

The Effect of Monomer Aggregation in the Photopolymerization of Styrenesulfonate

Miguel G. Neumann,* Carla C. Schmitt, and Hosana M. Maciel

Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780,
13560 São Carlos SP, Brazil

Received: September 18, 2000; In Final Form: January 25, 2001

The polymerization of styrenesulfonate photoinitiated with visible light in the presence of the dye safranin ($\lambda_{\text{max}} = 532 \text{ nm}$) has been studied at various monomer concentrations in aqueous solution ($>0.1 \text{ M}$). The elemental photochemical and ground state steps involved in the initiation were studied individually in order to obtain a general mechanism for the photoinitiation. Two important facts were found: first, the photopolymerization proceeds in the presence of air, whereas co-initiators like amines, inhibit the reaction; second, several evidences obtained from ground state and excited-state interactions, as well as from the polymerization products suggest the aggregation of the monomer in clusters containing a dye molecule. Similar evidences were found when using the nonpolymerizable anion toluenesulfonate.

1. Introduction

In recent years several papers have dealt with the photoinitiated polymerization of vinyl monomers. As most of the usual monomers only absorb in the UV region, the initiation by photochemical means could not be considered very useful for commercial means. Therefore, several systems commenced to be studied which included dyes (or other visible light absorbers) as radiation absorbers becoming known as photoinitiators. On the other hand, in many cases there seemed to be a thermodynamic incompatibility for the electron transfer between the excited initiator and the monomer, so that a third species was added to the polymerizing formulation. The latter, usually amines, or other easily oxidable compounds, acted as intermediaries, by transferring an electron to the excited initiator and starting the polymerization in a thermal way. The α -aminoalkyl radicals generated in these reactions are capable of initiating the polymerization of acrylates and methacrylates.

The photopolymerization of vinyl monomers in the presence of dyes absorbing in the visible region has been studied by various workers.^{1–4} Most of the earlier work dealt with the overall polymerization kinetics with little insight into the photochemical initiation mechanism. The present use of this procedure in the manufacture of printed circuits, encapsulation of electronic components, decorative coating, dental filler composites, stereolithography, and others, brought new interest into the subject. As a consequence, efforts are being made to provide better insight into the photophysical and photochemical process involved, to develop better and more efficient photoinitiator systems adapted to different problems and applications.^{5–10}

It seems to be desirable to establish a general mechanism involving all the reactions of the singlet and triplet states of the photoinitiators to be able to predict the influence of substituents and solvents, similarly to what has been done for the photoinitiation of vinyl polymerization by dyes in the presence of amines.^{11–14}

Normally, these polymers are obtained by sulfonation in extreme conditions of the noncharged polymer polystyrene.¹⁵

The thermal polymerization of styrenesulfonate (SS) was studied Kurenkov et al.¹⁶ Recently, Bhardbaj et al.¹⁷ studied the radiation-induced polymerization of SS in the steady state and by pulse radiolysis. On the other hand, the effect of radiation on PSS resins has been established several years ago.¹⁸ No work is known in which charged polymers, like poly(styrenesulfonate), PSS, were formed by the polymerization of the corresponding monomers by photoinitiated processes. Continuing our previous work, we present in this paper results for the polymerization of styrenesulfonate photoinitiated by the dye safranin (Sf) in aqueous solution. The photoinitiation is described in terms of the elemental reactions and processes involved in the mechanism leading to the polymerization initiating radicals.

2. Experimental Section

2.1. Chemicals. The dye Safranin (SfH^+ , Aldrich) and the monomer, sodium 4-styrenesulfonate (SS, Aldrich and Polysciences), were precipitated twice from methanol. Triethanolamine (TEAOH, Merck) was vacuum-distilled in the presence of metallic zinc before use. It was further treated with active carbon to eliminate eventual oxidation products. Other chemicals used were of the highest available purity and used as received. All solutions were prepared in Milli-Q purified water.

2.2. Polymerizations. Polymerizations were performed in 5 mL tubes to which an appropriate volume of a 0.5 M SS aqueous stock solution was added (around 2.5 mL), together with 0.5 mL of an aqueous solution of safranin ($1 \times 10^{-5} \text{ M}$). Pure water or amine solution was added to attain the desired monomer and amine concentrations.

The amine concentration was varied between 0 and 0.2 M. All solutions were protected from light prior to photolysis. When needed, the solutions were thoroughly degassed by bubbling oxygen-free nitrogen for 50 min. Irradiations were performed for 3 h in a dark box using two 100 W Philips Daylight lamps ($\lambda_{\text{max}} \sim 500 \text{ nm}$). The temperature was kept always below 28°C to ensure a minimum contribution of the thermal process.

The polymers were precipitated with acetone and washed thrice with the same solvent, after which they were dried in a

* Corresponding author. E-mail: neumann@iqsc.usp.br.

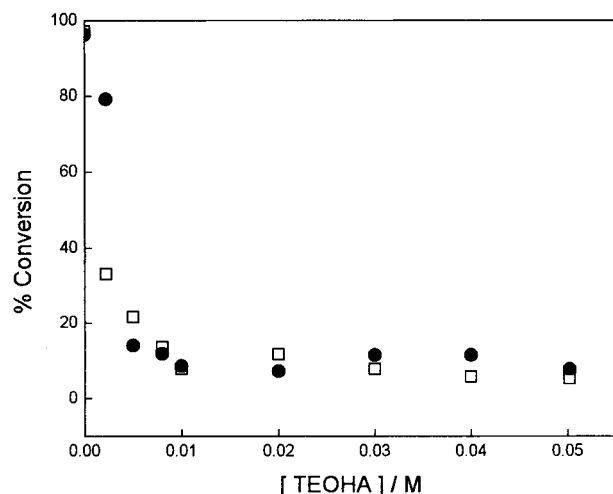


Figure 1. Photopolymerization of SS in the presence of amine. [SS] = 0.25 M; [Sf] = 5×10^{-6} M; irradiation time 3 h. Aerated (●) and deaerated (□) solutions.

vacuum for 3 days. The conversions were determined gravimetrically. Gel permeation chromatography (performed on a Shimadzu system with RI detector and using Asahipak (Shodex) GS 520 7E and GS-320H columns) showed the residual presence of monomer in the precipitate. The amount of the monomer was evaluated from the peaks of the chromatograms using a calibration done with known mixtures of polymer and monomer.

The solutions were also dialyzed for several days using cellulose membranes (14 000 D), until no fluorescence was detected in the range 290–450 nm (due to the aromatic rings). The purified polymers were also submitted to size analysis by dynamic light scattering using a Brookhaven Instruments BI9000-AT autocorrelator with a Uniphase Nd:YAG laser light source operating at 532 nm (125 mW).

2.3. Photophysical and Photochemical Determinations.

Fluorescence quenching experiments were carried out at room temperature (25 ± 1 °C) using an Hitachi F-4500 spectrofluorimeter. SfH^+ was excited at 532 nm and the emission was measured at its maximum. The lifetimes of the dye singlet in pure water and in concentrated SS solution were measured using single-photon counting with a CD-900 Edinburgh spectrometer operating with a nanosecond hydrogen-filled flash lamp at 25–30 kHz, at room temperature (25 ± 1 °C). In these experiments the excitation and detection wavelengths were 500 and 570 nm, respectively.

Transient absorption spectra and triplet lifetimes were determined with an Applied Photophysics kinetic laser spectrometer. Excitation at 532 nm was accomplished with Nd:YAG laser (Spectron) with frequency doubling. Detection was done with a Hamamatsu R928 photomultiplier.

The I_1/I_3 ratio of emission peaks of pyrene was determined using a 5.0×10^{-7} M concentration, and measured at 371 and 382 nm, respectively. Fluorescence experiments were performed on air-equilibrated solutions. The dye concentration used was always 1.0×10^{-5} M.

UV spectra were taken, at room temperature (25 ± 1 °C) on a Hitachi U2000 spectrophotometer linked to a PC computer.

3. Results and Discussion

Photopolymerization of styrenesulfonate is observed when irradiating monomer solutions containing safranin, even in the presence of oxygen or air, but suffers a marked inhibition in the presence amine. As can be seen in Figure 1 when

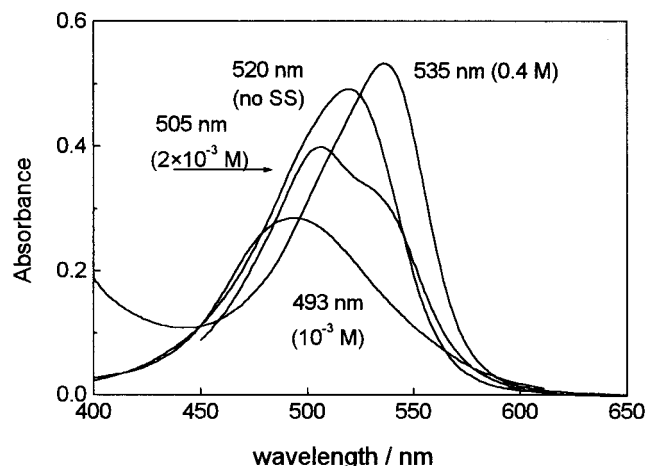


Figure 2. Absorption spectra of Sf in the absence and presence of different concentrations of SS.

the concentration of triethanolamine is above 0.01 M, the monomer conversion is less than 10% of that observed in its absence.

On the other hand, there is no detectable difference between the polymer yields in the presence or absence of oxygen (nondeaerated solutions). To explain these results a mechanism is proposed which involves the ground state association between the dye and the monomers. Active initiating radicals will be formed by an electron transfer process occurring in an already created molecular microdomain formed mainly by the monomer in which the dye molecule may be localized. An analysis of the different processes which may occur in these systems, in the ground and excited states, gives support to the mechanism.

3.1. Ground-State Interactions. Several ground state interactions between the components of the system should be considered. It is well-known that most cationic dyes, including Safranin, form aggregates in aqueous solution at sufficiently high concentrations.¹⁹ The presence of oppositely charged species in the solution, like ions or polyelectrolytes, will induce similar aggregations at lower concentrations due to the formation of ionic pairs by decreasing the electrostatic repulsion between the dye molecules. Additionally, the electrostatic repulsion will also be affected by the ionic strength effect.²⁰

Figure 2 shows the effect on the absorption spectrum of adding increasing amounts of SS to a solution of SfH^+ . Initially, the absorption at 520 nm decreases and the maximum gradually shifts toward shorter wavelengths. The shortest wavelength of the maximum absorption is reached at 493 nm, when the monomer concentration is 1×10^{-3} M. From there on, at higher monomer concentrations, the absorption rises again and shifts toward the red. A maximum is reached at [SS] ~ 0.2 M and is placed at 535 nm. The maximum absorptivity of the dye in the presence of SS 1×10^{-3} M is about 60% of that of a pure dye solution, whereas the peak found at higher SS concentrations has an absorbance 20% higher than that of the dye alone. These results can be interpreted assuming that the addition of low amounts of the charged monomer will form ion pairs with the dye, favoring its aggregation to form dimers and even higher dye aggregates, as also observed in aqueous solutions of the dye in the presence of poly(styrenesulfonate).^{20,21} The shift to shorter wavelengths and the decrease of the extinction coefficient is compatible with what is found for the aggregation of dyes in concentrated aqueous solutions.²² At higher concentrations, the excess of monomer molecules in solution will promote a redistribution of the dye molecules until only 1:1 associations

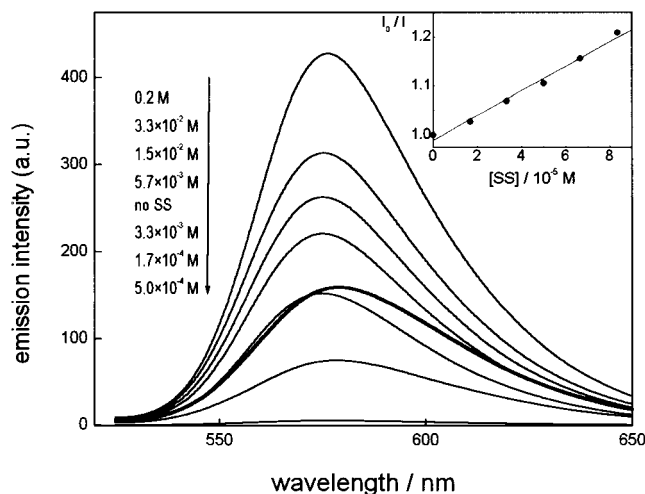


Figure 3. Fluorescence spectra of Sf in the absence (thick line) and presence of SS. Inset: Stern–Volmer plot at low SS concentrations.

will be present. Eventually, at even larger concentrations, the positive charged dye molecule may serve as a seed for the aggregation of the anionic monomers, similar to what has already been observed for the formation of premicellar surfactant aggregates induced by the presence of acridine orange.²³ Under these conditions, in principle, no more than one dye molecule should be present per monomer aggregate. Similar behavior has been also observed for the addition of polystyrenesulfonate to safranine solutions, for which the maximum absorption shifts and extinction coefficients show the same pattern.²¹

Addition of toluenesulfonate to aqueous safranine solutions shows a similar behavior to that described above. Furthermore, adding NaCl to the dye did not cause any significant changes, proving that the observed effects were not due to the increase of the ionic strength. When those experiments were performed in methanolic solutions practically no shift of the maximum or changes in the absorption spectra were observed, as expected from the exciton theory when applied to the formation of dye aggregates in low dielectric constant solvents.²⁴

The association constant of the dye in the presence of monomer at low concentrations was calculated using the Benesi–Hildebrand method and a value of 280 M^{-1} was obtained.

Addition of triethanolamine to a 1×10^{-5} solution of the dye caused only a slight decrease in the absorbance. For instance, adding 0.20 M of TEOH only decreased the absorbance by about 17%. A similar behavior of the spectrum could be observed when the same pH (10.6) was reached by adding NaOH, proving that the observed effect is only due to the decrease of the absorbing species because of deprotonation of the dye.

3.2. Excited-State Interactions. As shown in Figure 3 the fluorescence spectra of the dye also follow a nonconventional behavior when styrenesulfonate is added to it. At low concentrations, there is fast quenching of the emission, but for monomer concentrations above $\sim 10^{-3} \text{ M}$ the emission intensity increases dramatically, with a slight shift to the blue. The Stern–Volmer plot at low SS concentrations shows a positive deviation from the normal behavior, indicating the presence of an additional process to that of simple quenching. The emission intensity increases up to monomer concentrations of around $\sim 0.1 \text{ M}$, when the emission reaches its maximum (See Figure 4). Whereas the Stern–Volmer quenching constant at low monomer concentrations (inset of Figure 3) can be estimated as $2.5 \times 10^{-3} \text{ M}^{-1}$ (corresponding to a rate constant of $1.9 \times 10^6 \text{ M}^{-1}$

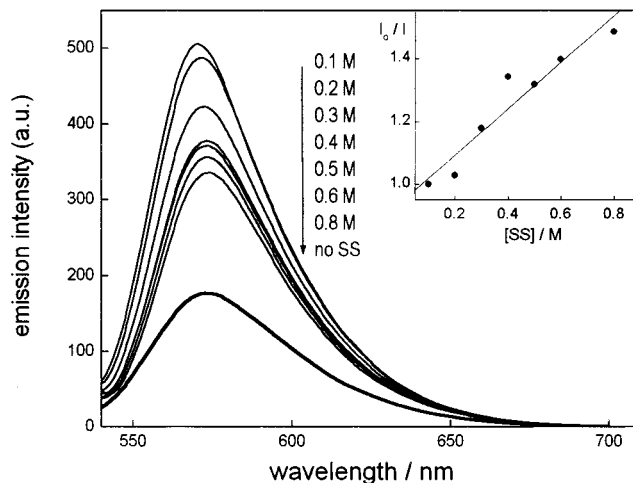


Figure 4. Fluorescence spectra of Sf in the presence of high SS concentrations. Inset: Stern–Volmer plot at high SS concentrations.

s^{-1}), at higher concentrations, like those used for polymerization, this constant was 0.76 M^{-1} ($4.75 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). The lifetimes used for the evaluations above were 1.3 and 1.6 ns (SS 0.5 M), respectively, measured by SPC. The decays were clearly monoexponential with χ^2 values of 1.096 and 1.192. The fact that the lifetime increases for the more concentrated SS solutions indicates that the effect of the new environment surrounding the dye molecule is larger than a conceivable static quenching.

The effect of amine on the Safranine fluorescence emission follows the usual pattern. The observed Stern–Volmer constant is around 4.8 M^{-1} , corresponding to $3.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the quenching rate constant, within what is expected for this type of reactions. Only a small difference was found when the quenching was performed in the presence of SS 0.5 M. In this case, the Stern–Volmer constant falls to 2.15 M^{-1} , rendering a quenching rate constant of $1.35 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, possibly reflecting a more difficult approach of the amine molecule to the dye (See Figure 4).

The decay of the triplet state of the dye in deaerated solution and in the absence of SS corresponded to a lifetime of around $27 \mu\text{s}$ ($k = 3.7 \times 10^4 \text{ s}^{-1}$). After the addition of SS $2.0 \times 10^{-5} \text{ M}$, it rose to about $40 \mu\text{s}$ ($k = 2.5 \times 10^4 \text{ s}^{-1}$), and fell with successive additions of the monomer, as expected for a normal quenching process. The quenching rate constant for this process is around $6.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The rise of the lifetime of the dye after the first addition of SS can be associated with the special configuration that the dye–SS pair, possibly with parallel π -orbital planes, as found for the association of safranine with the structural similar phenylglycines.²⁵

On the other hand, in aerated solutions and high SS concentrations the lifetime of the dye increases from 2 to $5 \mu\text{s}$, as shown in Figure 5, demonstrating a progressive protection of the dye to oxygen quenching when incorporated in the styrenesulfonate microdomain. Concurrently, the change of environment may also affect the triplet lifetime. But, on the other hand, the relatively small change in the lifetime of the singlet state suggests that the main effect is the protection of dye by the monomer cluster.

Similar results were also obtained when using toluenesulfonate instead of the monomer, although the dye lifetimes are somewhat longer in that media. This difference might be ascribed to the fact that when embedded in the SS clusters, the triplet excited dye will be quenched not only by the residual oxygen that reaches its position, but will also react with SS

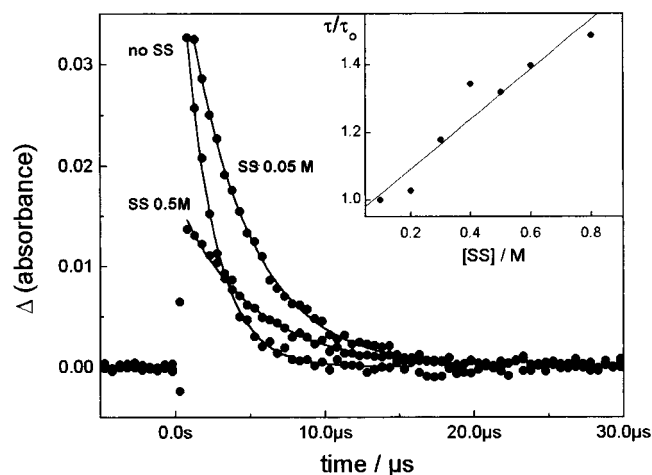
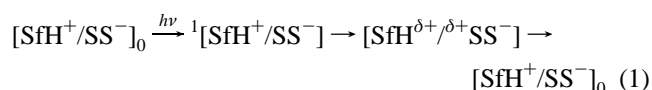


Figure 5. Sf triplet absorption decays (at 820 nm) in the absence and presence of high SS concentrations in aerated solutions. Inset: Ratio between the lifetimes of the triplet in the absence and presence of SS, up to [SS] 0.8 M.

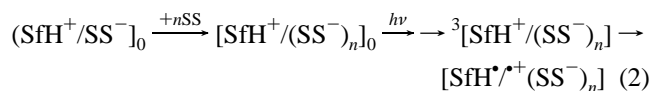
molecules to initiate the polymerization. On the other hand, the dye triplets in the clusters formed by toluenesulfonate will only be quenched by the residual oxygen.

3.3. Polymerization. Because of its rather low oxidation potential (1.57 eV), the styrenesulfonate monomer is able to donate an electron to the excited triplet state of the dye to form the initiating radical. A similar reaction has been found for other styrene derivatives, as described by Timpe et al.^{12,26} Other monomers, like MMA, cannot be photopolymerized by Safranine alone due to their higher oxidation potentials (3.07 eV). Similarly, the use of other dyes with lower reduction potentials does not lead to efficient photopolymerization either. In those cases a suitable co-initiator has to be used to photoreduce the excited dye.

At low SS concentrations the excitation will take place on a dye molecule situated in an ion pair or in a small SS microdomain. As expected, the charge separation in the singlet state will hardly lead to the formation of free radicals. Therefore, the singlet species is will be deactivated to its ground state by back electron transfer. In the presence of amine or oxygen the quenching will be even faster.



On the other hand, the addition of larger amounts of SS will form a microdomain which will protect the dye from oxygen quenching and ensure a longer lifetime to it.



The semireduced safranine $\text{SfH}^{\bullet+}$ will initiate polymerization by adding to a neighboring styrenesulfonate molecule.



Opposite to what happens in normal dye/monomer photoinitiations where the active radical originates from the reaction of the triplet dye with an amine electron donating co-initiator, here the active radicals seem to be the semireduced species. This is proved by the color of the polymer, which could not be bleached even after long time dialysis, or repeated washings with alcohol

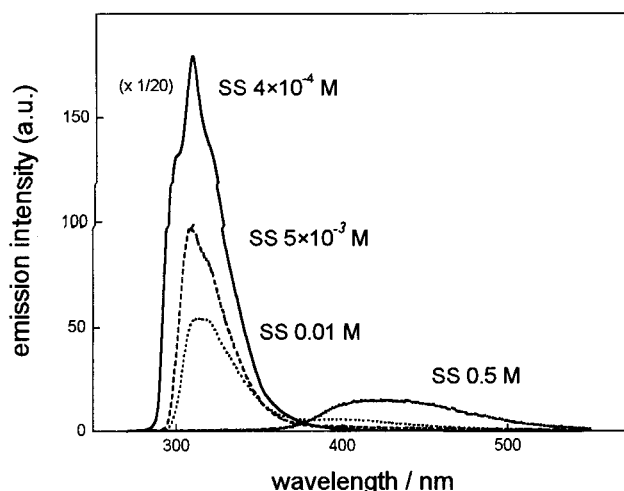


Figure 6. Emission spectra of SS ($\lambda_{\text{exc}} = 255$ nm) at different concentrations.

TABLE 1: I_1/I_3 Ratios of Pyrene Emission at Different SS Concentrations. $[\text{Py}] = 5 \times 10^{-7}$ M

[SS]/M	10^{-5}	0.01	0.1	0.2	0.3	0.4	0.5
I_1/I_3 ratio	1.80	1.60	0.81	0.72	0.67	0.66	0.63

or other solvents. Additionally, a progressive bleaching of the remaining solution can be observed, which proves the consumption of the dye during the polymerization process.

The inhibition by triethanolamine could be ascribed to two concurrent processes:

(i) The addition of amine will displace the prototropic equilibrium of the dye toward the deprotonated form Sf, which due to its lack of positive charge, may fail to induce aggregation of the anionic monomer molecules around it, thus decreasing the local concentration around the excited dye molecule. (ii) On the other hand, the high amine concentration will probably quench dynamically most of the dye in its singlet state. Quenching of the SS fluorescence by triethanolamine showed that the emission lifetime decreases from 4.1 to 2.9 ns for an amine concentration of 0.03 M. This result confirms the possibility of quenching of the excited SfH^+/SS species.

Therefore, it is believed that under the conditions used in this work, the polymerization will involve the following sequence of events.

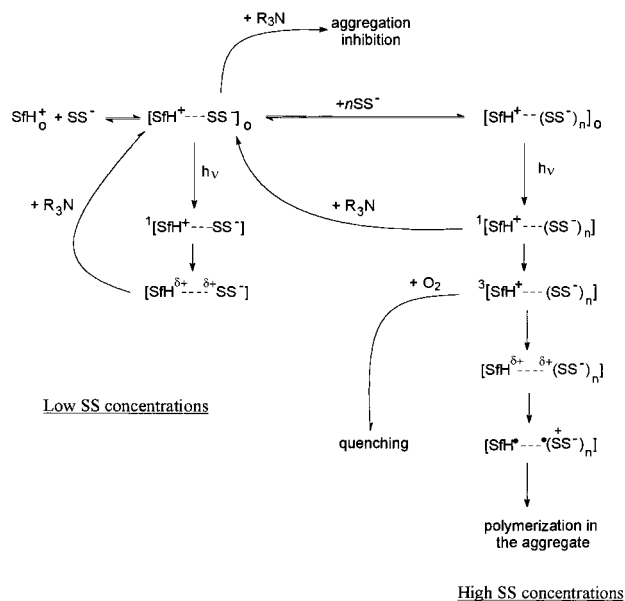
(a) Aggregation of the anionic monomer induced by the cationic dye molecule occurs. At the SS concentration used for the polymerizing formulation (~ 0.5 M), practically all dye molecules will be surrounded by monomer molecules forming a differentiated microenvironment with an extremely high local monomer concentration. Even in the absence of the dye, at SS concentrations higher than 0.01 M, the excimer emission can be observed (Figure 6). At even higher concentrations, like 0.5 M only the emission of excimers and higher aggregates is observed.

Additionally, the measurement of the I_1/I_3 ratio of the peaks of the fine structure of the emission of pyrene,²⁷ indicates an increasing hydrophobic character of the microenvironment surrounding the probe, when the SS concentration is increased, as illustrated by Table 1.

(b) After excitation, the dye will be able to abstract an electron from a neighboring styrenesulfonate ion. Although the interaction (quenching) of the dye by SS has a relatively low rate constant, its high local concentration will overcome this shortcoming, giving rise to the initial radical.

TABLE 2: Mean Diameter of PSS Particles Obtained by Photopolymerization of SS in the presence of Sf 1×10^{-5} M.

[SS]/M	0.8	0.6	0.3	0.1	0.05
mean diameter, nm	3780	2440	1670	790	470

SCHEME 1: Diagram of the Individual Steps Leading to Photopolymerization of SS in the Presence of the Photoinitiator Dye.

(c) Due to the high concentration, there will be a rapid propagation of the chain, which should consume most of the monomers present in the cluster around the dye.

(d) This last point is proved by the size of the precipitated polymer particles which increase by a factor of ca. 10 when the initial monomer concentration is increased from 0.05 to 0.8 M (Table 2), as there should be a reasonable correlation between the number of monomers in the cluster and the overall concentration. Any initiating dye radical will polymerize an amount of monomers proportional to the size of the cluster.

All the events described above are summarized in Scheme 1, which shows all the interactions present in the systems composed by SS, Sf, and TEAOH.

4. Conclusions

The photoinitiated polymerization of styrenesulfonate in the presence of safranin is possible at high SS concentrations (e.g., >0.1 M). There is no need for coinitiators, like amines, and the reaction also proceeds in air equilibrated solutions. The data obtained suggests that at high SS concentrations, the monomer forms aggregates or clusters, which incorporates a dye molecule which will be excited by light and produce the initiating free radical. Evidence for the formation of the aggregates were obtained at three different stages:

(i) In the Ground State. The absorption spectrum of Safranin changes according to the concentration of SS present in the solution in the sequence monomers, dye aggregates, ion pairs, and monomers in SS microdomains. The addition of pyrene to SS solutions with increasing concentrations, shows that the I_1/I_3 ratio of the emission peaks changes from 1.8 (practically aqueous solution) at low SS concentration to ~ 0.6 (hydrophobic medium) at SS 0.5 M.

(ii) In the Excited States. The emission spectra of pure SS solutions (excited at 255 nm) show peaks corresponding to excimers and higher aggregates at concentrations above 0.1 M.

The fluorescence of Safranin in SS solutions shows a pattern similar to that found for the absorption spectra: the pure monomer emission is initially quenched by SS, but increases and shifts to the red at higher concentrations, as expected for its localization in a more hydrophobic medium. Finally, the triplet of the dye in high SS concentration solution, when air equilibrated, increases its lifetime from 2 μ s to over ~ 5 μ s at SS 0.8 M, proving a lower local residual oxygen concentration (and quenching efficiency) as expected in more hydrophobic microdomains.

(iii) Polymerization Products. The size of the PSS particles formed during the dye photoinitiated polymerization in high SS solutions increases from ~ 500 nm at SS 0.05 M to ~ 4000 at 0.8 M, reflecting the size of the SS microdomain surrounding the excited dye.

Acknowledgment. Financial support by FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo, Brazil), Proc. 98/117521, is gratefully acknowledged. H.M.M. thanks the same Agency for a Graduate Fellowship (Proc. 97/00753-4).

References and Notes

- (1) Oster, G. *Nature* **1954**, 173, 300.
- (2) Eaton, D. F. *Advances in Photochemistry*; Volman, D., Gollnick, K., Hammond, G. S., Eds.; Wiley: New York, 1966; Vol. 13, Chapter 4.
- (3) Kustermann, E.; Timpe, H. J.; Gabert, K.; Schubert, H. *Wiss. Z. Technol. Hochsch. Meseburg* **1987**, 29, 287.
- (4) Chen, C. *J. Polym. Sci. A* **1965**, 3, 1107, 1127, 1137, and 1155.
- (5) Neckers, D. C. *Polym. Eng. Sci.* **1992**, 32, 1481. Kumar, G. S.; Neckers, D. C. *Macromolecules* **1992**, 24, 4322. Valdes-Aguilera, O.; Pathak, C. P.; Shi, J.; Watson, D.; Neckers, D. C. *Macromolecules* **1992**, 25, 541.
- (6) Böttcher, H.; Bendig, J.; Fox, M. A.; Hopf, G. H.; Timpe, H.-J. *Technical Applications of Photochemistry*; Dt. Verl. für Grundstoff: Leipzig, 1991; Chapter 2.
- (7) Dietliker, R. K. *Chemistry and Technology of UV and EB Formulation for Coating, Inks, and Paints*; SITA Technology Ltd.: London, 1991; Vol. 3.
- (8) Fouassier, J. P.; Lounnot, D. J. *Radiation Curing of Polymer Materials*; ACS Symposium Series 5; American Chemical Society: Washington, DC, 1990; p 417.
- (9) Allen, N. S.; Edge, M.; Bellobono, I. R.; Selli, E. *Current Trends in the Photochemistry of Polymers*; Ellis Horwood: London, 1995; Chapter 7.
- (10) Reiser, A. *Photoreactive Polymers: The Science and Technology of Resins*; Wiley: New York, 1989.
- (11) Timpe, H. J.; Kustermann, E.; Böttcher, H. *Eur. Polym. J.* **1991**, 27, 429; Timpe, H. J.; Müller, F. W.; Strehmel, B.; Panzner, G.; Schiller, K.; Reuter, H. *Angew. Makromol. Chem.* **1992**, 201, 49.
- (12) Timpe, H. J.; Neuenfeld, S. *J. Chem. Soc., Faraday Trans.* **1992**, 88, 2329.
- (13) Lemee, V.; Burget, D.; Jacques, P.; Fouassier, J. P. *J. Polym. Sci., Polym. Chem.* **2000**, 38, 1785. Fouassier, J. P. *Polym. Eng. Sci.* **1995**, 35, 1061. Fouassier, J. P.; Ruhlmann, D.; Graff, B.; Morletsavary, F.; Wieder, F. *Prog. Org. Coat.* **1995**, 25, 235. Cataliz, L.; Fouassier, J. P. *Angew. Makromol. Chem.* **1994**, 218, 81. Fouassier, J. P.; Ruhlmann, D.; Erddalane, A. *Macromolecules* **1993**, 26, 721.
- (14) Previtali, C. M.; Bertolotti, S. G.; Neumann, M. G.; Pastre, I. A.; Rufs, A. M.; Encinas, *Macromolecules* **1994**, 27, 7454. Encinas, M. V.; Rufs, A. M.; Neumann, M. G.; Previtali, C. M. *Polymer* **1996**, 37, 1395. Neumann, M. G.; Gehlen, M. H.; Encinas, M. V.; Allen, N.; Corrales; Peinado; Catalina, F. *J. Chem. Soc., Faraday Trans.* **1997**, 93, 1133. Rodrigues, M. R.; Neumann, M. G. *Polymer* **1998**, 39, 1657. Rodrigues, M. R.; Catalina, F.; Neumann, M. G. *J. Photochem. Photobiol. A* **1999**, 124, 29. Rodrigues, M. R.; Catalina, F.; Neumann, M. G. *J. Photochem. Photobiol. A* **1999**, 127, 147.
- (15) Duda, A.; Penczek, S. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Kroschwitz, J. I., Exec. Eds.; Wiley-Interscience: New York, 1989; Vol. 16, p 332ss.
- (16) Kurenkov, V. F.; Myachekov, V. A. *Eur. Polym. J.* **1979**, 15, 849.
- (17) Bhardwaj, Y. K.; Mohan, H.; Sabharwal, S.; Majali, A. B. *Radiat. Phys. Chem.* **2000**, 58, 373.
- (18) Wu, Ji-Lan; Zhang, Yu.-Hua *Radiat. Phys. Chem.* **1981**, 18, 1067.
- (19) Rabinowitch, E.; Epstein, L. F. *J. Am. Chem. Soc.* **1941**, 63, 69.
- (20) Vitagliano, V. In *Aggregation Processes in Solution*; Wyn Jones, E., Gormally, J., Eds.; Elsevier: Amsterdam, 1983; Chapter 11.

- (21) Neumann, M. G.; Gessner, F.; de Sena, G. *Dyes Pigm.* **1992**, 20, 255.
- (22) Neumann, M. G.; Hioka, N. *J. Appl. Polym. Sci.* **1987**, 43, 2829.
- (23) Neumann, M. G.; Gehlen, M. H. *J. Colloid Interface Sci.* **1990**, 135, 209.
- (24) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, 11, 371.
- (25) Neumann, M. G.; Gessner, F.; Souza, A. R.; Schmitt, C. C. *J. Photochem. Photobiol. A* **1988**, 45, 355.
- (26) Timpe, H. J.; Neuenfeld, S. *J. Polym. Sci., Polym. Chem.* **1993**, 31, 1347.
- (27) K. Kalyanasundaram, *Photochemistry in Microheterogeneous Systems*; Academic Press: New York, 1987.