Diphenyliodonium Salts with Pyranine Conk as an Environment-friendly Photo-acid Generator and Their Applications to Chemically Amplified Resists

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ABSTRACT: A diphenyliodonium salt with an environment-friendly dye as anion was designed. This salt was shown to possess photosensitivity suitable for use as a chemically amplified resist at both 365 and 405 nm. PAG of tris(diphenyliodonium) 9-hydroxy-pyrene-1,4,6-trisulfonate had a negative Ames test, showed good thermal stability, and had a decomposition temperature of 199.9 °C. The quantum yield of acid generation upon irradiation was 0.63. The mechanism of acid generation was intramoleculor electron transfer from the excited dye moiety to the iodonium structure. The photosensitivities of PAG in a polymer with a *t*-butoxycarbonyl protecting group were 31 and 58 mJ/cm^2 for 365 and 405 nm light, respectively.   [DOI 10.1295/polymj.37.545]
    KEY WORDS   Photo-acid Generator / Diphenyliodonium Salts / Environment-friendly Dye / Pyranine Conk /

Chemically amplified resists based on acid catalyzed reactions are used widely in semiconductor technology and resists.[1–4]

In these reactions, photo-acid generators (PAGs) that generate acids upon irradiation have played an important role.[5–8]

In general, PAGs must have a high sensitivity, a high thermal stability, ability to generate acid and high solubility in solvents and matrixes. It is important that PAGs and acid precursors are non-mutagenic.

PAGs are classified based on ionic structure, such as onium salts of sulfonate derivatives, and on their non-ionic structure, such as sulfonate derivatives of *N*-hydroxynaphthaleneimide.

Among PAGs, onium salts have several advantages such as a high sensitivity, good thermal stability, and easily modified structure for the purposes of altering their spectral absorption. This has led to various onium salts being applied as PAGs in photolithography. PAGs with photosensitivities at 193 and 248 nm have been studied, but there are few reports regarding the PAGs with photosensitivities at 365[9–13] and 405 nm. It is also difficult to find many reports describing safe and environmentally sensitive technologies regarding PAGs.

In this study, environment-friendly PAG photosensitive at both 365 and 405 nm was investigated. Tris-(diphenyliodonium) 9-hydroxy-pyrene-1,4,6-trisulfo-nate (PC-DPI, **1**) has an iodonium compound as a cation and an environment-friendly dye (pyranine conk, **2**) as an anion, which acts as spectral sensitizer for the iodonium ion and acid precursor. This dye (**2**) is referred to as a fluorescent whitening dye used in cosmetics and shampoos.

EXPERIMENTAL

Reagents

All solvents in this study were commercially available and used after being dehydrated with molecular sieves.

Materials

Pyranine conk, **2** (Hodogaya Chemical Co., Ltd.), and diphenyliodonium chloride (Tokyo Kasei Kogyo Co., Ltd. DPI-Cl) were used as received. Tetrabromo-phenol blue (TBPB) and *p*-toluenesulfonic acid were purchased from Wako Pure Chemicals. Tetrabutyl-ammonium hydroxide (TMAH, 2.38 wt% solution) was purchased from Tama Chemical Company.

Preparation of tris(diphenyliodonium) 9-hydroxy-pyr-ene-1,4,6-trisulfonate·3H$_2$O PC-DPI (1)

0.5 g (0.95 mmol) of **2** and 0.97 g (3.04 mmol) of DPI-Cl were dissolved together in water. The pyra-nine conk solution was added dropwise to the DPI-Cl solution. This solution was stirred at 40 °C for 2 h and then filtered. PC-DPI was recrystallized twice
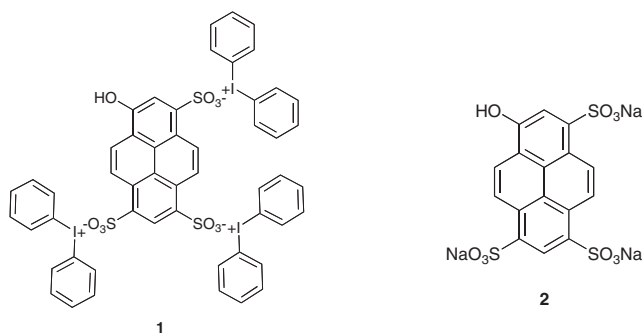
Figure 1. Structures of PAG (**1**) and Dye (**2**).

from water (1.02 g, 79.4%). No attempt was made to maximize the product yield. MP 199.9 °C (Decomposition temp.) Anal. Calcd for $C_{52}H_{43}I_3O_{13}S_3$: C, 46.17; H, 3.20; I, 28.14; S, 7.11. Found: C, 45.57; H, 3.17; I, 28.03; S, 7.14. ^{1}H NMR (400 MHz, DMSO) δ 2.54 (s, 6H), 7.52 (t, 12H), 7.64 (t, 6H), 8.15 (s, 1H), 8.24 (d, 12H), 8.28 (d, 1H), 8.86 (d, 1H), 8.98 (m, 3H) and 10.63 (s, 1H); IR (KBr pellet) 3250, 1475, 1440, 1200, 1060, 975, 740 and 670 cm^{-1}.

Mutagenic Test

The Ames test was used to examine the mutagenesic properties of PC-DPI and pyranine conk. The bacterium used in the test is a strain of *Salmonella typhimurium* that carries a defective gene making it unable to synthesize the amino acid histidine from the ingredients in its culture medium. However, some types of mutations can be reversed, referred to as a back mutation, with the gene regaining its function. These revertants grow on a medium lacking histidine.

A suspension of a histidine-dependent strain of *Salmonella typhimurium* was plated with a mixture of rat liver enzymes on agar lacking histidine. A filter paper disk was soaked with a DMSO solution with 10 or 50 μg of chemical (PC-DPI or pyranine conk). The control filter paper disk was soaked with DMSO only. The mutagenic effect of the chemical caused two bacterial strains (TA-100, TA-98) to regain the ability to grow without histidine, forming colonies around the disk. If the number of the scattered colonies was more than that of the control, the chemical was considered mutagenic. When the number of the scattered colonies was equal to or less than that of the control, the chemical was not considered mutagenic.

Measurements

UV–vis spectra were recorded in 1.00×1.00 cm quartz cells using a HITACHI U-3000 spectrophotometer.

Steady-state fluorescence spectra were recorded with samples in 1.00×1.00 cm quartz cells in a HITACHI MPF-2A fluorescence spectrophotometer.

Thermal stability was analyzed using a SEIKO thermal analysis system TG/DTA-200.

Redox potentials were measured by cyclic voltammetry with a Hokuto-Denko Function Generator HB-104 and a potensiostat/galvanostat HA-301. Electrochemical measurements were carried out using a three-electrode cyclicvoltammetric cell. The working electrode was a platinum wire and the reference electrode was a calomel electrode. The electrolyte was 0.1 M tetrabutylammonium perchlorate in DMF. The voltammograms were scanned at 50 mV s^{-1}. All potentials were calculated *vs.* SCE as $E_{1/2}$ values, where $E_{1/2} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.

Acid generation yield was measured using TBPB as an acid indicator.[12] An acetonitrile solution of PAG $(1.41 \times 10^{-5}$ mol dm$^{-3})$ in a quartz cell was irradiated with 405 nm light through a filter from a super high-pressure mercury lamp (405 nm, 2.5 mJ/cm^2). After irradiation, 3 mL of the solution were mixed with 1 mL of a TBPB acetonitrile solution $(5.59 \times 10^{-5}$ mol dm$^{-3})$, and the absorption spectrum of the mixture was measured. Changes in the absorption spectra of TBPB at 618 nm were compared.

Lithographic Evaluation

Photolithographic evaluation of the PAG photopolymer was based on the relationship between the exposure dose and the normalized film thickness after development. 1.0 μm thickness film consisting of poly(4-*t*-buthoxycarbonyl-styrene) and photopolymer with 3 wt % PAG was prepared on a silicon wafer and pre-baked at 110 °C for 2 min. Exposure was carried out using a super high-pressure mercury lamp (365 nm, 2.8 mJ/cm^2; 405 nm, 2.5 mJ/cm^2). Exposed resists were post-exposure baked at 110 °C for 5 min on a hot plate and developed in a 2 wt % TMAH solution for 12 s.

RESULTS AND DISCUSSION

The results of the Ames test are shown in Table I. The number of revertant colonies for pyranine conk and PC-DPI was equal to that of the control. Pyranine conk and PC-DPI are thus not mutagens.

Table I. Ames test of pyranine conk and PC-DPI used two bacteria (TA-100 and TA-98)

	The number of revertant colonies	
	TA-100	TA-98
DMSO	149	59
Pyranine conk	137	60
PC-DPI	123	61
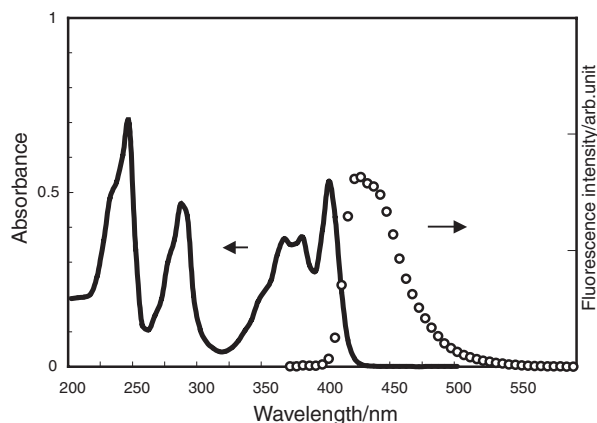
Figure 2. Absorption (–) and fluorescence (○) spectra of pyranine conk in MeOH. Absorption spectrum of DPI-Cl (●) in MeOH. The concentrations of pyranine conk and DPI-Cl were 2.18×10^{-5} and $2.28 \times 10^{-5} \, \mathrm{mol \, dm^{-3}}$, respectively; the excitation wavelength was 365 nm in the fluorescence spectrum.
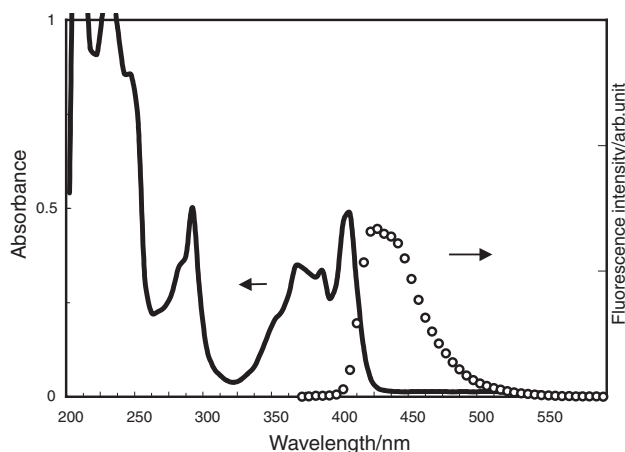
Figure 3. Absorption (–) and fluorescence (○) spectra of PC-DPI in MeOH. The concentration of PC-DPI was $1.47 \times 10^{-5} \, \mathrm{mol \, dm^{-3}}$; the excitation wavelength was 365 nm in the fluorescence spectrum. Absorption coefficient of PC-DPI at 365 nm: $2.36 \times 10^{4} \, \mathrm{M^{-1} \, cm^{-1}}$.

Figure 2 shows the absorption spectra of pyranine conk and DPI-Cl and fluorescence spectrum of pyranine conk in oxygen-free MeOH.

Pyranine conk has strong absorption peaks at 230 and 280 nm, a broad absorption with a vibrational fine structure in the wavelength region of 310–420 nm, and a broad and structureless fluorescence spectrum from 380 to 530 nm. The absorption spectrum of pyranine conk clearly extends to longer wavelengths than that of DPI-Cl. From these spectra, the lowest excited singlet state energy (ΔE_{00}) of pyranine conk was estimated as 69.6 kcal/mol.

PC-DPI was synthesized by reacting pyranine conk and DPI-Cl in water. Figure 3 shows the absorption and fluorescence spectra of PC-DPI in oxygen-free MeOH.

Electrochemical behavior was studied in DMF solution with tetrabutylammonium perchlorate as the supporting electrolyte. The oxidation potential ($E_{1/2ox}$) of pyranine conk was 0.79 V *vs.* SCE and the reduction potential ($E_{1/2}$ red) of DPI-Cl was -0.81 V *vs.* SCE. The standard free energy changes (ΔG^0) accompanying the electron transfer from the lowest excited single state of pyranine conk to that of DPI thus can be calculated according to the Rehm–Weller equation,

$$\Delta G^0 = 23.06\{E(D/D^{+\bullet}) - E(A^{-\bullet}/A)\} - \Delta E_{00} - C$$

where $E(D/D^{+\bullet})$ is the oxidation potential of the donor, $E(A^{-\bullet}/A)$ is the reduction potential of the acceptor, ΔE_{00} is the electronic energy corresponding to the excited singlet state of the donor, and C is the Coulombic interaction energy, in this case 1–2 kcal/mol in a polar solvent.

In the case of the pyranine conk anion and DPI cation in the PC-DPI molecule, ΔG^0 was calculated as -32.7 kcal/mol without taking coulombic interactions into consideration. This estimation indicates that the intramolecular electron transfer from anion to cation could take place quantitatively.

Table II shows the decomposition temperatures of DPI-Cl, Pyranine conk, and PC-DPI. The decomposition temperatures of fluoreny-lideneiminononafluorobutane sulfonate, fluorenylideneiminotrifluoro methane sulfonate and diphenyliodonium 9,10-dimethoxy-anthracene-2-sulfonate, other representative PAGs, are 146, 135, and 200 °C, respectively.[12] The thermal stability of the PAG developed in this study was equal to or higher than that of all of these other PAGs.

The thermal stability of PC-DPI may thus be considered adequate.

Acid generation yield was measured using TBPB as an acid indicator. The absorption band of TBPB at around 618 nm was changed by the presence of an acid. TBPB absorption changes were calibrated using *p*-toluenesulfonic acid as a standard material. Quantum yield was determined from the absorption changes at 618 nm due to acid generation. Quantum yield based on acid generation from PC-DPI was 0.63.

Quantum yields of diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate, *N*-trifluoromethylsulfonyloxy-1,8-naphthalimide and fluorenylideneiminotrifluoromethanesulfonate are 0.18, 0.17, and 0.32, respectively.[10–12]

Table II. Decomposition Temperatures of DPI-Cl, pyranine conk and PC-DPI

Compound	T_d (°C)
DPI-Cl	200
Pyranine conk	>400
PC-DPI	199.9
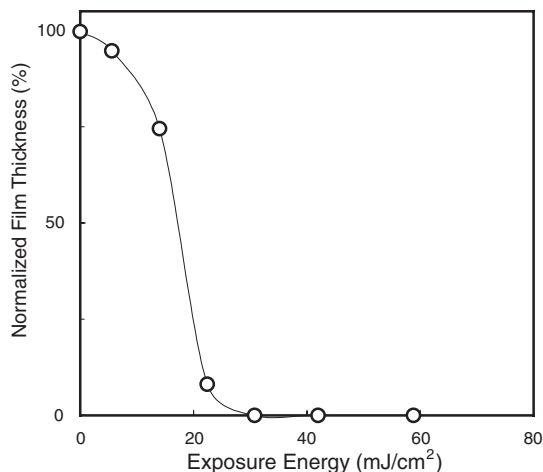
Figure 4. Characteristic curves of the photopolymer involved PC-DPI 3 wt % (365 nm wavelength light).
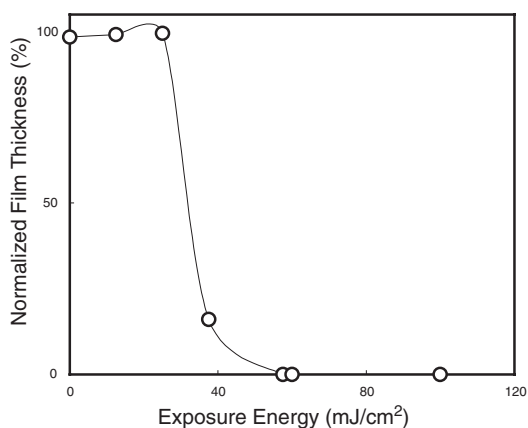
Figure 5. Characteristic curves of the photopolymer involved PC-DPI 3 wt % (405 nm wavelength light).

Figure 6. SEM photograph of the pattern from poly(4-*t*-buthoxycarbony-PHS) with PC-DPI 3 wt %.

mutagenic dye was designed. This new PAG possesses the necessary qualities for use as a chemically amplified resist.

The Ames test indicated the PC-DPI to be non-mutagenic. Mechanism of acid generation is considered intramoleculor electron transfer from the excited dye part of the molecule to the iodonium structure. The thermal stability of PC-DPI was adequate for use as a chemically amplified resist. Quantum yield of acid generation was 0.63. The photo-acid generating efficiency in a polymer with a *t*-buthoxycarbonyl protecting group was $31 \, \text{mJ/cm}^2$ (365 nm) and $58 \, \text{mJ/cm}^2$ (405 nm).

PC-DPI has sufficient potential at both 365 and 405 nm for use as a chemically amplified resist.

Quantum yield of the PAG in this study was thus much higher than that of these PAGs, indicating higher acid generation yield for PC-DPI, and, thus, a higher reactivity.
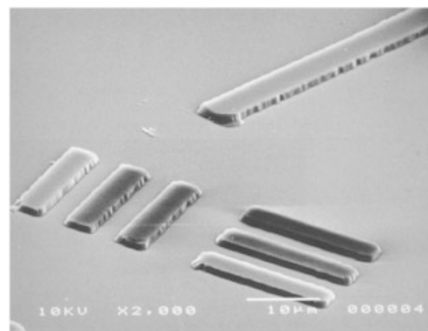
Figures 4 and 5 show the relationship between the light exposure intensity and normalized film thickness after development at 365 and 405 nm, respectively. The sensitivity of the new PAG was $31 \, \text{mJ/cm}^2$ (Figure 4) and $58 \, \text{mJ/cm}^2$ (Figure 5) for the two wavelengths. These results indicate that the photopolymer has sufficient sensitivity in the non-optimized step.

This is a positive working resist which shows solubility change due to deprotection by the acid from PAG and subsequent bake.

SEM micrograph of a pattern created from the photopolymer with 3 wt % PC-DPI is shown in Figure 6.

CONCLUSIONS

A new environmentally-friendly PAG with a non-

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