Photoinitiation Processes of Radical Polymerization in the Presence of a Three-Component System Based on Ketone–Amine-Bromo Compound

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ABSTRACT: The interactions between the different partners of a three-component system were studied by time-resolved laser spectroscopy and steady-state photolysis. The rate constants of the processes involved were measured. The primary steps of the photoinitiation reaction are mostly explained on the basis of an electron transfer between the ketone and the amine. The bromo compound, which acts as a quencher of the ketyl radicals known as scavengers of the growing polymer chains, decreases the rate of termination and generates new initiating radicals. Both effects lead to an increased rate of polymerization.

I. Introduction

Photoinduced polymerization reactions are widely used in the area of radiation curing technologies[1,2] for many applications in various industrial sectors. The key role played by the photoinitiator (PI) has been recognized for a long time, as discussed in several review papers.[3] The initiation of the radical polymerization may occur in the following manner:

(i) On unimolecular splitting of the photoinitiator

$$\mathrm{PI} \xrightarrow{h\nu} \text{radicals}$$

(ii) When a bimolecular reaction takes place between the photoinitiator and various additives, such as amines

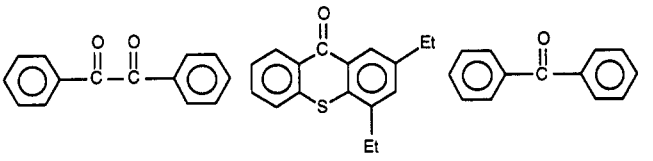
$$\mathrm{PI} \xrightarrow[\text{amines}]{h\nu} [\ ] \rightarrow \text{radicals}$$

The photochemistry, the excited-state processes, and the reactivity (in solution and bulk monomer medium) of PIs working through i or ii have been extensively studied in recent years, *e.g.*, in the case of substituted benzophenones,[4] hydroxylalkyl ketones[5] or aminoketones,[6] copolymerizable PIs,[7] polymeric PIs,[8] benzoylphosphine oxides,[9] sulfur-containing PIs,[10] water-soluble PIs,[11] mixtures of PIs,[12] and PIs in the presence of light stabilizers.[13]

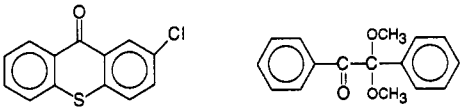
The development of UV curing, laser imaging, and 3D stereolithography requires the design of ever more efficient photoinitiating systems. One possible way to win this challenge is to conceive new mixtures, e.g., based on three components instead of two, that would exhibit a higher efficiency than any two-component combination. This has recently been achieved in dye (or ketone)/amine/onium salt systems where the dye can be a thioxanthene derivative,[14] eosin,[15] or a ketocoumarin.[16] The poor stability of the ketone/amine/onium salt system prompted us to change the onium salt for another substance. Bromo compounds appeared to meet this requirement, and a first report[17] described some preliminary experiments showing the promising capability of this three-component system. The present paper deals with (i) the performance of this system in photoinduced radical polymerization reactions and (ii) the mechanism of the initiation step (as deduced from time-resolved laser spectroscopy experiments) and the role of CBr_4. Only photopolymerization experiments will be reported for other bromo compounds due to experimental difficulties (see below).

II. Experimental Section

(1) The following compounds were used. (a) Ketones:

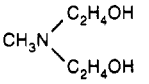


BZ DETX BP



CTX BDMK

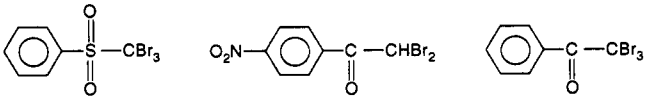
(b) Amine:



MDEA

(BZ: benzil. DETX: 2,4-diethylthioxanthen-9-one. BP: benzophenone. CTX: chlorothioxanthone. BDMK: 2,2-dimethoxy-2-phenylacetophenone. MDEA: 2,2′-(methylamino)diethanol.)

(c) Bromo Compounds: CBr_4.



BMPS DBAP TBAP

(BMPS: tribromomethyl phenyl sulfone. DBAP: 2,2-dibromoacetophenone. TBAP: 2,2,2-tribromoacetophenone.)

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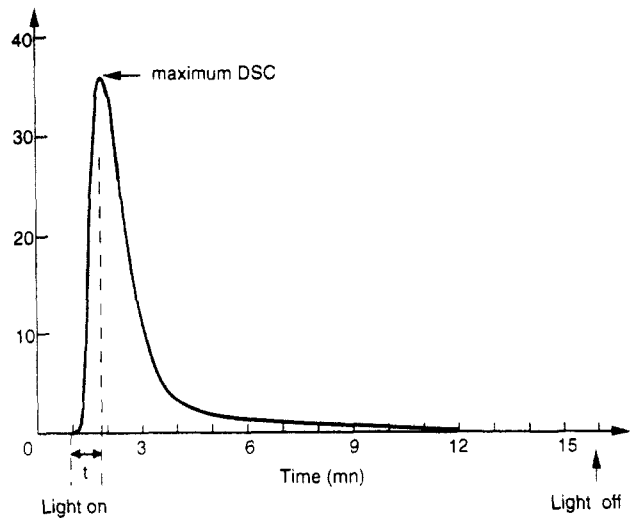
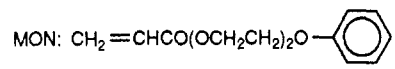


Figure 1. Typical DSC curve.

BMPS was purchased from Seitetu Kagaku Kogyo. DBAP and TBAP were synthesized as reported in ref 17b. BZ, BP, CTX, BDMK, and MDEA were purchased from Aldrich Chemical Co. DETX was supplied by Nippon Paint.

(d) Monomer:



diethylene glycol monophenyl ether monacrylate
(trade name Aronix M-101, produced by Toa Gosei)

(2) Techniques. (a) Time-Resolved Laser Spectroscopy. The Nd:YAG laser (BMI Corp.) flash photolysis apparatus (excitation wavelength λ = 355 nm, 3-ns fwhm pulse, 40 mJ/pulse; rise time of the detection system 3 ns) has been described in an earlier report.[18]

(b) Photopolymerization Experiments. The heat flow of the photopolymerization was measured by using a differential scanning calorimeter (DSC 220) equipped with a photoaccessory (200-W Hg–Xe lamp) produced by Seiko Instruments.

About 10 mg of a mixture of Aronix M-101 and a photoinitiator was placed in an aluminum DSC pan having a diameter of 5 mm. The sample was irradiated with the 200-W Hg–Xe lamp in air or N_2. When the measurements were performed in N_2, the sample was irradiated after flushing the closed sample chamber having a capacity of approximately 10 cm^3 with N_2 gas for 5 min. The N_2 flow (30 cm^3/min) was continued during the irradiation.

The light intensity was measured by using the International Light IL 1700 radiometer with a SED 400 detector.

The relative curing rate (RCR) was calculated by means of the following equation:

$$\mathrm{RCR} = \frac{t \text{ in BDMK}}{t \text{ in each photoinitiator}}$$

where t stands for the irradiation time required to reach the maximum heat flow (Figure 1).

(c) Acidity Measurements. Acidity measurements were performed by determining the potential difference of the solution during the photolysis under a HPK mercury lamp ($\sim 10^{16}$ photons cm^{-2} s^{-1}).

III. Results

III.1. Efficiency of the Three-Component System in Photopolymerization Reactions. The relative rates of curing (as defined in the Experimental Section) are shown in Table 1. BDMK is a well-known photoinitiator and is chosen as a reference. Because of the high efficiency of the cleavage process, amine and CBr_4 cannot interact with the excited states: this compound is usually employed without any additive. The following trends were observed. The ketone/bromo compound combination has a low efficiency (it becomes inefficient in air). The ketone/bromo compound/amine system is better than the ketone/amine system. In general, CBr_4 is the most suitable bromo compound. The loss of efficiency in the presence of TBAP is due to an inner filter effect because of the absorption of this compound in the near-UV wavelength range. In the presence of DBAP, this effect is presumably balanced by a higher reactivity of the additive. DETX is better suited than BZ or BP.

III.2. Ground-State Absorption. The well-known ground-state absorption spectra of DETX, BP, BZ, DBAP, TBAP, and CBr_4 in the near-UV have been recorded. The formation of complexes between amines and bromo compounds was observed as visualized in Figure 2 where the absorption of the complex is higher than the sum of the absorbances of the amine and the bromo compound (see caption of Figure 2). In the three-component system, the absorption of light will not only be due to the free molecules.

III.3. Fluorescence Measurements. Ketones such as BP and BZ are not fluorescent compounds. Thioxanthone derivatives, however, are known to exhibit a fluorescence emission in a polar environment because of a change in the excited-state configuration. Figure 3 shows the fluorescence emission spectrum of DETX and the Stern–Volmer plots for the quenching of the fluorescence by MDEA, the monomer, and the bromo compounds in acetonitrile according to

$$I^0_f/I_f = 1 + k_q\tau_f[Q]$$

(where I_f and I^0_f stand for the fluorescence intensities in the presence and in the absence of the quencher Q, τ_f stands for the S_1 singlet-state lifetime, and k_q stands for the rate constant of the bimolecular quenching reaction). The value of τ_f was evaluated by following the changes in fluorescence intensity for the aerated and the deaerated solutions and taking 3×10^{10} M^{-1} s^{-1} for the rate constant of quenching of the S_1 state by O_2. The quantum yield of fluorescence ϕ of DETX in acetonitrile is $\phi = 0.02$ (with reference to thioxanthone in methanol ($\phi = 0.12$)[19]). Table 2 shows that bromo compounds strongly interact with singlet fluorescent states. The apparent quenching process may be (a) a true fluorescence quenching

$$S_1 \rightarrow S_0$$

or (b) an indirect process where the fluorescence intensity decreases because of an enhancement of the intersystem crossing through the usual external heavy-atom effect (in the case of these ketones, where the quantum yield of intersystem crossing is already very high, this effect cannot be significant):

$$S_1 \rightarrow T_1$$

The first process should lead to a decrease of $[T_1]$, the second one to an increase, and the superposition of both processes either to an increase or a decrease (see below).

III.4. Excited-State Processes. (A) Transient Absorption Spectra. Laser excitation of the ketones BP, BZ, and DETX in deaerated acetonitrile solutions induces the S_0–S_1 transition and leads, through a fast intersystem crossing process, to the generation of a long-lived triplet state T_1 whose absorption decays in the microsecond time range according to a combination of first- and second-order kinetics. By way of example, the T_1–T_n absorption of DETX is displayed in Figure 4.

Table 1. Maximum DSC Peak, in Air and N_2 Flow, Enthalpy ΔH, and Relative Rate of Curing RCR (See the Experimental Section) (Monomer, MON; [Ketone] = 0.05 M; [Amine] = 0.25 M; [Bromo Compound] = 0.05 M)

	in air				in N_2	
photoinitiator	t (min)	max DSC (mW/10 mg)	ΔH (mJ/mg)	RCR	t (min)	max DSC (mW/10 mg)
BDMK	1.43	24.95	−213.6	1		
BDMK/CBr_4	no reaction					
BDMK/TBAP						
BDMK/BMPS						
DETX/MDEA	0.75	22.84	−316.3	1.91	0.44	34.04
DETX/CBr_4	no reaction					
DETX/CBr_4/MDEA	0.67	25.00	−324.0	2.13	0.29	36.09
DETX/DBAP	no reaction					
DETX/DBAP/MDEA	0.63	25.08	−317.8	2.27		
DETX/TBAP	no reaction					
DETX/TBAP/MDEA	2.31	7.66	−290.1	0.62		
DETX/BMPS	no reaction				3.25	1.21
DETX/BMPS/MDEA	0.79	23.97	−319.6	1.81	0.33	44.68
BZ/MDEA	1.39	5.57	−138.9	1.03	0.48	10.42
BZ/CBr_4	no reaction				1.47	1.02
BZ/CBr_4/MDEA	0.71	32.09	−304.5	2.01	0.37	45.77
BZ/DBAP	no reaction					
BZ/DBAP/MDEA	1.36	17.41	−237.8	1.05		
BZ/TBAP	no reaction					
BZ/TBAP/MDEA	1.66	11.47	−226.4	0.86		
BZ/BMPS	no reaction				2.00	0.80
BZ/BMPS/MDEA	0.82	35.85	−313.7	1.74	0.37	56.43
BP/MDEA	1.39	5.57	−138.9	1.03	0.33	46.86
BP/CBr_4	no reaction				2.95	6.99
BP/CBr_4/MDEA	0.75	29.19	−296.7	1.91	0.37	40.17
BP/DBAP	no reaction					
BP/DBAP/MDEA	1.01	24.51	−273.0	1.42		
BP/TBAP	no reaction					
BP/TBAP/MDEA	1.55	14.16	−259.4	0.92		
BP/BMPS	no reaction				2.15	9.19
BP/BMPS/MDEA	0.79	34.80	−298.2	1.81	0.37	54.01
CBr_4					2.31	3.27
BMPS					1.73	6.42
CBr_4/MDEA	1.58	8.96	−222.4	0.91	0.44	15.40
DBAP/MDEA	2.12	8.03	−209.9	0.68		
TBAP/MDEA	3.94	3.69	−159.4	0.36		
BMPS/MDEA	1.66	11.67	−224.2	0.86	0.48	32.29

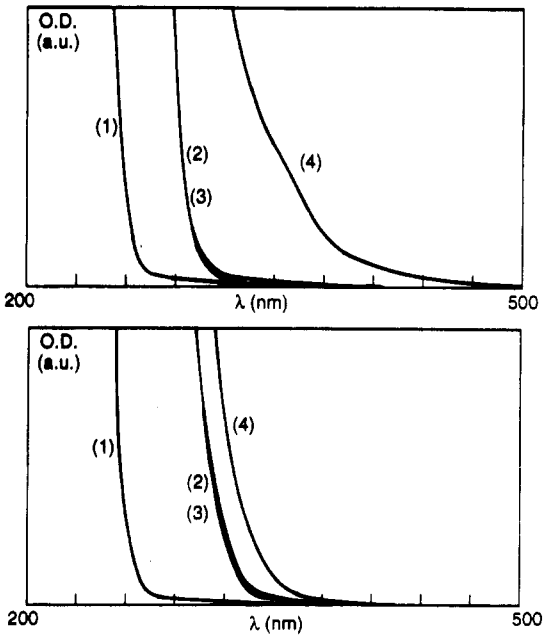


Figure 2. Formation of a complex between amines and bromo compounds in acetonitrile in air. Ground-state absorption spectra: (1) MDEA 0.08 M; (2) BMPS (top) or CBr_4 (bottom); (3) addition of spectra 1 + 2; (4) mixture of MDEA 0.08 M and BMPS (top) or CBr_4 (bottom) 0.015 M.

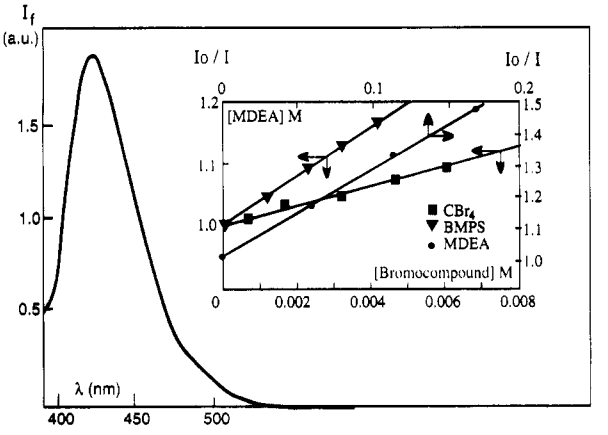


Figure 3. Fluorescence spectrum of DETX in acetonitrile (λ_{excit} = 370 nm). Typical Stern–Volmer plots for the fluorescence quenching of DETX in acetonitrile (λ_{excit} = 370 nm; λ_{ana} = 422 nm).

Table 2. Fluorescence Quenching Data for DETX/Q in Acetonitrile

Q	$k_q\tau_f$ (M^{-1})	$10^{-9}k_q$ (M^{-1} s^{-1})
MDEA	2.8	2.3
CBr_4	15	12.5
BMPS	38.5	32
MON	<0.025	<0.02

(B) Ketone/Amine Interaction. The reaction between the T_1 triplet state of the ketone and the amine MDEA was followed by laser spectroscopy. As is known, this reaction leads to the generation of a ketyl type radical on the ketone and an amine-derived radical through the formation of a charge transfer complex (CTC). A typical

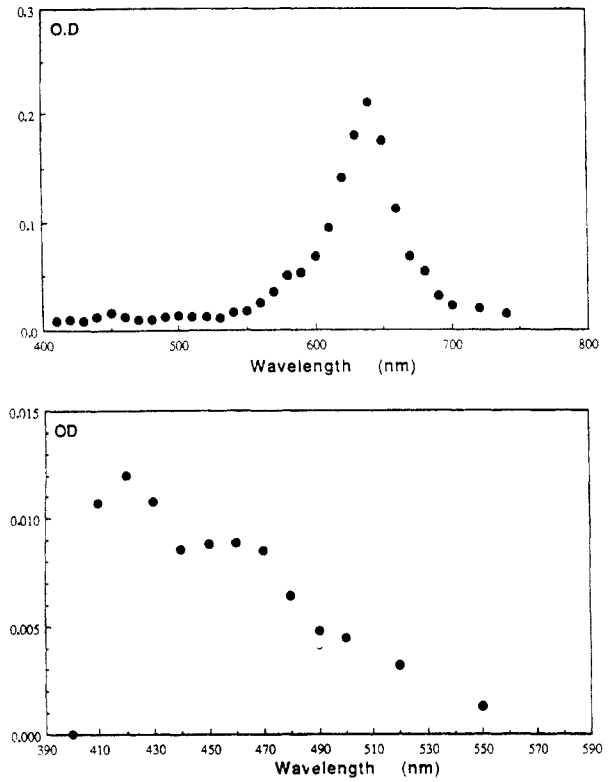


Figure 4. Triplet–triplet absorption of DETX in degassed acetonitrile (top). Ketyl radical transient absorption for DETX in acetonitrile/MDEA 0.1 M (bottom).

Table 3. Quenching Rate Constants by MDEA (k_e), MON (k_q), and BMPS or CBr_4 (k_{int}) in Acetonitrile

			$10^{-6}k_{int}$ (M^{-1} s^{-1})	
	$10^{-6}k_3$ (M^{-1} s^{-1})	$10^{-6}k_q$ (M^{-1} s^{-1})	BMPS	CBr_4
DETX	1400	2.4	740	2600
BZ	830	4	11	11.5
BP	2000	400	69	80
CTX			190	700

absorption spectrum of the ketyl structure is shown in Figure 4 for DETX.

$$T_1 + \text{MDEA} \xrightarrow{k_e} \text{CTC} \longrightarrow \text{OH} + \text{N}$$

The bimolecular rate constants k_e are displayed in Table 3 (solvent:acetonitrile): they reflect the highly efficient interaction between ketones and amines.

(C) Ketone/Monomer Interaction. In fluid media, the monomer interaction is usually efficient and competes with the radical generation processes. The rate constants k_q for the reaction

$$T_1 + \text{monomer} \xrightarrow{k_q} \text{quenching}$$

are listed in Table 3 for MON: as generally observed, this interaction is efficient for BP but rather low for benzil and thioxanthone derivatives.

(D) Ketone/Bromo Compound Interaction. (a) Triplet-State Quenching. Bromo compounds deactivate the triplet states of the different ketones used. As for the amine and the monomer quenching, a Stern–Volmer plot drawn for the triplet-state lifetime in the presence (τ_T) and the absence (τ^0_T) of the quencher Q (in that case, the bromo compounds)

$$1/\tau_T = 1/\tau^\circ_T + k_{int}[Q]$$

yields the rate constant of the reaction

$$T_1 + \text{bromo compounds} \xrightarrow{k_{int}}$$

Typical plots are shown in Figure 5; the k_{int} values are gathered in Table 3 for ketone/BMPS or CBr_4.

The quenching of T_1 by DBAP or TBAP cannot be followed with the present design of the laser spectroscopy apparatus (excitation wavelength: 355 nm). At λ = 355 nm, both the ketone and DBAP or TBAP absorb, which precludes any analysis because of the superposition of transients arising from the ketone and TBAP or DBAP. This investigation needs a complete set of experiments on the excited states of TBAP and DBAP and the interactions with ketones by using a new laser-pumped dye laser spectroscopy apparatus that is not available at the moment.

(b) Quenching Process. Bromo compounds may be expected to play the role of electron acceptors, according to

$$T_1\,(\text{DETX}) + CBr_4 \rightarrow \text{DETX}^{\bullet+} + CBr_4^{\bullet-}$$

or

$$T_1\,(\text{DETX}) + \text{BMPS} \rightarrow \text{DETX}^{\bullet+} + \text{BMPS}^{\bullet-}$$

The thermodynamic calculations were performed according to the Rehm & Weller equation: Ln $k_q = -\Delta E^3_{0,0} + E_{ox} - E_{red} + C$, where $\Delta E^3_{0,0}$, E_{ox}, E_{red}, and C are the electronic energy of the excited donor, the oxidation potential of the donor, the reduction potential of the acceptor, and the Coulombic term for the interaction between the radical ions, respectively. CTX is also used in this experiment due to the fact that its reactivity is similar to that of DETX and its redox potentials are known. The values of $\Delta E^3_{0,0}$, E_{red} (−1.5, −1.4, and −0.71 V for BP, CTX, and BZ, respectively), and E_{ox} (2.3, 1.5, and 2 V for BP, CTX, and BZ, respectively) are derived from refs 19–22, and the experimental data suggest that this reaction should occur in CTX, BP, BZ//BMPS or CBr_4 (Figure 6). By analogy, although no values are available for E_{red} and E_{ox}, the same holds presumably true for DETX/BMPS and DETX/CBr_4. The simultaneous occurrence of an energy-transfer process, however, cannot be ruled out at this stage (see below):

$$^3\text{DETX} + CBr_4 \rightarrow \text{DETX} + C^\bullet Br_3 + {}^\bullet Br$$

The electron-transfer process is supported by the fact that a new transient absorption was observed in the DETX/BMPS or DETX/CBr_4 system at approximately 430 nm (Figure 7). This transient is ascribed to the cation radical of DETX (the same species is formed on interaction of thioxanthone derivatives with onium salts[23].

In DETX/BMPS, the situation is obviously complex. In fact, formation of the tribromomethyl radical takes place in a first step and then the benzenesulfonyl anion presumably loses an electron: this might occur through reaction with DETX$^{\bullet+}$:

$$\text{BMPS}^{\bullet-} \longrightarrow \text{C}_6\text{H}_5\text{SO}_2^\bullet + {}^\bullet CBr_3$$

$$\text{DETX}^{\bullet+} + \text{C}_6\text{H}_5\text{SO}_2 \longrightarrow \text{DETX} + \text{C}_6\text{H}_5\text{SO}_2^\bullet \quad \text{(L)}$$

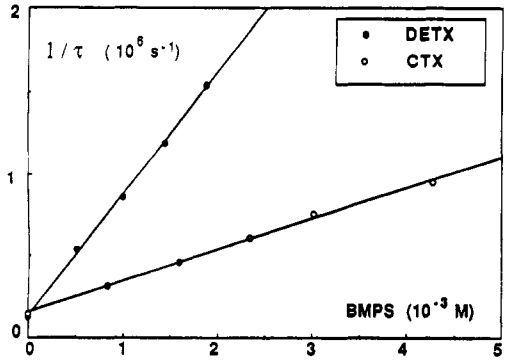


Figure 5. Typical Stern–Volmer plot for the quenching of the triplet state of the ketone by BMPS in acetonitrile.

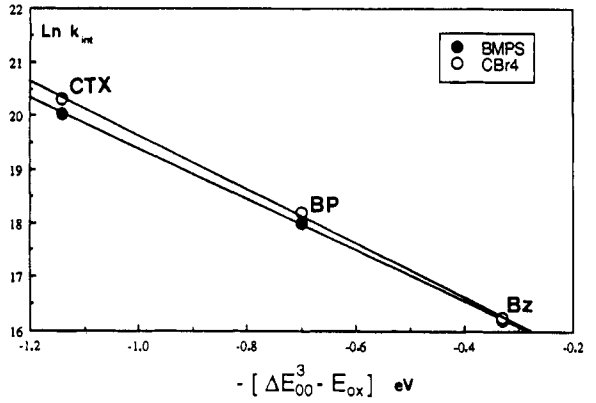


Figure 6. Ln k_{int} *vs* ΔG (see text).

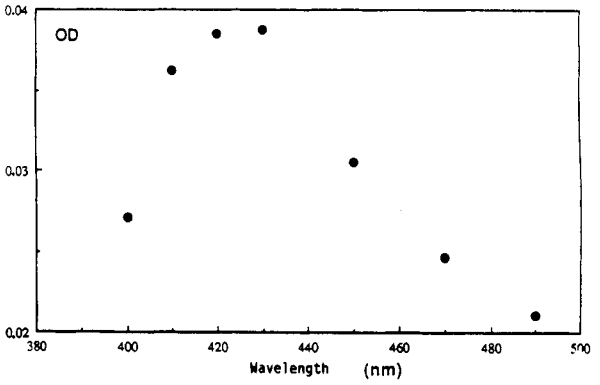


Figure 7. Radical cation transient absorption of DETX generated in DETX/BMPS 0.048 M in acetonitrile.

Qualitatively, the long-lived residual absorption L observed at the end of the decay of the cation radical of DETX (Figure 8) might contain a major contribution of the benzenesulfonyl radical, formed from the anion radical of BMPS in this set of complex reactions. This is well supported by the fact that the benzenesulfonyl radical is known to exhibit an absorption up to 500 nm.[24]

In DETX/CBr_4, a residual absorption is also clearly observed at approximately 430 nm. By analogy with the above-mentioned lines of thought with regard to DETX/BMPS, the formation of a Br• radical may be expected in the sequence of reactions:

$$CBr_4^{\bullet-} \rightarrow CBr_3^{\bullet} + Br^-$$

$$DETX^{\bullet+} + Br^- \rightarrow DETX + Br^{\bullet}$$

As recently reported,[25,26] the bromine anion and the bromine atom can recombine to yield $Br_2^{\bullet-}$, whose optical absorption lies in the UV–vis wavelength range with an absorption maximum at approximately 360 nm and a small

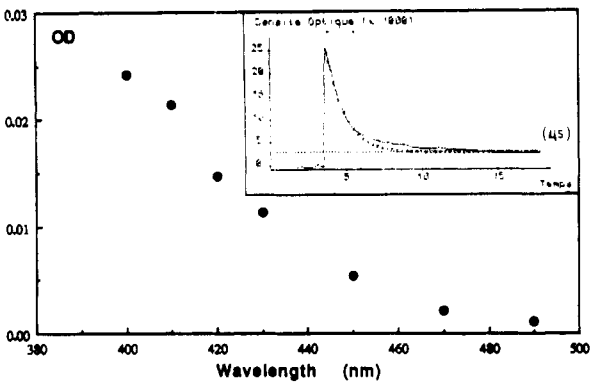
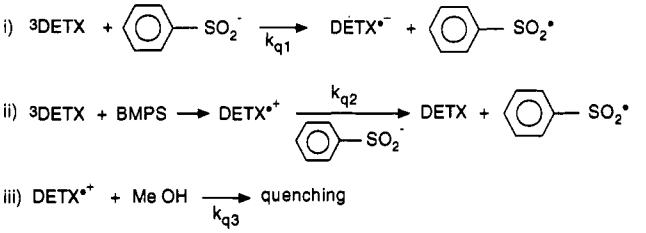


Figure 8. Residual absorption of L (see text) observed at t = 5 μs in DETX/BMPS 0.048 M in acetonitrile. Typical oscillogram showing the time-dependence of the absorption (λ_{ana} = 450 nm; λ_{excit} = 355 nm).

absorption at ~680 nm. The residual absorption is assumed to arise from this anion radical. The generation of Br• is supported by the fact that the evolution of Br_2 was observed during the photolysis of DETX/CBr_4.

Quenching experiments in DETX/sodium benzenesulfinate and DETX/BMPS/sodium benzenesulfinate in acetonitrile/MeOH 0.42 M solution were carried out in order to follow the interaction between the cation radical of DETX and the benzenesulfonyl anion. The following sequences of reactions were substantiated and support the role played by this benzenesulfonyl anion:



In fact, on addition of sodium benzenesulfinate to a DETX solution, the lifetime of the DETX triplet state decreases and the concentration of the benzenesulfonyl radical increases in agreement with reaction i; when sodium benzenesulfinate is added to a solution containing DETX and BMPS, the concentration of the cation radical of DETX decreases as expected from reaction ii. A weak effect of methanol on the species is observed (reaction iii).

The bimolecular quenching rate constants of these reactions were evaluated. The results lead to $k_{q2} \leq 2 \times 10^8$ M^{-1} s^{-1}, $k_{q1} \sim 2 \times 10^9$ M^{-1} s^{-1}, and $k_{q3} \sim 5 \times 10^6$ M^{-1} s^{-1}. The quenching of the DETX triplet state by MeOH in acetonitrile is unimportant ($k_{q4} \ll 10^5$ M^{-1} s^{-1}).

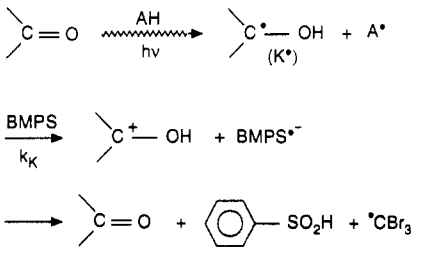
(c) Quenching of the Ketyl Radical. As is known, in the presence of amines, long-lived ketyl radicals are formed on the ketones and easily detected (Figure 4). Addition of BMPS to a solution containing, for example, DETX and MDEA 0.11 M leads to a faster disappearance of the ketyl radical. The value found for the bimolecular quenching rate constant of the ketyl radical of DETX by BMPS is $k_K \sim 4 \times 10^6$ M^{-1} s^{-1}. A similar behavior was encountered in the presence of CBr_4. The rate constants of quenching of the ketyl radical of BP and DETX by CBr_4 are 2×10^7 and $\sim 10^7$ M^{-1} s^{-1}, respectively.

At present, nothing can be said about the possible deactivation of $DETX^{\bullet-}$ (that might be generated from the CT complex) by BMPS (or CBr_4).

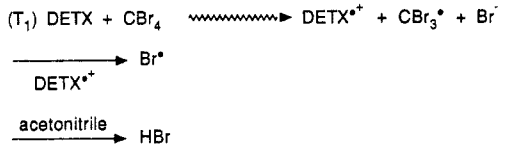
$$CTC \rightarrow MDEA^{\bullet+} + DETX^{\bullet-}$$

$$DETX^{\bullet -} + BMPS \rightarrow DETX + BMPS^{\bullet -}$$

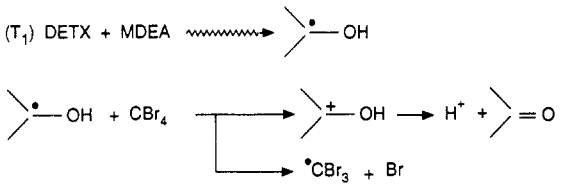
This quenching process by bromo compounds, *e.g.*, by BMPS, presumably occurs according to the following reaction and may lead to the formation of sulfinic acid (which leads to sulfonic acid):



(d) Generation of Acid. The generation of acid suggested in paragraph c is supported by the following experiment. Acidity measurements (Figure 9) show, for example, that acid is generated in DETX/CBr_4:



Addition of an amine increases the yield in acid because of the quenching of the ketyl radical through an electron transfer:



The initial slopes in Figure 9 are 80 and 20 mV/min for DETX/MDEA/CBr_4 and DETX/CBr_4, respectively. For longer irradiation times, secondary reactions may occur, as suggested in the benzoin ethers/CBr_4 system:[27]

$$DETX + CBr_3^{\bullet} \rightarrow DETX^{\bullet} + HCBr_3$$

but they cannot explain the strong increase of the acidity. Similar processes should occur in DETX/BMPS/amine. Comparison of the processes involved in the photolysis of DETX/MDEA and DETX/MDEA/BMPS or CBr_4 suggests that the ketone is recovered in the latter solution due to the ketyl radical quenching. Accordingly, the photodegradation reaction should be slower. This is well supported by the results shown in Figure 10: irradiation of DETX/MDEA in acetonitrile at $\lambda = 366$ nm in N_2 leads to a degradation of the ketone, while no degradation was observed in DETX/MDEA/CBr_4 (in the same time scale of observation), in agreement with the described reaction.

(e) Role of the S_1 Quenching. The possible effect of the S_1 quenching (see section III.3) on the concentration of the molecules in the triplet state T_1 and of the ketyl radicals K• was investigated by following the optical density of T_1 and K• formed upon laser excitation of various solutions. The experimental results were as follows: The ketyl radical concentration was 70% lower in DETX/MDEA 0.1 M/BMPS 0.047 M than in DETX/MDEA 0.1 M. The triplet state concentration was 65% lower in DETX/BMPS 0.05 M than in DETX. These effects can be evaluated from the values of the different rate constants

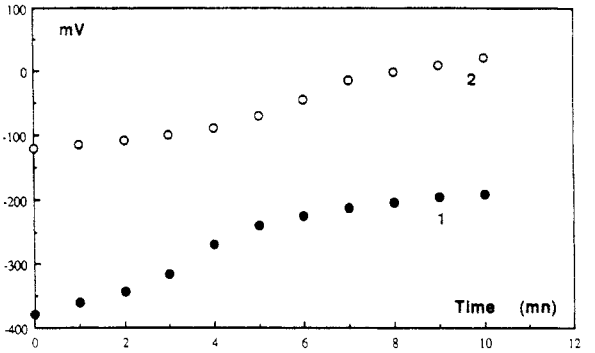
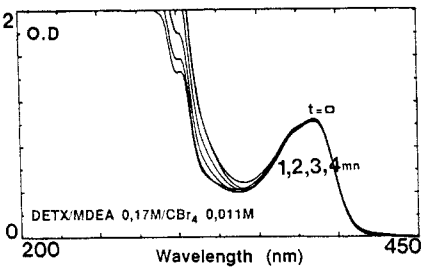


Figure 9. Acidity release of DETX in degassed acetonitrile in the presence of various additives: (1) MDEA 0.1 M – CBr_4 0.05 M; (2) CBr_4 0.05 M ($\lambda = 366$ nm).



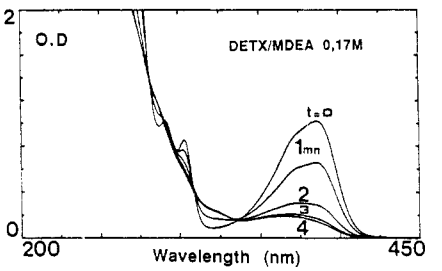
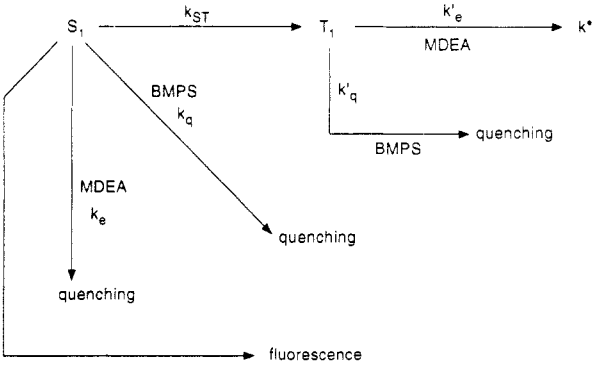


Figure 10. Changes of the absorption spectrum of DETX upon exposure to a mercury lamp ($\lambda = 366$ nm). Solvent: degassed acetonitrile.

Scheme 1



of the involved processes. Let us consider the following sequence of reactions (Scheme 1).

For DETX, $\tau_f = 1.2$ ns, $\phi_f = 0.02$; radiative lifetime = 60 ns, $\phi_{ST} = 0.98$, and $k_{ST} = 8.2 \times 10^8$ s^{-1} (the internal conversion was left out as suggested by earlier measurements[28]). It follows that

$$[T_1] = [S_1] = \frac{\phi_{ST}}{1 + k_q \tau_f [BMPS]}$$

Then

$$p = \frac{[T_1]}{[T_1]_0} = \frac{1}{1 + k_q\tau_f[BMPS]}$$

with [BMPS] = 4.7×10^{-2} M, τ_f = 1.2 ns, and $k_q = 3.2 \times 10^{10}$ M^{-1} s^{-1}; a value of 0.35 was found for p, which is in agreement with the observed 65% decrease. In the same way:

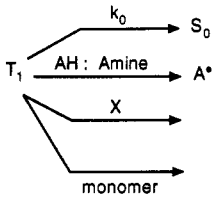
$$[K^\bullet] = [S_1]\frac{\phi_{ST}}{1 + k_q\tau_f[BMPS] + k_e\tau_f[MDEA]} \times \frac{k'_e\tau_T[MDEA]}{1 + k'_q\tau_f[BMPS] + k'_e\tau_f[MDEA]}$$

Then

$$p' = \frac{[K^\bullet]}{[K^\bullet]_0} = \frac{1 + k_e\tau_f[MDEA]}{1 + k_q\tau_f[BMPS] + k_e\tau_f[MDEA]} \times \frac{1 + k'_e\tau_f[MDEA]}{1 + k'_q\tau_f[BMPS] + k'_e\tau_f[MDEA]}$$

where $k_e = 2.3 \times 10^9$ M^{-1} s^{-1}, [MDEA] = 10^{-1} M, $k_q = 3.2 \times 10^{10}$ M^{-1} s^{-1}, [BMPS] = 0.05 M, $k'_q = 7.4 \times 10^8$ M^{-1} s^{-1}, $k'_e = 1.4 \times 10^9$ M^{-1} s^{-1}, and $\tau_T = 8$ μs. The calculated value of p' was 0.31 which compares well with the 70% decrease of [K•]. Accordingly, the main effect of BMPS on the fluorescent S_1 state is a quenching that reduces the yield of intersystem crossing (from almost 0.98 to 0.3; see below) and may enhance the generation of $BMPS^{\bullet-}$ species and, therefore, the yield of $CBr_3^\bullet$ through fluorescence quenching.

III.5. Discussion of the Proposed Mechanism. In the overall reaction scheme for DETX/BMPS 0.05 M/MDEA 0.1 M in CH_3CN monomer MON 5 M, the yield ϕ_x of the various processes is represented as follows (for example, for the quenching of the triplet state):

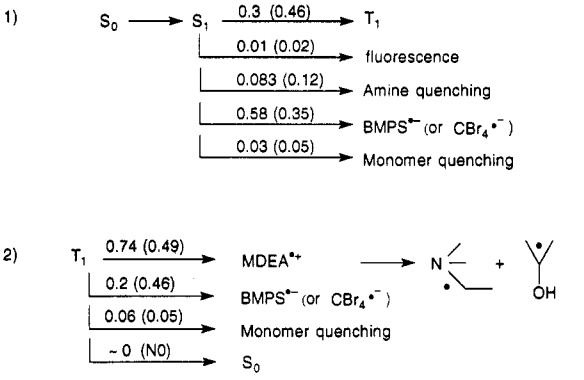


X being the bromo compound. The yield ϕ_x is expressed as:

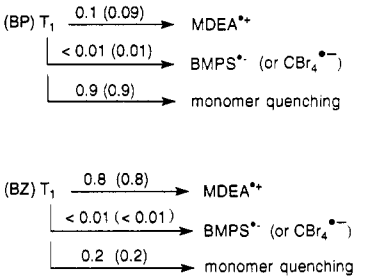
$$\phi_x = \frac{k_{int}[X]}{k_{int}[X] + k_0 + k_q[monomer] + k_e[amine]}$$

The calculated values found for the S_1 and T_1 quenching by BMPS and CBr_4 (the values in brackets correspond to CBr_4) are shown in Scheme 2 for DETX and Scheme 3 for BP and BZ. These results lead to the following trends: BMPS has a very strong effect on the S_1 state of DETX, which should result in the formation of a large amount of $CBr_3^\bullet$ radicals, capable of initiating new polymerization reactions. The triplet quantum yield is reduced, and amine quenching is the main deactivation pathway of T_1. The ketyl structure K• formed at the same time enhances the yield of $CBr_3^\bullet$. While the relative efficiency of the primary steps of the reaction is in the order DETX > BZ > BP, Table 1 shows that the practical efficiency of the three-component system ketone/BMPS/amine is almost the same. The lesson, is, therefore, that these primary steps are not the only driving factors affecting the reactivity:

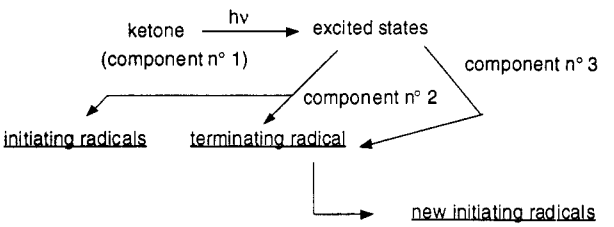
Scheme 2



Scheme 3



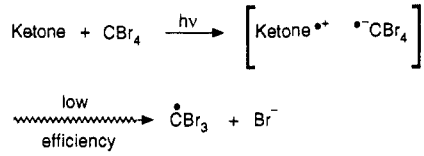
Scheme 4



the complex set of reactions occurring after the primary electron-transfer reactions is likely to have a strong effect on the ability of the three-component system to initiate the polymerization. Since ketyl radicals are known to act as terminating agents of the growing macroradicals in polymerization reactions, it is obvious that the electron transfer betweeen K• and BMPS has two benefits: a decrease of [K•] and an increase of $CBr_3^\bullet$. As a consequence, the rate of initiation should increase and the rate of termination should decrease. This marked effect of additives on K• has already been observed when using onium salts.[29] The higher efficiency observed in photopolymerization reactions in the presence of other bromo compounds shows that the demonstration performed in the case of BMPS or CBr_4 can be extended to DBAP or TBAP. In the same way, a general picture for ketone-containing three-component systems is shown in Scheme 4.

The mechanism depicted in Scheme 4 is operative when monochromatic or filtered lights (λ ≥ 350 nm) are used: in that case, the ketone is the only absorbing species. In polychromatic lights, however, where a fraction of the light can be absorbed by the system at short wavelength (λ < 350 nm), other mechanisms that are based on the interaction between two of the three components may occur. The first one, based on the initiation of the polymerization reactions through an interaction between CBr_4 and the ketone, should be inefficient (as shown by the results in Table 1). This suggests that the generation of the $CBr_3^\bullet$

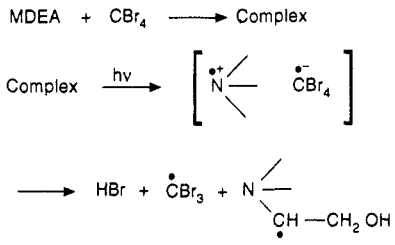
radical might be rather difficult because of an efficient back-electron-transfer reaction, e.g.:



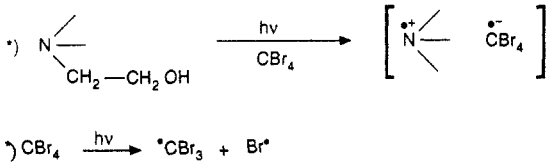
This result confirms that the energy transfer between the ketone and CBr_4 should not be taken into account, since such a process would form efficiently initiating radicals and lead to a high rate of polymerization (in contrast with the experimental results):

$$\text{ketone}^* + CBr_4 \rightarrow \text{ketone} + Br^\bullet + CBr_3^\bullet$$

Another mechanism relying on the interaction between an amine and CBr_4 leads to initiation (see Table 1). In agreement with the previous work on some complexes between aromatic amines and CBr_4,[30,31] a probable mechanism might be:



If free amines and free CBr_4 molecules are still existing, the following reactions may occur:



IV. Conclusion

This paper shows the superiority of a three-component system for the photopolymerization of acrylates. An explanation based on a careful examination of the excited-state processes of various ketones in the presence of CBr_4 has been proposed. A forthcoming paper will be devoted to a system based on ketone/amine/TBAP or DBAP.

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