Pure & Appl. Chem., Vol. 64, No. 9, pp. 1239–1248, 1992.
Printed in Great Britain.
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The photogeneration of acid and base within polymer coatings: Approaches to polymer curing and imaging

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Abstract: The photogeneration of acids and bases from soluble organic precursors can be used in polymer curing and imaging processes. Convenient photoprecursors of acids include the well know iodonium and sulfonium salts as well as a large number of halogenated aromatic compounds, sulfonate esters, and diazonaphthoquinone derivatives. The photogeneration of amine is possible from a variety of active carbamates, while hydroxide or alkoxide bases can be obtained by irradiation of hydroxy or alkoxy derivatives of triphenylmethane. Specially designed polymers that include acid or base sensitive groups have been prepared, mainly for use as imaging and resist materials for microlithography. Of particular interest are systems that incorporate *chemical amplification*. In these systems the initial radiation induced process, photogeneration of the acid or base catalyst within the polymer film, is followed by a cascade of reactions affecting the polymer. Overall this leads to highly sensitive photopolymer formulations in which the *effective* quantum yield is many times higher than that of the original photoevent. Practical examples of this concept in resists that operate on the basis of multiple main-chain cleavage processes, side-chain modification reactions, and electrophilic crosslinking are described.

The early designs of photopolymers used for microlithography borrowed much from the photopolymers that were used by the printing industry. As the demands of the two applications are quite different, new systems better suited for the high demands of modern microlithography have been developed. Issues of particular relevance in the design of new radiation-sensitive resist materials include high sensitivity and high resolution, good resistance to chemical etchants, high thermal stability, etc. Several reviews of resist materials and their chemistry are available [1-3].

Though numerous resists are used by the semiconductor industry today, by far the most widely used system is still that based on diazonaphthoquinone/novolac [4]. The photosensitive component in this system is the diazonaphthoquinone which, upon irradiation with UV light, undergoes a series of transformations that result in the eventual formation of an indene carboxylic acid. The large change in polarity that accompanies this radiation-induced sequence of reactions forms the basis of the imaging process as the initial diazonaphthoquinone is a powerful dissolution inhibitor for the novolac, while both the photoproduct and the novolac are very soluble in aqueous base. The quantum efficiency of the key transformation affecting the diazonaphthoquinone varies with its exact structure but is usually in the range 0.2-0.4. Though relatively high, this quantum efficiency places a fundamental limit on the photosensitivity of resists of this type as even an increase in quantum efficiency to the defined limit of 1.0 would only result in a moderate increase in resist sensitivity.

In order to circumvent this intrinsic limitation due to quantum yield, novel resist materials that incorporate a chemical amplification feature somewhat akin to that found in the silver halide photographic emulsion systems have been designed. In a chemically amplified resist, the original photoevent initiates a cascade of reaction affecting numerous sites or functional groups within the polymer. In practice, our approach [5] has been to use radiation to generate a catalyst within the polymer coating. The function of this catalyst is to act on the surrounding polymer in such a way that bonds are broken or formed in a chain-like process, resulting in a profound modification of the medium in the area surrounding the initial catalytic moiety. In turn, this modification translates into a large change in the solubility properties of the polymer film in the exposed areas of the film. The effective quantum efficiency is therefore magnified and is the product of the quantum yield for formation of the catalyst times the catalytic chain length.

There are several types of catalysts that can be photogenerated and used in chemically amplified imaging systems.

* (a) Free radicals
* (b) Acids
* (c) Bases

Of these, the free radicals are perhaps the best known as they are frequently used in the dry-film resists that are used in the fabrication of printed circuit boards. Typically, the photopolymers consist of free-radical precursors such as benzoin ethers 1 or aryl biimidazoles 2 in combination with suitable sensitizers 3 (Figure 1) as well as polyfunctional acrylates 4,5, all contained in an appropriate radiation inert matrix polymer (usually a co- or terpolymer containing monomers such as acrylic or methacrylic acid or esters, styrene, and maleic anhydride).

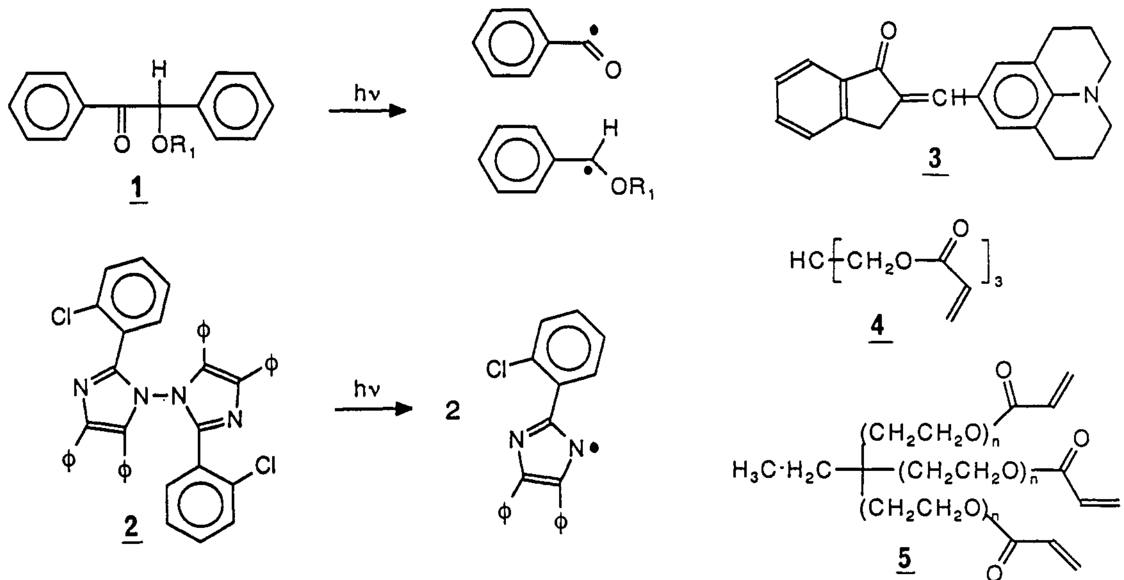


Figure 1. Typical active components of dry-film resists

Numerous compounds that generate acids upon irradiation have been described. These include the well known sulfonium and iodonium salts [6] which are thermally stable but may cause difficulties when used with non-polar polymers due to their ionic character. Other useful photoprecursors of acids include halogenated aromatic compounds such as 6 or triazine 7 (Figure 2) that release halogen acids upon irradiation [7]. Recent developments include *o*-nitrobenzyl esters 8-10 (Figure 3) that produce acids such as p-toluenesulfonic acid or trifluoromethane sulfonic acid upon UV irradiation [8].

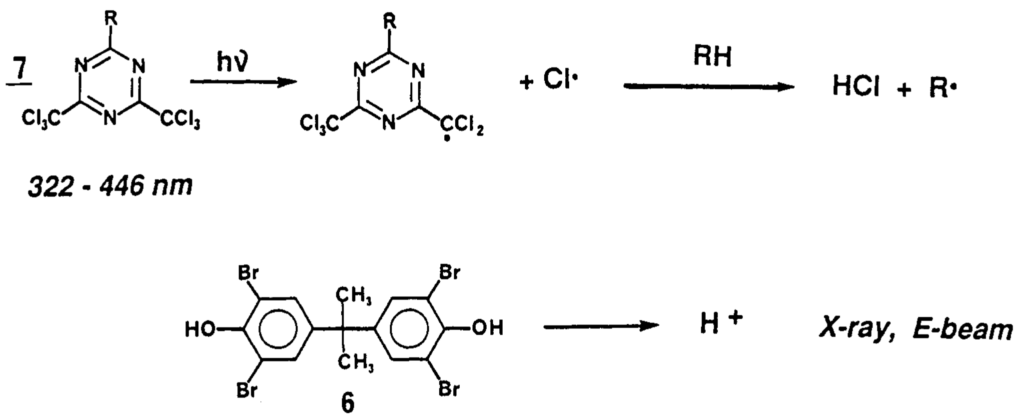


Figure 2. Halogen-containing aromatic compounds that release acid upon irradiation

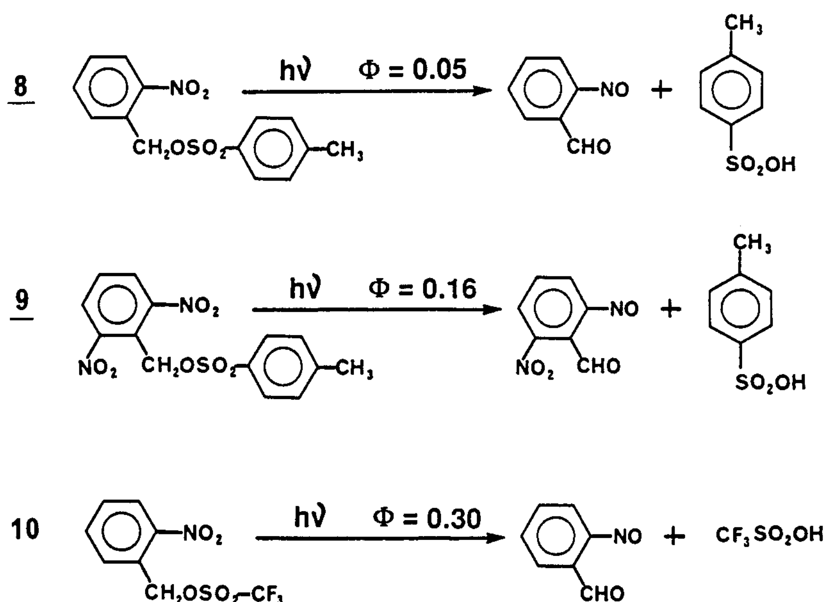


Figure 3. Photogeneration of sulfonic acids from their 2-nitrobenzyl esters

Another interesting photo precursor of acid is the recently described tris(methanesulfonyloxy)benzene which releases large amounts of methanesulfonic acid upon UV irradiation at 250 nm. The anomalously high quantum efficiency of this photo acid generator has been attributed to sensitization by the phenolic resin in which it is dispersed in resist applications [9].

Finally, aryl naphthoquinonediazide-4-sulfonates such as 11 [10] have been shown to produce highly acidic structures through a complex mechanism involving the addition of water (found in the polymer substrate) to an intermediate sulfene to afford a 3-carboxyindene-1-sulfonic acid 12 as shown in Figure 4.

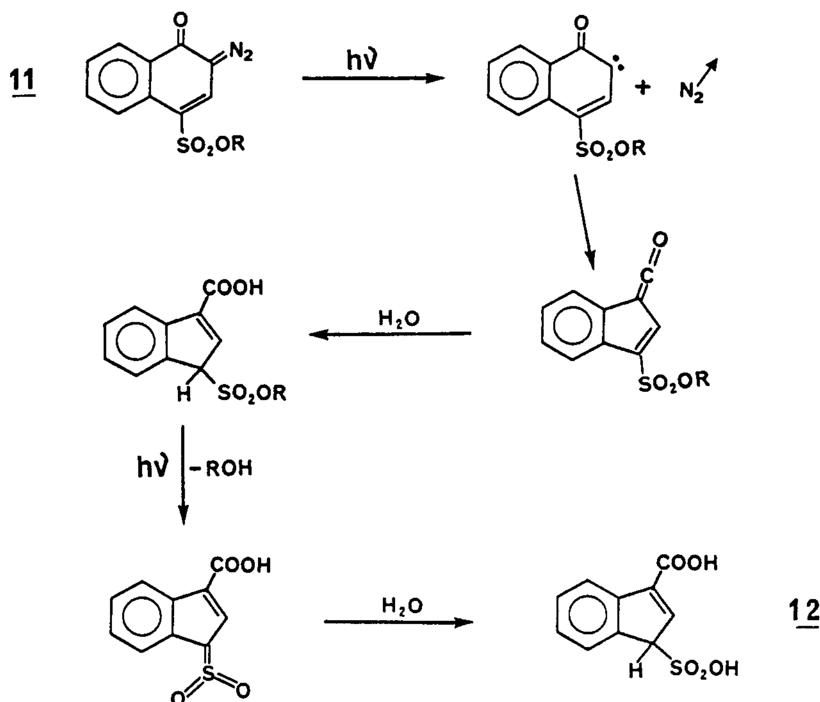


Figure 4. Formation of a 3-carboxyindene-1-sulfonic acid by UV irradiation of an aryl naphthoquinonediazide-4-sulfonates

The photogeneration of base from soluble organic precursors has received less attention than the photogeneration of acid. Early studies on photo removable protecting groups have shown that both the α,α-dimethyl-3,5-dimethoxybenzyloxycarbonyl group [11] and the 2-nitrobenzyloxycarbonyl group [12] can be used to protect the amine functionality of amino-acids. We have studied a number of photoactive carbamates based on 2-nitrobenzyl chemistry and have found that they could be used efficiently as photo base generators [13]. Light sensitive carbamates such as 13 can be obtained readily by reaction of an appropriate isocyanate 14 with a 2-nitrobenzyl alcohol 15 as shown in Figure 5. The importance of substituents R_1 and R_2 (Figure 5) on the aromatic ring and the benzylic position of the 2-nitrobenzyl moiety 13 cannot be underestimated as they affect both the quantum yields [13] for photogeneration of the amine 16 and its stability [14] in the presence of the carbonylated nitrosobenzene photo by-product 17. Therefore, quantum yields obtained with a variety of carbamates having structure 13 vary from 0.1-0.6 depending on the nature of R_1 and R_2. Best quantum yields are obtained for 2,6-dinitrobenzyl carbamates ($R_1 = NO_2$), while best stability in some reaction media [14] is achieved if the photo by-product 17 is a ketone ($R_2 = CH_3$) rather than an aldehyde (R_2 = H). It must be emphasized here that in most cases product recombination of the free amine 16 and carbonyl by-product 17 which was a problem with amino-acid substrates [12] is not significant for most of our applications in non-acidic media as imine formation is an acid catalyzed process.

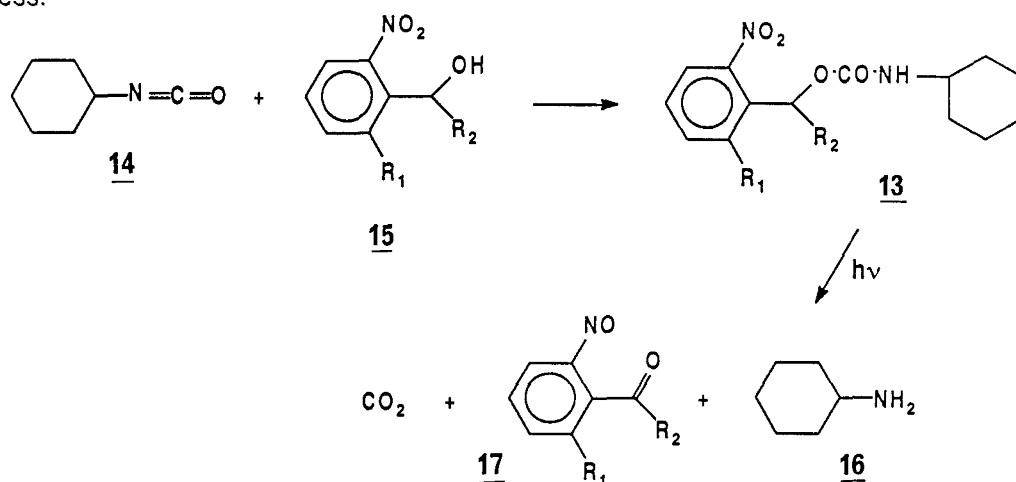


Figure 5. Preparation and photochemistry of 2-nitrobenzyl carbamates

Another approach [15] to photoactive carbamates such as 18 based on the α,α-dimethyl-3,5-dimethoxybenzyloxycarbonyl (Ddz) group is shown in Figure 6. Here again, the desired carbamates can be obtained from the corresponding alcohol and isocyanate though other routes are also possible. The quantum yields [16] for the photogeneration of amine from carbamates such as 18 is approximately 0.1.

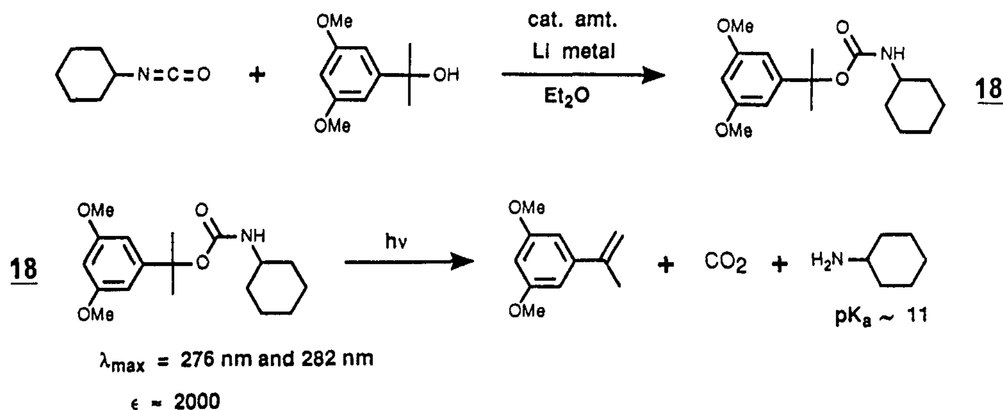


Figure 6. Preparation and photolysis of Ddz carbamates

Inorganic salts such as cobalt (III) ammines have been reported as sources of photogenerated ammonia [17], while polymers with photoactive side-chains that generate amine pendant groups upon irradiation have also been described [18,19].

PHOTOGENERATED ACID IN CHEMICALLY AMPLIFIED IMAGING MATERIALS

A large number of chemically amplified imaging and resist materials that owe their activity to the use of photogenerated acid have been developed recently. Our own work has focused on five types of acid-catalyzed reactions:

* Catalyzed thermolysis of polymer side-chains.
* Catalyzed thermolysis of polymer main-chains.
* Depolymerizations processes based on ceiling temperature phenomena.
* Electrophilic aromatic substitution reactions.
* Electrophilic rearrangements.

(A) Acid-catalyzed thermolysis of polymer side-chains

Perhaps the best known system developed to-date is that based on poly(p-t-butyloxycarbonyloxystyrene) 19 first prepared by Fréchet and Willson in 1979. The resist material consists of polymer 19 containing a small amount of a sulfonium or iodonium salt as the photo precursor of acid. Polymer 19 itself is hydrophobic and cannot be dissolved in the type of aqueous base that is commonly used for image development with standard resists. Upon heating near 200°C, 19 undergoes a very clean thermolysis reaction that liberates quantitatively base-soluble poly(p-hydroxystyrene) 20 while gaseous CO_2 and 2-methyl-propene are evolved. Key to the process is the fact that the thermolysis reaction is acid catalyzed and occurs at 100°C instead of near 200°C. Figure 7 shows a diagram of the imaging process.

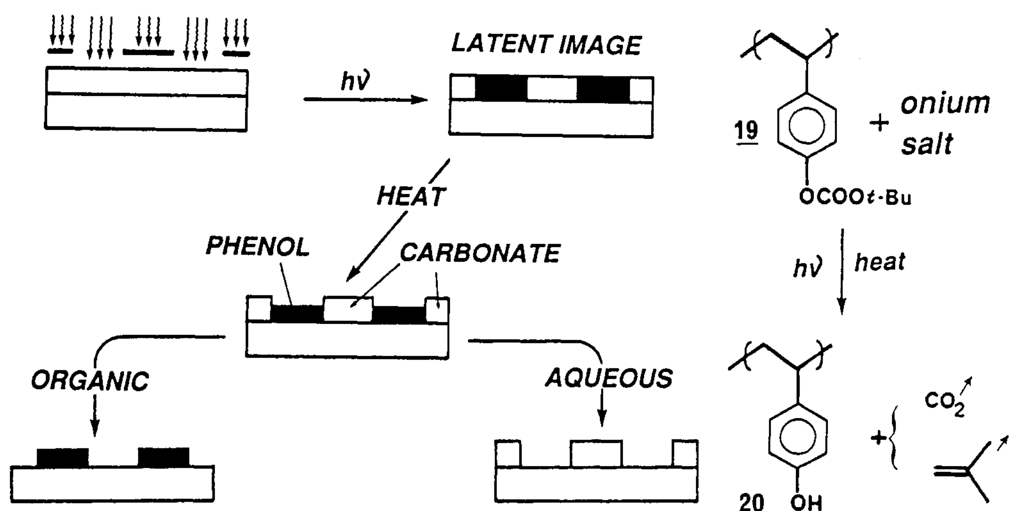


Figure 7. Imaging diagram for a resist based on poly(p-t-butyloxycarbonyloxystyrene)

After spin-coating the resist containing 19 and a photoacid generator onto a silicon wafer, the film is baked to remove the solvent, then irradiated though a mask using UV light near 250nm. Upon irradiation, acid is released in those portions of the film that have been irradiated (affording a latent image) but no appreciable reaction occurs until the exposed film is heated to 100°C. This causes thermolysis of the polymer side-chains to occur only where acid had been released. As a result of the thermolysis, some loss of film thickness (due to evolution of carbon dioxide and 2-methyl-propene) is observed in those areas where the phenolic polymer 20 has been formed. No changes are observed in the unexposed areas of the film which still contain unchanged lipophilic polymer 19 with carbonate pendant groups. Finally, image development is achieved through a selective dissolution process. A unique feature of this type of material is its ability to provide either a positive-tone image - through removal of the exposed (phenolic) areas of the film - using aqueous base, or a negative-tone image via selective dissolution of the unexposed lipophilic areas of the film using a solvent such as anisole [5, 20-21].

The mechanism of the process is shown in Figure 8. Protonation of the carbonate occurs followed by rapid breakdown of the protonated intermediate with formation of an unstable monoester of carbonic acid and a tertiary carbocationic intermediate. Key to the chemical amplification feature of this resist is the fact the proton that initiate the overall reaction sequence is not "lost". Stabilization of the t-butyl carbocationic intermediate is achieved through elimination of a proton that perpetuates the side-chain cleavage process.

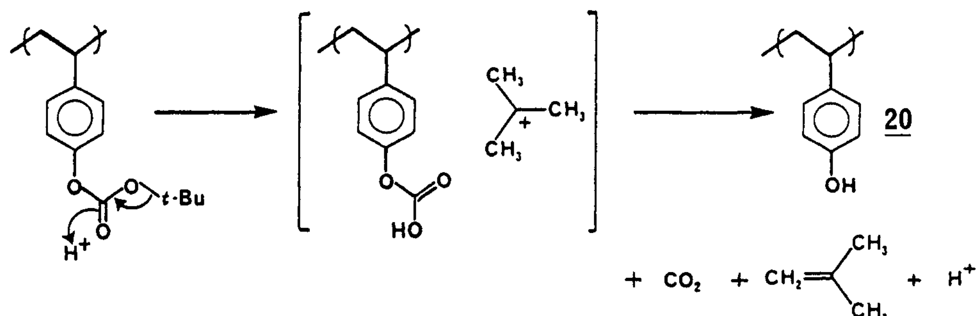


Figure 8. Mechanism of the acid-catalyzed side chain cleavage for polymer 19

Another interesting feature of this resist is that it can be used very effectively not only with UV radiation but also using E-beam or X-ray sources. Fortunately, the acid-catalyzed process is subject to side-reactions and the measured catalytic chain length for this system has been measured in the range between 800-1200 [22]. Though considerable, this amplification factor still allows for the production of very small images with an ultimate resolution below 300Å [23]. A significant consideration in the use of this type of resist material is their sensitivity to airborne chemical contamination [24] which may be overcome through a variety of approaches.

(B) Acid-catalyzed thermolysis of polymer main-chains

The general design features used in the acid-catalyzed thermolysis of polymer side-chains can be easily applied to effect multiple chain scissions within the backbones of polymers containing suitable carbonate [25], ester [26], or ether [27] linkages. For example, a polyether such as 21 can be used in combination with a photoacid generator to formulate an imaging material that can be dry-developed without the need for a separate solvent development step. Following photogeneration of acid within the polyether and protonation of the ether oxygen, heating of the polymer causes cleavage of the main-chain to afford stabilized cationic species that undergo successive eliminations to produce volatile small molecules. Additional driving force for the overall process is provided by the very favorable aromatization reaction that affords benzene as a final by-product (Figure 9).

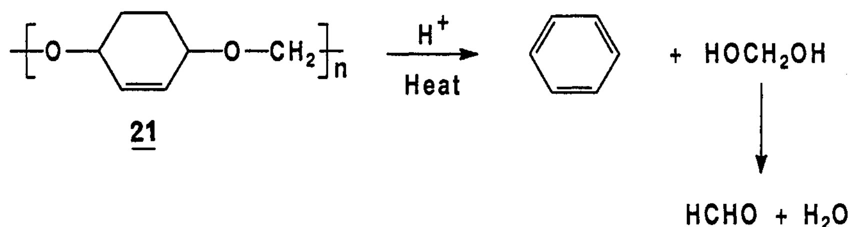


Figure 9. Imaging via acid-catalyzed main-chain cleavage of a bis-allylic polyether

(C) Depolymerizations processes based on ceiling temperature phenomena

The polyacetal derived from phthalaldehyde can be prepared by either anionic or cationic polymerization at low temperature. For example the anionic polymerization of phthalaldehyde 22 initiated with n-butyl lithium affords an alkoxy-terminated polyacetal with structure 23. This polymer is only stable below its ceiling temperature and reverts spontaneously to the more thermodynamically stable monomer if warmed above -40°C. However, a stabilized polyphthalaldehyde 24 is obtained if 23 is end-capped with acetic anhydride. Stability is due to the lack of a simple reversion mechanism. However, if a bond is broken within structure 24 while the material is at a temperature above -40°C, unzipping of the polymer chain is again expected to proceed spontaneously. The concept of imaging through depolymerization due to a ceiling

temperature phenomenon has been demonstrated [28] using a combination of polyphthalaldehyde and a photoacid generator. Upon exposure to radiation at room temperature, acid liberated within the polyphthalaldehyde causes its protonation which results in main chain scission. As the destabilized polymer is above its ceiling temperature, thermodynamic reversion to monomer is observed (Figure 10). Since the photogenerated acid is not consumed in the process a dual-stage chemical amplification process is observed.

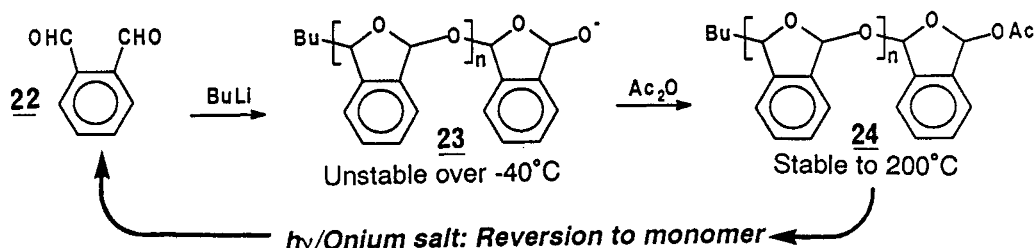


Figure 10. Preparation and acid-catalyzed unzipping of polyphthalaldehyde

(D) Acid-catalyzed electrophilic aromatic substitution reactions

A totally different design of chemically amplified resist materials makes use of the simple concept of electrophilic aromatic substitution. In this design, photogenerated acid is used to create carbocationic species that alkylate neighboring aromatic rings on a matrix polymer. The alkylation process, repeated many times with polyfunctional electrophiles, results in crosslinking and insolubilization of the aromatic polymer. The process is self-sustaining since each alkylation reaction results in the liberation of a new proton that perpetuates the reaction sequence. Several implementations of this concept have been described [29-30]. We have recently used copolymers containing both latent electrophilic groups, as well as activated aromatic rings, in combination with acid photo precursors to prepare negative-tone resists. For example, copolymer 25 containing 4-hydroxystyrene units as well as styrene units with pendant furfuryl alcohol moieties, crosslinks readily under the influence of photogenerated acid. The acid is responsible for the formation of stabilized carbocationic intermediates through the loss of water from the furfuryl alcohol sites. The resulting carbocations can then alkylate the very reactive furan nuclei of neighboring polymer pendant groups (Figure 11). Though essentially unreactive when compared to the highly activated furan rings, the 4-hydroxystyrene units of 25 are nevertheless essential as they provide for aqueous base development. During the development step, the unexposed areas of the film, consisting of the starting polymer, dissolve while the exposed areas remain insoluble due to their crosslinking. Once again this type of material can be used with many sources of radiation, from deep-UV light, to E-beam, to X-ray radiation. As was the case for all of the other systems described above, extremely high sensitivities (< 2 mJ/cm^2 at 254 nm) are obtained.

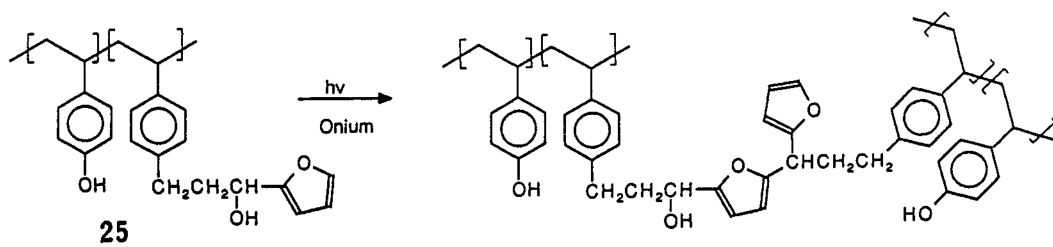


Figure 11. Photocrosslinking of polymer containing latent electrophiles

(E) Acid-catalyzed electrophilic rearrangements

A dual-tone (positive-negative) imaging system can be designed using a combination of poly(4-benzyloxystyrene) 26 and a photo precursor of acid. In the presence of photogenerated acid, the pendant benzyl ethers groups of polymer 26 are protonated. Subsequent attack of the electron rich phenolic moiety that results onto the incipient benzylic carbocation results in the formation of a C-alkylated product 27 (Figure 12). Polymer 27 is a phenolic resin that has very different solubility properties from those of the starting polymer. In particular, 27 is soluble in aqueous base while 26 is not. Differential dissolution of the type discussed earlier for resists based on 19 can be used to afford either negative or positive-tone images depending on the choice of developing solvent.

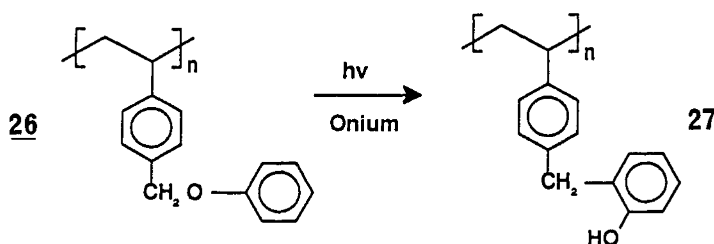


Figure 12. Acid catalyzed rearrangement of a polymer with pendant benzyl ether groups

Numerous other imaging materials based on acid-catalyzed chemistry have been developed, several excellent reviews containing additional examples of chemically amplified systems are available [5, 31]

PHOTOGENERATED BASE IN POLYMER CURING AND IMAGING

The use of photogenerated base in polymer curing and imaging has not been widespread due to the lack of commercial availability of photo precursors of bases. Yet the chemistry of basic compounds such as amines is of great importance in polymer chemistry as a number of commercially significant materials such as adhesives, foams, thermosets, etc, have relied on the reactivity of amines for chain formation, chain extension, or crosslinking.

Our first application [14] of photogenerated base in an imaging material involved the concept of image-tone reversal. The best known example of image reversal is the use of an amine, in the so-called "monazoline process" [1], for the production of a negative tone image from the classical positive-tone resist, novolac-diazonaphthoquinone. Though effective, this process is relatively cumbersome as several additional steps are required for image production. In contrast, the direct use of photochemically generated base can greatly simplify image reversal and extend the versatility of well known single-tone resists.

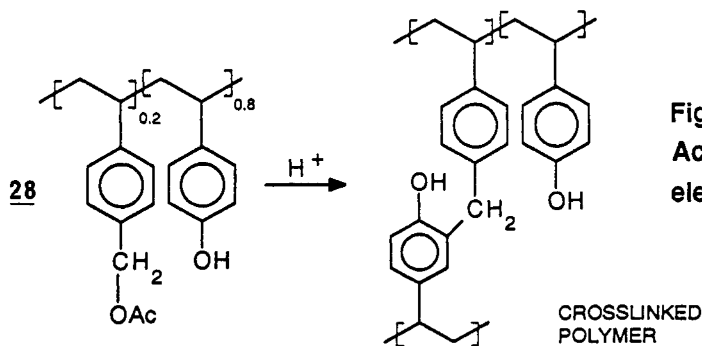


Figure 13.
Acid catalyzed crosslinking of 28 by electrophilic aromatic substitution

For example, a procedure analogous to that described above for 25 can be used to crosslink copolymer 28 via an acid-catalyzed electrophilic aromatic substitution reaction (Figure 13). When formulated with an acid photo precursor, this copolymer only affords negative-tone images. In order to accomplish image tone reversal, crosslinking of 28 must be effected only in those areas of the film that are *not* irradiated. This may be accomplished through the use of light to generate *not an acid, but a base* in exposed areas of the film. The purpose of this photogenerated base is to *protect* the exposed areas of the film from crosslinking. The unprotected (unexposed) areas of the film may then be crosslinked thermally as explained below. The resist formulation used consists of copolymer 28, a thermally stable base photogenerator 29, and a thermally labile acid precursor 30 [32]. Upon exposure to UV light, a latent image consisting of amine 31 dispersed into the copolymer 28 is created. Brief heating [32] of this image at a temperature sufficient to release acid from 30 results in acid catalyzed crosslinking of 28 in those areas where no base had been produced, while acid is neutralized by the photogenerated base elsewhere (Figure 14). The net result of this approach is the production of a positive tone image via a crosslinking process [14, 33]. It must be emphasized that unlike the monazoline process, this procedure does not add any processing step but only depends on the

normal exposure and post-bake operations to effect imaging with tone reversal. Chemical amplification does not play a role in this process as the key photochemical step is the photochemical release of amine. In this application the selection of an appropriate base precursor is important. For example higher resist sensitivities are observed with 29 than with 32 since, in the presence of acid, the photo by-product from 29 - a nitroso ketone - is less likely to form an imine with the photogenerated amine than is the case with the aldehyde photoproduct from 32.

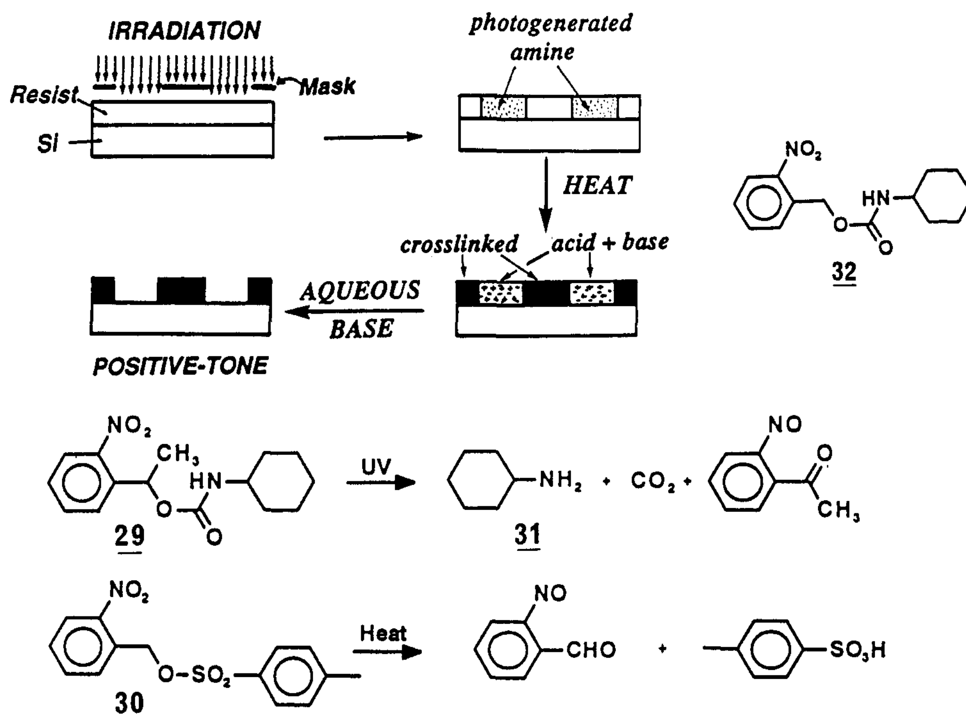
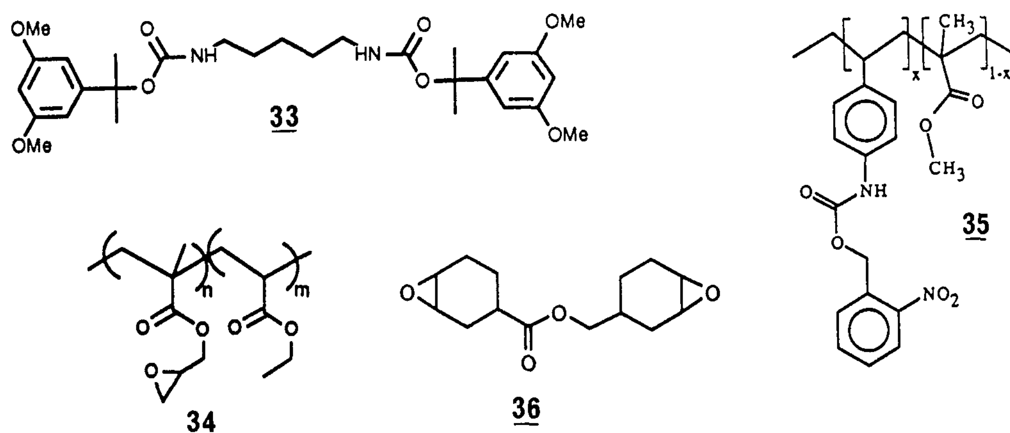


Figure 14. Image reversal in a photocrosslinkable resist using photogenerated base

Another approach to the use of photogenerated amines in polymer curing and imaging involves the direct crosslinking of polyfunctional epoxy compounds [19, 34]. For example, the diamine that is released from 33 upon exposure to UV light below 300 nm is useful in the crosslinking of polymer 34 that contains epoxy pendant groups [19]. Similarly, a mixture of copolymer 35 containing photoactive urethane groups and bis-epoxide 36 can be imaged effectively by exposure to UV light at 254nm affording negative tone images. While these chemically amplified processes using photogenerated bases are of some relevance to imaging chemistry, their value may lie more in the area of photosensitive curable coatings and adhesives.



Acknowledgements

The contributions of my coworkers whose names appear in the references are acknowledged with gratitude. The author also thanks IBM Corporation and the Office of Naval Research for continuing support of this research program.

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