ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 124 (1999) 29–34

Journal of Photochemistry and Photobiology A:Chemistry

Photoinitiation of MMA polymerization by thionine/amine systems in the presence of SDS micelles

Maira R. Rodrigues[a], Fernando Catalina[b], Miguel G. Neumann[a,*]

[a]*Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, 13560-970 São Carlos SP, Brazil*

[b]*Instituto de Ciencia y Tecnologia de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*

Received 27 February 1999; accepted 25 March 1999

Abstract

The photoinitiation of the polymerization of methylmethacrylate (MMA) by the dye thionine in the presence of triethylamine and triethanolamine has been studied in the presence of SDS micelles, and compared with similar studies in homogeneous methanol solutions. The conversion rates in the presence of micelles were significantly faster than in the homogeneous solutions, and the amine concentrations at which the maximum rates were observed (∼0.7) were higher than in methanol (∼0.1). Association constants of the dye, monomer, and amines to the micelles were determined, as well as the quenching rate constants of the dye's excited states by the monomer and the amines in these systems. An overall mechanism is proposed for the production of amine free radicals which includes the postulation of a triplex. An expression for the concentration of the initiating radicals was deduced from this mechanism, and when using the experimentally determined constants the fit to the polymerization data is quite good for amine concentrations up to the maximum conversion rate. At higher amine concentrations other processes may be participating in the process decreasing the efficiency of the production of free radicals.

Keywords: Photopolymerization; Photoinitiation; Thionine; Micellar solutions

---

1. Introduction

The relative efficiency of water and oil soluble photoinitiators in photopolymerization reactions carried out in micellar solutions has risen interesting questions. Photoinitiators have been used with great success in the polymerization of vinyl monomers in homogeneous and microheterogeneous systems. The dynamics of the excited states of several photoinitiators have been studied in an organized media, such as micelles or microemulsions and vesicles [1–5], as well as in homogeneous solution [6–13]. The presence of a pseudophase can modify the rate and the course of the photoprocesses due to the peculiar characteristics of the microenvironment. The inherent organization present in these systems allows the reactions to proceed in a specific way. The distribution of monomer, initiator and co-initiator among the aqueous and micellar phases has been proved to influence the monomer reactivity and constrain its molecular motion. Thus, in the presence of micelles, polymers with characteristics different from those obtained in homogeneous solution may be synthesized [3].

In this paper we report results for the photopolymerization of methyl methacrylate initiated by the thionine/amine pair. The polymerization efficiencies are explained and correlated with the photochemical events observed for the reactions in the presence of sodium dodecyl sulphate micelles.

2. Experimental

2.1. Chemicals

Methyl methacrylate (MMA, Aldrich), was distilled to an ice bath under reduced pressure in the presence of hydroquinone, washed with 5% NaOH in water and dried over $CaCl_2$. The amines (triethanolamine, TEOHA, Merck; and triethylamine, TEA, Aldrich) were vacuum-distilled before use. The dye thionine (ThH^+, Aldrich); sodium dodecyl sulphate (SDS, Aldrich) and the probes Pyrene (Py, Aldrich) and Acridine Orange (AO, Aldrich) were used as received.

2.2. Measurements

The light-induced polymerization was performed by irradiating 5 ml cells containing ThH^+ 0.8×10^{-5} M in SDS

---

*Corresponding author. Tel.: +55-16-273-9940; fax: +55-16-273-9952; e-mail: neumann@iqsc.sc.usp.br

1010-6030/99/$ – see front matter
PII: S1010-6030(99)00070-2

0.5 M/MMA 0.8 M aqueous solutions with two 26 W Osram Dulux D lamps, in the presence of known amounts of the amine. MMA was entirely solubilized in these solutions. The solutions were deoxygenated by thoroughly bubbling oxygen-free nitrogen. After irradiation the polymers were precipitated, washed with ice-cold methanol and dried. The conversions were determined gravimetrically.

Fluorescence quenching experiments were carried out at room temperature (25°C±1°C) using an Hitachi F-4500 spectrofluorimeter. ThH^+ was excited at 590 nm and the emission was measured at the emission maximum.

Transient absorption spectra and triplet quenching 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.

Photoreduction quantum yields were determined irradiating at 365 nm, selected from a Philips high-pressure Hg lamp (Hg–CS 500 W) with a Kratos 6M252 monochromator. Sample cells were thermostated at 25°C. Light intensities were measured using an International Light Model IL-700 radiometer, previously calibrated with Aberchrome 540 [14].

Fluorescence experiments were performed on air-equilibrated solutions. For triplet and photoreduction quantum yield studies, the solutions were deoxygenated by bubbling oxygen-free nitrogen.

3. Results and discussion

3.1. Polymerization

The conversion of monomers in the photoinitiated polymerization of MMA 0.8 M in SDS solution in the presence of ThH^+ and TEOHA or TEA, are shown in Table 1. These results are correlated with the respective pK_b of the amines and with the conversions in homogeneous methanolic solution after 4 h of irradiation [15]. Larger conversions are reached in the micellar solutions for both amine co-initiators, even at much shorter irradiation times.

The dependence of the conversion rates with the amine concentration after irradiation for 5 min is shown in Fig. 1 for TEA. For this amine the maximum conversion rate is reached at TEA concentrations around 0.75 M. Similar experiments with TEOHA showed a maximum at 0.7 M.

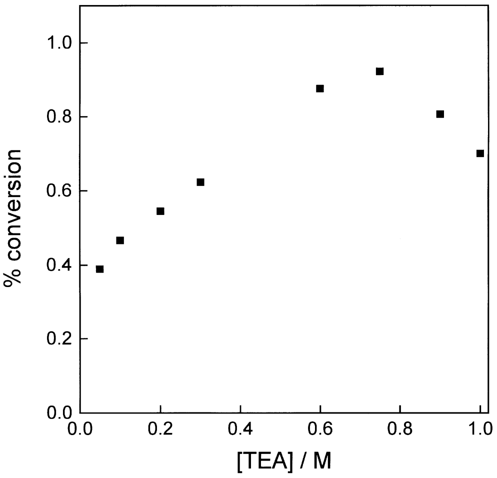

Fig. 1. Monomer conversion after 5 min in the ThH^+/SDS/TEA system.

Table 1
Photopolymerization conversions of MMA 0.8 M in ThH^+/amine in SDS and in methanol

Amine	SDS 0.5 M [a]		MMA/methanol (1:1) [b]	
	(%)	[max] (M)	(%)	[max] (M)
TEA	1.37	0.75	2.05	0.10
TEOHA	0.250	0.70	3.74	0.20

[a] [Amine]=0.6 M; t=15 min.
[b] [Amine]=0.1 M; t=4 h.

3.2. Association constants of ThH^+, TEOHA, TEA and MMA to SDS micelles

An important parameter needed to understand the effect of micelles on the polymerization kinetics is the degree of association of the monomer, the initiator and the co-initiator to the micelles. The association constants of TEA, TEOHA and MMA to SDS micelles were determined by the fluorescence quenching method of Encinas and Lissi [16], using pyrene as a probe for the amines and acridine orange for MMA. The K values, together with the exit rate constants (k_-) are shown in Table 2. The values for TEA and MMA are in good agreement with previous determinations (1370 for TEA [17] and 1000 for MMA [18]). These values also reflect the different solubility in water of the three species, TEOHA being more soluble in aqueous solutions than TEA and MMA.

The association constant of ThH^+ to SDS can be considered of the order of $10^5\ M^{-1}$, similar to those of other dyes like malachite green ($5\times10^5\ M^{-1}$) [19] and methyl viologen ($10^5\ M^{-1}$) [20]. Considering that value together with the constants in Table 2, the mean residence time of ThH^+ in the micelle can be estimated to be of the order of 10 μs, and that of the other species around 10^{-7} s. As the excited singlet state of the dye has a lifetime in the order of

Table 2
Association constants (K) of amines and MMA to SDS micelles, exit rate constants (k_-), and data for quenching of ThH^+ excited states by amines and MMA in SDS 0.5 M micellar medium

Quencher	K (M^{-1})	k_- (s^{-1})	$^1K_{SV}$ (M^{-1})	^3k_q ($M^{-1}s^{-1}$)
TEOHA	620	1.6×10^7	15.0	1.65×10^7
TEA	1100	0.9×10^7	0.94	2.1×10^8
MMA	1100	0.9×10^7		4.5×10^4

0.5 ns [21], the quenchers may be considered stationary during excitation and deactivation.

This data can be used to define the actual composition and distribution of the different species under photopolymerization conditions (SDS 0.5 M):

1. the concentration of ThH^+ is 0.8×10^{-5} M and that of the micelles is 8.0 mM, so that only one of every 1000 micelles will carry a dye molecule;
2. when using a MMA concentration of 0.8 M, 92% of the monomer will be incorporated to micelles;
3. at the concentration of TEA corresponding to the maximum conversion rate (0.75 M), 92% of the amine will be incorporated to the micelles;
4. similar calculations for TEOHA, lead to 86% of the amine incorporated to the micelles at the concentration of maximum conversion rate (0.70 M).

Making an analogy between the hydroxylic nature of TEOHA and alcohols the percentage of amine incorporated to the pseudophase can be reduced to 61%, as found for the partition of alcohols between SDS micelles and the intermicellar phase [22].

3.3. Quenching of the ThH^+ singlet in SDS micelles

The absorption spectrum of ThH^+ in water shows a maximum in the visible region around 600 nm. When adding SDS, an overall rise of the absorbance is observed, together with a bathochromic shift due to interactions between the micelles and the dye. This behaviour is characteristic for cationic dyes when placed in lower dielectric constant solvents. Local dielectric constants of the binding sites in organized systems have been determined by the shift of the absorption maximum of some dyes [23].

There is no change in the absorption spectrum of the dye in SDS 0.5 M after addition of MMA and at low amine concentrations. An overall decrease in the emission spectrum is only observed at amine concentrations where fluorescence quenching is effective, but without the indication of the formation of any other species. On the other hand, addition of NaOH lead to a new absorption around 500 nm with an isosbestic point near 550 nm, corresponding to the formation of the deprotonated species. Therefore, it seems that there is no abstraction of protons by the amine in the presence of SDS and that ThH^+ is not converted to the deprotonated species Th at these concentrations.

3.4. Quenching of the ThH^+ triplet in SDS micelles

The transient spectrum of the triplet state of ThH^+ in SDS micelles before and after the addition of TEA is shown in Fig. 2. The spectra show the typical triplet peaks at 780 and 415 nm. The decays at 780 nm are exemplified in Fig. 3, and are very similar to those observed at the shorter wavelength. The initial addition of TEA produced an increase in the lifetime of the triplet, probably due to a change in the environment of the dye. Further addition of the quencher showed a normal quenching behaviour with decrease of the lifetimes, as shown in Fig. 3. Stern–Volmer plots for the quenching of the ThH^+ triplet by TEA in methanol [15] and in the SDS 0.5 M micellar solutions are shown in Fig. 4, and the corresponding quenching rate constants are listed in Table 2.

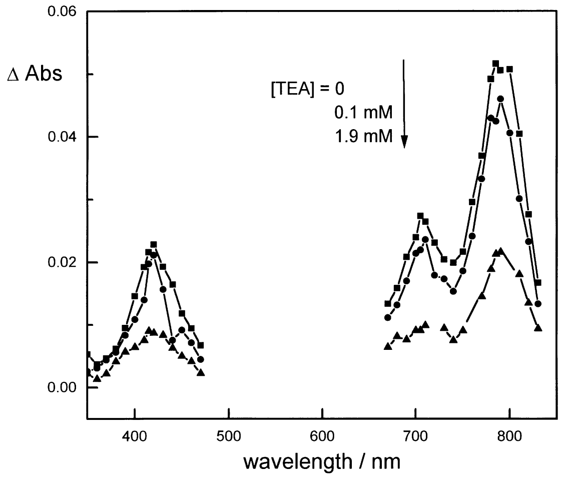

Fig. 2. Absorption spectra of the ThH^+ transient in micellar medium after additions of TEA, taken 2 μs after the laser pulse.

The quenching of triplet ThH^+ by amines in methanol proceeds by an initial proton transfer. At high amine concentrations, as those found in polymerizing formulations, the deprotonated triplet ${}^3Th$ is then quenched by electron transfer to form the semireduced dye. A similar mechanism was also found for the dye Safranine [24].

$$ {}^3ThH^+ + A \rightarrow {}^3T + AH^+ \qquad (1) $$

$$ {}^3T + A \rightarrow [T^{\bullet -}\cdots A^{\bullet +}] \rightarrow T^{\bullet -} + A^{\bullet +} \qquad (2) $$

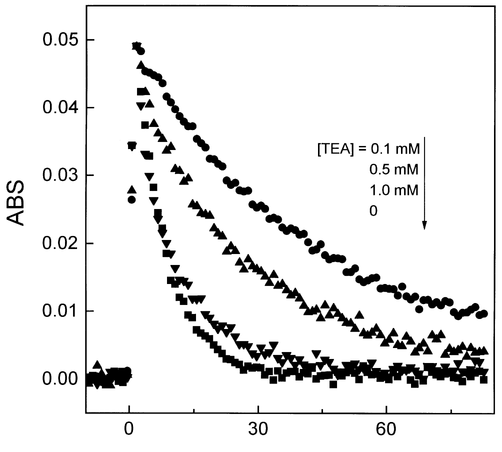

Fig. 3. Decay of the 790 nm absorption of triplet ThH^+ in micellar in SDS upon addition of TEA.

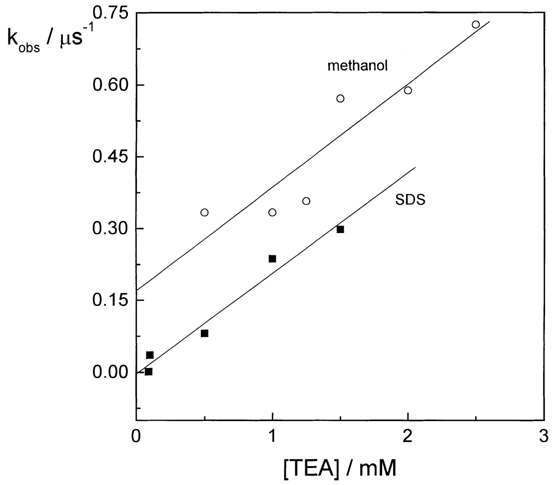

Fig. 4. Stern–Volmer plots of $1/\tau$ for the quenching of ThH^+ triplets by TEA in SDS micelles and methanol.

However, the proton concentration in the micellar interface is about 100 times higher than in an homogeneous solution [25], so that a proton transfer at relatively low amine concentrations will be precluded. Therefore, the mechanism involved in this case will be a direct electron transfer, to form the protonated semireduced species

$$^3ThH^+ + A \rightarrow [ThH^\bullet \cdots A^{\bullet +}] \rightarrow ThH^\bullet + A^{\bullet +} \quad (3)$$

The rate constant for the quenching of $^3ThH^+$ by MMA is various orders of magnitude smaller than that for amines, so that this reaction will not interfere with the quenching by amines leaving practically all the $^3ThH^+$ available for photoinitiation.

3.5. Photoreduction quantum yield

The polymerization process of MMA photoinitiated by ThH^+ in the presence of amines involves the reduction of the dye, detected by the bleaching of the solution. This reaction occurs after the electron transfer stage and leads to the formation of semithionine species which can abstract an hydrogen atom from the co-initiator or the solvent or disproportionate to form the leuco form of the dye and a molecule of the dye in the ground state

$$^3ThH^+ + A \rightarrow [ThH^\bullet \cdots A^{\bullet +}] \rightarrow ThH^\bullet + A^{\bullet +} \quad (4)$$

$$ThH^\bullet + A \rightarrow ThH_2 + A(-H)^\bullet \quad (5)$$

$$ThH^\bullet + ThH^\bullet \rightarrow ThH_2 + Th \quad (6)$$

In the conditions of the polymerization mixture, with high co-initiator concentration, the reaction that is likely to occur is the hydrogen abstraction from the amine. No photoreduction of ThH^+ was observed in the presence of oxygen, confirming that the triplet excited state is involved in this process. Table 3 shows the photoreduction quantum yields of ThH^+ by TEA and TEOHA in a nitrogen atmosphere under polymerization conditions.

Table 3
Photoreduction quantum yields of ThH^+ in polymerization conditions ([SDS]=0.50 M; [MMA]=0.80 M; [amine]=0.1 M; λ_{irr}=365 nm)

System	Φ_r
SDS/MMA/TEOHA	0.203
SDS/MMA/TEA	0.087

The amine will act as a bimolecular quencher of the dye triplet, as well as an hydrogen donor to the semireduced dye. Considering the rate constants for the natural decay of the triplet (k_d), the triplet quenching by the amine (k_q) and the photoreduction by the amine (k_r), and assuming that a fraction η of the triplet state species end up as semireduced molecules, the dependence of Φ_r with the amine concentration will be given by

$$\frac{1}{\Phi_r} = \frac{1}{\Phi_{isc}} + \frac{k_q}{\Phi_{isc} k_r} + \frac{k_d}{\Phi_{isc}\eta k_r[AH]} \quad (7)$$

A linear relationship between Φ_r and the inverse of the amine concentration is expected and has been obtained as shown in Fig. 5 for TEA. The slope of the line gives $k_d/\eta\Phi_{isc}k_r$. Considering that the intersystem crossing quantum yield (Φ_{isc}) of ThH^+ is 0.54 [21] and the lifetime of the triplet in SDS 0.5 M is 7.5 µs (corresponding to k_d=13.3×10^4 s^{-1}), the product of the photoreduction constant times η for TEA and TEOHA were found to be 2.86×10^5 and 6.57×10^5 M^{-1} s^{-1}, respectively. These values for the photoreduction rate constants are two to three orders of magnitude smaller than those for the quenching of the triplet dye by amines, suggesting very little interference between both processes. They are also confirmed by the fact that the traces of the transient decays, measured at 415 nm (where there is also an absorption of the semireduced species) show an initial rapid decay, followed by a levelling off, which only is observed to decay in the 100 ms time scale. An evaluation of the conditions present in the poly-

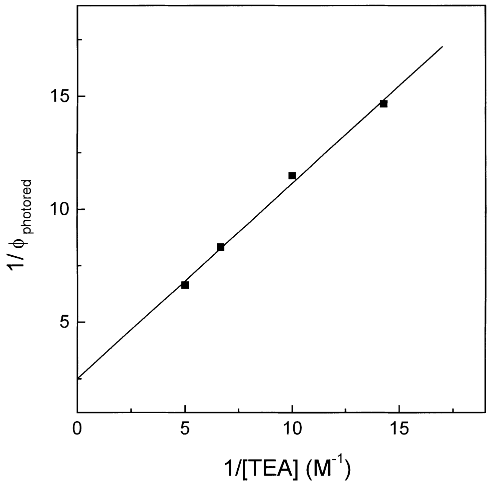

Fig. 5. Photoreduction quantum yield of ThH^+ as a function of TEA concentration.

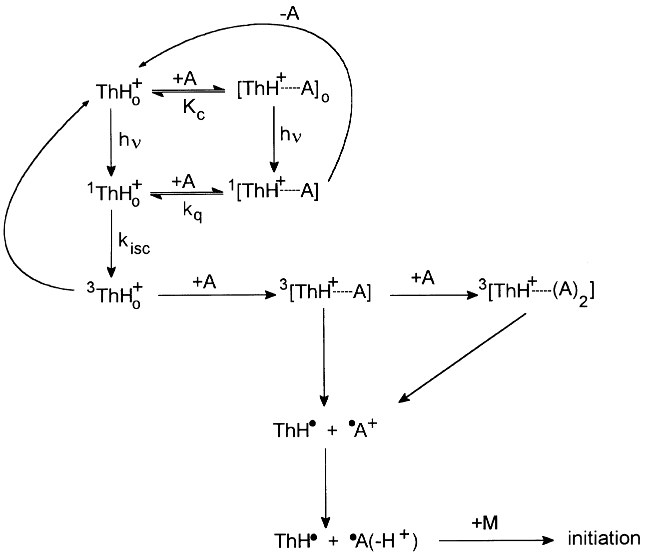

Fig. 6. Mechanism for the production of photoinitiating free radicals in the ThH^+/amine system in SDS micellar solution.

merizing mixture shows that the only effective H-atom supply for reducing the dye will be the co-initiator present in concentrations around 0.1–1.0 M. Disproportionation, in spite of having a lower activation energy will be less probable for two reasons, i.e.

1. the concentration of the semireduced species is at least a factor 10^5 lower than that of the amine, and
2. there is no more than one dye molecule per micelle, so that the encounters between semireduced molecules will be drastically hampered.

3.6. Polymerization mechanism

The mechanism shown in Fig. 6 is based on those proposed for similar systems [6,13,15] and is consistent with the photochemical behaviour of ThH^+ in SDS micellar solutions in the presence of amines. ThH_0^+, $^1ThH^+$ and $^3ThH^+$ correspond to the dye in the fundamental, excited singlet and monoprotonated triplet states, $ThH^\bullet$ refers to the semireduced radical species of the dye. $[ThH^+\cdots A]$ and $[ThH^+\cdots(A)_2]$ are dye–amine complexes, the former is an association complex that may be formed in the ground state, or in the excited states as exciplexes, and the latter is a triplex [26–28], frequently assumed to be present in this kind of reactions.

The amine radical, originated from the interaction of the co-initiator with the dye triplet, has been proved to be responsible for the chain initiation in several photoinitiated polymerizations. On the other hand, the interaction with the singlet state does not produce initiating radicals efficiently, so that its quenching will decrease the amount of radicals formed and hinder the polymerization efficiency. At the high concentrations of amine present in the formulation, the preferred pathway from the excited triplet to the radicals will go through an intermediate triplex. From this mechanism, the yield of active radicals can be deduced to be

$$\Phi_{\mathrm{rad}} = \beta\frac{\Phi_{\mathrm{isc}}}{1+{}^1K_{\mathrm{SV}}[\mathrm{A}]}\times\frac{{}^3K_{\mathrm{SV}}[\mathrm{A}]}{1+{}^3K_{\mathrm{SV}}[\mathrm{A}]}\times\frac{K_{\mathrm{SV}}^{\mathrm{triplex}}[\mathrm{A}]}{1+K_{\mathrm{SV}}^{\mathrm{triplex}}[\mathrm{A}]} \quad (8)$$

where K_{SV} are the Stern–Volmer constants, and β stands for the fraction of radicals that effectively lead to polymerization.

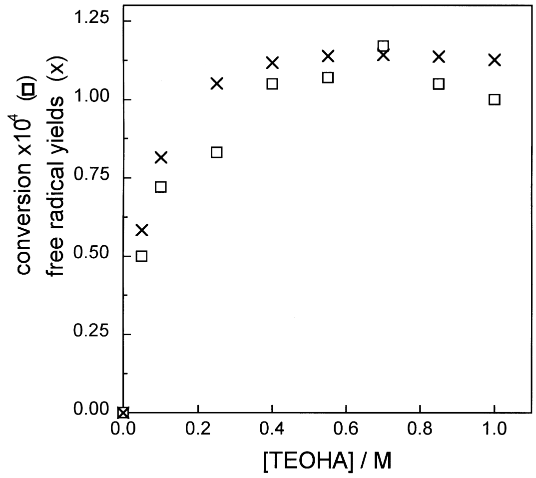

Fig. 7. Experimental conversion (□) and calculated free radical yields (×) for the ThH^+/MMA/TEOHA system.

The yield of polymerizing radicals, calculated with Eq. (8) using the data obtained from fluorescence quenching, laser flash photolysis experiments, and 0.15 M^{-1} for $K_{SV}^{triplex}$, is shown in Fig. 7 together with the polymerization conversion rates for the MMA/ThH/TEOHA system in SDS micelles. A similar behaviour was found for the system with TEA as co-initiator (using $K_{SV}^{triplex} = 1.5\,M^{-1}$).

Although the initial part (rise) of the conversion rate curve matches closely the calculated yield of radicals, after the concentration corresponding to the maximum conversion the conversion rate decreases faster than the calculated curve. Several factors can be pointed out as responsible for this. At higher amine concentrations the medium in which the dye is present will be more basic, possibly displacing the prototropic equilibrium of the dye towards its deprotonated form Th

$$ThH^+ + NR_3 \rightarrow Th +{}^+ HNR_3 \quad (9)$$

This species has a lower extinction coefficient than the protonated form and will, therefore, be less efficient in the final production of free radicals. The decrease at higher conversions has been attributed also to the increase of the viscosity of the solution and to the decrease of the monomer concentration [29]. Furthermore, the chain transfer reaction to the amine followed by an hydrogen abstraction may also contribute to decrease the actual rate of conversion. All these factors were not taken into account in the mechanism, as they are quite difficult to ascertain quantitatively, especially in micellar medium.

4. Conclusions

Photoinitiation of MMA by Th/amine systems is more efficient in the presence of SDS micelles than in homogeneous methanol solution. The maximum conversion rates are found for amine concentrations around 0.7 M, whereas for the same amines in alcoholic solutions these maxima were found at 0.1–0.2 M.

A mechanism is proposed for the photoinitiation process that includes the formation of a triplex involving the excited dye molecule and two amine molecules. This mechanism accounts well for the observed results up to the maximum conversion rate. Other processes, active at higher concentrations do probably diminish the concentration of initiating amine radicals at these conditions.

Acknowledgements

Financial support by FAPESP (94/3505-5) and FINEP (65/92.0063.00) is gratefully acknowledged. MRR thanks FAPESP for a graduate fellowship.

References

[1] M.S. El-Aasser, in: F. Candau, R.H. Ottewil (Eds.), An Introduction to Polymer Colloids, Chapter 1, Kluwer Academic Publishers, Dordrecht, 1990.
[2] F. Candau, in: F. Candau, R.H. Ottewil (Eds.), An Introduction to Polymer Colloids, Chapter 2, Kluwer Academic Publishers, Dordrecht, 1990.
[3] Q. Wang, S. Fu, T. Yu, Prog. Polym. Sci. 19 (1994) 703.
[4] A. Jayakrisnan, D.O. Shah, J. Polym. Sci., Polym. Lett. Ed. 22 (1984) 31.
[5] V. Vasková, V. Juranicová, J. Barton, Makromol. Chem. 191 (1990) 717.
[6] C.M. Previtali, S.G. Bertolotti, M.G. Neumann, I.A. Pastre, A.M. Rufs, M.V. Encinas, Macromolecules 27 (1994) 7454.
[7] J. Paczkowski, Z. Kucybala, Macromolecules 28 (1995) 269.
[8] J. Paczkowski, M. Pietrzak, Z. Kucybala, Macromolecules 29 (1996) 5057.
[9] A. Merlin, D.J. Lougnot, J.P. Fouassier, Polym. Bull. 3 (1980) 1.
[10] J.B. Rust, L.J. Miller, J.D. Margerum, Polym. Eng. Sci. 9 (1969) 40.
[11] J.P. Fouassier, P. Jacques, D.J. Lougnot, T. Pilot, Polym. Photochem. 5 (1984) 57.
[12] P.K. Sengupta, S.K. Modak, Makromol. Chem. 186 (1985) 1593.
[13] M.V. Encinas, A.M. Rufs, M.G. Neumann, C.M. Previtali, Polymer 37 (1996) 1395.
[14] H.G. Heller, J.R. Lanagan, J. Chem. Soc., Perkin Trans. 1 (1981) 341.
[15] M.G. Neumann, M.R. Rodrigues, Polymer 39 (1998) 1657.
[16] M.V. Encinas, E. Lissi, Chem. Phys. Lett. 91 (1982) 55.
[17] J.P. Fouassier, D.J. Lougnot, J. Appl. Polym. Sci. 32 (1986) 6209.
[18] M.V. Encinas, E. Guzmán, E. Lissi, J. Phys. Chem. 87 (1983) 4770.
[19] C.A. Burton, N. Carrasco, S.K. Huang, C.H. Paik, L.S. Romsted, J. Am. Chem. Soc. 100 (1978) 5420.
[20] S.G. Bertolotti, J.J. Cosa, H.E. Gsponer, M. Hamity, C.M. Previtali, Can. J. Chem. 64 (1986) 845.
[21] H.J. Timpe, S. Neuenfeld, J. Chem. Soc., Faraday Trans. 88 (1992) 2329.
[22] E.B. Abuin, E.A. Lissi, J. Colloid Interface Sci. 95 (1983) 198.
[23] M.G. Neumann, I.A. Pastre, A.M. Chinelatto, O.A. El Seoud, Colloid Polym. Sci. 274 (1996) 475.
[24] M.V. Encinas, C.M. Previtali, S.G. Bertolotti, M.G. Neumann, Photochem. Photobiol. 62 (1995) 64.
[25] I.A. Pastre, M.G. Neumann, J. Colloid Interface Sci. 179 (1996) 227.
[26] S.F. Yatesand, G.B. Schuster, J. Org. Chem. 49 (1984) 3350.
[27] D.J. Lougnot, C. Turck, J.P. Fouassier, Macromolecules 22 (1989) 108.
[28] R.S. Davidson, Adv. Phys. Org. Chem. 18 (1983) 1.
[29] P.J. Clapp, B.A. Armitage, D.F. O'Brien, Macromolecules 30 (1997) 32.