Sensitization Mechanisms of 1,7,13-Trimethyl-2,5,9,12-tetrahydro-2,5;9,12-diethano-isoindolomethene Difluoroborate in Photopolymer Coating Layer: Effect in Sensitization Mechanisms with Incorporating Bicyclo[2,2,2]octene Group into Bipyrrromethene Difluoroborate

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1. Introduction

The sensitization mechanisms for photocinitiations comprising a 1,7,13-trimethyl-2,5,9,12-tetrahydro-2,5;9,12-diethano-isoindolomethene difluoroborate (BBP) and a 2,8-diethyl-1,3,5,7,9-pentamethylbipyrrromethene difluoroborate (EBP), and a radical generating reagent; 3,3',4,4'-tetrakis(t-butyldioxycarbonyl)benzophenone (BTTB) in a poly(methyl methacrylate) (PMMA) film have been investigated by laser flash photolysis using a total reflection cell. Effect in sensitization mechanisms with incorporating bicyclo group into bipyrrromethene dye was discussed.

Keywords: bipyrrromethene, laser flash photolysis, cyclic voltammetry, sensitization mechanism, bicyclo group
To improve the sensitivity of photopolymers, we synthesized the new type bipyromethene dye with bicyclo[2,2,2]octane groups. The sensitivity at FD YAG laser, 532 nm, for photopolymer containing BBP was 0.6 mJ cm\(^{-2}\), which was ca. 2 times higher than that for EBP.

We present sensitization processes of BBP in a PMMA film and discuss the comparison of BBP to EBP.

2. Experimental

The dyes, BBP and EBP, were prepared according to the literature procedure in Ref. 4 and 5. The peroxide, BTTB, was purchased from NOF Corporation. Poly(methyl methacrylate) (PMMA), weight-average-molecular weight (Mw), Mw = 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.

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 \(\mu\)m photopolymer film as depicted in Fig. 1; details concerning the apparatus are described elsewhere [2]. 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 BTTB; 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 cyclohexane, BBP and EBP, were added to this solution either by dissolving the dyes directly in polymer solution or by mixing in a portion of concentrated dye solution. Films were made 1.2 \(\mu\)m 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 BTTB, 45 wt % of trimethylolpropane triacrylate and 45 wt % of poly(methylmethacrylate-methacrylic acid) (90:10 mol %, Mw= 50000) onto a grained aluminum plate and drying it at 80 °C to produce a 1 \(\mu\)m thick film, was exposed with various amounts of light energy by the 532 nm band of a xenon lamp, which was isolated using a monochrometer.

The incident energy required to insolubilize the last step of the layer was defined as sensitivity [3]. The incident energy was measured by a photoelectric cell (The Eppley Laboratory Inc).

Cyclic-voltammetric 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 an Ag/AgNO₃ (0.1 M) electrode as the reference electrode. An electrolyte solution of 0.1 M tetra-n-butylammonium perchlorate (TBAP) in acetonitrile was used to measure the redox potentials of the dyes. All solution were degassed.

3. Result and Discussion

Fig. 2 shows absorption and fluorescence spectrum on 355 nm excitation for BBP and EBP in acetonitrile. Absorption and fluorescence spectrum for BBP and EBP in acetonitrile has an analogous profile. Absorption maximum is 523 and 514 nm or HBP and EBP, and fluorescence maximum is 534 and 531 nm for HBP and EBP in acetonitrile.

In the fluorescence for the dyes on an excitation at different wavelength, 355 and 450 nm, no significant change on the fluorescence spectrum was observed.
Laser flash photolysis in a PMMA film

On the excitation of 355 nm pulse of the PMMA film containing BBP and EBP, though the strong fluorescence was observed, no transient absorption was detected for both dyes (Fig. 3). It is difficult to determine a decay time of the fluorescence due to too short laser pulse of 20 ns.

Fig. 4 shows the fluorescence intensity with various concentrations of BTTB.

The fluorescence intensity was reduced with the concentration of BTTB from 0 to 0.03 mol dm$^{-3}$.

As for the reduction of fluorescence by quencher in films, Kaneko et al. reported a multistep equilibrium model (Eq. (1)-(11)) [6]. In the equations, the multistep equilibrium between a Dye and more than two BTTBs within a quenching sphere are assumed (Eq. (1)-(2)). Dye and (Dye-iBTTB) is photoexcited to an excited state * (Eq. (3)) and (*Dye-iBTTB) (Eq. (7)) by absorbing a laser pulse. *Dye undergoes i) radiative (Eq. (5)) and nonradiative deactivation (Eq. (4)), and ii) dynamically sensitized decomposition of BTTB, forming radicals such as carboxyloxyl and t-butyloxyl radicals (Eq. (6)). (*Dye-iBTTB) undergoes i) radiative (Eq. (9)) and nonradiative deactivation (Eq. (10)), and ii) statically sensitized decomposition of BTTB, forming the radicals (Eq. (8)). The attenuation of fluorescence with the concentration of BTTB in film is described as an Eq. (11). When (*Dye-iBTTB) does not emit fluorescence, meaning $k_{qi}$ is much larger than any other decay rate. Eq. 13 is described as a combination equation (Eq. (12)) of dynamic and static quenching term (Perrin type [7]).

The logarithmic plots of the fluorescence intensity at various concentrations of BTTB exhibits a good linear relationship, indicating a (Perrin type) static quenching process [7]. The quenching radius (Rf), Rf = 10.4 and 11.1 Å for BBP and EBP, was determined from the slope of the logarithmic plots.

To elucidate the quenching mechanism by electron transfer from photo-excited BBP and EBP to BTTB, the redox potentials of dyes were measured by cyclic voltammetry. Fig. 5 shows cyclic voltammograms of an acetonitrile solution containing BBP and EBP, 0.01 mol dm$^{-3}$ for BBP and EBP, $E_{ox} = 0.79$ and 0.77 V (vs. Ag/AgN03) for BBP and EBP, which was corresponding to Eox = 1.13 and 1.11 V (vs. SCE).

The irreversible peaks during in the cyclic voltammogram indicated an unstable cation of the dye, the oxidation potential (Eox) was determined from the peak oxidation. The free energy change ($\Delta G$) for electron transfer was obtained from the Rhem and Weller equation [8], $\Delta G = -0.19$ and -0.21 eV for BBP and EBP, $\Delta G = E_{ox} - E_{red} - E_{oo} - C$ where $E_{oo}$ is the excitation energy of the dye-singlet-excited state, 2.4 eV for BBP and EBP, $E_{red} = -1.18$ V for BTTB [9] and C, coulombic
term, usually assumed to value ca. 0.1 eV for acetonitrile solvent. The low free energy change \((\Delta G)\) implies the possibility of electron transfer from the singlet excited state of the dye to the ground state of BTTB [9].

F. Li et al. reported molecular orbital calculation in respect 5-phenyl pyromethene-BF \(_2\) (PHP) using MINDO-AM1 and MNDO-psDI method [10]. The ground state \((S_0)\) of PHP has one stable conformer in which phenyl group is rotated 52° against the rigorously planer pyromethene framework, and the photoexcited state \((S_1)\) of PHP has two stable conformers; one conformer is a fluorescent metastable state with a phenyl ring rotated 37°, and the other is a nonfluorescent relaxed state with a significantly short lifetime, \(\sim 15\) ps, which has a phenyl ring not rotated against the plane defined by atoms 4, 5, and 6, and the pyromethene 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 PHP, the relaxation mechanism of photoexcited BBP and EBP can be predicted as depicted in Fig. 6. The ground state and photoexcited state for BBP and EBP have a stable conformer based on a planer pyrromethene framework; the large resonance stabilization of phenyl ring and atoms 4, 5, and 6, since there is no large resonance stabilization of phenyl ring and atoms 4, 5, and 6 for BBP and EBP. The ground state is photoexcited to a singlet excited state (S¹(A¹)), by absorbing a laser pulse. S¹(A¹) relaxes to a S¹(A) state accompanied with the nuclear configuration change dependent on substituents, and S¹(A) decays radiatively or nonradiatively, or is quenched by BTTB. The alkyl substituents at 2 and 8 atoms on BBP was fixed by bicyclo[2,2,2]octene. Thus the nuclear configuration change by the substituents for BBP should be smaller than that for EBP. The smaller stokes shift for BBP compared to that for EBP supported the substituent difference between BBP and EBP, stokes shift =11 and 17 nm for BBP and EBP.

The origin of increase in sensitivity for BBP at 532 nm FD Yag laser can be attributed to the higher absorbance at 532 nm for BBP, since the quenching radius for the dyes are almost same.

Fig. 6. Potential energy vs nuclear configuration.

4. Conclusion

It is suggested that the static-singlet-quenching process from the photoexcited BBP and EBP to BTTB is predominant in the sensitization, and the higher sensitivity for BBP at 532 nm laser exposure than that for EBP is caused by the higher absorbance at 532 nm for BBP than that for EBP.

5. References


