Effect of aggregates on the photochemical behavior of Rose Bengal peroxybenzoate initiator in PMMA film

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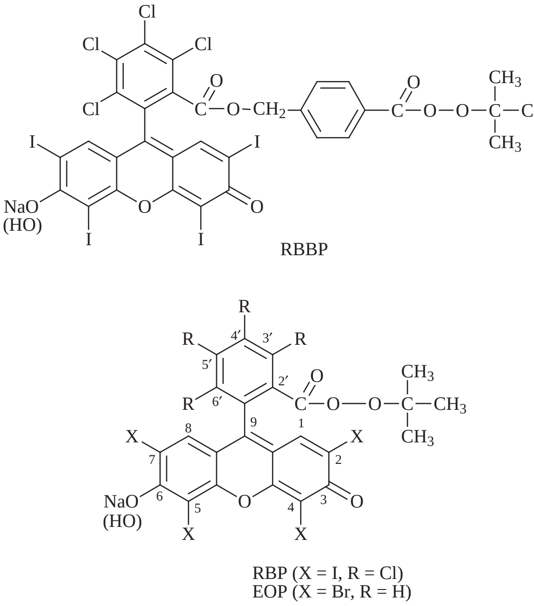
To reveal the sensitization mechanism of Rose Bengal peroxybenzoate (RBBP) in poly(methyl methacrylate) (PMMA) film, the behavior of RBBP was investigated by means of both fluorescence spectroscopy and laser flash photolysis in PMMA as well as in dilute solution for comparison. In the RBBP concentration range 2×10^{-3} to 9×10^{-2} mol dm^{-3} in PMMA film, the yields of the singlet and triplet excited states of RBBP are affected by dye aggregation which is enhanced by increasing RBBP concentration. Thus, in the (6–9) $\times 10^{-2}$ mol dm^{-3} RBBP concentration range, production of the fluorescent excited state is reduced, but formation of the triplet states is increased. This seems to be responsible for the radical generation during photoinitiation.

Introduction

Much attention has recently been paid to photoinitiation during visible light irradiation.[1,2] For this purpose, peroxides substituted with chromophores absorbing visible light have been investigated. For peroxyesters substituted with xanthene dyes, Neckers *et al.* showed that the 2′-*tert*-butyl peroxyester of Eosin Y (EOP, Scheme 1) in the presence of *N*-vinylpyrrolidone as an electron donor works as a high speed photoinitiator.[3] We found that the 2′-*tert*-butyl peroxyesters of other xanthene dyes, such as Rose Bengal (RBP, Scheme 1) and Erythrosine, could be effective photoinitiators, although the yield of their preparation from acid chlorides of the corresponding xanthene dyes and *tert*-butyl hydroperoxide was not satisfactory.[4] On the other hand, irradiation of Rose Bengal (RB) in the presence of a radical generating peroxide, *tert*-butyl 4-(bromomethyl)peroxybenzoate (BP), did not induce photopolymerization for photoresist-image formation.[5,6] However, we found that connection of the *tert*-butyl peroxyester group to RB with a phenylmethylene bridge as a spacer, that is, the 4-(*tert*-butylperoxycarbonyl)phenylmethyl ester of RB, described as RBBP in Scheme 1, brought about high speed photoinitiation in a polymer film under visible laser irradiation even without any electron donor additives such as amines.[5,6] Thus, the presence of a spacer between the RB chromophore and peroxyester group is effective in inducing decomposition of the peroxide bond during visible light excitation of the RB chromophore.


RBBP

RBP (X = I, R = Cl)
EOP (X = Br, R = H)

Scheme 1 Peroxyesters substituted with xanthene dyes.

To reveal the mechanism of photoinitiation with RBBP in a polymer film, we investigated by fluorescence and transient absorption spectroscopy the behavior of the excited states of RBBP dispersed in a poly(methyl methacrylate) (PMMA) film in the concentration range typical of an ordinary photoinitiation system and, for comparison, their behavior in dilute solution. It was found that increasing the RBBP concentration in the PMMA film enhances the aggregation of RBBP, which results in lower fluorescence efficiency and concurrently tends to increase the formation of the triplet state of RBBP. This might be responsible for efficient photoinitiation.

Experimental

RBBP was prepared according to the literature procedure.[6] Poly(methyl methacrylate) (PMMA), $M_n = 45370$, $M_w = 97720$, $M_w/M_n = 2.15$, estimated by GPC (RI), and all solvents were spectrograde and purchased from Wako Pure Chemical Industries, Ltd.

UV–VIS spectra were recorded with a Hitachi U-3000 spectrophotometer, and fluorescence spectra with a Hitachi F-4500 fluorescence spectrophotometer by using a solid sample holder, which was also used for a solution sample in order to minimize the effect of an internal light filter. Fluorescence lifetimes were measured by a Horiba NEAS-1100 time resolved fluorescence spectrometer (single photon counting). The excitation light was passed through a monochromator, and the emission light was detected through an O-56 cut-off filter to remove the scattering light from the excitation light at 560 nm. The solution sample was saturated with argon.

Laser flash photolysis in solutions was carried out with an excimer laser (Lambda Physik EGM 101, XeCl, 308 nm)-pumped dye laser (Lambda Physik FL-3002). The 530 nm excitation wavelength was obtained using a Coumarin 307 laser dye. As a monitoring light source, a pulsed 150-W Xenon arc (Wacom KXL-151) was employed, whose light was led to a 1 cm quartz cuvette containing the sample solution at a right angle to the excimer laser beam, passed through a monochromator (JASCO CT25) and was then detected by a photomultiplier (Hamamatsu R928). Transient spectra from nanoseconds to microseconds were obtained with the aid of a microcomputer (NEC PC-9801).[7] Sample solutions were bubbled with argon for 30 min before each measurement.

Laser flash photolysis in film was performed using a total reflection sapphire cell which was spin-coated with a 1.4 µm photopolymer film. An excitation light pulse (20 ns, 355 nm and 10 mJ per pulse) from a YAG laser (Spectron Laser Systems Model SL 402) was expanded and exposed over the entire sample cell. A monitoring light from a xenon lamp passed through the multireflection cell which was connected to the head of an optical fiber attached to a monochromator (Instruments Digikrom 240) equipped with a photomultiplier (Hamamatsu Photonics K.K. photomultiplier tube type R928) or to an SMA system (Princeton Instruments, Inc. model TRY-700G/R/Par).[8–11]

Films were prepared as follows. A 10 wt% PMMA solution was made up in cyclohexanone, RBBP was added to this solution either by dissolving the dye directly in polymer solution or by mixing in a portion of concentrated dye solution. Films were made 1.4 µm thick by spin-coating a solution onto a quartz glass or sapphire cell. The concentration of RBBP relative to PMMA in film was 11 times greater than that in solution. The photosensitivity was measured according to the procedure in ref. 6.

Cyclovoltammetric measurements were made on an HAB-151 potentiostat–galvanostat from Hokuto Denko, Ltd. utilizing a three-electrode system. A platinum disk served as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The SCE was separated from the bulk solution by a glass bridge. An electrolyte solution of 0.1 mol dm^{-3} tetra-*n*-butylammonium perchlorate (TBAP) in ethanol was used to measure the redox potentials of the dyes. All solutions were degassed with argon for 30 min before the experiment.

Results

For comparison with the results in PMMA film, the behavior of the excited state of RBBP was investigated in dilute solution. The results in dilute solution are shown in Figs. 1–4.

Fig. 1 depicts the excitation and emission spectra of RB and RBBP in acetonitrile. Fig. 2 depicts the absorption and fluorescence spectra of RBBP in cyclohexanone, cyclohexanone containing 10 wt% PMMA, neat film and PMMA film. In dilute cyclohexanone solution, RBBP shows essentially the same features in its absorption and fluorescence spectra, with two maxima of larger and smaller intensity, as the parent RB. In both the absorption and fluorescence spectra, the maxima showed a red shift of nearly 10 nm from RB. The addition of PMMA (10 wt%) to cyclohexanone slightly enhanced the absorbance and fluorescence intensity at a maximum wavelength but did not affect the bandwidth of these spectra.

In films, the absorption maxima shifted to red in the neat film, but to blue in the PMMA film. RBBP does not fluoresce in the former film, but fluoresces in the latter film.

The ratio of the absorbance at the absorption peaks for longer and shorter wavelengths, $\varepsilon_1:\varepsilon_2$, was determined since the aggregation of RB molecules is known to shift the absorption maximum and reduce the $\varepsilon_1:\varepsilon_2$ value.[12–18] These results are summarized in Table 1.

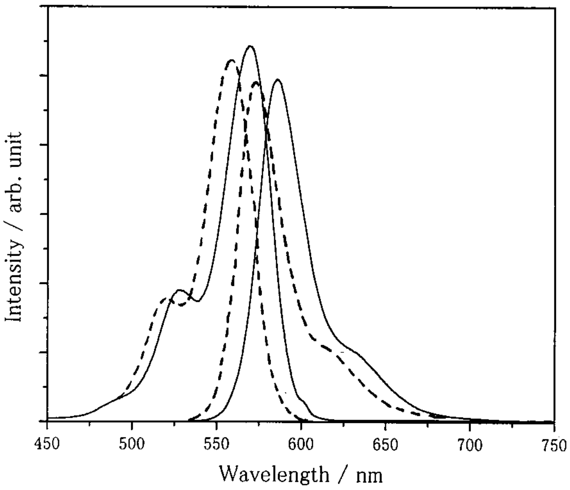


Fig. 1 Excitation (left) and fluorescence (right) spectra of RB (dashed line) and RBBP (solid line), 5×10^{-6} mol dm^{-3} in acetonitrile, fluorescence detected at the excitation of maximal absorption wavelength and excitation spectra observed at maximal fluorescence wavelength, respectively.

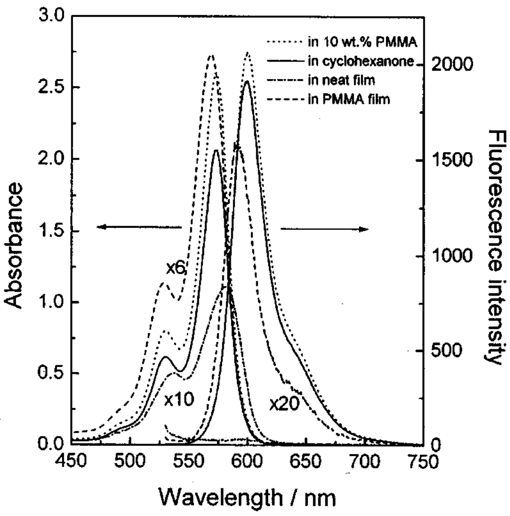


Fig. 2 Absorption and fluorescence spectra of 2.2×10^{-4} mol dm^{-3} RBBP in cyclohexanone (solid line), 2.4×10^{-4} mol dm^{-3} RBBP in cyclohexanone containing 10 wt% PMMA (dotted line), 3.5×10^{-3} mol dm^{-3} RBBP in neat film (dashed dotted line) and 3.9×10^{-3} mol dm^{-3} RBBP in PMMA film (dashed line); the corresponding fluorescence spectra were recorded upon excitation at 520 nm, the optical length of the solution is 1 mm, and the film thickness is 1.4 µm.

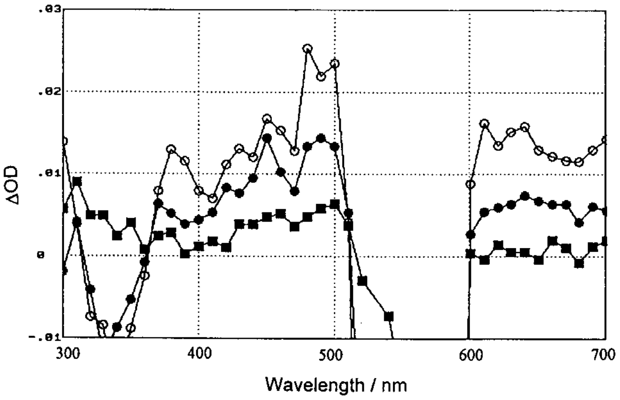


Fig. 3 Transient spectra of RBBP at a concentration of 2.7×10^{-5} mol dm^{-3} in acetonitrile observed at 50 ns (○), 9 µs (●) and 63 µs (■) after laser excitation at 530 nm.

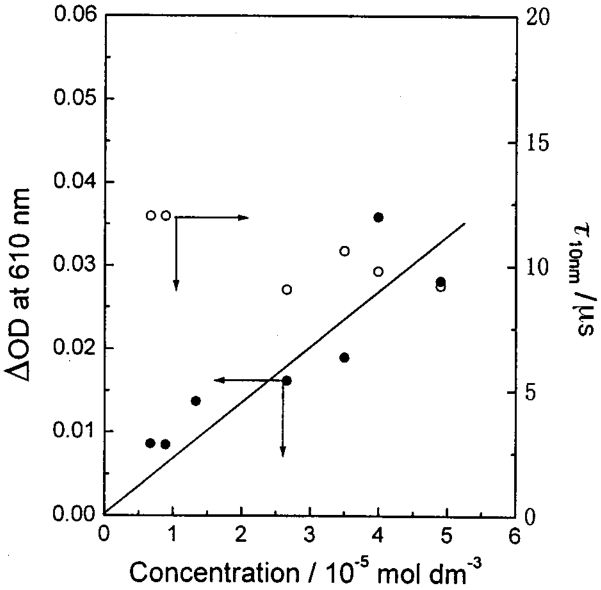


Fig. 4 The concentration dependence of both the initial T–T absorption (●) and triplet decay time (○) of RBBP in acetonitrile after laser excitation at 530 nm and detection at 610 nm.

The fluorescence lifetime of RBBP increased from 696 ps for 6.7×10^{-6} mol dm^{-3} in ethanol to 2.13 ns for 3.7×10^{-4} mol dm^{-3} in PMMA film.

Fig. 3 depicts the transient spectra of RBBP observed during laser flash photolysis at 530 nm in acetonitrile. The spectra show T–T absorption in the range beyond 600 nm together with the resulting radical ions between 360 and 500 nm, similar to those of RB as reported by Neckers.[19–21]

Fig. 4 shows the absorbance of the initial T–T absorption and the lifetime of the triplet state *versus* the RBBP concentration in acetonitrile. The absorbance of the initial T–T absorption increased linearly with increasing concentration of RBBP whereas the lifetime of the triplet state remained almost constant.

The results in film are depicted in Figs. 5–7. Fig. 5 shows the initial T–T absorption spectrum of RBBP in a PMMA film upon laser excitation at 355 nm. The absorption was observed only in the 630–680 nm region. As the insert to the figure indicates, the triplet state decayed almost exponentially. It is difficult to detect the transient absorption beyond this range due to high inherent absorption in the ground state below 630 nm and a high signal : noise ratio beyond 680 nm. The absorption due to the resulting radical ions was not detected in the range between 400 and 500 nm.

Fig. 6 depicts the absorption and fluorescence spectra of RBBP with varying RBBP concentration in the PMMA film and the concentration dependence of the absorbance at maximal wavelengths and their intensity ratio, $\varepsilon_1 : \varepsilon_2$. An increase in the RBBP concentration results in a red shift of the fluorescence maximum without any distinct change in the spectral shape.

Fig. 7 shows the dependence of the fluorescence intensity, the absorbance of the initial T–T absorption and the lifetimes of both the singlet and triplet excited states on the concentration of RBBP in the PMMA film.

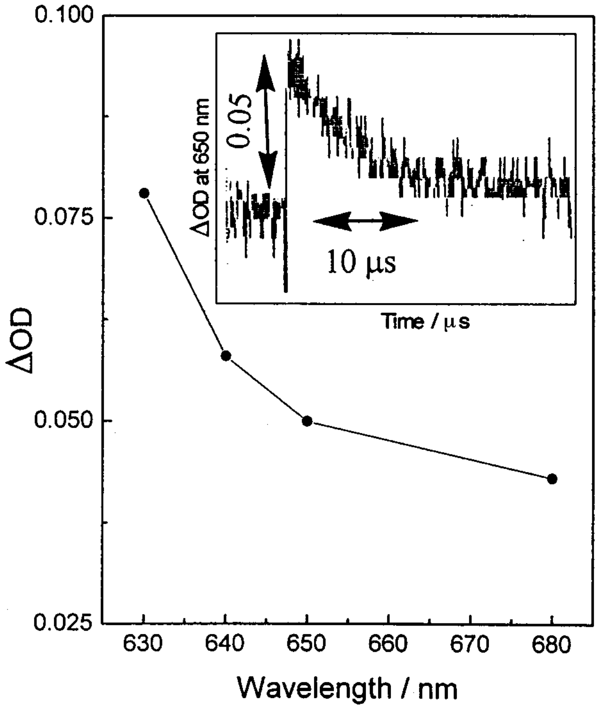


Fig. 5 T–T absorption spectrum of RBBP at a concentration of 8×10^{-2} mol dm^{-3} in PMMA film at 50 ns after laser excitation at 355 nm. Insert: time profile of RBBP at 650 nm.

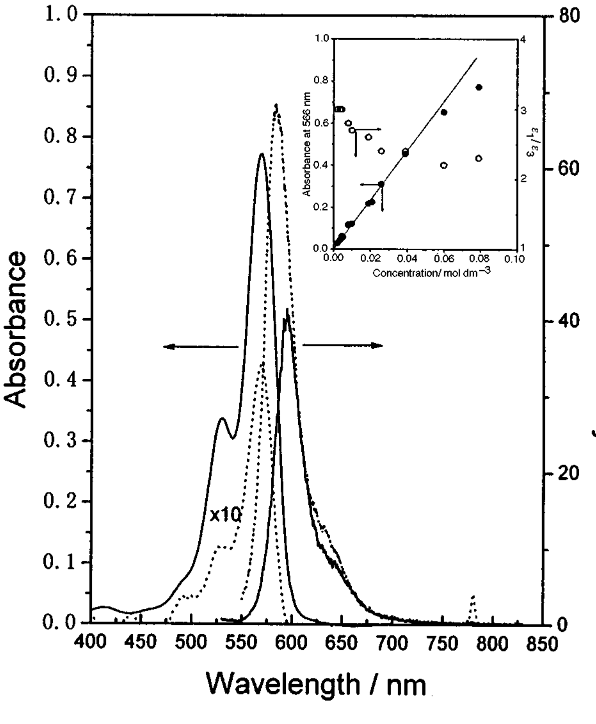


Fig. 6 The electronic absorption and fluorescence spectra of RBBP at concentrations of 7.9×10^{-2} (solid line) and 3.7×10^{-3} mol dm^{-3} (dotted line) in PMMA film (1.4 μm). Insert: the concentration dependence of both the absorbance of RBBP in the PMMA film at 568 nm and the $\varepsilon_1 : \varepsilon_2$ ratio; fluorescence spectra recorded after excitation at 520 nm.

Discussion

Like RB, RBBP shows two absorption peaks at longer and shorter wavelengths, that is, 574 and 530 nm in cyclohexanone. As for RB, the ratio of the absorption peaks at the longer and shorter wavelengths, $\varepsilon_1 : \varepsilon_2$, is known to decrease with aggregation.[12,22a] The results for RBBP in Table 1 and Fig. 6 show that this value decreases in both neat and PMMA film compared to that in dilute cyclohexanone solution. Fig. 6 indicates that in the PMMA film, the $\varepsilon_1 : \varepsilon_2$ value decreases with an increase in the RBBP concentration. Therefore, it is clear that RBBP aggregates in films and the degree of aggregation increases with increasing RBBP concentration.

Fig. 7 indicates that in the PMMA film, with an increase in the RBBP concentration, the fluorescence increases in intensity to a maximum at 1×10^{-2} mol dm^{-3} and then decreases; however, the lifetime of the singlet excited state, τ_S, rapidly decreases.

For the triplet state, with an increase in the concentration, the initial T–T absorption tends to continuously increase, but the lifetime of the triplet state, τ_T, is gradually reduced and attains a constant value when [RBBP] > 4×10^{-2} mol dm^{-3}.

These results indicate that in the PMMA film, an increase in the RBBP concentration from 0 to 1×10^{-2} mol dm^{-3} increases the amount of monomeric RBBP, thereby increasing the fluorescence intensity; however, further increasing [RBBP] to over 1×10^{-2} mol dm^{-3} enhances the aggregation and reduces the amount of monomeric RBBP. The aggregates do not fluoresce, as reported for RB by Neckers.[12,13] On the contrary, the remarkable decrease in the lifetime of the singlet excited state with an increase in the concentration from 0 to as little as 1×10^{-2} mol dm^{-3} suggests that the resulting singlet excited state suffers self-quenching.

Regarding the triplet state, the observed increase in the absorbance of the triplet state with an increase in the RBBP concentration throughout the entire range of concentrations examined suggests that in the lower concentration range, the singlet excited state of the monomeric RBBP undergoes intersystem crossing to the triplet state, but in the higher concentration range, the singlet excited state of the aggregated RBBP does not fluoresce but undergoes intersystem crossing to the triplet state with a higher quantum yield than that of the monomeric RBBP,[17,22] as has been reported for Rose Bengal, the C-2′ ethyl ester, C-6 sodium salt in 2% ethanol in the presence of KNO_3.[13] Gradual reduction of τ_T with the dye concentration attaining a constant value suggests that quenching of the triplet state occurs up to 4×10^{-2} mol dm^{-3} but then may be attenuated, when the triplet state arises mostly from the aggregates.

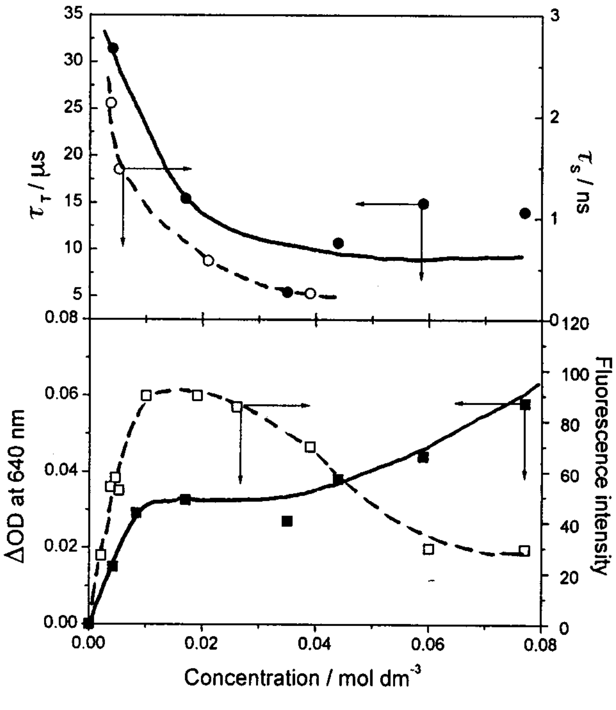


Fig. 7 Dependence of fluorescence intensity (□) and its lifetime (○) as well as the initial T–T absorption (■) and its decay time (●) of RBBP on the concentration in PMMA film (1.4 µm); fluorescence monitored at 586 nm upon 520 nm excitation and the triplet state monitored at 640 nm upon 335 nm laser excitation.

Fig. 8 shows schematically the photophysical processes of RBBP in terms of the equilibrium (*K*) between monomer (M) and dimer (D). The subscripts of Sq and Tq indicate singlet and triplet quenching, respectively; f, the fluorescence; S_0, S_1 and T_1, the ground, the excited singlet and the triplet state, respectively. The singlet excited state of the dimer (S_1^D) should be split into two levels in comparison with that of the monomer (S_1^M) according to the exciton theory.[14] As described above, in the high concentration range, only the singlet excited state of the non-fluorescent dimers gives the triplet states with a quantum yield higher than that of the monomer ($\varphi_{ST}^D > \varphi_{ST}^M$).[17]

In solution, xanthene dyes do not follow Beer's law at concentrations above about 10^{-4} mol dm^{-3} as dye molecules tend to aggregate.[15] In acetonitrile solution, RBBP does not seem to aggregate up to 3×10^{-4} mol dm^{-3}, since no change in the absorption and fluorescence spectra was observed. The addition of PMMA polymer did not affect the absorption and fluorescence spectra of RBBP in cyclohexanone, in which RBBP obeyed Beer's law for concentrations up to 3×10^{-4} mol dm^{-3}. The lifetime of the triplet state in acetonitrile, τ_T, was only slightly reduced in the examined concentration range (Fig. 4) and is comparable with that in PMMA film. Therefore, in dilute organic solution, RBBP monomer dominates the photochemical behavior of RBBP.[6,23,24]

As for the quenching process of the excited state of the dye, both energy transfer and electron transfer are considered to be responsible. Triplet energy transfer from the RB chromophore to the peroxyester moiety is unfeasible due to the higher triplet energy of BP than RB, as shown in Table 2. Electron transfer

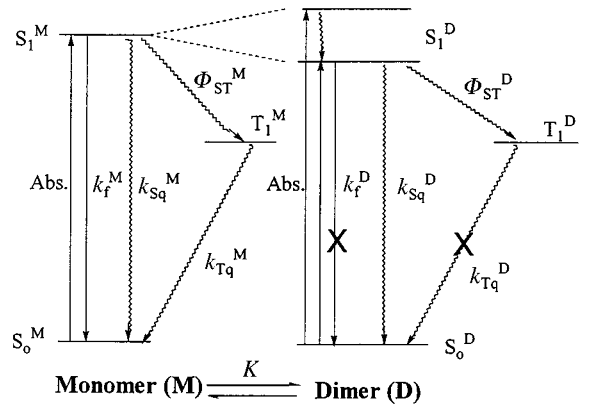


Fig. 8 Scheme for the photophysical processes of RBBP at equilibrium (*K*) between monomer (M) and dimer (D).

Table 1 Visible absorption and fluorescence spectra of RBBP in different media

[RBBP]/mol dm^{-3} in cyclohexanone	Medium	Absorption maximum/nm λ_{max1}	λ_{max2}	$\varepsilon_1 : \varepsilon_2$	Fluorescence maximum/nm
2.2×10^{-4}	Cyclohexanone	574	530	3.3	600
2.4×10^{-4}	Cyclohexanone containing 10 wt% PMMA	574	530	3.2	600
3.5×10^{-3}	Neat film	582	536	2.2	No fluorescence
3.9×10^{-3}	PMMA film	568	528	2.4	590

Table 2 Redox potentials, singlet and triplet excited energies of dyes and peroxyesters and free energy changes for electron transfer from the singlet and triplet excited states of dyes and to dyes in the ground state

	RBBP	RB	Eosin Y	BP
E_{ox}/V *vs.* SCE	+0.82	+0.86[a]	+0.84	*b*
E_{red}/V *vs.* SCE	−0.60	−1.03[a]	−1.05	−1.7
$^1E^c_{o-o}$/kcal mol^{-1}	48.7	50.7	53.6	
$^3E^c_{o-o}$/kcal mol^{-1}	*b*	39.7	43.1	68.1
ΔG_S/kcal mol^{-1}	−16	−7	−10	
ΔG_T/kcal mol^{-1}	−7[d]	4	0.5	

[a] The redox potentials of RB are identical to those in ref. 19. [b] Not observed. [c] In ethanol. [d] The triplet energy of RB was adopted.

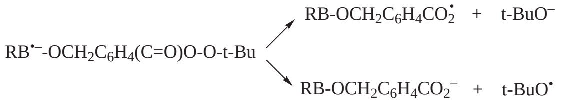
from the excited state of RB to the BP group seems endothermic since the free energy changes for the singlet and triplet excited states, ΔG_S and ΔG_T, are estimated as 8.3 and 19.3 kcal mol^{-1}, respectively, from the oxidation potential (E_{ox}) of RB and the reduction potential (E_{red}) of BP.

It is well known that the triplet state of xanthene dyes interacts with the ground state of the dyes through a D–D mechanism[25] to undergo either electron transfer giving one-electron oxidized and reduced species or bimolecular deactivation. For example, rate constants for electron transfer from the triplet to the ground state and bimolecular quenching for Eosin Y are 7×10^7 and 3×10^8 dm^3 mol^{-1} s^{-1},[26] respectively, in aqueous solution, though the rate constant for the unimolecular deactivation is 540 s^{-1}.[26] As indicated in Table 2, electron transfer between dye molecules in the triplet and the ground state seems to be slightly endothermic, and the above rate constant reflects the slightly endothermic nature of the process.

However, electron transfer between RBBP molecules in the excited and ground states seems feasible based on the values of ΔG_S and ΔG_T in Table 2. Therefore, it is reasonable to suppose that the triplet state of RBBP in which the triplet excitation is mostly located at the RB chromophore (RB*–BP) undergoes electron transfer with the RB chromophore of another RBBP molecule to give one-electron reduced (RB$^{\bullet-}$–BP) and oxidized species (RB$^{\bullet+}$–BP), as shown in eqn. (1).

$$\text{RB*–BP} + \text{RB–BP} \longrightarrow \text{RB}^{\bullet-}\text{–BP} + \text{RB}^{\bullet+}\text{–BP} \quad (1)$$

The resulting RB$^{\bullet-}$ group in the RBBP molecule will induce intramolecular reductive cleavage of the peroxide bond to give a free radical, either an aroyloxyl radical or a *tert*-butoxyl radical, as shown in eqn. (2). From a thermodynamic



(2)

$$\text{RB}^{\bullet-}\text{-OCH}_2\text{C}_6\text{H}_4\text{(C=O)O-O-t-Bu} \begin{cases} \nearrow \text{RB-OCH}_2\text{C}_6\text{H}_4\text{CO}_2^{\bullet} + \text{t-BuO}^- \\ \searrow \text{RB-OCH}_2\text{C}_6\text{H}_4\text{CO}_2^- + \text{t-BuO}^{\bullet} \end{cases} \quad (2)$$

viewpoint, production of the former radical seems to be more favorable than that of the latter.

Therefore, such electron transfers followed by intramolecular cleavage of the peroxide bond are enhanced with a higher concentration of dye, particularly in the dye aggregates. Probably, this aggregate effect in a photopolymer film results in the high photosensitivity of the RBBP system such as 0.14 mJ cm^{-2} determined at 0.08 mol dm^{-3} RBBP in a polymer which is comparable to or slightly better than the sensitivity of 0.20 mJ cm^{-2} determined for the system with RB and the fastest peroxyester, 3,3′,4,4′-tetrakis(*tert*-butyldioxycarbonyl)benzophenone (BTTB), during Ar$^+$-laser excitation at 514.5 nm.[5]

Summary

The photochemical behavior of RBBP in PMMA film is influenced by increasing concentration leading to aggregation. Thus, an increase in the RBBP concentration causes its aggregation, lowers the yield of the fluorescent singlet excited state but enhances the yield of the triplet state. The resulting triplet state seems to generate reactive free radicals for photoinitiation *via* electron transfer. Therefore, the excitation of RBBP aggregates is responsible for the high speed initiation of photopolymerization under visible-light laser irradiation.

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