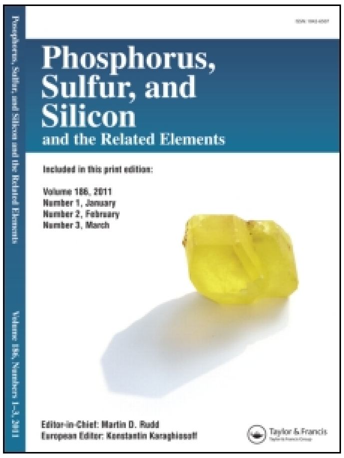

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Allcock, Harry R.(1999) 'Recent Developments with an Impact on the Future of Polyphosphazene Science and Technology', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 61 — 64
To link to this Article: DOI: 10.1080/10426509908546182
URL: http://dx.doi.org/10.1080/10426509908546182

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 61-64
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Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Recent Developments with an Impact on the Future of Polyphosphazene Science and Technology

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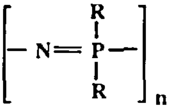
A new method for the synthesis of polyphosphazenes is described, together with the biomedical and electrochemical uses of phosphazene polymers with alkyl ether side groups

Keywords: phosphazenes; polymers; synthesis; applications

INTRODUCTION

Polyphosphazenes comprise the largest group of phosphorus-containing polymers and one of the most diverse of all the known synthetic macromolecular systems.[1] Most polyphosphazenes have the molecular structuure shown in **1**,



$$\left[-N=\overset{R}{\underset{R}{P}}-\right]_n$$

1

where the side groups, R, are mainly organic units, but can be inorganic or organometallic, and the degree of polymerization, n, can range as high as 15,000-20,000, which means that the molecular weights can be 2 to 4 million.

More than 700 different polymers of structure **1** are now known, all with the same backbone but with different side groups or different combinations of side groups along the phosphazene chain. Changes in side group structure have a profound effect on properties, and different phosphazene polymers are elastomers, high refractive index glasses, water-soluble or water insoluble macromolecules, hydrogels, fibers, films, or biomedically important materials. This last feature is of particular interest because different polyphosphazenes may be bioerodible to harmless products or biostable and biocompatible. Medical applications are being developed as drug delivery vehicles, vaccine adjuvants, tissue regrowth substrates, membranes, and dental materials. Overall, when developed to their full potential, polyphophazenes will constitute one of the most important fields based on phosphorus chemistry.

The most crucial fundamental and technological challenges in this field currently revolve around the synthetic chemistry. Three distinct pathways to polyphosphazenes exist at present. The first is based on the ring-opening polymerization of phosphazene cyclic trimers, either halogeno derivatives or organo-derivatives.[2] If the polymer bears halogen atoms linked to phosphorus, they must be replaced by organic groups to generate water-stable macromolecules. The second general approach make use of condensation reactions of phosphoranimines, in which organosilicon or $P(O)Cl_3$ molecules are eliminated.[3] All these polymerization processes require elevated temperatures and give broad molecular weight distributions. A third approach involves the denitrogenation of phosphorus azides.[4]

A NEW ROUTE TO POLY(DICHLOROPHOSPHAZENE) AND RELATED POLYMERS.

The classical route to useful polyphosphazenes is via macromolecular substitution reactions carried out on poly(dichlorophosphazene), itself produced by the ring-opening polymerization of $(NPCl_2)_3$.[2] A weakness of this route is the broad (often bimodal) molecular weight distributions of the polymers, the absence of control over the chain length, the need for high polymerization temperatures (210-250°C), and the inability of this route to allow block copolymer formation, especially with organic monomers.

Recently our group, working in association with the group of I. Manners at Toronto, have developed a new route to $(NPCl_2)_n$.[5] It involves the PCl_5-catalyzed, *room temperature*, solution polymerization of $Cl_3P{=}NSiMe_3$, with loss of $ClSiMe_3$ and concurrent formation of linear $(NPCl_2)_n$. Similar polymerizations occur with organophosphoranimines such as $Cl(R)_2P{=}NSiMe_3$. The advantages of this approach are: (1) it allows the polymer chain length to be controlled by the PCl_5 to phosphoranimine ratio (reduction of the PCl_5 concentration gives longer chains) and can give very narrow molecular weight distributions, (2) the reactions take place at 25°C, (3) the polymerization mechanism is "living" in the sense that the chains do not self-terminate but remain active for the addition of more of the same monomer, (4) the living mechanism allows the synthesis of block copolymers with other phosphazenes, (5) the reaction allows the growth of phosphazene chains from the ends of organic polymers, and (6) the process permits the synthesis of star-geometry polyphosphazenes.

Once synthesized, the poly(dichlorophosphazenes) produced by this route can be subjected to chlorine-replacement reactions to introduce a wide variety of organic side groups.. The development of this synthesis protocol is now a major effort in our research group.

THE SPECIAL IMPORTANCE OF ALKYL ETHER-SUBSTITUTED POLYPHOSPHAZENES

Of all the hundreds of different poly(organophosphazenes) known, some of the most interesting and useful are species with alkyl ether side groups. Most of these are soluble in water and stable to aqueous media. When crosslinked by gamma radiation they swell in water to form hydrogels, but do not dissolve. In the solid state these polymers are solvents for salts such as lithium- or silver triflate, and the solid solutions conduct electricity by an ionic mechanism.

Both the aqueous solutions and the hydrogels exhibit lower critical solution temperatures - they are soluble or swollen below a certain LCST temperature, but become insoluble or undergo gel contraction above this temperature. The LCST varies with the types of side groups and can range from 30°C to 80°C. This is a remarkable property that depends of the balance between the hydrophilic and hydrophobic components of the macromolecules, and makes these polymers of great interest in biomedicine. The hydrogels, in particular, have been used as enzyme immobilization substrates in which the enzymatic activity can be switched on or off by small changes in temperature.[6] Switching of a hydrogel by pH changes has also been accomplished.

The ionic conductivity of the solid solutions of salts in alkyl ether polyphosphazenes is also of great interest because these solid polymer electrolytes can be used in thin film, lightweight rechargeable lithium batteries.[7] Of the more than 30 of these polymers that we have designed and synthesized, those with branched alkyl ether side chains are of special importance because they resist crystallization, provide multiple oxygen sites to assist ion-pair separation, and generate materials that do not flow under pressure (which is a problem with the linear side chain species). One additional advantage of the polyphosphazenes for this application is their fire-retardant characteristics which result from the presence of the phosphorus-nitrogen backbone.

Acknowlegments

This work was supported by DOE, E.P.R.I., NSF, and NIH.
Coworkers are identified in the reference list.

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