Full Length Article

Photochemical study of Eosin-Y with PAMAM dendrimers in aqueous solution

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ABSTRACT

A steady-state and time-resolved study of the xanthene dye Eosin-Y (Eos) in the presence of amino-terminated polyamidoamine (PAMAM) dendrimers in alkaline aqueous solution is presented. Stationary photolysis experiments in deaerated and air equilibrated solutions were carried out. The absorption spectra of the photolyzed solutions in the absence of oxygen showed the formation of several intermediate species. With the aid of laser flash photolysis technique (LFP) those transients could be ascribed to semireduced and partially debrominated species of Eos. The triplet quenching rate-constant (^3k_q) and radical quantum yields (Φ_R) were determined by LFP. In the presence of PAMAM, the triplet lifetime of Eos is greatly decreased and the data fitted to a Stern–Volmer treatment. These experiments indicated that the electron transfer from dendrimers to Eos is a highly favored process. Based on the results found in this work, we concluded that Eos/PAMAM couple might act as a promising photoinitiator of vinyl polymerization with low ecological impact.

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1. Introduction

Nowadays, dendrimers and dendrons are considered one of the most attractive research fields in polymer chemistry because of their well-defined structures, versatility and potential applications [1–3]. These molecules can be modified by introducing functional groups and specific structural units at different levels of their structure: core, branches or periphery, giving rise to well-structured and highly functionalized molecules [4]. Due to this architecture, dendrimers can both encapsulate substrates and bind molecules at the periphery through branch termini by supramolecular interactions (H bonding, ionic bonding, coordination).

Some authors reported experimental evidence for covalently fixed unimolecular micelles, as well as for the encapsulation of several molecular guests at the end of the 1980s [5,6]. Subsequently, a variety of dendrimers and interdendritic (or dendronic) interactions were shown to contribute – eventually in synergy – to guest encapsulation by forming more complex supramolecular nanoassemblies [2]. Thereafter, guest encapsulation has appeared as one of the major dendritic capabilities because of the potential applications for drugs delivery [7,8] and nanomedicine [9,10].

Most of studies have concerned the polyamidoamine (PAMAM) dendrimers, because they are commercially available, are water-soluble and can be functionalized in the periphery. As an example, it was successfully proposed an on-demand drug delivery/release system that uses magnetothermally responsive of doxorubicin-encapsulated supramolecular magnetic nanoparticles for highly effective in vivo cancer treatment [11].

The use of synthetic dyes as probe molecules in a variety of organized systems is well documented [12–15]. In particular dyes were encapsulated in or covalently bound to dendritic structures for several applications [16–20]. It is of interest to investigate the photophysics and photochemistry of dyes in the presence of dendrimers. In particular, the use of dyes in photopolymerization has gained increasing relevance owing to the exploitation of visible radiation, less expensive than UV or thermal methods [21]. The system dye-dendrimer was proposed as photoinitiating system in order to synthesize nanoparticles of specific structural characteristics [20,22].

The most common photoinitiating systems for vinyl polymerization in the visible are composed by a dye and an amine as an electron donor (co-initiator). Our group has been studying for over a decade the electron-transfer reactions of several families of dyes, in both aqueous and microheterogeneous media [23–29]. We have been interested in the mechanistic aspects of these systems. By means of laser-flash photolysis, we found that the photo-initiation mechanism involves an electron transfer from the co-initiator to the triplet state of the dye [30–34]. Then, active radicals
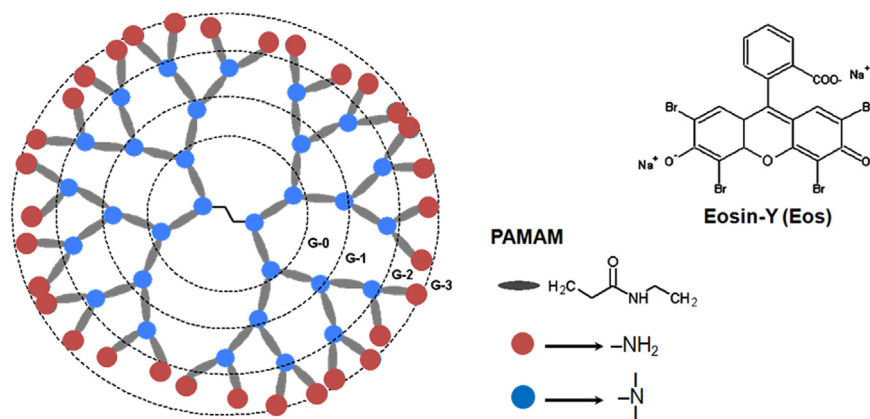
Scheme 1. Structures of Eosin-Y and PAMAM dendrimers.

derived from the amine are responsible for initiating the polymerization.

The xanthene dye Eosin-Y has been frequently used in several applications (laser dye, fluorescent probe, biological stain, sensitizer, etc.), and recently it has been employed in polymerization and the synthesis of nanoparticles [35,36]. It is known that the triplet state of Eosin-Y is efficiently quenched by electron donors and acceptors [37]. In a previous work, we studied the polymerization of acrylamide in reverse micelles of BHDC (benzyl-hexadecyl-dimethylammonium chloride), photoinitiated by Eosin-Y and triethanolamine [38]. The effect of the charge and localization of the dye in the reverse micelles on the polymer properties was assessed. We investigated the factors that affect the properties of polymeric particles obtained by this visible-light initiating system, and compared them with those previously reported on Safranine-O [39].

Due to the PAMAM dendrimers have many amine groups in their structure, we are interested in studying the dye-dendrimer interactions in particular the triplet state of the dye, because this environmentally-friendly system would be appropriate for potential applications in field of photopolymerization. We recently characterized the interactions between Eosin-Y and amino-terminated PAMAM dendrimers of low generations (0–3) in alkaline water solution [40]. In Scheme 1 are depicted the structures of Eosin-Y and PAMAM dendrimers, where each generation was demarcated with dash circles. The effect of concentration and generation of the dendrimer on the photophysics of Eosin-Y was evaluated by means of absorption and fluorescence spectroscopies. The observed spectral changes were ascribed to the dye/dendrimer association. The binding constants values indicated strong interactions between Eosin-Y and PAMAM, and suggested the formation of host/guest systems with larger dendrimers.

In this paper we studied for the first time the photochemistry and the triplet state properties of the xanthene dye Eosin-Y in the presence of amino-terminated PAMAM dendrimers, in alkaline aqueous solution. Steady-state photolysis was monitored by absorption spectroscopy. The formation of fluorescein as a final product of the reaction was confirmed by absorption and fluorescence spectroscopies, and by the respective singlet lifetimes. The effect of the dendrimer structure on the triplet excited state was investigated by laser flash photolysis. We have found that the dendrimers quench efficiently the dye and the photodecomposition is mediated by the triplet state.
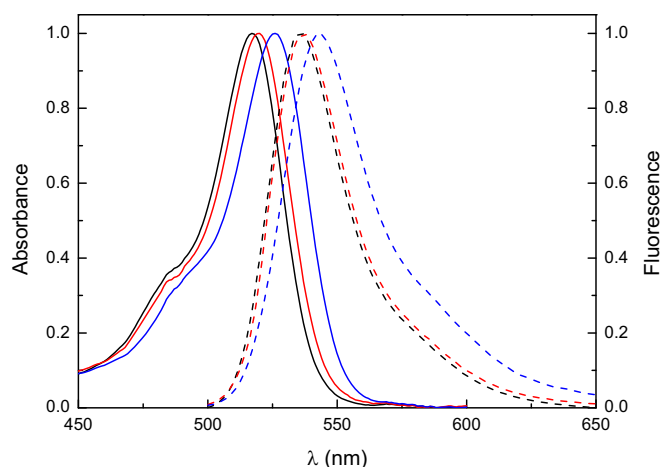

Fig. 1. Normalized absorption (solid line) and fluorescence (dash line) spectra (λ_{exc}=517 nm) of alkaline aqueous solution of Eos, in the absence (black) and in the presence of PAMAM-G0 16 mM (red) and PAMAM-G3 0.5 mM (blue). The concentrations of Eos were 5 and 1 μM for absorption and fluorescence experiments, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Materials and methods

Eosin-Y (Eos) and amino-terminated polyamidoamine dendrimers (20% in methanol) of generations 0–3 (from here on PAMAM-Gn, with n=0, 1, 2, 3) were from Aldrich and used without further purification. N-Acetyl-ethylenediamine (AEDA) from Aldrich was purified by sublimation. For dilutions, HPLC grade methanol (Sintorgan) and Milli-Q distilled water were used. The pH of the solutions was adjusted at 9.5 by analytical grade NaOH. Triethanolamine (TEOA) was commercially available and purified by standard procedures.

Absorption spectra were recorded on a Hewlett Packard 6453E diode array spectrophotometer. Fluorescence measurements were performed by means of a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer. Singlet lifetimes were registered by time-correlated single photon counting experiments on a FL 900 Edinburgh Instruments, equipped with a H_2 lamp. A 1-cm-pathlength quartz cuvette was used in all spectroscopic assays.

Dendrimers solutions were properly diluted with methanol as necessary. Throughout all experiments the addition of the
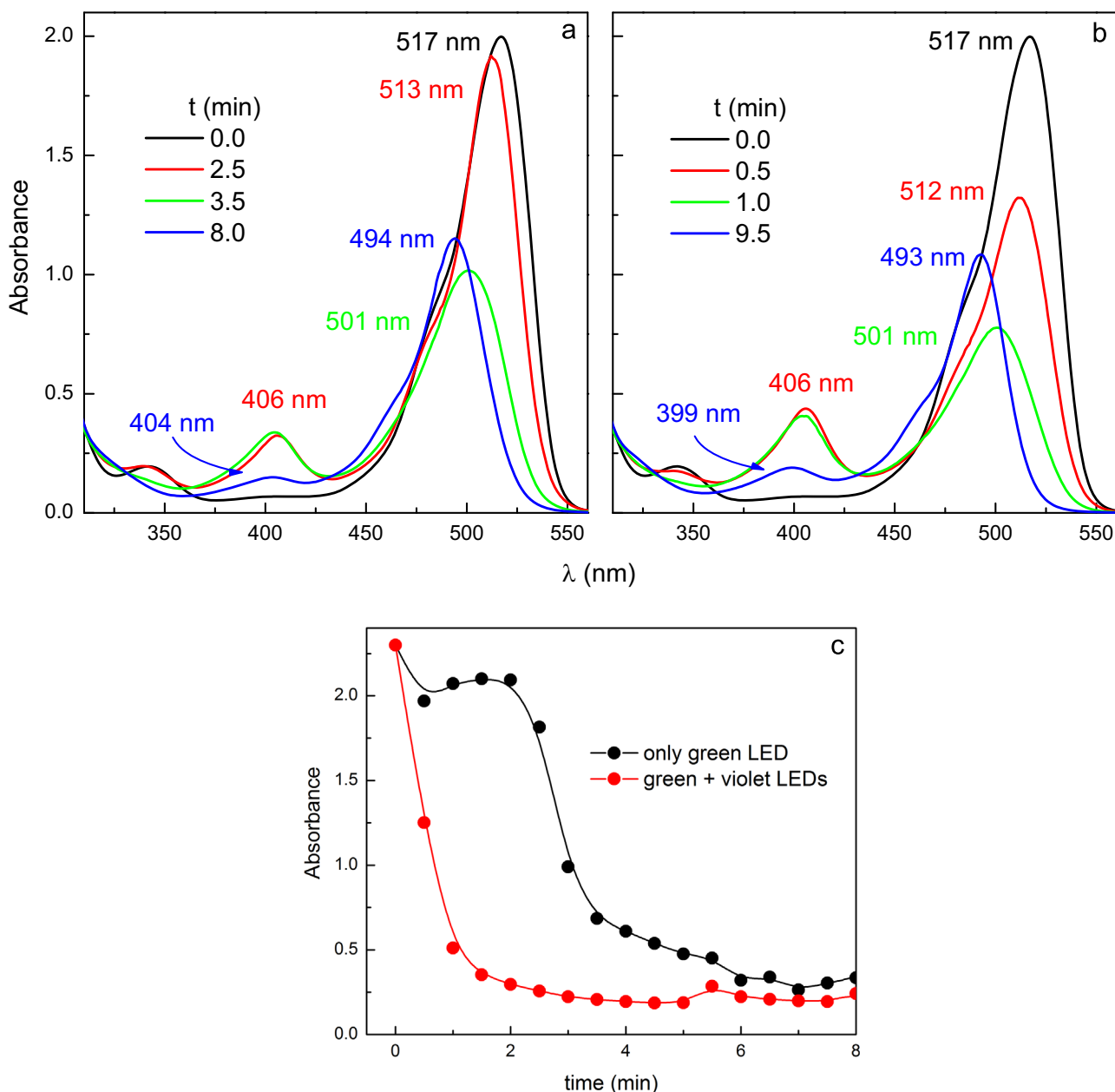
Fig. 2. Steady-state photolysis of deaereated alkaline aqueous solution of Eos (initial concentration 2×10^{-5} M) in the presence of PAMAM-G0 8×10^{-5} M: (a) Absorption spectra obtained by irradiating with only green LED; (b) Absorption spectra obtained by irradiating with green plus violet LEDs; (c) Absorbance at 517 nm vs. photolysis time for both experiments. The maxima of main bands are highlighted.

dendrimers was performed by microsyringes under constant stirring, such that the methanol content in the Eos solutions was < 5%. There were no changes in the spectra by this additional methanol, as verified through blank tests. Water solutions were prepared with bi-distilled water.

Steady-state photolysis were carried out by irradiation with light-emitting diodes (LEDs) of $\lambda_{max} = 510 \pm 22$ nm (green LED, 5.9 mW) and $\lambda_{max} = 412 \pm 9$ nm (violet LED, 4.5 mW). Transient absorption spectra and triplet quenching were determined by laser flash photolysis. A Spectron SL400 Nd:YAG laser generating 532 nm laser pulses (20 mJ per pulse, *ca.* 18 ns FWHM) was the excitation source. The experiments were performed with rectangular quartz cells with right angle geometry. The laser beam was defocused in order to cover all the path length (10 mm) of the analyzing beam from a 150 W Xe lamp. The detection system comprised a PTI monochromator coupled to a Hamamatsu R666

PM tube. The signals were acquired and averaged by a digital oscilloscope (Hewlett-Packard 54504) and then transferred to a computer. All the photolysis determinations were performed at 25 ± 1 °C and the solutions were de-oxygenated by bubbling with solvent-saturated high purity argon.

3. Results and discussion

3.1. Steady state photolysis

In alkaline aqueous solution (pH 9.5) Eos is in the dianionic form with $\lambda_{max} = 517$ nm [41] and binds strongly to PAMAM dendrimers [40], as reflected in the absorption and fluorescence spectra of the dye (Fig. 1). When Eos was irradiated with visible

light in the presence of PAMAM dendrimers, a photochemical process occurred.

Air saturated or air-free solutions (Ar atmosphere) were separately analyzed. No appreciable changes were observed in air atmosphere, whereas a different color was apparent in Ar equilibrated solutions after the same irradiation time. The course of the photolysis was monitored by UV–visible spectroscopy. Fig. 2 shows the changes in the absorption spectra of Eos in the presence of PAMAM-G0 at selected irradiation times. Similar results were found for other generations of PAMAM (not shown).

In a first test, the solutions were irradiated with a green LED, near to the absorption maximum of the dye. The main absorption band experienced an intensity decrease along with a progressive blue shift (Fig. 2a). Simultaneously, the growth of a new absorption band centered at 406 nm was observed. At the end of the photolysis the spectrum of the colored photoproduct showed a main band with $\lambda_{max}=494$ nm and a minor band at *ca.* 400 nm. In a second test (Fig. 2b) the Eos-PAMAM solutions were irradiated with a combination of one green LED plus one violet LED. Although Fig. 2b shows similar qualitative results as Fig. 2a, it can be seen that the photolysis occurred more quickly by irradiating with both LEDs. The absorbance of the band centered at 517 nm scarcely decreased after 2.5 min of irradiation with the green LED, whereas the intensity dropped around one-third in 5-fold less time with both LEDs. This difference in the rate of the photodecomposition of the dye is apparent on Fig. 2c, from which it may be inferred that the irradiating conditions determine the photolysis mechanism. By irradiating only around 517 nm a lag time in the decomposition is observed (slow mechanism), whereas by irradiating at 517 nm and at *ca.* 400 nm simultaneously, the photolysis process is accelerated (fast mechanism).

Similar spectral shifts were reported for the photolysis of Eos and other xanthene dyes in aqueous [42,43] and methanolic solution [44,45] in the presence of several electron-donor molecules, and were ascribed to the partial debromination of the dye. Some authors showed the formation of fluorescein as the final photoproduct, which has $\lambda_{max}=495$ nm and has no bromine substitution [42,44,45]. Zwicker and Grossweiner have studied the electron transfer from phenol to the triplet excited state of Eos in aqueous solution by flash spectroscopy [43]. They registered the absorption spectrum of the semireduced species of Eos and proposed that debromination of the dye occurs from its di-anion radical. Kimura et al. also demonstrated that the semireduced species is the precursor for the photodebromination [45]. The

authors showed the occurrence of a band at *ca.* 400 nm during photolysis of alkaline methanolic solution of Eos in the presence of tertiary amines [44,45]. From ESR experiments they ascribed this band to the semireduced eosin and proposed that semireduced forms of partial debrominated eosins are produced as intermediate species in the debromination process.

Based on these arguments, the bands registered at around 400 and 500 nm (Fig. 2) might be ascribed to the transient radicals and partially debrominated Eos species, respectively.

To determine if photolysis of Eos in the presence of dendrimers leads to fluorescein, deaerated Eos/PAMAM solutions were spectroscopically compared after ten minutes of irradiation with commercial fluorescein in alkaline aqueous solution. The normalized absorption and fluorescence spectra of the photolyzed samples coincide in shape and position with those of fluorescein (not shown for simplicity). Only slight shifts were detected mainly in the presence of PAMAM-G3, which could be due to an effect of the environment [40].

The fluorescence lifetime for the photolyzed solutions also equate that of fluorescein, within experimental error, as determined by singlet photon counting in air equilibrated atmosphere at pH 9.5. Therefore, spectroscopic measurements are in correspondence with fluorescein as a final photoproduct.

Summarizing, the experimental data presented in this section and the reports on this matter support the conclusion that photolysis of alkaline aqueous solution of Eos in the presence of PAMAM dendrimers is promoted by a debromination process. This photochemical reaction involves the formation of semireduced species from the dye as intermediates, generated by electron transfer from these amino dendrimers to excited Eos.

3.2. Laser flash photolysis

In order to characterize intermediate species formed by interaction between PAMAM dendrimers and Eos, laser flash photolysis experiments were carried out. The triplet-excited state of Eos has an apparent absorption maximum in 580 nm, plus a lower band around 400 nm [46]. In the absence of quenchers the triplet decays in tens of microseconds mainly by self-quenching or triplet–triplet annihilation, to give its respective semireduced and semioxidized forms [46]. These second-step intermediates absorb at 405 and 450 nm, respectively [46,47]. In Fig. 3 are exemplified the transient absorption spectra of Eos in the presence of dendrimers PAMAM-G0 and PAMAM-G3, obtained at several times after laser pulse in
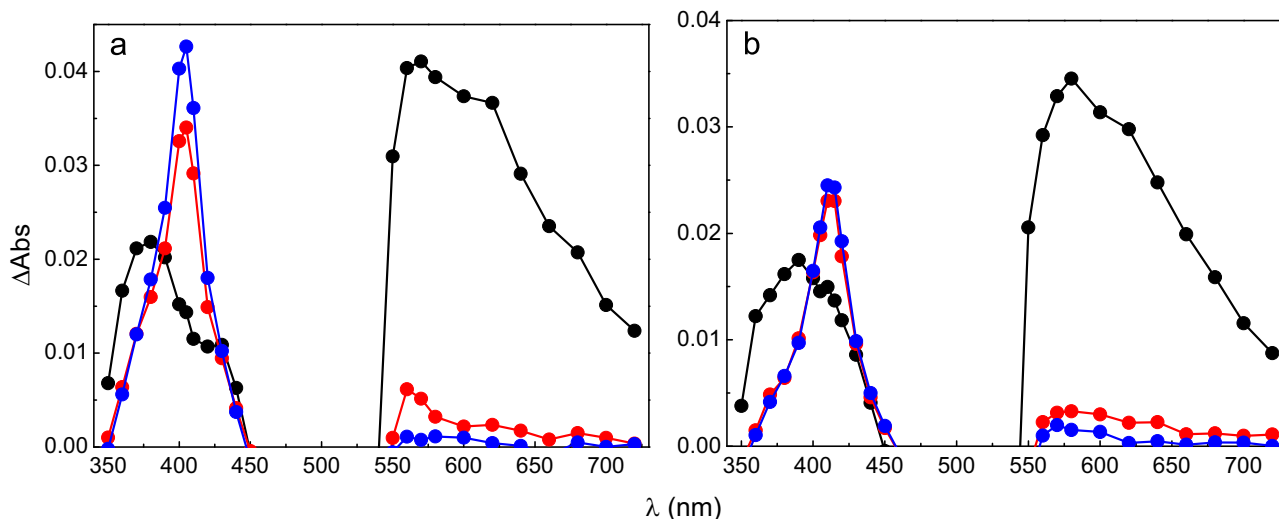

Fig. 3. Transient absorption spectra of alkaline aqueous solution of Eos *ca.* 1×10^{-5} M at 0 (black), 30 (red) and 100 μs (blue) after laser pulse, in the presence of: (a) PAMAM-G0 8.1×10^{-5} M, and (b) PAMAM-G3 1.2×10^{-5} M. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Time course of the absorbance for Eos *ca.* 1×10^{-5} M aqueous solutions in the presence of: (a) PAMAM-G0 8.1×10^{-5} M, and (b) PAMAM-G3 1.2×10^{-5} M. Blue lines correspond to the exponential fitting functions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
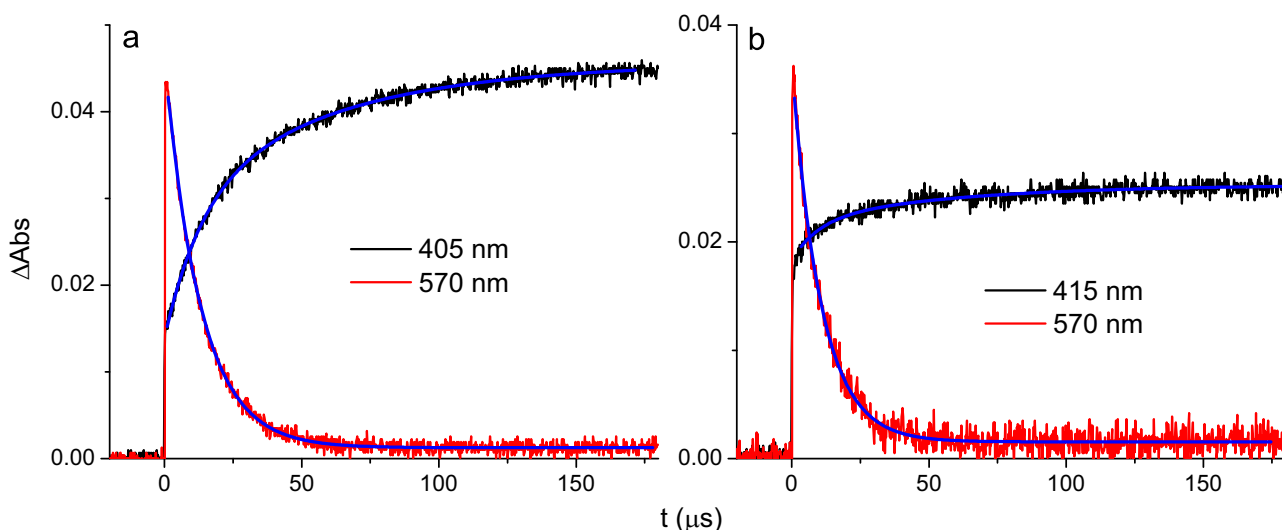
Table 1
Apparent lifetimes obtained from absorption profiles (all data in µs) shown on Fig. 4.

PAMAM	Triplet region (570 nm)	Radical region (~400 nm)	
	$^3\tau$	t_1	t_2
G0	13	13	58
G3	11	10	57

deaerated aqueous solution at pH 9.5. The dendrimer concentrations were chosen such that around 90% of the triplets were intercepted (PAMAM-G0 8.1×10^{-5} M, and PAMAM-G3 1.2×10^{-5} M). Since the triplet-state spectra of Eos at cero time in the absence and presence of PAMAM are superimposed, the respective spectrum with no additives was not included in Fig. 3 for simplicity. At short time, two main absorption bands are distinguished at 350–450 and 550–700 nm regions, for both dendrimer generations assayed. These spectra may be ascribed to the triplet state of Eos according to bibliographic data. The wavelength interval between 450–550 nm corresponds to the ground-state bleaching of the dye and is not shown for simplicity. At longer times the absorption in the region 550–700 nm is greatly decreased and a new band around 410 nm appears. Since PAMAM may act as electron donor [24] this sharp band may be ascribed to the anion radical of Eos, which seems to grow at the expense of the triplet state.

To discern the nature of the spectral bands, the kinetics of the transient formation in the presence of PAMAM-G0 and PAMAM-G3 were analyzed. Time profiles at 570 nm (Eos triplet) and around 410 nm (Eos anion radical) are shown in Fig. 4. For both generations used, the triplet depletion followed a first order kinetic and the lifetime decreased to about 10% of its value in pure water. However, signals in the radical absorption zone showed growths that were well fitted only with a biexponential function. The results of the fittings were similar in the presence of both dendrimers and are summarized on Table 1, where t_1 and t_2 correspond to the growth components. The shorter component of the growth at *ca.* 410 nm matches to the decay lifetime at 570 nm. This suggests a sequence of step reactions which forms a transient at the expense of the triplet state, and then this second transient originates another new species. The formation of this third intermediate is characterized by the longer time component of the
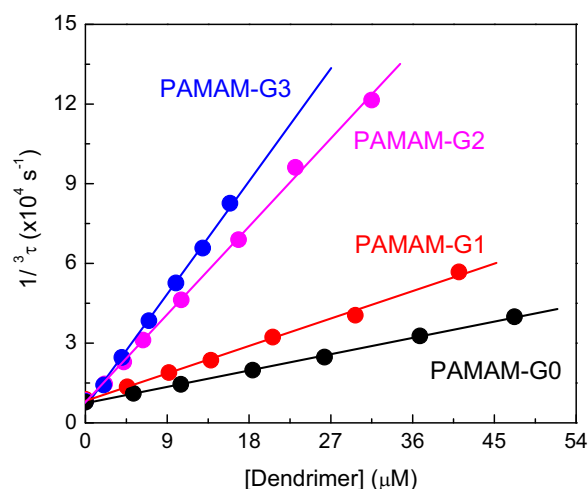

Fig. 5. Stern–Volmer plots for the quenching of triplet-excited state of Eos *ca.* 1×10^{-5} M with PAMAM dendrimers in aqueous solution at pH 9.5.

growth. However, the transient absorption spectra showed no qualitative changes at 10 and 60 µs, whereby the species that follow the triplet depletion could not be elucidated by laser flash photolysis.

It has been reported the formation of two different transient species from reaction between the triplet state of Eos and EDTA in aqueous solution [46]. The authors did not observe changes in the shape of the radical absorption band, but the decays after electron transfer process were biexponential. They suggested the formation of the radical anion of Eos and another loose semireduced species, which was unidentified. This unidentified species might be a partially debrominated radical, as proposed by Kimura et al. and discussed on previous section [44,45].

To check this, we evaluated the transient spectra of the 4,5-dibromofluorescein in alkaline aqueous solution. The molecular structure of this xanthene dye is between Eos (4 bromine substitution) and fluorescein (no bromine substitution). In the presence of TEOA dibromofluorescein showed transient spectra with a sharp band around 400 nm, typical of the semireduced anion of this family of dyes (data not shown). This absorption band superimposes with that obtained for Eos in the presence of TEOA, within experimental error. These results demonstrate that the

Table 2

Bimolecular quenching rate constants for the triplet state of Eos with several electron donors.

Quencher	^3k_q (M^{-1} s^{-1})
PAMAM-G0	6.8×10^8
PAMAM-G1	1.6×10^9
PAMAM-G2	3.7×10^9
PAMAM-G3	4.7×10^9
AEDA	5.2×10^4
TEOA/H_2O	4.2×10^{7}[a]
TEOA/MeOH	1.2×10^{6}[b]
TBA/MeOH	3.2×10^{6}[b]
EDTA/H_2O	5.0×10^{5}[c]

[a] Ref. [34].
[b] Ref. [29].
[c] pH 7.2 [46].

Table 3

Radical quantum yields for Eos in the presence of electron donors in homogeneous and microheterogeneous media.
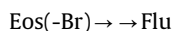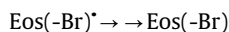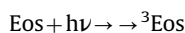
Donor/medium	[Donor] (M)	Φ_R
G0/H_2O	8.1×10^{-5}	0.186
G3/H_2O	1.2×10^{-5}	0.094
TEOA/H_2O	0.02	0.25[a]
TEOA/AOT	6×10^{-4}	0.006[b]
TEOA/BHDC	3.3×10^{-3}	0.024[b]

[a] Ref. [34].
[b] Ref. [29].

transient spectra of partially debrominated Eosins are qualitatively identical, regardless of the bromination degree.

The data collected by laser-flash photolysis experiments suggest that after light absorption, Eos in its excited triplet state (^{3}Eos) is reduced by electron transfer from the dendrimer to yield the radical anion (Eos$^•$) within the first 12 μs. Then, this radical generates another transient within the next 60 μs which we ascribed to partially debrominated species (Eos(-Br)$^•$). Although our time-resolved data are not enough to discern each transient species, we can to infer – based on the results of steady-state photolysis – that a sequence of successive debromination steps leading to fluorescein (Flu) is occurring. Therefore, the following simplified reaction mechanism can be proposed:

$$Eos + h\nu \rightarrow \rightarrow {}^3Eos$$

$${}^3Eos + e^- \xrightarrow{12\ \mu s} Eos^• \xrightarrow{58\ \mu s} Eos(-Br)^•$$

$$Eos(-Br)^• \rightarrow \rightarrow Eos(-Br)$$

$$Eos(-Br) \rightarrow \rightarrow Flu$$

In this scheme, the electron (e^-) comes from the dendrimer, Eos(-Br)$^•$ represents any debrominated radical and Eos(-Br) is any partially debrominated dye.

The quenching efficiency of four generations (PAMAM-G0 to PAMAM-G3) was evaluated recording triplet decays of deaerated aqueous solutions of Eos at 560 nm, near the absorption maximum. A shortening of the triplet lifetime was observed in the presence of dendrimers, which was registered as *ca.* 120 μs in pure alkaline water. All experimental decays were monoexponential and the bimolecular quenching rate constants (^3k_q) were evaluated according to Stern–Volmer equation:

$$^3\tau^{-1} = \tau_o^{-1} + {}^3k_q[PAMAM] \tag{1}$$

where τ_o is the lifetime in the absence of quencher. The Stern–Volmer plots were linear for all generations assessed, as it can be seen in Fig. 5.

Table 2 summarizes the ^3k_q values obtained by fitting the Stern–Volmer plots to straight lines, along with quenching rate constants previously reported by our group for some amines in homogeneous solution. It can be seen that ^3k_q correlates with the size of the dendrimer, and the lowest quenching rate constant obtained (with PAMAM-G0) is at least one order of magnitude higher than those reported for aliphatic amines. With the aim to obtain some insights about the nature of the quenching, the model compound AEDA was also used. This molecule mimics the peripheral arm of PAMAM dendrimers, because contains an amide moiety and a primary amino group in its structure. From Table 2 it can be seen that ^3k_q for AEDA is too small and practically no quenching is occurring. Such a result seems to point that the tertiary amino groups of the dendrimers are responsible for the electron transfer process.

To assess the capability of Eos/PAMAM to act as a highly efficient radical-generating system for polymerization-initiating process, radical quantum yields (Φ_R) were estimated according to:

$$\Phi_R = \frac{\Delta A_R \varepsilon_T}{\Delta A_T \varepsilon_R} \Phi_T \tag{2}$$

where ΔA_R is the absorption remaining after the total triplet depletion (400 μs) in the presence of dendrimers measured at 410 nm, and ε_R is the molar absorption coefficient of radical species. An alkaline aqueous solution of Eos in the absence of PAMAM was selected as a chemical actinometer. Thus, ΔA_T is the prompt T–T transient absorption of Eos measured at 570 nm immediately after the laser pulse; and the parameters ε_T (12,500 M^{-1} cm^{-1} at 570 nm) and Φ_T (0.61) were previously determined by our group [34].

The ε_R was determined by the ground-state depletion method [48]. The transient negative absorbance difference at the maximum wavelength of the ground absorption (ΔA_G) was compared with the absorption at the maximum of the spectrum of the semireduced dye (ΔA_R) with the aid of Eq. (3):

$$\varepsilon_R = \frac{\Delta A_R}{\Delta A_G} \varepsilon_G \tag{3}$$

here ε_G is the molar absorption coefficient of the ground state at the wavelength of its absorbance maximum. According to Eq. (3), a value of $\varepsilon_R = 27,700$ M^{-1} cm^{-1} at 405 nm was estimated. The Table 3 summarizes the Φ_R obtained in the present work along with those previously reported for Eos in another conditions, for comparison purposes.

Several assessments can be made from the results on Table 3. First, the Φ_R obtained for PAMAM-G0 is twice that for PAMAM-G3. These values do not reflect the trend showed with the ^3kq (Table 2). At dendrimer concentrations used there is about 10% of associated Eos in the presence of PAMAM-G3, whereas practically no binding occurs with PAMAM-G0. A possible explanation is that the rate of electron transfer depends on the relative number of amino groups in the dendrimers and therefore, it increases with the size of the dendrimer. On the other hand, in the presence of PAMAM-G0 the incipient radicals quickly diffuse into the bulk solution, whereas back-recombination of the radicals is favored in PAMAM-G3 due to that partial binding. Second, the radical efficiency with TEOA is barely two- and four-fold greater than those obtained with PAMAM-G0 and PAMAM-G3 respectively, although the amine concentration was more than 200-fold higher. Analogously, in reverse micelles of AOT and BHDC higher amine concentrations were used relative to those of PAMAM [29]. However, also in this case the greater Φ_R were obtained with dendrimers. Therefore, it can be inferred from Table 3 that the Eos/PAMAM

couple is efficient for the radicals formation, compared to another Eos/amine systems previously analyzed.

4. Conclusions

Summarizing, the photochemical behavior of the xanthene dye Eosin-Y in the presence of amino-terminated PAMAM dendrimers was characterized in alkaline aqueous solution. We were able to show that Eos photodecomposes in the presence of PAMAM to yield fluorescein as a final product. From steady-state photolysis we concluded that the process takes place from the triplet state of the dye, mediated by electron transfer reaction with dendrimers. Several transient species of partial debromination seem to be present throughout the photochemical reaction. The transient spectra obtained by laser flash photolysis experiments agreed with such hypothesis. All these findings are in agreement with previous reports concerning Eos and electron donors other than dendrimers in aqueous and methanolic solutions.

The electron transfer from PAMAM occurred with higher rate than with aliphatic tertiary amines, and correlated with the size of the dendrimer. The efficiencies of radical formation were quite high compared to another Eos/amine systems reported. These results suggest that Eos/PAMAM couple might act as a promising photoinitiator of vinyl polymerization with low ecological impact.

Acknowledgments

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