Inorganic & Organometallic Polymers

Introduction

- Type of materials- Indicator of human civilization
- stone age; metal age; Polymer age
- Conventional Materials are being replaced by polymers
- Growth of polymer Science is due to:
  1. Catenation of carbon
  2. Inexpensive petroleum raw materials

Inorganic Polymers

The most obvious definition for an inorganic polymer is a polymer that has inorganic repeating units in the backbone. The inter-mediate situation in which the backbone alternates between a metallic element and organic linkages is an area where differences in opinion occurs.

Currell and Frazer define an inorganic polymer as a macromolecule that does not have a backbone of carbon atoms. In fact, several other reviews define inorganic polymers as polymers that have no carbon atoms in the backbone.

Importance:

Uses for inorganic polymers abound, with advances being made continually. Polysiloxane and polyphosphazene elastomers, siloxane and metal-containing coupling agents, inorganic dental polymers, inorganic biomedical polymers, high temperature lubricants, and pre-ceramic polymers are examples of major applications for inorganic polymers. Conducting and superconducting inorganic polymers have been investigated as have polymers for solar energy conversion, nonlinear optics, and paramagnets. If we were to include inorganic coordination and organometallic species anchored to organic polymers and zeolites, catalysis would also be a major use.

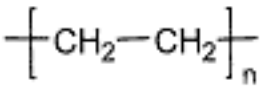
Why Inorganic & Organometallic Polymers

- Organic polymers are oxidatively degraded at high Temperature
- Becomes brittle at low temperature
- Inflammable
- Petroleum reserves are being depleted.
- Silicon is the second most abundant element in earth crust (27.2% by weight where as Carbon is at 17^{th} position. Even if carbon in oceans and atmosphere is included, it rises to 14^{th} position.
- This makes sense to consider inorganic elements for polymerization.

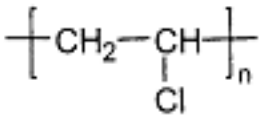
Procedures for Synthesizing Organic Polymers

1. Polymerization of unsaturated monomers

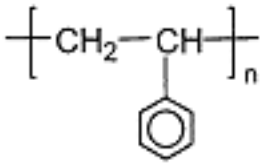
Vinyl monomers such as $CH_2=CH_2$ (and others such as $CF_2=CF_2$), mono substituted ethylenes $CH_2=CH(R)$ (such as propylene, styrene, vinyl chloride, acrylonitrile, methyl methacrylate, etc.), some disubstituted olefins $CH_2=CRR'$ (such as isobutylene), dienes (such as 1,3-butadiene, isoprene) and also monomers such as acetylene can be polymerized by various polymerization methods to afford linear chain polymers.



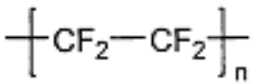
Polyethylene



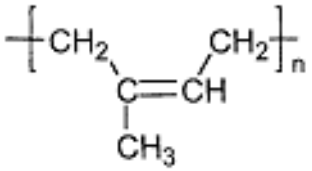
Poly(vinyl chloride)



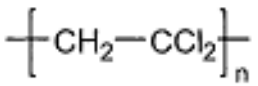
Polystyrene



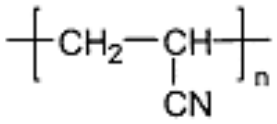
Polytetrafluoroethylene



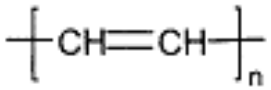
Polyisoprene



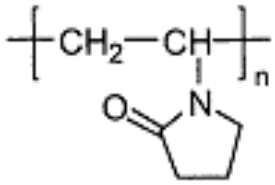
Poly(vinylidene chloride)



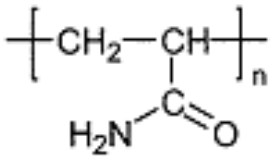
Polyacrylonitrile



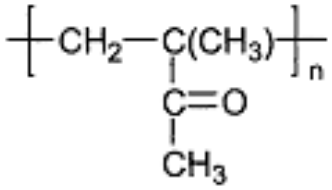
Polyacetylene



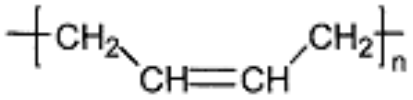
Poly(vinyl pyrrolidine)



Polyacrylamide



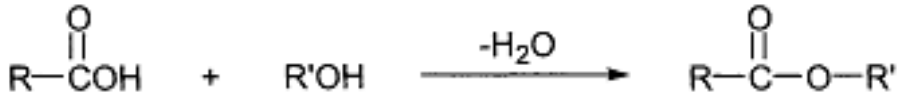
Poly(methyl methacrylate)



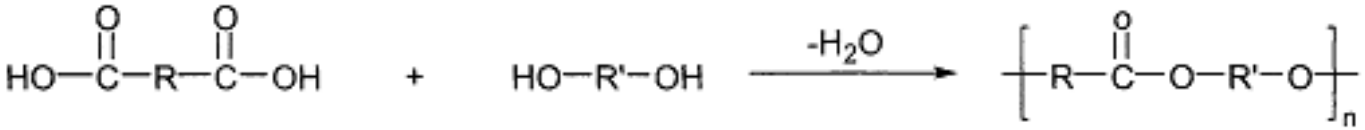
Poly(*cis*-butadiene)

2. Condensation of two difunctional monomers with each other

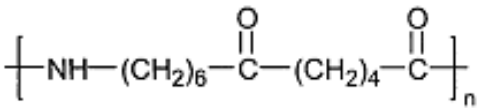
The second method of obtaining organic polymers involves the exploitation of functional group chemistry of organic molecules. Thus, for example the reaction of a carboxylic acid with an alcohol affords an *ester*. Instead of condensing two mono functional derivatives in reacting two difunctional compounds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



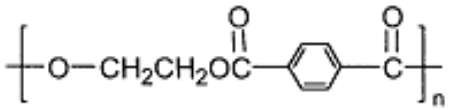
(1.1)



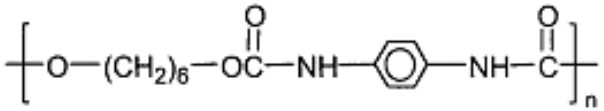
Polyester



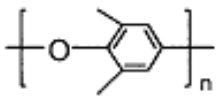
Polyamide



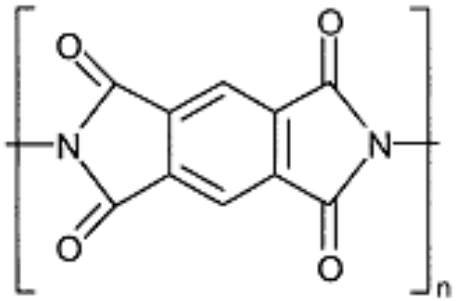
Polyester



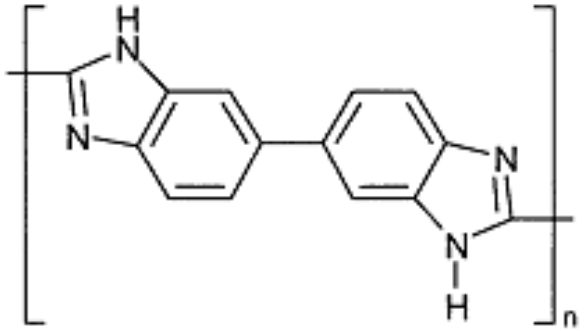
Polyurethane



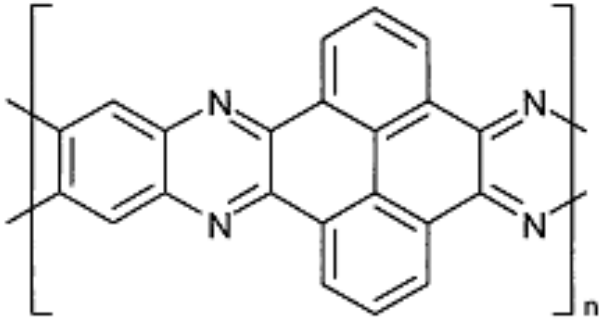
Polyether



Polyimide

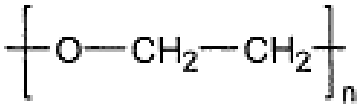


Poly(benzimidazole)

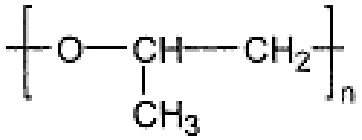


Polyquinoxaline

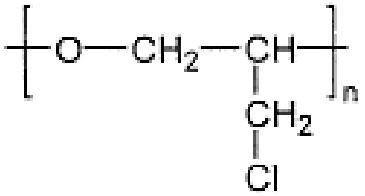
Ring Opening Polymerization



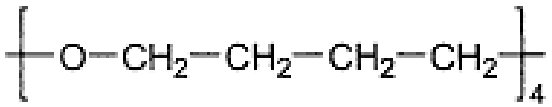
Poly(ethylene oxide)



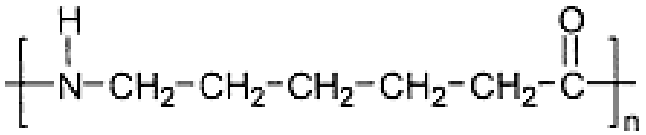
Poly(propylene oxide)



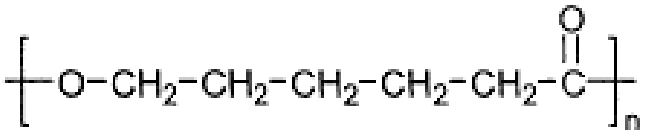
Poly(epichlorohydrin)



Poly(tetramethylene oxide)
[Poly THF]



Polycaprolactam (Nylon-6)

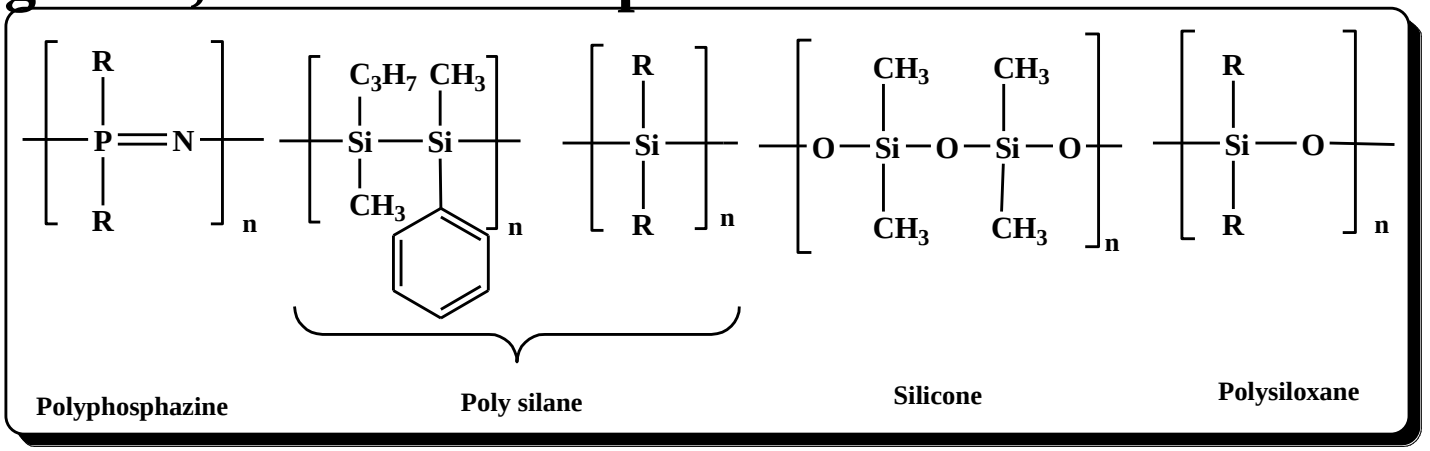


Polycaprolactone

Inorganic and Organometallic Polymers

Introduction

Inorganic polymers are polymers with a skeletal structure that does not include carbon atoms. Polymers containing inorganic and organic components are named hybrid polymers. One of the best known examples is polydimethylsiloxane, otherwise known commonly as silicone rubber. It has a repeat unit based on silicon and oxygen: —[O-Si(CH_3)$_2$]$_n$— Silicon and oxygen also occur widely in a range of inorganic minerals, including silica, mica and feldspar with other elements.



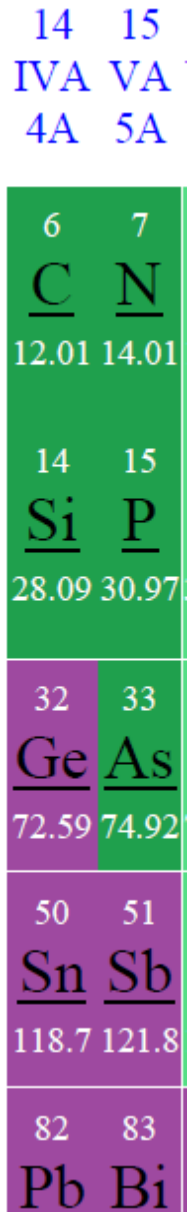
Uses for inorganic polymers abound, with advances being made continually.

- **Polysiloxane and polyphosphazene elastomers,**
- **siloxane and metal-containing coupling agents,**
- **inorganic dental polymers, inorganic biomedical polymers,**
- **high temperature lubricants, and preceramic polymers are examples of major applications for inorganic polymers.**
- **Conducting and superconducting inorganic polymers have been investigated as have polymers for solar energy conversion, nonlinear optics, and paramagnets**

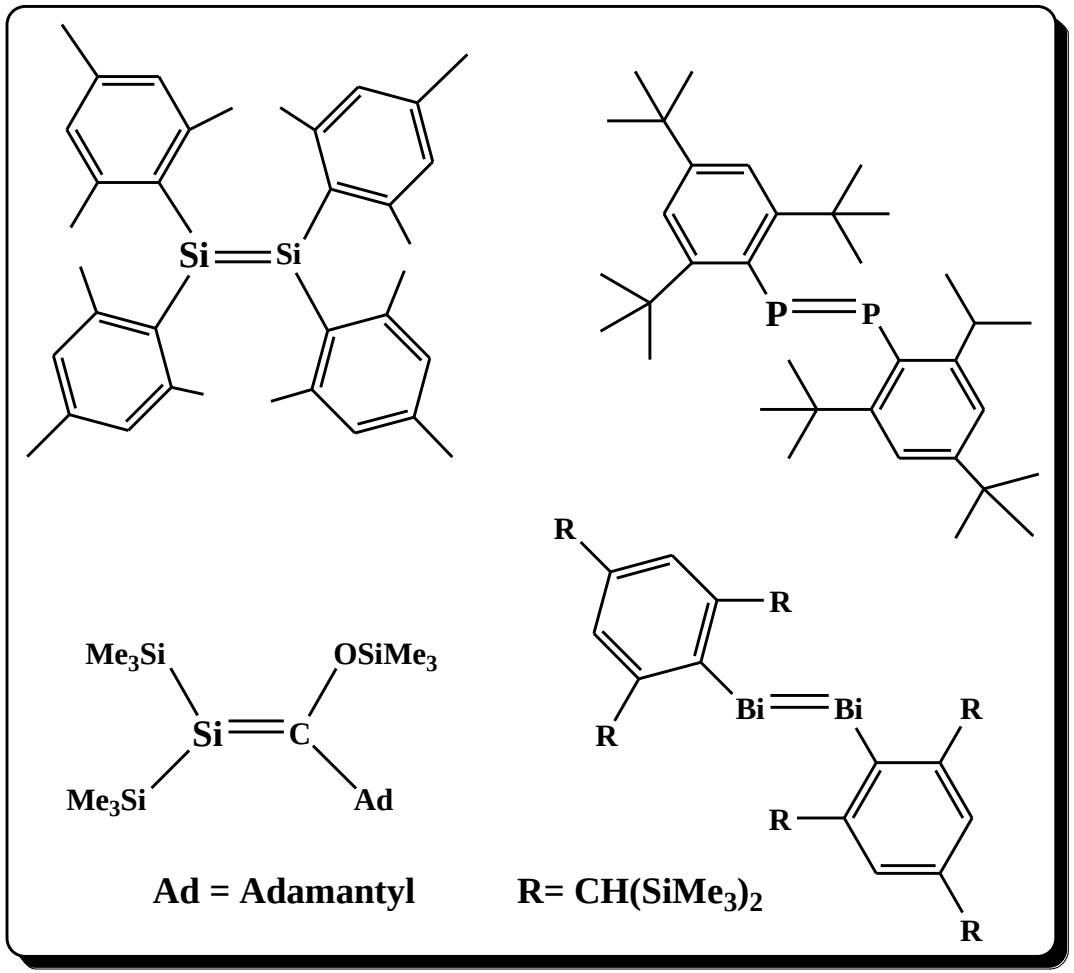
Synthetic Strategies for Inorganic Polymers

1. From Unsaturated Inorganic Compounds

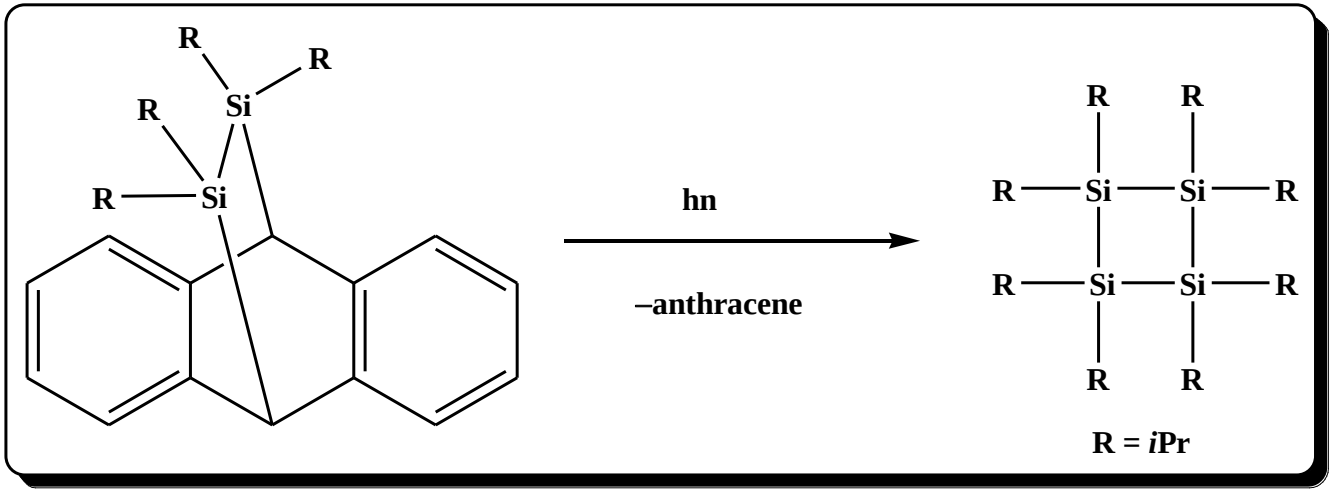
- German chemist Alfred Stock - Si_nH_{2n+2}
- Silanes were extremely reactive and burnt spontaneously in air. In fact, Stock had to develop hitherto unknown vacuum-line techniques for handling such pyrophoric compounds.
- For a long time compounds of silicon that contain double bonds between them could not be prepared and either cyc1ic- or oligomeric compounds, (or in some instances even some polymeric products) were the result of such investigations.
- Double bond rule.
- The double- bond rule held its own for a long time until its demise in 1981.



- **Utilization of sterically hindered groups for kinetically stabilizing these reactive compounds.**
- **Using this methodology stable compounds containing Si=C, Si=Si, P=C, P=P, P=As, Sb=Sb and even Bi=Bi double bonds were synthesized and characterized**



- *i*$Pr_2Si=SiiPr_2$ undergoes spontaneous oligomerization to the cyclic tetramer $[iPr_2Si]_4$



- Recently it was observed that $MesP=CPh_2$ could be polymerized by either radical or ionic initiators to afford moderate molecular weight polymers, $[MesPCPh_2]_2$ (Mes = 2,4,6-$Me_3C_6H_2$-)

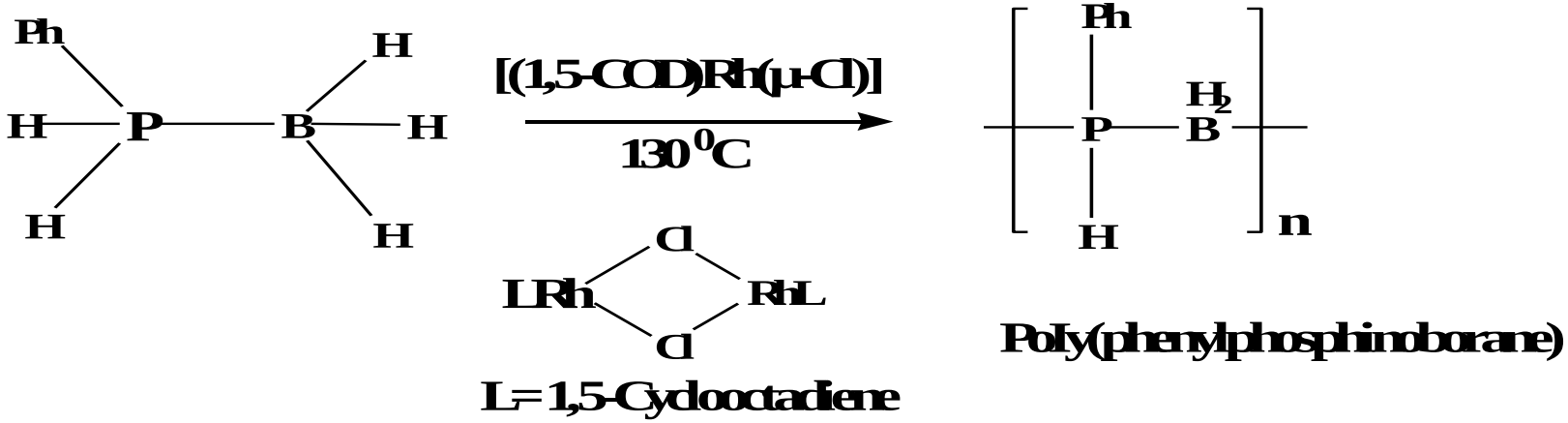
2. Inorganic Polymers from Acyclic Monomers

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.

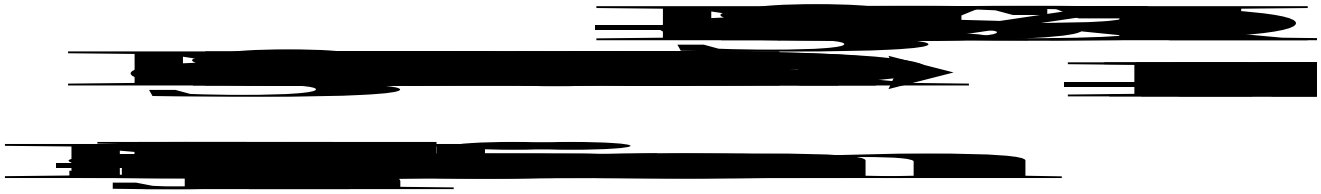
Polyphosphinoboranes- Polymers

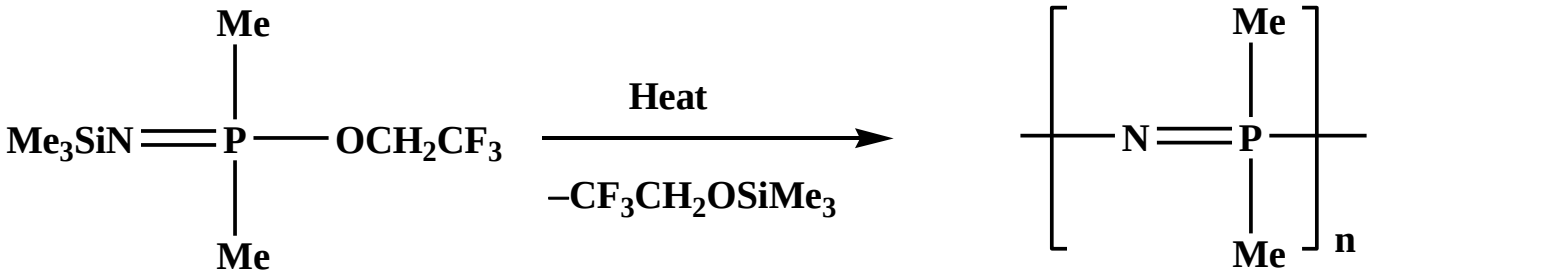


L= 1,5-Cyclooctadiene

Poly(phenylphosphinoborane)

Polyphosphazenes



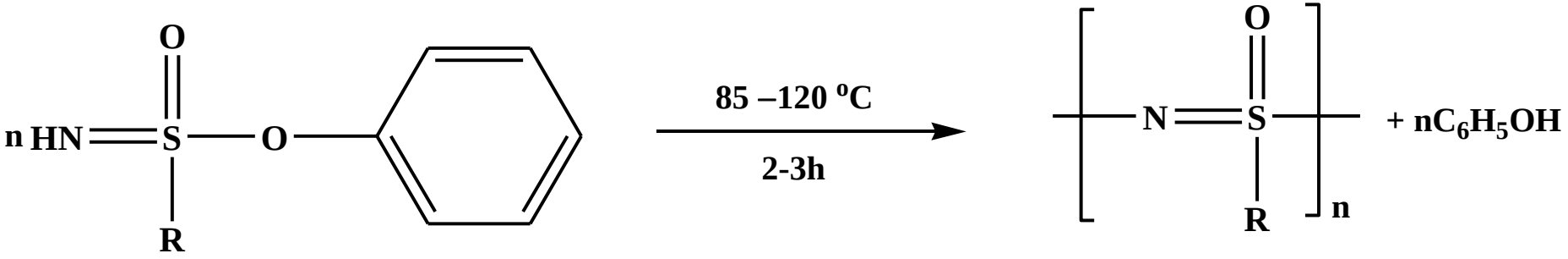


N-silylphosphoranimine

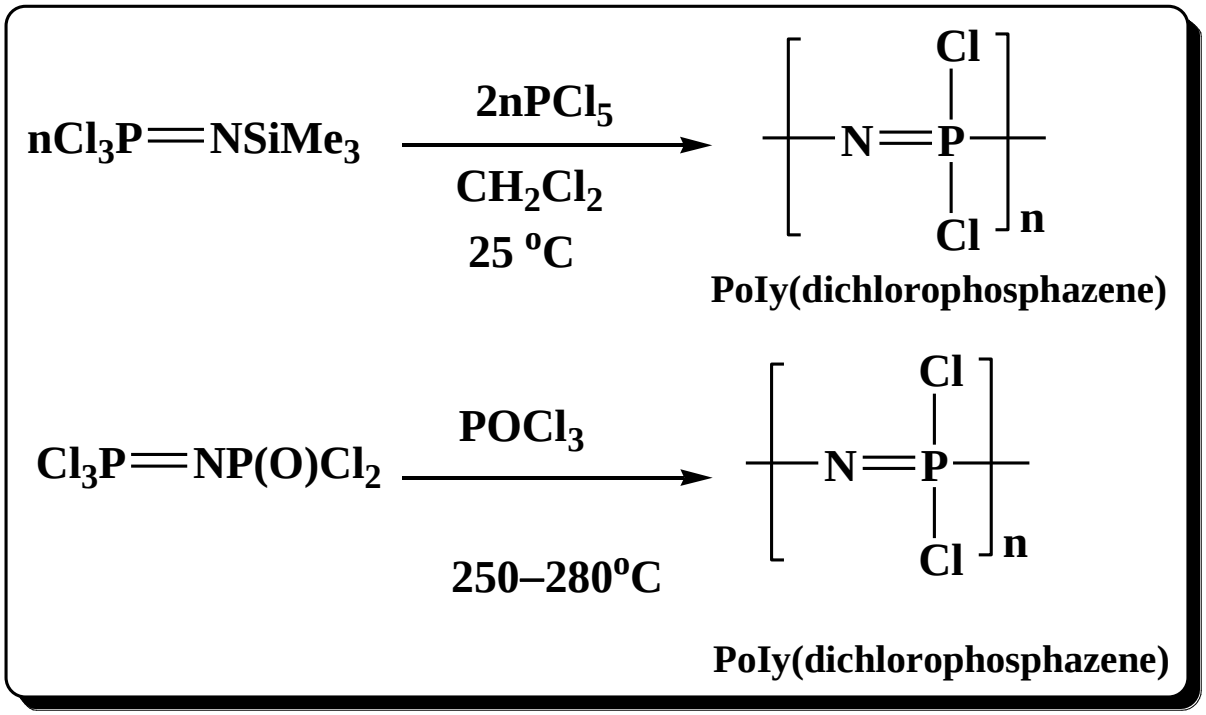
Poly(dimethylphosphazene)

Poly(oxothiazene)s

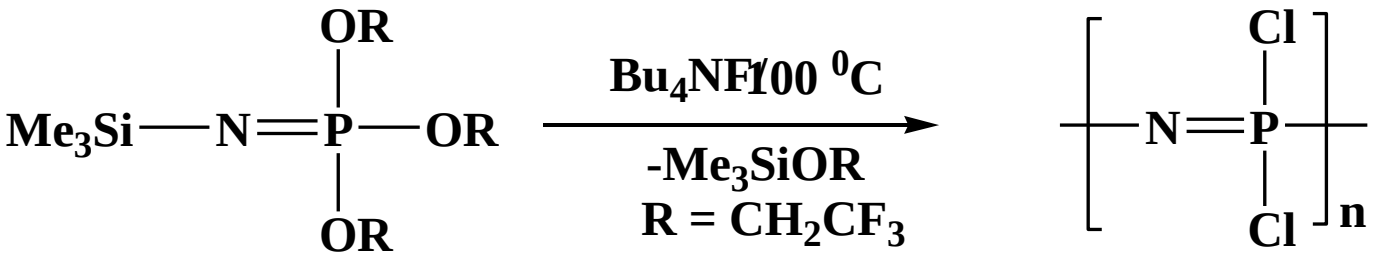
Elimination of silylethers from $Me_3SiN=S(O)R(OR')$ or even phenols from $HN=S(O)R(OPh)$ leads to the formation the high polymers



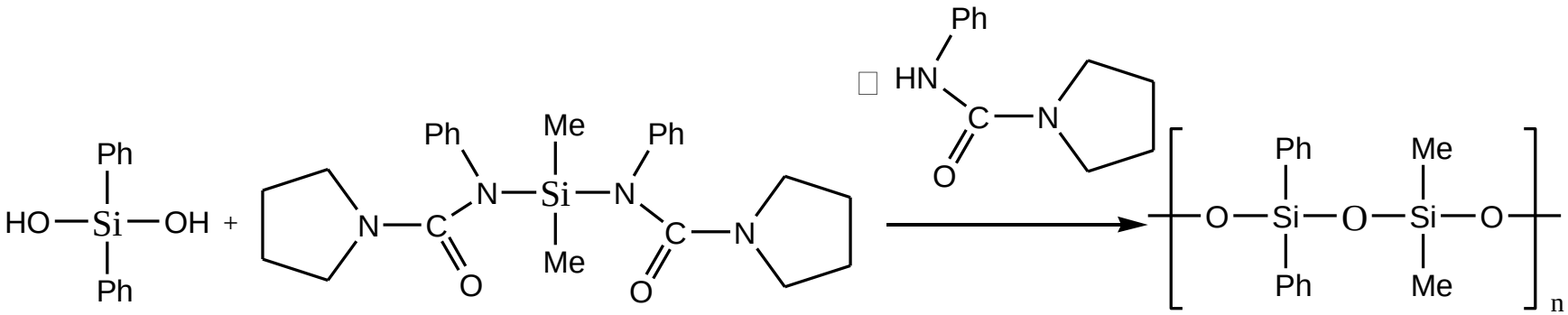
Acyclic monomers have also been used for the preparation of poly(dichlorophosphazene). For example, heating the acyclic phosphazene derivative $Cl_3P=N\text{-}P(O)Cl_2$ leads to the elimination of $P(O)Cl_3$ as the byproduct and a linear polymer, polydichlorophosphazene,$[NPCl_2]_n$ is obtained



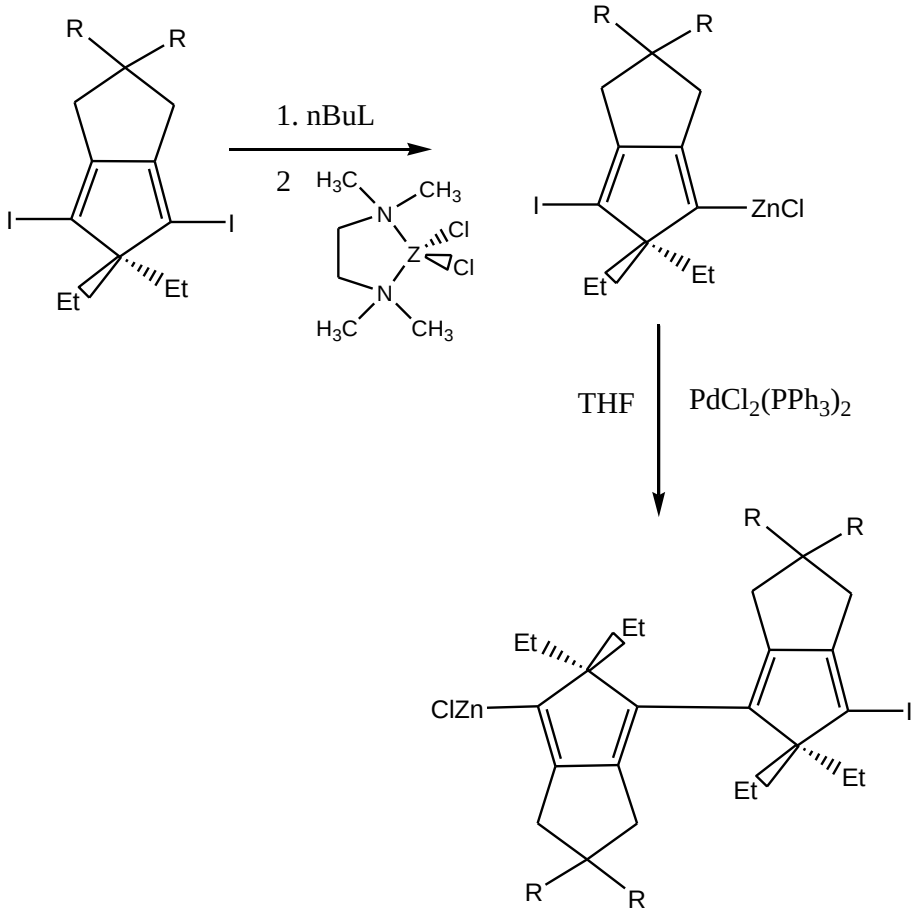
Anionic polymerization also can be used for preparing polyphosphazenes from acyclic monomers. Thus, treatment of $Me_3SiNP(OCH_2CF_3)_3$ with Bu4NF leads to the formation of the polymer $[NP(OCH_2CF_3)_2]n$

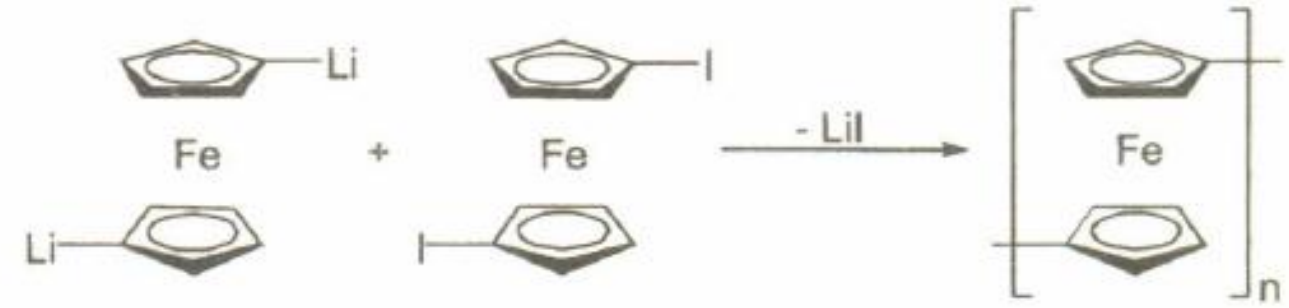


Polymer Synthesis from two Monomers

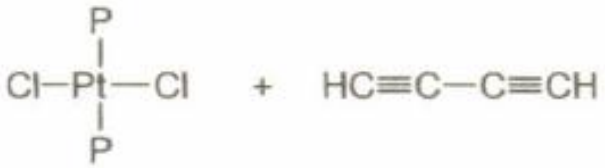


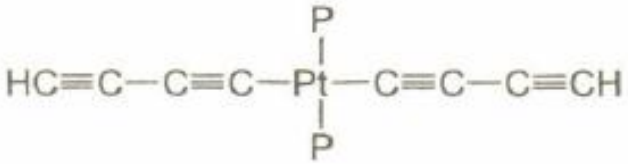
In contrast to poly(1,1′-silole)s which are prepared by the dehalogenation of the silole dichlorides, the preparation of poly(2,5-silole)s has to be carried out by a multi-step procedure (see Eq. 1.20) [36]. Thus, 2,5-diiodosilole can be selectively converted in situ to the monozinc derivative. Palladium-mediated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





Poly(ferrocene)

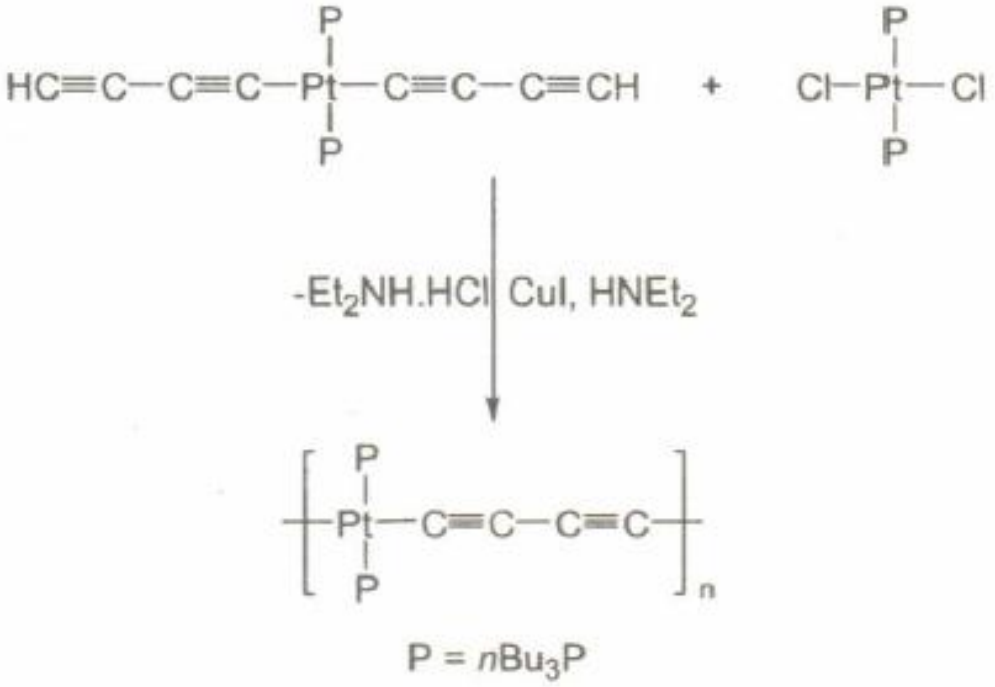




P = nBu$_3$P

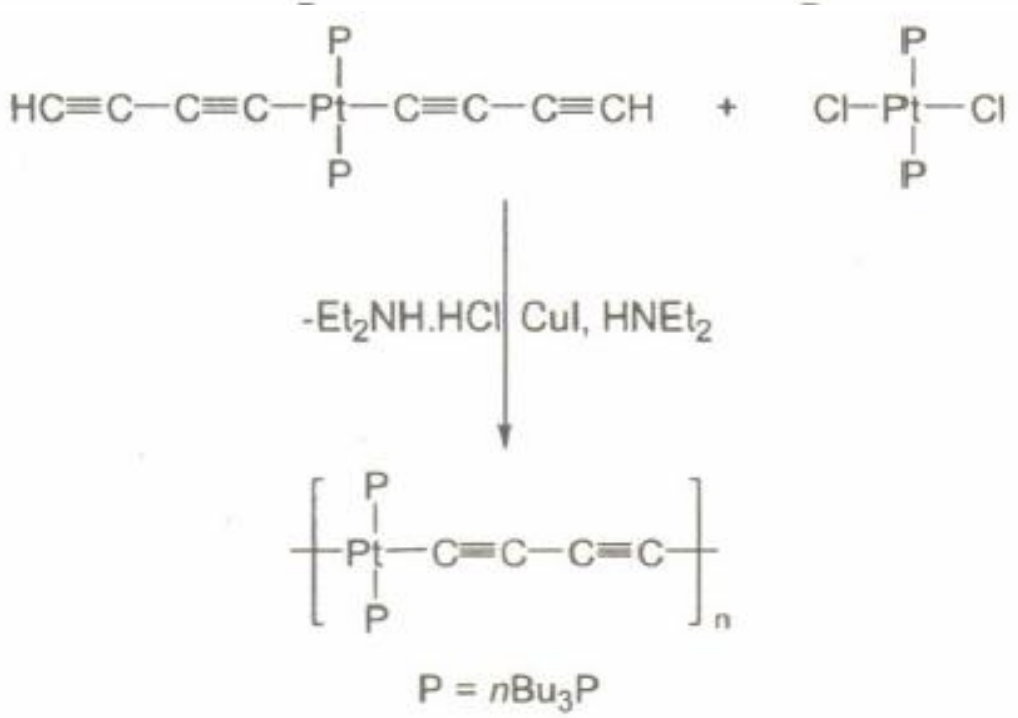
Difunctional Metal Complex
Containing Terminal Acetylides

Organometallic polymers with a rigid-rod architecture have been prepared by using the condensation strategy involving the condensation of *trans*-$Pt(PnBu_3)_2(CCCCH)_2$ with *trans*-$Pt(PnBu_3)_2Cl_2$. 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*-$Pt(II)Cl_2(nBu_3P)_2$ with 1,3-butadiyne to afford the alkynylated metal derivative *trans*-$Pt(PnBu_3)_2(CCCCH)_2$ containing a M-C σ bond (see Eq.



Rigid-rod organometallic polymer

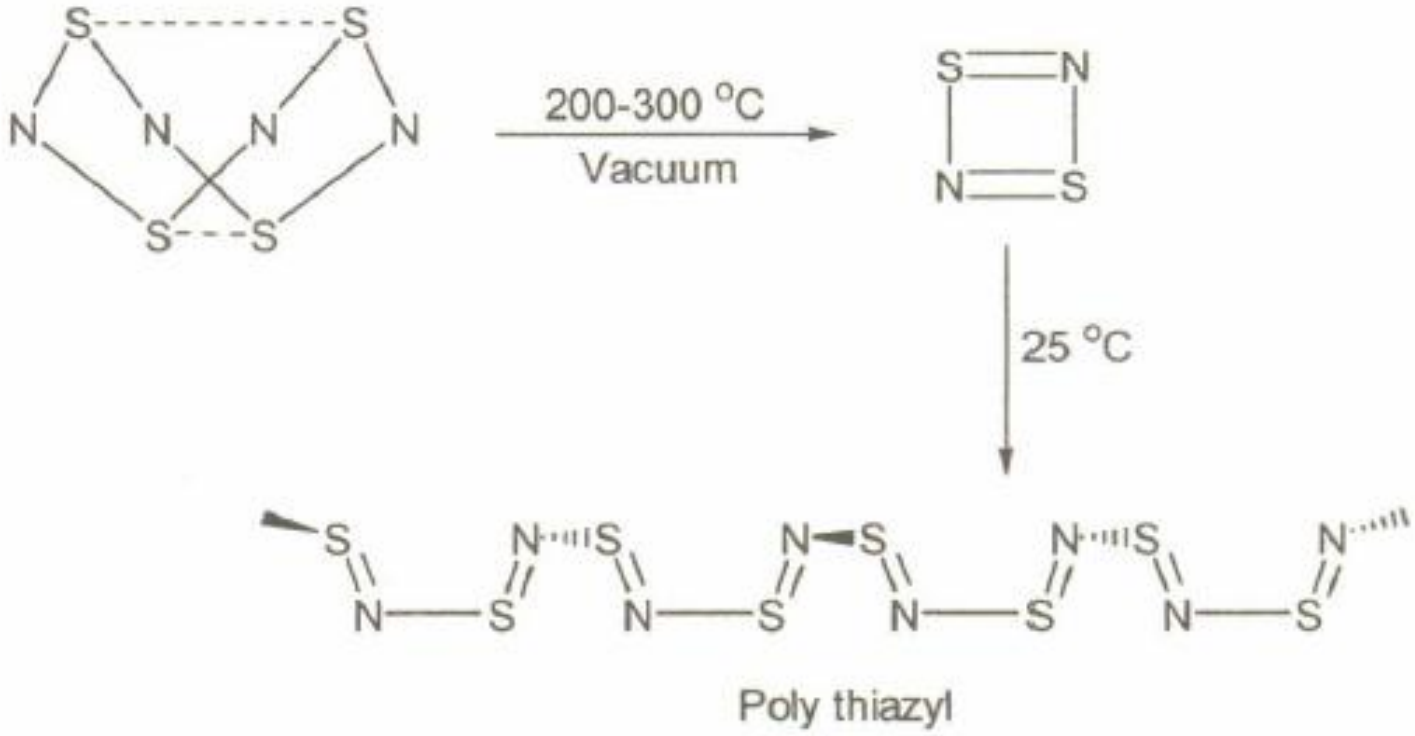
1.22). The difunctional derivative *trans*-Pt($P n Bu_3$)$_2$(CCCCH)$_2$ can be coupled with Pt(II)Cl_2($n Bu_3 P$)$_2$ to afford linear high-molecular-weight polymers (see Eq. 1.23) [39]. These polymers have rod-like structures because of the rigidity imposed by the alkynyl groups. This type of synthetic 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.



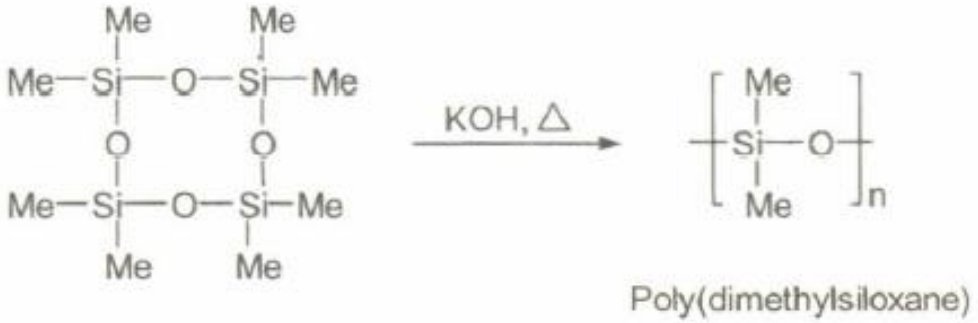
Ring-Opening Polymerization of Cyclic Inorganic Compounds

The earliest example is the polymerization of rhombic sulphur. Heating S_8 at about 160 °C causes its ROP to lead to the formation of a linear polymer

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].



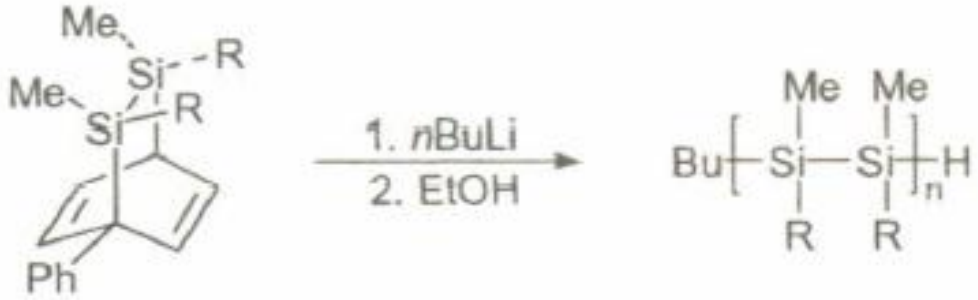
The inorganic siloxane rings can be polymerized by both cation and anion initiators to lead to polymeric siloxanes. Thus, for example, the octamethylcyclotetrasiloxane, $[Me_2SiO]_4$ can be polymerized by the use of KOH as an initiator to afford poly(dimethylsiloxane). The polymer $[Me_2SiO]_n$ prepared in this way has a very high molecular weight ($2\text{-}5\times10^6$) (see Eq. 1.26) [15-17]. Polysiloxanes are the most important family of inorganic polymers from the commercial point of view.



Poly(dimethylsiloxane)

Poly(phenylmethylsilane)

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].

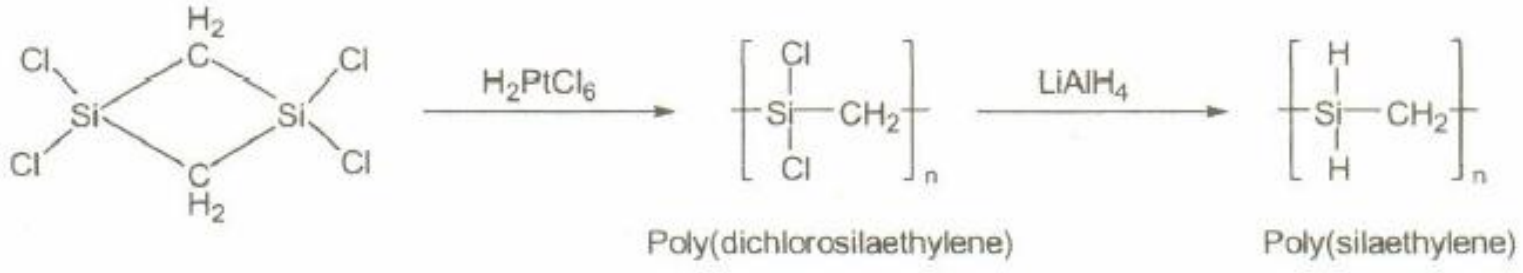


Masked disilene

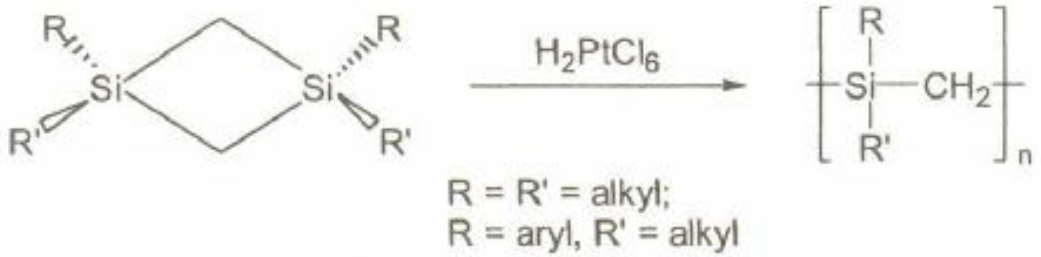
Polysilane

Polymers containing alternate silicon and carbon centers known as carbosilanes or silylene ethylenes have been originally prepared by the thermal rearrangement of polydimethylsilane, [Me-Si].
These polymers have been prepared by a ROP of four-membered disilacyclobutanes

The ROP of cyclo- $[Cl_2SiCH_2]_2$ can be carried out by using H_2PtCl_2as the catalyst to afford the polymer poly(dichlorosilaethylene),$[Cl_2SiCH_2]n$. It is possible to reduce the latter with $LiAlH_4$ to afford poly(silaethylene) $[H_2SiCH_2]_n$. The latter can be considered as an analogue of polyethylene where every alternate CH_2 group has been replaced by a SiH_2 group.

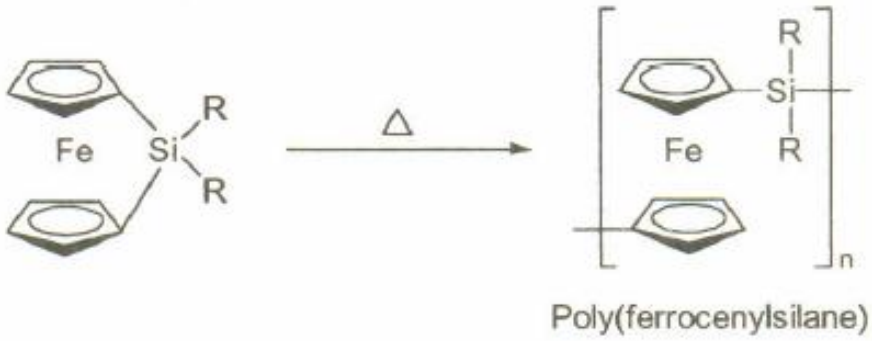


Polysilaethylenes that contain alkyl groups on the silicon can also be prepared by the H_2PtCl_6 catalyzed ring-opening polymerization of the corresponding silacyclobutanes, $[RR'SiCH_2]_2$ (see Eq. 1.30) [42].



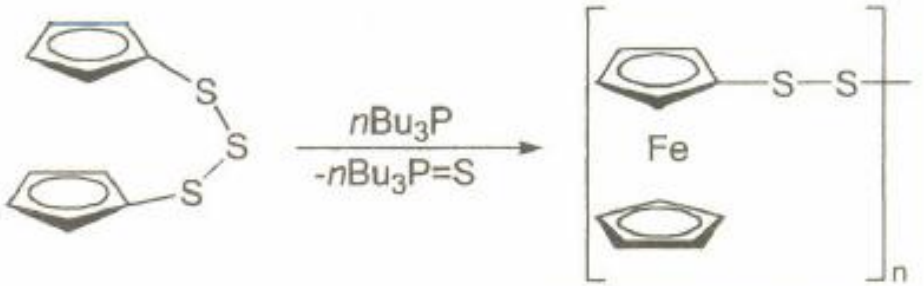
(1.30)

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].



(1.31)

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].



(1.32)

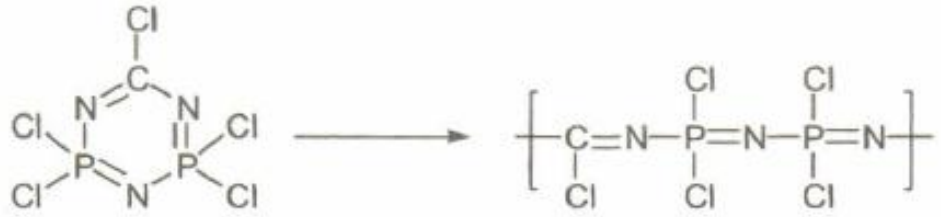
Poly(ferrocenyldisulfide)

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 $[NP(NRR')]_n$.

(1.33)

Poly(dichlorophosphazene)

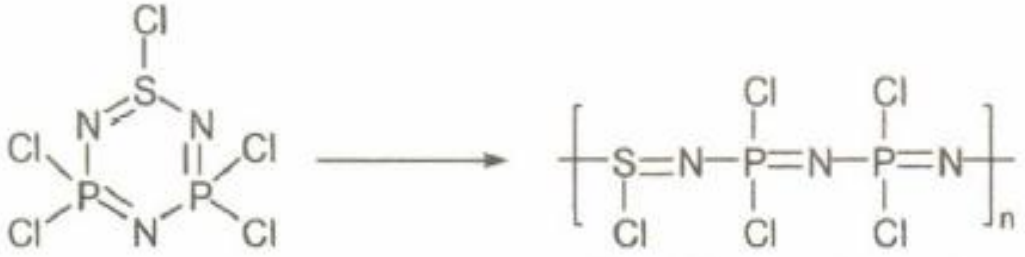
Pentachlorocarbocyclophosphazene, $N_3P_2CCl_5$, which contains a heteroatom in the form of carbon (in place of phosphorus) can also be polymerized by a thermal treatment to afford the hydrolytically sensitive poly(carbocyclophosphazene) (see Eq. 1.34) [49].



(1.34)

Poly(carbophosphazene)

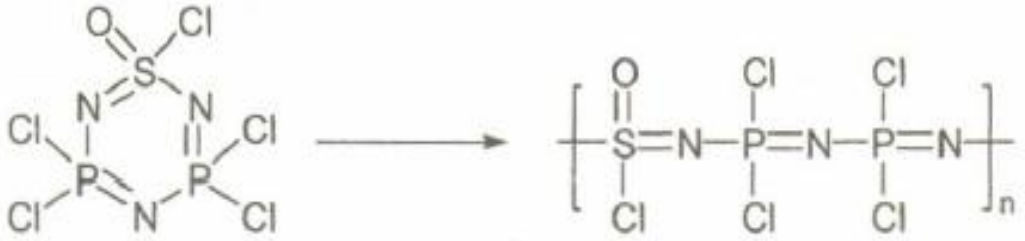
Pentachlorothiophosphazene, $N_3P_2SCl_5$, which contains a S(IV) as the heteroatom can be polymerized by the ROP to afford the linear polymer, poly(thiophosphazene) (see Eq. 1.35) [50].



Poly(thiophosphazene)

(1.35)

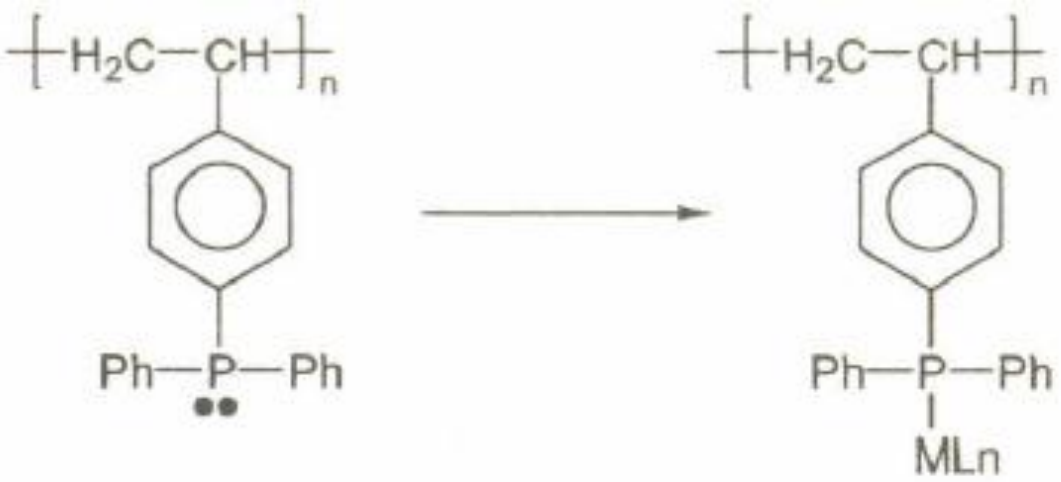
Pentachlorothionylphosphazene, $N_3P_2S(O)Cl_5$, also can be polymerized by the thermal ROP (see Eq. 1.36) [51].



Poly(thionylphosphazenes)

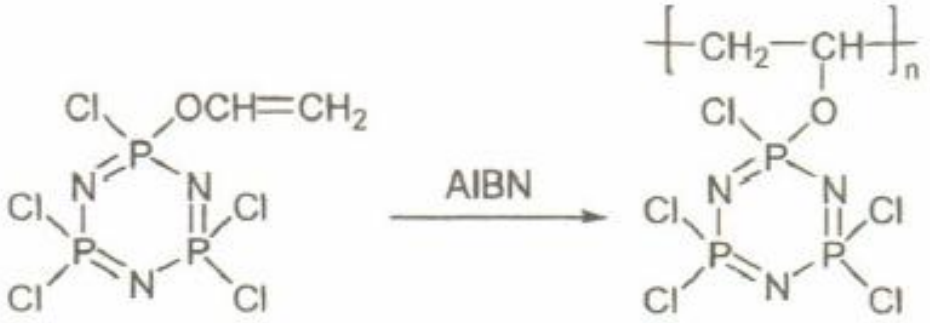
(1.36)

Polymers Containing Inorganic Rings or Motifs as Pendant Groups



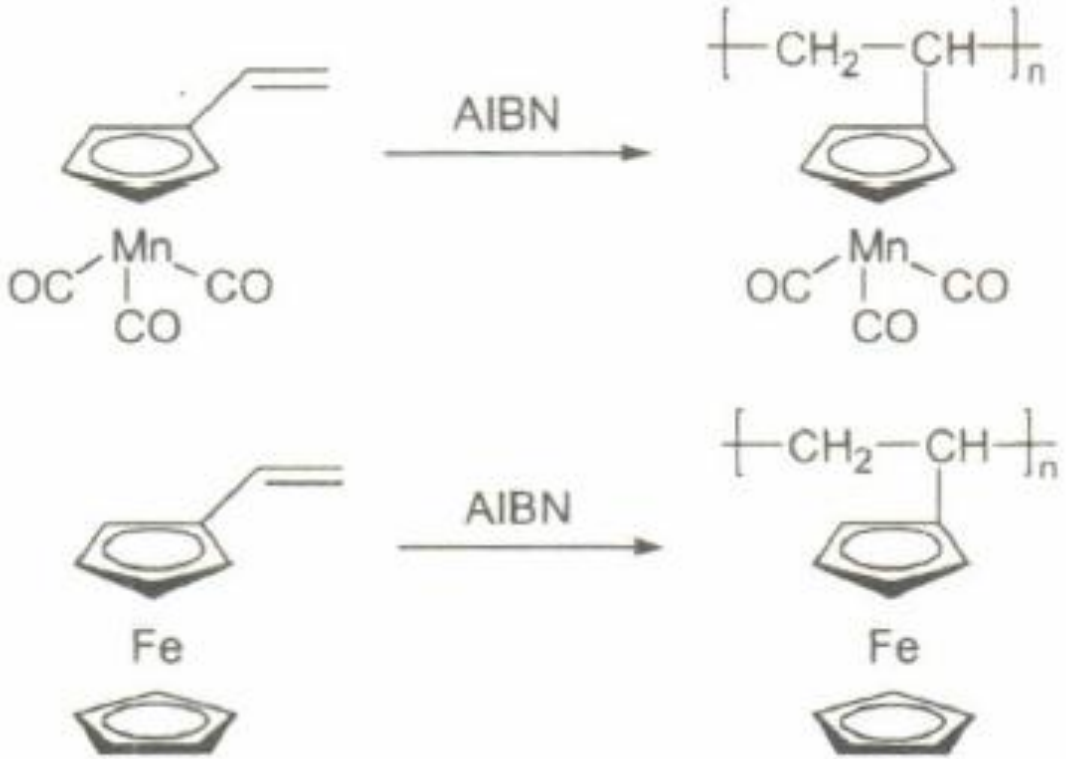
These polymers contain a carbon backbone. The inorganic units are attached to the backbone as a side chain. In principle almost any inorganic compound can be designed so that it can be a side chain on an organic backbone. The most important of this type of polymer is polystyrene that contains phosphino groups suitable for coordination

The above strategy has been applied to anchor other inorganic motifs as side-chains. For example, the cyclophosphazene, $N_3P_3Cl_5(OCH{=}CH_2)$ 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].



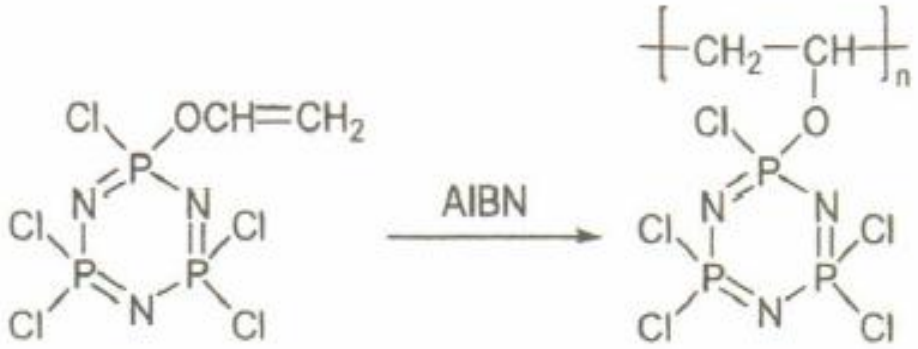
(1.38)

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].


AIBN
Mn
OC
CO
CO
CH2
CH
n
AIBN
Fe
Fe

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, $N_3P_3Cl_5(OCH{=}CH_2)$ 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].



(1.38)