The results reported here lend strong support to the original CK algorithm. The CK movement algorithm, which was designed for computational efficiency, does not seem to introduce any spurious effects.

Unfortunately, we are not able to answer the question of whether the mere existence of the two-bead motion somehow distorts the time scale. The question can perhaps be answered by comparing the cubic lattic results with the dynamics of chains on a face-centered cubic (FCC) lattice. One can construct an ergodic Monte Carlo algorithm for FCC chains using only one-bead moves. This work is currently in progress.[8]

We have also shown that the interchain entanglement effects observed by Crabb and Kovac are due to more than just the simple suppression of the crankshaft motion. We are currently investigating these enganglement effects in more detail.[9] By analyzing the dynamics in terms of the Rouse normal coordinates we hope to get a better understanding of the precise nature of the entanglements.

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Heterogeneous and Semiheterogeneous Photosensitization: Photochemical Processes Using Derivatives of Rose Bengal. 13

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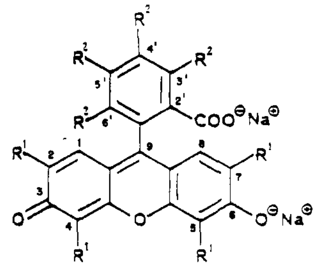
ABSTRACT: In this paper we outline the photochemical and spectroscopic properties of rose bengals immobilized to Merrifield resins and compare the properties of various heterogeneous photosensitizers with monomeric models as well as with soluble rose bengals.

Introduction

Heterogeneous photosensitizers that form singlet oxygen have proven most useful since the idea was introduced by Blossey, Neckers, Thayer, and Schaap.[1] The original idea derived from Merrifield's work[2] in which a polymer bead was used as a handle in a synthetic sequence—in the Merrifield case, the synthesis of a polypeptide. Essentially, the photosensitizer rationale was that if one could immobilize an energy-transfer donor to an insoluble bead and if the spectroscopic properties of the immobilized sensitizer were similar to those of the sensitizer in solution, one might effect heterogeneous energy transfer. At the time, heterogeneous energy transfer was unknown. Though a number of other dyes have been immobilized to polymer beads first by Blossey[5] and later by others[6,7] and some of these systems produced singlet oxygen, Ⓟ-RB[38] gave the highest quantum yield of singlet oxygen formation and was patented by Neckers, Blossey, and Schaap.[8] It has been commercially available for about a decade.

In retrospect, Ⓟ-RB—the first heterogeneous photosensitizer[9–11]—had at least three specific properties that made it unique: it was, by virtue of the polymer backbone, compatible with nonpolar solvents in contrast to the dye in solution; immobilized rose bengal was not bleached by the action of light and oxygen;[12] in contrast to the soluble dye, the excited states of the polymer-based dye were essentially isolated from one another by the polymer backbone.



It was on the basis of the acceptance of Ⓟ-RB that we began new studies on the dye rose bengal some three years ago.[13] Rose bengal, 3′,4′,5′,6′-tetrachloro-2,4,5,7-tetraiodouranine (4), was introduced as a singlet oxygen sensitizer by von Tappeiner[14] and used extensively by Schenck and Gollnick in their many mechanistic studies of dye-sensitized photooxidation.[15] It has been used as much as it has because of the high quantum yield of singlet oxygen that it produces ($\phi_{^1O_2} = 0.76$).[16,17]

The organic chemistry of rose bengal has been clarified by Lamberts and Neckers,[18–20] who synthesized a series of new derivatives of the dye. The rose bengal ammonium salts, for example, are soluble in nonpolar solvents like methylene chloride and even pentane in contrast to the parent dye, which is only soluble in water, low molecular weight alcohols, and polar solvents like DMF and Me_2SO. Since the ammonium salts are soluble in solvents of varying polarity, both the photochemistry and spectroscopy could be studied under varied conditions. This has allowed the first examples of nonpolar solvent photochemistry using rose bengal as the photosensitizer. Nonpolar derivatives and many others have been completely characterized in a full paper in *Free Radicals in Biology and Medicine*.[21] Lamberts and Neckers[17,18] also established

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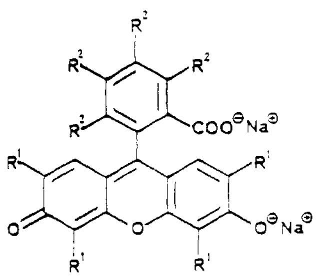
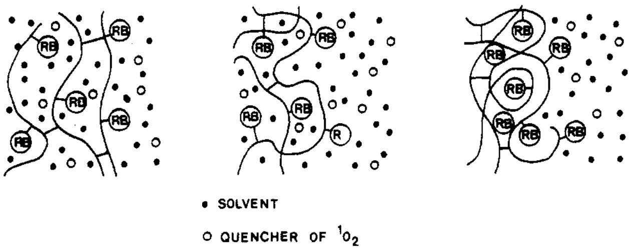
Table I



		R^1	R^2	λ_{max}, nm	ϕF[9]	ϕST[9]	$\phi_{^1O_2}$[9]	ϕST[62]
1	uranine[a]	H	H	491	0.93	0.03	0.1	0.03
2	eosin	Br	H	514	0.63	0.3	0.4	0.32
3	erythrosin	I	H	525	0.08	0.6	0.6	0.69
4	rose bengal	I	Cl	548	0.08	0.76	0.76	0.86

[a] Uranine is the disodium salt of fluorescein. The systematic name of fluorescein in its quinoid form is 2-(6-hydroxy-3-oxo-3*H*-xanthen-9-yl)benzoic acid. The systematic name of fluorescein in its lactonic form is 3′,6′-dihydroxyspiro[isobenzofuran-1(3*H*),9′-[9*H*]xanthen]-3-one.

Scheme I



that the reaction of the chloromethylated Merrifield polymer with rose bengal produced a covalent bond to the polymer bead only at the C-2′ carboxylate position of the dye. Polymeric derivatives of rose bengal are generally prepared via nucleophilic displacement of chloride from a chloromethyl function chemical bound to the copolymer.

Soluble polymeric derivatives of rose bengal were also prepared based on Lamberts' work.[22,23] It was observed that singlet oxygen formation in these soluble polymers depended on the number of rose bengal units attached to the polymer chain. Absorption and emission spectra of the polymers indicated that for lightly loaded polymers (that is polymers to which few rose bengals were attached) self-quenching processes are controlled by solution concentration effects only. For more highly functionalized polymers, self-quenching becomes significant between rose bengal molecules on the same polymer chain. These self-quenching effects are most significant when the polymer is used as a heterogeneous sensitizer, i.e., in a solvent in which it is not soluble—such as MeOH. Under these conditions both intramolecular and intermolecular self-quenching processes, i.e., a dye excited-state being quenched by a proximate dye ground-state, decrease the quantum yield of singlet oxygen formation.

All the xanthane dyes exist in different structural modifications as a function of solution pH. The commercial xanthene dyes, along with the currently accepted numbering system for the ring skeleton, are shown in Table I.

The spectroscopic properties of these dye isomers[24-33] are dependent on their structure.[18-20]

Results and Discussion

Rose Bengal Polymers: Preparation and Synthesis. Soluble polymer-bound rose bengals were obtained from the reaction of (poly(styrene-*co*-vinylbenzyl chloride), molecular weight 107 000) with rose bengal in DMF.[21,22] The starting reaction mixture contained 305 mg of rose bengal per 1.07 g of poly(styrene-*co*-vinylbenzyl chloride), and as elementary analysis has shown, 75% of the original rose bengal became attached to the polymer chain in the process.[23] This percentage yield is virtually independent of the relative ratio of copolymer to dye in the reactant solution.

In order to obtain polymer beads to which differing concentrations of rose bengal were immobilized, varying quantities of rose bengal were allowed to react with the same quantity of chloromethylated poly(styrene-*co*-divinylbenzene) beads in the Merrifield/Blossey[1,2] protocol. The quantity of rose bengal that became covalently bonded to the polymer beads could be calculated from the absorption of the dye remaining in solution ($RB_{max} = 1.625 \times 10^5$ in DMF) and analysis based on a developed spectral technique (see Experimental Section).

Figure 1 shows the relation between amount of RB used in the reaction mixture for 1 g of Merrifield's resin and the quantity of RB eventually attached to 1 g of the polymer beads. The minimum loading of polymer beads obtained in this process is 9.2 mg of rose bengal for 1 g of polymer carrier. The highest loading achieved (Figure 1 does not include this because a different set of conditions were required—see Experimental Section) is 284 mg of rose bengal for 1 g of the polymer beads.

The data show that at low concentration levels of RB in solution (i.e., to prepare lightly loaded polymer beads) about 30% of the rose bengal ends up attached to the polymer backbone (see Table II). When the rose bengal in the solution to be reacted with the copolymer is increased, the percentage yield of rose bengal that becomes immobilized decreases to about 20%. For solutions containing the highest concentration of rose bengal per gram

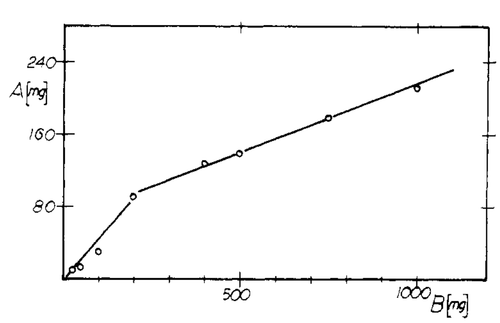


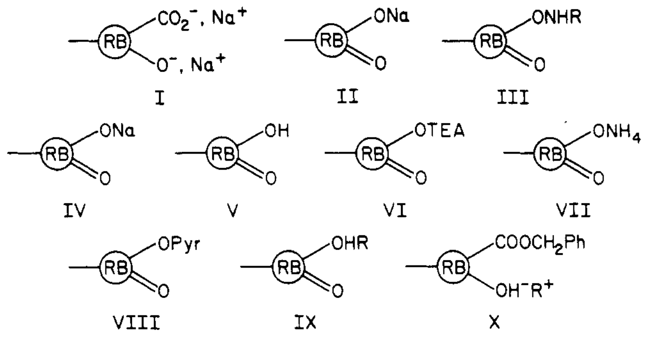
Figure 1. Relationship between amount of RB used in the reaction mixture for 1 g of resin (B) and quantity of RB attached to 1 g of polymer beads (A).

Table II
Quantum Yield for Singlet Oxygen Formation for Ⓟ-RB in CH_2Cl_2 with Various Rose Bengal Loading

type of Ⓟ-RB	amt of RB used in reactn with 1 g of polym[a] beads, mg	amt of RB attached to 1 g of polym beads, mg	$\phi_{^1O_2}$
Ⓟ-RB-0.1	25.0	9.2	0.82
Ⓟ-RB-0.2	50.0	12.5	0.82
Ⓟ-RB-0.4	100.00	33.4	0.91
Ⓟ-RB-0.8	200.00	95.5	0.88
Ⓟ-RB-1.6	400.00	127.8	0.77
Ⓟ-RB-2.0	500.00	138.1	
Ⓟ-RB-3.0	750.00	179.8	
Ⓟ-RB-4.0	1000.00	213.0	0.76
Ⓟ-RB-2/4	2000.00	284	0.82

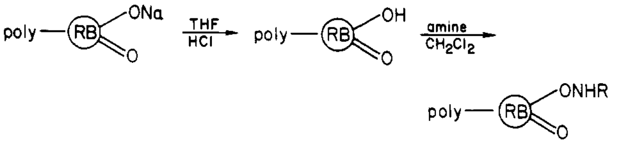
[a] Cl = 0.75 mequiv/g ≈ 12% of the chloromethyl groups react with rose bengal. Four grams of RB for every 210 g of beads.

Chart I



of Merrifield polymer (i.e., to prepare the highest loaded polymer beads), only 14% of the employed rose bengal is eventually attached to the polymer carrier. Since the copolymer beads used in Merrifield procedures are not soluble in DMF (styrene-divinylbenzene copolymer with 1% cross-linking) and since the rose bengal molecule is very large, we suggest that steric effects prevent rose bengal penetration inside swollen polymer beads. These difficulties are less severe for lightly loaded beads but increase as the quantity of RB to be attached to the bead increases.

With the method described by Lamberts and Neckers,[1,13,16,21] poly-II was converted to poly-III 1. The same procedure was applicable for both the soluble and the insoluble polymers to which rose bengal was attached. The acid form of the immobilized dye was neutralized—in methylene chloride—with the amine.



(1)

Quantum Yield of Singlet Oxygen Formation. The quantum yields of singlet oxygen formation for each of the poly-RB's and for the Ⓟ-RB's were obtained by using the relative actinometric method developed by Schaap, Thayer, Blossey, and Neckers.[3,33] The rate of photooxidation of 2,3-diphenyl-*p*-dioxene is compared for the various poly-RB's or Ⓟ-RB's with the rate of photooxidation of 2,3-diphenyl-*p*-dioxene for rose bengal in MeOH ($\phi_{^1O_2} = 0.76$). The important experimental parameter that must be controlled when using this method to study the energy-transfer process from the triplet state of the sensitizer to oxygen is to assure that it be a zero-order reaction. The singlet oxygen quenching process by 2,3-diphenyl-*p*-dioxene must also be a zero-order reaction. As Gottschalk and Neckers have shown,[33] this depends on the lifetime of singlet oxygen in the solvent in question. Below the defined crucial quencher concentration, the Schaap/Thayer relative actinometric method is not a valid measure of the quantum yield of $^1O_2$ formation.

Figure 2 shows the observed efficiency of singlet oxygen formation (using Ⓟ-RB-2.0 as a sensitizer) as a function of the flow of oxygen in the cell.

There is no effect of oxygen flow on a reaction sensitized by rose bengal *in solution*. The rate of 2,3-diphenyl-*p*-dioxene photooxidation using RB dissolved in MeOH as the sensitizer essentially does not change as a function of the rate of flow of oxygen. The rate of 2,3-diphenyl-*p*-dioxene photooxidation using Ⓟ-RB as sensitizer, however, increases as the oxygen flow increases. It is clear that there is a barrier to penetration of oxygen into the Ⓟ-RB beads, and said penetration occurs at a rate that is slower than is the rate of thermal diffusion in the fluid solution. Higher rates of oxygen flow influence the quantum yield of the product of photooxidation formation in the heterogeneous polymer sensitizer case but have no influence on the rate sensitized by RB in solution, because in solution the quantum yield of quenching by O_2 is diffusion controlled. For purposes of quantum yield studies all solvents have the same viscosity. For a Ⓟ-RB, however, two different phases exist: a solution of the $^1O_2$ acceptor in CH_2Cl_2 solution outside the bead and another within the swollen polymer beads. The bead/solution interface and the solvent/acceptor system in the bead have a much higher effective overall viscosity. Since diffusion of oxygen into the beads from the solution is a function of the effective viscosity in the bead's interior, the rate of oxygen flow must be much higher to force O_2 to quench all of the rose bengal triplets formed in the interior of the bead. The pertinent observation is that there is a critical oxygen flow rate below which not all RB^3 in the interior of the beads is quenched by O_2. Thus $^1O_2$ formation is also dependent on oxygen pressure.

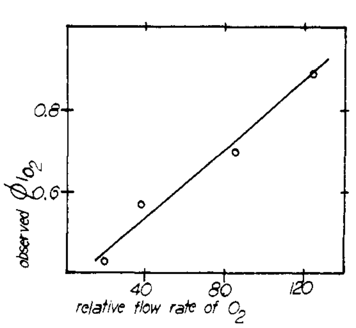


Figure 2. Observed efficiency of singlet oxygen formation for Ⓟ-RB-2.0 as a function of the flow of oxygen.

Rose bengal loading on Merrifield beads does not affect the quantum yield of singlet oxygen formation significantly. The highest observed value is 0.91 (for Ⓟ-RB-0.4); other values are only 15% lower, e.g., ($\phi_{^1O_2} = 0.76$ for Ⓟ-RB-0.2). Both these values are unexpectedly higher than those observed by Schaap, Thayer, Blossey, and Neckers[3] and their co-workers ($\phi_{^1O_2} = 0.43$). The original value obtained for the quantum yield of singlet oxygen formation from Ⓟ-RB must have been obtained under conditions in which the energy-transfer process from the sensitizer to oxygen and quenching processes were not zero order. Under the conditions of the original measurement, the concentration of oxygen in the bead was therefore not sufficient to quench all of the rose bengal triplets. Even for the highest loaded polymer beads (284 mg RB/g), the observed quantum yield of singlet oxygen formation is unexpectedly high (0.82). This value suggests, importantly, that no self-quenching processes occur even with the most heavily loaded Merrifield beads. This is easy to explain by considering the results obtained with soluble poly-RB's[34] and by comparing these results to those obtained with insoluble beads. The quantum yield for singlet oxygen formation observed for poly-RB-450 with loading about 337 mg of rose bengal per 1 g of polymer is slightly lower than is the maximum value obtained in solution. Self-quenching processes are most distinct when the loading of the soluble polymers is in the range 330–400 mg of rose bengal for 1 g of polymer. This loading value is much higher than is the loading even of the most highly loaded polymer beads (Ⓟ-RB-2/4). In Merrifield beads, no self-quenching is observed because the dyes are effectively "site-isolated".

We observed that the amine used as the cation at C-6 has significant influence on the quantum yield of singlet oxygen formation from the polymer-based reagent. The observed efficiency of singlet oxygen formation from Ⓟ-RB

Table III
Quantum Yield for Singlet Oxygen Formation for Poly-RB Soluble in CH_2Cl_2 Containing Various Cations at C-6 Phenolate Group

poly-RB	$\phi_{^1O_2}$
poly-IV	0.38[a]
poly-VIII	0.41
poly-VI	0.61

[a] From ref 3.

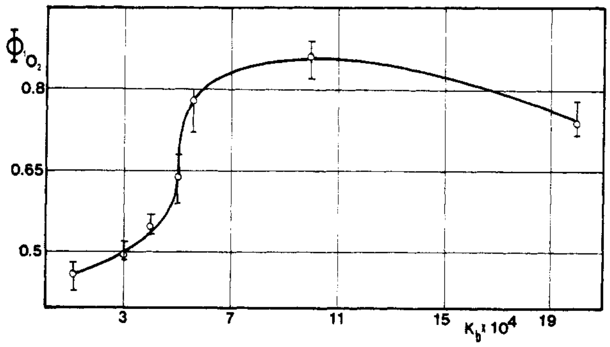


Figure 3. Relationship between basicity of amines used and quantum yield of singlet oxygen formation for Ⓟ-RB's in which different ammonium ions are substituted at C-6.

in which different ammonium ions are substituted at C-6 is shown in Table III. For the sodium and pyridinium salts the quantum yield is lower, while for triethylammonium salts the quantum yield of $^1O_2$ formation is much greater and comparable to the value observed by Lamberts and Neckers for rose bengal (C-2′ benzyl ester triethylammonium salt) in CH_2Cl_2 solution (0.67).

The efficiency of singlet oxygen formation for Ⓟ-III is actually a function of the K_b of the amine. Salts of stronger bases give higher quantum yields of singlet oxygen formation in CH_2Cl_2; see Table IV and Figure 3.

We attribute the effect of the amine at C-6 as deriving from the extent of dissociation of the ammonium salt at C-6, and it is an equilibrium effect that depends on the relative concentrations of the protonated phenolate group and the dissociated salt form. Strongly basic amines remove the proton completely and form the ammonium salt. Weakly basic amines do not cause complete ionization of the C-6 phenol. This same effect has been observed for monomeric models in solution. (We can ignore free amine quenching because the concentration of the amine is very low.)

As we pointed out in the introduction, in the case of Ⓟ-IV the hydrophobic polymer serves to carry an essentially polar dye into nonpolar solvents, but it does so only by virtue of the polymer backbone. Since rose bengal C-2′ benzyl ester sodium salt is not soluble in nonpolar solvents such as CH_2Cl_2, we could say that the hydrophobic polymer in nonpolar solvents produces a heterogeneous sensitizer with the bead swollen by the solvent but with the dye essentially not knowing what to do. It is an insoluble component of the swollen gel. The polymer chain produces essentially an ideal dispersion of the insoluble rose bengal moieties in the nonpolar solvent. For this reason we consider Ⓟ-IV *to be an essentially pure heterogeneous sensitizer, and the photooxidation process is indeed heterogeneous.*

The situation differs when the rose bengal moiety itself is soluble in nonpolar solvent as it is in the case of the appended rose bengal C-6 triethylammonium salt. When the C-2′ (polystyryl) ester is converted to the C-6 ammonium salt, the solubility of the appended moiety in nonpolar solvents is increased and the efficiency of singlet oxygen formation is now limited (a) by the effective isolation of the polymer-appended dye and (b) by the possibility of formation of the dissociated form, i.e., by equilibrium between the protonated phenol group and dissociated salt form. For Ⓟ-III the efficiency of singlet oxygen formation is not dependent on the rate of oxygen flow because the system is more like a homogeneous solution than a heterogeneous process. Ⓟ-III shows very similar behavior to the corresponding homogeneous sensitizers containing rose bengal in this regard, and the shape of the curve shown in Figure 3 is the same for different rates of oxygen flow, whereas Ⓟ-IV drastically changes its efficiency of singlet oxygen formation as a function of oxygen flow.

Table IV
Quantum Yield of Singlet Oxygen Formation of Semiheterogeneous Type of Sensitizer with the General Structure Ⓟ-IX

R^1	$\phi_{^1O_2}$	$K_b \times 10^4$[a]
TMA[b]	0.46	0.6
iso-BA[c]	0.50	3.0
sec-BA	0.55	4.0
tert-BA	0.64	5.0
TBA[d]	0.66	
Pip[e]	0.74	20.0
TEA[f]	0.78	5.6
DEA[g]	0.86	10.0
NH_3	0.27	1.8×10^{-1}
Pyr[h]	0.35	2.3×10^{-4}

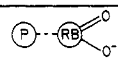
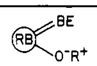
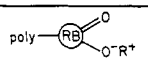
[a] From Morrison, R. T.; Boyd, R. N. "Organic Chemistry"; New York, 1983; p 889. [b] Trimethylamine. [c] Butylamine. [d] Tributylamine. [e] Piperidine. [f] Triethylamine. [g] Diethylamine. [h] Pyridine.

There are two probable explanations for this behavior. Since both the polymer chain and the appended rose bengal are soluble in CH_2Cl_2, an increase in swelling of the beads may result, allowing more efficient oxygen and quencher diffusion into the beads. Alternatively, the triplet lifetime of the dissociated rose bengal trialkylammonium salt may be longer than is the lifetime of the sodium salt in these same solvents. Under these conditions, the rate of oxygen flow can be lower in the case of the ammonium salt polymer than in the case of the sodium salt polymer and still allow all of the rose bengal triplets to be quenched.

Though Ⓟ-III show the typical properties observed for homogeneous photosensitizers, the cross-linked polymer chain does not allow the soluble sensitizer molecule to dissolve in the solvent to form an authentically homogeneous solution. The polymer-based ammonium salts are not pure heterogeneous photosensitizers nor are they purely homogeneous sensitizers. In this case a soluble dye is appended to an insoluble, but swollen, polymer bead. We choose to call this type of photosensitizer a *semiheterogeneous photosensitizer.*

The results obtained for Ⓟ-IV used as heterogeneous photosensitizers in MeOH are also important. This solvent system was not studied by Neckers, Schaap, and their co-workers because they reasoned that a polymer bead needed to be swollen by the solvent in which it was dispersed in order for it to function effectively as a heterogeneous sensitizer. Only the most lightly loaded Ⓟ-RBs (Ⓟ-IV-0.1 and -0.2 with loading of 9.2 mg RB/g and 12.5 mg RB/g, respectively) were viable photosensitizers when used in MeOH, and quantum yields were low ($\phi_{^1O_2} = 0.21$). When loading by dye is increased, the efficiency of singlet oxygen formation decreases (for Ⓟ-IV-0.4 with loading of 33.4 mg RB/g, $\phi_{^1O_2}$ less than 0.05). Ⓟ-IV in MeOH is a semiheterogeneous photosensitizer (rose bengal C-2′ benzyl ester sodium salt is soluble in MeOH), but the hydrophobic

Table V
Spectral Data of ⓟ-RB's, Their Monomeric Models, and poly-RB's

							
R	λ_1	λ_2	λ_1	λ_2	λ_1	λ_2	A^b of 1 mg/2
Na	570	522			572	532	22.35×10^{-3}
TMA	567	522	566.5	528.0			
iso-BA	573	523	563.0	529.0			
sec-BA	573	522	563.0	529.0			
tert-BA	510	522	559.0	530.0			
TBA	566	522					
TEA	571	523	564.0	527.0	573	531	11.21×10^{-3}
DEA	573	522	561.0	530.0			
Pip	572	520	552.5	526.5	573.5	533	
NH_3	573	524					
Pyr	575	525					9.55×10^{-3}

[a] Excitation spectra are not corrected. [b] Calculated absorption for 1 mg of poly-RB dissolved in 1 L of solvent.

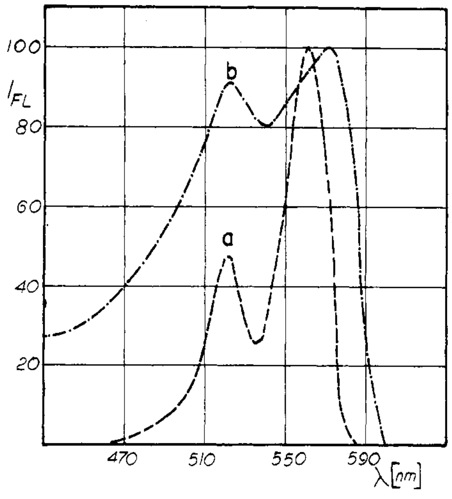


Figure 4. Fluorescence excitation spectra for rose bengal (curve a) and for ⓟ-VI (curve b) in MTHF at 77 °K (λ 605 nm).

polymer chain does not swell in MeOH, and the distance between rose bengal molecules is controlled by polymer environment only. There is no ideal dispersion of rose bengal molecules, and self-quenching processes (intermolecular aggregate formation) decrease the efficiency of singlet oxygen formation.[25] A more precise explanation of those observations is possible through analysis of certain spectral properties of ⓟ-RBs.

Spectral Properties of Heterogeneous Photosensitizers. Direct measurement of the absorption spectra of heterogeneous photosensitizers is impossible because of light dispersion from the polymer surface. Schaap, Thayer, Blossey, and Neckers reported the use of diffuse reflectance techniques to approximate absorption spectra,[3] but this technique does not produce "true" absorption spectra. The sample for reflectance is prepared in a MgO tablet. The ⓟ-RB is not therefore dispersed in a solvent and the spectra obtained are the spectra of ⓟ-RB without ideal dispersion of the rose bengal moieties solution. It is impossible to observe these spectra with reflectance techniques.

The shape of the excitation spectra of ⓟ-RB in a frozen nonpolar solvent (MTHF) do closely resemble the absorption spectra. This can be seen by comparing the absorption spectra of monomeric and soluble polymeric models for ⓟ-RB under identical conditions.

Figure 4 shows the fluorescence excitation spectra for rose bengal and for ⓟ-VI in MTHF recorded at 77 K (λ_{ex} 605 nm).

The general structure of the fluorescence excitation spectra for rose bengal and for ⓟ-VI are similar. Table V shows the fluorescence excitation data for ⓟ-RB's, absorption spectra data for monomeric models of ⓟ-RB's, and absorption spectra data for soluble poly-RB's. The results are also similar.

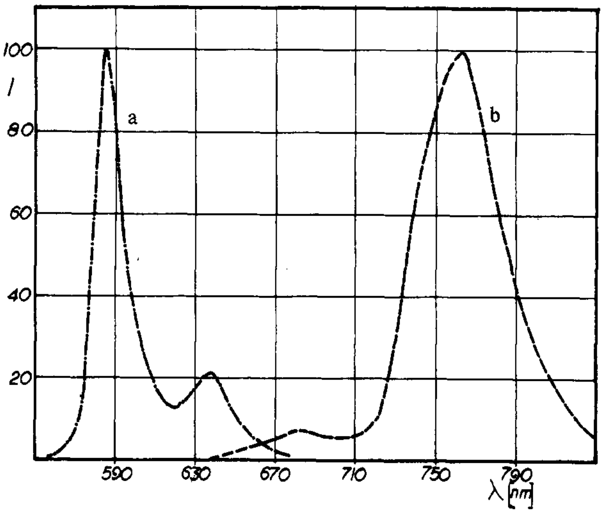


Figure 5. Total emission spectra for ⓟ-RB-0.1 recorded in MTHF at 77 °K: fluorescence spectrum (curve a); phosphorescence spectrum (curve b).

From this observation one can predict that the absorption properties of a heterogeneous photosensitizer will be comparable to the absorption spectrum of its soluble equivalent. Thus if one knows the absorption properties of a monomeric model, takes into regard corrections for solvent and microenvironment, and measures the excitation fluorescence (or phosphorescence) spectrum of the polymer at low temperatures, these spectra should be essentially comparable.

As the data of Table V show, the absorption maxima for soluble poly-RB's are shifted about 10 nm to the red when compared with monomeric models. The longest wavelength maximum of fluorescence excitation spectra for ⓟ-RB's and the longest wavelength maximum of absorption for soluble poly-RB's occur at virtually the same wavelength.

Soluble poly-RB's (triethylammonium salt and pyridine salt) show a decrease in absorption for 1 mg of polymer compared with the absorption observed for poly-IV. Similar behavior is observed for monomeric models of poly-RB's.[9,13,21]

Table VI shows fluorescence and phosphorescence data for ⓟ-RB's with different loadings (in MTHF). The data in the table and the information in the figure give still more information about the differing behaviors of ⓟ-RB's as

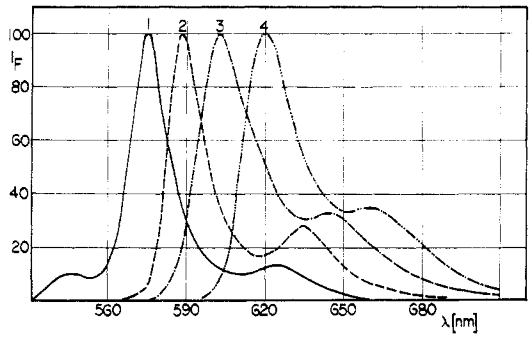


Figure 6. Fluorescence spectra recorded at 77 °K: (1) rose bengal C-2′ benzyl ester diethylamine salt; (2) Ⓟ-RB's in MTHF; (3) Ⓟ-RB-0.1 in EtOH; (4) Ⓟ-RB-2/4 in EtOH.

Table VI
Fluorescence and Phosphorescence Data for Ⓟ-IV with Different Loading of Rose Bengal

		MTHF		EtOH,
type of IV	loading, mg RB/1g Ⓟ	Fl λ_{max}, nm	Ph λ_{max}, nm	Fl λ_{max}, nm
Ⓟ-RB-0.1	9.2	588	758	602–603
Ⓟ-RB-0.2	12.5	585	753	603–604
Ⓟ-RB-0.4	33.4	589	758	608–604
Ⓟ-RB-0.8	95.5	585	759	608–609
Ⓟ-RB-1.6	127.8	591	759	612–613
Ⓟ-RB-2.0	138.1	590	760	612–613
Ⓟ-RB-3.0	179.8	591	759	613–614
Ⓟ-RB-4.0	213.0	592	760	615–616
Ⓟ-RB-2/4	284.0			620

a function of the cation at C-6. RB loading essentially does not change the position of the fluorescence and the phosphorescence maximum. The maximum fluorescence emission for rose bengal C-2′ benzyl ester sodium salt is at 575 nm (see Figure 6). An increase of more than 20 times in rose bengal loading on a polymer bead shifts the maximum of fluorescence emission only 3 nm, and the shape of the fluorescence spectrum does not change. Thus the loading of Ⓟ-RB does not influence the energy level of the singlet state in nonpolar solvents. The total shift of the fluorescence emission maximum from the rose bengal C-2′ benzyl ester sodium salt (13–16 nm) is likely connected with a different type of microenvironment[35,37] in which the rose bengal is located. Similar behavior was also observed for soluble poly-RBs with loading less than 400 mg RB for 1 g of polymer carrier.[11,34]

A similar situation is observed with the phosphorescence spectra. Rose bengal C-2′ benzyl ester sodium salt shows a maximum phosphorescence emission at 719–720 nm in MTHF. The most lightly loaded Ⓟ-IV shows a maximum at 758 nm. The total shift is about 40 nm in the case of the polymer. This relatively large shift results either from a different type of microenvironment of the dye in the polymer or emission from aggregate forms of the dye. The same spectral observations were obtained for soluble poly-RBs with variable loading.[11,34]

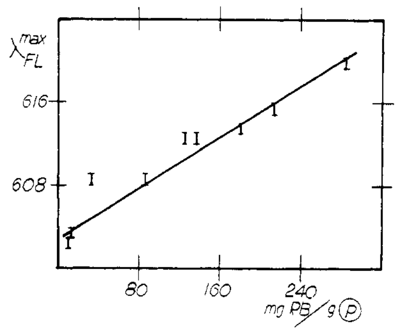


Figure 7. Relationship between the shift in the fluorescence maximum and the degree of loading for Ⓟ-RB's (recorded in EtOH at 77 °K).

The fluorescence spectra of Ⓟ-RB's were also measured for beads frozen in polar solvents (EtOH). In EtOH the beads are not swollen, there is no solvent between the polymer chains, and the rose bengal molecules are isolated by polymer chain only. Even for the most lightly loaded Ⓟ-IV, a large shift of fluorescence emission maximum is observed (see Figure 6). When the loading is increased, this shift is increased also. Figure 7 shows the relationship between the shift in the fluorescence emission maximum and the degree of loading. It is a linear relationship and may be used for calculating the degree of loading of the bead with dye.

Since the microenvironment is the same for all of the Ⓟ-RB's, the red shift of the fluorescence emission is the result of emission from aggregates. The phosphorescence emission maximum for Ⓟ-RB's observed in EtOH essentially does not change position when compared with the phosphorescence emission obtained for Ⓟ-RB's in MTHF. Since there is no difference between the phosphorescence spectra obtained in MTHF and in EtOH, it suggests that self-quenching processes must be taking place from the singlet state. As was stated earlier, as powders in MeOH only the most lightly loaded Ⓟ-RB's (0.01, 0.2) give detectable singlet oxygen formation. When dye loading is increased, the efficiency of singlet oxygen formation in MeOH is decreased. Since this loading essentially influences the fluorescence properties of the Ⓟ-RB's, we can assume that self-quenching processes occur from the singlet state of excited rose bengal molecules, and it is this type of self-quenching process that decreases the efficiency of singlet oxygen formation.

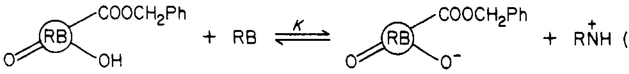
Semiheterogeneous photosensitizers generally show similar spectral properties to those that are observed for heterogeneous sensitizers. Table VII shows the fluorescence and phosphorescence data recorded for Ⓟ-III and their monomeric models (rose bengal C-2′ benzyl ester ammonium salts). The shift of fluorescence and phosphorescence emission maximum between monomeric models and Ⓟ-III is similar as to the cases of Ⓟ-IV and

Table VII
Fluorescence and Phosphorescence Data for Ⓟ-IX and for Their Monomeric Models with Structure Ⓟ-X

	fluorescence			phosphorescence		
R	Fl λ_{max} (IX), nm	Fl λ_{max} (X), nm	red shift, nm	Ph λ_{max} (IX), nm	Ph λ_{max} (X), nm	red shift, nm
tert-BA	589	574	15	738	700	38
iso-BA	587	575	12	759	701	58
sec-BA	588	574	14	738	703	35
TEA	588	576	12	761	713	48
DEA	585	574	11	738	703	38
TMA	590	577	13	758	704	54
Pip	593	574	19	740	703	37
NH_3	591			760		
Pyr	588			761		

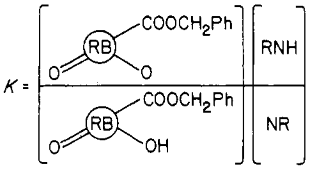
to that of rose bengal C-2′ benzyl ester sodium salt.

As we have previously pointed out, the quantum yield of singlet oxygen formation for semiheterogeneous sensitizers is dependent on the employed amine. In order to explain this, the emission spectra at monomeric models of Ⓟ-RB's (ammonium salts) were also studied. Figure 6 (curve 1) shows the fluorescence emission spectra recorded for rose bengal C-2′ benzyl ester diethylamine salt. In the case of rose bengal C-2′ benzyl ester diethylamine salt, an additional emission band is observed. This extra band becomes more obvious in the spectrum of the bis ammonium salts.[11] As we reported earlier,[11] we can write an equilibrium expression for this rose bengal ammonium salt



(2)

and



(3)

Expression 3 is the expression that characterizes the equilibrium constant for the amine when it acts as a base with the rose bengal C-2′ benzyl ester protonated form as the acid. Obviously, this equilibrium is controlled by the basicity of the amine. Stronger amines form higher concentrations of dissociated rose bengal molecules, and these can produce singlet oxygen at 566 nm.

Experimental Section

General Remarks. Rose bengal, 92% dye content, was used in all synthetic processes. Methanol, ethanol, and methylene chloride were spectroscopic grade and purchased from Aldrich. These were used without further purification. 2-Methyltetrahydrofuran (MTHF) was obtained from Aldrich and distilled before use.

Absorption spectra were measured with a Varian-Cary 219 UV-vis spectrometer. Emission and excitation spectra were measured on a Perkin-Elmer MPF-44A fluorescence spectrophotometer with a Perkin-Elmer phosphorescence accessory.

Low-temperature fluorescence and phosphorescence spectra were measured with 4-mm-diameter glass tubes. The dye solution and Ⓟ-RB's dispersion were degassed (three cycles freeze–thaw under high vacuum).

Synthetic Procedures. Rose bengal C-2′ benzyl ester ammonium salts were prepared with the procedure described by Lamberts and Neckers.[13,21]

General Procedure for the Preparation of Polymer-Bound Sensitizer Ⓟ-IV. To 4.0 g of chloromethylated styrene–divinylbenzene copolymer beads (Bio-Beads SX-1, 0.75 mequiv of Cl/g of polymer, 200–400 mesh) in 50 mL of dimethylformamide was added 100, 200, 400, 800, 1000, 2000, 3000 and 4000 mg of rose bengal. The reaction mixture was stirred magnetically and heated (60 °C) for 24 h. The reaction mixture was filtered, and the residue was washed thoroughly with DMF until no visible color appeared in the solvent. The polymer-sensitizer was additionally washed with MeOH and dried. The DMF/unreacted rose bengal solution was used for the colormetric measurement of unreacted rose bengal.

Preparation of Heavily Loaded Ⓟ-IV-2/4. A procedure similar to that used for the polymer-bound sensitizer was used with the exception of the following conditions: 2 g of Bio-Beads, 4 g of rose bengal, 100 mL of DMF, and temperature 72 °C.

Polymer Beads Bonded to Rose Bengal—Protonated Form Ⓟ-V. Ⓟ-RB sodium salt (10 g) was placed in 250 mL of tetrahydrofuran (THF). After 20 min 20 mL of 2 N HCl was added. The red dispersion of Ⓟ-IV turned orange. The mixture was filtered and the residue thoroughly washed with THF to remove residual HCl. Then it was washed with water and then with MeOH, and it was finally filtered and dried.

Polymer Beads Bonded Rose Bengal Triethylammonium Salt Ⓟ-VI. Ⓟ-V (protonated form) (2.19) was placed in 50 mL of CH_2Cl_2, yielding an orange dispersion. Upon addition of 2 mL of the dried amine, the dispersion turned deep red. The mixture was stirred for an additional hour and filtered, and the residue was thoroughly washed with CH_2Cl_2 and with MeOH.

A similar procedure was used for the other Ⓟ-RB ammonium salts by using the following amines: trimethylamine (TMA), diethylamine (DEA), *sec*-, *tert*-, and *iso*-butylamine (*sec*-, *tert*-, *iso*-BA), tributylamine (TBA), pyridine (Pyr), and piperidine (Pip).

Polymer Beads Bonded Rose Bengal Ammonium Salt Ⓟ-VII. Ⓟ-RB protonated form (2.0 g) was placed in 50 mL of THF and 5 mL of 30% NH_4OH was added. The mixture was stirred for 1 h and filtered, and the beads were thoroughly washed with THF to remove the excess NH_4OH. Subsequent washing was with water and, finally, with MeOH. The mixture was then filtered and dried.

Soluble Polymer Bonded Rose Bengal Sodium Salt Poly-IV. This polymer was prepared according to the method described in our earlier paper.[34]

Soluble Polymer Bonded Rose Bengal Protonated Form Poly-V. Poly-RB sodium salt (2.0 g) was dissolved in 50 mL of THF and 5 mL 2 N HCl was added. The red solution turned orange. The polymer was precipitated 3 times with an excess of MeOH.

Soluble Polymer Bonded Rose Bengal Triethylammonium Salt Poly-VI. The poly-RB protonated form (2.0 g) was dissolved in CH_2Cl_2 and then 2 mL of dry triethylamine was added. The orange solution turned deep red. The polymer was precipitated 3 times with an excess of MeOH.

Soluble Polymer Bonded Rose Bengal Pyridine Salt Poly-VIII. A similar procedure as in the case of poly-VI was used.

Quantum Yield Measurement. Ⓟ-RB beads (75 mg) were placed in a rectangular cell and 2.5 mL (2.9×10^{-2} M) of 2,3-diphenyl-*p*-dioxene was added. The dispersion was stirred, and a continuous flow of oxygen was passed through the mixture. After 10 min of initial saturation with oxygen, the dispersion was irradiated at 566 nm with a high-intensity Bausch and Lomb monochromator fitted with an Osram HBO 200W-L2 superpressure lamp. The product of the photooxidation (ethylene glycol dibenzoate) was monitored by a 5880A Hewlett-Packard gas–liquid chromatograph fitted with a glass capillary column, containing a cross-linked methylsilicone film. The quantum yield of $^1O_2$ formation was calculated with the method described in our earlier paper.[3]

The quantum yield of singlet oxygen formation for Poly-RB's was measured for CH_2Cl_2 polymer solutions, with a measured absorption at 566 nm of about 3. 2,3-Diphenyl-*p*-dioxene (2.9×10^{-2} M) was used as singlet oxygen quencher.

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Registry No. RB = BE(OH)·Na, 88157-09-9; RB = BE(OH)·TMA, 100045-57-6; RB = BE(OH)·*iso*-BA, 100045-58-7; RB = BE(OH)·*sec*-BA, 100045-59-8; RB = BE(OH)·*tert*-BA, 100045-60-1; RB = BE(OH)·TBA, 100045-61-2; RB = BE(OH)·TEA, 91491-53-1; RB = BE(OH)·DEA, 100045-56-5; RB = BE(OH) · pip, 100045-62-3; RB = BE(OH)·NH_3, 100045-63-4; RB = BE(OH)·pyr, 100045-64-5; 2,3-diphenyl-*p*-dioxene, 4344-45-0; oxygen, 7782-44-7.

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(18) Rose bengal is a commercial name deriving from the similarity in its color to the cosmetic dye, *sincur*, used as a dot or a line in the center of the forehead of Bengali women. Von Tappeiner used the name tetrachlorotetraiodofluorescein in his 1904 paper. Strictly speaking, that name is closer to what was known about the structure of rose bengal then than is the *Chemical Abstracts* name today. Von Tappeiner clearly used synthetic samples rather than the commercial dye or he would have used the commercial name. The original red Indian dye may be either a root extract or *cinnabar*. The dye was originally to symbolize marriage ("happiness wart") but in recent years has become more cosmetic than symbolic. We are uncertain if rose bengal is actually used today for this cosmetic purpose, but it may be.

(19) The *Chemical Abstracts* name for rose bengal is 4,5,6,7-tetrachloro-3′,6′-dihydroxy-2′,4′,5′,7′-tetraiodospiro[isobenzofuran-1(3*H*),9′-[9*H*]xanthen]-3-one disodium salt. This represent the cyclized form of the dye. The "Color Index" form of the dye (noncyclized) is the structure of the dye that we have chosen to use in this paper. Its *Chemical Abstracts* name is 2,3,4,5-tetrachloro-6-(6-hydroxy-2,4,5,7-tetraiodo-3-oxo-3*H*-xanthen-9-yl)benzoic acid disodium salt. We make no apologies for not using it or for using the commercial name instead. Rose Bengal should, we suppose, always be capitalized. We also opt to use the lower case—rose bengal.

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(38) Throughout this paper we shall use the following abbreviations: rose bengal, RB or I; soluble polymeric rose bengals, poly-RB; Merrifield polymer beads to which rose bengal is immobilized, Ⓟ-RB.

Thermal Degradation of Aromatic–Aliphatic Polyethers. 1. Direct Pyrolysis–Mass Spectrometry

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ABSTRACT: The thermal degradation of eight aromatic–aliphatic polyethers has been studied by direct pyrolysis–mass spectrometry (DP–MS) and by thermogravimetry. The effect of ammonium polyphosphate was also examined. Polyethers I–III undergo an intramolecular exchange process, which produces cyclic compounds, and a thermal rearrangement, producing compounds with aldehyde and phenyl end groups. Polyethers IV–VI decompose mainly through a β-CH hydrogen transfer to the oxygen atom, producing compounds with hydroxy and olefin end groups. A thermal rearrangement leading to compounds with aldehyde and pentyl end groups is also active in polymers V and VI. Polymers VII and VIII decompose with extensive hydrogen-transfer reactions, leading to compounds with hydroxy and methyl end groups, and through a β-CH hydrogen transfer from the methylene to the phenyl ring, generating compounds with aldehyde and phenyl end groups. Ammonium polyphosphate lowers the thermal stability of polymers I–VI, whereas the other polymers remain unaffected. Our data show that ammonium polyphosphate sometimes changes the distribution of the pyrolytic compounds by inducing an acid-catalyzed thermal degradation of the polymer chain.

Introduction

Direct pyrolysis of polymers in the mass spectrometer (DP–MS) is an excellent method for monitoring the initial thermal fragmentation processes occurring when polymers are heated to decomposition.[1]

We have investigated several classes of polymers by the DP–MS technique to ascertain primary thermal decomposition mechanisms operating in each case.[2–6] Effects of structural factors and/or of the presence of a particular agent on the thermal degradation behavior of polymers have been also studied.[3,5]

Previous MS accounts in the literature on polyethers are confined to totally aromatic polymers[7–9] and some aliphatic oligomers.[10]

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