Synthesis of Alkyl and Aryl Phosphazene High Polymers

New elastomers have been synthesized that contain a polyphosphazene chain and both alkyl and alkoxy side groups. In addition, new classes of polyphosphazenes have been developed that are high refractive index glasses or have second order nonlinear optical activity.
SUMMARY OF WORK PERFORMED

During the past three years, the following progress has been made through the work of Gayanne Schrubbe-McDonnell (former graduate student, now at the du Pont Marshall Laboratories), Michael N. Mang (former graduate student, now at the Dow Laboratories in Midland, Michigan), Alexa A. Dembek (graduate research assistant), Michael L. Turner and Ian Manners (postdoctoral fellows), and Masood Parvez (postdoctoral staff crystallographer). James L. Desorcie, whose name appears on some of the publications, is a former student who graduated before the start of the grant period.

(1) New high performance elastomers have been synthesized by the polymerization of cyclic phosphazenes that bear organic side groups and halogen atoms, followed by replacement of the halogen atoms by trifluoroethoxy groups. These polymers are alternatives to the fluorophosphazene elastomers currently used in military technology and biomedicine.

(2) Detailed studies have been made of the reasons why some cyclic organophosphazenes polymerize when heated and why others do not. A new polymerization mechanism has been postulated that explains ring-ring oligomer equilibrations when all or most of the side groups are organic units, but allows polymerization when most of the side groups are halogen atoms. This work is important because of its relationship to the elastomer syntheses mentioned in item (1).

(3) Work has continued on the development of synthesis methods for the preparation of polyphosphazenes with biphenyl and related side groups linked to the phosphazene chain. A total of 42 different polymers in this series were synthesized and their solid state properties investigated. The main problem was to design and prepare polymers with two or more different side groups (to prevent crystallization and ensure transparency), while at the same time obtaining a maximum loading of pi-electron units in the side groups (to maximize the refractive index). Twenty-nine of the polymers proved to be non-crystalline. The refractive indexes ($\lambda$ 632 nm) were as high as 1.686. These polymers are candidates for a number of optical engineering applications, including optical waveguides and tough, lightweight lenses.

(4) As an adjunct to the above project, a series of cyclic trimeric and tetrameric phosphazenes have been synthesized with biphenyl and related side groups, and the molecular structures have been solved by X-ray crystallography. The purpose of this work was to study side group packing and stacking in these small-molecule model compounds and to use that information to predict circumstances under which crystalline or amorphous structures might be found in the analogous high polymers.

(5) The concept of stacking and the alignment of aromatic side groups in a polyphosphazene has been extended to include systems with side groups that are capable of second-order nonlinear optical behavior. Specifically, side chains that contain an electron-donor and acceptor separated by conjugated
units such as \(-\text{C}_6\text{H}_4-(\text{C}==\text{C})_x-\text{C}_6\text{H}_4-\) have been linked to phosphazene ring systems and high polymers via flexible oligoethyleneoxy spacer groups. Films of the polymers have been poled and their second-order NLO activity measured. For species with \(-\text{C}_6\text{H}_4-(\text{C}==\text{C})_x-\text{C}_6\text{H}_4\text{NO}_2\) units the \(d_{33}\) coefficients were near 5 pm/V. (Values above 30 pm/V have been found for related aromatic azo units.) Rapid relaxation of the side groups following cessation of poling, and locking the side groups into poled orientation, is a major challenge for future work.

PUBLICATIONS RESULTING FROM THIS WORK

Report #45

An Overview of the Current Status of Polyphosphazene Chemistry
Harry R. Allcock
Polymer Preprints 1987, 28, 437.

Report #46

The Current Status of Polyphosphazene Chemistry
Harry R. Allcock

Report #47

Alkylation of Cyclic and High Polymeric Phosphazenes via Reactions Between Aluminum Alkyls and Aminophosphazenes
Harry R. Allcock, James L. Desorcie, and J. Steven Rutt


Report #48

Reactions of Inorganic High Polymers as a Route to Tailored Solids
Harry R. Allcock

Report #49

Organometallic and Bioactive Cyclophosphazenes, and the Relationship to Inorganic Macromolecules
Harry R. Allcock
Report #50

Poly(aryloxyphosphazenes) with Phenylphenoxy and Related Bulky Side Groups. Synthesis, Thermal Transition Behavior, and Optical Properties
Harry R. Allcock, Michael N. Mang, Alexa A. Dembek, and Kenneth K. Wynne

End-of-year report covering the period June 1, 1988 - June 1, 1989.

Report #51

Chemical Synthesis at the Boundary Between Polymer Chemistry and Inorganic Materials
Harry R. Allcock
The Chemist, January 1990, 10-16.

Report #52

Synthesis of New Polyphosphazene Elastomers
Harry R. Allcock, Gayann Schrubbe-McDonnell, and James L. Desorcie

Report #53

A Second-Order Nonlinear Optical Poly(organophosphazene)
Alexa A. Dembek, Chulhee Kim, and Harry R. Allcock (Penn State)
Robert L. S. Devine, William H. Steier (U. Southern California)
Charles W. Spangler (Northern Illinois University)

Report #54

Ring-Expansion and Equilibration in Organophosphazenes, and the Relationship to Polymerization
Harry R. Allcock, Gayann Schrubbe-McDonnell, and James L. Desorcie
Inorganic Chemistry 1990, 29, 3839-3844.

Report #55

End-of-year report covering the period June 1, 189 - May 31, 1990
Second-Order Nonlinear Optical Poly(organophosphazenes)
Alexa A. Dembek, Harry R. Allcock, Chulhee Kim (PSU), William H. Steier,
Yongqiang Shi, William H. Steier (USC), and Charles W. Spangler (NIU).
ACS Symp. Ser. (in press).

Second-Order Nonlinear Optical Poly(organophosphazenes): Synthesis and
Nonlinear Optical Characterization
Harry R. Allcock, Alexa A. Dembek, Chulhee Kim (PSU), Robert L. S. Devine,
Yongqiang Shi, William H. Steier (USC), and Charles W. Spangler (NIU).
Macromolecules (in press).

Synthesis and Structure of Cyclic and Short Chain Linear Phosphazenes
Bearing the 4-Phenylphenoxy Side Group.
Harry R. Allcock, Dennis Ngo, Masood Parvez, Robert Whittle, and William J.
Birdsall (Albright College).
J. Am. Chem. Soc. (in press)
<table>
<thead>
<tr>
<th>Office of Naval Research</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry Division, Code 1113</td>
<td></td>
</tr>
<tr>
<td>800 North Quincy Street</td>
<td></td>
</tr>
<tr>
<td>Arlington, Virginia 22217-5000</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Commanding Officer</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naval Weapons Support Center</td>
<td></td>
</tr>
<tr>
<td>Dr. Bernard E. Douda</td>
<td></td>
</tr>
<tr>
<td>Crane, Indiana 47522-5050</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dr. Richard W. Drisko</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naval Civil Engineering Laboratory</td>
<td></td>
</tr>
<tr>
<td>Code L52</td>
<td></td>
</tr>
<tr>
<td>Port Hueneme, CA 93043</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>David Taylor Research Center</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dr. Eugene C. Fischer</td>
<td></td>
</tr>
<tr>
<td>Annapolis, MD 21402-5067</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dr. James S. Murday</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry Division, Code 6100</td>
<td></td>
</tr>
<tr>
<td>Naval Research Laboratory</td>
<td></td>
</tr>
<tr>
<td>Washington, D.C. 20375-5000</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Defense Technical Information Center</th>
</tr>
</thead>
<tbody>
<tr>
<td>Building 5, Cameron Station</td>
</tr>
<tr>
<td>Alexandria, VA 22314</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dr. Robert Green, Director</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry Division, Code 385</td>
<td></td>
</tr>
<tr>
<td>Naval Weapons Center</td>
<td></td>
</tr>
<tr>
<td>China Lake, CA 93555-6001</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chief of Naval Research</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Special Assistant for Marine Corps Matters</td>
<td></td>
</tr>
<tr>
<td>Code 00MC</td>
<td></td>
</tr>
<tr>
<td>800 North Quincy Street</td>
<td></td>
</tr>
<tr>
<td>Arlington, VA 22217-5000</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dr. Bernadette Eichinger</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naval Ship Systems Engineering Station</td>
<td></td>
</tr>
<tr>
<td>Code 053</td>
<td></td>
</tr>
<tr>
<td>Philadelphia Naval Base</td>
<td></td>
</tr>
<tr>
<td>Philadelphia, PA 19112</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dr. Sachio Yamamoto</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naval Ocean Systems Center</td>
<td></td>
</tr>
<tr>
<td>Code 52</td>
<td></td>
</tr>
<tr>
<td>San Diego, CA 92152-5000</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dr. Harold H. Singerman</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>David Taylor Research Center</td>
<td></td>
</tr>
<tr>
<td>Code 283</td>
<td></td>
</tr>
<tr>
<td>Annapolis, MD 21402-5067</td>
<td></td>
</tr>
</tbody>
</table>
Dr. Harry R. Allcock  
Department of Chemistry  
Pennsylvania State Univ.  
University Park, PA 16802

Dr. E. Fischer  
DTNSRDC Code 2853  
Annapolis, MD 21402

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

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

Dr. J. M. Augl  
Naval Surface Weapons Center  
White Oak, MD 20910

Dr. Henry K. Hall  
Department of Chemistry  
University of Arizona  
Tucson, AZ 85721

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

Dr. T. J. Reinhart, Jr.  
Nonmetallic Materials Div.  
AF Materials Lab. (AFSC)  
Wright-Patterson AFB, OH 45433

Dr. Len J. Buckley  
Naval Air Development Center  
Code 6063  
Warminster, PA 18974

Dr. Richard M. Laine  
Washington Technology Center  
University of Washington  
Seattle, WA 98195

Dr. Ivan Caplan  
DTNSRDC Annapolis  
Code 0125  
Annapolis, MD 21401

Dr. Robert W. Lenz  
Polymer Sci. and Eng. Dept.  
University of Massachusetts  
Amherst, MA 01002
Dr. Krzysztof Matyjaszewski
Department of Chemistry
Carnegie-Mellon University
Pittsburgh, PA 15213

Dr. Dietmar Seyferth
Department of Chemistry
Massachusetts Inst. of Techn.
Cambridge, MA 02139

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

Dr. L. E. Sloter
Code Air 931-A
Naval Air Systems Command
Washington, D. C. 20361-9310

Dr. William B. Moniz
Code 6120
Naval Research Laboratory
Washington, DC 20375-5000

Dr. James M. Tour
Dept. of Chemistry
Univ. of South Carolina
Columbia, SC 29208

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

Dr. David M. Walba
Dept. of Chem. & Biochem.
Univ. of Colorado
Boulder, CO 80309

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

Dr. Richard R. Schrock
Department of Chemistry
Massachusetts Inst. of Techn.
Cambridge, MA 02139