Novel water soluble copolymers based on thioxanthone: photochemistry and photoinitiation activity

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Abstract

The absorption, luminescence and photoreduction properties of five novel water soluble thioxanthone copolymers are reported. The new polymers have been prepared by copolymerization of 1-methyl-4-(3-acryloxypropoxy) thioxanthone (TX3), 1-chloro-4-acryloxy thioxanthone (TX4), 1-chloro-4-oxyethylacrylate thioxanthone (TX5), and 1-chloro-4-allyloxy thioxanthone (TX6), with two water soluble comonomers, acrylamide (AAm) and 2-acryloxyethyl trimethylammonium iodide (MI).

The photoinitiation effectiveness of these new copolymers was studied by photocalorimetry and photodilatometry for acrylamide photopolymerization in aqueous solution and in the presence of a tertiary amine. The results compared to those of the corresponding low molecular weight model compounds, (TX1), 1-methyl-4-(2-hydroxy-3-N,N,N-trimethylammoniumpropoxy) thioxanthone chloride salt, and TX2, 1-chloro-4-(2-hydroxy-3-N,N,N-trimethylammoniumpropoxy) thioxanthone chloride salt. The new copolymers show high polymerisation rates under the experimental conditions used, and confirm that these compounds operate as effective photoinitiators of polymerization. The data are discussed in relation to their photophysical and photochemical properties.
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1. Introduction

In recent years, there have been many new developments in the synthesis and photochemical studies of novel polymeric photoinitiators. This is associated with the advantages derived from their macromolecular nature, in comparison with their corresponding low molecular weight analogues. The presence of the polymer chain in many cases improves their compatibility in the formulation and reduces the migration onto the film surface. This is one advantage, contributing to the manufacture of low-odour and non-toxic coatings. Polymeric photoinitiators can be defined as macromolecular systems that contain pendant or in-chain chromophores. Therefore, the incorporation of a photoinitiator moiety into a polymer may be accomplished by inclusion of the chromophore as a pendant or in a terminal position on the polymer chain, or alternatively by copolymerizing the chromophore. The copolymerization of photosensitive monomers with conventional comonomers offers the possibility of macromolecular design, in the context of nature and distance from the backbone of the pendant photosensitive moieties and nature of the comonomer. Recently, the

advances on a wide variety of macromolecules containing the two main types of free radical photoinitiators: photofragmenting and hydrogen-abstracting chromophores polymeric photoinitiators for UV curing has been reviewed [1], with particular reference to the water soluble macrophotoinitiators, since in aqueous systems problems such as low activity and poor solubility arise with polymeric photoinitiators.

Thioxanthones (TXs) are hydrogen-abstracting photoinitiators, and most widely used in processes such as printing inks, surface coatings, microelectronics, and photoresists [2], for particular applications in UV curing of heavily pigmented resins where the pigment (TiO_2) screens out much of the UV light from the irradiation source. Their activity as photoinitiators is based on the radical production from the interaction of the thioxanthone excited triplet state with tertiary amines which proceeds through a charge transfer intermediate in the excited state (normally a triplet exciplex) [3,4].

In this paper, five new water soluble copolymers with a thioxanthone moiety as a pendant group have been prepared by the copolymerization of: 1-methyl-4-(3-acryloxypropoxy) thioxanthone (TX3), 1-chloro-4-acryloxy thioxanthone (TX4), 1-chloro-4-oxyethylacrylate thioxanthone (TX5), and 1-chloro-4-allyloxy thioxanthone (TX6), with two water soluble comonomers, acrylamide (AAm) and a previously synthesized monomer, 2-acryloxyethyl trimethylam-
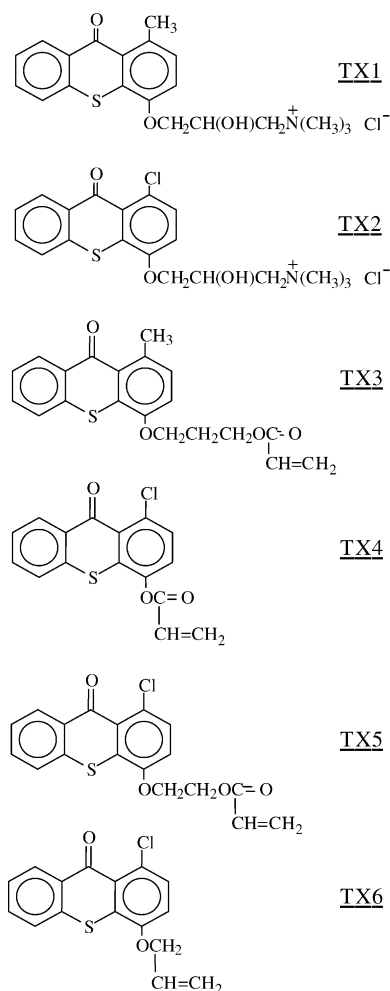
Fig. 1. Structures of the low molecular weight photoinitiators used as model compounds and monomers bearing TX chromophore.

Fig. 2. Structures of water soluble copolymers based on thioxanthone.

monium iodide (MI). The iodide counter-ion was replaced by chloride on the polymer by the use of an ionic exchange resin as described elsewhere [5]. Here, the photochemical and photopolymerization activity of novel water soluble copolymers on an aqueous system, acrylamide/water, have been examined. The data were compared with those obtained with: 1-methyl-2-hydroxy-3-(9-oxo-9H-thioxanthene-4-yloxy)-*N*,*N*,*N*-trimethyl-1-propanaminium chloride salt (TX1) and 1-chloro-2-hydroxy-3-(9-oxo-9H-thioxanthene-4-yloxy)-*N*,*N*,*N*-trimethyl-1-propanaminium chloride salt (TX2), used as low molecular weight model compounds.

The structures of the model compounds and the new copolymers are shown below with their corresponding reference abbreviation in Figs. 1 and 2.

2. Experimental procedures

2.1. Materials

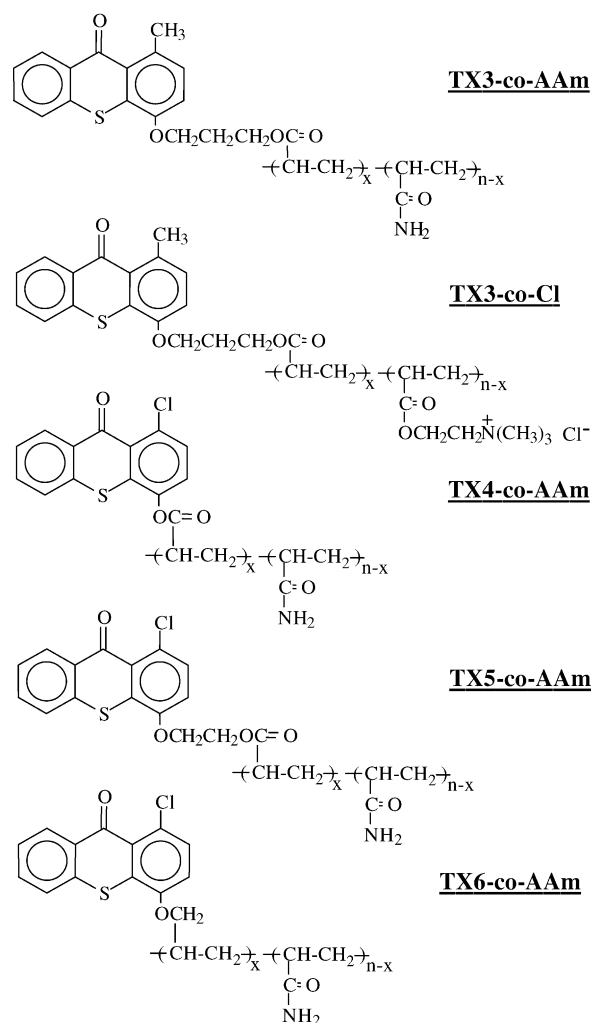Samples of the thioxanthones TX1–TX6 were supplied by Great Lakes Ltd, Widnes, Cheshire, UK. Acrylamide (AAm) was obtained from Merck and was purified by recrystallization in acetone. The water-soluble comonomer 2-acryloxyethyltrimethylammonium iodide (MI) was prepared following the method previously described [5]. The anionic exchange resin, Amberlite IRA 400, was used to exchange the iodide anion by chloride in the copolymers with MI. The solvent used in the copolymerisation, *N*,*N*-dimethylformamide was obtained from the Aldrich Chemical Co. and distilled under reduced pressure. 2,2′-Azo-bis-isobutyronitrile (AIBN), from Aldrich Chemical Co. was purified by recrystallisation from diethyl ether prior to use. Triethylamine (Aldrich) was purified by vacuum distillation. 2-(dimethylamino)ethyl acrylate from Tecal Co. was used as received.

In all the experiments MilliQ grade water was used and the other solvents were Analar or spectroscopic grades from Aldrich Chemical Co., Ltd.

2.2. Copolymerization procedure

Five new copolymers were obtained by radical copolymerization of thioxanthones TX3–TX6 with acrylamide

Table 1
Ultraviolet absorption in water and percentage of thioxanthone in the water soluble copolymers

Compound	λ_{max} (nm) in H_2O	TX content (w/w)
TX1	392	–
TX2	394	–
TX3-co-AAm	394	3.7
TX3-co-Cl	392	1.2
TX4-co-AAm	388	2.1
TX5-co-AAm	394	5.0
TX6-co-AAm	399	0.6

(AAm) and TX3 with 2-acryloxyethyltrimethylammonium iodide (MI). The copolymerization reactions were carried out in Pyrex ampoules under nitrogen at 70 °C for 40 min using *N,N*-dimethylformamide/water (8/2, v/v) as solvent and azo-bis-isobutyronitrile as the thermal initiator (0.3%).

Molar fractions in the feed were chosen to yield a low content of the chromophore in the copolymers such as f_{TX} = 0.017 and 0.983 for the remaining comonomers.

All the copolymers were purified by successive precipitations from aqueous solutions into methanol and acetone. The copolymer TX3-co-MI was precipitated in methanol, filtered, dissolved in water and then passed through an anionic exchange resin Amberlite IRA 400 to give the corresponding polyelectrolyte, TX3-co-Cl, with chloride as the counter-ion. The solvent was removed by evaporation and then the copolymers dried to constant weight. Hence, with this anion exchange more stable polymers are obtained and the possible heavy atom effect is avoided in their photochemical behaviour.

The weight percentages of thioxanthone chromophore in the copolymers were determined in water by UV spectroscopy, using the molar absorption coefficient of the corresponding model compound, TX1 for TX3-copolymers and TX2 for the copolymers containing TX4–TX6 in their structure. In water ε_{TX1} = 5248 L mol^{-1} cm^{-1} at λ_{max} = 392 nm, and ε_{TX2} = 5495 L mol^{-1} cm^{-1} at λ_{max} = 394 nm. The data are collected in Table 1. These results indicated that the composition of the copolymers is basically controlled by the monomer feed ratios.

2.3. Spectroscopic measurements

UV absorption spectra were recorded by means of a Shimadzu UV-265-FS spectrophotometer. Fluorescence and phosphorescence emission spectra were obtained using a Perkin-Elmer LS-50B luminescence spectrophotometer, and corrected by means of using the response curve of the photomultiplier. Fluorescence quantum yields were obtained at 300 K using the relative method employing quinine sulphate as a standard and assuming a quantum yield of 0.55 in 0.1 M sulphuric acid [6]. Phosphorescence quantum yields were obtained by the same method using benzophenone as a standard assuming a quantum yield of 0.74 in ethanol glass at 77 K [7].

Fluorescence emission spectra were also obtained at different pH and were measured by adding sodium hydroxide for basic media and hydrochloric acid for pH lower than 7.

2.4. Photoreduction quantum yields

Absolute quantum yields of photoreduction, ϕ_r, were determined in water at a initial chromophore concentration of 10^{-5} M, in the absence and presence of triethylamine (10^{-3} M) as a hydrogen donor. Irradiations were carried out at 365 nm from a medium pressure Hg lamp, under nitrogen as described previously [8].

2.5. Photodilatometry

Acrylamide photopolymerizations were carried out in a mixture of water:acetonitrile (5:2, v/v) at 0.4 M, using the synthesized thioxanthone copolymers or the water soluble model compounds (thioxanthone concentration: 10^{-5} M) together with triethylamine (TEA = 10^{-3} M) as a photoinitiator system. Nitrogen was purged through the dilatometer, filled with such photopolymerizable solutions, and then irradiated at 365 nm. A detailed description of the dilatometer and employed irradiation system, experimental procedure and determination of polymerization rates, R_p, were published earlier [9].

2.6. Photocalorimetry

The initial rates of polymerization, R_p, of acrylamide (AAm = 2.81 M) were determined by photocalorimetry in aqueous solution in air at 35 °C using 365 nm as monochromatic light. The thioxanthone derivatives were dissolved in the monomer-solvent mixture at a concentration of 10^{-5} M. In such conditions total absorption by the thioxanthone is assured. In all cases triethylamine was used as the co-synergistic amine at a concentration of 10^{-2} M. Samples (10 μl) were placed on aluminium pan sealed with quartz glass in order to avoid evaporation of the monomer and oxygen renovation through the atmosphere. The kinetics of photoinitiated polymerization were monitored using a Perkin-Elmer DSC-4 calorimeter. Experimental details of the system and the procedure have been reported elsewhere [8–10].

3. Results and discussion

3.1. Spectroscopic measurements

The absorption and luminescence (fluorescence and phosphorescence) properties of the novel five water soluble copolymers and their corresponding models, are compared in Table 2. The phosphorescence spectra were recorded in ethanol due to problems with freezing water cracking the quartz tubes used in the measurement at 77 K.

Table 2
Spectroscopic properties of novel water soluble copolymers and model compounds

Compound	Absorption in H_2O	Fluorescence in H_2O		Phosphorescence (77 K) in ethanol		
	λ_{max} (nm)	λ_{max} (nm)	ϕ_F	λ_{max} (nm)	ϕ_P	τ (ms)
TX1	392	495	0.15	465	0.11	9
TX2	394	483	0.32	470	0.45	169
TX3-co-AAm	394	489	0.04	507	0.06	7
TX3-co-Cl	392	490	0.04	492	0.01	7
TX4-co-AAm	388	453	0.03	491	0.03	—[a]
TX5-co-AAm	394	486	0.07	504	0.06	4
TX6-co-AAm	399	489	0.08	540	0.16	—[a]

[a] Not detected after 20 µs of delay.

The absorption wavelength maxima were little influenced by the nature of the 1-substitution. The copolymers exhibited similar properties to those corresponding to the low molecular weight compounds, indicating that there was no interaction between neighbouring groups in the ground state. Also, a blue shift was observed for TX4-co-AAm due to the hypsochromic effect of the ester group directly attached to the chromophore. Likewise, there was a small red shift in the absorption maximum for the TX6-co-AAm due to the absence of ester groups in the 4-position of the thioxanthone.

The longest wavelength emission maxima and quantum yield of fluorescence are shown in Table 2. From the data it was seen that all the compounds exhibited fluorescence emission indicating that the lowest excited singlet state had some degree of $\pi-\pi^*$ character. In general, the fluorescence quantum yields of the copolymers were lower than those of the model compounds. This effect could be due to the efficient radiationless process of deactivation of the lowest singlet state, which would be more favourable in the polymeric photoinitiators than in the low molecular weight compounds. Intra-molecular self quenching may also be operative.

The fluorescence emission maxima of the low molecular weight water soluble thioxanthones were strongly dependent on pH. The pH-effect for TX1, TX3-co-AAm and TX3-co-Cl is shown in Fig. 3, by plotting the obtained fluorescence quantum yields for these compounds at different pH media. As was previously described [11], in acidic pH the fluorescence quantum yield of compound TX1 was reduced markedly and this may be due to a change in the equilibrium of the emitting species. At a basic pH value the quantum yield seemed to decrease and then remain constant after pH 11. This effect could be related to the counter-ion interchange of the chloride by the hydroxide ion. A lower pH dependence of the quantum yield of fluorescence was observed for the copolymers studied, and for TX3-co-AAm the values obtained were nearly constant.

The phosphorescence quantum yield and triplet lifetime for the new compounds were measured in ethanol, Table 2. A similar effect to that found for the singlet state could be observed; the phosphorescence quantum yield and triplet lifetime for the copolymers were found to decrease with respect to the model compounds. This trend could be due to the efficient radiationless process of deactivation of the triplet state. The compound TX1 exhibited a lower phosphorescence quantum yield and triplet lifetime than the compound TX2. This result has been justified earlier for
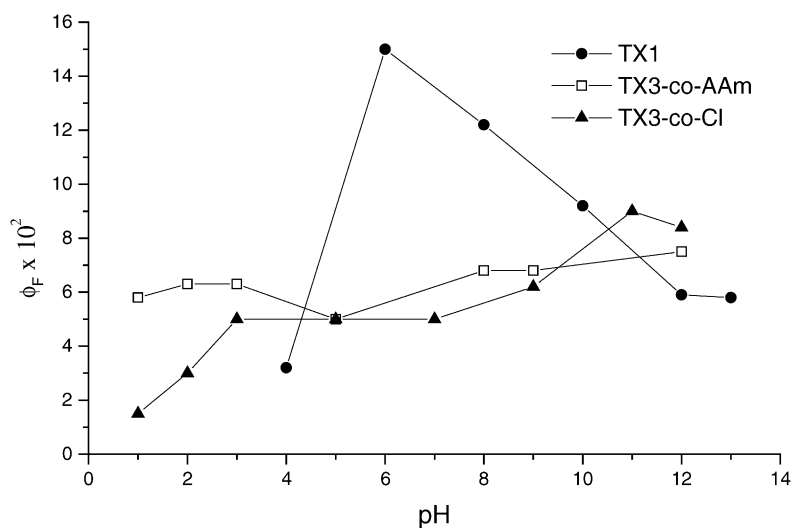

Fig. 3. Evolution of the fluorescence quantum yield of compounds TX1 (●), TX3-co-AAm (□) and TX3-co-Cl (▲) with the pH in water solution.

Table 3
Photoreduction quantum yields of thioxanthone derivatives (10^{-5} M) in water, using triethylamine as a hydrogen donor (10^{-3} M), under nitrogen

Compound	ϕ_r
TX1	0.010
TX2	0.025
TX3-co-AAm	0.037
TX3-co-Cl	0.020
TX4-co-AAm	0.005
TX5-co-AAm	0.043
TX6-co-AAm	0.034

$\lambda_{irrad} = 365$ nm.

the 1-methyl-substituted derivatives by an intramolecular hydrogen-bonding on the excited state between the carbonyl and the methyl hydrogen neighbouring groups [8].

3.2. Photoreduction quantum yields

The photoreduction quantum yields for all the products in deoxygenated water were determined in the presence and absence of triethylamine used as a hydrogen donor. The photoreduction quantum yields were low ($<10^{-4}$) in the absence of amine, and enhanced in the presence of triethylamine. This was consistent with photoreduction of the excited thioxanthone with the amine via a low lying triplet exciplex involving charge transfer. The data are summarised in Table 3. In general, higher photoreduction quantum yields were found for the copolymers than these for the models, and would indicate the role of the macromolecular chain as a hydrogen donor in the photoreaction.

3.3. Photodilatometric study

Photopolymerizations of acrylamide in a solvent mixture of water and acetonitrile (5/2, v/v) were carried out in a photodilatometer as described in the experimental part. The rate of polymerization (R_p) was calculated from conversion-time profiles up to conversion lower than 10%. The photoinitiation quantum yield (ϕ_i) was calculated using the general equation:

$$R_p = \frac{k_p}{k_t^{1/2}} R_i^{1/2}[M] = \frac{k_p}{k_t^{1/2}} \phi_i^{1/2} I_a^{1/2}[M]$$

where k_p and k_t are the propagation and termination rate constants and, for acrylamide at 19 °C have the values [12], $k_p = 8.2 \times 10^3$ L mol^{-1} s^{-1} and $k_t = 5.5 \times 10^6$ L mol^{-1} s^{-1}, I_a the absorbed intensity and [M] is the monomer concentration. The data obtained using TX1, TX3-co-AAm and TX3-co-Cl as photoinitiators are summarised in Table 4.

Photopolymerization rates and photoinitiation quantum yields were found to be similar for the model compound TX1 and the copolymer TX3-co-AAm. However, TX3-co-Cl exhibited a lower photopolymerisation activity. The presence of a large density charge in this copolymer may induce sev-

Table 4
Polymerization rates, R_p (mol L s^{-1}), and quantum yields of photoinitiation (ϕ_i) determined by photodilatorimetry

Photoinitiator	R_p ($\times 10^5$ mol L^{-1} s^{-1})	ϕ_i ($\times 10^2$)
TX1	8.3	0.7
TX3-co-AAm	7.8	1.1
TX3-co-Cl	3.3	0.2

Polymerization of AAm (0.4 M) in water/acetonitrile (5/2, v/v) irradiating under nitrogen at 365 nm using thioxanthones (10^{-5} M) and triethylamine (10^{-3} M).

eral effects affecting its photoinitiation activity. As for example the presence of chloride ions solvated in the medium which may react with primary initiating radicals reducing its effectiveness as photoinitiator. This feature also diminished the photoinitiation quantum yield of TX1. Moreover, the adopted conformation of the copolymer TX3-co-Cl seemed to cause restrictions to radical formation via exciplex.

3.4. Photocalorimetric study

The polymerization of acrylamide (AAm = 2.81 M) photoinitiated with these new water-soluble thioxanthones was carried out in water solutions using a thioxanthone concentration of 10^{-3} mol L. In absence of amine, no polymerisation was detected due to the poor hydrogen donating ability of the solvent. Triethylamine was used as the coinitiator in all cases. Moreover, this enhanced the effectiveness on the polymerization, since this was related to the ability of the amine group to scavenge oxygen via alkylamino radicals produced by the lowest excited triplet state of the thioxanthone abstracting a hydrogen atom from the amine. The polymerisation rates (R_p) and quantum yields (ϕ_m) on the photopolymerisation using the thioxanthones as photoinitiators, are shown in Table 5. The photopolymerisation quantum yield (ϕ_m) was calculated from the slope on the plot of moles of polymerized monomer versus the absorbed light intensity (I_a).

The polymerization quantum yields are quite high for all the compounds and the values of the polymerization rates were also similar for all of them. The polymer TX4-co-AAm showed the lowest value and this was in agreement with

Table 5
Polymerization rates, R_p (mol L s^{-1}), and quantum yields of photopolymerization (ϕ_m) determined by photocalorimetry

Photoinitiator	R_p ($\times 10^2$ mol L s^{-1})	ϕ_m ($\times 10^{-2}$)
TX1	2.5	1.1
TX2	3.5	1.5
TX3-co-AAm	4.5	2.0
TX3-co-Cl	2.1	0.9
TX4-co-AAm	0.9	0.4
TX5-co-AAm	4.1	1.9
TX6-co-AAm	1.2	0.6

Polymerization of AAm in water (2.81 M) irradiating at 365 nm using thioxanthones (10^{-3} M) and triethylamine (10^{-2} M).

its low photoreduction quantum yield shown in Table 3. Again, in comparison of the behaviour of TX3-co-AAm and TX3-co-Cl, the same feature as in the photocalorimetric study was observed. This was related to the polyelectrolyte nature of macromolecular main chain in TX3-co-Cl.

Several factors may account for the observed differences in photopolymerisation efficiency using these novel water-soluble photoinitiators bearing thioxanthone as chromophore. Considering acrylamide based copolymers, TX3-co-AAm, TX4-co-AAm, TX5-co-AAm and TX6-co-AAm, thioxanthone content increase seemed to favour photopolymerisation of AAm. Moreover, structural changes may influence the conformation of lateral thioxanthone pendant groups. For example, the presence of a mid-chain ester group in the 4-position of the TX moiety in TX3-co-AAm and TX5-co-AAm should allow better accessibility to the coinitiator to give rise the alkylamino initiating radicals.

Special attention merited TX3-co-Cl as a polyelectrolyte bearing a photoinitiator moiety. As it is well known, polyelectrolytes represent a unique class of polymer which are both macromolecules and electrolytes. The special properties of these polymers are determined by their electrochemical and macromolecular parameters and their chemical structure. The copolymerisation of the corresponding TX derivative acrylic monomer with MI (and then anion exchange) may result in a hydrophobically modified polyelectrolyte, TX-co-Cl. Owing to the presence of both ionizable and hydrophobic groups, electrostatic and hydrophobic interactions lead to a rich variety of structures and, therefore, photoinitiation activity is affected. In this regard, these types of polymeric photoinitiators may also act as a surfactant, thus becoming of interest for the polymerisation of emulsion systems.

4. Conclusions

Five new polymers have been prepared by copolymerization of 1-methyl-4-(3-acryloxypropoxy) thioxanthone, 1-chloro-4-acryloxy thioxanthone, 1-chloro-4-oxyethylacrylate thioxanthone, and 1-chloro-4-allyloxy thioxanthone, with two water soluble comonomers, acrylamide and 2-acryloxyethyl trimethylammonium iodide. Their properties and photoinitiation effectiveness were compared with those of low molecular weight model compounds (TX1), 1-methyl-4-(2-hydroxy-3-_N,N,N_-trimethylammoniumpropoxy) thioxanthone chloride salt, and TX2, 1-chloro-

4-(2-hydroxy-3-_N,N,N_-trimethylammoniumpropoxy) thioxanthone chloride salt. The new copolymers exhibited similar absorption to those corresponding to the models compounds, indicating that there was no interaction between neighbouring groups in the ground state. The luminescence quantum yields of the copolymers were lower than those of the models, due to the efficient radiationless process of the deactivation of the singlet and triplet states in the copolymers. Otherwise, the new copolymers containing TX3 showed higher polymerisation rates than TX1 model. This result confirmed that these novel compounds operate as effective photoinitiators of polymerization. The copolymers TX3-co-AAm and TX5-co-AAm exhibited the highest photoinitiation effectiveness. It has been associated with the presence of a mid-chain ester group in the 4-position of TX moiety, which should allow better accesibility to the coinitiator to give rise the alkylamino initiating radicals.

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