

# Thioxanthone Derivatives as Photoinitiators in Micelle Photopolymerization

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## Synopsis

This paper provides a complete survey of the primary processes involved in typical oil- and water-soluble thioxanthone derivatives dissolved in sodium dodecyl sulfate micelles, in the presence of monomers and amines. Special emphasis is laid on the determination of the rate constants of the different processes and the absorption spectra of the transients. Relevant data are shown and discussed with reference to the effectiveness of these molecules as photopolymerization initiators.

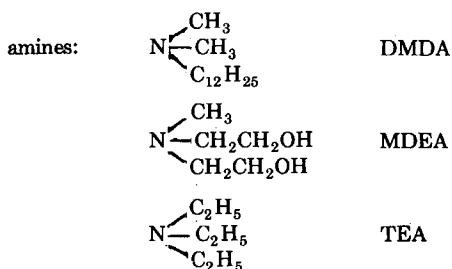
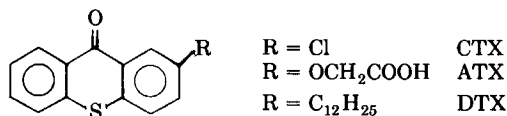
## INTRODUCTION

Polymerization in the presence of surfactants is a very attractive way to prepare polymers displaying both a high rate  $R_p$  and a high degree of polymerization,  $DP_n$ . This reaction has so far been mainly conducted using the conventional thermal initiation process, and very few papers deal with UV-light photoinitiation of the reaction. It is apparent, however, that such processes exhibit interesting features, as demonstrated by recent experiments, for example, in micelles,<sup>1-3</sup> microemulsions,<sup>4</sup> reverse micelles,<sup>5</sup> reverse microemulsions,<sup>6</sup> emulsions,<sup>7</sup> and vesicles.<sup>8</sup> The influence of several parameters were investigated: the reactant concentrations, the light intensity, the temperature, the presence of a magnetic field, and the nature of the photoinitiator. Among them, special emphasis was placed on the role played by the photoinitiator, because it governs to a large extent the efficiency of the reaction.<sup>9</sup> Attempts were made, using time-resolved laser spectroscopy, to determine the processes involved in the excited states of the photoinitiator in the presence of direct micellar assemblies (e.g., benzophenones in sodium lauryl sulfate micelles).<sup>10</sup> An investigation in reverse micelles and microemulsions showed the primary processes involved in the interaction taking place between a water-soluble photoinitiator, the surfactant, and possibly the cosurfactant environment.<sup>3-5</sup> The localization of the photoinitiator was recognized as the most important factor.<sup>11</sup>

This paper deals with an investigation of the primary processes involved during the initiation step of methyl methacrylate (MMA) polymerization in micelles in the presence of thioxanthone derivatives, which were used as photoinitiators on account of their expected "solubility" in the aggregate environment.

## EXPERIMENTAL

The following thioxanthenes were used mostly in the presence of typical amines:



CTX and ATX are laboratory grade products from Ward Blenkinsop; DTX, kindly donated by Sherwin, was purified by liquid chromatography; the dodecyl substituent is predominantly an *n*-propyl *n*-octyl methyl group as revealed by NMR spectroscopy.

The experimental procedure for steady-state measurements and laser spectroscopy has been described elsewhere.<sup>1,9</sup>

## RESULTS

## Localization of the Photoinitiation in the Micellar Assembly

Typical UV-absorption spectra of ATX, CTX, and DTX in various solvents [water, méthanol, MMA, sodium lauryl sulfate (NaLS), NaLS + MMA] are shown in Figures 1–3. The study of the solvatochromacy of this transition is used to assess a micropolarity to the solubilization site and thus to provide information regarding the depth of this site into the aggregate.<sup>8,11</sup> However, this approach is often fraught with ambiguity: in fact, the probe is regarded as being anchored in a given position of the microheterogeneous structure which corresponds only to a static description of the micellization process. A description taking into account the dynamic aspects of this structure would be probably much more accurate. However, the low solubility of TXs in the bulk water phase, which goes along with high binding constants to NaLS micelles, causes the probe to strongly interact with the aggregate. On that account, the mobility of the solute is restricted and the static approach used here provides a simplified view of its localization. Thus, the carboxylic derivative (ATX) is seen to interact weakly with the micellar assembly in the water layer surrounding the aggregate; the chlorothioxanthone (CTX) exhibits an absorption spectrum similar to that recorded in methanol and seemingly is in the polar

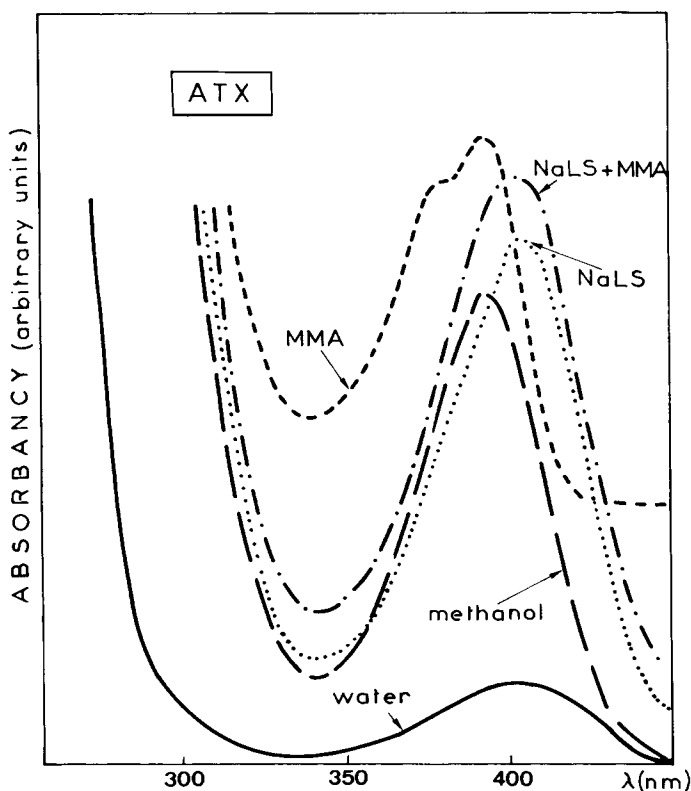


Fig. 1. UV-absorption spectra of ATX in different solvents.

region of the micellar aggregate; the long alkyl-chain substituted thioxanthone (DTX) is considered as lying in a slightly less polar environment of the micelle. Addition of amines or MMA causes the aggregate to swell and an apparent decrease of the solubilization site is observed as in the case of benzophenones.<sup>12</sup> The solvatochromacy of the UV absorption of thioxanthones seems complex; a complete investigation on this subject will be published in a forthcoming paper.

#### Emission Properties of the First Excited Singlet State

Upon laser excitation of the  $S_0 \rightarrow S_1$  transition, light emission is observed. The intensity-time dependence of the emitting species (first excited-singlet state) follows exactly the shape of the pumping train of pulses in the case of CTX and DTX. The lifetime of this species appears to be determined by the time response of the detection system; an accurate measurement through single photon counting yields  $\tau_f = 2.3$  ns for CTX. The singlet lifetime of ATX is longer ( $\tau_f = 13$  ns), whereas the emission spectrum of CTX in SDS micelles shown in Figure 4 is similar to that recorded with a spectrofluorimeter. The ATX spectrum exhibits a red shift of about 30 nm. The fluorescence quantum yields in methanol follow the order ATX > DTX > CTX.

The fluorescence intensities  $I_f$  were recorded as a function of the solvent (Table I) at a constant dose of excitation.  $I_f$  decreases significantly in

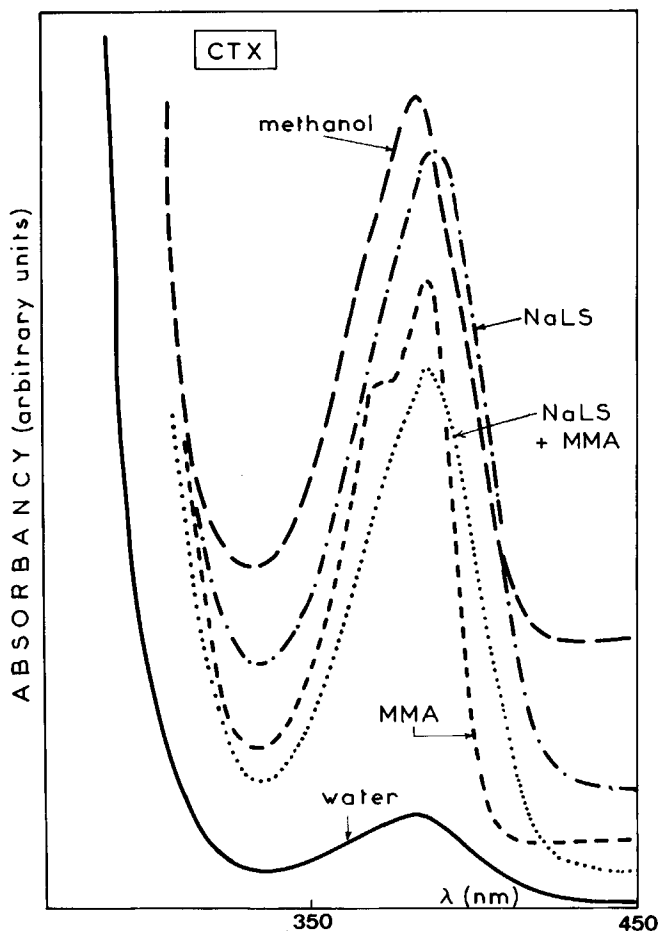


Fig. 2. UV-absorption spectra of CTX in different solvents.

nonpolar media, as a result of a change in the spectroscopic nature of the lowest excited singlet state. Similar results were found in micellar assemblies. CTX and ATX, located in the polar region of the micelle, exhibit the same  $I_f$  values in methanol and SDS, whereas  $I_f$  decreases for DTX, which exchanges more interactions with a slightly less polar environment.

### Excited State Processes

The generation of transient absorptions by laser excitation was investigated over the UV and visible region, and all the molecules were observed to exhibit the same general behavior.

**Triplet State Formation and Deactivation in Toluene Solution.** The typical oscillogram in Figure 5(a) shows the relaxation of the excited triplet molecules after intersystem crossing from the first excited state.

The triplet-state absorption was recorded as a function of the wavelength [Fig. 5(a)]; the position of the absorption maxima (Table II)—about 610 nm for CTX—confirms the localization of the thioxanthenes in the polar environment [Fig. 5(b)]. As reported elsewhere,<sup>13</sup> the absorption maximum shifts from

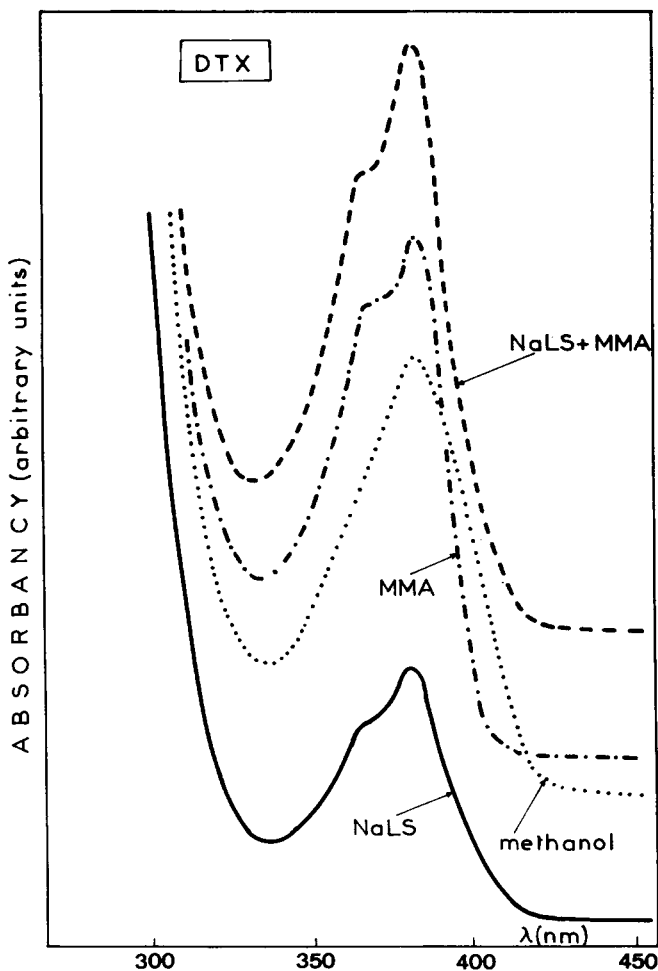
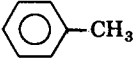


Fig. 3. UV-absorption spectra of DTX in different solvents.

660 to 615 nm when going from toluene to methanol, whereas no significant ketyl radical absorption was detected; similar results were recorded with thioxanthone itself.<sup>14</sup> This behavior involves presumably a change in the nature of the lowest lying triplet state<sup>15</sup>: from a mixed  $n\pi^*-\pi\pi^*$  or a  $n\pi^*$  character (in toluene) to a more pronounced  $\pi\pi^*$  character (in polar solvents), due to a very low energy gap between the two states (such a behavior was clearly demonstrated in the case of xanthone). From our data and considering triplet-triplet absorptions, DTX seems to be localized in a rather polar environment. A blue shift ( $\lambda_{\max} = 590$  nm) was observed for ATX, both in methanol and NaLS-micellar solution, as compared with the absorption maxima of CTX and DTX. These results clearly suggest that the absorption properties should not be investigated on the basis of a simple and usual analysis in terms of substituent effects on the thioxanthone structure. The analysis of the building up of the triplet population leads to a lifetime of the singlet state in the nanosecond range and confirms the short lifetime of the first excited singlet state.



TABLE I  
Relative Emission Intensity as a Function of the Solvent

	ATX	CTX	DTX
SDS	4.4	0.9	0.7
MeOH	4	1	2
	0.3 <sup>a</sup>	< 0.05	< 0.1

<sup>a</sup>In MMA.

The absorption (Fig. 7) of the long-lived transient (in the  $\mu\text{s}$  range), which is similar to that reported in homogeneous solution,<sup>13,14</sup> was ascribed to the ketyl radical of the thioxanthone derivatives. In addition, the ketyl structure of ATX exhibits a substantial red shift of the absorption maximum, which confirms that this substance does not behave like the other oil-soluble thioxanthenes substituted in position 2. A possible contribution of the ketyl radical anion of the thioxanthone structure to the overall transient absorption cannot be definitely ruled out.

The initial optical density ( $\text{OD}_T$ ) of the triplet-state measured immediately after the laser pulse decreases upon increasing amine concentration (AH), thus indicating a quenching of the precursor (the singlet state) by the amine. A usual Stern–Volmer treatment according to

$$\frac{1}{\text{OD}_T} = K [1 + k_{sv}[\text{AH}]] \text{ with } k_{sv} = k_e\tau_T^0$$

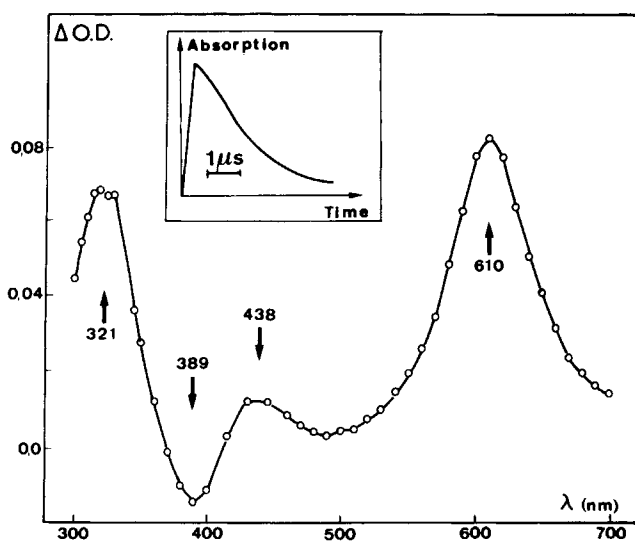
yields a  $k_{sv}$  of  $18 M^{-1}$  for ATX and  $8 M^{-1}$  for DTX. The singlet-charge transfer complex generated by this reaction is expected to mainly undergo a back electron transfer and deactivation rather than proton transfer and initiation. Though not very efficient in the case of the compounds investigated here, this process could appear as a detrimental pathway.

No significant magnetic effect on the exit of ketyl radicals from the radical pairs which can be formed in the presence of amines was observed; such effects have been detected in water-soluble benzophenones.<sup>16</sup>

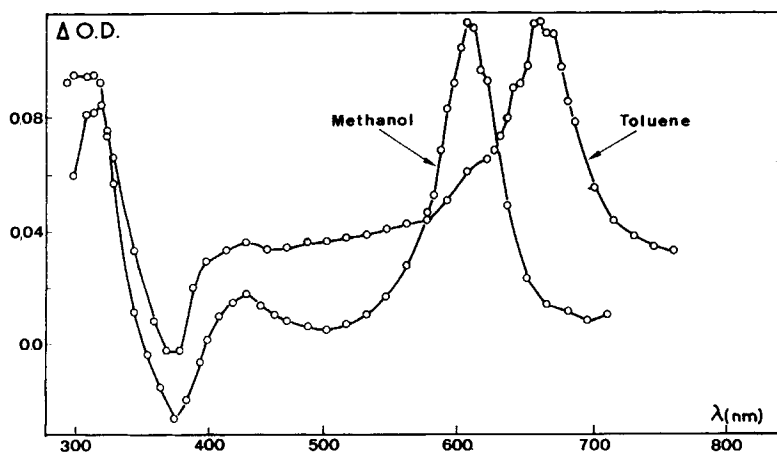
**Monomer Quenching.** It is a well-known fact that monomers (M) deactivate the triplet state of ketones. This was recognized as a detrimental effect on the efficiency of the photoinitiation. In order to minimize this effect, the triplet state must exhibit competitive processes of radical generation. Usually a plot of  $k$  (reciprocal value of the triplet lifetime) against  $[\text{M}]$  gives the bimolecular quenching rate constant.

In micelles as in homogeneous solution, the  $k_q$  values (Table II) are significantly lower than those reported in the case of the ketones (such as benzophenone in NaLS environment<sup>11</sup>), thus resulting in a favorable yield for the formation of the CT complex. No significant interaction between the ketyl type radical and the monomer was observed, which suggests that the amine derivative species  $\text{A}^{\cdot}$  is the only initiating radical.

**Overall Diagram.** The overall, simplified diagram showing the elementary processes that take place in the decay on the excited states of thioxanthenes



(a)



(b)

Fig. 5(a). Neat transient absorption change, mainly due to triplet-triplet absorption of CTX in NaLS micelle. Insert is triplet relaxation.

Fig. 5(b). Shift of the triplet-absorption spectrum of chlorothioxanthone (CTX) as a function of the solvent.



TABLE II  
Maximum Wavelength Absorption of the Triplet ( $\lambda_{TT}$ ) and Bimolecular Quenching Rate Constants of Monomer ( $k_q^M$ ) and Amine ( $k_e$ ) in NaLS Solution (0.5M)

	$k_q^M \times 10^{-6}$ ( $M^{-1} s^{-1}$ )	$k_e \times 10^{-8} M^{-1} s^{-1}$			$\lambda_{TT}^{max}$ (nm)
		MDEA	DMDA	TEA	
CTX	1.4	3.4	5.4	7.1	610
DTX	8	4.2	5	4.4	610
ATX	1	0.4	0.2	1.2	590

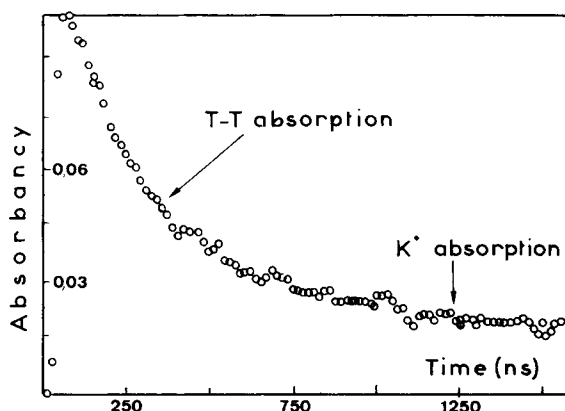


Fig. 6. Quenching of DTX triplet by amine ( $10^{-2}M$ ) in NaLS micelle.

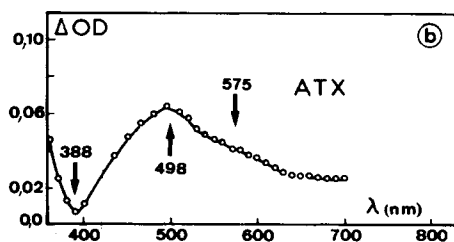
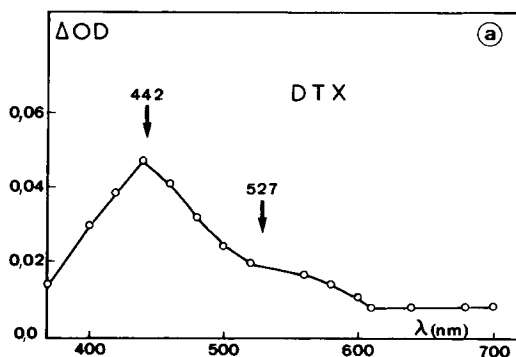
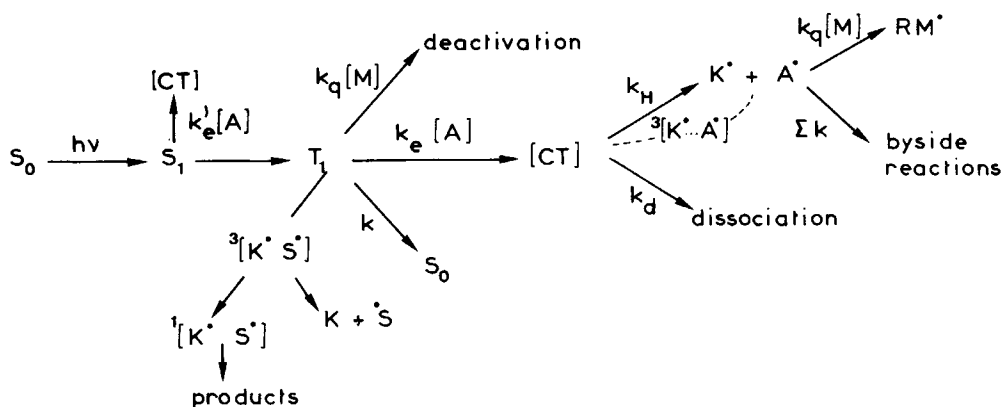


Fig. 7. Neat transient-absorption change mainly due to typical ketyl species absorption: DTX (a) and ATX (b) in the presence of MDEA (0.1M).



Scheme 1. General diagram of the excited states and transient radicals involved in the initiation process by thioxanthenes in micelles.

in micellar solution approximates closely that described in Scheme 1: Other processes of deactivation of the triplet state, usually observed with ketones in homogeneous solution or micellar environment (triplet-triplet annihilation, self-quenching, generation of a triplet radical pair<sup>10,17</sup>), have not been taken into account. As a matter of fact, in the presence of additives (e.g., amine AH), and under the usual experimental conditions of the polymerization reaction ( $k_q[\text{AH}] \gg k$ ), they are completely outstripped and appear as minor deactivation pathways.

### Photopolymerization Experiments

Rates of polymerization  $R_p$  were determined from the percent conversion-time curves in model systems that contain MMA (0.5M) in a NaLS-water solution, in the presence of substituted thioxanthenes and particular amines. The results are shown in Table III, together with the data recorded when DMPA is used as a photoinitiator under similar experimental conditions. In homogeneous solutions, DTX and CTX exhibit very similar efficiencies, whereas the rates are very different in a NaLS environment and appear to depend on the couple thioxanthone/amine.

TABLE III  
Rates of Polymerization

Amine	Homogeneous solution (toluene), [MMA] = 7M			SDS solution (0.5M), [MMA] = 0.5M,	
	$10^5 R_p (M s^{-1})$	$10^5 R_p (M s^{-1})$		$10^5 R_p (M s^{-1})$	
	none or < 0.1	MDEA <sup>a</sup>	TEA <sup>a</sup>	MDEA <sup>b</sup>	DMDA <sup>b</sup>
CTX	16	11	7	78	33
DTX	15	11	7	190	70
ATX				70	15
DMPA	41 <sup>c</sup>			95 <sup>c</sup>	

<sup>a</sup>[Amine] = 0.1M.

<sup>b</sup>[Amine] =  $5 \times 10^{-3}$ M.

<sup>c</sup>Without amine.

The quantum yield of initiation (number of starting chains per photon absorbed) can be expressed to a first approximation by using the kinetic model shown in Scheme 1 (on disregarding other possible minor ways of initiation, which could arise from triplex, singlet state quenching):

$$\phi_i = K \phi_{ST} \phi_{CT} \phi_{A'} \phi_{RM'}$$

where the  $\phi$ 's are the yield of intersystem crossing ( $\phi_{ST}$ ), formation of the charge transfer complex ( $\phi_{CT}$ ), generation of radicals through a CT complex ( $\phi_{A'}$ ), and formation of the first monomeric radical ( $\phi_{RM'}$ ):

$$\phi_{ST} = \frac{1}{1 + k_{sv} [AH]} \phi_{ST}^0$$

$$\phi_{CT} = \frac{k_e [AH]}{k_e [AH] + k + k_q [M]}$$

$$\phi_{A'} = \frac{k_H}{k_H + k_d}$$

$$\phi_{RM'} = \frac{k_q [M]}{k'_q [M] + \Sigma k}$$

From the values of the rate constants in Table II and under the experimental conditions of these photopolymerizations, it may be readily inferred that  $\phi_{CT}$  approaches unity. Moreover, in the presence of 0.005*M* of amine (e.g., MDEA)  $\phi_{ST}$  is almost unaffected:  $\phi_{ST} = 0.95 \phi_{ST}^0$  and  $0.9 \phi_{ST}^0$  for CTX and ATX respectively. This suggests that the electron-transfer reaction is not the predominant factor affecting the efficiency of the initiating system. As in the case of water- and oil-soluble substituted benzophenones,<sup>3</sup> the explanation should be found in other decisive parameters: the proton transfer efficiency ( $\phi_{A'}$ ), the reactivity of the amine-derived radical towards the monomer double bond ( $\phi_{RM'}$ ), the acid-base equilibrium of the ketyl radical, the presence of ketyl radical and ketyl radical anion, the localization effects of both the thioxanthone and the amine (which considerably affect the exit of the initiating radical from the radical pair), the electronic effects of the substituents, the electrostatic effects in the case of ATX and the micropolarity effects on the rate constants. Each of these parameters is not independent of the others, and, unfortunately, no simple and direct correlation has been demonstrated so far between one of them and the efficiency of the system. The problem is certainly complex, especially as the experimental probes required to investigate these factors are rather scarce.

## CONCLUSION

This study shows the general behavior of thioxanthenes in oil/water microheterogeneous monomer solutions. It provides a means for characterizing the primary processes involved in the excited states and discussing the

photochemical reactivity observed during the initiation step. Further unpublished data concerning the evolution of the excited states as a function of a large family of thioxanthenes and a number of amines, solvents, monomers, and environments support this general trend.

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### References

1. A. Merlin and J. P. Fouassier, *Polymer*, **21**, 1363 (1980).
2. N. J. Turro, M. F. Chow, C. J. Chung, and C. H. Tung, *J. Am. Chem. Soc.*, **105**, 1572 (1983).
3. J. P. Fouassier and D. J. Lougnot, *J. Appl. Polym. Sci.*, **32**, 6209 (1986).
4. S. S. Atik and J. K. Thomas, *J. Am. Chem. Soc.*, **103**, 4279 (1981).
5. J. P. Fouassier, D. J. Lougnot, and I. Zuchowicz, *Eur. Polym. J.*, **22**, 933 (1986).
6. F. Candau and C. H. Holtzschler, *J. Chim. Phys.*, **82**, 691 (1985).
7. E. D. Suddol and J. W. Vanderhoff, *Org. Coat. Plast. Chem.*, **42**, 162 (1980).
8. J. H. Fendler and P. Tundo, *Acc. Chem. Res.*, **17**, 3 (1984).
9. J. P. Fouassier and D. J. Lougnot, *Polym. Photochem.*, **3**, 79 (1983); D. J. Lougnot, P. Jacques, J. P. Fouassier, H. L. Casal, N. Kim-Thuan, and J. C. Scaiano, *Can. J. Chem.*, **63**, 3001 (1985).
10. P. Jacques, D. J. Lougnot, and J. P. Fouassier, *Surfactants in Solution*, Vol. 2, K. L. Mittal and B. Lindman, Eds., Plenum, New York, 1984.
11. P. Jacques, D. J. Lougnot, J. P. Fouassier, and J. C. Scaiano, *Chem. Phys. Lett.*, **127**, 469 (1986).
12. D. J. Lougnot, D. Floret, P. Jacques, and J. P. Fouassier, *J. Chim. Phys.*, **82**, 505 (1985).
13. W. Schnabel and G. Amirzadeh, *Makromol. Chem.*, **182**, 2821 (1982).
14. S. F. Yates and G. B. Schuster, *J. Org. Chem.*, **49**, 3349 (1984).
15. J. C. Scaiano, *J. Am. Chem. Soc.*, **102**, 7747 (1980); P. Jacques, D. J. Lougnot, and J. P. Fouassier, unpublished results.
16. J. C. Scaiano and D. J. Lougnot, *J. Phys. Chem.*, **88**, 3379 (1984).
17. J. C. Scaiano, E. B. Abuin, and L. C. Steward, *J. Am. Chem. Soc.*, **104**, 5673 (1982).

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