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REACTIONS OF INORGANIC HIGH POLYMERS AS A
ROUTE TO TAILORED SOLIDS

by

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Reactions of Inorganic High Polymers as a Route to Tailored Solids

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Abstract

A new class of reactive inorganic polymers--the polyphosphazenes--can be used as macromolecular intermediates for the synthesis of a wide range of inorganic-organic solids. By reactions that change the polymer side groups, it is possible to bias the properties toward elastomers or microcrystalline polymers, liquid crystalline materials, bioerodable solids, solids with bioactive surfaces, solid electrolytes, semi-conductors, or ultrastructures.

1. Purpose and Rationale

Linear macromolecules provide both an intellectual and a synthetic starting point for the development of new solid state systems. First, a study of the interactions between independent macromolecules in the solid state allows an understanding of the way in which van der Waals, polar, or ionic forces affect the physical properties of the bulk material. Second, the joining of macromolecules through covalent crosslinks provides a method for a progressive change of solid state properties from those of loosely associated molecules toward those of amorphous ultrastructure ceramics. And third, for both uncrosslinked and crosslinked polymers, changes in the composition and geometry of the

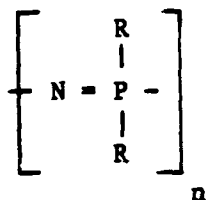
backbone and side groups bring about profound changes in the solid state properties.

Most of the known polymer-based solids are derived from organic polymers, synthesized from petrochemical monomers. Although some similarities can be detected between organic polymeric solids and totally inorganic materials, such as ceramics or metalloid semiconductors, in general a broad gap in properties exists between the totally organic and the completely inorganic solid systems. The thermooxidative instability of most carbon-based solids provides one example of the differences.

An objective of our work has been the synthesis of new macromolecules that possess a backbone of inorganic elements, flanked by side groups that have either organic or inorganic character. Such polymers occupy a zone of structures and properties between those of classical organic polymers and those of inorganic solids. The method of inorganic-organic polymer synthesis employed in this work allows the side groups to be varied over a wide range of structures. By changing the side groups, the solid state properties can be biased either toward those typical of organic polymers (elastomers, microcrystalline polymers, liquid crystalline solids) or toward those of totally inorganic solids, such as amorphous ceramics, solid electrolytes, semiconductors, or metals.

2. Synthetic Method

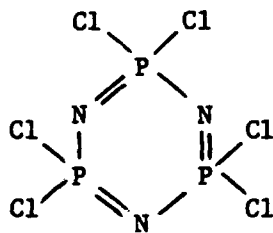
The polymers discussed here are called polyphosphazenes. They have the general molecular structure shown in 1, where n , the degree of



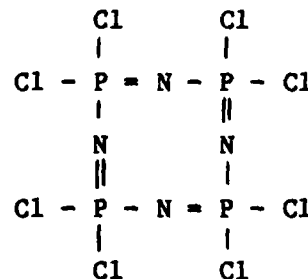
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polymerization, can be as high as 15,000-20,000, and the side groups, R, can comprise a wide variety of different organic, organometallic, or inorganic units. Depending on the experimental conditions, the inorganic backbone may be essentially linear, or highly branched.

The synthetic pathway starts from phosphate rock and atmospheric nitrogen. Phosphate rock is converted first to elemental phosphorus and thence to phosphorus pentachloride. Nitrogen is converted to ammonia and subsequently to ammonium chloride. Phosphorus pentachloride and ammonium chloride are then allowed to react in a chlorinated organic solvent to yield the two products shown as 2 and 3. Both materials are available commercially.



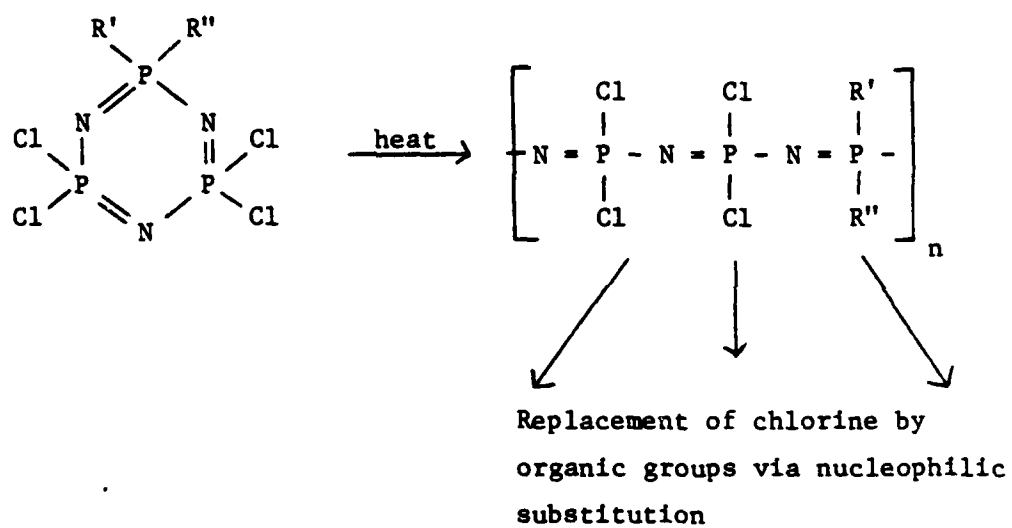
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Scheme II

Initially, conditions were found that allowed 2 or 3 to be polymerized thermally to a linear, uncrosslinked, high polymer (4).²⁻⁴ Polymer 4, a rubbery elastomer in the solid state, is highly reactive toward reagents that will cleave phosphorus-chlorine bonds. Thus, 4 functions as a macromolecular reaction intermediate for the replacement of all the chlorine atoms along each chain by organic, organometallic, or inorganic side groups. In nearly every case, the replacement of chlorine by an organic unit yields a polymer that is very stable in the atmosphere and often stable at elevated temperatures.

The physical and chemical properties depend on the side groups introduced.²⁻¹⁰ In addition, two or more different types of side groups can be incorporated, and this further widens the property variations that can be generated. The overall synthesis pathway is summarized in Scheme I. Further variations are possible by the polymerization of organo-substituted cyclic trimers or tetramers, and this option is illustrated in Scheme II.

Schemes I and II

The main advantage of this synthesis route for the preparation of new solids is as follows. Because the side group structure determines the solid state character and, because the side groups can be changed so readily by logical variations in chemical reagents used in the synthesis, both subtle and gross changes in properties can be generated. This provides an excellent tool for the study of structure-property relationships and for the design of improved materials. The following examples illustrate the manner in which different side groups affect the

bulk properties of polyphosphazene solids, and how the reactivity of the surfaces can be used to modify the biological activity of the material.

3. Effect of Different Side Groups on Bulk Properties and Materials Chemistry

3.1 Elastomeric solids and microcrystalline materials and glasses.

The linear polyphosphazene backbone has an inherent flexibility that results from a low barrier to torsion of the -P-N-backbone bonds. Provided the side groups attached to the phosphorus are small in size or are themselves flexible, these molecular characteristics give rise to elastomeric solid state properties.¹¹ Random mixed substitution that destroys molecular symmetry also favors elasticity by preventing the growth of microcrystalline domains.^{6,7,11,12} Polyphosphazene elastomers that bear alkyl ether side groups function as solid coordinative "solvents" for salts such as lithium triflate.¹³ Such systems are currently under investigation for use in lightweight rechargeable batteries.

However, increases in the size and rigidity of the side groups retards macromolecular reorientation and favors microcrystallization. Polyphosphazenes such as these (for example, those with OCH_2CF_3 or OC_6H_5 side groups) superficially resemble organic microcrystalline polymers, such as polyethylene, in appearance, but are more resistant to photolysis or oxidation.^{1,2} Flat, "stackable" side groups, such as those bearing metal phthalocyanines,¹³ impose additional ordered character which, in some cases, can be utilized to generate weak electrical semi-conductivity. Aromatic azo side groups linked to the chain via flexible spacer groups yield liquid crystalline materials.^{15,16}

Species that combine some of the properties of polymers and metals have also been synthesized. Examples include polyphosphazenes with transition metals bonded directly to the backbone,¹⁷ and others with ferrocene and/or ruthenocene units that function as side groups.¹⁸ Species such as these are of interest as polymeric electrode mediator solids.¹⁹

3.2 Surface reactivity. The surface character of a solid is an important factor that determines its suitability for many technological and biomedical applications. Use of the macromolecular substitution route (Scheme I) provides the primary means for modification of surface hydrophilicity or hydrophobicity. For example, fluoroalkoxy side groups generate hydrophobic surface character, whereas, methylamino,²⁰ glucosyl,²¹ or glyceryl²² side groups generate hydrophilicity.

However, a secondary method of surface-tailoring involves the reactions of side groups that lie at the surface of the solid. For example, the aryloxyphosphazene polymer $[NP(OC_6H_5)_2]_n$ undergoes surface nitration. The aryl nitro units formed then serve as sites for further surface chemistry. For example, subsequent conversion of the nitro groups to amino units has provided sites for the covalent binding of enzymes²³ or dopamine²⁴ to the surface, with retention of the biological activity.

3.3 Crosslinking as a route to membranes or ceramics. Lightly crosslinked polymers possess many of the characteristics of uncrosslinked macromolecules. The main difference is that the crosslinks prevent dissolution of the polymer in suitable solvents, although the

solid may absorb appreciable amounts of solvents and swell to a gel. Light crosslinking of a water-soluble polyphosphazene will yield a polymer that swells in water to form a hydrogel.²⁵

On the other hand, extensive crosslinking yields non-swellable ultrastructures. Poly(aminophosphazenes) of formula $[NP(NHR)_2]_n$ react at moderate temperatures (200–500°C) by side group elimination reactions with concurrent formation of P–N–P crosslinks.²⁶ Some of the resultant ceramics have compositions approaching that of phosphorus nitride. Other polyphosphazenes with carborane side groups have been pyrolyzed to ceramic coatings containing phosphorus, nitrogen, boron, and carbon.²⁷⁵

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