MMA photopolymerization initiated by thionine/triethylamine

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Abstract

The polymerization of MMA photoinitiated by the dye thionine (ThH^+) in the presence of triethylamine as co-initiator, has been studied in methanol. Polymerization rates increase with amine concentration up to a maximum at ~ 0.1 M, after which they decrease. A general mechanism for the photoinitiating process is proposed which leads to an equation relating the yield of initiating radicals to the concentration of amine. When using the rate constants and other data determined for the elemental photochemical steps involved in the photoinitiating mechanism, the behaviour of the yield of initiating radicals as a function of amine concentration is similar to that of the polymerization conversion. In agreement with that mechanism, no polymerization products were observed in the absence of amine, or in the presence of oxygen. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Thionine; Photopolymerization; Photoinitiation

1. Introduction

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, in order to develop better and more efficient photoinitiator systems adapted to different problems and applications [5–9].

It has recently demonstrated [10–19] that the presence of amines in formulations containing basic dyes, induces the photopolymerization process. The α-aminoalkyl radicals generated in these reactions are capable of initiating the polymerization of acrylates [16–20] and methacrylates [10–15].

Continuing our previous work, we present in this paper results for the polymerization of methyl methacrylate (MMA) photoinitiated by the dye thionine (ThH^+) in the presence

of triethylamine (TEA) as co-initiator in methanol solution. The photoinitiation mechanism is described in terms of the elemental reactions involved in the processes that lead to polymerization initiating radicals.

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 $CaCl_2$. Triethylamine (TEA, Aldrich) was vacuum-distilled before use. The dye thionine (ThH^+, Aldrich) was used as received.

2.2. Measurements

MMA in methanolic solution and the photoinitiator system (ThH^+/TEA) were placed in a dilatometer and irradiated with a mercury arc lamp (Philips Hg-CS 500 W). The dilatometer consisted of two capillary branches (i.d. 0.336 cm) attached to a cylindrical reaction vessel (i.d. 2.5 cm; volume 15 ml). The set-up was placed in a constant temperature bath. A radiometer, previously calibrated with Aberchrome 540 [21,22], was used to measure light intensity changes. The solutions were deoxygenated by thor-

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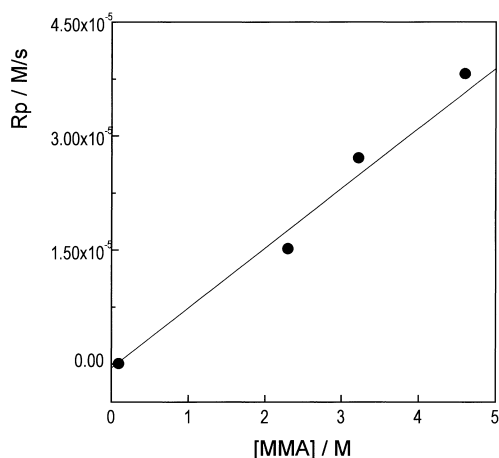*E-mail address:* neumann@iqsc.sc.usp.br (M.G. Neumann)

Fig. 1. Photopolymerization rates of MMA in methanol (1 : 1) at different monomer concentrations using the ThH$^+$/TEA 0.2 M photoinitiating system.

Fig. 2. Dependence of the MMA photopolymerization rates with TEA concentration.

oughly bubbling oxygen-free nitrogen and the experiments were carried out at $30 \pm 0.01°$C.

The rates of polymerization (R_P) were calculated using the standard expression [23]

$$R_p = \frac{h}{F \cdot t \cdot f} [M] \tag{1}$$

where h is the contraction in volume in the capillary at time t (s), F ($= 100 \times (d_p - d_m)/d_p$) relates the volume contraction with the molar densities of the polymer and the monomer in solution, [M], is the concentration of monomer, and f is the volume fraction of monomer in the solution. The rates of all photoinitiated polymerizations were corrected for the changes in absorption.

After each irradiation the reaction mixture was removed from the dilatometer and the polymer was precipitated, washed with ice-cold methanol and dried. Molecular weight distributions were measured by gel permeation chromatography (GPC) using a M-45 Waters high pressure pump with a U6K injector and Ultrastyragel permeation columns (Waters) placed in series (pore sizes: 10^3, 10^4, 10^5, 10^6 Å). A R-401 Waters differential refractometer detector was used, previously calibrated with a series of polymer standards of narrow molecular weight distribution.

Fluorescence quenching experiments were carried out at room temperature ($25 \pm 1°$C) using an Hitachi F-4500 spectrofluorimeter. ThH$^+$ was excited at 590 nm and the emission was measured at the maximum. The lifetime of the dye singlet was measured by single-photon counting with a CD-900 Edinburgh spectrometer operating with a nanosecond hydrogen-filled flash lamp at 25–30 kHz, at room temperature ($25 \pm 1°$C). 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.
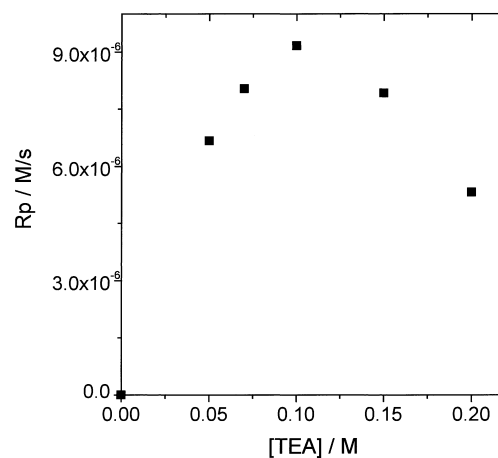
Photoreduction quantum yields were determined in methanol solution in the presence and absence of amine irradiating at 365 nm, selected from the Philips high-pressure Hg lamp with a Kratos 6M252 monochromator. Sample cells were thermostized at 25°C. Light intensities were measured with an International Light Model IL-700 radiometer, previously calibrated with Aberchrome 540 [21,22].

Fluorescence experiments were performed on air-equilibrated solutions. For photoreduction quantum yield, polymerization and laser studies, the solutions were deoxygenated by bubbling oxygen-free nitrogen. The dye concentration used was always 0.8×10^{-5} M.

3. Results and discussion

3.1. Polymerization

The dye photoinitiated polymerization of MMA in methanolic solution could only be achieved in the presence of an appropriate co-initiator. The rates of polymerization of MMA in methanol (1 : 1) using the photoinitiating ThH$^+$/TEA system were determined as a function of monomer concentration (Fig. 1) and of amine concentration (Fig. 2). The analysis of the rate data shows that the polymerization rate increases linearly with the monomer concentration. These results are in agreement with the general kinetic equation for photoinitiated polymerizations

$$R_p = \left(\frac{k_p}{k_t^{1/2}} \right) \cdot (I_a \Phi_i)^{1/2} [M] \tag{2}$$

where k_p and k_t are the propagation and termination rate constants, respectively; I_a is the absorbed light intensity and [M] is the monomer concentration.

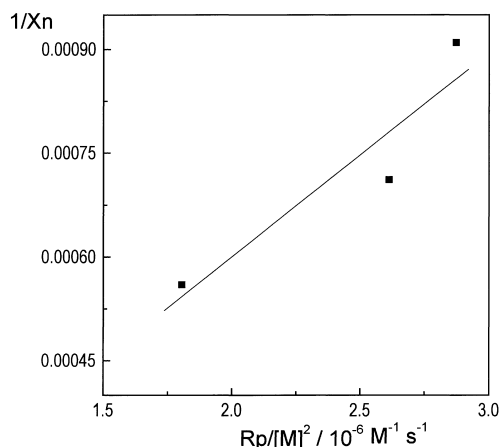The polymerization rate increases with amine concentration and reaches a maximum around TEA 0.1 M, decreas-

Fig. 3. Mayo equation plot for MMA in methanol at different monomer concentrations using the ThH$^+$/TEA 0.2 M photoinitiating system.

ing afterward. Similar experiments with triethanolamine (TEOHA) showed a maximum at 0.2 M [10].

The $k_p/k_t^{1/2}$ ratio was calculated using the Mayo equation [24]

$$\frac{1}{\bar{X}_n} = 1.72\frac{R_p k_t}{k_p^2[M]^2} \tag{3}$$

where $\bar{X}_n$ is the number average degree of polymerization. The coefficient 1.72 for MMA polymerization was obtained at 30°C interpolating [25] in the values reported by from Melville [26], assuming that chain termination only occurs by combination or disproportionation of the macroradicals, with negligible contribution of chain transfer.

The zero ordinate of the Mayo plot shown in Fig. 3, corresponds to 1.12×10^{-5}, suggesting that practically no chain transfer to the monomer or to the solvent takes place. The slope of the plot, corresponding to the ratio $k_p/k_t^{1/2}$ is 0.07. This value is quite similar to that reported in the literature (0.066) for MMA at 30°C, assuming that no primary radical-polymer radical termination takes place [24].

The polymerization quantum yield Φ_m can be obtained from the relation between polymerized monomer and absorbed energy. In the absence of chain transfer reactions

$$\Phi_m = \Phi_i \bar{X}_n \tag{4}$$

Table 1 lists the polymerization (R_p) and initiation (R_i) rates, the polymerization (Φ_m) and initiation quantum yields (Φ_i) and the monomer conversions for the photopolymerization of MMA, together with the molecular weight averages ($\bar{M}_n$) of the polymers obtained at different TEA concentrations. In general, these values are about a factor 3–5 smaller than those obtained when using TEOHA [10].

It can be seen that the polymerization rate increases with the amine concentration up to a maximum (at ~0.10 M and ~0.20 M for TEA and TEOHA, respectively), after which it decreases. This decrease is ascribed mainly to the quenching of the ThH$^+$ singlet excited state, which

decreases the amount of triplets produced by intersystem crossing and, therefore, the yield of initiating radicals. This same behaviour has been described for other monomer/initiator/amine systems, like the hydroxyethylmethacrylate photopolymerization initiated by Safranine/TEOHA in methanol [13]. This suggests that the polymerization initiating radicals originate from the interaction of the amine with the triplet excited state of the dye.

3.2. Quenching of the ThH$^+$ excited states

No changes were observed in the absorption spectrum of ThH$^+$ in methanol after addition of MMA [10]. Addition of TEA produces a decrease of the absorption at 600 nm and a new absorption band around 500 nm, with an isosbestic point near 550 nm. The new band does correspond to the unprotonated form of the dye, as proved by the addition of NaOH.

The Stern–Volmer rate constant for the quenching of the singlet state of the dye by TEA in methanol was 11.00 M^{-1}, which corresponds to 1.9×10^{10} M^{-1} s^{-1}, using 0.57 ns for the lifetime of singlet ThH$^+$ determined by single photon counting. This value is within the range expected from the correlation between rate constants and oxidation potentials of amines. The quenching experiments were performed at amine concentrations where practically all the dye was in the protonated form (ThH$^+$). The deprotonated form is only observed at amine concentrations large than those used for this determination.

In the actual photopolymerization system (MMA/methanol, 1:1), the Stern–Volmer constant for the quenching of the dye singlet by TEA was found to be 5.00 M^{-1}, smaller than that obtained in pure methanol. Under these conditions the lifetime was 3.7 ns, which renders a quenching rate constant of 1.35×10^9 M^{-1} s^{-1}, about ten times smaller than in pure methanol. A similar effect was observed for the quenching by TEOHA, where the quenching constants changed from 4.0 to 1.47 M^{-1}. As has been suggested before, this decrease in the values of K_{sv} in the reaction medium is caused by the change of the solvent polarity when adding the monomer [27].

The quenching of the protonated dye triplet (^{3}ThH$^+$) by TEA in MMA/methanol (1:1) was determined following the decay of the transient absorption at 780 nm. The quenching rate constant in this solvent was 1.35×10^7 M^{-1} s^{-1} (using the lifetime of 54 μs), as compared with 2.4×10^8 M^{-1} s^{-1} for the quenching in pure methanol. The corresponding Stern–Volmer constants were 728 and 2900 M^{-1}, respectively, for the process in the reactional medium and in pure solvent. These constants are resumed in Table 2.

The quenching of the deprotonated dye triplet (^{3}Th) in MMA/methanol (1:1) solution was performed by monitoring the transient decay at 430 nm, in a basic solution (pH ~ 12) obtained by addition of NaOH. The corresponding Stern–Volmer constant under these conditions was 331 M^{-1}. No quenching by the MMA was observed for this species.

Table 1
Data for the polymerization of MMA in methanol (1 : 1) at 30°C photoinitiated by ThH$^+$/TEA

[TEA] (M)	R_p (M/s) $\times 10^6$	$R_i \times 10^8$	Φ_m	Φ_i	$\bar{M}_n \times 10^{-4}$	Conversion
0.05	6.67	1.02	12.5	0.018	6.9	0.003
0.07	8.03	1.15	15.2	0.020	7.5	0.008
0.10	9.16	1.55	18.7	0.027	10.0	0.008
0.15	7.92	5.92	13.0	0.010	12.4	0.005
0.20	5.32	4.20	8.8	0.007	11.8	0.002

Table 2
Constants for the quenching of the excited states of Thionine

Species	TEA in reactional medium		MMA; k_q (M^{-1} s^{-1})	TEA in pure methanol	
	k_q (M^{-1} s^{-1})	K_{SV} (M^{-1})		k_q (M^{-1} s^{-1})	K_{SV} (M^{-1})
^{1}ThH$^+$	1.35×10^9	5.00	$< 10^3$	1.9×10^{10}	11.00
^{3}ThH$^+$	1.35×10^7	728	5.0×10^4	2.4×10^8	2900
^{3}Th	4.36×10^7	331	$< 10^3$		

3.3. Photoreduction of ThH$^+$

Bleaching of the dye is observed during the photoinitiated polymerization, similar to what occurs in the polymerization co-initiated with TEOHA [10], or in aqueous SDS solution [12]. This bleaching originates from reactions of the semithionine species (ThH$^\bullet$), which appears in the reaction scheme after both the proton and electron transfer stages

$$^3ThH^+ + A \rightarrow {}^3Th + AH^+ \tag{6}$$

$$^3Th + A \rightarrow {}^3[Th \cdots A] \rightarrow ThH^\bullet + A^\bullet(-H) \tag{7}$$

The radicalar semithionine can form the leuco form of the dye by abstracting a hydrogen atom from the co-initiator or the solvent, or disproportionating to form the uncoloured species and a molecule of the dye in the ground state.

$$ThH^\bullet + RH \rightarrow ThH_2 + R^\bullet \tag{8}$$

$$ThH^\bullet + A \rightarrow ThH_2 + A^\bullet(-H) \tag{9}$$

$$ThH^\bullet + ThH^\bullet \rightarrow ThH_2 + Th \tag{10}$$
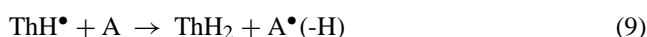
At the high co-initiator concentrations used in the polymerization mixtures, the reaction that is likely to occur is the hydrogen abstraction from the amine. No photobleaching of ThH$^+$ was observed in the presence of oxygen, confirming that the triplet excited state is involved in this process. The photoreduction quantum yield of ThH$^+$ under polymerization conditions at [TEA] = 0.1 M was found to be 0.012, which is lower than for TEOHA ($\Phi_r = 0.067$), as expected from the polymerization rate values.

The rate of photoreduction of the dye can be evaluated from a plot of the photoreduction quantum yield as a function of amine concentration using the double reciprocal plot of Eq. (10)

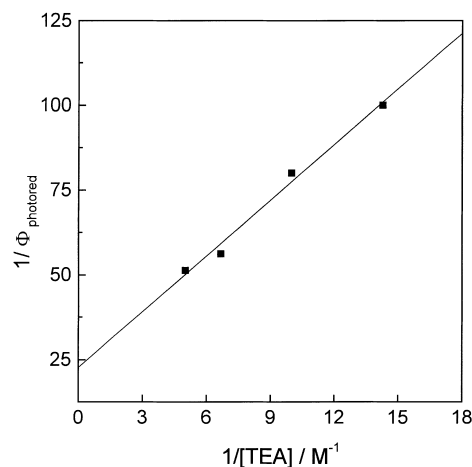$$\frac{1}{\Phi_r} = \frac{1}{\Phi_{isc}} + \frac{k_q}{\Phi_{isc}k_r} + \frac{k_d}{\Phi_{isc}\eta k_r[AH]} \tag{10}$$

Fig. 4. Photoreduction quantum yields of ThH$^+$ as a function of TEA concentration.

where k_d, k_q and k_r are the rate constants for the decay of the dye triplet in the absence of quencher, the quenching of the dye triplet by the amine and the photoreduction of the dye, respectively; and η is the fraction of the dye triplets that end up semireduced thionine.

The values of k_r and the fraction η can be obtained form the slope and the extrapolation to zero shown in the plot in Fig. 4. Using 0.54 for the intersystem crossing quantum yield of ThH$^+$ [28] and 10.5 μs for the lifetime of the triplet in methanol, the product of the photoreduction constants times η for TEA and TEOHA were found to be 3.22×10^4 and 2.38×10^5 M^{-1} s^{-1}, respectively. On the other hand, from the extrapolation to zero and using the quenching rate constant shown above, the photoreduction rate constant is found to be about 1.2×10^6 M^{-1} s^{-1}. A comparison of both values indicates that about 5% of the formed triplets will end up as semireduced species.
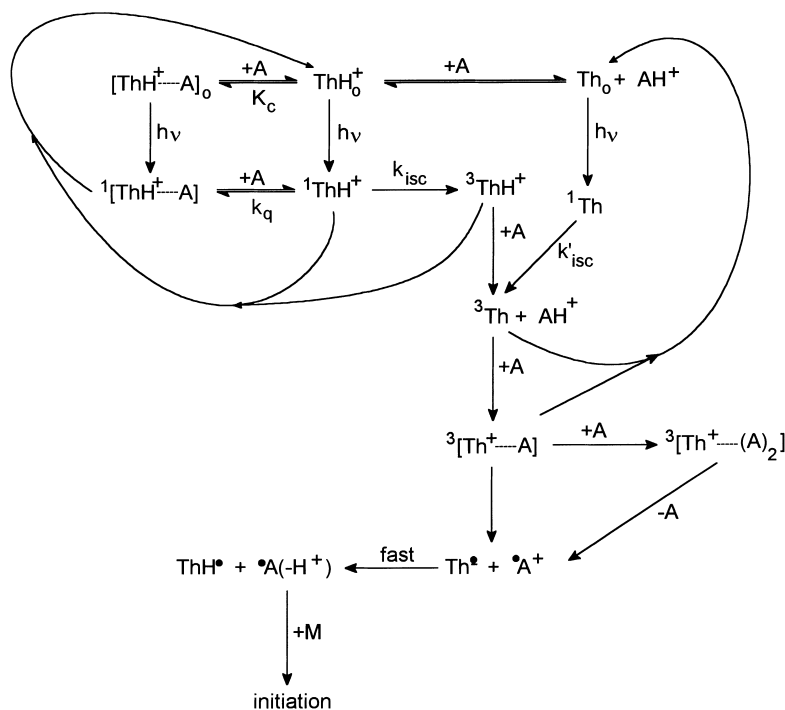
Fig. 5. Mechanism for the production of photoinitiating free radicals in the ThH$^+$/TEA system in methanolic solution.

3.4. Polymerization mechanism

A mechanism consistent with the results of photochemical behaviour of the singlet and triplet states of ThH$^+$ in presence of amine in methanol solution is shown in Fig. 5. [ThH$^+\cdots$A] and [Th$\cdots$A] refer to dye-amine complexes which may be formed in the ground state, or in the excited states as singlet and triplet exciplexes. An alternative pathway including a triplex [ThH$\cdots$(A)$_2$] is also introduced in the scheme. This intermediate is frequently assumed to be present in this kind of reactions, specially due to the high concentration of amine present in the reactional system [29–31].

Radicals originated from amines have been proved to be responsible for the chain initiation in many photoinitiated polymerizations. From the mechanism shown in Fig. 5, and taking into account that the interaction between the singlet state of ThH$^+$ and MMA does not lead to polymerization, the yield of active radicals is given by:

$$\Phi_{\text{rad}} = \beta \frac{\Phi_{\text{isc}}}{1 + {}^1K_{\text{SV}}[A]} \times \frac{{}^3K_{\text{SV}}[A]}{1 + {}^3K_{\text{SV}}[A]} \times \frac{{}^{3d}K_{\text{SV}}[A]}{1 + {}^{3d}K_{\text{SV}}[A]}$$
$$\times \frac{K_{\text{SV}}^{\text{triplex}}[A]}{1 + K_{\text{SV}}^{\text{triplex}}[A]} \tag{11}$$

where K_{SV} are the Stern–Volmer constants, and β stands for the fraction of radicals that effectively lead to polymerization. This yield can be calculated using the data obtained from fluorescence quenching and laser flash photolysis experiments in the reactional medium. The fit to the experi-
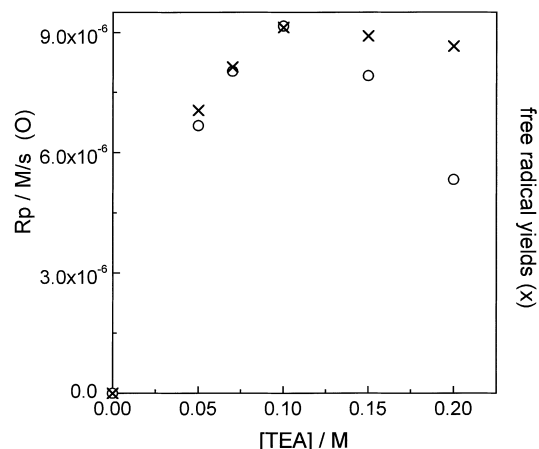

Fig. 6. Polymerization rate (○) and calculated free radical yields (×) for the ThH$^+$/MMA/TEA system.

mental data, shown in Fig. 6 was obtained using the data in Table 2 and assuming 12.0 M^{-1} for $K_{\text{SV}}^{\text{triplex}}$.

As can be seem from Fig. 6, a close match between the experimental conversion rate and the calculated radical yield is obtained for amine concentrations up to the maximum at [TEA] ~ 0.1 M. The decrease of the polymerization rates, as well as that of the dye semireduced radical yield, observed at high amine concentrations, indicates that excited dye molecules will be increasingly quenched by the amine, precluding their conversion to triplets which originate the active radicals leading to polymerization. Due to multiplicity restrictions, singlet exciplexes are not supposed to lead to separated radicals [12–14].

At higher concentrations the conversion rate decreases faster than the calculated yield of radicals. Several factors can be assumed to be responsible for this difference [12]: (i) the medium in which the dye is present will be more basic, so that the initially excited form of the dye may be the unprotonated form; (ii) the increase of the viscosity of the solution and the faster decrease of the monomer concentration [32]; (iii) premature chain terminations by chain transfer reactions to the amine followed by hydrogen abstraction [17]. All these factors were not taken into account in the mechanism, as they are quite difficult to ascertain quantitatively.

Acknowledgements

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