

Photoreaction and photopolymerization studies on phenoxazin dyes/diphenyliodonium chloride salt

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Abstract

The photophysics and photochemistry of the dyes resazurin (Rz) and resorufin (Rf) in absence and presence of diphenyliodonium chloride (DPIC) were investigated in water at pH 10. The dye/DPIC combination undergoes photoreaction via intermolecular electron transfer, resulting in photobleaching of the dye and generation of active radical species released by subsequent decomposition of DPIC. The polymerization of acrylamide in aqueous solution on visible irradiation in the presence of resazurin without the onium salt was negligible. However, it proceeds efficiently in the presence of DPIC. The polymerization follows a typical radical chain mechanism with second order termination. In the case of Rf/DPIC the photobleaching is very important, and no appreciable polymerization occurs.

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1. Introduction

Resazurin (Rz) is a phenoxazin-3-one dye widely used for testing various biological materials such as biochemical antioxidants [1]. Other example of its use is the “resazurin test”; in this test the reduction of Rz to resorufin (Rf) (Scheme 1) depends on the ability of metabolically active spermatozoa. This reduction is manifested by a visible change in color from blue to pink, and this color change correlates significantly with concentration of motile spermatozoa [2]. Resorufin has also been used as a probe molecule to study the reorientation of solvent molecules, and has shown an interesting chemistry and photochemistry in protic solvents which strongly depends on temperature, viscosity and structure of the solvent [3–5].

We have previously reported the photoreduction of dyes (flavins, safranine, resazurin and resorufin) by amines [6–10]. In particular, in the case of Rz it was found that a clean photodeoxygenation to resorufin occurs from the quenching by amines of the triplet state of the dye. This photodeoxygenation is dependent on the amine structure and is efficient only in the presence of ter-

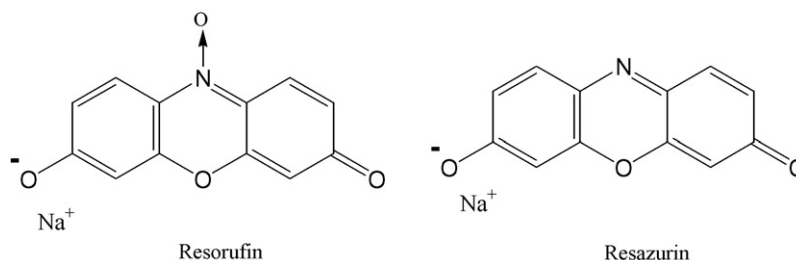
tiary aliphatic amines [10]. The photoinduced deoxygenation of N-oxides has been reported previously for other molecules [11] and was found to proceed on irradiation of N-oxide alone or in the presence of suitable electron donors such as amines [12,13]. In most cases the reaction is accompanied by side reactions and rearrangements of the N-oxide [14].

Water soluble photoinitiator systems of vinyl polymerization, especially those suitable for the visible region of the spectrum, have gained increasing interest in recent years [15]. 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. The efficiency of such a photoinitiator systems can be improved by the addition of a third component, the most commonly employed is an onium salt. Specifically, the photopolymerization of acrylamide (AA) initiated by the synthetic dye safranine-T in the presence of triethanolamine as co-initiator was investigated in aqueous solution. In the presence of diphenyliodonium chloride (DPIC) there is a marked accelerating effect on the polymerization rate [16,17].

Systems composed by a sensitizer and an onium salt have been widely employed in light-cured epoxy dental polymer systems, in this case used as photoinitiators for cationic polymerization [18–20]. On the other hand, few reports can be found

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Scheme 1.

dealing with dyes/onium salts as photoinitiator systems for radical polymerization [21,22].

Recently, we found that the related dyes resazurin and resorufin, in the presence of triethanolamine are efficient photoinitiators of aqueous acrylamide polymerization [23]. In this work we present the results of the study of the photophysics and photochemistry of Rz and Rf in the absence and in the presence of diphenyliodonium chloride in water solution at pH 10. The possible role as photoinitiators of the polymerization of acrylamide of these dyes in the presence of DPIC was investigated.

2. Experimental

2.1. Materials

Resazurin and resorufin were from Aldrich and were used as supplied. Diphenyliodonium chloride (Aldrich) and acrylamide (Sigma, >99% electrophoresis reagent) were used as received. Water was purified through a Millipore Milli-Q system. The pH was adjusted at pH 10 by the incorporation of concentrated solution of NaOH. In all cases, the solutions were deoxygenated by bubbling with high purity argon and the samples manipulation was carried out in a dark room.

2.2. Measurements

Absorption spectra were determined on a Hewlett Packard 6453E diode array spectrophotometer.

Fluorescence spectra determinations and fluorescence quenching experiments were carried out at room temperature in air equilibrated solutions ($25 \pm 1^\circ\text{C}$) with a Spex Fluoromax spectrofluorometer. Fluorescence quantum yields were determined relative to cresyl violet in methanol [24]. Fluorescence lifetime measurements were performed with an Edinburgh Instruments OB 900 time correlated single-photon counting fluorometer. The singlet quenching rate constant of Rf by DPIC was measured following the decrease of the lifetime as a function of DPIC concentration.

Transient absorption measurements were made using a laser flash photolysis equipment previously described [25]. Measurements were performed in samples subjected to a continuous bubbling with high purity argon. The triplet quenching rate constant of dyes by DPIC was measured following the decrease of the lifetime as a function of DPIC concentration.

Quantum yields of triplet species (Φ_T) were determined using zinc tetraphenylporphyrin (ZnTPP) triplet state as a reference

actinometer. Values of $7.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and 0.83 were used for the absorption coefficient and quantum yield of ZnTPP triplet state, respectively [26]. The molar absorption coefficients of triplet dyes were determined by the ground state depletion technique [27]. For both dyes, the negative absorption of the difference transient spectra matches the ground-state band. This is consistent with the lack of photoproduct formation under our conditions of laser experiments, and permits the application of the ground state depletion method to determine the molar absorption coefficients of the triplet state.

The photoreaction rates were measured by the decrease of the absorbance of the dyes at different irradiation times. Quantum yields were determined using Aberchrome 540 as actinometer [28].

The quantum yield of semioxidized dye (Φ_{rad}) was determined by laser flash photolysis, employing the triplet yield in the absence of quencher as relative actinometer, through Eq. (1).

$$\Phi_{\text{rad}} = \Phi_T \frac{A_R \varepsilon_T}{A_T \varepsilon_R} \quad (1)$$

where Φ_T is the triplet quantum yield in the absence of quencher, A_T the initial absorbance of the triplet in the absence of quencher and A_R the top absorbance of the semioxidized form, measured at the wavelength of maximum absorption. ε_T and ε_R are the absorption coefficients of the triplet and semioxidized form, respectively.

In the photopolymerization experiences, the irradiation was carried out with a Photon Technology International (PTI) illumination system comprising a 150 W Xe lamp and a monochromator. The irradiation wavelengths were at maximum of the dyes absorption and the bandwidth was 24 nm. Polymerization rates (R_p) were measured dilatometrically in deoxygenated solutions. 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 versus irradiation time plots.

Molecular weights distribution analysis was performed on a HP1100 liquid chromatography system equipped with diode-array UV-vis (DAD), refraction index (RID) and fluorescence (FLD) detection system. Separations were done at 25°C on a TOSHAAS, TSK-Gel (C0003-024) column (7.5 mm $\times$ 30 cm, 17 μm particle size). Water was used as mobile phase. The flow rate was 1.0 ml/min.

To calibrate the column seven standards of poly(ethylene-oxide) from TOSOH, TKS of different molecular weight were

Table 1
Photophysical parameters of the dyes in water at pH 10

	Resazurin	Resorufin
Absorption		
$\lambda_{\max}$ (nm)	602	572
ε ($\text{M}^{-1} \text{cm}^{-1}$)	$56,000 \pm 2800$	$55,000 \pm 2700$
Fluorescence		
$\lambda_{\max}$ (nm)	634	582
Φ_F	0.11 ± 0.01	0.38 ± 0.01
τ_F (ns)	0.7	2.8
$^1k_q \text{ DFI}^+ \text{Cl}^-$ ($\text{M}^{-1} \text{s}^{-1}$)	n.o.	2.85×10^9
$^1\eta_R$	~ 0	0.01 ± 0.001
Triplet		
Φ_T	0.07 ± 0.010	0.04 ± 0.005
$\lambda_{\max}$ (nm)	825	700
ε ($\text{M}^{-1} \text{cm}^{-1}$)	5400 ± 300	$15,000 \pm 1000$
τ_T (μs)	~ 90	~ 100
$^3k_q \text{ DFI}^+ \text{Cl}^-$ ($\text{M}^{-1} \text{s}^{-1}$)	2.6×10^6	3.0×10^6
$^3\eta_R$	0.08 ± 0.08	0.70 ± 0.07

employed. A linear relationship in a logarithmic plot between the retention times as a function of molecular weight was established.

3. Results and discussion

3.1. Fluorescence determinations

The UV–visible absorption spectrum of Rz in basic aqueous solutions consists of an intense absorption band at 602 nm ($\varepsilon = 56,000 \text{ M}^{-1} \text{cm}^{-1}$) and a weak band at 380 nm. This spectrum is similar to that reported in methanolic solution [10]. The bands are assigned to the $\pi\pi^*$ transition of the phenoxazin-3-one, and to the weak $n\pi^*$ transitions of the N-oxide, respectively. The visible spectrum of Rf is characterized by an intense band centered at 572 nm ($\varepsilon = 55,000 \text{ M}^{-1} \text{cm}^{-1}$) with a shoulder at 535 nm. The absorption of the dyes increases linearly with the concentration in the range 0.5–20 μM . This indicates that the aggregation of the dye is not appreciable in this concentration range.

Rz presents fluorescence emission with a band centered at 634 nm. The fluorescence quantum yield determined was 0.11. Rf exhibits a strong fluorescence emission with a maximum at 582 nm. A quantum yield of 0.38 was determined for this dye. The fluorescence lifetimes in water at pH 10, were 0.7 and 2.8 ns for Rz and Rf, respectively. The rather higher fluorescence quantum yield of Rf as compared to Rz, is in agreement with its longer lifetime. The photophysical data for both dyes are summarized in Table 1, and in the case of Rf they are comparable in magnitude with those reported by Flamigni et al. [5] in ethanol.

The singlet quenching rate constant for Rf by DPIC in water at pH 10 obtained by Stern–Volmer analysis was $2.85 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$. It was not possible to determine the quenching rate constant for Rz due to the short lifetime of the dye and the limited solubility of DPIC in water.

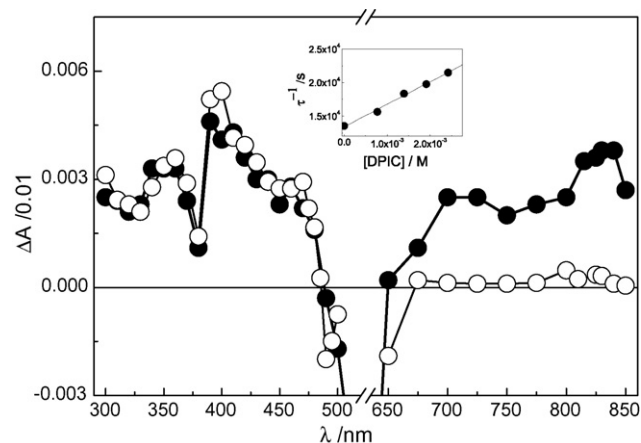


Fig. 1. Transient absorption spectra of Rz $1 \times 10^{-5} \text{ M}$ in absence (●) and presence (○) of 0.02 M DPIC in water at pH 10 (1 μs after laser flash). Inset: Stern–Volmer plot for the triplet quenching by DPIC.

3.2. Laser flash photolysis determinations

Transient absorption spectra of Rz at pH 10 were obtained in the absence and presence of DPIC (Fig. 1).

In the absence of DPIC at 1 μs after the laser pulse, two bands can be seen, one in the 650–900 nm region assigned to the triplet and the other at 300–490 nm assigned to the combined absorption of the triplet and the radical ions formed by an autoquenching process via electron transfer [10]. The negative absorption (500–620 nm) and the valley at 379 nm indicate the depletion of the ground state. A triplet quantum yield of 0.07 was measured at 825 nm using $\varepsilon_T = 5400 \text{ M}^{-1} \text{cm}^{-1}$ at 825 nm and $\varepsilon_G = 56,000 \text{ M}^{-1} \text{cm}^{-1}$ at 602 nm. The triplet lifetime in water at pH 10 was ca. 90 μs approximately (Table 1).

In the presence of DPIC a quenching of the triplet can be observed, while the absorption in the region 300–500 nm presents only slight changes. In the inset A of Fig. 1 it can be seen an increase in the absorption near 460 nm, which can be assigned to the semioxidized radical form of the dye [10]. These observations can be attributed to an electron transfer reaction

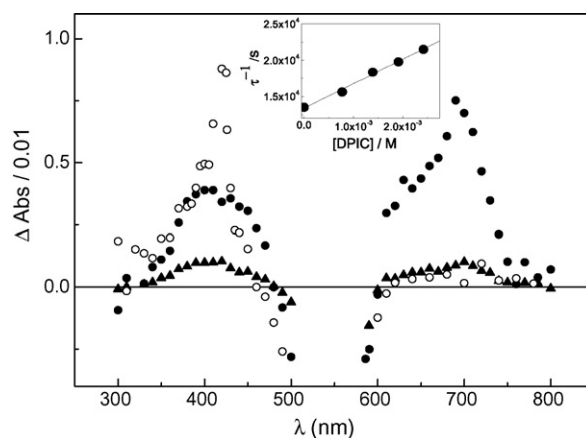


Fig. 2. Transient absorption spectra of Rf $1 \times 10^{-5} \text{ M}$ in absence (●, ▲) at 10 and 100 μs after flash respectively and in the presence (○) of $1 \times 10^{-3} \text{ M}$ DPIC in water at pH 10 at 100 μs after laser flash. Inset: Stern–Volmer plot for the triplet quenching by DPIC.

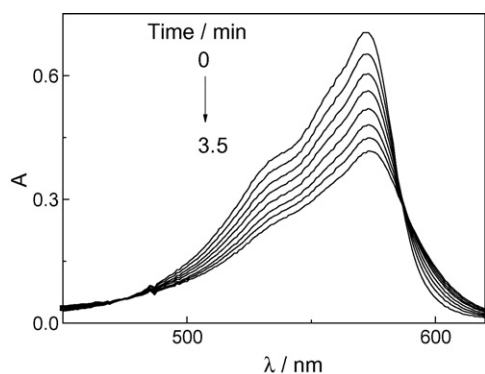


Fig. 3. Changes in the absorption spectrum of Rf with irradiation time (min). Rf 1.2×10^{-5} M and DPIC 1×10^{-3} M in water at pH 10.

from the triplet-excited state of the dye to the onium salt. The SV plot for the triplet quenching by DPIC is presented in the inset B in Fig. 1. The bimolecular quenching rate constant obtained was $2.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

In Fig. 2 the transient absorption spectra of Rf in aqueous solution at pH 10 in the absence and presence of DPIC are presented.

At $10 \mu\text{s}$ the spectrum obtained in absence of DPIC exhibits two positive absorption bands, one in the 600–750 nm region assigned to the T–T transition and the other in the 340–470 nm region due to the combined absorption of singlet and triplet state and the radicals formed by an autoquenching process via electron transfer [10]. A negative absorption band that corresponds to the ground state depletion in the 500–600 nm zone is also present. A triplet quantum yield of 0.04 was measured at 700 nm using $\varepsilon_{\text{T}} = 15,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 700 nm and $\varepsilon_{\text{G}} = 55,000$ at 572 nm and the triplet lifetime in water at pH 10 was ca. $100 \mu\text{s}$ (Table 1).

In presence of DPIC the quenching of the triplet state can be seen in the region of 600–750 nm, and a strong band appears with a maximum at 425 nm. This band can be attributed to the semioxidized radical ion of the dye [10]. The phenyl radical produced by fragmentation of the DPIC are not readily detectable in the spectral region near UV and visible [29]. The bimolecular quenching rate constant obtained was $3.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

3.3. Photochemical reaction

The photochemical reaction of Rf and Rz mediated by amines has been described [11]. No reports in literature describing the reaction of these dyes in the presence of electron acceptors were found. When Rf is exposed to visible light in the presence of DPIC, bleaching of the dye was observed (Fig. 3). This effect is considerably less for Rz. In Fig. 4 can be observed that the absorption changes of Rz under identical experimental conditions as employed in the experiment shown in Fig. 3 take a much longer time to occur. On the other hand, in the absence of DPIC, both dyes are photostable.

The kinetic of photobleaching was studied by monitoring the relative change in the absorbance of the dyes at their absorption maxima with the irradiation time.

The mechanism can be postulated (Scheme 2) in order to explain the results, where k_{F} , $^1k_{\text{d}}$, k_{ISC} , $^3k_{\text{d}}$, $^1k_{\text{q}}$ and $^3k_{\text{q}}$ are

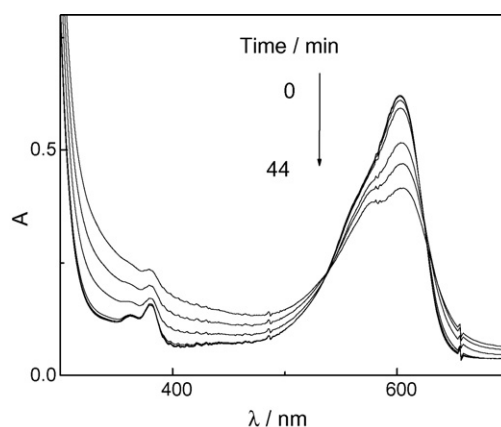
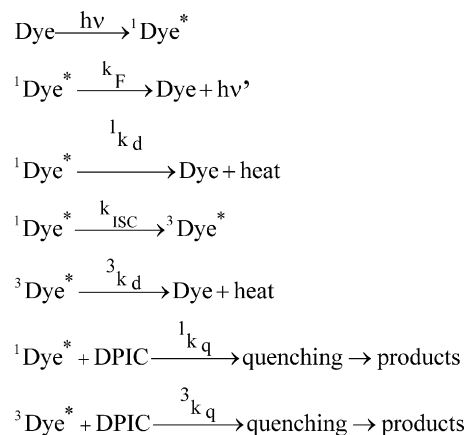


Fig. 4. Changes in the absorption spectrum of Rz with irradiation time (min). Rz 1.2×10^{-5} M and DPIC 1×10^{-3} M in water at pH 10.



Scheme 2.

the fluorescence, singlet non-radiative deactivation, intersystem crossing, triplet non-radiative deactivation, singlet quenching and triplet quenching rate constants, respectively.

Fig. 5 shows the photobleaching quantum yield (Φ_{R}) as a function of DPIC concentration. From a steady state analysis of the mechanism shown in Scheme 1, Eq. (2) can be obtained for Φ_{R} . The experimental results were fitted using the Eq. (2) with the kinetics parameters informed in Table 1. In this analysis it was considered that both singlet and triplet excited states are

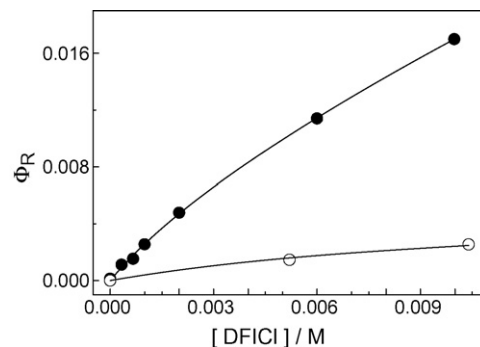


Fig. 5. Quantum yield of reaction between Rz (○) and Rf (●) with DPIC as a function of DPIC concentration in water at pH 10. Rf 1.2×10^{-5} M Rz. 1.0×10^{-5} M.

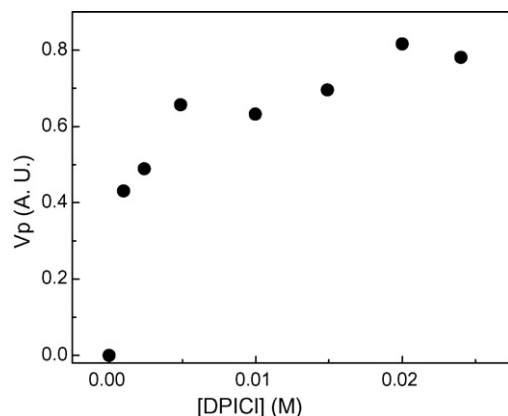


Fig. 6. Relative polymerization rates in arbitrary units vs. DPIC concentration for the polymerization of AA: 2M in water (pH 10) in the presence of RZ = 4×10^{-6} M.

involved.

$$\Phi_R = \frac{{}^1k_q[\text{DPIC}]}{{}^1k_q[\text{DPIC}] + ({}^1\tau_0)^{-1}} {}^1\eta_R + \frac{k_{\text{ISC}}}{{}^1k_q[\text{DPIC}] + ({}^1\tau_0)^{-1}} \frac{{}^3k_q[\text{DPIC}]}{{}^3k_q[\text{DPIC}] + ({}^3\tau_0)^{-1}} {}^3\eta_R \quad (2)$$

In Eq. (2) ${}^1\tau_0$ and ${}^3\tau_0$ are the singlet and triplet lifetimes of the dyes, and ${}^1\eta_R$ and ${}^3\eta_R$ are the efficiencies of photoreactions of the singlet and triplet states respectively. For the fitting k_{ISC} was calculated from the values of ${}^1\tau_0$ and Φ_T , and ${}^1\eta_R$ and ${}^3\eta_R$ were used as adjustable parameters.

The values of ${}^1\eta_R$ and ${}^3\eta_R$ obtained (Table 1) show that the efficiency of photoreaction from the triplet state is the principal contribution to Φ_R for Rf. In the case of RZ the contribution from the singlet state was negligible up to 0.01 M DPIC. The Φ_R of RZ is considerable less than the corresponding value of Rf. This fact is in agreement with the polymerizations results, discussed in the next section. The Φ_R determinations were made in absence of monomer, a slightly photoprotector effect was observed in the presence of acrylamide.

3.4. Photopolymerization results

In the absence of iodonium salt no photopolymerization of AA was observed for both dyes. When RZ is irradiated in the presence of DPIC, it is possible to observe that the photopolymerization proceeds efficiently. On the other hand, polymerization does not occur in the system Rf/DPIC. This is not unexpected, since the dye suffers a fast decomposition in the presence of the salt that is not inhibited by the monomer. Although the presence of radicals originated by electron transfer quenching of the excited states of the dye is evidenced by laser flash photolysis experiments, the very fast fading of the dye prevents a generation of active radicals sustained in time necessary in order to afford a measurable amount of polymeric material.

Fig. 6 shows the initial polymerization rate in arbitrary units measured dilatometrically against DPIC concentration.

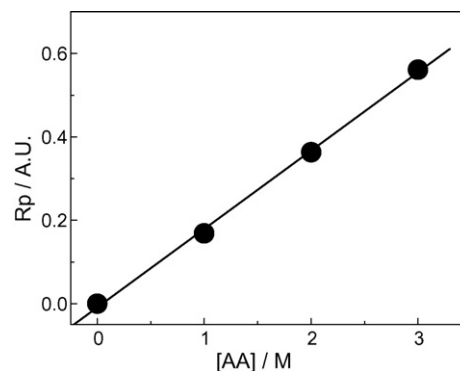


Fig. 7. Dependence of R_p on the monomer concentration for the polymerization of AA in water (pH 10) in the presence of RZ = 4×10^{-6} M and DPIC = 5×10^{-3} M.

The polymerization rate shows a sharp augment with the salt concentration up to 5×10^{-3} M; beyond this concentration the increment is less pronounced.

To check the polymerization kinetics, we investigated the dependence of the polymerization rate on the monomer concentration and light intensity for the system RZ/DPIC. The results are shown in Figs. 7 and 8, respectively.

The solid lines correspond to a unitary slope for the monomer concentration dependence and an order of 0.5 on the light intensity dependence. Therefore, the rate law conforms to the classic radical polymerization mechanism with second order termination, and may be written as:

$$R_p \propto [M]\Phi_{\text{rad}}^{1/2} \quad (3)$$

Based on the photochemical behavior of the RZ in the presence of DPIC and taking into account the negligible photoprotector effect observed in the presence of AA, a mechanism of initiation of polymerization is proposed in Scheme 3.

From the mechanism and assuming that the interaction between the singlet state of the RZ and DPIC does not lead to polymerization, the yield of active radical (Φ_{rad}) is given

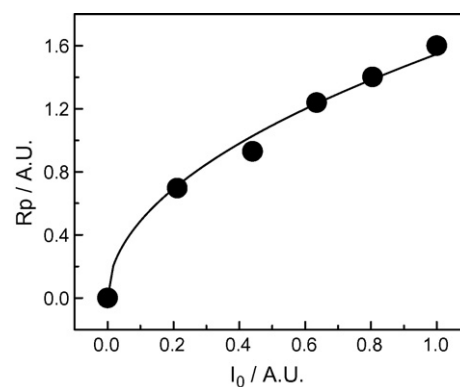
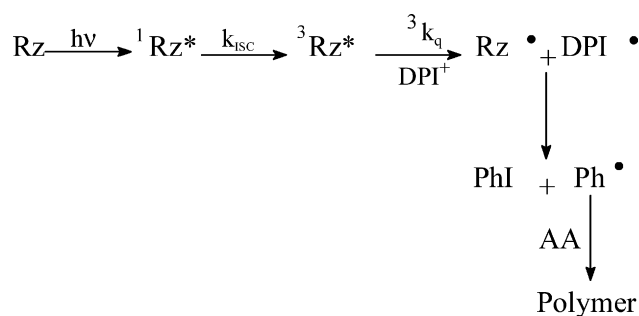


Fig. 8. Dependence of the light intensity (I_0) on the polymerization rate for the polymerization of AA: 3M in water (pH 10) in the presence of RZ = 4×10^{-6} M and DPIC = 5×10^{-3} M. The solid line was calculated assuming a square root dependence with light intensity.



Scheme 3.

by Eq. (4):

$$\Phi_{\text{rad}} = \Phi_{\text{T}} \left(\frac{{}^3k_q {}^3\tau_0 [\text{DPIC}]}{1 + {}^3k_q {}^3\tau_0 [\text{DPIC}]} \right) \beta \quad (4)$$

where Φ_{T} is the intersystem crossing quantum yield 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 radicals, as given by Equation (4) [16]. Fig. 9 shows a plot of the square of the polymerization rate (R_p^2) as a function of DPIC concentration. Employing as variable parameters ${}^3K_{\text{SV}} = {}^3k_q {}^3\tau_0$ and β , an appropriate fitting of the experimental results are obtained (solid line in Fig. 9), producing a value of 247 M^{-1} for ${}^3K_{\text{SV}}$. From the latter, and considering the experimental value of ${}^3k_q = 2.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ obtained in the absence of monomer as a good approximation for the quenching rate constant in the polymerizing medium, a value of $95 \mu\text{s}$ is obtained for ${}^3\tau_0$, being this similar to the experimental value in the absence of monomer. These results are in agreement with the mechanism proposed in Scheme 2, where the active radicals are formed exclusively from the triplet state of the dye, through an electron transfer reaction between Rz and DPIC.

Experiments were carried out in order to compare the polymerization of aqueous solutions of AA 2M initiated by Rz ($4 \times 10^{-6} \text{ M}$) and TEOHA or DPIC ($5 \times 10^{-3} \text{ M}$), it was found that the polymerization rate is twice higher using the amine as co-initiator system. However, in both cases a polymer of $1.3\text{--}1.4 \times 10^6 \text{ Da}$ of molecular weight was obtained. Thus, the

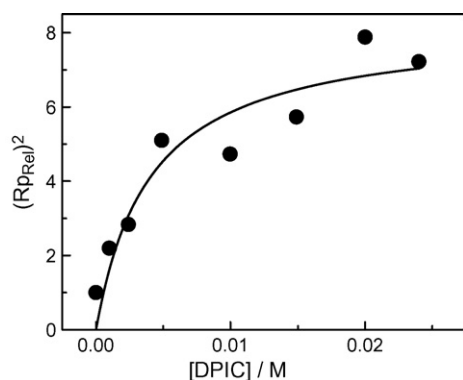


Fig. 9. Plot of R_p^2 as a function of DPIC concentration. The solid line corresponds to the free radical quantum yield calculated with Eq. (4).

photoinitiator system Rz/DPIC has the advantage of producing high molecular weight polymer with a lower rate of initiation allowing a suitable control of the reaction, which is valuable in many technological applications.

4. Conclusions

The Rz/DPIC combination system readily undergoes a fast photoreaction upon irradiation by visible light through electron transfer mechanism. For this system the photoreaction produces very significant photobleaching of the dye mainly from triplet state. Although the presence of radicals was observed by laser flash photolysis, the very efficient photobleaching of the dye prevents a generation of active radicals necessary to afford a measurable amount of polymeric material.

On the other hand, for the Rz/DPIC system, the photobleaching observed was notable less and the radicals were also observed by laser flash photolysis. In this case the polymerization takes place producing polyacrylamide with high molecular weight, following a typical vinyl polymerization mechanism with second order termination. From these experimental results an initiation mechanism was proposed, where the active phenyl radicals are formed by fragmentation of onium salt subsequent to an electron transfer from the triplet state of the Rz to DPIC.

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