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LASER FLASH PHOTOLYSIS OF DYED FABRICS AND POLYMERS—I

ROSE BENGAL AS A PHOTOSENSITIZING DYE

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Abstract—We report emission and transient absorption observed using diffuse reflectance following pulsed laser excitation of rose bengal in a variety of opaque heterogeneous environments. These include kinetic transient absorption studies for the first time on dyed fabrics and within cross-linked polymer beads to which rose bengal has been chemically attached. The transient absorption difference spectra which sometime show ground state depletion and isosbestic points upon decay are assigned to the production of triplet rose bengal. The transient decay is a mixture of first and second order kinetic processes. A strong contribution due to triplet–triplet annihilation is interesting in connection with the possibility of energy transfer between dyes attached to or adsorbed on polymers. These measurements illustrate that the primary photochemical processes of heterogeneous sensitizers and dyed fabrics can now be studied directly using diffuse reflectance flash photolysis.

INTRODUCTION

In a recent review of polymer photochemistry, Allen states "The role of singlet oxygen in the photofading of dyes appears to dominate the scene. It should be pointed out that most of the studies involved solution work and therefore the data though scientifically interesting may bear little relevance to actual fading processes in the polymer" [1]. It is indeed true that the need to use model systems when investigating the primary photochemical properties of polymers is a major disadvantage in attempts to understand the photodegradation of dyed and pigmented polymers. One of the most powerful techniques for investigation of primary photochemical properties is flash photolysis [2]. Until recently this technique was restricted to homogeneous transparent samples and many polymer studies were therefore made using dilute fluid solutions. However, we report here direct investigations of transient absorption spectra and decay kinetics from opaque heterogeneous dyed polymer and fabric samples using the new technique of diffuse reflectance laser flash photolysis [3–7]. Previously, we have applied this technique to the study of aromatic hydrocarbons adsorbed as fractions of a monolayer on catalytic, highly scattering, γ-alumina surfaces [3], of inorganic [4] and organic microcrystals [5, 6], of semiconductor powders [4, 7] and of sintered semiconductor electrodes with and without added dopants or coated with a sensitizing dye layer [7].

The present paper reports for the first time the successful direct detection of transient absorption spectra by electronically excited states within opaque polymer beads and from dyed woven fabrics. Since as mentioned in the review quoted above there is considerable interest in the generation and reactions of singlet oxygen $O_2^*(^1\Delta_g)$ within polymers, we have chosen to demonstrate the application of laser flash photolysis in diffuse reflectance mode to dyed polymers and to woven fabrics by studying the dye rose bengal in various environments including chemically bound within cross-linked polymer beads (i.e. as the commercially available heterogeneous photosensitizer known as Sensitox I and II), adsorbed on polyacrylamide and adsorbed on woven cotton and nylon fabrics.

EXPERIMENTAL

The essential features of the apparatus [5] to undertake diffuse reflectance laser flash photolysis comprise a pulsed Nd-YAG Laser (J.K. Lasers Ltd), delivering pulses of ~20 nsec duration of energy 150 mJ/pulse at 532 nm or 40 mJ/pulse at 354 nm to act as exciting source, a 250 W Xe arc lamp (Applied Photophysics Ltd) as monitoring source, pulsed (pulse width = 0.5 msec) to provide a high analysing intensity, and a Tektronix 7912 AD Programmable Digitizer to capture transient events. A "Minc" PDP11 minicomputer (Digital Equipment Ltd) is used to perform on line kinetic analysis and to extract spectral data from the transient information. Ground state spectral data were obtained with the diffuse reflectance attachment of a Pye-Unicam SP 8250 Spectrometer.

Sensitox I (rose bengal bound to chloromethylated styrene–divinyl copolymer beads) [8] and Sensitox II (rose bengal bound to polymer formed from copolymerisation of chloromethylstyrene and the monomethylacrylate ester of ethylene glycol) [9] were supplied by Hydron Laboratories, Inc. The samples of rose bengal adsorbed on to polyacrylamide and polystyrene were prepared by shaking suspensions of the polymer (0.5 g) and rose bengal dissolved in methanol (200 mg in 50 cm^3) for several hours. The suspensions were left to stand overnight, the solution was then decanted and the solid finally dried under vacuum. The cotton and nylon fabrics were dyed by soaking in a solution containing 0.02 g of rose bengal per 10 cm^3 of methanol and the solvent was allowed to evaporate to dryness. If the entire

volume of fabric was homogeneously dyed, this would correspond to a loading of 0.1 mg of rose bengal per 1 mm^3 of fabric. All samples are placed in holders and held under slight pressure against a quartz window.

RESULTS AND DISCUSSION

Spectral features

Time resolved emission spectra and transient changes in absorption spectra following pulsed laser excitation at 354 nm were recorded for rose bengal in various heterogeneous environments. Figures 1 and 2 present the results for chemically bound rose bengal, Sensitox I and II respectively [8, 9]. These show similar features except that the rates of decay of the transient absorption and the emission peaking at 765 nm are at least ten times faster in the case of Sensitox I. Between 510 and 570 nm where rose bengal absorbs strongly, no detectable change in transient diffuse reflectance was observed. With both Sensitox I and II the time resolved emission spectra show the presence of a shorter lived emission with a band centred at ~650 nm.

Physically adsorbed rose bengal on polyacrylamide, polystyrene and cotton fabric gave the time resolved spectra shown in Figs 3–5 respectively. Note the isosbestic points observed in the transient absorption difference spectra at ~510 and ~580 nm. Between these wavelengths negative transient absorption changes are observed. Ground state depletion and return obviously explains these observations and it follows that the extinction coefficient of the transient is less than that of ground state rose bengal in this region. The fact that the rate of the return of absorption in the 510–580 nm region is the same as that for the decay of the transient absorption above 600 nm is supporting evidence for these changes being attributable to the population and decay of triplet rose bengal. The zero change in transient absorption observed for Sensitox I and II in the 510–570 nm region suggests that the fractional conversion of ground state rose bengal is much less in the chemically bound samples probably because the effective rose bengal concentration is higher due to the high loading factor.

Microcrystals of rose bengal give the transient absorption spectrum changes shown in Fig. 6 but very little emission with a lifetime of greater than 20 nsec at any wavelength. Conventional ground state diffuse reflectance spectra were taken before and

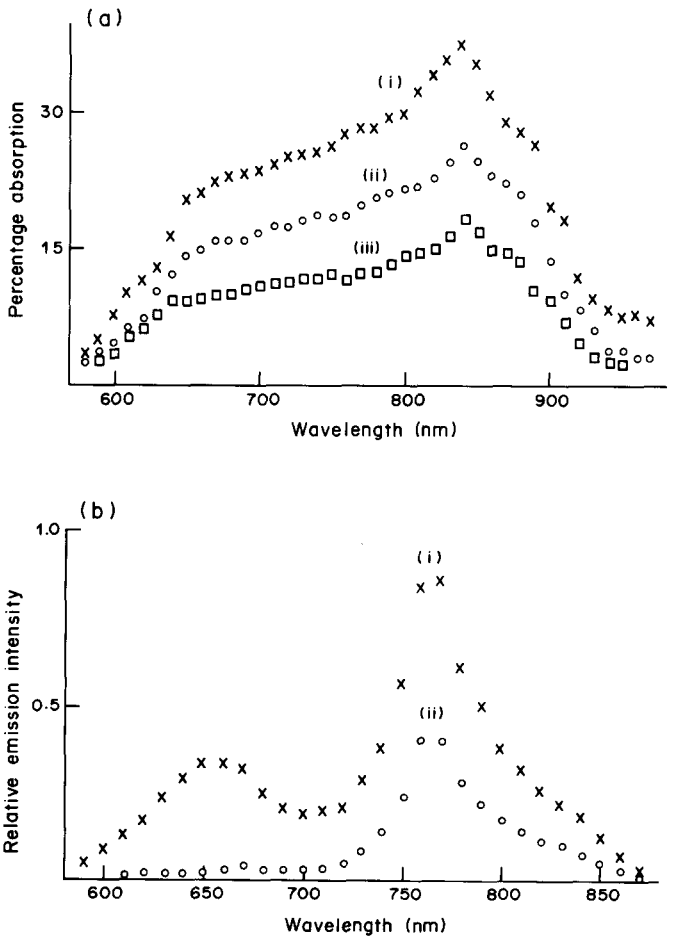

Fig. 1. Sensitox I: (a) transient absorption spectrum, (i) immediately after laser pulse, (ii) 1 μsec after excitation, (iii) 4 μsec after excitation; (b) emission spectrum, (i) immediately after laser pulse, (ii) 2.5 μsec after laser pulse.

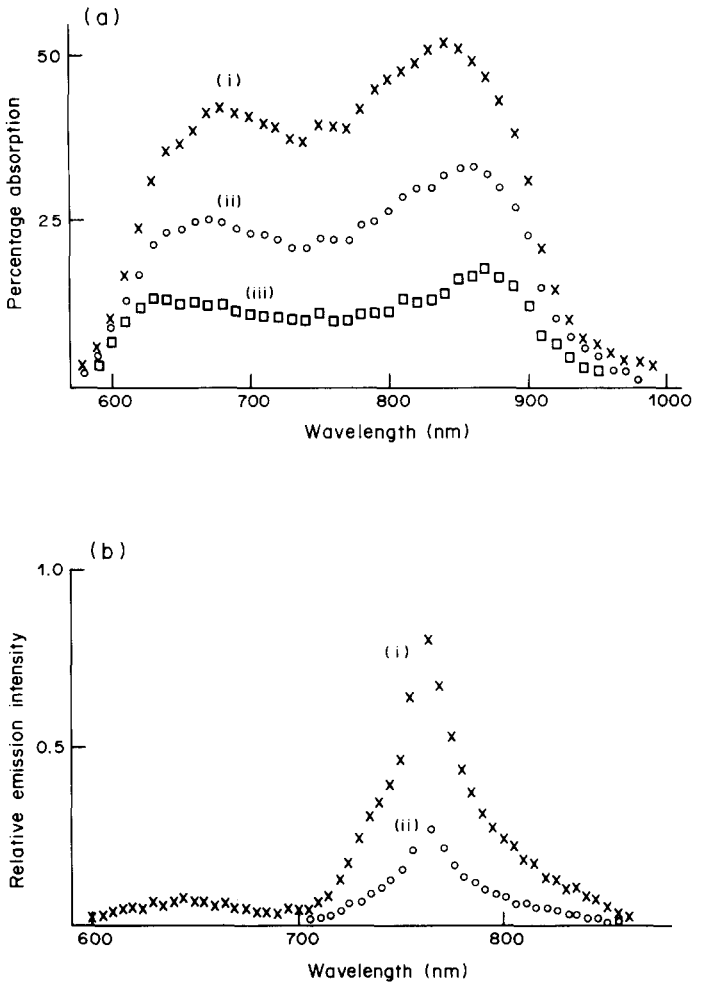

Fig. 2. Sensitox II: (a) transient absorption spectrum, (i) immediately after laser pulse, (ii) after 25 μsec, (iii) after 100 μsec; (b) emission spectrum, (i) immediately after laser pulse, (ii) after 100 μsec.

after laser excitation of all samples. With powdered microcrystalline rose bengal, considerable changes indicating an increased absorption in the region from 620 to 800 nm were observed due to laser exposure. In the case of all the other samples used to obtain the data in Figs 1–5, only slight changes in diffuse reflectance spectra were observed following laser excitation of the samples many times. Although the transient changes in absorption following laser excitation of powdered rose bengal (Fig. 6) does not show any negative changes, it is possible that the sharp peak at 620 nm is caused by the strong ground state absorption edge in this region since the difference spectrum shows a minimum where the ground state absorbs strongly. Thus, the difference spectrum could be due to overlapping transients with a negative contribution from ground state depletion. In view of the weak emission we think the transient absorption in this case is unlikely to be mainly due to triplet rose bengal. Radical cations and/or anions may be formed in the crystal (cf. Ref. 10) and more studies are needed to assign these transient absorption changes in the case of microcrystals of rose bengal.

The time resolved emission spectra from rose bengal on polyacrylamide and in cotton (Figs 3b and 5b) resemble those obtained from Sensitox I and II (Figs 1b and 3b). Although these emission spectra are uncorrected for changes in instrumental sensitivity at different analysing wavelengths, there can be little doubt that the band which peaks at ~765 nm corresponds to phosphorescence from rose bengal. Since the decays of the transient absorptions shown in Figs 1–5 are identical within experimental error or close to the corresponding decays of the emission at 765 nm (see later), we confidently assign these transient absorptions to changes due predominantly to the population of triplet rose bengal in these different environments. The presence of isosbestic points is confirmation of a single transient, the decay of which results in the return of ground state rose bengal. The transient absorption is similar to that observed by ourselves and others [10, 11] when rose bengal is subjected to nanosecond laser photolysis in dilute

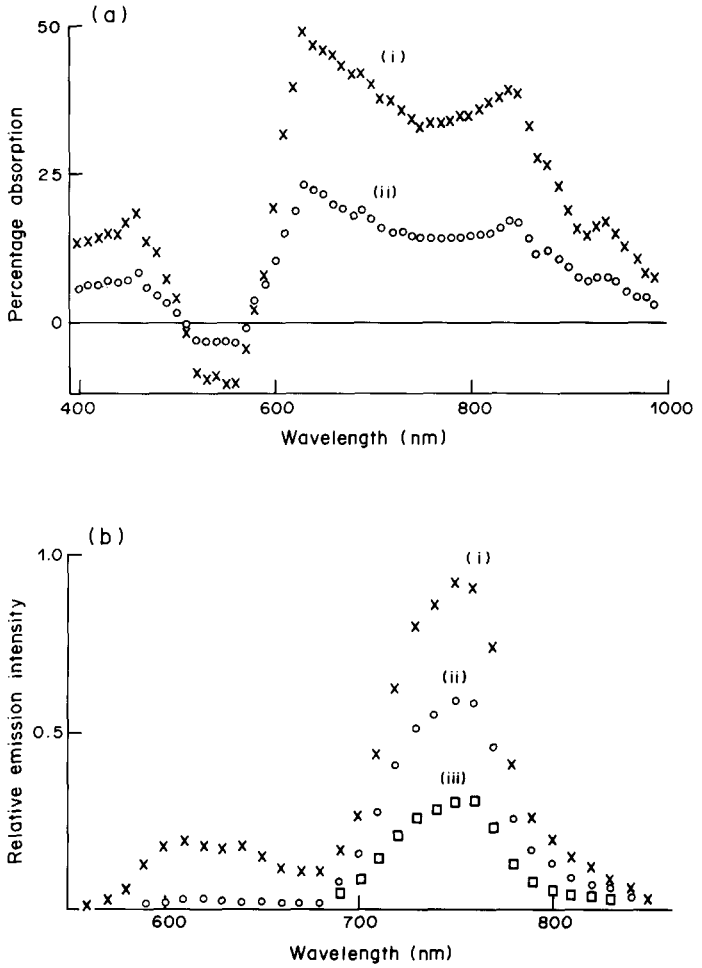

Fig. 3. Rose bengal adsorbed on polyacrylamide: (a) transient difference spectrum, (i) immediately after laser excitation, (ii) after 100 μsec; (b) emission spectrum, (i) immediately after laser excitation, (iii) after 40 μsec, (iii) after 160 μsec.

fluid solution using transient transmission spectroscopic measurements, and that transient spectrum has been assigned to the triplet state of rose bengal [11].

As far as the emission spectra are concerned, the spectra obtained from rose bengal on polystyrene (see Fig. 4b) are exceptional since the rapid decaying component which in this case peaks at 620 nm is much larger than the longer-lived phosphoresence at 765 nm. The ground state absorption by rose bengal which falls off rapidly above 620 nm means that the spectra of the more rapidly decaying emission which peak in the 620–650 nm region will be subject to distortion due to reabsorption to a greater or lesser extent. This emission is in the region expected for rose bengal fluorescence though its lifetime is too long to be assigned to prompt fluorescence and too short (relative to the phosphorescence lifetime) to be explained simply by E-type or P-type delayed fluorescence arising from the triplet state. Since the peak is most prominent for the polystyrene sample, where the diffuse reflectance ground state spectrum shows that this substrate absorbs the highest proportion of the laser pulse at 354 nm, we propose that this emission could be due to delayed fluorescence from the singlet state of rose bengal arising from energy transfer from excited states or traps in the substrate. There was no sign of any corresponding transient absorption changes on the timescale over which this emission occurred.

Kinetic analysis

General features. The decay of the laser induced transient absorption and the emission of triplet rose bengal in these environments cannot be fitted by simple first or second order kinetics. Although quite good linear plots were sometimes obtained as illustrated by inset (ii) in Fig. 7, usually the results indicated either multi-exponential decay, i.e. a range of first order decay constants or a mixture of first and second order decays. With so much kinetic information stored in the computer, the question of how best to report these non-linear decay curves presents a frustrating problem. We have already indicated in the previous section that more than 90% of the emission and transient absorption changes we have measured

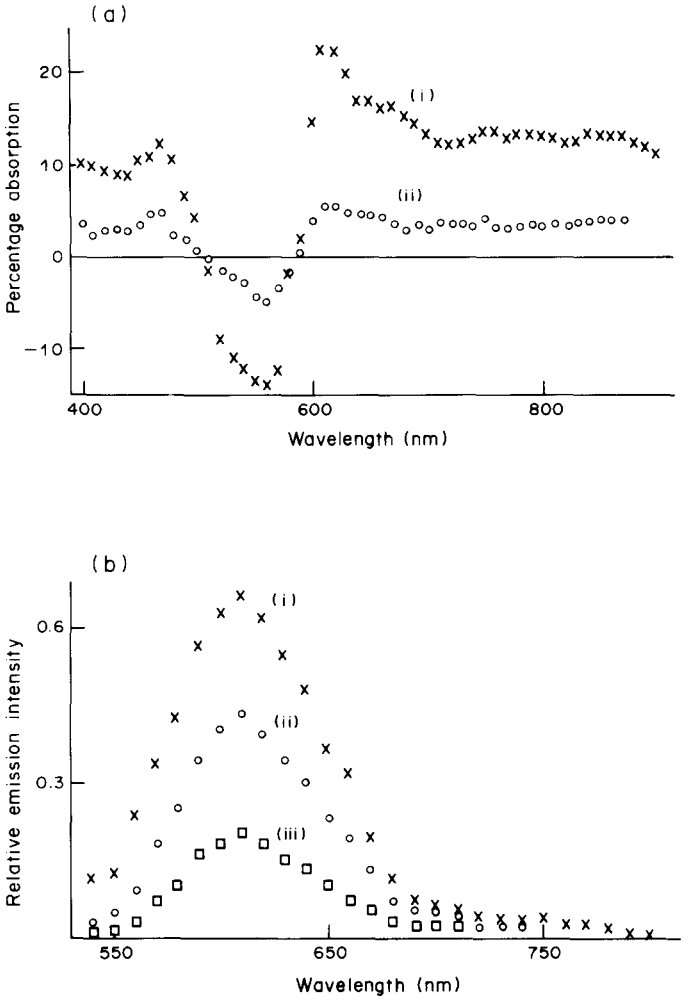

Fig. 4. Rose bengal adsorbed on polystyrene: (a) transient difference spectrum, (i) immediately after laser excitation, (ii) after 8 μsec; (b) emission spectrum, (i) immediately after laser excitation, (i) after 0.5 μsec, (ii) after 2 μsec.

can be explained in terms of the formation and decay of triplet rose bengal in various heterogeneous environments. Before examining the kinetic analysis in detail, we present in Table 1 a set of initial half-lives ($t1_{1/2}$) and second half-lives ($t2_{1/2}$), i.e. the time taken from traces to decay from $I_{max}/2$ to $I_{max}/4$, obtained from the various samples usually excited at two different wavelengths, and in each case quote values obtained using both emission and transient absorption changes relative to the pre-trigger value, i.e. before the laser fired. Although many of the pairs of values are within experimental error, differences of up to 30% occur for some pairs. If as Fig. 7 illustrates the decay has a strong second order component, then the half-life might be expected to depend on the initial concentration of the excited state and as can be seen in Table 1 this is often the case with ($t1_{1/2}$) being close to the value of ($t2_{1/2}$)/2. As mentioned earlier, emissions other than phosphoresence from rose bengal are detected. Although these peak at different analysing wavelengths, a small amount of overlap at the phosphoresence analysing wavelength could well account for the half-life differences observed. Analyses of the decay of the emission at different wavelengths showed varying amounts of the faster decaying component in the region 700–800 nm. In contrast we have good spectral evidence for only one decaying species in the transient absorption difference spectra. In addition, we have reported here that a close examination of decay traces such as that shown in Fig. 7 suggest a very small residual absorption change (less than 2%). This could be due, for example, to a small proportion of photochemical degradation. In which case, the kinetic analysis should use the final rather than the initial value to measure the half-lives which has the effect of reducing slightly the $t_{1/2}$ values measured by transient absorption measurements. It is apparent from Table 1 that changing the excitation wavelength from 354 to 532 nm (and consequently the laser intensity which is about five times greater at 532 nm) has little effect on the half-lives measured in the case of samples of adsorbed rose bengal on polystyrene and on polyacrylamide but reduces, by up to one half, the lifetimes for the chemical attached heterogeneous

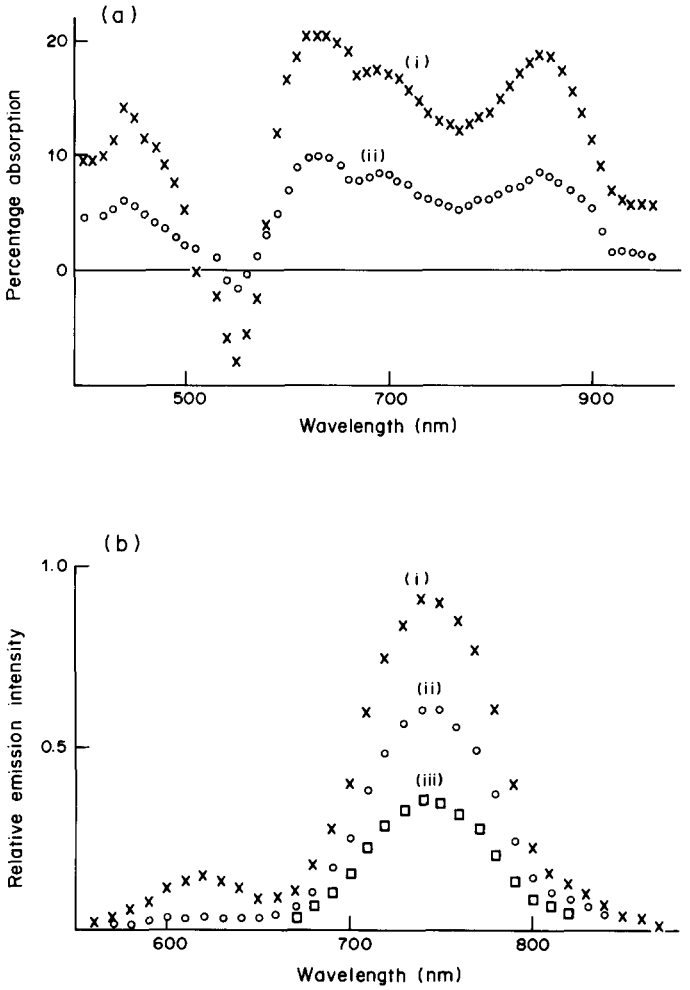

Fig. 5. Rose bengal dyed into cotton fabric: (a) transient difference spectrum, (i) immediately following excitation, (ii) after 50 μsec; (b) emission spectrum, (i) immediately following excitation, (ii) after 15 μsec, (iii) after 50 μsec.

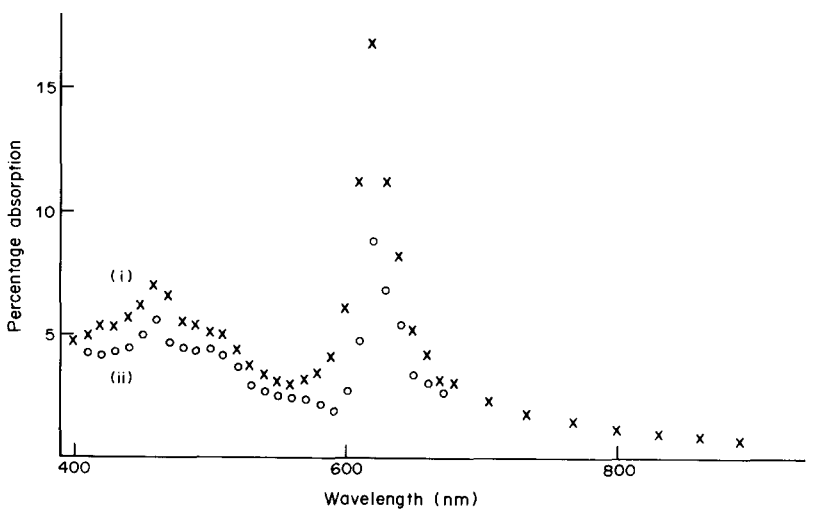

Fig. 6. Transient difference spectrum of pure rose bengal: (i) immediately following laser excitation; (ii) 200 μsec after excitation.

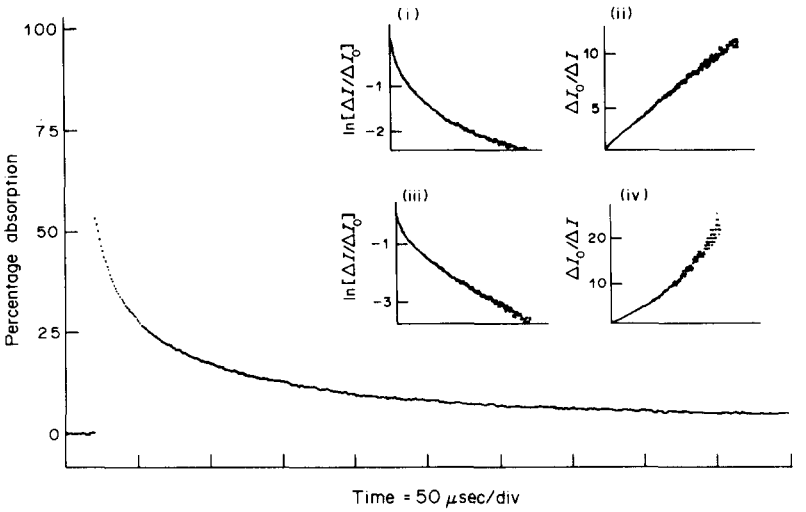

Fig. 7. Decay of transient absorption of Sensitox II, excited at 354 nm, monitored at 840 nm, (i) and (ii) are first and second order kinetic analyses relative to the pretrigger value, while (iii) and (iv) are the same kinetic analyses using a value between the pretrigger and the end of the decay, i.e. relative to an estimate of I_∞.

sensitizers, Sensitox I and II. Reducing the intensity of the laser excitation at 354 nm seven-fold only halved the initial amount of transient detected by both emission and diffuse reflection absorption for Sensitox I. The measured half-lives were only slightly reduced, i.e. by about 10%. This "saturation" effect could be due to singlet–singlet annihilation which does not produce triplet rose bengal being more significant at higher laser excitation intensities.

Before discussing in more detail the kinetic analysis, it is perhaps worth pointing out that if these heterogeneous samples have non-linear decays because of, for example, heterogeneity of site with rose bengal in different environments having different probabilities of decay, and given somewhat different emission and absorption spectra, then each analysing or emission wavelength will minotor different weighted contributions from the population of excited states at different sites. In such cases even if we knew how best to present the data, we would expect to find slight differences in any derived constants.

Analysis of decay curves

In previous publications [6, 12] we showed that the change in diffuse reflectance ΔI_d, is directly proportional to the concentration of a photoinduced transient in an opaque sample. The emitted intensity (change over background) ΔI_e is also directly propor-

Table 1. First and second half lives for the decay of transient absorption and of phosphorescence observed for rose bengal in different heterogeneous environments excited with 354 and 532 nm laser excitation

Sample	λ_{ex} (nm)	Method (λ_{an}/nm)	$t1_{1/2}$ (sec)	$t2_{1/2}$ (sec)
Sensitox I	354	Abs at 800	$4.0 \pm 0.4 \times 10^{-6}$	$1.0 \pm 0.2 \times 10^{-5}$
	354	Ems at 765	$3.3 \pm 0.3 \times 10^{-6}$	$0.7 \pm 0.1 \times 10^{-5}$
	532	Abs at 840	$2.9 \pm 0.3 \times 10^{-6}$	$7.5 \pm 1.0 \times 10^{-6}$
	532	Ems at 765	$2.5 \pm 0.2 \times 10^{-6}$	$6.5 \pm 0.2 \times 10^{-6}$
Sensitox II	354	Abs at 840	$3.3 \pm 0.3 \times 10^{-5}$	$8.9 \pm 0.6 \times 10^{-5}$
	354	Ems at 765	$4.2 \pm 0.4 \times 10^{-5}$	$8.8 \pm 0.2 \times 10^{-5}$
	532	Abs at 840	$1.7 \pm 0.2 \times 10^{-5}$	$3.5 \pm 0.5 \times 10^{-5}$
	532	Ems at 765	$2.2 \pm 0.2 \times 10^{-5}$	$4.3 \pm 0.2 \times 10^{-5}$
Rose bengal adsorbed on polystyrene	354	Abs at 860	$3.8 \pm 0.4 \times 10^{-6}$	$8.9 \pm 2.0 \times 10^{-6}$
	354	Ems at 765	$5.5 \pm 0.6 \times 10^{-6}$	$8.9 \pm 0.5 \times 10^{-6}$
	532	Abs at 860	$4.6 \pm 0.5 \times 10^{-6}$	$1.0 \pm 0.1 \times 10^{-5}$
	532	Ems at 765	$6.3 \pm 0.5 \times 10^{-6}$	$1.2 \pm 0.1 \times 10^{-5}$
Rose bengal adsorbed on polyacrylamide	534	Abs at 630	$1.3 \pm 0.2 \times 10^{-4}$	$1.7 \pm 0.3 \times 10^{-4}$
	534	Ems at 760	$0.8 \pm 0.1 \times 10^{-4}$	$1.3 \pm 0.2 \times 10^{-4}$
	532	Abs at 630	$1.2 \pm 0.1 \times 10^{-4}$	$1.8 \pm 0.4 \times 10^{-4}$
	532	Ems at 760	$0.7 \pm 0.1 \times 10^{-4}$	$1.0 \pm 0.1 \times 10^{-4}$
Cotton fabric dyed with rose bengal	354	Abs at 640	$7.4 \pm 0.6 \times 10^{-5}$	$1.4 \pm 0.2 \times 10^{-4}$
	354	Ems at 750	$9.5 \pm 0.5 \times 10^{-5}$	$1.4 \pm 0.2 \times 10^{-4}$
Microcrystalline rose bengal	354	Abs at 620	$8.9 \pm 1.5 \times 10^{-5}$	$2.6 \pm 0.5 \times 10^{-4}$

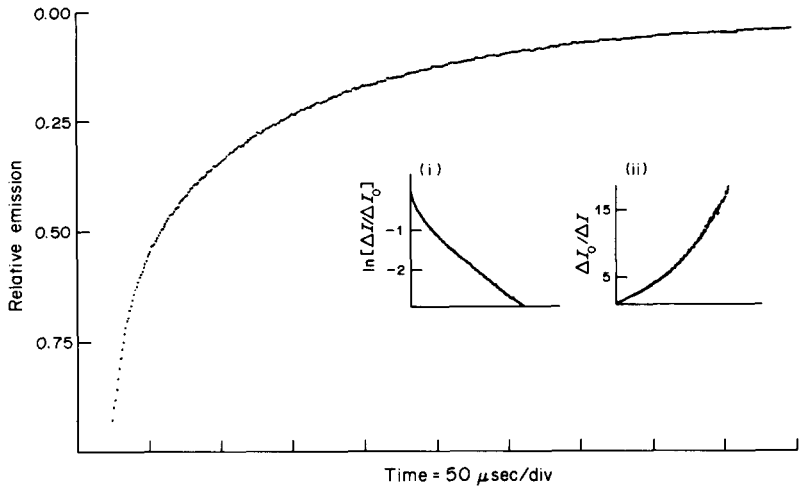

Fig. 8. Decay of emission of Sensitox II, excited at 354 nm, monitored at 765 nm, (i) and (ii) are first and second order kinetic analyses of the decay.

tional to the transient concentration, thus for a first order decay where the concentration of transient C is given by

$$C = C_0 \exp(-k_1 t) \quad (1)$$

a plot of $\ln(\Delta I/\Delta I_0)$ vs time will give a slope of $-k_1$ where ΔI represents the emission intensity or change in absorption of diffuse reflected light and ΔI_0 the initial change at time zero, when the laser fires. Note that if the transient decays to give some residual absorption or if a residual absorption is photoproduced on a much faster time scale then ΔI should be measured relative to the signal remaining after the decay, i.e. relative to the I_∞ rather than the I_p (pre-trigger) value.

For a second order decay,

$$\frac{-dC}{dt} = k_2 C^2 \quad \text{or} \quad \frac{C_0}{C} = 1 + k_2 C_0 t \quad (2)$$

Thus a plot of $\Delta I_0/\Delta I$ vs time is expected to be linear with a slope of $k_2 C_0$. Again, if the transient absorption signal in diffuse reflectance measured after the transient decay is different from that before, ΔI measured relative to I_∞ rather than I_p is more likely to give the correct kinetic analysis.

For decay by a mixture of first and second order, i.e. where:

$$\frac{-dC}{dt} = k_1 C + k_2 C^2$$

integration gives:

$$\ln\left[\left(\frac{\Delta I_0}{\Delta I}\right) + \frac{k_2 C_0}{k_1}\right] = k_1 t + \ln\left[1 + \frac{k_2 C_0}{k_1}\right] \quad (3)$$

Figure 7 shows a decay trace of the laser induced transient absorption obtained from Sensitox II. The insets (i) and (ii) show first and second order plots

Table 2. First and second order decay constants for the decay of transient absorption and of phosphorescence observed for rose bengal in different heterogeneous environments excited with 354 and 532 nm laser excitation

Sample	λ_{ex} (nm)	Method (λ_{an}/nm)	k_1 (sec^{-1})	$k_2 C_0$ (sec^{-1})
Sensitox I	354	Abs at 800	$(2.8 \pm 1.2) \times 10^4$	$(1.8 \pm 0.3) \times 10^5$
	354	Ems at 765	$(3.6 \pm 0.4) \times 10^4$	$(2.3 \pm 0.2) \times 10^5$
	532	Abs at 840	$(2.7 \pm 0.9) \times 10^4$	$(2.4 \times 0.3) \times 10^5$
	532	Ems at 765	$(5.0 \pm 0.5) \times 10^4$	$(3.2 \pm 0.3) \times 10^5$
Sensitox II	354	Abs at 840	$(4.2 \pm 0.7) \times 10^3$	$(1.6 \pm 0.4) \times 10^4$
	354	Ems at 765	$(4.3 \pm 0.3) \times 10^3$	$(1.1 \pm 0.1) \times 10^4$
	532	Abs at 840	$(4.0 \pm 1.5) \times 10^3$	$(6.1 \pm 1.0) \times 10^4$
	532	Ems at 765	$(5.6 \pm 0.5) \times 10^3$	$(3.0 \pm 0.3) \times 10^4$
Rose bengal adsorbed on polystyrene	354	Abs at 860	$(2.4 \pm 1.0) \times 10^4$	$(1.4 \pm 0.5) \times 10^5$
	354	Ems at 765	$(1.5 \pm 1.0) \times 10^4$	$(1.3 \pm 0.5) \times 10^5$
	532	Abs at 860	$(2.2 \pm 1.0) \times 10^4$	$(1.4 \pm 0.2) \times 10^5$
	532	Ems at 765	$(1.5 \pm 1.0) \times 10^4$	$(1.6 \pm 0.1) \times 10^5$
Rose bengal adsorbed on polyacrylamide	354	Abs at 630	$(5.0 \pm 0.5) \times 10^3$	$(6 \pm 1) \times 10^3$
	354	Ems at 760	$(3.7 \pm 0.4) \times 10^3$	$(1.4 \pm 0.2) \times 10^4$
	532	Abs at 630	$(4.9 \pm 0.5) \times 10^3$	$(7.5 \pm 1.0) \times 10^3$
	532	Ems at 760	$(3.6 \pm 0.3) \times 10^3$	$(1.3 \pm 0.2) \times 10^4$
Cotton fabric dyed with rose bengal	354	Abs at 640	$(3.6 \pm 0.4) \times 10^3$	$(2.2 \pm 0.5) \times 10^4$
	354	Ems at 750	$(3.6 \pm 0.2) \times 10^3$	$(1.3 \pm 0.2) \times 10^4$
Microcrystalline rose bengal	354	Abs at 620	$(1.3 \pm 0.4) \times 10^3$	$(5.1 \pm 0.5) \times 10^3$

respectively using ΔI values measured relative to the pretrigger value and insets (iii) and (iv) show the effect of using ΔI values relative to an extrapolated I_∞ value, i.e. using a value for I between I_p and the value shown at the end of the trace. The non-linear kinetic analysis curves (iii) and (iv) are very similar to those obtained from analysis of the phosphorescence decay of rose bengal from Sensitox II shown in Fig. 8 (i.e. as insets 8(i) and 8(ii) respectively). Values of k_1 and k_2C_0 obtained from fitting the decays to equation 3 are given in Table 2 for all the samples. The fact that similar or only slightly higher values of k_2C_0 are observed with excitation at 532 compared with excitation at 354 nm is probably due to the saturation effect concerning the dependence of the amount of transient on laser intensity mentioned earlier. The lifetimes and the fits obtained demonstrate a strong second order decay contribution from all cases except possibly for rose bengal on polyacrylamide. The occurrence of triplet–triplet annihilation is interesting in connection with the possibility of energy transfer between chromophores attached to polymers (see for example Ref. 13).

The reasons why the lifetimes and the extent of first and second order decay vary from the different environments is not obvious, but we feel the agreement between the values obtained using diffuse reflectance and emission is best in most cases when the kinetic analysis is for a mixture of first and second order decays. Examination of Tables 1 and 2 demonstrates that different half-lives for the different heterogeneous environments are reflected in different values for both k_1 and k_2C_0. Further systematic studies of adsorbed samples with different loadings of rose bengal are now proceeding; we hope that they will help clarify these effects.

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