Synthesis and Photochemical Behavior of Xanthene Dye-Peroxybenzoate Initiators

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A series of xanthene dyes bearing a *tert*-butyl peroxybenzoate moiety was synthesized. The fluorescence and phosphorescence spectra were measured to determine the photoproperties of xanthene dye peresters. The transient phenomena were also examined by nanosecond laser flash photolysis in organic solvents at room temperature. Furthermore, the photodecomposition behavior of these compounds was followed by UV-VIS absorption and the final decomposition products were distinguished by comparing IR spectra before and after the irradiation with an Ar⁺ laser at 514.5 nm. To prove their application to information recording materials, the sensitivities for the visible light initiating system are also reported.

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Introduction

Recently, LED and semiconductor lasers have developed rapidly and are promising compact and economical light sources, which emit long-wavelength light from the visible to the near-infrared (IR) region. Therefore, the development of materials that can absorb in the red and near-infrared (IR) region is of significant practical importance.

In the presence of appropriate coinitiator partners, xanthene dyes can be used to initiate photopolymerization.¹⁻⁸ The visible light photoinitiators have a number of advantages over those with UV light. As photoinitiators, peresters produce free radicals by UV light.9-17 Therefore, it is expected that the connection of a xanthene dye to a perester can give rise to the sensitivity of a peroxide group to the visible light absorbed by the xanthene dye. However, compounds of this kind were rarely developed and investigated even though significant structural changes have been sought to considerably increase the π system and extend the absorption maximum $(\lambda_{max}).^{9,18-20}$ Neckers et al. had reported that Eosin (2'-butyl peroxy ester) can be used as a photoinitiator in the presence of amines, but direct photochemical bond dissociation was not observed. The spacer between the xanthene dye 2'-ester bond and the perester group may affect the peroxide bond homolysis.

We have developed xanthene dye peresters that demonstrate high sensitivities in visible light photoinitiation even without amines. To understand the mechanism, photochemical experiments were carried out in a diluted organic solution. In a comparison with xanthene dyes, interesting transient phenomena were observed for their peresters. The fluorescence quantum yields of the xanthene dye peresters seem to relate inversely to the performance of these peresters as photoinitiators.

Experimental

¹H-NMR, MS, and FTIR spectra were recorded on a JEOL GSX 500 (500 MHz), a JEOL JMS-HX 110A, instrument, and a Horiba FT-200 spectrophotometer, respectively. The fluorescence and phosphorescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer and UV-VIS spectra with a Hitachi U-3000 spectrophotometer.

Materials. All solvents used were spectrograde and were purchased from WAKO Pure Chemical Industries, Ltd. Rose Bengal, Eosin Y, Erythrosine B, and Rhodamine B were used without further purification. *p*-Bromomethylbenzoic acid, xanthene dyes, and Florisil gel (mesh 100–200) were also obtained from WAKO, and *tert*-butyl hydroperoxide from Merck.

Preparation of Xanthene Dye Perester s p-Bromomethylbenzoic acid (21.5 g, 0.1 mol) was dissolved in 80 mL SOCl₂. The mixture was stirred and refluxed for 10 h at 80°C. The residual SOCl₂ was removed by distillation at 80 to 90°C. The p-bromomethylbenzoic chloride obtained was crystallized from hexane.

To a solution of *p*-bromomethylbenzoyl chloride (~23.4 g, 0.1 mol) in benzene (100 mL) was added a 0.2 mol dm⁻³ aqueous solution of NaOH (100 mL), and the mixture was cooled to 0 to 5 °C with an ice bath. *tert*-Butyl hydroperoxide (16 mL, 0.16 mol) was carefully added dropwise into the mixture. After stirring for 1 h, the mixture was stirred overnight at ambient temperature. The organic layer was separated and washed with 0.1 mol dm⁻³ NaOH aqueous solution several times, then dried with anhydrous MgSO₄, and the solvent was evaporated under reduced pressure. The resulting *tert*-butyl *p*-bromomethylperoxybenzoate weighed 14 g (50%).

tert-Butyl *p*-bromomethylperoxybenzoate (~5 g, 0.02 mol) and xanthene dye (2.5 g, ~0.003 mol) was dissolved in dimethyl sulfoxide (DMSO, 50 mL). The mixture was protected from the light and stirred overnight at 40°C. After adding water (50 mL), the resulting mixture was kept at ambient temperature for 7 h. The precipitate was filtered, washed with water, and dried under vacuum. The

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EOBP (EOBPH): $R_1 = H$, $R_2 = Br$ ERBP (ERBPH): $R_1 = H$, $R_2 = I$ RBBP (RBBPH): $R_1 = Cl$, $R_2 = I$

Scheme 1

xanthene dye peresters obtained were purified using column chromatography over Florisil gel (mesh 100–200) with ethanol-ethyl acetate as eluent. The ratio of ethanol and ethyl acetate was 1:4, 1:5, and 1:6 for Eosin Y perester (EOBP), Erythrosine B perester (ERBP), and Rose Bengal perester (RBBP), respectively. Their quality was confirmed by ¹H-NMR, MS, and FTIR spectra. The structure of these compounds is shown in Scheme 1.

- 1.*p*-(Bromomethyl)benzoic chloride: ¹H-NMR (acetone) δ 8.15 (s, 2H), 7.75 (s, 2H), 4.76 (s, 2H).
- 2. *tert*-Butyl *p*-bromomethylperoxybenzoate (BP): ¹H-NMR (acetone) δ 7.97 (m, 2H), 7.64 (m, 2H), 4.73 (m, 2H), 1.39 (s, 9H); FTIR (KBr) 1753 cm⁻¹ (v C = O, perester).
- 3. **EOBP:** ¹H-NMR (acetone) δ 8.31–7.04 (m, 10H), 5.11 (m, 2H), 1.43 (s, 9H); FTIR (KBr) 1753 cm⁻¹ (v C = O, perester), 1735 (v C = O, conjugated ester), 1618 (v C = O, C-6 ketone); MS m/e calculated for $C_{32}H_{21}O_8Br_4Na$ 876.08 (for $C_{32}H_{22}O_8Br_4$ 854.10); found 877 (854).
- 4. **ERBP:** ¹H-NMR (acetone) δ 8.30–7.16 (m, 10H), 5.13 (m, 2H), 1.43 (s, 9H); FTIR (KBr) 1753 cm⁻¹ (v C = O, perester), 1735 (v C = O, conjugated ester), 1618 (v C = O, C-6 ketone); MS m/e calculated for $C_{32}H_{21}O_8I_4Na$ 1064.08; found 1064.5.
- 5. **RBBP:** ¹H-NMR (acetone) δ 7.84–7.14 (m, 6H), 5.14 (m, 2H), 1.43 (s, 9H); FTIR (KBr) 1753 cm⁻¹ (v C = O, perester), 1735 (v C = O, conjugated ester), 1618 (v C = O, C-6 ketone); MS m/e calculated for C₃₂H₁₇O₈Cl₄I₄Na 1201.85 (for C₃₂H₁₈O₈Cl₄I₄ 1179.86); found 1202 (1180).

From the MS analysis of these compounds, the products of Eosin Y and Rose Bengal peresters were found to be mixtures of their protonated forms (EOBPH, RBBPH) and sodium salts (EOBP, RBBP) at the C-3 position.

Photoproducts. The sample solution was purged with argon for 30 min prior to irratiation. Argon was bubbled into the solution continuously during the irradiation. The irradiation with the light at 514.5 nm was performed using a Spectra Physics Stabilite 2016 Ar^+ laser . The laser beam diameter was expanded to 3 cm to eliminate intensity effects. The photoproduct analysis was carried out by withdrawing a 1 mL dye solution from the exposed samples and adding it to a 0.1 g sample of oven-dried KBr in a glass capsule. The solvent was evaporated under reduced pressure. A KBr pellet with dye was prepared in the usual manner.²¹ The UV-VIS and FTIR spectra were taken before and after the irradiation.

Laser Flash Photolysis. Laser flash photolysis (LFP) was performed at ambient temperature using an excimer laser (Lambda Physik EGM 101, XeCl, 308 nm)–pumped

dye laser (Lambda Physik FL-3002). Coumarin 307 was used as a laser dye to obtain visible laser pulses at a wavelength of 510 nm for exciting the xanthene dye peresters. A pulsed 150-W Xenon arc (Wacom KXL-151) was used as a monitoring light source. The monitoring light passing through the sample solution in 1 cm quartz cuvette at a right angle to the exciting laser beam was dispersed by a monochromator (JASCO CT-25C) equipped with a photomultiplier (Hamamatsu R928). Transient absorption spectra at particular delay times ranging from nanoseconds to microseconds were obtained with the aid of a storage oscilloscope (Iwatsu TS-8123) and a personal computer (NEC PC-9801VX21). Argon was bubbled into the sample solutions for 30 min before measurement.

Photosensitivity. The photosensitive layer was prepared by spin coating of 2-methoxyethanol solution, which consisted of poly(methylmethacrylate-co-acrylic acid) [i.e., P(MMA-AA)] as polymer, pentaerythritol triacrylate (PETA) as monomer, and the xanthene dye peresters synthesized as initiators. A 1-µm-thick film was produced on an aluminum plate and dried at 80°C. A protection overcoat of poly(vinyl alcohol) (PVP) could not be used because of the high solubility of xanthene dyes in water. Therefore, the photosensitive layer was exposed to 514.5 nm light from an Ar⁺ laser under a nitrogen atmosphere. The exposed photosensitive layer was developed in a 2% Na_2SiO_3 aqueous solution. The incident energy required to insolubilize a spot size equal to the visible laser beam diameter (1.36 mm) was defined as the sensitivity to visible light for sensitive photopolymers.

Results and Discussions

Preparation of Xanthene Dye Peresters. tert-Butyl *p*-bromomethylperoxybenzoate was allowed to react with xanthene dyes, Eosin Y, Erythrosine B, and Rose Bengal in DMSO at 40°C. The xanthene dye peresters obtained were purified by column chromatography on Florisil gel with ethanol-ethyl acetate as eluent. Their quality was confirmed by ¹H-NMR, MS, and FTIR spectra.

The photophysical properties of the xanthene dye peresters and their parent dyes are demonstrated in Table I. Esterification of the carboxyl group at the C-2' position of xanthene dyes leads to a red shift of about 10 nm in the absorption and fluorescence spectra. The introduction of the methylperoxybenzoyl group at the C-2' ester brought about only a slight decrease in the extinction coefficients at the peak wavelength in the xanthene dye peresters; they showed similar behavior in absorption, emission, and excitation spectra.

Transient Phenomena. Transient absorption spectra of EOBP and EO alone or in admixture with BP were observed in methanol, as shown in Fig. 1. The different transients and the lifetimes are summarized in Table II. It can be seen that the decay of the EOBP triplets was faster than that of both EO and the admixture with BP. This means that the EOBP triplets were quenched due to the intramolecular electron transfer that produced the radicals. However, the intermolecular electron transfer between the excited state EO and the ground state BP was not effective. For the xanthene dye, the transient peak around 460 nm has already been assigned to the formation of its one-electron oxidized radical cations,^{22–30} which appeared in EO and EOBP. The formation of one-electron reduced radical anions of the dye²⁴⁻³⁰ was observed at 420 nm. In comparison with the parent dye, the decay of EOBP radicals failed to recover to the ground state absorption in the 400- to 480-nm range. This indicates that the long-lived radicals produce the final bleached products, which might result from the fission of the attached peroxy bond.²⁹⁻³¹

TABLE I. The Photoproperties of Xanthene Dye Peresters, Their Parent Dyes and *p*-Bromomethyl-*t*-Butylperoxybenzoate (BP)*

	EOBP	EO	ERBP	ER	RBBP	RB	BP
I _{max} (abs.)/nm	534	524	544	532	568	558	246
$\epsilon_{max} imes 10^{-5}/M^{-1} \bullet cm^{-1}$	1.02	1.39	1.05	1.09	1.07	1.11	0.17
$\lambda_{max}(fl.)/nm$	554	544	563	552	584	572	285 (77 K)
$\phi_{\mathbf{F}}^{\mathbf{a}}$	0.54	0.60	0.12	0.12	0.13	0.12	
λ _{max} (phos. at 77 K)/nm	682	664	697	664	b	720	420
τ ₇ (77 K)/ms	31	1.4	26	0.2	<u>_b</u> _	0.5	210
ϕ_T^{c}		0.32		0.69		0.86	
¹ <i>E</i> * ₀₋₀ /kcal∙mol⁻¹	52.5	53.6	51.8	52.9	48.7	50.7	
³ E [*] ₀₋₀ /kcal•mol ⁻¹	41.9	43.1	41.0	43.1	_	39.7	68.1
E° _{red} /V versus SCE	-1.06	-1.05 ^f	-0.29 ^d	-1.04 ^f	-0.60 ^d	-1.03 ^e	
E°ox/V versus SCE	+0.85	+0.84 ^f	+0.80 ^d	+0.76-0.61 ^f	+0.82 ^d	+0.86°	

The measurements were carried out at the concentration of 5 × 10⁻⁷ M in ethanol at the room temperature, if not indicated.

^a Rhodamine B was the fluorescence quantum yield standard. The corrected integrated area of the fluorescence spectrum wasthakeneasurement of fluorescence yield.

^b Phosphorescence spectrum was not observed.

^{c, d, e, f} Data obtained from Refs. 3, 20, 22, and 23, respectively



Figure 1. Transient spectra of EOBP ($2 \times 10^{-5} \text{ mol dm}^{-3}$), EO + BP, and EO ($1.7 \times 10^{-5} \text{ mol dm}^{-3}$), in methanol, as observed at 0 μ s (*), 12 μ s (*) and 71 μ s (*) after laser excitation at 510 nm, respectively.

Figure 2 shows the transient spectra of ERBP and its parent dye or admixture with BP. The lifetimes of different transients and triplets are demonstrated in Table III. It is clear that the triplet of ERBP decayed faster than that of ER or the admixture with BP and independent of the concentration. It could be expected that the triplet decay of ERBP was significantly followed by a first-order process related to the presence of chromphore-linked peroxide whose electron transfer is intramolecular. The decay of the resulting radical transients did not recover to the ground state absorption in the range from 400 to 500 nm, which resembles the transient behavior of EOBP.

As shown in Fig. 3, RBBP transients appeared in the 350- to 500-nm region and were attributed to the xanthene dye radicals. Compared with Rose Bengal, the decay of RBBP transients did not return completely to the baseline. The failure in recovery of the ground state absorption was observed in the range from 400 to 500 nm. This indicates that the photodissociation occurred and led to bleaching products, ^{18,19,32–41} because residual absorption might result from the bleaching products related to the decomposition of the peroxy bond. The lifetimes of the radicals and triplets from Rose Bengal and its perester are given in Table IV. It can be seen that the lifetime of the RBBP triplet was shorter than that of RB. On the other hand, the concentration independence of the triplet decay indicates that the triplet of RBBP decayed by a first-order process due to the intramolecular electron transfer, which produces an intramolecular radical pair for further peroxy bond cleavage. However, this intramolecular pathway is unavailable to Rose Bengal for both the radical decomposition and triplet decay. Because the triplet decay of RB was enhanced with increasing concentration, the RB triplet decayed by a second-order process related to T-T annihilation and self-quenching.^{22,24} Because the lifetime of the RB radicals decreased with increasing concentration, the RB radicals possibly decay via disproportionation, and this leads to no residual absorption in the spectral range studied.²⁴

The mechanism of "intramolecular electron relay peroxide cleavage" is suggested for the formation of free radicals in the so-called phototunable perester systems.^{18,19} The xanthene dye peroxybenzoate shows the characteristics of the phototunable perester systems; however, it is difficult to analyze the transient behavior of the xanthene dye peresters due to overlap of the absorption of various species in the same spectral region.

dye	EO	EO + BP	EOBP
λ_{max} (T–T abs. in MeOH)	590 nm	580 nm	590 nm
τ_{τ} (dye concentration)	17 μs (8.5 μM)	18 μs (17 μM)	16 μs (10 μM)
	20 μs (17 μM)		13 μs (20 μM)
λ_{max} and lifetime of semioxidized form	450 nm	No peak	460 nm
(dye concentration)	19 μs (8.5 μM)		0.8 μs (10 μM)
	32 μs (17 μM)		27 μs (20 μM)
			$\Delta A_{\infty} \neq 0$
λ_{max} and lifetime of semireduced form	420 nm	420 nm	420 nm
(dye concentration)	16 μs (8.5 μM)	16 μs (17 μM)	(shoulder)
	24 μs (17 μM)		23 μs (10 μM)
			28 μs (20 μM)
			$\Delta A_{\infty} \neq 0$
λ_{max} and lifetime of transient 1	390 nm	360 nm	370 nm
(dye concentration)	22 μs (8.5 μM)	20 μs (17 μM)	22 μs (10 μM)
,	21 μs (17 μM)	,	12 μs (20 μM)





Figure 2. Transient spectra of ERBP ($2.8 \times 10^{-5} \text{ mol dm}^{-3}$), ER + BP, and ER, with the concentration of ($2 \times 10^{-5} \text{ mol dm}^{-3}$), in methanol, recorded at 0 µs (*), 13 µs (*) and 71 µs (*) after laser excitation at 510 nm, respectively.

Figure 3. Transient spectra of RBBP ($2.8 \times 10^{-5} \text{ mol dm}^{-3}$), RB + BP and RB ($2.4 \times 10^{-5} \text{ mol dm}^{-3}$), in methanol, recorded at 0 μ s (*), 13 μ s (*) and 66 μ s (*) after laser excitation at 510 nm, respectively.

TABLE III. Lifetimes of the Triplet States and Radicals from ERBP, ER and Admixture with BP

dye	ER	ER + BP	ERBP	
λ_{max} (T–T abs. in MeOH)	580 nm	580 nm	590 nm	
τ_{τ} (dye concentration)	18 μs (10 μM)	20 μs (20 μM)	11 μs (10 μM)	
	20 µs (20 µM)		12 μs (20 μM)	
λ_{max} and lifetime of semioxidized	450 nm	450 nm	460 nm	
form (dye concentration)	20 μs (10 μM)	21 μs (20 μM)	14 μs (10 μM)	
	25 μs (20 μM)		22 μs (20 μM)	
			$\Delta A_{\infty} \neq 0$	
λ_{max} and lifetime of semireduced form	410 nm	No distinct peak	No distinct peak	
(dye concentration)	23 μs (10 μM)			
	21 μs (20 μM)			
λ_{max} and lifetime of transient 1	370 nm	380 nm	390 nm	
(dye concentration)	15 μs (10 μM)	23 μs (20 μM)	14 μs (10 μM)	
,	17 μs (20 μM)		14 us (20 uM)	

TABLE IV. Lifetimes of the Triplet States and Radicals from RBBP, RB and Admixture with BP

dye	RB	RB + BP	RBBP	
λ_{max} (T–T abs. in MeOH)	600 nm	600 nm	610 nm	
τ_{τ} (dye concentration)	21 μs (12 μM)	21 μs (24 μM)	15 μs (14 μM)	
	17 μs (24 μM)		15 μs (28 μM)	
λ_{max} and lifetime of transient 2	480 nm	480 nm	480 nm	
(dye concentration)	23 μs (14 μM)	23 μs (24 μM)	17 μs (14 μM)	
	19 μs (28 μM)	$\Delta A_{\infty} \neq 0$	19 μs (28 μM)	
			$\Delta A_{\infty} \neq 0$	
λ_{max} and lifetime of semioxidized form	460 nm	460 nm	460 nm	
(dye concentration)	27 μs (12 μM)	24 μs (24 μM)	25 μs (14 μM)	
	18 μs (24 μM)	$\Delta A_{\infty} \neq 0$	22 μs (28 μM)	
			$\Delta A_{\infty} \neq 0$	
λ_{max} and lifetime of semireduced form	No distinct peak	No distinct peak	420 nm	
(dye concentration)	·		23 μs (14 μM)	
			none (28 µM)	
			$\Delta A_{\infty} \neq 0$	
λ_{max} and lifetime of transient 1	380 nm	380 nm	390 nm	
(dye concentration)	20 μs (12 μM)	22 μs (24 μM)	19 μs (14 μM)	
	18 μs (24 μM)	,	17 μs (28 μM)	

Photodecomposition Behavior. The photodecomposition of xanthene dye peresters was followed by monitoring the UV-VIS absorption of sample solutions during irradiation with an Ar⁺ laser at 514.5 nm. The influence of the irradiation time on the absorption of Rose Bengal, its perester and admixture with BP are described in Fig. 4. The decomposition of xanthene dyes exhibited an induction period in the absence and presence of BP. Table V summarizes the time required for the peak absorbance to decrease to a half of the initial value and the peak absorbance on prolonged irradiation. From Table V, it can be seen that the bleaching rate was decreased in the order of EOBP > RBBP > ERBP. The xanthene dye peresters bleached at a rate faster than the parent dyes and were almost independent of the concentration because the energy transfer is intramolecular. Therefore, it could be expected that the photobleaching of xanthene dye peresters is a first-order process related to the cleavage of the attached peroxy bond.²⁹⁻³¹ However, in the case of BP with either Eosin Y or Erythrosine B, an induction period appeared, and the absorption and fluorescence maximum was red-shifted by 10 nm after irradiating the mixture solution for about 50 min. It is clear that the photoinduced reactions take place between BP and Eosin Y or Erythrosine B during the prolonged irradiation.

The photodecomposition rate was much higher in acetonitrile than in methanol in the case of EOBP (see Table V), and a long induction period appeared in MeOH at room temperature. This solvent effect is in agreement with the lifetime decrease of EOBP phosphorescence from 31 ms in EtOH to 5.0 ms in MeCN at 77 K. It can also be explained by assuming that the hydrogen bonding between the EOBP radical anion and MeOH stabilized the radical anion to diminished its reactivity.^{42–44}

According to the IR spectra of xanthene dye peresters before and after irradiation at 514.5 nm, the remaining 1735 cm⁻¹ peak in the final photoproduct was stated as evidence of the existence of the ester function at the C-2' position,⁴⁵ but the attached peroxidic bond might be broken. Because of the overlap of two carbonyl stretching IR peaks due to the perester and ester linked to C-2', it is difficult to follow the cleavage of the peroxy bond by IR spectra. On the other hand, Rose Bengal and the admixture with BP were assumed to be bleached through an oxidative lactonization because the characteristic lactone carbonyl stretching frequency at 1771 cm⁻¹ was observed in their final photobleaching products.³¹ In the case of EOBP, only the 1735 cm⁻¹ IR peak remained in the final photobleaching products, but the other xanthene dye peaks disappeared after irradiation. Hence, the photodecomposition of EOBP should

TABLE V.Bleaching Rates and the Final Absorbances of Xanthene Dye Peresters and their Parent Dyes Under Continuous Irradiation with an Ar⁺ Laser at 514.5 Nm

	RBBP	RB	RB + BP	ERBP	ER + BP	EOBP	EO + BP
time (<i>A</i> ₀ /2 at λ _{max}) (concentration in MeCN)	30 min (20μM) 25 min (100 μM)	130 min (20 μM) 75 min (100 μM)	200 min (20 μM) 80 min (83 μM)	120 min (20 μM)	65 min (20 μM)	12 min (20 μM) 13 min (100 μM) 280 min (40 μM in MeOH)	100 min (20μM)
$A_{_{\infty}}$ (at $\lambda_{_{max}}$)	~A ₀ /2	→0	\rightarrow 0	\rightarrow 0	\rightarrow 0, but, the10-nm red shift of λ_{max}	ightarrow 0	$ ightarrow$ 0, but, the 10-nm red shift of λ_{max}



Figure 4. Plot of the maximum absorbance of solutions $(1 \times 10^{-5} \text{ mol dm}^{-3})$ in acetonitrile versus the irradiation time with Ar⁺ laser (514.5 nm, 200 mW); d = 1 cm.

take place in a different way from that of RBBP. RBBP cannot be completely bleached by irradiation with the argon ion laser at 514.5 nm; the residual absorbance of photoproduct is about half of its initial value (see Fig. 4).

Application. As visible light initiators, xanthene dye peresters were directly used to initiate photopolymerization in assembled systems. In comparison, the mixtures of xanthene dyes (XD) with 3,3',4,4'-tetra-kis(*t*-butylper-oxycarbonyl)benzophenone (BTTB) or BP were also applied as photoinitiators. The results are given in Table VI.

The sensitivity of xanthene dye peresters is obviously enhanced compared with mixtures of their parent dyes and peresters (BP or BTTB). The order of photoinitiator efficiency is ERBP > RBBP > EOBP, which is inversely related to the fluorescence quantum yield of the xanthene dye peresters (see Tables I and VI). This may be explained as follows: The triplet state formation of these peresters should dominate their efficiency as photoinitiators in the polymer matrix,^{8,45–47} It is reasonable that the triplet states of xanthene dye peresters might be also intercepted through intramolecular interaction because xanthene dyes are highly efficient in intersystem-crossing from the first excited singlet to the triplet state,³² the triplet states are long-lived, and have a tendency to transfer electrons in the excited states, yielding stable and long-lived radicals.33-³⁷ On the other hand, their performance as photoinitiators

also depends on the redox potential of the peresters. The more positive the reduction potential of the peresters, the more sensitive these peresters are as photoinitiators. Accordingly, the intermolecular electron transfer between the excited xanthene dye and BP should not contribute to effective radical generation, which efficiently initiates the photopolymerization in the visible light system. The inef-

TABLE VI. Sensitivities (mJ cm ⁻²) of Both Xanthene Dye Perester
(XDBP) and Xanthene Dye (XD) Perester Systems ²⁰

	Xanthene dye perester	XD + BP	XD + BTTB
Rose Bengal	0.14	<u> </u>	0.20
Erythrosine B	0.11	_	0.18
Eosin Y	0.31	—	0.59

^a not observed.

fectiveness of intermolecular electron transfer is also proved by the results of laser flash photolysis in dilute organic solution.

Conclusions

In this study we have shown that the synthesized xanthene dye peresters reveal the characteristics of so-called phototunable perester systems. Furthermore, intramolecular electron transfer takes place between the excited triplet state xanthene dye and the ground state peroxide moiety. The resulting radical intermediate could induce further cleavage of the attached peroxy bond. As visible light photoinitiators, these compounds demonstrated high sensitivities that are inversely related to the fluorescence quantum yield of xanthene dye peresters, that is, the photoinitiating efficiency depends on the efficiency of triplet formation in the polymer matrix. The reduction potentials of peresters also play an important role in photoinitiation.

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