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SEMESTR-VI

CHEMISTRY (Core – XIII)

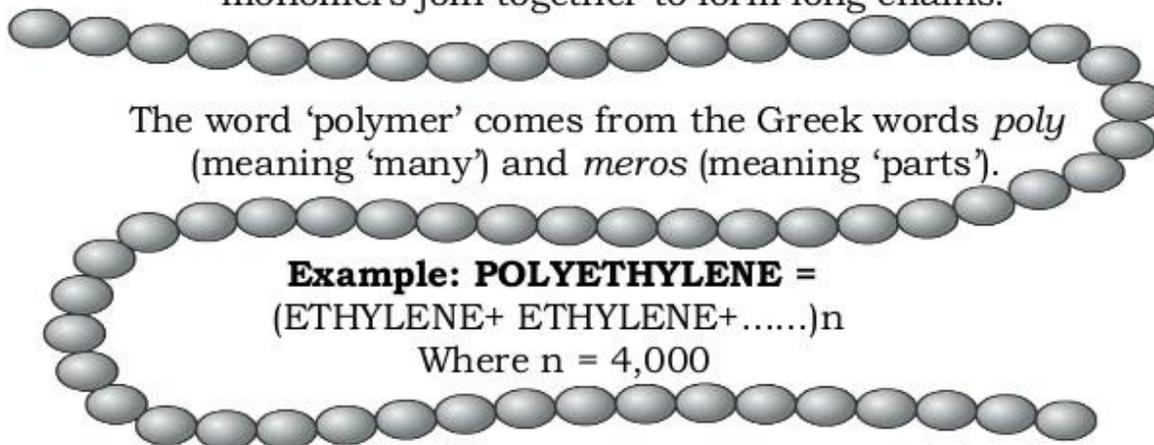
INORGANIC CHEMISTRY – IV

Chapter-2 Inorganic Polymers-a

Introduction:-

Polymers

Polymers are very large molecules made when hundreds of monomers join together to form long chains.



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Introduction

- Polymer chemistry impinges on nearly every aspect of modern life, from electronics technology, to medicine, to the wide range of fibers, films, elastomers, and structural materials on which everyone depends.
- Most of these polymers are organic materials. By this we mean that their long polymeric backbones consist mainly of carbon atoms linked together with covalent bonds.
- Organic polymers are derived either from petroleum or from plants, animals, or microorganisms. Hence, they are generally accessible in large quantities and at nominal cost. It is difficult to imagine life without them.
- After this much discussions the question comes in everyone's mind that Why, with the hundreds of organic polymers already available, should scientists be interested in the synthesis of even more macromolecules?

Introduction Of Inorganic Polymers

- Inorganic polymers by looking its name one can say that they are nonorganic or non-carbon containing polymers. The most obvious definition for an inorganic polymer is a polymers with a skeletal structure that does not include carbon atoms in the backbone.
- Polymer that has inorganic repeating units in their main polymeric backbone are known as inorganic polymers.
- It is a giant 3D or 2D network structure made up by number of covalent bonds but with an absence or near-absence of hydrocarbon units in the main molecular backbone.

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Why Do We Need Inorganic Polymers Over Organic Polymers?

- Many organic backbone polymers react with oxygen or ozone over a long period of time and lose their advantageous properties.
- Most organic polymers burn, often with the release of toxic smoke.
- Many organic polymers degrade when exposed to ultraviolet or gamma radiation.
- Organic polymers sometimes soften at unacceptably low temperatures, or they swell or dissolve in organic solvents, oils, or hydraulic fluids.
- Now in case of Inorganic polymers; inorganic elements can have different valencies than carbon, and this means that the number of side groups attached to a backbone may be different from the situation in an organic polymer. This will affect the flexibility of the macromolecule, its ability to react with chemical reagents, its stability at high temperatures, and its interactions with solvents and with other polymer molecules.
- The bonds formed between inorganic elements are often longer, stronger, and more resistant to free radical cleavage reactions than are bonds formed by carbon.

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Classification Parameters

- Inorganic polymers represent a rapidly growing field of chemical research and already have many applications and any classification is necessarily somewhat arbitrary.
- N. H. Ray, in his book on inorganic polymers, uses connectivity as a method of classifying inorganic polymers.
- Pittman uses dimensions as a parameter for the classification of inorganic polymers.
- The other classifying parameters are as following:
 1. wholly inorganic polymers
 2. inorganic-organic polymers
 3. organometallic polymers
 4. hybrid organic-inorganic polymers

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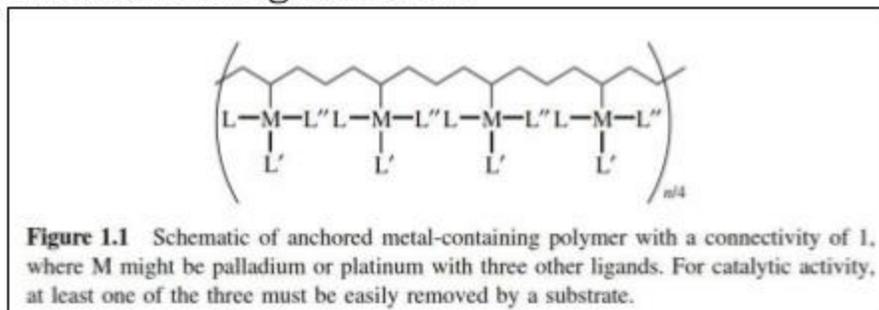
Classification On The Basis Of Connectivity

- Ray defines connectivity as the number of atoms attached to a defined atom that are a part of the polymer chain or matrix. This polymer connectivity can range from 1 for a side group atom or functional group to at least 8 or 10 in some metal-coordination and metal-cyclopentadienyl polymers, respectively.

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Connectivity of 1

- Anchored metal-containing polymers used for catalysis can have connectivity values as low as 1 with respect to the polymer chain as shown in Figure below.



- Note that the metal can have other ligands as well, but in as much as they do not affect the polymer connectivity, the metal is defined as having a connectivity of 1.

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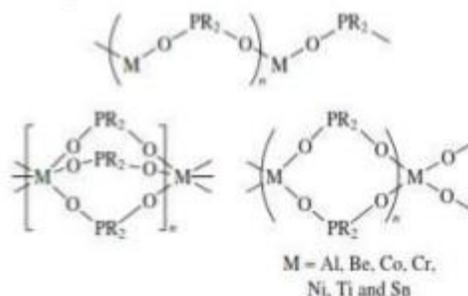
Classifications by dimensionality

- Another manner in which polymers can be classed is by dimensionality. Pittman use this classification for polymeric species containing metal atoms in their backbones. Here we will use the dimensionality for all types of inorganic polymers.
 - i. 1-D Polymeric Structures
 - ii. 2-D Polymeric Structures
 - iii. 3-D Polymeric Structures

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1-D Polymeric Structures

- A linear chain polymer is categorized as a one-dimensional (1-D) polymer even though it may have twists and turns in the “linear” chain. Simple polymer chains in which all of the atoms in the chain have a connectivity of 2 are classed as 1-D polymers.
- However, a linear chain polymer with one or more atoms of each repeating unit having a connectivity of more than 2 is also possible. For example, a polymer with benzene rings in the chain will have some carbon atoms with a connectivity of 3.

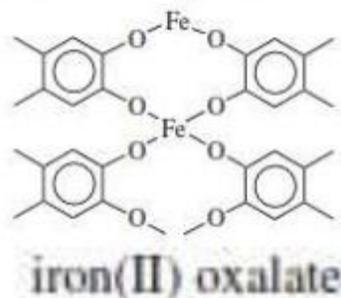


Schematic metal phosphonate 1-D polymers with connectivities of 2-6.

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2-D Polymeric Structures

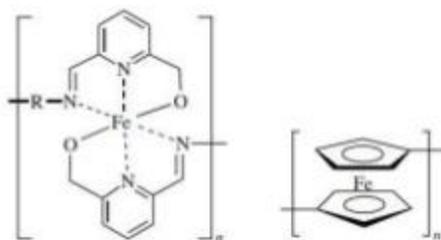
- Simple inorganic species with a connectivity of 3 often lead to sheet or two dimensional (2-D) polymers as shown in Figure for boric acid & arsenic sulfide.
- On the other hand, connectivities do not always determine illustrate this point, the aqueous iron(II) oxalate polymer has structure, but the analogous 2,5-oxyquinonate complex of istance as shown below in Figure.



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3-D Polymeric Structures

- Inorganic polymeric networks in which bonding occurs in three dimensions are well known. Starting with quartz (SiO_2) as a prime example, the most common characteristic of such species is insolubility — unless decomposition occurs during a dissolution process.
- To have a true 3-D polymer, at least some of the atoms must have a connectivity of 4 or more. Some polymers, such as some of the polysilynes are pseudo-3-D as a result of 3-D ring formation to relieve steric strain.
- Prussian blue is a classic example of a mixed Fe(II) and Fe(III) 3-D polymeric structure, with each iron ion surrounded octahedrally by six cyano ligands.



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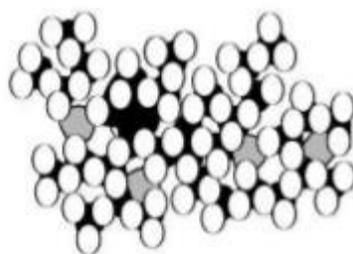
Classification On The Basis Of Chemical Constituents

- According to this classification method inorganic polymers are classified on the basis of parameters as following:
 1. wholly inorganic polymers
 2. inorganic-organic polymers
 3. organometallic polymers
 4. hybrid organic-inorganic polymers

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wholly inorganic polymers

- Inorganic polymers in this class constitute the major components of soil, mountains and sand, and they are also employed as abrasives and cutting materials (diamond, silicon carbide (carborundum), fibres (fibrous glass, asbestos, boron fibres), coatings, flame retardants, building and construction materials (window glass, stone, Portland cement, brick and tiles), and lubricants and catalysts (zinc oxide, nickel oxide, carbon black, silica gel, aluminium silicate, and clays).

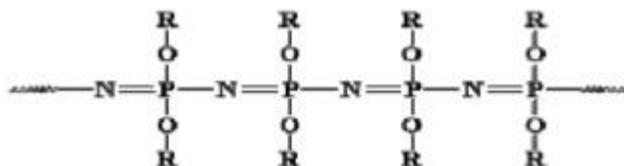
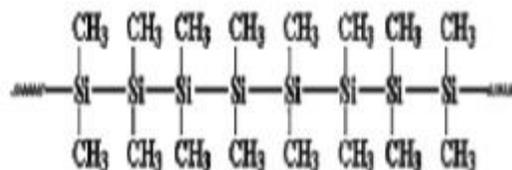
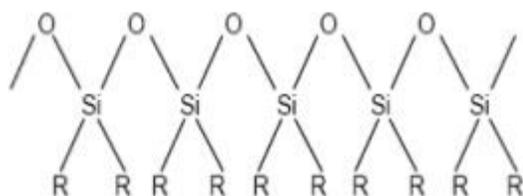


Structure of a typical silicon dioxide intensive glass

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Inorganic-organic Polymers

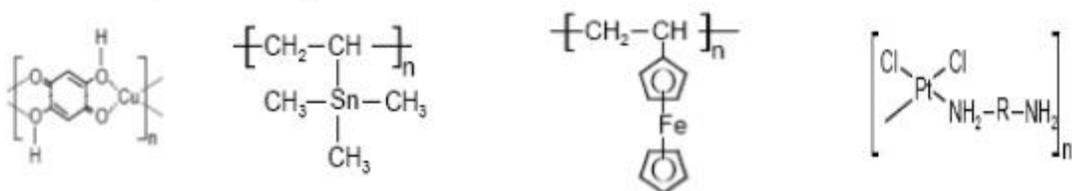
- Inorganic polymers containing organic portions attached to inorganic elements in their backbone. The area of inorganic-organic polymers is very extensive. Some examples of this class are: polysilanes, polysiloxanes, polyphosphazenes.



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Organometallic Polymers

- Organometallic polymers are made of over 40 elements including main group of metals (si or ge), transition metals or rare earth elements in addition to the 10 elements (C, H, N, O, B, P, halides) which is found in organic polymers. The variations of organometallic polymers seem endless.
- Organometallic polymers are new materials which combine the low density and structural variations and functional group varieties of organic materials with electrical conductivity and the high temperature stability features of inorganic compounds.

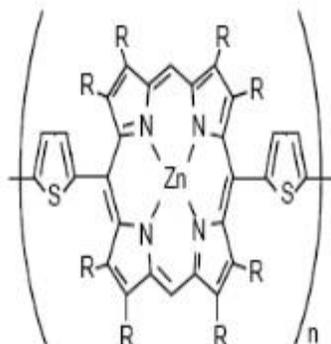


Different structures found in organometallic polymers

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Hybrid organic-inorganic polymers

- Hybrid organic-inorganic networks, prepared via sol-gel process, are multi-functional materials offering a wide range of interesting properties. Since there are countless different combinations of the organic and inorganic moieties, a large number of applications are possible by incorporation of inorganic building blocks such as silica networks, porous materials and metals.



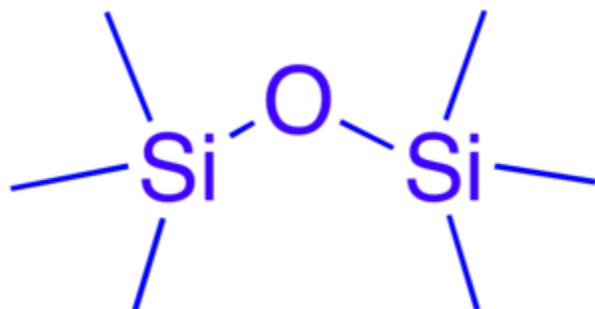
Π -conjugated polymers prepared via organometallic condensation reactions

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Siloxane

A **siloxane** is a functional group in [organosilicon](#) chemistry with the Si–O–Si linkage. The parent siloxanes include the [oligomeric](#) and [polymeric hydrides](#) with the formulae $\text{H}(\text{OSiH}_2)_n\text{OH}$ and $(\text{OSiH}_2)_n$.^[1] Siloxanes also include branched compounds, the defining feature of which is that each pair of silicon centres is separated by one oxygen atom. The siloxane functional group forms the backbone of [silicones](#), the premier example of which is [polydimethylsiloxane](#).^[2] The

[functional group](#) R_3SiO- (where the three Rs may be different) is called **siloxyl**. Siloxanes are manmade and have many commercial and industrial applications because of the compounds' hydrophobicity, low thermal conductivity, and high flexibility. ^[3]

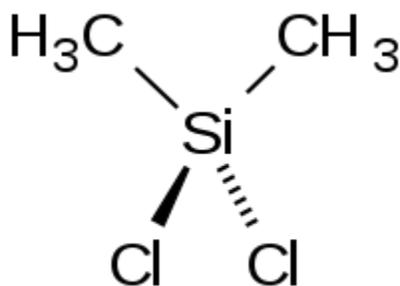


□

Structure

Siloxanes generally adopt structures expected for linked tetrahedral (" sp^3 -like") centers. The Si–O bond is 1.64 Å (vs Si–C distance of 1.92 Å) and the Si–O–Si angle is rather open at 142.5°. ^[4] By way of contrast, the C–O distance in a typical [dialkyl ether](#) is much shorter at 1.414(2) Å with a more acute C–O–C angle of 111°. ^[5] It can be appreciated that the siloxanes would have low barriers for rotation about the Si–O bonds as a consequence of low steric hindrance. This geometric consideration is the basis of the useful properties of some siloxane-containing materials, such as their low [glass transition temperatures](#).

Synthesis of siloxanes

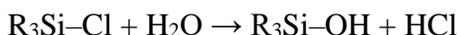


[Dimethyldichlorosilane](#) ($Si(CH_3)_2Cl_2$) is a key precursor to cyclic (D_3 , D_4 , etc.) and linear siloxanes. ^[6]

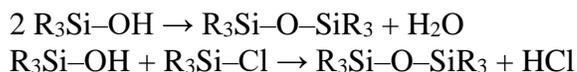
The main route to siloxane functional group is by [hydrolysis](#) of silicon chlorides:



The reaction proceeds via the initial formation of [silanols](#) (R_3Si-OH):



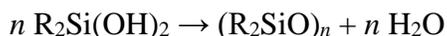
The siloxane bond can then form via a silanol + silanol pathway or a silanol + chlorosilane pathway:



Hydrolysis of a silyldichloride can afford linear or cyclic products. Linear products are terminated with silanol groups:



Cyclic products have no silanol termini:

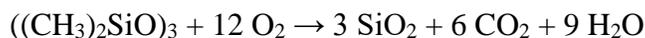


The linear products, [polydimethylsiloxane](#) (PDMS), are of great commercial value. Their production requires the production of [dimethylsilicon dichloride](#).

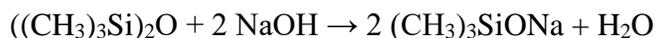
Starting from trisilanols, cages are possible, such as the species with the formula $(\text{RSi})_n\text{O}_{3n/2}$ with cubic ($n = 8$) and hexagonal prismatic ($n = 12$). $(\text{RSi})_8\text{O}_{12}$ structures. The cubic cages are [cubane-type clusters](#), with silicon centers at the corners of a cube oxygen centres spanning each of the twelve edges.^[7]

Reactions

Oxidation of organosilicon compounds, including siloxanes, gives [silicon dioxide](#). This conversion is illustrated by the combustion of hexamethylcyclotrisiloxane:



Strong base degrades siloxane group, often affording [siloxide salts](#):



This reaction proceeds by production of silanols. Similar reactions are used industrially to convert cyclic siloxanes to linear polymers.^[2]

Uses

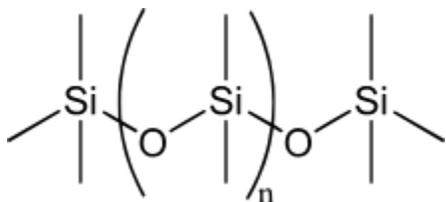
Polysiloxanes, upon combustion in an inert atmosphere, generally undergo pyrolysis to form silicon oxycarbide or [silicon carbide](#) (SiC). By exploiting this reaction, polysiloxanes have been used as preceramic polymers in various processes including additive manufacturing. The use of a poly-siloxane precursor in polymer derived ceramics allows the formation of ceramic bodies with complex shapes, although the significant shrinkage in pyrolysis needs to be taken into account.

Silicone

Silicone can be used as a basic sealant against water and air penetration

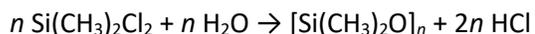
A **silicone** or **polysiloxane** are [polymers](#) made up of [siloxane](#) ($-\text{R}_2\text{Si}-\text{O}-\text{SiR}_2-$, where R = organic group). They are typically colorless, oils or [rubber](#)-like substances. Silicones are used in sealants, adhesives, lubricants, medicine, cooking utensils, and thermal and electrical insulation. Some common forms include [silicone oil](#), [silicone grease](#), [silicone rubber](#), [silicone resin](#), .

More precisely called [polymerized siloxanes](#) or polysiloxanes, silicones consist of an inorganic silicon-oxygen [backbone chain](#) ($\cdots-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\cdots$) with two organic groups attached to each silicon center. Commonly, the organic groups are methyl. The materials can be cyclic or polymeric. By varying the $-\text{Si}-\text{O}-$ chain lengths, side groups, and [crosslinking](#), silicones can be synthesized with a wide variety of properties and compositions. They can vary in consistency from liquid to gel to rubber to hard plastic. The most common siloxane is linear [polydimethylsiloxane](#) (PDMS), a [silicone oil](#). The second-largest group of silicone materials is based on [silicone resins](#), which are formed by branched and cage-like oligosiloxanes.



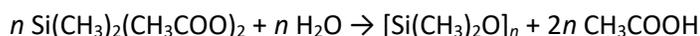
Synthesis

Most common are materials based on [polydimethylsiloxane](#), which is derived by hydrolysis of [dimethyldichlorosilane](#). This dichloride reacts with water as follows:



The polymerization typically produces linear chains capped with $\text{Si}-\text{Cl}$ or $\text{Si}-\text{OH}$ ([silanol](#)) groups. Under different conditions, the polymer is a cyclic, not a chain.^[1]

For consumer applications such as caulks silyl [acetates](#) are used instead of silyl chlorides. The hydrolysis of the acetates produces the less dangerous [acetic acid](#) (the acid found in [vinegar](#)) as the reaction product of a much slower curing process. This chemistry is used in many consumer applications, such as silicone [caulk](#) and [adhesives](#).



[Branches](#) or crosslinks in the polymer chain can be introduced by using organosilicone precursors with fewer alkyl groups, such as methyl trichlorosilane and [methyltrimethoxysilane](#). Ideally, each molecule of such a compound becomes a branch point. This process can be used to

produce hard silicone resins. Similarly, precursors with three methyl groups can be used to limit molecular weight, since each such molecule has only one reactive site and so forms the end of a siloxane chain.

Properties

Silicones exhibit many useful characteristics, including:^[1]

- Low [thermal conductivity](#)
- Low chemical reactivity
- Low [toxicity](#)
- Thermal stability (constancy of properties over a wide temperature range of -100 to 250 °C).
- The ability to repel water and form watertight seals.
- Does not stick to many substrates, but adheres very well to others, e.g. glass.
- Does not support [microbiological](#) growth.
- Resistance to oxygen, ozone, and [ultraviolet \(UV\) light](#). This property has led to the widespread use of silicones in the construction industry (e.g. coatings, fire protection, glazing seals) and the automotive industry (external gaskets, external trim).
- [Electrical insulation](#) properties. Because silicone can be formulated to be electrically insulative or conductive, it is suitable for a wide range of electrical applications.
- High [gas permeability](#): at room temperature (25 °C), the permeability of [silicone rubber](#) for such gases as oxygen is approximately 400 times^[citation needed] that of [butyl rubber](#), making silicone useful for medical applications in which increased aeration is desired. Conversely, silicone rubbers cannot be used where gas-tight seals are necessary such as seals for high-pressure gasses or high vacuum.

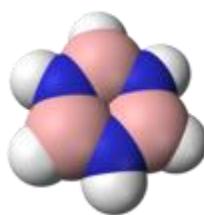
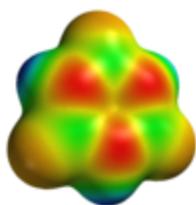
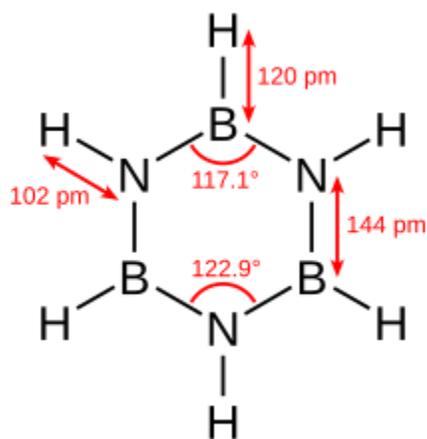
Silicone can be developed into rubber sheeting, where it has other properties, such as being FDA compliant. This extends the uses of silicone sheeting to industries that demand hygiene, for example, food and beverage and pharmaceutical.

Uses

Silicones are used in many products. [Ullmann's Encyclopedia of Industrial Chemistry](#) lists the following major categories of application: Electrical (e.g., insulation), electronics (e.g., coatings), household (e.g., sealants and cooking utensils), automobile (e.g., gaskets), airplane (e.g., seals), office machines (e.g., keyboard pads), medicine and dentistry (e.g., tooth impression molds), textiles and paper (e.g., coatings). For these applications, an estimated 400,000 tonnes of silicones were produced in 1991.^[clarification needed] Specific examples, both large and small are presented below.^[1]

Borazine

Borazine



Names

[Preferred IUPAC name](#)

1,3,5,2,4,6-Triazatriborinane (only preselected^[1])

Other names

Borazine

Cyclotriborazaneborazol

Inorganic benzene

Borazole

Identifiers

[CAS Number](#)

- [6569-51-3](#) ✓

3D model ([JSmol](#))

- [Interactive image](#)

[ChEBI](#)

- [CHEBI:33119](#) ✓

[ChemSpider](#)

- [122374](#) ✓

[ECHA InfoCard](#)

[100.169.303](#)

[PubChem](#) CID

- [138768](#)

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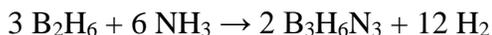
Properties	
Chemical formula	B ₃ H ₆ N ₃
Molar mass	80.50 g/mol
Appearance	Colorless liquid
Density	0.81 g/cm ³
Melting point	−58 °C (−72 °F; 215 K)
Boiling point	53 °C (127 °F; 326 K) (55 °C at 105 Pa)
Magnetic susceptibility (χ)	−49.6 · 10 ^{−6} cm ³ /mol

Borazine is a polar [inorganic compound](#) with the [chemical formula](#) B₃H₆N₃. In this [cyclic compound](#), the three BH units and three NH units alternate. The compound is [isoelectronic](#) and [isostructural](#) with [benzene](#). For this reason borazine is sometimes referred to as “inorganic benzene”. Like benzene, borazine is a colourless [liquid](#).^[2]

Synthesis

The compound was reported in 1926 by the chemists [Alfred Stock](#) and Erich Pohland by a reaction of [diborane](#) with [ammonia](#).^[3]

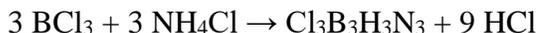
Borazine is synthesized from [diborane](#) and [ammonia](#) in a 1:2 ratio at 250–300 °C with a [conversion](#) of 50%.



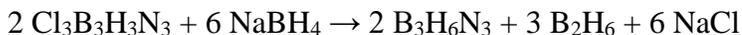
An alternative more efficient route begins with [lithium borohydride](#) and [ammonium chloride](#):



In a two-step process to borazine, [boron trichloride](#) is first converted to trichloroborazine:



The B-Cl bonds are subsequently converted to B-H bonds:

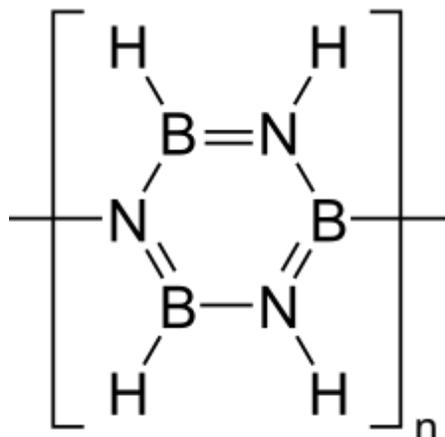


Properties

Borazine is a colourless liquid with an aromatic smell. In water it [hydrolyzes](#) to [boric acid](#), ammonia, and hydrogen. Borazine, with a [standard enthalpy change of formation](#) ΔH_f of −531 kJ/mol, is thermally very stable

Reactivity

Although often compared with benzene, borazine is far more reactive. With [hydrogen chloride](#) it forms an [adduct](#), whereas benzene is unreactive toward HCl.



Polyborazylene

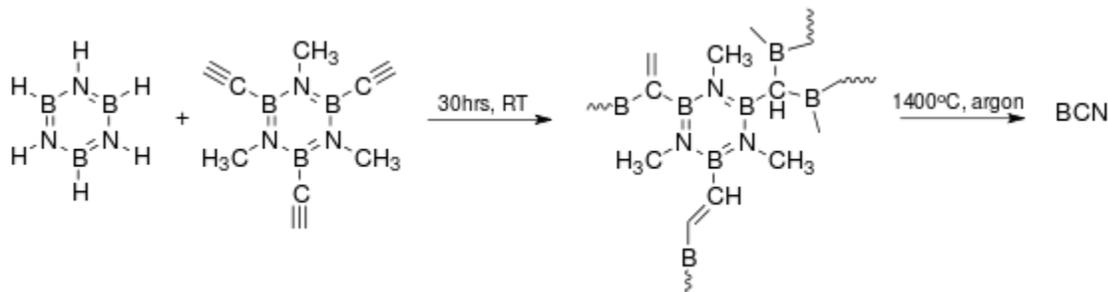


Addition reaction of borazine with hydrogen chloride



Reduction with [sodium borohydride](#)

The addition reaction with [bromine](#) does not require a [catalyst](#). Borazines undergo [nucleophilic](#) attack at boron and [electrophilic](#) attack at nitrogen. Heating borazine at 70 °C expels hydrogen with formation of a *borazanyl polymer* or *polyborazylene*, in which the monomer units are coupled in a [para fashion](#) by new boron-nitrogen bonds. [Boron nitride](#) can be prepared by heating polyborazylene to 1000 °C. Borazines are also starting materials for other potential ceramics such as *boron carbonitrides*. Borazine can also be used as a precursor to grow boron nitride thin films on surfaces, such as the [nanomesh](#) structure which is formed on [rhodium](#).



Polyborazylene has been proposed as a recycled [hydrogen storage](#) medium for [hydrogen fuel cell](#) vehicle applications, using a "single pot" process for digestion and reduction to recreate ammonia borane.^[8]

Among other B-N type compounds mixed amino-nitro substituted borazines have been predicted to outperform carbon based explosives such as [CL-20](#).^{[9][10]}