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Approaches to Polymer Curing and Imaging
Via the In Situ Generation of a Catalyst

by

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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-radicals 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).

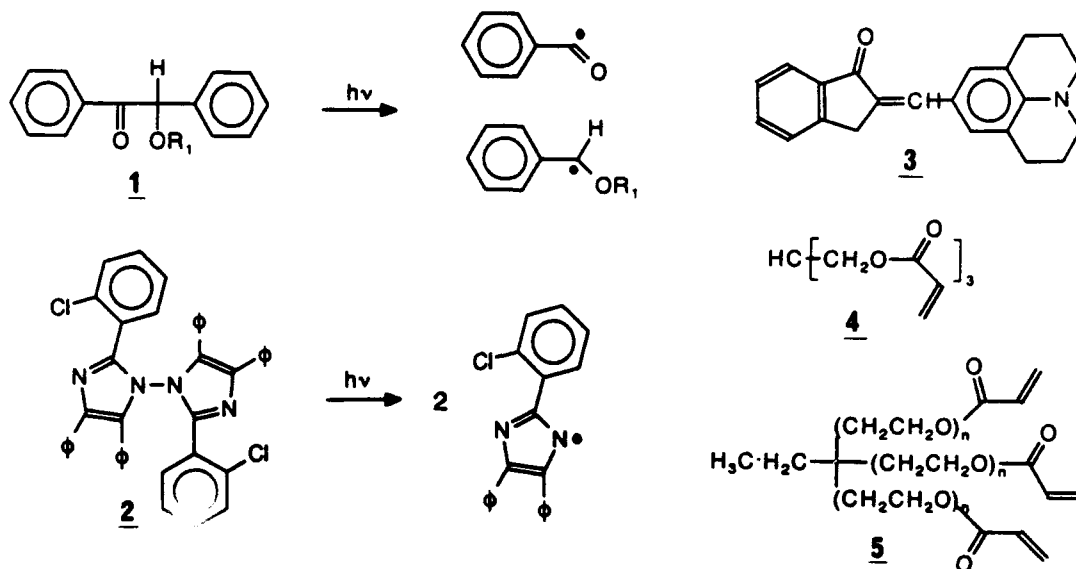


Figure 1. Typical active components of dry-film resists.

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].

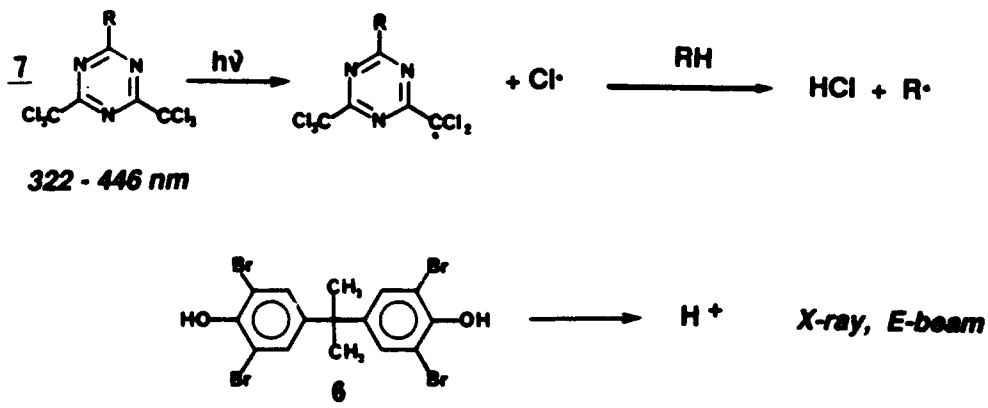


Figure 2. Halogen-containing aromatic compounds that release acid upon irradiation.

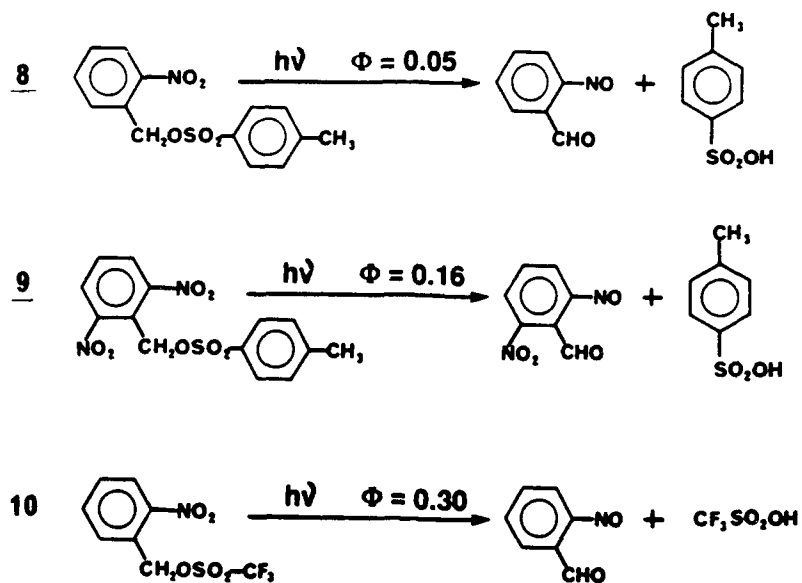


Figure 3. Photo generation of sulfonic acids from their 2-nitrobenzyl esters.

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.

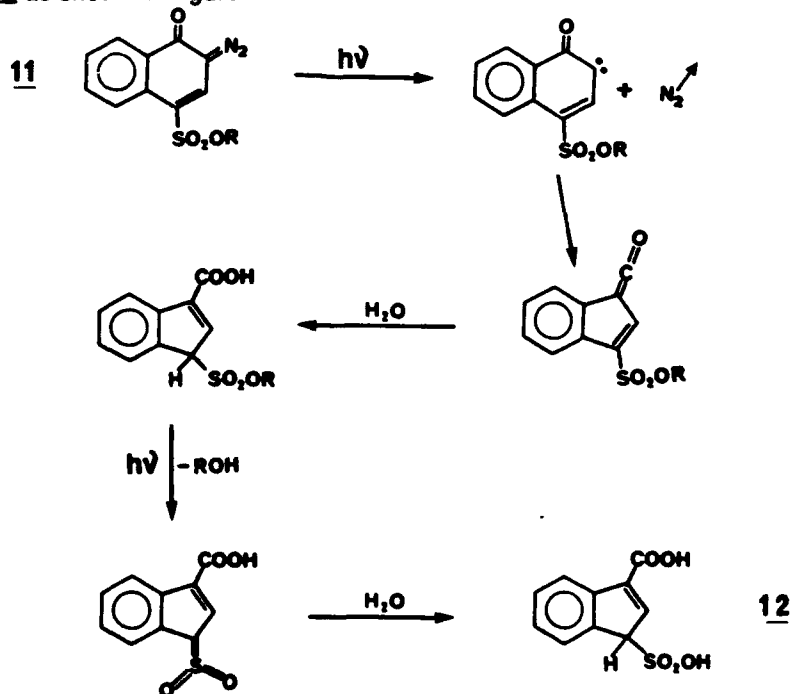


Figure 4. Formation of a 3-carboxyindene-1-sulfonic acid by UV irradiation of an aryl naphthoquinonediazide-4-sulfonates.

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 ($R_1 = \text{NO}_2$), while best stability in some reaction media [14] is achieved if the photo by-product **17** is a ketone ($R_2 = \text{CH}_3$) rather than an aldehyde ($R_2 = \text{H}$). 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.

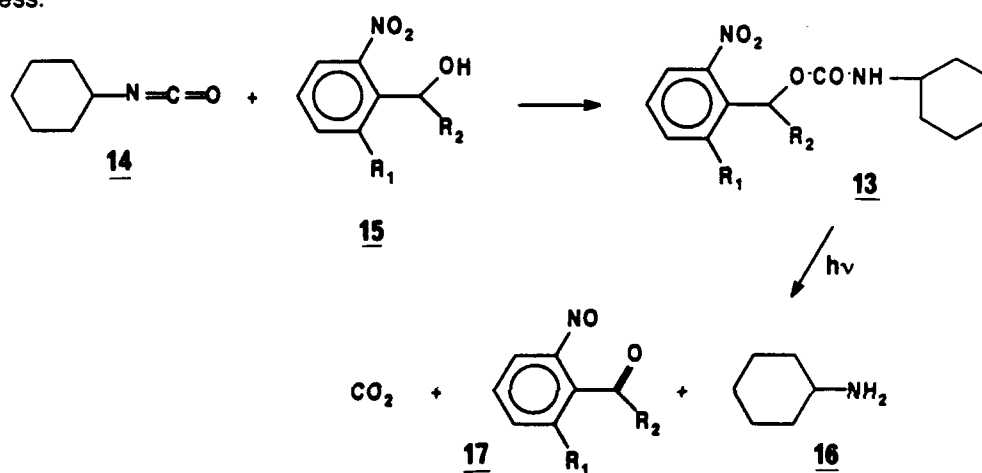


Figure 5. Preparation and photochemistry of 2-nitrobenzyl carbamates.

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.

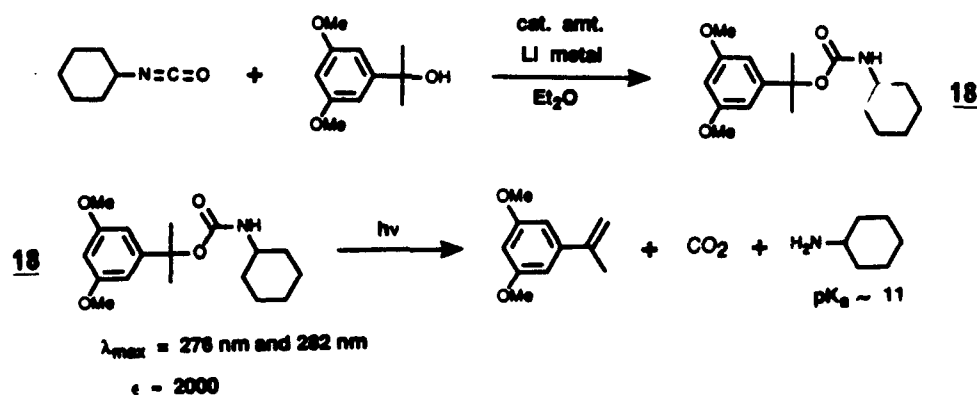


Figure 6. Preparation and photolysis of Ddz carbamates.

Inorganic salts such as cobalt (III) amines have been reported as sources of photo-generated 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 CO₂ 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.

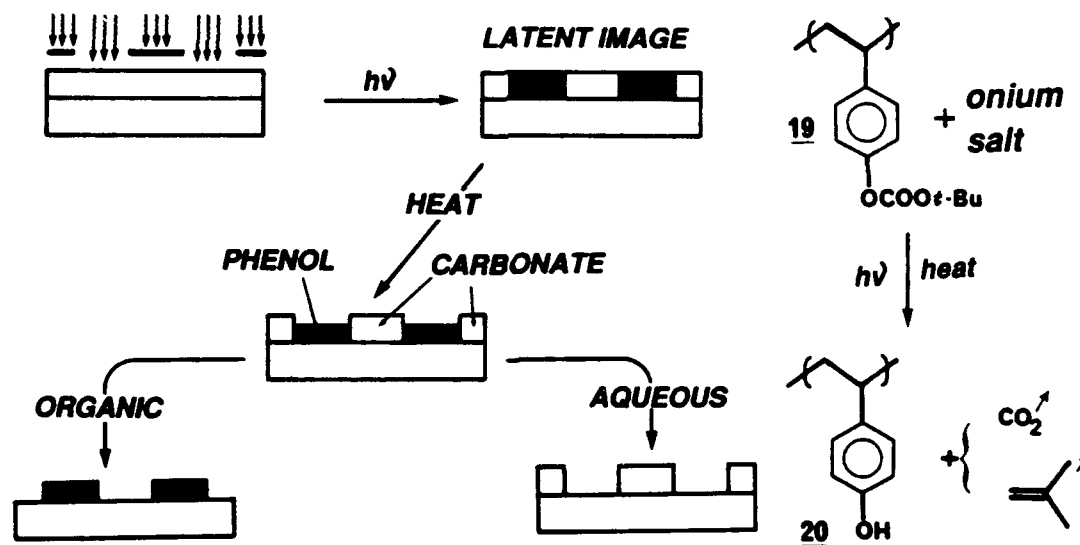


Figure 7. Imaging diagram for a resist based on poly(*p*-*t*-butyloxycarbonyloxystyrene).

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 through 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 initiates 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.

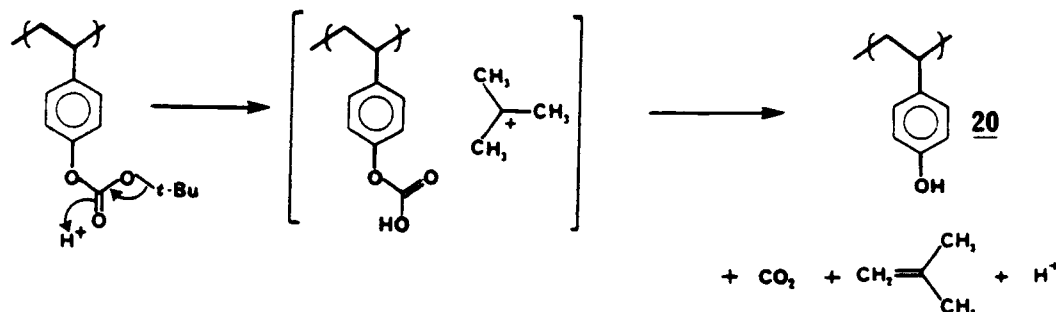


Figure 8. Mechanism of the acid-catalyzed side chain cleavage for polymer 19.

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).

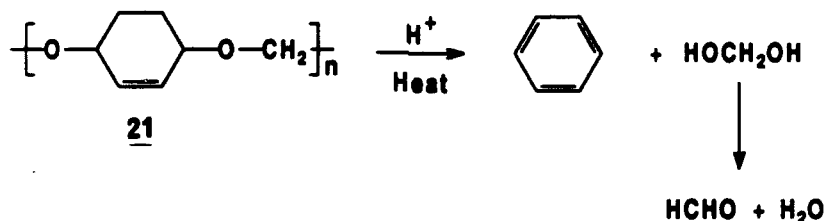


Figure 9. Imaging via acid-catalyzed main-chain cleavage of a bis-allylic polyether

(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.

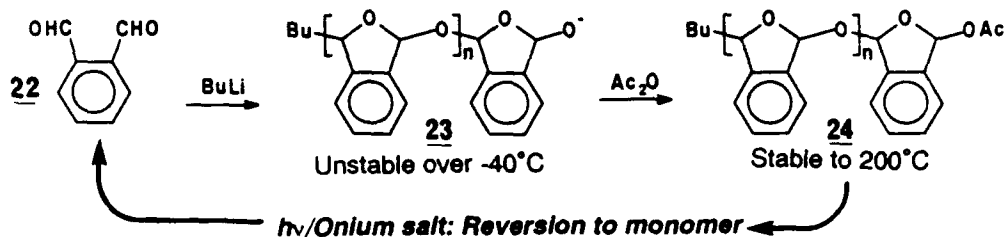


Figure 10. Preparation and acid-catalyzed unzipping of polyphthalaldehyde.

(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 ($< 2 \text{ mJ/cm}^2$ at 254 nm) are obtained.

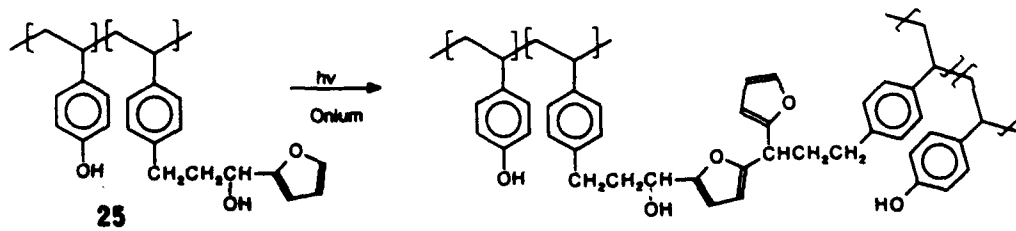


Figure 11. Photocrosslinking of polymer containing latent electrophiles.

(E) Acid-catalyzed electrophilic rearrangements.

A dual-tone (positive-negative) imaging system can be designed using a combination of poly(4-benzoyloxystyrene) **26** and a photo precursor of acid. In the presence of photogenerated acid, the pendant benzyl ether 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.

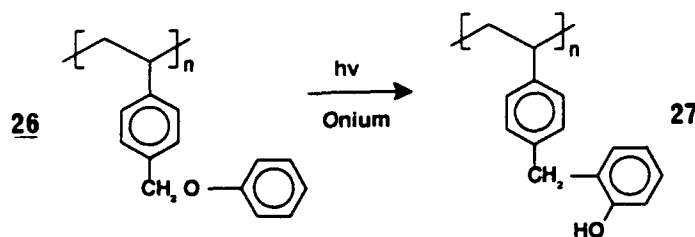


Figure 12. Acid catalyzed rearrangement of a polymer with pendant benzyl ether groups.

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.

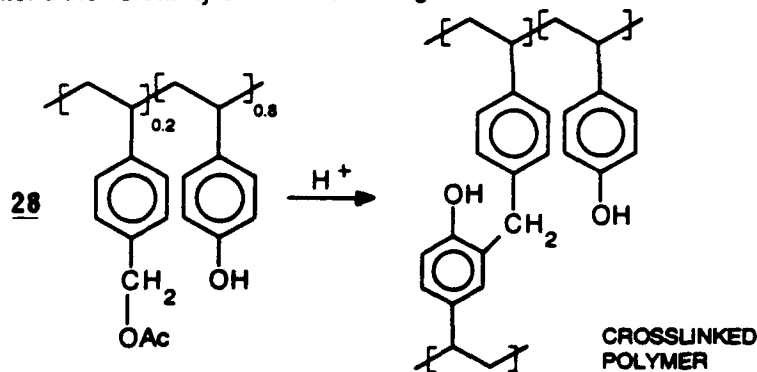


Figure 13. Acid catalyzed crosslinking of **28** by electrophilic aromatic substitution.

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 photo-generated 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**.

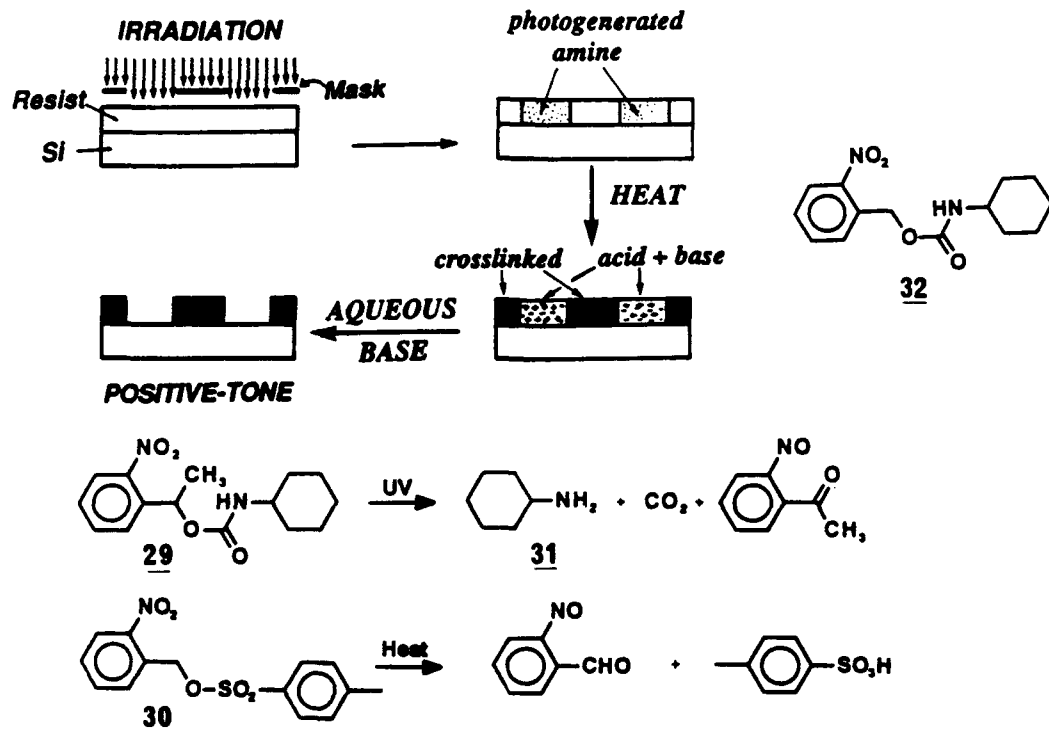
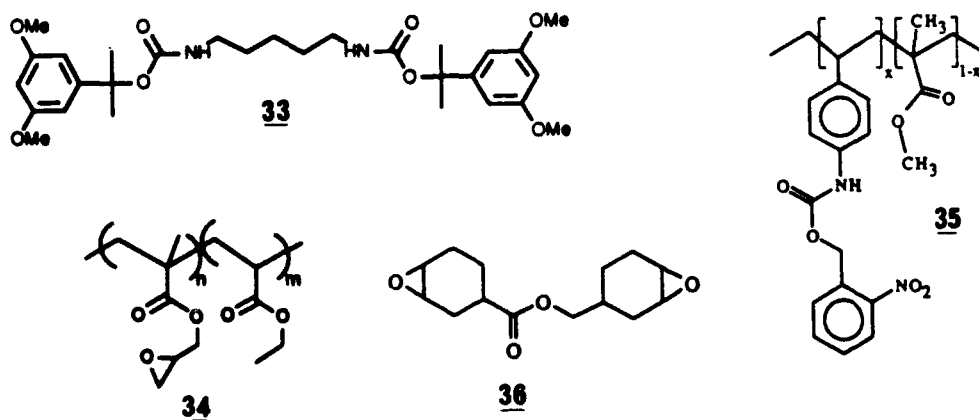


Figure 14. Image reversal in a photocrosslinkable resist using photogenerated base.

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.



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REFERENCES

- [1] Willson, C.G.; in "Introduction to Microlithography" (Thompson, L.F.; Willson, C.G.; Bowden, M.J., Editors) American Chemical Society Symp. Ser.#219, 1983, 87.
- [2] Reiser, A.; "Photoactive Polymers, The Science and Technology of Resists", J. Wiley and Sons, New York, 1989.
- [3] Moreau, W.M.; "Semiconductor Lithography, Principles, Practices, and Materials". Plenum Press, New York, 1988.
- [4] Süß, O.; Liebigs Ann. Chem. 1944, 556, 65.
- [5] Willson, C.G.; Fréchet, J.M.J.; Tessier, T.G.; Houlihan, F.M., J. Electrochem. Soc. 1986, 133, 181.
- [6] Crivello, J.V.; Lam, J. Macromolecules, 1977, 10, 1307
- [7] Smith, G.H.; Bonham, J.A., 1973, US Patent 3,779,778. Zimmerman, H.E.; Sandel, V.R.; J. Am. Chem. Soc., 1963, 85, 915. See also ref. 10 for a review.
- [8] Houlihan, F.M.; Shugard, A.; Gooden, R.; Reichmanis, E. Macromolecules 1988, 21, 2001.
- [9] Schlegel, L.; Ueno, T.; Shiraishi, H.; Hayashi, N.; Iwayanagi, T. Chem. Mater. 1990, 2, 299.
- [10] Buhr, G.; Dammal, R.; Lindley, C.R. Polym. Mat. Sci. Eng., 1989, 61, 269.
- [11] Birr, C.; Lochinger, W.; Stahnke, G.; Lang, P.; Liebigs Ann. Chem., 1972, 763, 162.
- [12] Patchornik, A.; Amit, B.; Woodward, R.B. J. Am. Chem. Soc., 1970, 92, 6333.
- [13] Cameron, J.F.; Fréchet, J.M.J. J. Am. Chem. Soc., 1991, 113, 4303.
- [14] Matuszczak, S.; Cameron, J.F.; Fréchet, J.M.J.; Willson, C.G. J. Mater. Chem. 1991, 1, 1045.
- [15] Cameron, J.F.; Fréchet, J.M.J. J. Org. Chem., 1990, 55, 5919.
- [16] Cameron, J.F.; Fréchet, J.M.J. J. Photochem. Photobiol. A: 1991, 59, 105.
- [17] Kutal, C.; Willson, C.G. J. Electrochem. Soc., 1987, 134, 2280.
- [18] Song, K.; Tonogai, S.; Tsunooka, M.; Tanaka, M. J. Photochem. Photobiol., A: 1989, 49, 269.
- [19] Beecher, J.E.; Cameron, J.; Fréchet, J.M.J.; Polym. Mat. Sci. Eng., 1991, 64, 71.
- [20] Fréchet, J.M.J.; Ito, H.; Willson, C.G. Proc. Microcircuit Eng. 1982, 260. Willson, C.G.; Ito, H.; Fréchet, J.M.J.; Houlihan, F. Proc. IUPAC 28th Macromol. Symp. Amherst, 1982, 448.
- [21] Ito, H.; Willson, C.G.; Fréchet, J.M.J., 1985, US Patent 4,491,628
- [22] McKean, D.R.; Schaedeli, U.; MacDonald, S.A. J. Polym. Sci., Polym. Chem. Ed., 1989, 27, 3927.
- [23] Umbach, C.P.; Broers, A.N.; Koch, R.; Willson, C.G.; Laibowitz, R.B.; IBM J. Res. & Develop. 1988, 32, 454.
- [24] S.A. MacDonald; Ciecak, N.J.; Wendt, H.R.; Willson, C.G. Proc. SPIE, 1991, 1466, 2.
- [25] Fréchet, J.M.J.; Bouchard, F.; Eichler, E.; Houlihan, F.M.; Iizawa, T.; Kryczka, B.; Willson, C.G. Polymer J., 1987, 19, 31. *Ibid.*, Macromolecules, 1986, 19, 13.
- [26] Fréchet, J.M.J.; Kryczka, B.; Matuszczak, S.; Reck, B.; Stanculescu, M.; Willson, C.G. J. Photopolym. Sci. Technol., 1990, 3, 235. *Ibid.* Polym. Mat. Sci. Eng., 1989, 60, 170.
- [27] Fréchet, J.M.J.; Willson, C.G.; Iizawa, T.; Nishikubo, T.; Igarashi, K.; Fahey, J. in "Polymers in Microlithography" American Chemical Society Symp. Ser. #412, 1989, 74.
- [28] Ito, H.; Willson, C.G.; Fréchet, J.M.J. Proc. Microcircuit Eng. 1982, 260. Willson, C.G.; Fréchet, J.M.J.; Houlihan, F. Proc. IUPAC 28th Macromol. Symp. Amherst, 1982, 448.
- [29] Feely, W.; Proc. SPIE, 1986, 631, 48. Dammal, R.; Dössel, K.F.; Lingnau, G.; Theis, J.; Huber, H.; Oertel, H.; Trube, J.; Microelectronic Eng., 1989, 9, 575. Bruns, A.; Luethje, M.; Vollenbroek, F.A.; Spiertz, E.J., Microelectronic Eng., 1987, 6, 467.
- [30] Stover, H.D.H.; Matuszczak, S.; Willson, C.G.; Fréchet, J.M.J.; Macromolecules 1991, 24, 1741. Fréchet, J.M.J.; Matuszczak, S.; Reck, B.; Stover, H.D.H.; Willson, C.G.; Macromolecules 1991, 24, 1746.
- [31] Reichmanis E.; Houlihan, F.M.; Nalamasu, O.; Neenan, T.X.; Chem. Mater., 1991, 3, 394.
- [32] Cameron, J.J.; Fréchet, J.M.J.; Polym. Bull. 1991, 26, 303.
- [33] Winkle, W.R.; Graziano, K.A., J. Photopolym. Sci. Technol., 1990, 3, 419.
- [34] Beecher, J.E.; Cameron, J.J.; Fréchet, J.M.J.; Submitted for publication, 1992