

A mechanistic and laser flash photolysis investigation of acrylamide polymerization photoinitiated by the three component system safranine-T/triethanolamine/diphenyliodonium chloride

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Abstract

The photopolymerization of acrylamide (AA) initiated by the synthetic dye safranine-T in the presence of triethanolamine (TEOHA) as co-initiator has been investigated in aqueous solution. It was found that the addition of diphenyliodonium chloride (DPIC) to the system has a marked accelerating effect on the polymerization rate. In the absence of DPIC an inhibiting effect of TEOHA is observed at high concentrations of the amine. This effect is suppressed by the presence of the onium salt. At the same time the photobleaching of the dye caused by the amine is suppressed by the presence of AA or DPIC. Laser flash photolysis experiments show that the presence of the onium salt increases the yield of triplet state of the dye. Also the yield of radicals in the quenching of the dye triplet by TEOHA increases by the presence of DPIC. The semi-reduced form of the dye decays faster in the presence of DPIC, suggesting a possible way of generating extra active radicals at the same time that the dye is regenerated. It is concluded that are several factors that contribute to the accelerating effect of DPIC on the polymerization rate.

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1. Introduction

Water soluble photoinitiator systems of vinyl polymerization, especially those suitable for the visible region of the spectrum, have gained increasing interest in recent years [1]. Among these, the most commonly employed photoinitiators are those where radicals are formed in a bimolecular process comprising an excited state of a synthetic dye or natural pigment, and a co-initiator that behaves as electron donor. Recently, it has been proposed that the efficiency of such a photoinitiator system can be improved by the addition of a third component, the most commonly employed is an onium salt. A system comprising an aromatic ketone, an amine and diphenyliodonium salt was investigated by Fouassier et al. [2] for UV curing of vinyl monomers. Later on, similar systems were extended to the visible region by using a synthetic dye derived from thioxanthene [3]. It was found

that the presence of a third component increases the sensitivity and a mechanism is proposed for this effect, in which the onium salt acts as an electron scavenger from the dye radical. Cationic polymerization of epoxides employing a three component system was investigated by Bi and Neckers [4]. They found that a system consisting of a xanthene dye, an aromatic amine and a diaryliodonium salt is an efficient photoinitiator. They also proposed a reaction between the semi-reduced form of the dye and the iodonium salt. More recently, radical polymerization photoinitiated by a three-component system based on methylene blue or eosin Y, methyldiethanolamine and diphenyliodonium chloride (DPIC) was investigated by Scranton et al. [5,6]. In general, it seems that the mechanism by which these systems attain higher efficiency is not general, and depends on the dye, solvent and even the monomer.

We have previously carried out a detailed analysis of the photoinitiator system formed by the dye safranine-T and aliphatic amines both in organic solvents [7] and in aqueous solution [8]. The polymerization of 2-hydroxyethyl methacrylate (HEMA) was investigated in methanol and in water

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as cosolvents. In the organic solvent it could be established that the active radicals are formed in the interaction of the unprotonated form of the dye triplet with the amine. At the same time it was suggested that the interaction with the excited singlet of the dye leads to the inhibition of the polymerization. A larger amine concentration was necessary for attaining the maximum rate in water, although the maximum polymerization rate is higher than in the alcohol [8]. With the aim of further improving the efficiency of this system for aqueous photopolymerization, we decided to investigate the possibility of employing an onium salt as a third component of the initiating system.

In this paper we present results on the effect of adding diphenyliodonium chloride (DPIC) to the photoinitiating system formed by safranine-T (SH^+) and triethanolamine (TEOHA) (see Scheme 1 for the structural formulae) for the polymerization of acrylamide (AA) in aqueous media. Results are presented that show that the presence of DPIC increases the polymerization rate by a factor of two or higher depending on the amine concentration. The photo-physics and photochemistry of these three components photoinitiating system is investigated by laser flash photolysis experiments and continuous irradiation in the absence and the presence of the monomer.

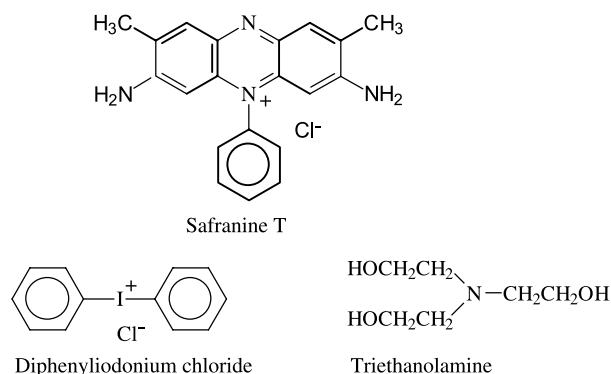
2. Experimental

2.1. Materials

Safranine-T chloride (SH^+Cl^-) (Merck) was recrystallized from methanol. Triethanolamine (TEOHA) (Aldrich) was purified by vacuum distillation before use. Diphenyliodonium chloride (DPIC) (Aldrich) and acrylamide (AA) (Sigma, >99% electrophoresis reagent) were used as received. Water was triply distilled. The solutions were deoxygenated by bubbling high purity argon. In all cases sample manipulations were carried out in a dark room.

2.2. Measurements

Fluorescence spectra determinations and fluorescence



Scheme 1.

quenching experiments were carried out at room temperature in air equilibrated solutions ($25 \pm 1^\circ\text{C}$) with a Spex Fluoromax spectrofluorometer. Fluorescence lifetimes were determined by the time-correlated-single-photon-counting technique using an OB-900 Edinburgh Instruments equipment. Triplet state properties were determined by the laser flash photolysis technique with a Spectron SL400 Nd:YAG laser generating 532 nm pulses (~ 18 ns pulse width) as previously described [9].

2.3. Polymerization procedure

Irradiation was carried out with a Photon Technology International (PTI) illumination system comprising a 150 W Xe lamp and a monochromator. The irradiation wavelength was 520 nm and the bandwidth was 8 nm. Polymerization rates (R_p) were measured dilatometrically in solutions degassed by several freeze and thaw cycles under vacuum. The polymerization cell was kept in a thermostatic bath equipped with a side window for illumination. Capillary readings were performed with a cathetometer. Initial polymerization rates were determined from the initial linear slopes of the volume contraction vs. irradiation time plots.

3. Results and discussion

The polymerization of AA (1 M in aqueous solution) on irradiation in the presence of SH^+Cl^- (1×10^{-5} M) was negligible. However, it proceeds efficiently in the presence of TEOHA. The initial polymerization rate, as determined by dilatometry, increases with the amine concentration reaching a maximum at TEOHA ca. 0.03 M. Further increase of TEOHA produces a decline of the polymerization rate, Fig. 1. This behavior is different to that observed in the polymerization of 2-hydroxyethyl methacrylate (HEMA) [8] with the same initiating system. In this case the plot of polymerization rate vs. [TEOHA] presented a slower increase with amine concentration, and the maximum is reached at amine ca. 0.1 M. The pronounced decline of the rate at higher amine concentration in Fig. 1, is not observed in the polymerization of HEMA. However, in this

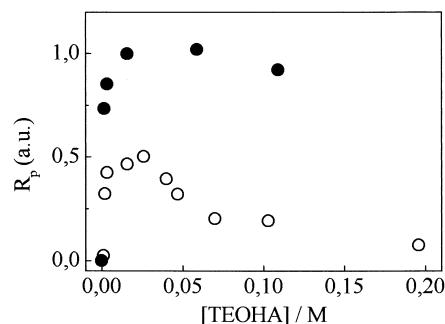


Fig. 1. Polymerization rates of AA in arbitrary units as a function of TEOHA concentration, in the absence (○) and presence (●) of DPIC 0.01 M.

case a much higher concentration of the monomer was used, and the distinct properties of the medium may be the cause of the difference. Fig. 1 also shows the effect of adding DPIC on the polymerization rate. It can be seen that the rate is significantly increased, and the decrease observed at high amine concentration is very much attenuated. The polymerization rate was found to be first order in monomer concentration, both in the absence and the presence of DPIC. Hence, assuming a second order termination, the polymerization rate may be written as

$$R_p \propto [M] \Phi_R^{1/2} \quad (1)$$

where $[M]$ is the monomer concentration and Φ_R is the quantum yield of initiating radicals.

In Fig. 2 the effect of varying DPIC concentration on the ratio R_p/R_p^0 , where R_p and R_p^0 are the polymerization rates in the presence and the absence of DPIC respectively, is shown. The effect is presented for two TEOHA concentrations, 0.027 and 0.1 M. It can be seen that when TEOHA is 0.1 M, the effect of DPIC is more important. This acceleration effect of DPIC could not be investigated at higher DPIC concentrations due to solubility limitation. With the aim of checking if the observed increasing in rate caused by the presence of DPIC was a general salt effect, the polymerization rate was measured in the presence of NaCl and tetrabutylammonium chloride both 0.01 M. In both cases the presence of the salt did not produce any noticeable increase in the rate.

In order to understand the mechanism by which the onium salt produces the acceleration effect on the polymerization rate, it is necessary to know the photochemical behavior of the system SH^+Cl^- –TEOHA under polymerization conditions. At this end, the excited state properties of aqueous solutions of the dye were investigated in the absence and the presence of DPIC and AA, and the quenching by TEOHA was measured in similar conditions. At neutral pH Safranin is in its monoprotonated cationic form, SH^+ , and is characterized by an absorption spectrum with $\lambda_{max} = 520 \text{ nm}$ and a fluorescence emission with $\lambda_{max} = 591 \text{ nm}$. The fluorescence lifetime, as determined by the single-photon-counting technique, is 1.3 ns in water and increases in less polar solvents. In the presence of AA

1 M the absorption spectra presents a red shift of 6 nm, while the emission maximum is now blue shifted to 586 nm. At the same time the fluorescence lifetime increases to 1.7 ns in the presence of the monomer. These changes are those expected for a less polar environment for the dye, and this distinct environment may be provided by a preferential solvation by AA molecules. In Table 1 are collected the fluorescence lifetimes of safranin measured in different media.

The effect of adding AA and DPIC on the triplet state properties was investigated by laser flash photolysis. Fig. 3 shows the transient absorption spectra observed after 532 nm laser excitation of SH^+ in water at neutral pH in the absence and in the presence of AA 1 M. The absorbance of the dye at 532 nm is identical in both solutions. In water a relatively intense band with maximum at 805 nm and a shoulder ca. 725 nm is seen. A less intense peak at 430 nm is also present. Negative absorbance was observed in the 460–550 nm region, which is assigned to the depletion of the SH^+ ground state. The absorption decay curves in the whole spectral range follow a first-order decay law with a lifetime of around 50 μs . All these observations agree with the general features of the triplet–triplet absorption spectrum of the dye, $^3SH^+$, in aqueous solution [10,11] and with those observed in organic polar solvents, such as methanol and acetonitrile [12]. In the presence of AA 1 M a red shift is observed in the T–T spectrum, similarly to that observed in the ground state absorption. The maximum is now at 820 nm while the spectral shape remains the same. The presence of AA slightly reduces the triplet lifetime. Changes in the shape of the T–T spectrum are not observed in the presence of DPIC up to 0.025 M. However, an increase in the triplet yield of more than 60% is observed in the presence of DPIC 0.022 M. At the same time the triplet lifetime becomes shorter.

It is well known that aliphatic amines quench the excited states of safranin-T. The quenching by TEOHA was investigated by stationary and time resolved fluorescence for the singlet, and by laser flash photolysis for the triplet. Bimolecular singlet quenching rate constants were determined by Stern–Volmer plots of fluorescence intensity according to Eq. (2)

$$\frac{I_0}{I} = 1 + {}^1k_q \tau_0 [\text{TEOHA}] \quad (2)$$

where I and I^0 are the fluorescence intensities in the presence and the absence of the amine, respectively; 1k_q is

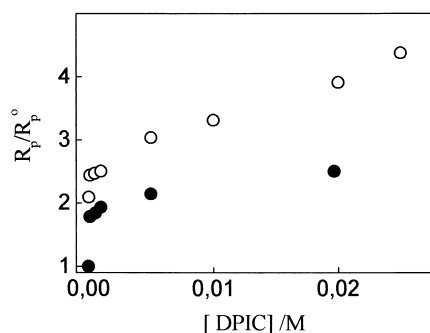


Fig. 2. Relative polymerization rates in arbitrary units vs. DPIC concentration. In the presence of TEOHA 0.027 M (●) and 0.1 M (○).

Table 1
Safranin-T fluorescence lifetimes

Solvent	Lifetime (ns)
H ₂ O	1.3
AA 1 M	1.7
Methanol	2.6
Acetone	3.4

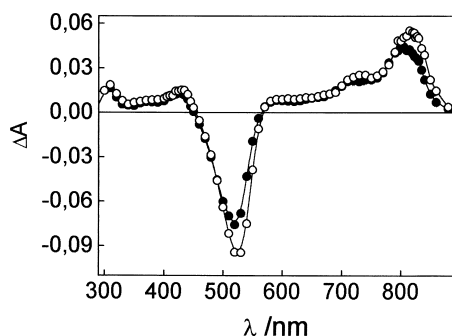


Fig. 3. Transient absorption spectrum of safranine-T in water at neutral pH taken at 2 μ s after the laser pulse at 532 nm in the absence (●) and the presence of AA 1 M (○).

the bimolecular quenching rate constant and τ_0 is the fluorescence lifetime in the absence of quencher.

Triplet quenching rate constants 3k_q , were obtained from a plot of the pseudo-first order decay rate constants at 805 nm, k_{obs} , as function of the quencher concentration [Q], Eq. (3)

$$k_{obs} = k^0 + ^3k_q[Q] \quad (3)$$

Quenching rate constants by the amine, the monomer and the iodonium salt are collected in Table 2.

The quenching of the monoprotonated triplet $^3SH^+$ by TEOHA does not follow a linear relationship with amine concentration as expected from Eq. (3) and the initial slope is abnormally high when compared with the singlet quenching rate constant. As previously discussed [8,13], this is due to an excited state proton transfer process involving the monoprotonated triplet and any of the bases present, leading to the deprotonated triplet state of the dye, Eq. (4):



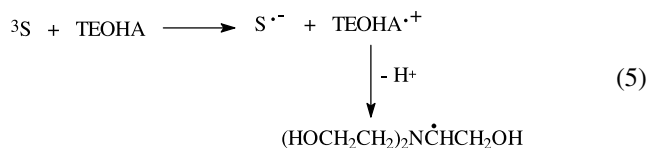
A posterior slower electron transfer process between 3S and the amine would lead to the formation of semi-reduced safranine in the form of radical anion, and the radical cation of the amine. The latter undergoes a second fast proton

Table 2
Singlet and triplet quenching rate constants

Quencher	Medium	1k_q ($M^{-1} s^{-1}$)	3k_q ($M^{-1} s^{-1}$)
TEOHA	H ₂ O	3.12×10^9	2.0×10^{10a}
TEOHA	AA 1 M	1.95×10^9	Not measured
TEOHA	DPIC 0.015 M	3.08×10^9	Not measured
AA	H ₂ O	Not observed	2.1×10^4
DPIC	H ₂ O	Not observed	1.0×10^6

^a From the initial slope of the Stern–Volmer plot.

transfer reaction leading to the active radicals, Eq. (5):



The mechanism is confirmed by the transient absorption spectra taken at 5 μ s after the laser pulse in the presence of TEOHA 0.1 M shown in Fig. 4. At this amine concentration the triplet is completely quenched and the resulting spectrum with $\lambda_{max} = 425$ nm and 600 nm, can be ascribed to the radical anion of safranine, $S^{\cdot-}$ [14]. The rate constant for the slow electron transfer step in reaction (5) is very difficult to be measured directly, since both species, the deprotonated triplet and the semi-reduced radical of the dye, absorb in the same spectral region, 400–440 nm. Also shown in Fig. 4 is the effect caused by the addition of DPIC 0.008 M on the transient absorption in this region. It can be seen that the presence of the iodonium salt increases the yield of the radical at short times, however, it decays faster in the presence of the salt (inset Fig. 4).

When SH^+ is continuously irradiated at the maximum of its absorption band at 520 nm in the presence of TEOHA, a fast photobleaching process takes place. In Fig. 5 the kinetics of the bleaching of the dye under different conditions is shown in the form of plots of the absorbance function $f(A)$ vs. time [15]

$$f(A) = \ln \frac{10^A - 1}{10^{A_0} - 1} = -\varepsilon I_0 \ell \Phi t \quad (6)$$

where A and A_0 are the absorbance of SH^+ at 520 nm at time t and time 0 respectively, ε is the molar absorption coefficient at the irradiation wavelength, I_0 the incident intensity, ℓ the irradiation path length and Φ is the photobleaching quantum yield. From the slopes of the plots in Fig. 5, and using aberchrome for the determination of I_0 , the quantum yields in Table 3 were determined. It can

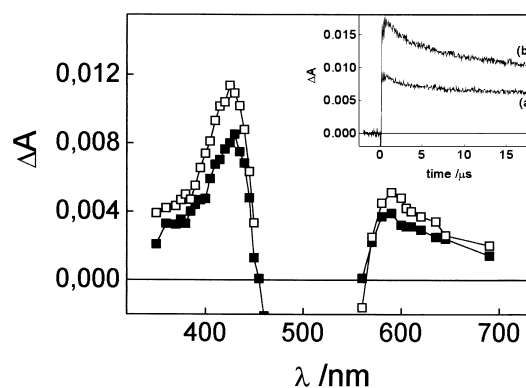


Fig. 4. Transient absorption spectra of safranine 10^{-5} M–TEOHA 0.1 M taken at 5 μ s after the laser pulse at 532 nm (■) and with the addition DPIC 0.008 M (□). Inset: decay of the absorption at 425 nm in the absence (a) and the presence (b) of DPIC 0.015 M.

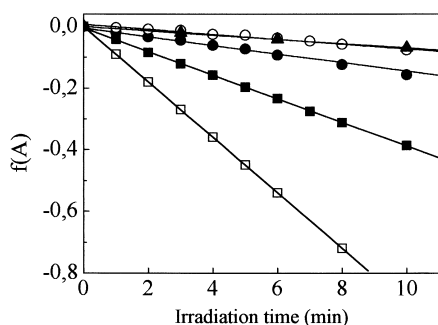


Fig. 5. Linear plot of the absorbance function vs. irradiation time of deaerated solutions of safranin 10^{-5} M–TEOHA 0.05 M (□), and with: DPIC 0.01 M (▲), AA 1 M (●), AA 1 M/DPIC 0.01 M (○). Excitation light: 520 nm. Actinometer: aberchrome 540 in toluene (■).

be seen that both AA and DPIC are efficient inhibitors of the photobleaching of the dye. This protective effect may be related to the trapping of reactive radicals.

According to Eq. (1) the square of the polymerization rate should be proportional to the quantum yield of initiating radicals. Assuming that the active radicals are formed in Eq. (5) in equal yield than the semi-reduced form of the dye, the quantum yield of initiating radicals can be estimated from the long-lived absorbance at 425 nm measured in the laser flash photolysis experiments. The yield increases in the presence of DPIC, becoming a factor of two larger at high concentrations of the salt. However, the square of the polymerization rate increases by a factor higher than 14 for the same concentration of DPIC. This is illustrated in Fig. 6. Therefore, the accelerating properties of the onium salt must be due to some secondary reaction with the radicals formed in the initiating steps or in a subsequent reaction in the propagation of the polymerization chain. This may be further assessed by a comparison of the experimentally determined polymerization rate, with the yield of initiating radicals predicted by the mechanism. The quantum yield of active radicals formed in reaction (5) may be estimated from the lifetimes and quenching rate constants, of singlet and triplet excited states of the dye, assuming that active radicals are produced only in the quenching

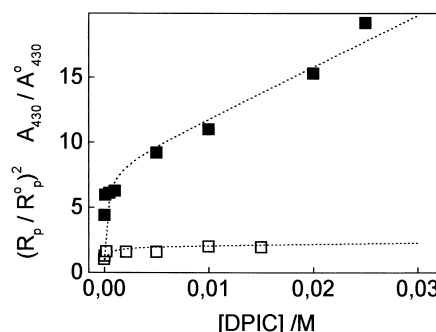


Fig. 6. Plot of the square of the polymerization rate (■) and the radical yield (□) measured as the long-lived absorbance at 425 nm in function of DPIC concentration relative to the values in the absence of DPIC. TEOHA concentration is 0.027 M.

of the triplet state, Eq. (7)

$$\Phi_R = \left(\frac{\Phi_{isc}^0}{1 + {}^1k_q {}^1\tau_0 [\text{TEOHA}]} \right) \times \left(\frac{{}^3k_q {}^3\tau_0 [\text{TEOHA}]}{1 + {}^3k_q {}^3\tau_0 [\text{TEOHA}]} \right) \beta \quad (7)$$

where Φ_{isc}^0 is the intersystem crossing quantum yield, ${}^1\tau_0$ and ${}^3\tau_0$ are the singlet and triplet lifetimes and 1k_q is the singlet quenching rate constant, 3k_q is the rate constant for reaction triplet electron transfer and β is a proportionality constant. It was previously shown that in many cases the square of the polymerization rate may be correlated with the theoretical quantum yield of initiating radical, as given by Eq. (7) [16].

In Fig. 7 it is shown a plot of the square of the polymerization rate R_p^2 as a function of TEOHA concentration. In the absence of DPIC it can be seen that R_p^2

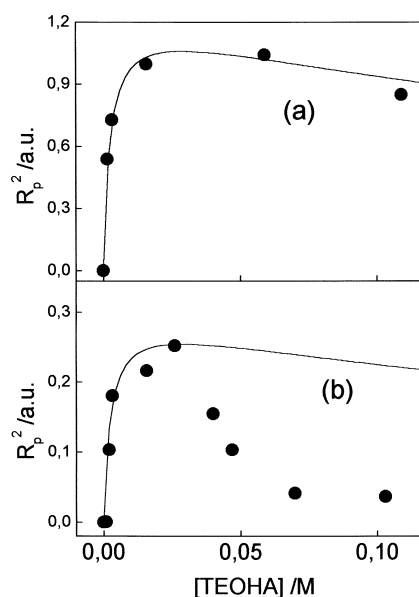


Fig. 7. Fitting of the square of the polymerization rate to Eq. 7 (b) in the absence and (a) in the presence of DPIC 0.01 M.

Table 3
Photobleaching quantum yields

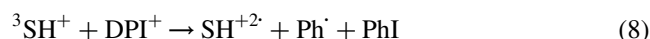
System	Φ
SH ⁺	~0
SH ⁺ + DPIC 0.01 M	~0
SH ⁺ + AA 1 M	~0
SH ⁺ + TEOHA 0.05 M	0.036
SH ⁺ + TEOHA 0.05 M + DPIC 0.01 M	0.003
SH ⁺ + TEOHA 0.05 M + AA 1 M	0.006
SH ⁺ + TEOHA 0.05 M + AA 1 M + DPIC 0.01 M	0.003

In all cases SH⁺ concentration was 1×10^{-5} M.

presents a fast decay as a function of the amine concentration after reaching a maximum at TEOHA ca. 30 mM. A similar behavior was previously observed in methyl methacrylate polymerization photoinitiated by fluorenone in the presence of triethylamine [17]. This can be ascribed to several factors, among them the interaction of the amine with a hypothetical radical ion pair formed in the electron transfer triplet quenching, reaction (5).

In the presence of the salt, the fast decay of the rate at high amine concentration is no longer present, and R_p^2 follows a similar trend to that of the theoretical radical yield as given by Eq. (7). The solid line in Fig. 7(a) was obtained by Eq. (7) with $^3k_q^3\tau_0 = 400 \text{ M}^{-1}$ and $^1k_q^1\tau_0 = 3 \text{ M}^{-1}$ and $\beta = 1.25$. The figure used for $^1k_q^1\tau_0$ results from the experimental determined values of singlet lifetimes and quenching rate constants. The values of β and $^3k_q^3\tau_0$ are those that afford the best fitting to the experimental data. With a lifetime of 50 μs for $^3\tau_0$ the quenching rate constants results $^3k_q = 8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ which is not an illogical value for reaction (5). The line in Fig. 7(b) is calculated with the same parameters than above, except that now $\beta = 0.35$. In order to fit the data in Fig. 7(b) to Eq. (7) an unreasonable high value must be adopted for $^1k_q^1\tau_0$.

Therefore, it seems that the effect of DPIC in increasing the polymerization rate may be due in part to a blocking of the inhibiting effect of high concentrations of TEOHA. Another possibility is the direct reaction of the triplet state of the dye with DPIC. The occurrence of the oxidative quenching of the triplet state, reaction (8) was investigated by monitoring the decay at 805 nm as a function of DPIC concentration. The small quenching observed, Table 2 might be ascribed to the reaction



However, in the polymerizing medium the presence of TEOHA makes the importance of reaction (8) negligible.

In other three component systems employing DPIC it was proposed that the accelerating action of the salt might be related to a secondary electron transfer reaction from the semi-reduced form of the dye formed in reaction (5) to the diphenyliodonium cation:



In the ground state S will be rapidly protonated to the form SH^+ .

It was suggested that the phenyl radicals produced in (9) would add to the monomer originating new polymer chains [3,6]. In fact, the inset in Fig. 4 shows that in our case the decay of the $\text{S}^{\cdot-}$ anion radical is faster in the presence of DPIC. However, as can be seen from Figs. 4 and 6, also the initial yield of radicals is increased by the presence of the onium salt. This increment in the radical yield is most likely related to the higher triplet yield in the presence of DPIC. Therefore, although reaction (9) is probably taking place, other factors may be also acting in increasing the efficiency

of the system. In addition to a specific effect of the salt on the yield of initiating radicals, it seems that a suppression of the inhibiting effect of high concentrations of the co-initiator TEOHA (Fig. 7) is brought about by the presence of DPIC. These effects may be related to the presence of some aggregates formed by the hydrophobic cations DPI^+ . We have observed a large increase in the scattered light in the fluorescence measurements carried out in the presence of DPIC. Also, the absorption and emission spectral changes of safranin-T in the presence of DPIC may be explained by the dye being in a less polar environment. The aggregation of this type of salts has been previously observed by Kunz and Calmettes [18]. Accordingly, the higher triplet yield in the presence of DPIC may be explained by an external heavy atom effect of the iodine atoms on the intersystem crossing efficiency. Moreover, it is well-known that in such microheterogeneous systems the excited state reactivity, and more specifically, the ion-radical yield in photoinduced electron transfer reactions, may be drastically altered [19].

In summary, the presence of the iodonium salt has a marked accelerating effect on the photopolymerization of AA initiated by safranin-T–TEOHA. There are several factors by which DPIC may act on the yield of initiating radicals, and on the photopolymerization mechanism of AA. Some of these are implied by the results of the present investigation, but to assess their relative importance in the several three components systems proposed as photoinitiator, requires a more detailed study of their photochemistry, in particular a through analysis of the several mechanistic aspects that are changed by the presence of the onium salt.

Acknowledgements

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