Macromolecules **2001,** *34,* 2845−2847 **2845**

Free Radical Polymerization Photoinitiated by Riboflavin/Amines. Effect of the Amine Structure

M. V. Encinas,*,† A. M. Rufs,† S. Bertolotti,‡ and C. M. Previtali‡

Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33,
Santiago, Chile; and Departamento de Química, Universidad Nacional de Río Cuarto,
800 Río Cuarto, Argentina

Received September 25, 2000; Revised Manuscript Received February 1, 2001

ABSTRACT: Polymerization rates of 2-hydroxyethyl methacrylate (HEMA) photoinitiated by riboflavin were investigated using as co-initiator several amines of different structure. The photoinitiation efficiency is highly dependent on the structure of the amine. The photochemical behavior of these systems was investigated under the polymerization conditions. The results are explained in terms of the dependence of the amino radicals production and the reactivity of these radicals toward monomer double bonds with the structural features of the amines.

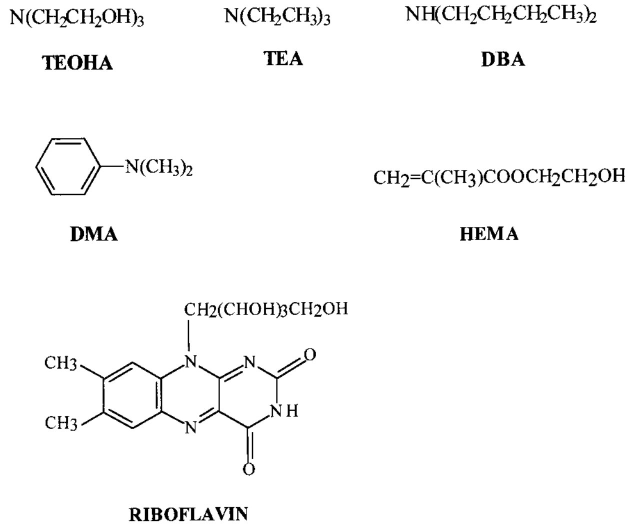
Introduction

The application of photoinitiated polymerization is extensive. Among the most commonly utilized photoinitiators for free radical polymerization stand those where radicals result from a bimolecular process comprising an excited chromophore and a co-initiator that behaves as electron donor.[1] Tertiary amines are the most frequently employed co-initiators in these processes. It is generally accepted that the α-amino radicals generated in these reactions are the species that add to the monomer.[2] In these reactions the yield of the primary photochemical processes is strongly dependent on the structure of the electron donor. Therefore, a strong dependence of the polymerization efficiency with the amine structural features can be expected.

Dependence of the polymerization rate with the structure of the amine has been reported for the acrylate polymerization using camphorquinone[3,4] and thioxanthones[5] as photoinitiators. However, there is not a general mechanistic explanation of the experimentally found dependence of the efficiency of the amine as co-initiator with its chemical structure. More recently, Davidson et al.[6] have proposed that for a particular aromatic ketone the efficiency of photoinitiation is determined by the structure and the molecular geometry of the α-aminoalkyl radical produced. On the other hand, Paczkowski et al.[7] have suggested that the initial electron-transfer reaction from an aromatic amines to the excited state of xanthene dyes, is the responsible of the variation of the photoinitiation efficiency.

In a previous work,[8] we have shown that riboflavin acts as an efficient photoinitiator of vinyl polymerization in the presence of triethanolamine (TEOHA). Radicals are produced with high yield by a photoinduced electron-transfer process. Therefore, the riboflavin−amine appears as an interesting system to study the effect of the amine structure on the photoinitiation efficiency. Here we report the polymerization of 2-hydroxyethyl methacrylate (HEMA) photoinitiated by riboflavin in the presence of several amines (Chart 1), with the aim of relating the efficiency of generation of radicals and their ability to initiate the polymerization with the structure of the amine.

Chart 1



Experimental Section

Riboflavin (Rf, Sigma) was used as received. 2-Hydroxyethyl methacrylate (HEMA, Aldrich) was distilled under reduced pressure. All the amines were from Aldrich and they were vacuum distilled before their use. 2,2′-Azobis(isobutyronitrile) (Fluka) was recrystallized from ethanol.

Photopolymerization rates (R_p) at low conversion were measured dilatometrically under anaerobic conditions at 25 °C. Irradiation was carried out with a medium-pressure Hg lamp fitted with a glass filter to isolate the 366 nm band.

Fluorescence lifetime measurements were performed with an Edinburgh Instruments OB 900 time-correlated single photon counting fluorometer. 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.

Results and Discussion

Polymerization rates of HEMA photoinitiated by riboflavin in the presence of several amines of different structure were measured in monomer/methanol (1/1). As previously reported with TEOHA,[8] the polymerization rate increases with the amine concentration reaching a constant value (Figure 1). For TEA the polymer-

---

† Universidad de Santiago de Chile.

‡ Departamento de Química, Universidad Nacional de Río Cuarto.

10.1021/ma001649r CCC: $20.00

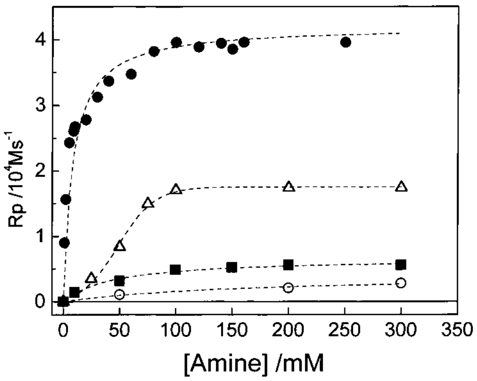


Figure 1. Polymerization rates of HEMA as a function of amine concentration: (●) TEOHA; (△) TEA; (■) DMA; (○) DBA. Monomer/methanol: 1/1 vol/vol.

Table 1. Polymerization Rates, and Efficiencies of Rf Excited States Quenching by 0.2 M Amines

amine	R_p, M/s $\times 10^{-4}$	f_T	f_S	ϕ_{rad}	E_{ox}, V[a]
DMA	0.6	1	0.92	0.16	0.81
TEOHA	3.9	0.9	0.68	0.25	0.90
TEA	1.8	0.88	0.67	0.14	0.99
DBA	0.2	0.57	0.30	0.05	1.1

[a] From refs 10 and 11.

ization rate as a function of amine concentration presents a sigmoidal dependence. This is most likely due to the labile proton on the hydroxyl group of HEMA[9] that protonates the amine at low concentration. Values of polymerization rate at 0.2 M amine, where the polymerization rates reach a constant value are given in Table 1. These results show that the photoinitiation efficiency depends markedly on the structure of the amine. Only aliphatic tertiary amines are efficient co-initiators, the hydroxy substituted amine is more efficient than the corresponding alkyl derivative. The aromatic amine, DMA, is much less efficient. A similar dependence of the polymerization rate with the structure of tertiary aliphatic amines was found for the polymerization of 1-vinyl-2-pyrrolidinone employing pyrene derivatives as photoinitiators.[12] In this case TEOHA is two times more efficient than TEA. The differences in polymerization rate for the different amines must be due exclusively to changes in photoinitiation quantum yield since addition of amine up to 0.2 M did not modify the polymerization rate of HEMA photoinitiated by 2,2′-azobis(2-amidinopropane). This azo compound produces radicals by a noncatalyzed unimolecular photocleavage, with minor dependence on the medium properties.[13]

To understand the different efficiency of these systems as photoinitiators it is necessary to know their photochemical behavior in the polymerization medium. This implies to know the efficiency of the interaction of dye excited states with the amine and the radical quantum yield that results from this interaction. These parameters were determined at 0.2 M amine, concentration where the polymerization rates reach a constant value.

The square of the polymerization rate will be proportional to the radical yield produced in the interaction of the dye excited states with the amine (ϕ_{rad}), and to the fraction of the radicals that add to the monomer (β), and hence

$$R_p^{\ 2} \sim \phi_{rad}\beta \qquad (1)$$

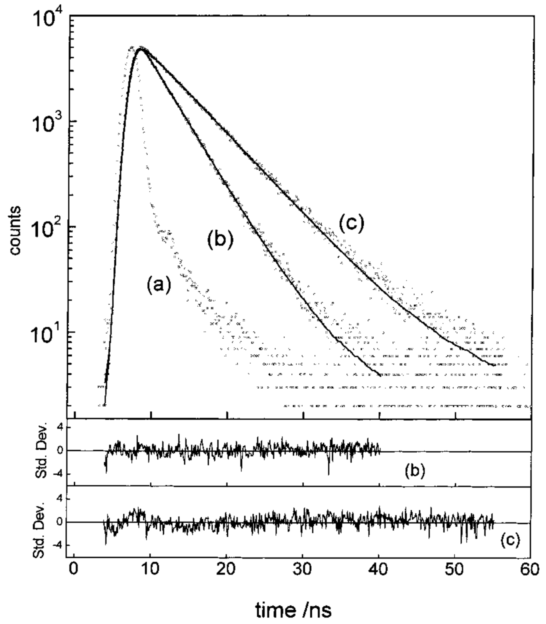


Figure 2. Fluorescence decay profiles of riboflavin in HEMA/methanol, in the absence (c) and in the presence of 0.2 M TEA (b). Part a is the lamp profile.

On the other hand, the fraction of dye excited states, singlet or triplet, that are deactivated by the amine (f) is given by eq 2,

$$f = k_q[\text{amine}]/(k_q[\text{amine}] + k_o) \qquad (2)$$

where k_q is the quenching rate constant and k_o is the decay rate of the excited states in the absence of amine.

The deactivation of riboflavin singlet excited state was evaluated from the fluorescence lifetime quenching. Figure 2 shows the shortened of the fluorescence decay by 0.2 M TEA. The fractions of excited singlets quenched by the different amines (f_S), calculated from eq 2 at 0.2 M amine, are summarized in Table 1. These data show a higher quenching efficiency for the aromatic amine, and the lower value corresponds to the secondary aliphatic amine.

The rate constant (k_q) for the riboflavin triplet quenching was measured from the triplet decay in the polymerization mixture, HEMA/methanol (1/1). The triplet decay, having lifetimes in the order of few microseconds in monomer/methanol, could be adequately fitted to first-order kinetics. The pseudo-first-order rate constants, k_{obs}, are related to the quenching rate constant by eq 3. Values of k_q determined from the slope of linear

$$k_{obs} = k_o + k_q[\text{amine}] \qquad (3)$$

plots of k_{obs} vs [amine] allowed us to calculate the fraction of riboflavin triplet excited states that are deactivated by the amine (f_T), eq 2. Results obtained at 0.2 M amine are also given in Table 1. These data show that the quenching efficiency for both excited states are in the order aromatic amine > tertiary amines > secondary amines, and they are not correlated with the photoinitiation efficiency. The trend in quenching efficiency is similar to that found in methanol as solvent,[8] and it agrees with the order of the oxidation potential of the amine; i.e., the quenching efficiency increases when the oxidation potential of the amine decreases.

The quenching of riboflavin excited states by amines is due to electron transfer from the amine to excited dye

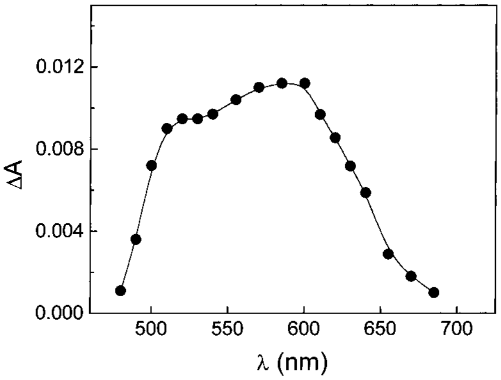


Figure 3. Transient absorption spectrum of riboflavin (1 × 10^{-5} M) in HEMA/methanol in the presence of 0.2 M TEOHA, at 20 μs after the laser flash.

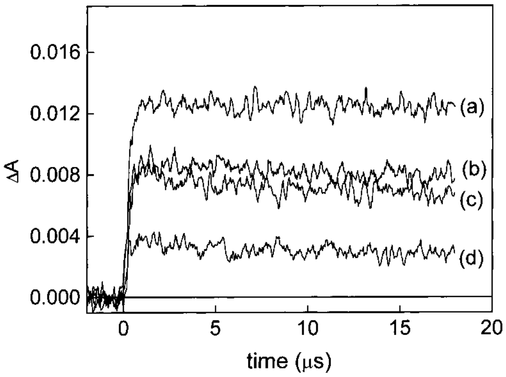
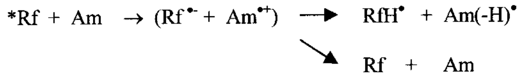


Figure 4. Transient absorption at 570 nm. Riboflavin (5 × 10^{-5} M) in the presence of 0.2 M amine: (a) TEOHA; (b) DMA; (c) TEA; (d) DBA.

Scheme 1



with the production of the semireduced dye ($Rf^{\bullet -}$) and semioxidized amine ($Am^{\bullet +}$). The neutral radical dye is formed by the protonation of the radical anion by proton transfer from the amine radical cation, Scheme 1.

Similar to that previously reported for the quenching of riboflavin by TEOHA in methanol or water,[8,14] the quenching in HEMA/methanol produces a residual absorption which remains over 100 μs. The transient absorption spectrum (Figure 3) in the presence of 0.2 M TEOHA taken 20 μs after the laser excitation showed the well-known absorption band of the riboflavin neutral radical, with $\lambda_{max} = 570$ nm.[15] The same spectra were obtained with all the amines.

We have previously demonstrated that the species that lead to polymerization are the amine radicals arising from the interaction of both singlet and triplet excited dye with the amine.[8] An estimation of the active radical quantum yield can be obtained from the riboflavin neutral radical yield at high amine concentration. Under this condition, it can be considered that riboflavin neutral radicals arise only from the interaction of the dye with the amine, self-quenching of the dye can be disregarded. Figure 4 shows the transient absorption of riboflavin at 570 nm in the presence of the different amines, where it is observed a much higher radical yield for the hydroxy substituted amine. The riboflavin radical yields (Φ_{rad}) were calculated relative to the triplet yield according to eq 4,

$$\Phi_{rad} = \frac{A_{570}\epsilon_T}{A_{670}\epsilon_{rad}}\Phi_T \qquad (4)$$

where A_{670} is the triplet absorption at 670 nm, and A_{570} is the absorbance of the riboflavin semiquinone radicals at 570 nm. The values for molar absorption coefficients (ϵ) were taken as 4400 and 5100 M^{-1} cm^{-1} for the triplet[16] and the neutral radical,[17] respectively. Values of Φ_{rad} measured at 0.2 M, using a value of 0.6 for the triplet quantum yield,[8] in monomer/methanol are included in Table 1. Radical yields do not correlated with the amount of excited states quenched by the amine, even when only aliphatic amines are considered. This suggests that the radical yield is determined mainly by the rate of the proton-transfer process.

On the other hand, data in Table 1 show that the radical yield is higher for the TEOHA, this is the amine that behaves as better photoinitiator. The lower value corresponds to the DBA, which gives very low polymerization rate. However, even when the trend in R_p is coincident with that obtained for radical yield, the correlation between R_p^2 and $\phi_{RfH^\bullet}$, according to eq 1, is very poor. This points to significant differences in the efficiency of the addition of the amino radicals to the monomer double bond, being the aromatic aminoalkyl radicals the less reactive.

In conclusion, the photochemical efficiency is strongly dependent on the structural features of the amines. This is consequence of both differences in the active radical yield generation and in the reactivity of these species. Otherwise, due to the electron-transfer characteristics of the primary photochemical process, it can be expected that these factors also are dependent on the structure of the photosensitizer.

Acknowledgment. This work was supported by Cátedra Presidencial en Ciencias 97, FONDECYT # 1000947, Fundación Andes, and CONICET (Argentina).

References and Notes

(1) Lissi, E. A.; Encinas, M. V. In *Photochemistry and Photophysics*; Rabek, J. F., Ed.; CRC: Boca Raton, FL, 1991; Vol. 4, Chapter 4.
(2) Hageman, H. J. *Macromol. Rapid Commun.* **1997**, *18*, 443.
(3) Cook, W. D. *Polymer* **1992**, *33*, 600.
(4) Mateo, J. L.; Bosh, P. *Polym. Adv. Technol.* **1994**, *5*, 561.
(5) Allen, N. S.; Catalina, F.; Luc-Gardette, J.; Green. W. A.; Green, P. N.; Chen, W.; Fatinikun, K. O. *Eur. Polym. J.* **1988**, *24*, 435.
(6) Bradley, G.; Davidson, R. S. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 528.
(7) Paczkowski, J.; Kucybala, Z. *Macromolecules* **1995**, *28*, 269.
(8) Bertolotti, S. G.; Previtali, C. M.; Rufs, A. M.; Encinas, M. V. *Macromolecules* **1999**, *32*, 2920.
(9) Beers, K. L.; Boo, S.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 5772.
(10) Ruiz, G.; Rodríguez-Nieto, F.; Wolcan, E.; Féliz, M. R. *J. Photochem. Photobiol. A: Chem.* **1997**, *107*, 47.
(11) Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7349.
(12) Encinas, M. V.; Lissi, E. A.; Majmud, C.; Cosa, J. J. *Macromolecules* **1993**, *26*, 6284.
(13) Alvarez, J.; Encinas, M. V.; Lissi, E. A. *Macromol. Chem. Phys.* **1999**, *200*, 2411.
(14) Orellana, B.; Rufs, A. M.; Encinas, M. V.; Previtali, C. M.; Bertolotti, S. *Macromolecules* **1999**, *32*, 6570.
(15) Land, E. J.; Swallow, A. J. *Biochemistry* **1969**, *8*, 2117.
(16) Schreiner, S.; Steiner, U.; Kramer, H. E. A. *Photochem. Photobiol.* **1975**, *21*, 81.
(17) Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9.

MA001649R