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David Brennan, Beverly Dunn, John Sisko, James Graaskamp, Michael Levin,
Alexa Dembek, Mark Welker, Jeffrey Dodge and William Coggio



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8. PUBLICATIONS

"Quaternized Cyclic and High Polymeric Phosphazenes and their Interactions with Tetracyanoquinodimethane," H. R. Allcock, M. L. Levin, and P. E. Austin, inorg. Chem., 25, 2281 (1986).

"Synthesis of Polyphosphazenes Bearing Covalently-Linked Copper Phthalocyanine Units," H. R. Allcock and T. X. Neenan, Macromolecules, 19, 1495 (1986).

"Synthesis and Molecular Structure of Methylsilane- and Methylsiloxane-Cyclotriphosphazenes," H. R. Allcock, D. J. Brennan, J. M. Graaskamp, and M. Parvez, Organometallics, 5, 2434 (1986).

"Poly(organophosphazenes). Synthesis, Unique Properties, and Applications," H. R. Allcock, Proc. of 5th. Intern. Symp. on Ring-Opening Polymerization, Blois, France, 1986, Makromol. Chem., Macromol. Symp., 6, 101 (1986).

"A Liquid Crystalline Poly(organophosphazene)," C. Kim and H. R. Allcock, Macromolecules, 20, 1726 (1987).

"The Organometallic Chemistry of Phosphazenes," H. R. Allcock, J. L. Desorcie, and G. H. Riding, Polyhedron, 6, 119 (1987).

"Ring-Opening Polymerization of Methylsilane- and Methylsiloxane-Substituted Cyclotriphosphazenes," H. R. Allcock, D. J. Brennan, and J. M. Graaskamp, Macromolecules, 21, 1 (1988).

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"Effects of Organic Side Group Structures on the Properties of Poly(organophosphazenes)," H. R. Allcock, M. S. Connolly, J. T. Suszko, and S. Al-Shali, Macromolecules, **21**, 323 (1988).

"Cyclotriphosphazenes with Geminal Trimethylsilylmethylene and Alkyl- or Aryl Side Groups," H. R. Allcock, D. J. Brennan, B. S. Dunn, and M. Parvez, Inorg. Chem., **27**, 3226 (1988).

"The Current Status of Polyphosphazene Chemistry," H. R. Allcock in Inorganic and Organometallic Polymers, Eds. M. Zeldin, K. J. Wynne, and H. R. Allcock, ACS. Symp. Ser. **360**, 1988, Chapter 19.

"Organosilicon Derivatives of Cyclic and High Polymeric Phosphazenes," H. R. Allcock and D. J. Brennan, J. Organomet. Chem., **341**, 231 (1988).

"Reactions of Inorganic High Polymers as a Route to Tailored Solids," H. R. Allcock, Proc. of 11th Intern. Symp. on Reactive Solids, Princeton, 1988, Solid State Ionics (in press).

"Polyphosphazenes and their Relationship to Ceramics and Metals," H. R. Allcock in Ultra Structure Processing of Advanced Materials, Eds. J. D. Mackenzie and D. R. Ulrich, John Wiley & Sons: New York, 1988, Chapter 53.

"Synthesis of Polyphosphazenes Bearing Geminal Trimethylsilylmethylene and Alkyl- or Phenyl Side Groups," H. R. Allcock, D. J. Brennan, and B. S. Dunn, Macromolecules (in press).

"Organometallic and Bioactive Cyclophosphazenes, and the Relationship to Inorganic Macromolecules," H. R. Allcock, Chapter in Phosphorus, Sulfur, and Related Elements, Proc. of Intern. Symp. on Inorg. Ring Systems, Amherst, Mass., 1988 (in press).

"Liquid Crystalline Phosphazenes--High Polymeric and Cyclic Trimeric Systems with Aromatic Azo Side Groups," H. R. Allcock and C. Kim, Macromolecules (in press).

"Organosilylphosphazene Oligomers and Polymers: Synthesis Via Lithioaryloxy-phosphazenes," H. R. Allcock, W. D. Coggio, R. S. Archibald, and D. J. Brennan, Macromolecules (in press).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this program was to develop new chemical synthesis methods for advanced polymers. The new polymers were to be hybrids at the molecular level of inorganic and organic materials. Attention was focused on polymers with an inorganic backbone of alternating phosphorus and nitrogen atoms (polyphosphazenes) that bore two organic side units on each phosphorus.

First, a major component of the project was to find synthetic methods that would allow the preparation of polymers with a polyphosphazene backbone and organosilicon side groups. This was accomplished by the development of reactions between cyclic six-membered ring phosphazenes and organosilyl organometallic reagents. The main pathway studied involved

phosphazenes and organosilyl organometallic reagents. The main pathway studied involved the reactions of chlorocyclophosphazenes with organosilyl Grignard reagents to replace one or more chlorine atoms by the organosilicon units. These derivative cyclic phosphazenes were then polymerized by a ring-opening process to yield high polymers bearing both organosilicon and unreacted chloro-side groups. The remaining chlorine atoms were then replaced by organic units using a macromolecular substitution reaction. The final polymers were stable, low-temperature elastomers with surface and bulk properties that were characteristic of both phosphazene elastomers and silicones.

The second aspect involved an exploration of ways in which the synthetic opportunities available for polyphosphazenes would allow the linkage of rigid, "stackable" organic and inorganic side groups to the flexible inorganic chain. The objective was to determine if the ordering of the side groups would allow the development of materials properties, such as electrical conductivity, liquid crystallinity, or high strength. Three classes of stackable side groups were used--copper phthalocyanine units, tetracyanoquinodimethane, and aromatic azo groups. The second system generated semiconductive materials. The third side group yielded liquid crystalline materials, provided a flexible spacer group was present to allow decoupling of the mesogenic side group motions from those of the main chain.

Finally, other side groups were examined as possible pyrolytic crosslink sites for the conversion of a flexible, formable polymer into an ultrastructure amorphous ceramic. Amino side groups fulfill this function. Controlled pyrolysis has yielded a number of ultrastructure products, some of which approach phosphorus nitride in composition.

AFOSR Program Manager: Dr. Anthony J. Matuszko

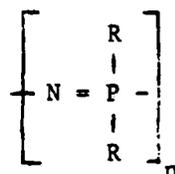
FINAL TECHNICAL REPORT

Background and Objectives

One of the most active areas of scientific research is the use of synthetic chemistry to produce new materials, such as polymers, ceramics, and synthetic metals or semiconductors. Our research program represents an attempt to advance this principle one step further, by the design and synthesis of new types of materials that combine the attributes of polymers, ceramics, and metals. A further objective was to design a system that would allow individual properties to be tailored in such a way that small changes in the synthetic procedure would bias the properties toward those of organic polymers, ceramics, or metals.

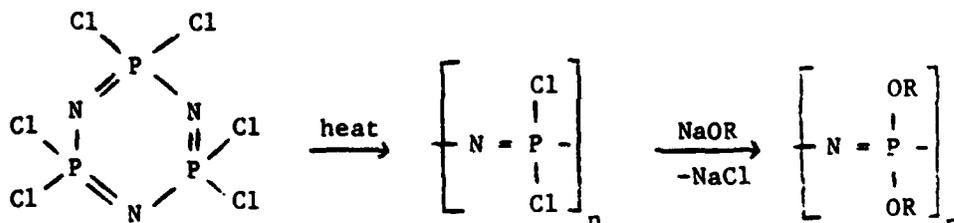
In order to do this, we have developed a synthesis route to linear polymers that contain inorganic elements in the backbone and a variety of organic and organometallic side groups attached to that backbone. This design provides the flexibility, toughness, and fabricability that is the main characteristic of linear polymers, with the "inorganic" properties of thermo-oxidative stability that is typical of most ceramics and metalloids. Variations in the side groups then confer specific properties on the system, such as hydrophobicity, electroactivity, or liquid crystallinity.

The polymer system used as a starting point is based on a backbone of alternating phosphorus and nitrogen atoms, with two side groups (R) attached to each phosphorus (1). These polymers are called polyphosphazenes.



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Polymers of this type are generally prepared by a two-step process, starting from a small-molecule cyclic phosphazene, such as 2.



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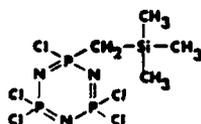
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Heating of 2 leads to polymerization to high polymer 3, which then functions as a macromolecular intermediate for substitution reactions to give stable, unreactive polymers, 4. As will be demonstrated, species that are derivatives of 2, but with several of the chlorine atoms replaced by organic or organometallic groups, also polymerize when heated. This provides a second method for the variation of the side group in the final derivative polymer.

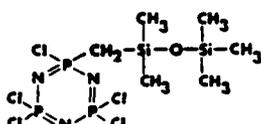
In the work just completed, three aspects of this chemistry have been explored. First, methods have been developed for the introduction of organosilicon side groups into the polymer, with the objective of preparing elastomers that are hybrids of polyphosphazenes and silicones. Second, by variations in the general synthesis process shown above, rigid, stackable side groups have been incorporated into the macromolecular structure. These polymers are designed to show hybrid materials properties such as electrical conductivity with polymer processability, or liquid crystallinity. Finally, attempts have been made to move a step beyond the use of side group packing to create solid state properties, and instead to generate ceramic-type ultrastructures by forming covalent crosslinks.

Polyphosphazenes with Organosilicon Side Groups

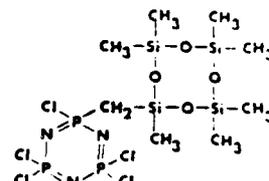
The details of this work will be found in papers 3, 7, 9, 11, 14, and 17 in the appended publication list. In summary, the following advances have been made. First, the reactions of organosilyl- and organosiloxy Grignard reagents with hexachlorocyclotriphosphazene (2) have yielded the organosilylphosphazenes shown as 5-13.



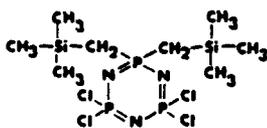
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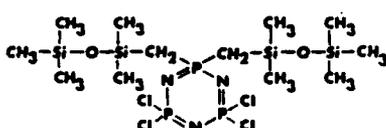
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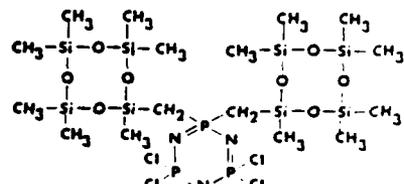
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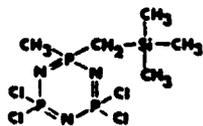
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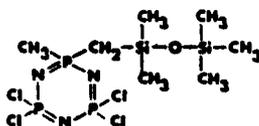
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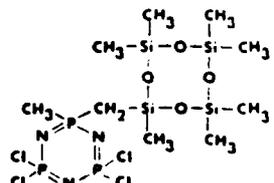
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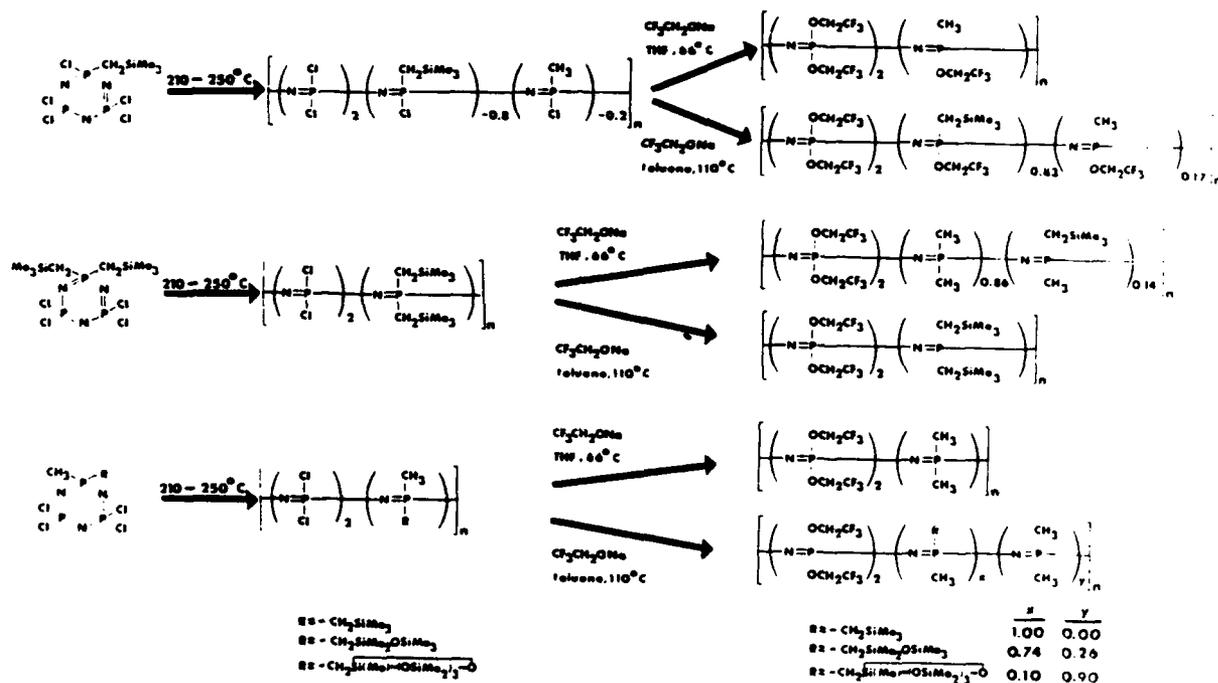


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Five of these compounds (5-8 and 11-13) polymerized when heated at 210°-250°C. The polymers formed by this process were then subjected to chlorine replacement reactions using sodium trifluoroethoxide to yield stable derivative macromolecules (Scheme 1).



Scheme 1

When toluene was used as a solvent, the organosilicon group survived as a side group. However, in tetrahydrofuran, carbon-silicon bond cleavage occurred to yield a methyl group in place of the organosilicon unit. Thus, by changing the reaction conditions, the structure of the product polymer can be modified.

The organosilicon-substituted polymers were elastomers with low glass transition temperatures (-63 to -40°C). The surface character was extremely hydrophobic. The gas transport properties of these polymers are currently being studied.

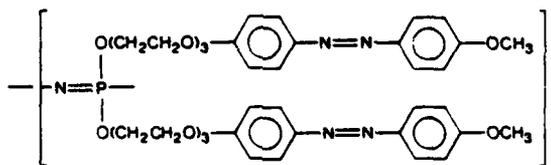
Similar polymers were prepared with unbranched alkyl groups geminal to a trimethylsilylmethylene group. The cyclic trimers required for these studies were prepared via a variety of organometallic pathways. All the macromolecular substitution work was preceded by model compound studies at the cyclic trimer level.

Polyphosphazenes with Stacking Side Groups

Certain flat molecules form stacks within a crystalline lattice. The stacked arrays generate properties that are characteristic of the lattice rather than of the molecules themselves. These properties range from structural rigidity to electrical conductivity. However, as single crystals such materials lack strength or flexibility. Hence, the attachment of such molecules to a flexible polymer chain may generate both the special properties of the stacked lattice and the strength, flexibility, and fabricability of the polymer. We have synthesized four different types of polyphosphazenes to test this idea.

First, a range of polymers has been synthesized with a polyphosphazene chain and various aryl side groups (paper 8). Some of these are shown in Table I. The single substituent aryl-substituted polymers were microcrystalline but not liquid crystalline. The mixed substituent polymers were neither microcrystalline nor liquid crystalline. It was clear that a specific combination of mesogen structure and spacer group length and flexibility would be needed to generate liquid crystalline character. To that end, a study was made of the effect of various alkoxy and alkoxy-ether side chains on the glass transition temperatures of the polyphosphazenes. It was found that alkoxy groups with 3-6 carbon chains, and alkoxy ether units with 2 to 3 ethyleneoxy chains provided the lowest glass transition temperatures, and possibly the greatest degree of side group decoupling from the motions of the main chain.

Thus, polymer 14 was then synthesized and its thermal transition behavior studied (papers 5 and 16). Polymer 14 shows typical microcrystalline behavior below 118°C,

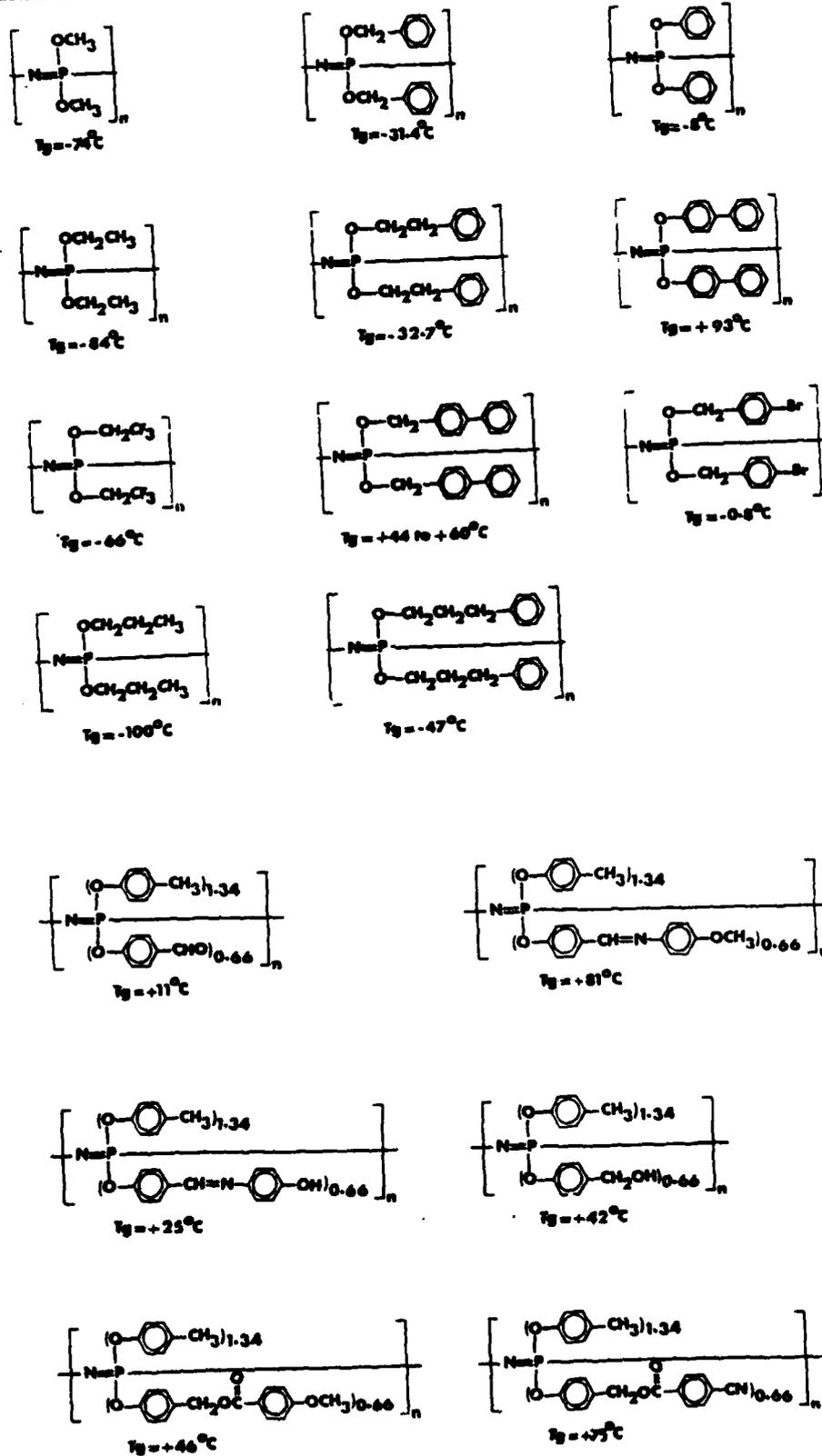


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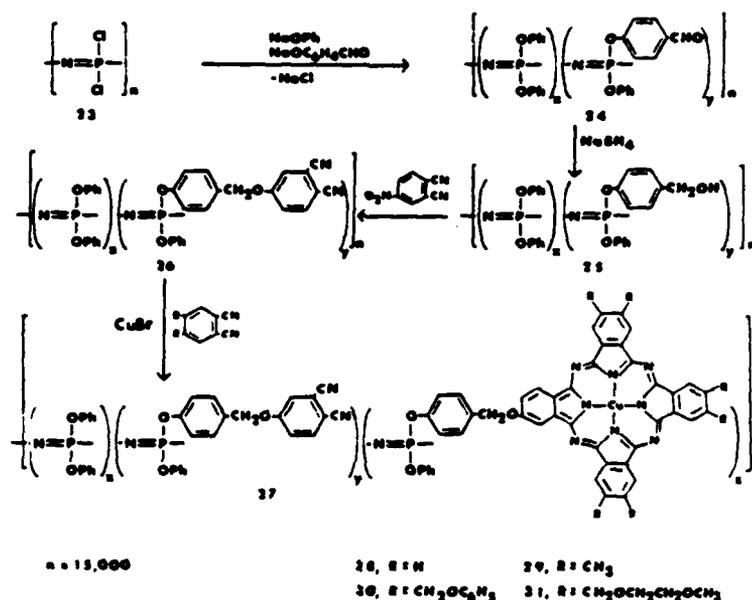
but is liquid crystalline between this temperature and 127°C. Further changes in macromolecular structure are being explored to widen the temperature range of the mesophase.

The third approach initiated was to bind tetracyanoquinodimethane (TCNQ) to a polyphosphazene skeleton by two methods (paper 1). Quaternization of an amino-phosphazene backbone, followed by treatment with lithium TCNQ, allowed TCNQ units to be ionically bound to the phosphazene. Alternatively, polyphosphazenes were synthesized with quaternizable amino or phosphino units at the ends of the side chains. These were then used as sites for ion exchange and binding of TCNQ units. The electrical behavior of these polymers varied with the loading of charged TCNQ groups and excess neutral TCNQ as dopant. A drawback of this system was that the conductivity increased with TCNQ loading, but the flexibility of the polymer decreased at the same time. Nevertheless, this approach does provide a method for preparing polyphosphazenes with a low but tunable conductivity.

Table I
 Variation in Glass Transition Temperature (T_g) with Polyphosphazene Side Group Structure



The fourth exploration within this concept involved an attempt to attach copper phthalocyanine units to a polyphosphazene chain (paper 2). Metal and metalloid phthalocyanines are well known for their ability to stack in a crystalline system, and for their ability when doped with iodine to function as good electrical conductors. The chemistry used for the linkage of the copper phthalocyanine groups to the polymer is illustrated in Scheme 2.



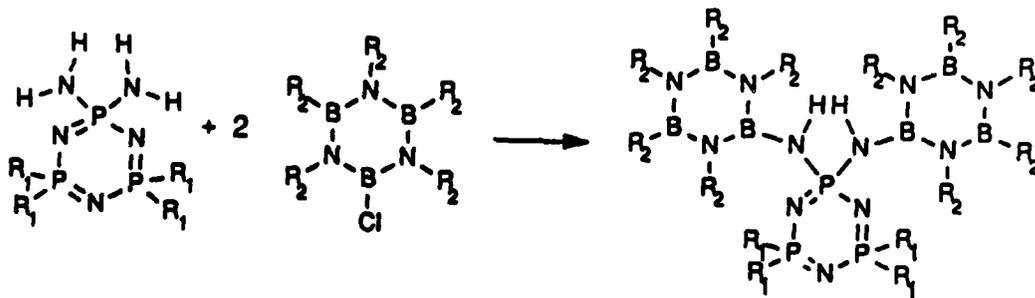
Scheme 2

Evidence for aggregation of the phthalocyanine units in the polymer was sought from electronic spectra and from conductivity measurements, as well as from electrochemical measurements in solution. At a level of 1 phthalocyanine per 25 repeating units, no evidence for aggregation was found. At higher loadings (1 phthalocyanine per 6-12 repeating units), agglomeration was evident, but it resulted in insolubility of the polymer and in the formation of brittle materials. Further development of this class of materials will require the use of a cosubstituent group that confers greater solubility and flexibility on the polymer. Based on the liquid crystalline studies, alkoxy or aryloxy ether side groups and spacer groups would be appropriate.

Polymeric Precursors to Ceramics

We have taken two approaches to the synthesis of preceramic phosphazenes. The first involved the synthesis of poly(aminophosphazenes) which, on pyrolysis would eliminate amines to form crosslinked ultrastructures. The polymer $[\text{NP}(\text{NHC}_3\text{H}_7)_2]_n$ was our prototype for the initial studies. Pyrolysis and loss of propylamine and other amines, led to the formation of species that approximated in composition to $\alpha\text{-P}_3\text{N}_5$. These were found both as domains within a graphitic matrix and as products formed by vapor deposition of volatile intermediates generated by the pyrolysis process. This product was exceedingly hard and had many ceramic-type properties. This project is being continued.

The second approach involved the linkage of borazine rings to phosphazene rings or chains. At the fundamental level, we have isolated the first borazine-cyclophosphazene hybrid compound. It has the structure shown in **15** where $\text{R}_1 = \text{NMe}_2$ and $\text{R}_2 = \text{Me}$. Similar chemistry is now being developed at the phosphazene high polymer level.



PUBLICATIONS

- (1) "Quaternized Cyclic and High Polymeric Phosphazenes and their Interactions with Tetracyanoquinodimethane," H. R. Allcock, M. L. Levin, and P. E. Austin, Inorg. Chem., **25**, 2281 (1986).
- (2) "Synthesis of Polyphosphazenes Bearing Covalently-Linked Copper Phthalocyanine Units," H. R. Allcock and T. X. Neenan, Macromolecules, **19**, 1495 (1986).
- (3) "Synthesis and Molecular Structure of Methylsilane- and Methylsiloxane-Cyclotriphosphazenes," H. R. Allcock, D. J. Brennan, J. M. Graaskamp, and M. Parvez, Organometallics, **5**, 2434 (1986).
- (4) "Poly(organophosphazenes). Synthesis, Unique Properties, and Applications," H. R. Allcock, Proc. of 5th. Intern. Symp. on Ring-Opening Polymerization, Blois, France, 1986, Makromol. Chem., Macromol. Symp., **6**, 101 (1986).
- (5) "A Liquid Crystalline Poly(organophosphazene)," C. Kim and H. R. Allcock, Macromolecules, **20**, 1726 (1987).
- (6) "The Organometallic Chemistry of Phosphazenes," H. R. Allcock, J. L. Desorcie, and G. H. Riding, Polyhedron, **6**, 119 (1987).
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- (8) "Effects of Organic Side Group Structures on the Properties of Poly(organophosphazenes)," H. R. Allcock, M. S. Connolly, J. T. Suszko, and S. Al-Shali, Macromolecules, **21**, 323 (1988).
- (9) "Cyclotriphosphazenes with Geminal Trimethylsilylmethylene and Alkyl- or Aryl Side Groups," H. R. Allcock, D. J. Brennan, B. S. Dunn, and M. Parvez, Inorg. Chem., **27**, 3226 (1988).
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- (11) "Organosilicon Derivatives of Cyclic and High Polymeric Phosphazenes," H. R. Allcock and D. J. Brennan, J. Organomet. Chem., **341**, 231 (1988).
- (12) "Reactions of Inorganic High Polymers as a Route to Tailored Solids," H. R. Allcock, Proc. of 11th Intern. Symp. on Reactive Solids, Princeton, 1988, Solid State Ionics (in press).
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- (14) "Synthesis of Polyphosphazenes Bearing Geminal Trimethylsilylmethylene and Alkyl- or Phenyl Side Groups," H. R. Allcock, D. J. Brennan, and B. S. Dunn, Macromolecules (in press).
- (15) "Organometallic and Bioactive Cyclophosphazenes, and the Relationship to Inorganic Macromolecules," H. R. Allcock, Chapter in Phosphorus, Sulfur, and Related Elements, Proc. of Intern. Symp. on Inorg. Ring Systems, Amherst, Mass., 1988 (in press).
- (16) "Liquid Crystalline Phosphazenes--High Polymeric and Cyclic Trimeric Systems with Aromatic Azo Side Groups," H. R. Allcock and C. Kim, Macromolecules (in press).
- (17) "Organosilylphosphazene Oligomers and Polymers: Synthesis Via Lithioaryloxyphosphazenes," H. R. Allcock, W. D. Coggio, R. S. Archibald, and D. J. Brennan, Macromolecules (in press).