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Photopolymerization of methyl methacrylate initiated by thioxanthone derivatives: photoinitiation mechanism

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Abstract

The photopolymerization of methyl methacrylate initiated by substituted thioxanthones in the presence of an amine has been investigated. The polymerization rates in acetonitrile were measured at several amine concentrations. The dependence of the polymerization rates with the amine concentration and the photoinitiation efficiency at a given amine concentration are highly dependent on the ketone structure. The rate constants for the quenching of thioxanthones excited states by the monomer and the amine were measured by fluorescence and laser flash photolysis, under the polymerization conditions. These data show that the reactivity of the ketone is also highly dependent on the ketone structure. The values of the quenching rate constants show that the initiation efficiency is controlled by the competition between the quenching of the excited states by the monomer and also the amine. From the latter a mechanism is proposed to simulate the dependence of the polymerization rates with amine concentration. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Methyl methacrylate; Thioxanthone derivatives; Photopolymerization

1. Introduction

Thioxanthones (TXs) are among one of the most widely used bimolecular photoinitiators in vinyl polymerizations [1]. The photoinitiation activity of these compounds is well known to be promoted by the presence of tertiary amines. Many studies have been devoted to gain an understanding of the initiation efficiency of these compounds and the nature of the mechanism involved [2]. It is well established that the TX excited states interact with amines forming a charge transfer intermediate, the formation of amine and ketyl radicals being one of its decomposition steps [3–6].

In a previous work [7] we reported that TXs with electron acceptor substituents in position 2 are significantly more reactive than those with donor substituents, while a methyl substitution in position 1 decreases the reactivity. Therefore, it may be expected that the photoinitiation efficiency will be influenced by the nature of the substituents on the TX ring. Furthermore, the behaviour of the charge transfer complex would be dependent on the nature of the carbonyl–amine pair.

The present work is devoted to study the behaviour of several substituted TXs as photoinitiators of methyl methacrylate polymerization. Also, some new TX derivatives substituted with acrylic group are analysed. These compounds may incorporate the TX moiety into the polymer chain, avoiding formulation and migration problems [8]. The results presented here allowed us to relate the photochemical behaviour of these compounds with their efficiencies as photoinitiators for MMA polymerization at low conversion. The structures of the TXs studied here are shown in Scheme 1.

2. Experimental

2.1. Materials

All the solvents used in this work were obtained from Aldrich, and were of Analar spectroscopic or high performance liquid chromatography (HPLC) grade quality. The 2-(*N*,*N*-diethylamino)ethanol (DEOHA) and methyl methacrylate (MMA) were obtained from Aldrich and were purified by vacuum distillation before use. The

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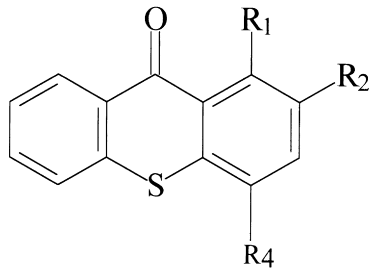

TX1 R_1 = $-CH_3$ R_4 = $-OCH_2CH_2CH_3$

TX3 R_1 = $-CH_3$ R_4 = $-O(CH_2)_3OCOCH{=}CH_2$

TXC R_1 = -H R_2 = $-OCOCH_3$

TX6 R_1 = -H R_2 = $-OCOCH{=}CH_2$

TX2 R_1 = -H R_2 = $-OCH_2CH_2CH_3$

TX4 R_1 = -H R_2 = $-O(CH_2)_3OCOCH{=}CH_2$

Scheme 1.

thioxanthone derivatives were synthesized following the procedures described in Refs. [7,9].

2.2. Instruments

UV spectra were recorded on a Shimadzu UV-265-FS spectrophotometer. Fluorescence measurements were carried out in a Spex Fluorolog Spectrofluorimeter. Transients decay were determined using an Applied Photophysics laser kinetics spectrometer with a 20 ns excitation pulse at 355 nm using Nd-YAG laser (Spectron) with frequency trebling. Detection was performed with a Hamamatsu R925 photomultiplier.

2.3. Molar mass measurements

Molar mass distributions of the obtained polymers by photodilatometry were measured using gel permeation chromatography (GPC); a model M-45 Waters high pressure pump with a U6K injector was employed and Ultrastyragel gel permeation columns were placed in series (pore sizes: 500, 10^3, 10^4, and 10^5 Å). A previous calibration was carried out with a series of poly(methyl methacrylate) standards with narrow molar mass distributions.

2.4. Photodilatometry

MMA photopolymerization rates were measured dilatometrically in acetonitrile solutions using thioxanthones together with 2-(*N*,*N*-diethylamino)ethanol as the photoinitiator system. The dilatometer, filled with the photopolymerizable 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 ($<5\%$). The dilatometer was calibrated relating the volume contraction with the amount of the formed polymer.

3. Results and discussion

3.1. Polymerization studies

Polymerization rates (R_p) were obtained from the initial slope of the conversion versus time plots. Polymerization rates of MMA in acetonitrile using thioxanthone (10^{-5} M) and DEOHA (10^{-3} M) as the photoinitiator system are shown in Table 1. The poly(methyl methacrylates) that are obtained from this experiment were characterized by GPC and the number average molar masses are summarized in Table 1. The ratios between propagation rate constant and the square root of the termination constant, $k_p/k_t^{1/2}$, were obtained from these data using the well-known simplified Mayo equation in the following form [10]:

$$\frac{1}{X_n} = 1.72\frac{k_t R_p}{k_p^2[M]^2} \tag{1}$$

The values obtained for the ratio $k_p/k_t^{1/2}$ (Table 1) are close to that reported in the literature (0.066 $M^{-1/2}\,s^{-1/2}$) for the polymerization of methyl methacrylate at 30°C initiated by azo-bis-isobutyronitrile, where chain transfer reactions or primary radical termination are negligible [11]. This result, together with the half-order with respect to the photoinitiator and first-order respect to the monomer, previously found for 2-acryloxy and 2-benzoyloxy thioxanthones [12,13] indicates that chain transfer or termination by primary radicals can be considered negligible. Thus, the polymerization

Table 1
Polymerization of MMA (2.8 M) photoinitiated by thioxanthone derivatives at 30°C (acetonitrile as solvent; thioxanthone 10^{-5} M; DEOHA 10^{-3} M)

Thioxanthone	Substituents	R_p (10^{-5} $M^{-1}\,s^{-1}$)	M_n (10^4)	$k_p/k_t^{1/2}$ ($M^{-1/2}\,s^{-1/2}$)	Φ_i (10^{-2})
TX1	$1-CH_3$ $4-OCH_2CH_2CH_3$	1.7	9.2	0.058	4.5
TX3	$1-CH_3$ $4-O(CH_2)_3OCOCHyCH_2$	1.7	7.8	0.054	3.5
TX2	$2-OCH_2CH_2CH_3$	2.6	7.1	0.063	6.6
TX4	$2-O(CH_2)_3OCOCHyCH_2$	2.3	8.2	0.064	7.8
TX6	$2-OCOCHyCH_2$	1.8	10.7	0.064	3.4
TXC	$2-OCOCH_3$	1.7			

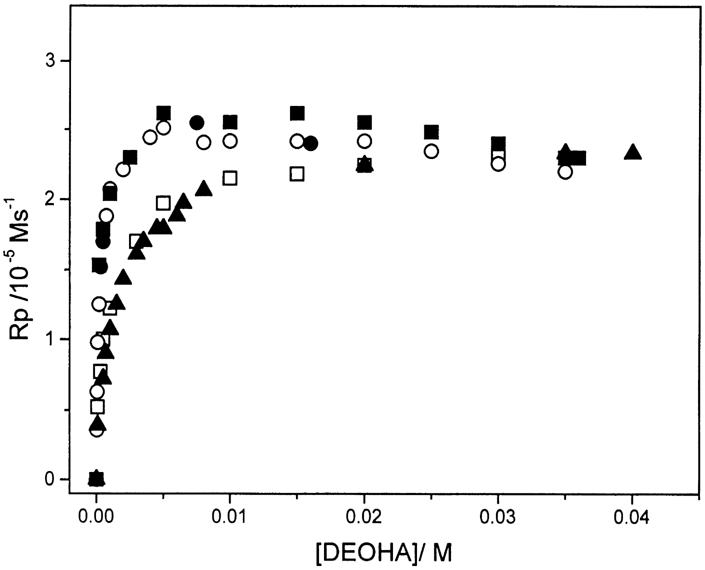

Fig. 1. Polymerization rates of MMA as function of the amine concentration, photoinitiated by: TX1 (A); TX6 (O); TX2 (W); and TX4 (B) in monomer/acetonitrile (1/1). TX2 (X) in monomer/benzene (1/1).

rate can be expressed by the classical expression

$$R_p = (k_p/k_t^{1/2})\Phi_i^{1/2} I_a^{1/2}[M] \quad (2)$$

Photoinitiation quantum yields (Φ_i) calculated from Eq. (2) are shown in Table 1. These data show that at a 10^{-3} M amine concentration, 2-propoxy TXs appear as more efficient photoinitiators.

Polymerization rates were also measured as function of DEOHA concentration (Fig. 1). These results show that the dependence of R_p on the amine concentration is similar for TX1 and TX6. The polymerization rate increases with the amine concentration reaching a constant value. However, this behaviour is different for TX2 and TX4, the rate increases more deeply and then decreases slowly at higher amine concentrations.

Polymerization rate of HEMA photoinitiated by TX2 was also measured in less polar media, such as benzene (Fig. 1). These values were similar to that obtained in acetonitrile. Since, the $k_p/k_t^{1/2}$ values for MMA polymerization in acetonitrile and benzene are similar [14], these results indicate a negligible effect on the photoinitiation efficiency when changing the solvent from a more polar acetonitrile to a less polar benzene.

Initiation efficiencies were compared to that obtained using AIBN as photoinitiator. This compound produces radicals by a single photocleavage bond. Under matched absorption conditions, and at the same monomer concentration, Eq. (2) leads to Eq. (3)

$$(\Phi_i)_{TX} = \{(R_p)_{TX}/(R_p)_{AIBN}\}^2(\Phi_i)_{AIBN} \quad (3)$$

Taking a value of 0.4 for the photoinitiation efficiency of AIBN [15], the values of 0.075 and 0.12 for TX1 and TX2, respectively, are obtained at a 10^{-2} M amine concentration. This is the concentration where the polymerization rates reach their maximum.

3.2. Photochemical studies

Fluorescence spectra of TX derivatives were recorded in acetonitrile, acetonitrile/ethyl acetate (1/1), and acetonitrile/MMA (1/1) mixtures under an argon atmosphere. The later mixture was chosen to mimic the solvent of the polymerization mixture. Typical spectra are shown in Fig. 2. In all cases, the fluorescence quantum yields were higher in acetonitrile than in the solvent mixture. Slightly higher values were obtained for the mixture containing the monomer. This indicates that quenching of the excited singlet state of the thioxanthone by the monomer is almost negligible. As already reported for the TX chromophore, the dependence of emission yield on the medium could reflect the solvent effect on the intersystem crossing quantum yield [16,17].

The rate constants for singlet quenching (^1k_q) by DEOHA were obtained from the decrease of fluorescence intensity by gradual amine addition, using the previously determined singlet lifetimes [7]. In all cases the Stern–Volmer plots were linear over a wide range of amine concentrations. Rate constants in acetonitrile are shown in Table 2. The rate constant values show the same trend with the substituents as those previously reported for the quenching of these carbonyl compounds by TEOHA [7]. Whereas 1-methyl substitution decreases the reactivity, the 2-acetoxy substituents give a higher quenching rate constant. Due to the solvent effect on the fluorescence quantum yield, Stern–Volmer constants ($^1K_{SV}$) were evaluated in acetonitrile/MMA (1/1) (Table 2). These values allow a real estimation of the interaction of the TX singlet with the amine in the polymerization medium.

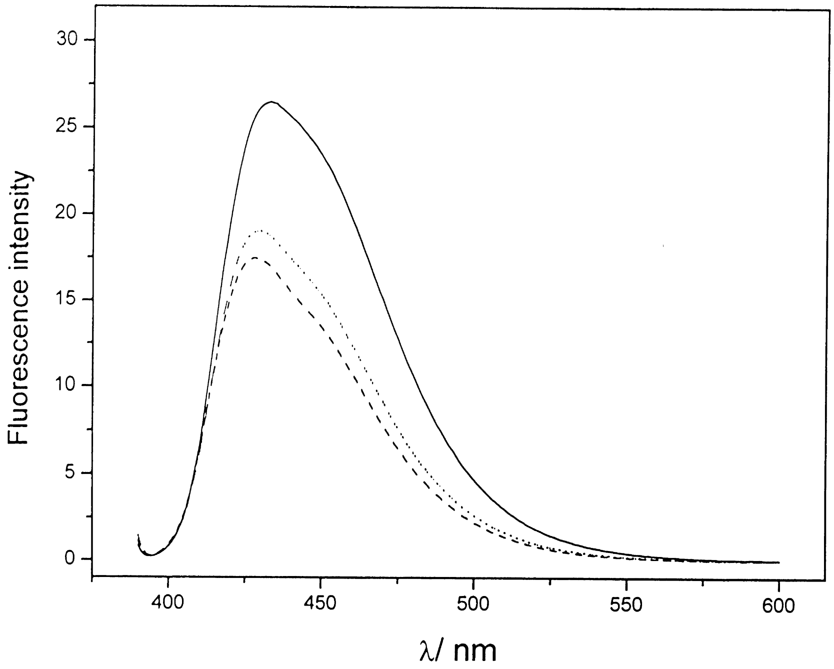

Fig. 2. Fluorescence spectra of TX4 in acetonitrile (—); acetonitrile/MMA (1/1) (· · · ·); and acetonitrile/ethyl acetate (1/1) (- - -).

Triplet quenching rate constants, ${}^3k_q$, were obtained from the experimental measured first order decays, k_{exp}, of thioxanthone triplets at 620 nm by Eq. (4)

$$k_{\text{exp}} = ({}^3\tau_0)^{-1} + {}^3k_q[\text{DEOHA}] \qquad (4)$$

where ${}^3\tau_0$ is the lifetime of the TX triplet in the absence of quencher. Typical experimental traces for the triplet decay are shown in Fig. 3. Values of ${}^3k_q$ for the quenching by DEOHA are included in Table 2. As found for the singlet quenching, 2-acetoxy substituents give the highest quenching efficiency. The 2-propoxy electron donating group could stabilise the $\pi\pi^*$ triplet relative to $n\pi^*$ state, thus, reducing its reactivity. Furthermore, the lifetimes of the TX triplets are significantly shortened by the presence of MMA. Bimolecular rate constants by the monomer are collected in Table 2. These values follow the same trend as that described for quenching by an amine.

Ketyl radicals, which have a characteristic absorption in the 380–430 nm region [3,18], were detected after reduction of the TX derivatives by the amine. The optical density of these radicals measured at 400 nm and 0.01 M DEOHA was slightly higher for 2-propoxy derivatives. The absorption of ketyl radicals for TX2 measured in acetonitrile and benzene was the same. Since the ketyl radical extinction coefficient can be considered similar in these solvents, the negligible solvent effect on the ketyl yield formation could explain the lack of solvent effect on the photoinitiation efficiency of TX2 described before.

3.3. Photoinitiation mechanism

The photochemical behaviour of TXs in the presence of amine (Am) and MMA, can be represented by a mechanism involving the formation of a charge transfer complex (CT)

Table 2
Rate constants for the quenching of singlet and triplet states of thioxanthones by diethylethanolamine and methyl methacrylate in acetonitrile

Thioxanthone	Substituent	DEOHA			MMA
		${}^1k_q$ (10^9 M^{-1} s^{-1})	${}^1K_{SV}$ (M^{-1})[a]	${}^3k_q$ (10^9 M^{-1} s^{-1})	${}^3k_q$ (10^6 M^{-1} s^{-1})
TX1	1-CH$_3$ 4-OCH$_2$CH$_2$CH$_3$	1.1	0.86	0.16	0.045
TX3	1-CH$_3$ 4-O(CH$_2$)$_3$OCOCHyCH$_2$	1.4			
TX2	2-OCH$_2$CH$_2$CH$_3$	4.0	16.6	0.58	0.027
TX4	2-O(CH$_2$)$_3$OCOCHyCH$_2$	3.3	13.9	0.5	0.02
TX6	2-OCOCHyCH$_2$	8.5	2.8	1.6	1.8
TXC	2-OCOCH$_3$	8.2		2.0	1.3

[a] In acetonitrile/MMA (1/1) (v/v).

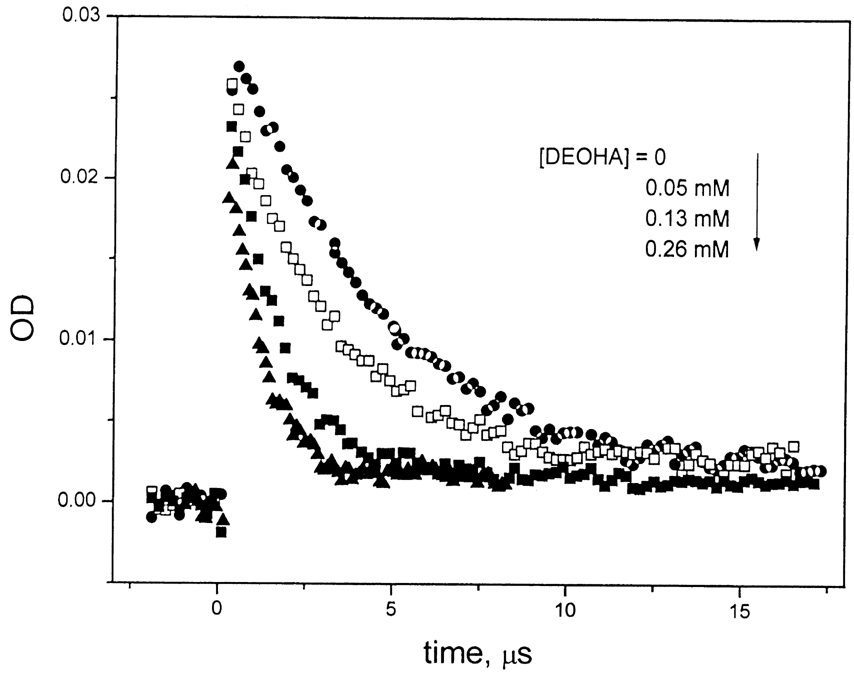

Fig. 3. Decay of the 620 nm absorption of TX6 triplet upon addition of DEOHA.

between the carbonyl triplet and the amine, through Eqs. (5)–(11)

$$\mathrm{TX} + h\nu \rightarrow {}^{1}\mathrm{TX}^{*} \tag{5}$$

$$^{1}\mathrm{TX}^{*} \rightarrow \text{deactivation} \tag{6}$$

$$^{1}\mathrm{TX}^{*} + \mathrm{Am} \rightarrow \text{quenching} \tag{7}$$

$$^{1}\mathrm{TX}^{*} \rightarrow {}^{3}\mathrm{TX}^{*} \tag{8}$$

$$^{3}\mathrm{TX}^{*} \rightarrow \text{deactivation} \tag{9}$$

$$^{3}\mathrm{TX}^{*} + \mathrm{MMA} \rightarrow \text{quenching} \tag{10}$$

$$^{3}\mathrm{TX}^{*} + \mathrm{Am} \rightarrow \underset{\mathrm{CT}}{(\mathrm{TX}^{\cdot -}\ \mathrm{Am}^{\cdot +})} \tag{11}$$

It is well known that one of the decomposition steps of the charge transfer complex is proton transfer from the amine to the carbonyl giving the ketyl and the alkyl amine radicals. The latter species is the active radical for the polymerization initiation. The lack of polymerization in the absence of amine indicates that the interaction of the TX triplets with the monomer does not lead to polymerization. From the above mechanism the amine radical quantum yield ($\Phi_{\mathrm{Am}^{\cdot}}$) is given by Eq. (12)

$$\Phi_{\mathrm{Am}^{\cdot}} = \frac{\Phi_{\mathrm{isc}}^{0}}{(^{1}K_{\mathrm{SV}}[\mathrm{Am}] + 1)} \frac{^{3}k_{\mathrm{q}}\,[\mathrm{Am}]}{((^{3}k_{\mathrm{q}})_{\mathrm{Am}}[\mathrm{Am}] + (^{3}k_{\mathrm{q}})_{\mathrm{MMA}}[\mathrm{MMA}] + (^{3}\tau_{0})^{-1})}\beta_{\mathrm{T}} \tag{12}$$

where Φ_{isc}^{0} stands for the intersystem crossing quantum yield in the absence of amine, and β_{T} for the fraction of triplet originated from the CT that decomposes to yield active radicals. Since β_{T} is not known, it is not possible to determine absolute values of $\Phi_{\mathrm{Am}^{\cdot}}$. However, relative values that simulate the dependence of the polymerization rate with the amine concentration can be obtained. The polymerization results obtained with TX1 and TX6 can be fitted quite well with Eq. (12) (Fig. 4), indicating that the radicals that lead to polymerization are those originated from the interaction of ketone triplet with the amine. Other deactivation processes like deactivation of the charge transfer intermediate by the amine can be considered as negligible [19].

On the other hand, TXs bearing 2-propoxy substituents could not fit to Eq. (12). Although nearly 25% of the excited singlet of these ketones are quenched in 20 mM amine, the R_{p} values remain almost constant. This indicates that the interaction of the singlet state with the amine may also lead to radicals that add to the monomer. The quantum yield of amine radicals originated from the singlet interaction is given by Eq. (13)

$$^{1}\Phi_{\mathrm{Am}^{\cdot}} = \frac{^{1}K_{\mathrm{SV}}[\mathrm{Am}]}{(^{1}K_{\mathrm{SV}}[\mathrm{Am}] + 1)}\beta_{\mathrm{S}} \tag{13}$$

where β_{S} is the fraction of the radicals that lead to polymerization. For both, TX2 and TX4 a better fitting to the experimental data was obtained considering that the active radicals come from both excited states, as represented by Eqs. (12) and (13). The fitting using $\beta_{\mathrm{S}} = 0.15$ and $\beta_{\mathrm{T}} \times \Phi_{\mathrm{isc}}^{0} = 0.7$ is shown in Fig. 4. If it is assumed that the sum of the quantum yields of fluorescence (0.2) [7] and intersystem

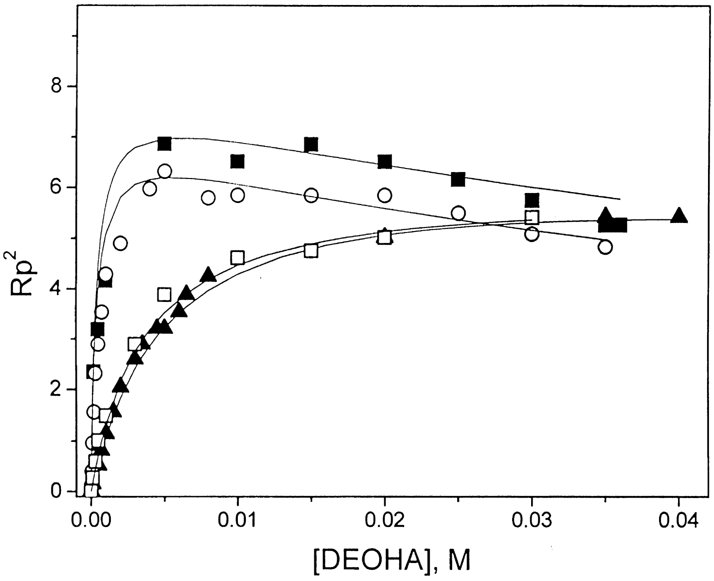

Fig. 4. Plot of the square of the polymerization rate in arbitrary units. Thioxanthone derivatives: TX1 (A); TX6 (O); TX2 (W); and TX4 (B). The solid line corresponds to the amine free radical quantum yield calculated according to Eq. (12) and/or Eq. (13).

crossing is close to unity [16], it can be estimated $\Phi^0_{\mathrm{isc}} \sim 0.8$ and then $\beta_{\mathrm{T}} \sim 0.9$. The higher value of β_{T} with respect β_{S} is in agreement with the high back electron transfer expected for the geminate radical ions originated from singlet state. The $\pi\pi^*$ character of the excited states of the 2-propoxy TXs could then increase the proton transfer within the radical ion pair, leading to the formation of neutral amine radicals in acetonitrile as solvent.

The role of the radicals coming from the singlet is, in this case, different from that reported for the photoinitiator system fluorenone-amine [19], where the interaction of the singlet with the amine leads to the inhibition of the methyl methacrylate polymerization. Fouassier et al. [20] have also reported an inhibition effect for the polymerization of acrylamide in aqueous solutions photoinitiated by TXs with electron-donating substituents. This points to a significant effect of the medium on the free radical formation from the charge transfer complex originated from the singlet excited state.

The comparison of the results found for TX2 and TX4 shows another interesting feature. In spite of the acryloxy group substitution in the side chain in TX4, both compounds show the same photoinitiator behaviour. This indicates that interaction between the chromophore and the double bond, separated by a spacer like the propoxy group, is negligible.

Data in Table 1 simulate the experimental conditions frequently used in industrial formulations [21]. However, although these results show the same general trend of those shown in Fig. 1, it is difficult to establish a real comparison between the efficiencies of the different TX derivatives. The photoinitiation efficiency of the TX derivatives will be dependent on the competition of triplet quenching by the monomer and the amine. This competition depends on the amine concentration as well as on the ketone structure. Furthermore, differences in absorbed light must be considered when using fixed ketone concentrations.

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