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# The influence of the photophysics of 2-substituted thioxanthones on their activity as photoinitiators

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## Abstract

The polymerization of methyl methacrylate photoinitiated by thioxanthones (TXs) substituted in the position 2 of the chromophore ring in the presence of 2-(*N*,*N*-diethylamino)ethanol has been investigated. The photoinitiation efficiency of these systems is highly dependent on the structure of the 2-substituent. At high amine concentrations, compounds with electron-withdrawing substituents appear as more efficient photoinitiators. The photophysics of the ketones was studied in the polymerization medium. These data show that the singlet excited state of TXs is deactivated by the amine with a rate constant near the diffusional control limit. The triplet rate constants for quenching by the amine and the monomer are highly dependent on the ketone structure. Compounds with electron-withdrawing substituents in the position 2 are more reactive. These studies allow to simulate the dependence of the photoinitiation efficiency with the amine concentration and indicate that the active radicals are produced by the interaction of the ketone triplet with the amine. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords*: Photoinitiator; Chromophore; Free radical polymerization

## 1. Introduction

Compounds based on the thioxanthone (TX) chromophore are among the most used photoinitiators for free radical polymerization. They have been introduced in processes such as printing inks, surface coating, microelectronics, and photoresists [1]. Several TX derivatives have been synthesized and have been examined in terms of their efficiency as photoinitiators [2].

It is well known that the activity as photoinitiators of these compounds is based in the radical production from the interaction of the TX excited triplet state with tertiary amines which proceeds through a charge transfer intermediate [3,4]. Due to the charge transfer characteristics of this intermediate its decomposition steps are highly dependent on the donor–acceptor capability of the photoinitiator and the co-initiator. Then, it is expected that the radical production will be markedly dependent on the substituents on the TX chromophore. In spite of the numerous works on this subject there are only few systematic studies on the relation of the photochemical behaviour and the photoinitiation efficiency of these compounds.

In a previous work [5], we described the behaviour as photoinitiators of TXs with propoxy and acetoxy groups in the position 2. In this work, we have extended our previous studies to a series of TXs with electron-donor and electron-withdrawing substituents in the position 2 of the TX chromophore (Scheme 1). The initiation efficiency of these compounds is related to their photochemical behaviour in the polymerization conditions.

## 2. Experimental

### 2.1. Materials

The 2-(*N*,*N*-diethylamino)ethanol (DEOHA), the rest of amines, and methyl methacrylate (MMA) were obtained from Aldrich, and were purified by vacuum distillation before use. The TX derivatives were synthesized following the procedures described in Refs. [4,6]. 2,2′-Azobis(isobutyronitrile) (AIBN) from Fluka, was recrystallized from

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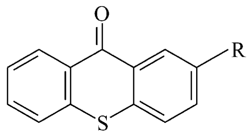

TX R = -H

ClTX R = -Cl

AcTX R = $-OCOCH_3$

MeTX R = $-CH_3$

PTX R = $-OCH_2CH_2CH_3$

TXOH R = -OH

Scheme 1.

ethanol. All the solvents used were obtained from Merck, and were of spectroscopic or HPLC grade quality.

### 2.2. Instruments

UV spectra were recorded on a Hewlett Packard diode array spectrophotometer. Steady-state fluorescence measurements were carried out in a Spex Fluorolog spectrofluorimeter. All emission spectra were recorded using the corrected mode.

Fluorescence lifetimes were measured with an Edinburgh Instruments OB 900 time-correlated single photon counting fluorometer. Transient absorption measurements were carried out 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 R928 photomultiplier.

### 2.3. Photopolymerization rates

MMA polymerization rates ($R_p$) were measured dilatometrically in MMA/acetonitrile (1/1, v/v) solutions using TXs together with DEOHA 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. The absorbance of all TXs was 0.2 at 366 nm. Rates were measured at low conversion (<10%). The dilatometer was calibrated relating the volume contraction to the amount of the formed polymer.

## 3. Results and discussion

### 3.1. Polymerization rates

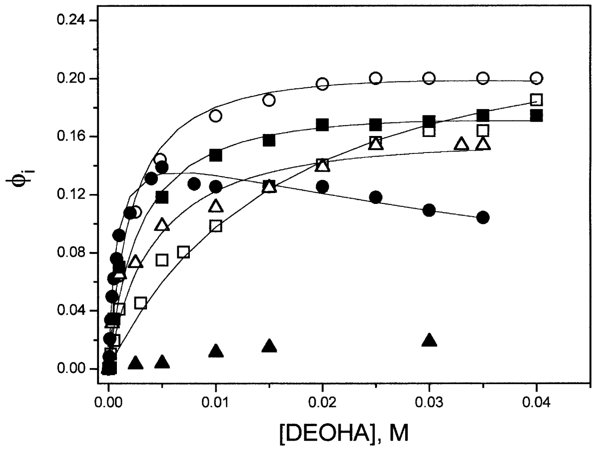

Fig. 1. Photoinitiation quantum yields as function of the amine concentration for the MMA polymerization photoinitiated by ClTX (○); TX (□); AcTX (■); MeTX (△); PTX (●); TXOH (▲). The solid lines correspond to the radical quantum yield calculated from Eq. (5).

The initial rates of MMA polymerization at 20 °C in monomer/acetonitrile (1/1, v/v) using DEOHA as co-initiator were measured at several amine concentrations. To evaluate the initiation efficiency, polymerization rates were referred to those obtained with AIBN as reference photoinitiator. At low conversion, it can be considered that the MMA polymerization rate follows the classical expression for free radical addition mechanism [7],

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

Then, working under matched absorption conditions and at the same monomer concentration Eq. (1) leads to Eq. (2),

$$\Phi_{TXs} = \left\{(R_p)^2_{TXs}/(R_p)^2_{AIBN}\right\}\Phi_{AIBN} \qquad (2)$$

Photoinitiation quantum yields of TXs at different amine concentrations were determined taking the photoinitiation efficiency of AIBN equal to 0.4 [8] (Fig. 1). These data show that the photoinitiation efficiency is dependent on the amine concentration and this dependence is characteristic of the nature of the 2-substituent. Values obtained at 30 mM DEOHA, a concentration where the polymerization rate reaches an almost constant value for most of the ketones, are given in Table 1. These data show that TXs with electron-withdrawing substituents in the position 2 appear as more efficient photoinitiators. The propoxy substituent in

Table 1
Photoinitiation quantum yield of 2-substituted thioxanthones in the presence of 30 mM DEOHA

| TXs | $\phi_i$ |
|---|---|
| TX | 0.17 |
| ClTX | 0.20 |
| AcTX | 0.17 |
| MeTX | 0.15 |
| PTX | 0.11 |
| TXOH | 0.02 |

this position decreases the photoinitiation efficiency. The TX with the hydroxyl substituent appears as a poor photoinitiator. Also, a low photoinitiation activity has been reported for the 1-chloro-4-hydroxythioxanthone [9].

### 3.2. Photochemical studies

The deactivation of the singlet excited state of TXs by the DEOHA was measured from the decrease of the fluorescence intensity combined with the fluorescence lifetime. Since the singlet decay is strongly dependent on the medium properties [10,11], the quenching efficiencies were measured in the monomer/acetonitrile (1/1) mixture.

Fig. 2 shows the shortening of the fluorescence decay of TXOH when the solvent is changed from acetonitrile to the MMA/acetonitrile mixture. In both cases the best fitting was obtained with a biexponential decay with components of 5.5 ns (98.5%) and 1.26 ns (1.5%) in acetonitrile, and 4.33 ns (95.1%) and 1.7 ns (4.9%) in MMA/acetonitrile (Table 2). The quenching of singlet lifetime cannot be due to the presence of the monomer. Measurements of the fluorescence lifetime using a mixture of solvents, acetonitrile/ethyl acetate (1/1), which provides a similar polarity medium to that offered by MMA/acetonitrile, gave similar singlet lifetimes. Then, this shortened lifetime in the monomer mixture must be due to a solvent effect and is in agreement with the decrease in fluorescence quantum yield when the solvent polarity decreases [4].

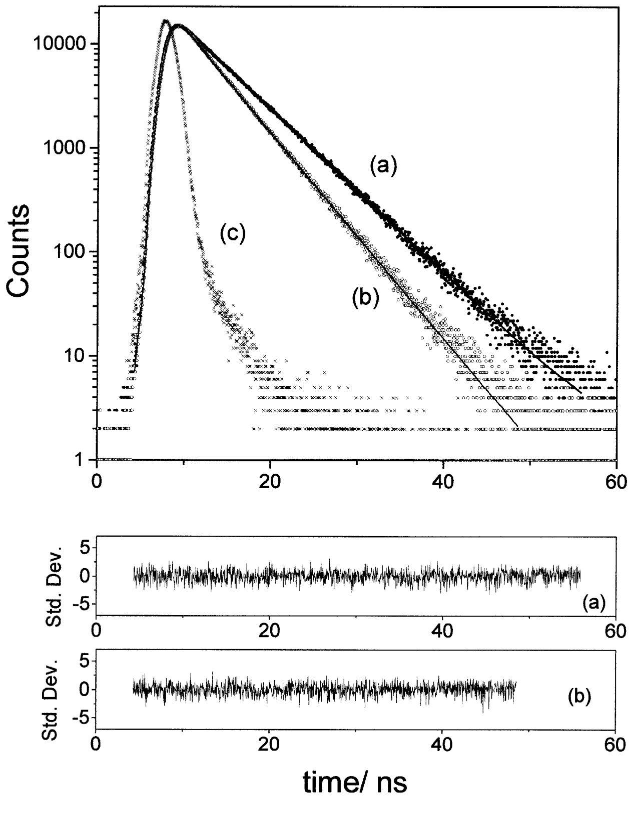

Fig. 2. Fluorescence decay profiles for TXOH in acetonitrile (a), and in MMA/acetonitrile (1/1) (b). The continuous line is the fitted curve following a biexponential analysis. (c) is the instrument response.

Table 2
Singlet lifetimes and quenching rate constants for the singlet quenching of 2-substituted thioxanthones by DEOHA in acetonitrile/MMA (1/1)

| TXs | $\tau_S$ (ns) | $^1k_q(10^9\ M^{-1}\ s^{-1})$ DEOHA |
|---|---|---|
| TX | 0.22 | 4.6 |
| ClTX | 0.91 | 1.9 |
| AcTX | 0.36 | 8.1 |
| MeTX | 0.46 | 3.6 |
| PTX | 4.52 (76.5%); 1.79 (23.5%) | 4.6 |
| TXOH | 4.33 (95.1%); 1.7 (4.9%) | 4.3 |

Emission lifetimes of TXs in the employed polymerization medium are summarized in Table 2. These data show that singlet lifetimes are very short for most of the TX derivatives, with the exception of TXOH and PTX. The longer lifetimes of the later derivatives are consistent with a reduction of the intersystem crossing quantum yield associated to the increased $\pi\pi^*$ character of the compounds bearing strong electron-donor substituent in the position 2. The presence of the short-lived component for the ether and hydroxy substituents may be due to solvent relaxation of the excited singlet influenced by the presence of a polar group in the vicinity of the C=O group.

Data of singlet quenching rate constants ($^1k_q$) in monomer/acetonitrile (1/1) are shown in Table 2. Values for PTX and TXOH were obtained using the average fluorescence lifetime [12]. These results show that the singlet quenching by DEOHA is nearly a diffusional controlled process. Rate constants for the quenching of TXOH excited singlet were also measured for amines of higher oxidation potential. A value of $5 \times 10^9\ M^{-1}\ s^{-1}$ was obtained for di-*n*-butylamine and *n*-butylamine. These results show that even for amines of high oxidation potential the quenching rate constants are close to the diffusional control.

The transient spectrum of TXs exhibits an intense absorption in the 580–640 nm region, which has been assigned to the triplet–triplet absorption [13,14]. The decay at 600 nm was used for determining the quenching rate constants of the triplet states ($^3k_q$). These bimolecular rate constants were measured from the experimental first-order rate constants, $k_{exp}$, determined from the triplet decay in the absence and presence of DEOHA, and they were related to the quenching rate constant by Eq. (3):

$$k_{exp} = k_0 + {}^3k_q[\text{Amine}] \tag{3}$$

where $k_0$ stands for the decay in the absence of amine. The values of $^3k_q$ determined from the linear plots of $k_{exp}$ vs [Amine] are given in Table 3. These data show that the reactivity of the TX triplets towards amines is not significant affected by the introduction of electron-withdrawing substituents in the position 2 of the TX chromophore. However, a considerable decrease of the triplet reactivity is observed

Table 3
Quenching rate constants for the triplet quenching of 2-substituted thioxanthones in acetonitrile

| TXs | ${}^3k_q$ ($10^9$ M$^{-1}$ s$^{-1}$) DEOHA | ${}^3k_q$ ($10^6$ M$^{-1}$ s$^{-1}$) MMA |
|---|---|---|
| TX | 2.4 | 9.3 |
| ClTX | 2.3 | 1.0 |
| AcTX | 2.1 | 1.3 |
| MeTX | 0.83 | 0.7 |
| PTX | 0.58 | 0.027 |

when electron-donating groups are in this position. As previously we reported for ether and ester substituents [4], this behaviour can be explained in terms of electron-donating resonance effects that stabilize the $\pi\pi^*$ states leading to less mixing of $n\pi^*$ and $\pi\pi^*$ triplets. This indicates a lower reactivity of the $\pi\pi^*$ triplets relative to the $n\pi^*$ triplets of TXs. Ketones having low $\pi\pi^*$ triplets are known to be substantially less reactive than those having low lying $n\pi^*$ states [15–17].

In the case of TXOH under the same experimental conditions, no triplet signal has been detected at the same time scale of our experiments. This indicates a very short triplet lifetime (<300 ns). A rapid intermolecular hydrogen abstraction could prevent the build-up of an appreciable concentration of triplets. In a related system, Favaro [18] has reported that *p*-hydroxybenzophenone undergoes efficient self-quenching with a rate constant of $1 \times 10^{10}$ M$^{-1}$ s$^{-1}$ in benzene. Also, Das et al. [19] have observed an efficient head-to-tail hydrogen abstraction in the photolysis of 4-hydroxypropiophenone in non-protic solvent.

Addition of MMA to TXs solutions produced the shortening of the triplet decay as shown in Fig. 3 for the ClTX. Quenching rate constants were determined according to Eq. (3) and the values are summarized in Table 3. In this case quenching rate constants are more sensitive to the substituent effects than that observed for the quenching for DEOHA, since the rates are much lower than the values for diffusion controlled limit. Substituents in the position 2 of the TX chromophore decrease the reactivity of TX, this effect being more notable for electron-donor substituents. As discussed earlier for quenching by amines, the favourable resonance stabilisation of the electron-donor groups decreases the $\pi\pi^*$ triplet energy.

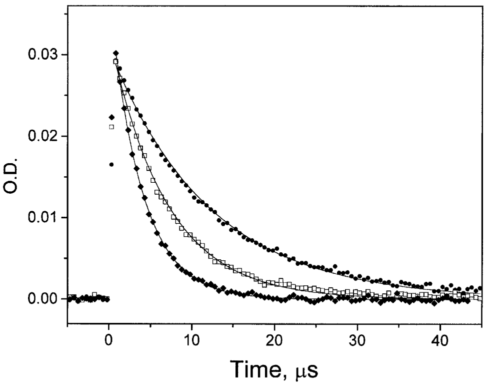

Fig. 3. Triplet decay of ClTX in acetonitrile, in the absence (●), and in the presence of MMA: (□) 0.057 M; (◆) 0.17 M.

### 3.3. Photoinitiation mechanism

It is well known that TX excited states are quenched by amines through a mechanism that involves electron transfer from the amine to the ketone forming a charge transfer intermediate. Rapid proton transfer from the amine radical cation to the ketone radical anion gives the ketyl and amine neutral radicals.

$$\begin{tikzcd} \mathrm{TX^* + Am} \arrow[r] & (\mathrm{TX^{\bullet -} + Am^{\bullet +}}) \arrow[r] \arrow[dr] & \mathrm{TXH^\bullet + Am(\text{-}H)^\bullet} \\ & & \mathrm{TX + Am} \end{tikzcd} \qquad (4)$$

Amine radicals (Am(−H)$^\cdot$) originated from the interaction between the carbonyl triplet and the co-initiator have been proved to be responsible for the initiation in several polymerizations photoinitiated by aromatic ketones [20]. The quenching of the singlet excited state frequently leads to the inhibition of the polymerization [21,22]. This is consequence of a reduced decomposition of the charge transfer intermediates to radicals, due to the rapid back electron transfer of the singlet radical ion pair.

The lack of polymerization when amine is not present, shows that the TX triplet quenching by the monomer does not lead to polymerization. Then, the active radical quantum yield is given by Eq. (5):

$$\phi_{\mathrm{rad}} = \phi_{\mathrm{T}} \frac{\left({}^3k_q\right)_{\mathrm{Am}}[\mathrm{Am}]}{\left({}^3k_q\right)_{\mathrm{Am}}[\mathrm{Am}] + \left({}^3k_q\right)_{\mathrm{MMA}}[\mathrm{MMA}] + 1/\tau_{\mathrm{T}}} \beta_{\mathrm{T}} \quad (5)$$

where $\beta_{\mathrm{T}}$ stands for the fraction of radicals originated from the triplet charge transfer intermediate that decomposes to yield active radicals, $\phi_{\mathrm{T}}$ is the yield of triplet formation, and is given by Eq. (6)

$$\phi_{\mathrm{T}} = \frac{\phi_{\mathrm{T}}^0}{\left({}^1K_{\mathrm{SV}}[\mathrm{Am}] + 1\right)} \quad (6)$$

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

The polymerization results obtained with TX, AcTX, ClTX, and MeTX can be fitted quite well with Eq. (5) (Fig. 1). This indicates that the radicals that lead to polymerization are those originated from the interaction of the ketone triplet with the amine. Other deactivation processes like quenching of the charge transfer intermediate by the amine can be considered as negligible [22]. On the other hand, the ketone bearing 2-propoxy substituent could be better fitted with a small contribution (10%) of radicals coming from the interaction of the singlet state with the amine [5]. The increased $\pi\pi^*$ character of the excited states of TXs with strong electron-donor substituents in the position 2, could increase the proton transfer within the singlet charge transfer intermediate, leading to the formation of neutral amine radicals. This contribution could be more important for the compound bearing the 2-hydroxy substituent.

The effect of the substitution in the position 2 of the TX chromophore on the photoinitiation efficiency can be analysed at high amine concentration, i.e. 30 mM. At this amine concentration nearly 90% of the triplet are deactivated by the amine. Data of Table 1 and Fig. 1 show that ClTX is the more efficient photoinitiator. This high reactivity could be due to dechlorination photoreactions. However, it has been previously shown that the irradiation of the TX with 2-chloro substituent in the presence of amines gives less than 1% of dehalogenation [23]. Furthermore, we found that the irradiation of ClTX in the absence of amine did not lead to MMA polymerization.

The difference in photoinitiation efficiencies for the different substituted TXs can be fairly well explained in terms of the triplet formation (Eq. (6)). The increase of the Stern–Volmer constant ($K_{SV}$) for the singlet quenching by amines due to the longest fluorescence lifetime found for PTX reduces the triplet formation, and consequently the yield of radicals that are able to add to the monomer. An estimation of $\phi_T$ can be obtained from Eq. (6) assuming that $\phi_T^0 = 1 - \phi_F$. This gives, at 30 mM DEOHA, $\phi_T$ value of ~0.95 for TX, ClTX, AcTX, and MeTX, and ~0.55 for PTX and TXOH.

The polymerization by TXOH could be due to the polymerization by the radicals formed in the interaction of the excited singlet of the ketone and the amine. However, at high DEOHA concentrations the triplet quenching by the amine could compete with the self-quenching process, as discussed before, and contributes to the formation of active radicals.

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