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Polymer-Based Sensitizers for the Formation of Singlet Oxygen. New Studies of Polymeric Derivatives of Rose Bengal

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ABSTRACT: We outline herein the synthesis and photochemical properties of a new series of polymeric derivatives of rose bengal. These polymers are made from poly(styrene-*co*-vinylbenzyl chloride) by nucleophilic displacement using the C-2′ carboxylate of the dye[1,3] and are soluble in nonpolar solvents. The possibility of aggregation of the rose bengal (RB) molecules along the polymeric backbone is indicated by changes in absorption spectra which occur with the loading of the rose bengal on the polymer. Singlet oxygen formation from sensitizers of increased RB loading in methylene chloride solution (the polymers are soluble in this solvent) suggests that the quantum yield of singlet oxygen formation is dependent on the number of RB units attached to the polymer chain. At low concentrations of RB, the quantum yield of singlet oxygen formation increases with RB loading, reaching a maximum value when 1 RB is attached per 30 chain units. Subsequent increases in the RB content cause a sharp decrease in the quantum yield of singlet oxygen formation. Electronic absorption spectra and quantum yields of singlet oxygen formation by the monomeric rose bengal model RB C-2′ benzyl ester suggest that hydrogen bonding between rose bengal moieties and protic solvents leads to blue shifts in the absorption maxima and an increase in the yield of singlet oxygen formation. Absorption and emission spectra indicate that, for lightly loaded rose bengal polymers, self-quenching processes are prevented by the lack of proximate aggregation of the bound RBs and the photochemistry is controlled by solution concentration effects only. For heavily loaded polymers, self-quenching becomes significant between RBs on the same polymer chain, and concentration effects in solution become less important in controlling the photochemical processes.

Introduction

The synthesis, use, and basic photochemical properties of the first heterogeneous sensitizer for singlet oxygen formation was outlined by Neckers, Schaap, and their co-workers in 1973.[1,2] This sensitizer, called Ⓟ-rose bengal, could be used to form singlet oxygen in solvents in which rose bengal itself was not soluble.[2,3] Polymer-based sensitizers have a number of important practical advantages over soluble sensitizers. The polymer may be used as a handle for easy separation and to carry a polar sensitizer into a nonpolar solvent. Ⓟ-rose bengal itself, marketed as Sensitox I, is much more stable to photochemical bleaching than is virtually any other analogue of rose bengal.[5,6] And, as we shall demonstrate in this paper, the polymer forces an isolation of individual dye molecules, thus decreasing self-quenching effects.

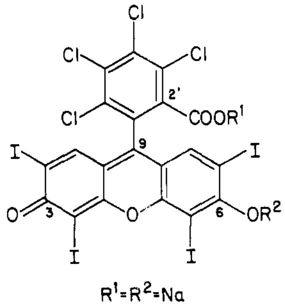
There are three general ways to prepare a polymer-based photosensitizer. The sensitizer may be covalently bound either to a cross-linked polymer gel prepared from styrene and divinylbenzene or to silica gel.[1,2,4,5] These polymeric sensitizers are synthesized by a chemical reaction of the rose bengal with the support. As Lamberts and Neckers have recently shown, that reaction involves the C-2′ carboxyl of rose bengal as the nucleophile[3,9,10] when rose bengal is the immobilized dye. In the second general method, the sensitizer is absorbed on the solid support such as silica gel.[6,7] This technique is easy, except that the dye may be eluted by polar solvents. In still another method, the sensitizer dye is incorporated into a thin polymeric film. This is done by dissolving the sensitizer and the polymer in a solvent and evaporating the solvent from the polymer/sensitizer solution on a flat surface.[8] This technique suffers—for reasons which we shall see later—from the polar properties of rose bengal and the degree of aggregation of the dye which occurs in the process of laying the film on the surface. Quantum yields of singlet oxygen formed, therefore, are not high, though this is almost certainly the result of self-quenching.

Although Ⓟ-rose bengal was first reported in 1973, essentially nothing was known about the chemistry of rose bengal until the studies of Lamberts and Neckers.[3,9,10] These workers established that rose bengal could be converted, by using standard organic processes, to monomeric nonpolar derivatives which behaved—spectrochemically and photochemically—as rose bengal itself did in polar solvents, and established by the study of model compounds how rose bengal reacted with chloromethylated polystyrene.

The original polymer rose bengal was prepared by Blossey and Neckers from chloromethylated polystyrene/divinylbenzene beads by using the following reaction:

$$Ⓟ\text{-}CH_2Cl + RB \rightarrow Ⓟ\text{-}RB$$

Initial control experiments by Schaap and Thayer made it clear that rose bengal immobilized on beads by the above process was a singlet oxygen source; nevertheless, the quantum yield of singlet oxygen formation from Ⓟ-rose bengal from these polymer beads (sodium salt) in methylene chloride was lower (0.43) than the quantum yield of singlet oxygen formation from rose bengal in MeOH (0.76), a polar solvent that is the only kind in which rose bengal itself dissolves. Other studies[11] indicated that other polymers gave rose bengal sensitizers which produced singlet oxygen in higher yield, though Sensitox I has a major advantage—it does not bleach significantly.[11,12]



$R^1 = R^2 = Na$

rose bengal

It is our intention in this work to outline the influence of the polymer support on the photochemistry of rose bengal and to compare the behavior of the polymer-bound dye to the behavior of a model dye free in the same solvent. In the present paper, therefore, we report on the photo-

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Table I
Yields, Percent CH_2Cl Corresponding to the Number of Rose Bengals Added to the Reaction Mixture of Poly-CH_2Cl, and the Frequency of C=O in Poly-RB

polymer	yield, g	% of CH_2Cl group	$\nu_{C=O}$, cm^{-1}
poly-RB-51[a]	0.85	1.65	1725.0
poly-RB-102	0.95	3.30	1725.0
poly-RB-152	0.77	5.00	1725.0
poly-RB-305	1.03	10.0	1741.4
poly-RB-450	1.15	15.0	1728.1
poly-RB-610	0.90	20.0	1738.3
poly-RB-1520	1.05	50.0	1739.8

[a] The quantity of rose bengal actually attached to the polymer chain cannot be easily estimated for very heavily loaded polymers. Solubility precludes actual measure of unreacted rose bengal; the spectra of both the bound and unbound dyes are almost the same. At higher concentrations, highly absorbing dyes do not follow Beer's law.[15,16]

chemical and spectral properties of new singlet oxygen sensitizers based on soluble polystyrenes. These derivatives are referred to as poly-RB. We compare their behavior with that of a model-RB C-2′ benzyl ester.

Results and Discussion

Polymer rose bengals were obtained in soluble form from the reaction of poly(styrene-*co*-vinylbenzyl chloride) with rose bengal in DMF. The ratio of styrene units to vinylbenzyl chloride units (60% meta, 40% para), was 3:1. Polymer-based rose bengals containing differing concentrations of rose bengal in the backbone were obtained by allowing differing amounts of rose bengal to react with an identical quantity of the copolymer. The yields of the obtained polymers, the percent of chloromethyl groups which corresponds to the number of RB moieties in the reaction mixture, and the wavenumber of the carbonyl stretching frequency of the obtained polymers are given in Table I.

Because of the substantial excess of chloromethyl groups in the polymer relative to the quantity of added rose bengal (Table I), it is assumed that essentially all of the RB becomes attached to the polymer chain as the styryl ester. The elegant work of Lamberts[3] clearly demonstrated that the esterification of RB with benzyl chloride formed the benzyl ester only. There was no reaction at the C-6 phenolic center.

When the produced poly(styrene-*co*-vinylbenzyl chloride) (molecular weight 107 000) was treated with rose bengal in DMF without protection from light or oxygen, partial decomposition of the polymer resulted, as shown by the gel permeation chromatography of the final polymer. Poly-RB, synthesized in the dark in DMF solution under nitrogen via the standard nucleophilic displacement process, produced little or no polymer decomposition. These degradations are those of known polystyrene oxidation processes.[13,14]

In order to determine how the photooxidation of the polymer was occurring, both the polymer which had been prepared in the absence of oxygen and light and the polymer which had been functionalized in the presence of oxygen and light were irradiated at the maximum rose bengal absorption, 566 nm at room temperature for 5 h. Poly-RB-51 obtained by the reaction in the absence of light and air was irradiated for an additional 10 h in refluxing methylene chloride. The molecular weight distribution curves for the polymer which was not protected from light and air during its synthesis showed some change of molecular weight from continued irradiation. The polymer which was prepared under anaerobic conditions was stable to continued irradiation and showed no change in molecular weight. This suggests that polymer degradations during preparation are sensitized mostly by monomeric rose bengal derivatives and likely are more important with the monomers than with the polymer. When the polymer is essentially all formed, the polymer becomes relatively photostable.

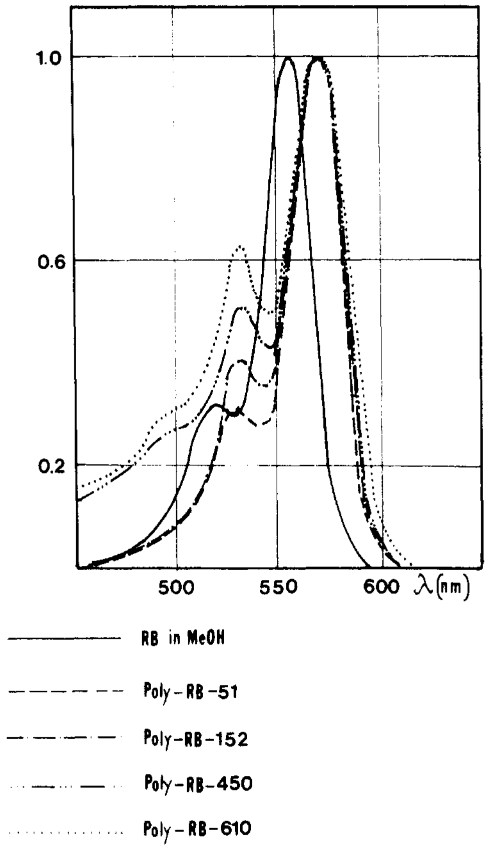


Figure 1. Electronic spectra in the visible region of poly-RB samples.

All the polymeric rose bengals are soluble in nonpolar solvents like methylene chloride and chloroform, but are not soluble in MeOH. An exception to this is the most highly loaded poly-RB, poly-RB-1520, which is soluble only in a mixture of MeOH/methylene chloride (1:1). All of the polymers show the typical ester carbonyl absorption between 1725 and 1741 cm^{-1} (Table I).

Electronic Absorption Spectra

Figure 1 shows the absorption spectra in the visible region of the analyzed polymers in methylene chloride solution. These data are summarized in Table II. The polymers separate into three different groups, each having differing absorption properties. The first, poly-RB-51, which is the lowest in rose bengal content, has an absorbance ratio of the two absorption maxima—at 571 and 530 nm—which is essentially the same as the ratio of these two peaks in the spectrum of rose bengal (Figure 1). The second group of polymers, poly-RB-102, poly-RB-152, and poly-RB-305, have ratios of these two maxima which are similar, but much lower than are those of either RB or poly-RB-51. In the cases of higher loading, the third group, the ratio of the two maxima is reduced even further. These effects can be seen with the eye; the lightly loaded polymers are purple; the more highly loaded polymers become much darker red in color.

In order to measure the spectra quantitatively, the absorption at the maximum of a 1 mg/L polymer solution was calculated. In other words, the concentration of the polymer was kept the same, although the concentration

Table II
Electronic Absorption Data in the Visible Region of Analyzed Polymers

polymer	$10^3 A_{1\ \mathrm{mg/L}}$	$\lambda_{1_{\max}}$, nm	$\lambda_{2_{\max}}$, nm	$A_{\lambda_1}/A_{\lambda_2}$	$\lambda_{3_{\min}}$, nm
poly-RB-51	4.63	571.0	529.0	3.165	541.0
poly-RB-102	6.33	572.0	532.0	2.685	544.0
poly-RB-152	9.11	572.0	532.0	2.418	544.0
poly-RB-305	22.35	572.0	532.0	2.674	544.0
poly-RB-450	11.0	572.5	532.0	1.935	546.0
poly-RB-610	11.5	572.5	532.0	1.593	547.0
poly-RB-1520[a]	18.2	570.0	531.0	2.057	541.0

[a] The electronic absorption in mixture of methanol and methylene chloride (1:1).

Table III
$\lambda_{\max}$ Positions (nm) for RB Benzyl Ester in Different Solvents and Mixture of Solvents

solv	$\lambda_{\max}$	solv	$\lambda_{\max}$	solv	$\lambda_{\max}$	solv	$\lambda_{\max}$
DMF	572	DMF-NMF (90:10)	571	acetone	570.5	CH_2Cl_2-MeOH (96:4)	
DMF-MeOH (50:50)	568			acetone-H_2O (50:50)	566		568[b]
		DMF-NMF (50:50)	568.5			CH_2Cl_2-MeOH (50:50)	566
DMF-MeOH (25:75)	565.5	NMF[c]	566.5	acetone-MeOH (50:50)	565.5		
MeOH[a]	564						

[a] From ref 19. [b] Saturated solution, RB benzyl ester is insoluble in pure CH_2Cl_2. [c] N-Methylformamide.

of the rose bengal attached to the polymer actually increased from sample to sample. There are two different types of behavior for these polymers (Table II). At low concentrations of RB on the polymer, the absorption of a 1 mg/L polymer solution increased regularly with RB content. In the intermediate range, poly-RB-305 and poly-RB-450, the absorbance is much too low based on that anticipated simply from the expected absorption of the rose bengal moieties if they were behaving independently. At higher loadings, A again increases with loading in a regular fashion, though not according to Beer's law. We rationalize that in the cases of the lower loadings, the RBs are far apart and "*site isolated*". Statistically poly-RB-51 has one RB per every 200 styrene units and poly-RB-305 has one rose bengal for every 30 styrene units. It seems apparent at these low loadings of dye on the polymer chain that the absorption spectra resemble that of a rose bengal derivative in diluted solution.

The situation is completely different when the effective distance between the immobilized dyes is diminished. There is then the possibility of aggregation along the polymer chain and one dye molecule influences another. In the higher concentration cases both the shape and the molar absorptivity (as measured for a 1 mg/L solution) no longer appear like that of a simple rose bengal[15,16] and RB–RB aggregates affect the absorption spectra.

The absorption maxima are also influenced by solvent. This can be observed from model systems. Every poly-RB, no matter the degree of loading, shows a maximum at 571–572 nm in methylene chloride. Although the polymers are not soluble in MeOH, RB C-2′ benzyl ester is and shows a maximum absorption in that solvent at 564 nm. Thus, there is a relatively large influence of hydrogen-bonding solvents on the absorption maximum. This can also be shown by measuring the maximum absorption of the benzyl ester (essentially a monomeric rose bengal polymer unit) in solvents of differing polarity (Table III). Data in Table III indicate that the red shift of the poly-RB maximum is a typical solvent effect and that the hydrogen bonding between the RB benzyl ester and protic solvents leads to a blue shift in the maximum absorption of the benzyl ester.[17,18] Small differences between the position of the maximum of poly-RB (571-572 nm) and a saturated solution of RB C-2′ benzyl ester in methylene chloride–MeOH (568 nm) result from the presence of the methanol, the effect of the polymer microenvironment,[19] and RB–RB interactions.

Quantum Yields of Singlet Oxygen Formation of Soluble Polymeric Rose Bengals in Solution. The intermediacy of singlet oxygen in photosensitized oxidations was originally postulated by Kautsky.[20,21] The sequence of events involves excitation of the sensitizer, intersystem crossing, energy transfer from the triplet of the sensitizer to molecular oxygen, and reaction of the formed singlet oxygen with the substrate.

$$\mathrm{Sens} \xrightarrow{h\nu} {}^1\mathrm{Sens} \tag{1}$$

$$\mathrm{Sens} \xrightarrow{k_2} {}^3\mathrm{Sens} \tag{2}$$

$${}^3\mathrm{Sens} + O_2 \xrightarrow{k_3} {}^1O_2 + \mathrm{Sens} \tag{3}$$

$$A + {}^1O_2 \xrightarrow{k_4} AO_2 \tag{4}$$

$${}^1O_2 \xrightarrow{k_5} {}^3O_2 \tag{5}$$

The quantum yields of singlet oxygen formtion from polymer rose bengals (poly-RB) in solution were obtained by using the actinometric method described by Schaap and Thayer.[2] The steady-state treatment of the kinetic scheme given (eq 1–5) yields the following result:[6]

$$\Phi(AO_2) = \Phi({}^1O_2)\frac{k_4[A]}{k_5 + k_4[A]} \tag{6}$$

where $\Phi({}^1O_2)$ is the quantum yield for singlet oxygen formation, and $\Phi(AO_2)$ is the quantum yield of product formation. If a relatively reactive acceptor is used in high concentrations, then $k_4[A] \gg k_5$ and the reaction is zero order in [A], i.e., $\Phi(AO_2) = \Phi({}^1O_2)$. Since all photooxidation reactions were carried out under similar experimental conditions in solution both for oxidations sensitized by RB and for reactions sensitized by poly-RB, the ratio of the rate of photooxidation with RB and the rate of photooxidation with poly-RB is equal to the ratio of the quantum yield for singlet oxygen formation with RB to that of the quantum yield for singlet oxygen formation with poly-RB.

$$\frac{V(AO_2)_{\mathrm{RB}}}{V(AO_2)_{\text{poly-RB}}} = \frac{\Phi(AO_2)_{\mathrm{RB}}}{\Phi(AO_2)_{\text{poly-RB}}} \tag{7}$$

The quantum yield of singlet oxygen formation is

$$\Phi(AO_2)_{\text{poly-RB}} = \Phi(AO_2)_{\mathrm{RB}}\frac{V(AO_2)_{\text{poly-RB}}}{V(AO_2)_{\mathrm{RB}}} \tag{8}$$

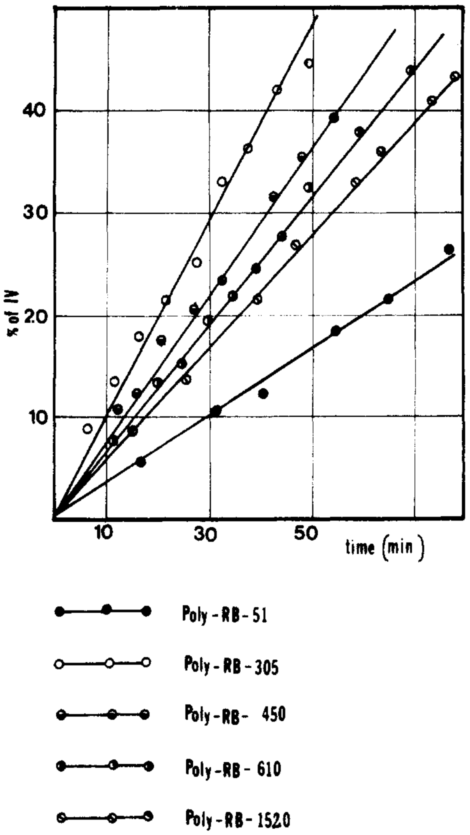
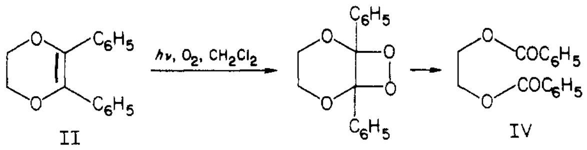


Figure 2. Photooxidation of 2,3-diphenyl-*p*-dioxene with poly-RB (photooxidation with poly-RB-1520 was carried out in a 50% MeOH and 50% CH_2Cl_2 solution).

Gollnick has reported that the quantum yield $\Phi(^1O_2)$ for RB in MeOH is 0.76. Therefore, the quantum yield of singlet oxygen formation for poly-RB is

$$\Phi(AO_2)_{\text{poly-RB}} = 0.76\frac{V(AO_2)_{\text{poly-RB}}}{V(AO_2)_{\text{RB}}} \tag{9}$$

The photooxidation or 2,3-diphenyl-*p*-dioxene was used to define the quantum yield of singlet oxygen formation.



(10)

The conversion of **II** to IV was monitored by gas chromatography. Irradiation under identical conditions of a mechanically stirred methylene chloride solution of II with poly-RB gives the results shown in Figure 2.

The data (Figure 2) indicate a different quantum yield of singlet oxygen formation for each of the synthesized polymers. The calculated quantum yields of singlet oxygen formation are plotted against the amount of rose bengal used in the synthesis of the polymer in Figure 3.

It is clear that as the amount of rose bengal attached to the polymeric support increased in the regime where the polymer can be called "*lightly functionalized*", the quantum yield of singlet oxygen formation increases also, reaching a maximum value for the polymer functionalized with one rose bengal for every 30 styrene units (poly-RB-305; $\Phi(^1O_2) = 0.38$).

There are at least two possible explanations for the observed increase in $(^1O_2)$ in the so-called lightly functionalized regime. First, it could be that singlet oxygen is quenched by the polystyrene. This quenching might lead either to a chemical product as, for example, the formation of the tertiary hydroperoxide on the polymer backbone, or to a physical quenching of the singlet oxygen by the polymer. If polymer quenching were important, then it would be anticipated that a monomeric model of the polymeric backbone might also retard formation of singlet oxygen. To test the point, the quantum yield for singlet oxygen formation from rose bengal benzyl ester in MeOH in the presence of added excess quantities of a polystyrene model, cumene, was measured. The results are clear—cumene does not quench the formation of singlet oxygen from RB benzyl ester. ($\Phi(^1O_2) = 0.72$ in the absence of cumene under standard conditions and $\Phi(^1O_2) = 0.71$ in the presence of a large excess of cumene.)

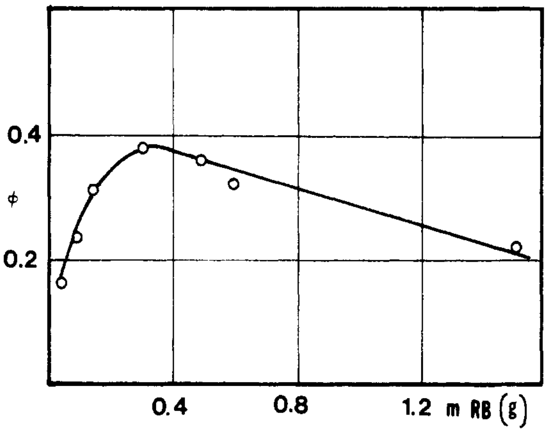


Figure 3. Quantum yield of singlet oxygen formation as a function of the amount of RB attached to a polymer.

A second explanation for the changes in quantum yield in the lightly functionalized regime, and one we confirmed experimentally, is that there is a substantial effect of solution viscosity on the apparent quantum yield of singlet oxygen formation in the case of the polymeric sensitizers. The polymers used in our experiments were studied such that the apparent rose bengal concentration, in every instance, was kept constant in the cell. Much more polymer lightly loaded with rose bengal was required than was required for polymers of higher loading to achieve identical effective RB concentrations in solution. Thus, 8.2 mg equivalent of rose bengal in a 25-mL solution required 180 mg of poly-RB-51, 94.2 mg of poly-RB-102, 65.8 mg of poly-RB-152, and 35.2 mg of poly-RB-305. As the loading of the polymer is increased, the actual amount of polymer required to achieve a fixed concentration of rose bengal became less.

That the photooxidation is actually being controlled by solution viscosity was confirmed by measuring the quantum yield of singlet oxygen formation from solutions of RB benzyl ester containing quantities of standard polystyrenes. The actual polystyrene weight was gradually incremented in the mixed solvent system methylene chloride/MeOH (4:1), containing RB benzyl ester to approximate the amount of polymer in the comparable poly-RB system. The relative viscosity of poly-RB and RB benzyl ester solutions containing polystyrene standards could be calculated and the singlet oxygen yields measured. Results are shown in Figure 4.

The curve for poly-RB as a function of RB loading and that for RB benzyl ester in the presence of polystyrene have similar—almost identical—shapes. It is clear, therefore, that the photooxidation process is controlled by the diffusion of oxygen into the rose bengal sites in the polymer solution. These results suggest that when a small amount of rose bengal is attached to the polymeric backbone (poly-RB-51, -102, -152, -305), the actual quantum

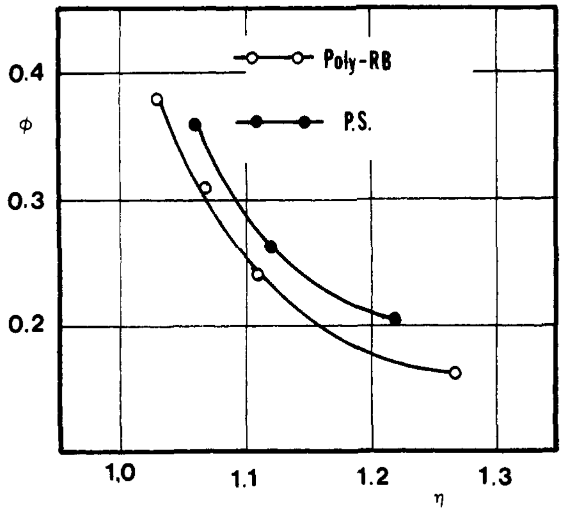


Figure 4. Quantum yield of singlet oxygen formation as a function of viscosity.

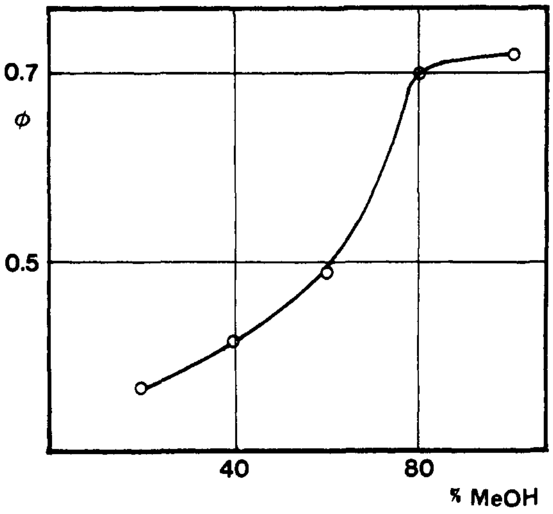


Figure 5. Quantum yield of singlet oxygen formation for RB C-2′ benzyl ester in a mixture of MeOH and CH_2Cl_2 as a function of MeOH concentration.

yield of singlet oxygen formation is essentially the same (about 0.38). The decrease from that value is neither sensitizer nor solvent controlled, but diffusion controlled.

The polymeric rose bengal derivatives are soluble only in nonpolar solvents such as methylene chloride, and the maximum quantum yield of singlet oxygen formation which can be achieved in these solvents with these sensitizers is 0.38. Rose bengal benzyl ester, on the other hand, can be studied in methanol solution and produces a quantum yield for singlet oxygen formation which reaches 0.72 in that solvent. In order to check how the solvent affects singlet oxygen formation, we measured the quantum yield for singlet oxygen formation from RB benzyl ester in methylene chloride/MeOH mixtures. Results are shown in Figure 5. Hydrogen bonding between the rose bengal benzyl ester and MeOH obviously influences the quantum yield. This effect is particularly distinct in the range of solvent concentrations between 40% and 80% MeOH. Since the RB benzyl ester is insoluble in pure methylene chloride, the direct measurement of the quantum yield in the pure solvent is impossible, but likely the quantum yield approximates that in 80% methylene chloride/20% MeOH, ($\Phi(^1O_2)$ = 0.37). Figure 3 shows that the quantum yield of singlet oxygen formation is affected differently at high loadings of rose bengal on the copolymer support than at low loadings. The highest value of the quantum yield of singlet oxygen formation is observed for poly-RB-305 (Φ = 0.38). As additional rose bengals immobilize to the poly(styrene-*co*-vinylbenzyl chloride) backbone, the quantum yield of singlet oxygen formation again decreases from the maximum value. This result derives from excited-state "self"-quenching, and these are influenced by dye loadings and polymer structure. They can be probed by emission spectroscopy.

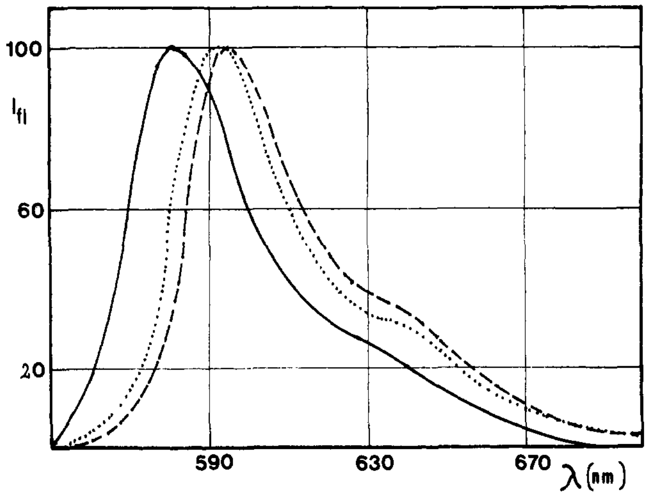


Figure 6. Fluorescence emission spectra at ambient temperature. Concentration corresponds with 4 × 10^{-5} mol/L of RB molecules: (—) RB C-2′ benzyl ester in MeOH; (---) poly-RB-610; (···) poly-RB-51.

Emission Spectra. Figure 6 compares the fluoresence spectrum at room temperature in methylene chloride of poly-RB-51 and of poly-RB-610. The spectrum of RB C-2′ benzyl ester in MeOH is shown for comparison. (Concentrations of rose bengal are normalized in each case to about 4.0 × 10^{-5} M.)

There is little difference between the emission spectra and the fluorescence maximum of the heavily loaded polymer and the lightly loaded polymer. (Poly-RB-610 (595 nm) is only slightly shifted from that of the lightly loaded polymer poly-RB-51 (593 nm).) There is a minor difference in the longer wavelength region. It appears that poly-RB-610 has a stronger emission at longer wavelength. Perhaps an excimer is formed from dye aggregates, but more likely this is just the result of the difference in the absorption spectra of the two differently loaded polymers. In essence, the effect of rose bengal loading on the polymer backbone on the fluorescence spectrum in solution at room temperature is small.

The fluorescence spectrum of rose bengal C-2′ benzyl ester, taken in MeOH, is more greatly shifted; but this is purely the result of the previously suggested solvent effect. Hydrogen bonding not only alters the absorption maximum of the dye, but also shifts the fluorescence maximum toward the blue.

Since the ambient temperature fluorescence spectra are basically nonstructured, the spectra were also measured at liquid-nitrogen temperature. Two different effects were probed: the concentration of polymer containing dye in a glass at that temperature and the effect of RB loading on the low-temperature emission spectra. (See Figure 7.) There are no differences in the structure of the fluorescence emission at low temperature as a function of polymer loading. Thus, if the concentration of rose bengal in the glass is made constant, the spectra are identical for both poly-RB-51 and poly-RB-610. There is an effect of the actual concentration of the polymer-based dye in the glass on the spectrum, however. At a higher concentration of poly-RB-51 in the glass, the fluorescence maximum shifts

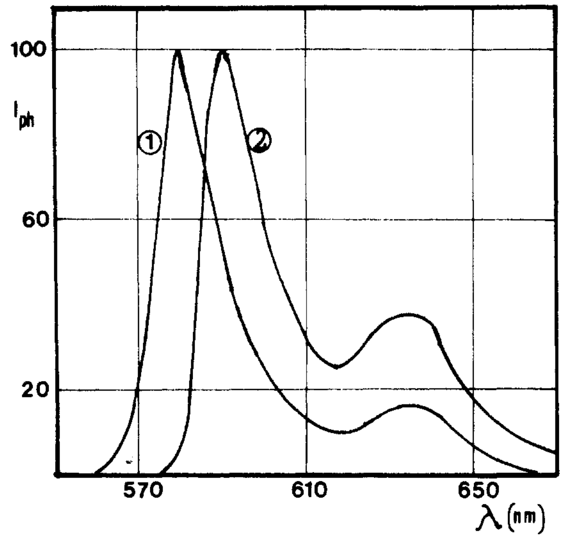


Figure 7. Fluorescence emission spectra for poly-RB-51 at 77 K in MTHF: (1) concentration corresponds with 4×10^{-5} mol/L of RB molecules; (2) concentration corresponds with 3×10^{-4} mol/L of RB molecules.

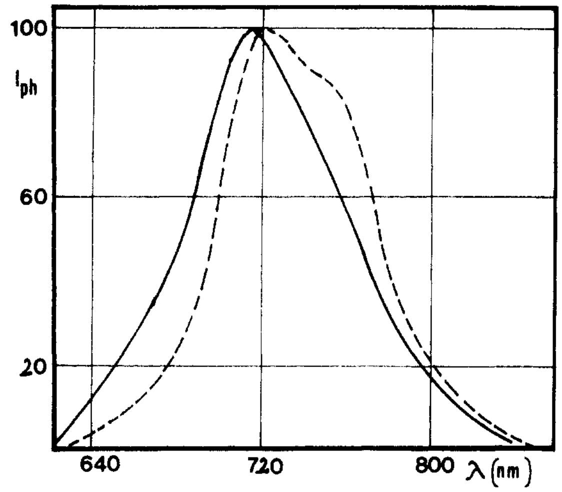


Figure 8. Phosphorescence emission spectra for RB C-2′ benzyl ester in MTHF at 77 K: (—) $c = 4 \times 10^{-5}$ mol/L; (- - -) $c = 4 \times 10^{-4}$ mol/L.

toward the red (maximum at 580 nm for [RB] which corresponds to 4×10^{-5} and maximum at 589 nm [RB] corresponding to 3.3×10^{-4}). This relatively large shift is attributed to intermolecular dye/dye aggregation.[23] This seems confirmed by the increase observed in the intensity of emission for the longer wavelength emission. If the longer wavelength emission is from an aggregated form or an excimer, its intensity of emission will increase with a higher concentration of polymer-based dye in the glass. Whatever, it is obvious that the concentration of the dye in the glass (i.e., intermolecular polymer strand interactions) affects the singlet state of the polymer-based dye, but intramolecular interactions (site–site effects) have no influence on the spectra because polymer loading has little influence on the fluorescence spectrum.

The quantum yield of fluorescence for rose bengal is not large (0.08 in MeOH);[23] more significant by far are the longer lived emissions of the dye, phosphorescence and delayed fluoresence. The phosphorescence spectrum of RB C-2′ benzyl ester in the MTHF glass at liquid-nitrogen temperature is shown in Figure 8.

At low concentrations, the maximum occurs at 721–722 nm. It shifts at higher concentrations to longer wavelengths (730 nm), and a new emission in the long-wavelength region is observed also. Since the new long wavelength band appears at high concentration, we suggest it derives from aggregates of more than one rose bengal moiety also.

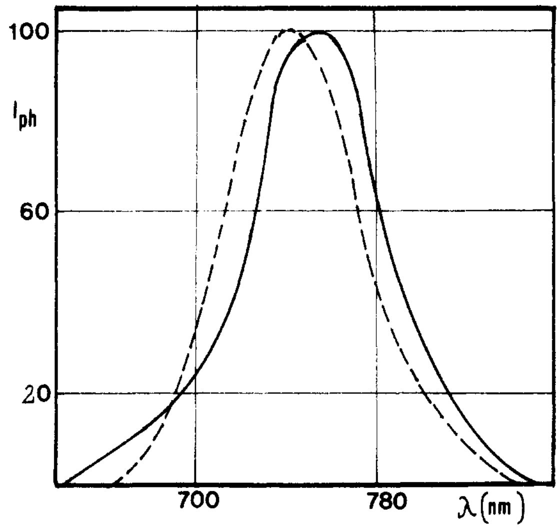


Figure 9. Phosphorescence emission spectra for poly-RB-51 in MTHF at 77 K: (—) concentration of polymer corresponds to 3×10^{-4} mol/L RB molecules; (- - -) concentration of polymer corresponds to 4×10^{-5} mol/L RB molecules.

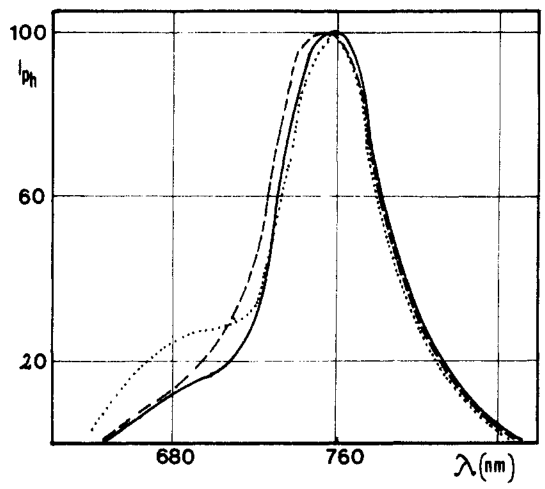


Figure 10. Phosphorescence emission spectrum for poly-RBs in MTHF at 77 K. Concentration of polymers corresponds to 3×10^{-4} mol/L of RB molecules: (- - -) poly-RB-51, (—) poly-RB-305, (···) poly-RB-450.

The effect of the polymer backbone on phosphorescence was examined as follows: the phosphorescence of poly-RB-51 was measured at different concentrations (Figure 9). In the case of both a low concentration of poly-RB-51 in a MTHF glass and a higher concentration, the phosphorescence maximum is greatly shifted from the model compound rose bengal benzyl ester (maximum of poly-RB-51 is 742–743 nm at lower concentrations; 755 nm at higher concentrations). Clearly the polymer backbone has a major effect on the triplet state of the rose bengal, and it forces a much more substantial contribution from aggregates to the emission spectra.

Figure 10 shows the long-lived emission spectra of poly-RB's which have differing loadings of rose bengal. Three different effects are observed: (1) when the concentration of RB attached to the polymer chain is increased, the emission maximum shifts toward longer wavelengths (for poly-RB-51 the phosphorescence maximum is at 755–756 nm; for poly-RB-450 the maximum is

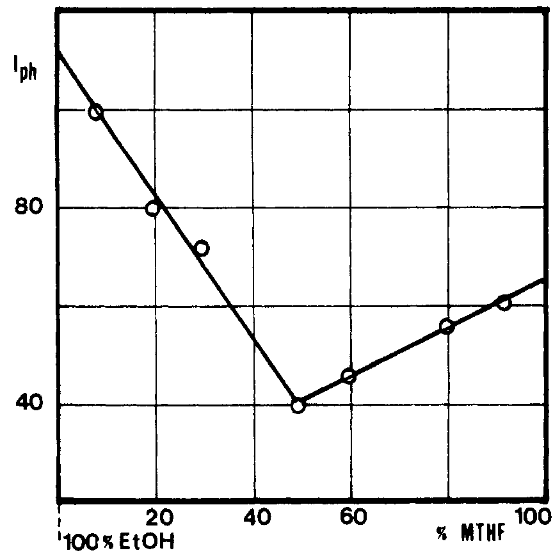


Figure 11. Intensity of phosphorescence emission for RB C-2′ benzyl ester in mixture of EtOH and MTHF as a function of MTHF concentration.

at 760–761 nm); (2) when the loading of rose bengal is increased, the intensity of the emission decreases; and (3) there is no difference in the shape of the emission spectra in the cases of the lightly loaded polymers (poly-RB-51, poly-RB-152, and poly-RB-305), but when the amount of rose bengal attached to the polymer is increased, a new emission band is observed *in the short-wavelength region* of the emission spectrum (poly-RB-450; poly-RB-610).

There are several reasonable explanations for this behavior. When the amount of rose bengal attached to the polymer chain is increased, the distance between two rose bengals diminishes and the probability of the formation of aggregates increases, both in the ground state and in the excited state. Triplet–triplet annihilation of the aggregates may lead to delayed fluorescence, which occurs at shorter wavelengths than phosphorescence. When the number of aggregates increases, the probability of triplet–triplet annihilation also increases and the intensity of the phosphorescence of the monomer decreases.

For lightly loaded polymers, the distance between two dye molecules is likely large, the probability of aggregation is less, and the number of unquenched triplets of the dye is high and constant. The rate of singlet oxygen formation is not, therefore, controlled by the intramolecular quenching process, i.e., between this excited rose bengal monomer and its nearest neighbor on the polymer chain. Again, it seems clear that for lightly loaded polymers, the extent of observed aggregations is controlled by intermolecular effects, and dilute solutions of lightly loaded polymers behave like monomeric rose bengals in dilute solution. For polymers heavily loaded, the distance between the two rose bengals is controlled by the coiling of the interspersed polymer chain, and the degree of aggregation is directly controlled by the extent of polymer chain loading with the dye. For polymers with high loading (poly-RB-450 and polymer-RB-610), the new emission band which is observed is likely that of a delayed fluorescence (triplet–triplet annihilation of triplet aggregates). The degree of loading can also influence the lifetime of the rose bengal triplet state.[24]

Since both the absorption spectra of the polymers and their corresponding emission spectra independently suggest that polymer-bound rose bengals interact—either excited-state with ground-state aggregate or to form an excimer—more frequently as a function of polymer loading, it seems clear that this same aggregation effect should also influence intermolecular energy-transfer processes involving dye excited states; i.e., energy transfer to oxygen. A kinetic study of the quenching of photooxidation as a function of polymer loading, and hence of ground-state aggregate formation and triplet–ground-state effects, takes the form

$$\mathrm{RB} \xrightarrow{h\nu} {}^1\mathrm{RB} \tag{11}$$

$$^1\mathrm{RB} \xrightarrow{k_2} {}^3\mathrm{RB} \tag{12}$$

$$^3\mathrm{RB} + {}^3\mathrm{O}_2 \xrightarrow{k_3} {}^1\mathrm{O}_2 + \mathrm{RB} \tag{13}$$

$$\mathrm{A} + {}^1\mathrm{O}_2 \xrightarrow{k_4} \mathrm{AO}_2 \tag{14}$$

$$^1\mathrm{O}_2 \xrightarrow{k_5} {}^3\mathrm{O}_2$$

and additionally for ground-state aggregation

$$^3\mathrm{RB} + (\mathrm{RB{-}RB}) \xrightarrow{k_6} \mathrm{RB} + {}^3(\mathrm{RB{-}RB}) \tag{15}$$

for triplet excimer

$$^3\mathrm{RB} + \mathrm{RB} \xrightarrow{k_7} {}^3(\mathrm{RB{-}RB}) \tag{16}$$

Now eq 6 takes the following form:

$$\Phi(\mathrm{AO}_2) = \Phi(^1\mathrm{O}_2)\frac{k_3}{k_3 + k_6 + k_7}\,\frac{k_4[\mathrm{A}]}{k_5 + k_4[\mathrm{A}]} \tag{17}$$

If a reactive singlet oxygen acceptor is used in high concentrations, then $k_4[\mathrm{A}] \gg k_5$ and the reaction is independent of [A], i.e.

$$\Phi(\mathrm{AO}_2) = \Phi(^1\mathrm{O}_2)\frac{k_3}{k_2 + k_6 + k_7} \tag{18}$$

where k_6 is the rate constant of triplet-state quenching by rose bengal ground-state aggregates and k_6 is the rate constant of triplet-state quenching by monomeric rose bengal ground state (excimer formation). When no self-quenching occurs, then

$$\Phi(\mathrm{AO}_2) = \Phi(^1\mathrm{O}_2) \tag{19}$$

but when $k_6 + k_7$ is comparable to k_2, the rates of photooxidation are controlled by intramolecular dye–dye self-quenching processes which involve proximate dye molecules on the polymer backbone. On the basis of our results, proximate dyes may be 30–50 individual styrene monomer units apart.

An additional observation of interest is the effect of solvent on singlet oxygen formation as indicated by the quantum yield of singlet oxygen formation over a range of solvent polarities from RB C-2′ benzyl ester. This study, which is only possible with the benzyl ester because it is soluble in solvents of such differing polarities, indicates why the quantum yield of singlet oxygen formation can reach a value for the polymers in methylene chloride no higher than 0.40. Thus, though the quantum yield of singlet oxygen formation is only 0.37 for the benzyl ester in methylene chloride (80%)/MeOH (20%), it reaches 0.72 in MeOH. Either the quantum yield of triplet formation is higher in the hydrogen-bonding solvent, or the lifetime of singlet oxygen must be longer. Since the latter is not the case, it must be the former.

This can be shown from the integrated phosphorescence intensities in polar and non-polar solvents (Figure 11).

It is clear from Figure 11 that the integrated phosphorescence intensity is a function of solvent. In the polar hydrogen-bonding solvent, the phosphorescence intensity is about 40% greater than in the nonpolar solvent. Assuming that the quantum yield of phosphorescence from the benzyl ester in EtOH is 0.72, from the quantum yield of singlet oxygen formation from the benzyl ester in the same solvent, the calculated value of the quantum yield of phosphorescence in the nonpolar solvent is $\Phi = 0.41$. This is essentially the value of the quantum yield for singlet oxygen formation for poly-RB (light loading) in a similar solvent, methylene chloride.

Conclusions

In conclusion, we have outlined the properties of soluble polymer-based rose bengal derivatives as singlet oxygen sensitizers and shown that the quantum yield of singlet oxygen formation from these sensitizers is lower in methylene chloride than is that of rose bengal itself in polar solvents. We have shown that there is a substantial effect of solution viscosity on the quantum yield of singlet oxygen formation for very lightly loaded poly-RBs, in which case the observed quantum yield of singlet oxygen formation is controlled by the rate of oxygen diffusion. The absorption and emission spectra of the polymer-bound dyes indicate that, for lightly loaded rose bengal polymers, self-quenching processes are controlled by solution concentration effects only, and these self-quenching processes occur between polymer chains. In the case of more highly functionalized polymers, the probability of the formation of aggregates between dyes bound on the same polymer backbone also increases, in both the gound state and the excited states. This can affect the quantum yield of singlet oxygen formation and, in fact, decreases it. Finally, electronic absorption spectra, emission spectra, and quantum yields of singlet oxygen formation of the polymeric analogue, RB C-2′ benzyl ester, suggest that hydrogen bonding between rose bengal moieties and protic solvents leads to a blue shift in the absorption maxima, an increase in the quantum yield of phosphorescence, and an increase in the quantum yield of singlet oxygen formation.

Experimental Section

Rose bengal, dye content 92%, was used as received or purified according to the method of Lamberts.[10] Solvents used for preparation of solutions for quantum yield measurement were spectroscopic grade and were purchased from Aldrich.

Infrared spectra were obtained by using a Nicolet 20DX Fourier transform infrared spectrometer and electronic absorption spectra by using a Varian Cary 219 instrument. Quantum yields were measured with a Bausch and Lomb high-intensity monochromator with an Osram HBO-200L2 super-pressure mercury lamp. GLC analysis was performed on a Hewlett-Packard 5800 gas chromatograph fitted with a glass capillary column (0.20-mm i.d., 12-m length) containing a cross-linked methylsilicone film (film thickness 0.33 mm) and a flame ionization detector. High-pressure gel permeation chromatograms (GPS) were run on a Waters Associates instrument with UV detection and μ-styragel columns having pore sizes of 10^5, 10^4, and 500 Å arranged in series.

Emission spectra were obtained by using a Perkin-Elmer MPF-44A fluoresence spectrophotometer with a Perkin-Elmer phosphorescence accessory for phosphorescence emission measurements.

Synthetic Procedures. Purification of Monomers. Commercial monomers were washed 3 times with 2% NaOH and 4 times with distilled water. The monomers were dried over anhydrous $CaCl_2$ and were distilled under vacuum before use.

Polymerization of Poly(styrene–vinylbenzyl chloride) Copolymer. In order to obtain poly(styrene–vinylbenzyl chloride) copolymer, a mixture of 10.4 g (0.1 mol) of styrene, 7.6 g (0.05 mol) of vinylbenzyl chloride (mixture of 60% meta isomer and 40% para isomer), and 90 mg of benzoyl peroxide was used. Polymerization was carried out in degassed (three cycles of freeze–thaw under high vacuum) sealed ampules at 60 °C. The polymer was precipitated with excess methanol, filtered, and dried.

Polymer-Bound Rose Bengal (Poly-RB). To 1.07 g of poly(styrene–vinylbenzyl chloride) copolymer in DMF was added respectively 51 mg of RB for poly-RB-51, 102 mg of RB for poly-RB-102, 152 mg of RB for poly-RB-152, 305 mg of RB for poly-RB-305, 450 mg of RB for poly-RB-450, 610 mg of RB for poly-RB-610, and 152 mg of RB for poly-RB-1520. The mixtures were stirred magnetically and heated (80 °C) for 24 h. The reaction mixtures were then cooled to ambient temperature. All the polymers were precipitated by addition of an excess of distilled water. They were then purified by precipitating from DMF solution by excess of methanol and washed continuously with methanol until the final filtrates were colorless. The polymers were dried under vacuum.

2,3-Diphenyl-*p*-dioxene was prepared according to the method of Summerbell and Berger, and the solid thus obtained was recrystallized twice from ethanol, mp 93–94 °C (uncorrected).[25]

Rose bengal benzyl ester was prepared according to the method described by Lamberts and Neckers in a previous publication.[10]

Quantum Yield Measurements of Singlet Oxygen Formation. For qunatum yield measurement, the procedure was as follows: Poly-RB solutions in 25 mL of CH_2Cl_2 were prepared so that the amount of RB attached to the polymer corresponded to 8.2 mg of RB in solution. In order to obtain these solutions, we used 180 mg of poly-RB-51, 94 mg of poly-RB-102, 65.8 mg of poly-RB-152, 35.2 mg of poly-RB-305, 27.6 mg of poly-RB-450, 22.6 mg of poly-RB-610, and 13.8 mg of poly-RB-1520 (solution of poly-RB-1520 prepared in a mixture of 50% MeOH and 50% CH_2Cl_2). To the polymer solution was added 172 mg of 2,3-diphenyl-*p*-dioxene. The solution (2.5 mL) in a rectangular cell was irradiated with a high-intensity monochromator at 566 nm. The solution was stirred, and a continuous flow of oxygen over the surface of the solution was maintained throughout the irradiation. The formation of the photooxidation product ethylene glycol dibenzoate (IV) was followed by analysis of the solution by GLC at 225 °C. $\Phi(^1O_2)$ was calculated from the ratio of the rate of formation of IV for poly-RB compared to the rate for RB and using the known quantum yield for RB ($\Phi(^1O_2) = 0.76$) according to eq 9.

The same procedure was used to measure singlet oxygen formation from RB benzyl ester under different conditions. The following solutions (25 mL) were prepared: (1) 8.2 mg of RB benzyl ester, 172 mg of 2,3-diphenyl-*p*-dioxene (II) in MeOH; (2) 8.2 mg of RB benzyl ester, 172 mg of II, 172 mg of cumene in MeOH; (3) 8.2 mg of RB benzyl ester, 172 mg of II in a 20% MeOH and 80% CH_2Cl_2 mixture; (4) 8.2 mg of RB benzyl ester, 172 mg of II in 40% MeOH and 60% CH_2Cl_2; (5) 8.2 mg of RB benzyl ester, 172 mg of II in 60% MeOH and 40% CH_2Cl_2; (6) 8.2 mg of RB benzyl ester, 172 mg of II in 80% MeOH and 20% CH_2Cl_2. In order to describe the influence of viscosity, the following solutions (25 mL) were used: (1) 8.2 mg of RB benzyl ester, 172 mg of II, 100 mg of polystyrene molecular weight 200 000; (2) 8.2 mg of RB benzyl ester, 172 mg of II, 100 mg of polystyrene molecular weight 110 000; (3) 8.2 mg of RB benzyl ester, 172 mg of II, 100 mg of polystyrene molecular weight 35 000. Solutions were prepared in a 20% MeOH and 80% CH_2Cl_2 mixture.

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Elucidation of the Proton Nuclear Magnetic Resonance Spectrum of Poly(propylene oxide) by Two-Dimensional *J*-Resolved Spectroscopy

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ABSTRACT: Two-dimensional *J*-resolved spectroscopy is applied to the separation of overlapping multiplets in the 500-MHz proton spectrum of poly(propylene oxide). Chemical shifts and homonuclear coupling constants are reported for protons in different stereochemical environments. These values are consistent with spectral parameters previously determined for selectively deuterated polymers. Proton chemical shifts in atactic poly(propylene oxide) are observed to be sensitive to triad stereosequences, but the homonuclear coupling constants for head-to-tail monomer units are the same regardless of stereosequence.

1. Introduction

Proton NMR spectroscopy is potentially a powerful tool for studying the microstructure of synthetic polymers since proton chemical shifts are sensitive to structural variables. Furthermore, proton–proton scalar coupling constants are sensitive to molecular conformation. However, the proton spectra of polymers are often complex because of extensive spectral overlap of multiplets with similar chemical shifts. Homonuclear two-dimensional (2D) *J*-resolved spectroscopy has been widely applied to the separation of overlapping multiplets in the proton spectra of peptides,[1–3] proteins,[4–6] and oligosaccharides.[7–10] However, because of scalar coupling between protons of different monomer units as well as coupling within the monomer unit, the coupling patterns associated with synthetic polymers are generally very complex. Consequently, 2D *J*-resolved spectra of synthetic polymers, especially vinyl polymers, can be difficult to interpret. This was observed by Macura and Brown[11] in the 2D *J*-resolved spectrum of poly(vinyl chloride). Poly(propylene oxide) represents a simpler case for 2D *J*-resolved spectroscopy since scalar coupling between protons of different monomer units is prevented by the oxygen. We report the application of 2D *J*-resolved spectroscopy to the elucidation of the 500-MHz proton spectrum of poly(propylene oxide).

2. Experimental Section

2.1. Materials. The atactic poly(propylene oxide) was a commercial sample supplied by Aldrich Chemical Co. in liquid form (molecular weight ca. 4000). It was initially characterized by ^{13}C NMR and found to have an approximately random stereochemical structure (see section 3). Isotactic poly(propylene oxide) was prepared from (*S*)-propylene oxide (99%, Aldrich Chemical Co.) by using a KOH catalyst and the method of Price and Osgan.[12] This procedure yielded a white crystalline substance with a sharp melting point of 60–61 °C. The intrinsic viscosity, measured in toluene at 25 °C, was 0.171 dL g^{-1}, corresponding to a viscosity–average molecular weight of ca. 14 500.

2.2. NMR Spectroscopy. Two-dimensional *J*-resolved spectroscopy, first performed in 1976 by Ernst and co-workers,[13] employs the spin-echo pulse sequence $90°–t_1/2–180°–t_1/2–t_2$. The 90° pulse flips the net magnetization vector into the xy plane, and the individual components dephase during the first interval of length $t_1/2$. The 180° pulse refocuses the spin isochromats which have dephased because of chemical shift differences but not those which have dephased because of J coupling. The individual components of a multiplet continue to dephase during the second interval of length $t_1/2$. This results in an apparent precession frequency during t_1 which is dependent only on the scalar coupling constants. At the end of the time t_1, the chemical shift components are completely refocused, and a spin echo is produced. This spin echo is detected as a free induction decay in the time variable t_2. As in all 2D NMR experiments, the evolution time t_1 is systematically incremented and the resultant free induction decay is detected in t_2 for a series of t_1 values. The resultant data matrix is Fourier transformed in both time variables; the first Fourier transform is with respect to t_2 and the second is with respect to t_1. This yields a 2D spectrum as a function of two frequencies, ω_1 and ω_2. In 2D *J*-resolved spectroscopy, the ω_1 frequency reflects only scalar coupling, while the ω_2 frequency reflects both chemical shift and scalar coupling effects. After a "tilt" of 45°,[14] the ω_2 axis reflects only chemical shifts, and the ω_1 axis reflects only J coupling. Hence, multiplets which are overlapped in the conventional proton spectrum are separated in the 2D *J*-resolved spectrum.

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