Functionalized Polysiloxanes with Thioxanthone Side Groups: A Study of Their Reactivity as Radical Polymerization Macroinitiators

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ABSTRACT: Functionalized silicone copolymers containing thioxanthone side groups were prepared and evaluated as radical polymerization photoinitiators in the presence of 4-(dimethylamino)benzoate ester derivatives as coinitiators and acrylic esters as monomers. Compared to low molecular weight thioxanthone analogues, the functionalized polysiloxanes exhibit a polymer effect similar to that observed with polysiloxanes containing benzophenone side groups: the photoinitiating efficiency is enhanced when thioxanthone chromophores are present as pendant groups on polymer chains and when the tertiary amine is a free reactant in the medium. This effect disappears when the chromophores and the amino groups are attached to the same chains. Time-resolved spectroscopy was used to compare the quenching of thioxanthone triplets in several systems where the ketone and the amine reactants are present in the form of pendant groups in copolymers or as low molecular weight reactants. The photophysical study performed in media different in their nature and viscosity indicates that the polymer effect is not to be found in the efficiency of the primary deactivation process.

Introduction

We have previously reported on the initiating activity in radical polymerization of functional polysiloxanes containing 2-benzoylbenzoate (2-BBA) side groups submitted to UV light irradiation in the presence of tertiary amine coinitiators.[1] By comparing the various functional polymeric systems to the low molecular weight (LMW) analogues, we have evidenced a neat polymer effect inducing a greater efficiency, especially when a polysiloxane containing only 2-benzoylbenzoate side groups at the functional units is associated with LMW esters of 4-(dimethylamino)benzoic acid (4-DMABA) in the photosensitive composition. This positive effect on the initial rate of polymerization of acrylic esters mixtures is lost when the benzophenone chromophore and the tertiary amine are both attached to the same polymeric chain.

The photoinitiation process following the type II generation of free radicals is the result of a complex sequence of fast reactions following photon absorption. It is generally considered that chain polymerization is essentially initiated by the α-amino radical that adds more efficiently to acrylate monomers than the ketyl radical deriving from the aryl ketone.[2] The initial investigation based on practical measurements of the overall merit of different photosensitive compositions does not allow us to propose an immediate and solid interpretation of the observed phenomenon. Because of the current interest devoted to polymeric photoinitiating systems,[3] we have followed up on this preliminary work and have prepared a new series of functionalized polysiloxanes bearing thioxanthone (TX) side groups. TX derivatives are benzophenone analogues in free radical photogeneration and receive special attention in the field of UV curing by virtue of their absorption characteristics.[4] The present investigation was undertaken to obtain confirmation of the peculiar behavior of polymer-bound aromatic ketones in an analogous series of photoreactive polymers. The polymeric or LMW nature of the chromophore may have a determining influence on the first photophysical or photochemical steps of the initiation process. In this connection, TX derivatives offer the opportunity to perform time-resolved spectroscopy experiments for studying the quenching of the carbonyl triplet after selective photoexcitation.[5]

Experimental Part

Starting Materials. Photoreactive polymers **2a–d** were obtained by multistep functionalization[6] (Scheme 1) of trimethylsiloxy-terminated poly(dimethylsiloxane-*co*-methylsiloxane) of M_n = 15 000 and containing Si–H functions (3.63 mmol·g^{-1}, 25 mol %). The epoxy content of modified polymer **1** determined by chemical titration was 2.45 mmol·g^{-1}. 2-Hydroxythioxanthone[7] was converted into the corresponding ethyl aroxyacetate **3** by reaction with ethyl bromoacetate. The reaction was carried out in DMF with an excess of K_2CO_3 as a base and tetrabutylammonium bromide as a phase tranfer catalyst. The acid was obtained from **3** after basic hydrolysis by 1 M NaOH in a water–methanol mixture (60:40 v/v) and subsequent acidification and extraction with chloroform.

The epoxy–carboxy reaction was performed under stoichiometric conditions at 100 °C in DMF according to known procedures. After 24 h of reaction of the convenient carboxylic acid in the presence of 5 mol % of tetrabutylammonium bromide as a catalyst, a 2-fold excess of acetic anhydride was added. The mixture was then allowed to react for another 24 h period at the same temperature. After evaporation of the solvent, the viscous products were repeatedly washed with aqueous sodium bicarbonate solutions. Standard extraction, neutral washing, and drying afforded polymers **2a–d** as amber resins. ^{1}H and ^{13}C NMR analysis of the purified products indicates a quantitative conversion of epoxy group and a structure of the spacers in total agreement with our previous reports.[8] Pendant functional groups derived from (9-oxo-2-thioxanthenyl)acetic acid (2-TXA) and from 4-(dimethylamino)benzoic acid (4-DMABA) showed the resonance signals observed with the corresponding model esters.

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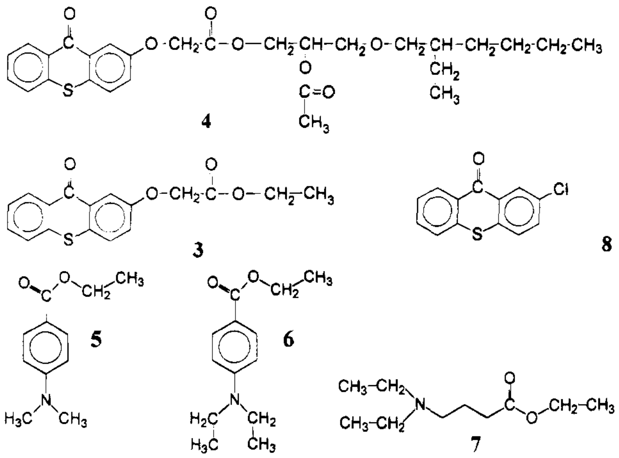
Chart 1. Low Molecular Weight Compounds



2-Acetoxy-3-((2-ethylhexyl)oxy)propyl ((9-Oxo-2-thioxanthenyl)oxy)acetate (4). Model compound **4** was prepared by reacting 2-TXA with 2-ethylhexyl glycidyl ether in the presence of triethylamine[9] and subsequent acetylation. It was obtained as a yellow oil after purification by column chromatography on silica gel.

^{13}C NMR (CDCl$_3$): δ 10.9 (q), 14.0 (q), 20.6 (q), 23.0 (t), 23.7 (t), 29.0 (t), 30.4 (t), 39.5 (t), 62.8 (t), 65.2 (t), 68.9 (t), 71.6 (d), 111.4 (d), 122.9 (d), 125.9 (d), 126.1 (d), 127.5 (d), 128.5 (s), 129.8 (d), 130.1 (s), 130.2 (s), 132.1 (d), 137.3 (s), 156.5 (s), 167.8 (s), 170.6 (s), 179.3 (s). Anal. Calc for $C_{27}H_{34}O_7S$ (514.57): C, 65.29; H, 6.60; S, 6.20. Found: C, 65.18; H, 6.80; S, 5.86.

Ethyl 4-(dimethylamino)benzoate (**5**) (Aldrich) was twice recrystallized from ethanol. Ethyl 4-(*N*,*N*-diethylamino)benzoate[10] (**6**) and ethyl 4-(*N*,*N*-diethylamino)butyrate[11] (**7**) were obtained by esterification in ethanol of the corresponding acid and were purified by standard procedures. The determination of the chromophore content in the polymers was performed by UV titration of chloroform solutions of the samples, using the following absorption coefficients measured with model compounds: $\epsilon(\mathbf{4})/\mathrm{L \cdot mol^{-1} \cdot cm^{-1}} = 7000$ at 398 nm; $\epsilon(\mathbf{5})/\mathrm{L \cdot mol^{-1} \cdot cm^{-1}} = 29\,500$ at 311 nm. Unsaturated monomers 2-ethylhexyl acrylate (EHA) and 1,6-hexanediol diacrylate (HDDA) from Aldrich were rendered free from stabilizers by elution through a column removing hydroxyaromatic inhibitors.[12] 2-Chlorothioxanthone (**8**) (Aldrich) was recrystallized from hexane before use. UV-sensitive compounds and formulations were prepared and stored in dark rooms.

Photopolymerization of the Samples. The photopolymerizable compositions were spread over a NaCl plate. The liquid film (10–30 μm thick) was covered with another NaCl plate, and the cell was submitted to the frontal beam of a 900 W Xenon lamp. Because of the sandwich nature of the cell, the polymerization proceeds under essentially anaerobic conditions. Irradiation times were controlled by an electronic shutter. The progress of the polymerization was monitored by quantitative IR spectroscopy after each of the cumulated short exposures to the UV beam. The variations of the acrylate concentration were deduced from the decrease of optical density OD_t measured at 810 cm^{-1} with the baseline set at 785 and 830 cm^{-1} after an exposure of duration t. The initial value of the optical density of the sample OD_0 at 810 cm^{-1} was adjusted to 1.00 ± 0.07. The conversion times of exposure curves shown in the following section represent the average variations of $\alpha = OD_t/OD_0 = [=]_t/[=]_0$ averaged from three different experiments.

Time-Resolved Laser Spectroscopy. The laser spectroscopy device[13] and the experimental procedure have been described elsewhere. The measurements of photoinitiator solutions including monomer were performed with fresh solutions, even when the monomer was diluted in a solvent (spectrograde toluene or methanol from Aldrich). The samples were prepared in a 4 mL solution and deaerated by an argon flow. The optical density of the solution was adjusted to 0.5 at 355 nm (third harmonic of Nd YAG emission).

Results and Discussion

Functionalized Polymers and Model Compounds. The photoreactive polysiloxanes studied in the present work were prepared according to the modification procedure depicted in Scheme 1.[6] Functional carboxylic acids were grafted onto polysiloxane **1** of $\overline{DP}_n = 200$ and containing 25 mol % [3-((2,3-epoxypropyl)oxy)propyl]methylsiloxane units by means of the epoxy–carboxy reaction. Under conditions quite similar to those we used to prepare the series with 2-BBA chromophores,[1] we have reacted ((9-oxo-2-thioxanthenyl)oxy)acetic acid (2-TXA) to introduce the TX chromophore and 4-(dimethylamino)benzoic acid to introduce a tertiary amino group.

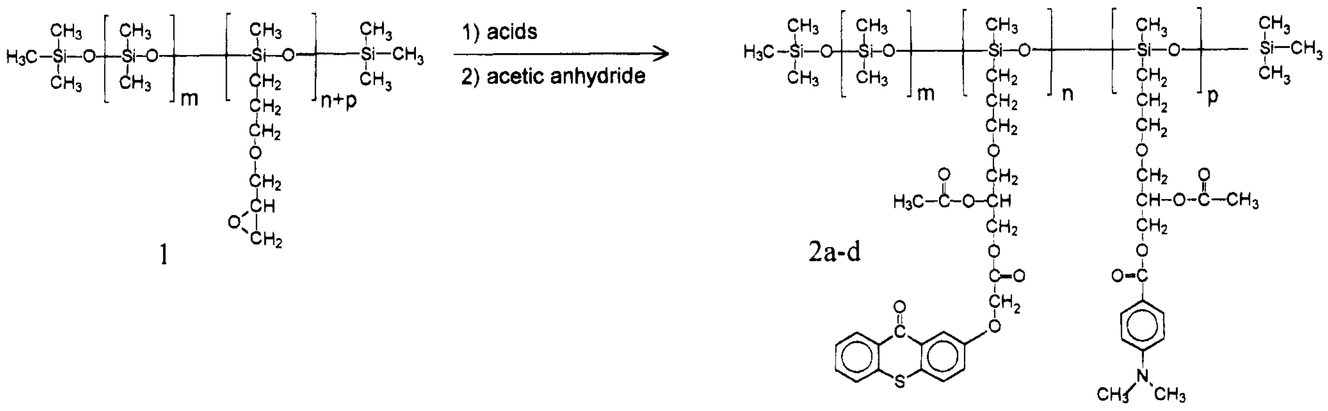
Polymers containing a single type of functional pendant group (**2a,d**) or containing both types of esters bound to the main chain (**2b,c**) were purified carefully after the last acetylation step. They were submitted to ^{1}H and ^{13}C NMR analysis that indicated the absence of unreacted epoxy groups and fully supported the claimed structure. As an example, the proton-decoupled ^{13}C NMR spectrum of polymer **2a** is shown in Figure 1. The signals appearing in the range 50–70 ppm are unambiguously assigned to the oxyalkyl side chain connecting the functional ester to the backbone. The isomeric structure of the spacer gives rise to the additional signals starred in Figure 1 and corresponding to the formal exchange of acyl radicals at methine (C_g) and methylene (C_h). For the synthesis of polymers **2b** and **2c**, the mole fraction of 4-DMABA in the mixture of acids introduced was 0.5 and 0.1, respectively. The presence of two types of aromatic side groups in polymer **2c** is easily evidenced in the 100–200 ppm region of the ^{13}C NMR spectrum of Figure 2. The absence of impurity—unreacted acid, ammonium catalyst, trace of solvent—can be checked on the spectra recorded after careful precipitation from methanol.

The sequence distribution of reactive side groups could not be determined on the basis of these NMR data. The functional ester groups are nevertheless believed to be randomly distributed along the polymer backbone since the parent polysiloxane presented originally a statistical arrangement of Si–H units[14] and since the carboxylic acids exhibit similar reactivities for the epoxy–carboxy reaction.[6]

The composition of the resulting copolymers was determined by UV spectroscopy using the extinction coefficients of esters **4** and **5** as LMW standards. The representative UV spectra presented in Figure 3 show that accurate determination of chromophore content can be achieved after simple calculations. It is also confirmed that the TX chromophore can be selectively excited by UV light of wavelength longer than 350 nm. The nature and content of the functional groups present in the different polysiloxanes **2a–d** prepared for this study are collected in Table 1.

Photopolymerization. Four compositions named C1–4 were prepared to evaluate comparatively the initiating efficiency under UV light of the TX–tertiary amine systems introduced under various forms. The reactive mixtures that were used contained equimolar amounts of monofunctional and difunctional acrylic esters, namely 2-ethylhexyl acrylate and 1,6-hexanediol diacrylate. The initial acrylate concentration in the formulated compositions was typically between 7.1 and 7.3 mmol·g^{-1}. The photoinitiating system was intro-

Scheme 1. Synthesis of Functionalized Polysiloxanes



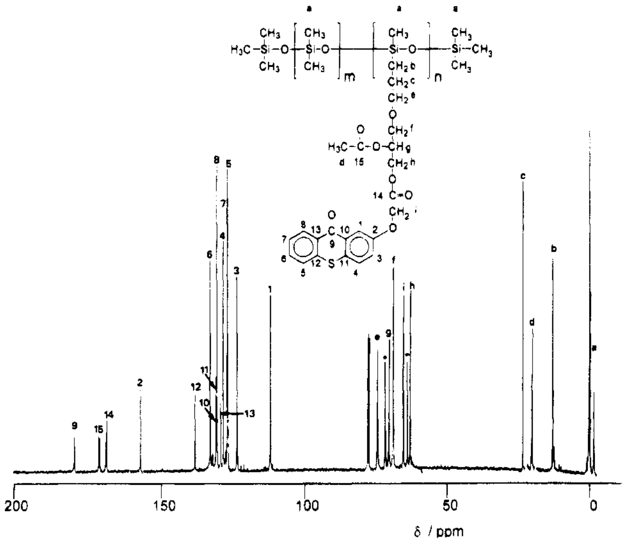


Figure 1. Proton-decoupled ^{13}C NMR spectrum of polysiloxane **2a**.

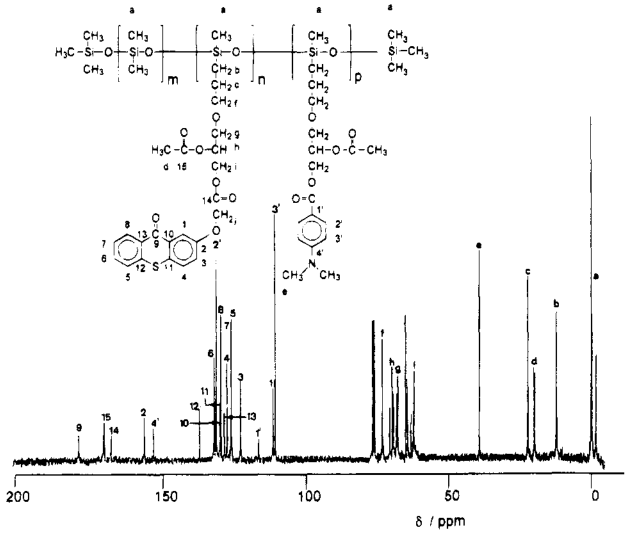


Figure 2. Proton-decoupled ^{13}C NMR spectrum of polysiloxane **2c**.

duced at a concentration of 62 μmol·g^{-1} of thioxanthone chromophore and a stoichiometric amount of DMABA ester. The final mole concentration of 2-TXA esters is equivalent to the chromophore concentration in a formulation with 1 wt % benzophenone.

Four different sources of TX chromophores were used, as indicated in Table 2 where the main data describing the tested compositions are gathered. The disappearance of acrylic functions upon irradiation of the samples was followed by discontinuous IR analysis of the reactive composition sandwiched between NaCl cells. The variations of conversion $\pi = 1 - [=]_t/[=]_0$, as a function of the cumulated time of exposure are reported in the curves of Figure 4. The initial rate of polymerization $(R_p)_0$ deduced from the slope measured at 2 s of exposure to the UV light is indicated in Table 2. This criterion allows us to compare quantitatively the efficiency of the photoinitiating systems during the first instants when the polymerization is believed to develop in a homogeneous liquid state. Previous investigations have shown that comparing polymeric systems to the LMW analogues could also put into evidence some strong differences at medium to high conversion. The limiting value of conversion π_∞ is the second criterion that can be used to evaluate comparatively the four initiating systems. Compositions C1 and C2 containing a couple of LMW TX and amine reactants initiate acrylate polymerization at similar rates. Repeated experiments have allowed us to measure for both systems and after 2 s of exposure a $(R_p)_0$ value of 1.4 mol·L^{-1}·s^{-1} under the used conditions. Comparing the two systems over a longer period of exposure nevertheless shows that long chain ester **4** can induce a faster consumption of acrylates, especially during the first moments of the photopolymerization. With both compositions, the conversion tends toward completion in spite of the expected gelation and vitrification of the acrylate matrix.

In a previous study the value of $(R_p)_0$ measured for the analogous system including benzophenone chromophore under the form of a benzoylbenzoic ester connected to the same branched alkoxy chain as in compound **4** was 0.4 mol·L^{-1}·s^{-1}. Although these results are consistent with the general trend to recommend TX derivatives for industrial use in UV curable inks and coatings, further comments on this point would not be relevant at this place, since several factors control the overall efficiency of the system. In the present case, enhanced absorption characteristics could well dominate any effect revealing the intrinsic reactivity of the various partners.

Composition C3 including polymer **2a** with 2-TXA esters side groups associated with LMW amine **5** exhibits a faster polymerization. The initial rate measured for the same concentration of TX chromophores is $(R_p)_0 = 2.3$ mol·L^{-1}·s^{-1}. The limiting conversion estimated from the value measured at 50 s of exposure is 90%. When the chromophore and the amine coinitiator coexist as pendant groups on the same chain (composition C4), the lowest value of $(R_p)_0$ is observed and π_∞ is close to 80%. The polymer effect described in

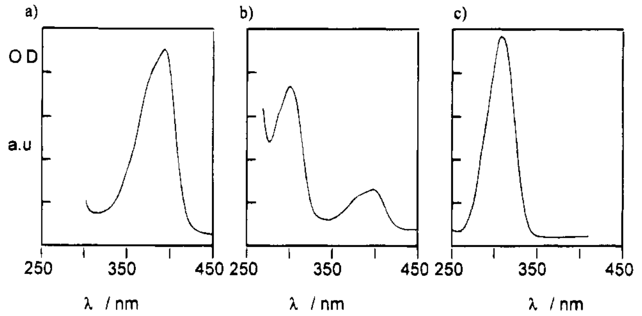


Figure 3. UV spectra of functionalized polysiloxanes **2a,c,d** in chloroform solutions, labels a, b, and c, respectively.

Table 1. Constitutional Characteristics of Functionalized Polysiloxanes 2a–d

	Nature and content of functional units					
	2-TXA ester			4-DMABA ester		
polymer	n[a]	mol %[b]	mmol·g^{-1}	p[a]	mol %[b]	mmol·g^{-1}
2a	50	25	1.23			
2b	42	21	0.94	8	4	0.17
2c	28	14	0.66	22	11	0.52
2d				50	25	1.52

[a] Average number of functionalized units in polymers **2a–d** of $\overline{DP}_n$ = 200. *n* and *p* as defined in Scheme 1. [b] Molar content of the functionalized siloxane unit in the copolymer.

Table 2. Reactivity of the UV Polymerizable Compositions[a]

composition	source of thioxanthone	source of tertiary amine	$(R_p)_0$[b]	π_∞[c]
C1	3	5	1.4	91 (→100)
C2	4	5	1.4	96 (→100)
C3	2a	5	2.3	90
C4	2c	2c	0.9	80

[a] Including equimolar amounts (62 μmol·g^{-1}) of 2-TXA ester and amine coinitiator (4-DMABA ester) submitted to the polychromatic light of a 900 W Xenon lamp. [b] Initial rate of polymerization (mol·L^{-1}·s^{-1}). [c] Limiting conversion of acrylate monomers (mol %).

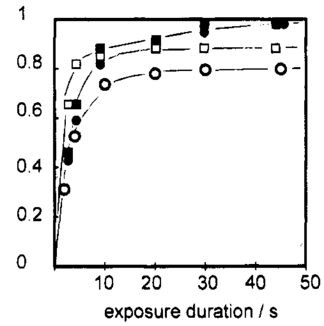


Figure 4. Variations of the conversion of acrylate monomers π as a function of the exposure duration. Photoinitiating system in an EHA–HDDA mixture: **3** + **5** (●); **4** + **5** (■); **2a** + **5** (□); **2c** (○).

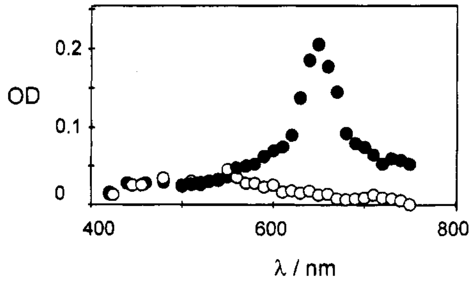
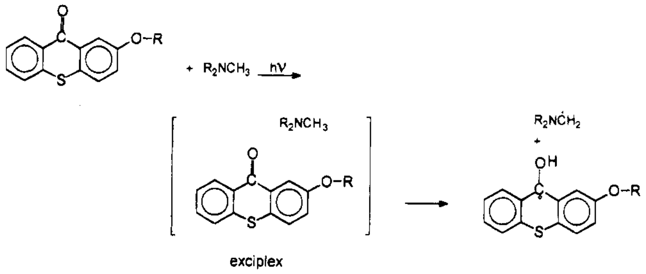


Figure 5. Transient absorption spectra of excited species derived from 2-TXA ester **4** in the presence of amine **5** after 355 nm laser pulse: delay 0 μs (●); 4 μs (○).

Scheme 2. Generation of Free Radicals by Photoreduction of Thioxanthone



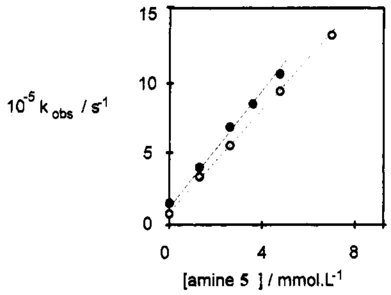


Figure 6. Stern–Volmer plot of the apparent first-order rate constant k_{obs} for the quenching of the 2-TXA triplet: **4** + **5** (●); **2a** + **5** (○).

Table 3. Rate Constants k_Q of the Thioxanthone Triplet Quenching by Amines in Toluene Solution

source of thioxanthone	$10^{-8}k_Q$ (L·mol^{-1}·s^{-1}) by amine			
	5	**6**	**7**	**2d**
2a	1.75	0.15	0.7	1.6
3	1.9		0.55	
4	1.3		0.6	

the previous study is thus confirmed and can be considered as a general feature of these type II systems.

Time-Resolved Spectroscopy. The absorption characteristics of 2-TXA and aminobenzoate esters offer the opportunity to excite selectively the aromatic ketone by the 355 nm light emitted by a YAG/Nd laser. Pulse photolysis of polymeric **2a** or the LMW 2-TXA derivative (**4**) photoexcited in deaerated toluene solutions allows us to observe the transient absorption of the resulting triplet. A strong maximum at 650 nm (Figure 5a) is characteristic of this species.[15] The triplet lifetimes measured from the first-order decay of the T–T absorption in deaerated toluene solutions are 12.5, 8, and 7 for the long-lived triplet of TX of **2a**, **3**, and **4**, respectively. If significant, the decrease of the triplet lifetime of **4** compared to that of **3** probably results from the presence of the branched ester substituent which provides several structural units favoring intramolecular hydrogen transfer.[16] On the other hand, polymer-bound chromophores in **2a** apparently show greater stability which may result from an energy migration process.[17,18] The long-lived triplet is efficiently quenched by ethyl (dimethylamino)benzoate (**5**), the coinitiator used for the photopolymerization experiments. The ketyl radical resulting from electron transfer and hydrogen abstraction (Scheme 2) gives the broad absorption of Figure 5.[19]

Stern–Volmer plots can be drawn after computation of the first-order decay of the triplets, as exemplified in Figure 6 for concentrations of **5** ranging from 10^{-2} to 10^{-3} mol·L^{-1}. We have collected in Table 3 the corresponding values of the bimolecular reaction rate constant k_Q determined for various TX–amine sytems. The results obtained from this first series of experiments conducted with toluene solutions, indicate that both LMW and polymer-bound TX triplets are quenched with a similar efficiency by amine **5**.

Changing the dimethylamino substituent of the benzoate for the diethylamino group of **6** causes a severe reduction of the quenching efficiency. This behavior is intriguing when trying to correlate quenching aptitude and first ionization potential of the amine.[20] It can nevertheless be related to the increase in steric hindrance at the nitrogen atom. Aliphatic *N*,*N*-diethylamino ester **7** was also shown to quench 2-TXA derivatives with a value of k_Q between the values just given. This fact is more consistent with the lower ionization potential of aliphatic amines compared to the substituted anilines.[21] Surprisingly, the bimolecular quenching reaction of the polymer-bound TX triplet of **2a** by the polymer-bound amine of **2d** was observed with the same efficiency as with LMW amines. It is remarkable that in the present conditions, the quenching rate does not appear sensitive to the expected lower mobility that results from the polymeric nature of the two reactants. The major outcome deduced from these experiments is the relative independence of the quenching efficiency with the nature of the molecule carrying the TX chromophore.

No polymer effect can therefore be evidenced from the results of flash photolysis experiments and further correlated to the behavior evidenced during photopolymerizations. The time-resolved spectroscopy experiments described above were carried out in toluene, a good solvent of the system. The physico-chemical characteristics of the medium can be criticized to some extent since they do not reproduce the actual reactive medium used to determine the initial polymerization rate. The solventless mixture of acrylic monomers indeed exhibits strongly different viscosities, polarities, and reducing powers.[22] A second series of measurements was thus undertaken to measure the kinetics of TX deactivation by tertiary amines in the reactive mixture of monomers.

In the monomer solution, the TX triplet exhibits a strong absorption centered on 620 nm. The blue shift of the maximum can be primarily interpreted as a direct consequence of the change of polarity of the medium.[23] The TX triplet in polymer 2a is not quenched by amine **5** more efficiently than the LMW excited chromophore. The value of the quenching constant is even slightly lower ($k_Q(\mathbf{2a}) = 1.6 \times 10^8$ L·mol^{-1}·s^{-1}) than that measured for the model ester ($k_Q(\mathbf{4}) = 2.2 \times 10^8$ L·mol^{-1}·s^{-1}). The reduction of the solvating power of acrylates for the modified polysiloxanes[24] may well affect the expansion of the polymer coils and thus control the access of amines to excited chromophores.

The presence of both amine and chromophore on the same chain was expected to deactivate the triplet with a higher rate, as a consequence of the possibility of intramolecular quenching. This is actually quite confirmed by comparing the lifetimes τ measured for TX chromophores. They were shown to decrease in the order $\tau(\mathbf{2a}) > \tau(\mathbf{2b}) > \tau(\mathbf{2c})$ in toluene as well as in the monomers solution (Table 4). As indicated by additional experiments performed on TX triplet deactivation in monomer–toluene mixtures, the shorter lifetimes measured in the polymerizable medium are due to efficient quenching by acrylate monomers.

Table 4. Lifetimes of the Polymer-Bound Thioxanthone Triplet

	τ (μs)			
solvent	**4**	**2a**	**2b**	**2c**
toluene	7	12.5	9	4
monomers[a]	2.6	3	1.5	0.7

[a] Mixture of 1,6-hexanediol diacrylate and 2-ethylhexyl acrylate (50:50 v/v).

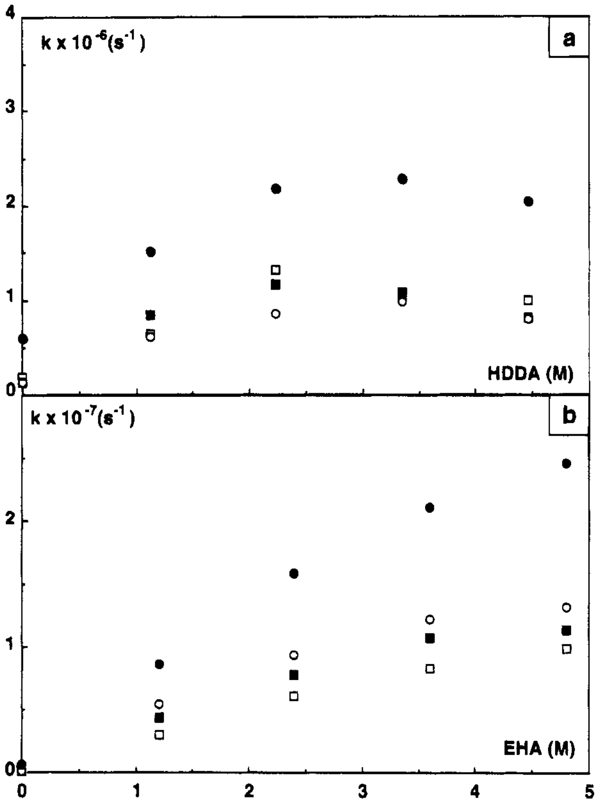


Figure 7. Rate constants of the thioxanthone triplet state deactivation by HDDA (a) and by EHA (b) measured at 620 nm in an argon-saturated toluene solution: **2a** (□); **4** (■); **3** (O); **8** (●).

The rate constants of quenching by EHA and HDDA of the triplet TX chromophore in **2a**, **3**, **4**, and **8** placed in toluene or methanol solution were tentatively determined. All the data were obtained from first-order fitting of the transient decays monitored at 620 nm near the T–T absorption maximum. The composition of the solvent-monomer mixtures ranged from 0–100 to 100–0 parts in volume by steps of 25 parts.

Computation of the data indicated that the Stern–Volmer model was not obeyed by these systems in toluene solution (Figure 7) as well as in methanol solution (Figure 8). Actually, several basic properties of the medium are changing strongly in the range of composition that was explored.

The increase of EHA concentration in polar methanol solution as well as in low-polarity toluene induces a continuous increase of the pseudo-first-order rate constant k_Q (Figures 7b and 8b). In the presence of HDDA, the variations of k_Q are represented by the bell-shaped curves of Figures 7a and 8a. Obviously, the situation is complex and several effects are combined. Chlorothioxanthone **8** was used as a reference model to rule out any effect inherent to the specific constitution of the ester moiety of **2a**, **3**, and **4**. The general behavior described above was observed with a value of k_Q significantly higher than for the 2-TXA chromophores. A detailed interpretation of the phenomena is beyond

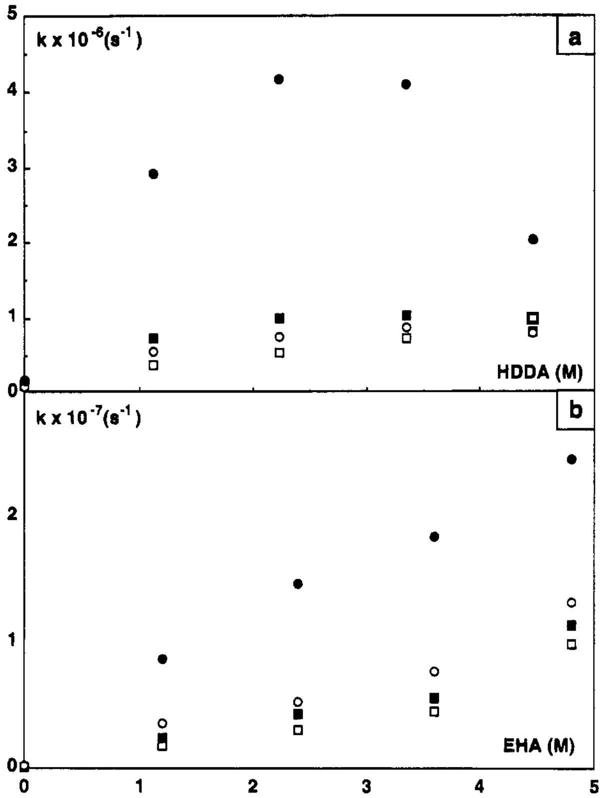


Figure 8. Rate constants of the thioxanthone triplet state deactivation by HDDA (a) and by EHA (b) measured at 620 nm in an argon-saturated methanol solution: **2a** (□); **4** (■); **3** (○); **8** (●).

Table 5. Pseudo-First-Order Rate Constants of the Triplet State Deactivation of TX Derivatives Measured at 620 nm in an Argon-Saturated Solution of Monomer

TX derivative	$10^{-6}k^{\mathrm{EHA}}$ (s^{-1})	$10^{-6}k^{\mathrm{HDDA}}$ (s^{-1})
2a	9.9	1.0
3	13.2	0.8
4	11.4	0.8
8	24.6	2

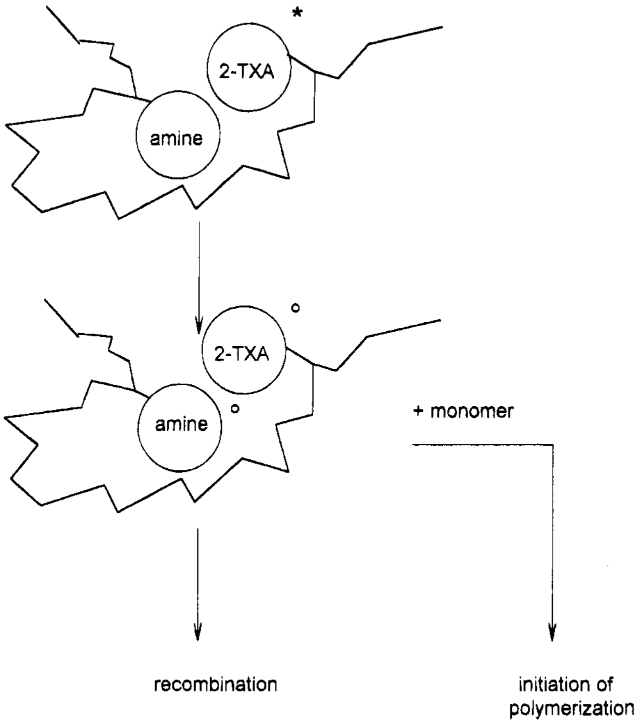
the scope of the present work. The following properties of the medium are subject to drastic changes of chemical properties (concentration of acrylate and of hydrogen-donating groups) as well as of physical chracteristics (polarity and viscosity). The major result is the absence of significant difference for the value of k_Q measured for **2a**, **3**, and **4** at various concentrations of acrylates in the solvent–monomer mixtures. This is also presented in Table 5 where the values of k_Q measured in pure monomers can be compared more precisely.

Conclusion

The present work was undertaken for investigating more deeply the peculiar effects associated with the use of polymer-bound chromophores in type II photoinitiating systems. The results concerning cross-linking polymerization initiated by such systems are from a phenomenological point of view in agreement with several recent studies on this topic. The observation that polymeric chromophores can induce an increase of the initial polymerization rate is confirmed for two series of type II systems including 2-BBA or 2-TXA chromophores.

Interestingly, despite the nonsymmetrical role of both types of free radicals produced in the type II process, the generation of macromolecular amino or ketyl radicals[1] was found to improve the initial value of R_p except when both types of radical are most likely produced by interaction of two partners binding the same macromolecule. These features were confirmed in the present study. The conversion does not go to completion when a polymeric reactant is used. Obviously, the presence of several chromophores and/or coinitiators on the same polymers is detrimental to the initiation process during the late stage of the polymerization. Gelation and vitrification of the polymerizing acrylate system most likely render the diffusion of the various partners of the complex initiation step more difficult. Our previous experiments with polymeric photoinitiators including additional acrylic functions in order to favor premature cross-linking and immobilization of the 2-BBA chromophores indeed showed that even lower values of π_∞ are obtained.

Scheme 3. Schematic Representation of the Competing Processes Taking Place with Polymer 2c



The close proximity of both the 2-TXA chromophore and the tertiary amine attached to the same polymer chain was expected to offer good conditions for generating the free radicals initiating chain polymerization. Time-resolved spectroscopy performed with these systems indeed indicates that triplet quenching proceeds with a greater efficiency than for the intermolecular deactivation observed with the LMW amine placed at the same macroscopic concentration. In spite of this beneficial influence on the first step of the process, the initial polymerization rate is not much different from that observed with the initiating system made of LMW reactants. The competition between recombination of primary free radicals and addition to monomer is a general feature of free radical polymerization, whatever the type of initiation process. It is likely that intramolecular deactivation by recombination[25] proceeds with greater probability when the radicals are generated on the same polymer chain (Scheme 3), thus canceling the benefit of intramolecular quenching of the excited chromophore.

The more intriguing aspect of the reactivity of the photoinitiators is the favorable effect on the initial polymerization rate when the chromophores are attached to a polymeric carrier. Time-resolved spectroscopy reveals that it is not correlated with the rate of quenching of the triplet excited state by a tertiary amine. It is still unclear whether the polymer effect acts on the initiation step or has an influence on some important parameters of the propagation chain.

A general interpretation of the peculiar behavior of polymeric photoinitiators described by several authors[26-29] is lacking. The study of viscosity effects on the rates of the various steps of the kinetic chain on one hand and of the evaluation of the average distance between propagating centers for various modes of initiation on the other seems of particular interest for this problem.

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