Recent Progress in Photo-Acid Generators for Advanced Photopolymer Materials

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Photopolymer materials have been widely used in some advanced industries owing to their practicability, low-cost, and ecological advantage. One of the key components of these photopolymer materials is a molecule that releases acidic species upon a photon trigger (known as Photo-acid generators, PAGs). Recently, PAGs have attracted much attention with novel technologies such as near-infrared CTP imaging, 3D printing, and EUV lithography, and are required to have various functions and sophisticated features. This review article summarizes recent advances in the molecular design and function of PAGs, which are required to respond to the increasing applications of the photopolymer materials in advanced industries.

Keywords: Photo-acid generator, PAG, Acid amplifier, Photoinitiator, Photopolymer, Photopolymerization, Photoresist

1. Introduction

Photopolymer materials [1,2] that can react only in the area irradiated with light are widely used in advanced industrial fields such as electronics, graphics, displays, and biomedical applications. Among photopolymer materials, photo-acid generators (PAGs) [3-7] are one of the key materials to affect the properties of photopolymer materials. PAGs have been extensively investigated in view of improving the efficiency of acid generation and polymerization enhancement. However, in recent years, PAGs with more sophisticated and diverse functions are required in order to respond to the emergence of various exposure light sources (e.g., light-emitting diode (LED), laser diode (LD)), novel applications such as computer-to-plate (CTP) imaging, 3D printing, and extreme ultraviolet (EUV) lithography. This review article describes advanced newly proposed design and functions of PAGs, focusing on the research on PAGs that meet the demands of advanced industries.

2. Photo-acid generators (PAGs)

Compounds that generate active species (initiating species) with light energy to trigger subsequent reactions are called photoinitiators [8-10]. The initiating species can be classified mainly to radicals, bases (anions), and acids (cations). PAGs are photoactive molecules that release acidic species via the photochemical process. The photopolymer materials using PAGs enables reactions to strictly control in view of time, space compared to materials using a thermal process. Such unique features can make highly functional photopolymer materials and environmentally friendly processes.

PAGs are widely used as cationic photoinitiators for photopolymerization of epoxies monomers and vinyl ethers (Fig. 1). Research by Crivello et al. in the 1970s has led to the spread of PAGs in various UV-cure applications.

![Fig. 1. Photoinitiated cationic polymerization system.](image-url)
PAGs are also used in various photopolymer materials such as acid-catalyzed deprotection reaction [11], depolymerization reaction [12] and crosslinking reaction [13,14]. In this section, types of general PAGs are classified into non-ionic compounds and ionic compounds, and their characteristics are described, including acid amplifiers.

2.1. Non-ionic PAGs

Typical structures and photochemical reaction mechanisms of non-ionic PAGs are shown in Table 1 [15-30].

Non-ionic PAGs have the advantage of good solubility in organic solvents but have slightly low thermal stability compared to ionic PAGs. In particular, a compound that generates an acid with strong acidity, such as perfluoroalkylsulfonic acid, has a remarkably low thermal stability. Therefore, molecular design for improving thermal stability is an important point for practical use. Moreover, non-ionic PAG molecules extended π-conjugated system have been developed to increase the absorption at visible wavelengths (Fig. 2) [31,32].

![Fig. 2. Structures of non-ionic PAGs extended π-conjugated system.](image)

Table 1. Structures and photochemical reaction of non-ionic PAGs.

| Type                      | Structure                                      | Reaction                                                                 |
|---------------------------|-----------------------------------------------|--------------------------------------------------------------------------|
| a) Nitrobenzylsulfonate   | ![Structure](image)                            | ![Reaction](image)                                                      |
| b) Midosulfonate          | ![Structure](image)                            | ![Reaction](image)                                                      |
| c) Oximesulfonate         | ![Structure](image)                            | ![Reaction](image)                                                      |
| d) Diazosulfone           | ![Structure](image)                            | ![Reaction](image)                                                      |
| e) Arylsulfonate          | ![Structure](image)                            | ![Reaction](image)                                                      |
| f) β-Ketosulfonate        | ![Structure](image)                            | ![Reaction](image)                                                      |
| g) N-Arylsulfonimid      | ![Structure](image)                            | ![Reaction](image)                                                      |

2.2. Ionic PAGs

An ionic PAG is composed of a cationic moiety (onium ion) and an anionic moiety (Fig. 3). Ionic PAGs have the disadvantage of slightly low solubility in reactive monomer components and organic solvents. However, onium compounds are able to have various types of anionic moieties such as superacids and inorganic acids besides sulfonic acids.

![Fig. 3. Schematic functions of anion and cation moieties on ionic PAG.](image)

Regarding the design of cationic polymerization initiators, the anionic moiety of ionic PAGs plays an important role in controlling initiation efficiency and reaction conversion. Thus it is necessary to consider the influence on the polymerization initiation ability (e.g. acidity, molecular size, nucleophilicity) and the deactivation of the propagation reaction. Typically, anions of BF₄⁻, PF₆⁻, and SbF₆⁻ are well known as anionic structures of ionic PAGs. However, in order to overcome the problems of high toxicity and low solubility of these anions, novel anionic structures have been developed (Table 2) [33-38]. Anionic structures have been extensively investigated as weakly coordinating anions [39].

The cationic moiety of ionic PAGs plays an important role in controlling photoreactivity and thermal stability. Various structures of onium compounds are able to use as PAGs (Table 3) [3, 40-49].
Among onium compounds, diaryliodonium and triarylsulfonium ions have enough the efficiency of acid generation and thermal stability. Thus these are widely spread as PAGs for industrial use [50].

The photochemical reaction mechanism of triphenylsulfonium salt is shown in Fig. 4 [8]. There are two cleavage paths either 1) heterolytic cleavage via direct excitation by π-σ* transition (C-S bond) or intramolecular electron transfer from π-π* transition to σ* molecular orbital (C-S bond) and 2) homolytic cleavage via intersystem crossing to the triplet state. After cleavage, the active species recombine in-cage or out-of cage to react with a hydrogen donor, forming a Brønsted acid. Sulfonium compounds have also a feature as radical generators to generate radical species that promote radical polymerization.

Table 2. Anionic moieties in ionic PAGs.

| Class      | Structure |
|------------|-----------|
| Borate [33, 34] | ![Structure](image) |
| Phosphate [35] | ![Structure](image) |
| Gallium [36] | ![Structure](image) |
| Sulfonylimido [37] | ![Structure](image) |
| Sulfonylethido [37] | ![Structure](image) |
| Aluminate [38] | ![Structure](image) |

Table 3. Cationic moieties in ionic PAGs.

| Class      | Structure |
|------------|-----------|
| Halonium [3] | ![Structure](image) |
| Sulfonium [3] | ![Structure](image) |
| Diazonium [3] | ![Structure](image) |
| Ammonium [40, 41] | ![Structure](image) |
| Oxonium [42] | ![Structure](image) |
| Carbenium [43, 44] | ![Structure](image) |
| Phosphonium [45] | ![Structure](image) |
| Ferrocenium [46] | ![Structure](image) |
| Others [47-49] | ![Structure](image) |

2.3. Acid amplifiers

An acid amplifier is a kind of acid generator that generates a strong acid such as sulfonic acid by auto-catalytically decomposing itself using a trigger acid (Fig. 5). They were studied by Ichimura et al. systematically [51]. Acid amplifiers are not PAGs, but a system is commonly used that utilizes an acid generated from a PAG as an initial
trigger. They thus are useful in high sensitivity techniques capable of image formation, curing, and patterning. Examples of acid amplifiers in Fig. 6 have been developed [52-56].

Fig. 5.  Schematic reaction process (a) and function (b) of acid amplifier.

Fig. 6.  Structures of acid amplifiers.

3. Design of photo-acid generation system corresponding to long-wavelength light source

In general, diaryliodonium salts and triarylsulfonium salts hardly absorb light near 300 nm or more (Fig. 7). It is not possible to use long-wavelength light of 300 nm or more emitted from high-pressure mercury lamps.

In addition, LED light sources consuming less power and LD light sources capable of scanning at high speed have been developed, and long-wavelength light in the visible region and near-infrared (NIR) region are increasingly used in advanced industries. The development of acid generation system compatible with these long-wavelength light has been a recent focus of research [50,57-59].

3.1. Shift to long-wavelength in light absorption of onium compounds

Onium salts can absorb light in the long-wavelength region by extending a π-conjugated system of onium salts (Fig. 8) [50, 60-68].

Fig. 7.  UV/Vis absorption spectra of triphenylsulfonium compound.

Fig. 8.  Onium compounds extended π-conjugated system (A) and linked sensitizer (B).
However, in a long-wavelength light, the available light energy is lower, and thus it is difficult for the bond cleavage to generate the acid. Thus sophisticated sulfonium PAGs with a π-extended conjugated system have been designed to induce an efficient bond cleavage reaction [65,69]. In addition, these compounds have a high absorption cross-section, and thus are useful as two-photon absorption-type PAGs [70]. Molecules have been developed in which a sulfonium salt and a long-wavelength photo-sensitizer are linked via a proper covalent bond to utilize intramolecular photoelectron transfer [71-73].

Recently, a sulfonium salt linked with ferrocene, an organometallic complex, has been revealed (Fig. 9) [74]. The absorption wavelength has been extended to around 430 nm by using the d-d transition of ferrocene, and further development is expected.

Fig. 9. Organometallic complex-type sulfonium compound.

3.2. Utilization of photo-sensitizers

Ionic PAGs such as iodonium salts and sulfonium salts are susceptible to photoelectron transfer sensitization when used in combination with a photo-sensitizer and are sensitive to light in the long-wavelength region, which is not absorbed by PAGs inherently (Fig. 10).

Fig. 10. UV/Vis absorption spectra of anthracene (sensitizer) and diphenyliodonium compound (PAG).

Figure 11 shows the photosensitized electron transfer reaction mechanism using anthracene as a photo-sensitizer [75-77]. Anthracene functions as an electron donor and onium salt functions as an electron acceptor. Besides anthracene, polycyclic aromatic compounds and heterocyclic compounds such as perylene and phenothiazine, and photoredox catalysts are used as photo-sensitizers (Fig. 12) [57-59,78-84].

Fig. 11. Photosensitized electron transfer reaction mechanism between anthracene and iodonium compound.

Fig. 12. Photo-sensitizers for visible to near-infrared light.
The photoelectron reaction rate is able to explain based on Marcus' theory [85]. The possibility that a thermodynamic reaction occurs can be estimated from the free energy change ($\Delta G_{et}$) obtained by the Rehm-Weller equation (1) [86]. Increasing $-\Delta G_{et}$ (Fig. 13) is an effective approach for design which improves acid generation efficiency.

$$\Delta G_{et} = E_{ox} - E_{red} - E_{00} - \frac{e^2}{\varepsilon R}$$  \hspace{1cm} (1)

($E_{ox}$: oxidation potential of photo-sensitizer, $E_{red}$: reduction potential of PAG, $E_{00}$: excitation energy of photosensitizer, $\varepsilon$: dielectric constant of medium, $R$: intermolecular distance between photo-sensitizer and PAG)

Fig. 13. Photo-sensitized electron transfer system between sensitizer (anthracene) and PAG (sulphonium).

Equation (1) shows that it is preferable to enhance the electron acceptability of PAGs. To enhance electron acceptability, the design of sulphonium compounds which have extended electron-withdrawing groups and $\pi$-conjugated systems are effective. In the photoinitiation system shown in Fig. 13, the more easily sulphonium salts are reduced, the more efficiently acids are generated (Fig. 14) [87]. Using these compounds, photocurable inks have been developed which are cationically polymerizable, highly sensitive, highly stable, and compatible with visible LED light sources.

As an application of the photoelectron transfer sensitization system, attention has recently been paid to a photoinitiation system using NIR light [88-90]. The use of NIR light source with high power is advantageous for productivity and the curing of the deep portion of materials such as materials containing thick films for which it is difficult to transmit a UV light [91]. In graphic materials, a CTP imaging technology has been developed which uses 830 nm NIR LD as a light source [92,93]. A photoinduced electron transfer sensitization initiation system is used which utilizes a cyanine-type NIR absorbing dye as a photo-sensitizer and an iodonium PAG. In this system, in order to control the efficiency and thermal stability of the electron transfer cleavage reaction, an iodonium salt with three methoxy groups which are introduced in the vicinity of an iodine atom has been designed to realize a highly sensitive and highly stable CTP imaging material (Fig. 15) [90].

Fig. 15. NIR dye-sensitized photoinitiation system.

A radical-induced acid generator system that combines an onium salt with a photo-radical generator that absorbs visible light has also been developed (Fig. 16) [94]. The electron generated by the decomposition of the photo-radical generator is transferred to the onium salt, which initiates oxidative decomposition [95,96]. In this system, an onium salt with improved electron acceptability is effective. In addition, an application to a light-induced frontal polymerization system for curing of the deep
portion that light does not reach has been recently reported [97]. Further, novel photoinitiating systems such as a photoelectron transfer initiation system using upconversion and a photoinitiating system using photoredox catalysts have been proposed [57-59].

Fig. 16. Radical-promoted photosensitization of onium ion.

4. Highly functionalized PAGs

The design of PAGs has advanced highly in progress focusing on acid species, the efficiency and the photochemical process of acid generation. Highly functionalized PAGs are described, focusing on recent advances.

PAGs that sophisticatedly control the photochemical reaction process of acid generation have also been studied. PAGs utilizing photo-tautomerization reaction [98-100] or cis-trans photo-isomerization reaction [101] are known (Table 4A and B), and the reversible acid generation by light and heat, or the control of acid generation according to the irradiation wavelength is possible.

PAGs utilizing a diarylethene structure, which are photocromic structures showing the high efficiency of intramolecular photo-cyclization reaction, have been designed recently. High quantum yield and proton release of a self-completed type which were not possible in conventional PAGs have been achieved (Table 4C) [102].

In addition, PAGs using a tandem reaction by photo-isomerization and photo-cyclization has been developed (Table 4D) [103]. These molecules show the reversible pH-photo-switching compounds, which are known as “photoacids” to control acidity by light [104]. These PAGs are expected to utilize for polymer synthesis by ring-opening cationic polymerization [105], ATP synthesis, and biological systems [106,107].

The acid generated from the PAGs is generally a Brønsted acid, but PAGs that generate tris (pentafluorophenyl) borane or carbocation which are strong Lewis acids have been designed (Scheme 1) [108-110]. Interestingly, these compounds have been utilized as photo Lewis acid catalysts for reactions such as polysiloxane formation and Mukaiyama-aldol reaction.
5. PAGs for advanced EUV resist materials

Lithography technology using photoresists is used to create semiconductor-integrated circuits that support the high performance of computers [111,112]. Extreme ultra-violet (EUV; 13.5 nm) resists are expected to form high-resolution patterns lower than 20 nm [113-115].

Chemically amplified resists are advantageous for high sensitivity and are mainly used for advanced photoresists [116]. The main components of the chemically amplified resist are the acid-labile polymer and PAG (Fig. 17). In processes for pattern formation, the PAG is decomposed by EUV exposure to generate an acid. In the baking step, the acid serves as a catalyst and the deprotection reaction of the acid-labile polymer proceeds in a chain reaction. In the alkali development step, only the exposed portion where the dissolution rate has been enhanced is developed to form a pattern.

The mechanism of acid generation of PAGs used in EUV resists is based on radiation chemistry (Fig. 18) [117,118]. When EUV photons are incident on the resist material, energy is provided via ionization of the polymer which is the main component of the resist, and secondary electrons are generated. Subsequently, while losing energy, secondary electrons become thermalized electrons and attach to the PAG. Then, acid is generated during the decomposition of PAG.

In order to improve the trade-off relation among line edge roughness (LER), resolution, and sensitivity, it is necessary to effectively utilize a few photons in EUV exposure and to precisely control the deprotection reaction mediated by PAGs. Recent progress of PAGs in EUV resist is described (Table 5). For improving the efficiency of acid generation in the EUV exposure process, acid generators have been designed to increase the efficiency of the cleavage reaction and the electron acceptability (Table 5A) [119-122].

In the acid-catalyzed reaction process, it is necessary to precisely control the nanometer-scale reaction field between the PAG and the acid-labile polymer to form the high resolution. In order to control the diffusibility of an acid, compounds having a ballast function (Table 5B) [122-124] and PAGs linked to polymer structures have been studied (Table 5C) [125]. PAGs generating highly fluorinated alkyl sulfonic acids (Table 5B) [123,124] to reduce the activation energy of the deprotection reaction. PAGs have been designed with a function of polarity conversion by introducing an acid-labile group and a function of photo-acid generation in one molecule, and a
molecular resist containing one of these PAGs as a single component has also been proposed (Table 5D) [126,127].

Table 5. Structures of PAGs on EUV resist.

| Class | Structure |
|-------|-----------|
| A) PAGs regarding acid generator efficiency (119-122) | ![Structure](image1) |
| B) PAGs having fluorosulfonate and sulfonate (123-124) | ![Structure](image2) |
| C) PAG bound polymer (125) | ![Structure](image3) |
| D) PAGs having acid active (126, 127) | ![Structure](image4) |

Acid amplifiers generating superacids (Fig. 19) [128,129] and photo-sensitizer precursors (Scheme 2) [130] have been designed to improve the sensitivity of resists.

Single nanometer-scale lithography is expected to emerge in the future, and thus PAG design is required that thoroughly reduces the inefficiency in the processes of energy provision, acid generation, acid-catalyzed reaction, and development [118].

Fig. 19. Structures of acid amplifiers on EUV resist.

Scheme 2. Structure and photochemical reaction of photo-sensitizer precursor.

6. Conclusion

This review article describes advanced newly proposed design and functions of PAGs, focusing on the research on PAGs that meet the demands of advanced photopolymer materials. Although PAGs function to release the required amount of the desired acid at the appropriate timing, attempts are still ongoing to sophisticatedly control the reaction of acid generation in view of time, space, irradiation wavelength, reversibility. In addition, the functions required for PAGs are on the increase with the emergence of novel applications such as an advanced EUV resist. Although not described in this review article, PAGs are also progressively utilized in new fields such as thermoelectric conversion materials [131], photodynamic therapy [67] and photo processing of cultured cells [132]. The development of innovative PAGs is expected to lead to the creation of novel applications in advanced industries.

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