*Kirk-Othmer Encyclopedia of Chemical Technology.*

# INORGANIC HIGH POLYMERS

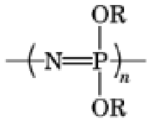
In a broad sense, inorganic polymers embrace a very large number of elements and compounds that are constructed of units bonded together in some type of repetitive fashion, with the requirement that the element carbon be excluded from the backbone of these repeating units. Some of the most common examples are the metals, as well as the naturally occurring silicate minerals and silica, where the $SiO_4$ tetrahedral moiety often forms the repeating unit of the one-, two-, or three-dimensional structure by sharing oxygen atoms with neighboring units (see Silica). This article covers linear, mainly covalent macromolecules where the skeletal repeat unit is composed of primarily noncarbon elements.

The most commercially successful inorganic polymers to date are the polysiloxanes, owing to their unique high temperature stability, low temperature flexibility, and a number of other advantageous properties such as low surface energy and room-temperature vulcanizability (see Silicon compounds, silicones). Despite the commercial success of polysiloxanes, however, the development of new inorganic polymers has not kept pace with that of their organic counterparts. The principal reasons for this are that a large variety of inorganic monomers has not been readily available, and extensive research and development with organic polymers have quickly provided many articles of commerce.

However, the rapid advancement of technology between the 1970s and the 1990s has created a need for materials whose special properties are unlikely to be obtained from carbon-based polymers alone. Thus, there has been a growing interest in the synthesis and development of new inorganic polymers, and there has been an almost explosive growth in the number of publications and patents dealing with the inorganic polymers, polyphosphazenes and polysilanes. These two polymer systems have been extensively studied, both with respect to new materials development via basic synthesis and chemical modification, and with respect to some of the intrinsic properties associated with the polymers; they are discussed here in detail. In addition, some newer inorganic polymers on the horizon are briefly covered. Other materials, eg, the polysilazanes, boron–nitrogen polymers, and other areas of inorganic polymers, are discussed elsewhere (1).

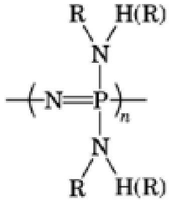
## 1. Polyphosphazenes

The polyphosphazenes, sometimes also referred to as polyphosphonitriles, are the most chemically versatile inorganic polymers known to date. A new class of phosphazene polymers, with only phosphorus–carbon bonded substituents, has been developed. Thus, based on their method of synthesis, two different types of phosphazene polymers are now in existence and are undergoing parallel development. The first type, bearing substituents on phosphorus bonded mostly via phosphorus–oxygen **(1)** and phosphorus–nitrogen **(2)** linkages, was developed in the mid-1960s as soluble, hydrolytically stable polymers (2–4). These polymers have seen steady growth in the diversity of polymers made throughout the 1970s and 1980s. Polymers of the second type, with substituents linked via direct phosphorus–carbon bonds **(3)** were first reported in the early 1980s (5–7) and since then have also seen significant development.

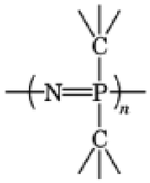


$$-\!\!\left(N{=}\overset{OR}{\underset{OR}{P}}\right)_{\!n}\!\!-$$

**(1)**



**(2)**

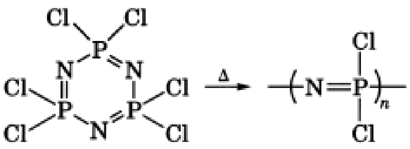


**(3)**

### 1.1. P—O- and P—N-Substituted polyphosphazenes

#### *1.1.1. Synthesis*

The synthesis of poly(dichlorophosphazene) [25034-79-1], $(N{=}PCl_2)_n$ **(4)**, the parent polymer to over 300 macromolecules of types **(1)** and **(2)**, is carried out via controlled, ring-opening polymerization of the corresponding cyclic trimer, $(N{=}PCl_2)_3$ [940-71-6].



(1)

**(4)**

Various inorganic, organic, and organometallic compounds are known to catalyze this polymerization (4, 8, 9). Among these, $BCl_3$ is a very effective catalyst, although proprietary catalysts that significantly lower polymerization temperature from the usual, sealed-tube reaction at 250°C are involved in the industrial manufacture of the polymer. A polycondensation process has also been developed for the synthesis of **(4)** (10–12). This involves elimination of phosphoryl chloride from a monomer prepared from $(NH_4)_2SO_4$ and $PCl_5$.

$$(NH_4)_2\,SO_4 + PCl_5 \longrightarrow Cl_3P{=}N{-}P\,(O)\,Cl_2 \xrightarrow[-P(O)Cl_3]{\Delta} (4) \qquad (2)$$

The very high reactivity of the P—Cl bonds in **(4)** forms the basis for the now well-known macromolecular substitution method, which has been used to synthesize polymers of types **(1)** and **(2)** and some polymers that are hybrids of these and **(3)**. The method involves nucleophilic reactions of **(4)**, and to some extent of its difluoro analogue, with alkoxides or amines.

$$(4) + \mathrm{NaOR} \longrightarrow (1) \text{ or } (4) + \mathrm{RNH(R)} \longrightarrow (2)$$

### *1.1.2. Properties*

One of the characteristic properties of the polyphosphazene backbone is high chain flexibility which allows mobility of the chains even at quite low temperatures. Glass-transition temperatures down to −105°C are known with some alkoxy substituents. Symmetrically substituted alkoxy and aryloxy polymers often exhibit melting transitions if the substituents allow packing of the chains, but mixed-substituent polymers are amorphous. Thus the mixed substitution pattern is deliberately used for the synthesis of various phosphazene elastomers. On the other hand, as with many other flexible-chain polymers, glass-transition temperatures above 100°C can be obtained with bulky substituents on the phosphazene backbone.

The thermal stability of polymers of types **(1)** and **(2)** is also dependent on the nature of the substituents on phosphorus. Polymers with methoxy and ethoxy substituents undergo skeletal changes and degradation above about 100°C, but aryloxy and fluoroalkoxy substituents provide higher thermal stability (4). Most of the P—N- and P—O-substituted polymers either depolymerize via ring-chain equilibration or undergo cross-linking reactions at temperatures much above 150–175°C.

Phosphazene polymers are inherently good electrical insulators unless side-group structures allow ionic conduction in the presence of salts. This insulating property forms the basis for applications as wire and cable jackets and coatings. Polyphosphazenes also exhibit excellent visible and uv radiation transparency when chromophoric substituents are absent.

Another valuable characteristic of many phosphazene polymers is their flame-retardant behavior and low smoke generation on combustion (13). This property is utilized in commercial applications.

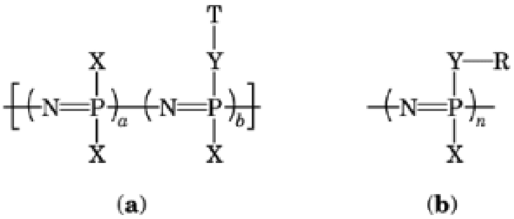
A remarkable feature of phosphazene polymers of types **(1)** and **(2)** is that appropriate substituents (which are readily attached) can be used as toggle switches to turn several properties, such as hydrolytic stability and electrical conductivity, on and off (1).

### *1.1.3. Applications*

Among the P—O- and P—N-substituted polymers, the fluoroalkoxy- and aryloxy-substituted polymers have so far shown the greatest commercial promise (14–16). Both poly[bis(2,2,2-trifluoroethoxy)phosphazene] [27290-40-0] and poly(diphenoxyphosphazene) [28212-48-8] are microcrystalline, thermoplastic polymers. However, when the substituent symmetry is disrupted with a randomly placed second substituent of different length, the polymers become amorphous and serve as good elastomers. Following initial development of the fluorophosphazene elastomers by the Firestone Tire and Rubber Co., both the fluoroalkoxy (EYPEL-F) and aryloxy (EYPEL-A) elastomers were manufactured by the Ethyl Corp. in the United States from the mid-1980s until 1993 (see Elastomers, synthetic–phosphazenes).

The fluoroelastomers possess good rubber properties with the added advantages of being nonburning, hydrophobic, and solvent- and fuel-resistant. In addition to these, because of flexibility down to about −60°C, these polymers have been used in seals, gaskets, and hoses in army tanks, in aviation fuel lines and tanks, as well as in cold-climate oil pipeline applications. These polymers have also found application in various types of shock mounts for vibration dampening (14, 17).

The aryloxyphosphazene polymers, on the other hand, have been used primarily in wire and cable coatings and jackets and as fire-resistant, low smoke, closed-cell foams and sound-barrier sheets.



(a) (b)

**Fig. 1.** Schematic bioactive polyphosphazenes. (**a**) General structure, where X=hydrophilic/hydrophobic group that hydrolyzes with concurrent polymer breakdown, Y=difunctional group for attaching bioactive agent to polymer, and T=bioactive agent. (**b**) Actual example where X= $-OC_6H_5$, Y= and R=$(CH_3)_2C(SH)$-$CH(NHCOCH_3)$, 4-$(C_3H_7)_2NSO_2-C_6H_4$, etc.

### *1.1.4. Biomedical Applications*

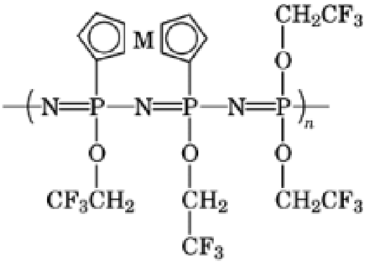
In the area of biomedical polymers and materials, two types of applications have been envisioned and explored. The first is the use of polyphosphazenes as bioinert materials for implantation in the body either as housing for medical devices or as structural materials for heart valves, artificial blood vessels, and catheters. A number of fluoroalkoxy-, aryloxy-, and arylamino-substituted polyphosphazenes have been tested by actual implantation in rats and found to generate little tissue response (18).

The second type of biomedical application utilizes the versatile chemistry of polyphosphazenes to generate bioactive polymers. Two approaches have been developed: one is to tie or physically entrap biologically active molecules using the phosphazene backbone as the carrier or encapsulant. The other is to attach bioactive molecules to a hydrolyzable (degradable) phosphazene backbone that releases the active species on breakdown of the backbone to harmless species that can be metabolized or directly excreted. Thus the first method has been used to attach a polymer-bound equivalent of the well-known anticancer agent cisplatin, heparin, dopamine, various enzymes, local anesthetics such as benzocaine, and a number of other bioactive molecules (19–26). The second approach utilizes cleverly designed polyphosphazenes that completely hydrolyze in water to small molecules. Thus, phosphazene polymers containing amino acid ester (eg, ethylglycinato) or imidazolyl substituents hydrolyze at body temperature and blood pH conditions to phosphate, ammonia, ethanol, and the corresponding amino acid or imidazole (27–30). The rate of hydrolysis can often be controlled by the presence of another substituent on phosphorus that does not allow ready hydrolysis. In this manner, bioactive agents can be released in a controlled fashion. Successful release of steroids, the antitumor agent melphan, and of naproxen has been obtained in *in vitro* and *in vivo* studies (31–36). The attachment of oligopeptides to a specially designed side-group on polyphosphazenes has also been reported (37), and could lead to the development of useful biomaterials.

Two crucial aspects of the design of bioactive polyphosphazenes have been carefully developed. One involves the hydrophilicity or hydrophobicity of the polymer, and the other is the stability of the polymer or tactical substituent linkages that allow release of the active agent or ensure its potency to be retained in the bound form. For example, methylamino-, glyceryl-, glucosyl-, (hydroxyalkyl)amino-, and alkyl ether-substituted polyphosphazenes are water-soluble, whereas fluoroalkoxy or aryloxy phosphazenes are hydrophobic. On the other hand, chemical bonds like Schiff's base linkages are hydrolytically unstable. Thus, the release rate or activity of bioactive molecules attached to a phosphazene polymer can be fine-tuned to obtain desired effects by balancing substituent characteristics on the polymer and the nature of the linkage used to attach the bioactive species. The general structure in Figure 1**a** shows the chemical architectural characteristics that have been employed in the design of these polymers and 1**b** exemplifies some bioactive molecules that have been attached to the phosphazene backbone through an amido linkage, in each case.

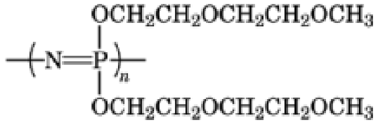
### 1.1.5. Polymers Bearing Metal Complexes

A large number of polymers with side groups containing metal complexes have been reported. The complexes are linked to the phosphazene backbone primarily through a ligand on a substituent (38–42), although linkages through the skeletal nitrogen (19) or through direct metal–phosphorus bonding with the skeletal phosphorus atoms (43) have also been utilized. The impetus for the synthesis of these metal–polymer hybrids is the potential for generating materials using particular properties of metals such as catalysis, electrical conduction, magnetism, and in some instances biological activity, with the inorganic polymer support providing features such as solubility, chemical protection, control of activity, biocompatibility, prevention of leaching, etc. Biological activity is exhibited by the platinum complex cisplatin, and catalytic activity has been demonstrated with polymer-bound species such as **(5)**. Polymers **(5)** and **(6)** are representative of metal-containing polyphosphazenes where the metal is linked through a ligand on a side-group.



where M = Fe, Ru

**(6)**

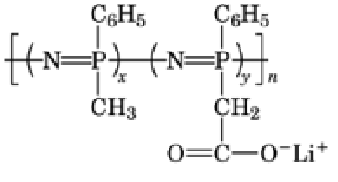


$$\left(\mathrm{N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2}\right)_n$$

**(7)**

### 1.1.6. Solid Electrolyte Applications

Among other potentially useful polymers synthesized by the versatile macromolecular substitution process are polymers based on oligoether substituents or heterocyclic substituents that have been under intense investigation for solid electrolyte battery applications (44–47). The most promising of these is poly[bis(methoxyethoxyethoxy)phosphazene (MEEP) **(7)**. This polymer is an excellent solid solvent for salts like lithium or silver triflate, and the resulting solid solution has an ionic conductivity three orders of magnitude greater than a similar composition based on poly(ethylene oxide). Lightweight, prototype rechargeable batteries based on cross-linked **(7)** have been successfully tested and are approaching commercialization.



$$\left[\left(\mathrm{N{=}P(C_6H_5)(CH_3)}\right)_x\left(\mathrm{N{=}P(C_6H_5)(CH_2C({=}O){-}O^-Li^+)}\right)_y\right]_n$$

**(11)**

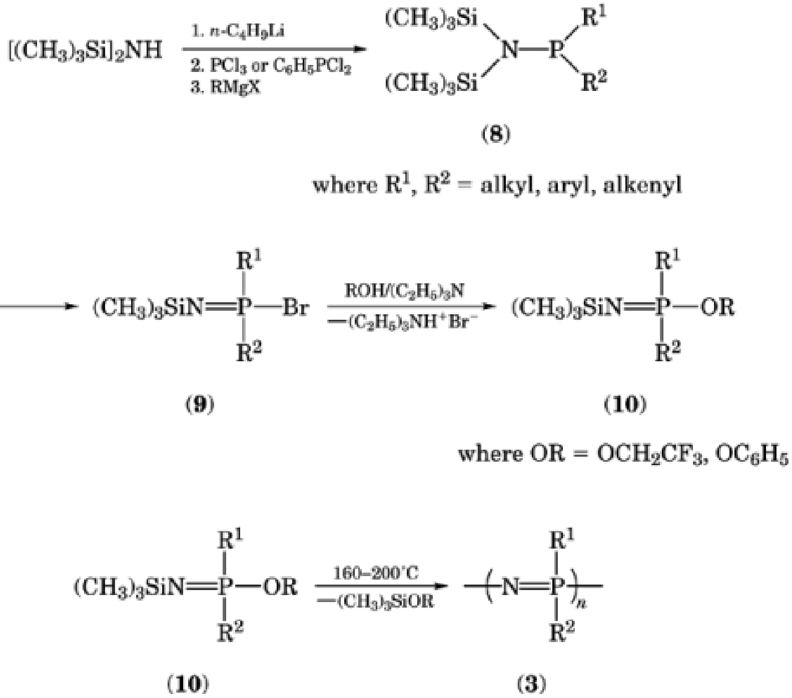


**Fig. 2.** Synthesis of polyphosphazenes with P—C bonds.

A number of liquid crystalline polyphosphazenes with mesogenic side groups have been prepared (48–50). Polymers with nonlinear optical activity have also been reported (51). Polyphosphazene membranes have been examined for gas, liquid, and metal ion separation, and for filtration (52–54). There is interest in phosphazene–organic copolymers, blends, and interpenetrating polymer networks (IPNs) (55–61) to take advantage of some of the special characteristics of phosphazenes such as flame retardance and low temperature flexibility. A large number of organic polymers with cyclophosphazene substituents have been made (62).

### 1.2. Polymers with Alkyl and Aryl Substituents on P

Even though partially alkyl- and aryl-substituted polyphosphazenes are accessible via the ring-opening polymerization followed by the macromolecular substitution route (63), polymers in which all substituents are attached through direct phosphorus–carbon bonds **(3)** are not yet accessible by this method. Reaction of organolithium or organomagnesium compounds with polymers such as polydichlorophosphazene **(4)** leads to incompletely substituted polymer as well as polymer degradation, and fully alkyl/aryl-substituted cyclic phosphazenes do not undergo ring-opening polymerization (4).

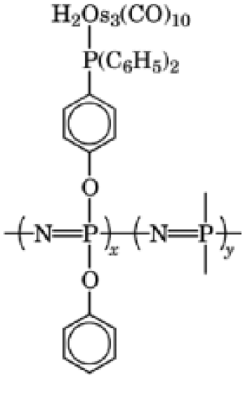
#### *1.2.1. Synthesis*

The first fully alkyl/aryl-substituted polymers were reported in 1980 via a condensation–polymerization route. The method involves, first, the synthesis of organophosphine-containing alkyl or aryl substituents, followed by the ready oxidation of the phosphine to a phosphorane with leaving groups suitable for a 1,2-elimination reaction. This phosphorane is then thermally condensed to polymers in which all phosphorus atoms bear alkyl or aryl substituents. This condensation synthesis is depicted in Figure 2 (5–7, 64).

The three steps in equation 2 are carried out in one vessel. This affords a wide variety of disilylaminoorganophosphines 2, including those with vinyl substituents (65), in yields of 40–85%. The oxidation of 2 to 2 and the reaction of 2 with alcohol (eq. 2) are carried out in a second reactor to provide the "monomer" phosphoranimines 2 in overall 30–65% yield based on starting $PCl_3$ or $C_6H_5PCl_2$. The use of $C_2Cl_6$ in place of $Br_2$ in the conversion of 2 to 2 makes it possible to carry out all the reactions leading to 2 in one vessel, and this has significantly increased yields of the monomer, with overall yields up to 80% (66).

The bulk polycondensation of 2 is normally carried out in evacuated, sealed vessels such as glass ampules or stainless steel Parr reactors, at temperatures between 160 and 220°C for 2–12 d (67). Two monomers with different substituents on each can be cocondensed to yield random copolymers. The by-product silyl ether is readily removed under reduced pressure, and the polymer purified by precipitation from appropriate solvents. Catalysis of the polycondensation of 2 by phenoxide ion in particular, as well as by other species, has been reported to bring about complete polymerization in 24–48 h at 150°C (68). Catalysis of the polycondensation of phosphoranimines that are similar to 2, but which yield P—O-substituted polymers **(1)**, has also been described and appears promising for the synthesis of **(1)** with controlled structures (69, 70).

In addition to providing fully alkyl/aryl-substituted polyphosphazenes, the versatility of the process in Figure 2 has allowed the preparation of various functionalized polymers and copolymers. Thus the monomer 2 can be derivatized via deprotonation–substitution, when a *P*-methyl (or $P—CH_2—$) group is present, to provide new phosphoranimines some of which, in turn, serve as precursors to new polymers (64). In the same vein, polymers containing a $P—CH_3$ group, for example, poly(methylphenylphosphazene), can also be derivatized by deprotonation–substitution reactions without chain scission. This has produced a number of functionalized polymers (64, 71–73), including water-soluble carboxylate salts **(11)**, as well as graft copolymers with styrene (74) and with dimethylsiloxane **(12)** (75).



**(5)**

REPLACEThus alkyl- and aryl-substituted polyphosphazenes and their immediate precursors are also quite amenable to synthetic modifications, with the potential for the synthesis of a wide variety of materials being quite evident.

### 1.2.2. Properties

The condensation–polymerization reaction (eq. 2) yields alkyl- and aryl-substituted polymers with average molecular weights in the range 40,000 to 250,000 ($\overline{M}_n$ ranges from 20,000 to 100,000). In addition to routine size exclusion chromatography (sec), membrane osmometric, viscometric, and light-scattering experiments have been used in representative cases to determine absolute molecular weights and to obtain polymer chain

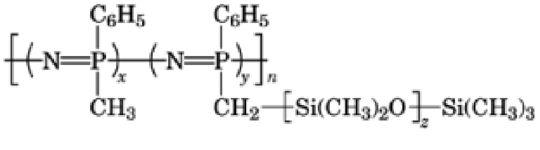
**Table 1. Thermal Analytical Data[a] for Some Poly(alkyl/arylphosphazenes)**

| Polymer | Structure number | CAS Registry Number | $T_g$, °C | $T_g$, °C | $T_{\mathrm{onset}}$, °C |
|---|---|---|---|---|---|
| polydimethyl-phosphazene | **(13)** | [88718-77-8] | −46 | 143 | 401 |
| polydiethyl-phosphazene | **(14)** | [107037-73-0] | | 217 | 353 |
| poly(methylphenyl-phosphazene) | **(15)** | [88718-66-5] | 37 | | 354 |
| poly(dimethylphos-phazene-*co*-methyl-phenylphosphazene) | **(16)** | [96743-50-9] | −3 | | 390 |
| polymer salt | | | 51[b] | | 320 |
| poly(phosphazene-*g*-siloxane) | **(12)** | | −123, 38 | −45[c] | 436[d] |

[a] $T_g$ and $T_m$ by dsc, $T_{\mathrm{onset}}$ (onset of decomposition) Thermogravimetric analysis in argon at 10°C heating rate.
[b] Estimate.
[c] Melting transition for poly(dimethylsiloxane) graft segment.
[d] In air.

dimensions (76). In general, the polymers are soluble in chlorinated solvents such as $CH_2Cl_2$ and $CHCl_3$. Polymers with phenyl substituents are also soluble in tetrahydrofuran.

The P—N backbone remains quite flexible with small, unbranched alkyl substituents on phosphorus. For example, polydimethylphosphazene **(13)** exhibits a glass-transition temperature ($T_g$) at −46°C. Bulkier substituents like phenyl cause significant increases in $T_g$, however. Symmetrically substituted dialkyl polymers exhibit varying degrees of crystallinity by x-ray diffraction (76). Polymer **(13)** shows both amorphous and crystalline domains, whereas the diethyl analogue **(14)** is so highly crystalline that it is insoluble in all common solvents, and does not exhibit a glass-transition temperature. Asymmetrically substituted polymers such as poly(methylphenylphosphazene) **(15)** are amorphous, which is probably a result of their atactic structure (76).REPLACE



$$\left[ \left( N{=}\overset{C_6H_5}{\underset{CH_3}{P}} \right)_x \left( N{=}\overset{C_6H_5}{\underset{CH_2-\left[Si(CH_3)_2O\right]_z-Si(CH_3)_3}{P}} \right)_y \right]_n$$

**(12)**

Alkyl- and aryl-substituted polyphosphazenes **(3)** exhibit onset of decomposition at between 350 and 400°C, as determined by thermogravimetric analyses (tga) (76) under argon atmosphere. Interestingly, the decomposition temperature for the graft copolymer **(12)** (Table 1) is higher than that of either of the component homopolymers. Even though it had long been predicted that the P—C bonded polymers **(3)** were likely to be more thermally stable than the P—O- **(1)** and P—N-bonded **(2)** polymers, a detailed study (77) suggests there may not be significant differences between the thermal stabilities of P—O- and P—C-bonded polymers. However, information on the thermooxidative stability of **(3)** as cross-linked polymers, in filled or unfilled systems, is not yet available.

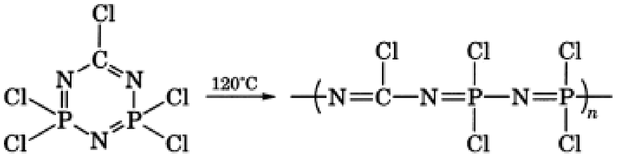
### *1.2.3. Applications*

Polymers with small alkyl substituents, particularly **(13)**, are ideal candidates for elastomer formulation because of quite low temperature flexibility, hydrolytic and chemical stability, and high temperature stability. The ability to readily incorporate other substituents (in addition to methyl), particularly vinyl groups, should provide for conventional cure sites. In light of the biocompatibility of polysiloxanes and P—O- and

P—N-substituted polyphosphazenes, poly(alkyl/arylphosphazenes) are also likely to be biocompatible polymers. Therefore, biomedical applications can also be envisaged for **(3)**. A third potential application is in the area of solid-state batteries. The first steps toward ionic conductivity have been observed with polymers **(13)** and **(15)** using lithium and silver salts (78).

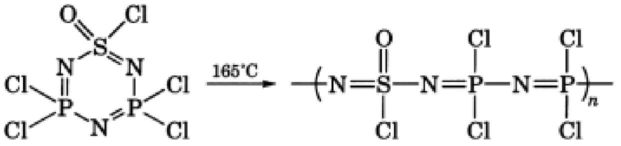
### 1.3. Phosphazenes Containing Skeletal Carbon, Sulfur, and Metal Atoms

The first phosphazene polymers containing carbon (79), sulfur (80, 81), and even metal atoms (82) in the backbone have been reported. These were all prepared by the ring-opening polymerization of partially or fully chloro-substituted (or fluoro-substituted) trimers containing one hetero atom substituting for a ring-phosphorus atom in a cyclotriphosphazene-type ring.



(6)

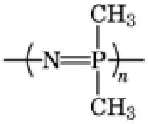
**(16)**



(7)

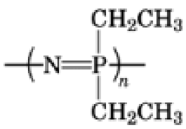
**(17)**

Apparent ring strain in these trimers of a magnitude greater than in the corresponding cyclotriphosphazene causes the former to polymerize at significantly lower temperatures. From the halo-substituted polymers, aryloxy-substituted polymers have been made for the carbon- and sulfur-containing systems, and these polymers show glass-transition temperatures ($T_g$) higher than the corresponding phosphazene homopolymers when carbon is a skeletal atom, but lower or higher $T_g$ (depending on the nature of the aryloxy group) when sulfur(VI) is a skeletal atom. The copolymers containing skeletal sulfur(VI) substitution appear especially promising from a materials standpoint. equations **6** and **7** are representative of the ring-opening polymerization route used to prepare the heterophosphazene polymers. Macromolecular substitution, eg, on **(16)** and **(17)**, then yields **(18)** and **(19)**, respectively.



$$-\!\!\left(N{=}\overset{CH_3}{\underset{CH_3}{P}}\right)_{\!n}\!-$$

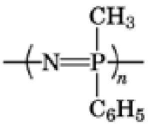
**(13)**



$$-\!\!\left(N{=}\overset{CH_2CH_3}{\underset{CH_2CH_3}{P}}\right)_{\!n}\!-$$

**(14)**

An example of a polyphosphazene incorporating metal atoms is **(20)**, where M = Mo or W.

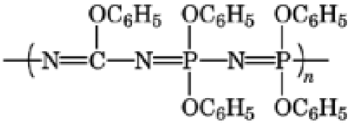


$$-\!\!\left(N=\overset{CH_3}{\underset{C_6H_5}{P}}\right)_{\!n}\!\!-$$

**(15)**

## 2. Poly(alkyl/aryloxothiazenes)

The synthesis of a new class of inorganic polymers **(21)** with a backbone consisting of alternating sulfur(VI) and nitrogen atoms, and with variable alkyl or aryl substituents as well as a fixed oxygen substituent on sulfur, has recently been accomplished (83–85). These polymers are structurally analogous to poly(alkyl/arylphosphazenes).

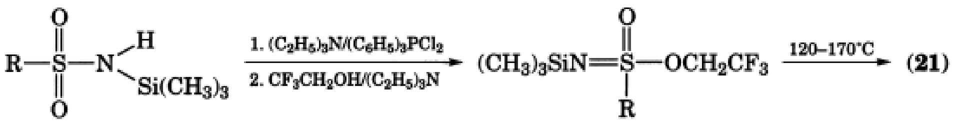


$$-\!\!\left(N=\overset{OC_6H_5}{C}-N=\overset{OC_6H_5}{\underset{OC_6H_5}{P}}-N=\overset{OC_6H_5}{\underset{OC_6H_5}{P}}\right)_{\!n}\!\!-$$

**(18)**

### 2.1. Synthesis and Properties

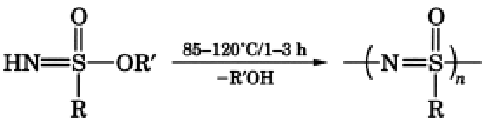
The synthesis of **(21)** follows a very straightforward route based on readily accessible starting materials and on some novel reactions in organo–inorganic sulfur chemistry (83–85), as well as on polycondensation chemistry analogous to that utilized in the preparation of poly(alkyl/arylphosphazenes). One preparation of **(21)** is as follows:



$$R-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-N\begin{matrix}H\\ Si(CH_3)_3\end{matrix}\xrightarrow[2.\ CF_3CH_2OH/(C_2H_5)_3N]{1.\ (C_2H_5)_3N/(C_6H_5)_3PCl_2}(CH_3)_3SiN=\overset{O}{\underset{R}{\overset{\|}{S}}}-OCH_2CF_3\xrightarrow{120\text{–}170^\circ C}\mathbf{(21)}\qquad(8)$$

**(22)** **(23)**

In step 2, phenol or trifluorethanol is used, but phenol is preferred. Examples of **(21)** prepared by this method include R = methyl [138815-47-1], ethyl [146525-87-3], phenyl [138815-48-2], and 4-fluorophenyl [146525-88-4]. Another preparation is shown in equation **9**, where R′OH is phenol or trifluoethanol.



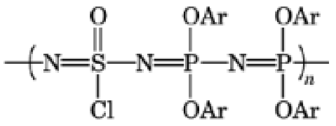
$$HN=\overset{O}{\underset{R}{\overset{\|}{S}}}-OR'\xrightarrow[-R'OH]{85\text{–}120^\circ C/1\text{–}3\ h}-\!\!\left(N=\overset{O}{\underset{R}{\overset{\|}{S}}}\right)_{\!n}\!\!-\qquad(9)$$

**(24)** **(21)**

Examples of **(21)** made by this route include R = methyl, phenyl, $ClCH_2CH_2CH_2$ [146525-89-5], and $C_6H_5{-}CH{=}CH$ [146525-90-8]. Both homopolymers and copolymers can be made by the polycondensation process. The polymers **(21)**, however, have not yet been studied in detail. Interesting properties include solubility of several polymers only in highly polar solvents like dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), as well as an unconventional lowering of $T_g$ in going from lower to higher alkyl substituents on sulfur. The highly polar S=O moiety, uniquely at every other linkage along the backbone, appears to play a role in polymer solubility and chain flexibility. As with phosphazenes, no backbone $\pi$-conjugation is apparent. From the quite general applicability of the synthetic approach to these new sulfur–nitrogen-backbone inorganic polymers, the development of a variety of these polymers with potentially many useful properties appears likely.

## 3. Polysilanes

The polysilanes or polysilylenes **(25)**, an unusual class of inorganic polymers, saw a very intense period of investigation during the 1980s.



$$\left( N{=}\overset{\overset{O}{\|}}{\underset{\underset{Cl}{|}}{S}}{-}N{=}\overset{OAr}{\underset{OAr}{P}}{-}N{=}\overset{OAr}{\underset{OAr}{P}} \right)_n$$

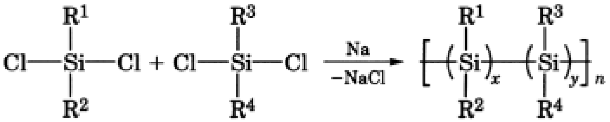
**(19)**

Research and development in the field are still continuing at a fast pace, particularly in the area of absorption and emission characteristics of the polymers. Several reasons account for this interest. First, the intractable polydimethylsilane [30107-43-8] was found to be a precursor to the important ceramic, silicon carbide (86–89). Secondly, a number of soluble polysilanes were prepared, which allowed these polymers to be studied in detail (90–93). As a result of studies with soluble polymers it became clear that polysilanes are unusual in their backbone $\sigma$-conjugation, which leads to some very interesting electronic properties.

### 3.1. Synthesis of Polysilanes

### *3.1.1. Wurtz-Type Coupling of Dihalosilanes*

Several approaches have been developed for the synthesis of polysilanes. However, the most commonly utilized method is based on the Wurtz-type alkali metal coupling of dichlorosilanes. Both homo- and copolymers can be prepared this way (eq. **10**).



$$Cl{-}\overset{R^1}{\underset{R^2}{Si}}{-}Cl + Cl{-}\overset{R^3}{\underset{R^4}{Si}}{-}Cl \xrightarrow[-NaCl]{Na} \left[ \left(\overset{R^1}{\underset{R^2}{Si}}\right)_x \left(\overset{R^3}{\underset{R^4}{Si}}\right)_y \right]_n \qquad (10)$$

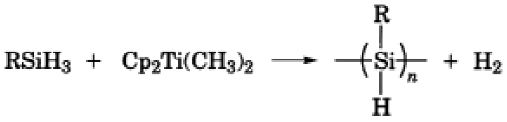
One of the constraints of this method is that only a limited number of functional substituents can be introduced because of the high reactivity of the alkali metal used in the coupling process. Despite this, a large number of homo- and copolymers have been made just from alkyl/aryl-substituted dichlorosilanes. Some polymers and copolymers containing heteroatoms, as well as fluorinated polymers, have also been reported (94–97). The sodium-coupling process is an extremely complex heterogeneous reaction, with profound effects on such properties as polymer yield, molecular weight, polydispersity, and the like brought about by the order of metal and chlorosilane addition, the nature of the alkali metal, the polar or nonpolar nature of the solvent used, the reaction temperature, polar additives used, and a number of other factors. Studies of these issues have been reviewed (94). An earlier article, though much smaller in scope, provides a very precise and comprehensible summary of the chemistry, properties, and potential applications of polysilanes (98).

In general, the sodium coupling reaction (often carried out in a refluxing hydrocarbon, such as toluene) produces a mixture of polymer, oligomers, and cyclic species, with polymer yields in the low to moderate range. The polymer molecular weight distribution is often bimodal or trimodal and broad, but this process produces high molecular weight material (average $M_{\mathrm{w}}$ can be as high as several million) that is not yet accessible via other routes. Polar solvents such as tetrahydrofuran as well as diethyl ether (99) and additives such as diglyme, crown ethers (100), and, more recently, ethyl acetate (101) have been shown to provide increased yields of polymers with lower polydispersity and unimodal distribution, although depending on specific conditions molecular weights can be significantly lower. Ultrasound has also been used to improve polymer yields (94, 102).

The mechanism of the polycondensation reaction remains unclear. A variety of possible reactive intermediates have been suggested, including silyl radicals and silyl anions. An anionic propagation mechanism (100, 101, 103) has been strongly suggested, although the case is by no means settled (104).

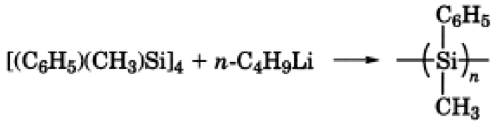
### *3.1.2. Other Synthetic Methods*

*3.1.2.1. Dehydrogenative Coupling.* Transition-metal catalyzed polymerization of silanes appears to hold promise as a viable route to polysilanes. A number of transition-metal complexes have been investigated, with titanium and zirconium complexes being the most promising (105–108). Only primary silanes are active toward polymerization, and molecular weights are rather low. The dehydrogenative polymerization is depicted in reaction **11**, where Cp = cyclopentadienyl:



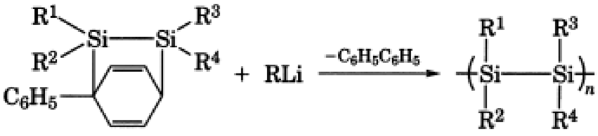
$$\mathrm{RSiH_3} + \mathrm{Cp_2Ti(CH_3)_2} \longrightarrow -\!\left(\overset{\mathrm{R}}{\underset{\mathrm{H}}{\mathrm{Si}}}\right)_{\!n}\!- + \mathrm{H_2} \qquad (11)$$

*3.1.2.2. Ring-Opening Polymerization.* As with most other inorganic polymers, ring-opening polymerization of cyclotetrasilanes has been used to make polysilanes (109, 110). This method, however, has so far only been used for polymethylphenylsilane (eq. **12**). Molecular weights (up to 100,000) are higher than from transition-metal catalyzed polymerization of primary silanes.



$$[(\mathrm{C_6H_5})(\mathrm{CH_3})\mathrm{Si}]_4 + n\text{-}\mathrm{C_4H_9Li} \longrightarrow -\!\left(\overset{\mathrm{C_6H_5}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\right)_{\!n}\!- \qquad (12)$$

*3.1.2.3. Polymerization of Masked Disilenes.* A novel approach, namely, the anionic polymerization of masked disilenes, has been used to synthesize a number of poly(dialkylsilanes) as well as the first dialkylamino substituted polysilanes (eq. **13**) (111, 112). The route is capable of providing monodisperse polymers with relatively high molecular weight ($\overline{M}_n = 10^4 - 10^5$), and holds promise of being a good method for the synthesis of alternating and block copolymers.



(13)

*3.1.2.4. Electrochemical Synthesis.* Electrochemical methods have also been investigated for the synthesis of polysilanes, but these have so far yielded low molecular weight materials (113, 114).

*3.1.2.5. Polymer Modification.* The introduction of functional groups on polysilanes using the alkali metal coupling of dichlorosilanes is extremely difficult to achieve. Some polymers and copolymers with 2-(3-cyclohexenyl)ethyl substituents on silicon have been made, and these undergo hydrogen halide addition to the carbon–carbon double bond (94, 98).

An easier approach to functionalizing polysilanes utilizes the ready cleavage of phenyl groups from silicon in polymethylphenylsilane using a strong acid such as HCl or, better, triflic acid (98, 115, 116). The resulting polymers containing Si—Cl or Si—triflate linkages can then be used as electrophilic substrates for attaching various functional groups to silicon.

The functionalization of poly(phenylsilane) [99936-07-9] by reaction with $CCl_4$ and with $CBr_4$ has also been reported (117). This yields polymers containing Si—Cl or Si—Br bonds, but leaves the Si—$C_6H_6$ bonds intact.

### 3.2. Properties

As with many polymer systems, the properties of polysilanes vary considerably depending on the nature of the substituents on the silicon atoms in the backbone. Polymers symmetrically substituted with the smallest alkyl groups are highly crystalline and, therefore, insoluble. This is also true of poly(diarylsilanes), unless crystallinity is disrupted by the introduction of appropriate substituents on the ring (118, 119). However, most unsymmetrically substituted dialkyl and alkyl/aryl homopolymers as well as copolymers are soluble in solvents such as tetrahydrofuran or toluene. The longer Si—Si bond length, compared with the C—C bond length, allows quite a bit of flexibility in the backbone such that glass-transition temperatures as low as 76°C (for poly(*n*-hexylmethylsilane)), have been observed. On the other hand, as expected, aryl substitution brings about significant increases in $T_g$. Thus polysilanes cover the range from rubbery elastomers to brittle solids. Thermal stability studies on polysilanes have not been carried out in any systematic fashion, but most polymers start to degrade in the temperature range 250–300°C (94).

Polysilanes are chemically inert to air and water at ordinary temperature, but their reactivity increases in solvent. In a solvent such as tetrahydrofuran, degradation of the Si—Si backbone by strong bases is quite rapid. Strong oxidizing agents like *m*-chloroperbenzoic acid insert oxygen atoms between the silicons to produce Si—O—Si linkages in the backbone (120).

#### *3.2.1. Electronic Properties*

What distinguishes polysilanes from virtually all other polymers is their backbone $\sigma$-conjugation. This leads to strong electronic absorption in the near-uv from a $\sigma$–$\sigma*$ transition. For most homo- and copolymers the absorption maximum ($\lambda_{max}$) lies between 300 and 400 nm. Dialkyl substituted polymers absorb in the 300–325 nm range in solution (94). A fluoroalkyl polymer with a shorter wavelength absorption at 285 nm has been reported (96). Aryl/alkyl and diaryl substituted homo- and copolymers, on the other hand, absorb between 330 and 400 nm. The lowering of transition energy with aryl substituents has been attributed to the mixing of aryl-$\pi$ and SiSi-$\sigma$ orbitals (94, 98). Both the absorption maximum and the extinction coefficient (per Si—Si bond) increase till the chain length reaches about 40–50 silicon atoms (94). Some representative uv absorption data are provided in Table 2. Many polysilane homopolymers exhibit thermochromism (as well as piezochromism) in

**Table 2. Ultraviolet Absorption of Polysilanes in Solution**

| Polymer | CAS Registry Number | $\lambda_{max}$, nm |
|---|---|---|
| $(n\text{-}C_3H_7SiCH_3)_n$ | [109926 – 38 – 7] | 306 |
| $(n\text{-}C_6H_{13}SiCH_3)_n$ | [88002 – 83 – 9] | 306 |
| (cyclohexyl $SiCH_3)_n$ | [88002 – 85 – 1] | 326 |
| $(n\text{-}C_{12}H_{25}SiCH_3)_n$ | [88002 – 84 – 0] | 309 |
| $(CF_3CH_2CH_2SiCH_3)_n$ | [31324 – 76 – 2] | 285 |
| $[(n\text{-}C_4H_9)_2Si]_n$ | [97036 – 65 – 2] | 314 |
| $[(n\text{-}C_6H_{13})_2Si]_n$ | [97036 – 67 – 4] | 317 |
| $[(n\text{-}C_{10}H_{21})_2Si]_n$ | [117652 – 57 – 0] | 324 |
| $(C_6H_5SiCH_3)_n$ | [76188 – 55 – 1] | 335 |
| $(CH_3O{-}C_6H_4{-}SiCH_3)_n$ | [97464 – 14 – 7] | 337 |
| $[(CH_3)_2N{-}C_6H_4{-}SiCH_3]_n$ | [122644 – 41 – 1] | 361 |
| $[(n\text{-}C_4H_9{-}C_6H_4{-})_2Si]_n$ | [111939 – 58 – 3] | 395 |
| $\{[(n\text{-}C_6H_{13})_2Si]_{1.17}[(CH_3)_2Si]_1\}_n$ | [118338 – 24 – 2] | 310 |
| $\{[(CH_3)_2Si]_{1.13}[(C_6H_5)_2Si]_1\}_n$ | [70926 – 75 – 9] | 351 |

their electronic absorption behavior (94, 98, 121, 122), both in solution and in the solid state (see Chromogenic materials). Significant red shifts are often observed in variable temperature uv spectra of the polymers. This lowering of transition energy has been attributed primarily to increases in the trans arrangement of the Si—Si bonds in the backbone at lower temperature, although other structural factors are also thought to be involved. Understanding of the dependence of electronic transition in polysilanes on conformation of the backbone as well as on intra- and intermolecular forces is still evolving (123).

The polysilanes are normally electrical insulators, but on doping with $AsF_5$ or $SbF_5$ they exhibit electrical conductivity up to the levels of good semiconductors (qv) (98, 124). Conductivities up to 0.5 $(\Omega\cdot cm)^{-1}$ have been measured. However, the doped polymers are sensitive to air and moisture thereby making them unattractive for practical use. In addition to semiconducting behavior, polysilanes exhibit photoconductivity and appear suitable for electrophotography (qv) (125–127). Polysilanes have also been found to exhibit nonlinear optical properties (94, 128).

Polysilanes absorb electromagnetic energy and undergo chain scission (94, 98, 129). This is an extremely important property of these polymers in terms of applications. Photochemistry is exhibited both in solution and in the solid state. The quantum yields for photoscission in solution are quite high, ranging from 0.5 to 1.0. Some cross-linking is observed with aryl-substituted polymers, but even with these scission predominates. During irradiation (for example, with 254-nm photons), the absorption maximum for a polymer is gradually blue shifted and decreases in intensity due to breakdown of the polymer into fragments with increasingly smaller catenation, with a corresponding decrease in backbone $\sigma$-conjugation. This has been termed photobleaching and is a key characteristic of polysilanes for microlithographic applications. Photolysis also occurs with uv photons of wavelength over 300 nm.

## 3.3. Applications

### *3.3.1. Manufacture of β-Silicon Carbide*

A commercially utilized application of polysilanes is the conversion of some homopolymers and copolymers to silicon carbide (130). For example, polydimethylsilane is converted to the ceramic in a series of thermal processing steps. Silicon carbide fibers is commercialized by the Nippon Carbon Co. under the trade name Nicalon (see Refractory fibers).

### 3.3.2. Microlithography, Xerography

Because of their photosensitivity, polysilanes are under intense investigation for use as positive photoresist materials (94) (see Lithographic resists). They are particularly attractive because both wet and dry development techniques can be used for imaging (131, 132). The use of polysilanes for xeroprinting has been reported (133). Thermal and optical sensors based on the photodegradation of polysilanes have been developed (134).

### 3.3.3. Photoinitiation

Since photolysis of polysilanes generates silyl radicals, which can add to carbon–carbon double bonds, these polymers have been used for the free-radical polymerization of unsaturated organic monomers (135, 136). Though about one-tenth as efficient as other organic photoinitiators, polysilanes are nevertheless quite insensitive to oxygen effects, which somewhat compensates for their lower efficiency.

## 4. Polygermanes

Soluble and well-characterized polygermane homopolymers, $(R_2Ge)_n$, and their copolymers with polysilanes have been prepared by the alkali metal coupling of diorgano-substituted dihalogermanes (137–139), via electrochemical methods (140), and by transition-metal catalyzed routes (105), as with the synthesis of polysilanes.

The polygermanes exhibit many of the same electronic properties as polysilanes, including near-uv photoabsorption, thermochromism, photobleaching, as well as nonlinear optical activity, and have seen a fair amount of theoretical and experimental investigation (137, 138, 141–143). However, despite similarities with polysilanes, polygermanes appear to be unlikely candidates for commercial exploitation, mainly because of higher monomer costs for germanium compounds and the lack of clear superiority over polysilanes in any area of application sufficient to offset the cost disadvantage.

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