

1 Inorganic Polymers: Problems and Prospects

1.1 Introduction

One of the indicators of the progress of human civilization is the type of materials that are accessible to society. Just as the Metal (Bronze and Iron) Age marked the beginning of a new chapter of human civilization at the end of the Stone Age, the advent of organic polymers in the last century has heralded a new era. Conventional materials such as iron, steel, wood, glass or ceramics are today being either supplemented or replaced by polymeric materials. From commonplace and routine (elastomers, fibers, thermoplastics) to special and high technology applications (electronic, electrical, optical, biological) polymers are being increasingly utilized. This dramatic impact of polymers has become possible because of two important factors. Firstly, the intrinsic versatility of carbon to form bonds to itself and to other hetero atoms such as oxygen, nitrogen or sulfur has enabled the extension of the principles of organic chemistry to polymer synthesis. This methodology has allowed the assembly of a large variety of polymers that possess varying properties which can fulfill wide and diverse needs. Secondly, the accessibility of inexpensive petroleum feed stocks from the beginning of the last century has allowed a large-scale availability of the building blocks of polymer synthesis and this in turn has helped the mass production of polymeric materials. From exotic laboratory materials polymers have become bulk commodities [1-3].

In spite of such wide-ranging applications and ubiquitous presence carbon-based polymeric materials probably do not have the capability to fulfill *all* the demands and needs of new applications [2]. For example, many organic polymers are not suitable for applications at extreme temperatures. Typically, at very low temperatures they become very brittle while at high temperatures they are oxidatively degraded. Also, most organic polymers are a fire hazard because of their excellent flammability properties. Most often it is required to blend fire-retardant additives to organic polymers to make them less hazardous with respect to inflammability. Another impor-

tant limitation is that the petroleum feed stocks are not going to last for ever. Clearly this stock is going to run out fairly quickly given the rate of its consumption. Even if one considers that coal reserves are much larger and hence may provide the necessary basis for the continuation of the organic polymers there is going to be a need for supplementing these conventional systems with polymers that contain inorganic elements. It is to be noted that silicon is the second most widely present element in the earth's crust (27.2 % by weight), while carbon ranks seventeenth in the order of abundance (180 ppm). If one takes into account the presence of carbon in oceans and atmosphere also, its abundance goes up to the fourteenth position [4]. Thus, it makes chemical sense to look for alternative polymeric systems based on non-carbon backbones. Lastly, another compelling reason to look for newer polymeric systems containing inorganic elements is the line of thinking that if organic polymers themselves are so diverse in terms of their structure and property, it should be possible to find entirely new types of polymeric systems with completely different properties in some combination of inorganic elements. These are a few reasons that have motivated research scientists across the world to find ways of assembling new types of polymers that are based on inorganic elements [5-9]. It must be stated at the outset that most of these efforts have resulted in polymers which not only contain inorganic elements but also have organic groups either as side groups or in the main-chain itself. While there are some examples of *pure inorganic polymers* they still remain *rare*. In order to appreciate the problems of inorganic polymer synthesis it is worthwhile to briefly examine the synthesis of organic polymers. A more detailed survey of organic polymer synthesis is presented in Chap. 2.

1.2 Procedures for Synthesizing Organic Polymers

Most organic polymers can be synthesized by using any of the following three general synthetic methods: (1) Polymerization of unsaturated organic monomers. (2) Condensation of (usually) two difunctional monomers with each other. (3) Ring-opening polymerization of cyclic organic rings to linear chain polymers [1-3].

Vinyl monomers such as $\text{CH}_2=\text{CH}_2$ (and others such as $\text{CF}_2=\text{CF}_2$), mono substituted ethylenes $\text{CH}_2=\text{CH}(\text{R})$ (such as propylene, styrene, vinyl chloride, acrylonitrile, methyl methacrylate, etc.), some disubstituted olefins $\text{CH}_2=\text{CRR}'$ (such as isobutylene), dienes (such as 1,3-butadiene, isoprene) and also monomers such as acetylene can be polymerized by various polymerization methods to afford linear chain polymers. In all of these po-

lymerization reactions two new C-C single bonds are created in place of one C=C double bond. This process is thermodynamically favorable. Representative examples of polymers that have been synthesized by this method are shown in Fig. 1.1.

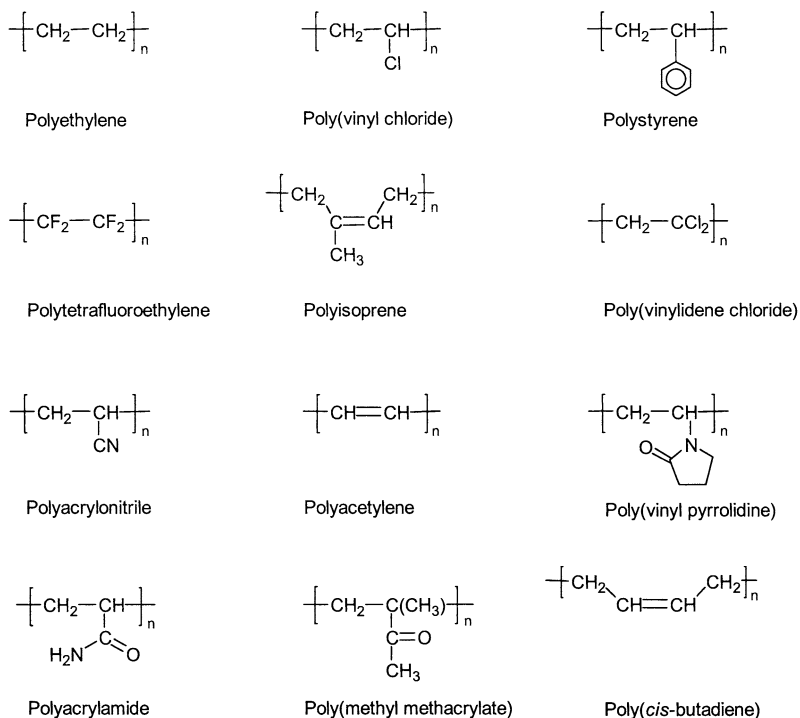
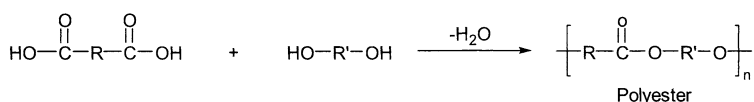
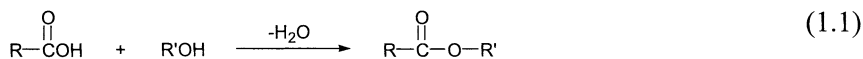


Fig. 1.1. Representative examples of organic polymers prepared from unsaturated organic monomers

The second method of obtaining organic polymers involves the exploitation of functional group chemistry of organic molecules. Thus, for example the reaction of a carboxylic acid with an alcohol affords an *ester*. Instead of condensing two mono functional derivatives in reacting two difunctional compounds (dicarboxylic acids and diols) one obtains a *polyester* (see Eq. 1.1).



This methodology is quite general and can be utilized to prepare several types of polymers such as polyamides, polyimides, polyurethanes, polyethers etc. The polymer properties depend on the type of functional groups that link the polymer building blocks. Further modulation is achievable by varying the nature of the difunctional monomer within each class of polymers. It is not always necessary to condense two difunctional monomers. Some polymers such as polyethers are prepared by the oxidative coupling of the corresponding phenols. A few examples of polymers that can be prepared by the condensation reactions are shown in Fig. 1.2.

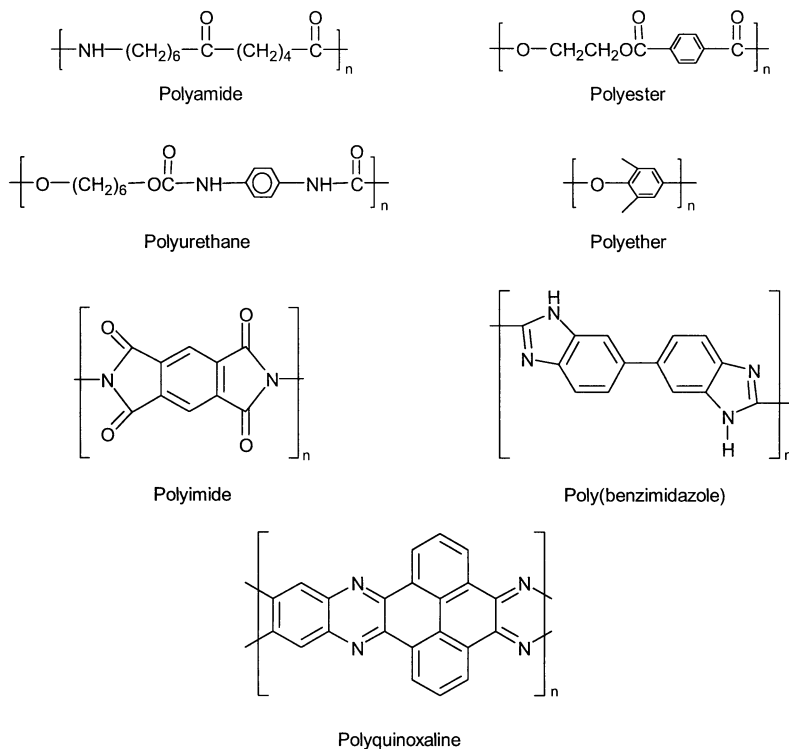


Fig. 1.2. Polymers prepared from the condensation reactions of organic monomers

The third method of polymer preparation involves a ring-opening polymerization (ROP) of cyclic monomers to polymeric chains. Thus, monomers such as ethylene oxide, propylene oxide or even tetrahydrofuran can be used as monomers for ROP. Cyclic amides (lactams) and cyclic esters (lactones) can also be polymerized. It is important to note that all cyclic organic compounds cannot be converted into linear chains. For example, well-known organic molecules such as benzene, cyclohexane, dioxane, tetrahydropyran etc., cannot be polymerized to the corresponding

polymers. Some examples of organic polymers that can be obtained by ROP are shown in Fig. 1.3.

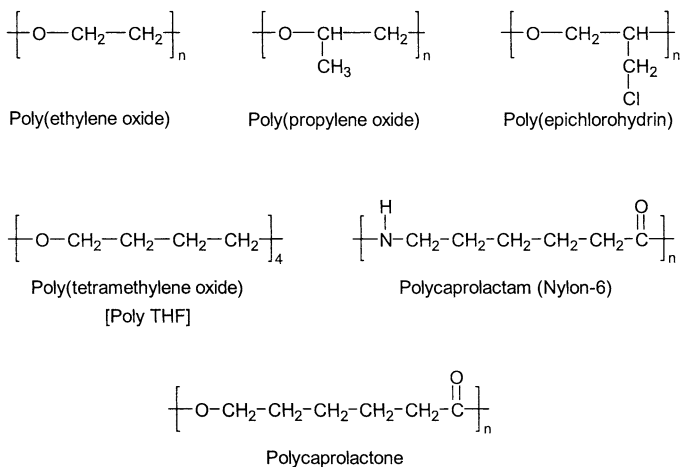


Fig. 1.3. Polymers prepared by the ring-opening polymerization of cyclic organic monomers

1.3 Inorganic Polymers: A Review of Synthetic Strategies

In light of the previous discussion on the synthesis of organic polymers we can now look at the strategies that would be needed for assembling inorganic polymers. It must be borne in mind that many inorganic compounds such as inorganic oxides (for example, SiO_2 , B_2O_3 , Al_2O_3 etc.,) or inorganic nitrides (for example, Si_3N_4 , BN etc.,) are technically polymeric substances which are built from simple structural blocks [4]. However, substances of this type are not considered in this discussion. Only inorganic polymeric substances that are analogous in terms of their solution behavior to organic polymers are considered. Thus, most organic polymers are soluble in some kind of organic solvents (some such as Kevlar are soluble in mineral acids) and more importantly they retain their macromolecular structure in solution. Further, many organic polymers retain their properties upon melting. These properties are possible because of the essentially covalent linkages that are present in these organic polymer chains. Inorganic polymer synthesis needs to address the issue of formation of covalent bonds between similar or dissimilar inorganic elements so that polymeric structures are realized. As will be shown in subsequent sections such element-element linkages can be accomplished in many ways.

1.3.1 Unsaturated Inorganic Compounds

We will first look at the possibility of utilizing inorganic compounds that contain double or triple bonds between them, as monomers for organic synthesis. In order to keep the discussion simple we can limit ourselves by looking at such compounds belonging to the elements of Groups 14 and 15. Thus, the silicon analogue of ethylene is $\text{H}_2\text{Si}=\text{SiH}_2$. Even before we consider this compound it is worthwhile to note that many silicon analogues of alkanes viz., $\text{Si}_n\text{H}_{2n+2}$ have been prepared by the German chemist Alfred Stock [4]. He noted that these silanes were extremely reactive and burnt spontaneously in air. In fact, Stock had to develop hitherto unknown vacuum-line techniques for handling such pyrophoric compounds. From this reactivity behavior it is anticipated that the corresponding silicon analogues of ethylene in particular and other olefins in general would be extremely reactive. For a long time compounds of silicon that contain double bonds between them could not be prepared and either cyclic- or oligomeric compounds, (or in some instances even some polymeric products) were the result of such investigations [10]. Similarly, it was not possible to isolate compounds of other main-group elements which contain double bonds between them. Several such failures have led to the *promulgation* of a *double-bond rule*. This stated that heavier main-group compounds containing double bonds cannot be prepared. The rationale for this rule emanates from two possible reasons. Heavier main-group elements are larger in size and hence their inter-atomic distances are also longer (in comparison to carbon). Consequently, the additional *p*-orbital overlap between heavier main-group elements to generate a double bond would be quite weak. The double-bond rule held its own for a long time until its demise in 1981. In this year the double bond rule was firmly thrown out and a series of main group compounds containing double bonds were isolated and characterized [10-11]. The synthetic technique that contributed to this success was the utilization of sterically hindered groups for kinetically stabilizing these reactive compounds. The idea was to use large-sized substituents to *sterically protect* the double bonds once they were formed. Using this methodology stable compounds containing $\text{Si}=\text{C}$, $\text{Si}=\text{Si}$, $\text{P}=\text{C}$, $\text{P}=\text{P}$, $\text{P}=\text{As}$, $\text{Sb}=\text{Sb}$ and even $\text{Bi}=\text{Bi}$ double bonds were synthesized and characterized [12] (Fig. 1.4). It can be seen that the size of the sterically hindered group increases with the increase in the size of the main-group element. Although, the problem of preparing multiple-bonded compounds containing heavy main-group elements was thus solved, the very method of stabilizing these compounds defeats the possibility of using them as monomers for polymer synthesis. For example, it was found that the *in situ* generated disilene

$i\text{Pr}_2\text{Si}=\text{Si}i\text{Pr}_2$ undergoes spontaneous oligomerization to the cyclic tetramer $[i\text{Pr}_2\text{Si}]_4$ (see Eq. 1.2) [13].

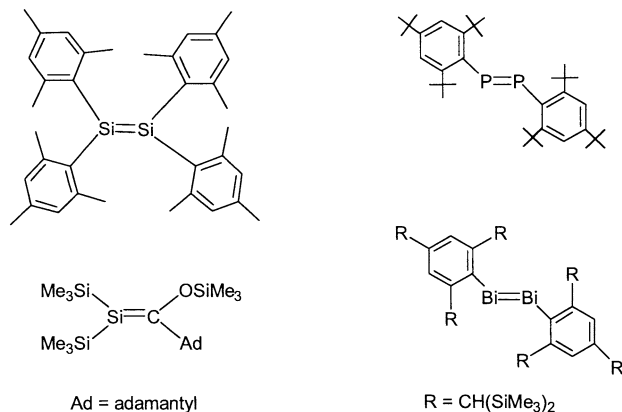
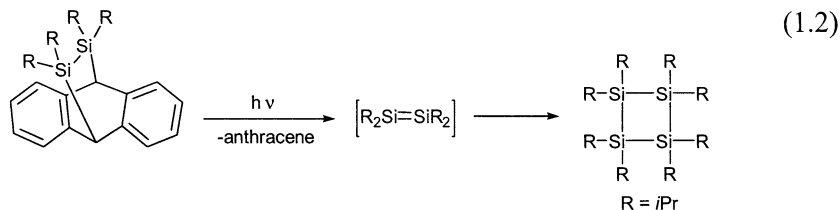


Fig. 1.4. Compounds of main-group elements that contain double bonds between them



Unsaturated organic compounds such as olefins also are reactive; however, their reactivity can be suitably directed to afford various kinds of products including polymers. Manipulating the reactivity of the newly discovered *unsaturated* inorganic compounds, to afford polymeric products still remains a synthetic challenge. Recently it was observed that $\text{MesP}=\text{CPh}_2$ could be polymerized by either radical or ionic initiators to afford moderate molecular weight polymers, $[\text{MesPCPh}_2]_n$ (Mes = 2,4,6-Me₃-C₆H₂-) [14].

1.3.2 Inorganic Polymers from Acyclic Monomers

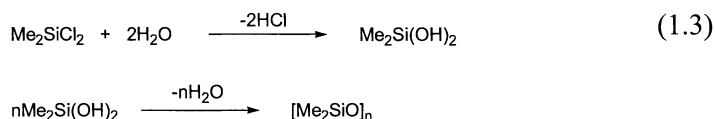
Various types of polymerization reactions involving appropriate *inorganic acyclic monomers* have been quite effectively utilized for the preparation of polymers containing inorganic elements or inorganic groups. Some of

these examples are illustrated in this section. These polymerization strategies are of two types.

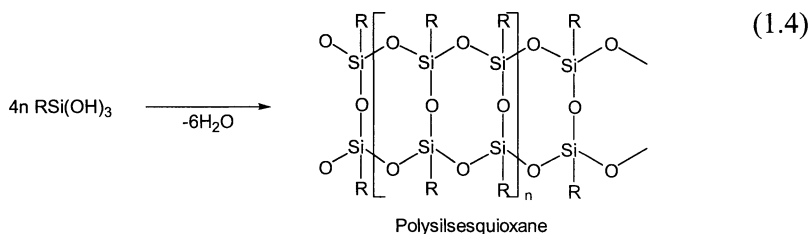
1. A reaction where a *small molecule* is eliminated from a *single monomer* to generate the polymer.
2. A reaction between *two appropriate difunctional monomers* to eliminate a small molecule and afford a polymeric material.

1.3.2.1 Polymer Synthesis from a Single Monomer

Various types of reactions have been used for the synthesis of polymers starting from a *single monomer*. Thus, for example, *dehydration* of diorganosilane diols affords the corresponding polymeric organosiloxanes. The most widely known inorganic polymer viz., poly(dimethylsiloxane), $[\text{Me}_2\text{SiO}]_n$, can be prepared in this manner (other routes for the synthesis of this polymer are also known) [15-17]. Although the reaction involved in the synthesis of poly(dimethylsiloxane) is the hydrolysis of dimethyldichlorosilane, the immediate product of the reaction is $\text{Me}_2\text{Si}(\text{OH})_2$ which is the actual monomer that undergoes self condensation by the elimination of water. This process of dehydration leads to the formation of $[\text{Me}_2\text{SiO}]_n$ (see Eq. 1.3).

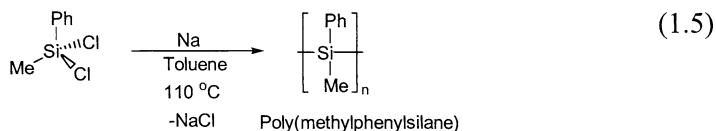


The dehydration reaction has also been used to prepare ladder-type polymers. Thus, the hydrolysis of PhSiCl_3 affords $\text{PhSi}(\text{OH})_3$ which undergoes a self condensation reaction to generate a ladder-like polymer which is known as polysilsesquioxane (see Eq. 1.4) [15, 16].

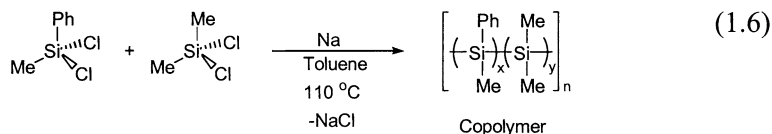


Metal-assisted *dehalogenation* reaction, analogous to the well-known Wurtz reaction has been very effectively employed for the preparation of polysilanes which contain catenated organosilicon units. Thus, the reaction of a variety of diorganodichlorosilanes with finely divided sodium in a

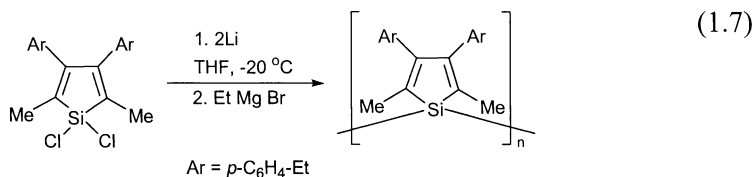
high boiling solvent such as toluene affords the corresponding polysilanes. The reaction involves elimination of sodium chloride. The yields of polysilanes vary from being low to moderate. For example, the reaction of phenylmethyldichlorosilane with sodium affords poly(methylphenylsilane) (see Eq. 1.5) [17-19]. This approach has been used for preparing many poly(dialkylsilane)s as well as poly(diarylsilane)s. Polysilanes containing mixed substituents have also been successfully assembled from this approach [19]. However, the Wurtz-type coupling reaction is not tolerant of reactive groups (such as halogens or the hydroxyl groups).



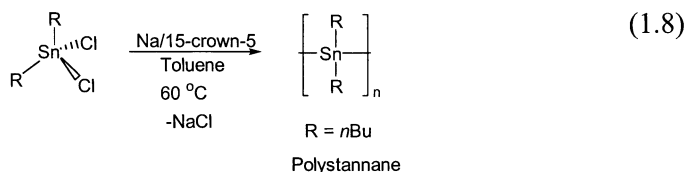
Wurtz-coupling has also been successfully employed for the preparation of a number of copolymers of polysilanes. For example, reacting a 1:1 mixture of phenylmethyldichlorosilane and dimethyldichlorosilane with molten sodium in toluene affords a high-molecular-weight copolymer containing a random arrangement of [PhMeSi] and [Me₂Si] units (see Eq. 1.6) [19]. A remarkable feature of the polysilanes is the presence of σ -conjugation in their backbone. Many of these polymers, consequently, are being increasingly investigated for novel electronic applications. Another interesting feature of polysilanes is their sensitivity to light. Thus, many polysilanes undergo photoscission upon exposure to light. This radiation sensitivity is far greater in solution than in the solid-state. Although this might at first sight sound detrimental for any applications, this property of photobleaching allows these polymers to be used as photoresists for micro-lithography [19].



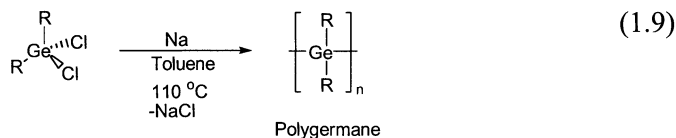
The dehalogenation reaction has also been used for preparing unusual polymers that contain the Si-Si σ -bonds in conjugation with an organic π -system. Thus, reaction of dichlorosiloles with lithium metal results in the formation of 1,1'-polysiloles (see Eq. 1.7) [20, 21]. Every silicon in these polymers is also a part of a five-membered unsaturated heterocyclic ring.



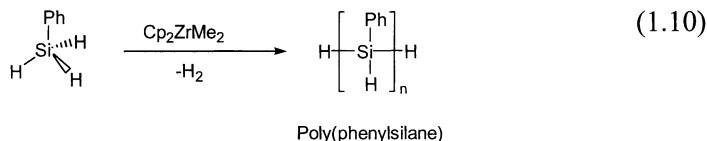
A high-molecular-weight *polystannane* was also prepared by using the dehalogenation reaction [22]. Di-*n*-butyltindichloride undergoes a dechlorination upon reaction with sodium metal in toluene. 15-Crown-5-ether was used as a structure-specific sequestering agent for sodium ions. It was found that the optimum reaction temperature for obtaining a high-molecular-weight polystannane, $[\text{R}_2\text{Sn}]_n$ was about 60 °C (see Eq. 1.8). Polystannanes are extremely sensitive to light and photo-bleach rapidly to form low-molecular-weight compounds. This can cause difficulties in synthesis unless precaution is taken to avoid light during the reaction and the subsequent work-up.



Similar to polystannanes a number of poly(dialkylgermane)s have also been prepared by the Wurtz-type coupling reaction (see Eq. 1.9) [23, 24].



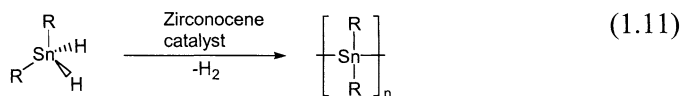
Catalytic dehydrogenation is an alternative method for the preparation of polysilanes. This reaction involves the dehydrogenation of RSiH_3 to afford polysilanes of the type $[\text{RSiH}]_n$ (see Eq. 1.10).



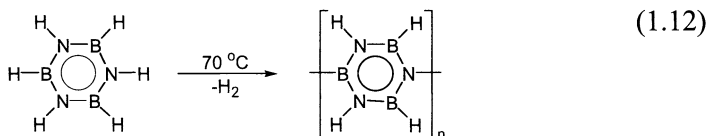
The dehydrogenation reaction is catalyzed by many types of organometallic complexes of titanium or zirconium [25]. The molecular

weights of the polysilanes obtained by dehydrogenation reactions are lower than those obtained by the Wurtz-type dehalogenation method. Another limitation of this methodology is that it seems to be applicable to only arylsilanes; many alkyl silanes with the exception of CH_3SiH_3 , are quite unresponsive towards this reaction. Secondly, this method is not very effective for preparing polysilanes of the type $[\text{RR}'\text{Si}]_n$. However, polysilanes prepared by the dehydrogenation reaction contain a reactive Si-H group that can be used for further elaboration involving hydrosilylation reactions.

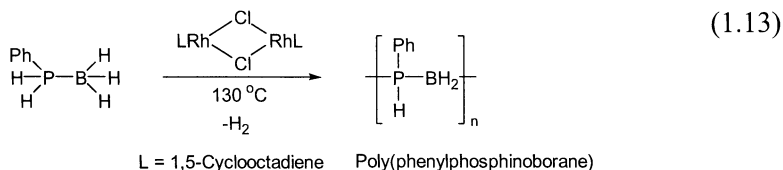
Catalytic dehydrogenation reactions have also been used for the preparation of polystannanes. Unlike polysilanes, polystannanes of the type $[\text{R}_2\text{Sn}]_n$ can be prepared by this method. Thus, the dehydrogenation of dialkyltindihydrides, R_2SnH_2 , by zirconocene catalysts provides a good route for the preparation of high-molecular-weight polystannanes, $\text{H}(\text{SnR}_2)_n\text{H}$ (see Eq. 1.11) [26]. These polymers contain reactive terminal Sn-H groups.



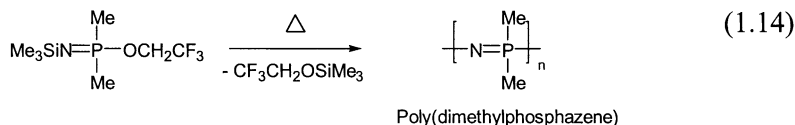
Heating the inorganic heterocyclic ring $\text{B}_3\text{N}_3\text{H}_6$ leads to the loss of hydrogen to afford a polymer where the borazine rings are interconnected with each other [27] (see Eq. 1.12). These types of polymers have been found to be useful as precursors for the preparation of the ceramic boron nitride.



Polyphosphinoboranes containing phosphorus and boron linked to each other in polymeric chains have remained elusive for a long time. Recently, catalytic dehydrogenation of the phosphine-borane adducts has been found to be effective to prepare the linear polymer. Thus, thermal treatment of $\text{PhPH}_2\cdot\text{BH}_3$ in the presence of catalytic amounts of $[(1,5\text{-COD})\text{Rh}(\mu\text{-Cl})]$ affords the linear polymer poly(phenylphosphinoborane), $[\text{PhHPBH}_2]_n$ (see Eq. 1.13) [28-30]. High polymers with M_w of about 33,000 have been isolated by this procedure.

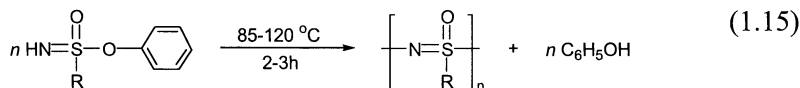


Polyphosphazenes containing alternate phosphorus and nitrogen atoms in the polymer backbone can be prepared by a variety of synthetic methods. These include condensation polymerization reactions which involve appropriate monophosphazene precursors such as $\text{Me}_3\text{SiNPRR}'\text{OR}''$. These compounds also known as *N*-silylphosphoranimines eliminate the silylether $\text{Me}_3\text{SiOR}''$, upon heating, with the formation of polymeric products. Many, poly(alkyl/arylphosphazene)s can be prepared by this procedure. For example, the preparation of poly(dimethylphosphazene) is accomplished by heating the *N*-silylphosphoranimine $\text{Me}_3\text{SiN}=\text{PMe}_2\text{-(OCH}_2\text{CF}_3)$ (see Eq. 1.14) [31, 32].

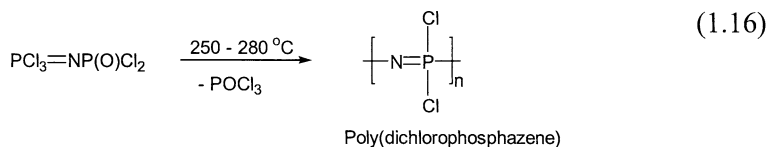


This method is fairly general and has been used for the preparation of a wide variety of high-molecular-weight poly(alkyl/arylphosphazene)s, $[\text{NPRR}']_n$ ($\text{R}, \text{R}' = \text{alkyl}; \text{R} = \text{alkyl}, \text{R}' = \text{aryl}$) [31].

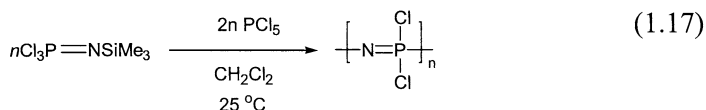
Using a similar strategy as above, poly(oxothiazene)s containing alternate sulfur and nitrogen atoms in the backbone have been prepared [33]. Elimination of silylethers from $\text{Me}_3\text{SiN}=\text{S(O)R(OR}'')$ or even phenols from $\text{HN}=\text{S(O)R(OPh)}$ leads to the formation of the high polymers (see Eq. 1.15).



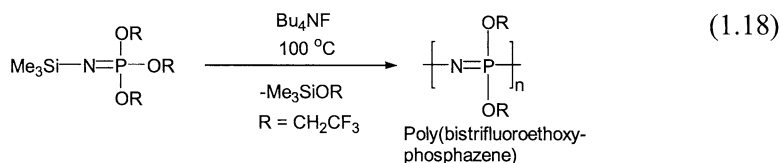
Acyclic monomers have also been found suitable for the preparation of poly(dichlorophosphazene). For example, heating the acyclic phosphazene derivative $\text{Cl}_3\text{P}=\text{N}-\text{P(O)Cl}_2$ leads to the elimination of P(O)Cl_3 as the by-product and affords the linear polymer, polydichlorophosphazene, $[\text{NPCl}_2]_n$ (see Eq. 1.16) [34].



Poly(dichlorophosphazene) has also been prepared by an ambient temperature process involving the reaction of $\text{Cl}_3\text{P}=\text{NSiMe}_3$ with PCl_5 . This process affords a high-molecular-weight *living polymer* (see Eq. 1.17) [32].

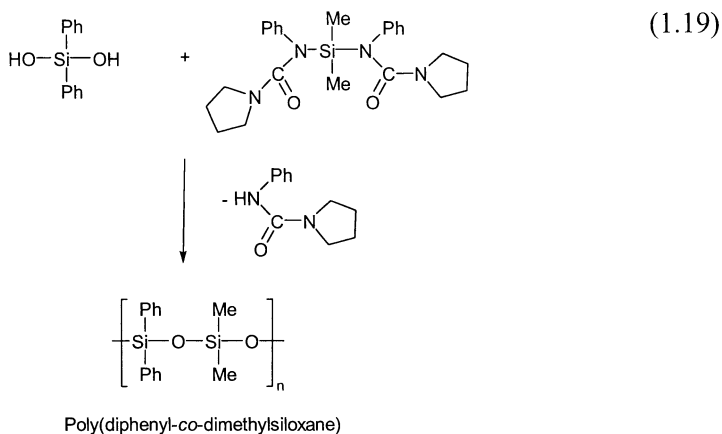


Anionic polymerization also can be used for preparing polyphosphazenes from acyclic monomers. Thus, treatment of $\text{Me}_3\text{SiNP}(\text{OCH}_2\text{CF}_3)_3$ with Bu_4NF leads to the formation of the polymer $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ (see Eq. 1.18) [32].

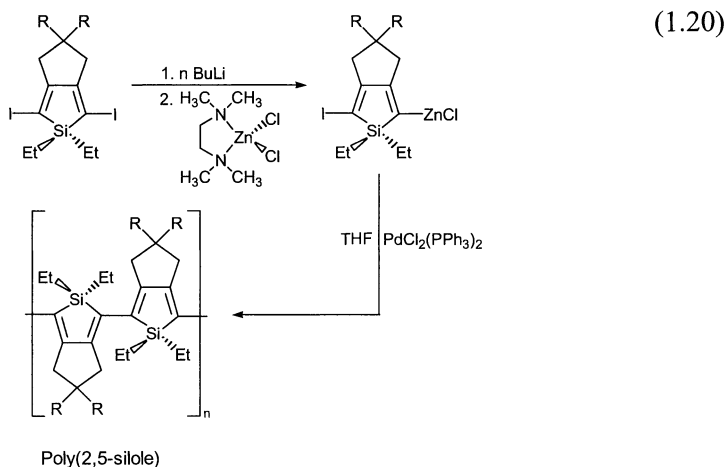


1.3.2.2 Polymer Synthesis from two Monomers

It is possible to design difunctional inorganic monomers that can react with each other to afford linear polymers. Although, in some cases these inorganic difunctional monomers are different from those encountered in organic polymer synthesis the polymerization principles are very similar. Thus, we have seen that the difunctional organic compounds involved in polymerization processes were diols, dicarboxylic acids, diamines etc. Reaction between them leads to the elimination of a small molecule (such as water, alcohol etc.) to afford long-chain macromolecules. Exact inorganic analogues containing these reactive functional groups are not always available. In many instances even if it is possible to prepare inorganic compounds containing such functional groups, they are too reactive to be used in a controlled polymerization process.



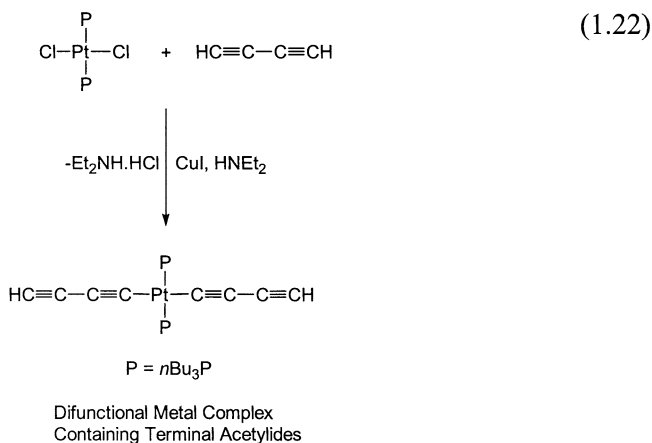
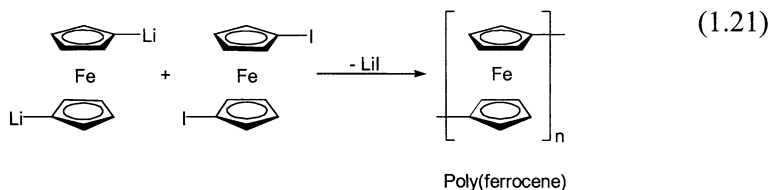
Compounds containing Si-OH and SiNR₂ are, however, known and have been employed for condensation reactions (compounds containing Si-NH₂ groups are still quite rare). However, it will be noticed that during condensation reactions between a compound containing a Si-NR₂ unit and a Si-OH unit, elimination of the amine R₂NH occurs to form a new Si-O-Si bond. For example, exactly alternating copolymers of the polysiloxane family, containing alternately Me₂SiO and Ph₂SiO units in the polymer backbone, have been prepared by the condensation of diphenylsilanediol with dimethylbis(ureido)silane. The cleavage of the weak Si-N bonds, formation of new thermodynamically favorable Si-O bonds and the elimination of urea as the insoluble by-product act as the driving force for the polymerization reaction (see Eq. 1.19) [35].



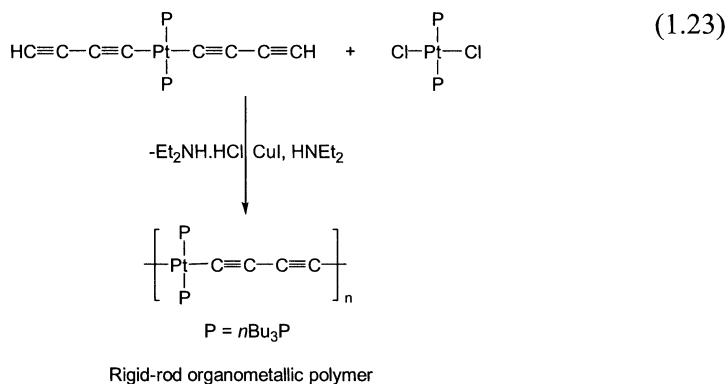
In contrast to poly(1,1'-silole)s which are prepared by the dehalogenation of the silole dichlorides, the preparation of poly(2,5-silole)s has to be carried out by a multi-step procedure (see Eq. 1.20) [36]. Thus, 2,5-diiodosilole can be selectively converted in situ to the monozinc derivative. Palladium-mediated cross-coupling reaction of the monozinc derivative affords poly(2,5-silole) which has a moderate degree of polymerization of about thirteen.

Recently, condensation polymerization has been used for preparing poly(*p*-phenylene phosphalkene) which contains P=C double bonds in the polymeric backbone. Thus, the reaction between the silylated phosphane, (Me₃Si)₂P-C₆H₄-*p*-P(SiMe₃)₂ and a diacid chloride affords an *E/Z* mixture of poly(*p*-phenylene phosphalkene) [37].

Condensation reactions have also been used to prepare poly(1,1'-ferrocenylene)s containing ferrocene units linked in a chain. Thus, the condensation of 1,1'-dilithioferrocene with 1,1'-diiodoferrocene affords a medium-molecular-weight polymer (see Eq. 1.21) [8, 38]. Condensation of alkylferrocenyldialdehydes such as [η^5 -C₅H₃RCHO]₂Fe is mediated by Zn/TiCl₄ catalysts to afford poly(ferrocenylvinylene)s. These polymers are interesting organometallic analogues of the well-known linear conjugated organic polymers such as poly(1,4-phenylenevinylene).



Organometallic polymers with a rigid-rod architecture have been prepared by using the condensation strategy involving the condensation of *trans*-Pt(*Pn*Bu₃)₂(CCCCH)₂ with *trans*-Pt(*Pn*Bu₃)₂Cl₂. This reaction is carried out in amine solvents and is catalyzed by Cu(I) salts (see Eqs. 1.22, 1.23) [39]. The monomer synthesis involves the reaction of *trans*-Pt(II)Cl₂(*n*Bu₃P)₂ with 1,3-butadiyne to afford the alkynylated metal derivative *trans*-Pt(*Pn*Bu₃)₂(CCCCH)₂ containing a M-C σ bond (see Eq. 1.22). The difunctional derivative *trans*-Pt(*Pn*Bu₃)₂(CCCCH)₂ can be coupled with Pt(II)Cl₂(*n*Bu₃P)₂ to afford linear high-molecular-weight polymers (see Eq. 1.23) [39]. These polymers have rod-like structures because of the rigidity imposed by the alkynyl groups. This type of synthetic strategy is in fact quite general and has been adapted to prepare other rigid-rod type of polymers containing transition metals such as ruthenium, nickel, cobalt etc., [8]. These types of rigid-rod polymers are often characterized by metal-to-alkyne charge transfer transitions. These polymers are also of interest from the point of view of their nonlinear optical properties.

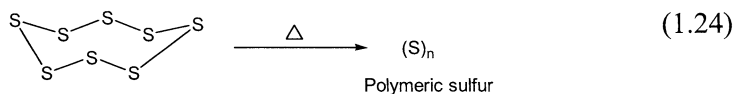


Although the condensation polymerization strategy has been employed quite successfully to prepare a number of inorganic polymers, one of the limitations of this method is the high demands on the purity of the monomer. Unless both the difunctional monomers are rigorously pure, condensation reactions do not lead to high-molecular-weight polymers.

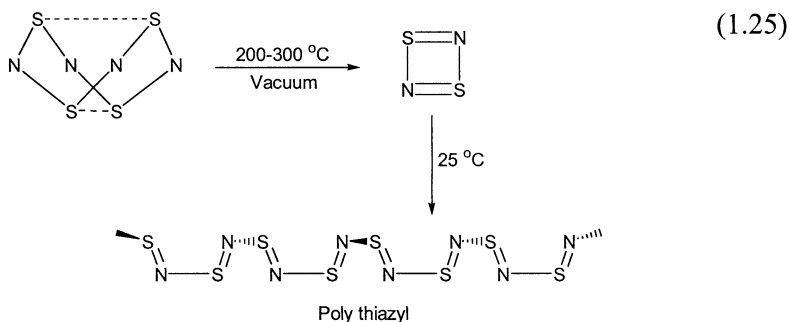
1.3.3 Ring-Opening Polymerization of Cyclic Inorganic Compounds

A number of inorganic rings can be successfully polymerized by the ROP method. The earliest example is the polymerization of rhombic sulfur. Thus, heating S₈ at about 160 °C causes its ROP to lead to the formation of

a linear polymer $(S)_n$ (see Eq. 1.24) [4,5]. This is one of the few *true* inorganic polymers. Unfortunately, polymeric sulfur, although elastomeric is not of much use because it undergoes depolymerization upon cooling to room temperature.

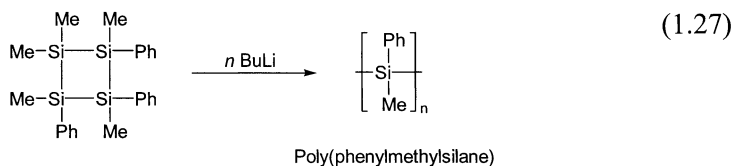
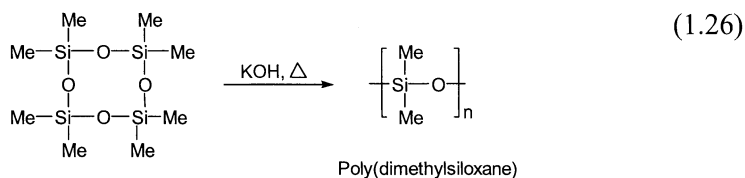


Sulfur combines with nitrogen to form several types of rings and cages that are either neutral or ionic [4]. One of the most well-known S-N cages is S_4N_4 . This compound, when heated, is converted into the four-membered ring S_2N_2 . The latter undergoes a polymerization in the solid-state to afford polythiazyl, $(SN)_n$ (see Eq. 1.25) [4, 5].



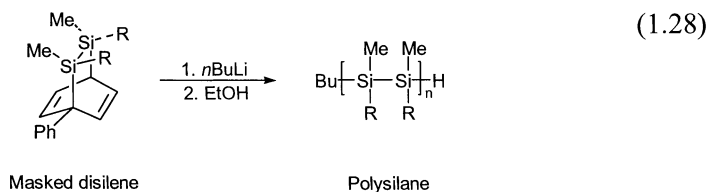
Polythiazyl, also a true inorganic polymer is not soluble in common organic solvents. However, it has attracted considerable interest because of its unusual electrical properties. Thus, $(SN)_n$ shows metal-like conductivity at room temperature and becomes a superconductor at 0.3 K [4, 5]. Although this material itself has not found any applications it has aroused considerable interest in the area of electrically conducting polymeric materials.

The inorganic siloxane rings can be polymerized by both cation and anion initiators to lead to polymeric siloxanes. Thus, for example, the octamethylcyclotetrasiloxane, $[\text{Me}_2\text{SiO}]_4$ can be polymerized by the use of KOH as an initiator to afford poly(dimethylsiloxane). The polymer $[\text{Me}_2\text{SiO}]_n$ prepared in this way has a very high molecular weight ($2-5 \times 10^6$) (see Eq. 1.26) [15-17]. Polysiloxanes are the most important family of inorganic polymers from the commercial point of view.



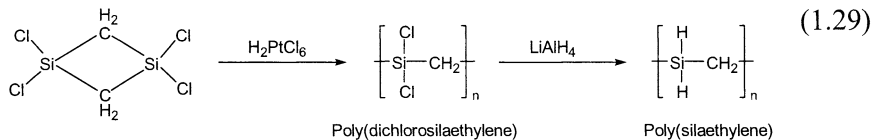
We have seen in the previous section that polysilanes, $[\text{RR}'\text{Si}]_n$ can be prepared by dehalogenation of $\text{RR}'\text{SiCl}_2$. These polymers can also be prepared by ROP of two different types of cyclic monomers. The tetrasilane $[\text{PhMeSi}]_4$ is polymerized to $[\text{PhMeSi}]_n$ by using $n\text{BuLi}$ as the initiator (see Eq. 1.27) [40].

n -Butyllithium has also been used as the initiator for polymerizing *masked disilenes*. The latter are essentially disilane compounds which can be viewed as *trapped or masked* disilenes. If the disilene is liberated from this trap it has many choices. It can form a disilene. It can cyclize or polymerize. By a careful choice of substituents on silicon it is possible to use masked disilenes as monomers for polymerization. This method of polymerization has been shown to be quite effective for the preparation of a variety of polysilanes (see Eq. 1.28) [41].

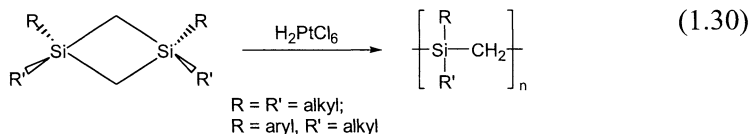


Polymers containing alternate silicon and carbon centers known as carbosilanes or silylene ethylenes have been originally prepared by the thermal rearrangement of polydimethylsilane, $[\text{Me}_2\text{Si}]_n$ [19]. More recently, these polymers have been prepared by a more rational route involving the ROP of four-membered disilacyclobutanes. Thus, the ROP of *cyclo*- $[\text{Cl}_2\text{SiCH}_2]_2$ can be carried out by using H_2PtCl_6 as the catalyst to afford the polymer poly(dichlorosilaethylene), $[\text{Cl}_2\text{SiCH}_2]_n$. It is possible to reduce the latter with LiAlH_4 to afford poly(silaethylene) $[\text{H}_2\text{SiCH}_2]_n$ (see Eq.

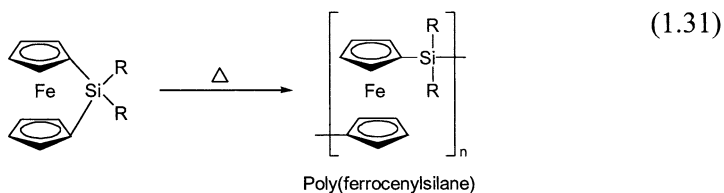
1.29) [42]. The latter can be considered as an analogue of polyethylene where every alternate CH_2 group has been replaced by a SiH_2 group.



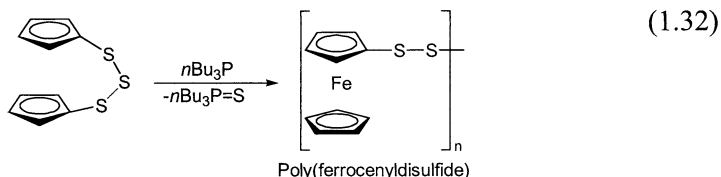
Polysilaethylenes that contain alkyl groups on the silicon can also be prepared by the H_2PtCl_6 catalyzed ring-opening polymerization of the corresponding silacyclobutanes, $[\text{RR}'\text{SiCH}_2]_2$ (see Eq. 1.30) [42].



Cyclic, silicon-bridged [1]ferrocenophanes have been found to undergo thermal ring-opening polymerization to afford high-molecular-weight poly(ferrocenylsilane)s (see Eq. 1.31) [8, 43]. Many other members of this family of polymers are now known including those where the silicon center is replaced by Sn(IV), P(III), Ge(IV), B(III) etc., [8].

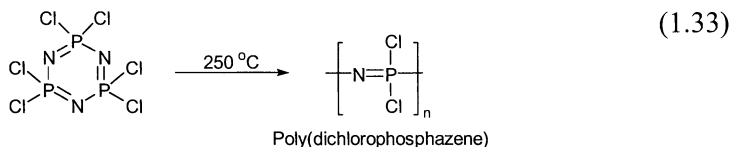


Another way of preparing ferrocenyl polymers consists of a sulfur-abstraction reaction from a ferrocene monomer where the two cyclopentadienyl units are linked by a trisulfide unit. Sulfur abstraction is brought about by the use of a tertiary phosphine which forms the corresponding phosphine sulfide and leads to a ROP (see Eq. 1.32) [44].

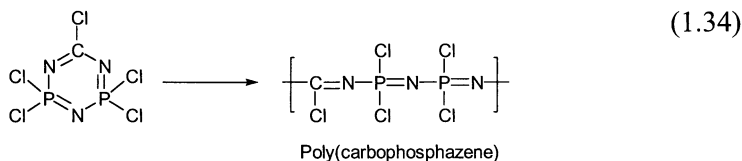


Cyclophosphazenes are a group of inorganic heterocyclic rings containing an alternate arrangement of phosphorus and nitrogen atoms [45-48].

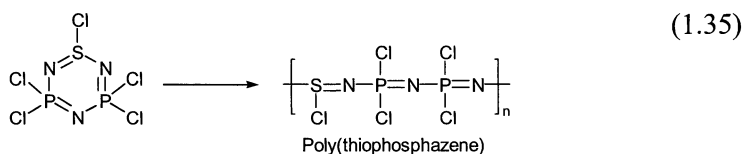
Hexachlorocyclophosphazene, $N_3P_3Cl_6$, undergoes a ring-opening polymerization at 250 °C to afford poly(dichlorophosphazene), $[NPCl_2]_n$ (see Eq. 1.33) [32, 48]. The latter is also one of the pure inorganic polymers. Although, $[NPCl_2]_n$ itself is hydrolytically sensitive, it can be used as a precursor for the preparation of a number of poly(organophosphazene)s such as $[NP(OR)_2]_n$, $[NP(NHR)_2]_n$ and $[NP(NRR')]_n$.



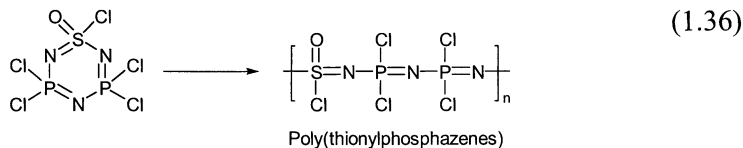
Pentachlorocarbocyclophosphazene, $N_3P_2CCl_5$, which contains a heteroatom in the form of carbon (in place of phosphorus) can also be polymerized by a thermal treatment to afford the hydrolytically sensitive poly(carbocyclophosphazene) (see Eq. 1.34) [49].



Pentachlorothiophosphazene, $N_3P_2SCl_5$, which contains a S(IV) as the heteroatom can be polymerized by the ROP to afford the linear polymer, poly(thiophosphazene) (see Eq. 1.35) [50].

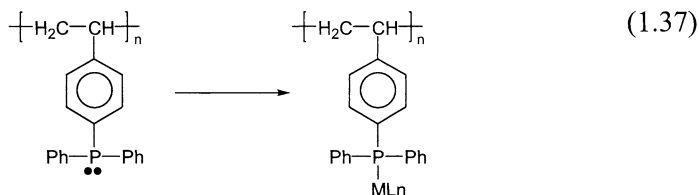


Pentachlorothionylphosphazene, $N_3P_2S(O)Cl_5$, also can be polymerized by the thermal ROP (see Eq. 1.36) [51].



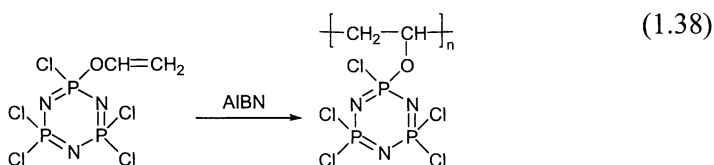
1.3.4 Polymers Containing Inorganic Rings or Motifs as Pendant Groups

Other types of polymers that contain inorganic elements or groups are those that have these units as pendant groups. These polymers contain a carbon backbone. The inorganic units are attached to the backbone as a side chain. In principle almost any inorganic compound can be designed so that it can be a side chain on an organic backbone. The most important of this type of polymer is polystyrene that contains phosphino groups suitable for coordination (see Eq. 1.37) [2, 5].

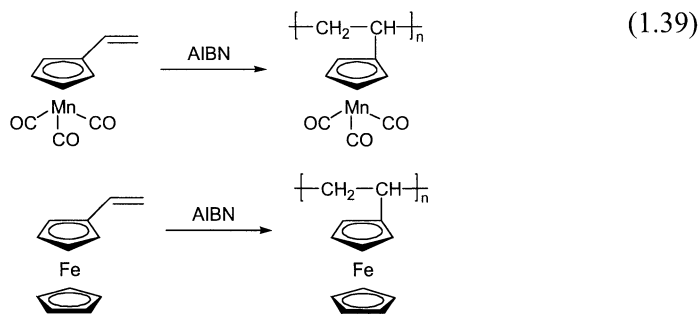


Such types of polymers, usually in their crosslinked forms have been used for interaction with transition metals. These heterogeneous metal-carrying polymers are quite valuable as catalysts for organic reactions.

The above strategy has been applied to anchor other inorganic motifs as side-chains. For example, the cyclophosphazene, $\text{N}_3\text{P}_3\text{Cl}_5(\text{OCH}=\text{CH}_2)$ can be readily polymerized by free-radical polymerization to afford a high-molecular-weight polymer which contains the inorganic heterocyclic ring as regular pendant groups (see Eq. 1.38) [52].



This methodology can also be used for preparing polymers containing organometallic side groups. Polymers containing ferrocene pendant groups have been prepared by the polymerization of ferrocenylethylene [8, 45]. Similarly polymers containing piano-stool type organometallic complexes as pendant groups can be readily prepared by adopting standard organic polymerization methods (see Eq. 1.39) [53].



1.4 Summary of Polymerization Procedures for Inorganic Polymers

In the foregoing we have seen a survey of various procedures that can be used for the preparation of inorganic polymers. Some of these methods are common to those found for the preparation of organic polymers. Some others are different. Many ring-opening polymerization methods are known that involve inorganic hetero- or homocyclic rings. Some of these ROP's are induced by thermal treatment, while some others are catalyzed by transition metal complexes. A number of polymerization methods depend on the loss of a simple molecule such as hydrogen, water, silyl ether, silyl chloride, sodium chloride, lithium iodide etc. Table 1.1 summarizes many of the major types of inorganic polymers and some of the methods utilized to prepare them. The most revealing aspect of the data presented in Table 1.1 is the large variety of inorganic polymers that are already known. The important question that needs to be addressed is as follows. Are these polymers different from organic polymers? Do they have any features that are distinct from organic polymers that make the endeavor of preparing new inorganic polymers worthwhile?

Even a preliminary investigation of the properties of some inorganic polymers reveals that some of them have unexpected properties. Polythiazyl is an anisotropic electrical conductor and shows conductivity that is comparable to metals. At 0.26 K this polymer becomes superconducting [4, 5]. Polysilanes which contain catenated silicon atoms in a polymeric chain have several unusual properties. These polymers have a σ -electron delocalization. They are radiation sensitive and many of them are thermochromic. Many members of this family also show nonlinear optical behavior [17, 19].

Polysiloxanes and polyphosphazenes are among the most flexible polymers known. Because of a combination of factors such as long skeletal bond lengths, wide angles at oxygen and poor intermolecular interaction, poly(dimethylsiloxane) shows many properties not found in organic polymers. These include hydrophobicity, high flexibility, low viscosity, good thermal stability etc., [15]. Such properties have enabled these polymers to be used in various types of applications such as high-temperature insulation, anti-foam applications, bio-transplants, drug-delivery systems, flexible elastomers, personal products etc. Similarly many poly(organophosphazene)s show low temperature flexibility. Besides, many of these polymers are fire-retardant in contrast to many organic polymers that are flammable [32].

Organometallic polymers such as poly(ferrocenylsilane)s have been shown to be precursors for new types of magnetic ceramics [9, 42]. Similarly poly(silyleneethylene)s [41] and some polysilanes are polymeric precursors for silicon carbide ceramics [19].

Thus, inorganic polymers have a unique and distinct place in the family of polymers and they have the potential to function as unique materials. In this book we will examine some of the prominent members of inorganic polymers. There are many polymer types where sufficient examples do not exist or whose synthesis has not yet been shown to be general. Some of these polymers have been alluded to in this Chapter. However, they will not be covered elsewhere in this book. Dendrimeric materials, which are not linear polymers, are also not considered here.

Table 1.1. Various kinds of inorganic polymers – summary of the methods of their preparation

S.No	Polymer	Structural unit	Method of preparation
1	Polyphosphazene	$\left[\begin{array}{c} \text{Cl} \\ \\ \text{P}=\text{N} \\ \\ \text{Cl} \end{array} \right]_n$	1. ROP of $\text{N}_3\text{P}_3\text{Cl}_6$ 2. Cationic polymerization of $\text{Me}_3\text{SiN}=\text{PCl}_3$ 3. Thermal treatment of $\text{Cl}_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$
2	Polyphosphazenes	$\left[\begin{array}{c} \text{R} \\ \\ \text{P}=\text{N} \\ \\ \text{R}' \end{array} \right]_n$ <p>R = R' = alkyl R = alkyl; R' = aryl</p>	Thermal polymerization of $\text{Me}_3\text{SiN}=\text{PR}(\text{R}')\text{OCH}_2\text{CF}_3$

Table 1.1. (contd.)

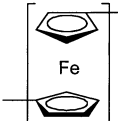
3	Poly(hetero-phosphazene)s	$\left[\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \quad \\ \text{M}=\text{N}-\text{P}-\text{N}=\text{P} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array} \right]_n$ <p>M = C(Cl); S(Cl) S(O)Cl</p>	ROP of $\text{N}_3\text{P}_2\text{MCl}_5$
4	Polysiloxanes	$\left[\begin{array}{c} \text{R} \\ \\ -\text{Si}-\text{O}- \\ \\ \text{R}' \end{array} \right]_n$	<ol style="list-style-type: none"> 1. ROP of $[\text{RR}'\text{SiO}]_{3,4}$ 2. Hydrolysis of $\text{RR}'\text{SiCl}_2$ followed by $\text{RR}'\text{Si}(\text{OH})_2$
5	Polysilanes	$\left[\begin{array}{c} \text{R} \\ \\ -\text{Si}- \\ \\ \text{R}' \end{array} \right]_n$	<ol style="list-style-type: none"> 1. Dehalogenation of $\text{RR}'\text{SiCl}_2$ 2. Anionic polymerization of cyclic poly silanes 3. Anionic polymerization of masked disilenes
6	Polysilanes	$\left[\begin{array}{c} \text{R} \\ \\ -\text{Si}- \\ \\ \text{H} \end{array} \right]_n$	Catalytic dehydrogenation of primary silanes RSiH_3
7	Poly(silylene-ethylen)s	$\left[\begin{array}{c} \text{R} \\ \\ -\text{Si}-\text{CH}_2- \\ \\ \text{R} \end{array} \right]_n$	ROP of $[\text{R}_2\text{SiCH}_2]_2$
8	Polystannanes	$\left[\begin{array}{c} \text{R} \\ \\ -\text{Sn}- \\ \\ \text{R} \end{array} \right]_n$	<ol style="list-style-type: none"> 1. Dehalogenation of Bu_2SnCl_2 2. Dehydrogenation of R_2SnH_2
9	Polygermanes	$\left[\begin{array}{c} \text{R} \\ \\ -\text{Ge}- \\ \\ \text{R} \end{array} \right]_n$	Dehalogenation of R_2GeCl_2
10	Poly(sulfurnitride)	$[\text{SN}]_n$	ROP of S_2N_2
11	Poly(oxo-thiazene)s	$\left[\begin{array}{c} \text{O} \\ \\ -\text{S}=\text{N}- \\ \\ \text{R} \end{array} \right]_n$	Thermal treatment of $\text{NH}=\text{S}(\text{O})\text{R}(\text{OR}')$ or $\text{Me}_3\text{SiN}=\text{S}(\text{O})\text{R}(\text{OR}')$
12	Poly(phosphino-borane)s	$\left[\begin{array}{c} \text{Ph} \\ \\ -\text{P}-\text{BH}_2- \\ \\ \text{H} \end{array} \right]_n$	Catalytic dehydrogenation of $\text{PhPH}_2 \cdot \text{BH}_3$
13	Polyferrocene		Condensation reaction of 1,1'-dilithioferrocene and 1,1'-diiodoferrocene

Table 1.1. (contd.)

14	Poly(ferrocenyl silanes)		ROP of strained ferrocenyl silanes
15	Rigid-rod organometallic polymers		Condensation reaction between <i>trans</i> -(P) ₂ PtCl ₂ and L ₂ Pt(P=Bu ₃ P; L = -C≡C-C≡CH
16	Pendant polymers		Polymerization of the vinyl group attached to the inorganic or organometallic group

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