56-5; PTAHQ-8 (SRU), 118476-44-1; PTAHQ-10 (copolymer), 118494-16-9; PTAHQ-10 (SRU), 118476-45-2; PTAHQ-12 (copolymer), 118476-57-6; PTAHQ-12 (SRU), 118476-46-3; PTAHQ-14 (copolymer), 118476-58-7; PTAHQ-14 (SRU), 118476-47-4; PTAHQ-16 (copolymer), 115563-54-7; PTAHQ-16 (SRU), 115563-57-0.

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Systems Containing Two Oppositely Charged Polyelectrolytes. Behavior of Ionic Photosensitizers and Quenchers

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ABSTRACT: Several photosensitizer–quencher systems containing both the negative polyelectrolyte poly(styrenesulfonate) (PSS) and the positive polyion polybrene (PB) have been investigated. At relatively low concentrations, solutions containing both PSS and PB are stable with respect to precipitation even at equivalent concentrations. Interactions of the polyelectrolytes with the photosensitizer zinc tetrakis(sulfonatophenyl)porphyrin ($ZnTPPS^{4-}$) and *meso*-tetrakis(*N*-methylpyridinium-4-yl)porphyrin, $ZnTMPyP^{4+}$, have been studied by spectrophotometric and spectrofluorimetric techniques. The concentration effect of the PSS induces the formation of charge-transfer complexes between a photosensitizer and the hydrophobic parts of the polymer, as well as photosensitizer dimers. The effects of the oppositely charged polyion on the absorption and emission spectra of the photosensitizers as well as the effect of several quenchers have been studied. The results lead to the conclusion that each of the two polyelectrolytes preserves part of its electrical field in its vicinity even when the oppositely charged polymer is in slight excess.

Introduction

Although mixing two solutions containing oppositely charged polyelectrolytes usually results with precipitation, there are well-known cases where the polymeric components remain in solution. Studies concerning the preparation, stability, and kinetic properties of polyelectrolyte complexation have been reported.[1-16] The term "complexation" in this context refers to the formation of pairs of the two oppositely charged polymers. Application of such complexes to other fields, such as medicine[17-19] and membrane science,[20-23] has been reported.

In the present manuscript we report the behavior of ionic photosensitizers and quenchers in a polyelectrolyte complex composed of poly(styrenesulfonate) (PSS) and polybrene (PB). This research has a potential importance in the application of microenvironments for the purpose of photochemical conversion and storage of light energy.

Experimental Section

Absorption spectra have been recorded by using a Bausch and Lomb Spectronic 2000 spectrophotometer. Emission was measured with a Perkin-Elmer LS-5 spectrofluorimeter. Laser photolysis was carried out with a Molectron DL200 dye laser, 450 μJ, 10-ns fwhm, pumped by a Molectron UV N_2 laser. The irradiation cell was 1 cm long. The analytical light and laser beam were oppositely coaxial as previously described.[24-26] The resolution time of this setup under our conditions was 2 μs. A 150-W Xe lamp was used as the analytical light source. The signal was transferred through a B&L monochromator to an IP28 photomultiplier and was digitized with a Tektronix 7912 AD digitizer.

Materials. All reagents were of the highest purity available. The sodium salt of $TPPS^{4-}$ and $TMPyP^{4+}$ (chloride form) were products of Strem Chemical Inc. and used as received. The Zn complex $ZnTPPS^{4-}$ was prepared and purified according to the method of Cheung et al.[27] $ZnTMPyP^{4+}$ was prepared according to the previously described procedure.[28] PB, as a bromide, was purchased from Sigma and was used as received. Poly(styrenesulfonate) (PSS), completely sulfonated, MW 70000, in the sodium salt form was purchased from Polysciences. It was purified by dialysis against 10^{-3} M EDTA followed by dialysis against water. Water was purified by passing through an ion exchanger, distilled, and finally passed through a Millipore Milli-Q water purification system. The temperature was 23 ± 2 °C. Polymer concentrations are given in terms of the monomer units.

Results and Discussion

When charge-equivalent concentrations of PSS and PB solutions are mixed together, turbidity is instantly pro-

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Table I
Precipitation Properties of Various Mixtures of PSS and PB[a]

[PSS] × 10^{-4} M	[PB] × 10^{-4} M											
	0.70	0.80	0.90	1.15	1.25	1.30	1.90	3.0	5.0	6.4	9.4	13.4
0.80			–									
1.40	–*						–					
2.30				–*		–		+				
2.50		–			–*							
2.60		–				–*						
5.30												+
10.00									+*			
18.80						–					+*	
27.00										+		+*
31.00									–			

[a] – deonotes that no precipitation occurs, + denotes that the mixture precipitates, and * denotes equivalence between [PSS] and [PB] in terms of charge.

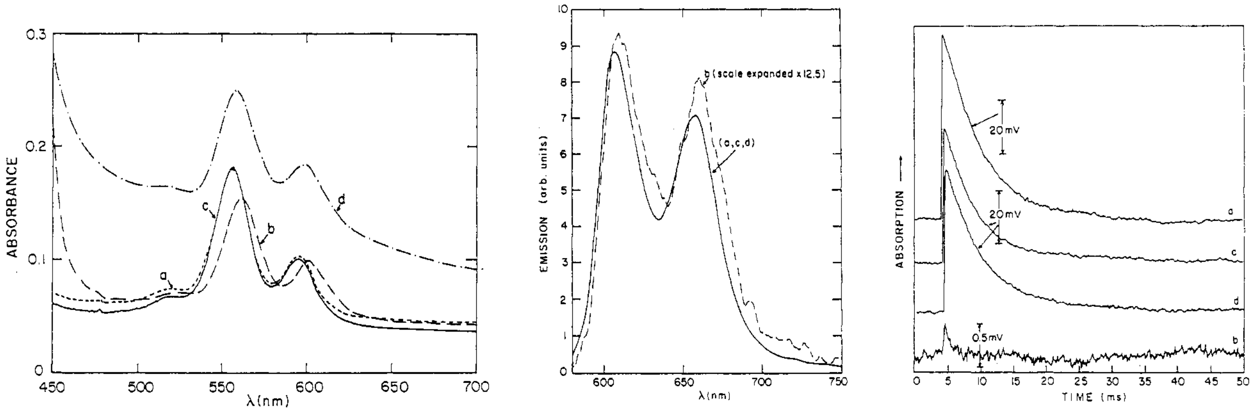

Figure 1. Absorbance, steady-state fluorescence, and laser photolysis of $ZnTPPS^{4-}$ in the presence of polyelectrolytes: (a) 5 × 10^{-6} M $ZnTPPS^{4-}$, polyelectrolytes absent; (b) 5 × 10^{-6} M $ZnTPPS^{4-}$ and 8 × 10^{-5} M PB; (c) 5 × 10^{-6} M $ZnTPPS^{4-}$ and 3.0 × 10^{-4} M PSS; (d) 5 × 10^{-6} M $ZnTPPS^{4-}$, 3.0 × 10^{-4} M PSS, and 8.0 × 10^{-5} M PB. Steady-state excitation wavelength was 562 nm. Laser photolysis kinetics was measured at 460 nm by using laser pulses at 540 nm. Light signals (mV): a, 150; b, 130; c, d, 125.

duced at PSS concentrations above 1 × 10^{-3} M. Note that the monomer unit of PSS is singly charged, while the monomer unit of the polybrene has a double charge; hence the concentration of an equivalent amount of PB is only one half of the PSS concentration. When one of the components is in excess, higher concentrations of both solutes can be employed without turbidity formation. In the absence of other additives, no time-dependent phenomena have been observed. Solutions which are clear immediately after preparation remain so for at least several days. Table I defines the concentration ranges where the solutions remain clear, and photophysical and photochemical experiments can be conveniently carried out. No formation of soapy bubbles, which is typical of micelle solutions, has been observed when solutions containing both PSS and PB are bubbled with He. The increased solubility of the two polymer systems when one of the polymers is in excess is attributed to the net charge of the polymer assembly. Some net local charges are likely to remain even at the equivalent point, since the polymer charges are different and the charged groups in the two polymers are not separated by exactly the same distances.

$ZnTPPS^{4-}$–Polybrene–PSS System. The photochemistry and photophysics of zinc tetrakis(sulfonatophenyl)porphyrin ($ZnTPPS^{4-}$) has been investigated previously.[29] Excitation of the porphyrin produces a singlet state, which shows fluorescence in the visible range. It is converted to a relatively long-lived triplet. The polyelectrolyte poly(vinyl sulfate) has been used in order to separate the $ZnTPPS^{4-}$ and MV^{2+} ions (which form an ion-pair complex in the absence of the negative polymer), resulting with quenching of the singlet. No work has been reported concerning the interactions between $ZnTPPS^{4-}$ and its excited state with oppositely charged polymers. In the following we will report our results in the mixed polymer system. We will show that in this system the positive PB retains part of its positive electric field even when the negative PSS is in excess.

$ZnTPPS^{4-}$ (5 × 10^{-6} M) has been dissolved in PB (8 × 10^{-5} M) solutions in the absence and in the presence of 3 × 10^{-4} M PSS. Control experiments have been carried out by using $ZnTPPS^{4-}$ alone as well as $ZnTPPS^{4-}$ and PSS with no PB. Figure 1 describes the appropriate absorption and emission spectra. Both absorption and emission spectra of $ZnTPPS^{4-}$ in the absence of PB remain unchanged upon addition of PSS. On the other hand, addition of polybrene to $ZnTPPS^{4-}$ in the absence of PSS results with red shifts of both the absorbance and emission spectra (ca. 5 nm) and efficient quenching of the singlet emission intensity. We have observed similar quenching in another positive polyelectrolyte system, namely, the poly((vinylbenzyl)tri-*N*-methylammonium chloride).

The red shifts observed in the absorption and emission spectra may be attributed to binding of the charged porphyrin to the polymer associated with changes in the electronic levels of the porphyrin by the influence of the electric field of the polymer. This may be accompanied with alterations of the singlet- and triplet-state properties, which may account for the strong reduction in the emission intensity upon addition of the polymer to the porphyrin solution. Another effect which has to be considered is the concentration of the porphyrin in the microvolume of the polymer field. This may induce the formation of dimer porphyrin molecules, which may show different photophysics as compared with the monomeric molecules. Note that in the presence of the electric field of the polymer, the dimer properties may be different from those which may be observed in polyelectrolyte-free solutions. The quenching of the emission by the polymer can be also attributed to a redox reaction involving the singlet porphyrin and the polymer molecule, such as oxidation of polymeric tertiary amino groups (if present as an impurity).

Addition of excess PSS (equivalents) to a $ZnTPPS^{4-}$–PB solution produces the following results: (a) The red shift described above for the optical absorption remains when corrected for the Rayleigh scattering background. On the other hand, the emission spectrum and its intensity are similar to those observed in the absence of PB (compare parts a, c, and d of Figure 1). (b) The solutions have been investigated by the pulsed laser technique. The triplet initial yield and its lifetime have been measured. The initial triplet absorption and its lifetime in the absence of PB (PSS present) is the same as in the presence of both PB and PSS. When PB is the only polyelectrolyte added, the triplet absorption is very low, showing that the quenching of the singlet emission by PB competes with the intersystem crossing (see Figure 1, computer traces).

The fact that the red shift in the absorption spectrum of $ZnTPPS^{4-}$ remains even upon addition of excess PSS (equivalents) to the PB solutions shows that the $ZnTPPS^{4-}$ still interacts with PB under these conditions. However, the PB electric field is no longer sufficient to induce the self-quenching of the excited $ZnTPPS^{4-}$, which is observed when PB is present in the absence of PSS.

We observe here that a polyelectrolyte (in this case PB) can retain part of its electric field properties, even when the counterpolymer is in excess. Note that the concentration of a counterion near a polyelectrolyte varies with the distance from the polymer backbone. The counterion distribution depends on its charge. The effect of the polymer field on a multicharged ion such as the porphyrin may also be described in terms of an ion pairing effect since the average distance of the counterions from the polymer may amount to condensation of the counterions at the polymer. This does not affect our basic conclusions. The oppositely charged polyelectrolyte has a much higher charge and higher charge density as compared with the porphyrin and has been added at much higher concentrations. It is expected to exchange with the porphyrin ions at the counterpolyelectrolyte. Since we observe that the porphyrin is still in the vicinity of the PB, despite of the presence of excess PSS, we conclude that the PB preserves some positive field properties (or a considerable fraction of positive ionic sites, in terms of ion pairing) under these conditions. In the following we will discuss our results in terms of the polymer field effects.

$ZnTMPyP^{4+}$ in the Presence of PSS, PB, and Cu^{2+} Ions. $ZnTMPyP^{4+}$ has been previously investigated in several donor and acceptor photochemical systems.[30] Here we report the effects of PSS (1.5×10^{-4} M), PB (1.8×10^{-4} M), and PSS/PB on the singlet and triplet quenching of excited $ZnTMPyP^{4+}$ (1×10^{-6} M, excited at the Soret band) by Cu^{2+} ions (5×10^{-5} to 10^{-3} M). Addition of PSS shifts the peak of the $ZnTMPyP^{4+}$ Soret band from 435 to 440.5 nm. Neither Cu^{2+} nor polybrene alone, in the absence of PSS, has an effect on the Soret band. The emission spectrum of $ZnTMPyP^{4+}$ is also changed by the addition of PSS. This is shown in Figure 2. The shoulder at 670 nm becomes a peak which is less intense than the 624-nm peak. (In the absence of PSS the emission peak is at 632 nm.) The emission intensity at the 624-nm peak is only about one-half of that measured in the absence of PSS at 632 nm (Figure 2b). Excitation was carried out at the respective Soret peak, the height of which does not change much upon addition of PSS. Addition of 5×10^{-5} M Cu^{2+} ions has no effect on the emission of $ZnTMPyP^{4+}$, neither in the presence nor in the absence of PSS (Figure 2c,d). In the absence of PSS, 1 mM Cu^{2+} decreases the emission at 635 nm by 38%. If PB is added to a solution containing $ZnTMPyP^{4+}$ and PSS, the emission spectrum typical of the PSS free solutions is restored (Figure 2e). These results can be explained by the interactions of the positive porphyrin with the negative polyelectrolyte, in a similar way to the $ZnTPPS^{4-}$–PB system. Formation of a charge-transfer complex involving the aromatic segments of the PSS and the monomer or dimer porphyrin which are concentrated by the negative field of the PSS is also possible here. Addition of excess PB neutralizes the negative field of the PSS and restores the emission spectrum, which is observed in the PSS free solutions. However, as will be seen in the following, the $ZnTMPyP^{4+}$ still remains in the polymer domain, although its average distance from the polymer apparently becomes larger as compared with the PB free solutions.

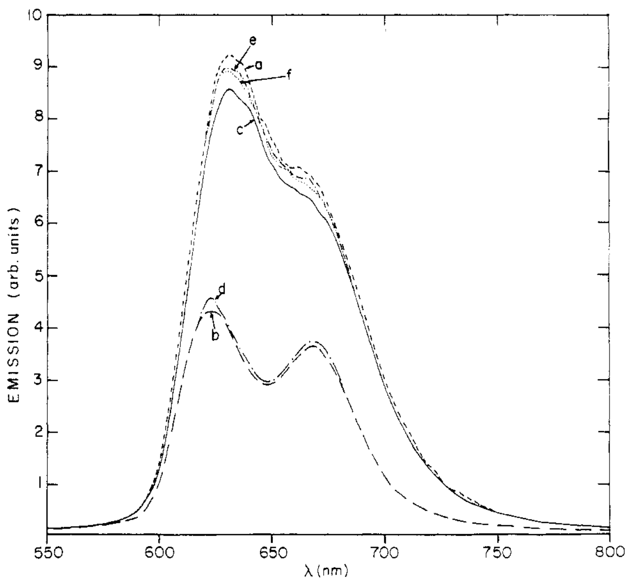

Figure 2. Emission spectra of $ZnTMPyP^{4+}$ in the presence of polyelectrolytes and cupric ions. Arbitrary units, $\lambda_{ex} = 436$ nm (Soret excitation); 1×10^{-6} M $ZnTMPyP^{4+}$. Measurements in PSS solutions were carried out at the Soret peak by slightly adjusting the excitation wavelength: (a) no additives (90); (b) 1.5×10^{-4} M PSS added (43); (c) 5×10^{-5} M Cu^{2+} (86); (d) 1.5×10^{-4} M PSS and 5×10^{-5} M Cu^{2+} added (45.5); (e) 1.5×10^{-4} M PSS and 1.9×10^{-4} M PB added (88); (f) 1.5×10^{-4} M PSS, 1.9×10^{-4} M PB, and 5×10^{-5} M Cu^{2+} (89). The numbers in parentheses represent the relative emission intensities at the higher emission peak (632 nm in the absence and 624 nm in the presence of PSS, respectively).

The effect of PSS and PB on the quenching of $^3ZnTMPyP^{4+}$ by Cu^{2+} ions has been investigated by the pulsed laser technique (Figure 3). Experiments were carried out using 1×10^{-6} M $ZnTMPyP^{4+}$ with and without 1.5×10^{-4} M PSS, 1.9×10^{-4} M PB, and 5×10^{-5} to 10^{-3} M Cu^{2+}. The initial absorbance change at 475 nm following a laser pulse (at 435 nm) was 0.019 ± 0.002, in the absence of the polymer additives as well as in the presence of PB and PSS together. When PSS is added in the absence of PB, the initial absorbance change decreases by about 2.5-fold. This observation parallels the decrease of emission observed in the steady-state excitation of the porphyrin (Figure 2).

The decay of $^3ZnTMPyP^{4+}$ is shown in Figure 3. In the absence of additives other than 1×10^{-6} M $ZnTMPyP^{4+}$, the half-life for the decay of the triplet was measured as

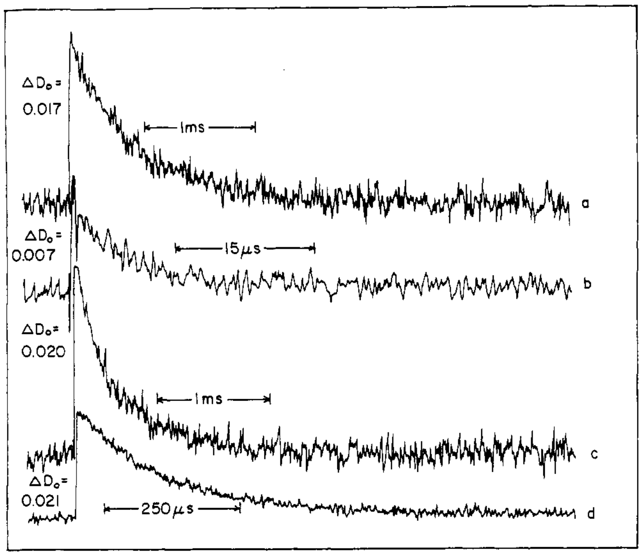

Figure 3. Kinetic effects of polyelectrolytes on the quenching of ^{3}ZnTMPyP^{4+} by Cu^{2+} ions. Laser pulses taken near 435 nm, slightly varied in order to remain at the peak of the Soret band. Detection at 475 nm; 1×10^{-6} M ZnTMPyP^{4+}: (a) no additives; (b) 1.50×10^{-4} M PSS added; (c) 1.5×10^{-4} M PSS and 1.9×10^{-4} M PB added; (d) 1.5×10^{-4} M PSS, 1.9×10^{-4} M PB, and 5×10^{-5} M Cu^{2+} added.

400 μs (Figure 3a). This decay is enhanced by over 2 orders of magnitude upon addition of PSS (Figure 3b). The enhancement can be explained by triplet–triplet annihilation or by dimer formation. (Note that the microvolume in the ZnTMPyP^{4+}–PSS system may involve several PSS polyions, since a porphyrin molecule may be bound to more than one polymer molecule.) Addition of excess PB such as in Figure 3c restores the relatively long half-life of ^{3}ZnTMPyP^{4+} (270 μs as compared with 3.6 μs in the presence of PSS and absence of PB; 400 μs in the absence of both polymers). This could be expected if the porphyrin is replaced by PB and moves to the bulk of the solution. However, when Cu^{2+} ions are also added to the solution (already containing both PSS and excess PB), such as shown in Figure 3d, the half-life for the quenching reaction becomes 106 μs, corresponding to an apparent quenching rate constant $k = 6 \times 10^7$ M^{-1} s^{-1} of the triplet porphyrin by the Cu^{2+} ions. The same rate constant has been measured at both 50 and 100 μM Cu^{2+}. In the absence of both polymers, the quenching rate constant has been measured as 2×10^6 M^{-1} s^{-1}, using up to 1 mM Cu^{2+}. These results indicate that both ^{3}ZnTMPyP^{4+} and Cu^{2+} are concentrated to some extent, by PSS, even in the presence of excess PB.

Conclusions

We have demonstrated that when PSS and PB are both present in the same solution, there exists a considerable range of concentrations where no precipitate is formed. Within this concentration range, photophysical and photochemical investigations were carried out. Each of the two oppositely charged polymers retains an electric field in its vicinity, although considerably smaller than in the absence of the other polymer. The effect of this electric field can be observed even when the oppositely charged polymer is in excess.

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Registry No. PB, 28728-55-4; PSS·Na, 9080-79-9; PSS·PB, 118892-35-6; ZnTPPS, 42712-11-8; ZnTMPyP, 28850-44-4; Cu, 7440-50-8.

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