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13. ABSTRACT (Maximum 200 words)  The aim of this work was the design and synthesis of new polymers for membrane applications. Specific uses are anticipated in high oxygen transmission films with the exclusion of organic liquids or vapors; in membranes for the capture of toxic or radioactive metal ions; and in "smart" membranes where the permeability can be controlled by temperature or pH changes. The new high oxygen transmission membranes synthesized are based on a polyphosphazene platform with both fluoroalkoxy and adamantyl side groups. The metal capture membranes utilize a polyphosphazene backbone and sulfur-containing aliphatic side groups. The "smart" membranes utilize a polyphosphazene backbone and hydrophilic alkoxy-ether side groups or side units with carboxylic acid terminal units. The permeability of these membranes is controlled by lower critical solution temperature (LCST) behavior and by pH changes. In addition, new methods for crosslinking membranes and modifying their surfaces have been developed. The new membranes are of potential utility in protective clothing, toxic waste cleanup, and in advanced protective surface coatings.			
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**THE SYNTHESIS AND STRUCTURE OF POLYPHOSPHAZENES**

**Final Progress Report**

**Harry R. Allcock**

**May 28, 1998**

**U.S. Army Research Office**

**DAAH-04-94-G-0403**

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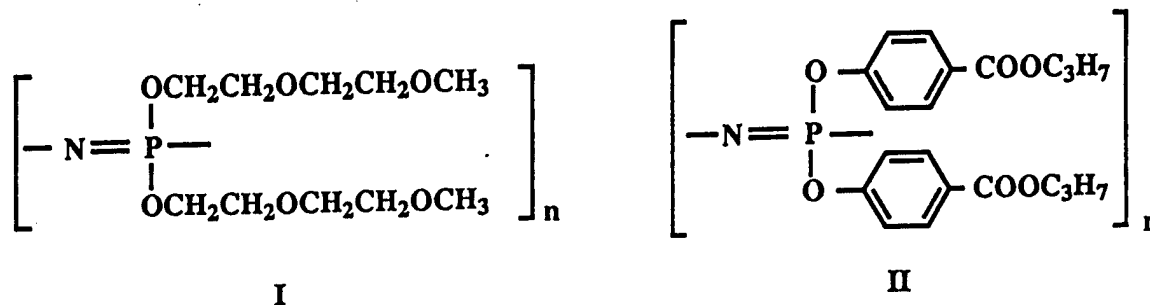
### Statement of the Problem Studied:

The aim of this work was the design and synthesis of new polymers for membrane applications. Specific uses are anticipated in high oxygen transmission films with the exclusion of organic liquids or vapors; in membranes for the capture of toxic or radioactive metal ions; and in "smart" membranes where the permeability can be controlled by temperature or pH changes. The new high oxygen transmission membranes synthesized are based on a polyphosphazene platform with both fluoroalkoxy and adamantyl side groups. The metal capture membranes utilize a polyphosphazene backbone and sulfur-containing aliphatic side groups. The "smart" membranes utilize a polyphosphazene backbone and hydrophilic alkoxy-ether side groups or side units with carboxylic acid terminal units. The permeability of these membranes is controlled by lower critical solution temperature (LCST) behavior and by pH changes. In addition, new methods for crosslinking membranes and modifying their surfaces have been developed. The new membranes are of potential utility in protective clothing, toxic waste cleanup, and in advanced protective surface coatings.

### Summary of the Most Important Results:

The program is based on the use of one of the most versatile polymer systems available--the polyphosphazenes--to generate a range of new properties that are needed for the development of advanced membranes. The underlying principle being used makes use of the unusual method of synthesis developed for these polymers. The process utilizes the high reactivity of poly(dichlorophosphazene) as a starting material for the introduction of different organic side groups by macromolecular chlorine replacement reactions. Different organic side groups generate different combinations of properties, including varying small-molecule permeation rates, the ability to coordinate to metal ions, the capacity to form hydrogels or water-insoluble materials, and surface hydrophobicity or hydrophilicity.

This project was initiated in an earlier phase of ARO support by an exploratory investigation of different ways to selectively remove cations from liquid phase media. The approach used two polyphosphazenes--one water-soluble (I) and the other water-insoluble (II), for the formation of



interpenetrating polymer networks (IPN's) with organic polymers that carried metal coordination sites such as phosphate, sulfonic acid, carboxylic acid, or amine units. Membranes derived from these polymers were characterized by a variety of techniques including electron microscopy and X-ray microanalysis. The IPN's were shown to selectively remove metal ions such as iron, copper, silver, or mercury. In principle, these or similar membranes may be useful for toxic waste cleanup procedures.

In the most recent work, a successful attempt has been made to prepare new membrane materials via the introduction of 2-butenoxy or 4-allylphenylphenoxy groups into polyphosphazenes. These unsaturated side units were then employed (a) as cross-linking sites to stabilize membranes and IPN's, and (b) as reactive units for the linkage of organosilicon side groups. The purpose of this latter approach was to provide a method for the preparation of hybrid polyphosphazene-silicone polymer systems. Silicone polymers are widely valued for their oxygen transmission properties, but suffer from ease of deformability and lack of physical strength. The hybrid polymers are designed to combine the strength of polyphosphazenes with the high oxygen permeability of silicones in systems that could perhaps be used in protective clothing or related devices.

### **Honors:**

Recipient of the American Chemical Society Herman Mark Award in Polymer Chemistry in November 1994 "for his outstanding contributions to polymer chemistry."

Humphrey Memorial Lecturer at the University of Vermont.

McGill University 175th Anniversary Lecturer in Chemistry.

Penn State University Graduate Commencement speaker.

Member of the Board of Directors of the Penn State Materials Research Institute.

Member of the Penn State Organizational Board for the commercialization of polyphosphazenes.

Member of the Advisory Editorial Boards of *Chemistry of Materials*, *Journal of Inorganic and Organometallic Polymers*, *Journal of Polymer Science (Chemistry)*.

Chaired ACS Committee to select the most recent editor of *Macromolecules*.

### **Patents Issued Resulting from ARO-Sponsored Research:**

"Polyphosphazene Blends"

Harry R. Allcock and Karyn B. Visscher

U.S. Patent 5,457,160 (1995), assigned to the Penn State Research Foundation.

"New Polyphosphazenes with Unsaturated Side Groups Useful as Reaction Intermediates, Cross-linkable Polymers, and as Components of Interpenetrating Polymer Networks"

Harry R. Allcock, Karyn B. Visscher, and Young-Baek Kim

U.S. Patent 5,747,604 (1998), assigned to the Penn State Research Foundation.

### **Manuscripts Prepared Under ARO Sponsorship:**

"Molecular Structures of Cyclic Mono- and Diphosphazophosphazenes: Small-Molecule Models for High Polymers"

H. R. Allcock, S. E. Kuharcik, K. B. Visscher, and D. C. Ngo

*J. Chem. Soc. (Dalton)* **1995**, 2785-2795.

"Synthesis and Structure of Small-Molecule Phosphazene Rings that Bear Fused-Ring Aryloxy Side Groups: Models for Optically-Useful High Polymers"

H. R. Allcock, S. Al-Shali, D. C. Ngo, K. B. Visscher, and M. Parvez  
*J. Chem. Soc. (Dalton)* **1995**, 3521-3532.

"Hybrid Phosphazene-Organosilicon Polymers. Part I. Background, Rationale, and Small-Molecule Model Compound Chemistry"

H. R. Allcock and S. E. Kuharcik  
*J. Inorg. and Organometl. Polymers* **1995**, 5, 307-342.

"The Synthesis and Characterization of pH-Sensitive Poly(organophosphazene) Hydrogels"

H. R. Allcock and A. M. A. Ambrosio  
*Biomaterials* **1996**, 17, 2295-2302.

"Lower Critical Solubility Temperature Study of Alkyl-Ether Based Polyphosphazenes"

H. R. Allcock and G. K. Dudley  
*Macromolecules* **1996**, 29, 1313-1319.

"Synthesis and Structure of Adamantane-Containing Phosphazenes"

W. E. Krause, M. Parvez, K. B. Visscher, and H. R. Allcock  
*Inorganic Chemistry* **1996**, 35, 6337-6338

"Hybrid Phosphazene-Organosilicon Polymers. Part II. High Polymer and Materials Synthesis and Properties"

H. R. Allcock and S. E. Kuharcik  
*J. Inorg. and Organometal. Polymers* **1996**, 6, 1-41.

"Synthesis of Polyphosphazenes with Ethyleneoxy-Containing Side Groups: New Solid Electrolyte Materials"

H. R. Allcock, S. E. Kuharcik, C. S. Reed, and M. E. Napierala  
*Macromolecules* **1996**, 29, 3384-3389.

"The Synthesis and Characterization of Amino-organosiloxane-Bearing Polyphosphazenes: New Properties by the Elimination of Hydrogen Bonding"

H. R. Allcock, S. E. Kuharcik, and C. J. Nelson  
*Macromolecules* **1996**, 29, 3686-3693.

"Polyphosphazenes and their Diversity"

H. R. Allcock  
Chapter in *Macromolecular Design of Polymeric Materials*  
(K. Hatada, T. Kitayama, and O. Vogl, eds.)  
Marcel Dekker: New York, **1996**, 477-492.

"Water-Soluble Polymers and their Hydrogels"

H. R. Allcock  
Chapter in *Hydrophilic Polymers* (J. E. Glass, ed.)  
ACS. Symp. Ser. **1996**, 248, 3-29.

"New Polyphosphazenes with Unsaturated Side Groups: Use of Reaction Intermediates, Cross-linkable Polymers, and as Components of Interpenetrating Networks"  
H. R. Allcock, K. B. Visscher, and Y.-B. Kim  
*Macromolecules* **1996**, 29, 2721-2728.

"The Design and Synthesis of New Biomaterials Via Macromolecular Substitution"  
H. R. Allcock  
Chapter in *Bioartificial Organs* (A. Prokop, D. Hunkeler, A. Cherrington, eds.)  
*Annals of the New York Academy of Sciences* **1997**, 831, 13-31.

"Polyphosphazenes with Adamantyl Side Groups"  
H. R. Allcock and W. E. Krause  
*Macromolecules* **1997**, 30, 5683-5687.

"Functional Polyphosphazenes"  
H. R. Allcock  
*ACS Symp. Ser.* (in press)

"The Synthesis of Functional Polyphosphazenes and their Surfaces"  
H. R. Allcock  
*Proc. Symp. Inorg./Organomet. Polymers, Kyoto, Japan, 1997* (in press).

"Synthesis and Reactivity of Methylthio-Containing Poly(organophosphazenes)"  
H. R. Allcock, A. M. Cannon, D. L. Olmeijer, U. Diefenbach  
(manuscript in preparation)

"Gas Transport of Poly(organophosphazene) Blends Containing Trifluoroethoxy and Adamantaneamino Substituents"  
H. R. Allcock, A. M. Cannon, W. E. Krause, and B. Freeman and K. Naagi (NCSU)  
(manuscript in preparation).

"Poly(aryloxyphosphazenes) as Ion-Exchange Membranes"  
(specifically tested as Aqueous Lithium Battery Membranes)  
H. R. Allcock, D. L. Olmeijer, A. M. Cannon, A. M. A. Ambrosio, S. D. Reeves, M. Urquidi-Macdonald, and J. Flores  
(work in progress).

**Scientific Personnel Supported by This Project and Degrees Awarded:**

Harry R. Allcock (principal investigator)  
Karyn B. Visscher (graduate student), Ph.D. (now at DuPont)  
Susan E. Kuharcik (graduate student), Ph.D. (now at DuPont)  
Archel A. Ambrosio (graduate student), Ph.D. (now at Allegheny Hospitals and Drexel University)  
Gary Dudley (graduate student), Ph.D. (now at Mobil Research Labs.)  
Angela Manders Cannon (graduate student)  
Wendy Krause (graduate student)  
Thomas Hartle (graduate student)

**Technology Transfer:**

Lecture to the Chemistry faculty at West Point Military Academy.

Discussions with Dr. Robert Singler at West Point regarding advanced polyphosphazene applications.

Initiation of a new company, "Phosphazene Custom Synthesis," for the production of advanced polymers for the engineering and medical industries. This company was formed following a one-and-a-half year planning process carried out by The Pennsylvania State University in conjunction with industrial and business advisors. The company is now producing polyphosphazene intermediates.

Discussions with Dr. Gary Hagnauer regarding the use of polyphosphazenes in advanced battery applications.

Conversations with Dr. Richard Paur regarding the use of polyphosphazenes in batteries and fuel cells.

Submission of polyphosphazene samples to Dr. Heidi Gibson at the Natick research laboratory for electro-spinning evaluations.