

i-Line sensitive photoacid generators

Haruyuki Okamura* and Masamitsu Shirai

Department of Applied Chemistry, Osaka Prefecture University, 1-1 Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan

ABSTRACT

Photoacid generator (PAG) is a key compound for the cationic UV curing and crosslinking system including epoxides and vinyl ethers. One of the drawbacks of photo-acid initiating system is a narrow selection of monomer structures and light sources. Many types of PAG have low sensitivity to i-line (365 nm) light from a medium-pressure mercury lamp or UV-LED (405 nm) light applicable to conventional and environment friendly UV curing system. In this paper, recent developments of PAG that is thermally stable and highly sensitive to i-line are reviewed. Furthermore, recent developments in the application of i-line sensitive PAG in contexts of photoresists, printing technology, and biology are introduced.

KEYWORD: photoacid generator, 365 nm light

1. INTRODUCTION

Photoacid generator (PAG) has been extensively studied because of their wide applications, especially in the field of polymeric photosensitive systems [1, 2]. PAG can be divided into two groups according to their characteristics, i.e., ionic- and non-ionic types. When these onium salts are irradiated with ultraviolet (UV) light, they undergo photolysis to form Brönsted or Lewis acids. Onium salts such as iodonium or sulfonium salts are thermally stable and may be structurally modified to change their spectral absorption characteristics.

On the other hand, non-ionic PAG has a much wider range of solubility in organic solvents and in polymer films compared to onium salt PAG. A disadvantage of the non-ionic PAG is that they are thermally less stable than the onium salt PAG.

PAG is a significant material for the photoinduced curing system using epoxides and such curing systems may be widely applied in coatings, adhesives, inks, and photoresists. Recently, the PAG sensitive to 365 nm light became important in relation to the application to UV curing and chemically amplified resists. Furthermore, emerging LED technology suggests new possibilities of applications in terms of low-energy consumption, low biological damage, effective curing of thick sample and sample having strong absorption at deep UV light. This review describes the recent developments and applications of i-line sensitive PAG.

2. i-Line sensitive ionic PAG

Ionic PAG basically involves onium salts such as aryldiazonium, diaryliodonium, triarylsulfonium, and triarylphosphonium salts that contain anions such as BF_4^- , SbF_6^- , AsF_6^- , PF_6^- , CF_3SO_3^- and $\text{C}_4\text{F}_9\text{SO}_3^-$. When these onium salts are irradiated with ultraviolet (UV) light, they undergo photolysis to form Brönsted or Lewis acids. Especially, iodonium [3] or sulfonium [4] salts are extensively studied by Crivello [5] because of their thermal stability and may be structurally modified to change their spectral absorption characteristics. A variety of onium salts as PAG have been prepared and the mechanism for their photolysis has been investigated in detail. The sensitivity of the onium

*Corresponding author: okamura@chem.osakafu-u.ac.jp

salts for i-line light was mainly accomplished by the aid of photosensitizers [6]. However, only a few reports are available for i-line sensitive PAG without photosensitizers. The limited solubility of the onium salts in common organic solvents that had been a serious disadvantage for their practical use was recently improved by modifying their chemical structures.

Figure 1 shows iodonium salts **1** [7] and **2** [8], sulfonium salts **3** [9, 10] and **4** [11], a ferrocenium salt **5** [12], and a cyclopropenium salt **6** [13] as a representative of i-line sensitive ionic PAG.

Iodonium salts, diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (**1**) and diphenyliodonium naphth[1,2-d][1,2,3]oxadiazole-5-sulfonate (**2**) were developed by Yamaoka *et al.* The absorption coefficients at 365 nm for **1** and **2** were of 10^3 order (7000 and 5300), originating in anthracene and diazoxide structures, respectively. The quantum yields for the acid formation of **1** and **2** with 365 nm irradiation were 0.29 and 0.21, respectively, in acetonitrile. The PAG **1** and **2** were applied to i-line sensitive chemically amplified resists.

Dectar and Hacker reported the photochemistry of diphenyliodonium salts investigated by product

analysis, measurement of acid, and determination of the consumption of the iodonium salts [3]. They revealed that the primary products formed upon direct and triplet-sensitized irradiation of diphenyliodonium salts are iodobenzene, 2-, 3-, and 4-iodobiphenyl, acetanilide, benzene, and acid. They also revealed that electron-transfer quenching and triplet quenching by the iodonium salt are competitive reactions for some sensitizers, which agreed with the results that the photolysis of diaryliodonium salts can be sensitized by several dyes [6].

Crivello reported (4-phenylthiophenyl)diphenylsulfonium hexafluoroarsenate having i-line sensitivity [9]. The PAG was more sensitive than triphenylsulfonium hexafluoroarsenate and 9-phenylthianthrenium hexafluoroarsenate on irradiation of a medium pressure mercury lamp. (4-Phenylthiophenyl)diphenylsulfonium hexafluoroarsenate has slight absorption at 365 nm. (4-Phenylthiophenyl)diphenylsulfonium hexafluorophosphate (**3**) was applied to i-line sensitive photoresist for screen printing plate [10].

We have developed an i-line sensitive sulfonium salt by the incorporation of thianthrene imide skeleton as a chromophore. The thianthrene imide

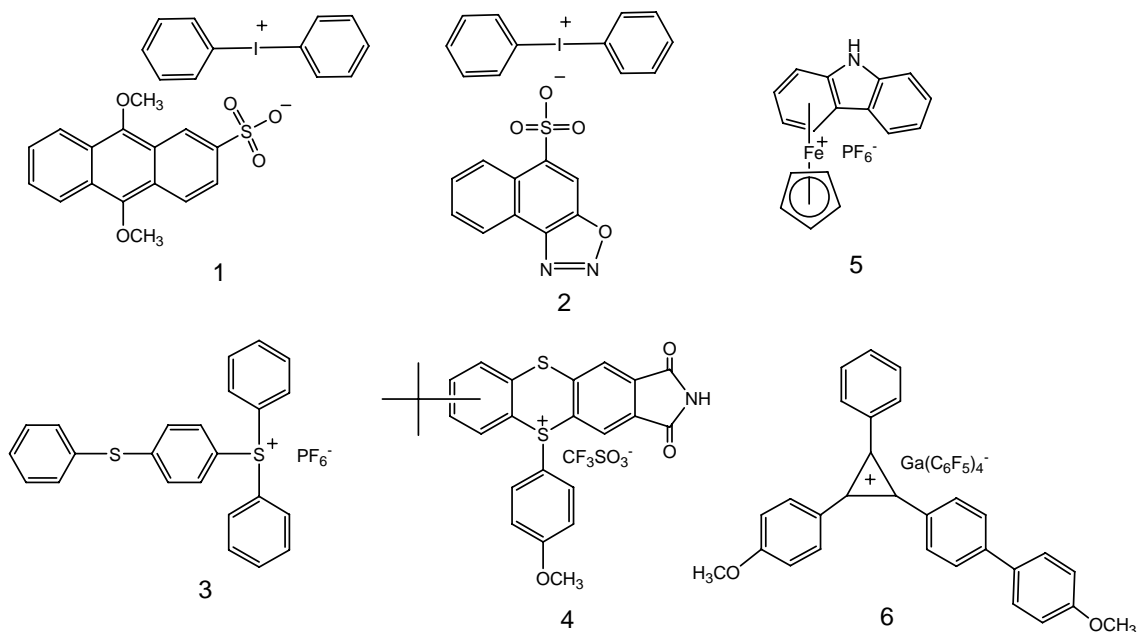


Figure 1. Chemical structures of i-line sensitive ionic PAGs.

chromophore has strong absorption at 365 nm. Synthesis of 7-(1,1-dimethylethyl)-5-(4-methoxyphenyl)-1,3-dioxo-1H-[1,4]benzodithiino[2,3-f]isindolium trifluoromethanesulfonate (**4**) [11] was carried out by the condensation of corresponding thianthrene *S*-dioxide and methoxybenzene and followed by exchange of anions. Thermal decomposition temperatures of **4** were around 300 °C. The good thermal stability is due to onium salt structures. Molar absorption coefficient of **4** at 365 nm was 3500, which was larger than that of *N*-trifluoromethanesulfonyloxy-1,8-naphthaleneimide (380), a conventional non-ionic PAG. Solubility of **4** at 20 °C was good (10 mg/mL) in common organic solvents such as benzene, chloroform, ethyl acetate, ethanol, and methanol. Incorporation of *tert*-butyl group in **4** was effective to enhance the solubility. The quantum yield of decomposition of **4** was 0.24 under N₂ in acetonitrile, which is consistent with the values of **1** and **2**.

Photolysis mechanism of sulfonium salt PAG was extensively studied by Dectar and Hacker [4]. They reported that direct irradiation of triphenylsulfonium salts produced new rearrangement products, phenylthiobiphenyls, along with diphenyl sulfide. The mechanism for direct photolysis is proposed to occur from the singlet excited state to give a predominant heterolytic cleavage along with some homolytic cleavage. The heterolytic cleavage gives phenyl cation and diphenyl sulfide, whereas homolytic cleavage gives the singlet phenyl radical and diphenylsulfinyl radical cation pair. These pairs of intermediates then produce the observed photoproducts by an in-cage recombination mechanism and also by reactions with the solvent.

Carbazole-bound ferrocenium salt (**5**) is a new class of i-line sensitive PAG [12]. The ferrocenium salt **5** has strong absorption at i-line region (λ_{max} : 347 nm, ϵ_{max} : 2170). The quantum yield of decomposition of **5** was 0.59. The photolysis of the compound with epoxide yields σ bonds of Fe-O and carbocations. The carbocation initiates the ring-opening reaction of epoxides.

Neckers *et al.* reported that a new series of triarylcyclopropenium tetrakis(pentafluorophenyl) gallates were synthesized by anion exchange [13].

The gallium salt **6** has strong absorption at 365 nm (ϵ_{365} : 8.0×10^4 in acetonitrile). Cationic photopolymerization of glycidyl phenyl ether (GPE) proceeded in the presence of **6** on irradiation. The polymerization afforded polyGPE with M_w of 4100-8100. The initiating species was identified as a proton produced from photolysis of the triarylcyclopropenium cation.

3. i-Line sensitive non-ionic PAG

Non-ionic PAG that can generate sulfonic acids upon irradiation involve (2 or 4)-nitrobenzyl esters of sulfonic acids, quinolones, *N*-hydroxyimide sulfonates, diazonaphthoquinone derivatives, and imino sulfonates. Non-ionic PAG has a much wider range of solubility in organic solvents and in polymer films compared to onium salt PAG. A disadvantage of the non-ionic PAG is that they are thermally less stable than the onium salt PAG. PAG is an important material for the photoinduced curing system using epoxides and such curing systems may be widely applied in coatings, adhesives, inks, and photoresists.

Recent developments of non-ionic PAG sensitive to i-line light were reviewed in [14, 15].

3.1. Nitrobenzyl esters

Protection of carboxylic acids with photolabile groups has been accomplished with the 2-nitrobenzyl group [16]. The photochemical deprotection of nitrobenzyl esters is believed to proceed via abstraction of a benzylic hydrogen atom by a nitro group oxygen. Subsequent rearrangement and cleavage regenerates the parent carboxylic acid and affords a nitrosoaldehyde as a by-product as shown in Figure 2.

Yamaoka *et al.* reported the direct photodissociation of *p*-nitrobenzyl esters instead of photolabile esters based upon *o*-nitrobenzyl photochemistry. *p*-Nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate (**6**) [17] (Figure 3) and other *p*-substituted benzyl 9,10-dimethoxyanthracene-2-sulfonate derivatives were photolyzed to give 9,10-dimethoxyanthracene-2-sulfonic acid. Suggested dissociation proceeds through an intramolecular electron transfer from the 9,10-dimethoxyanthracene moiety to the *p*-substituted benzyl moiety. The quantum yield for the photodissociation of **6** and **7** (Figure 3) with excitation at 365 nm in degassed acetonitrile

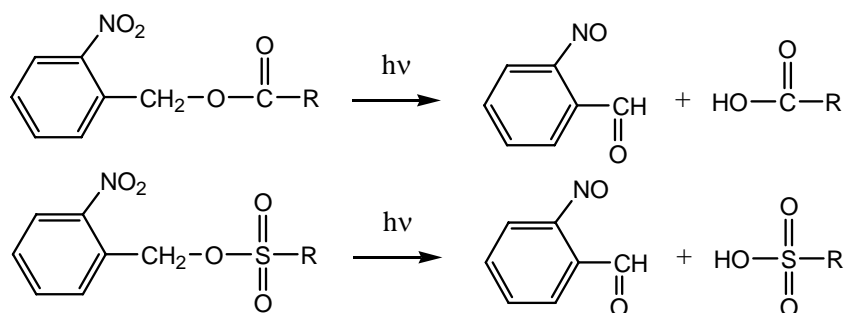


Figure 2. Photolysis of 2-nitrobenzyl esters.

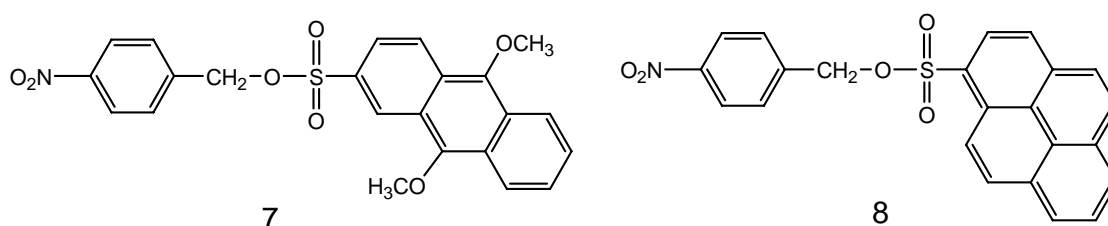


Figure 3. Chemical structures of i-line sensitive PAGs of 4-nitrobenzylsulfonates.

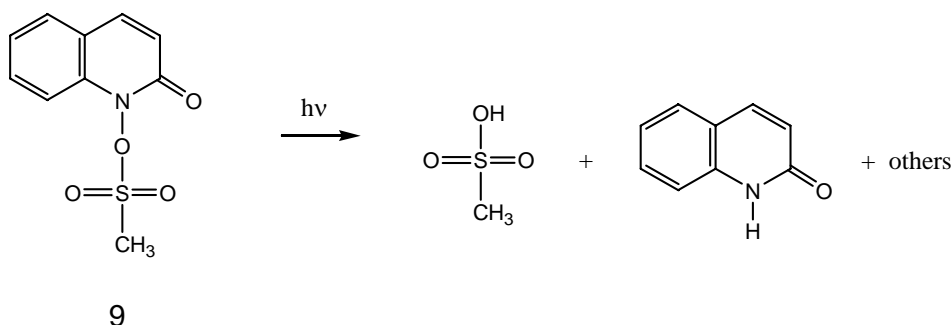


Figure 4. Photolysis of i-line sensitive PAG **9**.

is 0.14 and 0.16, respectively [17, 18]. The absorption coefficients at 365 nm for **6** and **7** were of 10^3 order, due to anthracene and pyrene structures, respectively.

3.2. Quinolone

A new class of carboxylate and sulfonate esters of 1-hydroxy-2(1H)-quinolone as nonionic PAGs was reported by Singh *et al.* [19]. Irradiation of carboxylates and sulfonates of 1-hydroxy-2(1H)-quinolone (**8**) by UV light ($\lambda > 310$ nm) resulted in homolysis of weak N-O bond leading to efficient generation of carboxylic and sulfonic acids,

respectively (Figure 4). The mechanism for the homolytic N-O bond cleavage was supported by time dependent DFT calculations. Photoresponsive copolymers of methyl methacrylate and 1-(*p*-styrenesulfonyloxy)-2-quinolone can successfully control surface wettability on irradiation.

3.3. Diazonaphthoquinones

Diazonaphthoquinone (DNQ) undergoes photolysis to produce a carbene, which then undergoes a Wolff rearrangement to form a ketene. The ketene reacts with water to generate indenecarboxylic acid (Figure 5).

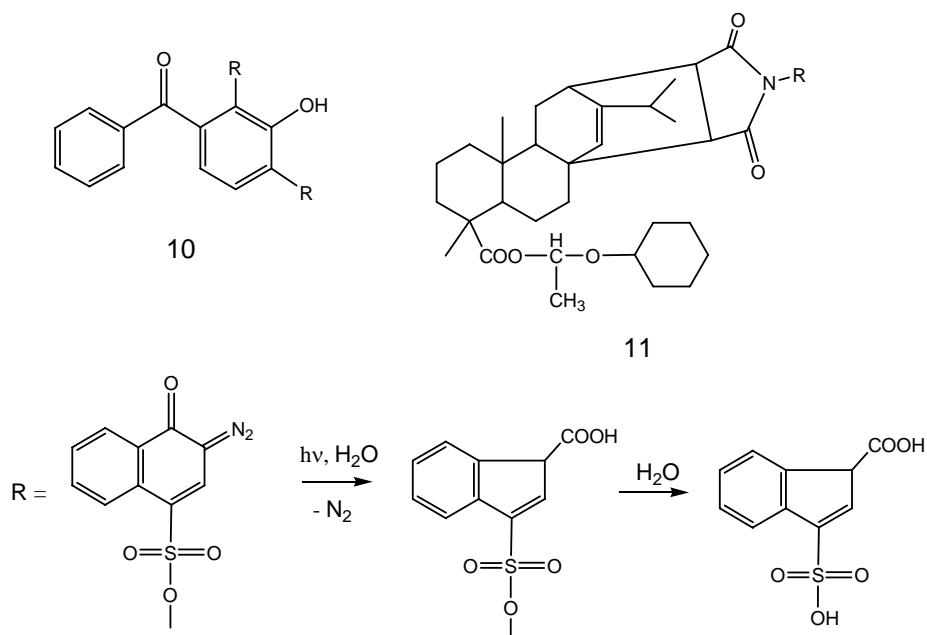


Figure 5. Chemical structures and photolysis mechanism of i-line sensitive DNQ type PAGs.

Wang *et al.* reported a series of i-line sensitive photoresists using diazonaphthoquinone [20, 21]. Polyaddition reactions of *N*-hydroxy maleopimarimide with divinyl ether compounds were carried out to give novel polymers with ester acetal linkages in the main chain. The polymers have good solubility in common organic solvents and relatively high T_g temperatures. Positive-tone chemically amplified i-line photoresists can be formed from them and 2,1-diazonaphthoquinone-4-sulfonate (9) (Figure 5). The photolithographic performance of the photoresists was evaluated using an i-line exposure system with high photosensitivity and resolution.

Wang *et al.* also reported that novel one-component positive-tone chemically amplified i-line photoresists can be formed by the molecular glass compounds. Maleopimaric acid was reacted with hydroxylamine to afford *N*-hydroxy maleopimarimide, which was then further esterified with 2-diazo-1-naphthoquinone-4-sulfonyl chloride (2,1,4-DNQ-Cl) to give *N*-hydroxy maleopimarimide sulfonate. The carboxylic acid group of the compound was then protected by the reaction of this compound with vinyl ether compounds to give the corresponding molecular glass compounds (10) (Figure 5). Upon irradiation of

365 nm light, the 2,1,4-DNQ group undergo photolysis not only to be converted into indene carboxylic acid but also generate a few amount of sulfonic acid which can catalyze the deprotection of the acid labile group. The lithographic performance of the resists was evaluated using i-line exposure system with high photosensitivity and resolution.

3.4. *N*-Hydroxyimide sulfonates

Certain sulfonic acid esters of *N*-hydroxyimides and *N*-hydroxyamides have been known to form sulfonic acid upon UV irradiation (Figure 6). *N*-trifluoromethanesulfonyloxynaphthalimide (12) which is sensitive to 248 and 365 nm light is thermally stable up to 225 °C. The absorption coefficient at 365 nm for **12** in acetonitrile is not so high (ϵ_{365} : 380). A reaction mechanism for the photolysis of **12** has been reported [22]. Photoreaction proceeds through homolytic cleavage of the N–O bond with subsequent hydrogen abstraction, leading to acid generation and formation of an amide compound with liberation of CO₂.

Singh *et al.* reported novel PAGs for sulfonic acids based on *N*-hydroxyanthracene-1,9-dicarboxyimide [23] (Figure 7). The PAG **13**

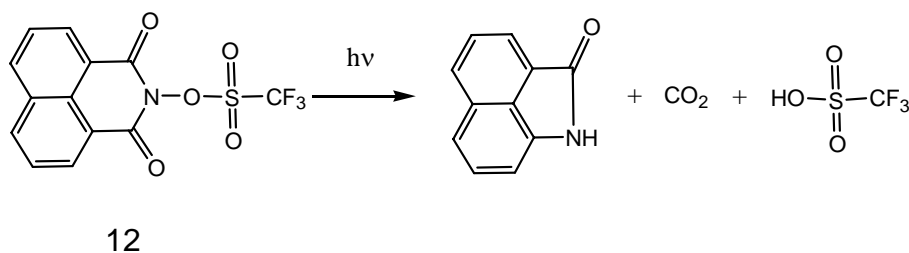


Figure 6. Photolysis of *N*-trifluoromethanesulfonyloxynaphthalimide (12).

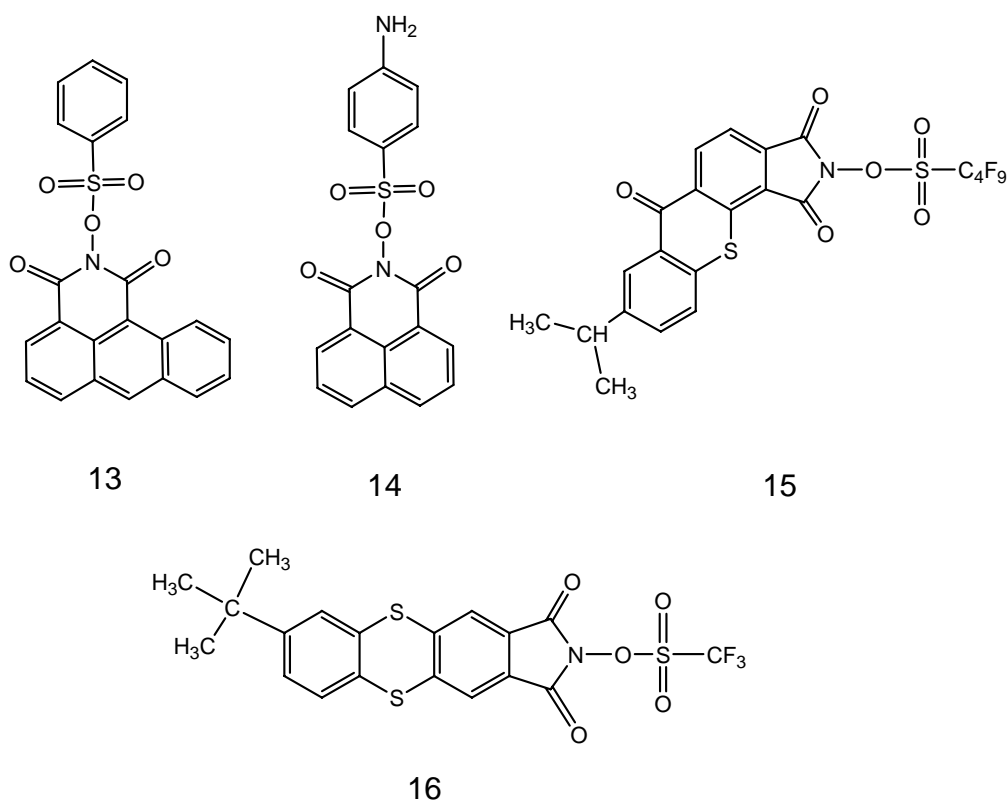


Figure 7. Chemical structures of i-line sensitive *N*-hydroxyimide sulfonate-type PAGs.

exhibited strong absorption at i-line and g-line light (λ_{max} (ethanol): 437 nm, $\log \epsilon_{\text{max}}$: 3.93). Irradiation of **13** in acetonitrile using UV light above 410 nm resulted in the generation of sulfonic acids in good quantum yield of acid generation (Φ_a : 0.33).

Takahara *et al.* reported *N*-(*p*-anilinesulfonyloxy)-1,8-naphthalimide (**14**) [24] (Figure 7) as fluorescence imaging material based on a novel fluorescence imaging mechanism. The PAG **14** generates an acid on irradiation. PAG **14** is an

analogous of the PAG **12**, which has weak absorption at 365 nm ($\lambda_{365} = 380$ in acetonitrile). The value of quantum yield of acid generation (Φ_a) of PAG **14** was 0.071. The fluorescence probe moiety then detects the acid and generates fluorescence. The self-contained photoreaction permits one-step fluorescence imaging without any wet or dry developing process.

We have developed a series of i-line sensitive PAGs having thioxanthone [25] and thianthrene [26, 27] chromophors (Figure 7). Molar extinction

coefficients were measured in acetonitrile. The PAG **15** showed low ϵ value at 365 nm (ϵ : 381), though a strong absorption at 436 nm (ϵ : 4030). Thus, **15** can work as g-line sensitive PAG. *N*-Hydroxyimide sulfonate PAG based on thianthrene chromophore **16** showed high ϵ value at 365 nm (ϵ : 1950). Thermal stability of PAG is a significant point for the practical use. The T_d values of PAGs **12**, **15**, and **16** were 225, 199, and 156 °C, respectively. The sulfonic acid ester moiety with electron withdrawing property decreased the thermal stability [26]. The PAGs **15** and **16** showed good solubility in solvents due to isopropyl or *tert*-butyl substituents in the PAGs.

The Φ_d values were obtained from UV and FT-IR spectral changes of PAG on irradiation at 365 nm. The PAGs **12** and **15** showed the same Φ_d values (0.18) and **16** showed a slightly lower Φ_d value (0.076). Thianthrene-based PAG strongly depended on the structure of the sulfonic acid ester units [26]. The PAG with the sulfonic acid ester unit having electron-withdrawing nature was highly photosensitive.

3.5. Imino sulfonates

Imino sulfonates can be photochemically dissociated to sulfonic acids. Upon UV irradiation the cleavage of -O-N= bonds in the compounds and the subsequent abstraction of hydrogen atoms from solvents leads to the formation of sulfonic acids, azines and ketones (Figure 8) [14, 15].

The absorption characteristics strongly depend on the structure of the imino moiety. For the photolysis of these compounds in polymer films in air, the reaction of imino radicals with oxygen is dominant compared to dimerization and hydrogen abstraction reactions. The quantum yields for the photolysis of these compounds were reported to be 0.2-0.3 [14, 15].

An imino sulfonate type PAG, (5-propylsulfonyloxyimino-5H-thiophen-2-ylidene)-2-methylphenylacetonitrile (**17**), applicable for g-line, i-line and DUV photoresists is reported by Asakura *et al.* [28] (Figure 9). The PAG **17** exhibit high solubility in PGMEA, thermal stability in a phenolic polymer matrix up to 140 °C, storage stability below 40 °C of more than 1 year, red-shifted absorption profile reaching to 490 nm, effective acid generation in terms of quantum yield (Φ_d = 0.15) and high sensitivity in resist formulations with various exposure wavelengths. Strong absorption at i-line and g-line light was observed for (5-methylsulfonyloxyimino-5H-thiophen-2-ylidene)-2-methylphenylacetonitrile, an analogous of the PAG **17** (ϵ_{405} : 9340 in acetonitrile). The PAG **17** was applicable to i-line sensitive photoresist [28], molecular glass resist [29] and a gate insulating layer in organic field-effect transistors [30].

We have developed a series of imino sulfonate type PAGs having fluorenone [31], thioxanthone [32, 33], and arylethynyl [34] chromophors

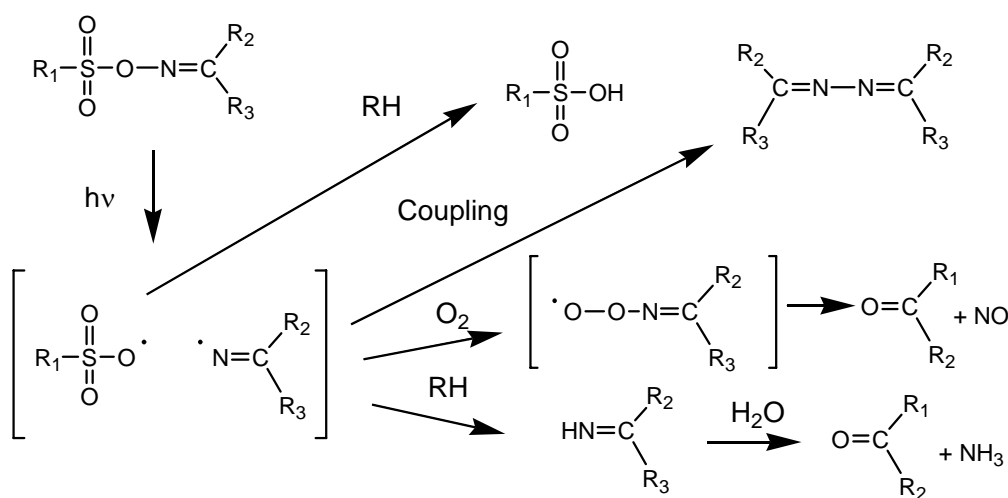


Figure 8. Reaction mechanism of photolysis of imino sulfonate-type PAGs.

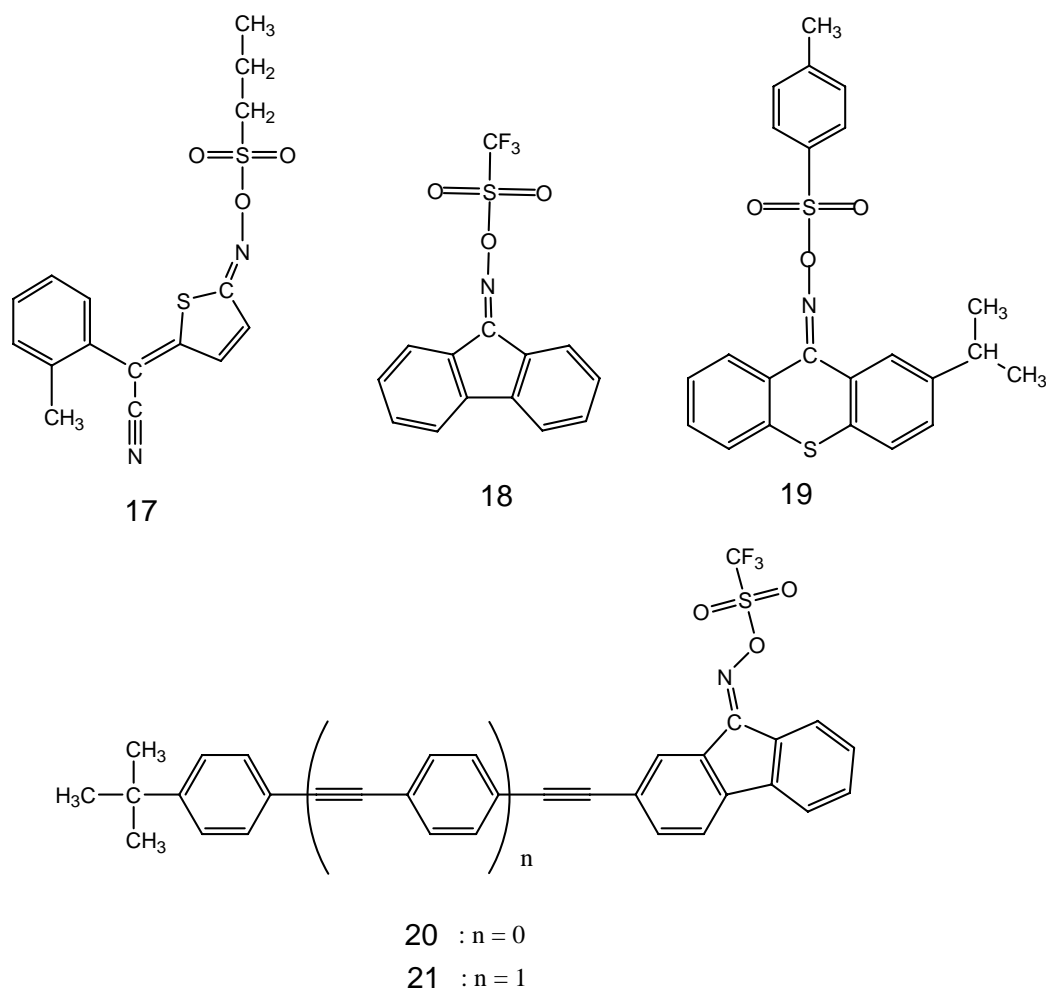


Figure 9. Chemical structures of i-line sensitive imino sulfonate-type PAGs.

(Figure 9). Incorporation of an isopropyl and *tert*-butyl groups in the chromophors was effective for enhancement of the solubility in organic solvents or polymer matrix. The PAG **18** showed a strong absorption at 257 nm, however, a weak shoulder was observed at 365 nm ($\epsilon_{365} = 300$ in acetonitrile). In contrast, PAGs **19**, **20**, and **21** show a strong absorption at 365 nm ($\epsilon_{365} = 4600$, 773, and 18500, respectively, in acetonitrile). PAGs **20** and **21** also show a strong absorption at 436 nm ($\epsilon_{436} = 1810$ and 3260, respectively, in acetonitrile). The absorption characteristics strongly depend on the structure of imino moiety. Thermal decomposition temperatures of **18** (135 °C), **20** (167 °C), and **21** (187 °C) were lower than that of **19** (206 °C). The structure of sulfonate esters strongly affected the thermal stability. Fluoroalkyl sulfonates decreased

their thermal stability. The solubility of PAG in chloroform, tetrahydrofuran, and cyclohexanone was 10 wt% or even higher. The clear PS film was obtained by mixing up to 20 wt% of PAG.

The Φ_d values were obtained from UV spectral changes of PAG in acetonitrile on irradiation at 365 nm. The PAGs **19** and **21** showed similar Φ_d values (0.080 and 0.081, respectively) and **18** and **20** showed slightly higher Φ_d values (0.32 and 0.22, respectively). The PAG with the sulfonic acid ester unit having electron-withdrawing nature was highly photosensitive except for the PAG **21**.

4. Application of i-Line sensitive PAG

Ueda *et al.* reported that positive-type chemical amplified resist was devised by a novel molecular

glass resist based on tetrahydropyran-protected G1 dendrimer in the presence of PAG **17** [29]. The resist showed a high sensitivity, high contrast, and successful fabrication of 3 μm line-and-space pattern with i-line exposure tool.

Ueda *et al.* also reported the fabrication of a highly dielectric and photo-patternable polymer material for a gate insulating layer in organic field-effect transistors (OFETs) [30]. PAG **17** was used as i-line sensitive PAG. The polymer material showed high sensitivity, good contrast, and high dielectric constants. The performance of OFET was improved using the polymer material.

Ober *et al.* report a new approach to solution-processable low-dielectric-constant materials including photolithographic patterning of these materials in chemically benign and environment friendly solvents [35]. A series of semiperfluorinated molecular glasses with styrenic substituents were successfully synthesized. The molecular glasses were patterned on irradiation at 365 nm in the presence of *N*-nonafluorobutanesulfonyloxy-naphthalimide, an analog of PAG **12**. The incorporation of semiperfluorinated substituents was effective in decreasing the dielectric constant.

Novel ester acetal polymers were applied to positive-tone chemically amplified i-line photoresists by Wang *et al.* [20]. By the combination of the DNQ-type PAG **10**, the excellent photolithographic performance also indicates that the chemically amplified system has the potential to achieve a better resolution of a quarter-micron.

Wang *et al.* also reported an i-line sensitive molecular resist compound **11** [21]. Fine positive-tone patterns with 0.75 μm line width were obtained under exposure doses of 50-60 mJ/cm^2 in the photolithography experiments.

DNQ-type PAGs were also applied to fabrication of contact holes [36]. The characteristics of the application of resolution enhancement lithography assisted by chemical shrink (RELACS) to i-line lithography were studied by conducting basic experiments on the addition of a PAG to an i-line resist and investigating the property of the cross-linking reactions involved in the pre-doping of various acids to RELACS film. Finally, we optimized RELACS materials to match i-line resist and realized the fabrication of contact holes less than 0.2 μm diameter by i-line lithography.

We have developed high-resolution screen printing using PAG **3** [10]. New resist formulation contains a base polymer, which consists of acid labile tetrahydropyranyl-protected carboxylic acid, hydroxyl, and methacrylic functions. A 10- μm feature size of resist on a screen plate was obtained on irradiation at 365 nm followed by development on a stainless steel screen. A 13-mm feature size silver circuit was successfully printed on poly(ethylene terephthalate) film without defect.

Matsumoto *et al.* demonstrated the validity of a new type of pressure-sensitive adhesion system [37] using block copolymers containing a poly(2-ethylhexyl acrylate) segment as the low glass transition temperature polymer and a poly(*tert*-butyl acrylate) or poly(isobornyl acrylate) segment as the reacting polymer in the presence of PAG **12**. This adhesion system can be easily debonded because of a change in the polymer properties of the adhesives by acid-catalyzed deprotection uniquely occurring during the photoirradiation followed by postbaking.

Maynard *et al.* reported that micron and submicron-scale features of aldehyde moieties were fabricated in polymer films by photolithography to develop a platform for protein immobilization and assembly at a biologically relevant scale [38]. Films containing the pH-reactive polymer poly(3,3'-diethoxypropyl methacrylate) and PAG **1** were patterned from 500 nm to 40 μm by exposure to i-line light. After the films were incubated with a biotinylated aldehyde reactive probe, the X-ray photoelectron spectroscopy results were consistent with biotin being attached to the surface. This methodology provides a platform for protein immobilization and assembly for various applications in biotechnology.

Sumaru *et al.* developed a novel method to kill adherent cells cultured on a substrate by micro-projection of incoherent visible light as a powerful tool of cell screening and cell purification [39]. The photo-responsive culture substrates functionalized with a photo-acid-generating polymer, which was an analogous of PAG **15**, was fabricated to kill the cells by the mild light irradiated by electrically controllable micro-projection systems currently available. In clear

contrast to the existing laser-based methods requiring point scanning, a real micro-projection of blue light with 436 nm light killed many CHO-K1 cells in the irradiated area on the substrate. The effect of the photo-generated acid was so confined that selective killing of targeted cells was achieved without critical damage to the neighboring cells. The photo-selective killing of the adherent cells was accomplished after preliminarily patterning through the photo-induced removal of cell adhesion-inhibiting polymer.

5. CONCLUSIONS

Recent developments of i-line sensitive PAGs were reviewed. A variety of ionic and non-ionic PAGs have been synthesized and mechanistic studies on photolyses of these materials have been evaluated. i-Line sensitive PAGs have been employed not only as catalysts for the photoinitiated polymerization of certain monomers but also in photoinduced cross-linking of polymers and oligomers, photoinduced degradation of polymers, and photoinduced transformation of functional groups in polymer chains. These applications are particularly important in the areas of photoresist, microelectronics technologies, and biological applications.

PAGs are a kind of photoremovable protecting groups (PPGs). PPGs offer excellent spatial and temporal control for the substrate release. Their applications span many scientific fields, from drug delivery to rheology, solid-phase synthesis, surface chemistry, and nanotechnology. Utilization of i-line and/or g-line light should contribute to the fields of polymer science, materials science, and biological science.

CONFLICT OF INTEREST STATEMENT

There are no conflicts of interest in the article.

REFERENCES

- Shirai, M. and Tsunooka, M. 1996, *Prog. Polym. Sci.*, 21, 1.
- Shirai, M. and Tsunooka, M. 1998, *Bull. Chem. Soc. Jpn.*, 71, 2483.
- Dektar, J. L. and Hacker, N. P. 1990, *J. Org. Chem.*, 55, 639.
- Dektar, J. L. and Hacker, N. P. 1990, *J. Am. Chem. Soc.*, 112, 6004.
- Crivello, J. V. 1999, *J. Polym. Sci. A: Polym. Chem.*, 37, 4241.
- Crivello, J. V. 2009, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 46, 474.
- Naito, K., Yamaoka, T. and Umehara, A. 1991, *Chem. Lett.*, 1869.
- Tarumoto, N., Miyagawa, N., Takahara, S. and Yamaoka, T. 2003, *J. Photopolym. Sci. Technol.*, 16, 697.
- Crivello, J. V. and Lam, J. H. W. 1980, *J. Polym. Sci., Polym. Chem. Ed.*, 18, 2677.
- Okamura, H., Kayanoki, M., Takada, K., Nakajiri, H., Muramatsu, K., Yamashita, M. and Shirai, M. 2012, *J. Photopolym. Sci. Technol.*, 23, 1151.
- Okamura, H., Naito, H. and Shirai, M. 2009, *J. Photopolym. Sci. Technol.*, 22, 583.
- Wang, T., Li, B. S. and Zhang, L. X. 2005, *Polym. Int.*, 54, 1251.
- Li, H., Ren, K. and Neckers, D. C. 2001, *Macromolecules*, 34, 8637.
- Shirai, M. 2007, *J. Photopolym. Sci. Technol.*, 20, 615.
- Shirai, M. and Okamura, H. 2009, *Prog. Org. Coat.*, 64, 175.
- Klán, P., Šolomek, T., Bochet, C. G., Aurélien Blanc, A., Richard Givens, R., Rubina, M., Popik, V., Kostikov, A. and Wirz, J. 2013, *Chem. Rev.*, 113, 119.
- Yamaoka, T., Adachi, H., Matsumoto, K., Watanabe, H. and Shirotsaki, T. 1990, *J. Chem. Soc. Perkin Trans.*, 2, 1709.
- Mishiki, M., Yamaoka, T. and Koseki, K. 1988, *J. Photopolym. Sci. Technol.*, 1, 102.
- Iqbal, M., Banerjee, R., Atta, S., Jana, A., Dhara, D., Anoop, A. and Singh, P. N. D. 2012, *Chem. Eur. J.*, 18, 11968.
- Yu, J., Xu, N., Wei, Q. and Wang, L. 2013, *J. Mater. Chem. C*, 1, 1160.
- Yu, J., Xu, N., Liu, Z. and Wang, L. 2012, *ACS Appl. Mater. Interfaces*, 4, 2591.
- Malval, J.-P., Suzuki, S., Morlet-Savary, F., Allonas, X., Fouassier, J.-P., Takahara, S. and Yamaoka, T. 2008, *J. Phys. Chem. A*, 112, 3879.
- Iqbal, M., Banerjee, R., Atta, S., Dhara, D., Anoop, A. and Singh, P. N. D. 2012, *J. Org. Chem.*, 77, 10557.

-
24. Endo, T., Suzuki, S., Miyagawa, N. and Takahara, S. 2008, *J. Photochem. Photobiol. A: Chem.*, 200, 181.
 25. Iwashima, C., Imai, G., Okamura, H., Tsunooka, M. and Shirai, M. 2003, *J. Photopolym. Sci. Technol.*, 16, 91.
 26. Okamura, H., Matsumori, R. and Shirai, M. 2004, *J. Photopolym. Sci. Technol.*, 17, 131.
 27. Okamura, H., Naito, H. and Shirai, M. 2008, *J. Photopolym. Sci. Technol.*, 21, 285.
 28. Asakura, T., Yamato, H. and Ohwa, M. 2000, *J. Photopolym. Sci. Technol.*, 13, 223.
 29. Ito, Y., Higashihara, T. and Ueda, M. 2008, *J. Photopolym. Sci. Technol.*, 21, 799.
 30. Saito, Y., Higashihara, T. and Ueda, M. 2012, *J. Photopolym. Sci. Technol.*, 25, 375.
 31. Okamura, H., Watanabe, Y., Tsunooka, M., Shirai, M., Fujiki, T., Kawasaki, S. and Yamada, M. 2002, *J. Photopolym. Sci. Technol.*, 15, 145.
 32. Okamura, H., Sakai, K., Tsunooka, M. and Shirai, M. 2003, *J. Photopolym. Sci. Technol.*, 16, 701.
 33. Okamura, H., Sakai, K., Tsunooka, M., Shirai, M., Fujiki, T., Kawasaki, S. and Yamada, M. 2003, *J. Photopolym. Sci. Technol.*, 16, 87.
 34. Kodama, S., Okamura, H. and Shirai, M. 2012, *Chem. Lett.*, 41, 625.
 35. Murotani, E., Lee, J.-K., Chatzichristidi, M., Zakhidov, A. A., Taylor, P. G., Schwartz, E. L., Malliaras, G. G. and Ober, C. K. 2009, *ACS Appl. Mater. Interfaces*, 1, 2363.
 36. Ishibashi, T., Toyoshima, T., Kanda, T., Yasuda, N., Katayama, K., Tanaka, M. and Tanaka, H. 2001, *Jpn. J. Appl. Phys.*, 40, 7156.
 37. Inui, T., Sato, E. and Matsumoto, A. 2012, *ACS Appl. Mater. Interfaces*, 4, 2124.
 38. Christman, K. L., Requa, M. V., Enriquez-Rios, V. D., Ward, S. C., Kenneth, A. Bradley, K. A., Turner, K. L. and Maynard, H. D. 2006, *Langmuir*, 22, 7444.
 39. Sumaru, K., Kikuchi, K., Takagi, T., Yamaguchi, M., Satoh, T., Morishita, K. and Kanamori, T. 2013, *Biotechnol. Bioeng.*, 110, 348.