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Photoacid generators. Application and current state of development

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Photoacid generators are used as components of photocurable polymer formulations and chemically amplified photoresists in microelectronics industry. In recent years, these compounds gained importance as components of various engineering materials. The review presents the classification of photoacid generators and summarizes data on photochemical processes giving photoacids. A special section is devoted to practical applications of photoacid generators and the current state of their development.
The bibliography includes 118 references.

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The following designations and abbreviations are used:
A — acceptor,
D — donor,
3D lithography — three-dimensional lithography,
ET — electron transfer,
EUV lithography — extreme ultraviolet lithography,
GM (Göppert-Mayer) unit — a unit for two-photon absorption, 1 GM = 1×10^{-50} cm^4 s photon^{-1},
hν — quantum of light,
LED — light-emitting diode,
PAG — photoacid generator,
R – H — hydrogen atom donor,
TfO — trifluoromethanesulfonate (triflate),
δ — two-photon absorption cross-section,
ε_{max} — molar absorption coefficient,
Φ_F — fluorescence quantum yield,
Φ_{H+} — quantum yield of acid generation.

1. Introduction

Photoacid generators (PAGs) are compounds that produce acids upon exposure to light

$$\text{PAG} \xrightarrow{h\nu} \text{H}^+ + \text{photoproducts} \quad (1)$$

These compounds should be distinguished from generators of metastable acids, which reversibly release a proton upon irradiation, with a lifetime of a few seconds to hours.[1,2]

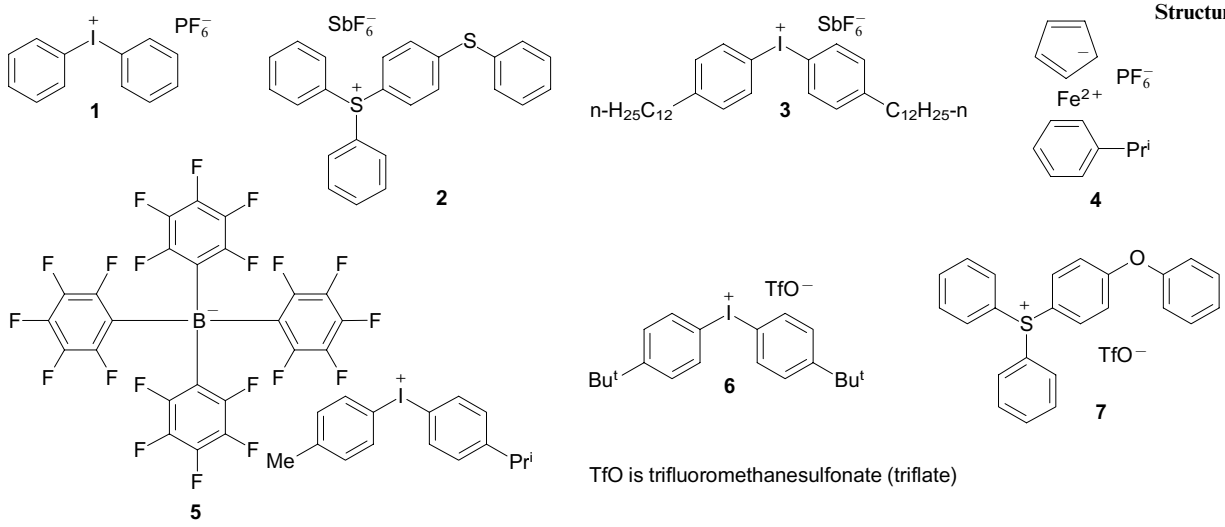
The efficiency of the photochemical generation of acid is defined as the quantum yield Φ_{H^+}. For PAGs, this value is calculated by Eqn (2)

$$\Phi_{H^+} = \frac{\text{number of generated acid molecules}}{\text{number of photons absorbed by photoacid generator}} \quad (2)$$

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Structures 1 – 7



A photoacid generator should have absorption at the excitation wavelength (generally in the UV region) and form a strong acid with high quantum yield.

In the last three decades, PAGs have gained importance as components of various engineering materials. As initiators for cationic photopolymerization of a broad range of vinyl monomers and cyclic compounds, PAGs are involved in photocurable coatings, adhesives, printing inks, varnishes and dental composites.[3–6] Photoacid generators have found increasing use as components of chemically amplified photoresists in microelectronic industry, for 3D printing[7] and the construction of microfluidic systems.[5,8]

In the review published in 1996, Shirai and Tsunooka[9] consider PAGs for cationic polymerization. Recently, Martin *et al.*[10] summarized the results of studies on PAGs performed in the past two decades. They analyzed data on the mechanisms of acid generation from PAGs obtained by laser pulse photolysis and considered development of long-wavelength sensitive PAGs. The present review focuses on the most extensively used photoacid generators and provides examples of their practical applications. Besides, approaches to the development of new PAGs are considered.

2. Classification of photoacid generators

Numerous diverse PAGs are classified into two groups — ionic and non-ionic. Ionic PAGs are composed of a cation and an anion. Onium (diaryliodonium and triarylsulfonium) salts containing BF_4^-, SbF_6^-, AsF_6^-, PF_6^- or RSO_3^- anions are the most widely used PAGs. Examples of commercial ionic PAGs are presented above (structures **1** – **7**). Salts with cations based on triarylselenonium and arene ferrocene derivatives are also known;[9] however, these salts have not been widely applied.

Diaryliodonium-based photoacid generators produce acids with higher quantum yields compared to triarylsulfonium salts. Hence, these PAGs are preferred when a high rate of the process is required, for example, for the manufacturing of photocurable coatings, printing inks and self-adhesive labels. On the other hand, high thermal stability of triarylsulfonium salts is the major factor governing the choice of PAGs for photoresists. Photoresists are subjected to pre- and post-exposure bake, which may impair the image quality in the case of insufficient thermal stability of the onium salt. Besides, the photolysis of diphenyliodonium-containing PAGs affords volatile iodo-substituted aromatic photoproducts, which are deposited on the optics of the equipment used for exposure of photoresists. The photolysis of triphenylsulfonium-based PAGs is not accompanied by the formation of volatile photoproducts.[11]

Numerous non-ionic compounds which generate carboxylic, sulfonic, phosphorus and hydrohalic acids upon exposure to light are described in the literature. The most important compounds of this class are sulfonic acid esters that give strong acids when exposed to light. They include iminosulfonates (**8**),[12–14] imidosulfonates (**9**)[12] and benzyl sulfonates (**10**).[10] Among benzyl sulfonates, only *p*-nitro- and *o*-nitrobenzyl esters of sulfonic acids **11** produce acids when exposed to light,[10,15] the photoacid generation by these isomers occurs through different mechanisms (see Section 3).

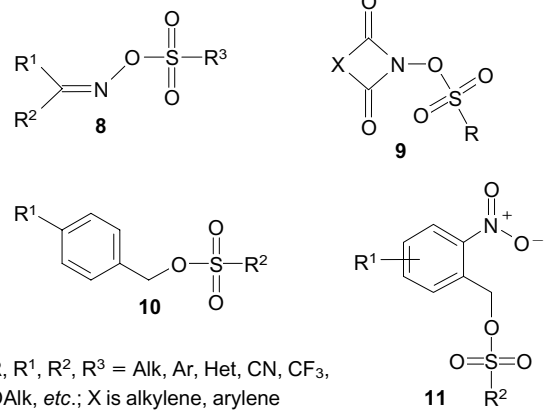
Non-ionic PAGs have higher solubility in organic solvents and polymer films but they are thermally less stable compared to onium salts.

Recently, Traven and Ivanov[16] proposed a new type of photoacid generators, dihydrohetarenes (in the presence of polychloroalkanes), which can be assigned to non-ionic compounds. As opposed to conventional PAGs, which decompose and produce acids under light irradiation, dihydrohetarenes are polychloroalkanes dehydrogenated in the presence of polychloroalkanes to release the acid (HCl).[17] In this group of compounds, 7-dialkylamino-3-(pyrazolin-3-yl)coumarins, including their julolidine analogue **12**

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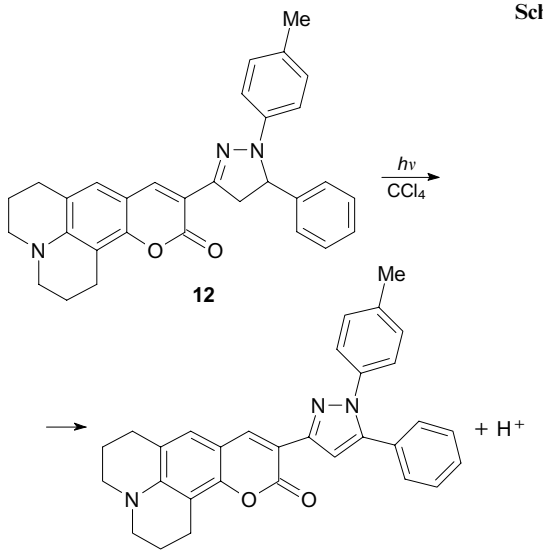
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Structures 8 – 11



(Scheme 1), are distinguished by high photoacid generation rates and two-photon absorption.[18] These compounds are promising for optical data storage and application in biochemical studies.

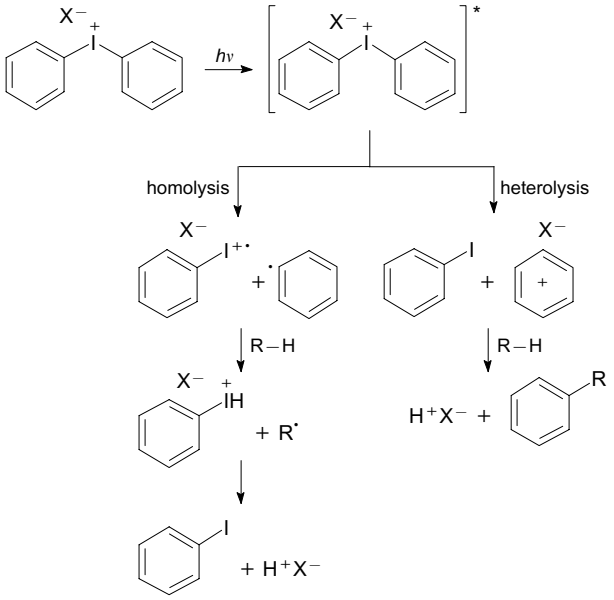
Scheme 1



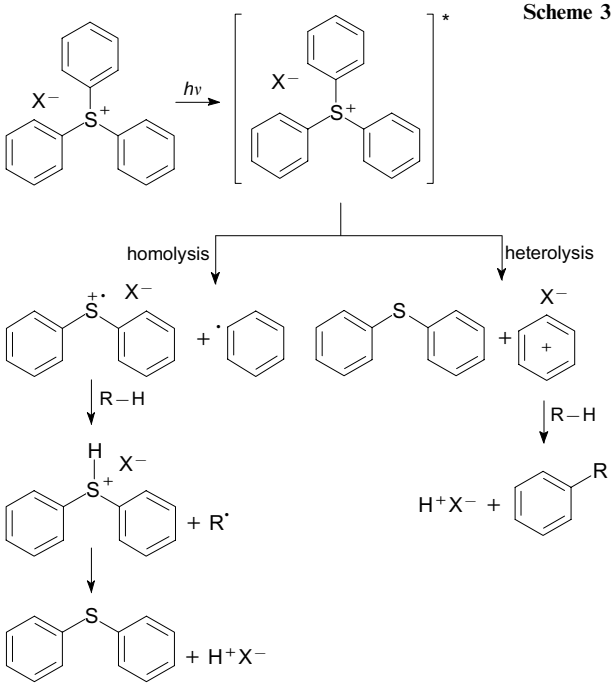
3. Mechanism of photoacid generation

Photochemistry of the most common ionic PAGs, such as diaryliodonium and triarylsulfonium salts, has been studied in detail[19,20] and has general features. The photochemical reaction mechanism for acid generation involves absorption of a light quantum by a salt cation and degradation of the resulting singlet excited state accompanied by the carbon – iodine or carbon – sulfur bond cleavage in the case of diaryliodonium and triarylsulfonium, respectively. The bond cleavage occurs simultaneously by two mechanisms (homolytic and heterolytic), resulting in the fragmentation of the cationic part of PAGs to form free radicals, cations and radical cations. The subsequent dark reactions between these species and with the solvent afford a number of final photolysis products. Both mechanisms involve the interaction with a hydrogen donor (solvent) and the photoacid generation from the anionic part of PAGs. Elementary steps of the acid formation under light irradiation of diaryliodonium and triarylsulfonium salts are presented in Schemes 2 and 3 (X^- is an anion).

Scheme 2

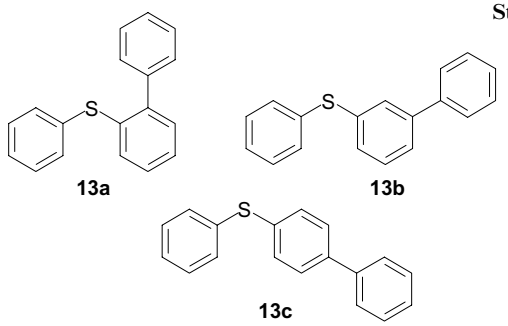


Scheme 3



These schemes include only the transformations giving a photoacid H^+X^-, where X^- is an anion of a strong acid (BF_4^-, SbF_6^-, AsF_6^-, PF_6^-, RSO_3^-). The quantum yields of acid generation through photolysis of onium salts in solution are 0.5 – 0.7,[20,21] whereas these values in real resist systems are lower (0.2 – 0.3).[21] Miscellaneous pathways of transformations of primary radicals, which are produced from an onium salt cation, are not shown in Schemes 2 and 3. Both diphenyliodonium and triphenylsulfonium produce phenyl radicals and cations, which can react with the starting compound, photoproducts, the solvent and oxygen giving mixtures of photolysis products. For example, the reaction of the phenyl radical with diphenyl sulfide (produced *via* photodestruction of triphenylsulfonium) affords

Structures 13

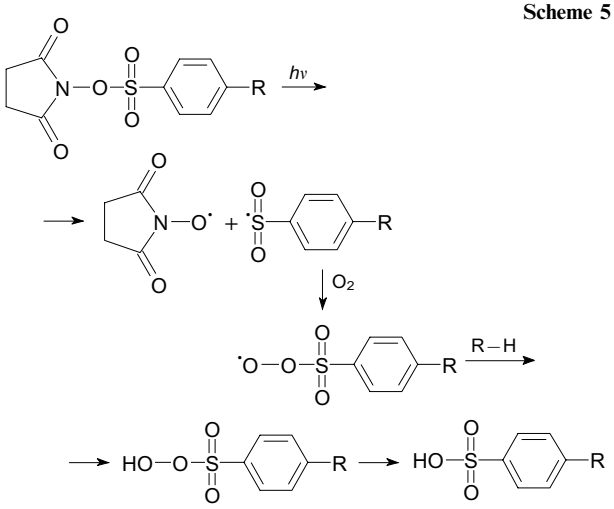


some identified photoproducts, such as isomeric (phenylthio)biphenyls **13a** – **c**.[20]

Under irradiation of non-ionic PAGs, such as iminosulfonates, N-hydroxyimidosulfonates and benzyl sulfonates, acids are formed *via* homolytic N – O, C – O and S – O bond cleavage followed by the hydrogen abstraction from the solvent by radicals.[22,23] The photoreaction occurs through the singlet excited state of PAGs. The formation of the major photolysis products in solutions of iminosulfonates is shown in Scheme 4.[12] The photochemical O – N bond cleavage followed by the hydrogen abstraction from the solvent or the polymer by the $ArSO_3^{\bullet}$ radical gives sulfonic acids. The process also involves the transformation of iminium radicals. The reaction of iminium radicals with oxygen predominates in the photolysis of these compounds in a polymer matrix in air.

The homolysis of many non-ionic PAGs affords $ArSO_2^{\bullet}$ radicals. Besides, sulfonic acids are released through the reaction of $ArSO_2^{\bullet}$ with oxygen.[24,25] This process with imidosulfonates is shown in Scheme 5. Recently, Torti *et al.*[26] demonstrated that the photolysis of aryl tosylates leads to homolytic $ArO-SO_2C_6H_4Me$-4 bond cleavage accompanied by generation of $^{\bullet}SO_2C_6H_4Me$ radicals. Apart from acids, such as 4-toluenesulfinic acid in deaerated solutions or stronger 4-toluenesulfonic acid in the presence of oxygen, the photolysis gave phenols and photo-Fries rearrangement products. The laser flash photolysis study showed that the ArO – S bond cleavage occurs through the singlet excited state. The photolysis of substrates containing a nitro group involves the competitive

Scheme 5



intersystem crossing to the triplet excited state as the predominant process, thereby suppressing the photoacid generation.

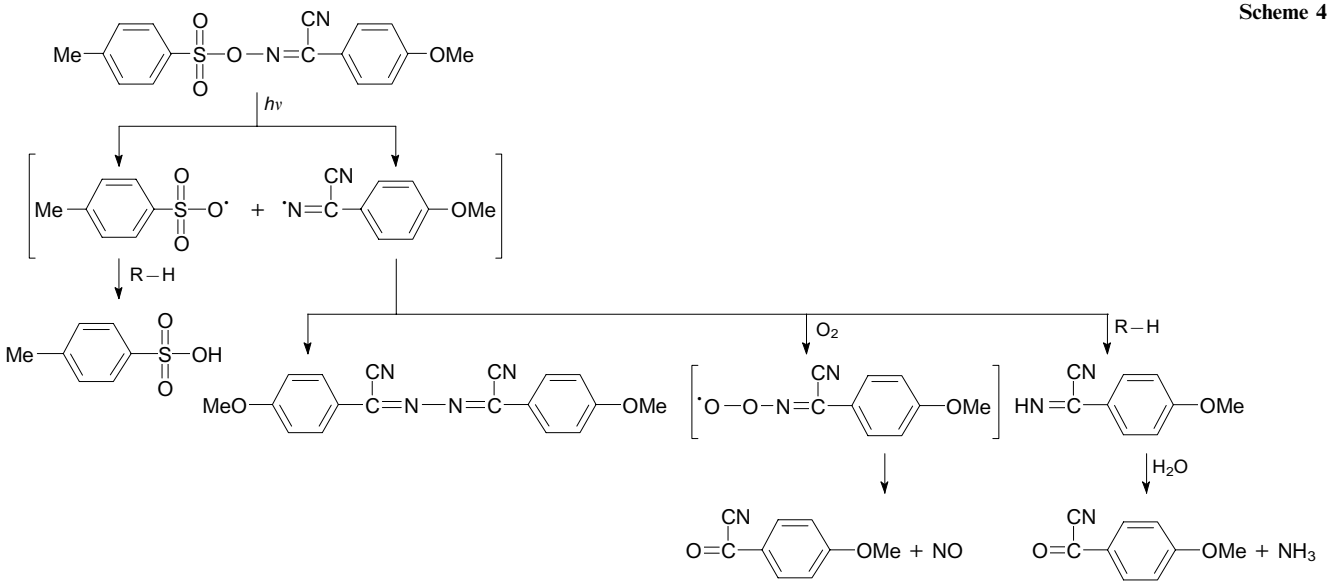
The quantum yields of acid generation from imino- and imidosulfonates vary from 0.23 to 0.46 depending on the structure.[14,22–24]

The mechanism of acid generation in the photolysis of *o*-nitrobenzyl sulfonates differs from that for other sulfonic acid benzyl esters. It involves the intramolecular oxidation of the C – H bond with a nitro group accompanied by the reduction of the latter to the nitroso group (Scheme 6). The quantum yields vary from 0.05 to 0.16 depending on the nature of substituents at the benzene ring and the wavelength of the excitation.[15]

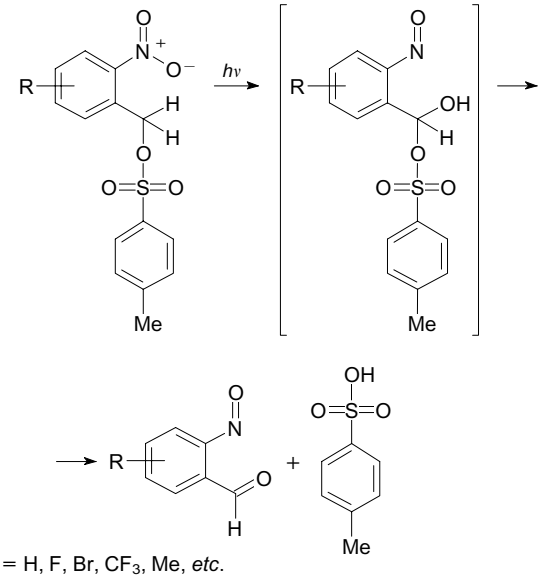
Nakashima *et al.*[27] prepared non-ionic PAGs that generate acids *via* photoinduced cyclization. Scheme 7 presents one of such processes. The quantum yield of acid generation is high (0.47).[28]

Some aspects of the mechanism of photoacid generation by (het)arylpyrazolines in the presence of perchloroalkanes are considered by Traven *et al.*[17] It was shown that oxygen is not involved in the reaction, polar solvents speed up the

Scheme 4

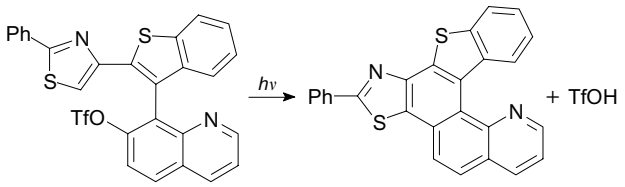


Scheme 6



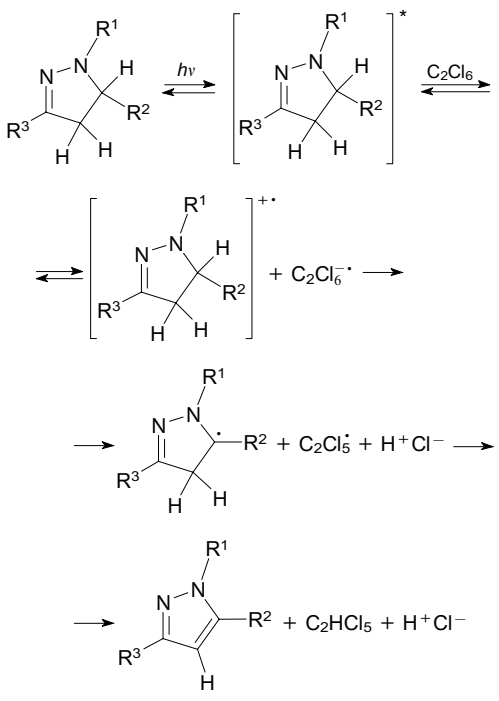
R = H, F, Br, CF_3, Me, *etc.*

Scheme 7



rate of the reaction, and the reaction rate correlates with the calculated first ionization potentials of pyrazolines. Based on these results, the authors proposed the mechanism of acid generation. It involves the formation of radical ions as intermediates (Scheme 8).

Scheme 8



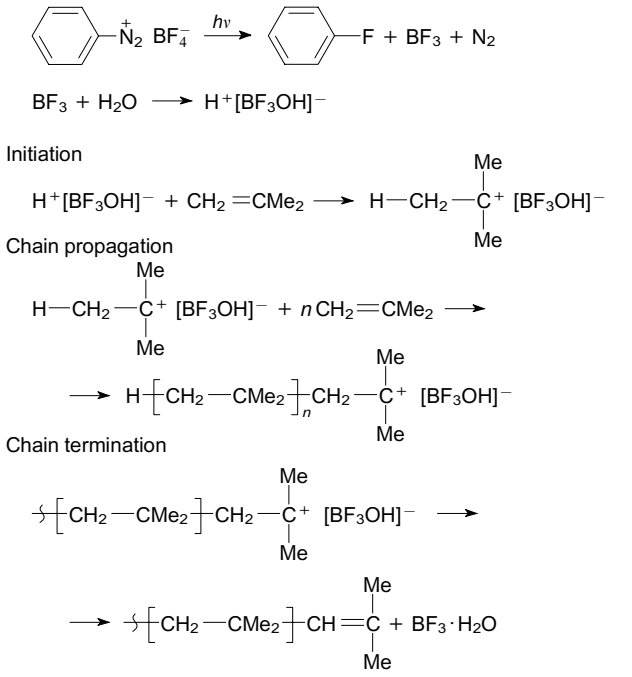
R^1, R^2 = Ar; R^3 is coumarin-3-yl

4. Photoacid generators for cationic photopolymerization

4.1. History of the development of photoacid generators and their application as initiators for cationic photopolymerization

Photoacid generators were first proposed in the 1970s as photoinitiators for cationic polymerization. Schlessinger[29] found that Lewis acids (*e.g.*, BF_3) generated by the photolysis of aryldiazonium salts can be used as photoinitiators for cationic polymerization. Generally, the Lewis acid-initiated cationic photopolymerization requires the presence of cocatalysts (water, alcohols, ethers) that form complexes with the catalyst. The reaction mechanism is exemplified in Scheme 9 for the cationic photopolymerization of isobutylene.

Scheme 9



The quantum yields of photodecomposition of aryldiazonium salts are rather high (they generally vary from 0.3 to 0.6).[19] However, the cationic photopolymerization initiated by this class of PAGs is not widely used because of thermal instability of these compounds and the release of molecular nitrogen in the course of the reaction, giving rise to defects in films.[19]

The breakthrough in technology and application of PAG-initiated cationic photopolymerization was achieved in 1980, when thermally quite stable diaryliodonium and triarylsulfonium salts were proposed as photoacid generators. Numerous compounds of these classes were synthesized. Photoacid generators with SbF_6^- and PF_6^- anions that produce superacids are most commonly applied. Compounds **1** – **4** are examples of this type of commercial photoinitiators. Ionic PAGs (*e.g.*, compounds **6** and **7**) capable of generating Brønsted acids (mainly trifluromethanesulfonic acid) by the photolysis are also widely used in cationic photopolymerization.

Properties of ionic PAGs depend on the nature of both ions. The cationic part absorbs light and is responsible for photochemistry. Hence, the structure of the cation should

be optimized with respect to the following parameters: the efficiency of absorption of excitation light, the quantum yield of photoacid generation and thermal stability. The nature of the anion is responsible for the strength and diffusion of the photoacid, its initiating ability, polymerization kinetics and the character of chain termination.

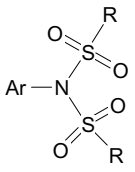
Photoacid generators are employed to initiate cationic polymerization of various monomers, including compounds of the vinyl series and compounds that undergo ring-opening polymerization. The use of onium salts as photoinitiators has resulted in an ever-increasing range of applications of photopolymerizable materials in many engineering processes. Numerous PAGs were structurally modified to tailor the solubility, reactivity and spectroscopic parameters for different technologies and sources of radiation.

The photopolymerization of epoxy-modified silicones intiated by PAGs **3** and **5** is an example of the large-scale industrial use of PAGs with tailored solubility and reactivity. This technology (Scheme 10) is employed to fabricate carriers for self-adhesive labels.[5] Alkyl substituents at the benzene rings of diphenyliodonium cations in these PAGs significantly improve their solubility and compatibility with silicone oligomers and polymers.[5] The $B(C_6F_5)_4^-$ anion (salt **5**) is weakly coordinating. It is not prone to form ion pairs, thereby accelerating photopolymerization[30] and the fabrication of silicone label carriers.[31]

Recently, Narcross *et al.*[32] reported the synthesis of triarylsulfonium-based epoxide-functionalized PAGs capable of participating in the cationic polymerization of epoxides.

Torti *et al.*[33] proposed N-aryl sulfonimides **14** as photoinitiators for cationic polymerization. Advantages of these compounds are their easy accessibility (facile synthesis from aniline derivatives) and the ability to generate photoacid in an amount of 2 equiv. per equivalent of the starting photoinitiator.

Structure 14



14

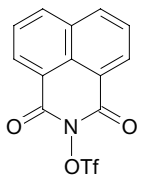
4.2. Current state of development of photoacid generators for cationic photopolymerization

Diaryliodonium and triarylsulfonium salts containing substituted and unsubstituted phenyl groups generally absorb light at 220 – 350 nm. The spectral sensitivity of diaryliodonium salts is low. For example, the simplest representative of this series, diphenyliodonium, has an absorption maximum at 227 nm. Trihenylsulfonium triflate has absorption maxima at 235 nm [the molar extinction coefficient (ε_{max}) = 18 600 L mol^{-1} cm^{-1}], 267 nm (ε_{max} = 3925 L mol^{-1} cm^{-1}) and 275 nm (ε_{max} = 2772 L mol^{-1} cm^{-1}).[21] The recently fabricated long-lasting and cost effective light-emitting diodes (LEDs) with a wavelength from 365 to 470 nm are currently widely used in apparatus for photocuring of polymers. This stimulated research on the extension of the spectral sensitivity range of onium salts to longer wavelengths. There are two main approaches to solve this problem: the introduction of a sensitizer into a formulation and the extension of the spectral sensitivity of PAGs by means of structural modification.

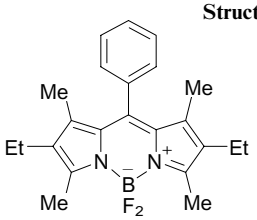
The long-wavelength sensitization of PAGs occurs by an intermolecular photoinduced electron transfer from the sensitizer to PAG. Consequently, the sensitizer in the excited state should reduce PAG, namely, the onium salt cation. Here it should be taken into account that the reduction potentials of diaryliodonium and triarylsulfonium are ~ -5 and -28 kcal mol^{-1}, respectively.[5] Hence, diaryliodonium PAGs are more easily long-wavelength sensitized compared to triarylsulfonium PAGs.

The possibility of extending the sensitivity range of conventional PAGs to longer wavelengths in the presence of photosensitizers was demonstrated in several publications. Suzuki *et al.*[34] reported the formation of trifluoromethanesulfonic acid upon photodecomposition of

Structures 15, 16

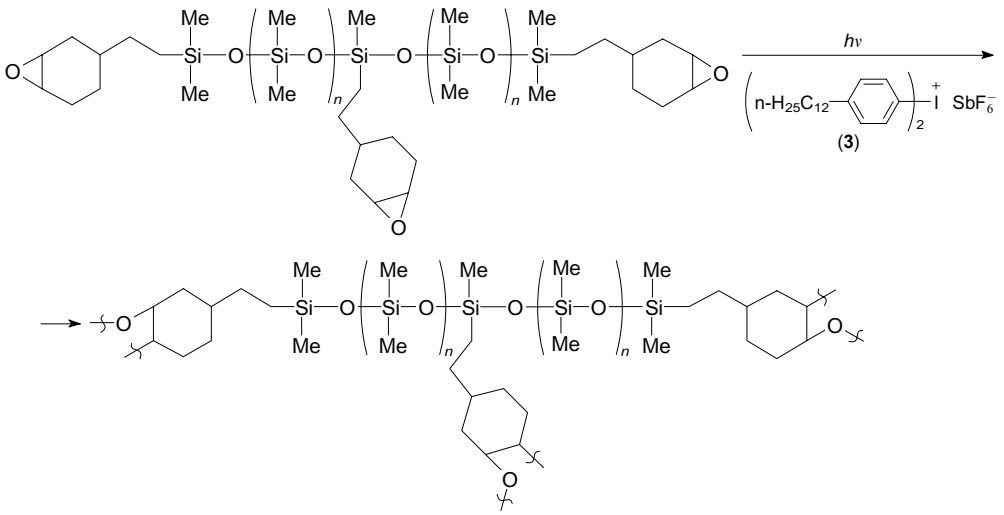


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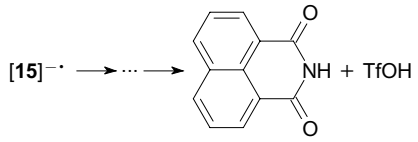


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Scheme 10



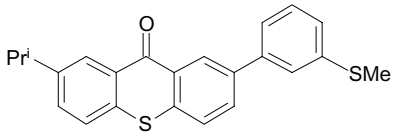
Scheme 11



N-hydroxynaphthalimide triflate (**15**) sensitized by pyrromethene dye **16** (Scheme 11). The electron transfer occurs from the singlet excited state of the sensitizer. The triplet state of the dye is not involved in the photoinduced electron transfer to naphthalimide.

Thioxanthone derivative **17** sensitizes diphenyliodonium hexafluorophosphate as PAG to LED radiation in the range of 405 – 450 nm.[35]

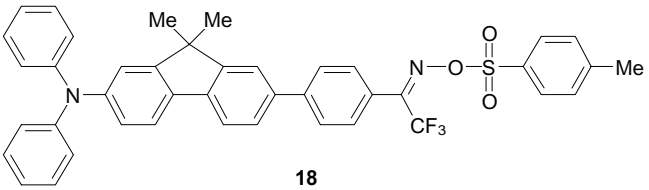
Structure 17



17

The spectral sensitivity range was extended directly for PAGs. For this purpose, a π-conjugated system is introduced into PAGs between an electron-donating site (generally di- or triphenylamino groups) and an electron-withdrawing site, thereby stabilizing the intramolecular photoinduced charge transfer. A series of D – π – A-type PAGs (D is a donor, A is an acceptor, π is a system of conjugated bonds), both ionic [36, 37] and non-ionic,[38, 39] were synthesized. Compound **18** is an example of D – π – A-type non-ionic PAGs.[39]

Structure 18



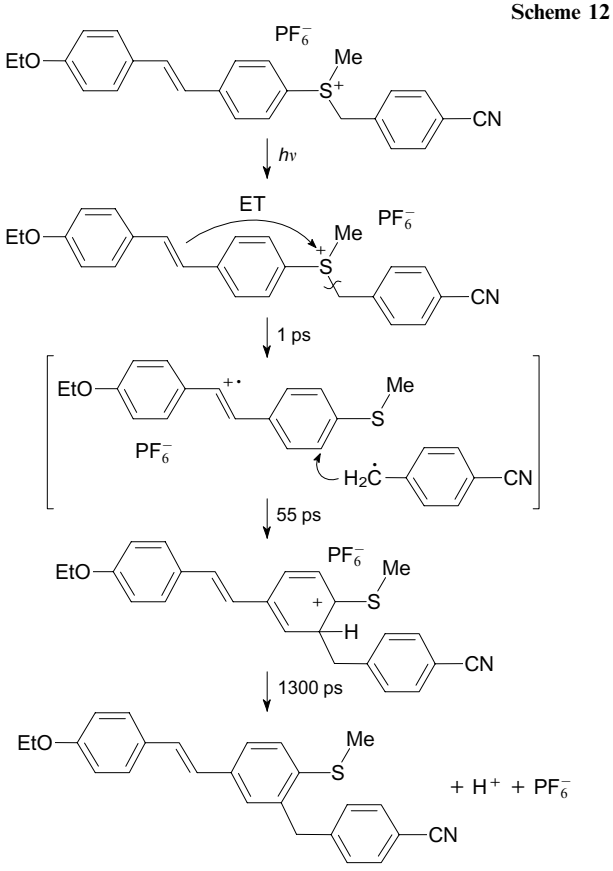
18

The absorption spectra of D – π – A-type sulfonium salts well match with the emission spectrum of LEDs, the appropriate photoacid being efficiently generated from these salts under LED irradiation. The yield of the photoacid increases in the presence of strong electron-donating groups, specific π-conjugated systems and electron-withdrawing substituents.[36]

Femto- and nanosecond laser flash photolysis was used to kinetically and spectrally resolve all successive elementary steps of the photoinduced proton generation by D – π – A-type sulfonium salts (Scheme 12). Waele *et al.*[37] confirmed that the mechanism of photoacid generation involves the intramolecular photoinduced charge transfer as the first step.

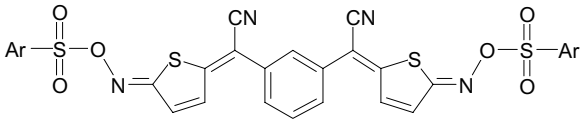
Recently, Sun *et al.*[40] proposed non-ionic PAGs with a long thiophene-containing conjugated system. An example is structure **19**. Light-emitting diode irradiation

Scheme 12



ET is electron transfer

Structure 19



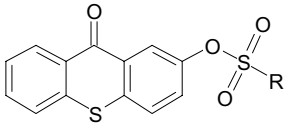
19

(λ = 365 – 475 nm) of these PAGs leads to generation of arylsulfonic acids with a good quantum yield.

The introduction of a chromophore with an appropriate absorption spectrum into a PAG molecule is worth noting among other approaches to the development of PAGs spectrally adapted to LED sources. An example is the development of non-ionic PAG **20** containing the thioxanthone ring.[41]

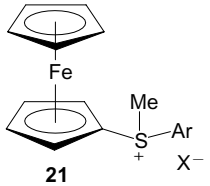
Takahashi *et al.*[42] reported the synthesis of ferrocene-based sulfonium salts **21** sensitive to visible light at λ = 436 nm.[42] The quantum yields of photoacid generation

Structures 20, 21



20

R = CF_3, n-C_8F_{17}



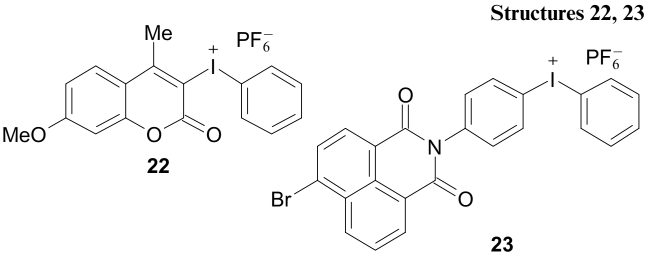
21

X = BF_4, PF_6, BPh_4^F

are at most 0.1;[42] however, these compounds are rare examples of ferrocene derivatives behaving as PAGs.

The replacement of one of the benzene rings in an iodonium salt with a coumarin-based chromophore (structure **22**) leads to a shift of the long-wavelength absorption band of PAGs to 350 nm.[43] The same results can be obtained by introducing bromo-substituted naphthalimide into the diphenyliodonium cation (compound **23**).[44] Chromophore-modified iodonium salts **22** and **23** initiate the cationic photopolymerization under LED irradiation at 395 nm.

Structures 22, 23



5. Photoacid generators for chemically amplified photoresists

5.1. Characteristic features of photoacid generators for photoresists

The development of PAGs for cationic photopolymerization made it possible to subsequently fabricate chemically amplified photoresists for modern microelectronics industry.

Photoresists are light-sensitive polymer materials, the physicochemical properties of which are changed upon exposure to light. When a positive photoresist is exposed to light, it becomes more soluble in the photoresist developer. After the development, the positive photoresist forms a resist pattern on a substrate with a desired accuracy. A negative pattern is created by a negative photoresist, when the exposed areas become less soluble in the developer. The developed areas of the substrate are then subjected to etching, metallization or any other treatment required for semiconductor device fabrication.

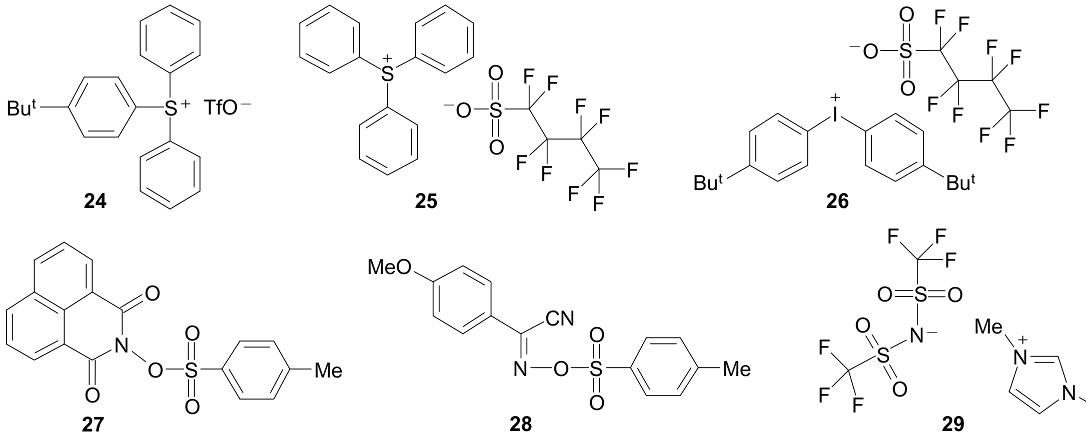
Both positive and negative PAG-containing photoresists are known. They function on the so-called chemical amplification principle proposed in 1982.[45,46] However, it took more than ten years to design the first commercial photoresist of this type. Currently, chemically amplified photoresists capture a large part of the market of these materials.

The term 'chemical amplification' arises from the fact that each photochemically generated acid molecule acting as a catalyst promotes numerous successive chemical transformation events in the photoresist film, thereby significantly increasing its sensitivity to actinic radiation. The resist pattern formation includes the exposure, post-exposure bake and development. During the exposure, the photolysis of PAG that is present in the resist formulation generates an acid. During the post-exposure bake, acid-catalyzed transformations involving functional groups of the polymer component, such as depolymerization, intramolecular dehydration, cross-linking, deprotection of acidic groups and so on, lead to a change in the polarity of the polymer and the chemical nature of its dissolution. The typical number of catalytic cycles per molecule of the resulting acid is ~ 1000. The subsequent development of the latent image yields a positive or negative relief image depending on the type of the photoresist and the developer.

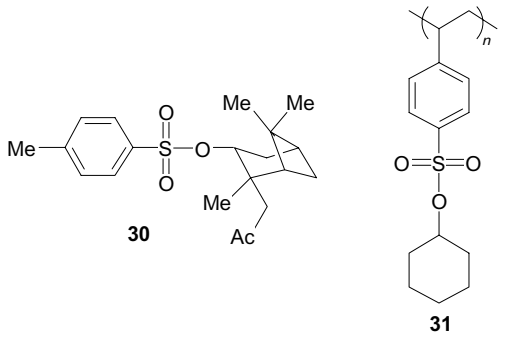
Photoacid generators used in photoresists should meet certain requirements. Thus, diphenyl[4-(phenylthio)phenyl]-sulfonium hexafluoroantimonate (**2**), the most popular PAG for cationic polymerization, is utilized as a photoinitiator for cross-linking in the photoresist SU-8.[47] However, PAGs containing SbF_6^- or PF_6^- anions generally dope the substrate and, consequently, are little used in photoresists. Chemically amplified photoresists involve onium salts of organic acids and non-ionic PAGs that generate sulfonic acids (*e.g.*, *p*-toluenesulfonic acid) or stronger organofluorine acids (*e.g.*, trifluoromethane- or perfluorobutanesulfonic acids) *via* photolysis. Let us refer to structures **24** – **29** as examples of commercially available PAGs for photoresists.

When choosing PAGs for photoresists, consideration should be given to numerous factors, such as the nature of radiation, quantum efficiency of generation and the strength of photoacid, the number of catalytic cycles, solubility and compatibility with the polymer, thermal and hydrolytic stability, the plasticizing effect, toxicity, the diffusion rate in the polymer matrix, the effect on dissolution rate behaviour of the photoresist film, the cost, *etc.* Chemically amplified photoresists are highly sensitive to actinic radiation; nevertheless, it may be additionally enhanced by introducing so-called acid amplifiers to the formulation.[48–51] An acid amplifier is a compound that undergoes acid-induced decomposition during post-exposure bake, resulting in the formation of an additional

Structures 24 – 29



Structures 30, 31



30 **31**

amount of the acid. Compound **30** (Ref. 49) and polymer **31** (Ref. 51) can be mentioned as examples of acid amplifiers.

5.2. Classification and examples of chemically amplified photoresists

Chemically amplified photoresists are classified according to the mechanism of image formation based on the cross-linking of a film-forming polymer, cationic polymerization or deprotection of acidic groups.

In the first commercial chemically amplified photoresist, the cross-linking of a film-forming polymer was used to produce a negative image. This photoresist is a three-component system composed of a novolac resin, PAG and a cross-linking agent. The acid is generated from PAG under irradiation and catalyzes the cross-linking of phenolic resin under dark conditions at ~110 °C. The resulting 3D structure is insoluble in an aqueous alkaline developer. Scheme 13 shows the mechanism of these transformations using PAG **28**.[52] In state-of-the-art resists, the photoacid-catalyzed cross-linking of phenolic resin is the dominant mechanism by which a negative image is formed. For example, the domestic negative photoresist FN-16U (Refs 53 – 55) and the photoresist AZ nLOF 2000 manufactured by MicroChemicals are employed for the metallization of a substrate by lift-off lithography.

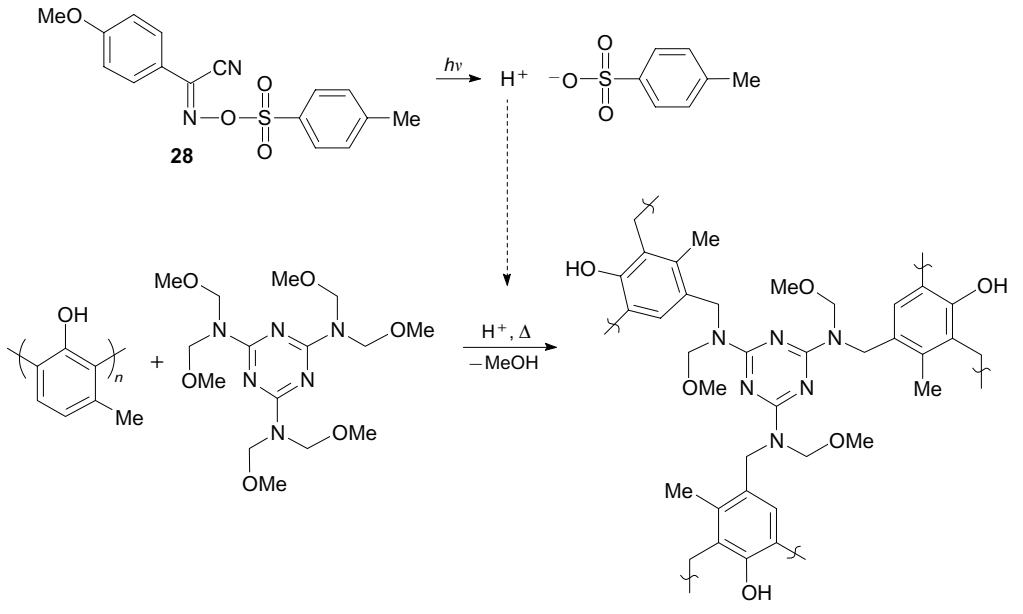
The photoresist SU-8 (MicroChemicals) operates by the cationic polymerization mechanism and is available as formulations that cover a film thickness range from 2 to 300 μm.[47] This photoresist is used for the creation of microfluidic devices,[56, 57] the fabrication of models by 3D photolithography,[47] pixel networks, printheads of jet printers and so on. The SU-8 composite includes the epoxidized Bisphenol A-based oligomer and diphenyl[4-(phenylthio)-phenyl]sulfonium hexafluoroantimonate (**2**) (Scheme 14). When exposed to light, PAG decomposes to form hexafluoroantimonic acid, which protonates epoxy groups of the oligomer. The protonated oxonium ions react with neutral epoxy groups in a series of cross-linking reactions on heating.[47]

A number of proposed photoresists contain PAGs directly inserted into a film-forming polymer and operate by the cationic polymerization mechanism (Scheme 15).[4]

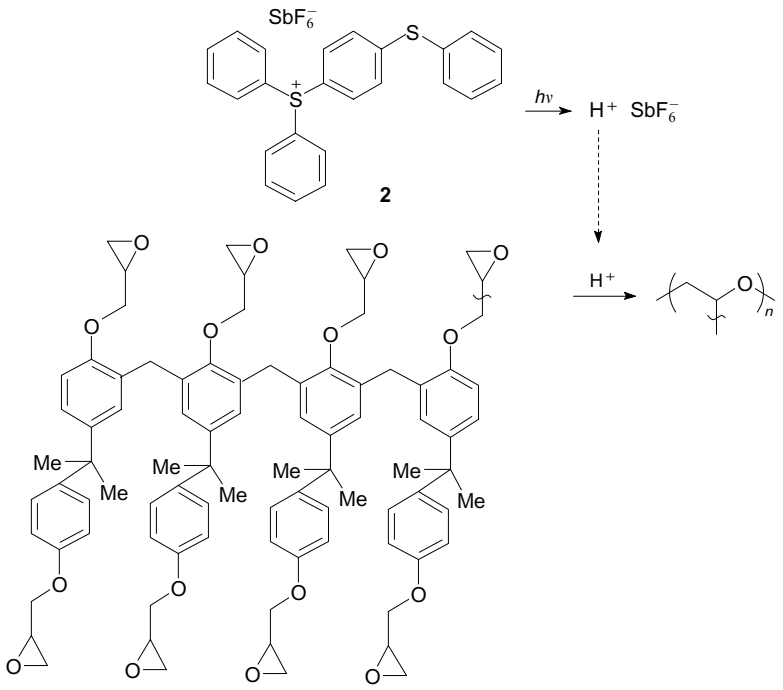
Chemically amplified positive photoresists for submicron photolithography, where images are formed by KrF and ArF excimer laser radiation (λ = 248 nm and 193 nm, respectively),[45] take a large part of the market of photoresists. Polymers of these photoresists contain protected acidic groups (hydroxystyrene groups or carboxylic acid moieties, *e.g.*, a methacrylic acid moiety). The deprotection of acidic groups changes the polarity of the polymer, thereby providing high solubility contrast between the exposed and unexposed areas. The development of these areas in an aqueous alkaline solution produces a positive image. Tertiary aliphatic or alicyclic ester moieties, the *tert*-butoxycarbonyl group, ketal and acetal moieties are generally used as protecting groups. Upon irradiation, a PAG in photoresist film generates an acid, and the latter catalyzes the cleavage of acid-labile protected groups of the polymer, generally at high temperature.

Molecular resists for next-generation lithography, EUV lithography (extreme ultraviolet lithography) using radiation at λ = 13.5 nm, also operate by the chemical amplification mechanism.[58] The difference is that the acid is generated upon interactions between PAGs and electrons, which are produced by ionization of the photoresist material (mainly, of the film-forming component), as opposed to KrF or ArF excimer laser lithography, where the acid is generated by direct absorption of a quantum of light by the photogenerator.

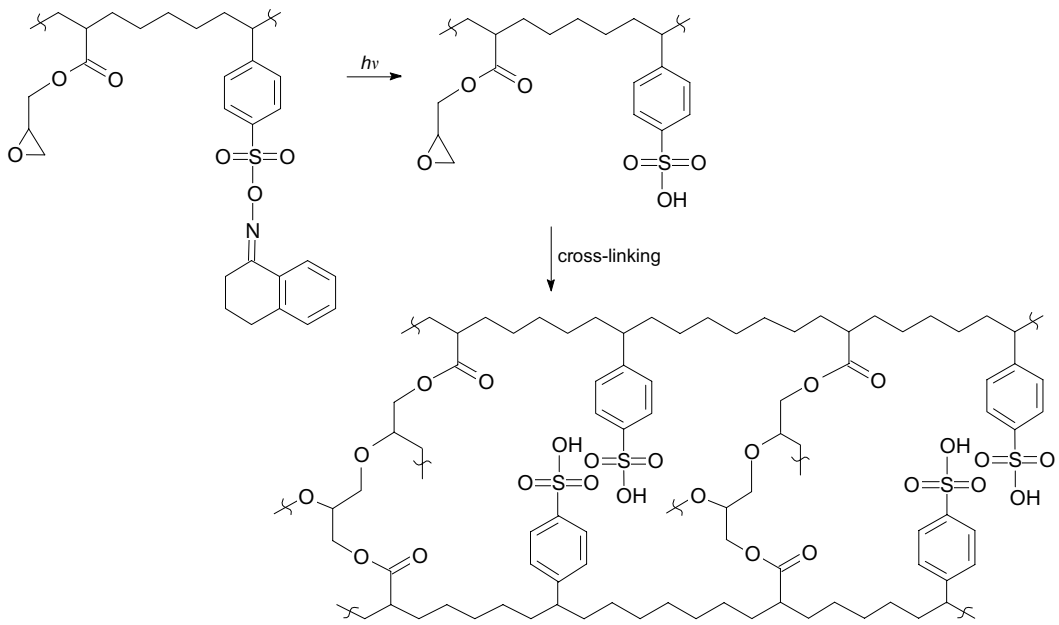
Scheme 13



Scheme 14



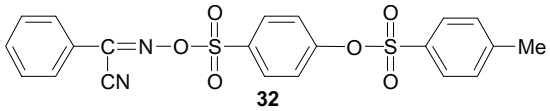
Scheme 15



The cleavage of ketals and acetals is characterized by a low activation energy. In this case, arylsulfonic acids generated by readily soluble iminosulfonates, *e.g.*, compound **32**, are utilized as PAGs.[59]

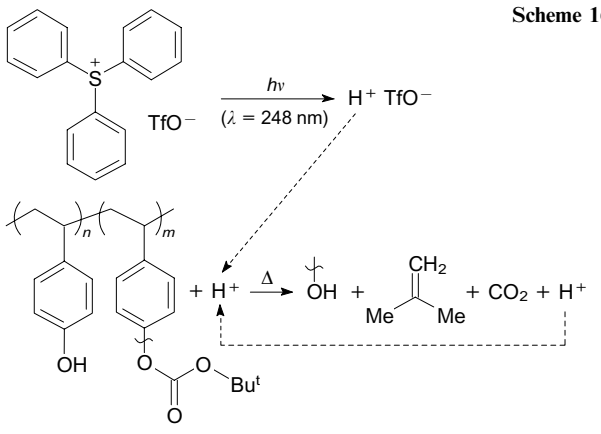
The acidic cleavage of tertiary esters with a high activation energy requires photoacid generators of superacids, such as perfluorosulfonic or arylsulfonic acids activated by electron-withdrawing substituents.

Structure 32

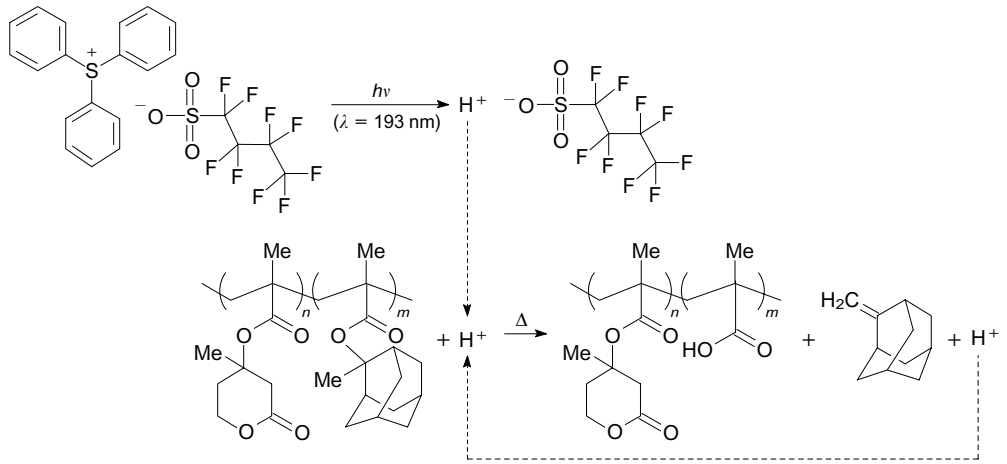


32

Scheme 16



Scheme 17

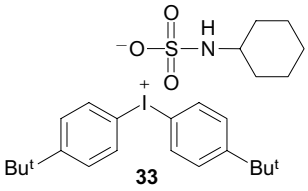


The deprotection of protected groups in typical polymers for photoresists sensitive to KrF and ArF excimer laser radiation is shown in Schemes 16 and 17, respectively.

It should be noted that all commercial chemically amplified photoresists contain a base component comprising from 10 mol.% to 20 mol.% of PAGs.[60] The base is added to bind small amounts of the acid, generated during storage, in the regions exposed to low doses of radiation and also the acid that diffuses to unexposed regions. This improves the contrast and resolution and increases the storage time of the photoresist.

The base moiety may be a part of the photoacid structure. Examples are photodegradable aminosulfonates, *e.g.*, compound **33**, capable of generating free N-substituted sulfamic acids.[61] These compounds can be employed as PAGs in photoresists with a low activation energy for deprotection of protected groups.

Structure 33

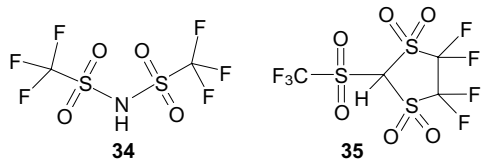


33

5.3. Current trends in the development of photoacid generators for photoresists

The currently used chemically amplified positive photoresists generally contain tertiary aliphatic or alicyclic ester moieties as protected acidic groups of the polymer. The cleavage of these groups requires high activation energy. *p*-Toluenesulfonic acid, which is generated by a broad range of available PAGs, proved to be insufficiently strong for catalysis. The process occurs in the presence of stronger acids, so-called superacids (*e.g.*, hexafluoroantimonic and hexafluorophosphoric acids) commonly used for photocuring of polymers. However, it is highly undesirable to introduce compounds containing boron, antimony or phosphorus atoms into the photoresist because these elements are silicon-doping impurities. Hence, it was recognized that the application of generators of strong fluorine-containing alkyl(aryl)sulfonic acids, bis(fluoroalkylsulfonyl)imides **34** and tris(fluoroalkylsulfonyl)methides **35**, which act as superacids due to the strong effect of electron-withdrawing perfluoroalkylsulfonyl groups, is a key factor for the development of chemically amplified positive photoresists. Photoacid generators capable of generating trifluoromethane-, perfluorobutane-, perfluorohexane- and perfluorooctanesulfonic acids are described in a patent.[62] In this series, trifluoromethanesulfonic acid is the most easily accessible one. A broad range of photoacid generators of this acid, which differ in the nature of the cationic part (*e.g.*, compounds **6**, **7** and **24**), are available in the world market.

Structures 34, 35

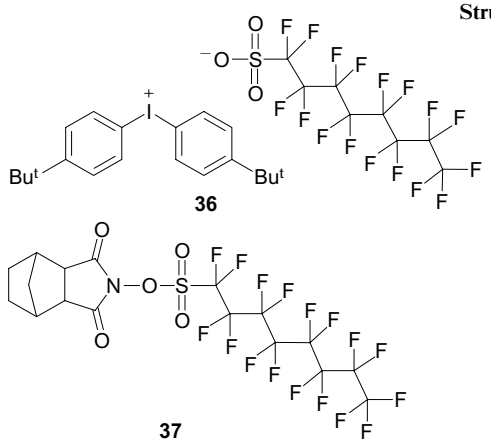


34 **35**

In chemically amplified photoresists, the photoacid molecule diffuses into the photoresist film and catalyzes hundreds of chemical transformations. The photoacid can migrate from exposed to unexposed regions, thereby causing alteration of the feature size and line-edge roughness.[63] This alteration is not significant when fabricating features with sizes >100 nm. However, in the case of smaller features, the diffusion of small trifluoromethanesulfonic acid significantly impairs the image quality. Different approaches are proposed to retard photoacid diffusion. The most evident one is to use PAGs that generate bulkier acids.

A patent[62] addresses photoacid generators that can generate perfluoroalkylsulfonic acids (perfluorobutane-, perfluorohexane- and perfluorooctanesulfonic acids) with longer perfluoroalkyl groups compared to trifluoromethanesulfonic acid. Foreign manufacturers offer a variety of photoacid generators of perfluorobutanesulfonic acid, in particular triphenylsulfonium perfluorobutanesulfonate (**25**) and bis(4-*tert*-butylphenyl)iodonium perfluorobutanesulfonate (**26**). It is worth noting that topological structures with a 16 nm line and space width can be produced by EUV nanolithography operating at 13.5 nm with molecular photoresists based on photoacid generators of perfluorobutanesulfonic acid.[64, 65] Even bulkier perfluorooctanesulfonates, *e.g.*, bis(4-*tert*-butylphenyl)iodonium perfluorooctanesulfonate (**36**), are not widely used. One of the factors that limit the application of such photoacid generators of

Structures 36, 37



36

37

perfluoroalkylsulfonic acids with long perfluoroalkyl groups is their low solubility. This drawback can be overcome either by modification of the cationic part of PAGs,[66] making the product much more expensive, or by employing mixtures with higher solubility (see, *e.g.*, the patent [67]), for example, a mixture of ionic bis(4-*tert*-butylphenyl)iodonium perfluorooctanesulfonate (**36**) and non-ionic norbornenedicarboximide perfluorooctanesulfonate **37**.

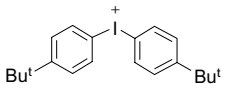
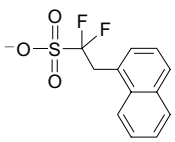
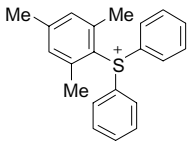
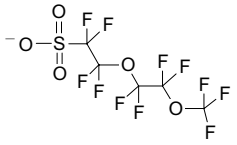
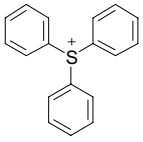
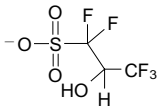
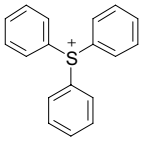
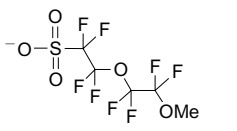
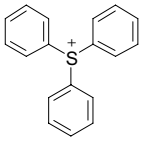
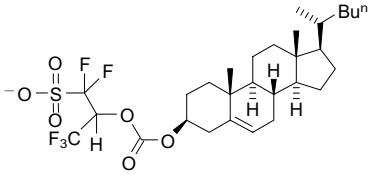
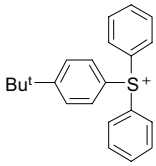
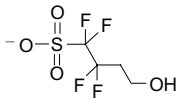
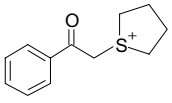
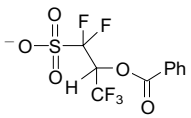
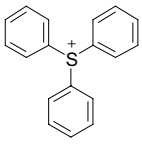
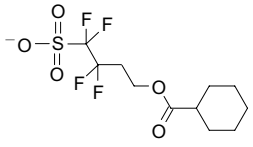
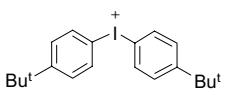
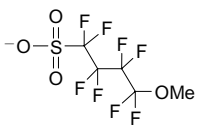
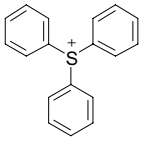
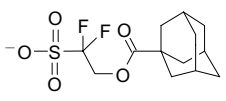
However, high chemical stability of perfluoroalkylsulfonic acids is a more serious problem than low solubility. For this reason, perfluorooctane-containing sulfonate and its salts are included in the list of restricted chemicals under Annex B of the Stockholm Convention on Persistent Organic Pollutants (production and use of chemicals in Annex B should be eliminated, except for 'acceptable purposes').[68] All perfluoroalkylsulfonic acids and their derivatives containing five or more carbon atoms are non-biodegradable and, due to high hydrophobicity, can accumulate in living organisms and the environment.

The problem of chemical stability of perfluoroalkylsulfonic acids has forced researchers to look for biodegradable PAGs as components of photoresists in a series of partially fluorinated alkylsulfonic acids. The optimization of the alkyl moiety in compounds containing the CF_2 group in the α position to the sulfo group, with retaining the strength of the acid, makes it possible to enhance the solubility of PAGs. The structures of such photoacid generators (compounds **38** – **47**) are given in Table 1.

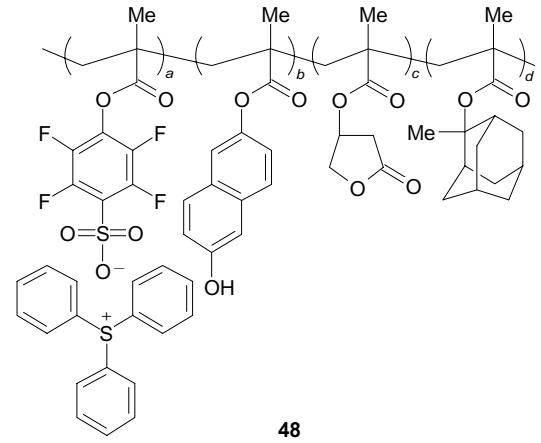
The covalent grafting of PAGs to film-forming polymers can also be employed to limit the photoacid diffusion. The most commonly used photoacid generators are ionic onium salts. These salts can be bound to a polymer through either a cation or anion. The grafting of a cation gives a little effect [78, 79] because an acid generated upon exposure is not bound to the polymer and is prone to diffusion, like in the case of free PAG. The incorporation of the anionic part of PAG into a polymer not only prevents photoacid diffusion [80, 81] but also offers many other advantages, for example, eliminates segregation of PAG in photoresist formulations, reduces outgassing giving rise to defects in films [82] and also reduces swelling.[83]

Structures **48** (Ref. 81) and **49** (Ref. 84) are examples of covalent grafting of the PAG anion to a film-forming polymer. The quantum yields of acid generation by photoacid generators incorporated into a film-forming polymer are high (0.5 – 0.8).[85]

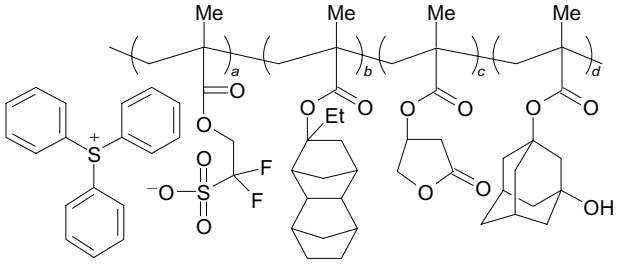
Table 1. Structures of photoacid generators of biodegradable partially fluorinated sulfonic acids **38** – **47**.

Compound	Cation	Anion	Ref.	Compound	Cation	Anion	Ref.
38			69	**43**			73
39			70	**44**			74
40			70	**45**			75
41			71	**46**			76
42			72	**47**			77

Structures 48, 49



48

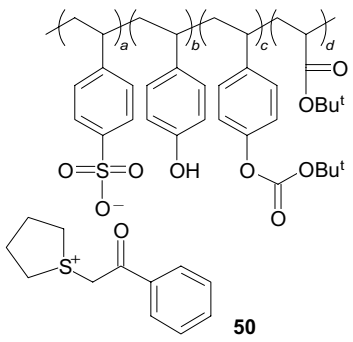


49

The covalent grafting of PAGs to a polymer significantly improves the properties of the photoresist, making it possible to achieve 15 – 20 nm resolution using electron-beam lithography or extreme ultraviolet photolithography.[81, 86, 87]

Polymer **50** is characterized by accessibility and exceptionally high resolution under exposure to KrF laser pulses (λ = 248 nm).[88]

Structure 50



50

Apart from the anion size, intermolecular interactions play a very important role in controlling photoacid diffusion.[63, 89] To utilize this principle, Kang *et al.*[90] synthesized hydroxyl-containing PAG $CF_3CH(OH)CF_2SO_3^-H^+$. The acid diffusion is restricted due to hydrogen bonding with other components of the photoresist. Besides, this PAG has such advantages as biodegradability and the facile method of synthesis.

The addition of weak (*e.g.*, carboxylic) acids was also proposed to inhibit photoacid diffusion. It was assumed that a salt exchange between weak and strong photoacids limits acid diffusion in the photoresist film.[91]

6. Miscellaneous applications of photoacid generators

In recent years, new applications of photoacid generators were developed, including stereolithography, two-photon data recording and biochemical assays.

6.1. Stereolithography and two-photon 3D lithography

Stereolithography is a 3D prototyping technique for the layer-by-layer fabrication of 3D structures from liquid photopolymerizable composites upon exposure to laser light. Stereolithography mainly utilizes conventional, including PAG-containing, negative photoresists used in semiconductor industry. The application of the photoresist SU-8 in stereolithography is mentioned in Section 5.2. The development of specific PAGs is required for 3D laser lithography based on two-photon polymerization to fabricate nanoscale structures (3D printing).[8]

In two-photon lithography, the chain polymerization of components of a liquid formulation is triggered only by the simultaneous absorption of two light quanta by PAGs. This unlikely process can take place exclusively at the centre of the focused laser beam or at the intersection of two laser beams in a nanometre-scale volume, where the highest photon density is achieved. The photoacid generation process considered in this Section should be distinguished from the photoacid generation by sequential (rather than simultaneous) absorption of two light quanta — by the main and intermediate states of PAGs.[92, 93] It is worth noting that both one- and two-photon excitation give the same excited state, which is a transient state in the photochemical reaction yielding acid. However, the efficiency of the two-photon process is determined, apart from Φ_{H^+}, by the two-photon absorption cross-section (δ) at the operating wavelength.

Commercially available PAGs have a low effective two-photon absorption cross-section in the near-IR region, which is employed in femtosecond laser-induced two-photon polymerization.[94] This entailed the development of new approaches for photoinitiated acid generation. One of these approaches is based on infrared sensitization of conventional PAGs using dyes with a higher effective two-photon absorption cross-section. In these systems, the intermolecular electron transfer occurs from the excited state of the sensitizing dye, which is generated by two-photon absorption, to PAG. The electron transfer induces the decomposition of PAG giving acid. Examples of such sensitizers are dyes **51** and **52**.[95]

Another approach is based on the development of PAGs with high δ at a femtosecond laser excitation wavelength (λ = 780 nm). Such compounds should absorb light with a wavelength two times shorter ($\sim$390 nm) than the laser excitation wavelength. The intramolecular charge transfer is known as the driving force for two-photon absorption,[96] which requires the presence of electron-donating and electron-withdrawing moieties in the molecule and a coplanar conjugated system between them. Therefore, PAGs sensitive to long-wavelength two-photon excitation were designed using bipolar D – π – A push-pull systems and symmetrical A – π – A, D – π – D and D – π – A – π – D chromophores. Symmetrical structures belong to quadrupolar systems composed of two branches with intramolecular charge transfer from the periphery to the centre (or *vice versa*). These compounds have higher absorption coefficients and

approximately two times higher values of δ compared to one-branch analogues.

Steidl *et al.*[97] synthesized symmetrical PAG **53**, which contains electron-withdrawing groups at the terminal benzene rings responsible for polarization of the molecule. This compound has a satisfactory two-photon absorption cross-section. When combined with IR sensitizer **54**, PAG **53** initiates two-photon cationic polymerization of a negative photoresist.

A series of A – π – A compounds containing diphenylsulfonium and nitro groups as acceptors were synthesized in order to prepare two-photon PAGs based on styryl-substituted fluorene.[98] The photoacid quantum yields of these PAGs are from 0.01 to 0.3 (for compound **55**),[98] the yields being increased with increasing length of the conjugated system.

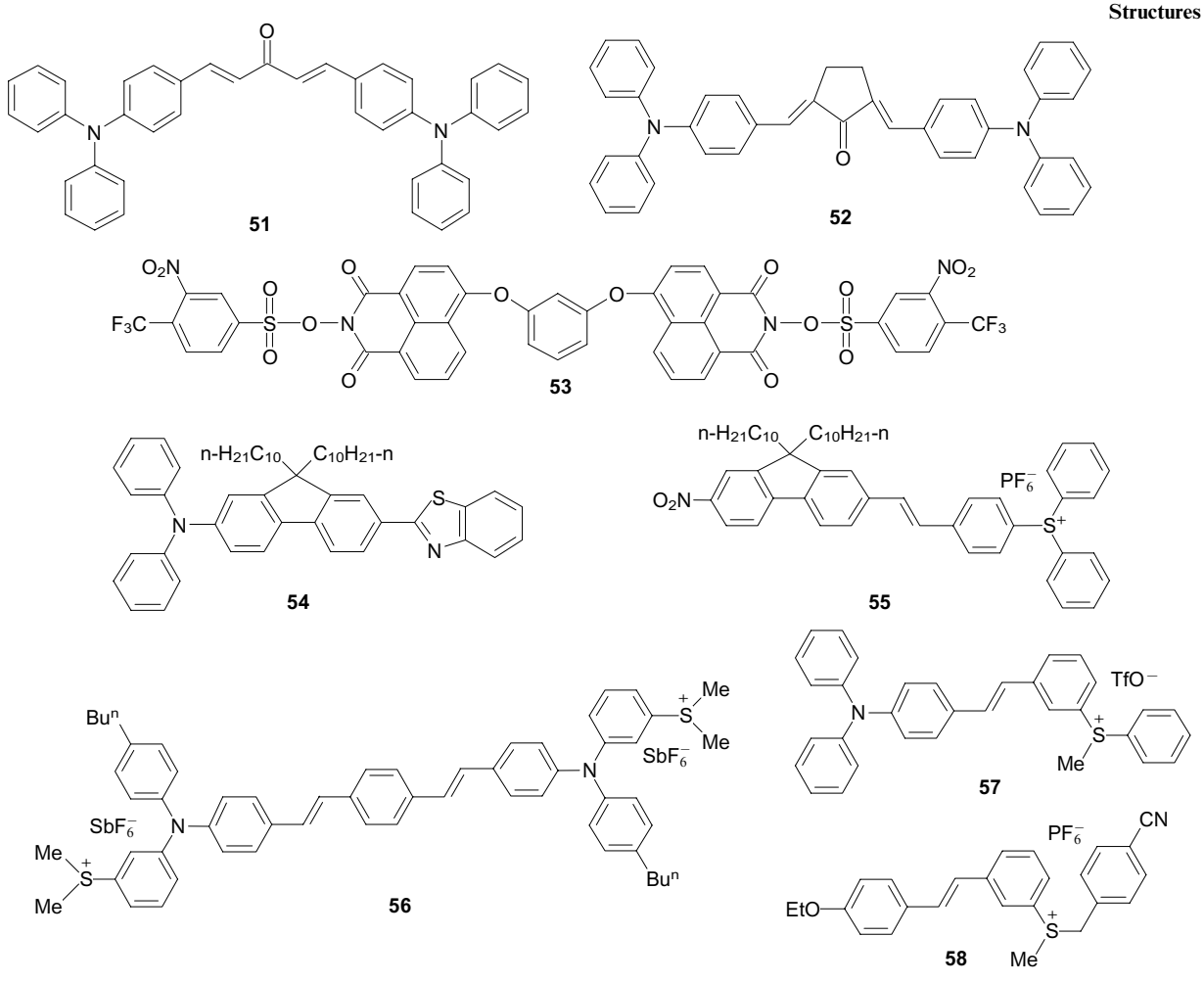
The design of D – π – D-type PAG **56** exhibiting the highest two-photon sensitivity was reported.[99, 100]

Unsymmetrical bipolar D – π – A molecules hold promise as compounds with a high two-photon absorption cross-section.[96] The synthesis of such PAGs was described.[101, 102] Compounds **57** and **58** exhibited high two-photon photoacid generation efficiency.

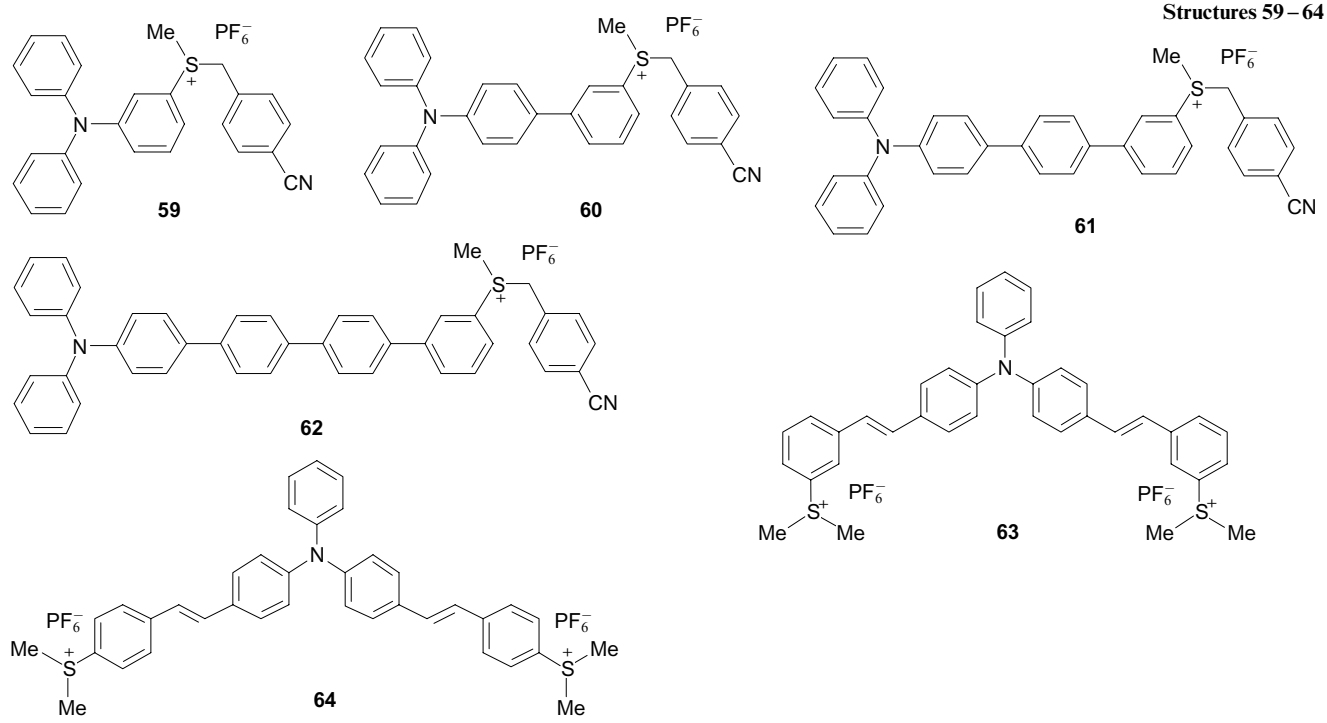
Jin *et al.*[103] synthesized a series of two-photon D – π – A-type PAGs (compounds **59** – **62**) with a conjugated system of different length consisting of a chain of benzene rings (from one to four). Compound **60** is characterized by a significant red shift (by 52 nm) of the long-wavelength absorption band compared to compound **59**, whereas a further increase in the number of benzene rings in the conjugated system leads to a modest long-wavelength shift of the band (by 5 and 2 nm for analogues **61** and **62**, respectively). Compounds **60** – **62** absorb in the 350 nm region corresponding to the LED emission spectrum. The photoacid quantum yields for PAGs **60** and **61** have unprecedented values (0.69 and 0.73, respectively).[103] Compounds **59** – **62** exhibit high efficiency as cationic photoinitiators of polymerization and also have a high two-photon absorption cross-section at > 700 nm. Therefore, these compounds hold promise in 3D printing of microstructures. As expected, an increase in the length of the conjugated system in the series of compounds **59** – **61** leads to an increase in the two-photon absorption cross-section. However, the latter value is somewhat lower when using PAG **62** apparently due to the deviation from coplanarity as a result of rotation of the benzene rings with respect to each other.

Wu *et al.*[104] synthesized A – π – D – π – A-type compounds **63** and **64**. These compounds have high cross-sections (δ = 745 and 816 GM, where 1 GM = 1×10^{-50} cm^4 s photon^{-1})[104] characteristic of branched structures. However, compound **63** generates acid with moderate quantum yield (0.40) in acetonitrile, whereas Φ_{H^+} for *para*-substituted isomer **64** is low (0.004).[104] Hence, the latter compound cannot be used for this purpose. Meanwhile, *meta*-analogue **63** shows efficiency as a photoinitiator of two-photon polymerization of epoxides induced by light at λ = 780 nm.

Structures 51 – 58



Structures 59 – 64



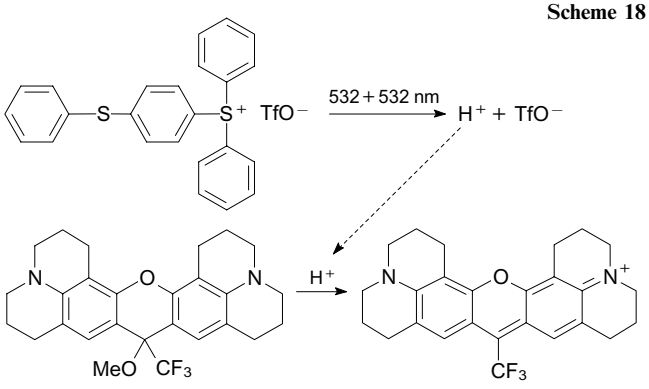
6.2. Use of photoacid generators in materials for fluorescence readout-based 3D optical data storage systems

Photoacid generators are components of materials proposed for archival storage in optical memory devices, including 3D optical memory elements for ROM (read only memory) devices.

The construction of 3D optical memory for archival storage applications requires the development of a light-sensitive recording medium with non-destructive readout. Recording media with fluorescence readout,[105] which are based on irreversible photochemical transformations of organic compounds into products with high fluorescence quantum yield (Φ_F), are of great interest for the development of these materials. In most of such media, colourless leuco compounds (precursors) are transformed into coloured fluorescent dyes in the presence of an acid generated from PAG at sites exposed to a particular radiation dose.[106 – 108] Photoacid generators used for this purpose should have high Φ_{H^+} and should be thermally stable and readily soluble in a polymer matrix. In the case of two-photon 3D optical recording, suitable for ultrahigh density recording, PAGs also should have high δ at the recording wavelength.

Rentzepis and co-workers[106, 107] utilized conventional PAGs (sulfonium salts, 1-nitro-2-naphthaldehyde) for the development of recording media for 3D optical data storage with fluorescence readout. Photoacid generators and a precursor of a fluorescent dye (generally rhodamine) were immobilized in a polymethacrylate matrix. The one- or two-photon excitation of a photoacid generator produces acid, which reacts with the precursor, resulting in its transformation into the fluorescent form. Scheme 18 shows transformations involved in the archival data recording in the material developed by Rentzepis and co-workers[107] based on sulfonium salt and the methoxy derivative of the laser dye rhodamine 700 as the precursor. Data were recorded using two-photon excitation with a picosecond laser pulse at

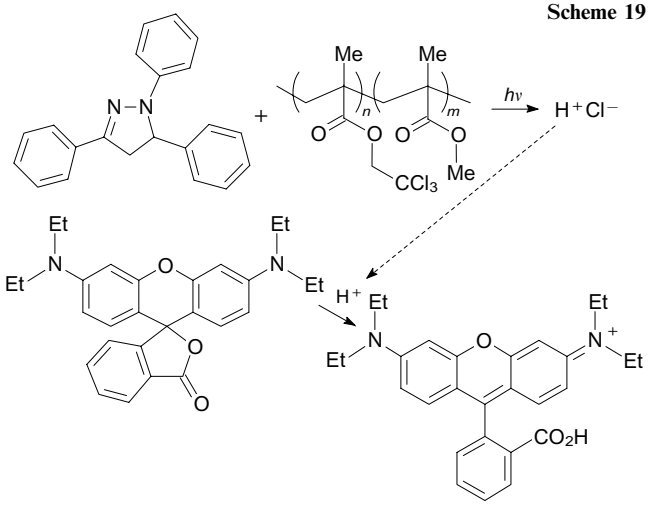
Scheme 18



λ = 532 nm. The system is characterized by high sensitivity. The data can be stored on a disc for years without changes.

The research team headed by Traven[109] patented a similar light-sensitive polymer material with fluorescence

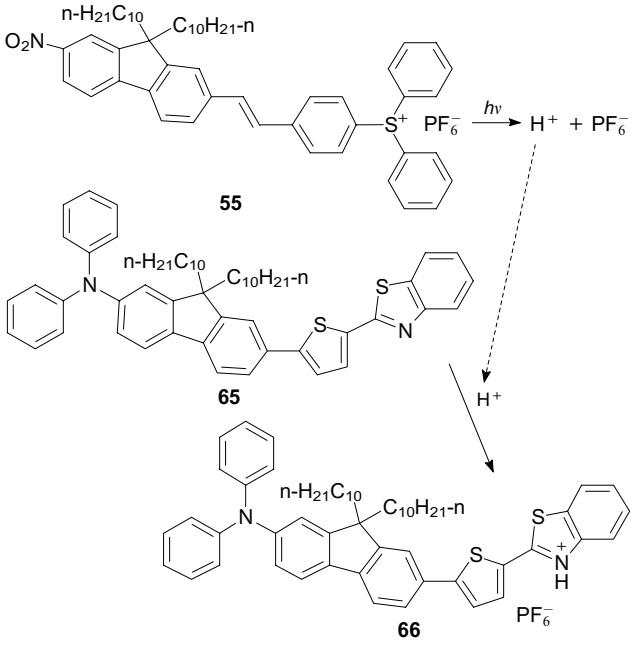
Scheme 19



readout. In this material, a pyrazoline – chloroalkane system with a copolymer of methyl methacrylate and 2,2,2-trichloroethyl methacrylate (polymer matrix) as chloroalkane serves as PAG. Scheme 19 gives an example of data recording, involving the lactone ring opening and the formation of highly fluorescent rhodamine B initiated by the acid that is generated by the pyrazoline – chloroalkane system under irradiation.

Yanez *et al.*[110] used both PAG and a dye (Scheme 20), which were developed for two-photon excitation, for data recording with fluorescence readout. Compound **55** generates acid with $\Phi_{H^+} = 0.40$. The data were recorded using two-photon excitation of PAG with laser irradiation at $\lambda = 710$ nm ($\delta_{710\ nm}$ is 240 GM for compound **55**).[110] Upon protonation with photoacid, dye **65** is transformed into **66**, which has high Φ_F (0.86) and δ at the readout wavelength ($\delta_{860\ nm} = 132$ GM).[110] This enables both one- and two-photon readout. The two-photon readout has advantages over the one-photon process since it provides better data readout over the whole volume of the 3D recording medium. The maximum recording storage density is *ca.* 1.8×10^{13} bit cm^{-3} (Ref. 110).

Scheme 20



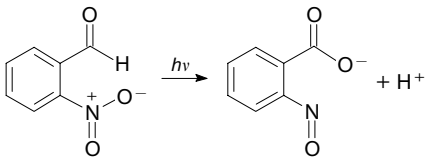
6.3. Use of photoacid generators in biology

Recently, three two-photon PAGs were tested as agents for photodynamic therapy of malignant tumours.[111] As opposed to conventional photodynamic therapy, where cytotoxic singlet oxygen is generated by a sensitizer, the cancer cell death in the proposed approach is induced by means of a pH imbalance caused by the acid generated by two-photon PAG. The long-wavelength radiation employed for two-photon excitation penetrates more deeply into tissues, which is important for therapy of cancer. Another advantage of utilization of PAGs in photodynamic therapy is that necrosis is independent of the presence of oxygen in tumour tissues.

In assays, HCT 116 adenocarcinoma cells were incubated overnight in phosphate buffer containing solubilized PAG. The photoacid generator was found to accumulate in tumour cells. Then the cell culture was irradiated with femtosecond laser pulses at $\lambda = 710$ nm, and the cell viability was evaluated. The best results were obtained for PAG **55**. Thus, lysosomal pH in cells decreased to < 4.5, resulting in necrotic cell death. It should be noted that the cell death was not observed in the presence of compound **55** without irradiation or upon irradiation in the absence of compound **55**. Fadhel *et al.*[112] modified compound **55** with polyethylene glycol and grafted it to aminopropylated silica nanoparticles. The viability of HCT 116 cells was approximately halved after incubation with these agents and irradiation, the efficiency of silica-grafted PAG **55** being higher than that of ungrafted PAG. Therefore, sulfonium-based PAGs were first demonstrated to be promising agents for photodynamic therapy.

Photoacid generators are increasingly used in biology. For example, the sectioning of the cell monolayer was performed by irradiating the monolayer on a PAG-modified polymer substrate. After cell death caused by pH imbalance in lines exposed to a certain rather low dose, sectioned monolayers of cells that remained viable with a size corresponding to the projected grid pattern are collected.[113] Photodegradable membranes for drug encapsulation and delivery were fabricated based on polymers grafted with PAGs.[114] Free PAGs are extensively used to study the response of various biochemical processes to changes in pH.[115–118] For example, Kohse *et al.*[118] used the intramolecular photorearrangement of 2-nitrobenzaldehyde to 2-nitrosobenzoic acid accompanied by proton release and pH change (Scheme 21) to activate acid phosphatase. It is suggested that this process can be applied to control the activity of other enzymes.

Scheme 21



7. Conclusion

Currently, PAGs are utilized as important components of many engineering materials. They also serve as components of photocurable polymer composites and chemically amplified photoresists and are applied in other fields.

Available PAGs used as photoinitiators for cationic photopolymerization generally meet the needs of modern photocuring technologies for polymers. The development of new PAGs for these purposes is aimed to extend their spectral sensitivity range to longer wavelengths corresponding to radiation of new cost-effective light sources — light-emitting diodes (LED).

Photoacid generators of trifluoromethanesulfonic acid are utilized in chemically amplified photoresists with a resolution > 100 nm. These PAGs are made by many foreign manufacturers. Photoacid generators of commercially available perfluorobutanesulfonic acid are generally suitable for photoresists with a resolution up to 20 nm (for EUV lithography). The development of new PAGs is performed along two lines of research. The first approach is based on the creation of photoacid generators with the general formula $RCF_2SO_3^-H^+$, in which the R group ensures solubility of PAGs in solvents for photoresists, low diffusion in a film-forming polymer and biodegradability.

There are several approaches to the fabrication of such structures. However, their synthetic accessibility is still an open issue. Another approach is based on the grafting of PAGs to film-forming polymers. Here a number of problems remain to be solved. In particular, it is unknown how PAGs grafted to the polymer influence the morphology of the photoresist. Despite the fact that this type of photoresists is not used in practice, many manufacturers initiated research and development work in this field.

Compounds that not only have high acid quantum yield and other properties depending on the specific features of their application, but also have a high two-photon absorption cross-section are required to realize the full potential of PAGs in two-photon 3D photolithography.

The new field of application of PAGs is their use in biology and medicine, for example, for the suppression of cancer cell growth and studies of the response of biochemical processes to changes in pH.

Evidently, the development of innovative materials which tailor the spectroscopic properties, solubility and reactivity for state-of-the-art technologies will give rise to new fields of application of PAGs in the nearest future.

References

1. Y.Liao. *Acc. Chem. Res.*, **50**, 1956 (2017)
2. V.K.Johns, P.K.Patel, S.Hassett, P.Calvo-Marzal, Y.Qin, K.Y.Chumbimuni-Torres. *Anal. Chem.*, **86**, 6184 (2014)
3. *Handbook of Photochemistry and Photophysics of Polymer Materials*. (Ed. N.S.Allen). (Hoboken, NY: Wiley, 2010)
4. J.P.Fouassier, J.Lalevee. *Photoinitiators for Polymer Synthesis: Scope, Reactivity and Efficiency*. (New York: Wiley, 2013)
5. J.V.Crivello, E.Reichmanis. *Chem. Mater.*, **26**, 533 (2014)
6. L.Song, Q.Ye, X.Ge, A.Misra, C.Tamerler, P.Spencer. *RSC Adv.*, **6**, 52434 (2016)
7. G.Fang, H.Cao, L.Cao, X.Duan. *Adv. Mater. Technol.*, **3**, 1700271 (2018)
8. A.A.Otroshchenko, I.Yu.Makarikhin. *Vestn. Perm. Univ., Fiz.*, **2** (36), 9 (2017)
9. M.Shirai, M.Tsunooka. *Prog. Polym. Sci.*, **21**, 1 (1996)
10. C.J.Martin, G.Rapenne, T.Nakashima, T.Kawai. *J. Photochem. Photobiol., C*, **34**, 41 (2018)
11. E.Reichmanis, O.Nalamasu, F.M.Houlihan, A.H.Gabor, M.O.Neisser, M.J.Bowden. *Mat. Res. Soc. Symp. Proc.*, **584**, 23 (2000)
12. M.Shirai, H.Okamura. *Prog. Org. Coat.*, **64**, 175 (2009)
13. Patent US 6916591 (2005)
14. M.Yamamoto, S.Takahara. *J. Photochem. Sci. Technol.*, **31**, 643 (2018)
15. F.M.Houlihan, O.Nalamasu, J.M.Kometani, E.Reichmanis. *J. Imaging Sci. Technol.*, **41**, 35 (1997)
16. V.F.Traven, I.V.Ivanov. *Russ. Chem. Bull., Int. Ed.*, **57**, 1063 (2008)
17. V.F.Traven, D.A.Cheptsov, M.V.Bulanova, N.P.Solovjova, T.A.Chibisova, S.M.Dolotov, I.V.Ivanov. *Photochem. Photobiol.*, **94**, 659 (2018)
18. V.F.Traven, D.A.Cheptsov, G.V.Vershinina, N.P.Solovjeva, T.A.Chibisova, S.M.Dolotov, I.V.Ivanov. *J. Photochem. Photobiol., A*, **351**, 8 (2018)
19. J.V.Crivello. *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 4241 (1999)
20. J.L.Dektar, N.P.Hacker. *J. Am. Chem. Soc.*, **112**, 6004 (1990)
21. Q.Lin. *IBM Research Report. Properties of Photoresist Polymers*. RC23689(W0508-036), August 5, 2005
22. P.A.Arnold, L.E.Fratesi, E.Bejan, J.Cameron, G.Pohlers, H.Liu, J.C.Scaiano. *Photochem. Photobiol. Sci.*, **3**, 864 (2004)
23. J.P.Malval, S.Suzuki, F.Morlet-Savary, X.Allonas, J.P.Fouassier, S.Takahara, T.Yamaoka. *J. Phys. Chem. A*, **112**, 3879 (2008)
24. F.Ortica, C.Coenjarts, J.C.Scaiano, H.Liu, G.Pohlers, J.F.Cameron. *Chem. Mater.*, **13**, 2297 (2001)
25. E.Torti, S.Protti, D. Merli, D. Dondi, M.Fagnoni. *Chem. – Eur. J.*, **22**, 16998 (2016)
26. E.Torti, G.Della Giustina, S.Protti, D. Merli, G.Brusatin, M.Fagnoni. *RSC Adv.*, **5**, 33239 (2015)
27. T.Nakashima, K.Tsuchie, R.Kanazawa, R.Li, S.Iijima, O.Galangau, H.Nakagawa, K.Mutoh, Y.Kobayashi, J.Abe, T.Kawai. *J. Am. Chem. Soc.*, **137**, 7023 (2015)
28. R.Li, T.Nakashima, T.Kawai. *Chem. Commun.*, **53**, 4339 (2017)
29. S.I.Schlessinger. *Polym. Eng. Sci.*, **14**, 513 (1974)
30. N. Klikovits, P.Knaack, D. Bomze, I. Krossing, R.Liska. *Polym. Chem.*, **8**, 4414 (2017)
31. F.Castellanos, J.P.Fouassier, C.Priou, J.Cavezzan. *J. Appl. Polym. Sci.*, **60**, 705 (1996)
32. H.Narcross, B. Sharp, L.Tolbert, C.Henderson. *J. Vac. Sci. Technol. B*, **35**, Art. ID 06GE02 (2017)
33. E.Torti, S.Protti, M.Fagnoni, G.D.Giustina. *Chem. Select*, **2**, 3633 (2017)
34. S.Suzuki, X.Allonas, J.P.Fouassier, T.Urano, S.Takahara, S.Yamaoka. *J. Photochem. Photobiol., A*, **181**, 60 (2006)
35. X.Wu, M.Jin, J.-P.Malval, D.Wan, H.Pu. *J. Polym. Sci., Part A: Polym. Chem.*, **55**, 4037 (2017)
36. X.Wu, M.Jin, J.Xie, J.-P.Malval, D.Wan. *Chem. – Eur. J.*, **23**, 15783 (2017)
37. V.De Waele, M.Hamm, T.Vergote, H.Chaumeil, M.Jin, J.-P.Malval, P.Baldeck, O.Poizat. *Chem. Mater.*, **27**, 1684 (2015)
38. X.Wu, M.Jin, J.Xie, D.Wan, J.-P.Malval. *Chin. J. Polym. Sci.*, **34**, 1456 (2016)
39. M.Jin, R.Zhou, M.Yu, H.Pan, D.Wan. *J. Polym. Sci., Part A: Polym. Chem.*, **56**, 1146 (2018)
40. X.Sun, M.Jin, X.Wu, H.Pan, D.Wan, H.Pu. *J. Polym. Sci., Part A: Polym. Chem.*, **56**, 776 (2018)
41. L.Huang, H.Liao, J.Yang, Z. Zeng. *Photochem. Photobiol.*, **367**, 124 (2018)
42. Y.Takahashi, S.Kodama, Y.Ishii. *Organometallics*, **37**, 1649 (2019)
43. H.Mokbel, J.Toufaily, T.Hamieh, F.Dumur, D.Campolo, D.Gigmes, J.Pierre Fouassier, J.Ortyl, J.Lalevee. *J. Appl. Polym. Sci.*, **132**, 42759 (2015)
44. N.Zivic, M.Bouzrati-Zerrelli, S.Villotte, F.Morlet-Savary, C.Dietlin, F.Dumur, D.Gigmes, J.P.Fouassier, J.Lalevee. *Polym. Chem.*, **7**, 5873 (2016)
45. H.Ito, C.G.Willson. *Polym. Eng. Sci.*, **23**, 1012 (1983)
46. H.Ito. *Adv. Polym. Sci.*, **172**, 37 (2005)
47. A.Del Campo, C.Greiner. *J. Micromech. Microeng.*, **17**, R81 (2007)
48. S.Kruger, C.Higgins, B. Cardineau, T.Younkin, R.Brainard. *Chem. Mater.*, **22**, 5609 (2010)
49. Patent US 8614047 (2013)
50. K.Arimitsu, M.Yonekura, M.Furutani. *RSC Adv.*, **5**, 80311 (2015)
51. K.Arimitsu, E.Hiraga, M.Furutani. *ACS Appl. Polym. Mater.*, **1**, 924 (2019)
52. Patent US 5627011 (1992)
53. Patent RU 2648048 (2017)
54. N.A.Kuznetsova, R.D.Erlikh, V.V.Solov'ev. *Elektronnaya Tekhnika. Ser. 3. Mikroelektronika*, (1), 44 (2017)
55. M.M.Afanas'ev, N.A.Kuznetsova, T.V.Chal'tseva. *Elektronnaya Tekhnika. Ser. 3. Mikroelektronika*, (3), 59 (2018)
56. M.L.Zanaveskin, A.A.Mironova, A.M.Popov. *Molecular Medicine*, **5** (2012); http://molmed.rusvrach.ru/archive/molecmed-2012-05-02.pdf (Last accessed on 22.01.2020)
57. A.A.Evstrapov. *Ross. Khim. Zh.*, **55** (2), 99 (2011)

58. J.W.Thackeray. *Front. Nanosci.*, **11**, 211 (2016)
59. Patent US 6916591 (2005)
60. C.M.Garza, W.Conley, J.Byers. In *Handbook of Semiconductor Manufacturing Technology*. (2nd Edn). (Eds R.Doering, Y.Nishi). (Boca Raton, FL, London, New York: CRC Press, 2008). P. 19
61. F.M.Houlihan, J.M.Kometani, A.G.Timko, R.S.Hutton, R.A.Cirelli, E.Reichmanis, O.Nalamasu, A.H.Gabor, A.N.Medina, J.J.Biafore, S.G.Slater. *J. Photopolym. Sci. Technol.*, **11**, 419 (1998)
62. Patent US 6048672 (2000)
63. V.M.Prabhu, S.Kang, D.L.Van der Hart, S.K.Satija, E.K.Lin, W.Wu. *Adv. Mater.*, **23**, 388 (2011)
64. A.Ya.Vainer, K.M.Dyumaev, A.M.Kovalenko, N.V.Barannik, R.M.Dragunskaya, S.V.Kotov, Ya.M.Pribysh. *Dokl. Chem.*, **486**, 126 (2019)
65. A.Ya.Vainer, K.M.Dyumaev, A.M.Kovalenko, L.E.Berenshtein, S.A.Krichevskaya, R.Z. Fridzon. *Dokl. Chem.*, **474** (Pt. 2), 129 (2017)
66. Appl. US 2017/0003587 (2017)
67. Patent US 6280911 (2001)
68. Z.K.Amirova, O.A.Speranskaya. *Novye Stoikie Supertoksikanty i ikh Vliyanie na Zdorov'e Cheloveka*. (New Persistent Supertoxicants and Their Effects on Human Health). (Moscow: Eko-Soglasie, 2016)
69. Patent US 6849374 (2005)
70. Patent EP 2033966 (2009)
71. Patent EP 1710230 (2006)
72. Patent US 6841333 (2005)
73. Patent US 6855476 (2005)
74. Patent US 7105267 (2006)
75. Patent US 8030515 (2011)
76. Appl. US 2008/0124656 (2008)
77. Appl. US 2010/0035185 (2010)
78. K.E.Lee, M.J.Kim, J.B.Yoo, H.S.Mondkar, K.Sohn, H.Lee. *J. Nanosci. Nanotechnol.*, **12**, 725 (2012)
79. S.Nandi, M.Yogesh, P.G.Reddy, S.K.Sharma, C.P.Pradeep, S.Ghosh, K.E.Gonsalves. *Mater. Chem. Front.*, **1**, 1895 (2017)
80. M.Wang, K.E.Gonsalves, M.Rabinovich, W.Yueh, J.M.Roberts. *J. Mater. Chem.*, **19**, 2797 (2009)
81. J.W.Thackeray, V.J.Jain, S.Coley, M.Christianson, D.Arriola, P.La Beaume, S.Kang, M.Wagner, J.Sung, J.Cameron. *J. Photopolym. Sci. Technol.*, **24**, 179 (2011)
82. T.Watanabe, Y.Fukushima, H.Shiotani, M.Hayakawa, S.Ogi, Y.Endo, T.Yamanaka, S.Tusa, H.J.Kinoshita. *Photopolym. Sci. Technol.*, **19**, 521 (2006)
83. H.Yamamoto, T.Kozawa, S.Tagawa. *Microelectron. Eng.*, **129**, 65 (2014)
84. Patent US 8062828 (2011)
85. M.Wang, W.Yueh, K.Gonsalves. *J. Fluorine Chem.*, **129**, 607 (2008)
86. H.Tamaoki, S.Tarutani, H.Tsubaki, T.Takahashi, N.Inoue, T.Tsuchihashi, H.Takizawa, H.Takahashi. *Proc. SPIE*, **7972**, Art. ID 79720A-1 (2011)
87. J.Yoo, S.Park, H.Kang, H.Mondkar, K.Sohn, H.Kim, K.Kim, H.Lee. *Polymer*, **55**, 3599 (2014)
88. Q.Wang, C.Zhang, C.Yan, F.You, L.Wang. *Eur. Polym. J.*, **114**, 11 (2019)
89. Y.Utsumi, T.Seshimo, Y.Komuro, A.Kawaue, K.Ishiduka, K.Matsuzawa, H.Hada, J.Onodera. *Jpn. J. Appl. Phys.*, **48**, 06FC07-1(2009)
90. H.N.Kang, J.H.Jung, H.S.Joo, D.C.Seo, H.Lee. *J. Nanosci. Nanotechnol.*, **14**, 9662 (2014)
91. Appl. US 20170329227 (2017)
92. M.D.Tham, D.E.Falvay. *J. Phys. Chem. A*, **122**, 3204 (2018)
93. P.S.Billone, J.M.Park, J.M.Blackwell, R.Bristol, J.C.Scaiano. *Chem. Mater.*, **22**, 15 (2010)
94. K.J.Schafer, J.M.Hales, M.Balu, K.D.Belfield, E.W.Van Stryland, D.J.Hagan. *J. Photochem. Photobiol., A*, **162**, 497 (2004)
95. H.Yuan, Y.Zhao, F.Wu. *Chem. Mater.*, **24**, 1371 (2012)
96. G.S.He, L.-S.Tan, Q.Zheng, P.N.Prasad. *Chem. Rev.*, **108**, 1245 (2008)
97. L.Steidl, S.J.Jhaveri, R.Ayothi, J.Sha, J.D.McMullen, S.Y.C.Ng, W.R.Zipfel, R.Zentel, C.K.Ober. *J. Mater. Chem.*, **19**, 505 (2009)
98. C.O.Yanez, C.D.Andrade, K.D.Belfield. *Chem. Commun.*, 827 (2009)
99. S.M.Kuebler, K.L.Braun, W.Zhou, J.K.Cammack, T.Yu, C.K.Ober, S.R.Marder, J.W.Perry. *J. Photochem. Photobiol., A*, **158**, 163 (2003)
100. T.Yu, C.K.Ober, S.M.Kuebler, W.Zhou, S.R.Marder, J.W.Perry. *Adv. Mater.*, **15**, 517 (2003)
101. M.Jin, H.Xu, H.Hong, J.P.Malval, Y.Zhang, A.Ren, D.Wan, H.Pu. *Chem. Commun.*, **49**, 8480 (2013)
102. R.Xia, J.P.Malval, M.Jin, A.Spangenberg, D.Wan, H.Pu, T.Vergote, F.Morlet-Savary, H.Chaumeil, P.Baldeck, O.Poizat, O.Soppera. *Chem. Mater.*, **24**, 237 (2012)
103. M.Jin, X.Wu, J.Xie, J.P.Malval, D.Wan. *RSC Adv.*, **5**, 55340 (2015)
104. X.Wu, M.Jin, J.Xie, J.P.Malval, D.Wan. *Dyes Pigm.*, **133**, 363 (2016)
105. V.A.Barachevsky, M.V.Alfimov, V.B.Nazarov. *Opt. Mem. Neural Networks*, **7**, 205 (1998)
106. A.S.Dvornikov, E.P.Walker, P.M.Rentzepis. *J. Phys. Chem. A*, **113**, 13633 (2009)
107. E.Walker, A.Dvornikov, K.Coblentz, P.Rentzepis. *Appl. Opt.*, **47**, 4133 (2008)
108. V.F.Traven, I.V.Ivanov, S.M.Dolotov, O.I. Kobeleva, T.M.Valova, V.A.Barachevsky. *J. Photochem. Photobiol., A*, **295**, 34 (2014)
109. Patent RF 2478116 (2011)
110. C.O.Yanez, C.D.Andrade, S.Yao, G.Luchita, N.V.Bondar, K.D.Belfield. *Appl. Mater. Interfaces*, **1**, 2919 (2009)
111. X.Yue, C.O.Yanez, S.Yao, K.D.Belfield. *J. Am. Chem. Soc.*, **135**, 2112 (2013)
112. A.A.Fadhel, X.Yue, E.H.G.Zadeh, M.V.Bondar, K.D.Belfield. *Int. J. Nanomedicine*, **11**, 6161 (2016)
113. K.Sumaru, K.Morishita, T.Takagi, T.Satoh, T.Kanamori. *Eur. Polym. J.*, **93**, 733 (2017)
114. Y.Wang, G.Li, R.Cheng, X.Zhang, J.Jiang. *Colloid Polym. Sci.*, **295**, 371 (2017)
115. K.Sumaru, T.Takagi, K.Morishita, T.Satoh, T.Kanamori. *Photomed. Photobiol.*, **37**, 25 (2015)
116. Y.Xu, J.Fei, G.Li, T.Yuan, J.Li. *ACS Nano*, **11**, 10175 (2017)
117. Y.Li, X.Feng, A.Wang, Y.Yang, J.Fei, B.Sun, Y.Jia, J.Li. *Angew. Chem., Int. Ed.*, **58**, 796 (2019)
118. S.Kohse, A.Neubauer, A.Pazidis, S.Lochbrunner, U.Kragl. *J. Am. Chem. Soc.*, **135**, 9407 (2013)