Ionic Photoinitiators for Radical Polymerization in Direct Micelles: The Role of the Excited States

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Synopsis

Radical photopolymerization reactions of MMA in direct anionic and cationic micelles are investigated in the presence of different types of ionic initiators, through steady state illumination experiments and time-resolved laser spectroscopy. The positively charged ionic photoinitiator BP^+ appears as the more efficient. The reactivity of the excited states involved as well as the behavior of the side radicals produced seem to govern for a large part the practical efficiency of these compounds. A general discussion on the role of the different factors (localization, electronic effects, monomer quenching, electron and proton transfer processes, radical exit from the micelle, and acid–base equilibrium) is presented.

INTRODUCTION

The relative efficiencies of water- and oil-soluble photoinitiators in the photopolymerization reactions carried out in direct micellar solutions became recently the subject of interesting questions. The dynamics of the excited states of such photoinitiators has been studied in organized media[1] and in homogeneous solutions as well.[2] Further investigations by UV spectroscopy and time-resolved laser spectroscopy have suggested that some typical substituent effects (electronic, steric, electrostatic, or localization) which influence the primary relaxation processes could have repercussions on the overall evolution of the polymerizable system.[3,4]

In the present paper, two water-soluble benzophenone derivatives are considered in the same way as their oil soluble parent compound. Some results obtained in polymerization experiments under stationary conditions will serve as probes of the overall reactivity of the system considered. Data derived from laser spectroscopy experiments on the processes occurring in the excited states are used to discuss the role played by the photophysical and photochemical events observed in the polymerization reaction of methyl methacrylate (MMA) mainly in dodecyl sulphate (SDS) or cetyltrimethylammonium chloride (CTAC) direct micelles.

EXPERIMENTAL

The experimental procedure for micelle polymerization has been previously described[5] as well as the laser spectroscopy apparatus.[6] Structures and ab-

breviations of the systems studied are the following:

	R = H	BP
	R = $CH_2SO_3^-$ Na^+	BP^-
	R = $CH_2N(CH_3)_3^+$ Cl^-	BP^+
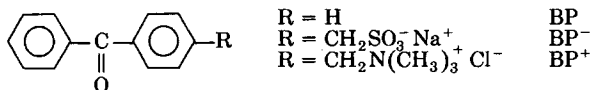
CH_3—$(CH_2)_{11}$—$SO_4^{\ominus}$ $Na^{\oplus}$
SDS = sodium dodecyl sulphate

CH_3—$(CH_2)_{15}$—$\overset{\oplus}{N}(CH_3)_3Cl^{\ominus}$
CTAC = cetyltrimethylammonium chloride

CH_3—$(CH_2)_{11}$—$\overset{\oplus}{N}(CH_3)_3Cl^{\ominus}$
DTAC = dodecyltrimethylammonium chloride

$N(C_2H_5)_3$
TEA = triethylamine

CH_3—$N(CH_2$—$CH_2OH)_2$
MDEA = methyldiethanolamine

CH_3—$(CH_2)_{11}$—$N(CH_3)_2$
DMDA = dimethyldodecylamine

$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}COOCH_3$$
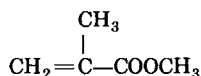
MMA = methyl methacrylate

RESULTS

Photopolymerization Experiments under Steady State Illumination

A set of typical results are reported in Table I; they are representative of the behavior of the photoinitiators under various conditions of reaction and sufficient to allow the behavior of the photoinitiators considered in this work to be understood. However, in this paper, we do not intend to report thoroughly on an overall investigation of the macroscopic dependence of the polymerization rate as a function of the usual parameters, i.e., concentration of the reactants, incident light intensity, and nature of the different elements of the system. Our attention will rather be focussed on some questions which

TABLE I
R_p vs. TEA in SDS Micelle[a]

	$R_p \times 10^5 M\ s^{-1}$	
	[TEA] = 0.005M	[TEA] = 0.05M
BP^+	35	220
BP^-	15	22
BP	3	18

[a] I_{abs} = 5×10^{15} phot cm^{-2} s^{-1} [SDS] = 0.5M; [MMA] = 0.5M.
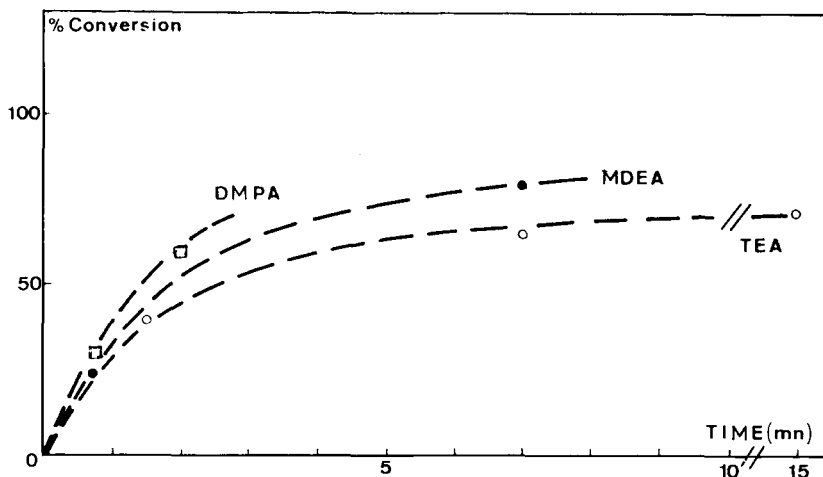
Fig. 1.   % conversion vs. time–BP$^+$–SDS–[amine] $= 0.05M$.

are specific of the micellar structures: localization of the reactants and partitioning of the active species. From a general point of view, it is interesting to note that high conversion (Fig. 1) as well as high polymerization rates are usually attained with all the systems tested in microheterogeneous media.

Rates of Polymerization

At first sight, BP$^+$ proves to be a very efficient photoinitiator; with this compound, the quantum yield of polymerization $\phi_m = R_p/I_{abs}$, which represents the number of monomer molecules polymerized per absorbed photon, is calculated to be 260: This result must be compared with the ϕ_m values obtained in the presence of 2,2-dimethoxy phenyl acetophenone ($\phi_m = 95$ [5]), hydroxy isopropyl acetophenone ($\phi_m = 200$ [7]), and chlorothioxanthone–TEA ($\phi_m = 180$ [7]). The derivative BP$^-$ is much less efficient than BP$^+$. The higher reactivity of BP$^+$ is observed both in SDS and cationic surfactants (CTAC and DTAC) (Table II). Thus, these results clearly shows that water-soluble photoinitiators are not always more efficient that the corresponding oil-soluble benzophenone (BP) in direct micelles.

Effect of the Amine Concentration

The change of R_p as a function of the amine concentration is reported in Figure 2: The initial slope of the curve as well as the plateau at high concentrations are strongly dependent on the nature of the photoinitiator;

TABLE II
Rate of Polymerization ($10^5 \times R_p$) vs. [TEA]
in CTAC and DTAC Micelles

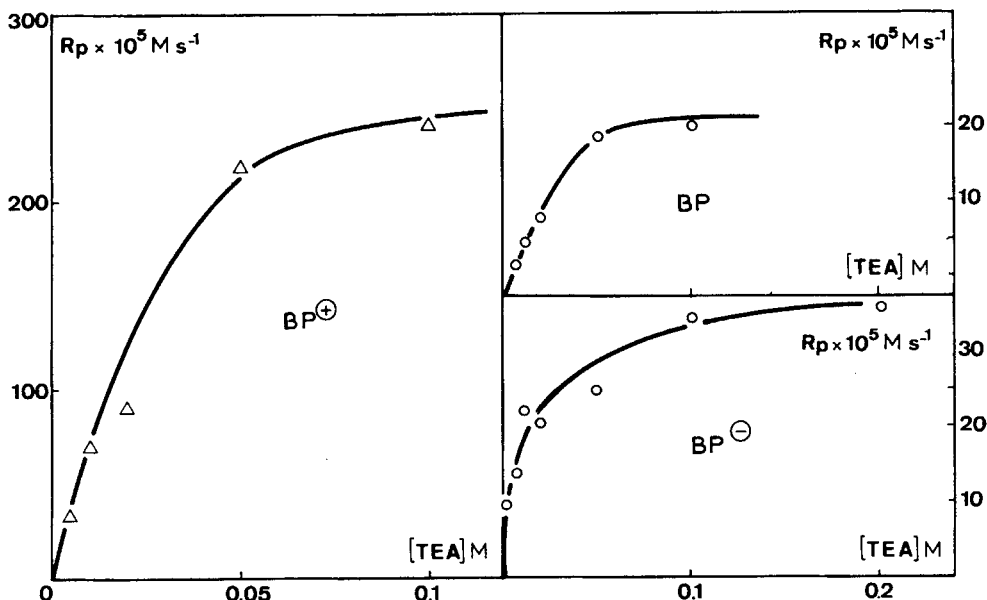| | CTAC | | DTAC |
	[TEA] = 0.005M	[TEA] = 0.05M	[TEA] = 0.005M
BP$^+$	120	230	70
BP$^-$	10	35	11

Fig. 2. R_p vs. [TEA] in SDS micelle of MMA (0.5M).

moreover, even in the absence of amine, BP$^-$ can initiate photopolymerization (such a behavior was also observed in AOT micelles[8]).

Role of the Amine

Whatever the photoinitiator, the influence of the nature of the amine on R_p (Table III) is basically the same; however, MDEA is "better" than TEA and DMDA (except for BP$^+$). In homogeneous toluene–MMA solution, the same type of behavior is observed.[7]

Degree of Polymerization

Some typical results concerning the degree of polymerization (DP) show that (Table IV):

—BP, BP$^-$, and BP$^+$ lead to comparable DP values, although the corresponding polymerization rates of BP$^+$ exceed those of BP and BP$^-$ by a factor of about 10;

—R_p and DP vary in the opposite direction;

TABLE III
$R_p(\times 10^5)$ Values in Various Benzophenone Derivative/Amine Combinations[a]

	MDEA	TEA	DMDA
BP$^+$	250	220	280
BP$^-$	45	22	15
BP	50	18	18

[a][Amine] = 0.05M; surfactant: SDS.

TABLE IV
Degrees and Rates of Polymerization in SDS Micelles

| | BP$^+$ | | | | | BP$^-$ | | BP, |
	TEA 0.05	DMDA 0.05	TEA 0.01	TEA 0.005, + 0.12M NaOH	TEA 0.005, 0.12M NaCl	TEA 0.005	TEA 0.05	TEA 0.005
DP	1500	1500	2200	1600	2100	1200	1300	1400
$R_p \times 10^5 M\ s^{-1}$	220	280	70	100	30	15	22	3

—upon increasing pH or ionic strength of the solution, DP has a tendency to decrease;

—with similar R_p values, the nature of the amine used has not significant influence;

—the polydispersity of the samples remains lower than 2 in every case, although a shoulder appears in the low molecular weight region when the initiator is BP$^-$; this fact suggests that the polymerization processes are rather complex and different depending on whether BP$^-$ and BP$^+$ are used.

Thus, in the case of BP and BP$^-$, the termination reactions seem to occur with a higher rate than in the presence of BP$^+$ since one could expect that the more efficient the initiation process (i.e., the higher the R_p) the lower the DP.

pH and Salt Effect

An increase of R_p (by a factor of about 2) is observed, upon addition of NaOH up to 0.1M (below this value, no deformation of the micelle has been noted[6]). Under the same conditions, NaCl produces no effect; however, in both cases, DP decreases; that would be more in favor of a pH rather than of a salt effect.

Magnetic Field Effect

In some cases, the rate R_p clearly changes (Table V) in the presence of a weak magnetic field ($\sim$ 800 G). By way of comparison, under similar experimental conditions, this rate increases by a factor of about two in the case of 2,2'-dimethoxy acetophenone.[1] The effect in SDS, CTAC, DTAC is strongly pronounced in the case of BP whereas it is less sensitive in the presence of the water-soluble BP derivatives. BP$^-$ and BP$^+$ play a symmetrical role in cationic and anionic environments.

TABLE V
Magnetic Field Effect on R_p[a]

Surfactant \ Initiator	BP	BP$^-$	BP$^+$
SDS	2.4	1.1	1.8
CTAC	2.3	1.5	$\sim$ 1
DTAC	2.6	1.6	$\sim$ 1

[a] Relative R_p obtained $R_p(H_0)/R_p(H_0 = 0)$ − [SDS] = 0.5M; [MMA] = 0.5M; [TEA] = 0.005M; H_0 = 800 G.

Interactions Solutes / Micelles in the Ground State

Localization of the Photoinitiators

A thorough investigation of this question[4] by UV spectroscopy led us to the determination of a microscopic polarity of the organized assembly; our approach is similar to that introduced by Fendler et al.[9] and the parameter which is used to denote the local polarities in these media is the Dimroth parameter $E_T(30)$.[10]

As expected, in SDS solution the absorption spectrum of BP^- resembles that observed in water; hence the conclusion that BP^- is actually located in the water phase. In the case of BP^+, a micropolarity equivalent to that of ethanol is deduced, hence the suggestion that BP^+ locates rather inside the micelle as compared with BP^-.

On the other hand, BP, which is regarded as an oil-soluble molecule, actually exchanges specific interactions with water: The micropolarity of the solubilization site is indeed observed to be similar to that of methanol. Thus, in SDS micelle, the penetration of the benzophenones in the aggregate is rather poor and their location are in the following order (from the oil to the water phase): BP^+, BP, BP^-. In the case of CTAC micelle, the reverse order is observed: BP^-, BP, BP^+. This result is obviously the consequence of the coulombic interaction between the charges of the benzophenone molecule and of the surfactant, rather than the effect of the water solubilizing group.

Addition of MMA or TEA leads to specific interactions with the photoinitiators. They are weak in the case of a derivative located "outside" the micelle (near the polar heads of the surfactant), viz., BP^- and BP^+ in SDS and CTAC micelle, respectively, whereas they are more important for the photoinitiators located "inside" the micelle (near the alkyl chain of the surfactant). Moreover, this interaction is stronger with BP than with the ionic benzophenones (BP^+ in SDS and BP^- in CTAC), a fact which could be accounted for by the better solubility of a nonionic compound in the organic microphase.

In conclusion, a great attention must be devoted to the concept of water- or oil-soluble solute in microheterogeneous solutions.

Interaction between Micellar Structures and Some Amines

The three amines used in the present work exhibit very different water solubility: MDEA is missible in all proportions whereas DMDA is almost insoluble in water. It is thus important to evaluate their binding constant K to the micellar structure

$$\text{micelle} + \text{amine} \underset{k^-}{\overset{k^+}{\rightleftharpoons}} \text{micellized amine}$$
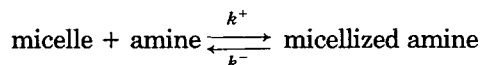
with $K = k^+/k^-$.

The procedure described by Encinas and Lissi[1] has been resorted to in order to determine those binding constants. It consists in measuring the quenching of a fluorescent probe completely micellized as a function of the total amount of a given quencher and of the micellar concentration.

The experimental results obtained in SDS are reported in Table VI along with the corresponding micellized fraction P.

TABLE VI
Binding Constants and Micellezed Fractions for
Some Amines in SDS Micelles

|	MDEA	TEA	DMDA
$K(M^{-1})$	450	1370	10,000
ρ	0.39	0.66	0.93

The binding constants corresponding to the micellization of methacrylates commonly exceed several tens of thousand,[11] hence the conclusion that methacrylates are completely incorporated into the micellar pseudophase. However, methyl methacrylate has been observed to depart from this general trend: Its binding constant to SDS micelle is $1000 M^{-1}$, which means that about 87% of MMA is incorporated for [SDS] = 0.5M. In CTAC, the conclusion is the same with about 80% incorporated.

Interaction of the Excited States of BP, BP$^+$, and BP$^-$ with Amine and Monomer as a Function of the Environment

In order to simplify the presentation of the results, a general scheme of evolution of the excited states is reported in Scheme 1.
Some specific points refering to BP has been discussed elsewhere.[3] Since the general scheme is well established, only the salient features and the results concerning complementary investigation will be considered.

Recalls

Upon UV excitation of the $n-\pi^*$ transition, the generation of the triplet state is very fast (presumably as fast in homogeneous solution); as previously reported in micelles,[3] it actually follows the picosecond laser excitation. Moreover, neither excitation intensity (which increases the number of excited
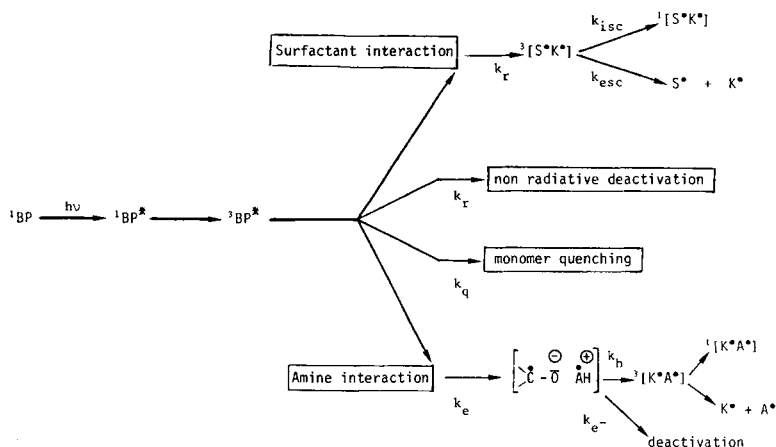
Scheme 1.

*Interaction between Micellar Structures and Monomers*

molecules) nor concentration effects (which varies the occupancy) are detected. This remark suggests that, owing the compartmentalization of the reactants, the bimolecular reactions which take place in homogeneous solution are avoided in micelles.

The photoinitiator in its triplet state decays according to four relaxation processes: deactivation through a nonradiative process (k), formation of a charge transfer complex with amine yielding a radical pair through proton transfer (k_h), generation of a radical pair through hydrogen abstraction from the surfactant (k_r), and quenching by monomer (k_q). The radical pairs are formed in their triplet state; they convert to singlet radical pairs, through intersystem crossing k_{isc} (yielding photolysis products) and to free radicals k_{esc} after decorrelation and exit.

The typical absorption spectra of the transient species—the triplet state and the ketyl radical K˙(either free or engaged in a radical pair)—have been reported.[3] The triplet lifetimes (Table VII) correlate mainly with the σ effect of neutral substituted benzophenones.[7] Recent works[12] have shown that the exit of a radical (from the corresponding radical pair after decorrelation) depends on the nature of solute (e.g., BP or BP$^-$), surfactant (e.g., SDS or DTAC), or counterradical R˙(surfactant or 1,4-cyclohexadiene); for instance, the yield of exit was observed to increase when a cyclohexadienyl counter-radical replaces the surfactant-derived radical, hence the conclusion that the "mobility" of the partners is a predominant factor for the escape of the radicals. (For example, in the case of BP, the yield of exit increases from 7 to 49% upon addition of 1,4-cyclohexadiene; with BP$^-$, it goes only from 45 to 59% because, above other effects, the exit is greatly favored by the location of BP$^-$, which is very close to the homogeneous water phase.) Higher yields of exit are obtained in the presence of a magnetic field: This magnetic field effect (MFE), first recognized in Ref. 13, results from the Zeeman splitting of the triplet sublevels: The external magnetic field H_0 decreases the intersystem crossing between the triplet and the singlet radical pair and thereby indirectly favors the yield of escape.

Electron Transfer with Amine

In the presence of amines, a strong decrease of the triplet state lifetime is observed (e.g., Fig. 3) whereas, in longer time scales, the relaxation process becomes complex; it appears as the superimposition of absorptions corresponding to several species—some ones growing and others decaying—and is thereby difficult to interpret. The behavior of this transient absorption must be governed by the formation of the radical pair, the exit of the free radicals, and an acid–base equilibrium between the excited species. The overall intensity of these absorptions increases with [AH] in agreement with:

$$^3BP + [AH] \rightsquigarrow A\dot{\ } + K\dot{\ }$$
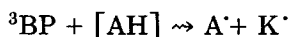
Moreover, the spectrum of the transient absorption changes as it decays: the maximum of this absorption clearly shifts from 530 nm (triplet absorption) to 540–560 nm (K˙absorption) and 610 nm (K˙radical anion absorption).
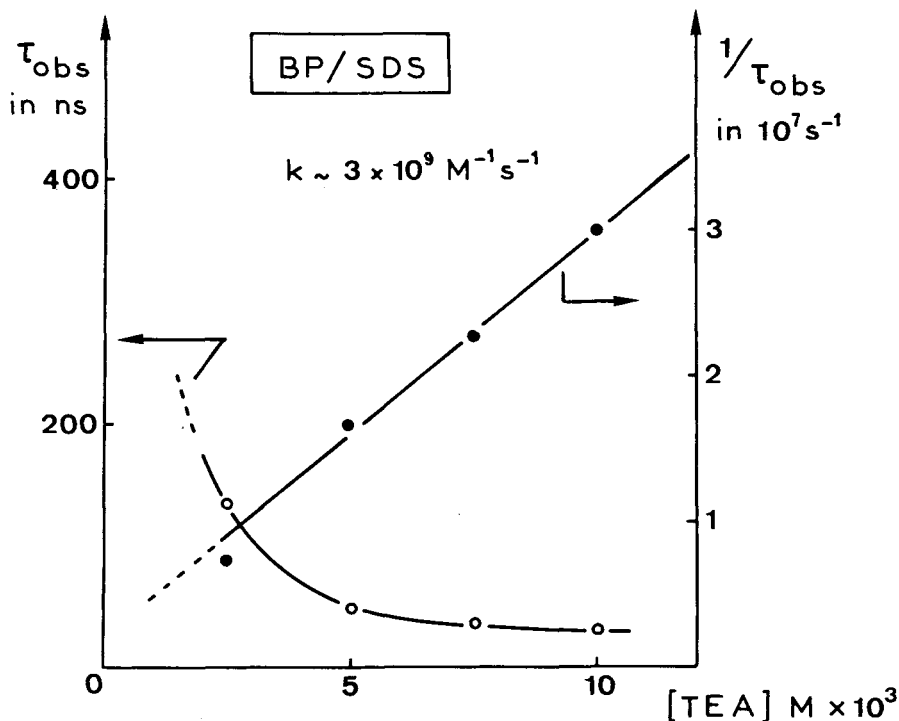
Fig. 3.   Triplet state lifetimes vs. [TEA].

Monomer Quenching

As in homogeneous solution, the quenching by monomer results only in a decrease of the triplet state lifetime (Fig. 4); neither long-lived residual absorption nor static quenching are observed. The quenching by monomer is a dynamic quenching. Moreover, the Stern–Volmer plot remains quite valid up to the important concentrations used during photopolymerization experiments. In the presence of increasing quencher concentrations, the triplet state lifetime decreases down to a few nanoseconds or less (the resolution time of the laser spectroscopy is 6 ns when using an N_2 laser as the exciting source).

Rate Constants

The whole data referring to the bimolecular quenching rate constants (by TEA and MMA) and the triplet state lifetimes are reported in Table VII, together with previously determined data. Due to the difficulties mentioned heretofore, the k_e values are estimated values. With MMA, the quenching rate constants obtained can be likely accounted for in terms of electronic effect of the substituent rather than by a specific localization of the solute in the microheterogeneous medium or by a compartmentalization of the species by the surfactant structure. Thus, by using the linear relationship between k_q and the Hammett constant σ, which holds in the case of neutral substituted benzophenones,[7] the quenching rate constants of BP^+ and BP^- by the monomer are estimated to be 0.6 and $1.1 \times 10^9 M^{-1}$ s^{-1}, respectively; they compare well with experimental results.
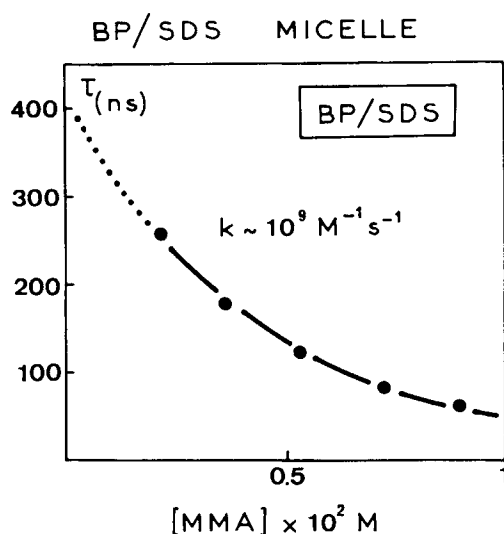
Fig. 4.   Triplet state lifetimes vs. [MMA].

TABLE VII
Rate Constants of Electron Transfer with TEA and of Monomer Quenching
and Exit Ratio of Radicals in SDS Solutions

	τ_T (ns)	Hammett's constant σ	$k_e \times 10^9$ $(M^{-1} s^{-1})$	$k_q \times 10^9$ $(M^{-1} s^{-1})$	% exit[a 10]		% exit[b 10]		% exit[c 10]	
					SDS	DTAC	SDS	DTAC	SDS	DTAC
BP^+	165	$+0.45$	6	0.7	49	59	6	61	70	82
BP^-	390	$+0.05$	4	1	59	53	45	22	78	81
BP	340	0	3	1.5	49	55	7	25	82	84

[a] In the presence of an H-donor (cyclohexadiene: CHD).
[b] From the surfactant-solute radical pair.
[c] In the presence of an H-donor (CHD) and a magnetic field.

The case of amine quenching is more complex. At first sight, the data reported in Table VIII seem to suggest a quenching constant increasing with σ; however, the experimental results referring to MDEA quenching are at variance with this *trend*. In effect, MDEA which is an hydroxylic amine, predominantly solubilizes outside the pseudophase, whereas the two other ones are rather oil-soluble; thus, in this case, the location of the amine, respectively, to the BPs and the local polarity of the quenching site become the decisive factors which govern the rate of the electron transfer. Moreover,

TABLE VIII
Quenching Constants of Ionic BPs by Different Amines

	TEA	DMDA	MDEA
BP^+	6	4.5	0.4
BP^-	4	2.5	1.5

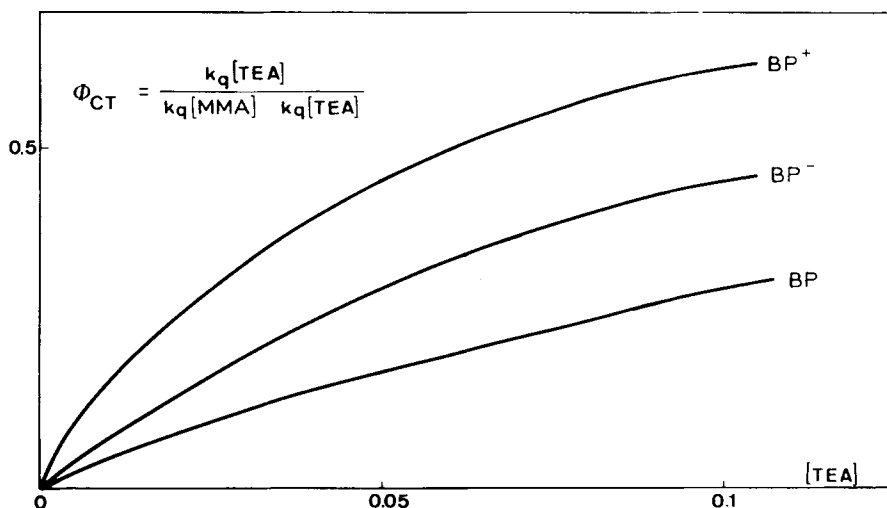$$\Phi_{CT} = \frac{k_q[TEA]}{k_q[MMA] \quad k_q[TEA]}$$

Fig. 5.   Electron transfer yield vs. [TEA].

slight variations of the ionization potentials of the amines considered in this work could also induce important changes in the rates of the charge transfer step. Unfortunately, no experimental data are available on this question.

The % exit in the presence of a small molecule is very slightly affected by the nature of either the surfactant or the solute. The exit from a radical pair formed with any partner of the micellar assembly seems to reflect the role played by the localization of the benzophenone derivatives.

Charge Transfer Yield

The yield of charge transfer complex ϕ_{CT} is calculated (Fig. 5) for each system according to:

$$\phi_{CT} = \frac{k_e[AH]}{\tau_T^{-1} + k_e[AH] + k_q[MMA]}$$

Before all, it must be emphasized that the quenching rate constants determined here are "bimolecular-like" constants: All the concentrations are defined relatively to the total volume of the sample, and thus comparisons are only valid in a given environment. The calculation of ϕ_{CT} is done by assuming a linear Stern–Volmer behavior in the range of quencher concentrations used. Figure 5 shows the evolution of ϕ_{CT} vs. the amine concentration. It is worth noting that the higher the quantum yield of the electron transfer process, the higher the rate of polymerization. However, this must not be the most determinant factor: for example, though the ϕ_{CT} value of BP–Cl is very close to that of BP$^+$, its reactivity is poor and rather compares with that of BP.

DISCUSSION OF THE PHOTOINITIATOR EFFICIENCY

The macroscopic rate of polymerization R_p in such an environment (and presumably the degree of polymerization DP) can be considered as depending on two factors: (i) the rate of the photochemical initiation event R_i which

generates the first monomer-derived radical; (ii) the chemical propagation and termination $C_{p,t}$ of the growing macromolecular chains. The latter should be affected by the nature of the aggregates and the role of the different radicals formed and trapped at the interface and which are able to ultimately terminate the polymer chains:

$$R_p = f(R_i; C_{p,t})$$

Hereafter, the discussion will be mainly focused on the initiation process which is the only photochemical step involved in the polymerization. From the results obtained before through laser spectroscopy, the macroscopic dependence of R_i can be expressed as follows:

$$R_i = \phi_{ST} I_{abs} \phi_{CT} \phi_{RP} \phi_A \beta$$

with ϕ_{ST} = quantum yield of intersystem crossing, ϕ_{CT} = yield defined above, ϕ_{RP} = yield of $^3[K^\cdot A^\cdot]$, $\phi_{RP} = k_h/(k_h + k_{e^-})$, ϕ_A = yield of initiating radicals; $\phi_A = k_{esc}/(k_{esc} + k_{isc})$, and β = parameter which denotes the efficiency of the chemical reaction between the amine-derived radical and monomer double bond.

Role of the Environment: Bulk and Micelle Polymerization

In homogeneous solution of MMA (in benzene or toluene), the rate of polymerization R_p has been shown[14] to obey the following relationship:

$$R_p = K\sqrt{I_{abs}}[\text{MMA}]^2 \frac{k_e[\text{AH}]}{k + k_e[\text{AH}] + k_q[\text{MMA}]} \frac{k_h}{k_h + k_{e^-}}$$

where I_{abs} is the incident light intensity absorbed and K a constant dependent on the rate constants of propagation k_p and of termination k_t.

By introducing the values k_e, k_q, k, $k_h/(k_h + k_{e^-})$ determined previously[14] in this relationship, the rate R_p (calculated for a homogeneous solution with [MMA] = $1M$ in the presence of BP and [TEA] = $10^{-2}M$) is about $6 \times 10^{-7}M$ s^{-1} under similar condition of irradiation. This result emphasizes the role of surfactant molecules. At first sight, if a parallel is drawn between the rates R_p measured in bulk or in homogeneous solution and the ϕ_{CT} values, one immediately observes that R_p is substantially higher in micellar polymerization, although the yield ϕ_{CT} corresponding to the first photophysical process (i.e. electron transfer reaction between the triplet state and the amine) is strongly unfavorable. Moreover, with the system BP–TEA, the product $\phi_{RP} \times \phi_A$ can be only lower than unity since in solution the yield in radical A$^\cdot$ formed in the decay of the CT complex by direct proton transfer reaches 1, its maximum value. It can be asserted that the higher rates R_p observed in the micellar media as compared with those reported in homogeneous solution are mainly ascribable to classical chemical effects of compartmentalization of the reactants (just as in the case of thermal initiation) rather than to an enhancement of the photoinitiation efficiency.

However, sharp differences in the efficiency of BP, BP$^+$, and BP$^-$ are noticed. The interaction of the photoinitiator with additives (amines or

monomers) is expected to depend on the respective localization of the partners and also on the effect of the substituents and/or the ionic charge on the dynamics and the evolution of the excited states.

Localization Effects

Two fundamental remarks hold: first, a water-solubilizing group is not sufficient to improve the efficiency of a given photoinitiator in micellar polymerization; second, the most important factor is not the sense of the interaction between the charges carried by the substituent and by the surfactant (which nonetheless governs the localization in the micelle) since BP^+ is observed to be more efficient both in SDS and CTAC micelles.

In SDS micelles, chloro-substituted benzophenone, which is located in a polar waterlike environment[15] (like BP^+) exhibits a photoinitiating efficiency comparable to that of BP: hence the conclusion that synthetizing an initiator which localizes "outside" the micelle is not the decisive condition to design an efficient photoinitiator.

Role of the Charge Transfer Complex

The amine concentration is experimentally observed to have an important influence upon the reactivity of the systems under study: the relative values of R_p's are as follows: $R_p(BP^+) \sim 2R_p(BP^-) \sim 10R_p(BP)$ at $[TEA] = 0.005M$ and $R_p(BP^+) \sim 10R_p(BP^-) \sim R_p(BP)$ at $[TEA] = 0.05M$. Thus, the ratio

$$\frac{R_{p([TEA]=0.05M)}}{R_{p([TEA]=0.005M)}}$$

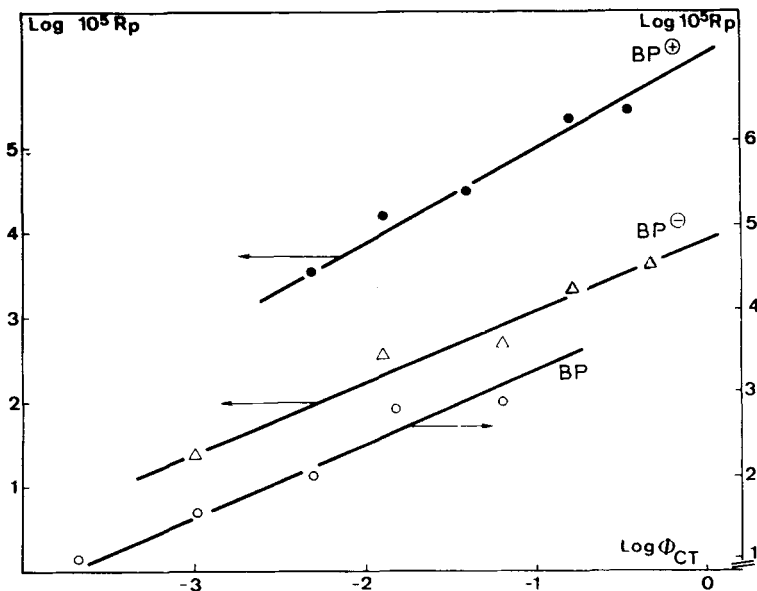which goes from 6 for BP^+ and BP to 1 for BP^- seems to indicate a saturation

Fig. 6.   Log–log plot of R_p vs. ϕ_{CT}. See text.

TABLE IX
Values of A and α Parameters (See Text)

	$A \times 10^5$	α
BP^+	420	1.04
BP^-	50	0.8
BP	55	0.8

effect. Mathematically, the evolution of R_p vs. ϕ_{CT} can be approximatively described by (Fig. 6)

$$R_p = A[\phi_{CT}]^\alpha \qquad \left(\text{or } R_p - R_p^0 = A[\phi_{CT}]^\alpha \text{ for } BP^- \right)$$

The A factor contains information on the development of the reaction (propagation and termination) and on the initiation efficiency $(\phi_{ST}, \phi_{RP}, \phi_A,$ and $\beta)$ whereas the exponent α expresses the contribution of the charge transfer reaction to the rate of polymerization. The following data have been obtained (Table IX).

Though no physical interpretation is yet available which would account for the observed dependence, it remains that (i) the behavior of the three benzophenones is clearly different and (ii) that less common processes have to be considered to account for the experimental A values (e.g., effect of the radical species on the termination reactions, efficiency of proton transfer or radical exit processes, etc.).

Moreover, if the experimental results reported in Table III (rates of polymerization) are paralleled with those of Table VIII (quenching rate constants by amines), no correlation comes out indicating that the quantum yield of the charge transfer complex is not the deciding factor: e.g., the systems BP^+/amine exhibit almost the same reactivity, although their quenching constants by amines is increased by a factor of 15 when going from MDEA to TEA. The difference in the reactivities of photoinitiating systems must rather be imagined as being the consequence (i) of different proton transfer rates in the charge-transfer complex, (ii) of variable radical exit ratios, (iii) of changes localization of the initiating species, or (iv) of different chemical reactivities towards the double bond rather as being merely determined by the quantum yield in charge transfer complex.

Radical Formation and Exit

The charge transfer complex (CTC) presumably undergoes proton transfer to yield a triplet radical pair between a ketyl radical ($K^\cdot$) and an amine derived radical ($A^\cdot$). This pair converts into a singlet radical pair and the separation of this pair leads to free radicals:
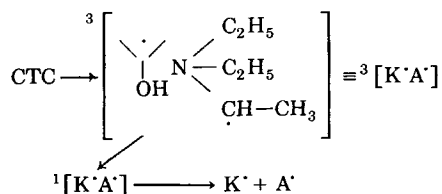
The separation of the radical pair (K· and A·) can be expected to happen almost similarly to that formed by a K· and cyclohexadienyl radicals. In that case, the data reported in Table VII (which show a substantial exit even in absence of MFE and a limit value of the % exit) points to the fact that the exit fraction in the presence of amine should be almost independent on the type of benzophenone and surfactant used: only a slight increase of R_p is therefore expected to occur.

In practice, the experimental results are somewhat at variance with this statement (Table V). However, it must be kept in mind that the exit ratio reported in this table corresponds to the sum of the exit ratio of the two radicals of the benzophenone–amine pair; therefore, a higher total exit ratio does not necessarily imply a more important exit of the amine radical.

As a general rule, the exit of the ketyl radical must be as high as possible, in order to favor the initiation of the polymerization. This exit actually depends (i) on the charge of the BP and of the surfactant used and (ii) on the magnetic field. The absence of significant influence of the nature of the amine considered on the rate of polymerization (Table III) and the "symmetric" behavior observed for BP^+ and BP^- in SDS and DTAC (Table VI) support this view.

Some other specific points are worth to be commented on: for instance, when going from SDS to DTAC, MFE increases the exit of $K^{·\ominus}$ ($BP^\ominus$ is located more "inside" in DTAC micelles) and decreases the exit of $K^{·\oplus}$ ($BP^\oplus$ is localized more "outside" in DTAC micelles); similarly, the use of a dodecyl–BP (whose exit of the K· radical is rather hindered) leads to a low rate of polymerization. However, the superiority of the system BP^+/DMDA compared with that of BP^-/DMDA is undoubtedly not related to the exit ratio of the corresponding K· radicals.

The efficiency of the proton transfer reaction depends presumably on the nature of the two partners (ketone and amine) and could explain the increase of R_p for BP^+ and the decrease for BP^- when going from MDEA to DMDA. Unfortunately, the yield of K· (in other words, the efficiency of the process leading to A· radicals) is not accessible by laser spectroscopy (see above).

Lastly, it must be emphasized that the water affinity of amine-derived radicals could affect the value of the overall exit ratio.

Acid Base Equilibrium

As shown above, an acid base equilibrium plays a part in the evolution process of the transient states; the following equilibrium is expected to take place in the presence of amines:
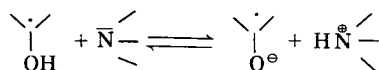
The role played by the basicity of the amine is corroborated by two observations: addition of NaOH enhances the amount of $K^{·-}$, whereas the use of a long chain amine (such as dodecyldimethylamine DMDA) with a basicity equivalent to that of TEA (pK = 10.67 [16]), but much less water-soluble, considerably reduces the $K^{·-}$ concentration. The consequence of the acid–base
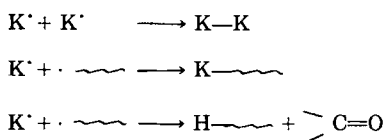
equilibrium is twofold: first it reduces the amount of amine molecules available to react with the triplet benzophenones (and thereby decreases the quantum yield ϕ_{CT}, which is calculated on the assumption that [A] is strictly equal to the concentration of amine introduced in the mixture). However, a simple calculation shows that this effect is negligible on the consumption of amine molecules; secondly, this equilibrium converts the $K^{\cdot}$ radicals into their anion form $K^{\cdot -}$. This reaction must presumably slow down the termination of the growing polymer chains by the $K^{\cdot}$ species: in THF solutions, $K^{\cdot}$ was effectively recognized to add to macro radicals.[14] As a consequence, both R_p and the degree of polymerization should increase. This behavior is effectively observed: in the presence of BP^+, if the amine concentration is increased by a factor of 5, then R_p increases by a factor of about 3 and DP decreases only by 30%; this would mean that the high decrease of DP expected from higher initiation rates is balanced by a local basicity effect which decreases the amount of free $K^{\cdot}$ that, as a consequence, slows down the termination reaction and increases the DP.

From laser spectroscopy experiments, the time necessary to reach the equilibrium appears to be longer for BP^+ than for BP^- and BP which denotes that

$$pK(BP^+) > pK(BP^-), pK(BP)$$

It is thereof expected that the effect of local basicity at higher amine concentrations would tend to saturate for BP^- and BP more rapidly than for BP^+. Though the relative rates R_p seem to behave as expected from this statement, nothing says whether acid base equilibrium is a predominant or a minor factor which must or not be taken into account.

Moreover, the effect of the $K^{\cdot}$ radical on the termination reactions should be more pronounced with BP^+, if we consider only the role of the $K^{\cdot}$ concentration. Since this assumption is at variance with the fact that BP^+ is experimentally observed to be much more efficient than BP^-, the differences of chemical reactivity must rather be accounted for by a more or less important tendency of the ketyl type derived radicals to terminate the growing chains rather than to self-dimerize:

$$K^{\cdot} + K^{\cdot} \longrightarrow K\!-\!K$$

$$K^{\cdot} + \cdot \,\sim\!\sim \longrightarrow K\!-\!\sim\!\sim$$

$$K^{\cdot} + \cdot \,\sim\!\sim \longrightarrow H\!-\!\sim\!\sim + \,{\textstyle\succ}C\!=\!O$$

Although an approach of these competitive reactions in terms of physical-organic chemistry is not easy, the behavior of the $K^{\cdot}$ species observed in the present work can be put together with previous conclusions obtained in the study of the role of structural parameters upon the R_p and DP in a photopolymerization by neutral benzophenone derivatives[17] in homogeneous solution.

The ketyl radical anion $K^{\cdot -}$ can well play also a part since DP is reduced upon addition of NaOH (which shifts the equilibrium to the neutral form $K^{\cdot}$). It is thereof inferred that the reactivity of $K^{\cdot}$ and $K^{\cdot -}$ rather than their concentrations will govern the efficiency of the termination reactions. The role

of K˙ could thus explain the values of the A factor.

Beside the considerations referring to the shape or the size of anionic and cationic micelles, the absence of a symmetric effect (Table II) in the R_p values when going from SDS to CTAC for BP^+ and BP^- (BP^+ remains more efficient in the two environments) implies that the ionic interactions induced by the surfactant assembly play a rather minor role in the excited states processes, in the mobility of the charged ketyl radicals, and in their efficiency as chain terminating radicals.

The use of amines with comparable basicity but with higher water solubility could lead to an increase of the deprotonation yield of K˙ and concomittantly to a decrease of the free K˙ concentration and also to an increase of the amount of radical anion K˙⁻. This effect on R_p is quite similar to that described previously. No dramatic influence is expected since the ϕ_{CT} values are only weakly dependent on the amine and since the more striking effect is governed by the ability of K˙ and K˙⁻ (and not to their concentration) to terminate the growing chains. The relative R_p values in Table III actually show that (i) the general behavior of the three benzophenones is not strongly dependent on the nature of the amine and (ii) that MDEA (pK ~ 8.5 [16]) as well as DMDA are slightly better as the additive. From the point of view of the acid–base equilibrium, a hydrophilic amine with a lower pK favoring the decrease of the K˙ concentration should increase the rates of polymerization. However, (i) nothing can be predicted as to the chemical reactivity of the monomer double bond towards the amine-derived radical and (ii) the concept of local basicity is rather difficult to handle in micellar aggregates.

CONCLUSION

This study clearly establishes that, in direct micellar photopolymerization reactions initiated, through electron and proton transfer processes, by ionic and nonionic molecules with benzophenone structures, more than one effect must be responsible of the reported results.

The respective localization of the reactants in the micellar assembly, the monomer quenching and the electron transfer (governed by substituent electronic effect), the proton transfer, the exit of the radical pair, the water-soluble character of the molecules used as photoinitiators, the ionic or dipolar interactions of charged molecules in ionic micelles—though playing a part in the overall process and mainly in the initiation event–do not seem to decisively influence the reactivity of the system.

Due to the A values obtained, an important chemical factor governing the reaction efficiency seems to be the reactivity of the ketyl species (radical and anion radical) which act as terminating agents of the growing polymer chains. Their concentration depend on the acid base equilibrium between the excited species and their efficiency in the termination reactions is strongly related to their chemical nature.

In direct micelles formed with anionic and cationic surfactants, BP^+ appears as the most efficient photoinitiator: the derived K˙ radicals are weakly reactive, the electron transfer process with amine is the most efficient, and the monomer quenching is the less pronounced. Similar trends are also observed (i) in homogeneous solution[18] and in reverse AOT micelles[8] photopoly-

merization of acrylamide and (ii) in SDS micelle polymerization of MMA where BP^-, BP, and neutral substituted BP behave as weakly efficient photoinitiators in comparison with BP^+.

References

1. D. J. Lougnot, P. Jacques, and J. P. Fouassier, *J. Photochem.*, **19**, 59 (1982).

2. J. P. Fouassier, *J. Chim. Phys.*, **80**, 339 (1983).

3. P. Jacques, D. J. Lougnot, and J. P. Fouassier, K. L. Mittal, Ed., Plenum, New York, 1984, Vol. 2, p. 1177.

4. D. J. Lougnot, P. Jacques, J. P. Fouassier, and D. Floret-David, *J. Chim. Phys.*, **82**, 505 (1985).

5. A. Merlin and J. P. Fouassier, *Polymer*, **21**, 1363 (1980).

6. J. Faure, J. P. Fouassier, D. J. Lougnot, and R. Salvin, *Nouv. J. Chim.*, **1**(1), 15 (1977).

7. J. P. Fouassier, D. J. Lougnot, and P. Jacques, unpublished data.

8. J. P. Fouassier, D. J. Lougnot, and I. Zuchowicz, *Eur. Polym. J.*, in press.

9. J. H. Fendler, E. J. Fendler, G. A. Infante, P. S. Shih, and L. K. Patterson, *J. Am. Chem. Soc.*, **97**, 89 (1975).

10. C. Reichardt, *Solvent Effects in Modern Chemistry*, Monographs in Modern Chemistry, 1979.

11. M. V. Encinas and E. A. Lissi, *Photochem. Photobiol.* **37**(3), 251 (1983).

12. J. C. Scaiano and D. J. Lougnot, *J. Phys. Chem.*, **88**, 3379 (1984).

13. N. J. Turro, M. F. Chow, C. J. Chung, and C. H. Tung, *J. Am. Chem. Soc.*, **102**, 7390 (1980).

14. A. Merlin, D. J. Lougnot, and J. P. Fouassier, *Polym. Bull.*, **3**, 1 (1980).

15. P. Jacques, D. J. Lougnot, J. P. Fouassier, and J. C. Scaiano, **127**(5), 469 (1986).

16. B. A. Korolev, M. A. Mal'tseva, A. I. Tarasou, and U. A. Vasnev, *J. Geh. Chem. USSR*, **44**, 833 (1974).

17. H. Block, A. Ledwith, and A. R. Taylor, *Polymer* **12**, 27 (1977).

18. J. P. Fouassier, D. J. Lougnot, I. Zuchowitz, P. N. Green, H. J. Timpe, K. P. Kronfeld, and U. Muller, *J. Photochem.*, in press.