**Title:** The Synthesis and Structure of Polyphosphazenes

**Author:** Harry R. Allcock

**Performing Organization:**
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

**Contract or Grant Number:** DAAG29-82-K-0045

**Type of Report & Period Covered:** Final 12/9/81 - 12/8/84

**Distribution Statement:** Approved for public release; distribution unlimited.

**Abstract:** New polyphosphazenes have been designed and synthesized, and the structure of these materials has been investigated.
THE SYNTHESIS AND STRUCTURE OF POLYPHOSPHAZENES

FINAL REPORT

Harry R. Allcock

January 29, 1985

U.S. Army Research Office

Grant Number DAAG-2982-K-0045

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802
Statement of the Problem Studied

Macromolecules (also known as polymers) are very large molecules that are integral components of structural plastics, elastomers, textile fibers, films, and coating materials—all of great importance to both the military and civilian sectors. With the exception of the silicones, virtually all polymers are "organic"-type substances derived either from petrochemicals or directly from living things.

A number of years ago, we discovered an entirely new class of polymers, called polyphosphazenes. These differ from conventional macromolecules because they have a backbone structure composed of inorganic elements in the form of alternating phosphorus and nitrogen atoms, and with two organic groups attached to each phosphorus atom.

These polymers have now been developed technologically in a number of different laboratories, including the Army Materials and Mechanics Laboratory at Watertown, Massachusetts, and by industrial companies.

During the grant period 1981 to 1984, we have sought to advance the knowledge of this field in three ways. First, we have explored the possibility that polyphosphazenes can be synthesized that will optimize film-forming properties. Such films could be of wide use in engineering applications, or as protective barrier materials in a hostile environment. Second, we have pioneered a new chemistry of polyphosphazenes that allows transition metals to be incorporated into the side groups attached to a polyphosphazene chain. Such new materials are of interest for their prospective electroactive properties and as polymer-bound catalysts, perhaps for use in batteries or fuel cells. Finally, we recognized that the design and synthesis of new polymers cannot be undertaken efficiently unless a thorough understanding is available of the reasons why specific molecular structural features give rise to certain properties, such as polymer strength, flexibility, or electrical conductivity. Thus, a critical part of our program has been to obtain molecular structural information for these new polymers and to correlate these data with the observed properties.

Summary of the Most Important Results

Film-forming polyphosphazenes have been developed based on mixed substituent polymers, especially those with both hydrophilic and hydrophobic substituents. The surface hydrophobicity of such polymers has been studied as a function of the side group ratios.

A variety of different synthetic methods have been devised and developed for the linkage of metal-containing groups to a phosphazene skeleton. These include the reactions of lithioferrocene or lithioruthenocene with halogenophosphazenes, the reactions of organometallic anions, such as NaFe(CO)2Cp, Na2Fe2(CO)8, Bu4NCr(CO)3Cp, Bu4NNb(CO)3Cp, and Bu4NW(CO)3Cp. Similar derivatives have been prepared by the reactions of phosphazene anions with organometallic halides. These metallophosphazenes constitute a new class of compounds which, at the high polymeric level, should give rise to unusual electronic, catalytic, or thermal behavior.
Finally, major progress has been made in understanding the relationship between molecular structure and physical properties of polyphosphazenes by the synthesis and X-ray diffraction study of a series of linear short chain analogues of the high polymers. The new structural data can now be applied to the high polymers to explore the reasons for unusual phenomena such as the low glass transition temperatures and the crystallization behavior.

List of Publications (grant # DAAG29-82-K-0045)


The Reaction of Mono- and Dilithioferrocene with Octachlorotetraphosphazene: The Crystal and Molecular Structures of \( \text{N}_4\text{P}_4\text{Cl}_6[(n-\text{C}_5\text{H}_4)\text{Fe}-(n-\text{C}_5\text{H}_5)]_2 \) and \( \text{N}_3\text{P}_3\text{Cl}_4(n-\text{C}_5\text{H}_4)\text{Fe}(n-\text{C}_5\text{H}_5)\text{N}_4\text{P}_4\text{Cl}_7 \), Organometallics 1984, 3, 663-669.

Chromium, Molybdenum, and Tungsten Chlorophosphazenes: Molecular Structures of $\text{N}_3\text{P}_3\text{Cl}_5(\text{Cr(CO)}_3(\text{n-C}_5\text{H}_5))$ and $\text{N}_3\text{P}_3\text{Cl}_4(\text{C}_5\text{H}_5)[\text{Mo(\text{n-C}_5\text{H}_5)}]$, H. R. Allcock, G. H. Riding, and R. R. Whittle, J. Am. Chem. Soc. 1984, 106, 5561-5567.


Progress Reports Sent to ARO (grant # DAAG29-82-K-0045)

Progress Report No. 26 (Period covered by report 7/1/82-12/31/82)
Progress Report No. 27 ("""""" 1/1/83-6/30/83)
Progress Report No. 28 ("""""" 7/1/83-12/31/83)
Progress Report No. 29 ("""""" 1/1/84-6/30/84)
Progress Report No. 30 ("""""" 7/1/84-12/31/84)

Personnel Supported by this Project and Degrees Awarded

<table>
<thead>
<tr>
<th>Name</th>
<th>Capacity</th>
<th>Degree Awarded</th>
</tr>
</thead>
<tbody>
<tr>
<td>H. R. Allcock</td>
<td>Principal Investigator</td>
<td></td>
</tr>
<tr>
<td>G. H. Riding</td>
<td>Postdoctoral Fellow</td>
<td></td>
</tr>
<tr>
<td>R. R. Whittle</td>
<td>Crystallographer</td>
<td></td>
</tr>
<tr>
<td>P. R. Suszko</td>
<td>Graduate Fellow</td>
<td>Ph.D. awarded 1983</td>
</tr>
<tr>
<td>L. J. Wagner</td>
<td>Graduate Fellow</td>
<td>Ph.D. awarded 1984</td>
</tr>
<tr>
<td>N. M. Tollefson</td>
<td>Graduate Fellow</td>
<td>Ph.D. awarded 1983</td>
</tr>
<tr>
<td>D. J. Brennan</td>
<td>Graduate Fellow</td>
<td></td>
</tr>
<tr>
<td>M. Mang</td>
<td>Graduate Fellow</td>
<td></td>
</tr>
<tr>
<td>G. Schrubbe</td>
<td>Graduate Fellow</td>
<td></td>
</tr>
</tbody>
</table>