Available online at www.sciencedirect.com

ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry 188 (2007) 329–333

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

The hydrotrope effect on the photopolymerization of styrenesulfonate initiated by Ru complexes

Isabel C. Rigoli, Carla C. Schmitt, Miguel G. Neumann *

Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, 13560-970 São Carlos, Brazil

Received 15 September 2006; received in revised form 7 November 2006; accepted 19 December 2006
Available online 27 December 2006

Abstract

Styrenesulfonate (StyS) was photopolymerized in the presence of tris(2,2′-bipyridine)ruthenium(II) chloride and triethylamine (TEA) or triethanolamine (TEAOH). Polymerization observed in both cases is obtained, but the rate is faster with triethylamine. The results are correlated with the ability of the monomer to form hydrotropic domains at sufficiently high concentrations (>0.1 M). The emission intensity behaviour and the lifetimes of the $[Ru(bpy)_3]^{2+}$ MLCT state confirm that the positively charged Ru complex is placed in those domains. At the same time, the amount of the reduced complex transient, $[Ru(bpy)_3]^{+}$, in solutions containing toluenesulfonate points to the presence of TEA in the same domains. On the other hand, the lower rate observed for the photopolymerization in the presence of TEAOH is attributed to the preferential placing of this amine in the bulk of the aqueous solution, outside the hydrotropic environment.

Keywords: Photopolymerization; Hydrotropes; Styrenesulfonate

1. Introduction

Polymerization of vinyl monomers are usually performed in homogeneous solutions and initiated thermally. In the case of charged monomers, like StyS, this procedure is less favourable due to the electrostatic repulsion between the ionic monomers. Therefore, polyStyS is usually obtained by sulfonating prepolymerized polystyrene [1]. Here the difficulty resides in the difficulty in obtaining complete sulfonation and in the homogeneity of the ring substitutions.

The photoinitiated polymerization of StyS using different initiators has been studied by us using cationic and anionic dyes (safranine and eosin, respectively) [2–4]. Copolymerization of StyS with methyl methacrylate has also been performed, albeit the practical difficulty of mixing homogenously hydrophobic and hydrophilic monomers [5]. In all these cases it has been proved that the hydrotropic properties of StyS, which forms aggregates above ∼0.1 M [4], plays an important role in the process. Two main factors are involved, on one side, the hydrotropic aggregates allow the solubilization of hydrophobic monomers, and on the other hand, the existence of a high negative charge density affects the local concentration of the charged photoinitiators near to the monomer aggregates.

Metallic complexes, especially Ru-derivates like tris(2,2′-bipyridine)ruthenium(II) chloride, have been frequently used as photoinitiators in the presence of aliphatic or aromatic amines to promote free-radical polymerization of various acryl monomers [6–9]. It is believed that the excited ruthenium MLCT state might lead to an electron transfer reaction involving the amine, which ultimately gives rise to an amino initiating radical [10–13].

Evaluation of the efficiency of photoinduced polymerization, requires studies of the chemical behaviour of the components of polymerization formulation. This involves the knowledge of the primary processes that lead to the formation of the initiation free radicals. It is also necessary to take into account any other processes that can compete with those reactions, or quench the excited states. An overall reaction mechanism for the polymerization photoinitiation can be proposed using these informations.

The photoinitiating system safranine/triethanolamine was proved to be efficient for the polymerization of neutral monomers such as acrylate and styrene derivatives [3]. However,

---

* Corresponding author.
E-mail address: neumann@iqsc.usp.br (M.G. Neumann).

doi:10.1016/j.jphotochem.2006.12.031

it was found less efficient for negatively charged monomers, as sodium styrenesulfonate, where amines inhibited the polymerization process [2]. In this system, an initiation mechanism was proposed, in which the electron transfer involving the triplet state of the dye occurred inside the hydrotropic aggregates formed by the monomers. This model was supported through the studies of the elementary reaction of the fundamental and excited states of the dyes, which indicated the aggregation of the negatively charged monomers and the localization of the dye in this domain.

In the present work the photoinitiated polymerization of sodium styrenesulfonate (StyS) in the presence of tris(2,2′-bipyridine)ruthenium(II) chloride, was studied. The main aim consisted in a assessment of the effect of the hydrotropic aggregates formed by StyS, in the presence of triethylamine and triethanolamine in aqueous solution.

2. Experimental

2.1. Materials

$[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (G. Frederick Smith Chemical Co.), sodium styrenesulfonate (StyS, Aldrich 99%) and sodium 4-toluenesulfonate (TS, Aldrich) were used as received. The aliphatic amines triethylamine (TEA, Fluka 99.5%) and triethanolamine (TEOHA, Merck) were distilled under reduced pressure. All solutions were prepared in Milli-Q purified water. The solutions were deoxygenated by bubbling argon or nitrogen.

2.2. Measurements

Fluorescence experiments were carried out at room temperature (25 ± 1 °C) using a Hitachi F-4500 spectrofluorimeter. Fluorescence lifetimes were determined by time-correlated single-photon-counting on a CD-900 Edinburgh Spectrometer. UV spectra were taken at room temperature on a Hitachi U-2000 spectrophotometer linked to a PC computer.

Transient absorption spectra and triplet lifetimes were determined with an Applied Photophysics kinetic laser spectrometer. Excitation at 355 nm was accomplished with a Nd-YAG laser (Spectron) with frequency doubling. Detection was done with a Hamamatsu R928 photomultiplier.

2.3. Polymerization procedure

The photopolymerization of StyS in the presence of the photoinitiator systems $[Ru(bpy)_3]^{2+}$/TEA and $[Ru(bpy)_3]^{2+}$/TEOHA was conducted in a dilatometer [14,15]. The solutions were thoroughly deoxygenated by bubbling argon. The dilatometer consisted of two capillaries attached to a cylindrical reaction cell, which was placed in a constant temperature bath (30.00 ± 0.01 °C) in front of the irradiation source (200 W Hg(Xe) lamp in an Oriel Universal Arc Lamp compartment). Depending on the experiment, a (440 ± 10) nm bandpath filter or a 395 nm cut-off filter was placed between the lamp and the reaction cell. The concentration of the photoinitiator was kept constant around 5.0×10^{-5} M. Different concentrations of co-initiators were used to optimize the polymerization rate.

The polymerization rates (R_p) were calculated using the following equation:

$$R_{\mathrm{p}} = \frac{\Delta V}{Fft}[M]\ (\mathrm{mol\,L^{-1}\,s^{-1}}) \tag{1}$$

where ΔV is the contraction in volume in the capillary (calculated from the variation in a cathetometer) at time t; f the volume fraction of monomer in the solution; F the volume contraction related to the densities of polymer and monomer in the solution, $F = [d_p - d_m/d_p]$; $[M]$ corresponds to monomer molar concentration. The densities of the monomer (d_m) and the polymer (d_p) were determined by picnometry in dodecene solution at 25 °C. The values found for the monomer and the polymer were 0.867 and 1.08 g cm^{-3}, respectively.

After irradiation, the poly(StyS) polymers were precipitated with methanol. The polymers were washed with the same solvent several times, filtered, and dried in desiccators.

3. Results and discussions

3.1. Photopolymerization of StyS in the presence of $[Ru(bpy)_3]^{2+}$/TEA

Aqueous solutions of StyS 0.3 M, deoxygenated with argon for 1 h, were irradiated using a 395 nm cut-off filter. This wavelength allows the excitation of the MLCT state of the complex [12,13].

The polymerization rate was obtained from the monomer conversion rate determined dilatometrically, as shown in Fig. 1. The calculated rate was 3.50×10^{-6} M s^{-1} for a conversion of 14%. Induction times were rather long and were assigned to the presence of residual oxygen. Longer degassing times lead to shorter induction times, but did not alter significantly the reaction rate. The shortest induction times (∼40 min) were obtained when the reaction mixture was degassed by several freeze-and-thaw cycles.

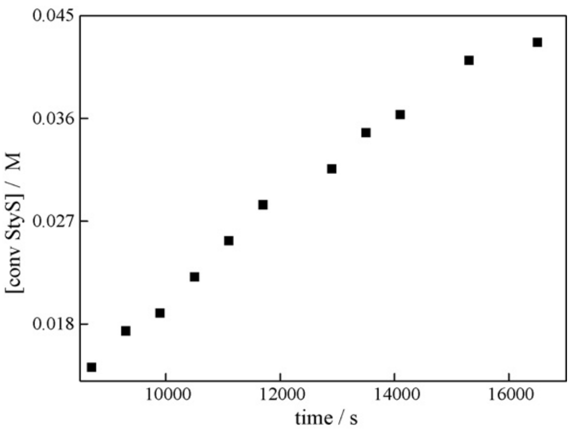


Fig. 1. Photoconversion of StyS in the presence of 5.0×10^{-5} M $[Ru(bpy)_3]^{2+}$ and TEA 0.2 M.

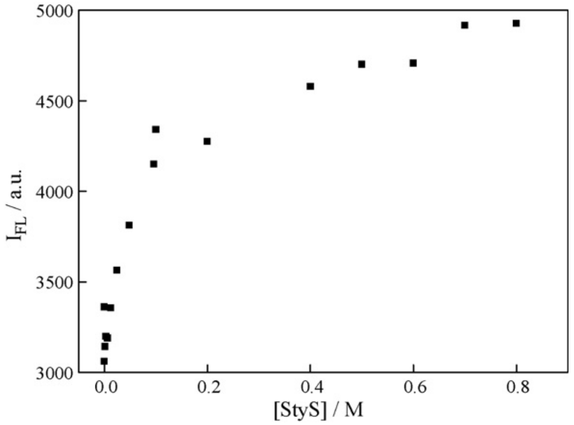


Fig. 2. Emission intensity of $[\mathrm{Ru(bpy)_3}]^{2+}$ band at 600 nm in the presence of StyS. $\lambda_{exc} = 452$ nm.

3.2. Elemental reactions

The absorption spectrum of a 5.0×10^{-5} M $[\mathrm{Ru(bpy)_3}]^{2+}$ complex solution remained practically unchanged in the presence of different concentrations of StyS and TEA. However, a small shift of the MLCT band of the complex is observed at the higher monomer concentrations.

An emission band at 600 nm is observed when exciting $[\mathrm{Ru(bpy)_3}]^{2+}$ at 452 nm (MLCT band). In the presence of low concentrations of StyS (1.0×10^{-3} to 0.1 M) there is a rapid increase of the emission (Fig. 2). Above these concentrations emission intensity grows slower, tending to a constant value. As observed for other compounds placed in solutions containing StyS, the formation of “hydrotropic clusters” of the monomer, provides a more rigid medium, in which the fluorescence emission is larger [2].

The lifetimes of the photoinitiator in aqueous solution, alone, and in the presence of StyS (hydrotropic monomer), triethylamine (co-initiator), and toluenesulfonate (hydrotrope) are shown in Table 1.

The lifetime of the photoinitiator in aqueous solution at room temperature is coincident with the value reported in the literature ($\tau = 0.6$ μs) [13,16]. There was no variation in the lifetime of the complex in the presence of the co-initiator TEA. On the other hand, there is an increase in the lifetime when in the presence of StyS or TS.

The transient absorption of $[\mathrm{Ru(bpy)_3}]^{2+}$ after laser excitation, shows two peaks with maxima at 313 and 360 nm, as shown in Fig. 3. These peaks correspond to the excited MLCT state of the complex [17].

Table 1
$[\mathrm{Ru(bpy)_3}]^{2+}$ lifetimes at photopolymerization conditions ($\lambda_{exc} = 452$ nm)

System	τ (ns)	χ^2
$[\mathrm{Ru(bpy)_3}]^{2+}$	600 ± 10	1.062
$[\mathrm{Ru(bpy)_3}]^{2+}$/TEA	590 ± 10	1.132
$[\mathrm{Ru(bpy)_3}]^{2+}$/StyS (0.5 M)	800 ± 10	1.051
$[\mathrm{Ru(bpy)_3}]^{2+}$/TS (2 M)	830 ± 10	1.058

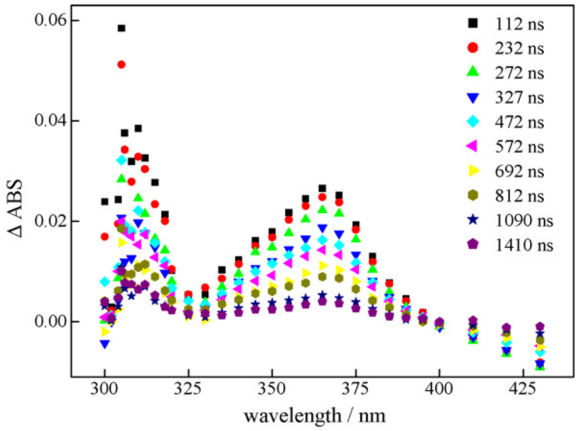


Fig. 3. Time evolution of the transient absorption of excited $[\mathrm{Ru(bpy)_3}]^{2+}$ in aqueous solution.

The lifetimes of the transient absorption at 360 nm in the presence of increasing concentrations of StyS and TS are plotted in Fig. 4. It can be seen that the lifetimes increase from 590 to 900 ns when increasing the hydrotrope concentration up to 2 M. The same effect was observed when placing the cationic dye safranine in high-concentration solutions of both sulfonates, as well as in other restricted microdomains, like micelles [2]. Therefore, it can be assumed that this increase in the lifetimes is due to the localization of the cationic complex in the hydrotropic domains of StyS and TS. As expected, the levelling off in TS occurs at higher concentrations than with StyS, due to the higher MHC (minimum hydrotrope concentration) of the former [18], which also reflects the aggregation ability.

It can be deduced from the results above that the complex species that reacts to give the initiating polymerization radicals is not the emitting triplet, as it does not change its lifetime in the presence of amine (see table). Several authors reported a non-emitting transient species formed from the singlet (possibly a ligand-centered state, LC) that can accept an electron from appropriate donors, like aliphatic amine co-initiators [19].

$$[\mathrm{Ru(bpy)_3}]^{2+} \rightarrow {}^{1}\mathrm{MLCT} \quad (2)$$

$$^{1}\mathrm{MLCT} \rightarrow \mathrm{LC} \quad (3)$$

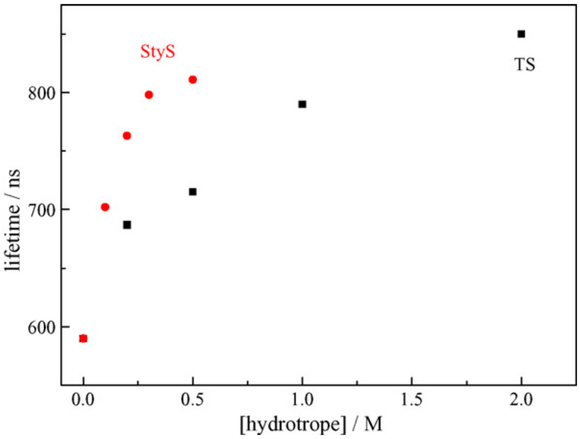


Fig. 4. Lifetimes of $^{*}[\mathrm{Ru(bpy)_3}]^{2+}$ transient (measured at 360 nm) at various StyS and TS concentrations.

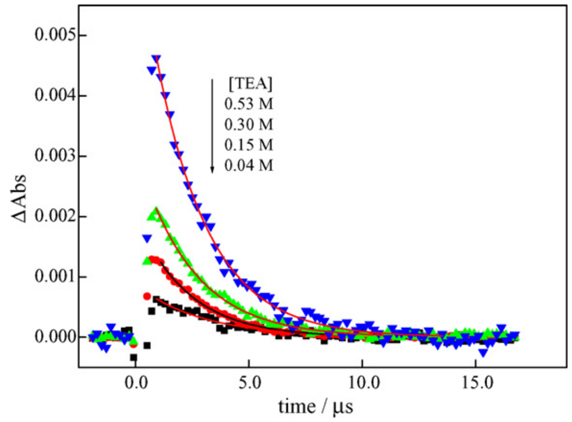


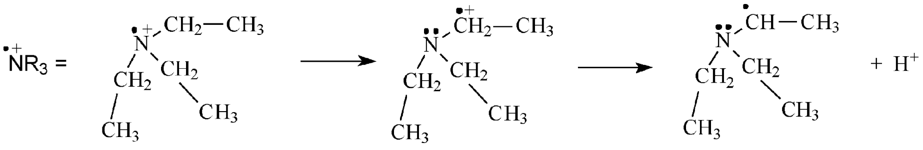
Fig. 5. Transient absorption at 530 nm after irradiation of $[Ru(bpy)_3]^{2+}$ 3.9×10^{-4} M, in the presence of different concentrations of TEA.

$$^1\text{MLCT} \rightarrow {}^3\text{MLCT} \quad (4)$$

$$^3\text{MLCT} \rightarrow [Ru(bpy)_3]^{2+} + h\nu' \quad (5)$$

$$\text{LC} + NR_3 \rightarrow [Ru(bpy)_3]^{+} + \overset{\bullet\,+}{NR_3} \quad (6)$$

Thus, the initiating radical can be believed to be the C-centred radical formed by the internal rearranging of the amino radical followed by the loss of a proton to the basic medium:



(7)

The mediating of a reduced Ru complex, $[Ru(bpy)_3]^+$, with a distinct absorption peak at ~530 nm is parallel to the formation of the initiating radical. As can be seen in Eq. (6), this species will be formed at the same rate that the amino radical. There is an increase in the amount of transients formed with increasing [TEA], and as expected, the decays are also faster (Fig. 5).

Thus, the amount of initiating radical will depend on the formation of an exciplex between the excited ligand-centered state of the Ru complex and the co-initiator, which might lead to charge transfer or deactivation.

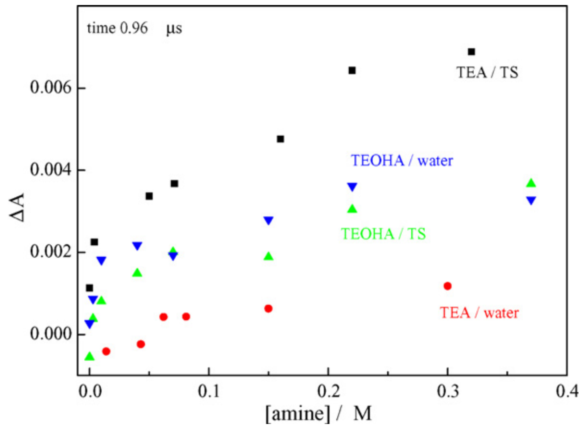


Fig. 6. Complex radical yields in solutions of $[Ru(bpy)_3]^{2+}$ in the presence of TEA and TEOHA, with and without the addition of TS (determined at 530 nm).

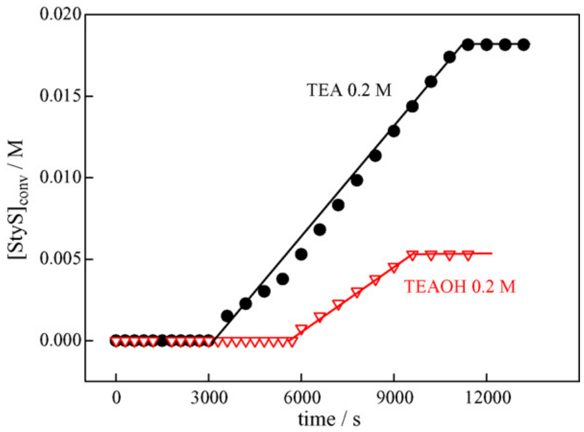


Fig. 7. Photopolymerization of StyS 0.3 M in the presence of 5.0×10^{-5} M $[Ru(bpy)_3]^{2+}$ and TEA or TEAOH 0.2 M.

$$\text{LC} + NR_3 \rightarrow ([Ru(bpy)_3]^{2+} \cdots NR_3) \quad (8)$$

$$([Ru(bpy)_3]^{2+} \cdots NR_3) \rightarrow [Ru(bpy)_3]^{+} + \overset{\bullet\,+}{NR_3} \quad (9)$$

$$([Ru(bpy)_3]^{2+} \cdots NR_3) \rightarrow [Ru(bpy)_3]^{2+} + NR_3 \quad (10)$$

$$([Ru(bpy)_3]^{2+} \cdots NR_3) \xrightarrow{+NR_3} [Ru(bpy)_3]^{2+} + 2NR_3 \quad (11)$$

The absorbance of the Ru complex transient measured after ~1 μs by laser flash photolysis shows that the amount of complex radical formed in the presence of TEA increases faster in TS solutions than in pure water (see Fig. 6). This is attributed to the presence of the cationic complex and the hydrophobic amine in the TS hydrotropic domains. On the other hand, when using the more hydrophilic triethanolamine, no variation in the radical yields was observed. In this case, it can be assumed that triethanolamine is preferentially located in the pure aqueous phase, outside the hydrotropic microdomains. This effect also helps to explain the difference between the polymerization rates observed for StyS 0.3 M in the presence of TEA and TEAOH 0.2 M, as shown in Fig. 7. For the former system the rate is about twice that observed for TEAOH (2.25 $M^{-1}\,s^{-1}$ versus 1.31×10^{-6} $M^{-1}\,s^{-1}$), which is practically the same proportion as that of the Ru-transient concentrations determined for this amine concentration, shown in Fig. 6.

Acknowledgements

Financial support by FAPESP, Brazil (Proc. 03/07770-4), is gratefully acknowledged. ICR also thanks the same agency for a doctoral fellowship (Proc. 00/10352-1).

References

[1] A. Duda, S. Penczek, in: J.I. Kroscwitz (Ed.), Encyclopedia of Polymer Science and Engineering, vol. 16, Wiley–Interscience, New York, 1989, p. ff. 332.

[2] M.G. Neumann, C.C. Schmitt, H.M. Maciel, J. Phys. Chem. B 105 (2001) 2939.

[3] M.G. Neumann, C.C. Schmitt, H.M. Maciel, J. Photochem. Photobiol. A: Chem. 175 (2005) 15.

[4] M.G. Neumann, C.C. Schmitt, H.M. Maciel, B.E. Goi, in: J.P. Fouassier (Ed.), Photochemistry and UV Curing: New Trends, The Dye Initiated Photopolymerization of Styrenesulfonate in Hydrotrope Medium, Research Signpost, Kerala, 2006 (Chapter 27).

[5] M.G. Neumann, C.C. Schmitt, H.M. Maciel, B.E. Goi, J. Photochem. Photobiol. A: Chem. 184 (2006) 335.

[6] A. Goswami, S.D. Baruah, Polym. Int. 43 (1997) 22.

[7] C.R. Rivarola, S.G. Bertolotti, C.M. Previtali, J. Polym. Chem. 39 (2001) 4265.

[8] K. Iwai, M. Uesegi, T. Sakabe, C. Hazama, F. Takemura, Polym. J. 23 (1991) 1005.

[9] S.D. Baruah, A. Goswami, J. Appl. Polym. Sci. 64 (1997) 2097.

[10] K. Kalyanasundaram, Photochemistry of Polypiridine and Porphyrin Complexes, Academic Press, London, 1992.

[11] D.M. Roundhill, Photochemistry and Photophysics of Metal Complexes, Plenum Press, New York, 1994.

[12] A. Juris, V. Balzani, F. Baricelletti, S. Campagna, P. Belser, A. Von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.

[13] A. Vlcek, Coord. Chem. Rev. 200 (2000) 933.

[14] I.C. Rigoli, C.C. Schmitt, M.G. Neumann, J. Photochem. Photobiol. A: Chem. 159 (2003) 145.

[15] M.G. Neumann, C.C. Schmitt, B.E. Goi, J. Photochem. Photobiol. A: Chem. 174 (2005) 239.

[16] D.P. Rillema, G. Allen, T.J. Meyer, D. Conrad, Inorg. Chem. 22 (1983) 1617.

[17] N.J. Turro, I.V. Khudyakov, K.R. Gopidas, Chem. Phys. 162 (1992) 131.

[18] D. Balasubramanian, V. Srinivas, V.G. Gaikar, M.M. Sharma, J. Phys. Chem. 93 (1989) 3865.

[19] C.R. Rivarola, S.G. Bertolotti, C.M. Previtali, Photochem. Photobiol. 82 (2006) 213.