Non-ionic Photoacid Generators for i-Line: Synthesis, Photochemistry and Application to Photocrosslinking System

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Abstract

Non-ionic photoacid generators (PAGs) based on imino sulfonates and N-hydroxyimide sulfonates were designed and synthesized. To obtain the PAGs Which are sensitive to i-line (365 nm light), fluorenone oxime, thioxanthone oxime and N-hydroxyimide derivatives of thioxanthone were selected as a chromophore. The PAGs obtained were thermally stable and highly photosensitive. A mechanism for the photolysis of the PGAs was discussed. Some of the thioxanthone-based PAGs were also sensitive to g-line (436 nm light). Photocrosslinking of poly(glycidyl methacrylate) film was studied using the PAGs.

Introduction

A large number of photoacid generators (PAGs) have been synthesized because of their wide applications, e.g. cationic UV coatings, adhesives, photoresists, and so on[1,2]. PAGs can be divided into two groups according to their characteristics, i.e. ionic- and non-ionic types. Ionic PAGs basically involve onium salts such as aryldiazonium, diaryliodonium, triarylsulfonium, and triarylphosphonium salts that contain anions such as BF_4^-, SbF_6^-, AsF_6^-, PF_6^- and $C_xF_ySO_3^-$. A variety of onium salts as PAG have been prepared and the mechanism for their photolysis has been investigated in detail. When onium salts are irradiated with ultraviolet (UV) light, they undergo photolysis to form Brönsted or Lewis acids. Onium salts such as iodonium or sulfonium salts have several advantages as PAG. They are thermally stable and may be structurally modified to change their spectral absorption characteristics. The limited solubility of the onium salts in common organic solvents that is a serious disadvantage for their practical use was recently improved by modifying their chemical structures.

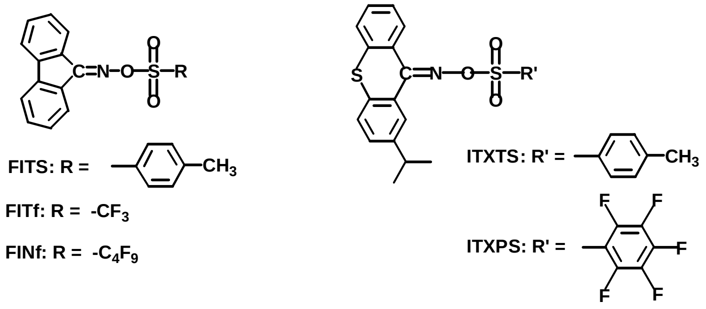
On the other hand, non-ionic PAGs that generate sulfonic acids upon irradiation involve 2-nitrobenzyl esters of sulfonic acids, imino sulfonates, 2-diazo-1-oxo-1,2- dihydronaphthalene derivatives, N-hydroxyimide sulfonates, and tris(methylsulfonyloxy)benzene, and its homologs. 2-Nitrobenzyl esters of carboxylic acids and 2-diazo-1-oxo-1,2-dihydro-5-naphthyl arenesulfonate derivatives can generate carboxylic acids upon irradiation. Triaryl phosphate derivatives generate phosphoric acids upon irradiation. Non-ionic PAG has a much wider range of solubility in organic solvents and in polymer films than onium salt analogs. A disadvantage of the non-ionic PAGs is that they are thermally less stable than the onium salt type PAGs.

PAG is widely used in the field of polymeric photosensitive systems. Although the polymerization initiated by the photoinduced radical species is prohibited by the oxygen molecule in the air, the cationic polymerization is not affected by oxygen molecule. PAG is also significant materials for the photoinduced curing system using epoxides and such curing systems may be widely applied in coating, adhesives, and inks. Another important application of PAG is observed in the development of the chemically amplified photoresist system where the reactions such as crosslinking of polymers and transformation of functional groups in polymer chains can be catalyzed by the photochemically generated acids.

Recently, PAGs sensitive to 365nm light became important in relation to the application to UV curing and chemically amplified resists for i-line lithography[3,4]. This paper describes the synthesis and photochemistry of i-line sensitive non-ionic PAGs based on imino sulfonates and N-hydroxyimide sulfonates[5-8]. Applications of these PAGs to novel photocrosslinking systems are also described.

Experimental

Synthesis of Imino Sulfonates



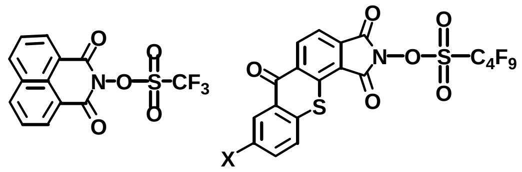
Scheme 1 Structures of imino sulfonates.

A series of PAGs of oxime sulfonates, FITS, FITf, FINf, ITXTS, and ITXPS shown in Scheme 1 were prepared. The PAG was easily synthesized by the reaction of corresponding oxime derivatives with appropriate sulfonyl chloride or sulfonic acid anhydride in relatively high yield. Synthesis of FITf was carried out as follows: Fluorenone oxime (0.25 g, 1.3×10^{-3} mol) and trifluoromethanesulfonic anhydride (0.40 g, 5.1×10^{-3} mol) were dissolved in benzene (5 mL), and heated at 50 °C for 30 min with vigorously stirring. The reaction mixture was cooled, diluted with benzene, washed with 15% sodium carbonate once and with water twice. The benzene layer was separated and dried over anhydrous sodium sulfate. The solution was evaporated to dryness and FITf was obtained by recrystallization with heptane as yellow crystal; yield 50%, mp: 114 ^{o}C, Td: 135 ^{o}C from TGA analysis. UV (acetonitrile) λ_{max} = 255 nm, log ε = 4.80 (L/mol・cm).

2-Isopropylthioxanthone oxime ester of *p*-toluenesulfonic acid (ITXTS) was prepared from 2-isopropylthioxanthone oxime and p-toluenesulfonyl chloride. A mixture of p-toluenesulfonyl chloride (0.46 g, 2.4 x 10^{-3} mol) and 2-isopropylthioxanthone oxime (0.65 g, 2.4 x 10^{-3} mol) was dissolved in benzene (10 mL). 4-Dimethylaminopyridine was slowly added to the solution with vigorous stirring. After 10 min, the reaction solution was passed through silica gel column (eluent: $CHCl_3$). The first fraction of the eluent was concentrated to dryness. The solid was purified by recrystallization from hexane; yield 67%, mp: 165 ^{o}C, T_d: 206 ^{o}C from TGA analysis. UV (acetonitrile) λ_{max} = 258 nm, log ε = 4.37 (L/mol・cm).

Preparation of pentafluorobenzensulfonic acid 2-isopropylthioxanthone oxime ester (ITXPS) was carried out as the same manner using 2-isopropylthioxanthone oxime and pentafluorobenzensulfonyl chloride; yield 32%, mp: 114 ^{o}C, T_d: 206 ^{o}C from TGA analysis. UV (acetonitrile) λ_{max} = 260 nm, log ε = 4.38 (L/mol・cm).

Synthesis of N-Hydroxyimide Sulfonates



NITf

THINf: X=H
iTHINf: X=isopropyl

Scheme 2. Structures of N-hydroxyimide sulfonates.

Thioxanthone-based PAGs are designed as i-line sensitive PAG. Structures of the PAGs are shown in Scheme 2. Nonafluorobutanesulfonic acid 1,3,6-trioxo-3,6-dihydro-1H-11-thia-2-azacylo-penta[a]anthracen-2-yl ester (THINf) was synthesized as follows: 2-Oxa-11-thiacylopenta[a]anthracene-1,3,6-trione (**1**) was prepared according to the literature[9)]. A mixture of **1** (0.5 g, 1.7 mmol), hydroxylamine hydrochloride (1.72 g, 1.7 mmol), and pyridine (20 ml) was kept at 100 ^{o}C for 15 h with stirring. The mixture was further mixed with 1N hydrochloric acid (200 ml). The precipitate was filtered, washed with water, dried, and recrystallized from ethanol to obtain 2-hydroxy-11-thia-2-azacylopenta[a]anthracene-1,3,6-trione (**2**): yield 76.6%.

A mixture of **2** (0.5 g, 1.7 mmol), nonafluorobuthanesulfonic anhydride (1.0 g, 1.7 mmol), and toluene (50 ml) was stirred at 25 ^{o}C for 1 h. The mixture was washed with 15% sodium carbonate aqueous solution, dried over anhydrous magnesium sulfate, evaporated to dryness and recrystallized from chloroform to obtain the product THINf: T_d 227 ^{o}C.

Nonafluorobutanesulfonic acid 8-isopropyl-1,3,6-trioxo-3,6-dihydro-1H-11-thia-2-

azacylopenta[a]anthracen-2-yl ester (iTHINf) was synthesized according to the same procedure as the preparation of THINf using 5-isopropyl-thiosalicylic acid [10] as a starting material. T_d 199 ^oC.

N-hydroxynaphthalimide triflate (NITf) was obtained from Midori Kagaku.

Results and Discussion

Characteristics of PAGs

Fluorenone oxime-based and thioxanthone oxime-based PAG are prepared as i-line sensitive PAGs. Imino sufonates are generally synthesized from sulfonyl chlorides and oximes which can be easily prepared from ketones. Thus, many types of imino sulfonates can be prepared by the combination of sulfonyl chlorides and oximes. The absorption region of the imino sulfonates depends on the structure of the oxime moiety.

FITS, FITf, and FINf have a fluorenone chromophor in a molecule. ITXTS and ITXPS contain thioxanthone skeleton. Incorporation of an isopropyl group in thioxanthone skeleton was effective for enhancement of their solubility in solvents or polymer matrices. FITS, FITf, and FINf showed strong absorption at 257 nm, however, only weak shoulder was observed at 365 nm. Molar absorption coefficients (ε) of FITS, FITf, and FINf at 365 nm were ranged from 270 to 400 L/mol・cm in acetonitrile. In contrast, ITXTS and ITXPS show strong absorption at 365 nm. The ε values of ITXTS and ITXPS were more than ten times larger than those of FITS, FITf, and FINf (Table 1).

Table 1 Characteristics of PAG

Sample	Yield (%)	T_m (^oC)[a]	T_d (^oC)[b]	ε (365 nm)[c]
FITS	45	161	225	400
FITf	50	114	135	300
FINf	74	62	146	270
ITXTS	67	165	206	4600
ITXPS	32	114	206	4480

[a] Melting point. [b] Onset temperature of thermal decomposition determined by TGA measurement under nitrogen. Heating rate ; 10 ^oC/min. [c] In acetonitrile.

Solubility of PAGs in solvents and polystyrene (PS) matrix was checked. More than 10 wt% of PAGs was soluble in chloroform, tetrahydrofuran, and cyclohexanone. By using the PAGs, the clear PS film was obtained by mixing up to 20 wt%.

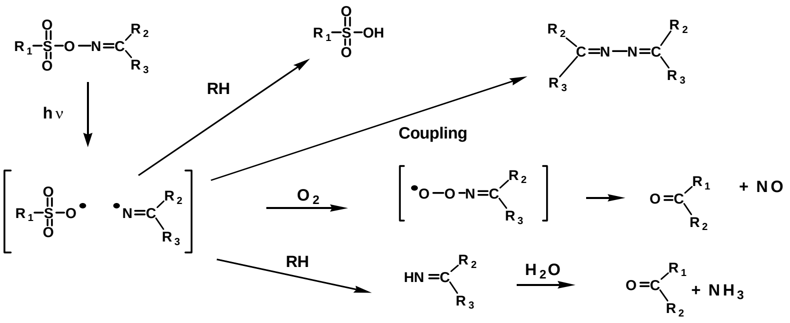
Thermal decomposition temperature of FITf (135 ^oC) and FINf (146 ^oC) was lower than that of other PAGs (206 ~ 226 ^oC) (Table 1). In PAGs having oxime ester skeleton, the structure of sulfoate esters strongly affected the thermal stability. Fluoroalkyl sulfonates decreased their thermal stability.

Certain sulfonic acid esters of N-hydroxyimides have been known to form sulfonic acids upon UV irradiation. N-hydroxyimide sulfonates are generally synthesized from sulfonyl chlorides or sulfonic acid anhydride and N-hydroxyimides. The absorption region of N-hydroxyimide sulfonates depends on the structure of the N-hydroxyimide moiety.

NITf showed a weak absorption at 365 nm (ε=380 in CH_3CN). THINf (ε=856 in CH_3CN) and iTHINf (ε=381 in CH_3CN) showed a similar ε value at 365nm. Interestingly, THINf (ε=4530 in CH_3CN) and iTHINf (ε=4030 in CH_3CN) showed strong absorption at 436 nm. Thus, THINf and iTHINf can also work as a g-line sensitive PAG. The solubility of THINf in organic solvents was lower compared to iTHINf.

Photochemistry of Imino Sulfonates

Imino sulfonates can be photochemically dissociated to sulfonic acids$^{11)}$. Upon UV irradiation the cleavage of -O-N= bonds in the compounds and the subsequent abstraction of hydrogen atom from solvents or polymer solid matrix leads to the formation of sulfonic acids, azines, and ketones (Scheme 3). The absorption characteristica strongly depend on the structure of imino moiety. For the photolysis of these compounds in polymer films in air, the reaction of imino radicals with oxygen is dominant compared to dimerization and hydrogen abstraction reactions.



Scheme 3 Photolysis mechanism for imino sulfonate.

Table 2 shows the results of product analysis for the photolysis of FITS in several media. The yield of fluorenone azine in solution was much higher than that in polymer films. This is due to high mobility of the imino radicals in solution. The formation of fluorenone azine in solution was not affected by atmosphere. The yield of p-toluenesulfonic acid in the presence of oxygen was 88% in solution and 52-61% in polymer films in air. These values were roughly consistent with the sum of the fluorenone yield and twice the fluorenone azine yield. The acid yield was not strongly dependent on the polymer matrix. The yield of p-toluenesulfonic acid in solution in vacuo was lower than that in solution in air. As shown in Scheme 3, this difference is due to the formation of NH_3 by the hydrolysis of imine. Thus, the acid yield was consistent with twice the fluorenone azine yield. The intermediary imine is known to be easily hydrolyzed to a carbonyl compound. In the presence of oxygen, the reaction of the imino radicals with oxygen molecules was greater than hydrogen abstraction by imino radicals from either polymer molecules or residual solvents.

Table 2 Products from the photolysis of FITS

Reaction Medium	Yield (%)[a)]		
	p-Toluenesulfonic Acid	Fluorenone	Fluorenone azine
CH_3CN/H_2O (92/8, v/v)			
In O_2	88	35	26
In vacuo	50	25	25
PMMA[b)] film in air	52	46	4.7
PBMA[c)] film in air	61	39	9.3

a) Based on photoreacted FITS. b) Poly(methyl methacrylate).
c) Poly(butyl methacrylate)

Table 3 Φ_d values for the photolysis of iminio sulfonates

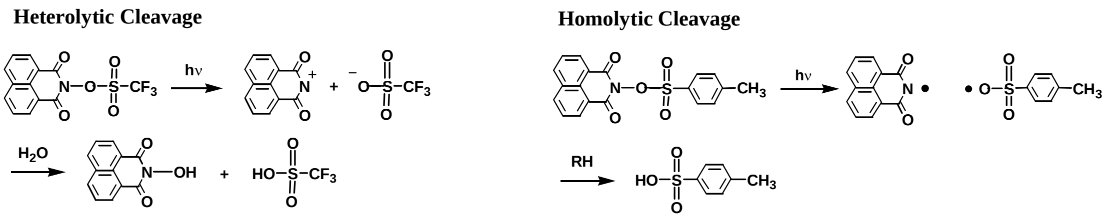
Sample	ε (366 nm)[a)]	Φ_d		
		in acetonitrile	in PS (UV)	in PS (in situ FT-IR)
FITS	400	0.16[c)]	0.065[c)]	0.065[c)]
FITf	300	0.32	0.19	0.17
FINf	270	0.24	0.19	0.19
ITXTS	4600	0.080	0.14	0.082
ITXPS	4480	0.10	0.28	0.28

[a)] In acetonitrile.

The Φ_d values for the photochemical decomposition of imino sulfonates were determined as the number of moles of imino sulfonate molecule photolyzed per einstein of light absorbed by the compounds (Table 3). The Φ_d values of FITf, FINf, ITXTS, ITXPS, and FITS are evaluated to be 0.32, 0.24, 0.080, 0.10, and 0.16, respectively, in acetonitrile. The Φ_d values of FITf and FINf were larger than those of other PAGs. The strength of –O–N= bonds of imino sulfonates in FITf and FINf may be lowered by the influence of the strong electron-withdrawing perfluoroalkyl groups. The result is consistent with the low thermal stability of FITf and FINf. The Φ_d values of ITXTS and ITXPS (0.08 and 0.10) were smaller than those of other PAGs regardless of their high molar absorption coefficients at 365 nm.

Photolysis of PAGs in PS film was also carried out. Photolysis degree was estimated by both UV spectral changes and in situ FT-IR measurements. The Φ_d values in PS film were slightly lower compared with the values obtained in acetonitrile.

Photochemistry of N-hydroxyimide Sulfonates



Scheme 4. Photolysis mechanism for N-hydroxyimide sulfonates.

Photoreaction proceeds through heterolytic cleavage of the N-O bond with subsequent production of ionic intermediates, leading to acid generation and formation of the corresponding N-hydroxyimide. This reaction pathway is possible for the compound having electron withdrawing acid moiety like triflic acid. On the other hand, in the case of tosyl ester, the reaction mechanism changes and photoacid generation occurs though homolytic cleavage of the N-O bond[12]. The reaction mechanism for NITf is shown in Scheme 4.

The photolysis rate of the PAGs in acetonitrile on irradiation at 365nm decreased in the order THINf > iTHINf > NITf. THINf and iTHINf were photolyzed on irradiation at 436 nm and the photolysis rate for THINf was slightly higher than iTHINf.

Application to Photocrosslinking System

PAG is widely used in the field of polymeric photosensitive systems[4]. PAG is utilized in the photoinitiated cationic polymerization of vinyl ethers and other cationically polymerizable monomers. PAG is significant materials for the photoinduced curing system using epoxides and such curing systems may be widely applied in coating, adhesives, and inks.

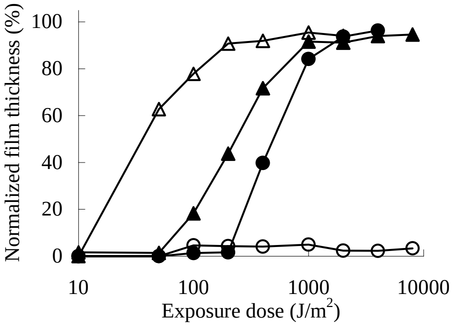


Figure 1. Insolubilization of PGMA film containing PAG on irradiation and followed by baking at 100 °C for 5 min. Developer: THF for 10 min.
PAG: NITf irradiated at 365 (●) and 436 nm (○); iTHINf irradiated at 365 (▲) and 436 nm (△).

Figure 1 shows the photocrosslinking properties of poly(glycidyl methacrylate) (PGMA) containing NITf and iTHINf on irradiation at 365 and 436 nm. The photocrosslinking efficiency of PGMA containing iTHINf on irradiation at 365 nm was higher than PGMA containing NITf. This is due to higher photoreactivity of iTHINf at 365 nm. The photocrosslinking properties of PGMA containing PAG were dependent on not only the acidity of acid generated from the PAG but also the photoreactivity of PAG. Moreover, the photocrosslinking efficiency of PGMA containing iTHINf on irradiation at 436 nm was higher than on irradiation at 365 nm because Φ value of iTHINf at 436 nm was higher than at 365 nm. Since NITf did not absorb the light at 436 nm, no photocrosslinking of PGMA containing NITf occurred.

Conclusion

Thixanthone oxime sulfonates were good photoacid generators sensitive 365nm light. The molar extinction coefficients of those photoacid generators at 365nm were about ten times larger than those of fluorenone oxime sulfonates. The thioxanthone-based imide sulfonates were also good photoacid generators which were sensitive to 365 and 436 nm light. The incorporation of isopropyl group into thioxanthone ring enhanced the solubility in organic solvents. Thioxanthone-based photoacid generators, ITXTS, ITXPS, THINf, and iTHINf were stable upto 200 ^{o}C. The photoacid generators shown here could be applied to the photocrosslinking of poly(glycidyl methacrylate) film and other cationically curable materials using 365 nm light or 436 nm light.

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