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Photoinitiated vinyl polymerization by safranine T/triethanolamine in aqueous solution

M. V. Encinas* and A. M. Rufs
Departamento de Química, Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 307-2, Santiago, Chile

M. G. Neumann
Instituto de Fisica e Quimica de Sao Carlos, Universidade de Sao Paulo, 13560 Sao Carlos SP, Brazil

and C. M. Previtali
Departamento de Química y Física, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Brazil

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The photolysis of safranine T in the presence of triethanolamine has been used as a source of free radicals in the polymerization of 2-hydroxyethyl methacrylate in aqueous solution. The polymerization rate was measured at several amine and dye concentrations. Flash photolysis studies of safranine in basic aqueous solutions indicate that the photoinitiation proceeds by the amine radicals formed in the interaction of the unprotonated form of the dye triplet with the hydroxyl amine. Primary radical termination does not play a significant role. Copyright © 1996 Published by Elsevier Science Ltd.

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INTRODUCTION

Water soluble formulations have gained increasing interest in recent years and many efforts have been devoted to the study of water soluble photoinitiators. Most of these photoinitiators are active when irradiated in the 300–400 nm region. Compounds absorbing in the visible region have been employed less frequently, in spite of the practical interest of using light in this spectral region. Xanthene, acridine and thiazine dyes in the presence of reducing agents have been used as photoinitiating systems for polymerization in aqueous solution[1,2]. However, these studies deal mainly with the kinetics of polymerization, whereas the photochemical mechanism received less attention.

In a previous work[3], we reported the behaviour of safranine in the presence of aliphatic amines as a photoinitiator system for the polymerization of 2-hydroxyethyl methacrylate (HEMA), in methanol as cosolvent. We have shown that the radicals that initiate the polymerization arise from the interaction of the amine with the triplet of the unprotonated form of safranine. On the other hand, the interaction of the singlet state of the dye leads to the inhibition of the polymerization. In the present work we extend these studies to the polymerization of the methacrylic monomer in aqueous solution.

EXPERIMENTAL

Safranine T chloride (Merck) was recrystallized from ethanol before use. Triethanolamine (TEOHA) and 2-hydroxyethyl methacrylate were from Aldrich and purified by vacuum distillation before use.

Transient absorption spectra and transient decays were measured on an Applied Photophysics laser kinetic spectrometer. Excitation at 532 nm was performed using the second harmonic of a Nd-YAG laser (Spectron). Solutions of safranine in water (1×10^{-5} M) were deoxygenated by nitrogen bubbling.

Polymerization rates (R_p) were measured dilatometrically in oxygen free solutions, as previously described[4]. Rates were determined at low conversion, and are reported in arbitrary units. Irradiations were done using a 100 W Phillips lamp ($\lambda > 500$ nm). The polymerization measurements were carried out at 25°C, in solutions containing equal volumes of HEMA and water. The solutions were adjusted to pH 10 by the addition of NaOH.

RESULTS AND DISCUSSION

The polymerization of HEMA in aqueous solution (monomer:water 1:1, pH = 10) in the presence of safranine was negligible. However, it proceeds efficiently in the presence of amines. Similar results have been reported for the photopolymerization of acrylates by eosin dye[5–7] and for the polymerization of HEMA in

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* To whom correspondence should be addressed

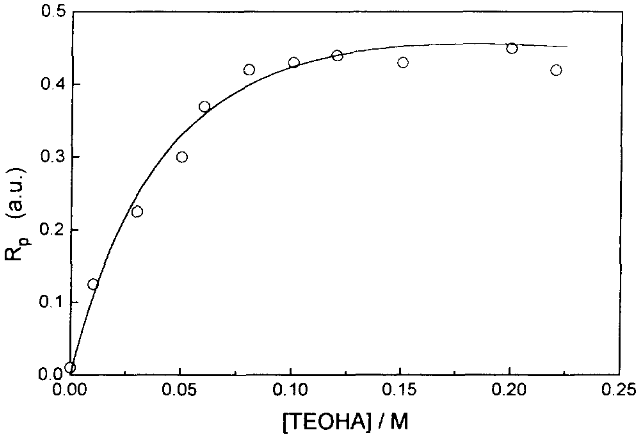


Figure 1 Polymerization rates in arbitrary units vs amine concentration. Rates calculated from equation (2) (solid line)

methanol using safranine[3], where the polymerization is only effective in the presence of amine. The initial polymerization rates of HEMA in an aqueous solution, in the presence of increasing concentrations of triethanolamine are shown in *Figure 1*. The rate increases with the addition of amine, reaching a maximum at 0.1 M of amine. Higher amine concentrations do not seem to affect the polymerization rate. This behaviour is somewhat different from that observed in methanolic solution[3]. In that solvent, high amine concentrations resulted in a moderate inhibition of the rate. The maximum polymerization rate in water is two times faster than that obtained in methanol under the same irradiation conditions. This difference is not only due to the effects in the photoinitiation process, but the propagation and termination rate constants will also be affected by the change of the solvent[8].

On the other hand, experiments carried out in aqueous solution at a pH below 8.0 (in the absence of added base, or at low TEOHA concentrations) showed very low polymerization rates.

Polymerization rates were also determined at different safranine concentrations, giving an order of 0.5. In order to disregard any effect of inhomogeneous free radical distribution[9], the absorbance of the dye in these experiments was kept in the range of 0.1–0.4. Then, these results indicate that primary radical termination does not play an important role. Chain termination by the semireduced form of the dye has been proposed for the vinyl polymerization initiated methylene blue[10] or eosin[6] in the presence of amines.

The absorption spectra of safranine in HEMA–water solutions at a pH between 7 and 10 show a maximum at 533 nm. The spectra do not show any shoulders and the absorbance follows Beer's law at least up to 60 μM. This is an evidence that no aggregation of the dye occurs under the conditions used in this work. Furthermore, the dimerization constant for safranine in water has been found to be 460[11], which means that less than 1% of the dye will be in the aggregate state. Additionally, it has been shown that the aggregation of this type of dyes decreases significantly in solutions containing organic solvents[12].

Excited state processes

A safranine excited singlet is quenched by amines through a mechanism that involves a charge transfer intermediate[13]. An exciplex intermediate has also been postulated for the quenching of the singlet states of other dyes, such as rose bengal and methylene blue by several amines[14,15]. Safranine steady-state fluoresence quenching by TEOHA was measured in basic HEMA/water (1:1) mixture giving a linear Stern–Volmer plot with slope of 1.6 M^{-1}. A value of 3.8 M^{-1} was reported for the same system in HEMA/methanol (1:1)[3]. The lifetime of the singlet state in the aqueous solvent was evaluated to be 1.4 times shorter than that in methanol, therefore, the deactivation rate constants of singlet state by amines can be assumed to be approximately 1.7 times lower in the presence of water than in the organic medium. This diminution of the quenching efficiency in aqueous media can be explained as due to the reduced capability of the amine to donate an electron in the presence of hydrogen bonding.

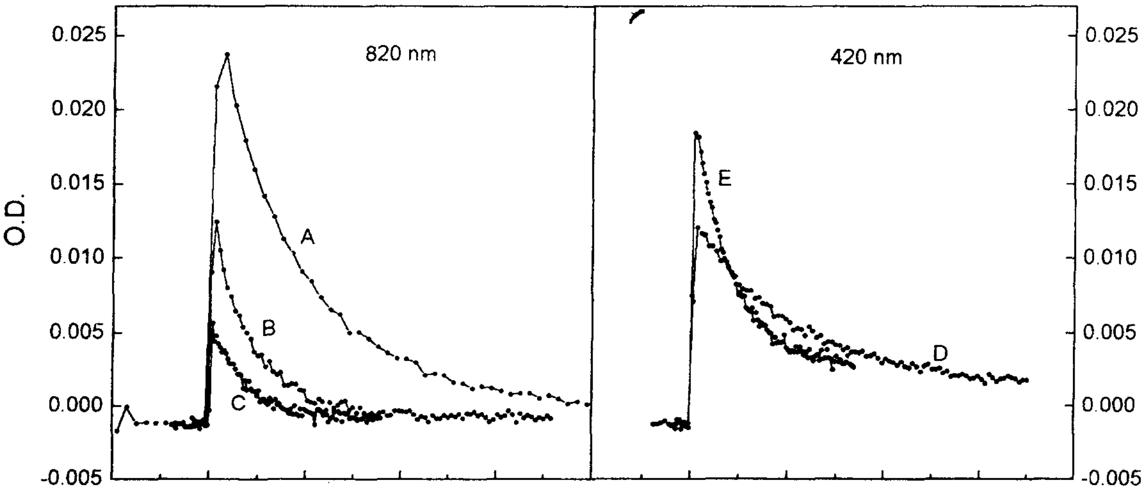


Figure 2 Effect of NaOH addition on the transient absorption decay of safranine at 820 nm and 420 nm in water. In the absence (curves A and D) and in the presence of NaOH (B, 0.15 mM; C, 0.2 mM; E, 0.2 mM)

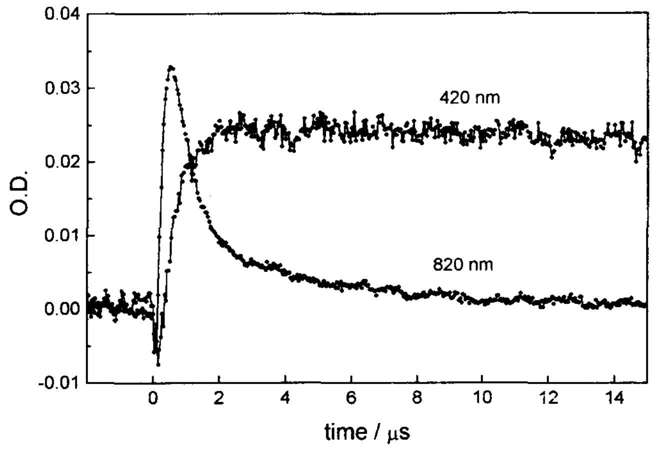


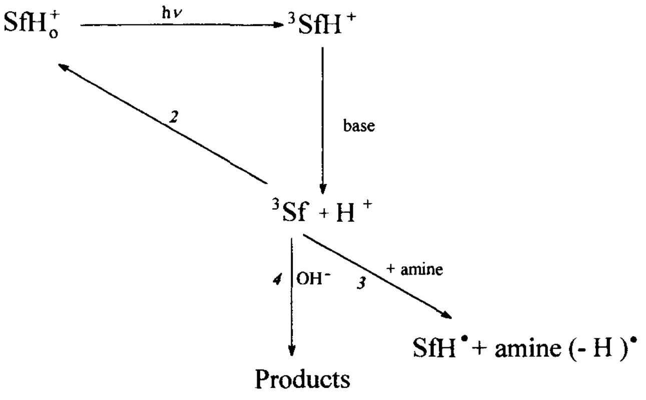
Figure 3 Transient absorption of safranine at 420 and 820 nm in water:HEMA (12% in monomer) at pH 10, in the presence of TEOHA 0.1 M

The transient absorption spectrum of safranine in neutral aqueous solution, in the absence of amine, is well characterized presenting two main absorption peaks at 420 and 820 nm. These peaks have been assigned to the monoprotonated triplet state of the dye, $^3\text{SfH}^+$ [13]. The deactivation of the monoprotonated triplet by the monomer was evaluated by following the shortening of the decay time of the signal at 820 nm. These measurements rendered a bimolecular rate constant of $4.8 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$. In spite of this rather high rate, this process does not lead to polymerization, as shown by the lack of polymer formation in the absence of amine.

A marked decrease of the decay times of both the 820 and 420 nm signals is observed when adding NaOH to neutral aqueous solutions of safranine (*Figure 2*). Furthermore, the initial optical density of the signal at 420 nm increases, whereas that of 820 nm decreases, being almost negligible at higher base concentrations. These effects can be ascribed to the transformation of the monoprotonated triplet form of the dye into its unprotonated form ^3Sf, which absorbs in the region of 410–430 nm[16],

$$^3\text{SfH}^+ \xrightarrow{\text{base}} {}^3\text{Sf} + \text{H}^+ \qquad (1)$$

The transient absorption at 420 nm (at pH 10) was measured in the presence of amine. The behaviour of this signal is rather complex. It presents an initial increase and a residual long-lived component which remains constant up to 500 μs (*Figure 3*). These results are consistent with the mechanism outlined in *Scheme 1*, that involves the initial formation of the monoprotonated triplet, followed by its transformation to the unprotonated form (as evidenced by the concomitant decay of the 820 nm signal), which may decay, react with amine to form the semireduced radical, or react with the base to form a long lived (or stable) species. All these species, $^3\text{SfH}^+$, ^3Sf, $\text{SfH}^\bullet$ and the unknown product absorb in the 420–430 nm region[13,16,17].



Scheme 1

Polymerization mechanism

The fact that the polymerization is ineffective at pH below the $\text{p}K_a$ of the transformation of the monoprotonated into the unprotonated form of the triplet, suggests that the radicals leading to polymerization are those formed in reaction 3 (*Scheme 1*). In this case, and considering that the interaction of the amine with the singlet does not lead to active species, the polymerization rate can be expressed as

$$R_p = \frac{1}{1 + (K_{sv})_s[\text{TEOHA}]} \times \frac{(K_{sv})_{420}[\text{TEOHA}]}{1 + (K_{sv})_{420}[\text{TEOHA}]} \times \beta \qquad (2)$$

where $(K_{sv})_s$ and $(K_{sv})_{420}$ stand for the Stern–Volmer constants for the quenching of the singlet and unprotonated triplet by the amine, respectively, and β is a constant that involves factors such as the intersystem crossing quantum yield of the dye and the fraction of produced radicals that lead to polymerization. The experimental points shown in *Figure 1* can be adjusted with equation (2). The best fit is obtained when using values of 2.0 and $15\ \text{M}^{-1}$ for the Stern–Volmer constants for the singlet and triplet quenching, respectively. The value for the singlet quenching agrees well with that determined directly from fluorescence quenching experiments (see above). The value for the triplet is somewhat lower than that found for methanolic solutions $(30\ \text{M}^{-1})$[13]. However, a similar decrease of the quenching efficiency for the singlet state with solvent is also observed, as expected for reactions proceeding through charge-transfer mechanisms. These results are in agreement with the mechanism proposed, where the radicals that lead to polymerization in an aqueous medium come almost exclusively from the interaction of the unprotonated form of the safranine triplet with the hydroxyl amine. Furthermore, the order of 0.5 obtained for safranine allows us to disregard the chain termination by the semireduced dye form.

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