2-5-19. Photoacid Generators

Overview

Photoacid generators (PAGs) are light-responsive molecules that produce acids upon irradiation, enabling acid-induced transformation of molecules and polymers. Since the development of sulfonium salts in the 1970s, PAGs have evolved from ionic to nonionic systems and, more recently, to reversible photoacids. Their applications now extend beyond advanced processing technologies, such as EUV lithography and 3D printing, to emerging areas including bio-related and medicinal targets as well as the regulation of enzymatic activity. Molecular design of PAGs has advanced to provide their precise control of photon absorption and acid generation.

Current Status and Frontiers

The concept of photoacid generators (PAGs) originated in the 1970s, when Crivello and co-workers reported cationic polymerization systems based on triarylsulfonium salts (J. V. Crivello, 1978). PAGs were first used for photocuring epoxy resins and then expanded to acid-catalyzed processes such as polymerization, deprotection, and crosslinking, driving broad adoption in photoresists, photopolymers, and adhesive materials. Ito and colleagues at IBM later introduced chemically amplified resists built on PAG chemistry, helping shape modern semiconductor manufacturing. Today, PAGs enable non-contact, localized generation of diverse acids under ambient conditions, and molecular design increasingly tunes acid strength, generation efficiency, and diffusion length for applications ranging from EUV lithography to medical area.

1. Structural classes and reaction mechanisms of conventional PAGs

PAGs are molecules that generate acids upon photoexcitation and are broadly classified into ionic, nonionic, and reversible types. Ionic PAGs consist of organic onium species, such as sulfonium and iodonium salts. Their dominant pathways are commonly understood to involve photoexcitation followed by triplet-state formation and electron-transfer processes, leading to C–S or C–I bond cleavage and subsequent formation of Brønsted acids. In contrast, nonionic PAGs are neutral molecules that directly produce acids upon photolysis and typically exhibit high compatibility with a variety of monomers and polymers. Representatively, imino ester–type PAGs generate acids via photolysis of N–O or S–O bonds. Both radical and ionic pathways would operate there in parallel.

2. PAGs with emerging functions

Recent "self-contained" PAGs place acid esters on photochromic scaffolds to release both a proton and a counter anion from a single molecule. Related concepts include photo-Lewis acid generators (PLAGs), which generate Lewis acids upon irradiation. Photosensitized electron-transfer systems enable activation with visible or near-infrared light, and two-photon-absorbing PAGs with D–π–D architectures can provide deeper penetration with high spatial resolution.

3. PAGs for EUV lithography

For PAGs used in EUV lithography, key challenges include improving sensitivity to compensate for the limited intensity of EUV exposure and suppressing acid diffusion to achieve higher pattern fidelity. Strategies under investigation include sensitization effects using oxide nanoparticles, metal-complex-type PAGs, and acid amplifiers—systems in which an initially generated acid acts catalytically to trigger further decomposition, leading to exponential amplification of acid production. Polymer-tethered PAGs have also been developed for suppressing diffusion and localizing acid, which are critical for simultaneously improving resolution and sensitivity.

4. Expansion into biological and medical applications

Irreversible PAGs enable photoacid therapy (PAT), and combinations with chemotherapeutics are being explored for tumor suppression. Fluorescent BODIPY-based PAGs can drive local acidification under LED irradiation and show activity against drug-resistant bacteria. Reversible photoacids (e.g., merocyanines, HPTS) allow pH to be switched reversibly with light exposure and deactivation, enabling temporally controlled modulation of ATP synthesis and enzyme activity.

References

1. C. J. Martin, et al., *J. Photochem. Photobiol. C: Photochem. Rev.*, **34**, 41–51 (2018).
2. N. Zivic, et al., *Angew. Chem. Int. Ed.*, **58**, 10410–10422 (2019).
3. T. Tsuchimura, *J. Photopolym. Sci. Technol.*, **33**, 15–26 (2020).
4. T. Sun, et al., *Adv. Sci.* **11**, 2302875 (2024).

Future Perspectives and Directions

Next-generation PAGs should combine sensitivity and absorption with short acid diffusion for lithography, while delivering both efficiency and safety for biomedical use. Integrating quantum-chemistry-informed machine learning with green, metal-free designs will accelerate optimization across electronics and bioengineering.

(Authors: Tsumoru Morimoto, Tsuyoshi Kawai)