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Photochemical Properties of Rose Bengal. 11. Fundamental Studies in Heterogeneous Energy Transfer

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ABSTRACT: Polymers deriving from nucleophilic displacement by rose bengal on poly(styrene-*co*-vinylbenzyl chloride) are studied as heterogeneous energy-transfer donors to oxygen. Self-quenching of rose bengal excited states by proximate rose bengal ground states is observed both in the singlet and in the triplet regime. These self-quenching effects are more significant for powders than they are for the same polymers in solution and affect the quantum yield of singlet oxygen formation. The rose bengal triplet lifetime for the poly-RB's is longer (1.5 ms) than is the lifetime of rose bengal in EtOH (90 μs). Upon irradiation in thick films an even longer lifetime product, which may be either a reduced quinomethine, a triphenylmethyl radical, or a radical ion, is observed. Formation of this intermediate is accompanied by cross-linking of the poly-RB matrix.

Introduction

The first use of an insoluble polymer bead as a support for rose bengal and its use as a photosensitizer was reported by Neckers, Schaap, and co-workers in 1978.[1,2] Their idea was conceptually based on Merrifield chemistry, i.e., solid-phase synthesis.[3–5] The original polymer-supported singlet oxygen sensitizer, called Ⓟ-rose bengal, could be used to form singlet oxygen in solvents in which rose bengal itself was not soluble[1,2] since the hydrophobic polymer support carried the basically polar dye into these nonpolar media. Ⓟ-Rose bengal could also be used in polar solvents.[6]

There are several ways to prepare polymer-based sensitizers from xanthene dyes. The sensitizer may be covalently bound to the polymer support.[1,3,7] Rose bengal is a xanthene dye that behaves as a nucleophile at the C-2′ carboxylate. The sensitizer may be absorbed onto a polymeric support.[8,9] The sensitizer may be incorporated into a polymeric film.[10,11] Or the sensitizer may be immobilized with an ion-exchange resin.[12]

We concentrate in this publication on the properties of rose bengal immobilized by covalent bonding to poly(styrene-*co*-vinylbenzyl chloride)—the soluble polymer analogous to Merrifield's resin. It is our purpose to assess the effect of polymer structure and the relationship and proximity of immobilized dye molecules on the photochemistry and the spectroscopy of the polymeric reagent.

The original polymer rose bengal produced singlet oxygen in methylene chloride but with a lower quantum yield (0.43) than did the dye dissolved in methanol (0.76). Lamberts and Neckers[13–15] established that rose bengal could be converted, using standard organic reactions, to monomeric derivatives that were soluble and produced singlet oxygen, in both nonpolar and polar solvents. These derivatives showed very similar quantum yields, and the essential component of the sensitizer molecule was shown to be the fully developed xanthene chromophore. Since rose bengal derivatives are usually soluble in methanol, they could be shown to produce singlet oxygen with essentially the same quantum yield that rose bengal dye (the disodium salt) did in that solvent.

Several structural factors can effect the photochemistry and the spectroscopy of polymetric sensitizers. These include intramolecular and intermolecular energy transfer between immobilized dye residues,[16–21] association between dye molecules and photochemical manifestations of such associations,[22–25] and specific interactions between the dye matrix and singlet oxygen.[26,27]

In this work we outline the influence of the polymer support on the photochemical properties of an immobilized rose bengal and compare the polymer-bound dye when it is used under heterogeneous conditions to the same polymer-bound dye used either in a film or in solution.

Results and Discussion

The preparation and basic photochemical properties of poly-RB's in solution were described in our previous paper.[28] Poly-RB's are derived from poly(styrene-*co*-vinylbenzyl chloride) by nucleophilic displacement in polar, non-hydroxylic solvents. The extent of functionalization can be controlled by the ratio of the two reagents—polymer and dye. As elementary analysis showed, about 75% of rose bengal used in the synthesis is attached to the polymer

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Table I
Quantum Yield of Singlet Oxygen Formation in Homo- and Heterogeneous Photooxidation

	poly-RB							
	25	51	102	152	305	450	610	520
CH_2Cl_2 soln		0.16	0.24	0.31	0.38	0.36	0.32	0.22
solid phase	0.41	0.41	0.32	0.24	0.12	0.11	0.11	0.04

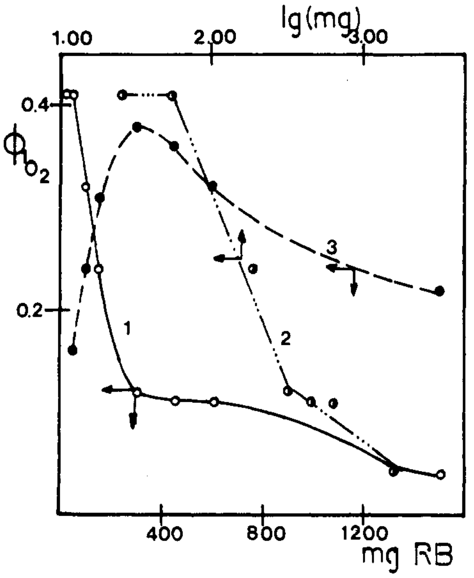


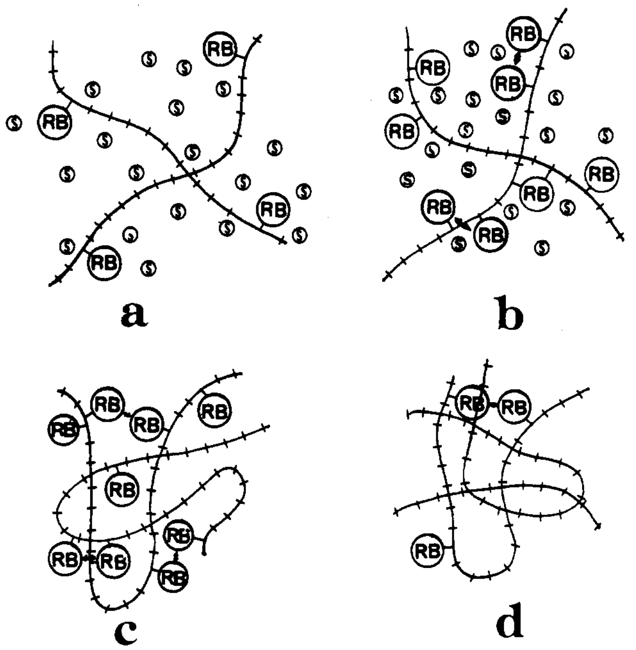
Figure 1. Quantum yield of singlet oxygen formation for heterogeneous and homogeneous (in CH_2Cl_2) photooxidation as a function of the amount of RB attached to a polymer backbone: (1) poly-RB powder in MeOH; (2) poly-RB powder in MeOH using semilogarithmic presentation; (3) poly-RB in CH_2Cl_2 solution.

chain, no matter how high the degree of loading. In our previous publication we[28] concluded that for highly loaded polymers, self-quenching interactions are influenced by the structure of the polymer and by the distance between two different rose bengal molecules immobilized to the macromolecule. Self-quenching interactions should be easy to see in the case of heterogeneous photooxidation, and because the polymers synthesized[28] are insoluble in methanol they can be so studied. In this latter case, energy transfer to oxygen takes place on the polymer surface only, and the distance between rose bengal dye residues is limited by the properties of the polymer chain. Intramolecular interaction should be minimized in the most lightly loaded polymer, i.e., poly-RB-51 (one rose bengal per 200 aromatic units), but would be expected to increase when the concentration of rose bengal moieties attached to the copolymer is increased. The maximum loading in our case is approximately one rose bengal in eight aromatic residues (poly-RB-1510).

We used diphenyldioxene as a singlet oxygen trap[2] and calculated the singlet oxygen quantum yield on the basis of its disappearance. Results of the measurement of singlet oxygen quantum yields as a function of polymer loading when poly-RB's are used as heterogeneous sensitizers in MeOH are given in Figure 1, and the data are shown in Table I.

The results clearly show that only those polymers that are very lightly loaded (poly-RB-25, poly-RB-51) show similar quantum yields in heterogeneous applications to those obtained under optimum conditions from poly-RB's in solution (0.41) (See Table I, $\phi_{^1O_2}$ = 0.38 in methylene chloride for poly-RB-305). When the concentration of rose bengal on the polymer backbone increases, the quantum yield for singlet oxygen drops off dramatically when these same polymers are used in the solid phase (0.12 for poly-RB-305 and 0.05 for poly-RB-1520).

Chart I



The highest value of the quantum yield of singlet oxygen formation was observed with the most lightly functionalized heterogeneous photosensitizers poly-RB-25 and poly-RB-51 (0.41) when the polymers were dispersed in MeOH. This quantum yield was, however, much lower than that of the monomeric model, the C-2′ benzyl ester in MeOH (0.72).[28] This reduced quantum yield clearly derives from rose bengal quenching between rose bengals immobilized on dissimilar polymer chains and, even though the dyes are isolated from one another on a single strand, interstrand dye*–dye quenching results in a decreased yield of singlet oxygen formation in the solid state. Although the polymer powder has a very large surface area, many more rose bengals exist inside the powder bead than are present on the polymer surface, and only a small percentage of the rose bengals actually contribute to the photochemical energy-transfer process.

This thesis can be confirmed experimentally by measuring singlet oxygen formation from a polymer rose bengal layer spread on a glass plate. A polymer layer was prepared from poly-RB-51 in such a way that the layer was thick and all of the incident radiation from a 566-nm source was absorbed by it (see Experimental Section). In this case the efficiency of singlet oxygen formation was very low (0.05 in the film compared with 0.41 for the polymer as a powder—both in MeOH).

The highest quantum yield of singlet oxygen formation from the poly-RB's was observed when poly-RB-305 was dissolved in methylene chloride (see Table I). Poly-RB's more highly loaded than poly-RB-305 gave a lower quantum yield because of intramolecular self-quenching. When the polymers were used under heterogeneous conditions in MeOH, the quantum yield of singlet oxygen formation maximized with very lightly loaded polymers and was seen to decrease for every increase in loading above poly-RB-51 (one RB in every 200 aromatics). In our previous paper we *assumed* that in solution the interaction between rose

Table II
Electronic Absorption Data in the Visible Region for Poly-RB's in CH_2Cl_2 Solution and Polymer Films

	in CH_2Cl_2 solution			polymer films		
polymer	λ_1(max)	λ_2(max)	$A_{\lambda_1}/A_{\lambda_2}$	λ_1(max)	λ_2(max)	$A_{\lambda_1}/A_{\lambda_2}$
poly-RB-51	571.0	523.0	3.165	576.5	534.5	2.19
poly-RB-102	572.0	532.0	2.685	578.0	537.0	1.83
poly-RB-152	572.0	532.0	2.418	578.0	537.0	1.79
poly-RB-305	572.0	532.0	2.674	577.5	537.0	1.67
poly-RB-450	572.5	532.0	1.935	578.5	537.0	1.72
poly-RB-610	572.5	532.0	1.593	578.0	536.5	1.63
poly-RB-1520	570.0[a]	531.0[a]	2.057[a]	580.5	537.0	1.54

[a] Obtained in MeOH–CH_2Cl_2 (1:7) mixture.

bengals on different polymer chains was controlled both by the structure of the polymer chain and by the dispersal of the polymer chain in that solvent[28] (see Chart I, parts a and b).

The situation is completely different when the polymers are used in MeOH, where they are not soluble or even swollen, and the energy transfer is heterogeneous. Because there is no solvent between the polymer chains, self-quenching processes are more likely to occur intermolecularly (Chart Ic). It seems clear that for very lightly loaded polymers, (poly-RB-25 and poly-RB-51) the moieties of rose bengal are sufficiently isolated by the interspersing aromatic residues of the polymer (styrene units) so that self-quenching, both intramolecular and intermolecular, does not occur. Photooxidation processes are not, therefore, interferred with by self-quenching. But when polymer loading is increased, both intramolecular and intermolecular interactions between the dyes are increased (Chart Ic). In this case, photooxidation is inhibited by self-quenching.

In order to determine the extent of intermolecular quenching, quantum yields of singlet oxygen formation for a solid blend of poly-RB-450 and polystyrene were measured. Poly-RB-450 and polystyrene was prepared as a powdered blend such that the concentration of rose bengal molecules in the total polymer blend was identical with that in poly-RB-51. In the case of the poly-RB-450/polystyrene blend, the observed quantum yield of singlet oxygen formation (0.30) was lower than in the case of poly-RB-51 (0.41). It seems clear that intermolecular quenching processes have a large impact on the photochemical processes, but even intermolecular effects can be greatly reduced by blending poly-RB with a polymer chain to which no dyes were attached. These observations suggest that in the case of poly-RB's in the solid state, the polymer chains are closer to one another than they are in solution and energy transfer between chains is observed. In the solid state, the effective photochemical energy-transfer radius is diminished by the presence of the second polymer chain—a polymer chain that lies much closer than it does in solution even with the same polymer. In solution the polymer chains are surrounded by solvent, and self-quenching processes are possible only for highly loaded polymers (Chart Ib). In the solid state, the polymer chains are coiled about one another (Chart I, parts a–c) and the distance between different rose bengal molecules diminishes. Eventually dye–dye self-quenching also increases even for polymer blends (Chart Id).

Self-quenching effects have a major influence on energy transfer to oxygen from polymer-immobilized rose bengals. Communication between dyes immobilized to the same polymer chain decreases the available rose bengal triplets for energy transfer to oxygen. The extent and kind of such self dye*–dye communication can be probed by *absorption* and *emission* spectroscopy.

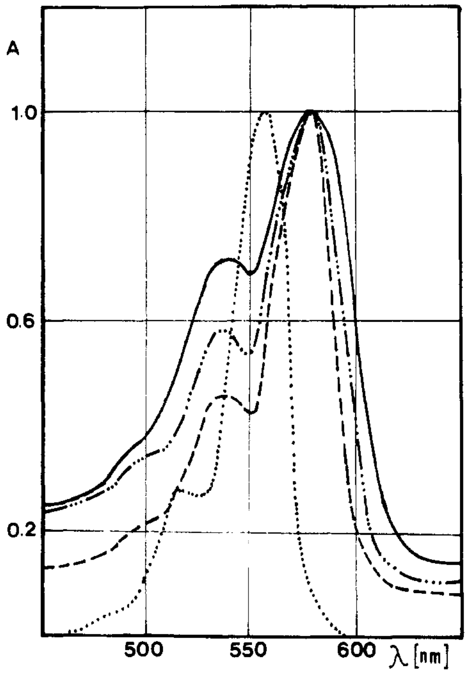


Figure 2. Electronic spectra in the visible region of poly-RB films: (···) rose bengal in MeOH; (---) poly-RB-51; (-···) poly-RB-305; (—) poly-RB-1520.

Figure 2 shows the absorption spectra for poly-RB films prepared on the surface of a rectangular spectroscopic cell, and Table II summarizes the spectroscopic data for poly-RB's in methylene chloride solution[28] as well as in films.

It is easy to see that in polymer films the rose bengal absorption is shifted toward the red when compared with the absorption spectra of the same polymers in methylene chloride solution. There are two different reasons for this. In the case of the polymer films, the individual rose bengal units are surrounded only by the polymer chain. This polymer chain may or may not contain another rose bengal unit. In solution, a single polymer chain is essentially all solvated and, basically, only surrounded by the solvent (Chart I). This suggests that the red shift in the film results from the polarity of the polymer-chain environment on the absorbing dye molecules.[29,30]

When dye polymer loading is increased on the polymer chain, an additional red shift is observed in solution as well as in the film. The red shift is the result not only of the environment but also of dye–dye interactions because the polymer chains are always polystyrenes and essentially the same in every case. We suggest that the distance between two dye molecules is likely large when the polymer is in solution and the possibility of interaction is low, but when polymer films are formed the extent of interaction must increase.

With lightly loaded polymers, the rate of singlet oxygen formation can not be controlled by intramolecular quenching of the dyes. For heavily loaded polymers in

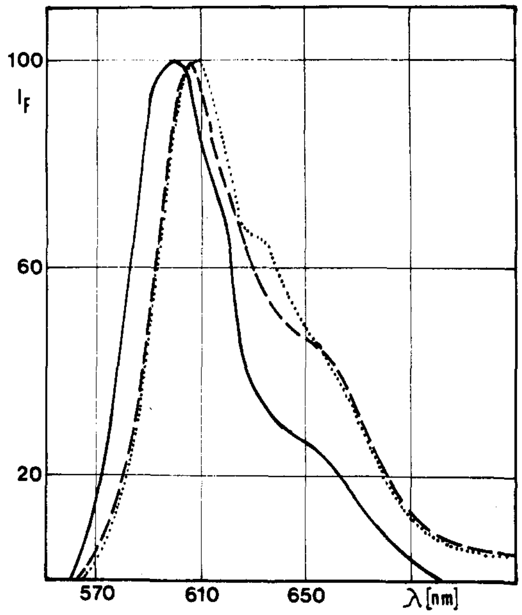


Figure 3. Fluorescence emission spectra at ambient temperature for poly-RB thin films (λ_{ex} 520 nm): (—) poly-RB-51 and polystyrene blend; (---) poly-RB-51, -102, and -152; (···) poly-RB-305.

solution, on the other hand, the distance between rose bengal moieties is a function of the coiling of the polymer chain and intramolecular quenching is much more probable (Chart Ib). Two different polymer molecules, both of which are immobilized rose bengals, are sufficiently separated by the solvent molecules so that the chains do not intertwine, and intermolecular polymer–polymer interactions that result in self-quenching of the dyes are improbable. Intramolecular effects, however, may be more significant.

For lightly loaded polymers, red shifts result from the proximity of dye molecules to one another along the backbone. These proximate dye molecules form aggregates or dye molecular pairs. Aggregate formation extends the absorption maximum and eventually causes a change in position of that maximum[22-25] (λ_{max} 576.5 nm for poly-RB-51 and 580.5 nm for poly-RB-1520). In addition, aggregate formation changes the ratio of $A_{\lambda_1}/A_{\lambda_2}$ for every polymer so that it is lower in the film than it is in methylene chloride solution (Table II). Only the highest value in the film approaches the average value of $A_{\lambda_1}/A_{\lambda_2}$ observed in solution for poly-RB's. For highly loaded polymers, this ratio is even further diminished in the film relative to the ratio in solution. It is clear that when the loading of the polymer with dye increases, the possibility of aggregate formation also increases, and this has an effect on the absorption spectrum of the system.

The influence of rose bengal loading on the poly-RB's in the film was studied by emission spectroscopy. Both fluorescence and phosphorescence were observed. Figure 3 shows the fluorescence spectra of the poly-RB's in films ($A < 0.2$) at ambient temperature. The emission spectrum of poly-RB-51 in a polystyrene-blend matrix shows a maximum fluorescence emission at 600 nm, while poly-RB-51 in methylene chloride solution shows a fluorescence maximum at 593 nm. This shift also results from the different environments around the dye molecules (Chart I, parts a and b). In the case of each of the poly-RB's, the environment is effectively identical in every case but the isolation between rose bengal dye molecules immobilized on that backbone is not as effective as it is in the case of poly-RB-51 blended into a polystyrene matrix where the isolation is enforced by the blended—but not functionalized—polymer. This isolation of the dye chromophore leads to an additional shift in the maximum (λ_{em} 605–610 nm).

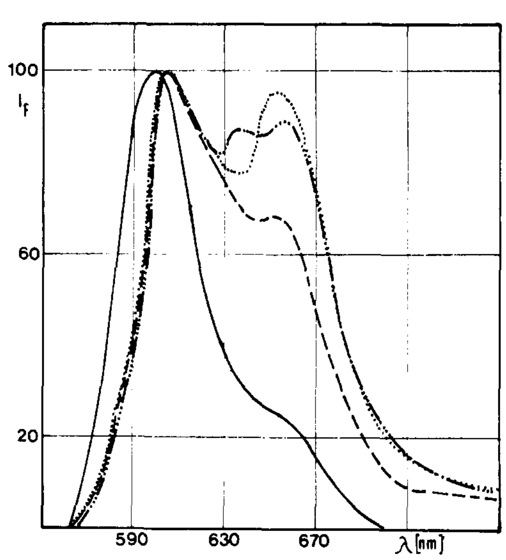


Figure 4. Fluorescence emission spectra at ambient temperature for poly-RB thick films (λ_{ex} 520 nm): (—) poly-RB-51 and polystyrene blend; (---) poly-RB-51; (—···) poly-RB-152; (···) poly-RB-305.

Moreover the structure of the emission spectra for pure poly-RB's in films is different from that of a polystyrene blend. For pure poly-RB films, the emission band in the red area is of increased intensity. This suggests that when the probability of dye–dye aggregation increases, the fluorescence spectrum shifts toward lower energy or longer wavelength. This shift is connected to emission from rose bengal aggregates.

Aggregation effects on the emission spectrum are more distinctly shown when the fluorescence emission spectrum is measured for thick films ($A > 2$), Figure 4. Since the emission spectrum and the absorption spectrum partly overlap in the shorter wavelength area of the emission spectrum, emission followed by reabsorption effects inside the polymer layer effectively emphasize the intensity of the longer wavelength emission band. Additionally, this emission band shows a maximum at about 650–655 nm and also derives from aggregates. When the rose bengal loading on the polymer backbone increases, the emission from aggregates clearly increases also. This effect is more distinct in the case of lightly loaded poly-RB's; for heavily loaded poly-RB's (poly-RB-450 and -610) long-wavelength emission increases but not as sharply.

Low-temperature fluorescence spectra are presented in Figure 5. The fluorescence emission curves with a maximum at 580 nm were obtained for poly-RB-51 in MTHF solution (the normalized contribution of rose bengal was 4×10^{-5} mol/L). RB-C'2 benzyl ester ($c = 2 \times 10^{-5}$ mol/L) in MTHF shows a fluorescence maximum at 575 nm. If we assume that in the case of poly-RB-51 in the solid phase the molecules of rose bengal are sufficiently isolated by the polymer chain (one rose bengal per 200 polymer monomer units), we can assume that the shift in the fluorescence emission for poly-RB-51 film is connected to a change in the microenvironment of the dye in the film (λ_{max} 598 nm). Dye–dye interactions are still possible, and this relatively large shift ($\simeq$ 18 nm) must be connected to a change in microenvironment and to interaction between rose bengal molecules on different polymer chains. When the loading of the polymer with dye increases, an additional shift is observed ($\lambda_{max_{em}}$ 618–619 nm for poly-RB-102 and -152 and 620–621 nm for poly-RB-450 and

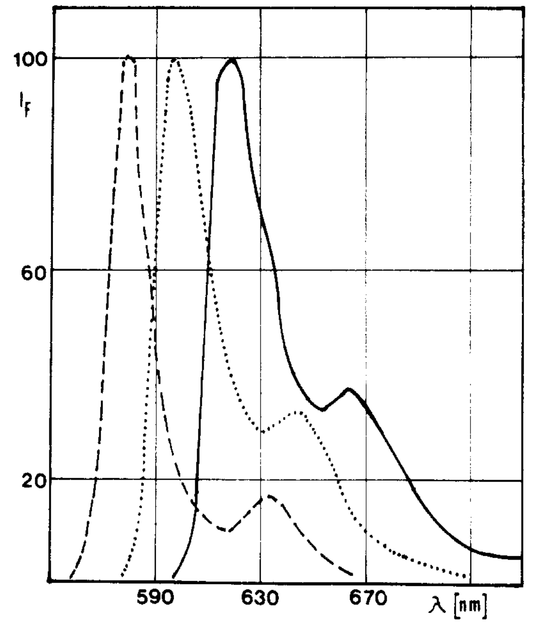


Figure 5. Low-temperature fluorescence emission spectra for poly-RB films and solutions: (---) poly-RB-51 in MTHF; (···) poly-RB-51 film; (—) poly-RB-450 and -610 film.

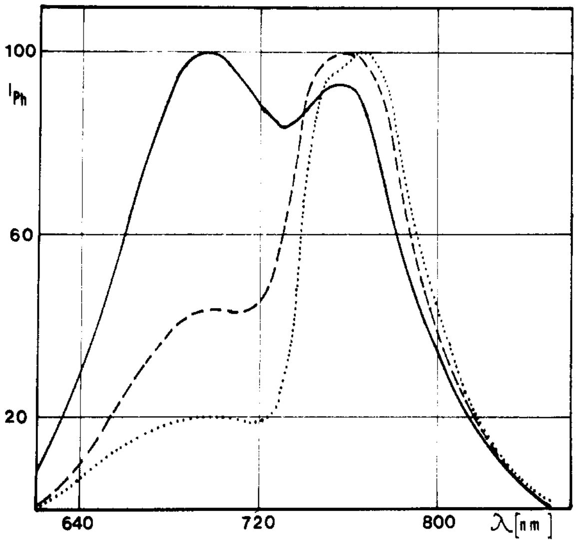


Figure 6. Phosphorescence emission spectra for poly-RB films (77 K): (···) poly-RB-51; (---) poly-RB-152; (—) poly-RB-450.

-610). Maximum monomer (i.e., nonaggregate) fluorescence emission in nonpolar solvents (RB-C′2-benzyl ester in MTHF) is observed at 575 nm and for poly-RB-450, 610 at 620 nm. This amounts to a total shift of 45 nm. The emission observed at 620 nm is obviously also that of dye aggregates.

The phosphorescence spectra for poly-RB films are shown in Figure 6. For all the poly-RB films, the maximum phosphorescence emission is observed at 765–766 nm (in MTHF at 755–756 nm for lightly loaded polymers and at 760–761 nm for heavily loaded polymers). In the case of phosphorescence emissions, there is no distinct difference in the position of the emission maxima in solution and in polymer films. The small shift (5–6 nm) is likely connected with different microenvironments for the dyes in the two cases.

On the other hand, the emission of the monomer as evidenced by the emission of C-2′-benzyl ester in MTHF shows a maximum emission at 720–721 nm, the difference between the C-2′-benzyl ester emission and that of the polymer being 40 nm. This large shift confirms that the polymer backbone has a major effect on the spherical interdependence of rose bengal molecules and this forces a larger contribution to the emission in the triplet time domain from rose bengal aggregates.

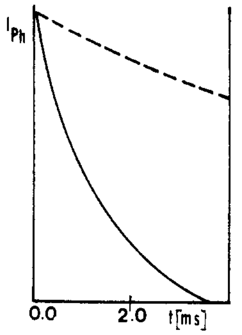


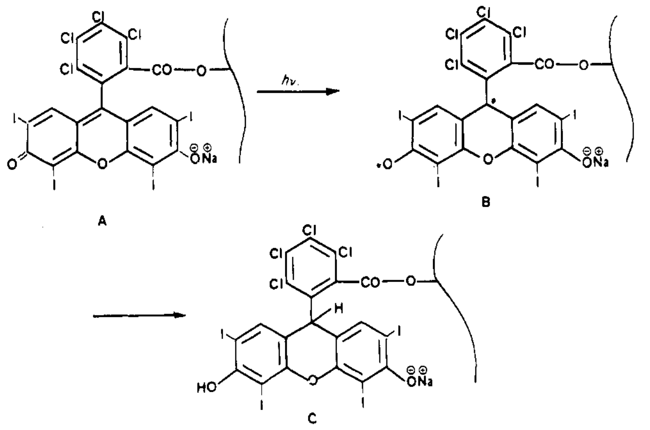
Figure 7. Long-lived emission decay curves for poly-RB films: (—) poly-RB-51 at 747 nm (λ_{ex} 530 nm); (---) poly-RB-450 at 685 nm (λ_{ex} 530 nm).

As we reported in our earlier paper,[28] when the amount of rose bengal attached to the polymer is relatively high (poly-RB-450 and -610 in MTHF), a new emission band is also observed in the short-wavelength region of the spectrum. This phenomenon is even more obvious in the case of rose bengal polymer films. As Figure 6 shows when the amount of rose bengal attached to the polymer increases, the intensity of the new shorter wavelength band is increased and it becomes more intense in the case of the most highly loaded polymers (poly-RB-450 and -610). Another possibility, however, is that the emission derives from a new rose bengal species being formed in the polymer film as the film ages.[28] It was this latter possibility that was confirmed experimentally. The decay curves for the phosphorescence spectrum and the new band were measured. The results are shown in Figure 7. It is interesting to note that the lifetime of the phosphorescence in the polymer rose bengal system is dramatically long (about 1.4 ms). Rose bengal in EtOH has a triplet-state lifetime of only 90 μs, while when rose bengal is present in a methanol–poly(4-vinylpyridine) solution, the lifetime is increased to 205 μs.[29] Since excited-state properties of xanthene dyes are greatly influenced by changes in viscosity, polarity, and physical site–site interactions, the triplet state is obviously stabilized by the structure of the polymer chain. Generally the environment around the dye is quite different from that around the polymer-based dye in solution.

The second decay curve for the longer lived emission, but of shorter wavelength, was also recorded. The lifetime for this emission is much longer than is that of the phosphorescence emission of rose bengal triplet. We assume that this emission is deriving from a photoproduct frozen in the polymer by virtue of its matrix structure, since all of the polymers were prepared in the light, rather than in the dark. In order to check this latter supposition, poly-RB-51 (poly-RB-51 shows almost none of the long-lifetime emission when initially prepared) film was placed in sealed tubes and irradiated. The long-wavelength emission was recorded. After 3 h irradiation, the emission spectrum was very similar to that of poly-RB-450. Moreover, the decay curve of the new emission band was identical in shape with that of poly-RB-450.

There are several structural possibilities for the photoproduct from rose bengal immobilized to polymer films. Photoreduction of the quinomethine, Scheme I, was suggested for other xanthenes many years ago by Oster.[31,32] Photoreduction occurs in stages and these involve first the triplet biradical, followed by reduction of the n,π* state

Scheme I



at the oxygen to produce the phenol radical. The radical center deriving at C-9 would then be reduced in the absence of oxygen. Another possibility is that the new emission observed from the film where oxygen deficiency is enforced is that of the triphenylmethyl radical at C-9. Still another possibility is that the new emission derives from electron transfer and is either the emission of the radical cation of rose bengal or its radical anion. It is well-known that the bleaching of rose bengal in the presence of oxygen is prevented by polymer immobilization. Since bleaching is thought to be the result of bimolecular electron transfer followed by oxidation, it may be that the rates of secondary reactions or the radical cation or radical anion are prevented by the polymer matrix. The photobleaching of rose bengal is a subject of intense interest in our laboratories, and though the chemistry is most complex, we are working toward the structure of the bleached product dye.

All of these processes also lead to different polymeric photochemical products. Abstraction of a proton from the polymer chain may lead to chain cleavage and oxidation of the backbone. Free radicals formed on the backbone can produce cross-linked chains. That this occurs was also confirmed experimentally. Poly-RB film after irradiation loses solubility in solvents in which the freshly prepared polymer is soluble.

Conclusions

Several structural factors can effect the photochemistry of polymer-bound sensitizers. In the case of homogeneous photooxidation, when the sensitizer used is monomeric, the photooxidation is influenced by the efficiency of triplet-state formation and energy-transfer processes from the excited dye to oxygen. The situation is more complicated when the dye is immobilized by covalent bonding to a polystyrene backbone. As results presented in this paper demonstrate, the main phenomenon that effects the efficiency of singlet oxygen formation is energy transfer, both inter- and intramolecular, between dye molecules.

Elimination of those processes deleterious to energy transfer to oxygen is possible by controlling polymer loading. This is particularly important in the case of intramolecular energy-transfer processes between dye molecules. Intermolecular energy-transfer processes can be regulated by the degree of dye loading on the polymer and better isolation of two different polymer-bound molecules by the presence of unreactive polymer molecules, e.g., poly-RB and polystyrene blend.

Self-quenching processes can be probed by both absorption and emission spectroscopy. Both showed that in the case of poly-RB's in the solid phase, self-quenching processes are observed both in the singlet and triplet states for excited rose bengal molecules. In the case of short-lived emissions, emission from aggregates is observed only (in solution this type of emission was not observed). Similar aggregate emission is also observed from the triplet excited state of rose bengal. These processes are most obvious when the loading of polymer is relatively high (more than 1 rose bengal molecule per 200 polymer units) and they can be reduced by the degree of loading.

Polymer-bound sensitizers have a particularly important property. The lifetime of the excited triplet state is much longer in the solid phase than is that of the monomeric dye in solution. This can increase the efficiency of energy-transfer processes from excited dye molecules to oxygen.

When the amount of rose bengal attached to the polymer is high (1 dye/10), a new emission band is also observed in the short-wavelength region of the long-lived emission spectra. This is an emission from photochemical products of rose bengal, which may also be excited in the same wavelength region as rose bengal. Likely these products can also form singlet oxygen.

Experimental Section

General Remarks. Electronic absorption spectra were obtained on a Varian Cary 219 UV-vis spectrometer. Emission spectra were measured with a Perkin-Elmer MPF-44A fluorescence spectrophotometer with the Perkin-Elmer phosphorescence accessory. Emission decay curves were obtained with the Perkin-Elmer phosphorescence accessory connected to an oscilloscope.

Quantum yields of singlet oxygen formation were measured with a Bausch and Lomb high-intensity monochromator fitted with an Osram HBO 2004-L2 superpressure mercury lamp. GLC analysis was performed on a Hewlett-Packard gas chromatograph fitted with a glass capillary column (0.20-nm i.d. 12-m length) containing a cross-linked methyl silicone film (0.33-nm film thickness) and a flame ionization detector.

Synthetic Procedure. The syntheses of the polymer-bound rose bengal has been described in a previous publication.[28] The polymers precipitated by MeOH were crumbled and washed with great care with MeOH. Elementary analyses of polymer loading were done by the Galbraith Laboratories, Inc. Results showed that about 75% of the rose bengal used in the syntheses end up attached to a polymer chain.

Quantum Yield Measurement of Singlet Oxygen Formation. To a 2.5-mL methanol solution of 2,3-diphenyl-*p*-dioxene (2.9×10^{-2} M) placed in rectangular cell was added 10 mg of poly-RB powder. The mixture was stirred, and a continuous flow of oxygen over the surface of the mixture was maintained throughout the irradiation. The mixture was irradiated with a high-intensity monochromator at 566 nm. The formation of the photooxidation product (ethylene glycol dibenzoate) was followed by GLC analysis of the solution at 225 °C. The quantum yield of singlet oxygen formation was calculated from the ratio of the rate of ethylene glycol dibenzoate formation for poly-RB's compared with the rate for RB under identical conditions and using the known quantum yield for RB ($\phi 1_{\mathrm{O}_2} = 0.76$) according to an equation described in a previous paper.[28]

Emission Spectra Measurements. Poly-RB's-coated glass plates were prepared by applying a dioxane solution of the appropriate poly-RB's and removing the solvent by evaporation at room temperature.

Poly-RB films for the measurement of low-temperature emission spectra were prepared in 4-mm-diameter glass tubes by solvent evaporation under vacuum at room temperature. Subsequently, polymer layers were degassed by using the high-vacuum apparatus at 40 °C. Finally the tubes were sealed.

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Photoresponsive Polymers. 7.[1] Reversible Solubility Change of Polystyrene Having Pendant Spirobenzopyran Groups and Its Application to Photoresists

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ABSTRACT: The solubility of polystyrene in cyclohexane was found to change reversibly upon ultraviolet irradiation by incorporating small amounts (~2 mol %) of spirobenzopyran into the pendant groups. Photoisomerization of the pendant spirobenzopyran groups to the polar merocyanine form decreased polymer–solvent interaction, resulting in fractional precipitation of higher molecular weight polymers. The molecular weight of the precipitated polymer ($M_w = 5.1 \times 10^4$) was twice that of the soluble polymer ($M_w = 2.4 \times 10^4$) when the spirobenzopyran content was 3.9 mol %. The fractional precipitation behavior was interpreted through the change in the molecular weight dependence of the critical miscible temperature owing to the configuration of the pendant groups. The copolymer with a high content of spirobenzopyran groups (12.5 mol %) worked as a negative photoresist with high contrast.

Introduction

In a previous paper[2] it was reported that polystyrene with azobenzene pendant groups changes its solubility in cyclohexane upon irradiation with light of a specific wavelength; ultraviolet light caused precipitation of the polymer, while visible light resolubilized it. Structural changes of the pendant azobenzene groups from the trans to cis form altered the balance of polymer–polymer and polymer–solvent interaction, resulting in contraction of the polymer chain and finally in its precipitation. Time-resolved light-scattering intensity measurement after a laser flash in the microsecond time range yielded evidence for the polymer chain contraction (indicated by an increase of the scattering intensity) with a rate constant of 10^3–10^4 s^{-1}. The precipitation was observed at several hundred milliseconds after the flash.[3]

In the present article, we report a reversible solubility change of polystyrene with spirobenzopyran pendant groups in cyclohexane and its application to photoresists. Our first paper on photoresponsive polymers[4] has shown that poly(methyl methacrylate) with spirobenzopyran pendant groups changes the viscosity reversibly in benzene upon ultraviolet irradiation. The decrease of viscosity due to photogeneration of the merocyanine form was explained by the intramolecular solvation of merocyanines by ester side groups.

Recently, Goldburt et al.[5] and Kalinsky and Williams[6] have reported intramolecular stack formation among pendant merocyanine groups upon irradiation of polymers with spirobenzopyran pendant groups. In these experiments, the pendant groups are attached to the polymer at the N position through an ester linkage. This photochemically induced reaction is in contrast to our observation[4] where the methacryloxy methyl substituent is introduced at the 8′ position of the spirobenzopyran group. This suggests that steric factors play an important role in the behavior of merocyanine forms in weakly polarizable solvents such as toluene. Analysis of the behavior in nonpolar solvents, such as cyclohexane, will provide a new insight into understanding the photoresponsive mechanism of spirobenzopyran polymers.

Experimental Section

Spirobenzopyran chromophores were incorporated into the pendant groups of polystyrene by copolymerization with 1,3,3-

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