

Photochemistry and photoinitiator properties of novel 1-chloro-substituted thioxanthenes Part I: Influence of 4-acyloxy substitution

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Abstract

The photoinduced polymerisation activities of five novel 1-chloro-4-acyloxy substituted thioxanthenes have been determined and compared to that of the 4-hydroxy and 4-*n*-propoxy derivatives in different monomers and prepolymers using RTIR and photocalorimetry methods. Absorption, fluorescence and phosphorescence analysis and photoreduction studies have also been undertaken on the compounds and the data inter-related to their photopolymerisation activities. Fluorescence and phosphorescence analysis indicates a high rate of intersystem crossing to the triplet state. The latter is essentially $\pi\pi^*$ in nature but strongly mixed with a close lying $n\pi^*$ as indicated by the phosphorescence lifetime data. Compared with the 1-chloro-4-hydroxy derivative used as a comparative model all 4-acyloxy derivatives exhibit much higher photoinitiation activity. The results are also consistent with a marked enhancement in photoreduction quantum yields, especially in the presence of an amine cosynergist. The enhanced photoactivity of the 4-acyloxy derivatives is associated with reduced fluorescence quantum yields and consequent increased $n\pi^*$ activity of the triplet state through the electron withdrawing effect of the acyl group. High photoconversion during polymerisation is observed in the presence of oxygen indicating the predominance of photodehalogenation which is enhanced by the presence of a tertiary amine cosynergist. Using RTIR higher degrees of conversion are observed under visible light irradiation than under UV exposure. © 1997 Elsevier Science S.A. All rights reserved.

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1. Introduction

Thioxanthone derivatives are widely used for the photoinitiated curing of pigmented acrylate formulations [1]. One successful compound in this regard is ITX, a 2-isopropoxy derivative. However, one major deficiency with these initiators is the requirement of a tertiary amine cosynergist, which aside from the additional cost, can cause unacceptable yellowing problems. Many new derivatives of thioxanthenes have been developed in recent years, not only to circumvent such problems but to also provide enhanced speed of cure and synergism with other active photoinitiators. One new initiator in this regard is the 1-chloro-4-propoxy derivative of thioxanthone, abbreviated to CPTX which exhibits photoinitiation in the absence of a tertiary amine cosynergist. In

blue screen printing inks it is claimed to exhibit twice the photocuring activity of ITX and is highly synergistic with benzophenone [2]. A more recent study on CPTX, in conjunction with other 1-halo derivatives, has shown evidence for an additional mechanism, involving dehalogenation to give a halogen radical [3]. This would account for the photoactivity of the initiator in the absence of an amine cosynergist.

In this series of papers we aim to examine the influence of a range of 4-oxy substituted groups on the photochemical and photoinitiation properties of 1-chloro-thioxanthone. Here we have examined the effect of a number of acyloxy groups either directly attached to the ring 4-position or displaced via an alkyl-ether link. The study includes a spectroscopic and photoinitiated polymerisation evaluation using real time infrared and photocalorimetry. The photoactivities of the initiators are compared with those of the standard industrial system, CPTX

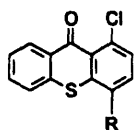
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and the basic 1-chloro-4-hydroxy derivative which was used to synthesise all the derivatives examined here.

2. Experimental

2.1. Materials

All the solvents, butyl acrylate, triethylamine, diethylethanolamine, benzophenone and quinine sulphate used in this work were obtained from Aldrich Chemical Co. Ltd., U.K and were of analar, spectroscopic or HPLC grade quality. The compounds, (1) 1-chloro-4-oxyethylacrylate (m.p. = 85–86 °C), (2) 1-chloro-4-acetyloxy (m.p. = 141–142 °C), (3) 1-chloro-4-acryloxy (m.p. = 164–165 °C), (4) 1-chloro-4-phenacyloxy (m.p. = 174–176 °C), (5) 1-chloro-4-benzoyloxy (m.p. = 171–175 °C), 1-chloro-4-*n*-propoxy (m.p. = 269–272 °C) and (7) 1-chloro-4-hydroxythioxanthenes were supplied by the Great Lakes Company, Widnes, UK. Their corresponding structures are shown below. All the compounds are chromatographically pure and have verified elemental C, H, O, Cl and S analysis as described previously [4]. The 4-hydroxy derivative was the starting compound used in the synthesis of all the structures and therefore a useful reference material in terms of activity studies.



- 1: R=OCH₂CH₂OCOCH=CH₂; mpt=85-86°C
 2: R=OCOCH₃; mpt=141-142°C
 3: R=OCOCH=CH₂; mpt=164-165°C
 4: R=OCH₂COC₆H₅; mpt=174-176°C
 5: R=OCOC₆H₅; mpt=171-175°C
 6: R=OCH₂CH₂CH₃; mpt=100-102°C
 7: R=OH; mpt=269-272°C

2.2. Spectroscopic measurements

Absorption spectra were obtained using a Perkin-Elmer Lambda 7 absorption spectrometer. Fluorescence and phosphorescence excitation and emission spectra were obtained using a Perkin-Elmer LS-50B research luminescence spectrometer. Fluorescence quantum yields were obtained by the relative method using quinine sulphate in 0.05 M sulphuric acid as a standard [5]. The quantum yield of quinine sulphate was assumed to be 0.55. Phosphorescence quantum yields were obtained in ethanol at 77 K using the relative method with benzophenone as a standard assuming a quantum yield of 0.74 in ethanol [5]. All spectra were corrected using a Perkin-Elmer IBM compatible GEM package with an appropriate file for this purpose.

2.3. Photoreduction quantum yields

Absolute quantum yields of photolysis (ϕ_f) of the initiators were determined in 2-propanol at 10⁻⁵ M using an irradiation wavelength of 365 nm, selected from a Philips high pressure Hg lamp (HB-CS 500 W) and a Kratos GM252 monochromator. Sample cells were thermostatted at 30 °C and the solutions were oxygen and nitrogen (< 5 ppm O₂) saturated. The absorbed light intensity was measured using an International Light Model 700 radiometer previously calibrated by the Aberchrome 540 actinometer [6,7].

3. RTIR

The thioxanthenes were dissolved in a minimum quantity (2–3 cm³ of tetrahydrofuran) followed by mixing with a prepolymer, Sartomer 348 (ethoxylated bisphenol-A-dimethacrylate) (Sartomer Company, Pennsylvania, USA) (0.001 M). Traces of solvent were then removed by flushing with argon for 30 min. followed by addition of 1 wt.% of the co-initiator *p*-ethyl dimethylaminobenzoate (EDB) (Great Lakes, Widnes, UK).

The resin was then placed between pieces of low density polyethylene using a separator to give a film thickness of 50 μm. The polyethylene holder was then placed between two infrared salt flats and placed in the sample beam. Two polyethylene film samples were used as the reference. The decrease in absorbance at 1638 cm⁻¹ of the vinyl absorption band was then monitored in real-time mode during irradiation using a fibre optic arrangement. The irradiation source used here was an ILC 302 UV (Laser Lines Ltd., Beaumont Close, Banbury, Oxon, UK) switchable between UV and visible light with a cut-off point at 400 nm. Plots of percentage conversion with time were obtained from which second plots of mol l⁻¹ versus time in seconds were obtained. From the initial slopes of the second plots R_p values (mol l⁻¹ s⁻¹) were obtained.

4. Photocalorimetry

The set-up for photocalorimetry is as described previously using a modified Perkin-Elmer differential scanning calorimeter [8]. The sample and reference are irradiated by way of two fibre optic cables carrying the light energy from a high pressure 100 W Hanovia mercury lamp and then by way of a monochromator for isolation of the 365 nm line. Heat evolution (mcal) with time of conversion is measured by maintaining the sample chamber at 40 °C. The exotherm curve for each experiment is integrated to calculate the area under the curve at given time intervals. Corrections are then made for reaction times and sample weights. Butyl acrylate was used as the monomer (Aldrich Chemical Co. Ltd., Spain) after distillation using a 20 ml sample in each case. Three experimental conditions were used, nitrogen, nitrogen and 2-die-

thylaminoethanol (amine) (6×10^{-3} M), air and air with amine at 3×10^{-3} M of initiator to give a constant absorbance at 365 nm.

Plots of percentage conversion with time were obtained from which second plots of mol l^{-1} versus time in seconds were obtained. From the initial slopes of the second plots R_p values ($\text{mol l}^{-1} \text{s}^{-1}$) were obtained. A third plot of moles converted versus energy absorbed, correcting for absorption differences, was also obtained. This plot compares the efficiency of the photoinitiators in converting the light energy into polymers. The slope of this graph gives the value of the quantum yield of photopolymerisation (Φ_p), i.e. the number of monomer molecules consumed per photon absorbed.

5. Results and discussion

5.1. Spectroscopic properties

Absorption maxima and extinction coefficients (logarithmic) of all the derivatives examined here are compared by the data in Table 1 for a range of solvents. In cyclohexane the 4-hydroxy derivative was not very soluble and consequently only a wavelength maximum is given. From cyclohexane to chloroform the long wavelength absorption maximum for all the compounds undergo a small bathochromic shift with no significant change in the extinction coefficient. In solvents of higher polarity there is a small

hypsochromic shift, again with no change in the extinction coefficient. This suggests the presence of a strongly mixed $n\pi^*/\pi\pi^*$ long wavelength transition. Thus, small patterns of substitution can have a marked influence on the excited state properties and activity of the thioxanthone chromophore. In comparison with the 4-propoxy derivative all the other compounds exhibit a small blue shifted absorption maximum associated with the electron withdrawing inductive effect of the acyl group. This is also likely to enhance the $n\pi^*$ activity of the molecule.

The fluorescence emission maxima and quantum yields of the thioxanthone initiators are compared in Table 2. A large bathochromic shift is observed in the emission wavelength maxima with increasing solvent polarity from cyclohexane to ethanol. Thereafter, there is a small hypsochromic shift, except for the benzoyloxy derivative, where the red shift continues to increase. This data is consistent with the absorption spectra and indicative of a lowest lying singlet $\pi\pi^*$ state with a close lying upper $n\pi^*$ state. All the fluorescence quantum yields are very low in non-polar cyclohexane, except that of the 4-hydroxy derivative, and show a tendency to increase in solvents of higher polarity. This is consistent with a lowest lying singlet $\pi\pi^*$ state decreasing in energy, and increasing distance, from that of the next upper singlet $n\pi^*$ state. However, the quantum yields in general are low and indicative of a high rate of intersystem crossing to the next lying triplet state. From our previous laser study CPTX had a relatively high rate of intersystem crossing of 0.80 [4]. The fluores-

Table 1
Absorption maxima and extinction coefficients of 1-chloro-4-acyloxy-substituted thioxanthenes (5×10^{-5} M)

Thioxanthone	Cyclohexane		Chloroform		Ethanol		Acetonitrile		DMF	
	λ max (nm)	Log ϵ	λ max (nm)	Log ϵ	λ max (nm)	Log ϵ	λ max (nm)	Log ϵ	λ max (nm)	Log ϵ
1-Chloro-4-oxyethylacrylate	374s/384	3.76	391	3.77	388	3.79	384	3.83	386	3.81
1-Chloro-4-acetyloxy-	369s/376	3.8	382	3.81	379	3.77	377	3.8	382	3.81
1-Chloro-4-acryloxy-	369s/377	3.82	381	3.8	379	3.79	377	3.82	383	3.81
1-Chloro-4-phenacyloxy-	380s/385	3.51	389	3.79	390	3.75	385	3.52	3.87	3.84
1-Chloro-4-benzoyloxy-	369s/377	3.81	383	3.8	379	3.81	377	3.82	380	3.82
1-Chloro-4-propoxy-	375s/386	3.8	391	3.78	390	3.79	386	3.81	387	3.81
1-Chloro-4-hydroxy	373	–	387	3.61	395	3.57	386	3.66	390	3.68

Table 2
Fluorescence emission maxima and quantum yields of 1-chloro-4-acyloxy substituted thioxanthenes

Thioxanthone	Cyclohexane		Chloroform		Ethanol		Acetonitrile		DMF	
	λ max (nm)	ϕ_f	λ max (nm)	ϕ_f	λ max (nm)	ϕ_f	λ max (nm)	ϕ_f	λ max (nm)	ϕ_f
1-Chloro-4-oxyethylacrylate	402	5.9×10^{-5}	440	2.0×10^{-3}	459	1.5×10^{-2}	441	6.8×10^{-4}	431	4.5×10^{-4}
1-Chloro-4-acetyloxy-	402	8.8×10^{-5}	424	1.1×10^{-4}	462	6.3×10^{-4}	443	8.7×10^{-5}	453	1.3×10^{-3}
1-Chloro-4-acryloxy-	403	7.6×10^{-5}	426	1.6×10^{-3}	446	7.0×10^{-4}	423	9.0×10^{-5}	448	1.6×10^{-3}
1-Chloro-4-phenacyloxy-	402	1.4×10^{-5}	430	1.6×10^{-3}	460	2.1×10^{-2}	438	5.2×10^{-4}	435	4.7×10^{-4}
1-Chloro-4-benzoyloxy-	402	8.5×10^{-5}	418	2.1×10^{-4}	436	5.1×10^{-4}	442	8.1×10^{-5}	450	1.2×10^{-3}
1-Chloro-4-propoxy-	402	6.0×10^{-5}	444	1.5×10^{-2}	464	2.2×10^{-2}	442	7.4×10^{-4}	436	7.1×10^{-4}
1-Chloro-4-hydroxy	403	3.8×10^{-3}	438	1.9×10^{-3}	477	4.5×10^{-3}	444	1.7×10^{-3}	450	3.2×10^{-3}

cence quantum yield of the 4-hydroxy derivative is consistent with solvent polarity and higher than the other derivatives, except chloroform and ethanol for the 4-*n*-propoxy derivative. This is associated with the electron withdrawing effect of the acyl group reducing the $\pi\pi^*$ character of the chromophore.

Phosphorescence emission maxima, quantum yields and lifetimes of the thioxanthenes are compared by the data in Table 3. The phosphorescence emission maxima are close to those of the fluorescence and thus indicative, of close lying singlet and triplet $\pi\pi^*$ states. The triplet lifetimes are also typical for those expected of a lowest lying triplet $\pi\pi^*$ state. It is also interesting to note that all the acyl derivatives exhibit higher phosphorescence quantum yields than both the 4-*n*-propoxy and 4-hydroxy derivatives. This is again consistent with a decrease in the π character of the chromophore.

Table 3
Phosphorescence emission maxima, lifetimes and quantum yields of 1-chloro-4-acyloxy substituted thioxanthenes in ethanol

Thioxanthone	λ max (nm)	ϕ_p	Lifetime τ (ms)
1-Chloro-4-oxyethylacrylate	472	0.11	273
1-Chloro-4-acetyloxy-	455	0.2	65
1-Chloro-4-acryloxy-	455	0.17	20
1-Chloro-4-phenacyloxy-	474	0.35	155
1-Chloro-4-benzoyloxy-	454	0.15	24
1-Chloro-4-propoxy-	474	0.06	209
1-Chloro-4-hydroxy	492	0.09	145

Table 4
Photoreduction quantum yields in anaerobic 2-propanol of 1-chloro-4-acyloxy-substituted thioxanthenes

Thioxanthone	No Amine ϕ_r	Amine ^a ϕ_r
1-Chloro-4-oxyethylacrylate	0.013	0.11
1-Chloro-4-acetyloxy-	0.015	0.12
1-Chloro-4-acryloxy-	0.069	0.18
1-Chloro-4-phenacyloxy-	0.0016	0.14
1-Chloro-4-benzoyloxy-	0.029	0.26
1-Chloro-4-propoxy-	0.009	0.28
1-Chloro-4-hydroxy	$< 10^{-4}$	$< 10^{-4}$

^a 10^{-3} M triethylamine.

Table 5
Photocalorimetry data in anaerobic and aerobic butyl acrylate of 1-chloro-4-acyloxy-substituted thioxanthenes (3×10^{-3} M)

Thioxanthone	Aerobic ^a		Anaerobic ^a	
	$R_p \times 10^{-2}$ (mol dm ⁻³ s ⁻¹)	ϕ_p	$R_p \times 10^{-2}$ (mol dm ⁻³ s ⁻¹)	ϕ_p
1-Chloro-4-oxyethylacrylate	3	102.9	3.1	131.7
1-Chloro-4-acetyloxy-	2.6	94.3	2.8	109.3
1-Chloro-4-acryloxy-	1.7	63.5	2.4	94
1-Chloro-4-phenacyloxy-	2.6	96.1	2.7	99.5
1-Chloro-4-benzoyloxy-	2.7	102.5	2.8	108.5
1-Chloro-4-propoxy-	1.75	64	2.3	96.5
1-Chloro-4-hydroxy	0.08	3	1.8	71.3

^a 6×10^{-3} M diethylethanolamine.

5.2. Photoreduction and photoinitiated polymerisation

The photoreduction quantum yields of the thioxanthenes in 2-propanol in the absence and presence of a tertiary amine (triethylamine) are compared by the data in Table 4. The quantum yields are generally low when irradiated alone in 2-propanol and enhanced in the presence of the amine. This is consistent with photoreduction of the excited thioxanthone via a low lying triplet exciplex with the amine involving electron transfer. In the case of the 4-hydroxy derivative there is virtually no photoreaction and may be associated with the strong $\pi\pi^*$ character of its lowest excited triplet state.

The photoinduced polymerisation data show a number of interesting features. Rates of propagation and quantum yields of monomer conversion during photocalorimetry are compared by the data in Table 5. The first interesting feature is that the presence of oxygen has little influence on the rate of conversion. Exclusion of the oxygen in the case of the 4-acyl derivatives has only a minor effect in enhancing the quantum yields. This may suggest a high rate of photoconversion via photodehalogenation [4]. In this case the chlorine radical would then hydrogen atom abstract from the amine to produce the active alkylamino radical. The electron withdrawing effect of the acyl group may enhance this reaction. The second interesting result is that the 4-propoxy derivative is somewhat less reactive in the presence of oxygen, with the 4-hydroxy derivative being even lower. The higher phosphorescence quantum yields in the case of the 4-acyloxy derivatives is consistent with the increased photoinitiation activity suggesting that dehalogenation may occur via the lowest excited triplet state. Under the conditions of irradiation used here the 365 nm Hg line would induce photoexcitation to the lowest excited singlet $n\pi/\pi\pi^*$ states.

The photopolymerisation data obtained via real time infrared (RTIR) analysis is shown in Table 6. Here the influence of UV versus visible light, as well as the effect of amine are examined. The first interesting feature is that the effect of amine is highly synergistic with all the thioxanthenes. In the absence of amine photoconversion is very low and is consistent with the photoreduction data in Table 4. We previously showed that photodehalogenation was enhanced in the pres-

Table 6
Photopolymerisation data R_p ($\text{mol dm}^{-3} \text{s}^{-1}$) in ethoxylated bisphenol A dimethacrylate (Sartomer 348) with 1 wt.% *p*-ethylidimethylaminobenzoate (EDB) using 1-chloro-4-acyloxy-substituted thioxanthenes ($1 \times 10^{-3} \text{ M}$)

Thioxanthone	UV light		Visible light	
	No amine	Amine	No amine	Amine
1-Chloro-4-oxyethylacrylate	3.48	17.57	2.51	22.02
1-Chloro-4-acyloxy-	6.77	13.54	0.18	16.08
1-Chloro-4-acryloxy-	7.02	13.91	5.35	12.73
1-Chloro-4-phenacyloxy-	3.64	19.82	3.57	19.86
1-Chloro-4-benzoyloxy-	7.18	18.72	5.04	16.9
1-Chloro-4-propoxy-	2.04	20.57	1.84	22.79
1-Chloro-4-hydroxy	0.95	14.64	0.48	17.92

ence of an amine [4]. The second interesting feature is that these thioxanthenes exhibit overall higher activity when irradiated with light above 400 nm. Owing to the polychromatic nature of the light source the involvement of several reaction paths is enhanced. Thus, with no amine present whilst photoreactivity is low all the acyloxy derivatives exhibit higher activity than both the 4-*n*-propoxy and 4-hydroxy derivatives. This effect is consistent with the photocalorimetry data. However, in the presence of an amine comparable, if not slightly higher activity is observed under these conditions.

6. Conclusions

Spectroscopic analysis on the 1-chlorothioxanthenes indicates a high rate of intersystem crossing to the triplet state. The latter is essentially $\pi\pi^*$ in character but strongly mixed with a close lying $n\pi^*$ state. Compared with the 4-hydroxy derivative used as a comparative model all the 4-acyloxy derivatives exhibit much higher photoinitiation activity. The 4-propoxy derivative was also less active except in the presence of an amine cosynergist. The enhanced photoactivity of

the 4-acyloxy derivatives is associated with reduced fluorescence quantum yields and consequent increased $n\pi^*$ triplet activity through the electron withdrawing effect of the acyl group. The results are also consistent with an enhancement in photoreduction quantum yields, especially in the presence of an amine cosynergist. High photoinitiated polymerisation activity is observed in the presence of oxygen indicating the predominance of photodehalogenation which is enhanced by the presence of a tertiary amine cosynergist. Higher rates of photoconversion are also observed under visible light irradiation with wavelengths > 400 nm than that with UV light < 400 nm. Laser flash photolysis and photoacid generation studies are currently underway and will follow through in future series.

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