited State Generated from the Excitation of Unprotonated (PS–AA), Singly Protonated (PS–AAH$^+$), and Doubly Protonated (PS–AAH$_2$$^{2+}$) Forms of Aminoacridine Covalently Linked to Polystyrene (Excitation: 355 nm)**

| substrate | $\Phi_T$ (±0.06) | T–T absorption max | $\tau_0$ (μs) |
|---|---|---|---|
| PS-AA | 0.22 | 400, 480 | 133 |
| PS-AAH$^+$ | 0.16 | 400, 480 | 150 |
| PS-AAH$^{2+}$ [a] | 0.29 | 380, ~520[a] | 220 |

[a] The shift in the absorption maximum is due to the bleaching in the 430 nm region.

**3.5. Triplet Quantum Yield Measurements.** The triplet quantum yields ($\Phi_T$) of the copolymer were measured employing an earlier described method[25] of energy transfer to β-carotene, using a tris(bipyridyl)-ruthenium complex, Ru(bpy)$_3$$^{2+}$, as the reference. DMF solutions of Ru(bpy)$_3$$^{2+}$ and the copolymer, optically matched at 355 nm, were mixed with a known volume of β-carotene in DMF. Transient absorbance (ΔA) of the β-carotene triplet was monitored at 520 nm. Comparison of the plateau absorbance following the completion of sensitized triplet formation with correction for the intrinsic decay of the donor triplet excited states enables one to determine the $\Phi_T$ of the copolymer (eq 3) where

$$\Phi_T^S = \Phi_T^R \left(\frac{\Delta A^S}{\Delta A^R}\right)\left(\frac{k_{obs}^S}{k_{obs}^S - k_0^S}\right)\left(\frac{k_{obs}^R - k_0^R}{k_{obs}^R}\right) \quad (3)$$

superscripts S and R designate the sample (copolymer) and reference (Ru(bpy)$_3$$^{2+}$), respectively, $k_{obs}$ is the pseudo-first-order rate constant for the growth of the β-carotene triplet, and $k_0$ is the rate constant for the intrinsic decay of the donor triplet. Experiments were carried out with excitation of the three different protonated forms of the copolymer. The results are summarized in Table 2. The quantum yields in all these three experiments were very similar (0.22 ± 0.06) to the one reported for the monoprotonated proflavine molecule ($\Phi_T$ = 0.22[26]). This shows that the presence of the polymer backbone does not alter the quantum yield of the triplet excited state.

**3.6. Photoelectrochemical Effect with PS–AA Films.** In order to investigate the photosensitizing properties of PS–AA, photoelectrochemical experiments were carried out with nanocrystalline SnO$_2$ films, coated with the copolymer. Illumination of this electrode in a photoelectrochemical cell with visible light resulted in the generation of photocurrent. The photoresponse of this electrode is shown in Figure 9. The photocurrent generation was prompt and was steady during the course of illumination. These results highlight the feasibility of using a PS–AA coated SnO$_2$ film as photosensitive electrode material.

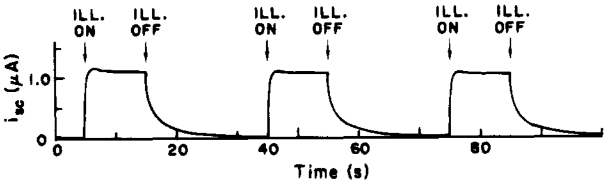


**Figure 9.** Photocurrent generation at a SnO$_2$ electrode modified with PS–AA with visible light excitation (electrolyte, 0.1 M LiI in acetonitrile; counter electrode, Pt gauge).

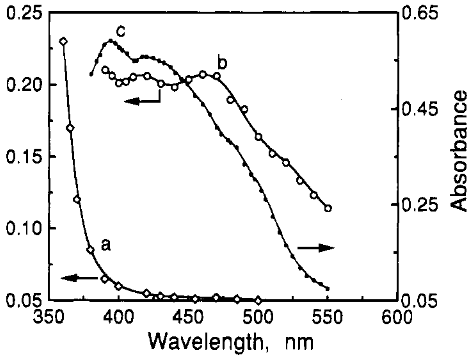


**Figure 10.** Action spectrum of (a) OTE/SnO$_2$ and (b) OTE/SnO$_2$/PS–AA in a photoelectrochemical cell. The absorption spectrum of a PS–AA-modified SnO$_2$ electrode is shown in c (electrolyte, 0.1 M LiI in acetonitrile; counter electrode, Pt gauze).

The photocurrent action spectra of bare SnO$_2$ and a PS–AA-modified SnO$_2$ electrode are shown in Figure 10 (spectra a and b). The values of photon-to-photocurrent conversion efficiency (IPCE) were evaluated from the short circuit photocurrent measurements at different excitation wavelengths and by using the expression (4), where $i_{sc}$ is the short-circuit photocurrent

$$\mathrm{IPCE}\ (\%) = \frac{i_{SC}}{I_{inc}}\frac{1240}{\lambda} \times 100 \quad (4)$$

(A/cm$^2$), $I_{inc}$ is the incident light intensity (W/cm$^2$), and λ is the excitation wavelength.

The photocurrent response of a semiconductor particulate film (spectrum a in Figure 10) is usually in the UV region. But the copolymer-modified electrode extends the photoresponse well into the visible region. The close match between the IPCE spectrum (spectrum b in Figure 10) and the absorption spectrum of the PS-AA film (spectrum c in Figure 10) shows that the photosensitization mechanism is operative in extending the photocurrent response of the OTE/SnO$_2$/PS–AA electrode into the visible region expressions (5–7).

$$\text{PS–AA} + h\nu \rightarrow \text{PS–AA*} \quad (5)$$

$$\text{PS–AA*} + \text{SnO}_2 \rightarrow \text{SnO}_2\text{(e)} + \text{PS–AA}^{\bullet+} \quad (6)$$

$$\text{PS–AA}^{\bullet+} + \text{I}^- \rightarrow \text{PS–AA} + \text{I}^\bullet \quad (7)$$

Upon excitation with visible light, the excited sensitizer molecules inject electrons into the SnO$_2$ particles. These electrons are then collected at the OTE surface to generate anodic photocurrent. The redox couple I$^-$/I$^\bullet$ present in the electrolyte quickly regenerates the sensitizer. The relevance of similar redox systems in sensitizer regeneration as well as bringing photocurrent stability has been addressed in earlier studies.[27]

The maximum IPCE observed in the present experiments was less than 1%. These IPCE values are smaller than the values obtained for $TiO_2$ and $SnO_2$ particulate films with ruthenium complex sensitizers but are comparable to those reported for other sensitization experiments with organic dyes.[27] Further optimization of the operating conditions is necessary to improve the performance of photoelectrochemical cells, employing such polymer films. The photoelectrochemical experiments described here show the ability of the polymer matrix in transporting electrons from the excited proflavine moiety to the $SnO_2$ nanocrystallites.

## 4. Conclusions

The copolymer, poly(styrene-*co*-3-acrylamido-6-aminoacridine) (PS−AA), exhibits interesting photochemical and photoelectrochemical properties. The absorption properties of this copolymer (PS−AA) are dependent on the acidity of the medium, as it can exist in neutral and singly and doubly protonated forms in solution. The fluorescence and triplet quantum yields are 0.1 ± 0.03 and 0.22 ± 0.06, respectively. The feasibility of employing these polymer films as photosensitive electrode material has been demonstrated.

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