B.Sc Sem-5 US05CCHE22 Inorganic Chemistry
Unit-4 Inorganic Polymers Lecture-5,6&7

By

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Polymers containing silicon :

Que-What are silicones. Discuss the types of silicones in details.2013, 2015, 2016,2018

Silicones are organo-silicon polymers containing ---O-Si-O—linkages, may be linear silicone cyclic silicone and cross-linked silicones.

Preparation: These are prepared by the hydrolysis of alkyl or aryl derivatives of SiCl4, like RSiCl3, R2SiCl2 and R3SiCl and polymerization of alkyl or aryl hydroxy-derivatives obtained by hydrolysis. Thus, this method consists of the following steps :

(i) To prepare alkyl or aryl derivatives of silicon tetrachloride. Examples of such derivatives are $RSiCl_3$, R_2SiCl_2 and R_3SiCl where R is an alky (e.g., CH_3, C_2H_5 etc.) or aryl (e.g., C_6H_5) group. These derivatives are prepared by the following methods :

(a) Methyl chlorosilanes like $(CH_3)SiC1_3$, $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$ are prepared by heating methyl chloride, $(CH_3)Cl$ with Si, catalysed by Cu, at 300°C. This reaction gives a mixture of methyl

$$2CH_3Cl + Si \xrightarrow{Cu,500^\circ C} (CH_3)SiCl_3 + (CH_3)_2 SiCl_2 + (CH_3)_3SiCl$$

It is mixture of CH_3Cl and HCl is heated with Si, catalysed by Cu, at 300°C, then $(CH_3)SiCl_3$ is

$$CH_3Cl + 2HCl + Si \xrightarrow{Cu,300^\circ C} (CH_3)SiCl_3 + H_2$$

(b) alkyl chlorosilanes can also be obtained by the action of Grignard reagent on $SiCl_4$.

$$3RMgCl\ (Grignard\ reagent) + SiCl_4 \longrightarrow RSiCI_3 + MgCl_2$$

$$2RMgC1 + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$$

$$3RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$$

(c) Phenyl(Aryl) chlorosilane, $(C_6H_5)SiCl_3$ is obtained by heating C_6H_6 with $HSiCl_3$ at

- $$C_6H_6 + HSiCl_3 + Si \xrightarrow{\Delta\ AlCl3} C_6H_5SiCl_3 + H_2$$

(ii) To prepare alkyl or aryl hydroxyl derivatives of silicon tetrachloride.

$$RSiCl_3 + 3H.OH \xrightarrow{Hydrolysis} RSi(OH)_3 + 3HCl$$

$$R_2SiCl_2 + 2H.OH \xrightarrow{Hydrolysis} R_2Si(OH)_2 + 2HCl$$

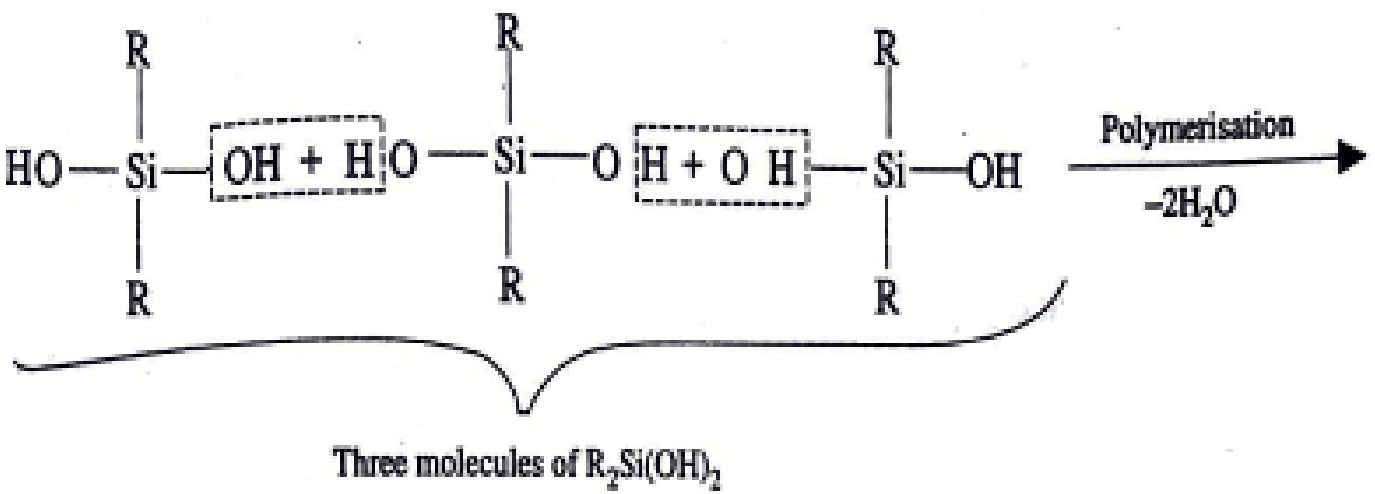
$$R_3SiCl + H.OH \xrightarrow{Hydrolysis} R_3Si(OH) + HCl$$

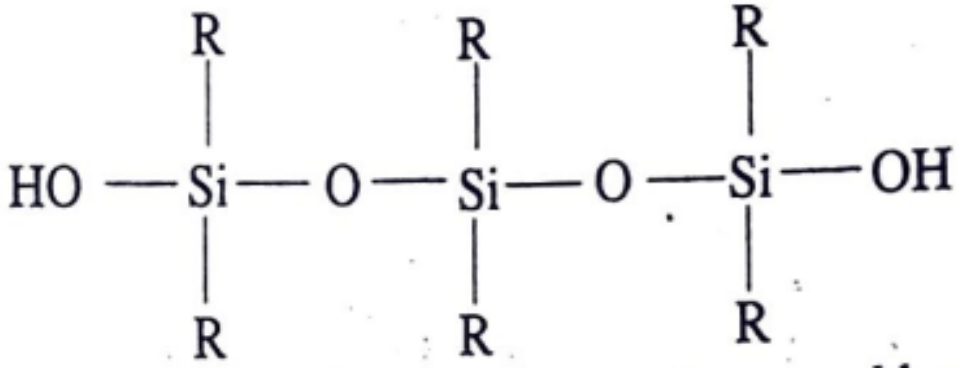
(iii) Polymerisation of silanols:

Que- write the polymerization process for dialkyl-dihydroxy-silane. 2-mark

The type of silicone obtained depends on the nature of alkyl or aryl hydroxy derivative and way in which the hydroxy-derivative undergoes Polymerisation.

(a) When many molecules of alkyl trihydroxy-silane, $R_2Si(OH)_2$ undergoes polymerization, a cross-linked two dimensional silicone is obtained.





Linear or straight chain silicone (Thermoplastic polymer) (siloxane)

Properties and uses of silicones :

Que- write the properties and uses of silicones.2013,

Que- write the properties of silicones. 2 mark 2013

- They have high thermal stability upto 300°C in the absence of air.
- Chemically inert, low mol wt. silicones dissolve in C_6H_6, ether and CCl_4.

- They do not become too viscous on cooling and are, therefore, used for low temp. Lubrication.
- They do not wetted by water so used, in making water proof cloth. and They have good insulating properties and thus used as insulator.

The silicone containing polymers have _____ thermal stability. 2015

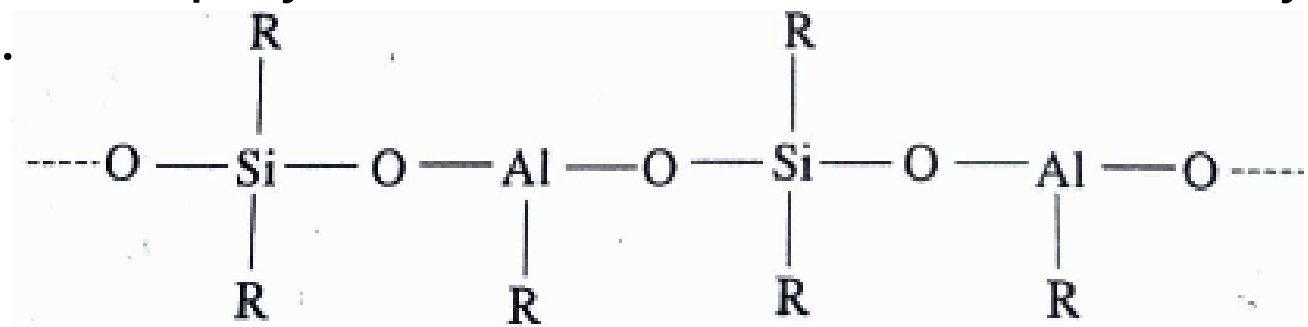
(a) **High** (b) low (c) medium (d) very low

Classification (types) of silicones :

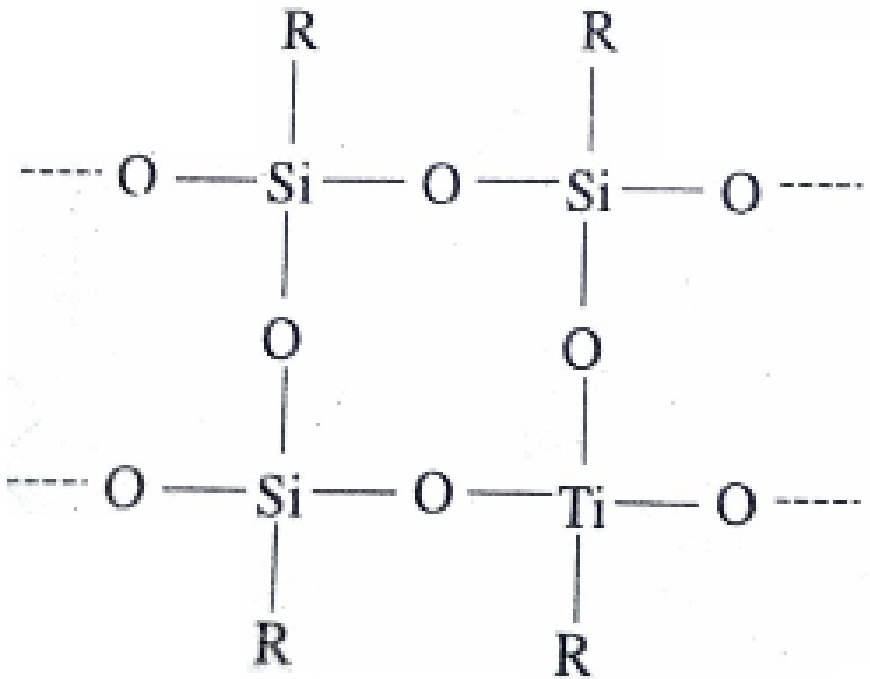
Depending upon the degree of polymerization, the length of the straight chain in cross-linked silicones and the nature of the alkyl or aryl groups attached with Si-atom in silicones, silicones can be obtained in the form of oils, viscous fluids, resin or rubber like solids as following types.

- **High thermal silicones**
- **Silicone resins**
- **Silicone fluids or oils.**
- **Silicone rubbers**
- **Silicone greases**

- **High thermal silicones.**
  When hydrolysis of an organo silicon halide followed by polymerization is carried out in presence of the halides or alkoxides of Al or Ti, two-dimensional linear or cyclic silicone polymer is obtained. In this polymer, some Si-atoms are replaced by Al or Ti atoms.
  High thermal silicones have exceptionally high thermal stability and remain unchanged, even in contact with a white-hot electrically-heated wire. The presence of Al and Ti atoms in the structure of the polymers increase the thermal stability of the polymers.

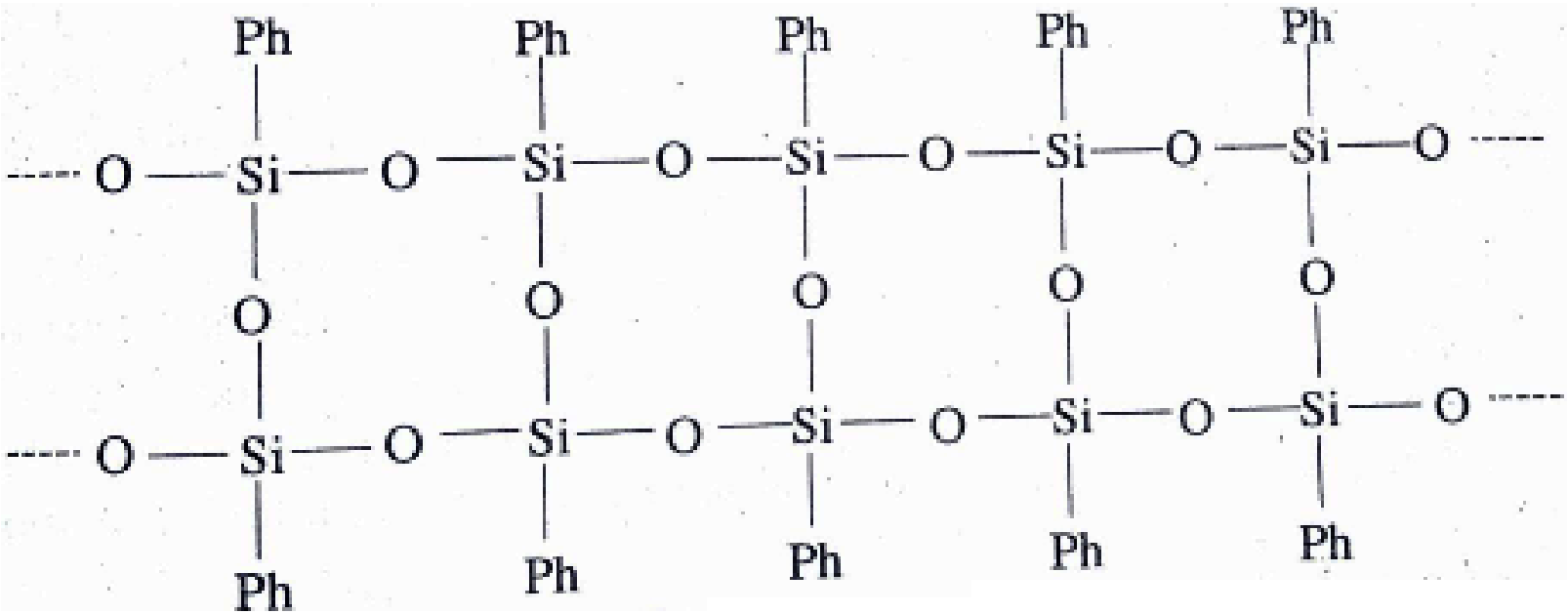


Linear polymer



Cyclic polymers

In l960, Brown at al reported the synthesis of a linear polymer. This polymer has exception all thermal stability. Its structure can be represented as:



Silicone resins:

They are obtained by blending(સંમિશ્રણ) silicone with organic resin, such as acrylic ester. They are of many types like coating resins, laminating resins, release resins, water-repellent resins, molding etc..

(3) Silicone fluids or oils:

Que- what are silicones ? Discuss silicone fluids and oils in details.) 2017

A silicone fluid is a mixture of equal proportions (1:1mix.of) of linear and cyclic polymers. These have low temperature-coefficient of viscosity and good insulating properties and high thermal stability used for high temp. oil bath, high vacuum pumps and low temp. lubrication.

A _____ is a mixture of equal proportions of linear and cyclic polymers. (2017)

(a) Silicone resins (b) silicone rubber
(c) **Silicone fluids** (d) silicone greases

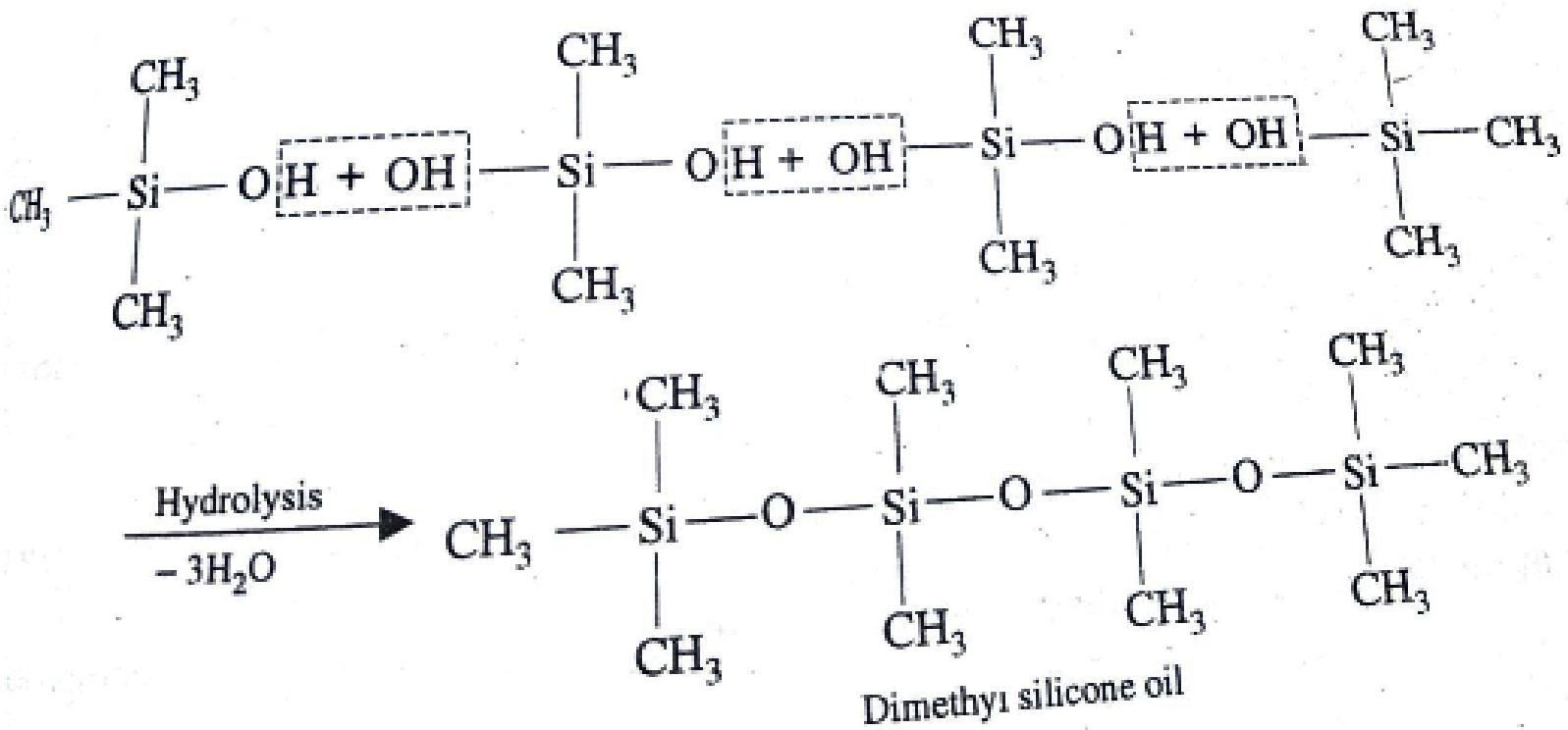
.

A _____ is a mixture of equal proportions of linear and cyclic polymers. (2015,2016)

(a) Silicone resins (b) silicone rubber
(c) **Silicone fluids** (d) high thermal silicone

Preparation of dimethyl silicone oil:

If a mixture containing $(CH_3)_3SiOH$ and $(CH_3)_2Si(OH)_2$ in proper ratio heated gets polymerized, dimethyl silicone oil is obtained,



4. Silicone rubbers:

Que-Explain Silicone Rubber, 2018

These are long chain polymers, with some cross-linking between chains, are made by the hydrolysis of $(CH_3)_2SiC1_2$ followed by polymer. $(CH_3)_3$-Si-O-Si$(CH_3)_3$ may be added to control length of the chain. Silicone rubbers consist of cross-linked type silicones with SiO_2 or ZnO as filler and vulcanizer, such as benzoyl peroxide.

The hydrolysis of followed by polymerization forms _____ .(2015)

(a) Silicon oil (b) **silicon rubber**

(c) silicon fluid (d) silicon resin

5. Silicone greases :

These are made by adding carbon black, special soaps or finely dispersed SiO_2 to silicone oils, used as lubricants in aeroplanes, since they do not freeze at as low temperature as -40°C and do not melt at 200°C.

The long chain vitreous sodium phosphate polymers are used in _____ industries.(2014)

(a) **Rubber** (b) electric (c) food (d) ceramic

Polymers containing phosphorus :

Classification or types of phosphorus polymers

Depending on the type of bonding existing between their atoms, these polymers can following two types :

1. Chain polymers :

2. Network polymers :

1. Chain polymers. These polymers include

(i) polyphosphazines, $[NPR_2]_n$ in which R=Cl, OCH_3 or OC_2H_5. Polyphosphazines may be of three types namely

(a) polyphosphonitrilic chlorides, $[NPCl_2]_n$

(b) polydimethoxy-phosphazines, $[NP(OCH_3)_2]_n$

(c) poly diethoxy-phosphazines,

(ii) polyphosphoryl chlorides, $P_nO_{2n-1}Cl_{n+2}$
(iii) vitreous polyphosphates
(phosphate glasses)
(iv) crystalline polymetaphosphates.
Examples are Maddrell's and Kuroll's salts
(v) platicised and flexible phosphates
(vi) polyphosphoric acids.
2. Network polymers.
These polymers include
(i) polymeric phosphorus pentoxide(P_2O_5)
(ii) polymeric boron orthophosphates, $[BPO_4]_n$
(iii) polymeric aluminium orthophosphate
$[AlPO_4]_n$
(iv) polymeric silver orthophosphate, $[Ag_3PO_4]_n$
(v) polymeric ferrous orthophosphate,
$[Fe_3(PO_4)_2.8H_2O]_n$

(vi) Sulphur phosphorus polymers
(vii) ultraphosphate glasses

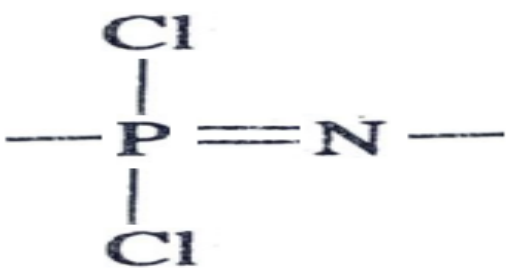
(viii) boron phosphate glasses.

Here, we shall discuss only polyphosphonitrilic chlorides, vitreous polyphosphates, crystalline polymetaphosphates, polyphosphoric acids and borophosphate glasses.

Polyphosphonitrilic chlorides, $[PNCl_2]_n$ n = 3 to 7)

Que-discuss the Preparation, properties of polyphosphonitrilic chloride molecules $(NPCl_2)_3$ 2013, 2016.

As a repeating unit, linear polymers are also called inorganic rubber.



Preparation. The following methods have been used for the preparation of these compounds:

(i) $(NPCl)_3$ and $(NPCl_2)_4$ can be prepared by the ammonolysis of PCl_5.

$$nPCl_5 + nNH_3 \rightarrow (NPCl_2)_n + 3nHCl$$

$$3PCl_5 + 3NH_3 \rightarrow (NPCl_2)_3 + 9HCl$$

(Tri phosphonitrilic chloride)

$$4PCl_5 + 4NH_3 \rightarrow (NPCl_2)_4 + 12HCl$$

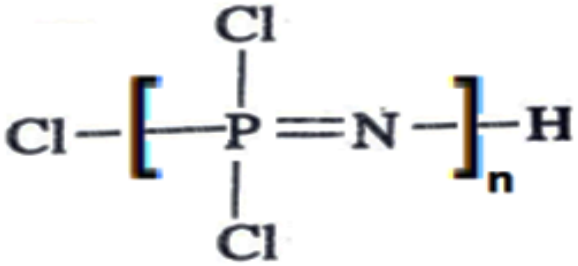
(Tetra phosphonitrilic chloride)

(i) °C.

$$nPCl_5 + nNH_4Cl \xrightarrow[\textit{ethelene chloride}]{\textit{Presence of}} (NPCl_2)_n + 4nHCl$$

Properties.

(i) Cylic trimer or tetramer when heated in vacuum at 250°C gives a chain polymer.

$n[NPCl_2]_3$ or $n[NPCl_2]_4$ $\xrightarrow{250°C,\Delta}$ 

Cylic

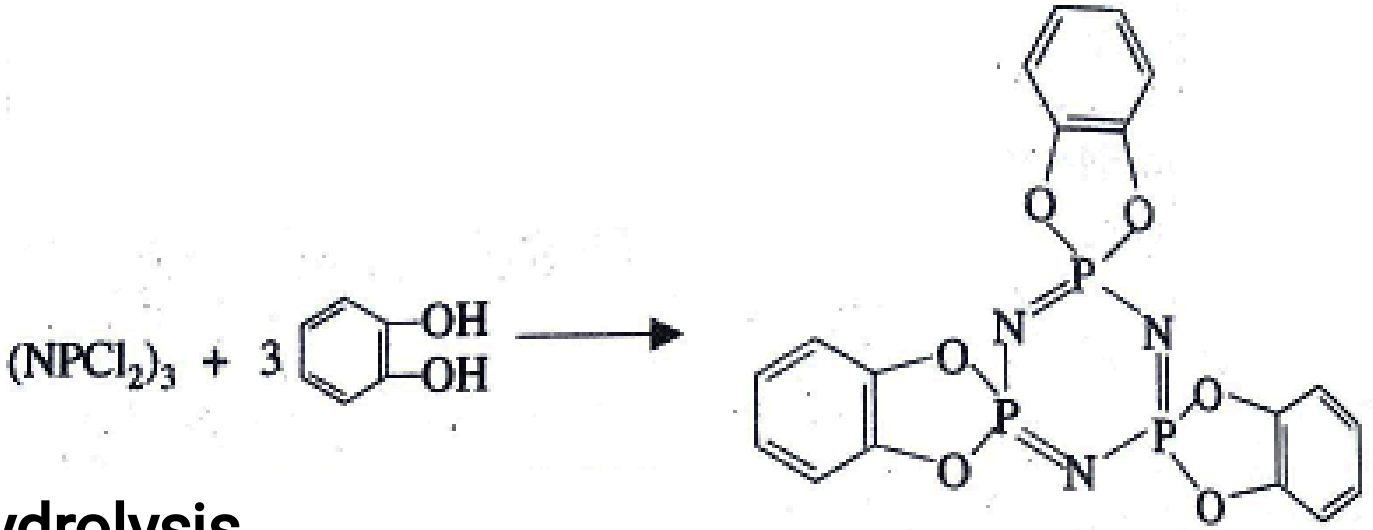
chain polymer

(ii)**Nucleophilic sub reaction:** involving replacement of Cl-atom of P-Cl bond. Cl-atom in P-Cl bond in fairly replaced by many nucleophiles.

$[NPCl_2]_3 + 6NaF \rightarrow (NPF_2)_3 + 6NaCl$

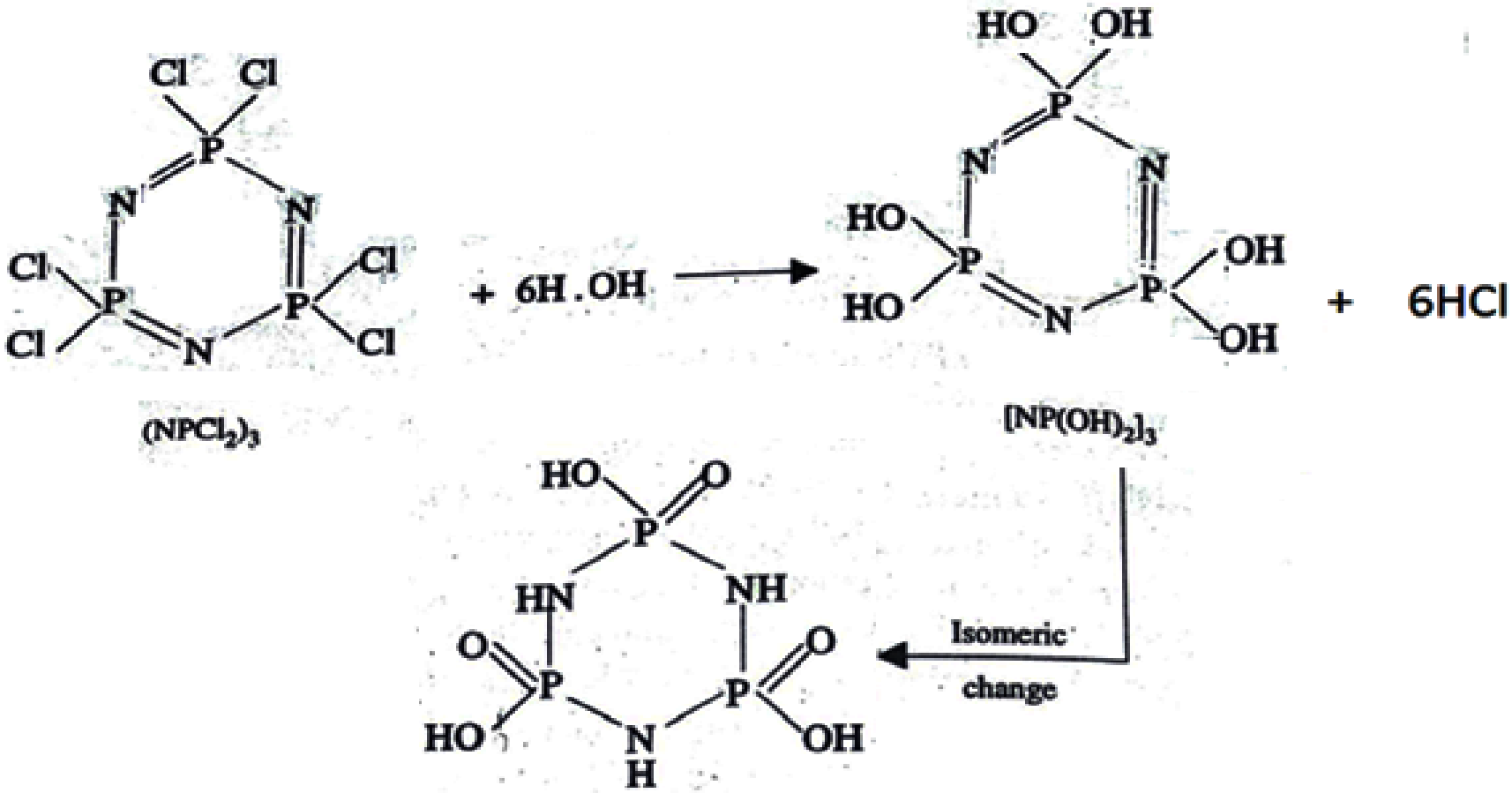
$[NPCl_2]_3 + 6NaOC_2H_5 \rightarrow [NP(OC_2H_5)_2]_3 + 6NaCl$

Tri (diethoxy)phosphazine



(iii) **Hydrolysis**.

(a) **Cyclic polymer**:- When $(NPCl_2)_3$ reacts with H_2O (aqueous ether), all Cl-atoms are replaced by OH groups.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+ 6HCl
(NPCl2)3
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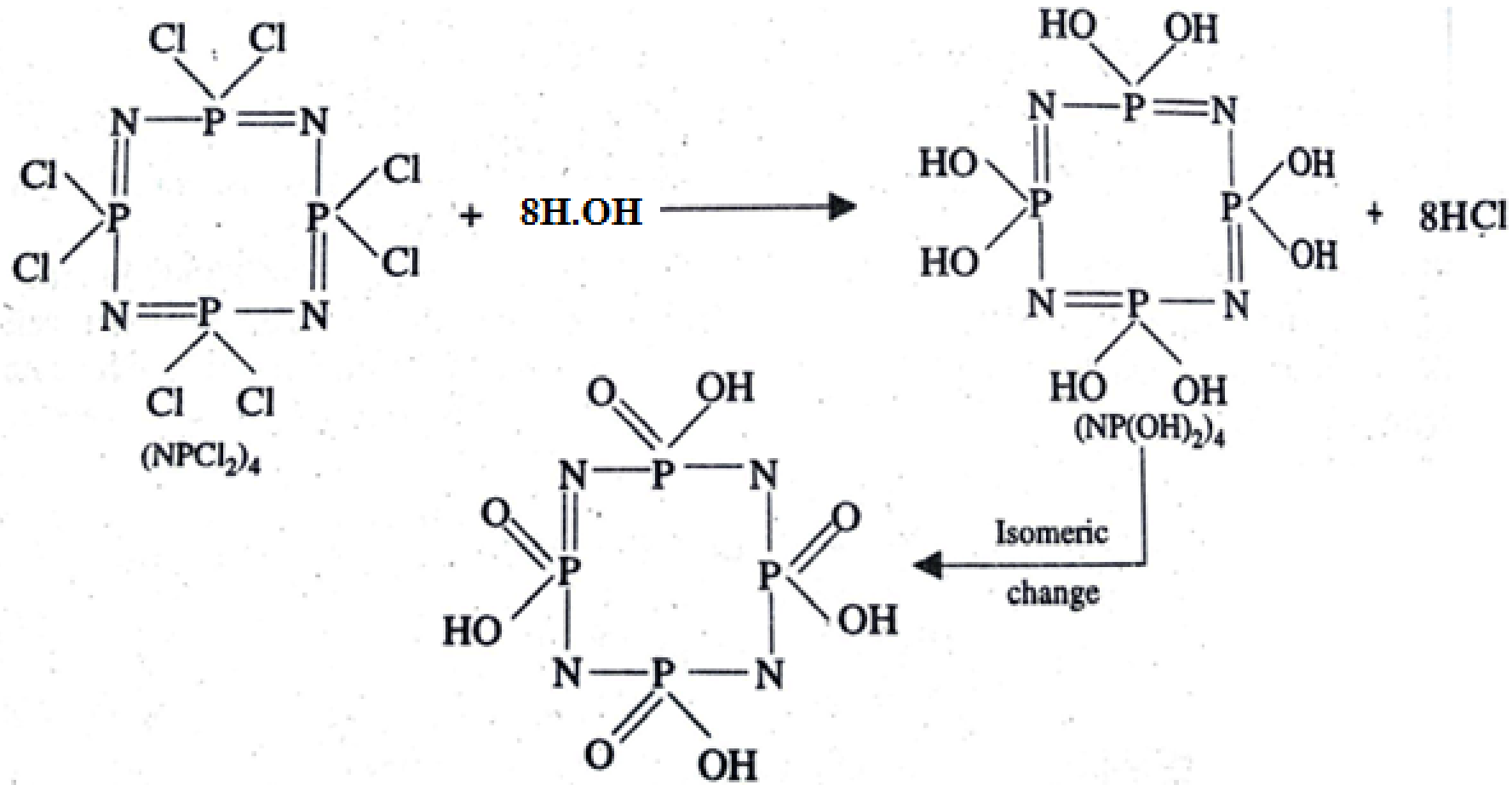
Isomeric
change


Cl Cl
N P N
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(NPCl2)4
+ 8H.OH
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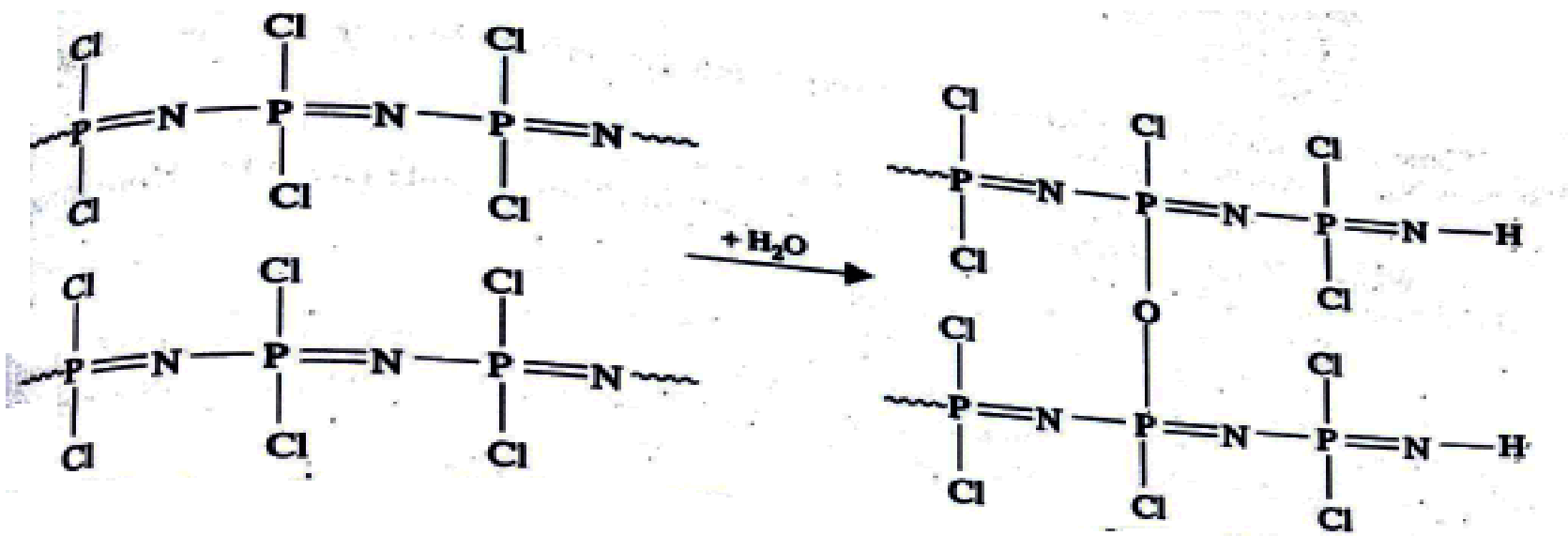
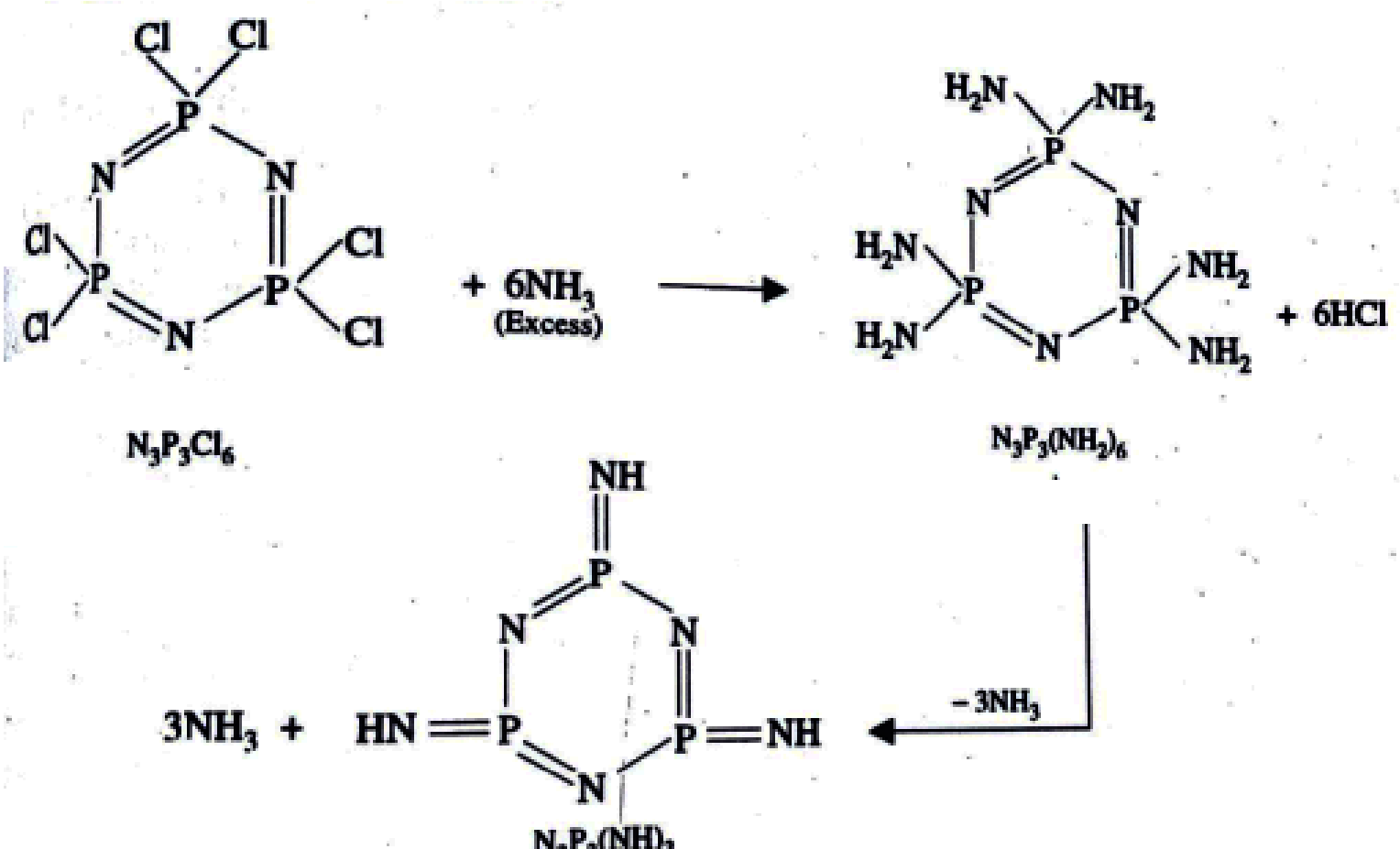
HO P P OH
N P N
HO OH
(NP(OH)2)4
+ 8HCl
Isomeric
change
O OH
N P N
O P P O
HO P P OH
N P N
O OH

(b) Linear polymer:

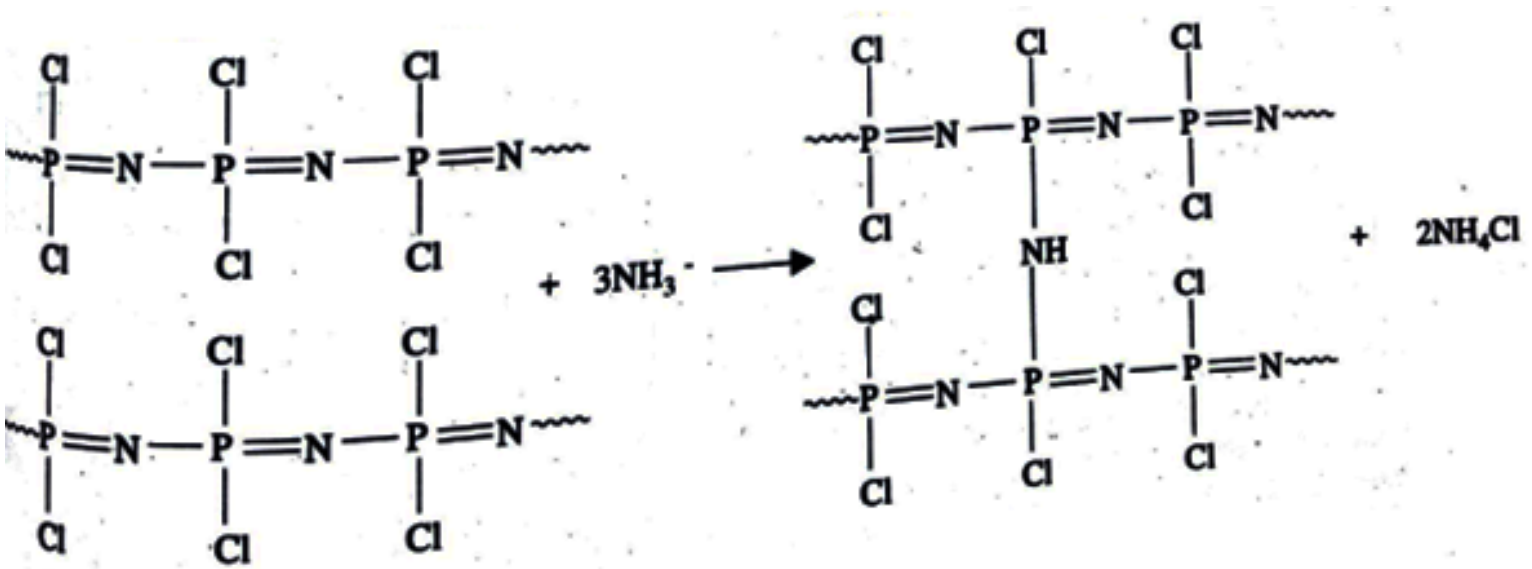
When linear $[NPCl_2]_n$ polymers are stored in air, they become brittle. This due to the action of H_2O which forms O-bridges between P-atoms,



- (iv) **Ammonolysis** (a) when $[NPCl_2]_3$ reacts with excess of NH_3, all the six Cl-atoms are replaced by NH_2 group and $N_3P_3(NH_2)_6$ is produced. This compound loses $3NH_3$ molecules, forming ph



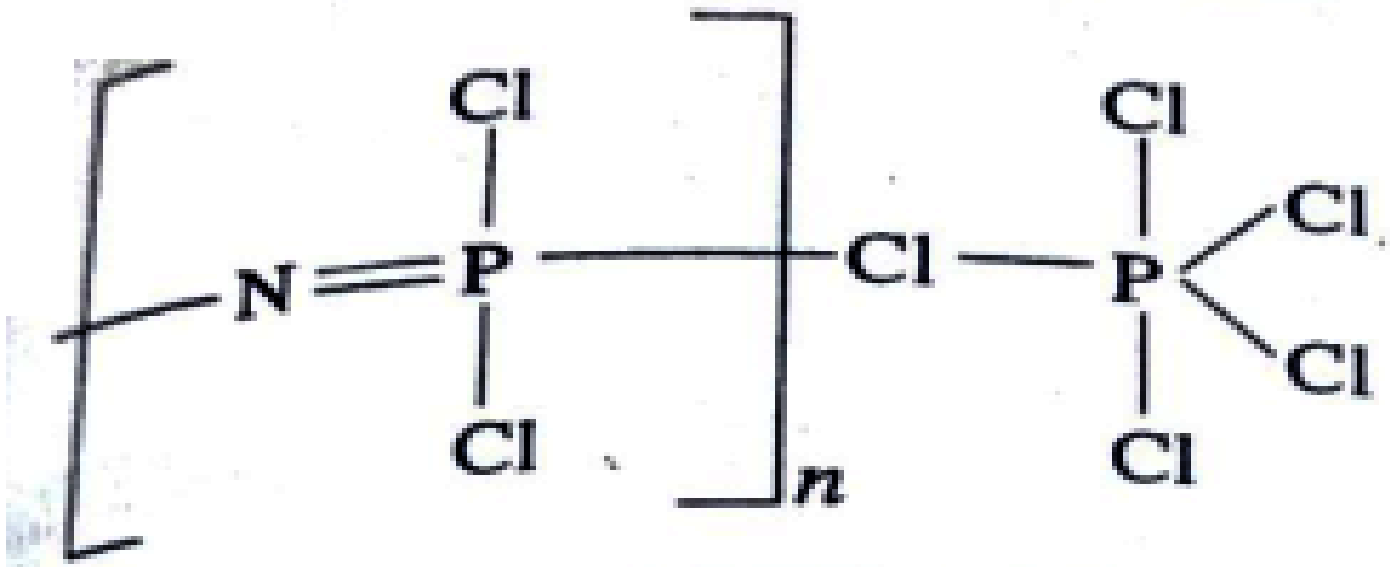
- (b) linear $[NPCl_2]_3$ gives crosslinked polymer



(v) in presence of $AlCl_3$ $N_3P_3Cl_6$ react with benzene form diphenyl derivative. These polymers exhibit high elasticity and can be stretched several fold with complete recovery. However they undergo degradation at normal temperature than do the organic rubber. Hence find much less

Linear polyphosphonitrilic chloride: [inorganic rubber]
Que- write note on inorganic rubber. 2-mark) 2014, 15, 16

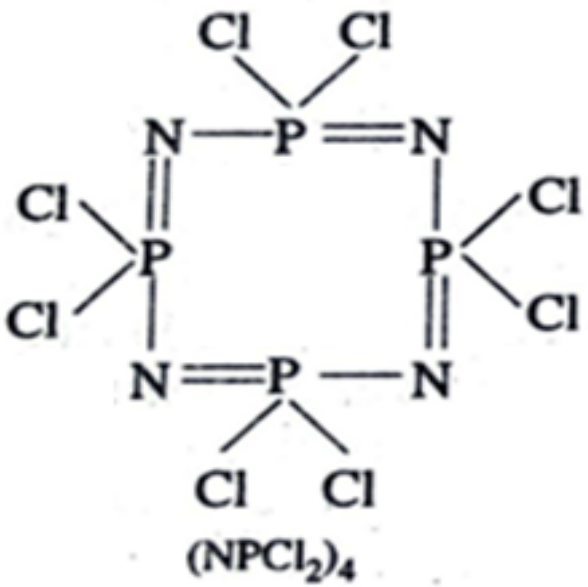
When PCl_5 and NH_4Cl are heated together in a refluxing 5-tetrachloro ethane, a product obtained insoluble in petroleum ethane has composition $[NPCl_2]_nPCl_5$, n=10 to 15. It is rubber like hence called inorganic rubber. It becomes brittle when kept in air for several hours, due to hydrolytic condensation by atmosphere.



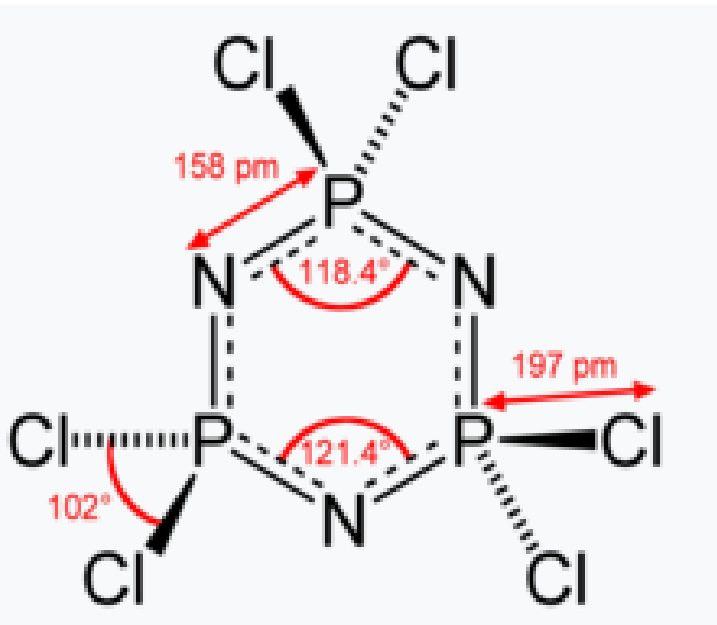
Structure of $[NPCl_2]_n \cdot PCl_5$

The bond angle of ClPCl in $[NPCl_2]_4$ is _____ .(2018)

(a) 102 º (b) **90 º** (C) 108 º(d) 45 º



$[NPCl_2]_4$



$[NPCl_2]_4$

THANK YOU