Riboflavin/Triethanolamine as Photoinitiator System of Vinyl Polymerization. A Mechanistic Study by Laser Flash Photolysis

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Received August 6, 1998; Revised Manuscript Received January 7, 1999

ABSTRACT: The polymerization of 2-hydroxyethyl methacrylate photoinitiated by riboflavin in the presence of triethanolamine was investigated. The polymerization was also studied using as photoinitiator lumichrome, the major product obtained in the anaerobic photoreduction of riboflavin. Photopolymerization rates were measured as a function of amine concentration in the UV (366 nm) and visible (>450 nm) regions. The quenching of the excited states of the dyes by triethanolamine was investigated by fluorescence lifetime and laser flash photolysis experiments. Quenching rate constants were determined in the absence and the presence of monomer. These rate constants and singlet and triplet lifetimes were used to fit the polymerization rate vs amine concentration curves. From the fitting it was concluded that the interaction of both singlet and triplet excited states with the amine led to the 2-hydroxyethyl methacrylate polymerization.

Introduction

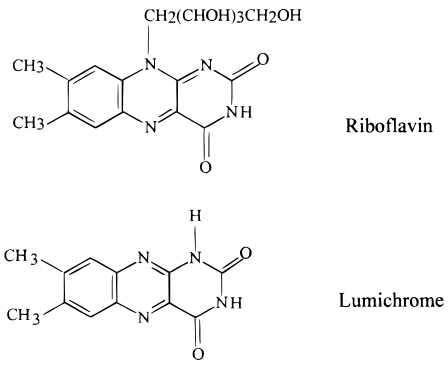
The extension of the absorption spectrum of photoinitiators to the visible light is now of great interest. Besides the practical interest of using light in this spectral region, they are found applications that range from lithography for integrated circuit manufacture to curing processes.

A wide variety of photoinitiator systems containing dyes have been described in the literature.[1,2] However, not many works have related the photochemical behavior of the dye with its efficiency as photoinitiator. Xanthene dyes in the presence of electron donors such as tertiary amines, borate salts, and *N*-phenylglycines photoinitiate the polymerization of acrylates. In these systems it has been proposed that radicals formed in the interaction of the excited dye with the amine are the initiating species.[3−6] Methylene blue sensitized photopolymerization of acrylamide and methyl methacrylate using triethanolamine as reducing agent has been explained on the basis of the triplet mechanism.[7] A study of the safranine photochemical behavior showed that the polymerization of methacrylic monomers proceeds through the radicals generated in the interaction of the unprotonated triplet form of the dye with the amine.[8,9]

Flavins are naturally occurring pigments with absorption bands in the near-UV and visible region. The photoreduction of flavin derivatives by electron donor compounds has been widely described in the literature.[10,11] The mechanism involves an initial one-electron reduction of the triplet state giving the flavin semiquinone radical. The values of the semiquinone radical quantum yield reported for several donors under different conditions are on the order of triplet quantum yield.[11,12] Thus, this high yield of radical formation could make flavins a suitable radical source for vinyl polymerization.

In this work we studied the 2-hydroxyethyl methacrylate (HEMA) polymerization photoinitiated by riboflavin in the presence of triethanolamine (TEOHA). The polymerization of HEMA was also studied using as photoinitiator lumichrome in the presence of TEOHA (Chart 1). Lumichrome is the mayor product obtained in the anaerobic photoreduction of riboflavin.[13] The aim of this work is to provide information on the photoinitiation mechanism.

Chart 1



Experimental Section

Chemicals. Riboflavin (Rf) and lumichrome were purchased from Sigma and were used without further purification. The amines, obtained from various commercial sources, were purified by vacuum distillation and kept under nitrogen. 2-Hydroxyethyl methacrylate (HEMA, Aldrich) was vacuum distilled before use. 4,4′-Azobis(4-cyanovaleric acid) (ABCV) from Aldrich was used as received.

Measurements. Polymerization rates (Rp) were measured dilatometrically in oxygen-free solutions, as previously described.[14] All measurements were carried out at 25 °C, in solutions containing equal volumes of HEMA and methanol. Irradiations were carried out using a medium-pressure mercury lamp (Black-Ray) with cutoff filters (Schott) to isolate the 366 nm line or with a 100 W Philips lamp with cutoff filters (λ < 450 nm). Low absorbances of initiators (1.5×10^{-5} M) were used to avoid the generation of an inhomogeneous free radical distribution.[15]

10.1021/ma981246f CCC: $18.00
Published on Web 04/14/1999

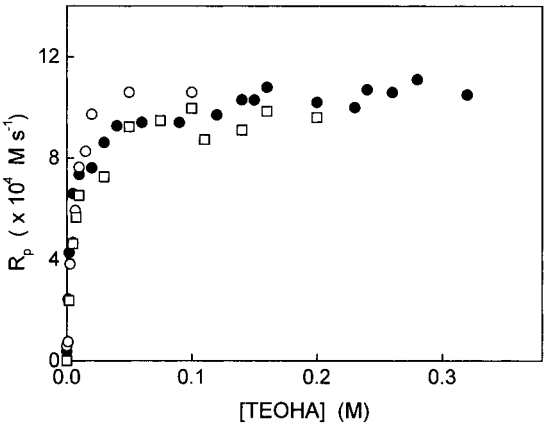


Figure 1. Polymerization rates vs TEOHA concentration: (●) riboflavin, $\lambda = 366$ nm; (□) riboflavin, $\lambda > 450$ nm (Rp × 12); (○) lumichrome, $\lambda = 366$ nm. HEMA/methanol (1/1) v/v.

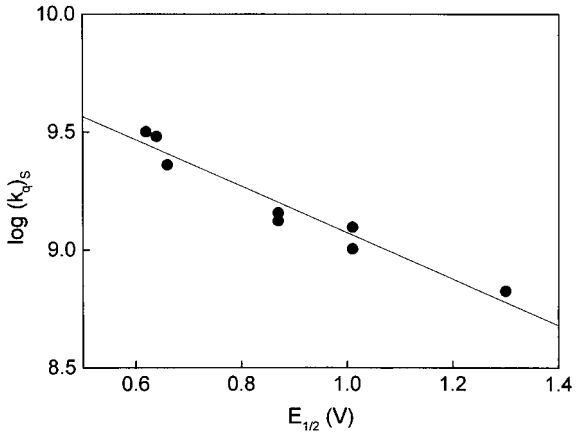


Figure 2. Correlation of the riboflavin singlet quenching rate constants with the oxidation potential of the amine.

Steady-state fluorescence experiments were performed at 20 °C in a Spex Fluorolog spectrofluorometer. The fluorescence lifetimes were measured with a Edinburgh Instruments OB 900 time-correlated single photon counting fluorometer. The singlet quenching rate constants were measured by following the decrease of the fluorescence intensity elicited by the amine addition combined with lifetime in the absence of quencher.

Transient absorption measurements were made using a laser flash photolysis apparatus. A nanosecond Nd:YAG laser system at 355 nm (Spectron Lasers, pulse width, 18 ns; laser power 5 mJ/pulse) was employed for sample excitation. The samples were deoxygenated prior to use by nitrogen bubbling. The bimolecular rate constants for the riboflavin triplet quenching were determined by measuring the transient decay at 670 nm as a function of quencher concentration. Transient quantum yields were determined as relative to the triplet yield of tetraphenylporphyrin (ZnTPP) in benzene. The triplet yield of ZnTPP was measured at 470 nm immediately after the laser pulse. Values of 7.3×10^4 M^{-1} cm^{-1} and 0.83 were used for ϵ_T and ϕ_T of ZnTPP, respectively.[16] The following molar absorption coefficients were used: flavin triplet,[17] $\epsilon_{670} = 1.1 \times 10^4$ M^{-1} cm^{-1}; neutral flavin radical,[18] $\epsilon_{570} = 4.7 \times 10^3$ M^{-1} cm^{-1}.

Results

Photopolymerization Rates. Studies of HEMA polymerization rates photoinitiated by riboflavin in methanol as solvent were carried out using irradiation wavelength of 366 nm and visible light (>450 nm). In both cases the polymerization of HEMA was negligible in the presence of riboflavin alone. However, it was efficiently activated by the presence of aliphatic amines.

Polymerization rates of HEMA in HEMA/methanol (1/1) at several TEOHA concentrations were measured from the linear part of conversion vs time plots. Rp values increase with the hydroxylamine concentration, reaching a maximum value at 0.08 M amine. Further amine addition did not lead to significant changes of the polymerization rate (Figure 1). Similar results were obtained when the solution was irradiated with wavelength of 366 nm or visible light.

To obtain an estimation of the polymerization efficiency under the same experimental conditions, we measured the polymerization rate photoinitiated by ABCV. Working under matched absorption at 366 nm, we obtained a value of 11×10^{-4} M^{-1} s^{-1} for Rp. Since the presence of amine in the ABCV photoinitiation system does not modify the $k_p/k_t^{1/2}$ value,[14] the initiation efficiency (f_i) can be evaluated from eq 1,

$$f_i = [\mathrm{Rp}/(\mathrm{Rp})_{AZO}]^2 (f_i)_{AZO} \qquad (1)$$

From eq 1 and taking $(f_i)_{AZO} = 0.28$,[19] an initiation efficiency of 0.27 was obtained at 0.1 M TEOHA.

The polymerization rates photoinitiated by lumichrome/TEOHA follow a similar pathway to that described for riboflavin/TEOHA. The polymerization rate increases with the amine concentration, reaching a maximum value at 0.06 M TEOHA. Matched solutions of riboflavin and lumichrome irradiated at 366 nm in the presence of 0.1 M hydroxylamine gave similar HEMA polymerization rates (Figure 1). These results indicate a similar photoinitiation efficiency for both dyes.

The effect of the amine concentration on the HEMA polymerization rates here described for riboflavin and lumichrome is somewhat different than that found using other dye/amine photoinitiating systems. Thus, for the system safranine dye in the presence of aliphatic amines in methanol as cosolvent, the polymerization rates slowly decrease at high amine concentration as a consequence of the quenching of excited singlet by a mechanism that does not lead to polymerization.[8] The same happens for the photopolymerization of methyl methacrylate initiated by fluorenone/triethylamine.[20]

Singlet Excited-State Processes. The fluorescence decay of riboflavin in methanol was monoexponential with lifetime of 5.75 ns. This value is in agreement with that previously reported in ethanol.[21] Similar behavior is followed by lumichrome with a lifetime of 1.04 ns.

Riboflavin excited singlet is efficiently quenched by amines. The decrease of fluorescence intensity gave linear Stern−Volmer plots, even at high amine concentration. Values of quenching rate constants for several amines show that the singlet quenching rate constants, $(k_q)_S$, depend on the oxidation potential of the amine, decreasing when the amine oxidation potential increases (see Figure 2). This behavior indicates that the quenching process takes place through a mechanism that implies a certain degree of electron transfer from the amine to the dye.

To evaluate the singlet quenching by the monomer, the fluorescence spectrum of riboflavin was recorded in methanol and methanol/HEMA (1/1) solutions. The fluorescence intensities and the shape of the spectra were similar in both media, indicating that the singlet quenching by the monomer can be disregarded. Singlet quenching by TEOHA was also measured in the polymerization medium HEMA/methanol (1/1) obtaining a value of $k_q = 1.4 \times 10^9$ M^{-1} s^{-1}. The lower value of quenching rate in methanol/HEMA than in methanol

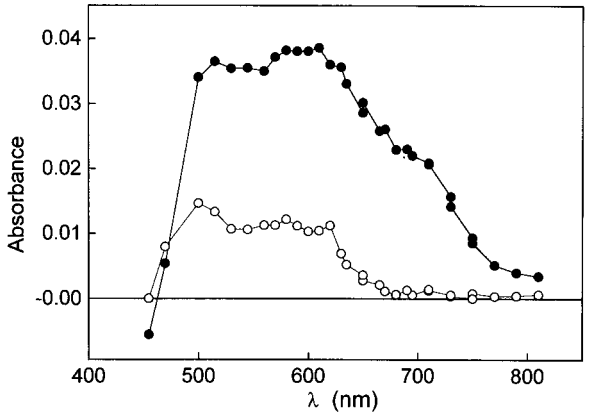


Figure 3. Transient absorption spectra of riboflavin (2.5×10^{-5} M) in methanol: (●) at 3 μs after the laser pulse; (○) after 70 μs.

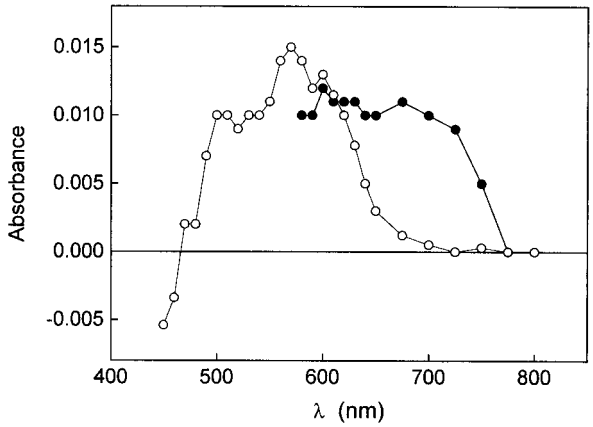


Figure 4. Transient absorption spectra of riboflavin (1×10^{-5} M) in the presence of 0.6 mM TEOHA: (●) at 2 μs after the laser pulse; (○) at 80 μs.

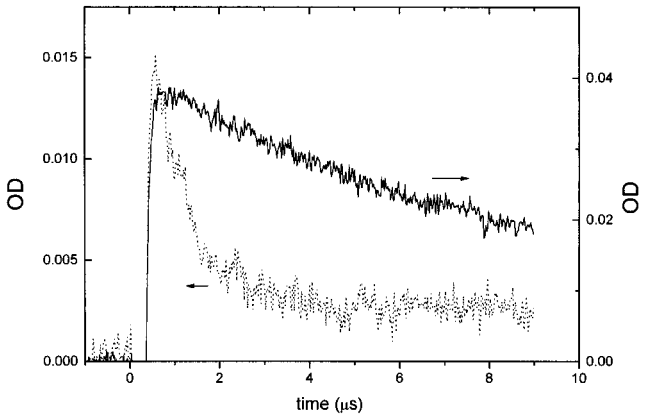


Figure 5. Transient absorption decay at 670 nm in the absence (solid line) and presence of 4.1 M HEMA (dashed line).

could be an effect of the decrease of the medium polarity in the presence of the monomer.

The fluorescence spectrum of lumichrome in methanol showed an unstructured band centered at 450 nm, which is similar in position and intensity when HEMA/methanol (1/1) is used as solvent. This emission was quenched by TEOHA with k_q values of 8.0×10^9 and 3.0×10^9 M^{-1} s^{-1} in methanol and HEMA/methanol, respectively.

Triplet Excited-State Processes. Laser flash irradiation of a deaerated riboflavin solution in methanol gives the transient absorption spectra shown in Figure 3. The spectrum recorded 3 μs after the laser pulse is ascribed to the triplet−triplet absorption of the dye.[22] The triplet decay was accompanied by the appearance of a long-lived absorption in the 500−600 nm region due to the formation of the semireduced riboflavin radical. The same behavior has been reported for lumiflavin in aqueous solution, and it has been explained in terms of the triplet quenching by the ground-state dye.[23] The triplet decay was measured at low dye concentration (1×10^{-5} M) in order to minimize the effect of the self-quenching and at enough low laser energy to eliminate any triplet−triplet annihilation. Under these conditions the triplet decay was a first-order process.

The triplet quantum yield (Φ_T) of riboflavin in the absence of amine was determined in methanol and in the polymerization medium, HEMA/methanol. In both cases it was obtained triplet quantum yield value of 0.6. The value obtained in methanol is in good agreement with those reported in the literature.[17]

The triplet decay at 670 nm is shortened by the addition of TEOHA or triethylamine, and a new long-lived transient species appears in the region 500−600 nm (Figure 4). This signal is identical to the long-lived spectrum found in the absence of amine and has been assigned to the riboflavin semireduced form.[22] Bimolecular quenching rate constants were measured from the decay of the triplet as a function of amine concentration; values of 8×10^8 and 3.4×10^8 M^{-1} s^{-1} were obtained in methanol for TEOHA and triethylamine, respectively. These values are an order of magnitude lower than the singlet quenching rate constants but follow the same dependence with the amine structure. These facts indicate that the triplet quenching by amines is due to electron transfer from the amine to the triplet of the dye with the production of semireduced dye ($Rf^{\bullet -}$) and semioxidized amine ($Am^{\bullet +}$). The neutral radical dye would be formed after protonation of the radical anion by proton transfer from the amine radical cation inside or outside the solvent cage.

$$^3Rf + Am \rightarrow (Rf^{\bullet -} + Am^{\bullet +}) \rightarrow RfH^{\bullet} + Am(-H)^{\bullet} \quad (2)$$

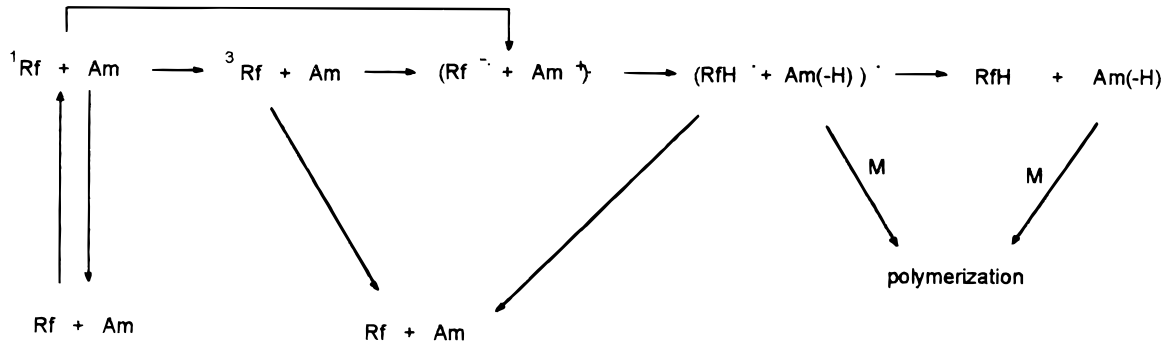
Triplet quenching by TEOHA was also measured in ethanol obtaining a value of $k_q = 1 \times 10^9$ M^{-1} s^{-1}. This solvent was considered to provide a medium of polarity similar to that afforded by HEMA/methanol (1/1) as measured by the pyrene polarity scale.[24] Quenching of excited states by amines through the charge-transfer mechanism has been reported for several dyes;[1,2] however, the quenching by the proton-transfer mechanism has been demonstrated only for the quenching of safranine[8] and thionine[25] triplets.

The triplet decay was also shortened by the addition of HEMA (Figure 5). A bimolecular rate constant of 2.2×10^5 M^{-1} s^{-1} was obtained from the triplet decay as a function of HEMA concentration. On the other hand, the optical density of the long-lived component observed in the 500−600 nm region in the presence of TEOHA increases with the addition of monomer (Figure 6). This indicates that the presence of monomer increases the formation of the flavin neutral radical.

The semireduced riboflavin quantum yield ($\Phi_{RfH^{\bullet}}$) was determined relative to the triplet yield according to eq 3

$$\Phi_{RfH^{\bullet}} = \frac{OD_T \epsilon_R}{OD_R \epsilon_T} \Phi_T \quad (3)$$

Scheme 1



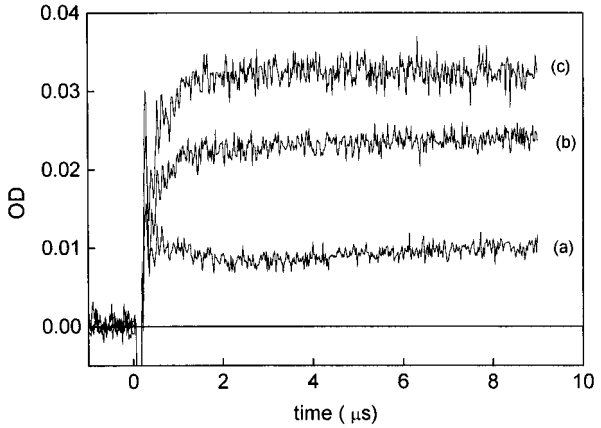


Figure 6. Transient absorption at 570 nm. Riboflavin (1×10^{-5} M) in the presence of 6 mM TEOHA in methanol: (a) in the absence of monomer; in the presence of (b) 1.14 M HEMA; (c) 1.8 M HEMA.

Table 1. Semireduced Flavin Quantum Yields as a Function of Monomer Concentration at 6 mM TEOHA

[HEMA] (M)	$\Phi_{RfH\cdot}$
0	0.16
1.1	0.37
1.8	0.55

where OD_T is the triplet absorbance at 670 nm in the absence of the amine immediately after the laser pulse and OD_R is the absorbance of the radical at 570 nm.

For 0.1 M TEOHA, where the polymerization rate reaches an almost constant value, $\Phi_{RfH\cdot}$ was 0.7. This value is higher than the triplet-state quantum yield under these conditions. For this amine concentration 45% of the excited singlets are quenched. Therefore, assuming a triplet quantum yield of 0.6 in the absence of the amine, the contribution of the triplet to $\Phi_{RfH\cdot}$ is at most 0.33. This points to a high contribution of the singlet quenching process to the production of free semireduced flavin. On the other hand, in pure methanol $\Phi_{RfH\cdot}$ at the same TEOHA concentration is only 0.04. Semireduced riboflavin quantum yields at 6 mM TEOHA, where a minimal fraction of excited singlets are intercepted, are shown in Table 1. In the absence of HEMA the yield is much lower than the triplet yield, due to an in-cage recombination process. The most likely explanation for the increase of the flavin free radicals with the HEMA concentration is the interception of the amine radical by the monomer before the radical escapes from the cage and recombines with the flavin radical.

Laser flash photolysis of lumichrome in methanol showed a transient species absorbing in the region 360−650 nm, with a sharp maximum at 370 nm and a broad absorption in the region 450−650 nm. This spectrum was similar to that previously reported in aqueous solution at pH 7 and has been assigned to the absorption of the neutral triplet state.[26] The triplet decay, measured at 370 nm, was shortened by TEOHA addition with a bimolecular rate constant of 3×10^8 M^{-1} s^{-1}. Lumichrome triplet was quenched by HEMA with a rate constant of 3.5×10^5 M^{-1} s^{-1}.

Discussion

The reaction of riboflavin excited states with aliphatic amines in methanolic solution is an electron-transfer process that results in the reduction of the dye. After initial electron transfer from the amine to the singlet and triplet dye, the riboflavin anion and amine cation radical pair are formed. Rapid proton transfer from the amine gives the dye and amine neutral radicals. This process probably occurs inside the solvent cage as shown in Scheme 1. This scheme is supported by the effect of HEMA concentration on the flavin radical yield as discussed in the previous section.

It is found that in nearly all cases the amine radical is the species that initiates the polymerization of vinyl monomers. This was further supported in the present system since spectroscopic measurements of the resulting polymer revealed a negligible incorporation of the flavin moiety to poly(2-hydroxyethyl methacrylate). The independence of Rp with the amine concentration in the range of high TEOHA concentrations suggests that the amine radicals from the singlet quenching also lead to polymerization. Thus, at 0.35 M TEOHA, where 74% of singlet are quenched by the amine, the polymerization rate is still constant. Then, the active radical yield (Φ_R) at constant monomer and initiator concentrations will be given by eq 4

$$\Phi_R = \beta_S \frac{(k_q)_S[\text{TEOHA}]}{(k_q)_S[\text{TEOHA}] + {}^S\tau_0^{-1}} + \Phi_T \frac{(k_q)_T[\text{TEOHA}]}{(k_q)_T[\text{TEOHA}] + {}^T\tau_0^{-1}} \beta_T \quad (4)$$

where $(k_q)_S$ and $(k_q)_T$ stand for the amine singlet and triplet quenching rate constants, respectively. ${}^S\tau_0$ and ${}^T\tau_0$ are the excited lifetimes in the absence of amine, in the polymerization medium, HEMA/methanol (1/1). Φ_T is given by eq 5

$$\Phi_T = \Phi^\circ_T/(1 + (k_q)_S {}^S\tau_0[\text{TEOHA}]) \quad (5)$$

and β stands for the fraction of radicals produced in each singlet or triplet riboflavin interaction with the amine

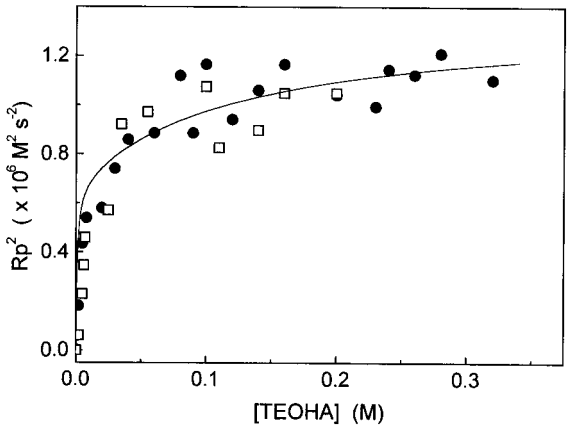


Figure 7. Plot of the square of the polymerization rate as a function of TEOHA concentration. Riboflavin, (●) $\lambda = 366$ nm; (□) $\lambda > 450$ nm; 4.1 M HEMA. The solid line corresponds to the free radical quantum yield calculated with eq 4.

that are able to add the monomer. The fitting of the polymerization rates to eq 4 using the measured values of k_q, τ_0, and Φ_T and as adjustable parameters β_S and β_T is shown in Figure 7. The best fitting was obtained with $\beta_S = 0.85$ and $\beta_T = 0.7$, indicating that the interaction of the amine with the singlet dye is an important process that leads to polymerization. The high value of β_S is somewhat surprising since back electron transfer is a very fast process from the singlet radical ion pair. With dyes such as eosin,[3] safranine,[8] and fluorenone[20] it has been proposed that the active radicals are those formed from interaction of the triplet state with the amine. In the photoreduction of rose bengal esters using as electron donor triphenyl *n*-butyl borate, it has also been proposed that the reactive excited species is the triplet state of the dye.[27] With regard to riboflavin, the polymerization through radicals arising from the interaction of both singlet and triplet states with the amine is in agreement with the high photoinitiation quantum yield of 0.27. High quantum yields of free flavin radicals also have been proposed in the interaction of the flavin mononucleotide singlet state with ascorbic acid.[28]

Finally, it is interesting to note that the same polymerization behavior is held when the samples are irradiated at 366 nm or >450 nm (Figure 1). This shows the applicability of flavins as photoinitiator either with near-UV or visible light. Furthermore, lumichrome photoinitiation behavior is similar to that of flavin. The fitting of the experimental data of Rp to eq 4 gives values of $\beta_S = 0.7$ and $\beta_T = 0.8$. This indicates the participation of the amine radicals generated from the interaction of both singlet and triplet excited dye with the amine. This similarity in the photoinitiation mechanism between riboflavin and lumichrome as well as the almost equal photoinitiation efficiency gives to the flavin dye a particular feature. Thus, at long irradiation time, a condition where the bleaching of the flavin dye acquires importance, the polymerization could continue with similar efficiency through the radicals generated by the photoproduct.

Acknowledgment. Thanks are given to Fundación Antorchas-Andes for a joint research grant (A-13219/1-000068). The financial support by Cátedra Presidencial en Ciencias 1997, FONDECYT (Grant 1970414), and CONICET is also gratefully acknowledged.

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MA981246F