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# Photogenerated base as catalyst for imidization reactions

## A new design of photosensitive polymers

**J. M. J. Fréchet[1,*], J. F. Cameron[1], C. M. Chung[1], S. A. Haque[1], and C. G. Willson[2]**

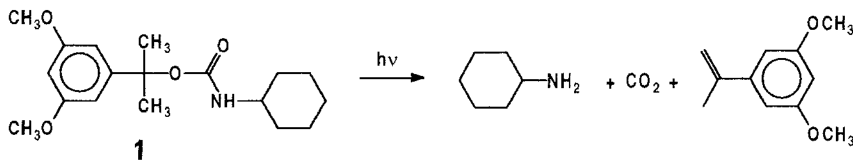
[1]Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853-1301, USA
[2]IBM Almaden Research Center, San Jose, CA 95120, USA

### *Abstract*

The photogeneration of free amines or diamines from soluble organic precursors such as photoactive 2-nitrobenzyl carbamates is useful for the imidization of polymers containing amic acid or amic ester moieties. The base-catalyzed reaction occurs at lower temperatures than the non-catalyzed thermal process and is applicable to the patterning of polymer coatings or thin films.

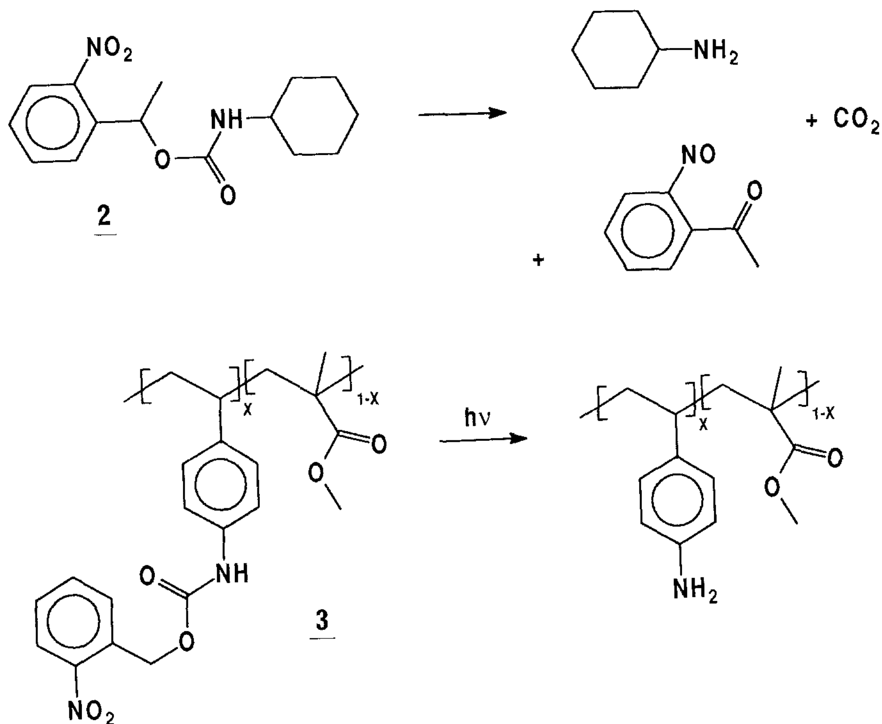
### *Introduction*

The photogeneration of active species such as free radicals within polymer thin films has long been used in the design of imaging systems (1) such as thick film resists or in photosensitive coatings. This approach has now been extended with the use of photogenerated acid or base in polymer curing and imaging systems (1). In particular, the use of acid catalysis in the design of chemically amplified resist materials has led to numerous advances in the field of microlithography (1, 2). A variety of sources of photogenerated acid have been explored including the triarylsulfonium salts of Crivello et al. (3) and a large number of other organic compounds (4). We have recently described (5-8) a number of photoactive carbamates that may be used as efficient photoprecursors of amines (e.g. compounds **1** and **2**), diamines, or polymers containing numerous amino pendant groups (e.g. structure **3**). The first family (5, 6) of carbamates is based on the photoactive Ddz (α,α-dimethyl-3,5-dimethoxybenzyl carbamoyl group) (9) and the second (7, 8) is based on carbamates incorporating the well-known 2-nitrobenzyl or related chromophores (10). For both of these families, removal of the photolabile protecting groups from their carbamate precursors has been demonstrated in the solid state through experiments in which polymer films containing small amounts of the carbamates were exposed to UV light (5-8). The quantum yields measured for carbamates based on the Ddz chemistry are near 0.10, while higher quantum yields varying from 0.11 to 0.62 are obtained with the 2-nitrobenzyl carbamates depending on the structure of the basic 2-nitrobenzyl chromophore.




*Corresponding author

For example, substitution of the 2,6-dinitrobenzyl for the 2-nitrobenzyl chromophore affords a five-fold increase in quantum yield, while the introduction of an α-methyl-benzyl group results in both increased quantum yield and reactivity enhancements in some applications (11). Other useful photoprecursors of amines have been described by Kutal and Willson (12).



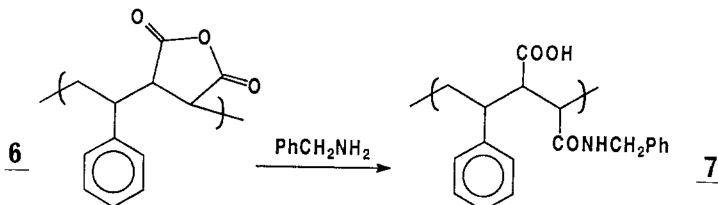

While the photogeneration of amines has found applications in image reversal processes (11) or in the patterning or photocuring of polymers formulations containing multifunctional epoxides (1), numerous other applications are possible (13).

For example, a survey of the literature reveals that the process of imidization of a variety of polyamic acids and derivatives may be base-catalyzed. Early work at Cornell University by Sondheimer and Holley (14) has shown the effectiveness of base-catalysis in the imidization of monoamide-monoester derivatives of asparagine and glutamine. Similarly, the cyclization of ortho-amidoesters to imides under catalysis by tertiary esters was reported (15) in 1978. Most interesting perhaps are the recent results of Volksen et al. who have provided conclusive evidence for the catalytic role of amines in imidization processes. These findings, combined with the use of our photoprecursors of amines (5-7) led to the development of a new class of photosensitive polyimides based on the amine catalyzed imidization of poly (amic esters) under mild conditions (17). This approach to photosensitive polyimides is quite different from that used by Rubner (18) as the key step of the process involves the *in situ* photogeneration of an amine and its subsequent use in low temperature imidization of a poly(amic ester), thus allowing its patterning (17).

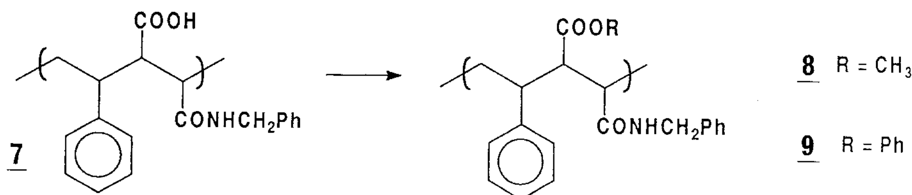
***Results and Discussion***

We have selected a novel poly(styrene maleic anhydride) derivative to demonstrate the concept of using photogenerated base in the patterning of polymer coatings and thin films. In this design, a radiation-sensitive coating is prepared using a soluble polyamic acid, or an ester derivative thereof, in combination with a base photogenerator such as **1**, **2**, **4**, or **5**. Exposure of the coating to light of the appropriate wavelength cause liberation of the base within the polymer and initiates the imidization reaction. As this reaction is very slow at room temperature, the exposed film is heated to a temperature which is sufficient to allow the base-catalyzed imidization process to take place, but is too low for appreciable imidization to occur in the absence of base. Therefore, a gradient of solubility is created as the exposed and unexposed areas of the film have different solubilities. Imaging is carried out by differential dissolution, and complete imidization can then be achieved thermally after image development.

Copolymer **7** containing carboxylic acid and amide functionalities on adjacent carbons is easily prepared by reaction of benzylamine with the regularly alternating copolymer of maleic anhydride and styrene **6**. This reaction can be carried out at room temperature using a modification of an earlier procedure (19).

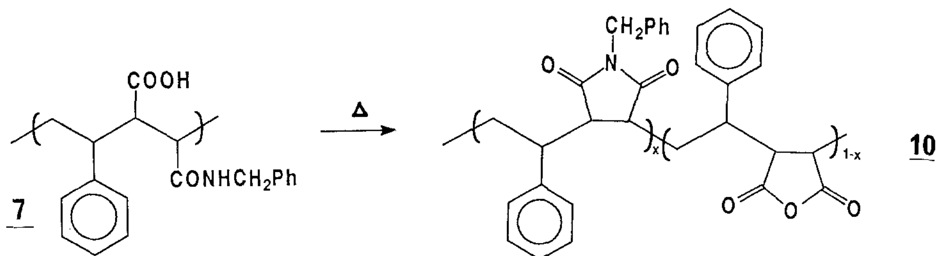



In order to facilitate its characterization, polymer **7** can be converted to an ester derivative such as **8** or **9**. Characterization of **8** and **9** is easily done using spectroscopic techniques as well as gel permeation chromatography (GPC). For example a styrene-maleic anhydride copolymer **6** with $M_n$ = 18,300 and $M_w/M_n$ = 1.9 (GPC data) afforded **8** with $M_n$ = 25,800 and $M_w/M_n$ = 1.6 (GPC data) after reaction with benzylamine followed by esterification using diazomethane. The structures proposed for the various polymers **6-9** are confirmed by NMR as well as IR spectrometry.

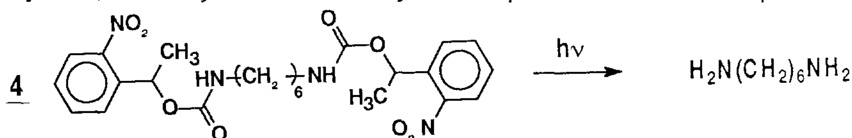



The imidization of copolymer **7** was first tested under purely thermal conditions by heating above 200°C. The reaction is readily monitored by infrared spectrometry. The broad bands corresponding to the COOH group of **7** disappear upon heating while the amide band near 1735 $cm^{-1}$ is replaced by an imide band near 1705$cm^{-1}$. However, in addition to the imide band, two other bands also appear in the carbonyl region of the spectrum: a small band at 1857 $cm^{-1}$ and a larger one at 1780 $cm^{-1}$. These absorptions are similar to those found in **6** and suggest the formation of a significant amount of anhydride units in the product. Therefore the product

of thermolysis of **7** would have structure **10** with both imide and anhydride groups. A similar observation of partial imidization accompanied by partial anhydride formation was made when **7** was heated to 180°C in the presence of 1,6-diaminohexane.

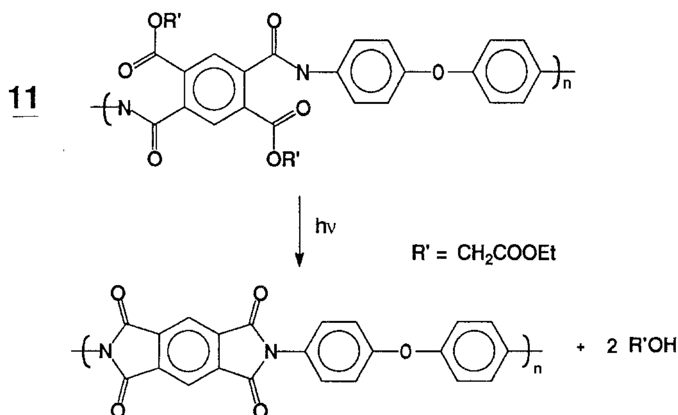



Since both the imidization reaction and the side reaction (anhydride formation) result in a significant change in the solubility properties of the polymer, the process can be used to image polymers **7-9**. In particular the change in solubility as **7** is transformed into **10** is interesting for imaging or resist chemistry as the starting polymer **7** is readily dissolved in very dilute aqueous base while the product is not.




Therefore, photobase generator **4** which affords a diamine upon exposure to UV light was tested in the photoinitiated thermal transformation of **7** into **10**. Thin films of copolymer **7** containing 10 mole % of photobase generator **4** were exposed through a mask to varying doses of 254 nm UV light. Despite the high quantum efficiency of the photobase generator itself (7), relatively high exposure doses were required due to the high absorbency of the medium. After exposure, the exposed films were heated at temperatures varying from 140 to 180°C to effect the base catalyzed thermal reaction. The use of silicon wafers polished on both sides allowed monitoring of the reaction by FT-IR. It was observed that the two reactions responsible for the formation of a product with structure **10** occurred to varying degrees depending on reaction conditions. Under some of the conditions that were tested, the amount of anhydride formation that was observed was estimated to exceed 50%. Attempts at accurate quantifying of the process were made difficult by the presence of some water in the starting polymer. Image development for the partly imidized films was made possible by the great solubility difference that exists between polymer **10** and its precursor **7**. While the latter, with its free carboxylic acid group, is soluble in very dilute aqueous tetramethylammonium hydroxide (ca. 0.005 M), the partly imidized structure **10** is not. Therefore a negative-tone image of the mask is obtained. Typical sensitivities for this system are not high, with doses of ca. 700 mJ/cm$^2$ required for complete insolubilization to be observed. However, since the exact structure of **10** varies with imaging and thermolysis conditions, it is difficult to measure accurately the ultimate lithographic sensitivity of the system.

This chemistry is directly applicable to the preparation of polyimides from polyamic acids or derivatives (17). Polyamic acid **11** was used in combination with a photobase generator such as **4** to pattern a polyimide as shown in Figure 1.




Irradiation through a mask liberates the amine in those areas of the film that have been irradiated and affords a latent image. Subsequent heating of this image effects the partial imidization of the polymer. Image development can then be achieved using solvent mixtures containing N-methyl-pyrrolidone. The partly imidized areas of the film are less soluble in the developer than the unexposed areas containing the starting amic ester moieties, as a result a negative-tone image is obtained. Since only some of the repeating units of polymer **11** are imidized, insolubilization of the exposed areas of the film is not complete and significant thinning of the film occurs during development. Due to the high absorbency of the starting polymers, the photochemical step is inefficient and very high doses near or in excess of 1J/$cm^2$ are required to obtain images such as that shown in Figure 1. Other base photogenerators such as **1** are not suitable for this application since they operate exclusively below 300 nm where the absorbency of polymers such as **11** is too high to allow penetration of the film. This is not a problem in solution as demonstrated by the rapid gelation of solutions containing the poly(amic ester) and **1** upon exposure to deep UV light. Significant improvements to this imaging system will be described shortly by Labadie et al. (20).

## *Experimental Procedure.*

Preparation of polymer **7**.

A mixture of styrene-maleic anhydride copolymer (10 mmoles, $M_n$ = 18,300 and $M_w/M_n$ = 1.9 by GPC with polystyrene calibration) and 50 mL methanol was treated with 40 mmoles of benzylamine while stirring vigorously at room temperature. All of the copolymer was dissolved within 20 minutes and stirring was continued for another 20 min. The solution was then concentrated and the polymer was precipitated in 1% aqueous acetic acid. After filtration and washing, the polymer was redissolved in methanol and precipitated again to afford the desired polymer **7** (71%). GPC (polystyrene standards $M_n$ = 25,800 and $M_w/M_n$ = 1.5). $^1$NMR analysis as well as FT-IR spectrometry are in agreement with the proposed structure; some water of hydration is tenaciously retained by the polymer.

Preparation of base photogenerator **4**.

This compound was prepared from 1,6-diisocyanatohexane and (2-nitrophenyl)-ethanol as described previously (7).

Imaging of a resist based on polymer **7** and base photogenerator **4**.

A 14 wt% solution of polymer 7 in ethylene glycol monomethyl ether was prepared. Compound 4 (10 wt% with respect to polymer 7) was dissolved and the solution was filtered then used to spin coat silicon wafers as well as KBr discs. The coated wafers were then pre-baked at 80°C for 10 min and the film thickness of the polymer coating was measured (0.95μm). The wafers were then exposed to various doses of 254nm UV light to photogenerate amine, and postbaked at temperatures varying from 140 to 180°C to effect the thermal imidization reaction. Development of the exposed images was accomplished using dilute aqueous base to remove the unexposed (unreacted) areas of the film. A typical developer was 1% aqueous AZ 312 MIF (AZ 312 is a commercial developer from Hoechst-Celanese consisting of 0.54 M aqueous tetramethylammonium hydroxide).

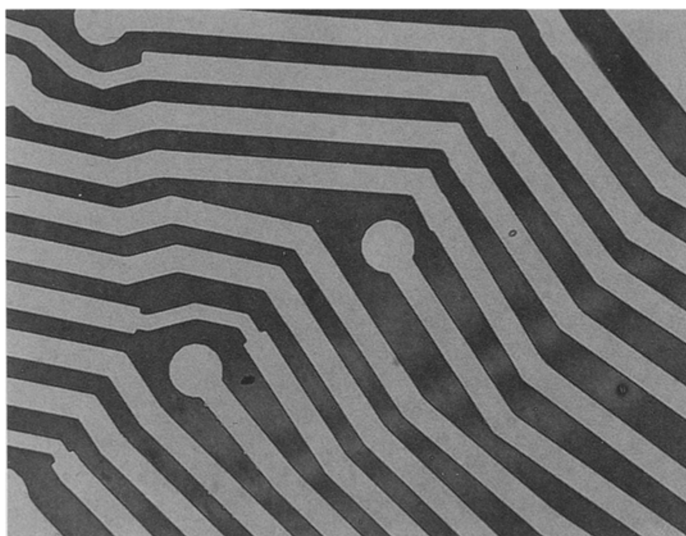


**Figure 1. Image obtained with a photosensitive polyimide using 4**

Imaging of polyamic ester **11**

This was done as described above using a more dilute solution (ca. 10 wt%) of the polyamic ester **11** (15) in N-methyl-pyrrolidone. The photobase generator **2**, prepared as described previously (7), was added to the solution in concentrations from 5 to 20% (with respect to polymer). After pre-baking for 5 min at 80°C, the films were exposed to varying doses of unfiltered UV light. A weak image observed after the exposure step intensified during post-bake at 150°C for 10 min. The exposed areas of the film became almost insoluble during the post-bake while the exposed areas remained soluble in solvents containing N-methyl-pyrrolidone. Therefore a negative image of the mask was obtained, though considerable film thinning was also observed during the development step.

***Conclusion***

The use of photobase generators such as 2-nitrobenzyl carbamates in the design of photosensitive polymers operating through base catalyzed imidization

processes has been demonstrated. The photogenerated amine acts as a catalyst in the imidization of precursor polymers containing active functionalities such as amic acid or amic ester groups. Though the reaction can be carried out in the solid state, sensitivity is low due to the high absorbency of the starting polymers at the wavelengths that are most effective for photogeneration of base. We are investigating several new promising photobase generators as well as the sensitization of existing compounds (5-8).

***Acknowledgements.***

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***References***

(1) Fréchet, JMJ, Pure & Appl. Chem. (1992) 64: 1239.
(2) Willson CG, "Introduction to Microlithography" ACS Symp. Ser. (1983) 219: 87. Fréchet JMJ, Ito H, Willson CG, Proc. Microcircuit Eng. (1982) 260. Willson CG, Ito H, Fréchet JMJ, Houlihan F, Proc. IUPAC 28th Macromol. Symp. Amherst (1982) 448. Willson CG, Fréchet JMJ, Tessier TG, Houlihan FM, J. Electrochem. Soc. (1986) 133: 181. Fréchet JMJ, Matuszczak S, Reck B, Stöver HDH, Willson CG, Macromolecules (1991) 24: 1746.
(3) Crivello, J.V.; Lam, J. Macromolecules (1977) 10: 1307.
(4) Reichmanis E, Wilkins CW Jr., Price DA, Chandross EA, J. Electrochem. Soc., (1983) 130: 1433. Houlihan FM, Shugard A, Gooden R, Reichmanis E, Macromolecules (1988) 21: 2001. Schlegel L, Ueno T, Shiraishi H, Hayashi N, Iwayanagi T, Chem. Mater. (1990) 2: 299. Buhr G, Dammel R, Lindley CR, Polym. Mat. Sci. Eng., (1989) 61: 269.
(5) Cameron JF, Fréchet JMJ, J. Org. Chem. (1990) 55: 5919.
(6) Cameron JF, Fréchet JMJ, J. Photochem. Photobiol. A: Chem. (1991) 59: 105.
(7) Cameron JF, Fréchet JMJ, J. Am. Chem. Soc. (1991) 113: 4303.
(8) Beecher JE, Cameron JF, Fréchet JMJ, Polym. Mat. Sci. Eng. (1991) 64: 71.
(9) Birr C, Lochinger W, Stahnke G, Lang P, Liebigs Ann, Chem., (1972) 763: 162.
(10) DeMayo P, Adv. Org, Chem. (1960) 2: 367. Patchornick A, Amit B, Woodward RB, J. Am. Chem. Soc. (1970) 92: 6333.
(11) Matuszczak S, Cameron JF, Fréchet JMJ, Willson CG, J. Mater. Chem. (1991) 1: 1045.
(12) Kutal C, Wilson CG, J. Electrochem. Soc.(1987) 134: 2280.
(13)Beecher, JM, Cameron, JF, Fréchet JMJ, J. Mater. Chem. (1992) 2: 811.
(14) Sondheimer E, Holley RW, J. Am. Chem. Soc., (1954) 76: 2467.
(15) Lavrov SV, Talankina OB, Kardash IE, Pravednikov AN, Vysokomol. Soedin, Ser. B. (1978) 20: 786.
(16) Volksen W, Pascal T, Labadie J, Sanchez M, Polym. Mat. Sci. Eng. (1992) 66: 235.
(17) McKean DR, Walraff GM, Volksen W, Hacker NP, Sanchez MI, Labadie JW; Polym. Mat. Sci. Eng. (1992) 66, 237.
(18) Rubner R, Adv. Mater. (1990) 2: 452 and references therein.
(19) Rätzsch M., Prog. Polym. Sci., (1988) 13, 277.
(20) McKean DR, Walraff GM, Volksen W, Hacker NP, Sanchez MI, Labadie JW; ACS Symposium Series, submitted for publication.

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