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Perspective

The expanding field of polyphosphazene high polymers

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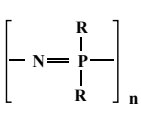
The importance of phosphorus in polymer chemistry is illustrated by the growth of the broad field of polyphosphazene science. Several hundred high polymers are now known with a phosphorus-nitrogen backbone and combinations or more than 250 different organic side groups. The properties of these polymers depend on both the character of the inorganic backbone and the structure of the organic side groups. This summary reviews the synthesis pathways to these materials, the often-unique structure-property relationships, and challenges for the future expansion of this field.

1. Background

Polyphosphazenes are macromolecules with a linear (or branched) backbone of ~15,000 alternating phosphorus and nitrogen atoms, and with two organic or inorganic side groups linked to each phosphorus (structure **1**).[1-3] The history of these polymers began in the 1890's with the report by H. N. Stokes[4] that the small molecule cyclic trimeric chlorophosphazene, $(NPCl_2)_3$ (**2**), or its larger ring analogues, when heated to 250 °C or higher was converted to a rubbery elastomer, later described as "inorganic rubber". This material proved to be insoluble in all solvents, but swelled in benzene, and was hydrolytically unstable in the atmosphere. Apart from a few experiments that were limited by the insolubility, little progress was made during the next 60 years.



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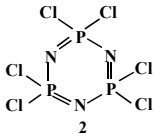

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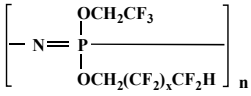

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A key development occurred in the mid-1960's[5-7] when it was realized that an insoluble but swellable elastomer is almost certainly a *cross-linked* high polymer and that, if the cross-linking could be prevented, this polymer would provide an excellent starting point for the synthesis of a wide range of stable polymers by making use of the known reactivity of phosphorus-chlorine bonds. Early experiments in the author's program verified this idea. Subsequently, replacement of the halogen atoms in the non-crosslinked polymer by reactions with alkoxides, aryloxides, primary or secondary amines, and a few organometallic species in THF solvent led to the synthesis of a wide range of new polymers with property combinations that in many cases, are improvements over classical organic polymers or silicones. Although theory might suppose that the replacement of say 30,000 chlorine atoms per molecule is statistically unlikely, the insolubility of sodium chloride or other salts in the solvent is a powerful driving force for this reaction. Thus, the reaction sequence outlined in Scheme 1 is the main basis of this chemistry. It allows the synthesis not only of polymers with one type of side group, but mixed-substituent derivatives with two or more different substituents. Each side group or combination of different side groups generates a different set of properties. This macromolecular substitution approach to polymer synthesis is

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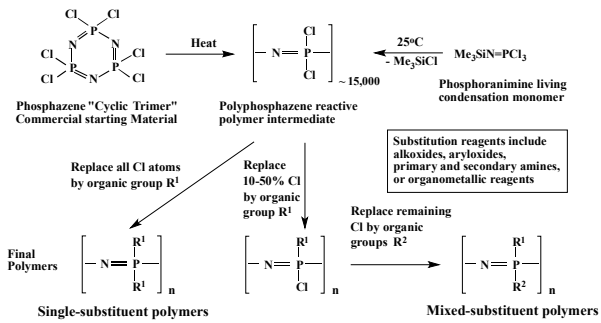
extremely rare in organic polymer chemistry.

Scheme 1



Scheme 1. Overall synthesis pathway to poly(organophosphazenes)

An alternative way to prepare poly(dichlorophosphazene) is via a living, room-temperature condensation polymerization of a chlorophosphoranimine.[8-11] This method provides access to block copolymers with organic macromolecules or organosilicon polymers. Another condensation route to poly(dichlorophosphazene) from Cl_3P=N-$POCl_2$ has also been developed[12] and the direct conversion of organophosphoraminines to organophosphazene polymers is also possible.[13-17] A few low to medium molecular weight phosphazene polymers are accessible by the ring-opening polymerization of cyclic trimeric phosphazenes with both halogen and organic side groups.[18] Moreover, under special circumstances it is possible to replace one organic group attached to phosphorus by another.[19,20] In addition to these possibilities there exists another type of polymer in which phosphazene rings are connected as side groups to an organic polymer chain.[20]

A large number of organic or organometallic nucleophiles participate in the reaction sequence shown in Scheme 1. More than 250 different side groups have been used and several hundred poly(organophosphazenes) have been prepared. Some typical side groups utilized in this synthesis manifold are shown in Table 1, together with properties they bring to the polymer.

2. Structure-Property Relationships

The properties of any polymer depend on the chemical characteristics of the backbone and the nature of the side groups. The polyphosphazene backbone bonds have a surprising high torsional freedom and a correspondingly high chain flexibility such that the polymer properties range from low temperature elastomers,[20] or film or fiber-forming polymers, to rigid solids depending on the side groups. Any factor that will raise the height of the barrier to torsion of the backbone bonds, such as side group bulk, ionic forces, hydrogen bonding, or coordination interactions, will raise the glass transition temperature. Thus, side groups can be chosen to tune the glass transition temperature over the range of -100 °C (alkoxy side groups[21]) to 200 °C or higher with adamantylamino groups.[22]

Table 1. Example polyphosphazene side groups and their influence on properties, and potential applications

Side group(s)	Properties	Actual or potential applications
-OCH_2CH_3	Elastomer	Possibly bioerodible to ethanol, phosphate , and ammonia
-$O(CH_2)_xCH_3$	Low Tg polymers	Elastomers or gums
-OCH_2CF_3	Opalescent, UV stable, microcrystalline, hydrophobic or superhydrophobic films and fibers.	Non-flammable, hydrophobic films and fibers. Medical device coatings
-$OCH_2CF_2CF_3$	Less soluble in organic media than side groups with CF_2H termini	Solvent and oil-resistant polymers
-$OCH_2(CF_2)_3CF_2H$	Soft, transparent films	UV stable films
-OCH_2CF_3/ -$OCH_2(CF_2)_xCF_2H$	Hydrophobic elastomer (when crosslinked)	Aerospace and biomedical devices
-$OCH_2CH_2OCH_2CH_2OCH_3$	Polymeric electrolyte and (when crosslinked) hydrogels	Lithium battery electrolytes and hydrogel applications
-OCH_2CF_3/metal phthalocyanine or azo dyes	Polymeric dyes	LCD displays or camera sensors
-OCH_2CF_3/polyaryleneoxy	Elastomer	Aerospace and medical
-OCH_2CF_3/spiropyran	Photochromic polymers	Photonics or eye protection
-OC_6H_5	Fire-resistant thermoplastic	Thermal and electrical insulation
-OC_6F_5	Highly crystalline polymers	Dielectric materials
Halogenated aryloxy groups	High refractive index	Photonic devices
-OC_6H_4COOH (PCPP)	Polyelectrolyte. Forms hydrogels in the presence of di- or tri-valent cations	Bioreactors, gold nanoparticle coatings, switchable membranes, vaccine adjuvant
-OC_5H_9 and other cycloalkanoxy groups	Strong films and membranes	CO_2 separations
-$NHCH_2COOEt$ and other amino acid esters	Hydrolyzes to H_3PO_4, NH_3, amino acid, and ethanol	Biomedical tissue engineering or drug release
-N-fluoroquinolone antibiotics	Fibers or films	Antibiotic polymers

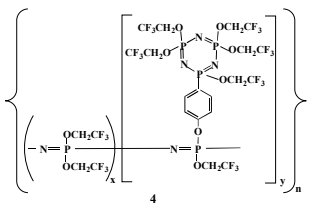
The stability of the polymer backbone depends on the side groups. For example, a few organic side groups can be displaced from phosphorus by hydrolysis to leave hydroxyl groups in their place. This opens a pathway to migration of the hydroxyl proton from oxygen to nitrogen, "saturation " of the backbone, followed by skeletal bond cleavage. Amino acid ethyl esters, linked via the nitrogen terminus to phosphorus, can undergo hydrolysis, and this has been used as a deliberate means to sensitize these polymers to breakdown to phosphate, ammonia, amino acid, and ethanol, a process of interest in tissue engineering and other biomedical processes.[23-28] Glucosyl[29] or glyceryl[30] side groups have the same effect. However, most of the other known poly(organophosphazenes) are stable to aqueous media.

The following examples illustrate how the polymer properties can be changed by the presence of different side groups.

3. Examples of Different Classes of Polyphosphazenes

3.1. New polyphosphazene elastomers

One group of poly(fluoroalkoxyphosphazene) elastomers, with the formula $[NP(OCH_2CF_3)(OCH_2(CF_2)_xCF_2H)]_n$ (Structure **3**) was the earliest attempt to utilize polyphosphazenes for a practical purpose.[31,32] Like other elastomers, its elasticity depends on the presence of both a high degree of intramolecular freedom and covalent crosslinks between the chains. We have recently shown that polymers with trifluoroethoxy side groups and low percentages of bulky cosubstituents such as tri-or tetra-phenyleneoxy, or cyclic trimeric phosphazene rings with trifluoroethoxy or phenoxy substituents display elasticity without having the chains connected by covalent crosslinks.[33-35] Instead, the bulky cosubstituents appear to associate by interdigitation or intermolecular clustering. Thus, polymers with the general structures shown in **4** and **5** have been synthesized with different of ratios of the trifluoroethoxy and bulky side groups. The advantage of a physical crosslinking option over covalent crosslinking is that it facilitates fabrication of the material and yields elastomers with fewer additives and the prospect of better biomedical compatibility than other phosphazene polymers currently in use.



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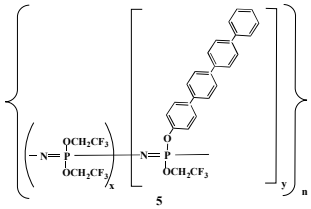

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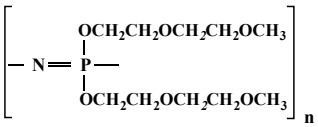
3.2. Polymers for use as electrolytes in lithium batteries, fuel cells, and dye-based solar cells

Alkyl ethers are solvents for salts such as lithium triflate, and the solutions can function as liquid ionic conductors for use in lithium batteries or dye-based solar cells. However, the liquid electrolytes in these devices are prone to leakage and may be a source of fires. The linkage of short etheric side groups to a polyphosphazene (for example, structure **6**) generates polymer-salt systems that have good ionic conductivity, are viscous enough to inhibit leakage, and are more resistant to combustion. [36-44] Similar polyphosphazenes with etheric side groups have been evaluated for use in dye-based solar cells.[45]



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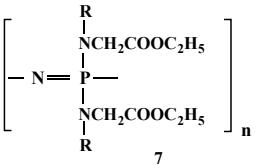

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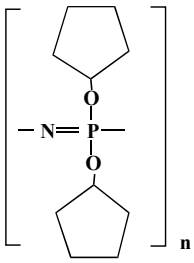
3.3. Bioerodible polymers designed for use in tissue engineering

Most synthetic polymers are stable to water. However, polymers that decompose when exposed to aqueous media may be useful for medical devices as in controlled drug release or tissue regeneration matrices. A few specialized polyphosphazenes, particularly those with amino acid ester side groups such as **7**, have been developed extensively as matrices for bone regeneration.[46-52] Thus, composites of the polyphosphazene with calcium hydroxyapatite microparticles, and seeded with osteoblasts and growth factors, accelerate the rate of bone repair both in the laboratory and in animal model tests. Recent publications describe the development of polyphosphazenes for ligament and tendon regeneration.

3.4. Membranes for gas separations

Many of the organic side groups that have been linked to a polyphosphazene chain generate polymers that are good film- and membrane-formers.[53] Films are usually prepared on a flat surface by evaporation of solvents from concentrated solutions of the polymers. A recent publication described the linkage of cycloalkanoxy side groups with from three-to eight-membered rings linked to the phosphorus atoms of the skeleton.[54] The polymer with cyclopentanoxy side groups (structures **8** and **9**) is especially effective for the selective transmission of carbon dioxide, and is under investigation for use in CO_2 capture equipment.



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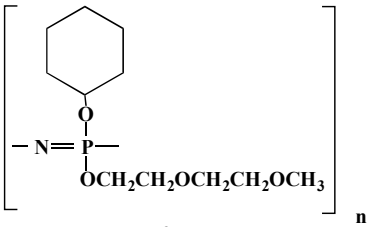

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3.5. Carrier polymers for dye molecules and liquid crystalline groups

Polymer dyes are useful in many applications including color filters for electronic display devices. The macromolecular synthesis method facilitates the synthesis of such molecules. For example, red, green, and blue dye molecules have recently been linked to polyphosphazenes (Figure 1).[55] This is an application where low loadings of the bulky dye molecules are sufficient to achieve the required optical densities, with the co-

substituents being chosen to optimize other physical properties such as transparency or high glass transition temperature. Liquid crystalline side groups have also been linked to the skeleton in a similar way.

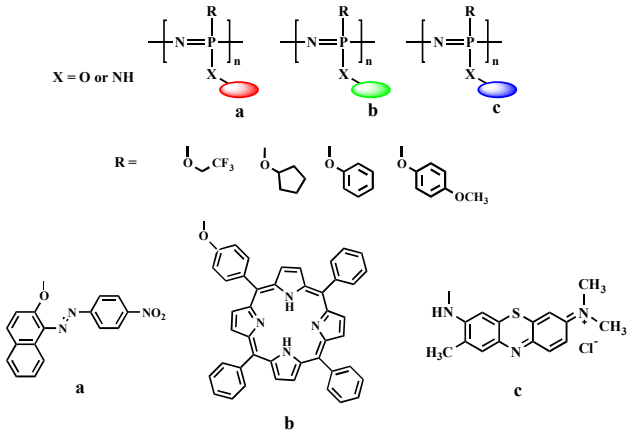

Figure 1. Colored filters are produced by the linkage of red, green, and blue dyes to the polyphosphazene chain together with major co-substituents of the type shown as R, chosen to maximize transparency

3.6. Hybrids of polyphosphazenes with organosilicon polymers

The field of organosilicon polymers (silicones) is a well-established discipline in general technology and medical science. Yet there are numerous property combinations that have not been accessible through these polymers. Some useful characteristics can be anticipated from hybrid polymers formed from polyphosphazenes and silicones. Thus, attempts have been made in our program to prepare hybrids of the two systems such as polyphosphazene chains with oligo-organosilicon side groups,[56] block copolymers,[58] and specialized macromolecules with both organic and polyhedral oligomeric silsesquioxane (POSS) side groups.[59]

3.7. Transition Metal Derivatives of Polyphosphazenes

Small molecule precious metal catalysts are often immobilized on surfaces or attached to polymers for facile recovery for environmental or economic reasons. The simplest approach with polyphosphazenes is to utilize the skeletal nitrogen atoms or amino side groups as ligands for transition metals as in the formation of platinum complexes.[60] Other examples of the attachment of transition metals to polyphosphazenes include the linkage of ferrocene molecules[61] and a variety other species such as chelated metals to the polymer skeleton.[62-66] These techniques offer new options for uses in catalysis, electronics, and electro-optics.

4. Applications

A large number of potential uses have been identified for poly(organophosphazenes).[1,2] These range from inert biomedical materials to bio-erodible solids, antibiotic polymers,[67] or hydrogels, to battery or solar cell electrolytes, gas separation membranes, or aerospace elastomers [68](see Table 1). Many of these applications appear promising at the research level but have not yet been advanced to a commercial manufacturing scale. However, polyphosphazene elastomers for medical and aerospace applications have been developed to a commercial level and they are undoubtedly the forerunners of other engineering or medical applications. Barriers to wide-scale commercial developments are the unfamiliarity of industrial chemists with the macromolecular substitution method of polymer synthesis, and cost issues especially when expensive nucleophiles are employed for the halogen replacement steps. Nevertheless, the main starting material, $(NPCl_2)_3$ (**2**) is now available in commercial quantities from China and Japan and this has removed a significant roadblock to future commercial advances. Overall, the chemistry of poly(organophosphazenes) has far outstripped the commercial utilization of these materials, although the large amount of research data already in the literature should make scale-up and commercialization very rapid in the future.

5. Future Challenges

With all the nucleophiles available for the macromolecular substitution process, an important question is this: "What organic or inorganic side groups cannot be linked to a polyphosphazene chain, and why?" Research so far has identified the following hurdles and solutions.

First, if each nucleophile has more than one functional group it is likely that the second functional site will react with another polymer molecule to cross-link the system and insolubilize the polymer before the rest of the chlorine atoms can be replaced. This would generate a polymer that is sensitive to hydrolysis in the atmosphere or in aqueous media. Thus, a multi-functional nucleophilic reagent must first have its secondary sites protected and then deprotected after that group has been connected to the backbone. This is the technique that has been employed for a range of side groups such as amino acids where, for example, the carboxylic acid moiety is first esterified, and the amino terminus is then utilized for attachment to the phosphorus atoms. This technique has also been used to assemble polymers with side groups such as para-hydroxyphenoxy or para-carboxyphenoxy units.

Second, many of the more interesting polymers foreseen for the future require the linkage of bulky side groups to the polyphosphazene skeleton, and these will encounter steric hindrance restrictions. Most of the nucleophiles used during the earlier exploratory phase of this field were relatively small units such as ethoxide, trifluoroethoxide, phenoxide, ethylamino, etc. However, even the introduction of biphenyloxy, or diethylamino side groups requires more forcing conditions (higher temperatures and/or longer reaction times) than for smaller nucleophiles. For example, extremely bulky side groups may replace only one chlorine per phosphorus. Recent attempts to widen the scope of this field have required the introduction of bulky side groups such as polyaryleneoxy-,[34] tyrosine, phthalocyanines, polyaromatic

dye molecules,[55] cyclotrimeric or tetrameric phosphazene rings,[33,35] polyhedral oligomeric silsesquioxanes (POSS), or some of the large biological molecules, mentioned above. These restrictions can be understood in terms of the well-known role of steric hindrance in Sn2 substitutions.

There are two strategies to cope with this challenge. It is often sufficient to separate the bulky group from the coupling amino or hydroxyl functional site by means of a flexible spacer unit. Even a trimethylene spacer is usually sufficient, since this relieves the steric crowding at the reaction site. An alternative approach is the use of two or more different side groups, one bulky and one smaller. In this way the steric crowding is less severe. This approach has been widely employed in our program via the prior replacement of fewer than 50% of the chlorine atoms by the bulky groups, followed by replacement of the remaining chlorine atoms by trifluoroethoxide or other smaller nucleophiles. In this way the effects of variable loadings of the larger side groups on the polymer properties can be investigated. Examples from our recent studies include the linkage of bulky side groups such as polyarylenes, fused aryl rings, phosphazene cyclic trimeric, or tetrameric rings, or bulky amino acid esters to a polyphosphazene chain, some of which are mentioned above.

It should also be noted that the low solubility of some organo-substituted phosphazene polymers in organic media is sometimes encountered when specific side groups are linked to the phosphazene skeleton. For example, the introduction of fluorinated aryloxy groups has a tendency to create insoluble polyphosphazenes. Thus, use of nucleophiles such as pentafluorophenoxide may cause precipitation of the polymer from solution before all the chlorine atoms have been replaced. Special strategies such as the use of high boiling solvents and pressure reactors may be needed to overcome this hurdle.[69] Another challenge for future work is when amino nucleophiles are employed for reactions with poly(dichlorophosphazene). For example, methylamine is a difunctional reagent, which can crosslink polymer chains during substitution. Moreover, when amino nucleophiles are used, hydrogen chloride is released as a side product, and this can coordinate to either the side groups or the skeletal nitrogen atoms and be difficult to remove in subsequent purification. A stronger base such as triethylamine is normally employed to capture the hydrogen chloride as the insoluble triethylammonium salt, but at elevated temperatures the equilibrium for this process may be unfavorable.

The existence of these challenges is the reason why a normal procedure in our program is to carry out preliminary fundamental exploratory research with small molecule phosphazenes, particularly with the cyclic trimer $(NPCl_2)_3$ or cyclic tetramer $(NPCl_2)_4$ as a prelude to studies with new high polymers.[70] Although these model systems are not ideal (they have rings that are considerably less flexible than polymer chains), they do provide hints about the need to follow one strategy or another during syntheses at the high polymer level. Clearly the use of small-molecule linear chlorophosphazenes would provide better models, and we have begun to explore this alternative.

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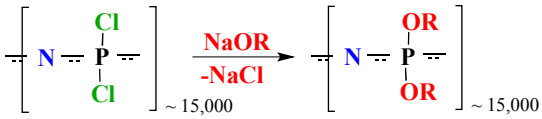
Journal Name

Perspective

Table of Content Entry

The wide variety of accessible poly(organophosphazenes) is a consequence of the unusual macromolecular substitution approach to their synthesis.



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