

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE June 30, 1996	3. REPORT TYPE AND DATES COVERED Technical Report # t # 25		
4. TITLE AND SUBTITLE DESIGN OF IMAGING MATERIALS FOR USE WITH PHOTOGENERATED BASE: RADIATION INDUCED β -ELIMINATION TO YIELD POLY(4-HYDROXYSTYRENE).		5. FUNDING NUMBERS C N00014-91-1338		
6. AUTHOR(S) Jean M.J. Fréchet, Edward J. Urankar, Isabella Brehm, Q. Jason Niu				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Cornell University Dept. of Chemistry, Baker Laboratory Ithaca, New York 14853-1301		8. PERFORMING ORGANIZATION REPORT NUMBER C N00014-91-1338		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000		10. SPONSORING / MONITORING AGENCY REPORT NUMBER 19960711 001		
11. SUPPLEMENTARY NOTES To appear in Polym. Mat. Sci. Eng. 1996, 75				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale, its distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) DESIGN OF IMAGING MATERIALS FOR USE WITH PHOTOGENERATED BASE: RADIATION INDUCED β -ELIMINATION TO YIELD POLY(4-HYDROXYSTYRENE). The search for chemically amplified resist and imaging materials that are resistant to airborne contaminants has led us to explore new routes to resist imaging. The use of photogenerated base is particularly attractive since several stable photoprecursors of amines and other bases have been developed. We have now designed a novel family of polymers that undergo base catalyzed β -elimination to afford poly(p-hydroxystyrene). Although the active units of the polymers are different, their basic design is analogous to that of the well known family of t-BOC resists [1] that operate on the basis of acid-catalyzed side chain deprotection. Several polymers and copolymers containing base labile pendant groups have been prepared. Their use as chemically amplified imaging and resist materials is described. [1] S. MacDonald, C.G. Willson, J.M.J. Fréchet, Acc. Chem. Res. 1994, 27, 151.				
14. SUBJECT TERMS Photoresist, Chemical Amplification, Photogenerated Base, solubility change, imaging, microelectronics, lithography photosensitive coating, radiation			15. NUMBER OF PAGES 2	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

OFFICE OF NAVAL RESEARCH

Grant # N00014-91-J-1338

R&T Code 313t003---07

Dr. Kenneth J. Wynne

Technical Report #25

Design of Imaging Materials For Use with Photogenerated Base: Radiation Induced β -Elimination to Yield Poly(4-Hydroxystyrene)

Jean M.J. Fréchet, Edward J. Urankar, Isabella Brehm, and Q. Jason Niu

Department of Chemistry Baker Laboratory Cornell University
Ithaca, New York 14853-1301

June 30, 1996

Reproduction in whole or in part is permitted for any purpose
of the United States Government.

This document has been approved for public release and sale,
its distribution is unlimited.

DESIGN OF IMAGING MATERIALS FOR USE WITH PHOTOGENERATED BASE: RADIATION INDUCED β -ELIMINATION TO YIELD POLY(4-HYDROXYSTYRENE).

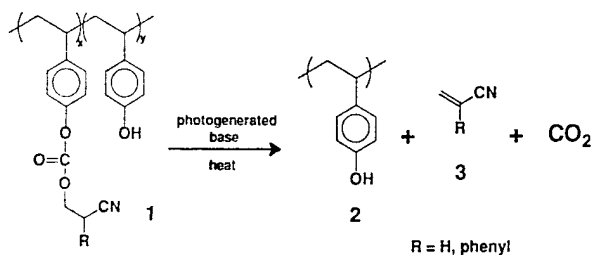
Edward J. Urankar, Isabella Brehm, Q. Jason Niu,
and Jean M.J. Fréchet

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, NY 14853-1301

Introduction

The concept of chemical amplification in microlithography was first described by Fréchet, Ito, and Wilson^{1,2} with the development of the poly(*t*-BOC-styrene) resist which was susceptible to acid catalyzed thermolysis to poly(4-hydroxy-styrene). Although chemically amplified resists have grown in importance because of their high performance capabilities³, they have been found to be affected by the presence of airborne contaminants. Since the resists operate on the basis of the photogeneration of acid within the polymer film, airborne traces of volatile bases such as *N*-methylpyrrolidinone may cause de-activation of the film surface with concomitant degradation of imaging characteristics. It is expected that a new family of resists designed to operate with photogenerated base, rather than acid, as the key catalyst should be immune from this problem.

Recently, families of photoactive precursors have been developed that upon exposure to ultraviolet irradiation liberate amines or other bases^{4,5}. This development has led to the use of photogenerated base in an image reversal process of a cationically curable resist material⁶. Photogenerated base has also been used to catalyze the thermal imidization of poly(amic esters) in the design of imageable polyimides^{7,8}. The development of the first chemically amplified resist utilizing a phototriggered basic catalyst involved the decarboxylation⁹ of a polymer side chain. More recent imaging systems utilizing photogenerated amines have dealt with the base catalyzed curing of polymers containing highly enolizable side chains¹⁰ and the intramolecular imidization of amide-esters¹¹. This report describes the design of a family of imageable polymers containing activated carbonate linkages in their side chains that are susceptible to base catalyzed β -eliminations to yield poly(4-hydroxystyrene).



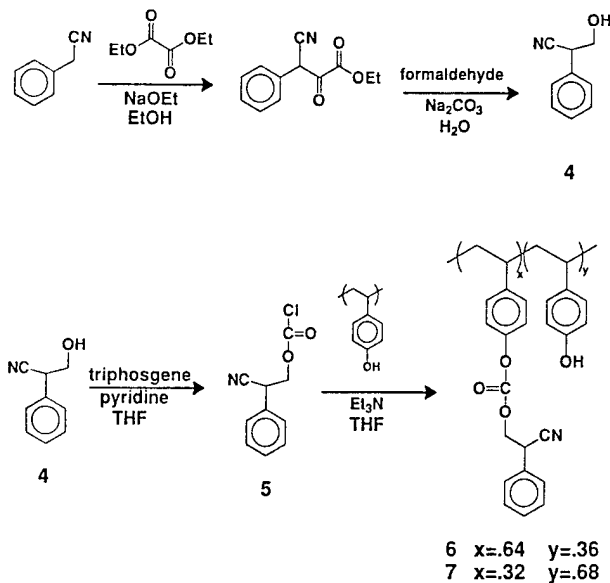
Results and Discussion.

In order to accommodate both desirable imaging characteristics and acceptable chemical reactivity, copolymers such as structure 1 were selected for this study. The "active" component of copolymer 1 contains functionalities that are susceptible to facile β -elimination to afford more polar phenolic units. The overall composition of the copolymer may be adjusted in such a way that removal of its base-sensitive functional groups leads to a significant change in solubility without excessive loss in film thickness.

Copolymer 1 is prepared by chemical modification of poly(4-hydroxystyrene) 2, a process that allows considerable latitude in the selection of the ratio x/y between base-active and inactive units. In order to facilitate the β -elimination process, the active

units incorporate a carbonate moiety that releases carbon dioxide together with the eliminated fragment, α -cyano-styrene 3.

Chloroformate 5 is obtained by reaction of its alcohol precursor 4 with triphosgene in the presence of pyridine. Coupling of 5 with poly(4-hydroxystyrene) 2, in the appropriate stoichiometry, affords copolymer 1. While several copolymers were prepared for this study, only results obtained with copolymers 6 and 7 containing 64 and 32% of base-sensitive carbonate units, respectively, will be given here. The composition of the copolymers is readily determined by thermogravimetric analysis since the carbonate groups are heat-labile. Therefore TGA analysis of 6 (Figure 1) shows a 48.2% weight loss occurring near 183°C. As expected, the thermal behavior of 6 is reminiscent of that for poly(*t*-BOC-styrene) since both materials are carbonates with labile β -hydrogens. Copolymer 7 containing fewer base-sensitive functionalities shows a significantly reduced loss of weight upon thermolysis, a feature that may be advantageous if film thickness retention is deemed to be of importance. In the presence of photogenerated amine, abstraction of a hydrogen atom located α to the cyano group leads to cleavage with loss of α -cyano-styrene followed by decarboxylation. Proton transfer from the protonated amine leads to the phenolic polymer while the amine itself is regenerated for further use. Therefore chemical amplification is achieved since a single molecule of photogenerated amine is capable of effecting the cleavage of several carbonate units.



The elimination reaction was easily monitored by FTIR spectroscopy under the conditions used during the imaging experiments. Figure 2 shows the IR spectrum obtained from a thin film of the resist containing 89 wt % of copolymer 6 and 11 wt % of the photobase generator. The characteristic carbonyl absorption at 1767 cm^{-1} from the carbonate structure of the polymer is evident (Spectrum a). Upon exposure to 84 mJ/cm^2 of 254nm irradiation and subsequent baking at 100°C for 3 minutes complete loss of the carbonyl absorption is seen in the IR, along with the appearance of the hydroxyl absorption at 3500 cm^{-1} due to the formation of poly(4-hydroxystyrene) (Spectrum b). As seen with the classical *t*-BOC resist systems, formation of poly(4-hydroxystyrene) in the irradiated areas leads to differential solubility as these areas are highly soluble in isopropyl alcohol or aqueous base developers. This type of development is used to obtain the desired positive-tone relief image.

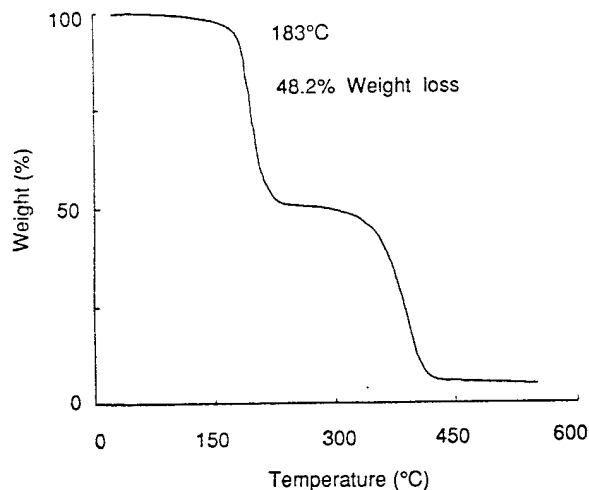


Figure 1: Thermogravimetric Analysis of copolymer 6

The sensitivity values for this system are quite high. Using the resist films described above, copolymer 6 afforded a sensitivity of 30 mJ/cm² when developed with 50% aqueous AZ312MIF after a post exposure bake of 120°C for 3 minutes. The sensitivity values seem to be highly dependent on the degree of modification of the matrix polymer. Copolymer 7 containing considerably more free phenol units demonstrated a much lower sensitivity of 250 mJ/cm² under conditions identical to those used previously with 6.

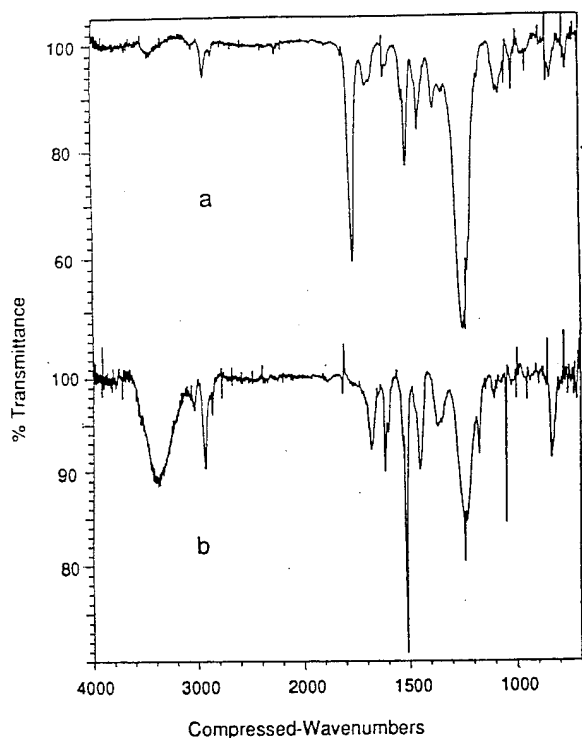


Figure 2: FTIR spectrum of resist containing copolymer 6

Experimental Procedure

Preparation of Copolymer 6

To an ice cooled solution of 3-hydroxy-2-phenylpropionitrile¹² **4** (3.0 g, 20 mmol) and triphosgene (2.08 g, 7 mmol) in dry THF is added pyridine (1.58 g, 20 mmol) producing a white precipitate. Solution stirred at room temperature for 12 hours, filtered from salts, and evaporated to dryness at reduced pressure to give 4.2 g (100%) of crude chloroformate **5** which was pure by ¹H and ¹³C NMR and used without further purification. Poly(4-hydroxystyrene) (1.56 g) and triethylamine (1.31 g, 13 mmol) in dry THF was added dropwise to a solution of chloroformate **5** (3.0 g, 14 mmol) in THF. Slight exothermic reaction and white precipitate are produced and solution stirred at room temperature overnight. The reaction is concentrated and quenched with water. The precipitated polymer is filtered, dissolved in acetone, and reprecipitated twice into ethyl ether to leave 2.70 g (70%) of white powder.

Imaging experiments: determination of resist sensitivity.

A resist solution was prepared from 0.1379 g (89 wt %) of the copolymer prepared above, 0.0178 g (11 wt %) of [(2-nitrobenzyl)-oxy]carbonyl[4,4'-trimethylenedipiperidine] in 0.430 g of diglyme. The filtered resist solution was spin-coated onto silicon wafers that were subsequently pre-baked at 120°C for 3 minutes affording films 1 micrometer in thickness. Exposure at 254 nm (interference filter) through a gradient multidensity mask (Ditric Optics) afforded a composite image with areas of different exposure doses. After postexposure baking at 120°C for 3 minutes, the image was developed by immersion into a stirred solution of 50% v/v of AZ312MIF in water for 45 seconds.

Acknowledgements

Financial support of this research by the Office of Naval Research is acknowledged with thanks.

Literature

- Fréchet, J.M.J.; Ito, H.; Willson, C.G., *Proc. Microcircuit Eng.* **1982**, 260.
- Willson, C.G.; Ito, H.; Fréchet, J.M.J.; Tessier, T.G.; Houlihan, F.M., *J. Electrochem. Soc.* **1986**, 133, 181.
- MacDonald, S. A.; Willson, C.G.; Fréchet, J.M.J., *Acc. Chem. Res.* **1994**, 27, 151.
- Cameron, J.F.; Fréchet, J.M.J., *J. Org. Chem.* **1990**, 55, 5919.
- Cameron, J.F.; Fréchet, J.M.J., *J. Am. Chem. Soc.*, **1991**, 113, 4303.
- Ackmann, A.; Fréchet, J.M.J., *J. Chem. Soc., Chem. Commun.*, **1996**, in press.
- Matuszczak, S.; Cameron, J.F.; Fréchet, J.M.J., *J. Mater. Chem.* **1991**, 1, 1045.
- McKean, D.R.; Briffaud, T.; Volksen, W.; Hacker, N.P.; Labadie, J.W., *Polym. Prep.* **1994**, 35, 387.
- Fréchet, J.M.J.; Cameron, J.F.; Chung, C.M.; Haque, S.A.; Willson, C.G., *Polymer Bull.*, **1993**, 30, 369.
- Leung, M.; Fréchet, J.M.J., *Polym. Mat. Sci. Eng.*, **1993**, 68, 30.
- Urankar, E.J.; Fréchet, J.M.J., *Polym. Prep.* **1994**, 35, 933.
- Leung, M.; Fréchet, J.M.J.; Cameron, J.F.; Willson, C.G., *Macromolecules*, **1995**, 28, 4693.
- Banerjee, D.K.; Kasturi, T.R.; Purushotham, J., *Indian J. Chem.*, **1984**, 23b, 395.