Polymer Bulletin 12, 119–126 (1984)

Polymer Bulletin

Photosensitizers

Quantitative Evaluation of Polymeric Photosensitizers

2. Preparation of a Soluble Polymer-Bound Rose Bengal and Determination of Its Singlet Oxygen Generation Efficiency

Roberto Martinez-Utrilla**, **José M. Botija*** **and Roberto Sastre***

* Instituto de Plásticos y Caucho, Juan de la Cierva 3, Madrid-6, Spain
** Instituto de Química Orgánica General, Juan de la Cierva 3, Madrid-6, Spain

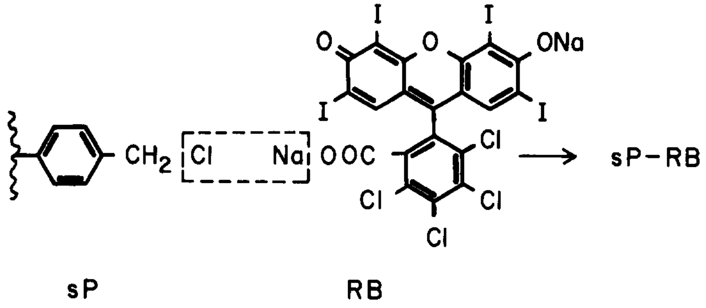
Summary

The xanthene dye Rose Bengal (disodium salt of 3', 4', 5', 6'-tetrachloro-2, 4, 5, 7-tetraiodofluorescein) has been covalently bound to a linear (soluble) copoly styrene-vinyl benzyl chloride. The chemical union takes place through alkylation of the carboxylate anion of the dye by one of the chloromethyl groups grafted on the polymer. The quantum yield of singlet oxygen generation results equal to that of the free dye and the photostability seems to be improved.

Introduction

The use of insoluble polymeric photosensitizers appears as an attractive technique in photochemical synthesis (NECKERS, 1978). The potential utility of these sensitizers has been also claimed in connection with the future development of chemical-based solar energy systems (HAUTALA and LITTLE, 1980). A relevant example of this type of sensitizers is constituted by the chemical union of a typical photosensitizing dye, Rose Bengal, to a cross linked styrene-divinyl benzene copolymer matrix as singlet oxygen generator (SCHAAP et al., 1975, 1979). Linear polystyrene, conveniently functionalized, is being currently used in our laboratory to attach to it different sort of molecular species which are recognized as efficient photosensitizers (CATALINA et al., 1982). The linear character of such polymeric supports allows the evaluation of their sensitizing properties to be effected in homogeneous solution, a condition which facilitates in high degree the achievement of quantitative measurements, particularly those concerning light absorption (MARTINEZ-UTRILLA and

SASTRE, 1982). Previous work with model molecules (AMAT et al.,) had shown that the esterification of the carboxylic function in Rose Bengal (RB) could be carried out by an alkyl halide without affecting the phenoxide anion:



Esterification of RB has also been the subject of a recent report (LAMBERTS and NECKERS, 1983). We had found out that decarboxylation of RB constituted the most serious secondary reaction limiting the ester formation. After this previous exploratory work, the chemical binding of RB to linear chloromethyl polystyrene was undertaken in the hope of obtaining a polymeric sensitizer that, being soluble in organic media, would retain the singlet oxygen efficiency of the free dye. As it will be shown later, our goal has been accomplished although the amount of dye bound to the polymer is much less than the stoichiometric one, as calculated from the chloromethyl content of the starting polystyrene. The efficiency in singlet oxygen generation is analogous to that of the free dye but with the advantage of its photostability being significantly better.

Experimental

Polystyrene (Mn = 143. 560) was functionalized through a reaction with chloromethyl methyl ether. The original procedure (PEPPER et al., 1953), modified by us in order to minimize the secondary reactions of the chloromethyl groups, was followed to obtain starting polymers of different chloromethyl contents. The soluble polymer-bound Rose Bengal, thereafter designed as s**P**-RB, was prepared by reacting the para-chloromethyl polystirene with RB of commercial origin (Fluka). In some cases, the purified lactonic form of the dye was employed in order to facilitate the identification of products. A general synthetical procedure consisted in mixing 0.2 g of the starting polymer and 0. 2 g of RB in 50 ml of cyclohexanone-water (49 : 1) or in 25 ml of dimethylformamide, DMF. Once all the dye was dissolved, the mixture was vigorously stirred and heated at 65°. The advance of reaction was monitored by TLC using chloroform-ethanol (2 :1) as eluent. After 24 hours, the mixture was poured into pentane-methanol (1 : 1) and the precipitated dark red polymer filtered off. Purification was carried out by dissolving the solid in tetrahydrofurane and subsequent reprecipitation in methanol. The recovered sP-RB was finally dried at vacuum for 48 hours at 40°. When precipitation was effected in the presence of mineral acid, the isolated orange coloured polymer corresponded to the acid (phenolic) form of the dye. The RB content of the polymer was spectrophotometrically determined in DMF, at 572 nm, taking 9.6 10^4 M^{-1} cm^{-1} for the value of the molar extinction coefficient of the esterified RB. This value had been obtained previously working with the monomeric esters.

Infrared spectra showed the apparition of the new ester band at 1730 cm^{-1}, while only minor changes were detected at the chloromethyl absorption band, 1270 cm^{-1}, due to the low degree of reaction reached in all the cases. The original high solubility of the chloromethyl polystyrene in benzene is strongly diminished when the RB content in the sample is increased. Nevertheless, the solubility of the sP-RB remains sufficient enough to yield benzene solutions of high absorbance, the necessary requisite to collect light in an efficient way. Kinetic runs for quantum yield determinations were carried out employing a 55 W tungsten-halogen lamp (Osram H3) provided with a lense and filter glass (Schot SFK 11) in order to isolate a band centered at 552 nm. Samples in conventional pyrex-glass cells (1 cm optical path) were irradiated in a merry-go-round apparatus which allowed the simultaneous irradiation of up to eight cells. 1, 3-Diphenylisobenzofurane (Aldrich), DPIBF, has been used to scavenge the singlet oxygen. The commercial product was employed as such, although a measurement of the molar extinction coefficient was made in order to check its purity. The obtained ϵ-value (23. 500 M^{-1} cm^{-1}), was in accordance with that in the literature at 410 nm in methanol (YOUNG et al., 1973). The relative photostability of the polymeric photosensitizers was determined by irradiating the free RB and the sP-RB samples with the entire output of a 500 W high pressure xenon lamp (Osram XBO) focalized on the cells with the aid of an special elliptic mirror. Before entering the samples, the IR part of the incident radiation was absorbed in a water-glass filter.

Results and Discussion

The results summarized in Table I show that the amount of RB linked to the polystyrene, through reaction with the chloromethyl functions, is far from the stoichiometric one. The two first samples have dye-contents indicating that only a 10 % of the reactive chloride has formed the ester with the carboxylate anion of the RB, the rest remaining intact. Preliminary results obtained using eosin (disodium salt of tetrachloro-2, 4, 5, 7-tetrabromofluorescein) instead of RB, indicate also a similar behaviour. These results can be interpreted assuming that the voluminous and electrically charged dye molecule exerts a kind of umbrella effect hindering the approach of new molecules to the reactive sites of the polymeric framework. Consequently, the formation of new ester-bonds is prevented. It is

TABLE I

Photooxidation of 1, 3-Diphenylisobenzofurane in DMF with polymer-bound Rose Bengal and Eosin

Photosensitizer	P-CH_2Cl (%)	Dye content (%)	λ_{max} (nm)	Relative quantum yield *
sP-RB 1	7	0.8	572	1 **
sP-RB 2	14	1.8	572	0.99
sP-RB 3	54	3.2	572	0.80
sP-Eosin	7	0.71	544	1

* Average of at least six experiences.

** A similar relative quantum yield was obtained when benzene was used as solvent.

worth noting that attempts to increase the dye content by reacting a sample of sP-RB with RB, under the standard experimental conditions, were unfruitful. Therefore, one can infer that the dye-content of the sample was the maximum attainable or, at least, very near to it. Furthermore, no increase is observed on working at higher temperatures. Under these conditions, the esterification rate grows as expected, but the decarboxylation process becomes then an important detrimental reaction.

The photooxidation efficiencies of the synthetized sP-RB samples were evaluated by measuring the relative quantum yields of singlet oxygen generation, taking the free RB as reference. The rate of disappearance of the trapping agent, in the present case DPIBF, is related to the quantum yield of singlet oxygen generation $\varphi_{^1O_2}$ by the general expression (1)

$$-\frac{dC}{dt} = I_a E_{IS} E_{O_2} E_{tr} = I_a \varphi_{^1O_2} E_{tr} \qquad (1)$$

where I_a stands for the light intensity absorbed (einsteins $s^{-1}L^{-1}$) and E_{IS}, E_{O_2} and E_{tr} are the efficiencies of the following processes: intersystem conversion, energy transfer to molecular oxygen and trapping of singlet oxygen. Multiplication of the two former give the quantum yield of singlet oxygen generation, which is the parameter normally used to characterize the effectiveness of a sensitizer when the mechanism is of the Type II. The above expression is transformed into (2), suitable for use in our particular case:

$$-\frac{dC}{dt} = I_m F \varphi_{^1O_2} \frac{C}{\beta + C} \qquad (2)$$

where I_m represents the maximum intensity of light which a sample in the merry-go-round apparatus is able to absorb i.e., when the dye concentration is high enough to absorb all the wavelenghts contained in the incident light. We use the parameter F to take into account the different absorbances of the irradiated samples and the values of the transmission coefficient of the filter at seven wavenlenghts (see Fig. 1). In this way, I_m times F gives the actual light absorbed for a particular sample. The changes occurring in the absorption spectrum during irradiation of a sample are shown in Fig. 1. The functional form of the transmission coefficient of the filter and the wavenlengths selected to calculate F are also included.

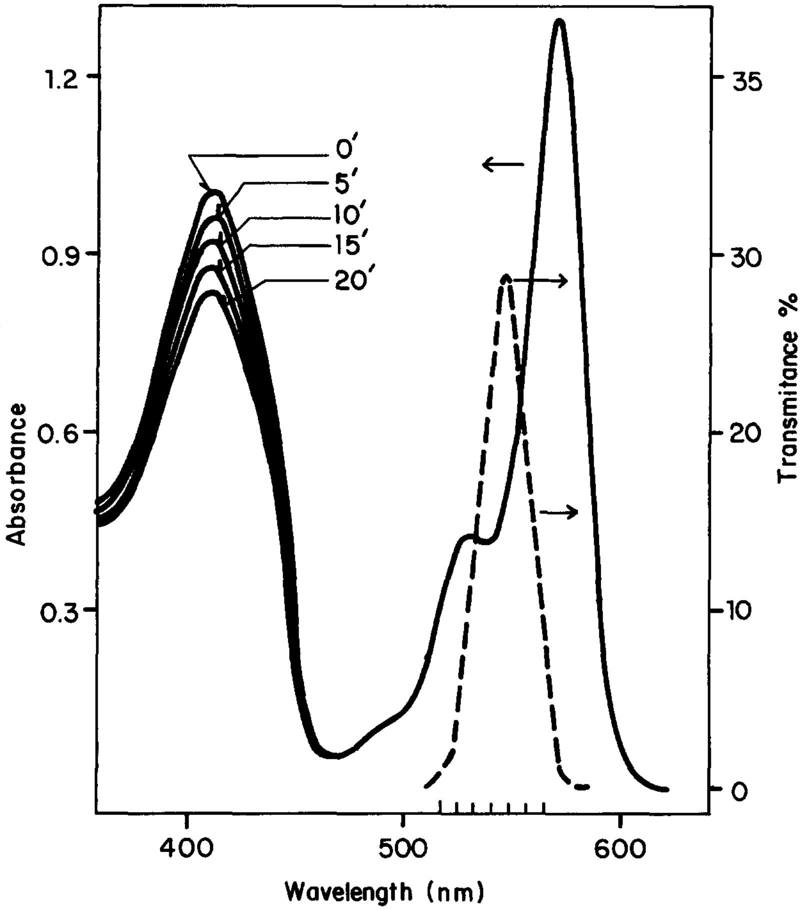


Fig. 1: Absorption spectra evolution under irradiation at 552 nm of mixture of sP-RB (1.35×10^{-5} M) and DPIBF (4.3×10^{-5} M) in DMF.

Initial kinetic runs on methanol and dimethylformamide solutions of free RB demonstrated that the β-value for DPIBF was the same in both solvents. Thus, we finally adopted the literature value of 7.3×10^{-5} M reported for methanol, (YOUNG et al., 1973). The relative quantum yield of singlet oxygen formation for a polymeric sensitizer is referred to the monomeric unbound sensitizer through expressions (3) and (4):

$$\varphi_r = \frac{Y}{X} \quad (3) \quad ; \qquad Y \text{ (or X)} = \frac{1}{F}\left[\frac{A_0 - A}{\epsilon} + \ln\frac{A_0}{A}\right] \quad (4)$$

where Y stands for the polymeric and X for the free sensitizer solutions which are simultaneously irradiated in the merry-go-round apparatus. A_o and A represent the absorbances, before and after irradiation, of each solution measured at the absorption maximum of DPIBF, ϵ being the molar extinction coefficient of this compound. Measurements at different doses of irradiation were taken for each sample. In all the cases, linear plots of Y versus X were obtained. The resulting φ_r-values are given in Table I. It can be observed that only the sample with the highest dye-content has a lower effectiveness in singlet oxygen generation than the free dye. DMF was used in all the experiments, but one result corresponding to benzene is also included. This one is only approximated because of the rough extrapolation made from literature values (YOUNG et al., 1973) in order to estimate β.

Finally, some exploratory work on the photostability of the bound dye was carried out. The absorbance decrease occurring at the dye absorption maximum (562 and 572 nm for RB and sP-RB, respectively) was followed after irradiating the samples with all the visible and UV output of a 500 W high pressure xenon lamp. As inspection of Fig. 2 shows, the lightfast-

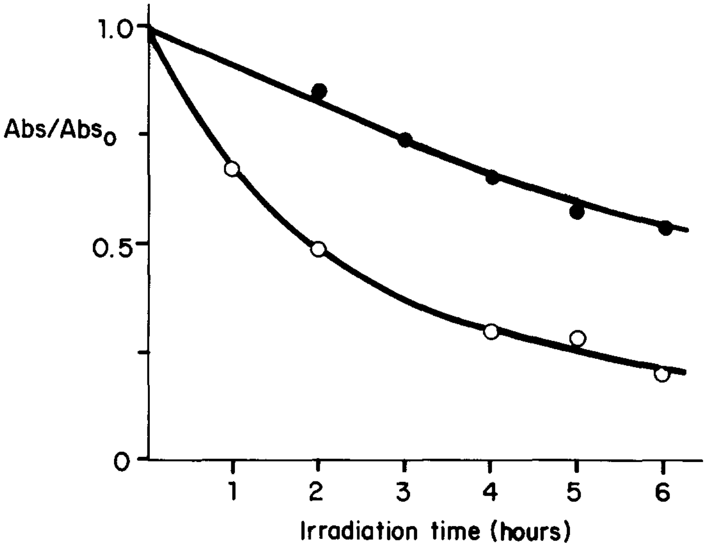


Fig. 2: Photobleaching under UV-VIS high intensity irradiation: o free RB; ● sP-RB (1.8 %).

ness of the linked RB appears to be greater that the one corresponding to the free dye.

Conclusions

A linear polymer-based Rose Bengal has been obtained which is soluble in organic media. This polymeric photosensitizer has the same or analogous effectiveness in sensitizing singlet oxygen formation to the unbound Rose Bengal. On the other hand, this soluble polymeric photosensitize presents remarkable advantages with regard to its insoluble and crosslinked counterpart such as: a) an easier preparation, purification and analysis; b) a more precise evaluation of its singlet oxygen photogeneration efficiency; c) the possibility of being used in solvents where both free-RB and crosslinked P-RB are insoluble and therefore unable to sensitize singlet oxygen formation in such an efficient way. Last but not least it posseses a higher photostability than the free-RB.

Financial aid by C.A.I.C.Y.T. is gratefully appreciated.

References

AMAT, F., LOPEZ, M. C., and MARTINEZ-UTRILLA, R., to be published.

CATALINA, F., MARTINEZ-UTRILLA, R., and SASTRE, R., Polym. Bull., 8, 369 (1982).

HAUTALA, R. R., and LITTLE, J. L., Adv. Chem. Ser. nº 184 (1980).

LAMBERTS, J. M., and NECKERS, D. C., J. Am. Chem. Soc., 105, 7465 (1983).

MARTINEZ-UTRILLA, R., and SASTRE, R., Rev. Plast. Modern., 43, 519 (1982).

NECKERS, D. C., Chemtech., 8, 108 (1978).

PEPPER, K. W., PAISLEY, H. M., and YOUNG, M. A., J. Chem. Soc., 4097 (1953).

SCHAAP, A. P., THAYER, A. L., BLOSSEY, E. C., and NECKERS, D. C., J. Am. Chem. Soc., 101, 4016 (1979).

YOUNG, R. H., BREWER, D., and KELLER, R. A., J. Am. Chem. Soc., 95, 375 (1973).

Accepted June 29, 1984