The Photoinitiation Mechanism of Vinyl Polymerization by Riboflavin/Triethanolamine in Aqueous Medium

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ABSTRACT: Free radicals produced in the photoinduced electron transfer from triethanolamine to excited riboflavin lead to the polymerization of 2-hydroxyethyl methacrylate in aqueous medium. Polymerization rates increase with the amine concentration, reaching a maximun value at 0.01 M amine. Further amine addition produces a decrease of the polymerization. Time-resolved photolysis studies of riboflavin were carried out under the polymerization conditions, monomer/water pH 9. These results indicate that the polymerization proceeds by the radicals formed in the interaction of the dye triplet with the amine. Meanwhile, the quenching of the excited singlet inhibits the polymerization. These results are discussed in terms of the dependence of the photoinitiation mechanism with the solvent employed in the polymerization.

Introduction

Most of the bimolecular photoinitiators used in the polymerization of vinyl monomers use as radical source the photoinduced electron transfer between the photoinitiator and aliphatic tertiary amines.[1,2] Because the primary photochemical processes in these reactions are strongly dependent on the solvent, also a strong dependence of the photoinitiation quantum yield can be expected.

The photoreduction of flavins by electron donor compounds has been widely described in the literature.[3−6] The rate constants and the nature of the primary reactions between the flavin excited states and electron donors have been studied in alcohol and in aqueous solutions in the pH range 3−14.[3,5−8] High quantum yields of the semiquinone flavin radical have been reported in most cases. Therefore, the system flavin/amines may be expected to act as an efficient photoinitiator of the vinyl polymerization. In particular, riboflavin (Rf) in the presence of aliphatic amines behaves as an efficient photoinitiator system of 2-hydroxyethyl methacrylate (HEMA) polymerization in methanolic solutions.[9] Then, it could be expected that riboflavin in the presence of amines could be also effective as photoinitiator in aqueous media. Although, dramatic changes are observed in polymerization rates when the media is changed from organic to aqueous solvent.[10]

In this work we studied the polymerization of HEMA photoinitiated by the system Rf/triethanolamine (TEOHA) in aqueous solution with the aim of obtaining information on the role of the solvent on the mechanism and efficiency of photoinitiation.

Experimental Section

Chemicals. Triethanolamine (TEOHA, Sigma) and 2-hydroxyethyl methacrylate (HEMA, Aldrich) were distilled under reduced pressure before their use. Riboflavin (Rf) was from Sigma and used as received. Water was purified through a Millipore Milli-Q system. 4,4′-Azobis(2-amidinopropane) (ABAP, Polysciences) was used without further purification.

Measurements. Riboflavin solutions, at concentrations ranging from 8 to16 μM, were purged with argon for 30 min before their use. The pH was adjusted after addition all reagents by NaOH addition.

Photopolymerization rates (R_p) were measured dilatometrically under anaerobic conditions at 25 °C. Rates were determined at low conversion (<5%). The irradiation was carried out with a medium-pressure Hg lamp using a glass filter with transmission band centered at 366 nm. Low photoinitiator absorbances (0.12) were used to avoid inhomogeneous free radical distribution.[11]

Steady-state fluorescence measurements were made using a Fluorolog-Spex spectrofluorimeter. Fluorescence lifetime measurements were performed with an Edinburgh Instruments OB 900 time-correlated single photon counting fluorometer. Singlet quenching rate constants were obtained from the decrease of the fluorescence intensity elicited by the quencher addition combined with the lifetime in the absence of quencher.

Transient absorption measurements were made using a laser flash photolysis equipment. The third harmonic of a Nd:YAG laser (355 nm, 5 mJ/pulse, 20 ns) was employed for sample excitation. The signals from the monochromator/photomultiplier system were initially captured by a HP54504 digitizing oscilloscope and transferred to a computer for storage and analysis. Bimolecular rate constants for riboflavin triplet quenching were determined by measuring the transient decay at 710 nm as a function of quencher concentration. Triplet quantum yield was determined relative to the triplet yield of zinc 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.[12] The molar absorption coefficient of the neutral riboflavin triplet in water at 670 nm was taken as 4400 M^{-1} cm^{-1}.[13]

Results and Discussion

Polymerization. The irradiation of Rf in the presence of TEOHA leads to the HEMA polymerization in aqueous solution. The polymerization rates were measured in HEMA/water (1:2) (v/v) at pH 9 at different amine concentrations. The rate increases with the TEOHA addition, reaching a maximum at 0.01 M

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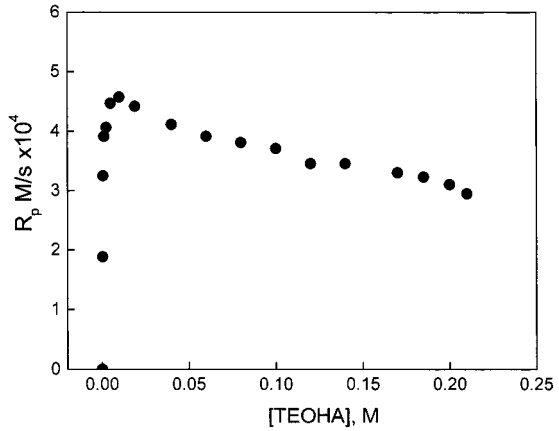


Figure 1. Polymerization rates vs amine concentration.

TEOHA. Further amine addition decreases the polymerization rate (Figure 1). This behavior is different from that previously described for the polymerization of HEMA in methanolic solution.[9] In the later system the polymerization rate increases with the increase of amine concentration, but it reaches a constant value.

The polymerization rates were also measured at several riboflavin absorbances (0.08−0.3), keeping the amine concentration constant (0.1 M). The order in riboflavin obtained by plotting log R_p against the log of riboflavin absorbance ($1 - 10^{-A}$) was 0.53 ± 0.03.

To evaluate the initiation efficiency, the polymerization of HEMA was carried out using ABAP as reference photoinitiator. This compound decomposes to give radicals by a homolitic cage fragmentation. For this initiator it is well established that it follows a classical kinetic law.[14] Since in our case the order in initiator is 0.5, the initiation efficiency, under matched absorption conditions, can be evaluated from eq 1,

$$\Phi_{inic} = (\Phi_i)_{ABAP}\{(R_p)_{Rf}/(R_p)_{ABAP}\}^2 \qquad (1)$$

An initiation efficiency of 0.16 was obtained from eq 1 for riboflavin in the presence of 0.01 M TEOHA, taking for the reference initiator ($(\Phi_i)_{ABAP}$) a value of 0.36.[10] This value decays to 0.13 at 0.1 M amine. The maximum initiation efficiency in this system is lower than that previously obtained (0.26) when methanol was used as cosolvent.[9] Furthermore, in the latter system the amine concentration required to reach the maximum photoinitiation efficiency is approximately 8 times higher than in the aqueous polymerization.

Excited-States Processes. To ascertain the photoinitiation mechanism, as well as the dependence of R_p with the amine concentration, it was necessary to carry out a detailed study of the riboflavin photochemical behavior under the polymerization conditions.

Since changes in the protonation state of Rf influence its photochemical behavior, all studies were carried out in water or HEMA/water (1:2) at pH 9. At this pH it can be considered that the dominant protolytic form of the ground and excited states of Rf is the neutral form.[13,15] In aqueous monomer solution an almost negligible change of fluorescence intensity was detected in the 4−9 pH range (data not shown). This is compatible with the lack of deprotonation of the flavin in both the ground and excited singlet states. Laser flash photolysis experiments of riboflavin in a HEMA/water (1:2) mixture at pH 9 gave the transient absorption spectra shown in Figure 2. This spectrum, recorded at

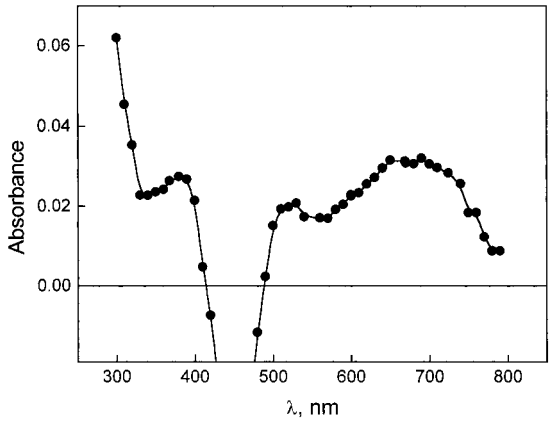


Figure 2. Transient absorption spectrum of riboflavin in HEMA/water (1:2), pH 9, at 1 μs after the laser flash in the absence of amine.

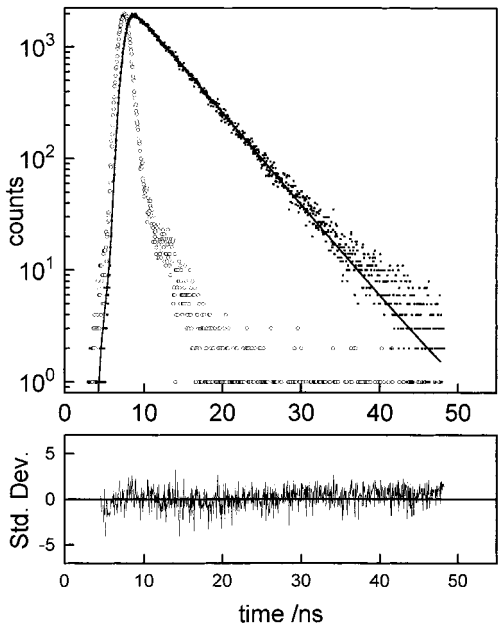


Figure 3. Fluorescence decay of riboflavin in HEMA/water (1:2), pH 9, with excitation and emission wavelengths of 440 and 525 nm, respectively.

1 μs after the laser pulse, reveals the presence of the well-known absorption bands of the riboflavin neutral triplet state.[3,13] From these results it is clear that in the HEMA/water mixture at pH 9 the predominant protolytic form for the excited states of riboflavin is the neutral form.

The triplet quantum yield under the polymerization conditions in the absence of amine was determined by measuring the initial triplet−triplet absorption at 670 nm in the HEMA/water mixture. $\Phi_{isc} = 0.5$ was obtained in HEMA/water (1:2), taking as reference ZnTPP in benzene. This value is similar to those reported in the literature in water at pH 7.[16]

The fluorescence emission decay of riboflavin was measured in the absence of amine in both water and HEMA/water mixture at pH 9. The fluorescence decay data could be fitted by a single-exponential function (Figure 3). The lifetimes obtained were 5.1 and 5.2 ns in water (pH 9) and HEMA/water (1:2), respectively. These results indicate that the riboflavin singlet excited state is not quenched by the monomer.

The rate constants ($^S k_q$) for the riboflavin singlet quenching by the amine were measured by the decrease

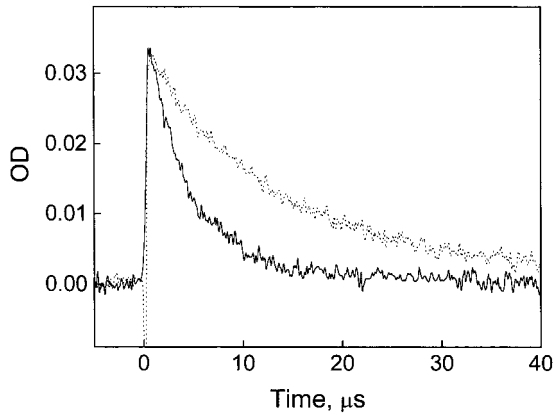


Figure 4. Transient absorption decay at 710 nm in water, pH 9 (dashed line), and in HEMA/water (1:2), pH 9 (solid line).

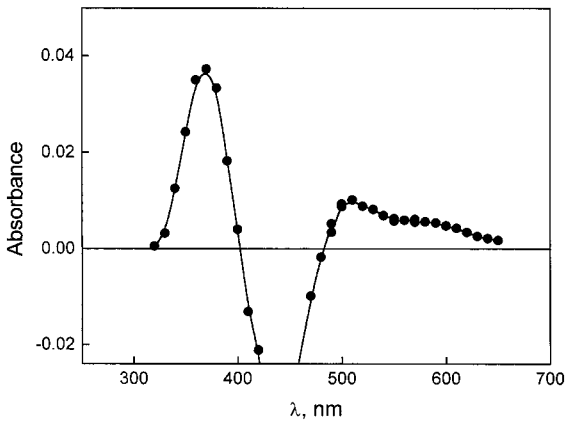


Figure 5. Transient absorption spectra of riboflavin in water, pH 9, at 20 μs after the laser flash in the presence of 6 mM TEOHA.

of the steady-state intensity produced by TEOHA addition. The Stern−Volmer plots were linear over the range of quencher concentrations used. Quenching rate constants of 2.7 and 1.6 × 10^9 M^{-1} s^{-1} were obtained in water and the HEMA/water (1:2) mixture, respectively. The lower value of the quenching rate constant in HEMA/water than in water can be due to an effect of the higher viscosity of the monomer mixture, reaching the diffusional limit in this medium.

The bimolecular rate constant for the triplet quenching by TEOHA was obtained from the experimentally measured first-order decay of the triplet state according to eq 2,

$$k = k_0 + k_q[Q] \tag{2}$$

where k_0 is the decay rate constant in the absence of amine. From the slope and intercept of the line, the values of k_q and k_0 were determined to be 1.7 × 10^8 M^{-1} s^{-1} and 1.6 × 10^5 M^{-1} s^{-1} in HEMA/water (1:2) at pH 9. The k_q value is lower than the value of 5.1 × 10^8 M^{-1} s^{-1} reported by Heelis et al.[5] for the triplet quenching of lumiflavin by TEOHA in water at pH 7. The small differences observed among the quenching efficiency of excited states of lumiflavin and Rf by TEOHA probably reflect small differences in the electron-withdrawing power of the substituents on the isoalloxazine nucleus.

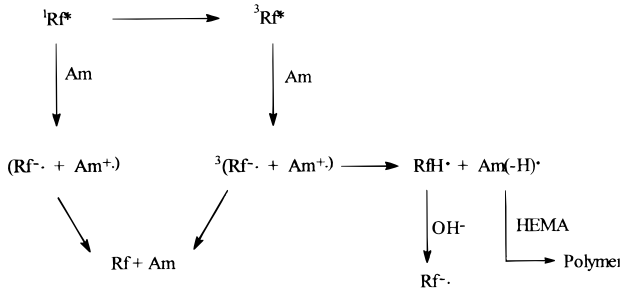
Riboflavin triplet decay also was shortened by the addition of HEMA (Figure 4). A bimolecular rate constant of 2.2 × 10^5 M^{-1} s^{-1} was obtained from the triplet decay as a function of monomer concentration. These results indicate that in the absence of amine 66% of Rf triplet states are quenched by the monomer; however, this process does not lead to polymerization as evidenced by the lack of polymerization in the absence of amine.

Riboflavin Semiquinone Radicals. Riboflavin excited states are quenched by amines through a mechanism that involves electron transfer from the amine to the flavin with the production of the semireduced flavin ($Rf^{\bullet -}$) and semioxidized amine ($Am^{\bullet +}$).[5,9] Rapid proton transfer from the amine radical cation to the $Rf^{\bullet -}$ gives flavin and amine neutral radicals, as the long-lived species at neutral pH

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

The quenching of excited triplet of Rf in aqueous solution at pH 9 by 6 mM TEOHA, where 90% of triplet are quenched by the amine, produces a residual absorption which remains over 100 μs. Figure 5 shows the spectrum obtained at 20 μs after laser excitation. Similar spectral properties were obtained when the spectrum was recorded at 2 μs. This transient is similar to that reported for the riboflavin radical anion, indicating that under these conditions (pH 9) the predominant form is the anionic radical form. These results are consistent with the pK 8.3 reported for the equilibrium between uncharged and monoanionic species of the radicals derived from riboflavin.[15,17,18] Furthermore, the similarity of the spectra in the range 2−20 μs indicates that the deprotonation of the neutral semireduced radicals occurs in a few hundred nanoseconds. El Hanine-Lmoume and Lindqvist[18] have reported that the initial neutral radical derived from flavin mononucleotide at pH 10.3 is deprotonated within 1 μs.

Scheme 1



Photoinitiation Mechanism. A mechanism consistent with the results found for the photochemical behavior of Rf in the presence of amine and monomer in aqueous solution at pH 9 is given in Scheme 1, where parentheses indicate reactive partners in the solvent cage. In this mechanism it is implied that the singlet quenching does not produced active radicals. Moreover, since the interaction between the Rf triplet and the monomer does not lead to polymerization, the only step leading to initiating radicals is the Rf triplet quenching by TEOHA. Accordingly, the active radical yield is given by

$$\Phi_r = \beta \frac{\Phi^o_{isc}}{1 + {}^S(K_{SV})[Am]} \frac{{}^T(K_{SV})[Am]}{1 + {}^T(K_{SV})[Am]} \tag{4}$$

where ${}^S(K_{SV})$ and ${}^T(K_{SV})$ stand for the Stern−Volmer constants for the singlet and triplet quenching by the amine, respectively. β represents the fraction of radicals produced in the triplet quenching process. The photo-

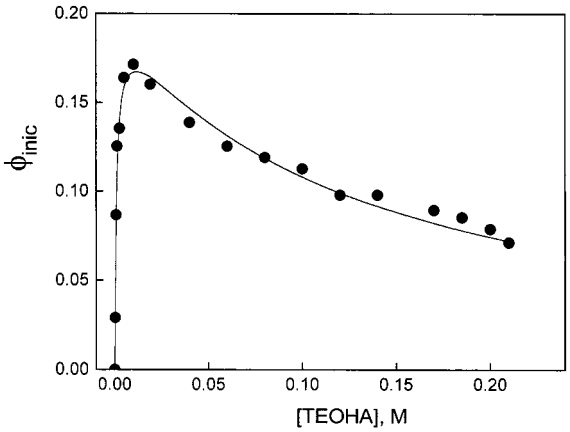


Figure 6. Photoinitiation quantum yields as a function of the TEOHA concentration. The solid line corresponds to the radical quantum yield calculated from eq 4 with $\beta = 0.4$.

initiation efficiency can be related to the active radicals quantum yield, through a constant that reflects the fraction of the radicals that effectively initiates a polymer chain. If this constant is included in the parameter β, then the experimental values of Φ_{inic} can be adjusted with eq 4 using Φ^{o}_{isc}, ${}^{S}K_{SV}$, and ${}^{T}K_{SV}$ measured values and β as an adjustable parameter. In Figure 6 the experimental values of Φ_{inic} (eq 1) are shown as a function of TEOHA concentration, and the solid line is the best fit of the data, using eq 4, with $\beta = 0.40$. The lack of photoinitiation through the singlet quenching process may be explained by a fast back electron transfer for the singlet radical ion pair. These results suggest a marked influence of the solvent on the back-electron-transfer reaction.

In conclusion, the nature of the solvent plays an important role in the polymerization of HEMA photoinitiated by the Rf/TEOHA system. The photoinitiation mechanism is markedly different when the solvent changes from water to methanol. In the aqueous medium the active radicals are those coming from the Rf triplet interaction with the amine. The singlet quenching leads to an inhibition of the polymerization. This is contrary to what we found using methanol as cosolvent,[7] where the active radicals are produced from both the singlet and triplet quenching. Moreover, in this case the fraction of active radicals originating from the singlet quenching is even slightly higher than the corresponding triplet quantity.

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