

Highlight Article

Photoactive Chitosan: A Step Toward a Green Strategy for Pollutant Degradation

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ABSTRACT

This article is a highlight of the paper by Ferrari *et al.* in this issue of *Photochemistry and Photobiology*. It describes the innovative use of rose bengal-conjugated chitosan as a reusable green catalyst that photo-degrades phenolic compounds in aqueous media, and thereby has decontamination potential of polluted waters. Whether a next-generation photoactive polymer that produces singlet oxygen is a solution to pollutant degradation can be argued. It is as yet unclear what polymeric sensitizer would be practical on a large scale. Nonetheless pursuing this goal is worthwhile.

COMMENTARY

The study of organic photoactive polymers for materials to oxidatively decontaminate polluted waters has attracted much interest (1,2). Oxidative methods that use atmospheric oxygen as a green, environmentally friendly route to highly reactive $^1\text{O}_2$ ($^1\Delta_g$) are of interest (3,4). However, a challenge is that the polymer's success for producing $^1\text{O}_2$ may lead it to "commit suicide" by self-oxidation. This highlight article of the paper by Ferrari *et al.* (5) in this issue of *Photochemistry and Photobiology* describes how this self-oxidation problem can be managed by the incorporation of rose bengal into chitosan.

Figure 1 shows the rose bengal-chitosan conjugate. Chitosan is an excellent polymer for exploring photosensitization phenomena. It is an aminopolysaccharide polymer that is nontoxic and biodegradable, and is available on large scales by chitin deacetylation of shellfish waste or fungal biomass (6). Synthetically, the amino group of chitosan can be functionalized (7).

SYNTHESIS

Ferrari *et al.* (5) functionalized chitosan by dehydrative coupling of its amino group and the rose bengal carboxy group, which provided a simple procedure to the corresponding conjugate. The resultant material was precipitated in NaOH solution and then redissolved in acetic acid solution, where rose bengal was introduced into the backbone of chitosan in the amount of about 0.3% w/v. The material's color is light red or pink due to two absorptions at 523 and 561 nm in acidic aqueous solution. Rose bengal also fluoresces red albeit only weakly.

The photolysis of the rose bengal-chitosan conjugate was studied with visible light (filtered white light from a halogen lamp) and green Nd:YAG laser light. The light was only absorbed by the rose bengal sites in the polymer, and not by the trihydroxybenzene compounds, 1–3 (Scheme 1), which served as model pollutants as will be discussed later. As a result of this selective irradiation, triplet rose bengal is efficiently quenched by O_2 to form $^1\text{O}_2$ with traces of superoxide anion ($\text{O}_2^{\cdot-}$) (8,9).

Until now, studies of rose bengal-chitosan conjugates for green chemistry applications have largely neglected analyses of surface properties to reduce problems of self-oxidation. Nevertheless, earlier studies are very instructive. In the 1970s, Neckers *et al.* discovered polymer rose bengal, research using Merrifield chloromethylpolystyrenes, and discovered it as a heterogeneous source of $^1\text{O}_2$ (10). Noteworthy properties of the rose bengal polymer included [1] unwanted intramolecular sensitizer–sensitizer interactions were controlled by lower loadings; [2] monomeric (isolated) rather than aggregated rose bengal sites produced higher yields of $^1\text{O}_2$ (11); and [3] ammonium salts formed at the "phenolic" positions of rose bengal by displacing the phenol proton produced tighter ion pairing and higher $^1\text{O}_2$ quantum yields (12). Studies of Ferrari *et al.* (5) on rose bengal-chitosan conjugate have since been concerned with preserving the photosensitizer sites on the polymer.

PRESERVATION OF THE CHITOSAN PHOTSENSITIZER SITES

The chitosan is found to protect the rose bengal sites. A longer service life was found, where the rose bengal-chitosan photodegraded some 5-times slower than free rose bengal in solution. A question could be posed: *Why is rose bengal-chitosan more resistant to degradation than free rose bengal?* A simple answer relates to a discussion of polymer shielding, which would result in a relatively inaccessible sensitizer site, even though rose bengal is chemically reactive with $^1\text{O}_2$, as are many photosensitizers such as bacteriochlorins (13). Singlet oxygen attack can lead to the formation of a hydroperoxide across the quinoid "A-ring" of rose bengal, which is reminiscent of reactions of $^1\text{O}_2$ with substituted phenols (14) and subsequent decomposition of the newly formed hydroperoxide (15,16). Depending on the reaction condition and solvent, rose bengal may also decompose by formation of radical cations or radical anions (17). The slower degradation values can result from reduced directions for access of $^1\text{O}_2$ to

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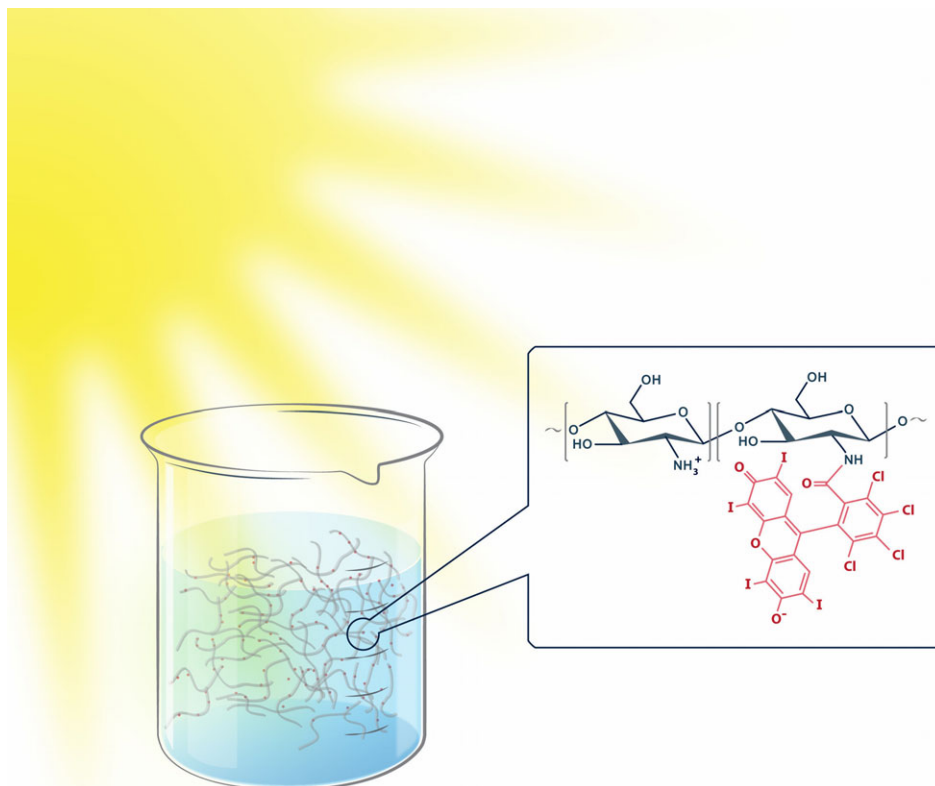
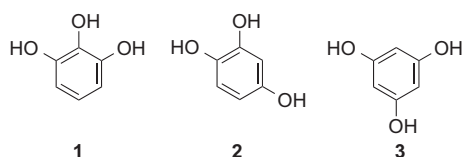


Figure 1. Image of the rose bengal-chitosan conjugate.



Scheme 1.

rose bengal in the heterogeneous sample contrary to the greater access of $^1\text{O}_2$ to rose bengal in fluid solution.

Efforts to insulate rose bengal sites to reduce $^1\text{O}_2$ contact have their limitations. Within chitosan are primary amine sites of glucosamine that can quench $^1\text{O}_2$ physically to form triplet dioxygen ($^1\text{O}_2 \rightarrow ^3\text{O}_2$) (18), although most sites are positively charged ammonium ions in aqueous solution. In a similar vein, polymers with diazabicyclo[2.2.2]octane (DABCO) covalently attached has been used as a stabilizing agent against $^1\text{O}_2$ -induced degradation (19).

PHOTODEGRADATION OF PHENOLIC POLLUTANTS

To study the polymer, Ferrari *et al.* irradiated it in the presence of trihydroxybenzene compounds, **1–3**, as test organic contaminants that were degraded by $^1\text{O}_2$ oxidation. Total quenching rate constants (k_t) were determined by time-resolved detection of $^1\text{O}_2$ at 1270 nm. The chemical quenching rate constants (k_r) of **1–3** were also measured. One tangible outcome was the enhanced chemical quenching efficiency of **1–3** by rose bengal-chitosan compared to free rose bengal, which they attribute to surface association with the polymer. Although not established in the

Ferrari study, phenols **1–3** may be oxidized to give *o*-quinones (20). Nonetheless, phenols quench $^1\text{O}_2$ by charge transfer and have quenching rate constants of $\sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (21), whereas phenolate anions are even more nucleophilic and reactive with electrophilic $^1\text{O}_2$ (22).

It is worth noting that rose bengal and rose bengal-chitosan conjugates have found other uses. Both have had success in tissue bonding and wound closure applications by photocrosslinking proteins (23–25). The bonding and closure effects were accompanied by protein stiffening and reduced wettability. Furthermore, researchers have also shown that rose bengal-chitosan compounds have the ability to photo-induce the killing of bacterial biofilms (26) and cancer cells (27). While rose bengal is also recognized as a cerebral stroke inducer due to closure of local blood flow upon irradiation (28,29), although rose bengal fails to localize well in organelles due to its high water solubility.

CHITOSAN PHOTOCATALYST IS RECOVERABLE, BIODEGRADABLE

Ferrari *et al.* report very promising results. They observe that after the photoreaction, only $\sim 2\%$ of the rose bengal units were lost. The dye content remained high, and provided good evidence for the polymer's durability. After use, acid workup, precipitation and simple filtration can be used to recover the catalyst. If not, the material is biodegradable, and when left in water it eventually degrades by hydrolysis.

In conclusion, the results of Ferrari and co-workers' with their rose bengal-chitosan degradation of trihydroxybenzene compounds will likely inspire the further development of photo-active polymers that are also environmentally friendly.

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