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B) Inorganic Polymers:
The polymers formed by the combination of atoms other than carbon in main chain or back bone.
- Elements like, Si, N, P, S, etc.
The elements in inorganic polymers are joint together by single or double covalent bonds.
eg: Silicone, polyphosphazine, polysulphur nitride.

General properties:
1) At the high temperature nearly above 600°C they only melt but do not burn except sulphur containing polymers.

2) They are usually stiffer, harder and more brittle as they form cross linked structures.

3) With cross-linked structures the chain segments between cross-links are, usually short, but stiff or not flexible & they are enough to swell reversibly by intercalation of molecules of solvent.

4) They dissolve only in polar solvents.

5) They are stiffer in nature.

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Classification of inorganic polymers:

On the basis of element present in monomer, they are classified as:

i) Polyphosphazines
ii) Sulphur based polymers
iii) Silicones

Preparation and applications of inorganic polymer.

1) Polyphosphazines:

The polymers which contain phosphorous atoms as central atoms of unit particles are polyphosphazines.

* General formulae:

$$+\left[\begin{matrix} R \\ | \\ P=N \\ | \\ R \end{matrix}\right]_n+$$

where:

R = - Cl in polyphosphonitrile chlorides.
R = - OCH_3 in polydimethoxy phosphazines
R = - OC_6H_5 in polydiethoxy phosphazine

* alternate nitrogen & phosphorous groups.

a) Polyphosphonitrile chloride:

They are prepared by heating of cyclic tetramer in vaccum above 250°C.

$$n\,PCl_5 + NH_4Cl \xrightarrow[-(4n-1)HCl]{C_2H_2Cl_2} Cl\left[\begin{array}{c} Cl \\ | \\ P=N \\ | \\ Cl \end{array}\right]_n + (PCl_2N)_3 + (PCl_2N)_4$$

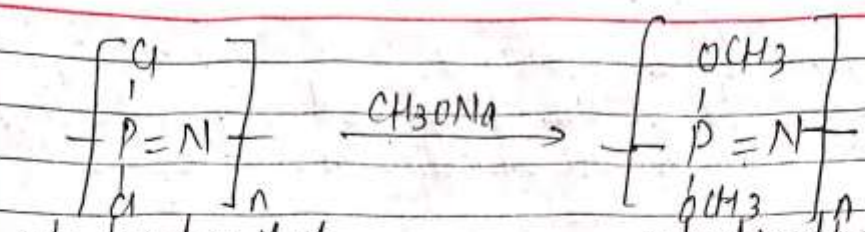
phosphorous pentachloride — ammonium chloride — cyclic trimer — cyclic tetramer.

$$n(PCl_2N)_4 \xrightarrow{250^\circ C\ \text{vaccum}} Cl\left[\begin{array}{c} Cl \\ | \\ P=N \\ | \\ Cl \end{array}\right]_{4n-4} Cl + \text{chain polymer}$$

$$(P_4 + 2N_2 + 3Cl_2)$$

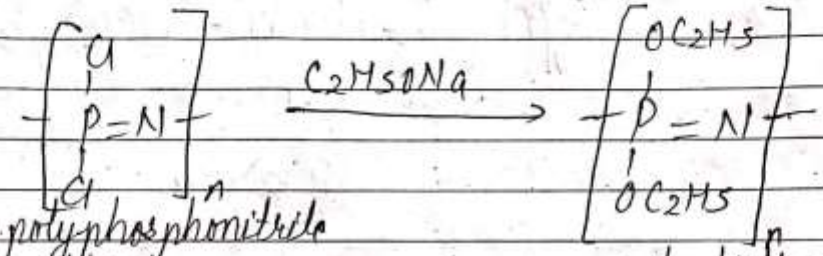
b) Polydimethoxy phosphazines & polydiethoxy phosphazines:

They are prepared by reacting of polyphosphonitrile chloride with sodium methoxide (CH_3ONa) & sodium ethoxide (C_2H_5ONa) respectively.



polyphosphonitrile chloride

polydimethoxy phosphazine.



polyphosphonitrile chloride

polydiethoxy phosphazine

Uses:

i) They are used for making transparent & film forming thermopolymers.
ii) Used for preparation of thermopolymers.
iii) Used in pipelines, & seals in oil, fuel delivery & storage systems.

2) Sulphur-based inorganic polymers:

The sulphur-based inorganic polymers are the polymers containing sulphur due to their catenation property.

They are categorized into 2 types as:

i) Linear chain polymers:

ii) Polymeric Sulphur (PS):

It is prepared by melting rhombic sulphur (S_8) at 165-168°C followed by pouring of molten sulphur into ice water. S_8 is converted into free radical which in combination with S_8 produces long chains. The solid product is washed with carbon disulphide to remove S_8 which if present converts polymeric sulphur to S_8.

$$S_8 \xrightleftharpoons{165-168^\circ C} {}^{\cdot}S-S_6-S^{\cdot}$$

$${}^{\cdot}S-S_6-S^{\cdot} \rightleftharpoons {}^{\cdot}S-S_{14}-S^{\cdot} \text{ and so on.}$$

It is unstable below the boiling point of sulphur i.e: 114°C and gets converted to rhombic sulphur.

Uses

i) It is used as flame proofing fabrics are known as plasticizers.

ii) It is used as catalyst in the silicones manufacturing process.

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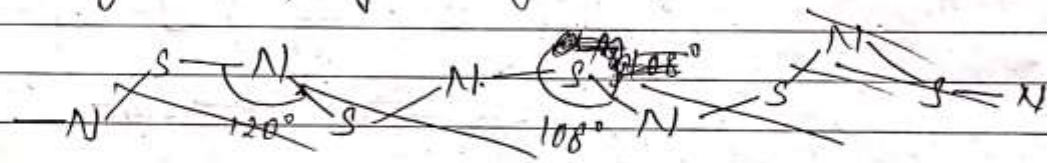
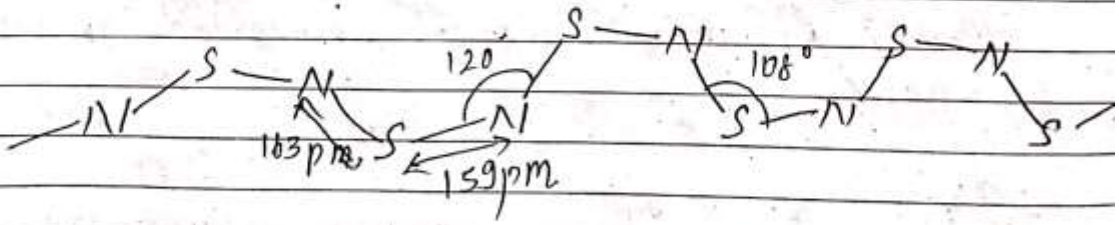
ii) Polymeric Sulphur nitride $(SN)_n$

Polythiazyl is also known as polymeric sulphur nitride $(SN)_n$ is an electrically conductive gold-coloured polymer with a metallic lustre.

S_4N_4 is the source for the preparation of $(SN)_n$. At first disulphur dinitride is formed when S_4N_4 is vapourised at reduced pressure and passed through silver wool followed by its slow polymerization resulting in polythiazyl $(SN)_n$.





It shows metallic conductivity and becomes a superconductor at 0.26 K so called as non-metallic superconductor.

Uses:

→ It is used for the construction of the digit circuit, digital computer, transformer, electric

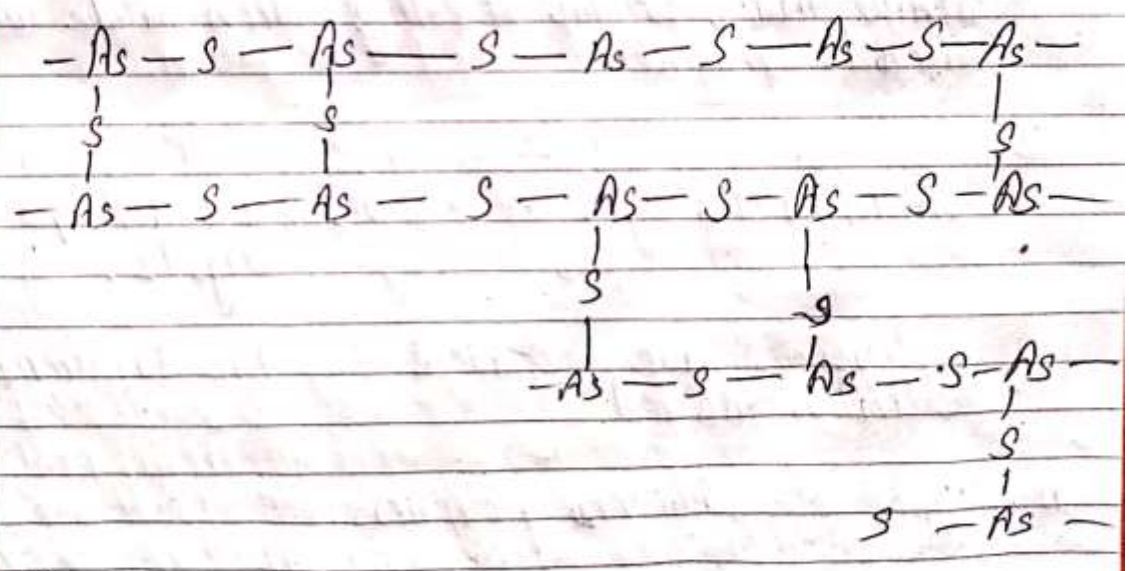
motor, etc

b) Chalcogenide glass or Network polymers.

They are cross-linked amorphous polymers formed by reacting polyvalent elements like As, Ge, In, P, Sb, etc., with chalcogens (S, Se, Te).

It is prepared under conditions for minimizing oxidation and loss of volatilization.

eg: $(SiS_2)_n$, $(As_2S_3)_n$ (best known chalcogenide) etc.



Uses:

→ They are used in ultrasonic delay lines, high energy particles detector, a memory device, electroluminescent displays.

→ Infrared transmitting windows are made from them

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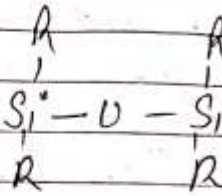
3) Silicones or Silicone polymer:

Silicones are inorganic polymer which contains alternate silicon, oxygen linkage. Organic radicals are attached with silicon atom.



Preparation:

Silicones are prepared by reacting alkyl halide or by reacting silicon halide with Grignard's reagent.

$$Si + CH_3Cl \longrightarrow CH_3SiCl_3 + (CH_3)_2SiCl_2$$

$$SiCl_4 + CH_3MgCl \longrightarrow (CH_3)_3SiCl + (CH_3)_4Si + MgCl_2$$

Silicones are prepared by the fractional distillation method.

Types of silicone polymers:

1) Monomethyl silicon trichloride $[CH_3SiCl_3]$
2) Dimethyl silicon dichloride $[(CH_3)_2SiCl_2]$
3) Trimethyl silicon trichloride $[(CH_3)_3SiCl]$

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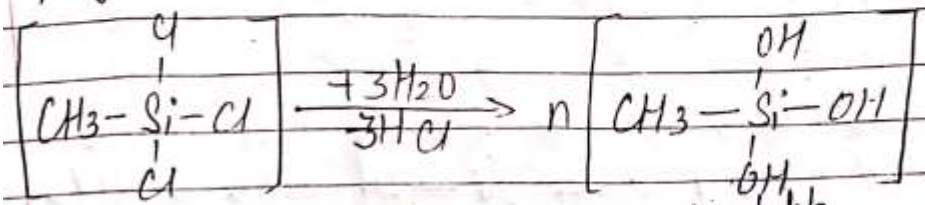
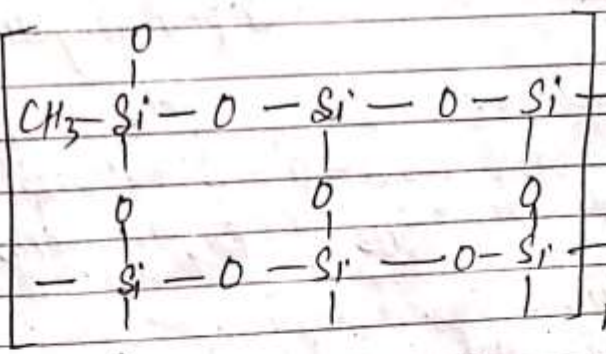
Monomethyl silicon trichloride $[CH_3SiCl_3]$

It is trifunctional ~~unit~~ unit particle and gives cross-linking to the final polymer.



Unstable

↓ polymerization

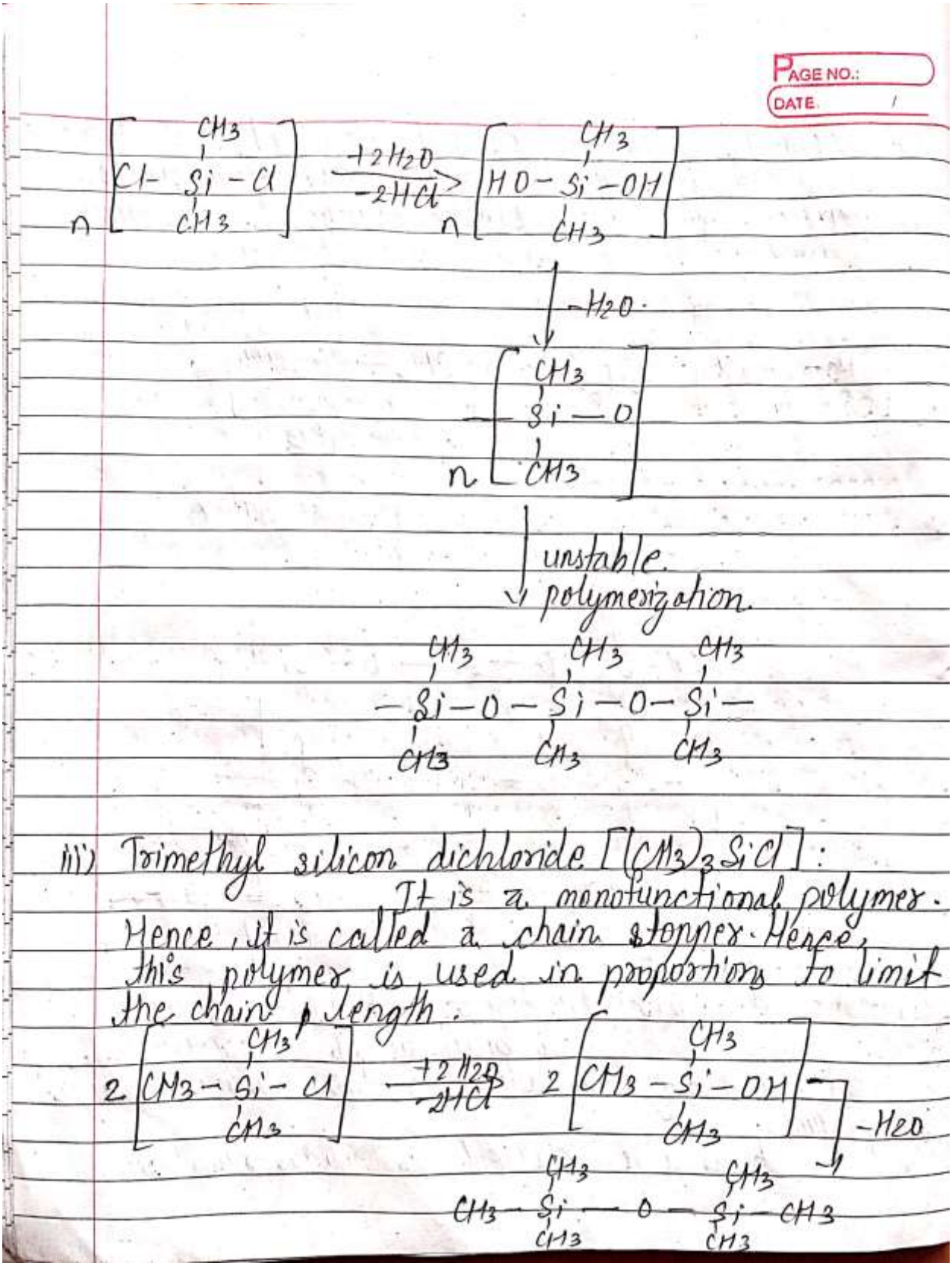


~~Monomethyl silicon trichloride~~
(cross linked)

ii) Dimethyl silicon dichloride $[(CH_3)_2SiCl_2]$

It is a bifunctional unit particle. After polymerization, it gives the linear chain polymer.

It is also called as silicon rubber.



iii) Trimethyl silicon dichloride [$(CH_3)_3SiCl$]:

It is a monofunctional polymer. Hence, it is called a chain stopper. Hence, this polymer is used in proportions to limit the chain length.

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Different types of silicone polymers and their uses:

a) Silicon oils / Liquid silicone polymer:
Generally, they are dimethyl silicone polymers having low molecular weight. They possesses low surface tension, a very small change in viscosity, etc.

Uses:
↳ They are used as high-temperature lubricants as they are highly stable and non-volatile.
↳ They are used in cosmetics and polishes.
↳ They are used in heat transfer media as damping and hydraulic fluids.
↳ They are used in high vaccum pump.

b) Silicon greases:
They are modified form of silicon oil. They are prepared by adding carbon black, silica, wood flour, china clay to silicone oil.

Uses:
↳ They are used as lubricants in airplanes.
↳ They don't freeze at low temperature (-40°C) and don't melt upto 200°C. So, silicone is used in cold as well as hot circumstances

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c) Solid silicone resins:

They are highly cross-linked polymers obtained by condensing bifunctional silicon polymer or trifunctional silicon polymer.

Uses:

↳ They are used for making high-temperature insulating materials and high voltage insulating materials.

↳ They are mixed with paints, pigment and enamel to make them resistant to the effect of high temperature, sunlight and chemicals.

d) Silicon rubber:

They are obtained by mixing high molecular weight of linear dimethyl silicon, fillers like silica, carbon black/metal, etc. which causes the formation of cross-linked between methyl groups of adjacent chains.

Uses:

-> They are used in ceiling joints of aircrafts and insulating electrical parts like transistors which cannot be heated.

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Properties of Silicones

i) They have high range of thermal stability (100°C - 250°C)
ii) They are able to repel water.
iii) They have excellent resistance to oxygen, Ozone, UV-rays, etc.
iv) They have low chemical reactivity.
v) They have low ionicity.
vi) They don't support micro-biological growth

Uses:

i) They are used as a sealing material in search lights and in aircrafts engines.
ii) As adhesive in electronic industry.
iii) For making artificial heart valves, transfusion tubing and padding for plastic surgery.
iv) For insulating the electrical wiring in ships.
v) For manufacturing tyres for fighter aircrafts.