Dye Sensitization Mechanisms in Photopolymer Layer for Laser-Printing Plate.

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To reveal bulky-substituent effect of pyromethene dye in sensitization mechanisms in photopolymer layer for laser-printing plate, the sensitization mechanisms of a pyromethene dye, which has a bulky *t*-butylmethyl group at 5 atom, with a radical generating reagent, 1,3,7,9-tetramethyl-5-*t*-butylmethylpyromethene-BF₂ (BHB) and with 3,3',4,4'-tetrakis(*t*-butyldioxy carbonyl)benzophenone (BP), in a poly(methylmethacrylate) (PMMA) film were investigated by means of both laser flash photolysis using total reflection cell and a single photon counting as well as in dilute solution, and compared to the sensitization mechanisms for a pyromethene dye, which has a non-bulky methyl group at atom 5, 1,3,7,9-tetramethyl-5-methylpyromethene-BF₂ (BHM) [1-i].

Keywords: Photoinitiator, photo-polymerization, sensitization, dispersive-excited state, energy hopping

1. Introduction

Much attention has recently paid to photoinitiation over visible light irradiation [1 and 2]. The photopolymer coating layer containing pyromethene dyes and a BP affords a sensitivity at 514 nm excitation of argon ion laser which was equipped to the laser imaging systems. The sensitivity, 0.5 mJ cm⁻² for the photopolymer containing BHB and BP on 514 nm was 2 times higher than that for BHM. To reveal the reason for increase of sensitivity as incorporating bulky *t*-butylmethyl group into pyromethene dye (fig. 1), dye-sensitization mechanisms for photopolymer coating layers have been investigated by means of both single photon counting and laser flash photolysis using a total reflection [3 and 4]. In the

investigation using a single photon counting, the stretched decay of fluorescence for BHB in the presence of BP in a PMMA film was observed, and no transient absorption was detected by the laser flash photolysis.

As for the stretched decay in a photoexcited state, stretched decays of phosphorescence in amorphous, anthraquinone, and phenanthrene were reported by Basseler et al [5]. In the report, orientational differences of asymmetric molecules (dipolar disorder) and abandon of lattice periodicity (amorphous structure) in amorphous-organic molecules caused energetic disorder by a fluctuation of the resonant and nonresonant energy between the molecules, affording the

Fig. 1. Laser flash photolysis and single photon counting in film.

Fig. 2. Schematic illustration of excitation

energy hopping across an array of sites with Gaussian energy distribution, and trapping in BP [1-1,7]. The dashed curve indicate the initial distribution of state densities after the excitation pulse, and full curve, the distribution in long time after the excitation.

inhomogeneously broadening of the photoexcited state (dispersive photoexcited state). Thus the excitation energy hopping from higher energy site to lower energy site in the dispersive photoexcited state efficiently occurred (Fig. 2). The decay of the dispersive photoexcited state accompanied with the hopping was simulated by Eq. (1) of stretched decay form comprised of the intrinsic decay term: lifetime τ and the decay term by the hopping of the energy sites in the dispersive photoexcited state.

$$I(t) = I_0 \exp[-t/\tau - c/(t/t_0)^{\alpha}] \quad (1)$$

where c is a relative concentration of deep traps, t_0 jumping time in an energetically-discrete-hopping system, and α , a dispersion parameter. Yamamoto et al. reported analyses of stretched decay of phosphorescences in Naphthalene and phenanthrene pendant poly(methyl methacrylate)s using Bassler's simulation [6], and Yamazaki et al. reported analyses of stretched decay of fluorescence using Basseler's simulation in N,N'-dioctadecylrhodamine B (DORB) in Langmuir-Blodgett monolayer where with increasing the concentration of DORB stretched decay became steeper, the fluorescence maximum was shifted to red, and fluorescence intensity was reduced significantly as well as the quenching of DORB by octadecyl crystal violet (ODCV) made the decay steeper [7].

We already reported the quenching of the dispersive photoexcited state of BHM by BP in a PMMA film, in which there were both a main-static-quenching process from a dispersive-singlet excited BHM to a ground state of BP, and a minimal-nonstatic quenching process competitive to the excitation energy hopping [1-1].

In this paper we describe the difference in

sensitization mechanisms between BHB and BHM, which were coated by bulky-substituent of pyrromethene dyes.

2. Experimental

The dyes, BHB, was prepared according to the literature procedure in Ref. 8. The peroxide, BP, was purchased from NOF Corporation. Poly(methyl methacrylate) (PMMA), $M_w = 40000$, was 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 spectrometer 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 decays were measured by a time resolved fluorescence spectrometer (single photon counting) (Horiba Corp. NAES-550). Fluorescence quantum yield (Φ_f) was measured in acetonitrile using quinine sulfate as an actinometer: dye concentration; $2 \times 10^{-3} \text{ mol dm}^{-3}$.

Laser flash photolysis in film was performed using a total reflection sapphire cell (10 X 30 mm, 1 mm thickness, and both short sides were cut at a 45 degree angle), which was spin-coated with a 1.2 μm photopolymer film as depicted in Fig. 1; details concerning the apparatus are described elsewhere [4]. 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 R 928) or to a spectral multichannel analyzer (SMA) system (Princeton Instruments, Inc. model TRY-700G/R/Par). The measurement was repeated five times within less than 3 wt% of the decomposition of the dye and BP; more than

90 % of the 355 nm-laser light absorbed in the sample film was absorbed by the dye.

Films were prepared as follows. A 10 wt % PMMA solution was made up in cyclohexanone, BHB 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 1.2 μm thick by spin-coating a solution onto a sapphire cell.

The photosensitivity of the photoinitiator systems was measured as follows, the sensitive layer which was prepared by coating a cyclohexanone solution of the photosensitive composition containing 5 wt % of the dyes, 5 wt % of BP, 45 wt % of trimethylolpropane triacrylate and 45 wt % of poly(methylmethacrylate-methacrylic acid)(90:10 mol %, weight-average-molecular weight, $M_w = 50000$) onto a grained aluminum plate and drying it at 80 $^{\circ}\text{C}$ to produce a 1 μm thick film, was exposed through a step tablet (Kodak photographic step tablet no. 2) by the 488 nm band of a super-high-pressure mercury lamp, which was isolated by using Y-47 and KL-49 filters. The incident energy required to insolubilize the last step of the layer was defined as sensitivity [9]. The incident energy was measured by a photoelectric cell (The Eppley Laboratory Inc).

Cyclovoltammetric measurements were made on a Hokuto-Denko Function Generator HB-104 and Potentiostat HA-301 using a three-electrode system. A platinum disk served as the working electrode, a platinum wire as the counter electrode and a saturated calomel separated from the bulk solution by a glass bridge. An electrolyte solution of 0.1 mol dm^{-3} tetra-n-butylammonium perchlorate (TBAP) in acetonitrile was used to measure the redox potentials of the dyes. All solution were degassed with nitrogen for 30 min before the experiment.

Fig. 3. Absorption spectra of () BHM and () BHB in (a) acetonitrile and in (b) PMMA, and fluorescence spectra of () BHM and () BHB in (c) acetonitrile and in (d) PMMA. Substrate concentration $1.5 \times 10^{-5} \text{ mol dm}^{-3}$ both for BHM and BHM; excitation wavelength 355 nm.

3. Result and Discussion.

Figure 3 shows absorption and fluorescence for BHB spectra in PMMA film and in acetonitrile, and, for comparison, that for BHM in PMMA film and in acetonitrile. The absorption maximum, 514 nm, of BHB at the concentration of $2 \times 10^{-2} \text{ mol dm}^{-3}$ in PMMA film was similar to that, 512 nm, $1.5 \times 10^{-5} \text{ mol dm}^{-3}$, in acetonitrile. Fluorescence maximum, 546 nm, of

BHB, $2 \times 10^{-2} \text{ mol dm}^{-3}$, in PMMA film was almost same as that of BHB, 545 nm, $1.5 \times 10^{-5} \text{ mol dm}^{-3}$ in acetonitrile, however the profile of fluorescence in PMMA film became wider than that in acetonitrile. The Stokes shift, 32 nm, for BHB in PMMA film was larger than that, 23 nm, for BHM. The profile of absorption of BHB in the concentration range of BHB from 2 to $6 \times 10^{-2} \text{ mol dm}^{-3}$ in PMMA film was almost same. Figure 4 shows

Fig. 4. Profile change of fluorescence spectrum in BHB in PMMA with the concentrations of BHB, (a)0.02 and (b)0.06 mol dm^{-3} ; excitation wavelength: 355 nm.

Fig. 5. Profile change of fluorescence spectrum in BHB in PMMA in the presence of BP with the concentrations of BP, (a)0, (b)0.0043, (c)0.0086, (d)0.017, and (e)0.043 mol dm^{-3} . Substrate concentration 1×10^{-1} mol dm^{-3} for BHB; excitation wavelength: 355 nm.

Fig. 6. Profile of fluorescence spectrum in BHB in acetonitrile in the presence of BP with the concentrations of BP, (a)0, (b)0.0031, (c)0.0060, (d)0.0092, (e)0.012 and (f)0.016 mol dm^{-3} . Substrate concentration 1.5×10^{-5} mol dm^{-3} for BHB; excitation wavelength: 355 nm.

Fig. 7. Fluorescence decay (If) and measurement of fluorescence (If) and transient absorption in PMMA film on 530 at excitation of 355 nm pulse. Substrate concentration: 1×10^{-1} mol dm^{-3} for BHB; Li, lamp profile.

fluorescence spectra of BHB at various concentrations in PMMA. As the concentration of BHB increased from 2 to $6 \times 10^{-2} \text{ mol dm}^{-3}$, the fluorescence maximum shifted to red, 4.8 nm, and the intensity of fluorescence was significantly reduced, and the profile of fluorescence became wider. Figures 5 and 6 show fluorescence spectra of BHB at various concentrations of BP in PMMA film and acetonitrile. As the concentration of BP increased from 0 to $4.3 \times 10^{-2} \text{ mol dm}^{-3}$, the fluorescence maximum in PMMA film was shifted to red, 4.5 nm, and the intensity of fluorescence was moderately reduced, and the profile of fluorescence became slightly wider, while the profile of fluorescence and fluorescence maximum in acetonitrile was almost same in the concentration range of BP from 0 to $1.6 \times 10^{-2} \text{ mol dm}^{-3}$.

Laser flash photolysis in photopolymer coating layer.

Figure 7 depicts the monitor trace on 530 nm at an excitation by 355 nm, 20 ns laser pulse. Strong fluorescence was observed, however no transient absorption was detected (insert in Fig. 7). The decay time of the fluorescence was too short to be determined using 20 ns laser pulse.

Figure 8 shows that the fluorescence intensity at 530 nm, which was decreased with the concentration of BP. Logarithmic plots of fluorescence apparently fitted the Perrin equation [10], indicating a static quenching. The slope of the plots afforded the quenching radius, $R_f = 12 \text{ \AA}$.

Analyses of Photopolymer coating layer using a single photon counting.

The profile of the decay of the fluorescence for BHB in the presence and absence of BP were analyzed by means of single photon counting in PMMA film as well as acetonitrile.

Figures 9 shows the logarithmic plots of fluorescence decay in the absence and presence of BP in PMMA film. Figure 10 shows the

logarithmic plots in the absence of

BP in acetonitrile. The logarithmic plots of fluorescence in acetonitrile reduced convexly over 10~20 ns and then reduced linearly over 20~50 ns. The convex curve of the fluorescence decay was due to the effect of the excitation-lamp profile, and exhibited a good fit to the curve simulated by deconvolution of the excitation lamp profile using a single-exponential-fluorescence-decay model, and the decay time, 5.2 ns, was determined.

The logarithmic plots of the fluorescence decay in the absence of BP in PMMA film reduced concavely over 10~50 ns and the curve of the plots did not fit the curve simulated by a single-exponential-decay model, and it apparently fitted a two-exponential-decay model. The two-decay times $\tau_1 = 3.7 \text{ ns}$ and $\tau_2 = 1.2 \text{ ns}$ and the ratio of two initial-decay intensities were determined, $A_1 : A_2 = 31 : 69$ for slow and fast decay. In the presence of BP, $1.7 \times 10^{-2} \text{ mol dm}^{-3}$, the two decay times and the decay-intensity ratio were $\tau_1 = 3.2 \text{ ns}$ and $\tau_2 = 0.9 \text{ ns}$, and $A_1 : A_2 = 36 : 64$.

Fig. 8. Quenching of fluorescence of BHB by BP in PMMA. Substrate concentration: $1 \times 10^{-4} \text{ mol dm}^{-3}$ for BHB; excitation wavelength 355 nm, detection 530 nm.

Fig. 9. Logarithmic plots of fluorescence of BHB obtained from single photon counting in PMMA in (A) the absence of BP, and in (B) the presence of BP; (—) simulation curve, and (---) logarithmic plots of excitation lamp. Substrate concentration 1×10^{-1} and 1.7×10^{-2} for BHB and BP; excitation wavelength 334 nm, detection wavelength 530 nm. Inserted Figures; logarithmic plots of deconvoluted fluorescence decays.

Fig. 10. Logarithmic plots of fluorescence of BHB obtained from single photon counting in acetonitrile, (—) simulation curve, and (---) logarithmic plots of excitation lamp. Substrate concentration 1.5×10^{-5} for BH; excitation wavelength 334 nm, detection wavelength 530 nm.

Inserts in Figure 9 show the deconvoluted-logarithmic plots of fluorescence in a PMMA film, exhibiting a nonlinear-concave curve in the presence and the absence of BP, and both logarithmic plots of fluorescence were almost same. The result was contrast to that for BHM [1-I], in which a nonlinear-concave curve of fluorescence-logarithmic plots for BHM in the absence of BP became more steep by incorporating BP, determining the quenching radius, $R_a = 18 \text{ \AA}$, which was obtained from below equations (2) and (3) as a nonstatic quenching of fluorescence by BP, competitive the excitation energy hopping [7];

$$I(t) = I_0 \exp\left[-t/\tau - C_0(t/\tau)^{1/2}\right] \quad (2)$$

$$C_0 = (4/3) \pi^{3/2} (n_0 R_0^3 + n_a R_a^3)$$

n_0 = the number of acceptors in unit volume in

the absence of BP

n_a = the number of BP in unit volume

R_0 = the quenching radius of photoexcited BHH by acceptors in the absence of BP

R_a = the quenching radius of photoexcited BHB by BP

τ = the intrinsic lifetime of photoexcited BHH without BP.

$$\ln(I(t)) = \ln(I_0) - t/\tau - C_0(t/\tau)^{1/2} \quad (3)$$

Taking the stretched decay mechanism of fluorescence into consideration, the nonlinear-concave curve of fluorescence-logarithmic plots, and the red-shift of fluorescence maximum versus the concentration of BHB and BP suggested a dispersive photoexcited state of BHB in a PMMA film.

The decay time, $\tau_1 = 3.7$ ns, in the fluorescence decay for BHB was one order of magnitude shorter than that for BHM, 31 ns, though the decay time, $\tau_2 = 1.2$ ns, for BHB was same order of magnitude of that for BHM, 3.4 ns.

The shorter decay time, τ_1 , for BHB compared to that for BHM is considered due to the efficient nonradiative-deactivation process from photoexcited BHB enhanced by rotation of bulky substituent, t-butylmethyl group on BHB.

Fig. 11. Normalized reaction coordinate for BHB.

In the molecular orbital of bipyrrromethene dyes

Loi et al. reported molecular orbital calculation in respect to 1,3,7,9-tetramethyl-5-phenyl pyrromethene-BF₂ (BHP) using MINDO-AM1 and MNDO-psDI method [11]. The ground state (S_0) of BHP has one stable conformer in which phenyl group is rotated 52° against the rigorously planar pyrromethene framework, and the

photoexcited state (S_1) of BHP has two stable conformers; one conformer is a metastable state with a phenyl ring rotated 37°, and the other is a relaxed state which has a phenyl ring rotated into the plane defined by atoms 4,5, and 6, and the pyrromethene framework significantly distorted 35° out of plane due to the large resonance stabilization of phenyl ring and atoms 4,5, and 6.

Considering the results of molecular orbital calculation for BHP, the relaxation mechanism of photoexcited BHB can be predicted as depicted in Fig. 11. The ground state has a stable conformer with an bulky t-butylmethyl group, which is fully rotated with respect to the rigorously planar pyrromethene framework. The ground state is photoexcited to an excited state ($S_1(A)$), by absorbing a laser pulse. $S_1(A)$ undergoes rotation of t-butylmethyl group to a relaxed state ($S_1(B)$), which is analogous to the metastable conformer of BHP, since the photoexcited state for BHB has no large resonance stabilization of phenyl ring and atoms 4,5, and 6 on BHP. $S_1(B)$ decays radiatively or nonradiatively, or is quenched by BP.

The rotated t-butylmethyl group of BHB increased the potential energy surface of the ground state by a larger repulsion between t-butylmethyl group and 3- and 7-methyl group on BHP, leading to decrease a singlet-excitation energy for BHB. Thus the longer wavelength of maximum in absorption for BHB than that for BHM (Figure 3) supports the relaxation mechanism in Figure 11. As S_1 surface for BHB approaches closely to a ground state, the nonradiative deactivation from S_1 to S_0 for BHB is accelerated, and then the fluorescence-decay time for BHB become short. The large conformation change in the singlet-excited-state surface from $S_1(A)$ to $S_1(B)$ for BHB affords the larger storks shift BHB than that for BHM, which is consistent with the experimental results in respect to storks shift, 32 and 23 nm for BHB and BHM in Figure 3. The shorter-fluorescence-decay time for BHB, 3.7 ns, suppresses a

nonstatic quenching over the decay time, while photoexcited BHM with the longer-fluorescence-decay time, 34 ns, was nonstatically quenched.

To elucidate the quenching mechanism by electron transfer from photo-excited BHB to BP, the redox potentials of dyes which were measured by cyclic voltammetry as $E_{ox} = 1.33$ V (vs. SCE) for BHP, and $E_{red} = -1.18$ V for BP [12]. The free energy change (ΔG) for electron transfer was obtained from Rhem and Weller equation [13], $\Delta G = -0.01$ eV; $\Delta G = E_{ox} - E_{red} - E_{00} - C$ where E_{00} is the excitation energy, 2.45 eV of the BHB-singlet-excited state, and C , coulombic term, usually assumed to value ca. 0.1 eV for acetonitrile solvent. The low free energy change (ΔG) implies the possibility of electron transfer from the singlet excited state of the dye to the ground state of BP [13].

The origin of increase in sensitivity for BHB at 514 nm argon ion laser, can be attributed to the higher absorbance at 514 nm for BHB compared to that for BHM, since the quenching radius for BHB is shorter than that for BHM, and fluorescence quantum yield (Φ_f) for MHB, $\Phi_f = 0.56$, was lower than that for MHM, $\Phi_f = 0.91$; absorption coefficient (ϵ) at absorption maximum in acetonitrile for the dyes is 4.7×10^4 at 497 nm and 9.3×10^4 at 512 nm for BHM and BHB.

Finally it is suggested that the static-singlet-quenching process from the dispersive photoexcited BHB to BP is predominant in the sensitization, and the higher sensitivity for BHB at 532 nm laser exposure than that for BHM is caused by the higher absorbance at 532 nm for BHB than that for BHM.

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