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Phenylonium salts as third component of the photoinitiator system safranine O/triethanolamine: A comparative study in aqueous media

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Abstract

The efficiency of the photoinitiator system composed of safranine and triethanolamine for the polymerization of acrylamide in water was improved by the incorporation of onium salts. The phenylonium salts employed were diphenyliodonium chloride, triphenylsulfonium triflate, tetraphenyphosphonium chloride and tetraphenylarsonium chloride hydrate. Among them, diphenyliodonium presents the highest efficiency, followed by triphenylsulfonium. In an appropriate concentration of triethanolamine, the behavior of the sulfonium salt resembles that of iodonium. Tetraphenyphosphonium and tetraphenylarsonuim have little effect over the polymerization rate; however, interesting effects over the photophysical properties of the system were found. Two important conclusions emanate from the work: the phenylonium salts studied aggregate in water in a behavior similar to hydrotropes and several factors contribute to the accelerating effect of the onium salt on the polymerization rate. The main differences in the observed efficiency of the salts might reside in the redox potentials of the salts and in their ability to prevent the photobleaching of safranine in the presence of triethanolamine.

Keywords: Photopolymerization; Onium salts; Three-component photoinitiators

1. Introduction

Photoinitiator systems for vinyl polymerization have been extensively studied because of their importance in industry, especially in lithography and photocuring [1,2]. Particularly, the employment of onium salts in sensitized cationic polymerization took great interest [3–5]. Their applications are several and very important, among them are UV curing of pigmented coating usable as paints, textile printing, glass reinforced fibers, UV curing of inks, laser-induced polymerization, and others [6]. Moreover, the use of water-soluble photoinitiator systems able to absorb visible light makes these systems environmentally friendly and more attractive [7]. The use of visible light instead of UV light is possible by the incorporation of a synthetic dye in the photoinitiator system.

In the last decade, the study and development of three-component photoinitiator systems, born as a manner of improvement of the known two-component photoinitiators studied at the moment, took great importance [5,8–13].

The most common photoinitiator systems in the visible for vinyl polymerization are composed of a dye and an amine as an electron donor. The reaction between the dye and the amine has been widely investigated and the mechanism for the generation of amino radicals able to initiate vinyl polymerization is well known [14–17]. Onium salts were generally employed as photoinitiators for cationic polymerization [3,8,18,19]. Cationic polymerization of epoxides employing a three-component system was investigated by Bi and Neckers [8]. They found that a system consisting of a xanthene dye, an aromatic amine and a diaryliodonium salt is an efficient photoinitiator.

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They proposed as the primary photochemical reaction the electron transfer from the dye to the iodonium salt. In radical photopolymerization the incorporation of an onium salt, generally a diphenyliodonium salt, as third component enhances the polymerization rate [10–13]. Fouassier et al. suggest that in three-component systems based on sensitizer/electron donor/radical scavenger the onium salt inhibits the ketyl radical regenerating the salt [9]. 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 Padon and Scranton [10,11]. 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.

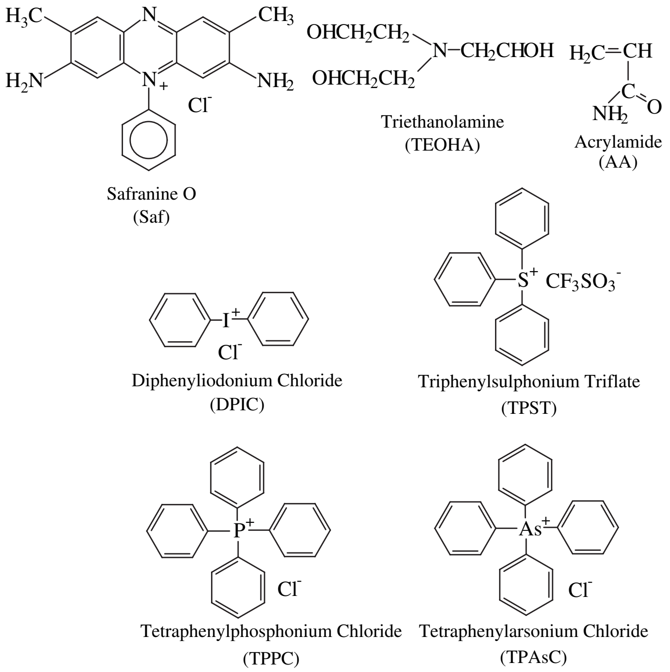
In previous works [20,21] we observed that the efficiency of the photoinitiator system composed by safranine (Saf) and triethanolamine (TEOHA) was incremented by the addition of DPIC. The mechanism by which DPIC acts is complex. Several alternatives were discussed, including an increase in the yield of active radicals, suppression in the inhibitory effect observed at high amine concentration and changes in the reactivity of the excited states. The accelerating effect was found to be much more important than the increase in the yield of radicals in the initiation process. We also found that DPIC aggregates in water at working concentrations and a correlation between the polymerization rate and the formation of aggregates could be established [21].

In most of the three-component systems studied an iodonium salt was the onium salt incorporated as third component. On account of the importance of the onium salts as third component in photoinitiator systems, we present here a comparative study for the polymerization of acrylamide (AA) in water photoinitiated by Saf and TEOHA, in the presence of four different phenylonium salts (On). The salts studied were DPIC, triphenylsulfonium triflate (TPST), tetraphenyphosphonium chloride (TPPC) and tetraphenylarsonium chloride hydrate (TPAsC). A comparative analysis between the efficiency of the different onium salts is performed in this paper. Results presented show that while DPIC and TPST increase the polymerization rate, TPPC and TPAsC have little effect. At the same time the four phenylonium salts investigated have significant effects on the photophysical properties of the dye. We also observed that the presence of the salts affects the photobleaching quantum yield of Saf/TEOHA system and that this effect is in line with the effect on the photopolymerization rates.

2. Experimental

2.1. Chemicals

Tridistilled water was used in all the experiments. Safranine O, provided by Merck, was recrystallized twice from methanol before use. TEOHA (Aldrich) was distilled in vacuum before use. AA, Aldrich electrophoresis grade, was used as received. The onium salts DPIC, TPST, TPPC and TPAsC, all of them provided by Aldrich were used without further purification (97–98% purity). Scheme 1 shows all structural formulae.



Scheme 1.

2.2. Measurements

2.2.1. Photopolymerization experiments

The initial rates of polymerization were measured dilatometrically. The solution to polymerize was placed in a dilatometric cell in a thermostatic bath (25 ± 0.5 °C) and irradiated with a 150 W Xenon lamp–monochromator system at 520 nm (24 nm bandwidth). The solution was previously de-oxygenated by nitrogen bubbling. No polymerization was observed in the absence of amine or the dye. To investigate the intensity dependence of the polymerization rate, the light intensity was attenuated with absorbing solutions of the dye. Polymers were characterized by gel permeation chromatography on an HP1100 liquid chromatography system equipped with a refraction index detector. Separations were done at 25 °C on a TOSOHAAS, TSK-Gel (C0003-024) column (7.5 mm × 30 cm – 17 μm particle size). Molecular weights were calculated from the elution volume by reference to polyethylene oxide standards.

2.2.2. Absorption spectra

The absorption spectra were obtained using a Hewlett–Packard 8453 diode array UV–vis spectrophotometer.

2.2.3. Steady state photolysis

These experiments were carried with the same illuminating system at 520 nm (8 nm bandwidth). All the experiments were performed at 25 ± 0.5 °C. Aberchrome 540 from Aberchromics LTD in toluene was used as actinometer.

2.2.4. Fluorescence determinations

The fluorescence spectra and relative fluorescence quantum yield were determined with a Spex Fluoromax spectrofluorometer. Scattering measurements were performed at 500 nm at right angle geometry. Fluorescence lifetimes were determined by time correlated single photon counting using an OB-900 Edinburgh Instruments spectrofluorometer.

2.2.5. Laser flash photolysis measurements

Triplet–triplet absorption spectra and triplet lifetimes were determined using the experimental set-up described before [22]. Excitation of the dye was carried out at 532 nm using the second harmonic of a ND–YAG laser. A flow cell was used when necessary, in order to avoid photodecomposition of sensitive components.

3. Results and discussion

3.1. Photopolymerization results

Fig. 1 shows the dilatometric measurements of the kinetics of photopolymerization of AA: 1 M, employing as photoinitiator system Saf: 1×10^{-5} M/TEOHA: 0.025 M/On: 0.02 M. The effect of NaCl is also represented in Fig. 1. No effect of NaCl was observed, permitting rejection a general salt effect by the incorporation of On in the photoinitiator system. An important effect is observed when On are employed, compared with the photoinitiator system without salt.

Fig. 2 presents the results for the photopolymerization rates of AA: 1 M employing Saf: 1×10^{-5} M, TEOHA: 0.025 M at different On concentrations. The ratios R_p/R_p^0, where R_p and R_p^0 are the rate in the presence and in the absence of On, respectively, are plotted against On concentrations. Fig. 2 reveals the important effect of DPIC on the initial polymerization rate, a lesser effect of TPST, whereas a minor effect by the incorporation of TPPC or TPAsC was observed. The polymerization rate increased 2.5 times in the presence of DPIC 0.02 M, while the rate increased 1.5 times at the maximum TPST concentration employed. The effect of TPST on the ratio R_p/R_p^0 at a higher TEOHA concentration is also shown in Fig. 2. It can be seen that when TEOHA 0.1 M is employed, the effect of TPST is more important and similar to the DPIC effect with TEOHA 0.025 M.

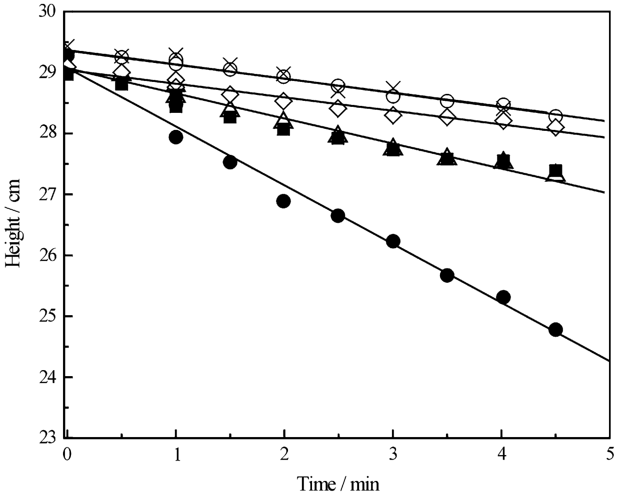


Fig. 1. Dilatometry: height vs. time. Salt effect on the polymerization rate of Saf: 1×10^{-5} M/TEOHA: 0.025 M in the absence (○) and in the presence of TPAsC (◇), TPPC (■), TPST (△), DPIC (●) and NaCl (×), all of them 0.02 M.

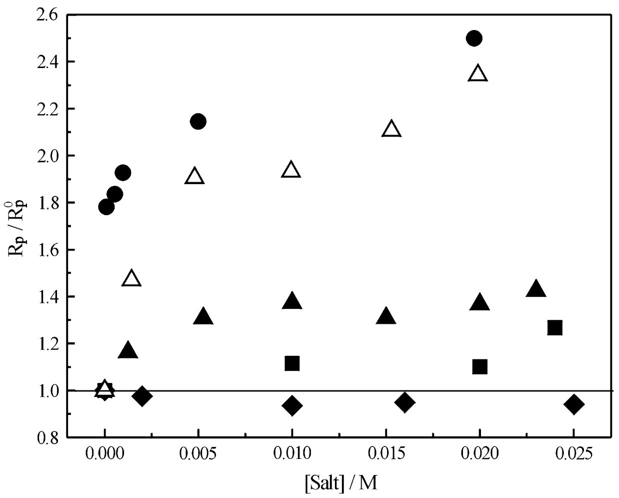


Fig. 2. Relative polymerization rate of AA 1 M as a function of onium salt concentration for Saf: 1×10^{-5} M/TEOHA: 0.025 M in the presence of DPIC (●), TPST (▲), TPPC (■), TPAsC (◆) and TPST in the presence of TEOHA: 0.1 M (△).

To check the polymerization kinetics, we also investigated the dependence of the polymerization rate on the monomer concentration and light intensity in the absence and in the presence of On. It was observed that, in all the cases, the polymerization rate was directly proportional to AA concentration and to the square root of incident light intensity. Hence, the polymerization rate may be written as:

$$R_p \propto [M] I^{1/2} \qquad (1)$$

Therefore, the rate law conforms to the classic vinyl polymerization mechanism with second-order termination.

The effect of TEOHA concentration was analyzed for TPST. Fig. 3 shows the effect of TEOHA concentration over

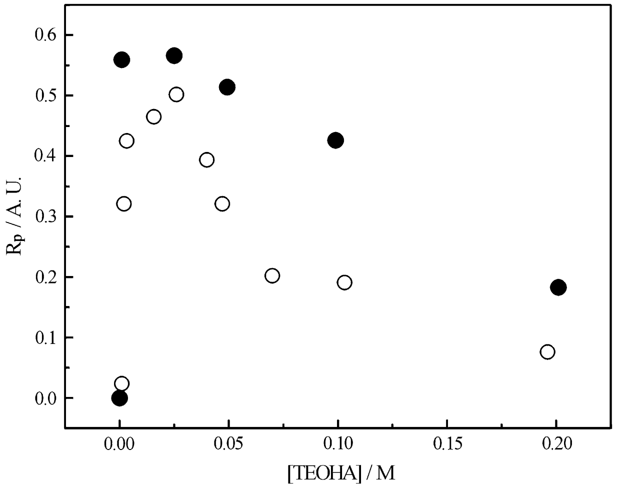


Fig. 3. Effect of TEOHA concentration over the polymerization rate of AA 1 M photoinitiated by Saf: 1×10^{-5} M, in the absence (○) and in the presence (●) of TPST 0.01 M.

Table 1
Molecular weight (MW) and initial polymerization rate (R_p) for [Saf]: 1×10^{-5} M, [TEOHA]: 0.025 M and [On]: 0.01 M

System	MW ($\times 10^6$)	R_p (A.U.)
Saf/TEOHA	2.30	3.1
Saf/TEOHA/TPST	2.33	4.1
Saf/TEOHA/DPIC	2.06	6.8

the polymerization rate of AA initiated by Saf: 1×10^{-5} M in the absence and in the presence of TPST: 0.01 M. The effect of TEOHA on the photoinitiator system containing DPIC was presented previously [20], where the pronounce decline of the rate at high amine concentration was suppressed by the presence of DPIC. In the case of TPST this effect is less important, however, it can be seen in Fig. 3 that at amine concentration higher than 0.05 M the presence of the salt has an important increasing effect on the rate.

Molecular weight determinations were made by size exclusion chromatography for the polymers obtained in the absence and the presence of DPIC and TPST. The entire chromatogram poses one single peak, the results are presented in Table 1 together with the maximum polymerization rate in each case. In spite of the differences observed in the polymerization rate, the three-photoinitiator systems analyzed produce polyacrylamide of similar high molecular weight.

3.2. Photochemical and photophysical characterization

To elucidate the effect of the onium salts on the polymerization rate, a detailed study of the photophysical and photochemical properties of these three-component systems was carried out. Fluorescence quantum yields and lifetimes (τ^1) of Saf were measured in the absence and in the presence of the onium salts. Quantum yields were determined as the integrated band of fluorescence of Saf in the presence of the salts relative to the value for Saf in water (Φ_f^R). Relative triplet quantum yields (Φ_T^R) were determined following the triplet–triplet absorption at 805 nm, assigned to the maximum absorption for the monoprotonated triplet (^{3}SafH$^+$) in water [23], for different onium salt concentrations relative to the value in the absence of the salt. These results are summarized in Table 2.

Table 2
Fluorescence quantum yield (Φ_f^R)[a], fluorescence lifetime (τ^1), shift of the maximum wavelength of fluorescence (λ_f shift) and triplet quantum yield for Saf (Φ_f^R)[a] in water by onium salts ([Saf]: 1×10^{-5} M and [On]: 0.02 M)

System	Φ_f^R (% Inc.)	τ^1 (ns)	λ_f shift (nm)	Φ_T^R (% Inc.)
Saf/DPICl	10	1.3	N.O.	60
Saf/TPST	10	1.3	N.O.	20
Saf/TPPCl	25	1.9	6 nm	30
Saf/TPAsCl	40	1.7	4 nm	40

N.O.: not observed.

[a] Percent increment with respect to the values of Saf in the absence of On.

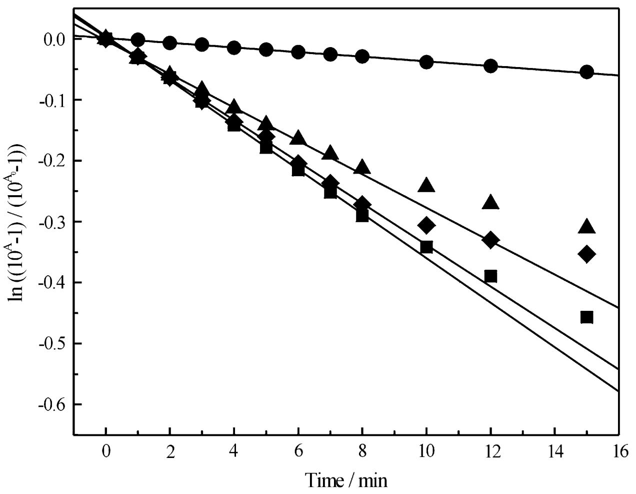


Fig. 4. Linear plot of the absorbance function vs. irradiation time of deareted solutions of Saf: 1×10^{-5} M/TEOHA: 0.05 M with DPIC (●), TPST (▲), TPPC (■) and TPAsC (◆), all of them 0.01 M.

The first important observation from the photochemical characterization is a fast photobleaching process, observed when Saf was irradiated in the presence of TEOHA. However, in the presence of DPIC an efficient inhibition of the photobleaching of the dye was observed [20]. In Fig. 4 the kinetics of the photobleaching of the dye with TEOHA 0.05 M in the presence of 0.01 M of On are shown in the form of plots of the absorbance function $f(A)$ vs. time [24]:

$$f(A) = \ln \frac{10^{A} - 1}{10^{A_0} - 1} = -\varepsilon I_o \ell \Phi_{PB} t \tag{2}$$

where A and A_o are the absorbances of Saf at 520 nm at time t and time 0, respectively, ε is the molar absorption coefficient at the irradiation wavelength, I_o the incident intensity, ℓ the irradiation path length and Φ_{PB} is the photobleaching quantum yield. From the slopes of the plots in Fig. 4, and using Aberchrome for the determination of I_o, the quantum yields were determined in Table 3. It can be seen that DPIC is the most efficient inhibitor of the photobleaching of the dye, followed by TPST with a less important protective effect. TPPC and TPAsC have little effect on the photobleaching quantum yield. These results correlate with the reduction potentials of the onium salts [25–27] regardless of the differences founded in the literature.

The occurrence of the oxidative quenching of the triplet state was investigated by monitoring the decay at 805 nm for Saf/AA: 1 M in the absence and in the presence of TPST and DPIC, the differences observed in the triplet lifetimes, Fig. 5, might be ascribed to reaction (3):

Table 3
Photobleaching quantum yield for Saf (Φ_{PB}), radical quantum yield ($\Phi_R^{\bullet}$) and the ratio R_p/R_p^0 for [Saf]: 1×10^{-5} M, [On$^+$]: 0.01 M, [TEOHA]: 0.05 M, [TEOHA]: 0.025 M

System	Φ_{PB} ([TEOHA]: 0.05 M)	$\Phi_R^{\bullet}$ ([TEOHA]: 0.05 M)	R_p/R_p^0 ([TEOHA]: 0.025 M)
Saf/TEOHA	0.036	1	1
Saf/TEOHA/DPICl	0.003	2	2.2
Saf/TEOHA/TPST	0.023	1.2	1.3
Saf/TEOHA/TPPCl	0.031	1.3	~1
Saf/TEOHA/TPAsCl	0.029	1.2	~1

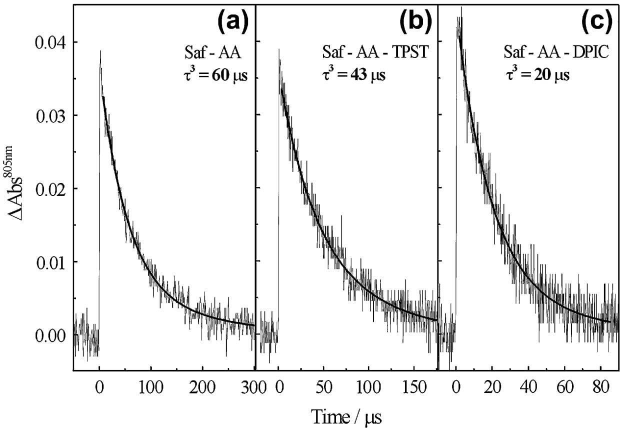


Fig. 5. Decay of the triplet–triplet absorption at 805 nm for Saf/AA: 1 M (a), Saf/AA: 1 M/TPST: 0.02 M (b), and Saf/AA: 1 M/DPIC: 0.02 M (c).

$$\begin{array}{l} {}^3\mathrm{SafH}^{+} + \mathrm{On}^{+} \rightarrow \mathrm{SafH}^{+2\bullet} + \mathrm{Ph}^{\bullet} + \mathrm{On(-Ph)} \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\quad \text{Initiation} \end{array} \tag{3}$$

However, in the polymerization medium reaction (3) cannot compete with the triplet quenching by TEOHA. The deactivation rate constants of $^3SafH^+$ in the presence of AA 1 M are in the order of $3 \times 10^5\ M^{-1}\ s^{-1}$ for TPST and $2 \times 10^6\ M^{-1}\ s^{-1}$ for DPIC; while the corresponding value for the deactivation rate constants in the presence of AA 1 M by TEOHA is $2 \times 10^{10}\ M^{-1}\ s^{-1}$. Since the same order of concentrations of the amine and the onium salts is used, reaction (3) becomes negligible.

According to the mechanism of generation of active radicals, proposed earlier [20], the active amino radicals are produced by an electron transfer reaction between the deprotonated triplet form of the dye and the amine, followed by a very fast deprotonation (reaction (4)), as proposed previously by Hassoon and Neckers [28].

$$\begin{array}{l} {}^3\mathrm{Saf} + \mathrm{TEOHA} \longrightarrow \mathrm{Saf}^{\bullet-} + \mathrm{TEOHA}^{\bullet+} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow -\mathrm{H}^{+} \\ \qquad\qquad\qquad\quad (\mathrm{HOCH_2CH_2})_2\mathrm{N}\dot{\mathrm{C}}\mathrm{HCH_2OH} \end{array} \tag{4}$$

Since the semireduced form of the dye and the active amino radical are generated with the same quantum yield, the quantum yield of initiating radicals can be estimated from the long-lived absorbance at 430 nm (assigned to the absorbance of the semireduced form of the dye) by laser flash photolysis in the presence of TEOHA. An example is presented in Fig. 6. From the figure it is possible to note, at short time, an increment of about 20% in the radical quantum yield (absorbance) when TPST is added. In all cases we observed that the radical quantum yield was enhanced by the presence of the onium salts (Table 3).

The results corresponding to the photobleaching quantum yield (Φ_{PB}), the radical quantum yield relative to that in the absence of onium salt ($\Phi^{\bullet}_{R}$) and the ratio R_p/R_p^0 are summarized in Table 3.

As mentioned above, and with the exception of DPIC, the rest of the onium salts enhance the radical quantum yield by about 20–30%; however, DPIC and TPST are only capable of incrementing the polymerization rate. These results allow disregarding the effect of the increment in $\Phi^{\bullet}_{R}$ as the only explanation for the increase in polymerization rate and might indicate that the protective effect of the onium salt on the photobleaching of the dye could be the most important factor in this regard. That the effect is not related to an increment of initiating radicals is also pointed out by the similar MW in the three cases. Padon and Scranton reported a similar effect of DPIC on the photobleaching of methylene blue when this dye was employed in conjunction with TEOHA for the photopolymerization of 2-hydroxyethylmethacrylate [10].

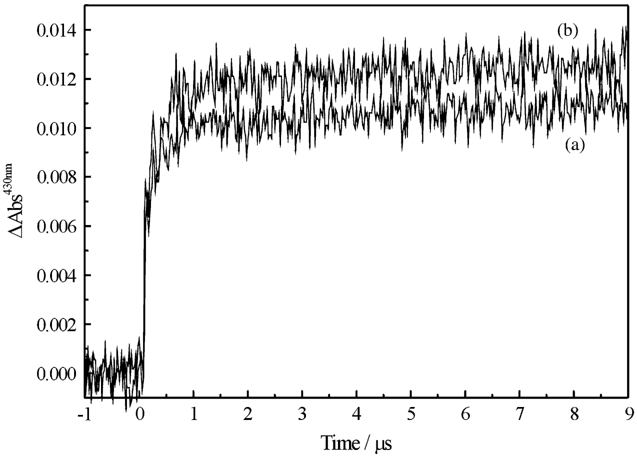


Fig. 6. Decay of the triplet–triplet absorption of Saf/TEOHA: 0.05 M at 430 nm in the absence (a) and in the presence (b) of TPST 0.01 M.

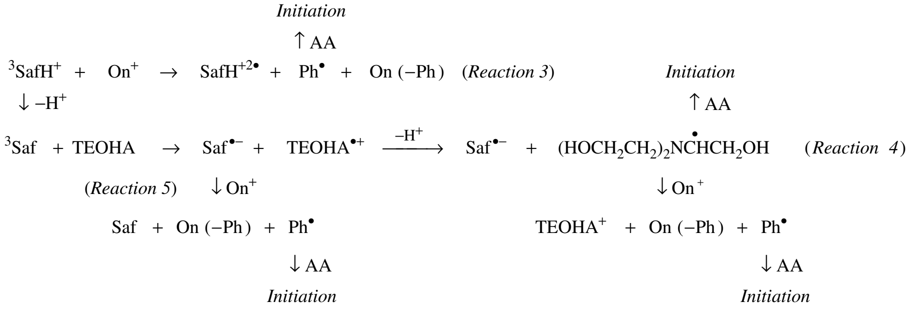
In other studies of three-component systems employing DPIC [11,13], it was proposed that the accelerating action of the salt may be related to a secondary electron transfer reaction from the semireduced form of the dye formed in reaction (4) to the diphenyliodonium cation, this behavior might be extended to the other On; in a general way this reaction is represented by reaction (5):

$$\begin{array}{l} \mathrm{Saf}^{\bullet-} + \mathrm{On}^{+} \longrightarrow \mathrm{Saf} + \mathrm{Ph}^{\bullet} + \mathrm{On(-Ph)} \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\quad \text{Initiation} \end{array} \tag{5}$$

The phenyl radicals produced in reaction (5) would add to the monomer originating new polymer chains [10,11,29]; besides, reaction (5) regenerates the dye in the ground state, preventing its photobleaching when it is irradiating in the presence of TEOHA.

Although the fate of the amino radicals could not be followed experimentally, the possibility of their reaction with the onium salts could not be disregarded. This electron transfer reaction was proposed by Bi and Neckers [8], from product analysis by GC; and could be an additional way of generation of phenyl radicals. The complete mechanism, with the different possible initiation paths, is summarized in Scheme 2.

Another important aspect to be considered when analyzing the effect of onium salts in photoinitiator systems is the formation of aggregates of the hydrophobic cations [21]. This effect produces changes in the photophysical parameters of Saf, as



Scheme 2.

can be observed in Table 2. Thus, when the onium salts are added to solutions containing Saf the triplet and fluorescence quantum yields of the dye increase, whereas the ground state absorption spectra remain almost unchanged. Also a shift in the maximum wavelength of fluorescence and changes in the fluorescence lifetime of the dye in the presence of the On are observed.

The changes in photophysical parameters shown in Table 2 could be attributed to the incorporation of the salt to a micro-heterogeneous domain of cluster of the hydrophobic cations of the salts (an increase in the fluorescence lifetime for Saf was previously observed in less polar solvents [30]). The shift of the maximum wavelength of fluorescence of Saf with respect to the value in the absence of salt is also indicative of a change in the polarity, as it was recently reported [30].

In addition, we observed an increment in the light scattering of the solution as the concentration of onium salt increases. The light scattering measured by nephelometry as a function of On salt concentration is presented in Fig. 7. The abrupt change in light scattering may be related to the formation of aggregates of the salt [21]. The changes in the photochemical properties shown in Table 2 are in line with the scattering behavior. The nature of the aggregates could not be clearly established with the experimental techniques available to us; however, as can be seen from Fig. 7, the light scattering due to On was much higher than that observed for a common surfactant as SDS in the same concentration range, in which normal micelles are formed.

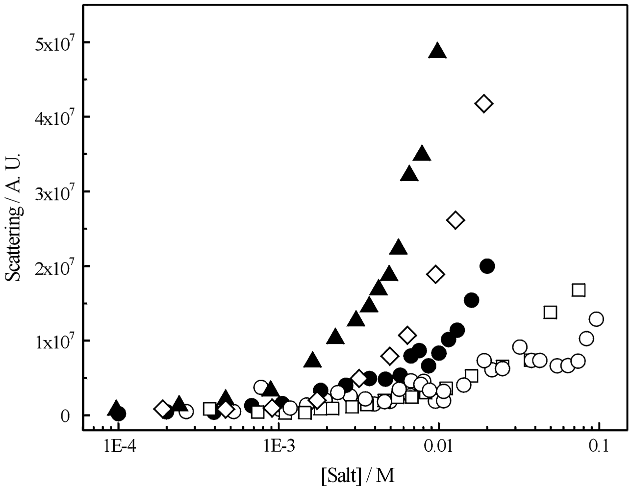


Fig. 7. Effect of onium salts' concentrations on the light scattering intensity of the solution in the presence of SDS (○), DPIC (●), TPST (▲), TPPC (□) and TPAsC (◇).

This effect is similar to that assigned to molecules designated as hydrotropes [31], so the onium salts might behave as hydrotropes, with a minimum hydrotrope concentration ca. 1×10^{-3} M, acting as efficient solubilizers of monomer.

However, while the micro-heterogeneity of the polymerizing solution may be of importance in explaining the acceleration effect of DPIC and TPST, the other two salts investigated also present a noticeable light scattering typical of an aggregation phenomena but they do not affect the polymerization rate. It is clear therefore that some other structural aspect may be acting.

The increase in polymerization rate can be correlated with the increase in the yield of radicals, as measured by laser flash photolysis of the semireduced form of the dye, Table 3. This could be related to a higher initiation efficiency. However, in the case of DPIC this augment is not reflected in the MW of the polymer, Table 1. The MW is practically the same in the absence and in the presence of DPIC. Since it is expected to decrease if the initiation efficiency and the number of growing chains increase, the results in Table 1 do not keep a relationship with those in Table 3. A possible explanation is a partial compensation with an increase in the propagation rate in the presence of DPIC. This could be due to a higher local concentration of monomer on the aggregates of the salt as previously proposed.

If the effect of DPIC and TPST is mainly due to the hydrotropic behavior, it is not easily explained why there is not effect of TPAsC and TPPC. In some way the facility of reduction of the cation must be involved. As mentioned above, the increase in polymerization rate follows the trend of reduction potentials. The possible participation of the On cations in reactions with the excited states of the dye or with radicals produced in the reaction with the amine must be considered (Scheme 2). This was previously discussed in the case of DPIC [21] and it was considered not to be the main factor. Nevertheless, it must be recognized that the only two salts that have an accelerating effect, i.e. DPIC and TPST are the most easily to reduce of the series.

4. Conclusions

Four different onium salts were studied as third component for the photoinitiator system Saf/TEOHA. While the incorporation of DPIC or TPST to the photoinitiator system Saf/TEOHA enhances the polymerization rate; TPPC and TPAsC have little effects, even though their effects on the photophysics of the dye. In all cases, polyacrylamide of high molecular weight was obtained. All the initiator systems follow the general kinetic mechanism proposed for photoinitiated vinyl polymerization.

Being DPIC and TPST the more easy salts to reduce, these may be the only species accomplished to produce active radicals by an additional way. In this way, the reaction between the semireduced form of the dye and the onium cations DPI^+ and TPS^+, replacing the inactive radicals of the dye by active species capable of initiate vinyl polymerization by an additional way, could be responsible for the observed increment in the polymerization rate. However, various secondary reactions with the onium salt might be cooperating, producing the final observed effect on the polymerization rate. A second aspect important to the use of onium salts as members of three-component system is their behavior as hydrotropes, allowing a higher local concentration of monomers and co-initiators, this characteristic being in particular suitable for aqueous systems.

Acknowledgments

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