Radiation-induced Modifications of Allylamino-Substituted Polyphosphazenes

M. F. Welker and H. R. Allcock (PSU)
G. L. Grune, R. T. Chern, and V. T. Stannett (NCSU)

Department of Chemistry
The Pennsylvania State University
152 Davey Laboratory
University Park, Pennsylvania 16802

Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217-5000

Chapter in "Polymers for Electronics", ACS Symposium Series (in press)

A collaborative effort to synthesize amino-substituted polyphosphazenes and examine their sensitivity to radiation has recently been undertaken. The objective was to determine the value of using such polymers as new and better resist materials for microlithographic applications. An initial study was carried out using elastomeric phenoxy-substituted polyphosphazenes as models for radiation and grafting. However, it became necessary to synthesize several new amino-substituted polyphosphazenes for several reasons. First, the usefulness of elastomeric polymers for resist applications is severely limited by their inability to remain dimensionally stable at normal temperatures. Glassy polymers have been shown to provide the necessary thermal properties required for resist films deposited on SiO₂ wafers. Second, the amino-substituted polyphosphazenes are excellent film-forming polymers with high molecular weights. Finally, it seemed possible that these polymers would exhibit similar reactive ion etching resistance to those of a phenoxy-substituted counterpart, and experimental work was performed to determine reactive ion etching values for the most radiation-sensitive of the new polymer candidates.

Polymers, synthesis, crosslinking, photolithography, phosphazenes, radiation

Security Classification of Report: unclassified
Security Classification of this Page: unclassified
Security Classification of Abstract: unclassified
Limitation of Abstract: unlimited
Radiation-Induced Modifications of Allylamino-Substituted Polyphosphazenes

by

M. F. Welker and H. R. Allcock (PSU)
G. L. Grune, R. T. Chern, and V. T. Stannett (NCSU)

Prepared for Publication in Polymers for Electronics
ACS Symposium Series

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

May 18, 1993

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.
RADIATION-INDUCED MODIFICATIONS OF ALLYLAMINO-SUBSTITUTED POLYPHOSPHAZENES

by

M. F. Welker and H. R. Allcock
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

and

G. L. Grune, R. T. Chern, and V. T. Stannett
Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27605

I. INTRODUCTION

A collaborative effort to synthesize amino-substituted polyphosphazenes and examine their sensitivity to radiation has recently been undertaken. The objective was to determine the value of using such polymers as new and better resist materials for microlithographic applications. An initial study was carried out using elastomeric phenoxy-substituted polyphosphazenes as models for radiation and grafting. However, it became necessary to synthesize several new amino-substituted polyphosphazenes for several reasons. First, the usefulness of elastomeric polymers for resist applications is severely limited by their inability to remain dimensionally stable at normal temperatures. Glassy polymers have been shown to provide the necessary thermal properties required for resist films deposited on SiO₂ wafers. Second, the amino-substituted polyphosphazenes are excellent film-forming polymers with high molecular weights. Finally, it seemed possible that these polymers would exhibit similar reactive ion etching resistance to those of a phenoxy-substituted counterpart, and experimental work was performed to determine reactive ion etching values for the most radiation-sensitive of the new polymer candidates.

II. EXPERIMENTAL

Syntheses of allyl amino-substituted polyphosphazenes were accomplished using nucleophilic substitution techniques described previously and represented in Figure 1. Following the synthesis of these polymers, molecular and materials' characterization was accomplished by means of ³¹P and ¹H NMR, and elemental analysis, followed by GPC for molecular weight determination, and thermal analysis by DSC for Tₙ measurements. Films of 0.0045-0.0065 inch thickness, prepared from solutions of the polymer in THF, were cast on clean glass plate using a precision blade to spread the 20 wt.% solution. Deionized water was used to remove the dried film from the glass substrate. To determine their sensitivity to radiation, the polymer films were irradiated in a Gammacell 220 ⁶⁰Co γ-ray source manufactured by Atomic Energy of Canada Ltd. Films weighing approximately 0.0100 g were placed in sealed glass evacuated vials (1 x 10⁻⁶ torr) before exposure. The dose rate was 0.52 kGy/hour. Extraction of the soluble portion was performed by placing irradiated films in fritted glass vials (20-50 μμ pore size) and refluxing with THF to constant weight.
II. EXPERIMENTAL

Syntheses of allyl amino-substituted polyphosphazenes were accomplished using nucleophilic substitution techniques described previously and represented in Figure 1. Following the synthesis of these polymers, molecular and materials' characterization was accomplished by means of 31P and 1H NMR, and elemental analysis, followed by GPC for molecular weight determination, and thermal analysis by DSC for Tg measurements. Films of 0.0045-0.0065 inch thickness, prepared from solutions of the polymer in THF, were cast on clean glass plate using a precision blade to spread the 20 wt.% solution. Deionized water was used to remove the dried film from the glass substrate. To determine their sensitivity to radiation, the polymer films were irradiated in a Gammacell 220 60Co γ-ray source manufactured by Atomic Energy of Canada Ltd. Films weighing approximately 0.0100 g were placed in sealed glass evacuated vials (1 x 10^-6 torr) before exposure. The dose rate was 0.52 kGy/hour. Extraction of the soluble portion was performed by placing irradiated films in fritted glass vials (20-50 μm pore size) and refluxing with THF to constant weight.

III. RESULTS AND DISCUSSION

Initially, model polymers were investigated for their sensitivity to both E-beam and gamma-radiation. Experimental determination of the G(X) (the number of crosslinks/100 eV) values for chemically different poly(organophosphazenes) was used as an initial indicator of their behavior as resist materials. In that study, it was found that the presence of an allylic substituent (8 mol%) could greatly enhance not only gelation, but also the grafting to the elastomers of reactive monomers. The first attempt to synthesize an amino-substituted polyphosphazene specifically
tailored to provide better resist properties was unsuccessful because the polymer was quite insensitive to radiation. Incorporation of the allylic groups into the amino-substituted polymers allowed for sufficient gelation after irradiation to suggest possible negative resist applications.

Experience with the irradiation of polyphosphazenes in any form (rubbery elastomer, fibrous glassy, or film) has been limited to that of only two or three groups of researchers, including those from both of these laboratories. Stannet et al. investigated eight different poly(organophosphazenes) and obtained Dg (the dose where the gel is first formed), G(X), and G(S) values for each. Depending on the nature of the substituent, the G(X) values found ranged from 0.050 to 2.49. The smallest G(X) value was found for the amino-substituted phosphazene, possibly due to the stabilizing influence of the "hindered amines" within its structure. Studies by Beggiato, Hiraoka, and Lora have reviewed the different aspects of irradiating polyphosphazenes, but neglected the use of irradiation grafting techniques. Recently, a study was conducted where dimethylaminoethyl methacrylate monomer was grafted to various poly(organophosphazenes) to increase biocompatibility. Synthesis and characterization of allyl amino-substituted polyphosphazenes were carried out using previously described techniques.

Initially, the polymer shown in Figure 1, containing only 4-ethyl anilino substituents, was synthesized, characterized, and exposed to varying dosages of gamma radiation.

\[
\text{Tg} = 86 \text{ C}
\]

**Figure 2.** *Structure of 4-ethyl-anilinophosphazene homopolymer.*

Unfortunately, this polymer was found to be very radiation-insensitive when exposed to gamma rays under vacuum (10^-6 torr) even at temperatures of 95°C—well above the T_g. This stabilizing influence has recently been confirmed by adding a small amount (1.25 - 2.5 wt %) of the polymer to styrene monomer. This resulted in small but significantly retarded polymerization yields and molecular weights of the polystyrene. Thus, several syntheses were subsequently performed to obtain polymers with the three structures shown in Figures 3 (a), (b), and (c) below.

Work has been performed for two of the polymers to determine G(X) values. This involves the use of the Charlesby-Pinner (CP) treatment which describes the determination of the gel fraction of the polymer as a function of radiation dose. Figures 4(a) and 4(b) illustrate that polymers with structures such as those shown for Polymers 1 and 2 are suitable for crosslinking when exposed to "Co radiation. Polymer 1 has been synthesized with approximately 7% of the allylic substituent, while the synthesis of polymer 2 allowed for 3-4% of the same allylic group.
The Charlesby-Pinner equation used to determine the G(X) values for these polymers is given as:

\[ s + s^{1/2} = p_0/q_0 + 2/q_0MwD \]  

(1)

where:
- \( p_0 \) = density of main chain fractures per unit dose
- \( D \) = radiation dose
- \( q_0 \) = density of crosslinks per unit dose
- \( s \) = soluble fraction of the polymer

and reduces to allow the simple determination of the G(X) value when \( p_0 \) is close to zero:

\[ G(X) = \frac{4.52 \times 10^8}{Dg \times Mw} \]  

(2)

where; \( Dg \) = dose at which the gel first appears
\( Mw \) = weight average molecular weight as determined by GPC

This equation is very dependent on proper determination of \( Dg \), which can be facilitated by using a method made popular by Lyons—that of a log-log plot of \( s + s^{1/2} \) vs. dose. Other restrictions in using this technique: (a) crosslinks are distributed randomly along molecular chains during irradiation, and (b) crosslinks are assumed independent of the absorbed dose. This was confirmed by the plots in Figures 4 (a) and (b), which indicate the best straight-line fit of the data goes through the origin.

Grafting experiments with purified acrylic acid have also been performed. We speculate that the stabilizing influence of the substituent has hindered the graftability of the allyl-amino-substituted polyphosphazenes. Attempted grafting with a 50/50 mixture of acrylic acid and water has resulted in little or no success. Pure acrylic acid was found to dissolve the polymer. The best polymer film candidate based on sol/gel analysis performed as described, was dissolved (5 wt.%) in methyl-isobutyl ketone (MIBK) and spin-coated onto a 4 in. \( \text{SiO}_2 \) wafer at 2000 r.p.m. using hexamethyldisilazane (HMDS) as a primer. Small sections of the optimum wafers were sectioned and subjected to a 15 KeV electron beam power source using an electron beam/scanning electron microscope lithography tool, as shown in Figure 5. The exposure was performed at \( 2 \times 10^{-6} \) torr. Subsequent development was achieved in 10 seconds, again using THF as the solvent.

![Figure 5. Schematic Diagram of ERC Electron Beam Lithography Tool.](image-url)
Polymers

Polymer 1
Figure 3(a).

Polymer 2
Figure 3(b).

Polymer 3
Figure 3(c).

Figures 4(a) and 4(b). Charlesby-Pinner Plots for Polymer 1 and Polymer 2
The Charlesby-Pinner equation used to determine the G(X) values for these polymers is given as:

\[ s + s^{1/2} = \frac{p_o}{q_0} + \frac{2}{q_0}MWD \]  

(1)

where: 
- \( p_o \) = density of main chain fractures per unit dose 
- \( D \) = radiation dose 
- \( q_0 \) = density of crosslinks per unit dose 
- \( s \) = soluble fraction of the polymer

and reduces to allow the simple determination of the G(X) value when \( p_o \) is close to zero:

\[ G(X) = \frac{4.52 \times 10^6}{D_g \times M_w} \]  

(2)

where; \( D_g \) = dose at which the gel first appears 
\( M_w \) = weight average molecular weight as determined by GPC

This equation is very dependent on proper determination of \( D_g \), which can be facilitated by using a method made popular by Lyons\textsuperscript{24}--that of a log-log plot of \( s + s^{1/2} \) vs. dose. Other restrictions in using this technique: (a) crosslinks are distributed randomly along molecular chains during irradiation, and (b) crosslinks are assumed independent of the absorbed dose. This was confirmed by the plots in Figures 4 (a) and (b), which indicate the best straight-line fit of the data goes through the origin.

Grafting experiments with purified acrylic acid have also been performed. We speculate that the stabilizing influence of the substituent has hindered the graftability of the allyl-amino-substituted polyphosphazenes. Attempted grafting with a 50/50 mixture of acrylic acid and water has resulted in little or no success. Pure acrylic acid was found to dissolve the polymer. The best polymer film candidate based on sol/gel analysis performed as described, was dissolved (5 wt.%) in methyl-isobutyl ketone (MIBK) and spin-coated onto a 4 in. SiO\textsubscript{2} wafer at 2000 r.p.m. using hexamethyldisilazane (HMDS) as a primer. Small sections of the optimum wafers were sectioned and subjected to a 15 KeV electron beam power source using an electron beam/scanning electron microscope lithography tool, as shown in Figure 5. The exposure was performed at \( 2 \times 10^{-6} \) torr. Subsequent development was achieved in 10 seconds, again using THF as the solvent.

![Figure 5. Schematic Diagram of ERC Electron Beam Lithography Tool.](image-url)
Figure 6 illustrates a cross-section of an SiO2 wafer with a 1780 Å film thickness of Polymer 1 spin-coated on its surface. Figure 7 is an E-beam lithographic pattern using a 15 KeV power source at 6 μC/cm² of the same wafer. Submicron resolution (0.1 - 0.5 μm) was achieved using THF as a developing solvent--development time was 10 seconds. No pre- or post baking of the wafer/resist was performed, yet adhesion of the polyphosphazene film was excellent.

Reactive ion etching rates as low as 585 Å/min. have been determined for this same water/film combination. These rates are compared in Tables 1 and 2 from a previous study and from the results of our work. The effect of the differences in vacuum and two types of equipment used for plasma etching is reflected in the etch rate differences shown.

Table 1. Reactive Ion Etching Rates for Various Negative Resist Materials Based on Work by Hiraoka (250 V Bias, 40 SCCM, 60 mTorr, 0.35 W/cm²).

<table>
<thead>
<tr>
<th>Resist Type</th>
<th>Etch Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(diphenoxyporphazene)</td>
<td>30 Å/min.</td>
</tr>
<tr>
<td>AZ-1350J</td>
<td>1300 Å/min.</td>
</tr>
<tr>
<td>Silyated AZ-1350J</td>
<td>30 Å/min.</td>
</tr>
<tr>
<td>Poly(chloromethylstylene)</td>
<td>1400 Å/min.</td>
</tr>
</tbody>
</table>

* UV-hardened films

Table 2. Reactive Ion Etching Rates (RIE) for Allyl-amino Sunstituted Polyphosphazenes and Commercially Available Resist (-250 V Bias, 40 SCCM, 900 mTorr, 0.08 W/cm²)

<table>
<thead>
<tr>
<th>Resist Type</th>
<th>Etch Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shipley 1400-31 Novolak Resin</td>
<td>4,224 Å/min.</td>
</tr>
<tr>
<td>Polymer 1 - Exposed w/E-beam</td>
<td>585 Å/min.</td>
</tr>
<tr>
<td>Polymer 1 - Unexposed</td>
<td>830 Å/min.</td>
</tr>
</tbody>
</table>
Figure 6. Cross-section Microphotograph (37,000 X Magnification) of Polymer 1 w/7% Allylic Substituent on SiO₂ Wafer Indicating 1780 Å Film Thickness.

Figure 7. Microphotograph (5,500 Magnification) of Patterned Wafer Using 15 KeV Electron Beam/SEM at 6 µCi/cm² illustrating submicron (0.1-0.5 µm) resolution for Polymer 1. Development solvent/time is THF/10 seconds.
IV. SUMMARY

It has been shown that allyl-amino substituted polyphosphazenes, specifically tailored to form films from suitable solvents can be used for negative resist/mask applications for microlithography. As suggested by earlier model studies, the addition of allylic double bonds to amino-substituted polyphosphazenes increases the sensitivity to radiation-induced crosslinking. However, it is probable that the stabilizing influence of the hindered amine substituent has reduced the graftability of these polymers. In addition, the inherent RIE resistance of the phosphazene family has been demonstrated, which underscores the potential usefulness of these systems for future resist work. Currently, other related polymer structures with higher allylic loadings are being investigated for enhanced radiation sensitivity.

V. ACKNOWLEDGMENTS

The work at North Carolina State University has been supported with an Shared University Research grant from the IBM Corporation. Drs. Sanwald and J. R. Kirby of IBM-RTP, N.C. and J. Shaw of IBM-Yorktown, N. Y. have been generous with financial and technical support for this effort. The polymer synthesis studies at The Pennsylvania State University were carried out with support from the Office of Naval Research.

The authors would like to thank Professor J. A. Moore of Rensselaer Polytechnic Institute for helpful advice and unpublished data involving the grafting enhancements, which can be accomplished for potential resist applications. In addition, R. Greer, an undergraduate in Chemical Engineering (NCU) was extremely helpful in preparing polymer forms for irradiation and grafting studies. Professor Phillip Russell and Ph.D. candidate Terry Stark (NCU) were responsible for E-beam writing of the SiO₂ wafers. Dr. Sam Nablo of Energy Sciences, Inc., Wilmington, Mass. has been helpful with technical information.
V. REFERENCES


Office of Naval Research (2)*
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Air Weapons Center
Weapons Division
China Lake, CA 93555-6001

Dr. Elek Lindner (1)
Naval Command, Control and Ocean Surveillance Center
RDT&E Division
San Diego, CA 92152-5000

Dr. Barnard E. Douda (1)
Crane Division
Naval Surface Warfare Center
Crane, Indiana 47522-5000

Dr. Richard W. Drisko (1)
Naval Civil Engineering Laboratory
Code L52
Port Hueneme, CA 93043

Dr. Harold H. Singerman (1)
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Eugene C. Fischer (1)
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Defense Technical Information Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

* Number of copies to forward
ABSTRACT DISTRIBUTION LIST

Dr. Harry R. Allcock
Department of Chemistry
Pennsylvania State Univ.
University Park, PA 16802

Dr. Chris W. Allen
Department of Chemistry
University of Vermont
Burlington, VT 05405-0125

Dr. Andrew R. Barron
Department of Chemistry
Harvard University
Cambridge, MA 02138

Dr. Kurt Baum
Fluorochem, Inc.
680 South Ayon Avenue
Azusa, CA 91702

Dr. Alexander S. Blumstein
Department of Chemistry
University of Massachusetts
Lowell, MA 01854

Professor Joseph M. DeSimone
Department of Chemistry
The University of North Carolina at Chapel Hill
Chapel Hill, NC 27599-3290

Dr. Jean M. Frechet
Department of Chemistry
Cornell University
Ithaca, NY 14853

Dr. Robert H. Grubbs
Department of Chemistry
California Inst. of Technol.
Pasadena, CA 91124

Professor Issifu I. Harruna
Morris Brown College
643 Martin Luther King, Jr. Drive, N.W.
Atlanta GA 30314-4140

Dr. Robert W. Lenz
Polymer Sci. and Eng. Dept.
University of Massachusetts
Amherst, MA 01002
Dr. Lon J. Mathias  
Department of Polymer Science  
University of Southern Mississippi  
Hattiesburg MS 39406-0076

Dr. Krzysztof Matyjaszewski  
Department of Chemistry  
Carnegie-Mellon University  
Pittsburgh, PA 15213

Pr. Alan G. MacDiarmid  
Department of Chemistry  
University of Pennsylvania  
Chemistry Building  
Philadelphia PA 19104-6323

Dr. James E. McGrath  
Department of Chemistry  
Virginia Polytechnic Inst.  
Blacksburg, VA 24061

Dr. James A. Moore  
Department of Chemistry  
Rensselaer Polytechnic Inst.  
Troy, NY 12180-3590

Dr. Bruce M. Novak  
Department of Chemistry  
University of California  
Berkeley, CA 94720

Dr. Virgil Percec  
Dept. of Macromolecular Sci.  
Case Western Reserve Univ.  
Cleveland, OH 44106-2699

Dr. Dietmar Seifert  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, MA 02139

Dr. Richard R. Shrock  
Department of Chemistry, 6-331  
Massachusetts Institute of Technology  
77 Massachusetts Avenue  
Cambridge, MA 02139

Dr. James M. Tour  
Dept. of Chemistry  
Univ. of South Carolina  
Columbia, SC 29208
Dr. David M. Walba
Dept. of Chem. & Biochem.
Univ. of Colorado
Boulder, CO 80309

Dr. Robert West
Department of Chemistry
University of Wisconsin-Madison
Madison WI 53706

Dr. Michael E. Wright
Department of Chemistry
Utah State University
Logan, UT 84322