ELSEVIER

Polymer 43 (2002) 4591–4597

polymer

www.elsevier.com/locate/polymer

Photochemical study and photoinitiation activity of macroinitiators based on thioxanthone

T. Corrales[a], F. Catalina[a], C. Peinado[a], N.S. Allen[b], A.M. Rufs[c], C. Bueno[c], M.V. Encinas[c,*]

[a]Instituto de Ciencia y Tecnología de Polímeros, C.S.I.C., Juan de la Cierva 3, 28006 Madrid, Spain
[b]Department of Chemistry, Faculty of Science and Engineering, Manchester Metropolitan University, Manchester M1 5GD, UK
[c]Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40 Correo 33, Santiago, Chile

Received 2 October 2001; received in revised form 16 April 2002; accepted 13 May 2002

Abstract

In this work we studied the photopolymerization of methyl methacrylate using polymeric initiators based on thioxanthone chromophore. As co-initiator were used low molecular weight tertiary amines and bound to a polymer chain. The photoinitiation efficiency of these systems was compared with that of the corresponding low molecular weight analogue. A higher efficiency was obtained with the system comprising the thioxanthone bound to a polymer chain and the free amine. The results carried out with low molecular weight TX and the polymeric co-initiator showed that the efficiency is independent of the amount of amine units in the polymer chain. The photophysics of the different systems show that the polymer chain does not affect the emission characteristics of the thioxanthone chromophore. Bimolecular rate constants for the singlet and triplet quenching of thioxanthone by the amine were determined using fluorescence and laser flash photolysis techniques. The dependence of the photoinitiation efficiency with the amine concentration was simulated from the measured quenching rate constants, and shows that the active radicals are produced from the interaction of the ketone triplet with the amine. The ketyl radical yield was slowly higher for the thioxanthone bound to the polymer. The difference between the photoinitiation activity of the polymeric system and the low molecular weight models is explained in terms of the effect of the polymer chain on the reactivity of the amino radicals. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Photoinitiation activity; Macroinitiator; Thioxanthone

1. Introduction

Recently polymeric photoinitiators have been the subject to an increased research interest since they offer some advantages compared with their corresponding low molecular weight analogues in the UV curing applications. These advantages are derived from the macromolecular nature of these compounds. The photoinitiation activity can be improved as a result from energy migration along the polymer chain. Intramolecular reactions can produce the formation of more reactive species. The macromolecular chain can protect the active species, similar to a cage effect. They offer the possibility of macromolecular design in content of the pendant photosensitive moieties and nature of the comonomer giving different properties to the polymeric photoinitiator. The presence of the polymer chain reduces the migration rates, and in many cases improves the solubility.

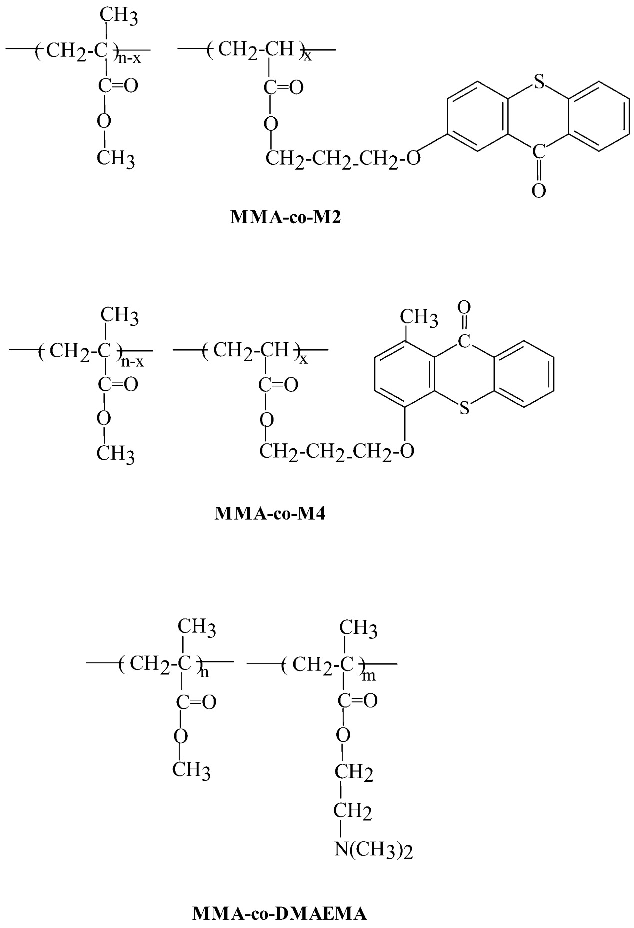
There are many studies concerning to bimolecular polymeric photoinitiators [1–3]. Most of them indicate an increase of the photoinitiation efficiency, compared with the low molecular weight system, when the photoinitiator is incorporated to a polymer backbone and the co-initiator is a free tertiary amine. This increase in photoinitiation efficiency is not observed when both the initiator and the amine are bound to the same macromolecule. In spite of this extensive work, there are few systematic studies on the relation between the photochemical behaviour and the photoinitiation efficiency of these systems.

In a previous work, we have synthesized two new acrylic derivatives of thioxanthone and we have found that the photoinitiation activity is similar to that of the corresponding structural model compounds [4]. In this paper we studied two novel polymeric photoinitiators obtained by copolymerization of these acrylic derivatives of the thioxanthone chromophore with methyl methacrylate

---

* Corresponding author.
E-mail address: mencinas@lauca.usach.cl (M.V. Encinas).

0032-3861/01/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(02)00310-5



Scheme 1.

(MMA). As co-initiators were used 2-(diethylamino)ethanol (DEOHA), and the homopolymer of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and its copolymers with MMA (Scheme 1). The aim of this work is to relate the initiation efficiency of these compounds with their photochemical behaviour under the polymerization conditions.

2. Experimental

2.1. Material

DEOHA, MMA, and DMAEMA were obtained from Aldrich and were purified by vacuum distillation before use. 2,2′-azobis-(isobutyronitrile) (AIBN) was recrystallized from ethanol. 2-(3′-acryloxy)propoxythioxanthone (M-2) and 1-methyl-4-(3′-acryloxy)propoxy-thioxanthone (M-4) were synthesized following the procedures described in Ref. [5]. Copolymers of M-2 and M-4 with MMA were prepared by radical polymerization using AIBN, as previously described [5]. The content of thioxanthone chromophore in the polymer was 2%. Homopolymer of DMAEMA and its copolymers with MMA were obtained by polymerization in benzene using AIBN as photoinitiator. The polymers were purified by precipitation from methanol. The composition of the copolymers was determined by ^{1}H NMR and is expressed as the fraction of DMAEMA units in the polymer chain.

2.2. Measurements

MMA polymerization rates (Rp) were measured dilatometrically in acetonitrile and benzene solutions (monomer/solvent (1:1) v/v), at 25 °C. The dilatometer, filled with the polymerizable solutions, previously degassed, was irradiated with a medium pressure Hg lamp using a glass filter with the transmission band centred at 366 nm. Rates were measured at low conversion ($<10\%$). The dilatometer was calibrated relating the volume contraction with the amount of the formed polymer.

The molar mass of the obtained polymers was measured using gel permeation chromatography (GPC), with a M-45 Waters high pressure pump and a U6K injector. Ultrastyragel gel permeation columns were employed. A previous calibration was carried out with a series of polymethacrylate standards with a narrow molar mass distribution.

UV spectra were recorded on a Hewlett-Packard diode array spectrophotometer. Steady-state fluorescence measurements were carried in a Spex Fluorolog spectrofluorimeter. Fluorescence quantum yields were obtained using quinine sulphate in 1N H_2SO_4 as standard. The absorbance values of the samples at the excitation wavelength were lower than 0.1 for 1 cm pathlength. Fluorescence lifetimes were measured with an Edinburgh Instruments OB 900 time correlated single photon counting fluorimeter, using an hydrogen filled lamp for excitation. Flash photolysis studies were done using a Nd-YAG laser with excitation pulse at 355 nm. The signals from the monochromator/photomultiplier system were captured by a HP54504 digitizing oscilloscope and transferred to a computer for storage and analysis.

3. Results and discussion

3.1. Polymerization studies

Rp were obtained from the initial slope of the conversion versus time plots. Rp of MMA in acetonitrile using the thioxanthone incorporated to the polymer chain and the low molecular weight ketone as photoinitiators in the presence of several DEOHA concentrations are shown in Fig. 1. These results show that using thioxanthones as photoinitiators with 2-propoxy substituent, the Rp increases with the amine concentration reaching a constant value at ~15 mM DEOHA. Further amine addition slowly decreases the Rp, whereas for the macroinitiator and the model with a methyl substituent at position 1 of the thioxanthone ring, the maxima Rp is reached at much higher

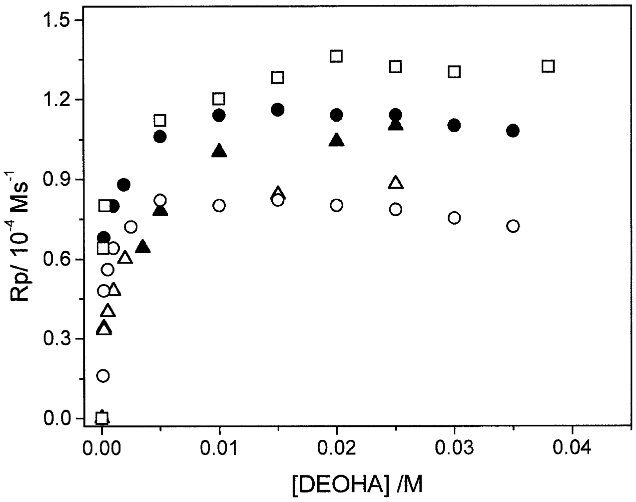


Fig. 1. MMA Rp as function of the amine concentration. Acetonitrile/monomer (1/1), photoinitiators: (•) MMA-*co*-M2; (○) M-2; (▲) MMA-*co*-M4; (△) M-4. Benzene/monomer (1/1): (□) MMA-*co*-M2.

amine concentrations. On the other hand, it is interesting to note that at all amine concentrations the macroinitiator is more efficient than the corresponding low molecular weight analogue. This increased activity has also been described for several bimolecular macroinitiators based on thioxanthone or benzophenone chromophores [6–10].

The poly(methylmethacrylates) obtained in the experiments carried out with the different photoinitiators and constant amine concentration (1 mM) were characterized by GPC. The ratios between the propagation rate constant and the square root of the termination rate constant, $k_p/k_t^{1/2}$, were obtained from these data using the well known simplified Mayo equation in the following form [11]

$$\frac{1}{X_n} = 1.72\frac{k_t\mathrm{Rp}}{k_p^2[M]^2} \qquad (1)$$

where X_n is the average chain length, and $[M]$ is the monomer concentration. The value obtained of $k_p/k_t^{1/2}$ was $0.060 \pm 0.007\ \mathrm{M}^{-1/2}\ \mathrm{s}^{-1/2}$, which is close to that reported in the literature ($0.066\ \mathrm{M}^{-1/2}\ \mathrm{s}^{-1/2}$) for the polymerization of MMA at 30 °C initiated by AIBN, where chain transfer reactions or primary radical termination are negligible [12]. This result, together with the half-order with respect to the initiator and first-order with respect to the monomer, previously found for related thioxanthone derivatives [4], indicate that degradative chain transfer or termination by primary radicals can be considered negligible irrespectively of the photoinitiator. Then, at low conversion, the Rp can be expressed by the classical kinetic law

$$\mathrm{Rp} = \left(k_p/k_t^{1/2}\right)\Phi_i^{1/2}I_a^{1/2}[M] \qquad (2)$$

The photoinitiation efficiencies were evaluated with respect to that obtained with AIBN as photoinitiator. Under matched absorption conditions, and at the same monomer concentration, Eq. (2) leads to Eq. (3)

Table 1
MMA Rp photoinitiated by M-2, in the presence of DEAEMA and MMA-*co*-DMAEMA copolymers, 20 mM amine. Monomer/benzene 1:1 (v/v), 25 °C

Fraction of amine units	Rp (10^{-4} M/s)
Monomer	1.0
0.11	1.2
0.40	1.3
1.00	1.3

$$\Phi_{\mathrm{TX}}/\Phi_{\mathrm{AIBN}} = (\mathrm{Rp})^2_{\mathrm{TX}}/(\mathrm{Rp})^2_{\mathrm{AIBN}} \qquad (3)$$

From Eq. (3) and taking the photoinitiation quantum yield of AIBN, $\Phi_{\mathrm{AIBN}} = 0.4$ [13], it was obtained at 20 mM DEOHA photoinitiation efficiencies (Φ_{TX}) of 0.24 and 0.11 for MMA-*co*-M2 and M-2, respectively. Thus, the thioxanthone with 2-propoxy substituent presents a photoinitiation efficiency two times higher when it is bound to a polymer chain.

Rp of MMA photoinitiated by MMA-*co*-M2 were also measured in benzene as solvent, Fig. 1. Benzene is a good thermodynamic solvent for MMA increasing the size of the polymer coil. These results show that Rp are higher than that found in acetonitrile, a θ solvent for the poly(methyl methacrylate) [14]. However, an increase on Rp in benzene also was found when it was used as photoinitiator M-2. Rp is 1.2 times higher in benzene. This increase in Rp cannot be due to changes in k_p or k_t values since the ratio $k_p/k_t^{1/2}$ for MMA polymerization in benzene and acetonitrile are similar [13]. Then, these results suggest a solvent effect on the initiation mechanism, similar for the low and high molecular weight photoinitiator. Thus, the expected polymer effect due to the thermodynamic quality of the solvent can be disregard in this system.

Rp were also measured using the M-2 low molecular weight thioxanthone derivative, and the homopolymer of DMAEMA and its copolymers with MMA as co-initiators. Table 1 shows data obtained with M-2 in benzene at 20 mM amine. It can be observed that the Rp is slightly higher for the polymeric co-initiator, and is almost independent of the amount of amine units in the polymer chain. This lack of polymer effect for systems where the co-initiator is incorporated to a macromolecule has also been reported for some photoinitiators based on benzophenone chromophore bound to silane and acrylic polymers [8,15].

3.2. Photochemical studies

UV absorption spectra of copolymers bearing thioxanthone groups, MMA-*co*-M2 and MMA-*co*-M4, are superimposed to those of their corresponding models, M-2 and M-4. So that there is no interaction between thioxanthone chromophores and the polymer chain in the ground state.

Table 2
Fluorescence quantum yields and fluorescence lifetimes for thioxanthone derivatives

Thioxanthone	Φ_F		$^1\tau$ (ns)	
	Acetonitrile	Acetonitrile/ethyl acetate	Acetonitrile	Acetonitrile/ethyl acetate
MMA-*co*-M2	0.22	0.17	4.93 (75.2%) 1.98 (24.8%)	4.66 (72.6%) 1.73 (27.4%)
M-2	0.20	0.16	5.1 (83.2%) 2.1 (16.8%)	4.52 (76.5%) 1.79 (23.5%)
MMA-*co*-M4	0.001	0.001	0.65	0.60
M-4	0.008	0.001	0.68	0.50

Fluorescence emission maximum wavelengths for copolymers MMA-*co*-M2 and MMA-*co*-M4 are in similar position to those of M-2 and M-4 models. The fluorescence quantum yield and fluorescence lifetimes of the copolymers and the corresponding models in acetonitrile and acetonitrile/ethyl acetate are shown in Table 2. The latter solvent mixture can be considered to provide a medium of polarity similar to that afforded by acetonitrile/MMA. These data show that the polymer chain does not affect the emission characteristics. The fluorescence quantum yield for the compounds with a methyl group in position 1 is more than one order of magnitude lower than that of thioxanthone with the propoxy group in position 2 (Table 2). These facts are similar to those we have described for low molecular weight thioxanthone derivatives [16]. Donor substituents in position 2 increase the separation of the nπ^* and $\pi\pi^*$ excited states, reducing the intersystem crossing associated to the increase of the $\pi\pi^*$ character of the S_1.

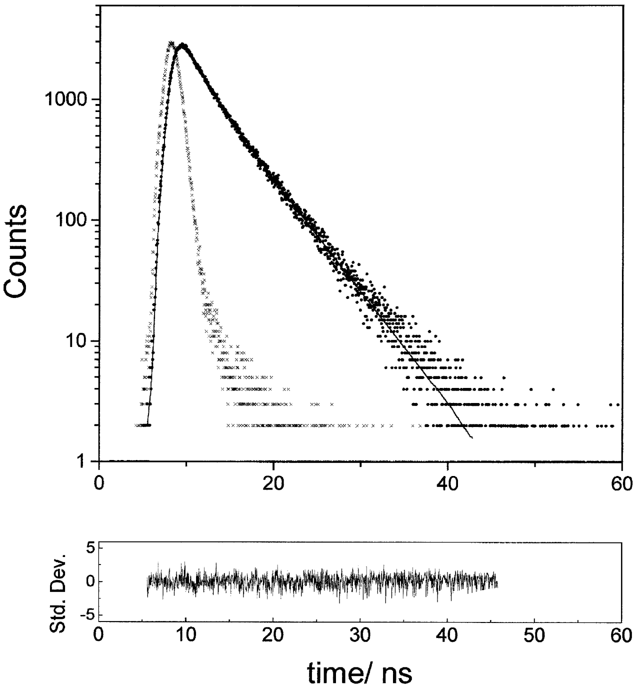


Fig. 2. Fluorescence decay of MMA-*co*-M2 in acetonitrile/ethyl acetate (1/1). (xx) is the lamp profile. The solid line is the fitting to a biexponential decay.

Fluorescence lifetimes of copolymers, similar to the model compounds, increase with the solvent polarity, and compounds with the *n*-propoxy group in position 2 have a biexponential decay. Fig. 2 shows the fluorescence decay of MMA-*co*-M2 in acetonitrile/ethyl acetate at room temperature and the biexponential fitting with two components of 4.66 and 1.73 ns. The presence of a short component in the decay of the thioxanthone chromophore with an ether group in position 2, has been explained in terms of solvent relaxation and intramolecular reorganization of the substituent in the excited state [16]. These effects are also present when the chromophore is bound to a polymer chain.

Singlet quenching rate constants (^1k_q) calculated from the decrease of the fluorescence intensity combined with the lifetime or average lifetimes are given in Table 3. The singlet quenching by DEOHA is a nearly diffusional controlled process, even in media of relative low polarity as benzene. This behaviour holds for both the copolymers and also the low molecular weight compounds. Fluorescence lifetimes of copolymers were similar in acetonitrile/ethylacetate and in acetonitrile/MMA, indicating that the quenching of the singlet excited state by the monomer is negligible.

On the other hand, rate constants for the singlet quenching of M-2 by the copolymers bearing the amine depend on the fraction of amine units in the polymer chain (Table 4). The quenching rate constants decrease when the amount of amine increases. Considering that the singlet quenching is a diffusional process, the decrease of ^1k_q can be explained in terms of the inhomogeneous distribution of the quencher units in the polymer coils [17].

The transient spectrum of the thioxanthone bound to the polymer presents a strong absorption in the 580–650 nm region which is similar to that observed for the low molecular weight thioxanthone derivative. The decay of this signal, that corresponds to the triplet–triplet absorption, follows a first-order kinetics. The triplet decay of TX bound to the polymer is similar to that of the respective models, indicating that intramolecular deactivation pathway of the triplet excited state through the macromolecule chain is negligible.

The bimolecular rate constants for the triplet quenching by the amine, ^3k_q, were determined from the linear least

Table 3
Quenching rate constants for the singlet and triplet excited states of thioxanthone derivatives by DEOHA

Thioxanthone	DEOHA			MMA
	^1k_q (10^9 M^{-1} s^{-1}) Acetonitrile	Acetonitrile/ethyl acetate	^3k_q (10^8 M^{-1} s^{-1}) Acetonitrile	^3k_q (10^6 M^{-1} s^{-1}) Acetonitrile
MMA-*co*-M2	5.2	3.5 (2.3)[a]	2.6 (3.2)[a]	0.09
M-2	5.1	4.1 (3.1)[a]	5.0 (4.0)[a]	0.02[b]
MMA-*co*-M4	1.6	1.0	0.77	0.045
M-4	1.6	2.1	1.6	0.045[b]

[a] In benzene.

[b] From Ref. [4].

square fits of the rate constant of the triplet decay (k_{obs}) at 620 nm versus [DEOHA] plots using the expression

$$k_{obs} = k_0 + {}^3k_q[\mathrm{DEOHA}] \tag{4}$$

where k_0 is the decay rate constant in the absence of quenching (Fig. 3). Values of ^3k_q for the quenching by DEOHA are included in Table 3. The quenching efficiency for the thioxanthone bound to the polymer is slightly lower than that of the corresponding model compound, indicating only a minor effect of the macromolecule chain in the triplet reactivity. Fouassier et al. [9,18] have also reported a small polymer effect for the triplet quenching of thioxanthone bound to siloxane and acrylic polymers. Triplet state of thioxanthones bound to the polymer are also quenched by MMA (Table 3). The rate constants are similar to that previously determined for the model compounds [4].

Ketyl radicals, which have a characteristic absorption in the 400–500 nm region were detected after reduction of the thioxanthone by the amine. The optical density of the radicals derived from the 2-propoxy thioxanthone derivatives in the presence of 20 mM DEOHA were measured at 430 nm. Experiments under matched absorption conditions gave absorption of 0.021 and 0.017 for MMA-*co*-M2 and M-2, respectively (Fig. 4). Since the ketyl radical absorption coefficient can be considered similar for the thioxanthone free or bound to the polymer chain, this result indicates a minor influence of the macromolecular coil on the radical yield.

Rate constants for the quenching of M-2 triplet by the copolymers bearing amine groups are included in Table 4. It can be observed that there are no significant changes with the amine content in the copolymers. Since, the triplet quenching by DMAEMA is not diffusion controlled, it will not be affected by an obstructive effect of the polymer segments towards the diffusion of the small molecule. In this case, any polymer effect must arise from differences in the free energy of the activated complex, which is expected to be relatively small since the amine is located in the pendant group far from the polymer chain. On the other hand, the lower value of quenching rate constant by the monomer with respect to that found for the DEOHA (Table 3) is in agreement with the higher oxidation potential of the amine (DMAEMA) due to the methyl substituents at the N atom.

Table 4
Rate constants for the quenching of excited states of M-2 by the monomer (DMAEMA), homopolymer and copolymers with MMA. Acetonitrile as solvent

Fraction of amine groups	^1k_q (10^8 M^{-1} s^{-1})	^3k_q (10^8 M^{-1} s^{-1})
Monomer	51	0.9
0.11	28.3	0.58
0.40	11	0.41
1.0	5.5	0.42

3.3. Photoinitiation mechanism

The photochemical behaviour of thioxanthones in the presence of amines (Am) can be represented by a mechanism involving the electron transfer from the amine to the excited thioxanthone (Scheme 2).

It is well known that amine radicals ($\mathrm{Am(-H)^{\cdot}}$) which originated from the decomposition of the charge transfer complex are the species that adds to the monomer. The lack of polymerization in the absence of amine indicates that the interaction of the thioxanthone triplet state with the monomer does not lead to polymerization. Then, the active

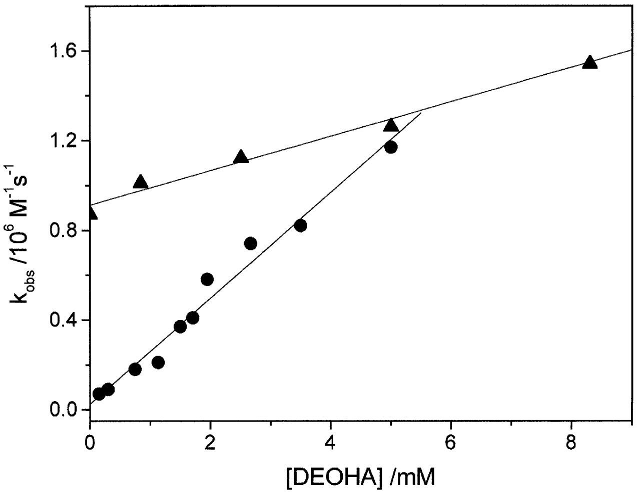


Fig. 3. Rate constant for the triplet decay as function of the amine concentration, in acetonitrile. (▲) MMA-*co*-M4; (●) MMA-*co*-M2.

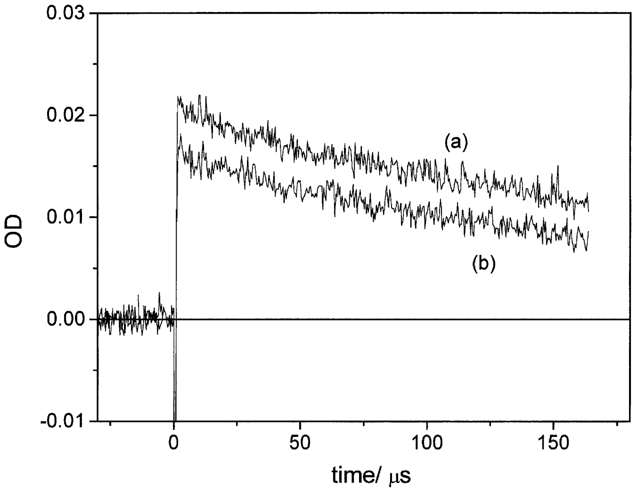


Fig. 4. Transient absorption at 430 nm of: (a) MMA-*co*-M2; (b) M-2. In the presence of 20 mM DEOHA in acetonitrile.

radical quantum yield is given by Eq. (5)

$$\Phi_{\rm rad} = \Phi_{\rm isc}\beta_{\rm T}\frac{\left({}^3k_{\rm q}\right)_{\rm Am}[\rm Am]}{\left(\left({}^3k_{\rm q}\right)_{\rm Am}[\rm Am] + \left({}^3k_{\rm q}\right)_{\rm MMA}[\rm MMA] + k_0\right)} \tag{5}$$

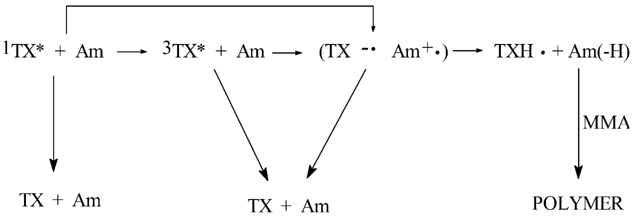
where $\beta_{\rm T}$ stand for the fraction of radicals originated from the triplet charge transfer intermediate that decomposes to yield active radicals, and $\phi_{\rm isc}$ is triplet quantum yield given by

$$\Phi_{\rm isc} = \frac{\Phi^0_{\rm isc}}{\left({}^1K_{\rm SV}[\rm Am] + 1\right)} \tag{6}$$

where $\phi^0_{\rm isc}$ is the triplet quantum yield in the absence of amine, and ${}^1K_{\rm SV}$ the Stern–Volmer constant for the singlet quenching by the amine in the polymerization mixture.

The polymerization data obtained with copolymers containing the thioxanthone chromophore and their models can be fitted quite well with Eq. (5) (Fig. 5). This indicates that the radicals that lead to polymerization are those originated from the interaction of the thioxanthone triplet with the amine. The singlet deactivation leads to the polymerization inhibition.

Also, it is interesting to note that the polymerization in benzene is not inhibited using thioxanthones with the ether group in position 2. This is in agreement with the low value of ${}^1K_{\rm SV}$ (4 $\rm M^{-1}$) in this solvent. Moreover, higher Rp are found in benzene than in acetonitrile, since the triplet quenching rate constants are similar in both solvents, this suggests a higher radical formation in the less polar solvent which is due mostly to a higher intersystem crossing quantum yield.



Scheme 2.

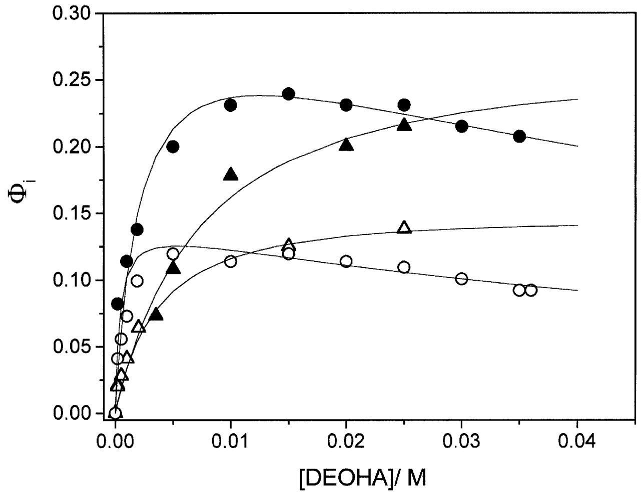


Fig. 5. Photoinitiation quantum yield as function of the amine concentration. Photoinitiators: (●) MMA-*co*-M2; (○) M-2; (▲) MMA-*co*-M4; (△) M-4. Solvent: acetonitrile. Solid line represents the fitting to Eq. (5).

On the other hand, the data obtained at high amine concentration, where it can be considered that >90% of the triplets are deactivated, show that the macroinitiator is almost two times more efficient than the corresponding low molecular models. This could be the consequence of an increased production of activity radicals and/or a high reactivity of the radicals towards the monomer double bond. The absorbencies measured for the ketyl radicals derived from the 2-propoxy thioxanthone derivatives show that the ketyl radical formation and then the amine radical formation, for the thioxanthone bound to the polymer is only 1.2 times higher than that of the free thioxanthone (Fig. 4). This indicates that the higher photoinitiation activity of the macroinitiator is due to a higher reactivity for the radicals produced in the macroinitiator system. Polymer chain could prevent the recombination of radicals favouring their reaction with the monomer, and could explain the improved activity of these macroinitiators. Also, a high monomer concentration on the locus, macromolecular coil, where the radicals are formed could lead to a high initiation activity of the systems comprising a macroinitiator and a low molecular weigh co-initiator.

Results obtained with monomeric compound M-2 and the co-initiator bound to a macromolecule, at concentration where more than 90% of the triplet are quenched, show a small increase in the Rp with respect to the low molecular weight co-initiator. It could be expected that polymer-bound radicals have a lower initiating activity, due to the steric hindrance, than that of low molecular weight radicals. However, Rp data show a similar reactivity or even higher for the macroradical. This could be explained by a reduction of the singlet quenching by the amine. Since, the radicals that lead to polymerization are only those that come from the deactivation of the thioxanthone triplet with the amine, the singlet quenching will lead to the inhibition of the polymerization. The latter effect is minor when the amine is incorporated to the polymer chain since the singlet quenching rate constants are lower.

Acknowledgments

This work was supported by FONDECYT (1000747) and Cátedra Presidencial en Ciencias 97, and Ministerio Ciencia y Tecnología (# MAT2000-1671).

References

[1] Davidson RS. J Photochem Photobiol A: Chem 1993;69:263.

[2] Davidson RS, Dias AA, Illsley DR. J Photochem Photobiol A: Chem 1995;91:153.

[3] Carlini C, Angiolini L, Caretti D, Corelli E. Polym Adv Technol 1996; 7:397.

[4] Corrales T, Peinado C, Catalina F, Neumann MG, Allen NS, Rufs AM, Encinas MV. Polymer 2000;41:9103.

[5] Corrales T, Catalina F, Peinado C, Madruga EL, Allen NS. Polym Int 1997;42:397.

[6] Carlini C, Ciardille F, Donate D, Gurzoni F. Polymer 1983;24:599.

[7] Carlini C, Toniolo L, Rolla PA, Barigelletti F, Bortolus P, Flamigni L. New Polym Mater 1987;1:63.

[8] Du FS, Zhang P, Li FM. J Appl Polym Sci 1994;51:2139.

[9] Pouliquen L, Coqueret X, Morlet-Savary F, Fouassier JP. Macromolecules 1995;28:8028.

[10] Pouliquen L, Coqueret X. Macromol Chem Phys 1996;197:4045.

[11] Begvington JC, Melville HW, Kuo C, Gallopo A. J Am Chem Soc 1978;100:393.

[12] Mc Ginnis VD, Melville HW, Taylor RP. J Polym Sci 1954;14:463.

[13] Alvarez J, Encinas MV, Lissi EA. Macromol Chem Phys 1999;200: 2411.

[14] Brandrup J, Immergut EH, Grulke EA, editors. Polymer handbook, 4th ed. New York: Wiley; 1999.

[15] Pouliquen L, Coqueret X, Lablace-Combier A, Loucheux C. Macromol Chem 1992;193:1273.

[16] Neumann MG, Gehlen MH, Encinas MV, Allen NS, Corrales T, Peinado C, Catalina F. J Chem Soc Faraday Trans 1997;93:1517.

[17] Olea AF, Encinas MV, Lissi EA. Macromolecules 1982;15:1111.

[18] Angiolini L, Caretti D, Carlini C, Corelli E, Fouassier JP, Morlet-Savary F. Polymer 1995;36:4055.