Substituent Effect in Sensitization Mechanisms of Pyrromethene Dyes in Solution

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The sensitization mechanisms for photo-initiations comprised a sensitizer dyes such as 2,8-diethyl-1,3,5,7,9-pentamethylbipyrrromethene difluoroborate (EBP), 1,3,5,7,9-pentamethylbipyrrromethene difluoroborate (HBP), and 2,8-diethyl-1,3,5,7-teramethyl-9-phenylbipyrrromethene difluoroborate (PBP), and a radical generating reagent 3,3',4,4'-tetrakis(t-butylperoxycarbonyl) benzophenone (BTTB) in acetonitrile have been investigated by single photon counting.

KEYWORDS: Sensitizer, pyrromethene, polymerization, liquid photoresist.

1. Introduction

Sensitization mechanisms by pyrromethene dyes were investigated by single photon counting. In the sensitized decomposition of 3,3',4,4'-tetrakis(t-butylperoxycarbonyl) benzophenone (BTTB), Fouassier reported that the sensitization mechanisms of photoinitiating system comprised of a sensitizing dye, thiopyrylium salt (TP), and BTTB, in which a triplet sensitization process was predominant with the triplet-quenching rate constant $k_q = 6.6 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, and a singlet-excited sensitization process was minor due to rather high triplet quantum yield (Φ_T), $\Phi_T = 0.3$ [1] and low fluorescent character [2]. In the contrast to the mechanisms between TP and pyrromethene dyes, the pyrromethene dyes are well known as highly efficient fluorescent dyes with fluorescence quantum yield (Φ_f), $\Phi_f > 0.8$, which can be applied to laser dyes [3, 4], fluorescent probes in biochemical procedure [5], and sensitizer dyes of solid and liquid photopolymer resists for visible-laser imaging systems such as visible-laser-printing plates and circuit boards [6, 7]. Though we reported BTTBs in a PMMA film in the earlier

investigation, there were both a main-static-quenching process from a singlet excited pyrromethene dyes to a ground state of BTTB and a minor-dynamic quenching [6-i]. The sensitization mechanism of solution containing the photoinitiators, which is under similar condition to that of liquid photopolymer resists, is not clear yet. In this paper we describe the substituent effect in sensitization processes of pyrromethene dyes in acetonitrile (Fig. 1).

2. Experimentals

EBP, HBP, PBP were prepared according to the literature procedure [8]. BTTB was purchased from NOF Corporation. Acetonitrile was spectrograde and purchased from Wako Pure Chemical Industries, Ltd.

UV-VIS and fluorescence spectra were recorded with a Hitachi U-3000 spectrophotometer and a Hitachi F-454500 fluorescence spectrometer, respectively. Fluorescence decays were measured by a time resolved fluorescence spectrometer Horiba Corp. NAES-550 (single photon counting). All samples solutions were degassed with nitrogen for 20 min. before the measurement.

Fig. 1. Photoinitiation systems.

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 sample solutions were degassed with nitrogen for 10 min before the experiment.

3. Results and Discussions

Fig. 2 shows absorption and fluorescence spectrum on 355 nm excitation for HBP in acetonitrile, and those for HBP and EBP in acetonitrile were described [9]. Absorption and fluorescence spectra for HBP, EBP and

PBP in acetonitrile have analogous profiles with absorption maximum at 491, 514, and 519 nm, and fluorescence maximum at 501, 531 and 534 nm for HBP, EBP and PBP, respectively.

In the fluorescence spectra in acetonitrile excited at different wavelength, 334 and 420 nm, no significant change on the fluorescence spectrum was observed for the dyes.

Single photon counting. The profile of the decay of the fluorescence for the dyes in the presence and absence of BTTB on the excitation of 5 ns pulse were analyzed by means of single photon counting.

Fig. 3 shows the logarithmic plots of fluorescence decay in the absence and presence of BTTB. The logarithmic plots of fluorescence for the dyes 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, and was fitted to the simulation curve simulated by single-exponential-fluorescence-decay model. The life times were 6.5, 7.3 and 6.1 ns for HBP, EBP and PBP, respectively.

The life times of the dyes were decreased with the concentration of BTTB. The ratio (τ_0/τ) of the life times against the concentration of BTTB

exhibited a good linear relationship, which was fitted to stern-volmer plots, as depicted in Fig.4. From the slope of the plots, quenching rate constants (k_q) were determined as 3.5, 3.0 and 4.3 mol⁻¹ dm³ s⁻¹ for HBP, EBP and PBP. The fluorescence-quenching rate constants for the dyes were 2 orders of magnitude greater than triplet quenching-rate constant for TP.

In the sensitization mechanisms accompanied with an electron transfer from photo-excited dyes to BTTB, the redox potentials of dyes were measured by cyclic voltammetry. The free energy change (ΔG) for electron transfer was obtained from Rhem and Weller equation [10] as $\Delta G = -0.29$, -0.21 and -0.22 eV for HBP, EBP and PBP; $\Delta G = E_{ox} - E_{red} - E_{oo} - C$, where the oxidation potential (E_{ox}) is determined from the peak oxidation potential, $E_{ox} = 0.74$, 0.77 and 0.76 V (vs. Ag/AgNO₃) for HBP, EBP and PBP, corresponding to $E_{ox} = 1.08$, 1.11 and 1.10 V (vs. SCE) for HBP, EBP and PBP, E_{oo} is the excitation energy of the dye-singlet-excited state, $E_{oo} = 2.45$, 2.40 and 2.40 eV for HBP, EBP and PBP, $E_{red} = -1.18$ V (SCE) for BTTB [11] and C , coulombic term, usually assumed to value ca. 0.1 eV for acetonitrile solvent. The low free energy change (ΔG) indicates the possibility of an efficient-electron transfer from the singlet excited state of the dyes to the ground state of BTTB.

The molecular orbital calculations of 5-phenyl pyrromethene-BF₂ (PHP) using MINDO-AM1 and MNDO-psDI method were reported by Li et al. [12]. The ground state (S_0) of PHP has one stable conformer in which phenyl group is rotated 52° against the rigorously planer pyrromethene framework. The photoexcited state (S_1) of PHP has two stable conformers; one is a fluorescent metastable state with a phenyl ring rotated 37°, and the other is a nonfluorescent relaxed state with a non-twisted-phenyl ring against the plane

Fig. 2. Absorption (solid line) and fluorescence (dashed line) spectra of PBP in acetonitrile.

Substance concentrations were 7.63, 6.28 and 7.63 $\times 10^{-6}$ mol dm⁻³ for PBP; excitation wavelength 355nm. Absorption coefficient (ϵ) at maximum; $\epsilon = 5.1 \times 10^4$ mol⁻¹ dm³ cm⁻¹ for PBP.

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, which has a significantly short lifetime of 15 ps.

Taking consideration into the bulky-substituent effect in molecular orbital calculation for PHP, the relaxation mechanism of photoexcited EBP and PBP can be predicted as depicted in Fig. 6. The ground state has a stable conformer with fully rotated ethyl and phenyl group for EBP and PBP with respect to the rigorously planer pyrromethene framework. The ground state is photoexcited to a singlet excited state ($S_1(A)$) by absorbing a laser pulse. $S_1(A)$ deactivates accompanied with the large nucleous change. $S_1(A)$ for EBP undergoes rotation of ethyl groups to a relaxed state ($S_1(B)$) with moderately rotated ethyl, and $S_1(A)$ for PBP undergoes rotation of phenyl group to a relaxed state ($S_1(B)$) with moderately rotated phenyl, subsequently going to a fully-relaxed state such as a ($S_1(C)$) with the less-twisted phenyl ring due to the large resonance stabilization between phenyl group and dye chromophore. In case of HBP, the repulsion between substituents is lower than that for EBP and HBP. Thus the relation-energy gap from

Fig. 3. Fluorescence decays of HBP (a), EBP (c), and PBP (e) in the absence of BTTB, and of HBP (b), EBP (d), and PBP (f) in the presence of BTTB. Dashed line curve is logarithmic plots of lamp. Substance concentration 6.1×10^{-6} , 1.3×10^{-5} , and 6.3×10^{-6} mol dm⁻³ for HBP, EBP and PBP, respectively and 10^{-2} mol dm⁻³ for BTTB; detection wavelength more than 550 nm using cut pass filter (Toshiba Electric Corp. Glass filter O-56); excitation wavelength of pulse lamp (I), 490, 515, and 520 nm for HBP, EBP, and PBP,

Fig. 4. Ratio (τ_0/τ) of fluorescence life time for HBP (a), EBP (b), and PBP (c) against BTTB (concentration).

Fig. 5. Potential energy vs. nuclear configuration.

$S_1(A)$ to $S_1(B)$ is lower, and there is no state such as a $S_1(C)$ due to no resonance stabilization such as phenyl ring. $S_1(B)$ for the dyes decays radiatively or nonradiatively, or is quenched by BTTB.

The repulsion energy between phenyl ring and methyl groups, or between ethyl and methyl groups should increase the potential energy of the ground state, shifting absorption and fluorescence maximum to red, and the rotation of the bulky substituents in relaxation from $S_1(A)$ to $S_1(B)$ induces large-nuclear-configuration change. Thus the longer absorption maximum for EBP and PBP than that for HBP, and the larger Stokes shift for EBP and PBP than that for HBP support the large effect of the bulky substituents (Figure 2). The absorption maximum in 490 – 520 nm of the dyes are useful for laser imaging system equipped with 532 nm FD-Yag laser, and especially the absorption maximum at 514 and 519 nm for EBP and PBP is fitted to the emission light wavelength of FD-YAG laser.

The quenching-rate constant for PBP is larger than that for HBP and EBP. The reason of the large rate constant for PBP is not clear yet. However, it is considered that the spread of chromophore in PBP by phenyl ring increased the probability of electron transfer from the dye to BTTB.

Generally, liquid photoresists are used under air atmosphere. Since triplet lifetimes of

general dyes under nitrogen atmosphere, 10^{-6} – 10^{-1} s [13], and are efficiently reduced to 1-10 ns by oxygen in solutions as assuming the quenching rate of triplets by oxygen; 10^{10} mol⁻¹ dm³ s⁻¹ and the concentration of oxygen pressure in solutions at one atmosphere of air; 0.03mol dm⁻³ [13], the lifetime of TP triplet under air atmosphere should be same order of magnitude as the fluorescence lifetime for the pyrromethene dyes. The highly efficient fluorescent character for pyrromethene dyes, and the two order of magnitude higher quenching rate constant of fluorescence for pyrromethene dyes by BTTB than the triplet quenching rate constant for TP by BTTB implies the efficient sensitization character of the pyrromethene dyes for liquid photoresists.

Finally it is suggested that the pyrromethene dyes have high performance as a sensitization dye for liquid photoresist due to the high quenching rate constant, and the absorption maximum fitted to argon ion laser or FD-YAG laser.

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