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The photopolymerization of styrenesulfonate initiated by dyes The effect of monomer aggregation

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Abstract

Styrenesulfonate was photopolymerized in the presence of the anionic dye Eosine Y. The study of the reactions of the excited- and ground states of the species involved in the photoinitiation process showed that the monomer aggregates forming hydrotropic domains in aqueous solution at concentrations above 0.1 M. Although the dye is distributed between these domains and the bulk of the solution, the main initiating pathway involves excited dyes outside the clusters. These results are opposite to those obtained using the cationic dye Safranine, which starts photopolymerization from the dye molecules incorporated in the monomer clusters.

Keywords: Polymer synthesis; Poly(styrenesulfonate); Monomer aggregation; Hydrotropes

1. Introduction

In recent years, several papers 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 containing dyes (or other visible light absorbers) commenced to be studied by various workers. The present use of this procedure in the manufacture of printed circuits, encapsulation of electronic components, decorative coating, dental filling composites, stereolithography, and others, brought new interest into the subject [1–6]. As a consequence, efforts are being made to provide better insight into the photophysical and photochemical process involved, in order to develop better and more efficient photoinitiator systems adapted to different problems and applications [7–10].

Sulfonated polyelectrolytes, and particularly poly(styrenesulfonate) (pStyS), are normally obtained by sulfonation in extreme conditions of the non-charged polymer polystyrene [11]. The thermal polymerization of StyS was studied by Kurenkov and Myachekov [12] and the effect of radiation on pStyS resins has been well established several years ago [13]. Bhardwaj et al. studied the radiation-induced polymerization of this compound in the steady state and by pulse radiolysis [14]. We recently reported on the photopolymerization of StyS in the presence of the cationic dye Safranine [15]. The monomer can be considered a hydrotrope due to the simultaneous presence of the hydrophobic phenyl ring and the hydrophilic sulfonate group [16,17]. As a result, monomer aggregates are formed at the relatively high StyS concentrations (>0.1 M) used for polymerization. These negatively charged clusters can be considered to be a good medium for the dissolution of cationic dyes like Safranine. The photoinitiation mechanism was described in terms of the ground and excited state elemental reactions involved in the system.

Continuing this work, we present in this paper results for the photopolymerization of styrenesulfonate in the presence of the anionic dye Eosine Y (Eos) in aqueous solution.

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2. Experimental

2.1. Chemicals

The dye Eosine Y (Aldrich) and the monomer, sodium styrenesulfonate (StyS, Polyscience), were precipitated twice from methanol. 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 an aqueous stock solution of StyS 0.5 M was added (around 2.5 mL), together with 0.5 mL of an aqueous solution of Eosine Y (1×10^{-5} M). Pure water, Milli-Q purified, was added to reach the desired monomer concentrations. Irradiations were performed for in a dark box using four 100 W Philips Daylight lamps ($\lambda > 500$ nm). The temperature was kept at 30 °C to assure a minimum contribution of the thermal process.

Polymerization rates were determined dilatometrically. The dilatometer consisted of two capillaries (i.d. 0.18 cm) attached to a cylindrical reaction vessel (i.d. 2.2 cm, volume 8.5 mL), which was placed in a constant temperature bath (25 °C) in front of a 200 W Hg(Xe) lamp in an Oriel Universal Arc Lamp source. A 395 nm cut-off filter was placed between the lamp and the reaction cell.The polymerization rates (R_p) were calculated using Eq. (1)

$$R_p = \frac{\Delta V}{F \cdot f \cdot t}[\text{StyS}] \quad (\text{M/s}) \tag{1}$$

where ΔV is the contraction in volume in the capillary (calculated from the variation in the cathetometer) at time t, f the volume fraction of StyS monomer in the solution, F the volume contraction related to the densities of polymer and monomer in solution $F = [(d_p - d_m)/d_p]$, and [StyS] corresponds to the monomer molar concentration.

All solutions were protected from light prior to photolysis. When needed, the solutions were vacuum-degassed by four freeze–thaw cycles with liquid nitrogen.

The polymers were precipitated with acetone and washed thrice with the same solvent, after which they were dried in vacuum for three days. 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 solutions were also dialysed for several days using cellulose membranes (14,000 D), until no fluorescence was detected in the range 290–450 nm (due to StyS aromatic systems).

2.3. Photophysical and photochemical determinations

Fluorescence quenching experiments were carried out at room temperature (25 ± 1 °C) using a Hitachi F-4500 spectrofluorimeter. Eos was excited at the maximum absorption wavelength (516–520 nm) and the emission was measured at the emission maximum (539–543 nm). The lifetimes of the dye singlet in pure water and in concentrated StyS solution were measured using single-photon timing with a CD-900 Edinburgh spectrometer operating with a nanosecond hydrogen-filled flash lamp at 25–30 kHz, at room temperature (25 ± 1 °C).

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

UV spectra were taken at room temperature on a Hitachi U2000 spectrophotometer linked to a PC.

Table 1
Photopolymerization of StyS 0.5 M by different dyes (conversions correspond to 3 h irradiation)

Dye	λ_{max} (nm)	Type	% converted
Rhodamine B	545	Xanthenic	0
Eosine Y	516	Xanthenic	55
Acridine Orange	490	Azinic	<13
Safranine	520	Phenazinic	97
Methylene Blue	610	Thiazinic	<10

3. Results and discussion

3.1. Polymerization

The photopolymerization of the ionic monomer styrenesulfonate in aqueous solution proceeds in the presence of various dyes.

It can be observed in Table 1 that the best conversions are obtained with Safranine and Eosine Y. The overall conversions also show a good correlation with the intersystem crossing quantum yields of the dyes. Whereas for Sf and Eos the Φ_{ISC} values are 0.28 and 0.50 [18,19], respectively, for Rhodamine the yield of triplets is generally less than 0.05 [20]. These results suggest that the initiation reaction path must involve the triplet state of the dyes.

Another interesting feature for these polymerizations is that no co-initiators are necessary to proceed with the reaction [8,21]. This behaviour is different from systems involving dyes and other monomers like methyl methacrylate and similars. Although the values for the oxidation and reduction potentials (the oxidation potential of the triplet is −1.11 V (versus NHE) [8,22], and a value for styrenesulfonate similar to that for styrene, around +1.60 V) render a positive value for ΔG, it seems that the slow rate at which the electron transfer would occur is sufficient to launch the polymerization process.

$$\text{Eos}^{2-} \xrightarrow{h\upsilon} \rightarrow {}^3(\text{Eos}^{2-}) \tag{2}$$

$${}^3(\text{Eos}^{2-}) + \text{StyS}^- \rightarrow {}^{\bullet}\text{Eos}^{3-} + {}^{+\bullet}\text{StyS}^- \tag{3}$$

Table 2
Rates, induction times and molecular weights for the photopolymerization of StyS in the presence of Eosine Y (1.2×10^{-5} M)

[StyS] (M)	t_{ind} (min)	R_p (10^{-6} M s^{-1})	10^6 (M_w)
0.1	9.8	3.43	nd
0.2	32.4	6.12	1.02
0.3	43.7	5.97	1.14
0.4	30.0	8.62	1.36
0.5	26.4	11.4	1.61
0.6	48.8	8.23	nd

In aqueous solution, the monomer cation radical is stabilized by bonding to the hydroxy ion

$$^{+\bullet}\mathrm{StyS}^- + \mathrm{H_2O} \rightarrow \mathrm{HO} - {}^{\bullet}\mathrm{StyS}^- + \mathrm{H}^+ \quad (4)$$

Both radicals derived from the monomer and from the dye are able to initiate the polymerization process. Possibly, due to the high negative charge present on the dye (two charges due to the original structure of Eosine, plus the charge resulting from the accepted electron), its efficiency to approach negatively charged monomers will be reduced, in comparison with the ion radical from the donor monomer. The fact that the polymers obtained by this method are practically colourless confirms this assumption. Additionally, this result can be compared with the polymers obtained by the same method using the cationic dye Safranine instead of Eosine. Ground state Safranine has a positive charge which is delocalized over the whole structure, and when reduced is converted to the semi-reduced neutral radical, which is efficient in initiating polymerization, so that the obtained polymers are intrinsically coloured [8]

$$\mathrm{Sf}^+ \xrightarrow{h\upsilon} \rightarrow {}^3\mathrm{Sf}^+ \quad (5)$$

$${}^3\mathrm{Sf}^+ + \mathrm{StyS}^- \rightarrow \mathrm{Sf}^{\bullet} + {}^{+\bullet}\mathrm{StyS}^- \quad (6)$$

Polymerization rates and other relevant data are shown in Table 2.

3.2. Photochemical properties of the initiator

In order to propose the reaction mechanism for the photopolymerization, it is necessary to know exactly which are the species present under the reaction conditions, as well as the rates of the elemental reactions included in the mechanism.

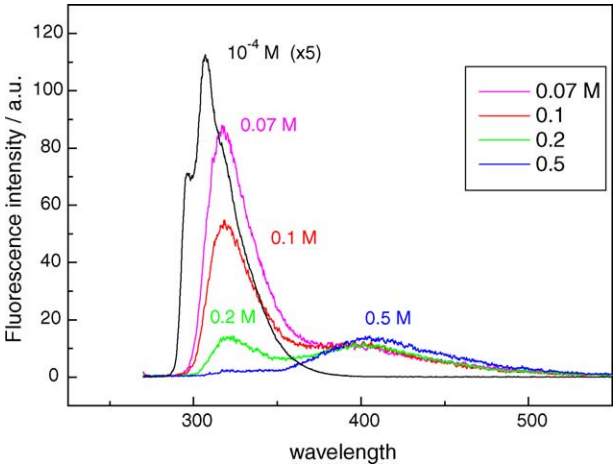


Fig. 2. Emission spectra of aqueous solutions of StyS at different concentrations.

3.2.1. The prototropic equilibrium

As stated above, Eosine Y is a dye that may take various protonation states according to the pH of the solution (Fig. 1).

At pH above 5.5 the dye presents an absorption spectra with maximum at 516 nm and at lower pH, a new peak appears around 485 nm. The pK corresponding to the monoprotonated–unprotonated equilibrium was found to be 4.3, and the diprotonated state (with a maximum absorption at 455 nm) is only present at pH < 3. Thus, the species present at the working conditions (pH ∼ 6) will always be the unprotonated dianionic form. Korobov and Chibisov [23] reported the pK_a^T of triplet Eosine at about 4, so that no excited state protonation will occur under the working conditions.

At the low concentrations used in this work there is practically no self-aggregation of the dye, so that it can be considered that all the dye is present in its monomeric form.

3.2.2. Aqueous solutions of styrenesulfonate

When dissolved in water, the emission spectrum of StyS (Fig. 2) shows a behaviour, which can be explained by the formation of aggregates. At concentrations below 1×10^{-3} M, the emission maximum is found at 307 nm. When increasing

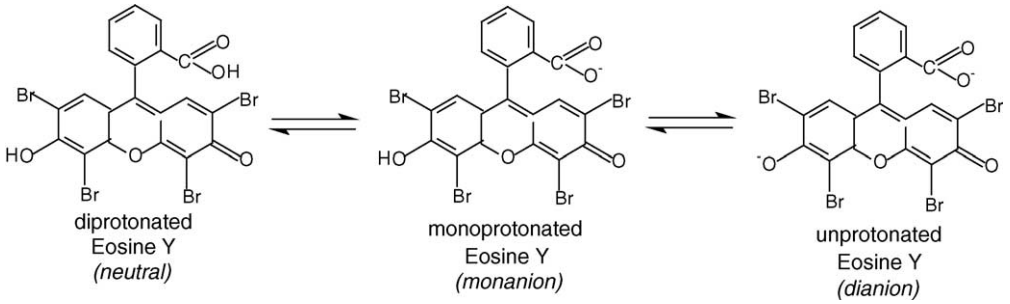


Fig. 1. Prototropic equilibria of Eosine Y.

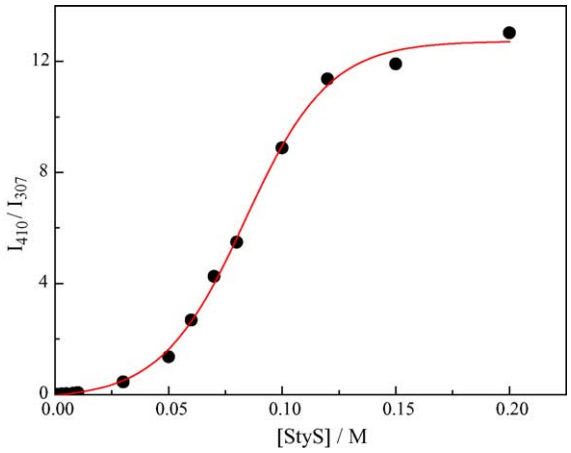


Fig. 3. Monomol/aggregate emission ratio for various concentrations of StyS. λ_{exc} = 255 nm.

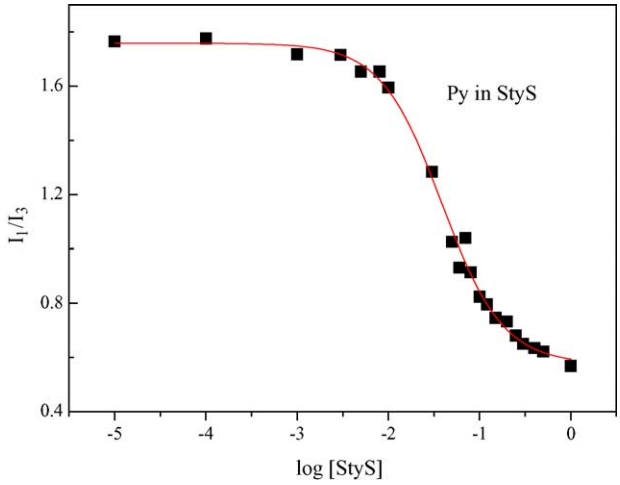


Fig. 4. I_1/I_3 emission ratio of pyrene (1×10^{-6} M) in StyS aqueous solutions.

the concentration to 3×10^{-3} M this maximum is shifted to 310 nm. From there on, higher concentrations promote a gradual shift towards 317 nm, and a consistent decrease of the emission. This shift in the emission can be assigned to the emitting monomers being in a different microenvironment. At concentrations around 0.05 M, a new broad emission band is observed with a maximum around 410 nm, which increases steadily with concentration. This peak is due to the emission of excimers and higher aggregates. At 0.5 M, only the longer wavelength peak is observed, as shown in Fig. 2. Fig. 3 describes the ratio between the monomol and aggregate emissions measured at 367 and 410 nm, respectively. A limiting value for the ratio can be estimated to be reached at concentrations around 0.1 M. This point can be considered to be the *minimum hydrotrope concentration* (MHC) [16] for StyS. This value is within those expected for similar hydrotropes, and should correspond to the concentration at which the hydrotrope effect begins to be apparent.

A similar conclusion can be reach by plotting the I_1/I_3 ratio of the pyrene emission (a parameter related to the microenvironment were the organic probe is placed) as a function of the StyS concentration, as seen in Fig. 4. The inflexion point of the curve is at about 0.04 M and it can be considered that the levelling-off occurs somewhere between 0.1 and 0.3 M, which is quite consistent with the value obtained from the monomol/aggregate emission ratio shown in Fig. 3. It is to be noted that the limiting value for the I_1/I_3 ratio is about 0.6, which corresponds to the value found for pyrene in hydrophobic organic solvents. It can also be observed that there is a self-quenching of the emission, as evidenced by the decrease of the total emission intensity.

Similar behaviour was observed for StyS in methanol: water (70:30) solutions, except that the onset of the excimer emission only occurs at higher StyS concentrations. Also, the increase of the ionic strength by addition of NaCl prevents the aggregation [24].

3.2.3. Ground state dye–monomer association

The absorption spectra of Eosine in the presence of increasing concentrations of styrenesulfonate up to 0.5 M show a gradual decrease of the absorbance, together with a shift of the maximum from 516 to 520 nm. The same effect was observed when placing the dye in a solution of toluenesulfonate. No effect at all was observed when adding NaCl 0.5 M to an aqueous solution of the dye, so that any ionic strength effects can be discarded. This change in the spectrum of the dye is similar to what is observed when dyes are put in micellar solutions, and are ascribed to the difference in the environment where the dye is localized. Therefore, it can be assumed that a part of the Eosine will placed within the microenvironments resulting from the clustering of the monomers.

3.3. Excited state reactions

The lifetimes of Eosine in aqueous solution and in the presence of StyS 0.5 M were 1.2 and 1.4 ns, respectively. The difference is within the experimental error confirming that there is no dynamic quenching of the singlet dye by the monomer, even at high concentrations. Furthermore, the small increase in the lifetime might also be ascribed to the lower oxygen solubility inside the clusters, compared to pure aqueous solution.

3.3.1. The triplet state

The triplet–triplet spectrum obtained for Eosine Y, shown in Fig. 5, is practically identical with that found in previous reports [25,26]. The absorption maximum is found at 575 nm, and the bleaching in the region of the ground state absorption between 450 and 540 nm can also be observed. The time evolution of the spectra shows the simultaneous decrease of the triplet absorption and the recovery of the ground state. The decay measured at 600 nm corresponds to a lifetime of 45.1 μs, whereas the bleaching recovery, measured at 480 nm, was found to be 63.8 μs (inset of Fig. 5). These values are

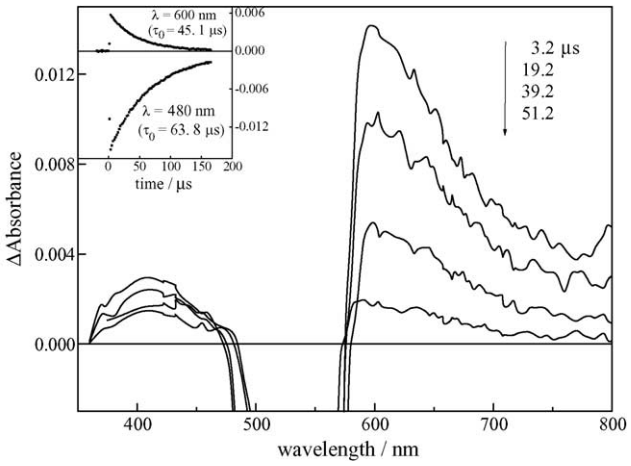


Fig. 5. Transient spectra of Eosine Y (1.2×10^{-5} M) in deaerated aqueous solutions at different times after laser excitation at 532 nm. Inset: decay and bleaching recovery at 600 and 480 nm.

in good agreement with those reported earlier from pulse radiolysis experiments [26].

The small absorption observed in the transient spectrum in the 380–450 nm region is attributed to semi-reduced species originated by self-quenching reactions. The decay in this region is somehow slower (a half-life of about 130 μs), confirming the presence of a different species. Additionally, it may be considered that the longer lifetime of the bleaching recovery measured at 480 nm may be due to the presence of semi-oxidized species which absorb at this wavelength [25,26].

3.3.2. Transients in the presence of monomer

The transient spectrum of Eosine Y in the presence of StyS is shown in Fig. 6. In the presence of monomer, the transient spectrum shows an increase in the absorption in the 355–440 nm region when compared to solutions without the monomer. The half-life for this absorption is rather long, as expected for a semi-reduced species originated by an

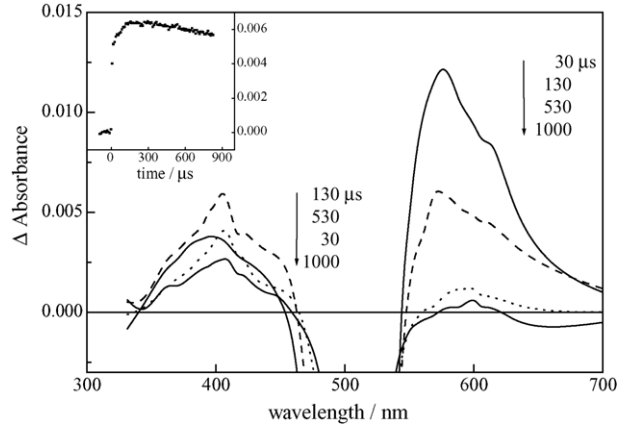


Fig. 6. Transient absorption spectra of Eosine Y (1.2×10^{-5} M) in deaerated aqueous solution containing StyS 0.5 M. λ_{exc} = 532 nm. Inset: time evolution of the 405 nm transient absorption.

Table 3
Lifetimes of the decay of transient absorptions of excited Eosine Y in different media measured at 600 nm

Medium	τ_1 (μs)	τ_2 (μs)
Water	45.1	–
+StyS (0.1 M)	47.7	161.4
+StyS (0.3 M)	12.0	128.4
+StyS (0.5 M)	9.2	123.6
+TS (0.1 M)	41.3	110.9
+TS (0.3 M)	43.9	118.1
+TS (0.5 M)	35.1	117.9
+O_2 (aq)	2.6	–
+StyS (0.1 M) + O_2	–	3.3
+StyS (0.3 M) + O_2	–	3.2
+StyS (0.5 M) + O_2	–	4.2
+TS (0.1 M) + O_2	–	2.9
+TS (0.3 M) + O_2	–	3.3
+TS (0.5 M) + O_2	–	4.7

electron transfer from the monomer to the dye. Additionally, as seen in the inset of Fig. 6, there is an initial in-growth of the absorption at 405 nm, followed by the decay of the species due to a secondary reaction. The decay of the absorption in the 550–820 nm is biexponential with lifetimes of 9.2 and 123.6 μs.

As proved for the system involving the same monomer and the dye Safranine, styrenesulfonate monomers may aggregate in aqueous solutions forming clusters, so that dye molecules will be placed in a more rigid medium and somehow protected from quenching by residual oxygen. In order to verify if a similar phenomenon occurred in the Eosine system, experiments were performed in which the styrenesulfonate was substituted by the structurally similar toluenesulfonate. The transient spectra are quite similar to those obtained with StyS. The decays measured at 405 and 600 nm are 1.1 ms (monoexponential), and 35.1 and 117.9 μs (biexponential), respectively.

Table 3 lists the lifetimes of the Eosine transients in different systems, including also the presence of oxygen. The following conclusions regarding the triplet state can be drawn from there:

- The triplet state of the dye in aqueous solution has a maximum around 575 nm and a lifetime of 45 μs. As expected, in aerated solutions the lifetime falls to 2.6 μs.
- When enough monomer or TS is added to the dye solution, hydrotropic domains are formed in the solution and some of the Eosine molecules will be placed in them, whereas others will remain in the "bulk" of the solution. The former feel a more rigid environment with lower oxygen solubility, resulting in longer lifetimes. The decay of the absorption at 575 nm was approached by a biexponential function, leading to two lifetimes. In TS solution, the shorter lifetime is between 44 and 35 μs, not too different from that of the dye in aqueous solution. The longer lifetime of around 110–120 μs is ascribed to dye molecules in the hydrotropic environment.

- In the presence of increasing amounts of StyS, the shorter lifetime is quenched from 47.7 to around 9 μs. This is due to the electron transfer reaction that leads to the initiation of the polymerization. This quenching is not observed with TS. On the other hand, the longer lifetime is not quenched significantly, possibly due to an arrangement that precludes the electron transfer.
- A triplet absorption is also found in the presence of oxygen. Monoexponential decays with short lifetimes (3–4 μs) are found in all cases, but no quenching due to monomers or TS is observed. These triplets might be placed within the clusters, and increasingly protected from oxygen as the size of the hydrotropic domain increases.
- Absorption at 405 μs is observed in all cases and is assigned to the semi-reduced form of the dye. In pure aqueous solutions, it is formed by the self-quenching reaction of the dye.
- The same species in the presence of StyS will be formed by electron transfer from the monomer to the dye triplet. This can be observed by the in-grow of the absorption. Its rather slow decay is due to its reaction with other monomer molecules in the chain propagation reaction.

The partition of Eosine between the StyS hydrotropic domains and the bulk of the solution is further confirmed by the fact that the polymerization rate constant is not directly proportional to the StyS concentration, as can be seen from Fig. 7. If all the newly added StyS would be available to the polymerization process, a five-fold increase of its concentration would result in a similar increase in the rate. The experimental results show that this increase is about half of what would be expected.

3.3.3. *Polymerization mechanism*

In water–methanol solution, the polymerization rate is larger than in pure water (Table 4). This can be ascribed to the fact that the presence of methanol prevents in some degree the formation of clusters, therefore increasing the amount of StyS and Eos in the bulk of the solution. The addition of TS to the StyS solution also results in an increase of the polymerization rate. In this case, the presence of TS will probably replace the monomer molecules in the hydrotropic domains, displacing the MHC towards higher concentrations and releasing StyS to the bulk of the solution.

The results of the photopolymerization are consistent with these findings, and the mechanism is summarized in reaction (Scheme 1).

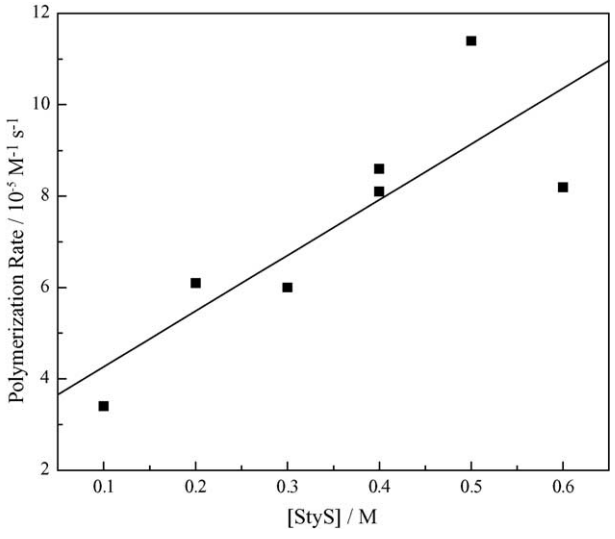
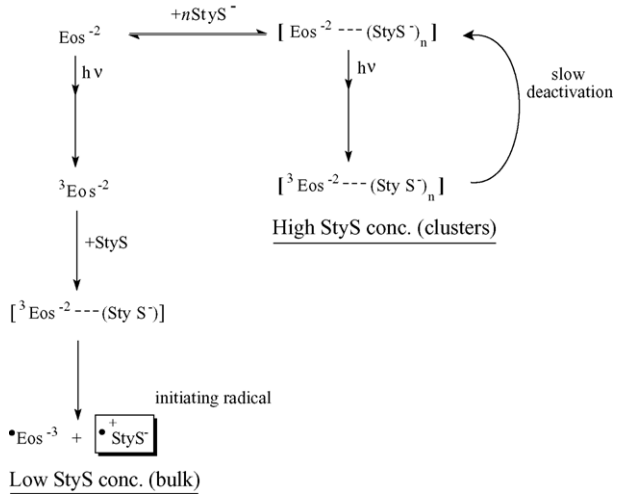


Fig. 7. Polymerization rate constants for StyS in the presence of Eosine Y (1.2×10^{-5} M) in aqueous deaerated solution.

Table 4
Rates for the photopolymerization of StyS in the presence of Eosine Y and added TS or methanol

Eos (1.2×10^{-5} M)	[ϕ-SO_3^-] (M)	R_p ($M^{-1}\,s^{-1}$)
+StyS (0.1 M)	0.1	3.43×10^{-6}
+StyS (0.1 M) + TS (0.2 M)	0.3	4.88×10^{-6}
+StyS (0.1 M) + TS (0.4 M)	0.5	9.04×10^{-6}
+StyS (0.1 M) [in methanol:water, 70:30]	0.1	4.84×10^{-6}



Scheme 1.

4. Conclusions

The photopolymerization of styrenesulfonate in aqueous solution, in the presence of Eosine Y, is initiated by dye molecules placed outside the monomer clusters. The excited triplet dye molecules placed in solution generate styrenesulfonate cation radicals by electron transfer. These radicals initiate the polymerization process more efficiently than the semi-reduced dye. Excited dye molecules placed in the clusters are preferentially deactivated to the ground state.

Solutions of the monomer in water–methanol solutions photopolymerize faster than those in pure water, due to smaller aggregation of the monomers, leading to a larger concentration in the regular solution.

The photochemistry of the Eosine dye in the presence of StyS proves the presence of different environments for the

dye, resulting in a biexponential decay of the triplet with lifetimes around 40 and 120 μs. This behaviour was confirmed for the dye in solutions of the structurally similar toluenesulfonate.

Acknowledgements

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