Laser Flash Photolysis Study of the Photoinitiator System Safranine T–Aliphatic Amines for Vinyl Polymerization

C. M. Previtali,[†] S. G. Bertolotti,[†] M. G. Neumann,[‡] I. A. Pastre,[‡] A. M. Rufs,[§] and M. V. Encinas*[,§]

Departamento de Química y Física, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina, Instituto de Fisica e Quimica de Sao Carlos, Universidade de Sao Paulo, 13560 Sao Carlos SP, Brazil, and Departamento de Química, Facultad de Ciencia, Casilla 307-2, Universidad de Santiago de Chile, Santiago, Chile

Received December 20, 1993; Revised Manuscript Received March 31, 1994[⊗]

ABSTRACT: The polymerization of 2-hydroxyethyl methacrylate, in a methanol solution, proceeds efficiently using the photoinitiator safranine T in the presence of tertiary aliphatic amines. Polymerization rates were measured at several amine concentrations. These values increase with the amine concentration, reaching a maximum, and further amine addition slowly reduces the polymerization rate. The quenching of the dye excited states by amines was analyzed by static fluorescence and laser flash photolysis. The excited singlet quenching involves a charge-transfer process with rate constants near the diffusional limit. Flash photolysis studies of safranine in the presence of amines, in a methanol solution, yield the triplet species $^3SH^+$ and $^3S^+$ and the unprotonated semireduced radical. This latter transient follows a dependence with the amine concentration similar to that found for polymerization rates. All these results indicate that polymerization involves the interaction of the excited triplet with the amine, while quenching of the excited singlet inhibits the polymerization.

Introduction

The photopolymerization of vinyl monomers in the presence of photosensitizers that absorb visible light has been studied by various workers.[1-3] Most of these studies deal with the polymerization kinetics, and no details concerning the photochemical initiation mechanism seem to exist.

Most photoinitiator systems consist of a dye and a reducing agent, where the excited triplet state of the dye acts as the oxidizing species. Amines are frequently used reducing agents.[2,3] The first comprehensive work using amines as reducing agents was reported by Chen.[4] This author studied the polymerization of acrylamide by methylene blue/triethanolamine, suggesting that the polymerization kinetics could not be explained by a simple steady-state analysis. Recently, Vedeneev et al.[5] examined the same system by analyzing the effect of a magnetic field, which led to an increase of the polymerization rate in viscous media. This fact was ascribed to the observed increase in the production of free radicals. Earlier work on the polymerization of methyl methacrylate with eosin/amine systems established an ideal kinetic law with respect to monomer and light intensity, but the dependence of the amine and dye concentrations could not be established.[6] In a more recent study, Fouassier and Chesneau[7] proposed that the deactivation of the excited triplet of eosin by triethanolamine produces radicals that initiate the polymerization. Neckers et al.[8,9] used eosin in the presence of different aliphatic amines to photoinitiate the polymerization of acrylic monomers.

The photochemical behavior of dyes in the presence of reducing agents has been evaluated in a few systems.[2] Steiner et al.[10] determined for the photoreduction of thionine triplets by amines an almost quantitative limiting semireduced dye yield. Kayser and Young[11] found that the photoreduction of methylene blue triplet by amines proceeds through a partial charge-transfer intermediate, formed between the dye triplet and the amines. Aliphatic amines lead efficiently to photobleaching of the dye.[12] Photobleaching by amines has also been described for other xanthene dyes.[13,14]

In this paper, we report the polymerization of 2-hydroxyethyl methacrylate (HEMA), photoinitiated by safranine T in the presence of aliphatic amines, as well as the photochemical behavior of this system. The aim of this work was to provide information on the photoinitiation mechanism.

Experimental Section

Chemicals. Safranine T chloride (Chart 1), from Merck, was recrystallized from ethanol before use. The amines, obtained from various commercial sources, were purified by fractional distillation or vacuum distillation and kept under nitrogen. 2-Hydroxyethyl methacrylate (HEMA; Aldrich) was vacuum distilled before use.

Measurements. Polymerizations rates (V_P) were measured dilatometrically in oxygen-free solutions, as previously described.[15] Rates are reported in arbitrary units. Irradiations were carried out using a 100-W Philips lamp ($\lambda > 500$ nm). All polymerizations were carried out at 25 °C, in solutions containing equal volumes of HEMA and methanol.

Fluorescence quenching experiments were carried out at room temperature (25 ± 1 °C) as previously described.[16] Transient absorption spectra and triplet quenching were determined with an Applied Photophysics laser kinetic spectrometer. Excitation at 532 nm was performed using a Nd:YAG laser (Spectron) with frequency doubling. All fluorescence quenching and laser photolysis experiments were made with 1×10^{-5} M safranine solutions in methanol. For the fluorescence quenching experiments the solutions were air-equilibrated. For triplet studies, they were deoxygenated by nitrogen bubbling.

In water, the safranine ground state exists in its cationic single charged form SH^+, in the pH range 2–10.[17,18] Therefore, it can be assumed that this is the species present in methanolic solutions, or in the polymerization mixture.

Results

Photopolymerization Rates. The polymerization of HEMA using methanol as cosolvent in the presence

---

[†] Universidad Nacional de Río Cuarto.

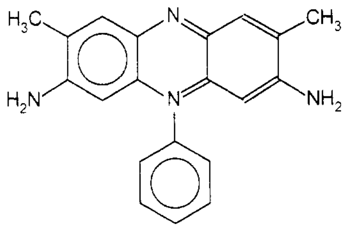
[‡] Universidade de Sao Paolo.

[§] Universidad de Santiago de Chile.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1994.

0024-9297/94/2227-7454$04.50/0

Chart 1



Safranine T

of safranine alone was negligible. However, it was efficiently activated in the presence of aliphatic amines. This result contrasts with that reported by Timpe and Neuenfeld[19] for the polymerization of styrene in methanolic solutions of safranine T, where the polymerization proceeds to some extent in the absence of any additives.

Polymerization rates of HEMA in methanol (1:1) photoinitiated by the system safranine–amine were measured for triethylamine (TEA) and triethanolamine (TEOHA) at several amine concentrations. Polymerization rates (V_P) obtained from the initial slope of the conversion vs time plots are shown in Figure 1. The V_P values increase with amine concentration, reaching a maximum. Further addition of amine slowly reduces the polymerization rates. Under the experimental conditions used in these experiments (low absorbance and high intensity), the maxima rates correspond to 11–13% of monomer conversion. An inhibition effect at high concentrations of amine on the photopolymerization of methyl methacrylate initiated by fluorenone–amine system has been reported before.[20] A similar effect was also detected for the photopolymerization of acrylamide in water initiated by thioxanthone in the presence of amines.[21] The decrease in the polymerization rates in these systems has been explained as due to quenching of the ketone singlet by the amines by a mechanism that does not lead to polymerization.

Singlet Excited State Processes. The deactivation of safranine singlet excited state by aliphatic amines of different electron-donor ability was measured by fluorescence quenching. Stern–Volmer plots were linear in all cases. The addition of the quenchers did not result in changes in the absorption or emission spectra of the dye. Thus, any interaction between quenchers and the ground state of safranine can be disregarded. Singlet quenching rate constants, $k_q(S)$, were evaluated from the slopes of the Stern–Volmer plots, using a lifetime of 2.3 ns.[16] The values obtained are collected in Table 1. It can be observed from these data that the rate constants depend on the oxidation potentials of the amines ($E_{1/2}$), decreasing when the amine oxidation potential increases (see Figure 2). This behavior indicates that the process takes place through a total, or partial, charge-transfer mechanism. However, the rate constants do not change significantly with $E_{1/2}$. This can be understood since these rate constants are near the diffusional limit in methanol. Therefore, according to the Rehm–Weller correlation for electron transfer quenching, large changes in this region should not be expected. A charge-transfer mechanism has also been reported for the safranine singlet quenching by aromatic amines.[16]

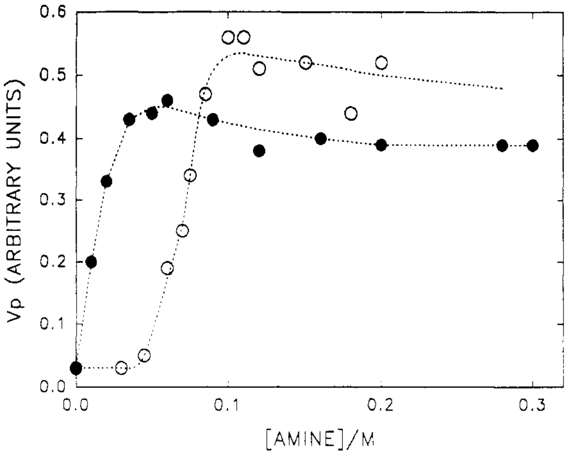


Figure 1. Polymerization rates in arbitrary units vs amine concentration: (●) TEOHA; (○) TEA.

Table 1. Singlet and Triplet Quenching Rate Constants by Aliphatic Amines in Methanol

amine	$E_{1/2}$ (V)[a]	pK_b	k_q(s) ($\times 10^8$ M^{-1} s^{-1})	k_q(T) ($\times 10^8$ M^{-1} s^{-1})
n-butylamine	1.3		3.0	9.4
di-*n*-propylamine	0.93	3.00	6.2	5.1
diisobutylamine	0.87	3.50	9.0	3.0
triethylamine	0.66	3.32	10.0	6.7
tri-*n*-propylamine	0.64	3.35	25.0	2.4
tri-*n*-butylamine	0.62	4.07	20.0	1.2
N-methyldiethanolamine		5.14		0.13
triethanolamine		6.24	32.0	

[a] In acetonitrile vs Ag/Ag$^+$ from: A. J.; Bard, H. Lund, *Encyclopedia of the Electrochemistry of the Elements*; Marcel Dekker: New York, 1984; Organic Section, Vol. XV. pK_b in water at 198 K from several sources.

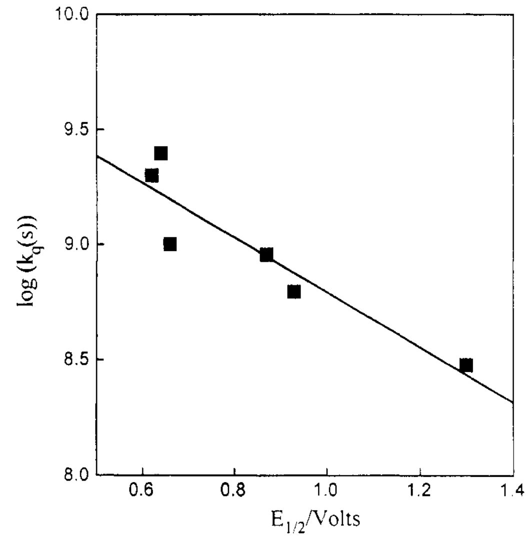


Figure 2. Correlation of the singlet quenching rate constants with the oxidation potential of the amine.

In order to evaluate the singlet quenching by the monomer, the fluorescence quantum yield of safranine was measured in methanol and in methanol/HEMA (1:1) solutions. Fluorescence intensities and the shape of the spectra are similar in both cases, indicating that the singlet quenching can be disregarded. Singlet quenching by TEA and TEOHA was also measured in the polymerization medium methanol/HEMA (1:1). The Stern–Volmer constants obtained were 2.0 and 3.8 M^{-1} for TEA and TEOHA, respectively. Lower values for the quenching rate constants are expected from the decrease of the polarity of the solvent in the presence of the monomer. The effect of the solvent properties on the quenching rate constant has been described in several reactions that proceed through a charge-transfer mechanism.[22,23]

Triplet Excited State Processes. The transient absorption spectra of safranine in methanol, in the

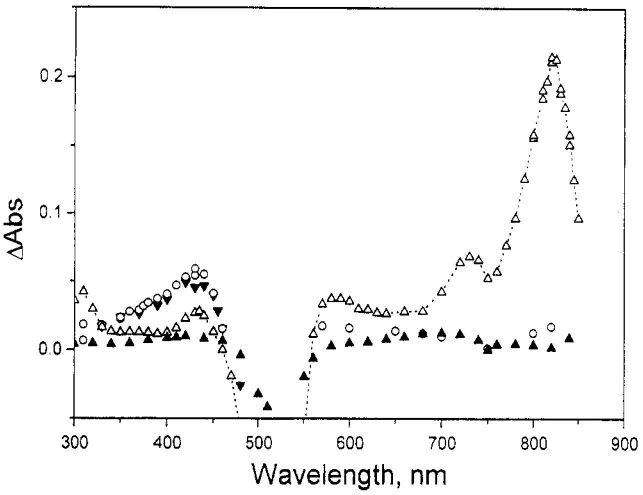


Figure 3. Transient absorption spectrum of safranine (10^{-5} M) in methanolic solutions: (△) at 0.8 μs after the laser flash in the absence of amine; (▲) 200 μs in the absence of amine; (○) 200 μs in the presence of TEOHA (0.25 M); (▼) 200 μs in the presence of TEA (0.45 M).

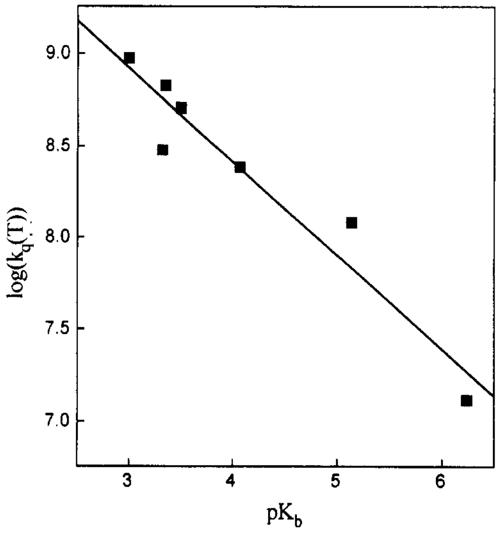


Figure 4. Correlation of the quenching rate constant of the safranine monoprotonated triplet measured at 830 nm with the basicity of the amine.

absence and in the presence of amine, are shown in Figure 3. In the absence of amine, a strong absorption with a maximum at 830 nm appears immediately after the laser pulse. This absorption is assigned to the monoprotonated triplet $^3H^+$.[16] It decays with first-order kinetics and has a lifetime of tens of microseconds. The decay is a function of the safranine concentration.[24] In our experiments, the safranine concentration was kept constant at 1×10^{-5} M^{-1}.

The triplet decay at 830 nm is markedly shortened by the addition of alkylamines, whereas this effect is considerably lower in the presence of hydroxylamines. In all cases, the decays follow first-order kinetics and a new long-lived transient species appears in the 420–430 nm region (Figure 3). This new transient absorption is in the same region where the unprotonated triplet and the semireduced safranine are known to absorb.[17] Bimolecular quenching rate constants were obtained from the decay of the triplet at 830 nm as a function of amine concentration. These values are included in Table 1, are less than an order of magnitude lower than the singlet quenching rate constants, and do not correlate with the oxidation potentials of the amines. On the other hand, quenching rate constant values of 10^5–10^6 M^{-1} s^{-1} would be expected if the triplet state quenching would follow a mechanism similar to that of singlet-state quenching. These facts indicate that a different mechanism must be operating for the triplet state. In Figure 4, the triplet-state quenching rate constants are plotted as a function of the amine basicity (pK_b). This figure shows that the rate correlates well with the amine basicity and permits the postulation of a proton transfer quenching mechanism

$$^3SH^+_{830} + A \rightarrow {}^3S_{420} + AH^+ \qquad (1)$$

where the subscripts indicate the maximum absorption wavelength for each species.

This proton transfer is not a *real* quenching process, since the amine promotes the transformation of the monoprotonated triplet to the unprotonated excited triplet $^3S_{420}$. This unprotonated species is known to absorb at 420–430 nm in water.[17] The time profile of absorption at 420 nm was measured at different TEA and TEOHA concentrations. For both amines, these decays are quite complex (Figure 5): they show a fast initial decay in the 10–20-μs time scale, followed by a long-lived residual absorption. The latter absorption can be ascribed to monoprotonated semireduced safranine that absorbs at 430 nm in water.[17] Figure 5 also shows that the faster decay is shortened with increasing the amine concentrations, whereas the residual absorption increases up to a maximum. The first decay, fitted to a monoexponential function, follows a Stern–Volmer relationship with amine concentration. From these data, Stern–Volmer constants (K_{SV}) of 30 and 70 M^{-1} can be obtained for TEOHA and TEA, respectively. These results can be explained in terms of the $^3S_{420}$ quenching by the amine through a process that involves an electron transfer from the amine to the unprotonated dye triplet, followed by a fast proton transfer in the ion pair inside the cage, to form the monoprotonated semireduced safranine and the amine radical,

$$^3S_{420} + A \rightarrow S^{\bullet -} + A^{\bullet +} \rightarrow SH^{\bullet}_{430} + A(-H)^{\bullet} \qquad (2)$$

On the other hand, the optical density of the long-lived component extrapolated to 60 μs increases up to a maximum and slowly decreases on further addition of amine. The optical densities as a function of TEOHA concentration are shown in Figure 6, in which are also included the polymerization efficiencies, expressed as the square of the polymerization rate. These results show that both the semireduced safranine yields and the polymerization efficiencies have a rather similar dependence on the amine concentration. The results obtained for TEA are also in good agreement concerning the dependence of the safranine radical yields and the polymerization efficiencies on amine concentration with a maximum reached at ca. 0.1 M TEA.

Discussion

A mechanism consistent with the results found for the photochemical behavior of safranine in the presence of amine in methanolic solution is given in Scheme 1. SH_0^+, $^1SH^+$, and $^3SH^+$ indicate the ground state, the excited singlet, and monoprotonated triplet of the dye, respectively. ^3S stands for the unprotonated triplet and $SH^{\bullet}$ for the semireduced radical.

The intermediate unprotonated semireduced form of safranine was not observed in aqueous solution. This

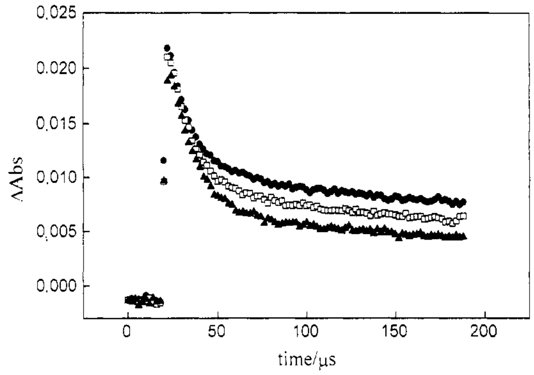


Figure 5. Decay of the transient absorption at 430 nm as a function of TEOHA concentration: (▲) 0.004 M; (□) 0.011 M; (●) 0.031 M.

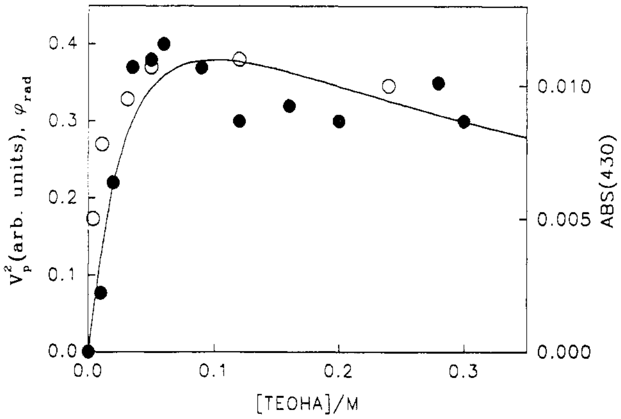


Figure 6. Plot of the square of the polymerization rate in arbitrary units (●) and the long-lived absorption at 430 nm (○) as a function of TEOHA concentration. The solid line corresponds to the free radical quantum yield φ_{rad} calculated with eq 4.

is probably due to its strong basicity. The radical originated from aliphatic amines has been proved to be responsible for the chain initiation in many photoinitiated polymerizations. The decrease of the polymerization rate, as well as that of the safranine semireduced radical yield, observed at high amine concentrations, indicates that the active radicals arise from the interaction of the safranine triplet with the amine. The quenching of the safranine singlet by the amine must lead to the inhibition of the active radicals.

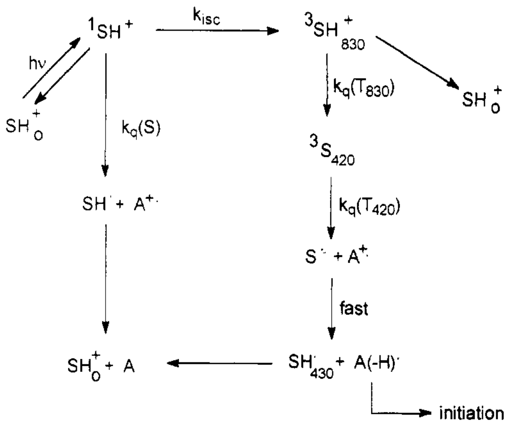
From the mechanism shown in Scheme 1, and taking into account that interaction between the safranine excited states and the monomer does not lead to polymerization, the active radical yield is given by

$$\Phi_{rad} = \frac{\Phi^0{}_{isc}}{1 + {}^1(K_{SV})[A]} \frac{(K_{SV})_{830}[A]}{1 + (K_{SV})_{830}[A]} \frac{(K_{SV})_{420}[A]}{1 + (K_{SV})_{420}[A]} \beta \qquad (3)$$

where the subscript on the Stern–Volmer constant indicates the wavelength at which the quenching was followed and β stands for the fraction of radicals produced that lead to polymerization. From the values obtained from laser flash photolysis experiments and fluorescence quenching, an apparent radical yield φ_{rad} can be defined

$$\varphi_{rad} = \Phi_{rad}/\beta\Phi^0{}_{isc} \qquad (4)$$

Scheme 1



The curve calculated from eq 4 for TEOHA is included in Figure 6. The results show that the theoretical curve has the same general shape as the measured polymerization efficiencies and the safranine semireduced radicals. All these parameters go through a maximum value at ca. 0.06 M TEOHA. These facts are in agreement with the mechanism proposed in Scheme 1, where the radicals are assumed to come almost exclusively from the interaction of the safranine triplet (420-nm absorption) with the hydroxyl-substituted amine. Other processes, such as the quenching of the intermediate charge-transfer complex by the amine, proposed for other systems,[20,25,26] give only a minor contribution.

The polymerization rates obtained with TEA show that the alkylamine, at high concentrations, is a more effective coinitiator than the hydroxylamine (Figure 1). However, the results obtained using TEA are more complex. The theoretical curve calculated from eq 4 shows a maximum at ca. 0.1 M amine, which is in good agreement with the maximum values found for the polymerization efficiencies and the safranine semireduced radicals. However, at concentrations of TEA below that maximum value, the theoretical curve predicts active radical yields higher than those obtained experimentally for the polymerization efficiencies or safranine semireduced radical yields. This difference can be due, at least partially, to the strong basicity of the tertiary alkylamine. In any case, this point deserves further attention.

Timpe and Neuenfeld[27] have proposed that styrene acts as an electron donor for the excited singlet state of safranine ($^1SH^+$), producing semireduced safranine radicals that initiate the polymerization. A rate constant of 3.2×10^7 M^{-1} s^{-1} was reported for the quenching of safranine singlet by styrene. The lack of polymerization that we found for HEMA in the absence of additives could be a consequence of the low rate of interaction of the safranine singlet with the methacrylic monomer. This is in agreement with the lack of safranine bleaching of acrylic or methacrylic acids reported by Timpe and Neuenfeld.[19] Furthermore, the quenching of the monoprotonated triplet by HEMA is very low; we determined a value of 3×10^4 M^{-1} s^{-1} in methanolic solution. Thus, our results indicate that the active radicals that lead to the methacrylic monomer polymerization in methanolic solutions proceed from the interaction of the safranine triplet with the amine.

Acknowledgment. We are grateful to Fundacion Antorcha-Andes (No. A-12659/1-5), DICYT (Universidad de Santiago de Chile), FONDECYT (No. 1930063), CNPq (Brasil), and CONICET and CONICOR (Argentina) for financial support.

References and Notes

(1) Oster, G. *Nature* **1954**, *173*, 300.

(2) Eaton, D. F. *Advances in Photochemistry*; Volman, D., Gollnick, K., Hammond, G. S., Eds.; John Wiley: New York, 1986; Vol. 13, Chapter 4.

(3) Kustermann, E.; Timpe, H.-J.; Gabert, K.; Schulert, H. *Wiss. Z. Tech. Hochsch. Merseburg* **1987**, *29*, 287.

(4) Chen, C. *J. Polym. Sci., Part A* **1965**, *3*, 1107, 1127, 1137, 1155.

(5) Vedeneev, A. A.; Khudyakov, I. V.; Golubkova, N. A.; Kuzmin, V. A.; Irinyi, G. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3545.

(6) Maiti, S.; Saha, M. K.; Palit, S. P. *Makromol. Chem.* **1969**, *127*, 224.

(7) Fouassier, J. P.; Chesneau, E. *Makromol. Chem.* **1991**, *192*, 245.

(8) Neckers, D. C.; Raghuveer, K. S.; Valdes-Aguilera, O. *Polym. Mater. Sci. Eng.* **1989**, *60*, 15.

(9) Sudesh Kumar, G.; Neckers, D. C. *Macromolecules* **1991**, *24*, 4322.

(10) Steiner, U.; Winter, G.; Kramer, H. E. A. *J. Phys. Chem.* **1977**, *81*, 1104.

(11) Kayser, R. H.; Young, R. H. *Photochem. Photobiol.* **1976**, *24*, 395.

(12) Kayser, R. H.; Young, R. H. *Photochem. Photobiol.* **1976**, *24*, 403.

(13) Oster, G.; Oster, G. K.; Kang, G. *J. Phys. Chem.* **1962**, *66*, 2514.

(14) Zakrzewski, A.; Neckers, D. C. *Tetrahedron* **1987**, *43*, 4507.

(15) Encinas, M. V.; Majmud, C.; Lissi, E. A. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 2465.

(16) Neumann, M. G.; Pastre, I. A.; Previtali, C. M. *J. Photochem. Photobiol. A: Chem.* **1991**, *61*, 91.

(17) Baumgartner, C. E.; Richtol, H. H.; Aikens, D. A. *Photochem. Photobiol.* **1981**, *34*, 17.

(18) Pilipenko, A. T.; Volkova, A. I.; Shevchenko, T. L. *Zh. Anal. Khim.* **1974**, *29*, 983.

(19) Timpe, H.-J.; Neuenfeld, S. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 1347.

(20) Encinas, M. V.; Lissi, E. A.; Rufs, A. M.; Previtali, C. M. *J. Polym. Sci., Polym. Chem.*, in press.

(21) Lougnot, D. J.; Turck, C.; Fouassier, J. P. *Macromolecules* **1989**, *22*, 108.

(22) Encinas, M. V.; Guzman, E.; Lissi, E. A. *J. Phys. Chem.* **1983**, *87*, 4770.

(23) Encinas, M. V.; Lissi, E. A. *J. Photochem.* **1985**, *29*, 385.

(24) Neumann, M.; Previtali, C.; Encinas, M. V., unpublished results.

(25) Hub, W.; Schneider, S.; Dorr, F.; Oxman, J. D.; Lewis, F. D. *J. Am. Chem. Soc.* **1984**, *106*, 701.

(26) Hamanoue, K.; Nakayama, T.; Ibuki, K.; Otani, A. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3731.

(27) Timpe, H.-J.; Neuenfeld, S. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2329.