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The mechanism of the photoinitiation of the polymerization of MMA by the thionine–triethanolamine system

Miguel G. Neumann* and Maira R. Rodrigues
Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, 13560-970 São Carlos SP, Brazil

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Methyl methacrylate (MMA) has been photopolymerized in methanol using the photoinitiation system formed by the dye thionine and triethanolamine as co-initiator. In the absence of amine no polymerization was observed, and at very high concentrations of the amine the polymerization rate decreased. The maximum polymerization rate was obtained with around 0.3 M amine. The individual rate constants for the reactions involved in the photoinitiation process have been determined by static fluorescence for the singlet state and flash photolysis for the triplet states. A mechanism is presented for the photoinitiation, from which polymerization rates could be calculated using the rate constants for each of the steps. These results were consistent with the measured experimental polymerization rates. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: photopolymerization; thionine; photoinitiation)

INTRODUCTION

Photoinitiated polymerization in the presence of photoreducing dyes and an electron donor has been studied quite frequently in the last few years[1–7]. The interest in these systems arises because of the possibility of initiating the polymerization with visible light fonts (arc lamps or lasers) in applications such as the manufacture of lithographic printing plates without film intermediates[8], the production of three-dimensional topographical maps[9], the manufacture of contact lenses and photopolymerizable resin composites for various uses. The use of dyes is especially interesting because of their high molar absorptivities, which allow the use of minimal amounts of the absorbing species, and their relatively low oxidation potential, which increases the initiating radical yields.

The first study using amines as reducing agents was reported by Chen, who investigated the polymerization of acrylamide by Methylene Blue/triethanolamine[10]. Photoinitiated polymerization has been described in homogenous aqueous solution, organic solvents, micelles and inverse microemulsion[11]. Quite a number of studies have been carried out on the photoinitiated polymerization of methyl methacrylate (MMA), in which the effects of the solvent, monomer, photoinitiator and co-initiator concentration were evaluated[12–15]. In the photoinitiated polymerization of MMA in SDS or CTAC micelles, the role of different factors, such as localization, electronic effects, monomer quenching rates, electron and proton transfer processes, radical exit from the micelle and acid–base equilibrium, have been discussed[16].

In general, not many studies have been carried out on the mechanism of the interaction of an excited dye with aliphatic amines, which is very important in order to understand the processes occurring in the early stages of photoinitiated polymerization. Timpe *et al.*[17–19] and Fouassier *et al.*[20] presented several studies in which relationships between the photochemistry of dyes were correlated with the yields of dye-initiated acrylic polymerizations. Recently, the effect of a magnetic field, which leads to an increase in the polymerization rate[21], has been studied.

Recently, we studied the photoinitiated polymerization of hydroxyethyl methacrylate by Safranine/aliphatic amine systems in organic[22] and aqueous solutions[23], and proposed a reaction mechanism based on studies of the elementary reactions of the excited species present in those systems[24,25]. A similar study of the reactions of derivatives of thioxanthones was also undertaken with the purpose of evaluating the initial steps in the photoinitiation by these compounds[26].

In the present work, we present results for the photopolymerization of methyl methacrylate (MMA) in the presence of thionine (TH^+) and triethanolamine (TEAOH), as well as a study of the mechanism leading to the initiating free radicals.

EXPERIMENTAL

Chemicals

The monomer, methyl methacrylate (MMA; Merck), was distilled on an ice bath under reduced pressure in the presence of hydroquinone, washed with 5% NaOH in water and dried over $CaCl_2$. The amines (diethanolamine, Merck; di-*n*-butylamine, Aldrich; di-*n*-propylamine, Aldrich; triethanolamine (TEAOH), Merck; triethylamine, Merck; *sec*-butylamine, Merck) were vacuum-distilled before use, and the dye thionine was used as received.

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* To whom correspondence should be addressed. Fax.: xx55-16-274-9205; e-mail: neumann@iqsc.usp.sc.br

Measurements

The light-induced polymerizations were performed by irradiating 5 ml cells containing thionine 0.8×10^{-5} M in methanol/MMA (1:1) solutions with two 26 W Osram Dulux D lamps, in the presence of known amounts of the amine. The solutions were deoxygenated by thoroughly bubbling oxygen-free nitrogen.

After irradiation the polymers were precipitated, washed with ice-cold methanol and dried. The polymerization rate was evaluated from gravimetric measurements[27] according to

$$R_p = \frac{W}{VtM_w} (M/s) \qquad (1)$$

where W is the weight of polymer formed, V is the volume of the solution (l), t is the time (s), and M_w is the molecular weight of the monomer.

The initial rate was determined from the initial slope of a plot of monomer conversion as a function of irradiation time[16,28].

Fluorescence quenching experiments were carried out at room temperature (25 ± 1°C) using an Aminco Bowman spectrofluorimeter. Thionine (0.8×10^{-5} M) in methanol was excited at 600 nm and the emission was adjusted at the emission maximum. Transient absorption spectra and triplet quenching were determined with an Applied Photophysics laser kinetic spectrometer. Excitation at 532 nm was accomplished using an Nd–YAG laser (Spectron) with frequency doubling, with detection by a Hamamatsu R928 photomultiplier.

Table 1 Rate constants for the quenching of the excited states of thionine by amines in methanol

Amine	^1k_q (M^{-1} s^{-1})	^3k_q (M^{-1} s^{-1})	$E_{1/2}$ (V)^a	pK_b
sec-Butylamine	3.44×10^{10}	3.38×10^{8}	1.62.	3.05
Di-*n*-propylamine	3.15×10^{10}	2.96×10^{8}	0.93	3.07
Di-*n*-butylamine	2.88×10^{10}	2.95×10^{8}	0.87	3.20
Triethylamine	2.60×10^{10}	2.41×10^{8}	0.66	3.22
Diethanolamine	1.21×10^{10}	2.27×10^{8}	–	5.11
Triethanolamine	0.80×10^{10}	1.64×10^{7}	–	6.15
Anisole	2.26×10^{9}	–	1.79	
MMA	–	5.02×10^{4}	–	

^{a}Determined in acetonitrile *versus* an Ag/Ag$^+$ electrode. Taken from Ref.[29]

For the fluorescence quenching experiments, the solutions were air- equilibrated. For the triplet studies they were deaerated by bubbling oxygen-free nitrogen.

The pK_b values of the amines in water were obtained potentiometrically at 25°C. When available, the values were very close to those found in the literature[29].

RESULTS AND DISCUSSION

Thionine quenching by amines

The absorption and emission spectra of thionine did not undergo any changes in the presence of the amines, indicating that there is no interaction between these compounds and the ground state of the dyes, at least in the range of concentrations used in this work. On the other hand, the formation of dimers of the dye could also be ruled out as no alteration in the spectrum was observed in the region corresponding to those aggregates. Note that the relatively low aggregation constant (around 800 in water), the use of organic solvents, and the low concentration of thionine (about 10^{-5} M) contribute to avoid the metachromatic effect.

The rate constants for the quenching of the singlet state of the dye by amines shown in *Table 1* were determined from the corresponding Stern–Volmer plots, using 0.5 ns for the lifetime of singlet thionine. These values are near the diffusional limit in methanol (about 1.2×10^{10} M^{-1} s^{-1}). No correlation is found with the pK_b of the amines[30], but when adding to the set the quenching by anisole, a clear correlation can be found with the quencher oxidation potential increase.

Thionine in methanol, in the concentration used, shows significant absorption at 532 nm. The absorption spectra measured after the addition of amines and MMA are similar to those in pure methanol.

The transient absorption spectrum of TH^+ in methanol (*Figure 1*), shows absorption peaks with maxima at 770 and 415 nm, which are assigned to the monoprotonated triplet $^3TH^+$[11,31,32]. The addition of alkylamines increases the transient absorption at the shorter wavelength, due to the fact that the unprotonated triplet (^3T) also absorbs in that region. The bimolecular quenching rate constants by amines ($k_q(T)$) were obtained from the decay of the absorption of the triplet at 770 nm as a function of amine concentration

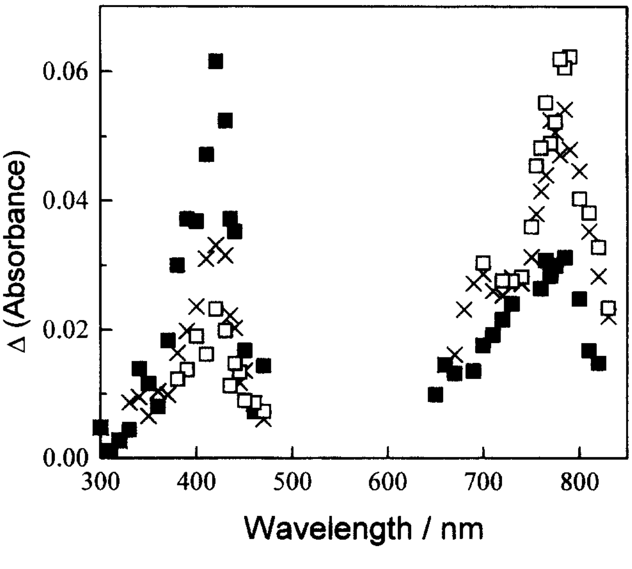


Figure 1 Transient spectra of 0.8×10^{-5} M thionine in methanol (□) taken 2 μs after the flash and in the presence of (×) 1×10^{-4} M TEAOH and (■) 2×10^{-3} M TEAOH

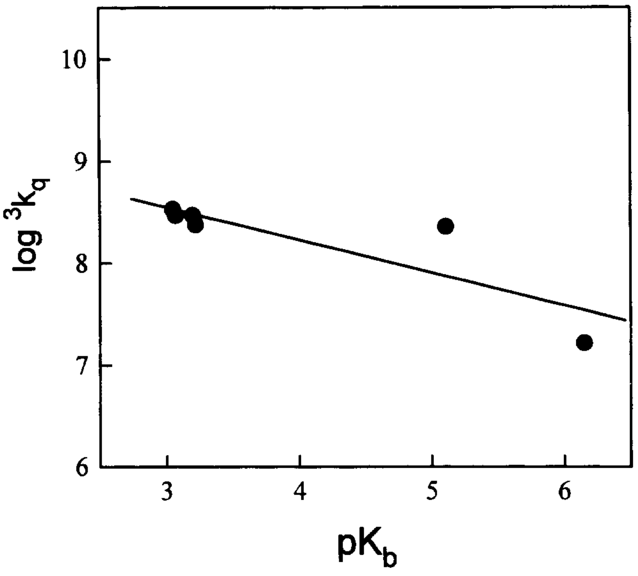


Figure 2 Dependence of the quenching rate constants of $^3TH^+$ by amines on their basicities

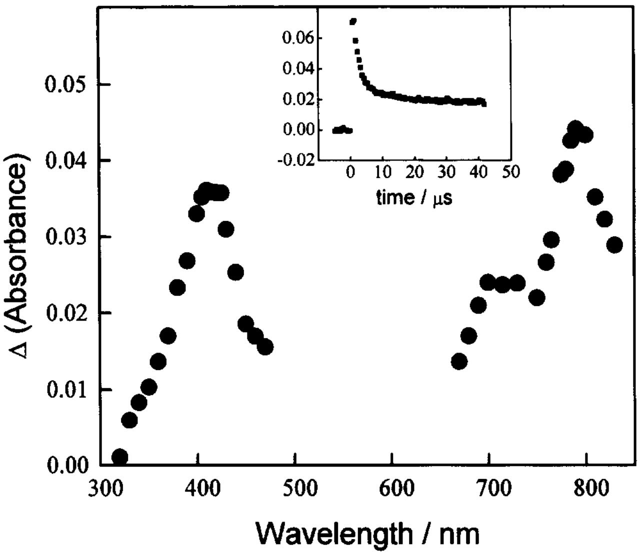


Figure 4 Transient spectrum of 0.8×10^{-5} M thionine in MMA/methanol (1:1) taken 2 μs after the flash. Inset: decay trace at 770 nm

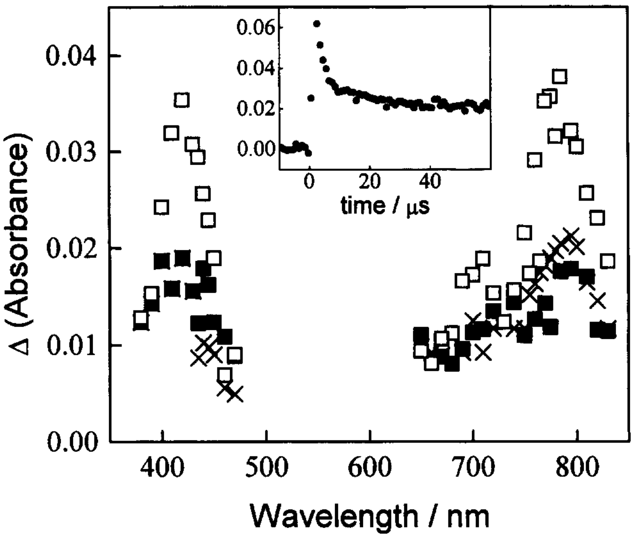


Figure 3 Transient spectra of thionine in 0.8×10^{-5} M methanol in the presence of 0.5×10^{-3} M TEAOH, taken (□) 2 μs, (×) 4 μs, and (■) 20 μs after the flash. Inset: decay trace at 415 nm

using 7.5 μs for the triplet lifetime, and are shown in *Table 1*. These values seem to be little affected by the oxidation potentials of the amines, and remain almost constant at about $3 \times 10^8\ M^{-1}\ s^{-1}$ for $V_{1/2}$ ranging from 1.66 to 0.62 V. These values are two orders of magnitude lower than the diffusional limit in the solvent used, and mean that the reaction is not controlled by diffusion. There seems to be no good reason for this non-dependence of the triplet quenching rate constants on the nature of the amines; nevertheless, the same effect was observed for the quenching of the triplet of the similar dyes Methylene Blue and some of the Azures[33] by aliphatic amines. On the other hand, there seems to be a certain dependence with those constants on the pK_b of the amines (shown in *Figure 2*), as is also found for the quenching of the dye Safranine by alkylamines.

It can be seen from the inset in *Figure 3* that, after an initial fast decay, the absorption at 415 nm remains reasonably constant, indicating the formation of a long-lived species that also absorbs at this wavelength. This absorption remains practically constant up to 100 μs. From its rather long lifetime, it has been concluded that it corresponds to the basic form of semireduced thionine TH•[30].

The Stern–Volmer constant for the quenching of the unprotonated triplet ^3T by TEAOH has been determined in solutions previously adjusted to pH 12 by the addition of a solution of NaOH. The K_{SV} measured for this system is $282\ M^{-1}$, whereas that for the protonated triplet was $198\ M^{-1}$.

Thionine quenching by methyl methacrylate

The addition of MMA to thionine did not change the absorption or emission spectra of the dye. Fluorescence was not quenched by the presence of the monomer.

On the other hand, when the solvent is MMA/methanol (1:1), the transient spectrum shows an increase in the 700–720 nm region (*Figure 4*). The decay at 770 nm corresponds to a lifetime of 2.5 μs (inset in *Figure 4*). A residual long-lived absorption is also observed, which is assigned to the protonated semireduced radical $TH_2^{•+}$[30].

Polymerization

Photopolymerization of MMA in methanolic solution (1:1) is negligible in the presence of TH^+ alone. However, when amines are added to the solution, the polymerization proceeded readily, with rates depending mainly on the pK_b of the amines, as shown in *Table 2*. The rates of the photoinitiated polymerization increased with amine concentration, reaching a maximum around 0.3 M. Further addition of amine slowly reduces the polymerization rates (*Figure 5*).

A mechanism consistent with the results found for the photochemical behaviour of thionine in the presence of amine in methanolic solution is given in *Scheme 1*. TH_0^+, $^1TH^+$ and $^3TH^+$ denote the ground state, the excited singlet and triplet forms of the monoprotonated dye, respectively, and ^3T denotes the unprotonated triplet and TH• the semireduced radical.

The amine radical originating from the deprotonation of the cation radical of the amines (reaction 9) has been proved to be responsible for the chain initiation in many photoinitiated polymerizations. Therefore, in order to be able to

Table 2 Photoinitiated polymerization rates for methyl methacrylate in the presence of 0.8 × 10^{-5} M thionine and 0.1 M amine in MMA/methanol (1:1) at 33.5°C

Amine	R_p ($M\ s^{-1}$)
Di-*n*-butylamine	0.0044
Triethylamine	0.0066
Diethanolamine	0.00029
Triethanolamine	0.012

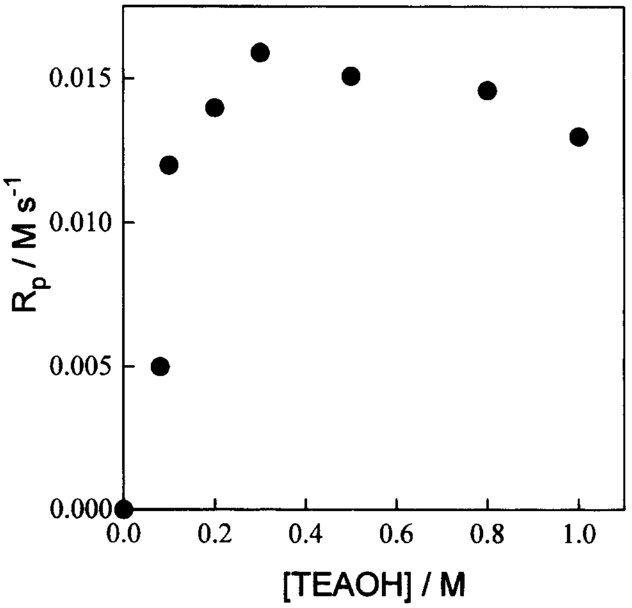
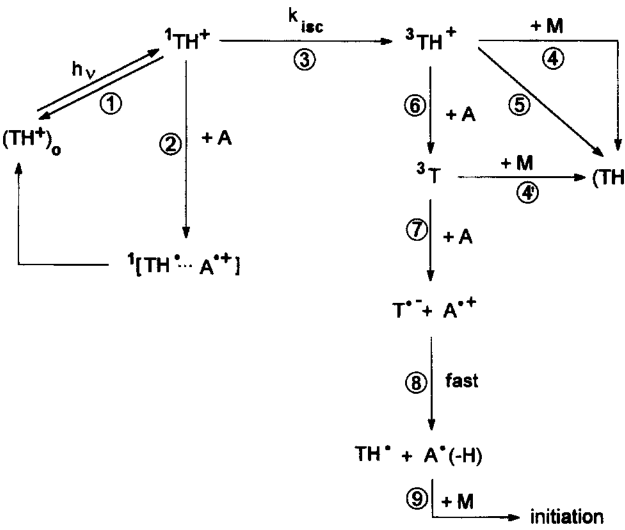


Figure 5 Polymerization rate (R_p) of MMA in the presence of TH^+/TEAOH as a function of TEAOH concentration, after 4 h irradiation



Scheme 1

predict the polymerization rate, one has to take into account all the reactions that lead (or precede) the formation of this radical. The decrease in the polymerization yield as well as the lower yield of semireduced thionine observed at high amine concentrations indicate that the active radicals arise from the interaction of the thionine triplet with the amine. The quenching of the singlet state (reaction 2), due to its spin characteristics, does not lead to the formation of free radicals but to deactivation of the dye to its ground state. Therefore, in the presence of high concentrations of amine, the excited dye molecules will be intercepted at the singlet level, avoiding its conversion to triplets and eventual formation of free radicals.

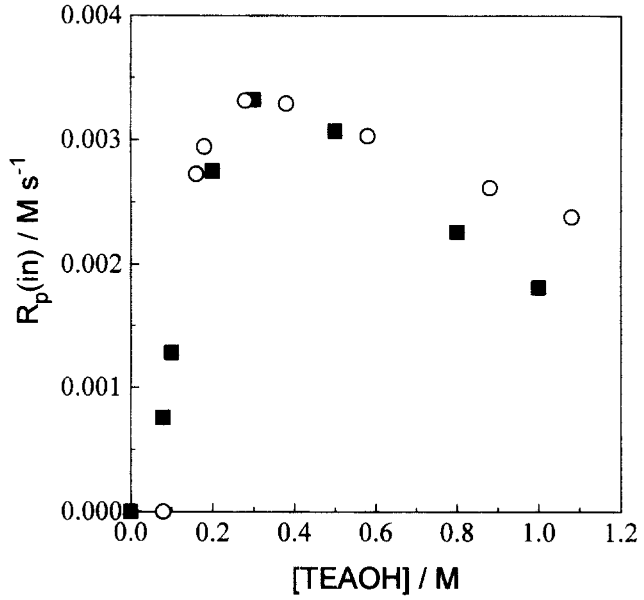


Figure 6 Initial polymerization rates for MMA in the presence of thionine and amine, compared with the normalized yield of semithionine (○) calculated using equation (2)

The interaction of the excited states of thionine with MMA does not lead to polymerization. As stated above, there is no reduction of the dye fluorescence in the presence of the monomer. The quenching of the triplet states by MMA (reactions 4 and 4′) has rate constants about 2–3 orders of magnitude lower than that for the quenching by amines, and seems not to provide additional radicals for the photoinitiation process. On the other hand, as the concentration of monomer is rather high, this interaction will divert some of the triplets from the pathway to the radicals.

The values of the initial polymerization rates R_p(in) were obtained from the zero-time extrapolation of plots of the polymerization rates (R_p), as defined in equation (1), *versus* irradiation time, as a function of TEAOH concentration. These values are plotted in *Figure 6* together with the radical yield φ_{rad} calculated from equation (2)

$$\varphi_{rad} = \eta \frac{1}{1 + {}^1K_{SV}[A]} \times \frac{{}^3K_{SV}[A]}{1 + {}^3K_{SV}([A] + r)} \times \frac{{}^{3d}K_{SV}[A]}{1 + {}^{3d}K_{SV}([A] + r)} \qquad (2)$$

where ${}^1K_{SV}$, ${}^3K_{SV}$, and ${}^{3d}K_{SV}$ are the Stern–Volmer constants for the quenching of the singlet and protonated and unprotonated triplets of the dyes: 1.47 M^{-1}, 197 M^{-1}, and 282 M^{-1}, respectively; η is a proportionality factor that includes the initiation efficiency of the radicals; and r is a correction factor that takes into account the quenching of triplets by the monomer. This factor is obtained from the ratio between the rate constants for the quenching of the triplets by the amine and the monomer

$$r = \frac{k_{q,M}}{k_{q,A}} \times [M] \qquad (3)$$

Using the values in *Table 1* and considering that the concentration of monomer in a MMA/methanol (1:1) solution is about 5 M, a value of 0.02 can be evaluated for *r*. Although the quenching rate constant for the deprotonated triplet by the monomer was not determined, the ratio between both quenching rates can be assumed to be similar to that for the other triplet.

A good coincidence can be observed between both sets of points, as shown in *Figure 6*. There seems to be a small induction concentration that could be traced to the consumption of some radicals by residual oxygen or some other radical trap dissolved in the solution. The larger decrease at higher amine concentrations can be ascribed to the presence of unprotonated ground state thionine even before the onset of the photoreaction.

CONCLUSIONS

The quenching of the singlet state of thionine by amines takes place by a charge-transfer mechanism while a different mechanism seems to be operating for the triplet state quenching, showing quenching rate constants of about $10^8\ M^{-1}\ s^{-1}$. The transient absorption observed at 415 nm, after addition of the amine, is assigned to basic semithionine (TH•). These results can be explained assuming that the ^3T quenching by the amine proceeds by a process that involves an electron transfer from the amine to the unprotonated dye triplet, followed by a fast proton transfer to form the monoprotonated semireduced thionine and the amine radical.

Triethanolamine is the most efficient co-initiator for the thionine photoinitiated polymerization of methyl methacrylate in methanol (1:1). The polymerization rates increase with amine concentration, reaching a maximum around 0.3 M; further addition of amine reduces the rates, due to the decrease in the concentration of initiating radicals caused by the quenching of the singlet state of the dye.

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REFERENCES

1. Oster, G., *Photogr. Eng.*, 1953, **4**, 173.
2. Yoshida, Z., *Kogyo Kagatu Zasshi*, 1957, **60**, 1161.
3. Toppet, S. and Delzenne, G., *J. Polym. Sci., Part A*, 1964, **2**, 1539.
4. Koizumi, M. and Kumora, Z., *J. Inst. Polytech., Osaka City Univ., Ser. C*, 1951, **2**, 1.
5. Lenka, S., Navak, P. L. and Mohanty, I. B., *Polym. Photochem.*, 1986, **7**, 49.
6. Tsibouklis, J. and Feast, W. J., *Trends Polym. Sci.*, 1993, **1**, 16.
7. Neckers, D. C., *J. Chem. Educ.*, 1987, **64**, 649.
8. Vollman, H. W., *Angew. Chem. Int. Ed.*, 1980, **19**, 99.
9. Claus, C. J., Krohn, I. T. and Swanton, P. C., *Photogr. Sci. Eng.*, 1966, **5**, 211.
10. Chen, C., *J. Polym. Sci., Part A*, 1965, **3**, 1107, 1127, 1137, 1155.
11. Lissi, E. A. and Encinas, M. V., *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17**, 2791.
12. Encinas, M. V., Lissi, E. A., Majmud, C. and Cosa, J. J., *Macromolecules*, 1993, **26**, 6284.
13. Encinas, M. V., Majmud, C. and Lissi, E. A., *J. Polym. Sci., Part A*, 1990, **28**, 2465.
14. Li, Z., Kubota, H. and Ogiwara, Y., *J. Appl. Polym. Sci.*, 1982, **27**, 1465.
15. Encinas, M. V., Garrido, J. and Lissi, E. A., *J. Appl. Polym. Sci.*, 1989, **27**, 139.
16. Lougnot, D. J., Tyrck, C. and Fouassier, J. P., *Macromolecules*, 1989, **22**, 108.
17. Timpe, H.-J., Jockush, S. and Körner, K., in *Radiation Curing in Polymer Science and Technology*, Vol. II, ed. J. P. Fouassier and J. F. Rabek, Elsevier Applied Science, London, 1993, p. 575.
18. Timpe, H.-J. and Neuenfeld, S., *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2329.
19. Timpe, H.-J. and Neuenfeld, S., *J. Polym. Sci. A, Polym. Chem.*, 1993, **31**, 1347.
20. Fouassier, J. P. and Chesneau, E., *Makromol. Chem.*, 1991, **192**, 245.
21. Vedeneev, A. A., Khudyakov, I. V., Golubkova, N. A., Kuzmin, V. A. and Irinyi, G., *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 3545.
22. Previtali, C. M., Bertolotti, S. G., Neumann, M. G., Pastre, I. A., Rufs, A. M. and Encinas, M. V., *Macromolecules*, 1994, **27**, 7454.
23. Encinas, M. V., Rufs, A. M., Neumann, M. G. and Previtali, C. M., *Polymer*, 1996, **37**, 1395.
24. Encinas, M. V., Previtali, C. M., Bertolotti, S. G. and Neumann, M. G., *J. Photochem. Photobiol. A*, 1995, **62**, 65.
25. Encinas, M. V., Previtali, C. M., Gehlen, M. H. and Neumann, M. G., *Photochem. Photobiol.*, 1996, **94**, 237.
26. Neumann, M. G., Gehlen, M. H., Encinas, M. V., Allen, N. S., Corrales, T., Peinado, C. and Catalina, F., *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 1517.
27. Lenka, S. and Mohanty, J., *J. Polym. Photochem.*, 1986, **7**, 447.
28. Kumar, S. G. and Neckers, D. C., *Macromolecules*, 1991, **24**, 4322.
29. Bard, A. J. and Lund, H., *Encyclopedia of the Elements, Organic Section*, Vol. XV, Marcel Dekker, New York, 1984.
30. Vogelmann, E., Schreiner, S., Rauscher, W. and Kramer, H. E. A., *Z. Phys. Chem., Neue Folge*, 1975, **101**, 21.
31. Wildes, P. D. and Lichtin, N. N., *J. Phys. Chem.*, 1978, **82**, 981.
32. Ferreira, M. I. C. and Harriman, A., *J. Am. Chem. Soc.*, 1976, **21**, 1085.
33. Previtali, C. M., personal communication, 1997.