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# Synthesis of a new polymer containing Rose Bengal

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## Summary

Rose Bengal (4,5,6,7-tetrachloro-2′,4′,5′,7′-tetraiodofluorescein, RB), a xanthene dye well-known as singlet molecular oxygen photosensitizer, was bound to the polymeric matrix poly(butadiene-hydroxyethylmethacrylate-epichlorhydrin) (PB-HEMA-ECH). The new polymer-bound dye (P-RB) was investigated as sensitizer for the photooxidation in air equilibrated solutions of model compounds (Q). Comparative results of degradation of these compounds suggest the generation of singlet oxygen. Also P-RB showed good stability and was reused.

## Introduction

Reactions involving the first excited state of molecular oxygen, $O_2$ ($^1\Delta_g$) (denoted $^1O_2$ below), play an important role in many natural photochemical and photobiological processes. Molecular oxygen is more electrophilic in its singlet excited state and can react with substrates that are unaffected by oxygen in its ground state [1-3].

Photosensitization is one of the most common ways of $^1O_2$ generation in laboratory and in the nature [4]. This process requires the simultaneous presence of light, oxygen and a light absorbing substance (Sens). By absorption of light, the Sens reaches an electronic excited state ($^3$Sens*), which can react with a substrate (Type I reaction) or transfer its energy to ground state molecular oxygen ($^3O_2$) producing $^1O_2$ (Type II pathway, see the photochemical scheme shown in reaction 1).

$$\text{Sens} + h\upsilon \rightarrow {}^3\text{Sens}^* + {}^3O_2 \rightarrow \text{Sens} + {}^1O_2 \qquad (1)$$

Xanthene dyes, like Rose Bengal (RB, Figure 1), Eosin or Erythrosine, soluble in water and in polar solvents, are often used as Sens because they have high absorption coefficients in the visible spectral region, high quantum yields of $^1O_2$ generation ($\Phi_\Delta$) and are stable after photosensitization. We selected RB as Sens, which in water has the maximum of the absorption band at 548 nm and $\Phi_\Delta = 0.75$ [5].

Generation of $^1O_2$ is possible in homogeneous solution or in heterogeneous system. The use of inmobilized Sens has several practical advantages: a) $^1O_2$ could be separated from its precursors and only the reactions that occur in solution could be studied, b) solvents in which the Sens is insoluble could be used and c) the Sens can be removed at the end of the reaction and reused [6]. Polymer-bound Sens were successfully employed in the photooxidation of different substrates [3, 7-9].

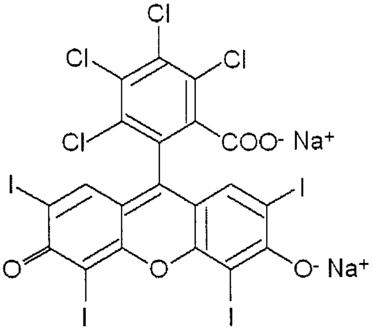

Figure 1. Chemical structure of Rose Bengal.

In this work, we report the synthesis and characterization of Rose Bengal coupled to a highly insoluble synthetic matrix (P-RB). The polymer was used as Sens for the photooxidation of well-characterised $^1O_2$ acceptors (Q), *i. e.* compounds that react with $^1O_2$ with a high rate constant of chemical reaction ($k_r$, reaction 2) and a low rate constant of physical quenching ($k_q$, reaction 3).

$$^1O_2 + Q \xrightarrow{k_r} {}^3O_2 + \text{products} \qquad (2)$$

$$^1O_2 + Q \xrightarrow{k_q} {}^3O_2 + Q \qquad (3)$$

Presence of singlet molecular oxygen generated by irradiation with visible light was inferred from indirect measurements, in order to test if the new polymer could act as Sens in air equilibrated solutions.

## Experimental

### *Materials*

Rose Bengal (RB), furfuryl alcohol (FFA), histidine (HIS) and 9-anthracene carboxylic acid (ACA) were purchased from Sigma Chem. Co. Sodium azide ($NaN_3$) was from Aldrich. For the synthesis, all solvents (Merck) were used as received. Aqueous solutions were prepared with bidistilled water and, where indicated, were alkalinised with 10 mM NaOH (Merck).

### *Instruments*

The IR spectra of the polymeric matrix and P-RB were recorded on a Nicolet 5-SXC FT-IR spectrometer.

The sensitized photooxygenation was analysed by following oxygen consumption with a specific oxygen electrode (Orion 97-08) and spectral changes. The UV-Vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer.

*Synthesis*

The polymer was synthesized employing poly(butadiene-hydroxyethylmethacrylate-epichlorhydrin) (PB-HEMA-ECH) provided by Bertorello et al. [10, 11]. The epoxy-activated gel was washed repeatedly in a batch system with water, ethanol, acetone and benzene. After drying, 0.85 meq of oxirane groups per gram of dry product were determined using the pyridinium chloride method [12]. The PB-HEMA-ECH, previously swollen in water, was mixed with an aqueous solution of RB ($2x10^{-4}$ meq of RB per gram of polymeric support) and NaOH (1 M) at room temperature for 48 hours with stirring. The product PB-HEMA-ECH-RB (P-RB) was purified by washing in a batch system with water, ethanol and acetone.

*Photooxidations*

Static photolysis were carried out in a home-made photolyser described previously [13]. Briefly, the sample solution was irradiated with a quartz-halogen lamp (150 W) through a water filter, focusing optics and a cut-off filter (500 nm). Photooxidations were carried out in a Pyrex tube and the solutions were stirred with a magnetic bar during the irradiation. Concentrations of Q, P-RB or RB for the photooxidations were 0.1 mM, 1 mg/ml and $5x10^{-3}$ mM, respectively.

The deaerated solutions were prepared by bubbling solvent-saturated $N_2$ for 30 minutes. All measurements were made at room temperature.

## Results and discussion

The aim of this work was the synthesis of a new sensitizer for singlet oxygen production in heterogeneous media. RB was covalently incorporated as a result of the opening of oxirane groups of the activated beads. The amount of dye attached to the polymer was low (0,1 mg/g), in order to avoid its aggregation. Signals of the IR spectra of P-RB showed a relative increase at 1167.1 and 1033.5 $cm^{-1}$ (ether group), 749 $cm^{-1}$ (aromatic groups) in comparison with PB-HEMA-ECH matrix.

The polymer-bound RB (Figure 2) was a powder of uniform red coloration. The product was a solvent-swollen gel, stable during several hours of sonication and stirring in neutral and alkaline aqueous solutions.

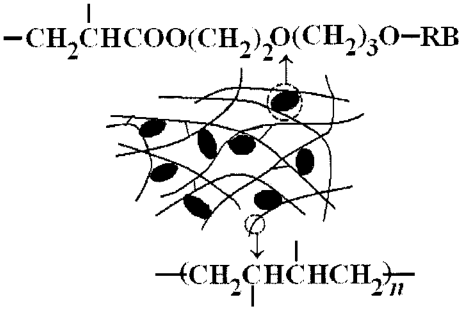

Figure 2: Schematic drawing of the structure of PB-RB.

The evidence of $^1O_2$ formation and removal was collected using indirect methods employing selected singlet oxygen quenchers: FFA, ACA or HIS [14].

Air equilibrated solutions containing the Sens plus Q were irradiated with visible light and oxygen uptake was measured. In order to check the stability of P-RB, after irradiation the solutions were filtered and the UV-Vis spectra were registered. No loss of RB was detected.

In parallel, the photooxidation of ACA was followed by spectrophotometry. Spectral changes for ACA and oxygen consumption for all the quenchers, were not observed in the absence of light or when the solutions were previously bubbled with $N_2$. These observations suggest the participation of reactive oxygen species in the photopromoted process.

Indirect experiments for testing singlet oxygen presence are based on the inhibiting effects of additives on the rate of photooxidation reaction. Frequently employed physical quenchers of $^1O_2$ are azide ion ($N_3^-$) and 1,4-diazabicyclo[2.2.2]octane (DABCO) in aqueous media or α-tocopherol and β-carotene in organic media. Degradation rate of FFA in the presence of $NaN_3$ (1 mM) was slower than degradation rate without $NaN_3$ (Figure 3), supporting the involvement of singlet oxygen. The data were obtained from identical samples under identical conditions.

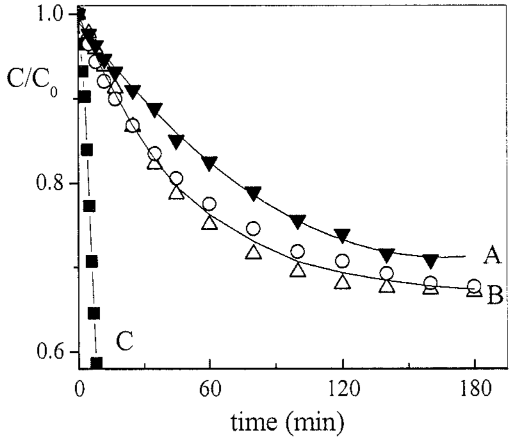

Figure 3. Evolution of oxygen uptake upon sensitized photoirradiation of different aqueous solutions: (A) P-RB + FFA (0.1 mM) + $NaN_3$ (1 mM); (B) P-RB + FFA (0.1 mM) (circles correspond to experiences with re-used P-RB) and (C) RB + FFA (0.1 mM). C and $C_0$ represent the oxygen concentration at time= t and time=0, respectively.

The data in Table 1 and Figure 3 obtained for the photooxidation of the selected Q suggest that, under our experimental conditions, the behaviour of P-RB is similar to that of RB in homogenous solution. However, when P-RB is the Sens, as shown in Figure 3, the photooxidation rate is slower. Similar results were previously reported for other inmobilized sensitizers when compared with their unbound counterparts, probably by the need of oxygen to diffuse into and out of the polymer matrix in order to be sensitised and quenched [3].

For economic reasons, the reused polymeric matrix was also tested by successive photooxidations of FFA (see Figure 3 and Table 1). P-RB shows an acceptable photostability, allowing at least two repetitions without a significant degradation. However, P-RB photodegradation could not be neglected.

Table 1. Conversion (%) of different substrates employing P-RB as photosensitiser

| Probe | Time (m) | Conversion (%) | | |
|---|---|---|---|---|
| | | P-RB | P-RB1[a] | P-RB+ $NaN_3$ |
| FFA | 5 | 3(22)[b] | 3 | 2 |
| | 120 | 32 | 30 | 26 |
| HIS | 120 | 25 | | |
| ACA | 120 | 37 (39)[c] | | |

[a] P-RB reused; [b] photosensitiser: RB in homogeneous solution; [c] followed by spectrophotometry

## Conclusions

The results indicate that P-RB is a novel polymeric sensitizer for photooxidations via singlet oxygen. P-RB was found to photosensitize oxidation reactions in a comparable manner to RB in homogeneous media. After irradiation, it can be filtered off, which is a practical advantage of P-RB. It can be used for several applications in heterogeneous system, such as wastewater treatment, bleaching processes, chemical synthesis or photodynamic blood sterilization.

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