

## MICROHETEROGENEOUS PHOTSENSITIZERS FROM WATER-SOLUBLE POLYMERS

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(Received November 13, 1985; in revised form March 9, 1986)

### Summary

Poly(ethylene glycol) has been functionalized with rose bengal and its photochemical properties and spectra studied in solvents ranging from toluene to water. The compound is a microheterogeneous photosensitizer in that the dyes attached to the polymer aggregate in solvents in which they are not normally soluble. This effects both the quantum yield of singlet oxygen formation and the spectral shapes of the dye.

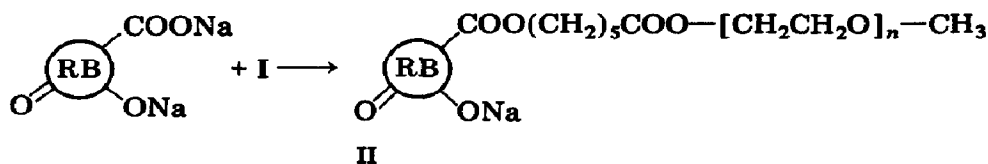
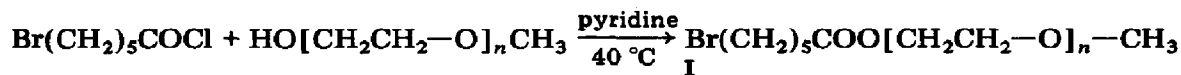
### 1. Introduction

Many methods, both thermal and photochemical, have been developed for the generation of singlet oxygen [1, 2]. The most common method employs a dye with a high intersystem crossing quantum yield such as rose bengal or methylene blue. These dyes, particularly rose bengal, can be used either as heterogeneous or homogeneous sensitizers [3 - 6] and they can also be attached to soluble polymer chains [7].

Rose bengal has among the highest efficiencies of <sup>1</sup>O<sub>2</sub> formation (quantum yield, 0.76 in MeOH [8]). Though its universal use has been limited by its insolubility in non-polar solvents, the work of Lamberts and Neckers [9 - 11] has alleviated that problem and a number of sensitizers based on the rose bengal moiety and soluble in virtually every organic solvent are now known.

In this paper we describe perhaps the most unusual polymer sensitizer in the rose bengal series, one based on a water-soluble polyglycol. This new rose bengal polyglycol is obtained by the reactions in Scheme 1 and is soluble in solvents from toluene to water. Essentially it is a rose bengal esterified with a low molecular weight polyglycol through the C-2 carboxylate function.

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Scheme 1.

## 2. Results

The shape of the electronic absorption spectrum of II is typical for a rose bengal (see Fig. 1.) Spectral data reported for measurements in a variety of solvents are given in Table 1.

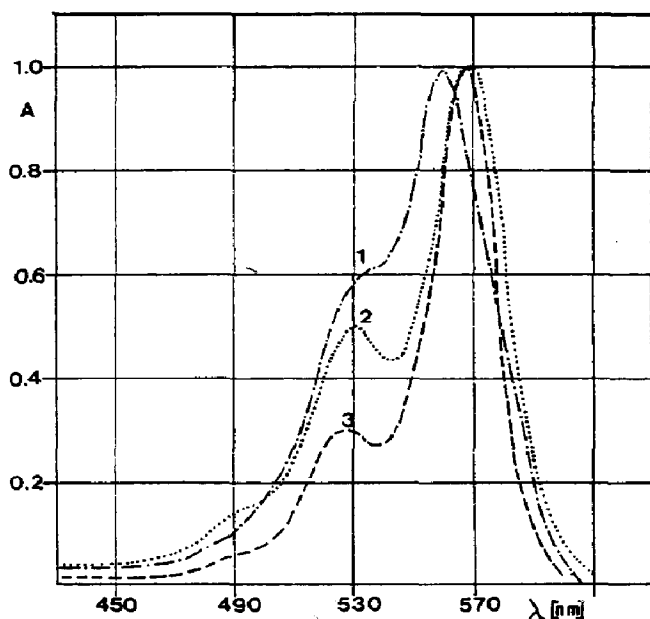


Fig. 1. Electronic absorption spectra for II in  $\text{H}_2\text{O}$  (curve 1), benzene (curve 2) and EtOH (curve 3).

The formation of singlet oxygen by II was tested using our relative actinometric method [4, 5]. The  $^1\text{O}_2$  quencher 1,2-diphenyl-*p*-dioxene (DPDO) was used in these studies, and its photo-oxidation product was monitored by vapour phase chromatography. The results are given in Table 2.

As the data in Table 1 indicate, II is soluble in various solvents varying from the non-polar solvent toluene on the one hand to water on the other hand. This derives from the fact that II contains both a hydrophobic side chain (the polyether) and a hydrophilic rose bengal moiety.

TABLE 1

Electronic absorption data for II obtained in various solvents

Solvent	$\lambda_1$ (nm)	$\lambda_2$ (nm)	$\epsilon_{\lambda \text{ max}}$	$A_{\lambda_1}/A_{\lambda_2}$
EtOH	568.5	526 - 527	$9.84 \times 10^4$	3.21
CH <sub>2</sub> Cl <sub>2</sub>	571.5	528	$9.12 \times 10^4$	2.99
Benzene	569.2	530	$4.93 \times 10^4$	2.02
Toluene	568.5	528 - 529	$4.52 \times 10^4$	1.93
H <sub>2</sub> O	561.5	a	$5.65 \times 10^4$	—

Calculated molecular weight of II, 1660.

a Only a shoulder is observed.

TABLE 2

Quantum yield of singlet oxygen formation for II ( $c = 1.0 \times 10^{-4}$  M)

Solvent	$\lambda(^1\text{O}_2)$
EtOH <sup>a</sup>	0.75
CH <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>	0.76
CH <sub>2</sub> Br <sub>2</sub> <sup>b</sup>	0.81
Benzene	0.40
Toluene <sup>a</sup>	0.30

<sup>a</sup>Concentration of DPDO,  $2.5 \times 10^{-2}$  M.<sup>b</sup>Concentration of DPDO,  $3.0 \times 10^{-2}$  M.

Since rose bengal C-2' esters in the C-6 sodium salt form are not soluble in highly non-polar solvents such as CH<sub>2</sub>Cl<sub>2</sub>, toluene and benzene, it is apparent that the poly(ethylene glycol) residue serves to carry an essentially polar dye into an essentially non-polar solvent. In addition, the polymeric side chain is able to carry the rose bengal C-2' ester into water.

The quantitative values obtained for the formation of singlet oxygen from II (Table 2) indicate that for polar and protic solvents the quantum yield of singlet oxygen formation is comparable with that obtained from rose bengal in methanol ( $\phi = 0.76$ ). In non-polar solvents the quantum yield of singlet oxygen formation varies from 0.30 in toluene to 0.81 in CH<sub>2</sub>Br<sub>2</sub>. Analysis of the absorption spectrum indicates that for II in benzene and toluene the ratio between the intensity of the two bands ( $A_{\lambda_1}/A_{\lambda_2}$ ) is much smaller than is the same ratio in EtOH or CH<sub>2</sub>Cl<sub>2</sub>. This suggests that in benzene and toluene the polar dyes of II are aggregated [12, 13]. In view of the fact that the dye is generally not soluble in these solvents it seems clear why this should be so. The polar dye moieties are more compatible with each other than they are with the bulk solvent. It is another example of a microheterogeneous effect on polar dye behavior in solution [14].

Aggregation effects can be responsible for decreases in quantum yields of singlet oxygen formation, because aggregation enhances self-quenching.

The high values of the quantum yield in  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_2\text{Br}_2$  are likely to be the result of an external heavy-atom effect.

II may be compared in its properties with polymer-(rose bengal) [4, 5]. In the case of (P)-rose bengal, the non-polar polymer chain carries a polar dye into a non-polar solvent. In the case of (P)-rose bengal, hundreds of rose bengal molecules are attached to one polymer chain, whereas in the case of II each rose bengal possesses its own small polymer residue.

The (P)-rose bengal system based on poly(styrene-co-divinylbenzene) beads is a heterogeneous photosensitizer and is truly an example of heterogeneous photochemical catalysis. The poly(ethylene glycol) system II is an example of a microheterogeneous system. Even though the polymer solubilizes the dye in various solvent systems, the dye aggregates in solvents in which it is not soluble. Under those conditions, the dye is essentially dispersed in the solvent. In solvents in which the dye is soluble, self-quenching effects are ameliorated by solvation of the dissolved dye as well as the polymer chain.

### 3. Experimental details

Poly(ethylene glycol) monomethyl ether (11.0 g; average molecular weight, 550; Aldrich) was dissolved in 50 ml dry pyridine. 6-Bromohexanoyl chloride (6.4 g; 3 mmol; Aldrich) was added. The reaction mixture was stirred at 40 °C. After 12 h the precipitated pyridine hydrochloride was filtered and the residual pyridine evaporated. The residue was washed with a 50vol.%hexane-50vol.%(methyl *tert*-butyl ether) mixture until product I was rid of all residual acid chloride (as shown by IR).

I (7.4 g) was dissolved in 100 ml 50vol.%acetone-50vol.%water and 2 g (2.0 mmol) rose bengal was added. The mixture was stirred at 80 °C for 24 h. After the reaction was complete, the acetone and water were evaporated *in vacuo* and the final product was purified using column chromatography.

The quantum yields of singlet oxygen formation were monitored as reported previously [7].

### Acknowledgment

This work was supported by the National Science Foundation (DMR 8404001). The authors are grateful for this support.

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