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Photoinduced Polymerization Reactions in the Presence of Light Stabilizers: Reactivity of the Photoinitiator in Solution and in Bulk[†]

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ABSTRACT: Excited-state interactions between light stabilizers (LS) and photoinitiators were investigated, for the first time, through time-resolved laser spectroscopy (TRLS), both in solution and in bulk monomer. The lifetimes of the photoinitiator triplet states and the rate constant of the interactions with oxygen, monomers, and amines in a bulk matrix became available. Fairly long-lived triplet states were detected even in the presence of high acrylate concentrations in the highly viscous monomer/oligomer medium. The practical effects of the addition of LS were evaluated in solution and in film photopolymerization experiments. An excellent agreement was found between the expected effect (from TRLS) and the observed practical behavior of the polymerized system, as evaluated by the rate of polymerization (R_p) or the superficial hardness of the coating: addition of LS leads to a decrease of R_p in solution but does not affect the curing rate in practical film photopolymerization performed in air.

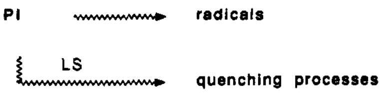
1. Introduction

Photoinitiators (PI) used to start a radical photoinduced polymerization reaction on exposure to UV light have been recognized as playing one of the most important roles in reaching high conversions of the monomer (M) in short irradiation times:[1–6]

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{PI}^* \longrightarrow \mathrm{R}^\bullet \xrightarrow{\mathrm{M}} \mathrm{RM}^\bullet \xrightarrow{\mathrm{M}} \mathrm{Polymer}$$

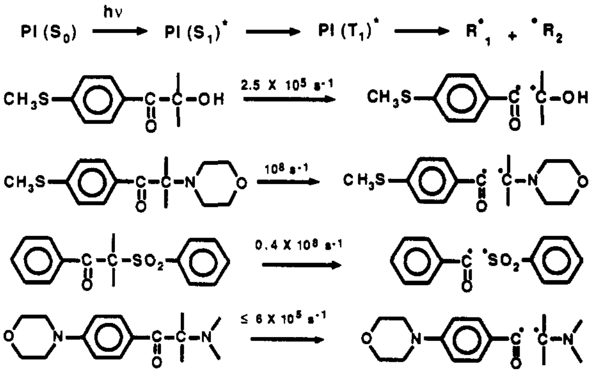
This reaction finds many applications in the UV curing of coatings, varnishes, paints, inks, ...[7–9] Considerable endeavors have been made to develop weather-resistant systems, particularly their ability to withstand sunlight exposure. In that case, one has to prevent, or at least to slow down, the photooxidation reactions, by means of a strategy called photostabilization.[10–16] Several major mechanisms can be operative: UV screening (compounds designed as UV absorbers, able to absorb light instead of the polymer backbone, are incorporated into the system); excited-state quenching (deactivation of detrimental species by appropriate quenchers); chain breaking by antioxidants (such compounds have to react with peroxide radicals; hindered amine light stabilizers (HALS) exemplify this behavior; they are also able to decompose hydroperoxides and to quench carbonyl groups.[17–21]

Incorporation of these light stabilizers (LS; UV absorbers, quenchers, or HALS) has to be carried out during the formulation of the photopolymerizable mixture, before the UV light exposure that leads to the ultimate coating. As a consequence, one might expect a detrimental interaction of LS with the excited states of PI, thus reducing the yield of production of the initiating species:



The present paper is devoted to an investigation of these primary fast processes in solution and in bulk (in the presence of UV absorbers and HALS).

The first part will describe original and new experiments on the kinetics of the excited states in bulk (i.e., in the viscous monomer/oligomer matrix usually employed on an industrial scale) in the presence of amines, multifunctional acrylate functions, and oxygen. The second part will show the interactions between PI and LS and their consequence on the polymerization reaction. These experiments were performed with the usual photoinitiators (whose photochemistry is well-known) working through α cleavage [hydroxyalkyl phenyl ketones (HAP);[22] morpholino ketones (MK);[23–26] sulfonyl ketones (SK);[27] and amino ketones (AK)[24–28] (the rate constants of the cleavage process in organic solvents are briefly reviewed in the following scheme)]



(1)

or through electron transfer in the presence of amines (AH) (benzophenone (BP);[6,29] chloro thioxanthone (CTX)[6].

$$\begin{tikzcd} \mathrm{PI}\,(S_0) \arrow[r, "h\nu"] & \mathrm{PI}\,(S_1)^* \arrow[r] & \mathrm{PI}\,(T_1)^* \arrow[r] & {} \arrow[d, "\mathrm{AH}"] \\ \mathrm{PIH}^\bullet + \mathrm{A}^\bullet & & & \mathrm{PI}^{\bullet-}\ \mathrm{AH}^{\bullet+} \arrow[lll] \end{tikzcd} \qquad (2)$$

2. Experimental Section

(a) Materials. The photoinitiators (PI) and light stabilizers (LS) which were used are shown in Tables I and II. They were purchased from Aldrich (CTX, BP), Merck (HAP), Fratelli

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[†] Part of this paper (corresponding to the practical aspects) has been presented at the RadTech North America Meeting, Boston, in April 1992 and was reprinted with permission from RadTech'92 North America Conference Proceedings, copyright 1992, RadTech International North America, 60 Revere Dr., Suite 500, Northbrook, IL 60062.

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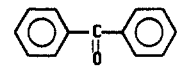
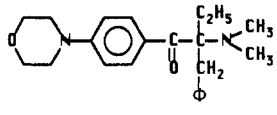
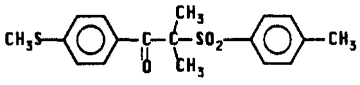
Table I
Investigated Photoinitiators



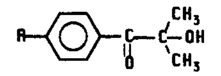
BP



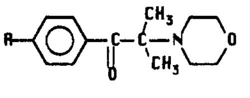
AK



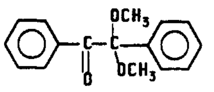
SK



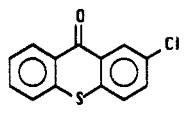
HAP N : R= $(CH_3)_2N$
HAP S : R=CH_3S



MK H : R=H
MK N : R=$(CH_3)_2N$
MK S : R=CH_3S

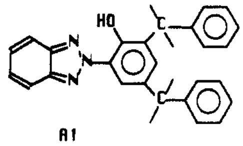


DMPA

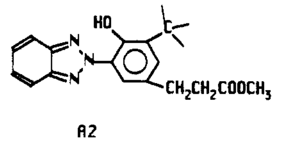


CTX

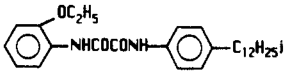
Table II
Investigated Photostabilizers



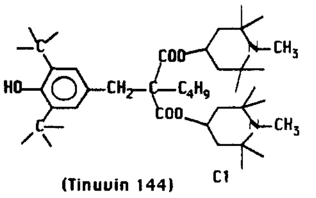
A1
(Tinuvin 900)



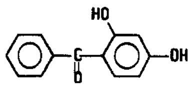
A2
(Tinuvin 1130)



(Sanduvor 3206)
B1



(Tinuvin 144)
C1



D1

Lamberti (AK), Sandoz (B1), and Ciba-Geigy (AK, MK, DMPA, A1, A2, C1). The molecular weights were calculated according to the formula and the compositions assigned to the commercial samples. Typical ground-state absorption spectra are shown in Figures 1 and 2.

(b) Techniques. 1. Time-Resolved Laser Spectroscopy. The typical device of laser spectroscopy used with a nanosecond time resolution was described in ref 23. The excitation source consists of a Nd/YAG laser Q-switched by a Pockels cell which produces a 3-ns pulse at 1064, 532, or 355 nm. The monitoring system consists of a xenon arc, a monomchromator, a photomultiplier at the detection end, a transient digitizing system, and a computer station (time resolution, 3 ns).

Table III
Relative Rate of Polymerization of [MMA] = 7 M in Deaerated Toluene in the Presence and the Absence of C1 (10^{-2} M)

	$r = R_p/R_p^\circ$		$r = R_p/R_p^\circ$
DMPA	1	AK	0.88
HAP S	1	BP[a]	0.65
MK S	1	CTX[a]	0.75
SK	0.85		

[a] In the presence of [MDEA] = 0.05 M.

Table IV
Persoz Hardness of a UV-Cured Film (Epoxy Acrylate/HDDA, 60:40) at a Belt Speed of 10 m min^{-1} (2 Passes)[a]

	pendulum hardness (s)			pendulum hardness (s)	
	[LS] = 0	[LS] = 1% w/w		[LS] = 0	[LS] = 1% w/w
DMPA	306[c]	308	AK	310	308
HAPS	214	214	BP[b]	126	124
MK S	280	289	CTX[b]	242	246
SK	238	290			

[a] LS is C1; [photoinitiator] = 3%. [b] [MDEA] = 2% w/w. Glass hardness is ≈430 s. [c] Average value; the error is estimated to be ±5 s from a series of measurements on a given film.

2. Solution Photopolymerization. Methyl methacrylate (MMA) was purified as described in ref 30. The MMA concentration was 7 M in degassed toluene. The samples were prepared and irradiated (as described in ref 29) using a 125-W medium-pressure mercury lamp equipped with a band-pass glass filter centered at $\lambda = 366$ nm, with $\Delta\lambda = 25$ nm). The incident light intensity was typically 10^{16} photons $cm^{-2}\,s^{-1}$. The polymerization rates (R_p) were determined using a dilatometric method.

3. Film Photopolymerization. A typical formulation consists of epoxy acrylate (Actilane 70 from SNPE)/HDDA (hexanediol diacrylate from Norsolor), 60:40 (w/w); a photoinitiator, 3%; amine MDEA (methyldiethanolamine), 2%; and a light stabilizer if used, 1% (as usual, in film photopolymerization, the concentrations are expressed in weight percent). This formulation is coated onto a glass plate (film thickness, 50 μm) and then polymerized in air by means of an industrial UV-curing line source (80 W cm^{-1}). (The photon flux is ca. 10^{18} photons $cm^{-2}\,s^{-1}$ at the sample.) The hardness of the scratch-free cured sample was measured with a Persoz pendulum (Erichsen 3000 NFT 30016).[31]

3. Results

3.1. Photopolymerization Experiments. A. Solution Photopolymerization. The rates of polymerization R_p of [MMA] = 7 M in a deaerated toluene solution were followed by dilatometry (Figure 3). The relative values recorded in the presence and absence of C1 are listed in Table III. In some cases, the presence of LS leads to a decreased rate of polymerization.

B. Film Photopolymerization. A 50-μm film formulation consisting of a mixture (60:40, w/w) of epoxy acrylate/HDDA in the presence and the absence of the HALS derivative C1 (1% w/w) was polymerized in air by means of a 80 W cm^{-1} mercury lamp. Figure 4 and Table IV show that the hardness of the film reaches the same value. This result holds true whatever the type of photoinitiator used and is obviously different from that observed for R_p in solution. Monitoring the changes of the double-bond content of a photopolymerizable film formulation (which actually gives that rate of polymerization) through real time IR spectroscopy[32] leads to the same conclusion: if bulk experiments are performed in air, the addition of HALS compounds does not reduce the rate of polymerization R_p. On the contrary, if UV absorbers

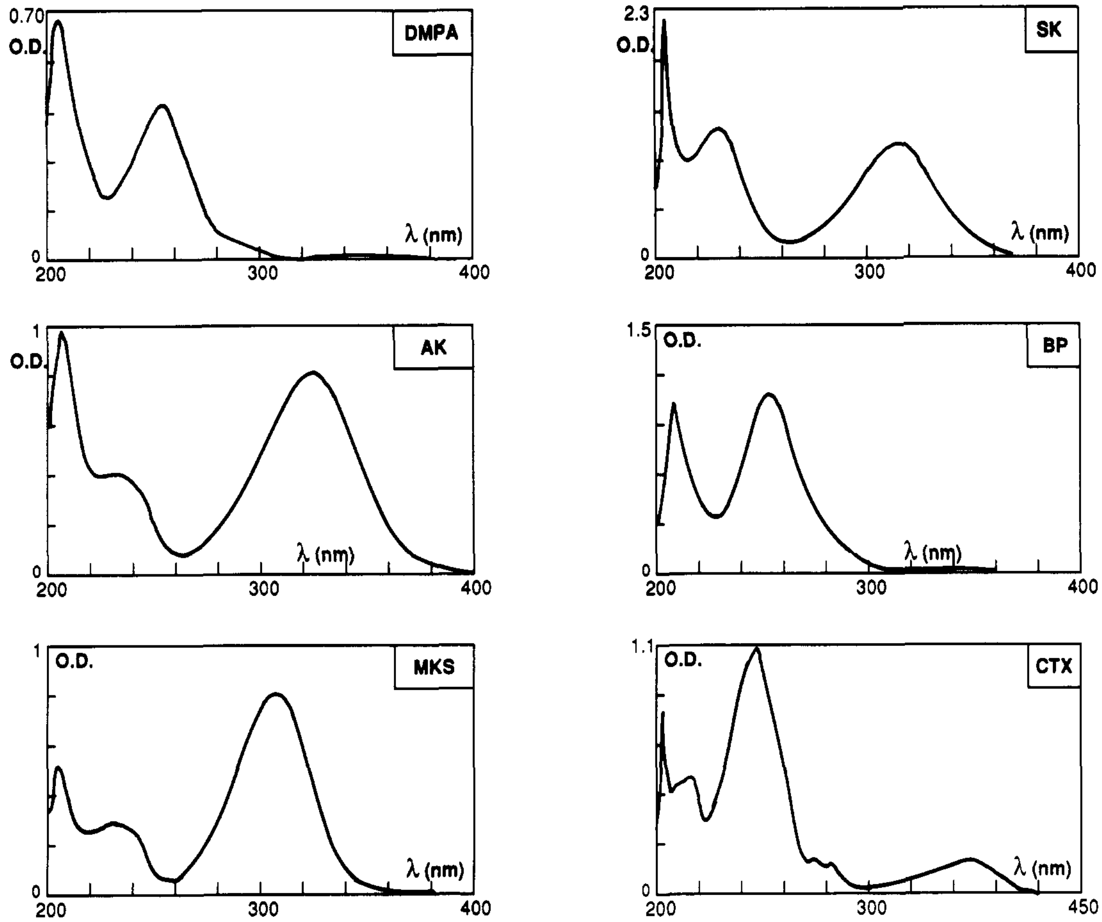


Figure 1. Ground-state absorption spectra of various typical PI (0.001%) in methanol (1-cm-path-length cell).

Table V
Triplet-State Quenching of BP by LS in Acetonitrile

LS	$10^{-6}k_a$ (M^{-1} s^{-1})	LS	$10^{-6}k_a$ (M^{-1} s^{-1})
A_1	8550	C_1	6500
A_2	10300	D_1	7050
B_1	15000		

are incorporated, R_p decreases at least because of a screening effect resulting in the absorption of light (see absorption spectra in Figure 2).

3.2. Excited-State Interactions. A. Triplet-State Quenching by Light Stabilizers. On laser excitation of the $S_0 \rightarrow S_1$ transition and after intersystem crossing, the triplet states T_1 of the photoinitiators were generated and their decays monitored as a function of the light stabilizer concentration. The value of k_a was determined by means of a Stern–Volmer plot

$$k = 1/\tau = 1/\tau_0 + k_a[\mathrm{LS}]$$

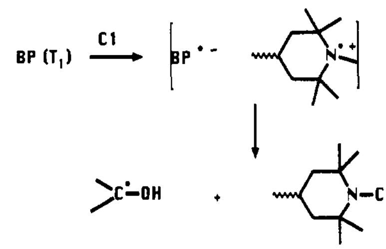
(where τ and τ_0 are the triplet-state lifetimes in the presence and the absence of LS; k_a stand for the rate constant of the bimolecular quenching of T_1 by LS). Fairly high values of k_a were recorded, thus revealing a strong interaction. The decay of T_1 was recorded at the following wavelengths: 520 nm (BP); 630 nm (CTX); 450 nm (HAP N); 420 nm (HAP O); 460 nm (HAP S); 460 nm (MK N); 400 nm (MK O); 470 nm (SK); 480 nm (AK).

(a) Interaction BP/LS. The results are listed in Table V, and typical Stern–Volmer plots are shown in Figure 5. It is apparent that the LSs interact very strongly with the benzophenone triplet state. In the case of C1, and only then, a long-lived residual absorption (which increases with [LS]) was observed (Figure 6): this absorption is very similar to that recorded on excitation of BP in isopropyl alcohol and, therefore, was assigned to a ketyl radical.

Table VI
Triplet-State Quenching in Various Couples of Photoinitiator/Light Stabilizer in Acetonitrile

PI	LS	$10^{-6}k_a$ (M^{-1} s^{-1})	PI	LS	$10^{-6}k_a$ (M^{-1} s^{-1})
HAP N	A1	5600	CTX	A1	12000
HAP N	C1	≤320	CTX	C1	10000
HAP S	C1	290	SK	A1	6400
MK N	A1	4850	SK	C1	520
MK N	C1	270	AK	A1	270

This species is presumably formed through an electron and proton transfer:



(3)

(b) Interaction between Various Photoinitiator/Light Stabilizer Couples. Similar experiments were carried out, in various combinations, in acetonitrile (Table VI). In CTX/C1, an electron and proton transfer occurs since the ketyl radical was observed (Figure 7). In other PI/C1 couples where the same process takes place (HAP N, HAP S, MK N, SK, AK), the k_a values are lower by almost an order of magnitude: this is easily accounted for by the low reactivity of these photoinitiators in electron-transfer reactions, as already shown when studying their interactions with amine compounds.[22,24,27] Except for AK, quenching by A1 exhibits a very high efficiency. Substituting toluene for acetonitrile leads (Table VII) to an increased quenching rate constant k_a for MK N, AK, SK,

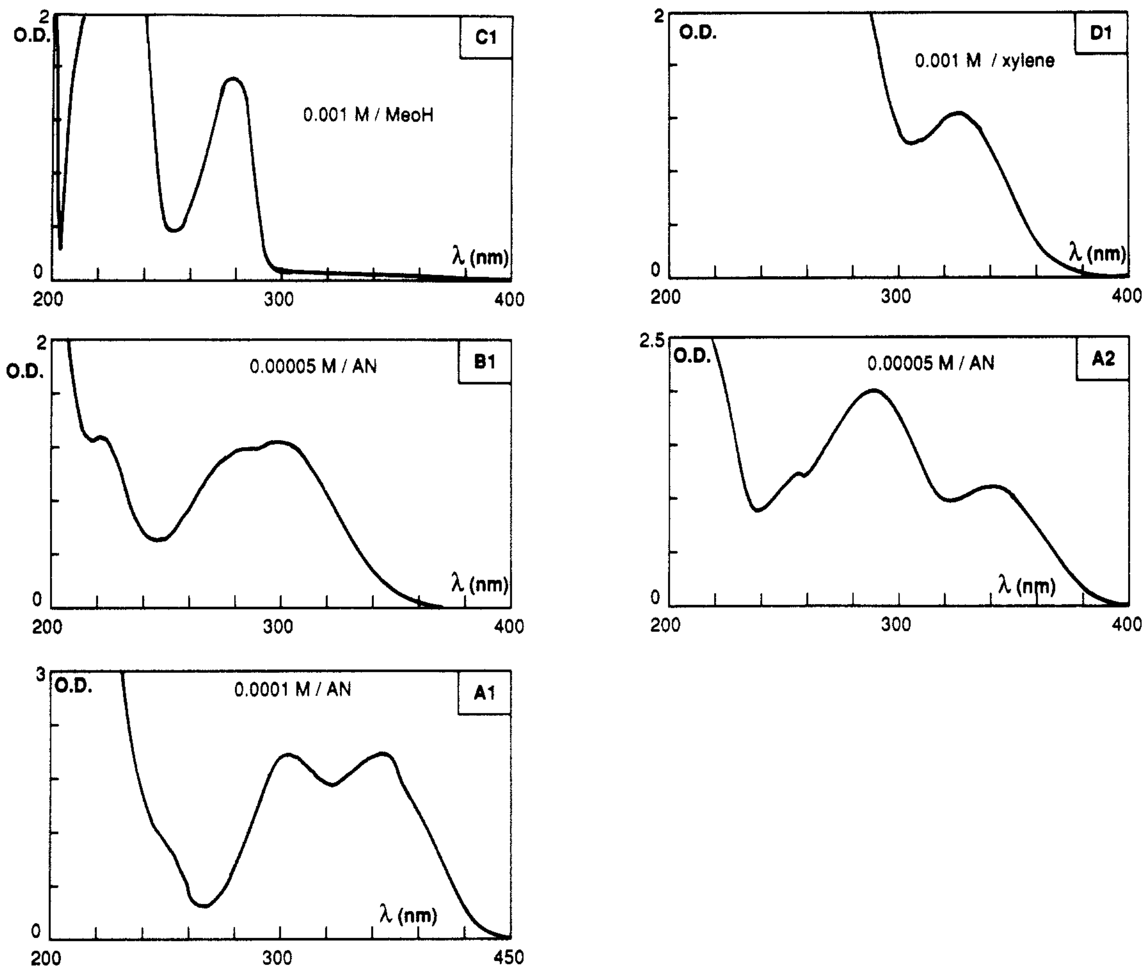


Figure 2. Ground-state absorption spectra of various LS in organic solvent (1-cm-path-length cell).

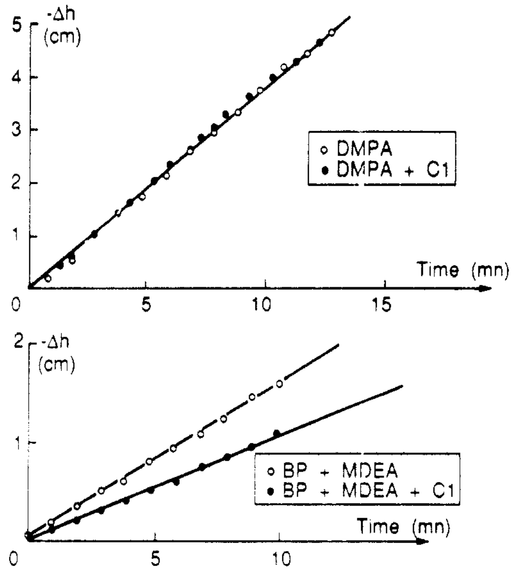


Figure 3. Typical monomer conversion curves as followed by dilatometry. [MMA] = 7 M; the OD of PI is 0.1 on 1 cm at λ = 365 nm; [C1] = 10^{-2} M; [MDEA] = 0.05 M. A volume contraction of 1 cm corresponds to a conversion of ≈2%.

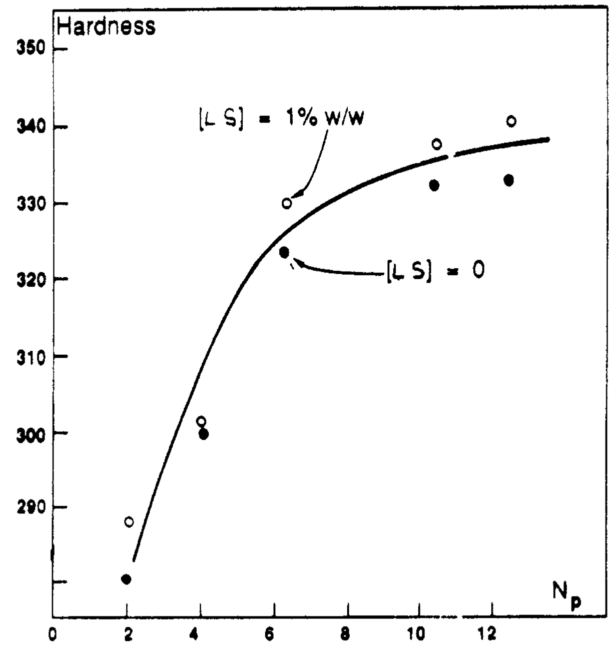
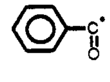
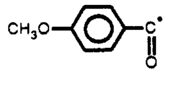


Figure 4. Typical hardness vs N_p curve (where N_p is the number of passes under the lamp). Belt speed 10 m min^{-1}. PI is MK S; LS is C1. Experimental conditions are given in Table IV.

and HAP S (whose lowest-lying triplet states exhibit a Π–Π^* charge-transfer character) and to a decreased k_a for BP (n–Π^* triplet state) and CTX (n–Π^* triplet state in toluene and Π–Π^* in acetonitrile). In the presence of LS such as the UV absorbers A1 and A2, the optical density (OD) of the triplet state decreases with increasing LS concentrations, because the ground-state absorption of A1 and A2 at the excitation wavelength (λ = 353 nm) reduces the yield in excited BP (inner filter effect).

B. Quenching of Radicals by Light Stabilizers. In a general way, a very weak interaction between radicals and light stabilizers was observed. For example, the bimolecular quenching rate constant k is $<10^7$ M^{-1} s^{-1} for





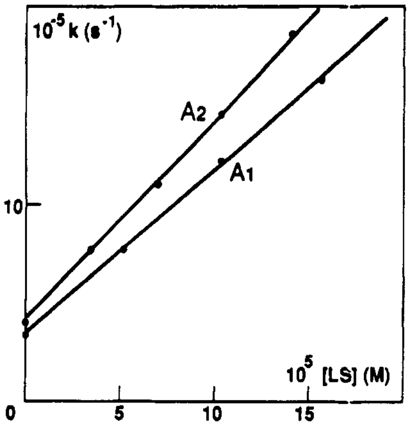


Figure 5. Examples of Stern–Volmer plot curves for the quenching of BP triplet state by typical LS in acetonitrile.

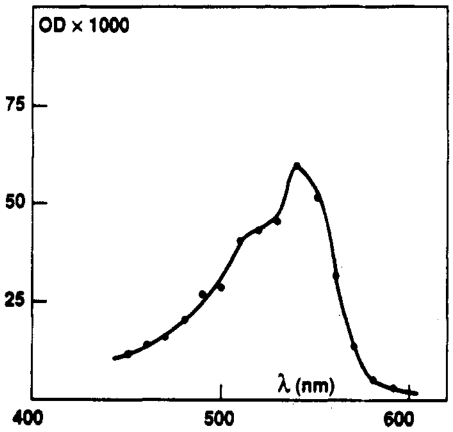


Figure 6. Long-lived residual absorption observed in the system BP/C1 in acetonitrile. The OD of BP is 0.5 on 1 cm at λ = 353 nm; [C1] = 4.7 × 10^{-4} M.

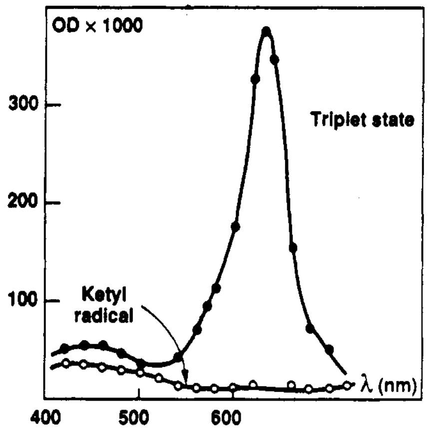


Figure 7. Triplet state of CTX in acetonitrile and long-lived residual absorption in the presence of C1. The OD of CTX is 0.45 on 1 cm at λ = 353 nm; [C1] = 1.5 × 10^{-4} M.

Table VII
Quenching of Triplet States by C1 in Toluene

PI	$10^{-6}k_a$ (M^{-1} s^{-1})	PI	$10^{-6}k_a$ (M^{-1} s^{-1})
BP	5800	AK	670
CTX	4050	SK	975
MK N	1600	HAP S	500

in the presence of C1 and B1.

4. Reactivity in Solution

The determination of the different rate constants of the processes involved provides a means for evaluating the effect of the light stabilizer on the primary process of radical formation, through either α cleavage or electron transfer (in the presence of an amine such as MDEA, methyldiethanolamine). The yields in radicals $\Phi_\alpha{}^\circ$ and Φ_α in the absence and the presence of LS can be evaluated for a given photopolymerization reaction in solution (methyl methacrylate (MMA) in deaerated toluene with monochromatic light centered at λ = 366 nm). Figure 8 shows the UV absorption of the different components of the polymerizable mixture. Under these experimental conditions where the optical densities are low at the excitation wavelength, the screening effect of HALS is negligible.

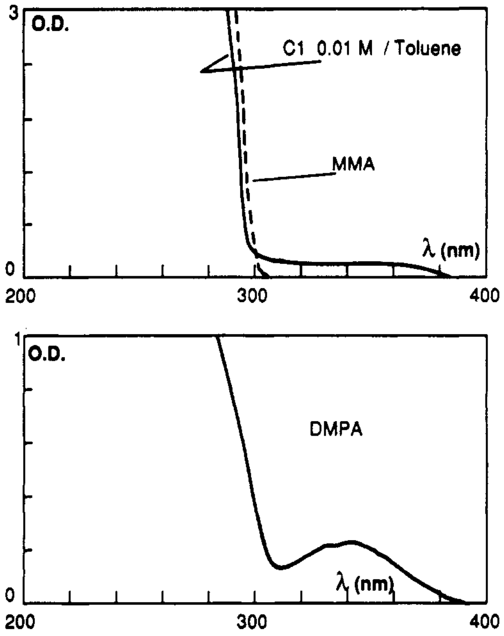
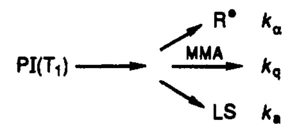


Figure 8. Ground-state absorption of monomer (MMA in bulk, a given photoinitiator (DMPA), and C1 (10^{-2} M) in toluene (1-cm optical path-length cell)).

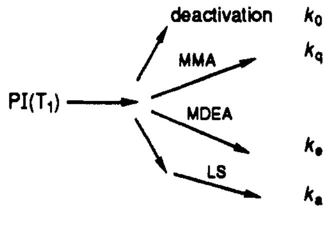
The yields Φ for the cleavage or the electron-transfer process can be calculated:

(i) α cleavage process



$$\Phi_\alpha = \frac{k_\alpha}{k_\alpha + k_q[\mathrm{MMA}] + k_a[\mathrm{LS}]}$$

(ii) electron-transfer process



$$\Phi_e = \frac{k_e[\mathrm{MDEA}]}{k_0 + k_e[\mathrm{MDEA}] + k_q[\mathrm{MMA}] + k_a[\mathrm{LS}]}$$

Typical calculations are summarized in Tables VIII and IX for various photoinitiators in the presence of C1. The changes of Φ_e or Φ_α parallel fairly well the changes of *r* obtained in Table III: a decrease of the yields is accompanied by a decrease of *r*. In some cases, the decrease of *r* is less important than expected: this behavior may be due to chemical reactions between the PIs and the LS (after the electron-transfer process), leading to new initiating radical species.

Table VIII
Quenching Rate Constants and Calculated Φ_e Values (See Text) in Toluene[a]

PI	$10^{-6}k_e$ ($M^{-1}\,s^{-1}$)	$10^{-6}k_q$ ($M^{-1}\,s^{-1}$)	$10^{-6}k_a$ ($M^{-1}\,s^{-1}$)	$100\Phi_e^\circ$	$100\Phi_e$
BP	1300	66	5800	12.3	11.1
CTX	3000	2	4050	91.5	73.3
SK	140	0.8	975	55.5	31.3

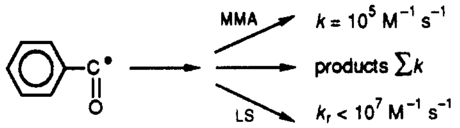
[a] [MDEA] = 5×10^{-2} M. [MMA] = 7 M. [LS] = 10^{-2} M. LS is C1.

Table IX
Quenching Rate Constants and Φ_α Values (See Text) in Toluene[a]

PI	$10^{-6}k_\alpha$	$10^{-6}k_q$	$10^{-6}k_a$	$100\Phi_\alpha^\circ$	$100\Phi_\alpha$
MK H	≥1000	200		40[b]	40[b]
DMPA	≥10000			100[b]	100[b]
MK N	0.5	5	1600	1.4	1.0
AK	0.6	0.3	670	22.2	6.4
SK	0.15	0.8	975	2.6	1.0
HAP S	0.25	8	500	0.4	0.4

[a] [MMA] = 7 M. [LS] = 10^{-2} M. LS is C1. [b] If $k_a = 5 \times 10^9$ $M^{-1}\,s^{-1}$.

Almost no effect of LS on the efficiency of an initiating radical is expected. For example, the following rate constants are obtained for the benzoyl radical:



The efficiency of the monomer interaction Φ_{RM} is

$$\Phi_{RM} = \frac{k[MMA]}{k[MMA] + \Sigma k + k_r[LS]}$$

Values of 1 and 0.9 were calculated for [LS] = 0 and [LS] = 10^{-2} M; [MMA] = 7 M.

5. Reactivity in a Film Matrix

The same calculations can be made for a bulk medium such as a photopolymerizable film matrix. The triplet-state lifetimes τ_T° and τ_T in the absence and the presence of C1 were determined in bulk, for the first time, through laser spectroscopy: τ_T° stands for the triplet-state lifetime in the degassed bulk medium (epoxy acrylate/HDDA, 60:40 w/w). These values are weakly affected by oxygen. The rate constant of the bimolecular quenching $k_a{}^b$ of the triplet state by C1 in bulk can be derived from

$$k_a{}^b = \frac{1}{[C_1]}\left[\frac{1}{\tau_T} - \frac{1}{\tau_T^\circ}\right]$$

In α cleavable PIs such as DMPA, HAP S, MK S, AK, and SK, the relative yield of cleavage (Y_c) in the presence and the absence of LS is expressed by

$$\frac{1}{\tau_T^\circ} = k_\alpha + k_q[M]$$

$$\frac{1}{\tau_T} = k_\alpha + k_q[M] + k_a{}^b[LS]$$

In an aerated bulk medium, Y_c is defined by

$$Y_c = \frac{k_a/(1/\tau_T^\circ) + k'_q[O_2]}{k_\alpha/(1/\tau_T) + k'_q[O_2]}$$

The term $k'_q[O_2]$, which stands for the quenching of triplet states by O_2, is computed from

$$\frac{1}{\tau_T^\circ(\text{air})} = \frac{1}{\tau_T^\circ(N_2)} + k'_q[O_2]$$

Thus

$$Y_c = \frac{1/\tau_T^\circ(\text{air})}{1/\tau_T + 1/\tau_T^\circ(\text{air}) - 1/\tau_T^\circ(N_2)}$$

Table X
Values of τ_T°, τ_T, $k_a{}^b$, Y_c, and Y_e (See Text) Determined in Bulk[a]

	τ_T° (ns)		τ_T (ns)	$10^{-6}k_a{}^b$		
	air	N_2	in N_2	($M^{-1}\,s^{-1}$)	Y_c	Y_e
HAP S	410	470	470	≤5	1	
AK	2000	4200	4000	0.85	0.98	
SK	2000	3300	2000	14	0.72	
CTX	1900	4000	1750	23		1

[a] Epoxy acrylate/HDDA 60:40, w/w; [C1] = 0.014 M (1% w/w). BP behaves like CTX and Y_e is ≈1. In MK H, MK S, and DMPA, triplet states have such a short lifetime that they cannot be detected: quenching by the monomer, O_2, and LS is totally inefficient and Y_c is equal to 1.

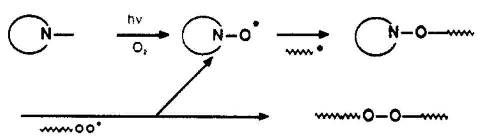
The results gathered in Table X show that, in a bulk and aerated medium based on multifunctional acrylates (similar to that used in practical applications), (i) the quenching of the triplet states by the monomer and oxygen is not as important as shown by the fairly long-lived triplet states in air and nitrogen; (ii) the rate constants of quenching by LS and, of course, by the monomer and O_2 become low compared with those measured in organic solvents, because of the well-known viscosity effect on the diffusion rate constant k_{diff} that will reduce the bimolecular quenching rate constants k_q, k_a, or k'_q (η is the viscosity)

$$k_{diff} = \text{cte}\frac{1}{\eta}$$

$$k_q = \alpha k_{diff}$$

(iii) the primary step of the radical generation from the photoinitiator is not significantly affected by the presence of LS, which explains the absence of any significant effect on the hardness measured in Table IV. The situation observed with SK is particular: decrease of Y_c and increase of the hardness.

Additional effects might be taken into account, such as the direct absorption of light by the HALS derivative C1 and its role in an oxygenated medium:



Typical absorption spectra of the matrix, PI, and C1 shown in Figure 9 reveal that the light is mainly absorbed by the photoinitiator at λ ≥ 300 nm and demonstrate that the HALS might have no other effect than to quench the excited states. A weak contribution, however, cannot be ruled out, due to its direct light absorption; as already pointed out,[32] it can explain the increased rate of polymerization because of the rapid consumption of O_2 by HALS.

In PIs working through an electron-transfer bimolecular process, whose efficiency is dependent on the viscosity (e.g., BP and CTX), the determination of the rate constant of electron transfer with amines in bulk is required. For CTX, the triplet-state lifetime in air is shortened to 280

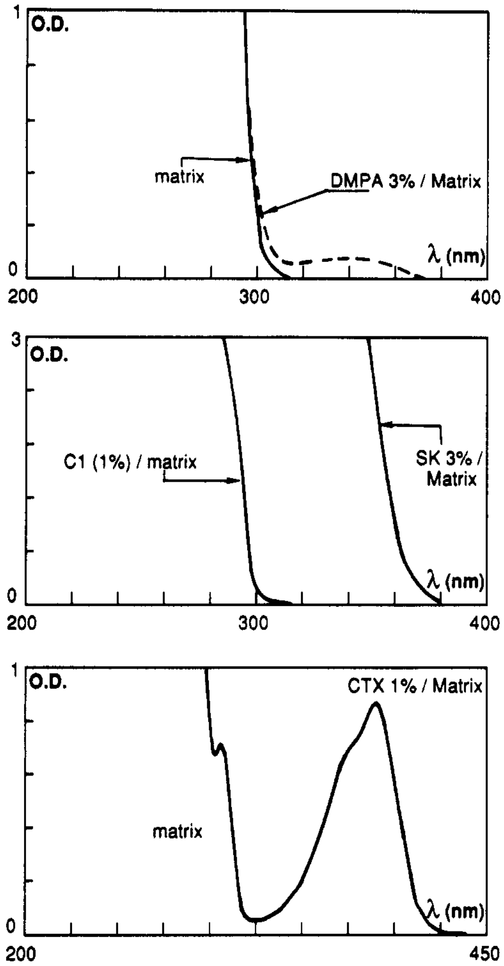


Figure 9. Ground-state absorption spectra of a 50-µm film of epoxy acrylate resin/HDDA (60:40, w/w) alone or containing C1 (1%) or DMPA 3%, CTX 1%, or SK (3%).

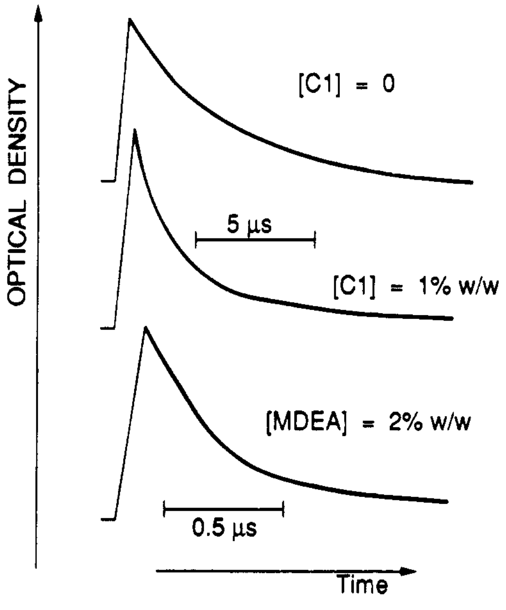


Figure 10. Typical oscillogram trace for the decay of the triplet state of CTX in epoxy acrylate/HDDA 60:40, w/w, in N_2. The lifetimes are calculated according to a first-order kinetic analysis. ln OD = $f(t)$. The lifetime is considered as the reciprocal value of the first-order rate constant.

ns upon addition of MDEA 2% w/w (Figure 10). In the definition of $\tau_T°$ and τ_T, k_α has to be replaced by k_e[MDEA], and Y_c becomes Y_e (relative yield of electron transfer). A value close to 1 is easily calculated for Y_e: no effect was expected, and no effect was observed (Table IV).

6. Conclusion

This study provided information, for the first time, on the interaction of photoinitiators (PI) with light stabilizers (LS), both in solution and in a film matrix. While the results obtained in an aerated UV-curable formulation show that the presence of LS should not affect the curing rate (and confirm previous works as already noted[32]) or the film hardness, the rate of the reaction decreases in degassed solution polymerization. These different behaviors are well understood on the basis of kinetic measurements performed through time-resolved laser spectroscopy, notably those carried out in bulk media, which predict that the interaction PI/LS should have almost no effect on the yield of radical production.

Another important facet of the present work is concerned with the effect of a photopolymerizable monomer/oligomer matrix (used in coating technology) on the excited-state processes of PI. The lesson is as follows:

(i) The O_2 quenching of high-reactivity triplet states (e.g., in MK S or DMPA) can be disregarded. In less reactive triplet states (e.g., in AK or SK), however, the yield in the initiating radical (Y_R) becomes lower in aerated bulk medium:

$$Y_R(\text{air}) = k_\alpha \tau_T°(\text{air})$$

$$Y_R(N_2) = k_\alpha \tau_T°(N_2)$$

$$\frac{Y_R(\text{air})}{Y_R(N_2)} = \frac{k_\alpha \tau_T°(\text{air})}{k_\alpha \tau_T°(N_2)}$$

This ratio is ~0.5 for AK and ~0.6 for SK. In organic solvent, this ratio is lower than 0.1 (and is more unfavorable to the generation of initiation radicals).

(ii) In efficient cleavable PI, the monomer quenching in bulk cannot compete;

(iii) In PI/amine combinations, the primary step of the electron transfer remains much more efficient than the monomer quenching even if a high concentration of acrylates is present, as encountered in bulk.

(iv) As a consequence, the yield Φ_α or Φ_e of the primary process in photoinitiators having short-lived triplet states should be similar to that determined in deaerated solution but nothing can be said about the quantum yield of initiation which takes into account Φ_α (or Φ_e), ϕ_{RM} (yield in starting polymer chains), the quantum yield of intersystem crossing Φ_{ST}, and the yield of escaping radicals formed in the radical pair (see eq 1)

$$\left[R_1^{\bullet}\ R_2^{\bullet}\right] \longrightarrow R_1^{\bullet} + R_2^{\bullet}$$

or in the charge-transfer complex (see eq 2)

$$PI^{\bullet -}AH^{\bullet +}$$

(that might be affected by the viscosity or the polarity or the H-bonding character of the matrix).

Other aspects concerned with the direct investigation of photochemical processes in multifunctional monomers or oligomers in bulk have been recently discussed in a preliminary paper[33] (and will be treated at greater length in forthcoming papers), such as the effect of the viscosity or the polarity of different matrices, the behavior of PI sensitive to the polarity of the medium, and the interaction between a photosensitizer and a photoinitiator in a bulk monomer/oligomer medium.[34,35] These investigations are of primary importance for the understanding of what takes place in end-use industrial formulations.

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