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Accounts

Photoacid and Photobase Generators: Prospects and Their Use in the Development of Polymeric Photosensitive Systems

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This article describes the recent progress in the preparation of a set of compounds which can generate acids or bases upon irradiation of light. These compounds are called photoacid generators and photobase generators, respectively. Photoacid generators can be divided into two groups according to their characteristics; i.e., ionic- and non-ionic compounds. Photobase generators are fewer than photoacid generators. These compounds are widely used in the field of polymeric photosensitive systems such as photoinitiated polymerization, photoinduced crosslinking of polymers and oligomers, photoinduced degradation of polymers, and photoinduced transformation of functional groups in polymer chains. In particular, this article focuses on the applications of photoacid and photobase generators to promote the development of photoresist and UV curing materials.

Compounds that can generate acids upon irradiation of light are called photoacid generators. A large number of these compounds have been synthesized because of their wide applications, especially in the field of polymeric photosensitive systems. Photoacid generators can be divided into two groups according to their characteristics, i.e. ionic- and non-ionic compounds. Ionic photoacid generators involve onium salts such as aryldiazonium, diaryliodonium, triarylsulfonium, and triarylphosphonium salts that contain complex metal halides such as BF_4^-, SbF_6^-, AsF_6^-, and PF_6^-. Although the existence of these onium salts has been known for nearly a century, many years had passed before the usefulness of these compounds was realized. A variety of onium salts as photoacid generators have since been prepared and the mechanisms for their photolysis have 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 photoacid generators. 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 had been a serious disadvantage for their practical use was recently improved by introducing long alkyl chains on the phenyl ring of the onium salts.

Non-ionic photoacid generators that generate sulfonic acids upon irradiation involve 2-nitrobenzyl esters of sulfonic acids, imino sulfonates, 2-diazo-1-oxo-1,2-dihydronaphthalene derivatives, *N*-sulfonyloxyimides, 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 generate carboxylic acids upon irradiation. Triaryl phosphate derivatives generate phosphoric acids upon irradiation. Non-ionic photoacid generators have a much wider range of solubility in organic solvents and in polymer films than onium salt analogs. A disadvantage of the non-ionic photoacid generators is that they are thermally less stable than the onium salts.

Photobase generators are not so popular as photoacid generators. They are compounds which can generate basic compounds such as amines upon UV irradiation. Cobalt amine complexes, nitrobenzyl carbamates, formamides, and *O*-acyloximes have been known as photobase generators. Since the first papers on photobase generators appeared in the latter half of the 1980s, the studies have been increasing. At present, different from photoacid generators, they are not used as initiators for anionic polymerizations but as catalysts for the base-catalyzed reactions.

Photoacid and photobase generators are widely used in the field of polymeric photosensitive systems. Photoacid generators are utilized in the photoinitiated cationic polymerization of vinyl ethers and other cationically polymerizable monomers. Although the polymerization initiated by the photochemically generated radical species is prohibited by oxygen molecules in the air, the cationic polymerization is not affected by oxygen molecules. Photoacid and photobase generators are also significant materials for the photoinduced curing system using epoxides and such curing systems may be widely applied in coating, adhesives, and inks. One of the most important applications of photoacid and photobase generators is observed in the development of photoresist materials. The highly sensitive photoresist systems contain the reactions such as crosslinking of polymers and transformation of functional groups in polymer chains which can be catalyzed by the photochemically generated acids or bases. Characteristics of photoacid and photobase generators and their uses in the polymeric photosensitive materials are briefly summarized as follows (Tables 1 and 2).

In this paper we will describe the chemistry of photoacid generators and photobase generators and their applications to the polymeric photosensitive systems. Emphasis will be placed on our own studies on the chemistry and applications of imino sulfonates as a photoacid generator and *O*-acyloximes as a photobase generator.

1. Photoacid Generators and Their Applications

1.1 Photochemical Generation of Acids. **Ionic Photoacid Generators.** Aryldiazonium salts ($ArN_2^+ X^-$; $X = BF_4^-, AsF_6^-, PF_6^-$) have been shown to undergo a fast fragmentation under UV irradiation with formation of free Lewis acids. The quantum yields for the photolysis of diazonium salts are high (ca. 0.5) and depend on the nature of substituents on the aryl ring. The photodecomposition can be sensitized by xanthene dyestuffs. Disadvantages of aryldiazonium salts include poor thermal stability and the evolution of nitrogen gas.[1)]

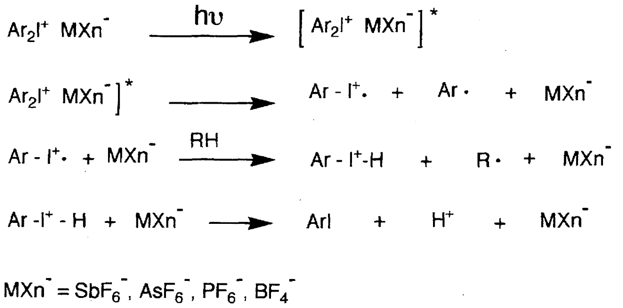
The stable diarylhalonium salts consist of three members: the diaryliodonium, diarylbromonium, and diarylchloronium salts with complex metal halide anions. Diaryliodonium salts generate a Brönsted acid upon UV irradiation. In contrast to aryldiazonium salts, the iodonium salts show high thermal stability, as well as low hydrolytic reactivity. The absorption maximum of compound (**1**) falls near 250 nm. The quantum yield for the photolysis of **1** ($Y = CH_3$, $MXn = AsF_6^-$) was 0.2 for irradiation at 313 nm in acetonitrile. A mechanism for the photolysis of diaryliodonium salts was reported based on product analysis (Scheme 1).[2)] A slightly different mechanism was also reported.[3a,3b)] The photolysis of diaryliodonium salts can be sensitized by several dyes such as Acridine Orange, Acridine Yellow, Phosphine R, and Benzoflavine, which absorb light in the wavelength region of 411—539 nm.[4)] While diaryliodonium salts are significant photoacid generators, simple diaryliodonium salts have some problems: very limited solubilities in non-polar solvents and toxicity. Diphenyliodonium hexafluoroantimonate has an oral LD_{50} of 40 mg kg^{-1} (rats). However, the toxicity of iodonium salts was reduced by substituting AsF_6^- or SbF_6^- with $B(C_6F_5)_4^-$. Long alkyl groups attached the phenyl rings in this compound greatly enhance its solubility in hydrocarbons. Diaryliodonium salts with alkoxy chain lengths

Table 1. Photoacid Generator

Type	Generated acid	Solubility in common organic solvents	Thermal stability	Application
Ionic				
Diaryldiazonium salt	Lewis acid	Good	Poor	Photoinitiator (UV curing material)
Diaryliodonium salt	Brönsted acid	Poor	Good	
Triarylsulfonium salt	Brönsted acid	Poor	Good	Catalyst for polymer reaction (Photoresist)
Non-ionic				
2-Nitrobenzyl ester of sulfonic acid	Sulfonic acid	Good	Depend on structure	Catalyst for polymer reaction (Photoresist)
Imino sulfonate				
N-Sulfonyloxyimide				
Aromatic sulfone				

Table 2. Photobase Generator

Type	Generated base	Solubility in common organic solvent	Thermal stability	Application
Ionic				
Cobalt amine complex	Ammonia Alkyl amine	Poor	Good	Catalyst for polymer reaction and curing (Photoresist and UV curing material)
Non-ionic				
Carbamate	Alkylamine	Good	Depend on structure	
O-Acyloxime	Aralkyl amine			
Formanilide	Aromatic amine			



Scheme 1. Photodecomposition mechanism of diaryliodonium salts.

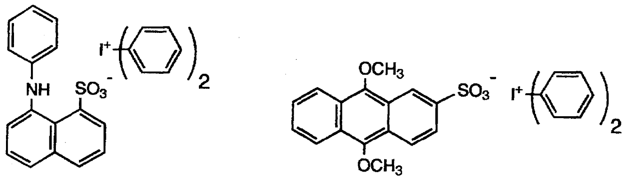


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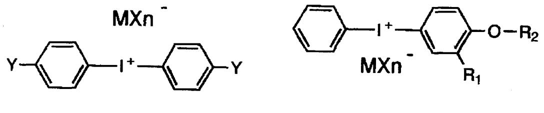
Chart 2.

of up to six carbon atoms are soluble only in polar solvents and are insoluble in aromatic hydrocarbons. In contrast, alkoxy-substituted diaryliodonium salts (**2**) having alkoxy groups of eight carbon atoms or more are insoluble in water, but are soluble in aromatic hydrocarbons such as toluene and styrene (Chart 1); they also have some solubility in hot cyclohexane.[5] However, they are insoluble in straight chain paraffinic solvents such as petroleum ether and hexane. Diphenyliodonium 8-anilinonaphthalene-1-sulfonate (**3**) and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (**4**) have been known to generate sulfonic acids on irradiation (Chart 2). The quantum yields for the acid formation of **3** and **4** with 365 nm irradiation were 0.18 and 0.22, respectively, in novolak films.[6] Diarylchloronium and diarylbromonium salts are efficient photoacid generators with quantum yields of photolysis even higher than those reported for diaryliodonium salts. However, due to the difficulty of their synthesis and their poor thermal stability, these compounds have not been extensively studied.

Triarylsulfonium salts (Ar_3S^+ MX_n^-) with complex metal halide anions such as BF_4^-, AsF_6^-, PF_6^-, and SbF_6^- comprise a class of highly efficient photoacid generators. When these compounds are irradiated with UV light, carbon–sulfur bond cleavage occurs to form radical fragments. At the same time, the strong Brönsted acid HMX_n is also produced. The mechanism for the photolysis of triphenylsulfonium salts was studied in detail.[7—12] When the photolysis of a solution of tris(4-methoxyphenyl)sulfonium hexafluoroarsenate (**5**) in acetone was carried out with UV light, the products identified were anisole, bis(4-dimethoxyphenyl)sulfide, three isomeric dimethoxybiphenyls, and $HAsF_6$. The quantum yield for the photolysis of tris(4-methoxyphenyl)sulfonium haxafluoroarsenate was observed to be 0.17 at 313 nm and 0.19 at 365 nm in acetonitrile.[13] Compounds (**6**, **7**) that have two and three photoactive triarylsulfonium groups in the same molecules are good photoacid generators.[14] A series of alkyl(methyl)-1-naphthylsulfonium salts (**8**) undergo photoinduced 1,3-sigmatropic rearrangements to form 1-(methylthio)-2-substituted alkylnaphthalenes and the corresponding acid with quantum yields falling between 0.24 and 0.10 (Chart 4).[15,16] 3,5-Dialkyl-4-hydroxyphenylsulfonium salts (**9**) are a class of useful photoacid generators (Chart 5). On irradiation these salts undergo reversible ylid formation with the simultaneous generation of strong Brönsted acids.[17,18]

Triarylselenonium salts with complex metal halide anions such as BF_4^-, AsF_6^-, and SbF_6^- have been shown to be efficient photoacid generators. The mechanism by which triarylselenonium salts decompose appears to be identical to that which has been proposed for the photolysis of triarylsulfonium salts.[19] Certain triphenylphosphonium salts with complex metal halides are also useful photoacid generators.[20—22] Iron arene complexes with complex metal halides (**10**) are a new class of photoacid generators (Chart 6). Upon irradiation, a photoinduced ligand-transfer reaction occurs with the displacement of the arene ligand.[23,24] The photolysis of these compounds yields relatively weak iron-based Lewis acids compared to the Brönsted acids generated by the photolysis of triarylsulfonium and diaryliodonium salts. *N*-Alkoxypyridinium salts are a new class of photoacid generators.[25,26] Some sulfonium salts such as benzyl(*p*-hydroxyphenyl)methylsulfonium hexafluoroantimonate were developed as thermal-latent initiators for cationic ring-opening polymerization of epoxides. However, these compounds also worked as photo-latent initiators for the cationic polymerization of epoxides because they photochemically generated a benzyl cation with SbF_6^- as a counter anion.[27,28]

Non-ionic Photoacid Generators. Non-ionic photoacid generators that generate sulfonic acids upon irradiation involve 2-nitrobenzyl ester of sulfonic acids, imino sulfonates, 2-diazo-1-oxo-1,2-dihydro-4-arenesulfonate derivatives, *N*-sulfonyloxyimides, and tris(methylsulfonyloxy)benzene and its homologs. 2-Nitrobenzyl esters of carboxylic acids[29] and 2-diazo-1-oxo-1,2-dihydro-5-arenesulfonate derivatives[30]



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R_1 : H , CH_3

R_2 : C_8H_{17} , $C_{10}H_{21}$, $C_{11}H_{23}$

$C_{12}H_{25}$, $C_{14}H_{29}$, $C_{14}H_{29}$

$C_{15}H_{31}$, $C_{16}H_{33}$, $C_{18}H_{37}$

MXn^- : SbF_6^- , PF_6^- , OTs^-

Chart 1.

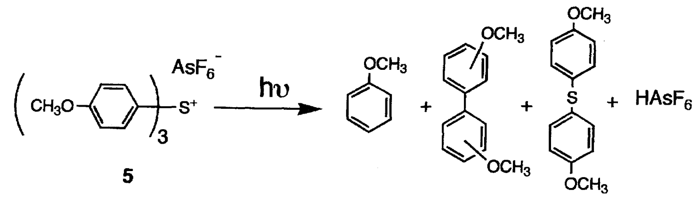

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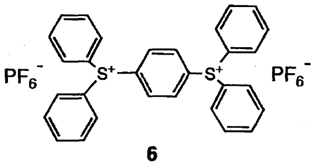
Chart 3.



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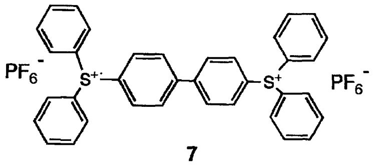

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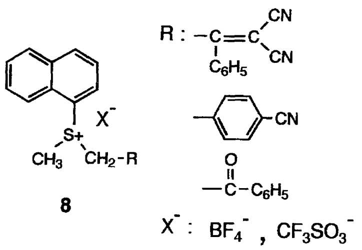

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Chart 4.

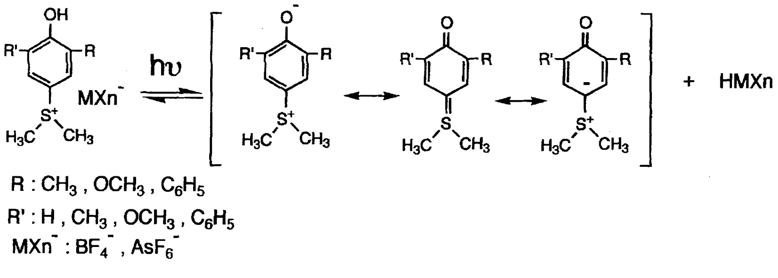

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Chart 5.

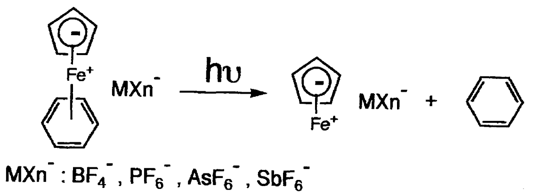

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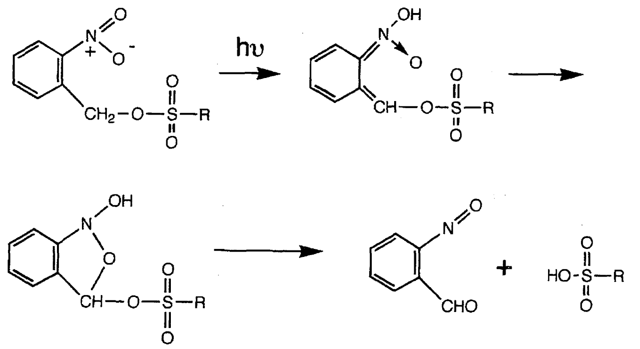
Chart 6.

generate carboxylic acids upon irradiation. Non-ionic photoacid generators have a much wider range of solubility in solvents and in polymer films than onium salt analogs. A disadvantage of the non-ionic photoacid generators arises because they are thermally less stable than the onium salts. 2-Nitrobenzyl esters of sulfonic acids generate sulfonic acids upon UV irradiation (Scheme 2).[31] A variety of 2-nitrobenzyl sulfonate derivatives were prepared and the thermal stability and quantum yields for the photolysis were reported. The thermal stability of 2-nitrobenzyl esters is governed by substituent effects that may be steric, resonance, or inductive in nature, or a combination of all three. In general the addition of electron-withdrawing groups (CF_3, F, NO_2, SO_3R) to the benzenesulfonate moiety leads to an increased acidity of the sulfonic acid and decreased thermal stability of the corresponding esters.[31] The substituents to the benzenesulfonate moiety do not strongly affect the quantum yields for the photolysis of 2,6-dinitrobenzyl benzenesulfonate derivatives. No significant variation in quantum yield was observed with decreasing the size of the acid group.



Scheme 2. Photorearrangement of 2-nitrobenzyl sulfonate.

4-Nitrobenzyl esters of sulfonic acids with electron-donating aromatic moieties (**11**) are photodissociative to form sulfonic acids, while 4-nitrobenzyl tosylate and benzenesulfonate are not photodissociative (Chart 7). The mechanism for the photolysis of 4-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate was evaluated (Scheme 3).[32,33] A class of compounds which are structurally related to the nitrobenzyl class of photoacid generators has been reported. The photoacid generating ability of pentafluorobenzyl sulfonates (**12**) parallels the electron-donating character of the sulfonic acid component of the molecule (Chart 8).[34]

Sulfone compounds (**13**) are another class of photoacid

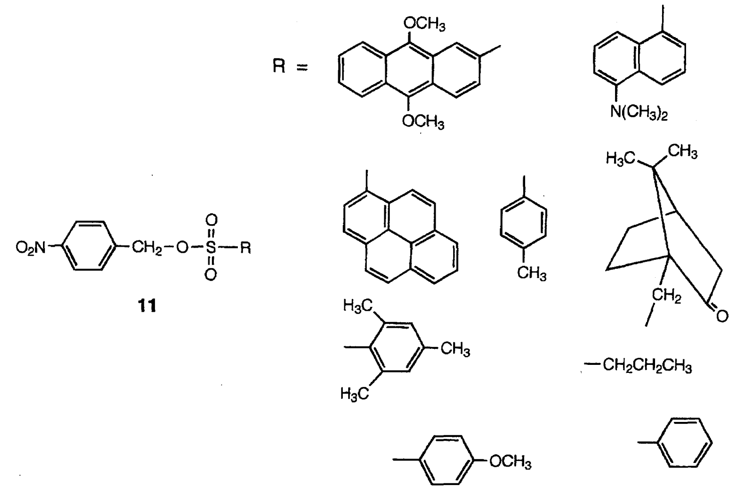
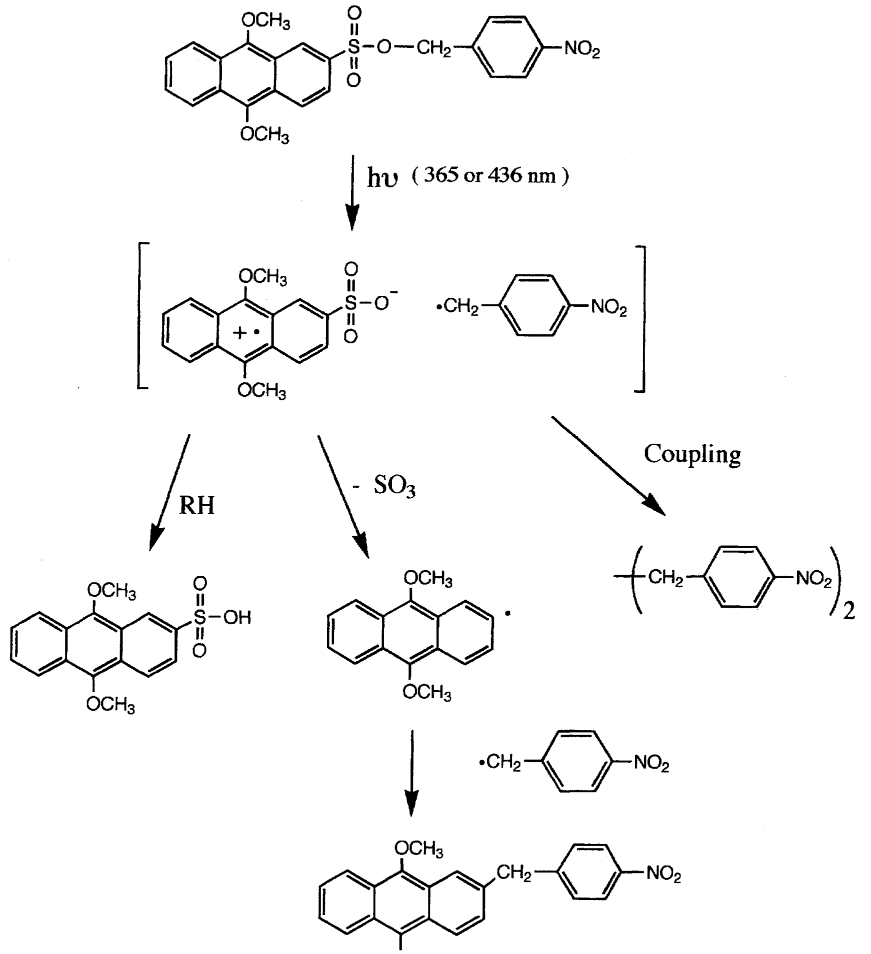


Chart 7.



Scheme 3. Photoreaction of 4-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate.

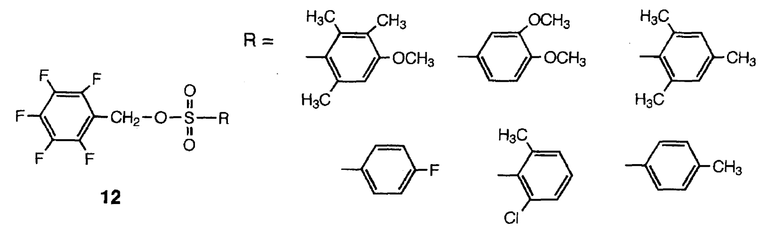


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Chart 8.

generators.[35,36] They are thermally very stable (Chart 9). These compounds primarily generate sulfinic acids upon deep-UV irradiation. Diaryl disulfones (**14**) also generate sulfinic acid upon UV irradiation (Chart 10).[37]

Photoirradiation of triaryl phosphate and its homologs with 254 nm light generates a biaryl and phosphoric acid or its monoaryl ester equivalently with relatively good quantum yields ($\Phi = 0.02$—0.19).[38,39] The photolysis was suggested to proceed via intramolecular excimer formation between the aryl moieties.

Certain *N*-sulfonyloxyimides have been known to form sulfonic acid upon UV irradiation.[40,41] The photoacid generation efficiency decreased in the order *N*-(methylsulfonyloxy)phthalimide > *N*-(*p*-tolylsulfonyloxy)- > *N*-(nitrobenzylsulfonyloxy)- > *N*-(dinitrobenzylsulfonyloxy)-. Hydroxy substituted benzenes such as hydroquinone and bisphenol A work as a photosensitizer for the photolysis of these photoacid generators. The reaction was also efficiently sensitized by benzophenone, suggesting that this photoreaction proceeds through its triplet excited state.

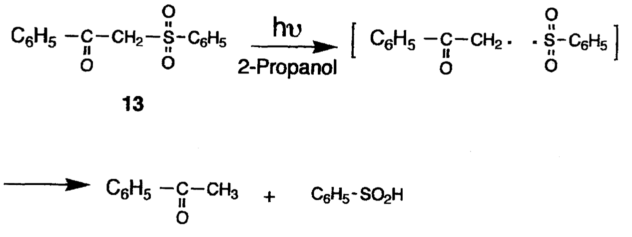

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Chart 9.

Alkane- and arenesulfonic acid esters of pyrogallol and its analogs generated sulfonic acids upon UV irradiation.[42] The quantum yields for acid generation from alkyl and aryl sulfonic acid esters of pyrogallol decrease in the order methanesulfonate > ethanesulfonate > propanesulfonate > benzenesulfonate > toluenesulfonate > naphthalenesulfonate. The photosensitivity of methanesulfonic acid esters of monohydroxy-, dihydroxy-, and trihydroxybenzene isomers indicated the importance of the number of sulfonyloxy groups attached to the benzene ring.

Organic compounds containing vicinal dibromides represent a particular subset of hydrogen bromide photogenerators (Scheme 4). Upon irradiation with 365 nm light, trans-10,11-dibromodibenzosuberone generates HBr along with dibenzosuberenone.[43]

Imino sulfonate compounds (**15**—**28**) are a particular subset of photoacid generators. These compounds can be synthesized from oximes and sulfonyl chlorides. Many types of oximes can be derived using different types of ketones. The absorption characteristics strongly depend on the structure on the oxime moiety. 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. A representative photolysis mechanism for 9-fluorenilideneamino *p*-toluenesulfonate (**18**) is shown in Scheme 5 and

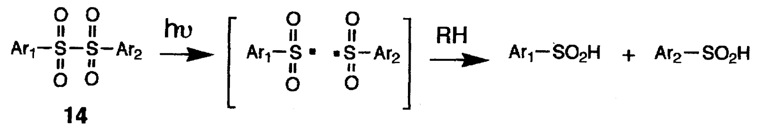

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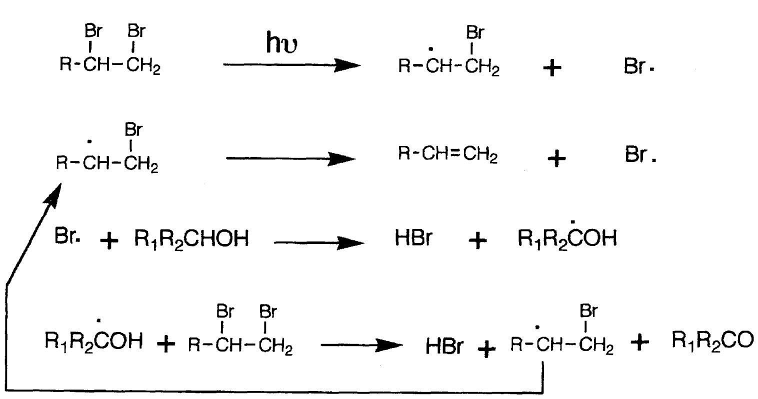
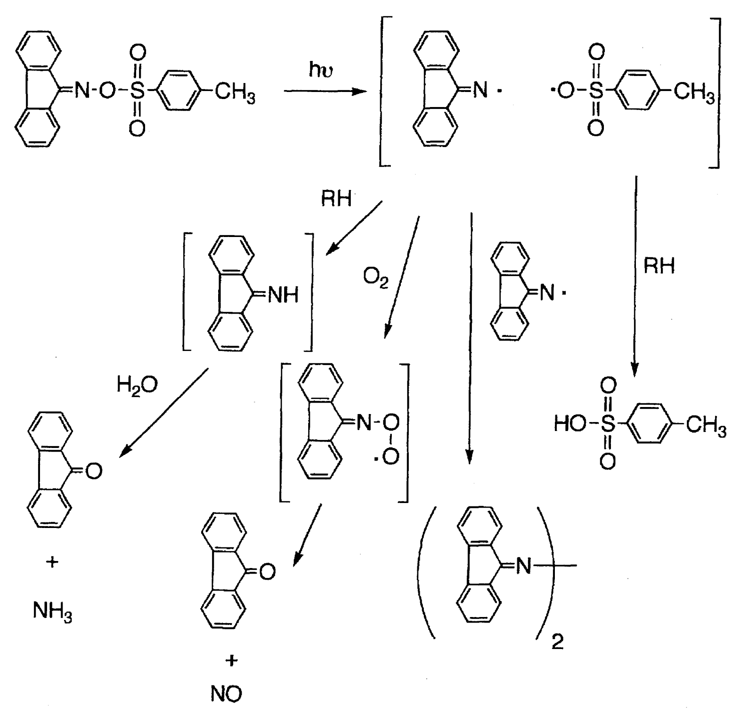
Chart 10.



Scheme 4. Photoinduced HBr formation from vicinal dibromides in the presence of alcohols.



Scheme 5. Mechanism for the photolysis of **18**.

Chart 11.[44]Table 3 shows the results of product analysis for the photolysis of **18** in several media. The yield of fluorenone azine in solution was much higher than that in polymer films. This difference is due to the high mobility of the imino radicals in solution. The formation of fluorenone azine in solution was not affected by the atmosphere. The yield of *p*-toluenesulfonic acid in the presence of oxygen was 88% in solution and 52—69% 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 5, this difference is due to the formation of NH_3 by the hydrolysis of

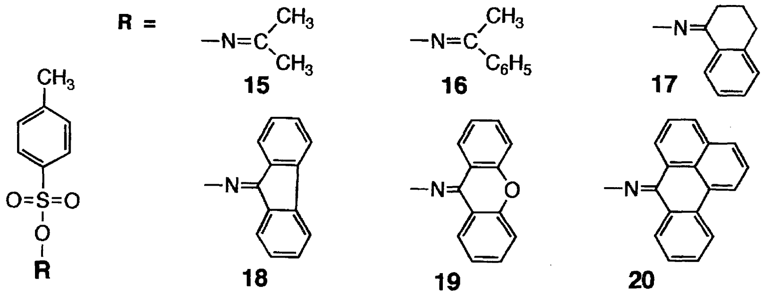


Chart 11.

Table 3. Products from the Photolysis of **18**

Reaction medium	Yield (%)[a)] *p*-Toluenesulfonic acid	Fluorenone	Fluorenone azine	Photolysis degree (%)
CH_3CN/H_2O (92/8, v/v)				
In O_2	88	35	26	55
In vacuo	50	25	25	55
PBOS[b)] film in air	69	56	5.3	78
PMMA[c)] film in air	52	46	4.7	64
PBMA[d)] film in air	61	39	9.3	34

a) Based on photoreacted **18**. b) Poly[*p*-(*t*-butoxycarbonyloxy)styrene]. c) Poly(methyl methacrylate). d) Poly(butyl methacrylate).

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. A similar mechanism has been reported for the photolysis of carboxylic acid esters of oximes.[45)]

The amount of acids generated photochemically can be determined using a colorimetric method.[44)] In this method, acid-sensitive dyes such as tetrabromophenol blue and a merocyanine dye, 1-hexadecyl-4-[2-(4-oxo-2,5-cyclohexadienylidene)ethylidene]-1,4-dihydropyridine, were used. The Φ_a values for the sulfonic acid were determined as the number of moles of sulfonic acids formed per einstein of light absorbed by the compounds. The Φ_d values for the photochemical decomposition of imino sulfonates were also determined as the number of moles of imino sulfonate molecule photolyzed per einstein of light absorbed by the compounds. Although the Φ_a and Φ_d values were dependent on the structure of imino sulfonates, the Φ_a/Φ_d ratio was observed to be about 0.6—0.8 for most imino sulfonate compounds studied (Tables 4 and 5).

The thermal stability of imino sulfonates was strongly dependent on the structure of imino moiety. Roughly speaking, the imino sulfonates that were prepared from sulfonyl chlorides and cyclic ketone oximes with aryl moiety showed relatively higher thermal stability. The absorption peaks for imino sulfonates strongly depended on the structure of the compounds. The compounds studied here are sensitive to 254 nm light, except **25** and **28** (Chart 12). The compounds **18**, **19**, **20** are sensitive to 365 nm light. The compounds **25** and **28** are sensitive to the light at wavelength below 254 nm, e.g. 185-nm light from a low-pressure mercury lamp.

Table 4. Characteristics of Imino Sulfonates **15**—**20**

	Imino sulfonate					
	15	**16**	**17**	**18**	**19**	**20**
T_m (°C)[a)]	85	70	98—99	160—162	164	165—168
T_d (°C)[b)]	118	77	145	225	250	210
Abs. peak (nm)	227	235	228 254	257 299	230 334	228 253 376
Φ_a [c)]	0.094	0.09	0.027	0.13	—[d)]	0.03

a) Melting point. b) Thermal decomposition temperature. c) Quantum yield for the photochemical acid generation using 254 nm light. d) Not measured.

Table 5. Characteristics of Imino Sulfonates **17** and **21**—**24**

	Imino sulfonate				
	17	**21**	**22**	**23**	**24**
T_m (°C)[a)]	98—99	82	138	127	139
T_d (°C)[b)]	145	152	144	137	139
Abs. peak (nm)	254 269(sh)	243 296(sh)	256 295(sh)	255 296(sh)	253 297(sh)
Φ_a [c)]	0.027	0.039	0.064	0.06	0.023

a) Melting point. b) Thermal decomposition temperature. c) Quantum yield for the photochemical acid generation using 254 nm light.

Recently a review on photoacid generators was published.[46)]

1.2 Applications of Photoacid Generators to Polymeric Photosensitive Systems. Photoinitiated Cationic Polymerization and Crosslinking. Photoacid generators, which generate acids on UV irradiation, are utilized in the

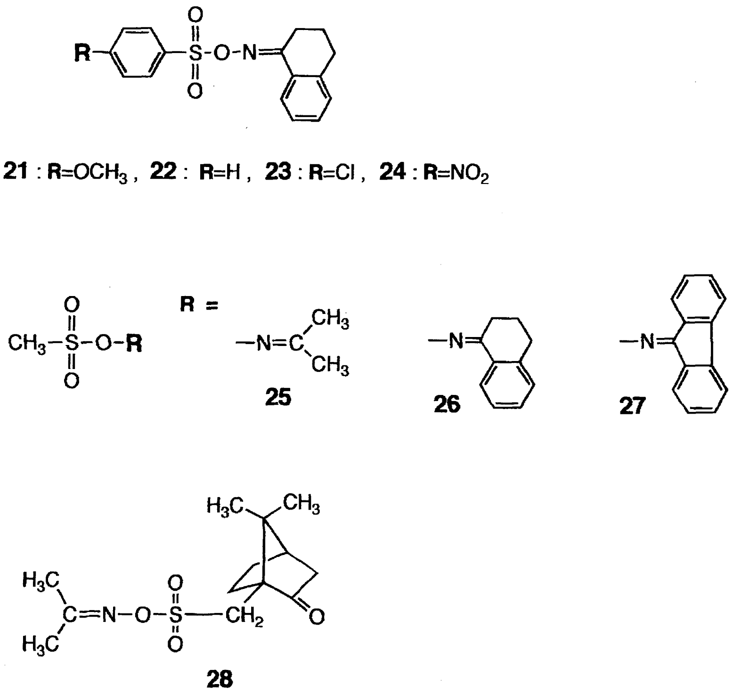


Chart 12.

photoinitiated cationic polymerization of epoxy monomers as well as other cationically polymerizable monomers such as vinyl ethers, the crosslinking and degradation of polymers, the transformation of functional groups in polymer chains, and modification of polymer surfaces. These reactions are very interesting in the field of photoresists, coatings, adhesives, and inks.

In recent years, the photoinitiated cationic polymerization of epoxides and vinyl ethers has become an important technique with applications toward coating, inks, and adhesives. Cation-induced polymerization is not sensitive to oxygen in air so that, by contrast to photochemically induced radical polymerization, the chain reaction continues in the dark after irradiation. Aryldiazonium salts with complex metal halides such as BF_4^-, AsF_6^-, or PF_6^- have been shown to undergo a fast fragmentation under UV irradiation with the formation of acids which are known as efficient initiators for the polymerization of epoxy monomers such as 1,2-epoxypropane and 1,2-epoxybutane. The effectiveness of the salts in the polymerization of epoxyalkanes was dependent on the complex metal halides and decreased in the order $SbF_6^- > PF_6^- > BF_4^-$.1,47) Because of their poor thermal stability and evolution of nitrogen gas that causes bubbles in UV-cured films, these systems have now been replaced by diaryliodonium or triarylsulfonium salts.

Photoinitiated cationic polymerizations of cyclic sulfides,2) cyclic acetals,2) lactones,2) styrene oxide,13) cyclohexe oxide,13) tetrahydrofuran,13) trioxane,47) 2-chloroethyl vinyl ether,47) limonene oxide,14) styrene,48) and 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate49) using a variety of triarylsulfonium salts with complex metal halides have been studied. Although diaryliodonium and triarylsulfonium salts are highly efficient photoinitiators for cationic photopolymerization of epoxy monomers and vinyl ethers, photolysis of these photoinitiators does not occur upon irradiation with light at wavelengths greater than 400 nm. The combination of a dye and an onium salt makes it possible to initiate a number of cationic polymerization using visible light.50) The miscibility of triarylsulfonium and diphenyliodonium salts with epoxy resins is an important factor for effective polymerization. To enhance the miscibility, diphenyliodonium derivatives with long alkyl chains on the phenyl ring were prepared. Recently, iodonium salts with $B(C_6F_5)_4^-$ as a counter anion were prepared. They showed good miscibility with epoxides and also showed higher activity for the curing of epoxides compared with iodonium salts with SbF_6^- as a counter anion.51,52) The toxicity of $B(C_6F_5)_4^-$ was reported to be lower than SbF_6^-. Combination of iodonium salts and photoradical generators such as 1-hydroxycyclohexyl phenyl ketone induced the efficient photopolymerization of vinyl ethers.53) In this system, in addition to the photochemical generation of acids from iodonium salts, the radical species formed by the photolysis of photoradical generators were oxidized by iodonium salts to generate cationic species which initiated the cationic polymerization. Although sulfonium salts can be used for the same purpose, the reactivity of sulfonium salts toward radicals is lower than that of iodonium salts.54)

Photoinduced acid- catalyzed crosslinking has been achieved through various mechanisms. These include cationic polymerization, condensation polymerization, and electrophilic aromatic substitution. The photoacid induced crosslinking of polymeric materials can be applied to negative tone photoresists and coating materials. The photoinduced acid-catalyzed crosslinking of polymers bearing epoxy or epithio groups was reported. Photocrosslinking of polymer films (**29**) was reported with both 2,3-epoxypropyl or 2,3-epithiopropyl groups and imino sulfonate units (0.3—3.0 mol%) (Chart 13), the latter of which form *p*-styrenesulfonic acid units upon irradiation with 254 nm light.55) The photocrosslinking efficiency of the polymers with 2,3-epithiopropyl groups was higher than those with 2,3-epoxypropyl groups. The insoluble fraction of the irradiated films increased with increasing post-heating time at 80 °C in the dark.

Copolymers (**30**) of 4-(1-hydroxy-1-methylethyl)styrene and styrene or 4-hydroxystyrene became insoluble in solvents (Chart 14), when films of the polymer containing 5—10% of triarylsulfonium salts were irradiated and followed by heating.56) In this system, crosslinking occurs by the electrophilic aromatic substitution of benzylic carbocationic species or by the cationic polymerization of vinyl groups generated by the photoinduced acid-catalyzed dehydration of the pendant alcohol groups.

Polymers (**31**) bearing pendant β-keto sulfone units together with vinyloxy groups were reported to be photocrosslinkable (Chart 15).57) In this system, photoinduced sulfinic and/or sulfonic acids generated by the photolysis of β-keto sulfone units induced the polymerization of vinyl ether units in the side chain, which resulted in insolubilization of the polymer.

Photoinitiated Degradation and Transformation of Polymers. If poly(phthalaldehyde) is prepared at temperatures below −40 °C by the use of butyllithium as an initiator and the chain ends are capped by reaction with an alkylating or acylating reagent, the polymer can be isolated and han-

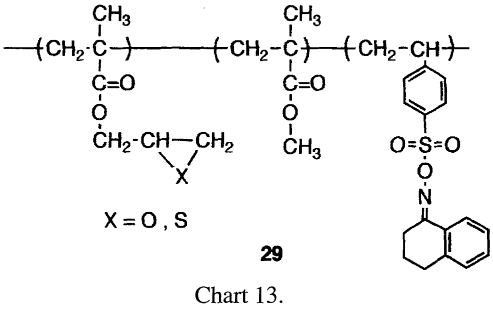


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Chart 13.

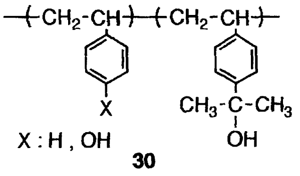

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Chart 14.

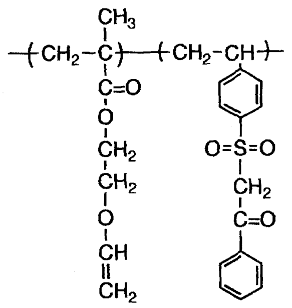

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Chart 15.

dled conventionally at temperatures above 100 °C.[58] When a film of poly(phthalaldehyde) containing a photoacid generator is irradiated, the polymer rapidly depolymerized back to the monomer, phthalaldehyde. The monomer sublimes away during exposure even at room temperature to spontaneously produce relief images in positive tone. Similarly, the photoinduced acid-catalyzed degradation of polycarbonate (**32**)[59] and polymers (**33**) containing 2,4-dialkoxypyrimidine units[60] was observed (Chart 16). These degradation systems are named "chemically amplified systems".

Photoinduced acid-catalyzed deprotection of pendant groups on polymers results in an alteration of polarity of the repeat units, which changes the solubility of polymers. A polarity change from a non-polar to a polar state provides positive imaging with aqueous base or negative imaging with non-polar organic solvents. A variety of polymer bearing COOH or phenolic OH groups which are protected were prepared and their applications to photoresists were widely studied. A class of resists that achieve differential solubility by an acid catalyzed chemical reaction were discovered. The process typically involves photogeneration of acids that catalyze many subsequent chemical reactions such as deblocking of a protective groups or crosslinking of matrix resins. This system is also called a chemically amplified system. Irradiation of poly[4-(*t*-butoxycarbonyloxy)styrene] (**34**) films containing small amounts of photoacid generators and subsequent heating lead to cleavage of the protecting group to generate poly(4-binylphenol) and regeneration of acid, making it available for subsequent deprotection reactions (Chart 17).[61—63] Aqueous base developers selectively remove the irradiated regions affording a positive image and organic solvent developers remove the unirradiated portions of the film, giving a negative image. Acetal-protected poly(4-vinylphenol),[64] tetrahydropyranyl-protected poly(4-vinylphenol),[65] and silylated poly(4-vinylphenol)[66] liberated poly(4-vinylphenol) by the deprotection reactions catalyzed by the acids formed photochemically.

Polymers (**35**) having pendant imino sulfonate units can be photochemically converted into *p*-styrenesulfonic acid units (Chart 18); then the irradiated polymers become soluble in aqueous base and polar solvents.[67—72] A copolymer of 4-(*t*-butoxycarbonyloxy)styrene and 9-fluorenilideneamino *p*-styrenesulfonate as photoacid generating units was reported. The polymer was converted to a copolymer of 4-vinylphenol and *p*-styrenesulfonic acid upon irradiation and subsequent heating.[73]

Surface Imaging Resists. Photoacid generating polymers which have imino sulfonate units in their side chains were used as surface imaging resists.[74—80] The methodology of the system for the surface imaging is shown in Scheme 6. Upon irradiation, the surface of the polymers having photoacid generating units becomes hydrophilic because of the formation of acid. Water sorption from the atmosphere occurs at the surface of the irradiated films. When the irradiated surface was exposed to the vapor of alkoxysilanes under hu-

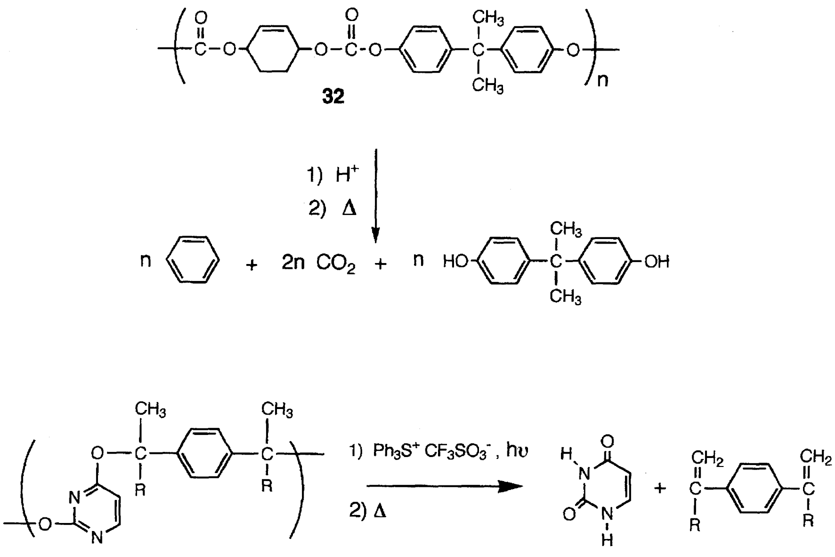

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Chart 16.

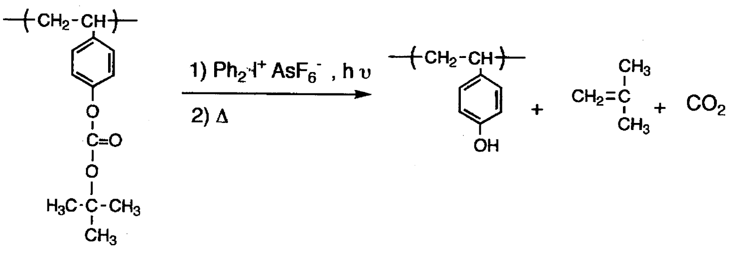

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Chart 17.

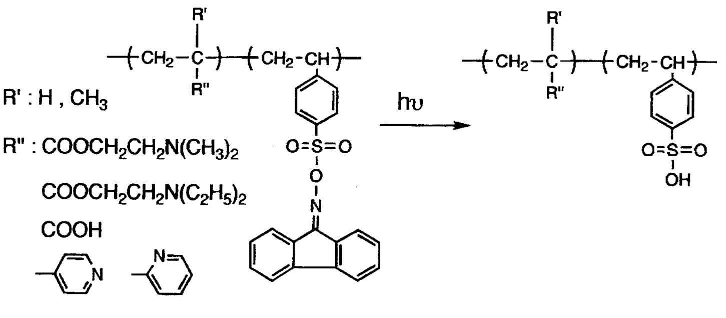

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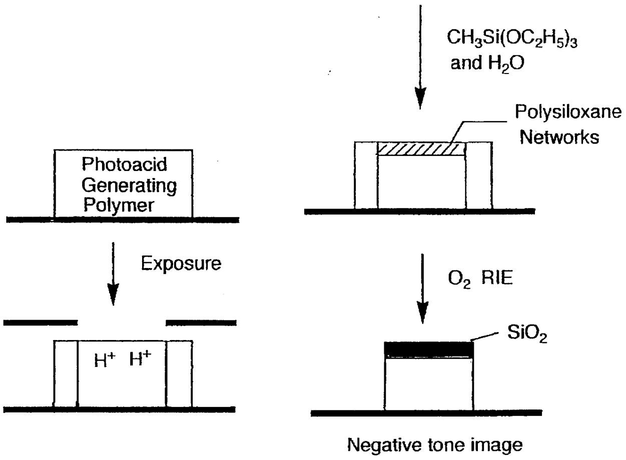
Chart 18.



Scheme 6. Surface imaging photoresist system.

mid conditions, polysiloxane networks were formed near the surface of the polymer films. No polysiloxane networks were formed at the unirradiated surface, since the photoinduced acids are essential for catalyzing the hydrolysis of alkoxysilanes. A negative tone image was obtained by using

$$n\mathrm{CH_3Si(OC_2H_5)_3} + 3n\mathrm{H_2O} \xrightarrow{\mathrm{H^+}} n\mathrm{CH_3Si(OH)_3} + 3n\mathrm{C_2H_5OH}$$
$$n\mathrm{CH_3Si(OH)_3} \longrightarrow \mathrm{Polysiloxanes} + 1.5n\ \mathrm{H_2O}$$

oxygen reactive ion etching (O_2 RIE), since the polysiloxanes formed at the irradiated polymer surface act as a good etch barrier. In the microlithographic process, the use of deep UV light to provide higher resolution causes new problems due to decreased depth of focus and increased substrate reflectance. The surface imaging system is expected to eliminate or alleviate these problems.

When the films of copolymers (**36a**—**36c**) of methacrylates with 1,2,3,4-tetrahydro-1-naphthylideneamino *p*-styrenesulfonate were irradiated with 254-nm light, *p*-styrenesulfonic acid units were generated by the photolysis of 1,2,3,4-tetrahydro-1-naphthylideneamino *p*-styrenesulfonate units (Chart 19). The fraction of the photoacid generating units were 15—25 mol%. The hydrophobic polymer surface became hydrophilic upon irradiation and water sorption from the atmosphere occurred, which was checked by a quartz crystal microbalance. The relationship between irradiation time and water sorbed into the irradiated **36a** film at various relative humidities was shown in Fig. 1. Water sorption began the moment that the polymer film was irradiated with 254-nm light. It increased with irradiation time and more gradually increased after irradiation. The amount of water sorbed increased exponentially with increasing relative humidity. Furthermore, if the relative humidity and irradiation time were the same, the water sorption ability of the irradiated polymer films decreased in the order **36a** > **36b** > **36c**. When the irradiated **36a** film was exposed to the vapor of alkoxysilanes such as $Si(OR)_4$ or $R'Si(OR)_3$ at 30 °C, SiO_2 or polysiloxane was formed in the near surface region of the films. The amounts of SiO_2 or polysiloxanes increased with increasing the amount of acid in the film and the period of vapor treatment with alkoxysilane vapor (CVD treatment). The ester structure of **36a**—**c** strongly affected the SiO_2 formation rate at the irradiated surface (Fig. 2). The hydrophobic nature of the ester units strongly reduced the SiO_2 formation rate. The structure of alkoxysilanes also strongly affected the SiO_2 or polysiloxane formation rate. Among the selected alkoxysilanes, the formation rate decreased in the order $CH_3Si(OCH_3)_3 > Si(OCH_3)_4 > CH_3Si(OC_2H_5)_3 > Si(OC_2H_5)_4 > Si(OC_3H_7)_4$. It was confirmed that the SiO_2 or polysiloxane formation rate in the irradiated surface

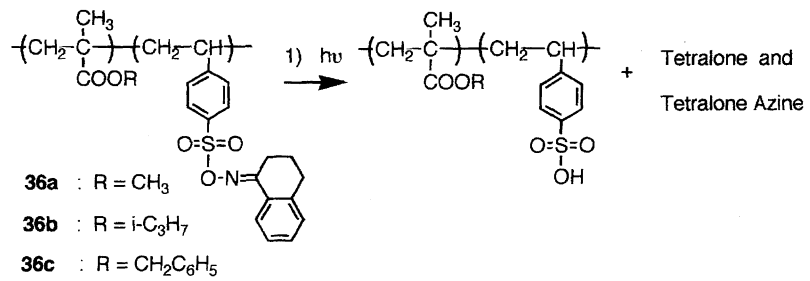


Chart 19.

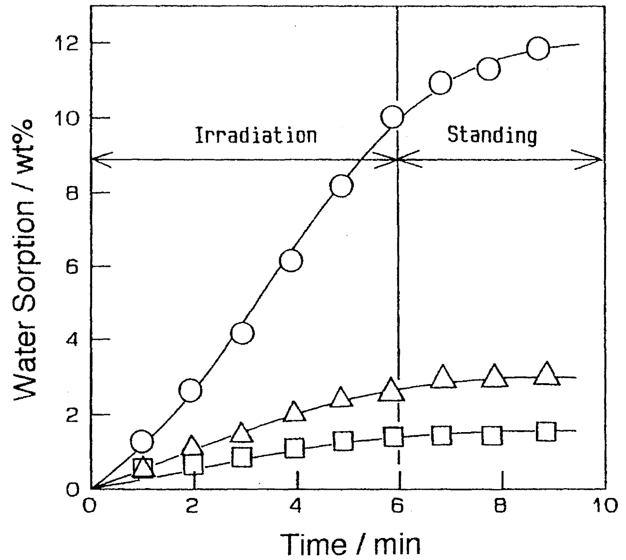


Fig. 1. Relationship between irradiation time and water sorption to **36a** film. Relative humidity: (○) 95, (△) 58, (□) 32%.

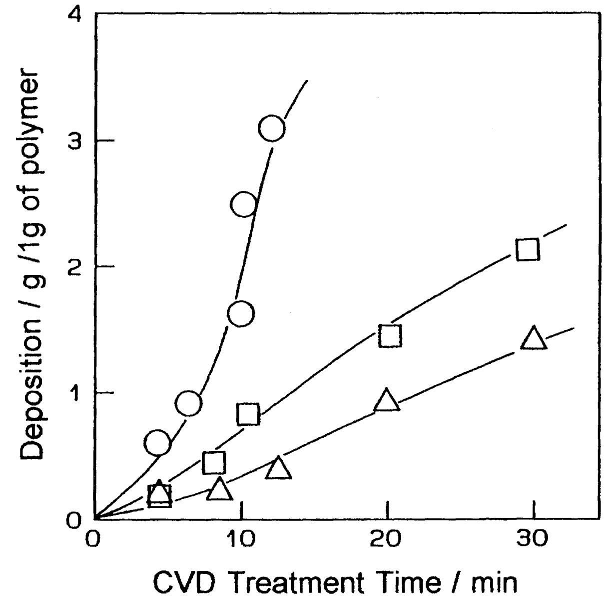


Fig. 2. Effect of the polymer structure on the SiO_2 deposition at the irradiated film surface. Surface modification was carried out with $Si(OCH_3)_4$ vapor. Polymer: (○) **36a**, (△) **36b**, (□) **36c**.

was determined by both the rate constant for the hydrolysis of alkoxysilanes in the presence of acid and boiling points of alkoxysilanes. The etching rate of **36a** film with O_2 plasma decreased after alkoxysilane vapor treatment. Based on the present system, 0.25 μm line and space images were obtained using **36a** and KrF excimer laser lithography.[81] Furthermore, using **37** and ArF excimer laser lithography, 0.13 μm line and space images were obtained (Chart 20).[82]

2. Photobase generators and Their Applications.

2.1 Photochemical Generation of Bases. Typical examples of photobase generators are listed in Scheme 7 and their quantum yields of photolysis are shown in Table 6.

Cobalt amine complexes (**38**) are ionic compounds, which show poor solubility in organic polymers and solvents. Thus, halide ions are changed to perchlorate ions in their use as a photobase generators.[83—85] Their UV absorption is under 300 nm and the quantum yield of formation of an amine or ammonia is about 0.01. In the photolysis of oxime esters (**39**) amines are formed as shown in Scheme 7. In this reaction, imines formed after their photolysis are easily hydrolyzed to amines by water vapor in air.[86—88] Triplet sensitizers such as benzophenone are very effective for the photolysis; their quantum yields for amines formation are 0.3 and 0.5 for **39a** and **39b**, respectively. Their values increase for bifunctional

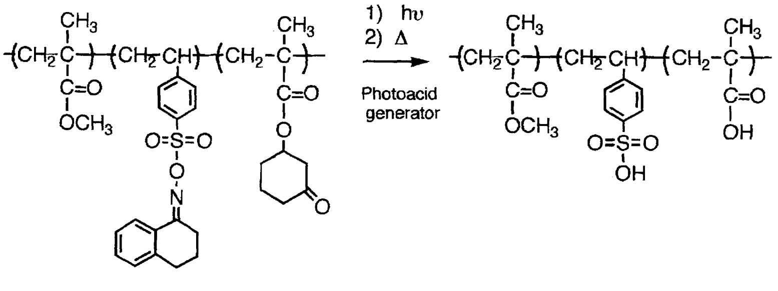


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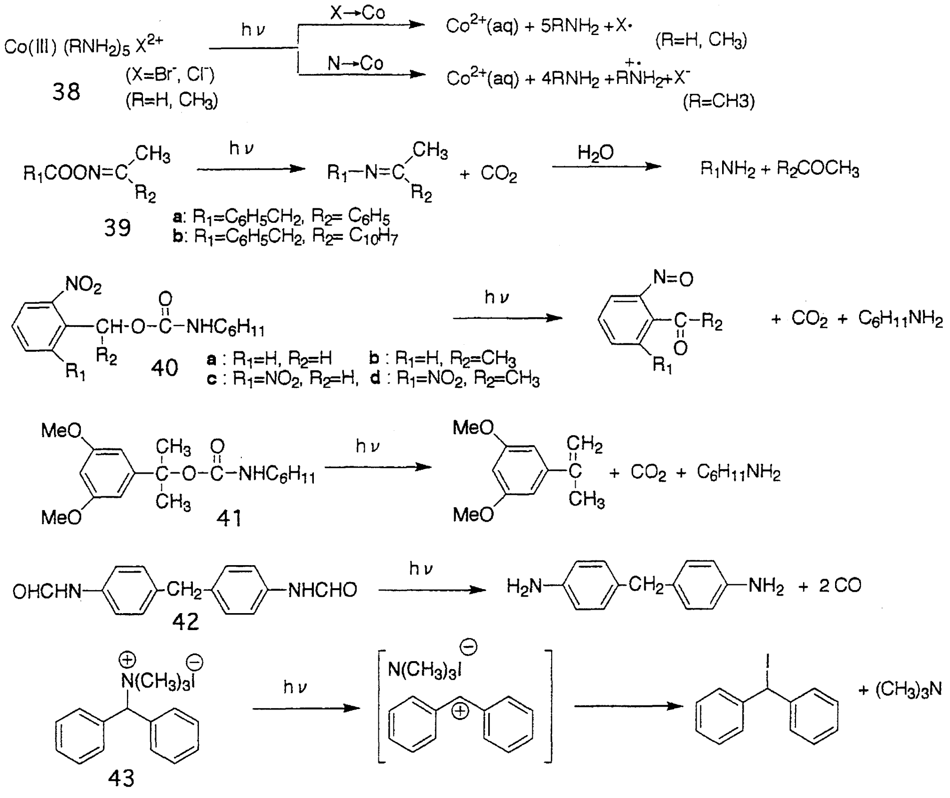
Chart 20.



Scheme 7. Photobase generators.

Table 6. Quantum Yields of Amine Formation in Polymer Matrix (Φ)

Photobase generator	Φ	Irradiation wavelength (nm)	Polymer matrix
38	ca. 0.01	254	Glycidyl methacrylate/ ethyl acrylate copolymer
39a	0.30	366	Polystyrene[a)]
39b	0.50	366	Polystyrene[a)]
40a	0.13	254	Poly(methyl methacrylate)
40b	0.11	254	Poly(methyl methacrylate)
40c	0.62	254	Poly(methyl methacrylate)
40d	0.35	254	Poly(methyl methacrylate)
41	0.10	280	Polymethacrylonitrile

a) in the presence of benzophenone.

oxime esters (e.g. **39e** in Table 7) and pendant acyloxyimino groups in polymers (e.g. (AAPO(26.3)-St)) from 0.3 to 0.6 and 0.5, respectively.[89)]

In the photolysis of *o*-nitrobenzyl carbamates (**40a**), amines are formed in a similar manner, as shown in Scheme 2. Their quantum yields of amine formation is about 0.1 for **40a** and **40b** and the values for *o*-dinitro derivatives (**40c** and **40d**) increase to 0.62 and 0.35, respectively.[91)] The quantum yields for carbamates such as **41** is 0.10.[92,93)] Photolysis of formamides (**42**) generates amines.[91,94)] However, the change of formyl groups to acyl or benzoyl groups reduces the yields, because the resulting *O*-acetyl or *O*-benzoyl-substituted benzene units absorb UV light strongly.[94)] Although it is reported that the photolysis of an onium salt (**43**) generates a tertiary amine, the details are not known.[95)]

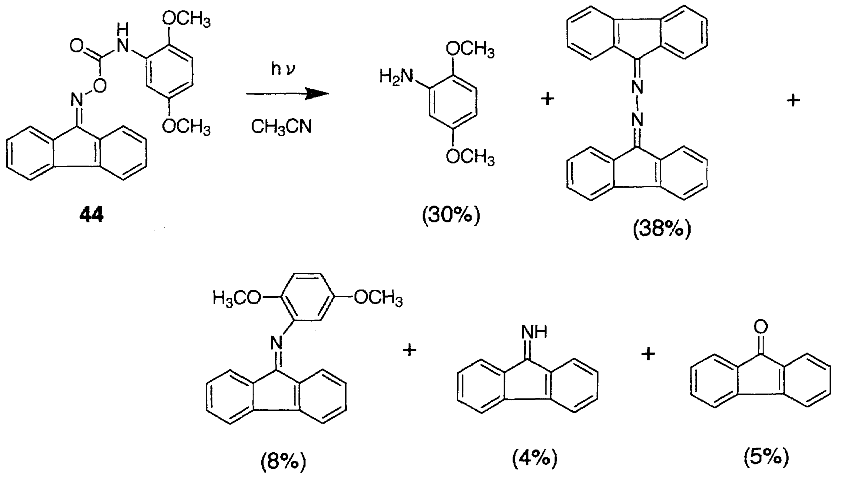
Table 7. Yields of Amines for Oxime Esters under N_2

Compound[a)]	Condition	Resulting Amine	Yield (%)
39a	PSt film	Benzylamine	72
39c	PSt film	*t*-Butylamine	7
39d	PSt film	Aniline	3
39e[b)]	PSt film	Ethylenediamine	68
39f[b)]	PSt film	1,3-Propanediamine	13
AAPO[c)] (26.3)–St[d)] (copolymer)	Film	Amino groups	70
MAAPO[e)] (28.3)–St (copolymer)	Film	Amino groups	22

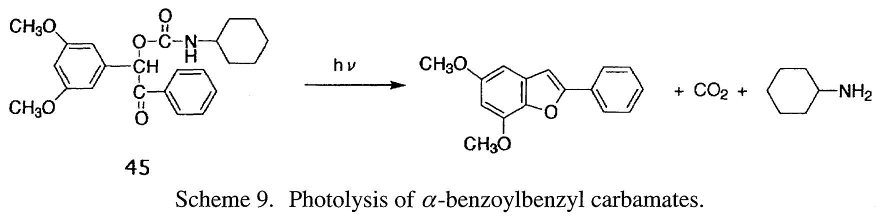
a) $R_1COON{=}C(CH_3)C_6H_5$: **39a**: $R_1 = C_6H_5CH_2$, **39c**: $R_1 = (CH_3)_3C$, **39d**: $R_1 = C_6H_5$. b) $R_1(COON{=}C(CH_3)C_6H_5)_2$: **39e**: $R_1 = CH_2CH_2$, **39f**: $R_1 = CH_2CH_2CH_2$. c) Acetophenone *O*-acryloyloxime. d) Styrene. e) Acetophenone *O*-methacryloyloxime.

In the photolysis of a carbamate (**44**) derived from fluorenone oxime shown in Scheme 8, 2,5-dimethoxyaniline and fluorenone azine are main products.[96] Although it is expected that 2,5-dimethoxyphenylhydrazine is formed from the structure of carbamate, no hydrazine derivatives were detected. That may be due to the fact that this photolysis was carried out in solution. When 2,5-dimethoxyanilino groups were changed to cyclohexyl groups, the yield was ca. 5%. Furthermore, the photolysis of α-benzoylbenzyl carbamates yields efficiently cyclohexylamine with the corresponding substituted benzo[*b*]furan photocyclization product, as shown in Scheme 9.[97] Their quantum yields depended on the irradiation wavelengths: the values were 0.067, 0.080, 0.054, and 0.028 at 254, 313, 336, and 365 nm, respectively.

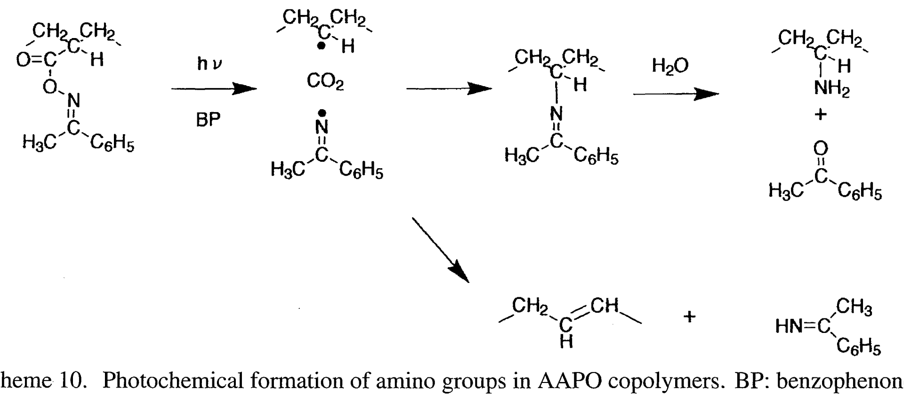
The yields of amines in the photolysis of oxime esters depended on their *O*-acyl groups. Table 7 shows the relation between oxime esters and yields of amines in polymer matrixes. In this table, the results of acetophenone *O*-acryloyloxime (AAPO) or acetophenone *O*-methacryloyloxime (MAAPO) copolymers are also shown. As seen in Scheme 10, pendant amino groups are formed in the photolysis of acyloxyimino (AOI) groups in AAPO copolymers, followed by hydrolysis, and at the same time double bonds in main chains are also formed as the other product.[87—89] The yield of amino groups for the copolymer of AAPO and styrene (St), that is, AAPO(26.3)–St is 70%. The same yields for amine formation were obtained for **39a** and **39e**. On the other hand, the yield of amino groups for MAAPO(28.3)–St was 22%. The lowering of the yield was explained by the intramolecular hydrogen abstraction of iminyl radicals, as shown in Scheme 11. Scheme 12 shows the relation between structures of oxime esters and yields of amines. The formation of six-membered rings of azomethine units in oxime esters reduces the yield as seen in **39c**, **39d**, and **39e**. However, the yield for **39f** was 68%. This result was explained by the difference in the reactivity of hydrogens: That is, the



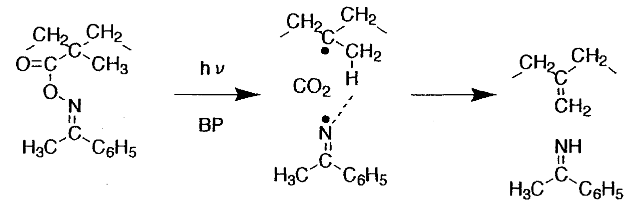
Scheme 8. Photolysis of oxime *O*-carbamates. ( ): yield.



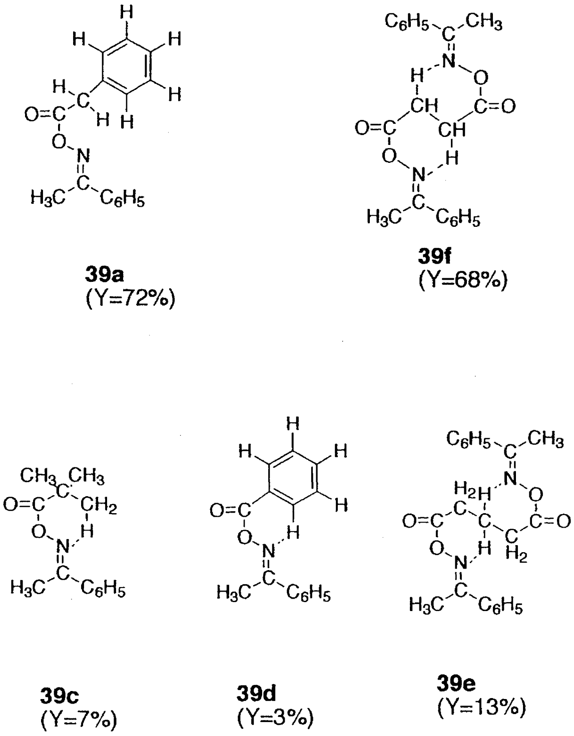
Scheme 9. Photolysis of α-benzoylbenzyl carbamates.



Scheme 10. Photochemical formation of amino groups in AAPO copolymers. BP: benzophenone.



Scheme 11. Photochemical formation of vinylidene-type double bonds in MAAPO copolymers. BP: benzophenone.



Scheme 12. Relation between structure of oxime esters and yield of amines. (Y: yield)

polar hydrogen at α-position of ester groups is difficult to abstract by iminyl radicals compared with β-hydrogen. It is not apparent whether the same explanation can be applied for **39d**.

As seen in Scheme 10, the coupling efficiency of the resulting radicals in the photolysis of oxime esters determines the yield of amines. In the photolysis of **39a** in polystyrene films and in benzene, such yields were 72 and 43%, respectively.[99]

In the photolysis of pendant AOI groups in AAPO copolymers, the content of AAPO affects the yield. Figure 3 shows the relation between AAPO content in St copolymers and the yield of amino groups.[87,89] The yield decreased with increasing contents of AAPO. This result was explained by an increasing formation of double bonds in main chains.

2.2 Applications of Photobase Generators to Photosensitive Polymer Systems. As mentioned before, the acids derived from photoacid generators are widely used as catalysts not only for polymer modification but also for cationic polymerization in UV curing of epoxides and vinyl ethers.

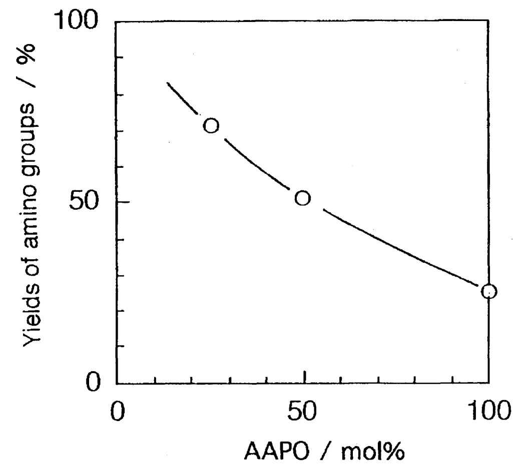


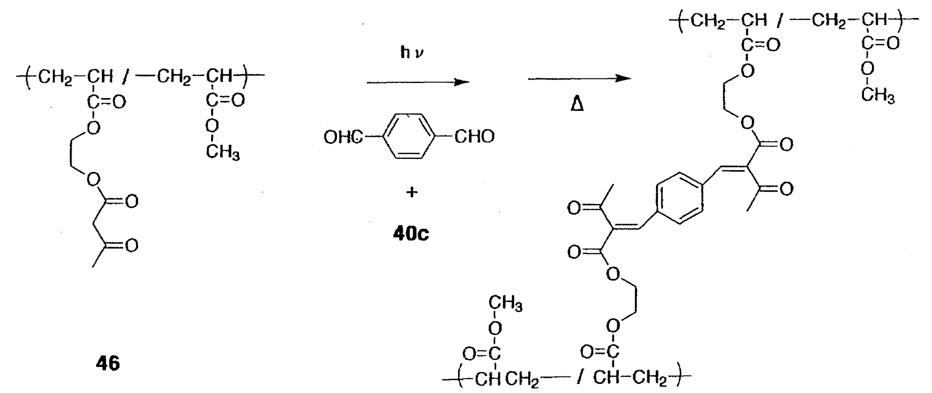
Fig. 3. Relation between AOI group contents in AAPO–St and yields of amino groups.

Similarly, photobase generators are expected to be applied to several photochemical processes, including photocrosslinking and photomodification of polymers. From such viewpoints, several applications of the use of photobase generators are described.

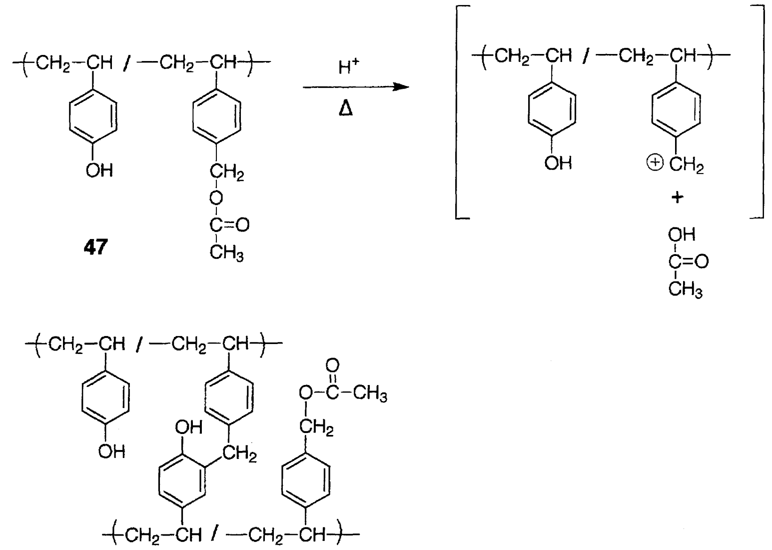
Photoinitiated Thermal Crosslinking. Photoinitiated thermal crosslinking of polymers or oligomers bearing epoxy groups[83—86,94,100—102] or isocyanate groups[94] is induced in the presence of photobase generators.

A new crosslinking system by the use of Knoevenagel condensation in the presence of photobase generators was investigated.[103] Copolymers of 2-acetoacetoxyethyl methacrylate (AAEM) and methyl methacrylate (MMA) (**46**) were chosen as a polymer bearing active methylene units, as shown in Scheme 13. Polymer films were irradiated in the presence of terephthalaldehyde and **40c** and then heated. The resulting amines amplified the thermal crosslinking. The copolymer of 50 mol% AAEM could be developed in an aqueous alkaline solution. Furthermore, when the acetoacetyl units were replaced by cyanoacetyl units, the activity of methylene units in the copolymer (CAEM–MMA) could be increased. However, as thermal crosslinking of active methylene units with terephthalaldehyde occurred, the polymer could not used as a photoresist. When a dialdehyde which has a steric hindrance such as 2-methoxy-5-methyl-isophthaldehyde was chosen, the high sensitivity (20 mJ cm^{-2} at 254 nm) was obtained. The CAEM–MMA is also insolubilized by the reaction of methylene units with cyano groups in the presence of amines without dialdehydes.

The addition of photobase generators in the photoresists which use thermal crosslinking by acids formed thermally can reverse the image of the mask (from negative type resists to positive type resists). As shown in Scheme 14, the acids can induce the thermal crosslinking of a copolymer of 4-vinylphenol-4-(acetoxymethyl)styrene (**47**). If a base is introduced in the copolymer films photochemically before the thermal crosslinking, the acid in irradiated parts is neutralized by the base, and thermal crosslinking does not proceed. On the basis of this principle, thermal acid gener-



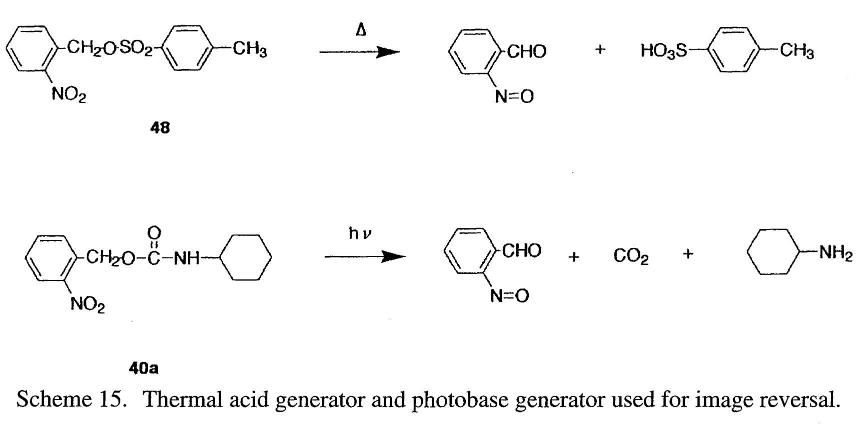
Scheme 13. Photo-induced thermal crosslinking by the use of Knoevenagel condensation.



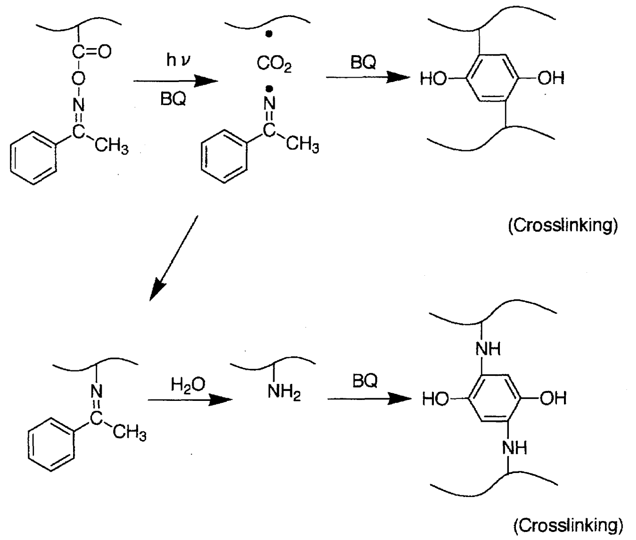
Scheme 14. Acid-induced thermal crosslinking of 4-(acetoxymethyl)styrene-4-hydroxystyrene copolymer.

ator (**48**) and photobase generator (**40a**) in Scheme 15 are mixed in the copolymer and heated after irradiation. Upon development, a positive pattern of the copolymer can be obtained. As the thermal acid generator can also generate the acid photochemically, a little higher amount of **40a** should be used.[105] Poly(vinylphenol)/hexakis(methoxymethyl)melamine blends can be used as polymer systems using acid-induced thermal crosslinking.[106]

As shown in Scheme 10, pendant amino groups can be introduced in the photolysis of AAPO copolymers. Quinones such as 1,4-benzoquinone (BQ), 1,4-naphtoquinone (NQ), and dodecylthio-1,4-benzoquinone (DSBQ) were used as crosslinkers in the photolysis of AAPO copolymers.[107—110] The outline of the reactions are shown in Scheme 16. Upon UV exposure, the reaction of resulting polymer radicals and BQ induced the crosslinking, and the degree of the crosslinking was depressed in the presence in air. After the UV exposure, thermal reaction of pendant amino groups with BQ proceeded upon heating. Such photoinduced and thermal crosslinking reactions are novel hybrid crosslinking reac-



Scheme 15. Thermal acid generator and photobase generator used for image reversal.



Scheme 16. Hybrid type photoinitiated thermal crosslinking of AAPO copolymers/BQ systems. BQ: 1,4-benzoquinone.

tions thanks to the use of both free radicals and amino groups. Furthermore, in the investigation of crosslinking processes, the quinones were found to work as photosensitizers for the photolysis of AOI groups. The sensitization efficiency of these quinones were less than that of benzophenone, and the order of sensitization for decomposition of AOI groups was BP > NQ > BQ > DTBQ.[108,110] Effective irradiation wavelengths for the quinones are 254 and 313 nm and the order of sensitization was parallel to the intensity of absorption at the wavelengths. The light at 436 nm was not effective for DSBQ, even though this compound has an absorption band around this wavelength.

When AAPO(28)–MMA films in the presence of quinones were irradiated, NQ and BQ induced the photocrosslinking. Although DSBQ did not induce the crosslinking, the thermal insolubilization after irradiation was induced.[108] This result was explained by the difference in the reactivity of the resulting polymer radicals with the quinones. That is, it is deduced that polymer radicals reacted with iminyl radicals more effectively than with DSBQ, and much higher amounts of pendant amino groups were introduced in the polymers compared with results with BQ or NQ.

Furthermore, copolymers bearing both pendant AOI groups and epoxy groups which were prepared by the copolymerization of AAPO with glycidyl (2.3-epoxypropyl) methacrylate (GMA) were very effective for photoinduced and thermal crosslinking. As shown in Fig. 4, photocrosslinking of AAPO(33)–GMA films proceeded very effectively compared with the results of AAPO(28)–MMA films and the insolubilization after the irradiation was increased thermally.[111] It was thought that the thermal reactions were due to the reactions of pendant amino groups with NQ and pendant epoxy groups as shown in Scheme 17.

In fact, thermal crosslinking of polymers bearing amino groups and epoxy groups which were prepared by the photolysis of AAPO(33)–GMA films with BP, proceeded very rapidly with or without NQ (Fig. 5). Moreover, reduction of NQ and a decrease in an amount of epoxy groups after heating were observed in their IR spectra.

Photoinduced Transformation of Functional Groups. When pendant amino groups formed by photolysis of almost of all AOI groups in AAPO(50.3)–MMA films were transformed to ammonio groups by an acid, the copolymers became soluble in water.[114] This result suggests that the AAPO copolymers can be applied to photoresists. In fact they could be used as dual tone photoresists by choosing developer.[112—115]

In the photolysis of pendant β-keto sulfone (β-KS) groups in p-(phenacylsulfonyl)styrene (PSSt) copolymers,

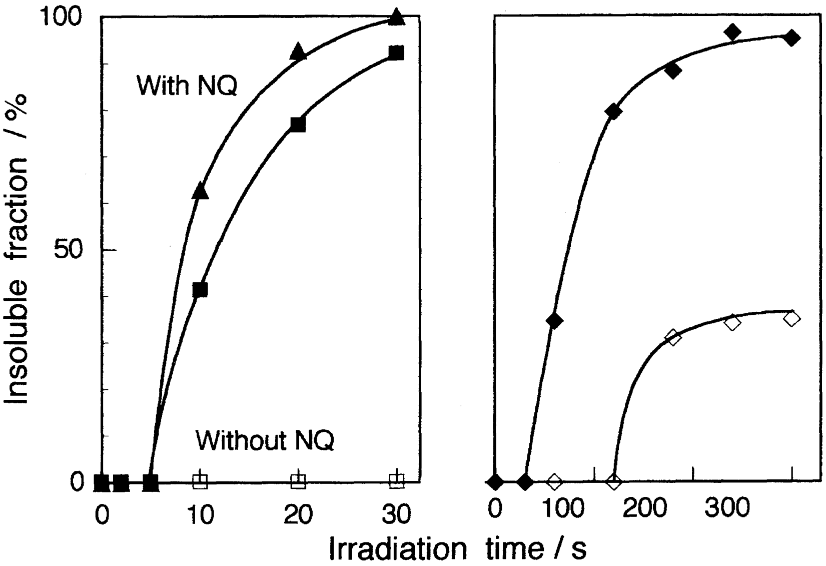
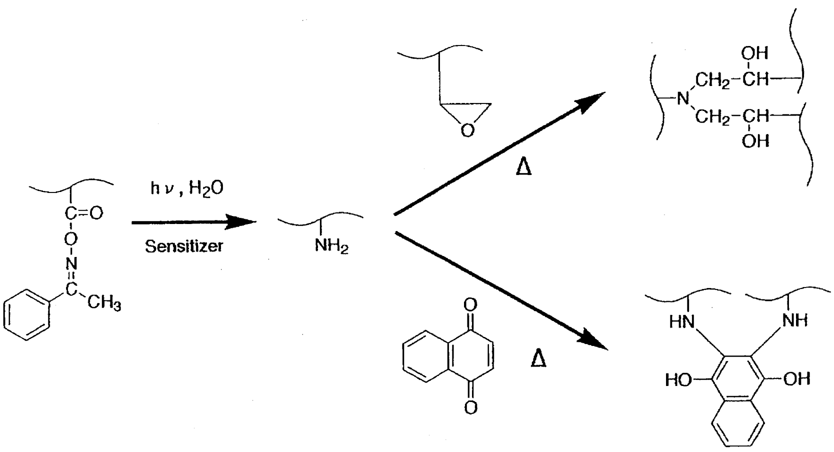


Fig. 4. Photoinduced and thermal insolubilization of AAPO copolymers. (a) AAPO(33)–GMA films: (■, □) Only irradiation, (▲, △) Heated for 10 min. (b) AAPO(28)–MMA films with NQ: (◆) Only irradiation, (◇) Heated for 10 min.# # at 100 °C after irradiation.



Scheme 17. Thermal crosslinking mechanism of copolymer bearing both amino and epoxy groups in the presence of 1,4-naphthoquinone (NQ).

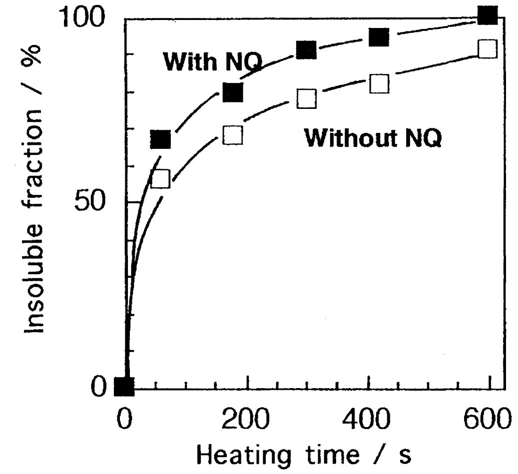


Fig. 5. Effects of NQ on thermal crosslinking of polymers bearing amino groups and epoxy groups at 120 °C: (■, □) Decomposed fraction of AOI groups in the AAPO-(33)–GMA films irradiated in the presence of benzophenone: 60%.

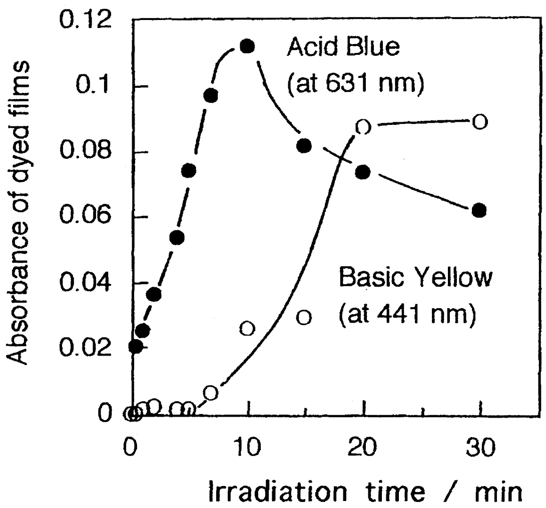
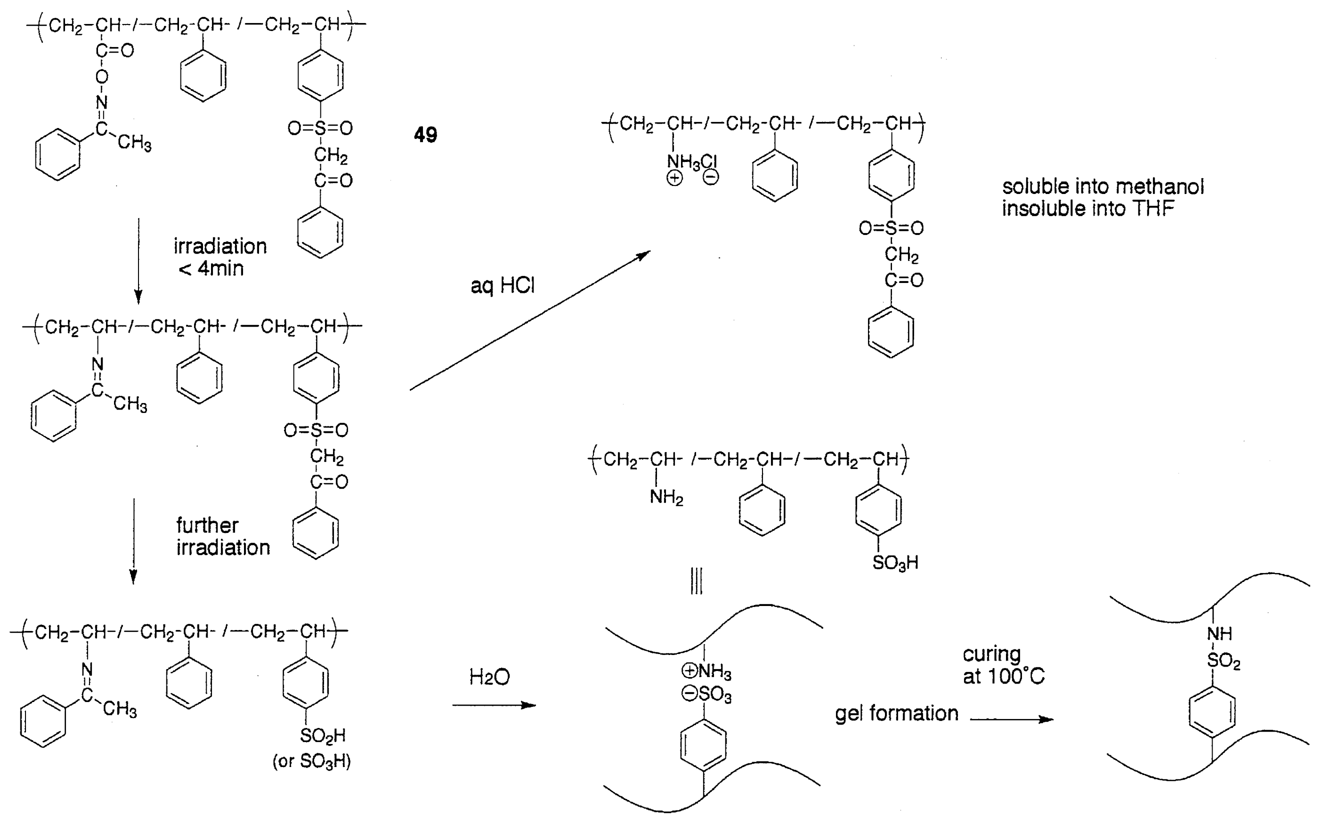


Fig. 6. Dyeing of irradiated AAPO(25)–PSSt(23)–MMA films by Acid Blue 40 and Basic Yellow 2.

acid groups (sulfinic and sulfonic acid groups) are introduced. Thus, it is expected that in the photolysis of polymers bearing both AOI groups and β-KS groups, both acid and base groups are introduced in the same polymers. As shown in Scheme 18, the terpolymer of AAPO(33)–PSSt(4)–St (**49**) was prepared. Interestingly, in the photolysis of this polymer film, stepwise photolysis of AOI groups and β-KS groups was observed.[116,117)] That is, the film became soluble in an aqueous HCl solution at an earlier stage by UV irradiation. The further irradiation induced the film to be insoluble in water, and irradiated parts swelled well in water. This behavior suggests that the photolysis of AOI groups occurs at first, and then that of β-KS groups does. Furthermore, this explanation was also verified by dyeing of irradiated films. Although the degree of dyeing of the film with C. I. Acid Blue 40 which has $-SO_3Na$ groups increased with increasing irradiation time at an earlier stage, the film was not dyed by C. I. Basic Yellow 2 which has $-N(CH_3)_2HCl$ groups (Fig. 6). On the other hand, further irradiation made it possible for the film to be dyed by both dyes (Fig. 6). This result also supports the sequential formation of basic and acidic groups. The photochemical gradual introductions of basic and acidic groups are very interesting from the viewpoint of changing the physical properties of polymers.

One of the recent trends in a polarity alteration is the introduction of the concept of chemical amplification. The presence of bases induced the decrease of the temperature of decarboxylation in the polymer (**50**) shown in Scheme 19. Although the decarboxylation occurs at 130—150 °C without amines, it starts at 100 °C with them. The thermolysis after irradiation of the polymer film with a photobase generator induces polarity alteration and the development of the film with alkaline developer gives a negative image. Image reversal is accomplished by in situ silylation of the unirradiated parts with (dimethylamino)trimethylsilane, followed by dry development by O_2 plasma. The resist shows high sensitivity to deep UV, ca. 10 mJ cm^{-2}.[118—120)] Thus this polymer can be used not only as an alkaline-developable photoresist but also as a surface imaging photoresist.

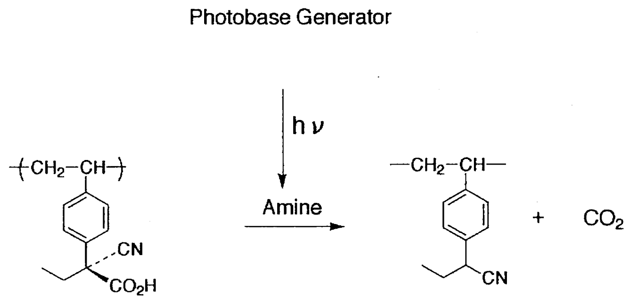
In the polymer (**51**) shown in Scheme 20, pendant amido-



Scheme 18. Photoreaction of copolymer bearing both β-KS and AOI groups.

ester groups are removed thermally by amine-catalyzed intramolecular imidization of polymer side chains and pendant hydroxy groups are introduced in the polymers.[121] The order of imidization was **51d** > **51a** > **51c** > **51b**. The **51** and photobase generator system was used as a positive photoresist.

Photosensitive Polyimides. They are very attractive polymers, which can be used both as photoresists and insulators. At present, soluble poly(amic ester)s with methacrylate or benzophenone units are cured by UV irradiation and then irradiated-insoluble parts are imidized at high temperature. The UV curing is carried out by the use of radical processes. This polyimide has unfavorable features such as low photolithographic contrast (ca. 1) and a high percentage of shrinkage on final cure (>50%). As the use of amines can decrease the temperature of imidization, e.g. from 170 to 150 °C, poly(amic ester)s (**52**) with a photobase generator **40b** were investigated as photosensitive polyimides. A coumarin derivative was used as a sensitizer which has an absorption to 400 nm, because the poly(amic ester) has an absorption to 360 nm. The thermal imidization of the poly(amic ester) by the resulting amine is performed selectively as shown in Scheme 21. The differential dissolution between poly(amic ester)s and partially imidized polymers (20—80%) was possible. Finally, complete imidization was carried out. Final shrinkage was 37% and contrast was 3.[122,123]



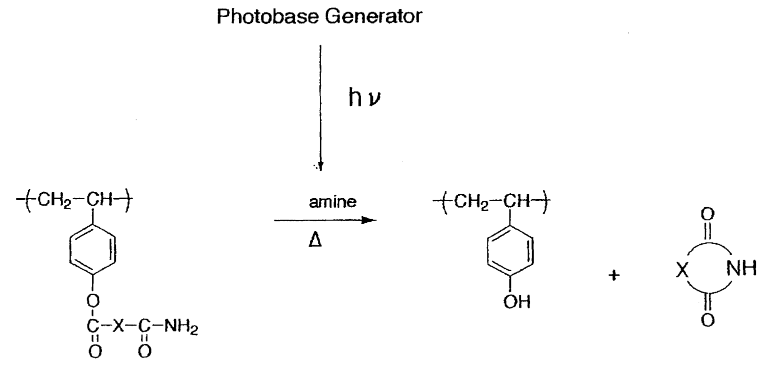
50

Scheme 19. Polarity alteration by base-catalyzed decarboxylation.

Polyisoimides (**53**) are soluble in organic solvents different from polyimides, and amines can catalyze their transformation to polyimides. On the basis of this idea, the photobase generator (**54**) which was developed for this purpose was used in the imidization of polyisoimides (Scheme 22).[124] Dimethyl groups were introduced in the piperidine lest the piperidine should react with the polymer.

Although the dissolution rate of polyisoimide (**55**) films with nifedipine (**56**) shown in Scheme 23 was very low, the rate was increased by the photochemical oxidation of nifedipine to a pyridine derivative. That is, the nifedipine was found to act as an dissolution inhibitor for photosensitive polyimide.[125,126]

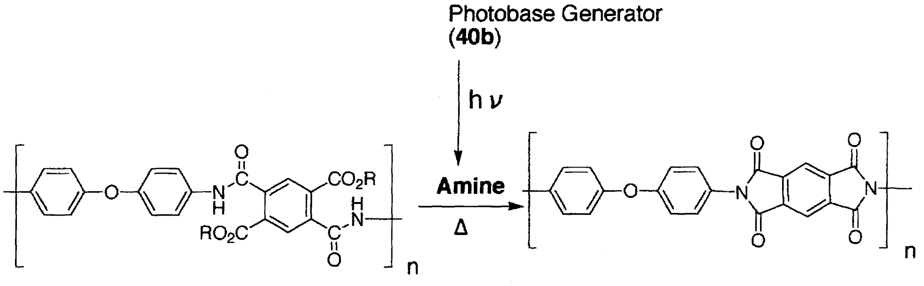
Photoinitiated Thermal Curing of Epoxides. UV curing is a very promising technology; at present photoinitiated radical polymerization is the main process. On the other hand, recently photoinitiated cationic polymerization of epoxides and vinyl ethers are put into practical use. Although amines are well known as curing agents for epoxides, it is a disadvantage for their use that they should be mixed just



51

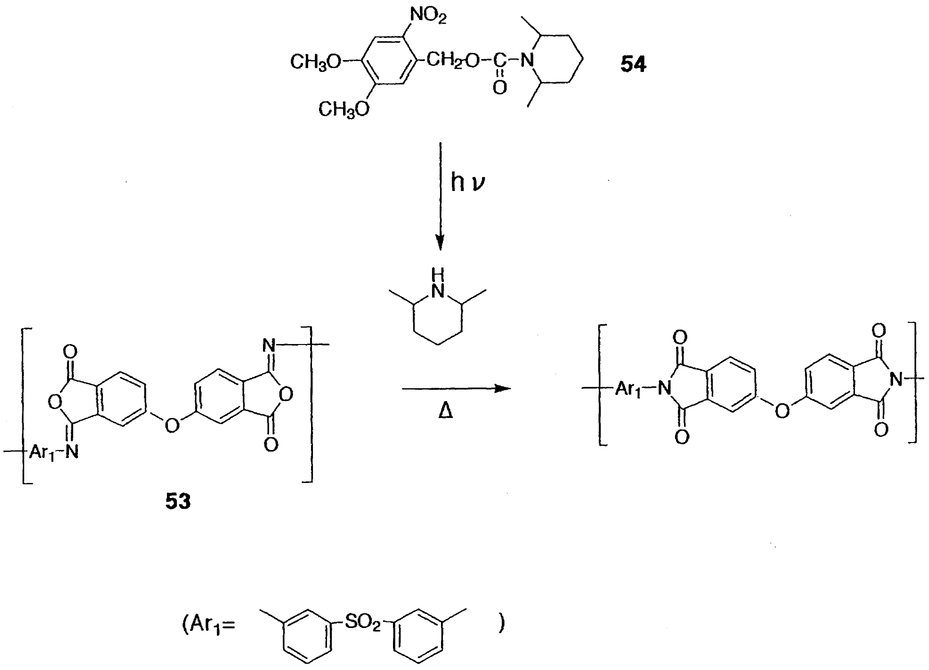
a : X=$(CH_2)_2$, b : X=$(CH_2)_3$
c : X=$(CH_2C(CH_3)_2CH_2)$, d : *o*-phenylene

Scheme 20. Removal of pendant amido-ester groups by base-catalyzed intramolecular imidization.



52 (R=CH_2CH_3, CH_2CF_3)

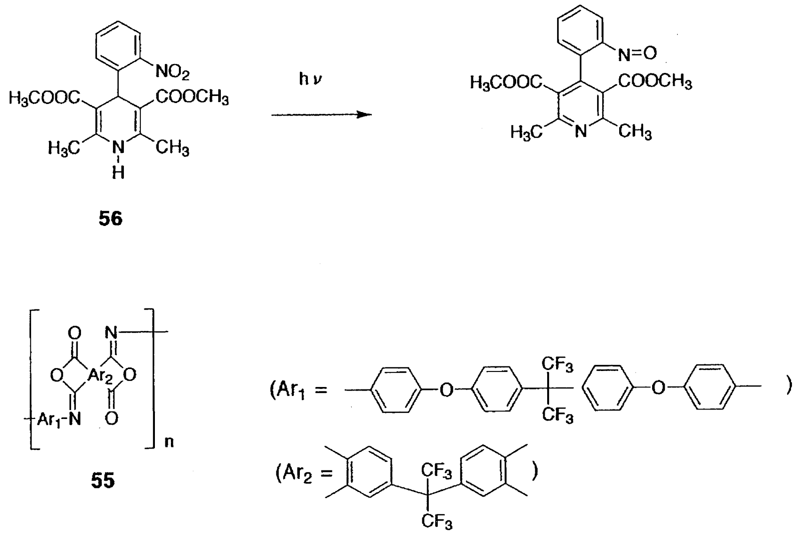
Scheme 21. Base-catalyzed imidization of poly(amic ester)s.



Scheme 22. Base-catalyzed isomerization of polyisoimide to polyimide.

before use because the curing starts when they are mixed. Thus, the use of photobase generators is very promising for the initiation control.

Oxime esters (**39**) are very active for the photoinitiated thermal crosslinking of polymers bearing pendant epoxy groups.[100,102] However, one must make a slight modification of oxime esters to use them for curing of epoxy resins such as *o*-cresol novolac epoxy resins (M.W. ca. 3000) (**57**). That

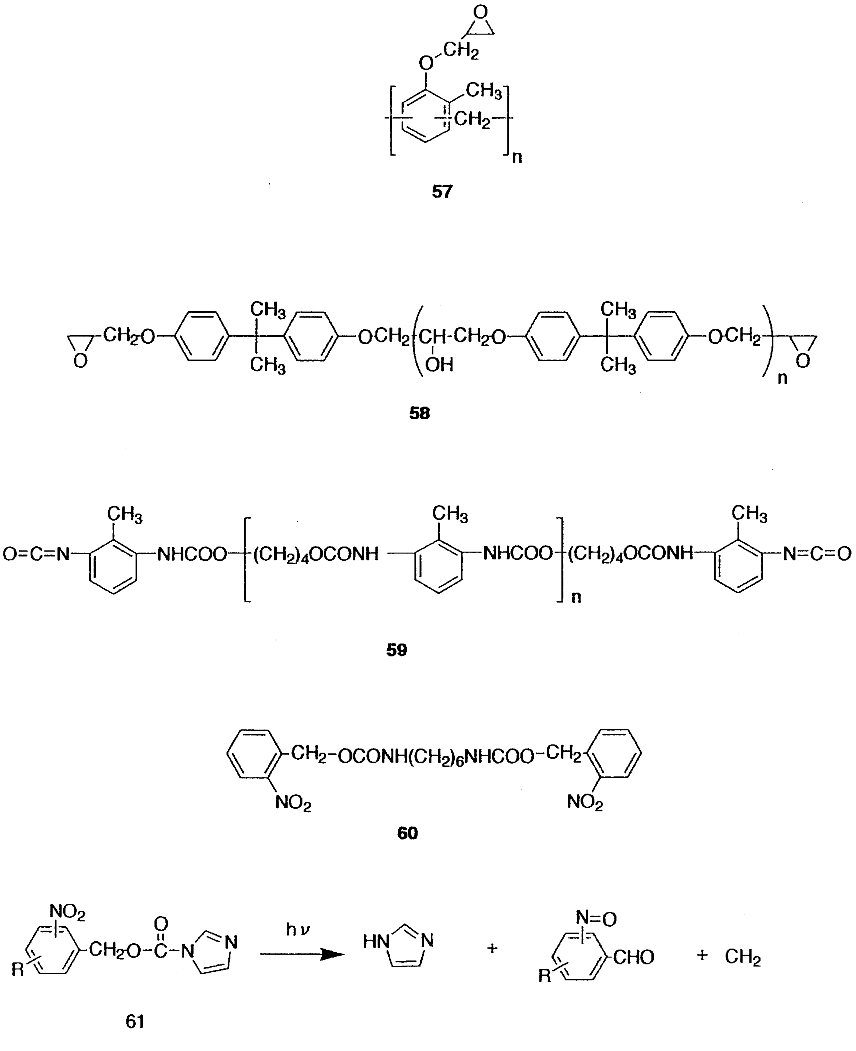


56

55

Scheme 23. Photobase generator as dissolution inhibitor for photosensitive polyimide.

is, polymeric photobase generators,[127] AAPO copolymers were found to be useful for the curing of the epoxy resins (Scheme 24); furthermore the combination of AAPO–GMA and NQ was much more effective for the curing.[128]



57

58

59

60

61

(R=Cl, CH_3, CH_3O)

Scheme 24. Epoxy resins, urethane oligomers, and photobase generators.

Curing of epoxy resins of bisphenol A (**58**) and polyurethane oligomers with isocyanate groups (**59**) were investigated by the use of **42** or **60** as a photobase generator. In the curing of the epoxy resin, **60** gave better results than **42**. So it is deduced that the rate of amine formation is much higher compared with **42** and the resulting amine is aliphatic.[94)]

The amines generated from photobase generators mentioned above are mainly primary or secondary amines, except the amine from **44**, and the reaction in curing of epoxides is the step-wise addition of amines to epoxides. The photochemical formation of tertiary amines which can be used as an catalyst of chain polymerization of epoxides is of interest. Photochemical formation of imidazole was investigated by the use of photobase generator (**61**). The resulting imidazole is effective for the curing of the epoxy resins and more effective compared with the results with **60**. Heating at 120—150 °C is needed for curing after irradiation.[129)]

Recent reviews on photobase generators are listed in the end of references.[28,46,130—133)]

3. Concluding Remarks

Chemistry of photoacid generators and photobase generators and their uses in the polymeric photosensitive systems were described. A variety of photoacid generators have been prepared and mechanistic studies on the photolysis of these materials have been evaluated. Several disadvantages of some photoacid generators for the practical use have been improved since they were first discovered and have been employed as catalysts for the photoinitiated polymerization on certain monomers, photoinduced crosslinking of polymers and oligomers, photoinduced degradation of polymers, and photoinduced transformation of functional groups in polymer chains.

On the other hand, photobase generators, which are not so familiar as photoacid generators, have been synthesized and mechanisms for the photolysis were also investigated. At present they are expected to act as curing agents for epoxides and a catalyst for imidization; further applications are under investigation. These applications are particularly significant in the development of UV curing materials and photoresists in microelectronic technologies.

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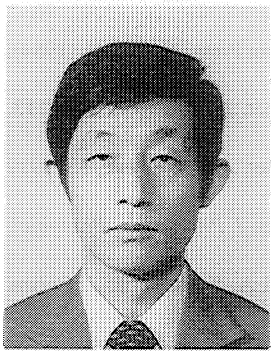

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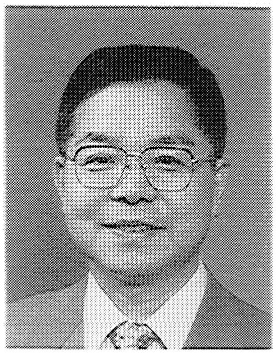

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