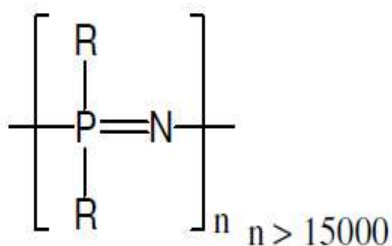


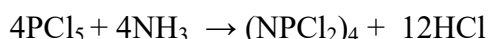
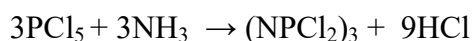
# polyphosphazene

**Definition:** Polyphosphazenes are largest class of inorganic polymers because of ease of side group modification. Inorganic polymers containing alternate phosphorous and nitrogen atoms with two substituent on each phosphorous atom are polyphosphazene. Side groups (R) can be organic, inorganic or organometallic. Method of synthesis allows modification of side groups. The three main structural types are cyclic trimer, cyclic tetramer and the oligomer or high polymer. A few cyclic pentamers and hexamers are also known. Each macromolecule typically contains from 100 to 15,000 or more repeating units linked end to end, which means that (depending on the organic side groups) the highest molecular weights are in the range of 2 million to 10 million.

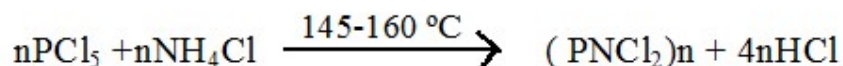
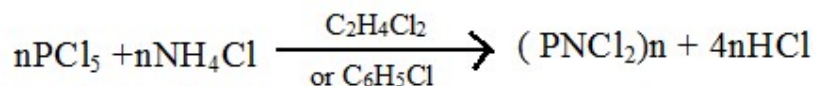


## Preparation of polyphosphazene:

(i)  $(\text{NPCl}_2)_3$  and  $(\text{NPCl}_2)_4$  can be prepared by ammonolysis of  $\text{PCl}_5$



(ii) These compounds can be prepared by the reaction between  $\text{PCl}_5$  and  $\text{NH}_4\text{Cl}$  in presence of  $\text{C}_2\text{H}_4\text{Cl}_2$  or  $\text{C}_6\text{H}_5\text{Cl}$  or by heating  $\text{PCl}_5$  with solid  $\text{NH}_4\text{Cl}$  at 145-160 °C.

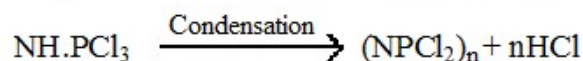
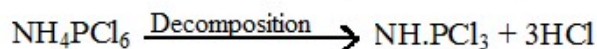
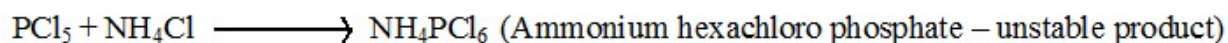


Both the above reactions produce a mixture of various phosphonitrilic chlorides, but under controlled condition, high yields of  $(\text{NPCl}_2)_3$  and  $(\text{NPCl}_2)_4$  can be obtained. These two

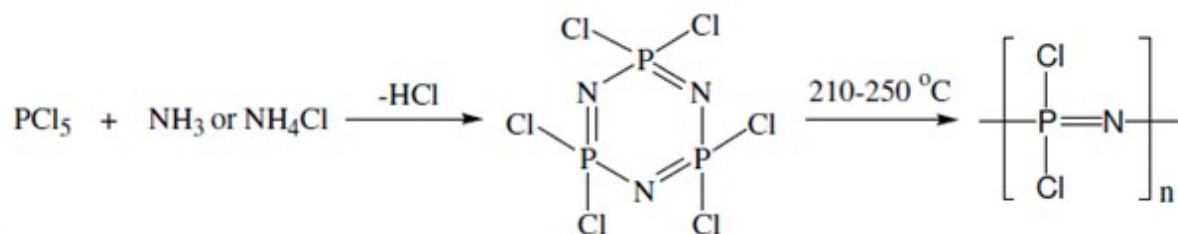
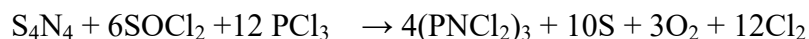
# polyphosphazene

compounds can be separated from each other by using the fact that  $(\text{NPCl}_2)_3$  sublimes in vacuum at  $50^\circ\text{C}$  as a white crystalline solid whereas  $(\text{NPCl}_2)_4$  does not do so under these condition.

The formation of  $(\text{NPCl}_2)_n$  takes place through the following steps.

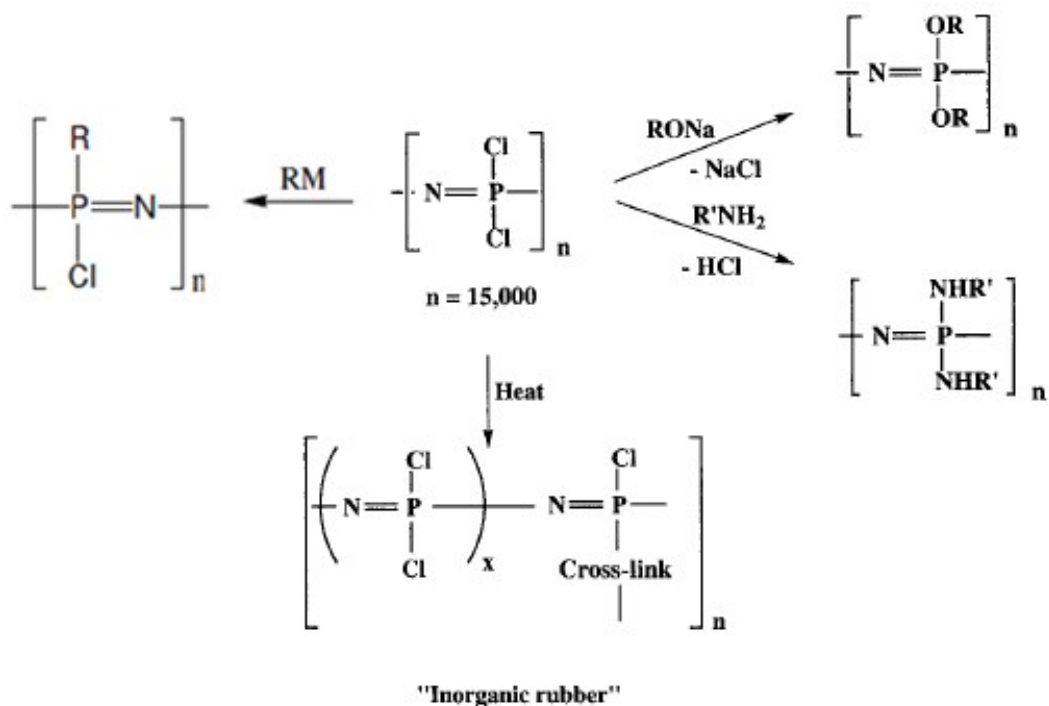


(iii)  $\text{S}_4\text{N}_4$  reacts with  $\text{SOCl}_2$  in  $\text{PCl}_3$  to give  $(\text{NPCl}_2)_3$

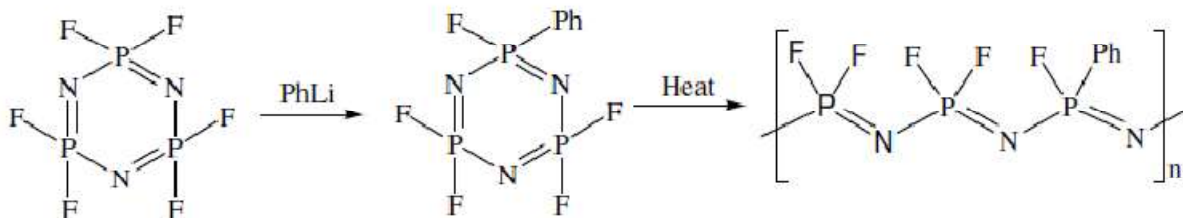


**Macromolecular Substitution:** Careful control of the time, temperature, and cyclic trimer purity, and termination of the reaction before it reached approximately 70% conversion to polymer, yielded an essentially linear high polymer that dissolved completely in organic solvents such as benzene, toluene, or tetrahydrofuran. Solutions of poly(dichlorophosphazene) in benzene, toluene, or tetrahydrofuran react rapidly and completely with nucleophiles such as sodium trifluoroethoxide to yield derivative polymers as shown in reaction sequence. However, further heating of this polymer caused cross-linking of the chains and yielded the insoluble inorganic rubber.

# polyphosphazene

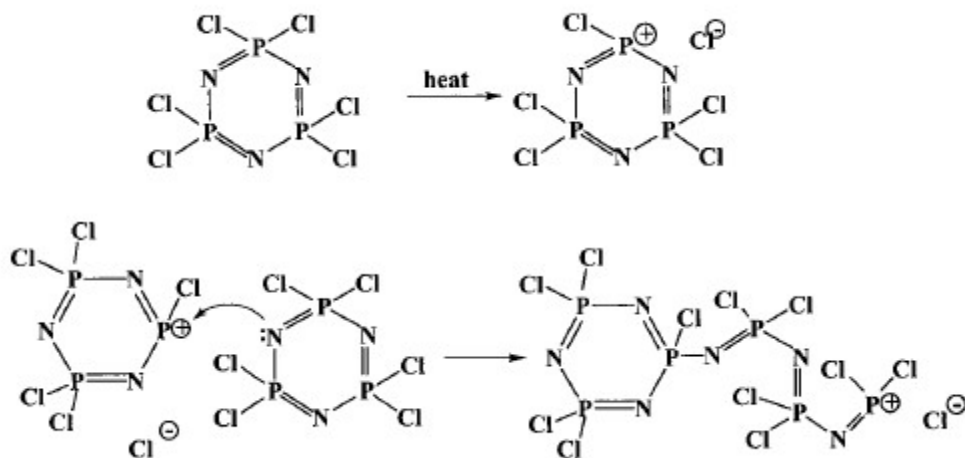


$(\text{NPF}_2)_n$  is prepared by polymerization of the trimer,  $(\text{NPF}_2)_3$ , which itself is obtained from  $(\text{NPCl}_2)_3$  by treatment with sodium fluoride. In principle,  $(\text{NPF}_2)_n$  is a very useful macromolecular intermediate. However, in practice, its insolubility in all solvents except specialized fluorocarbon media limits its usefulness. This problem can be overcome by the use of a fluoro-polymer that has one phenyl side group for every three repeating units. This macromolecule is soluble in several ordinary organic solvents and is, thus, an excellent substrate for fluorine replacement reactions.



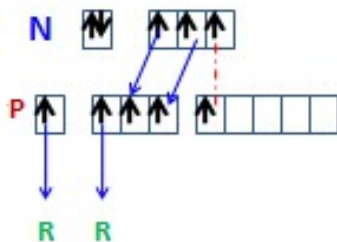
# polyphosphazene

**Mechanism of ring opening polymerization:** In this mechanism it is assumed that polymerization is induced by ionic species, generated by the ionization of P-Cl bonds to form a cyclic (or linear) phosphazanium ion. The phosphazanium ion would then act as a cationic initiator by attack on the skeletal nitrogen atom of an  $(\text{NPCl}_2)_3$  molecule, inducing ring opening and chain propagation by a cationic mechanism.



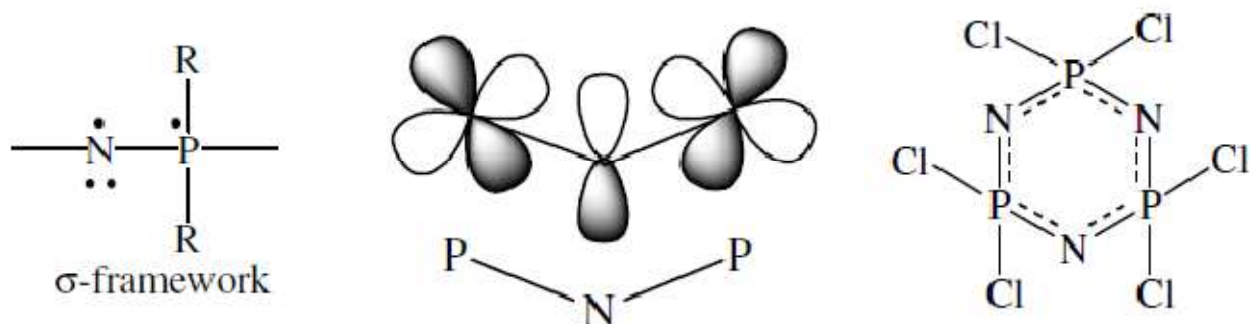
## STRUCTURE

The halide trimers consist of planar six membered rings. The bond angles are consistent with  $\text{SP}^2$  hybridization of the nitrogen and  $\text{SP}^3$  hybridization of the phosphorous. Two of the  $\text{SP}^2$  orbital of nitrogen, containing one electron each, are used for 's' bonding and the third contains a lone pair of electron. This leaves one electron for the unhybridised PZ orbital. The four  $\text{SP}^3$  hybrid orbital (containing four electrons) of phosphorous are used for 's' bonding leaving a fifth electron to occupy a 'd' orbital. Resonance structures can be drawn like benzene ring indicating aromaticity . The Planarity of the ring, the equal P-N bond distances and the shortness of the P-N bonds, and the stability of the compounds suggest delocalisation. All phosphazenes are not planar.



# polyphosphazene

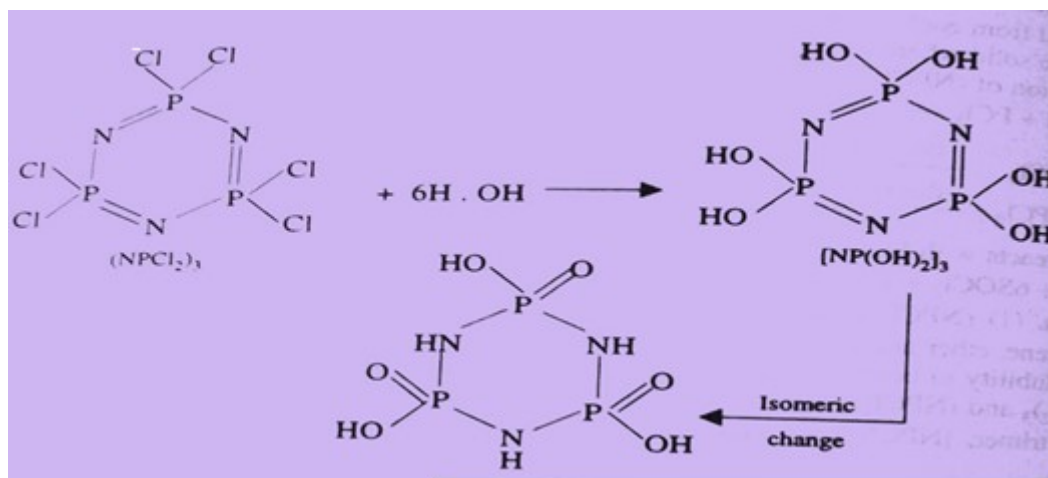
**Bonding in Polyphosphazenes:** Each phosphorus atom provides five valence electrons per repeating unit, and each nitrogen contributes an additional five. If two of the electrons from nitrogen are confined to a lone-pair orbital, and electron pairs are assigned to the sigma bond framework, two electrons are left unaccounted for—one from phosphorus and one from nitrogen. These electrons do not remain unpaired. It is believed that the electron on nitrogen is accommodated in a  $2p_z$  orbital, and the one from phosphorus in a  $3d$  orbital to generate an arrangement. Thus, although the pi-bonds are delocalized over “islands” of three skeletal atoms, they are not broadly delocalized over the whole chain because of the orbital mismatch and nodes that occur at every phosphorus. Moreover, because each phosphorus can use as many as five  $3d$ -orbitals, torsion of a P-N bond can bring the nitrogen p-orbital into an overlapping position with a d-orbital at virtually any torsion angle. Hence, the inherent torsional barrier is much smaller than in a  $\pi\pi$  double bond of the type found in organic molecules. Polyphosphazenes are not coloured and do not conduct electricity that is characteristic of extensive conjugation.



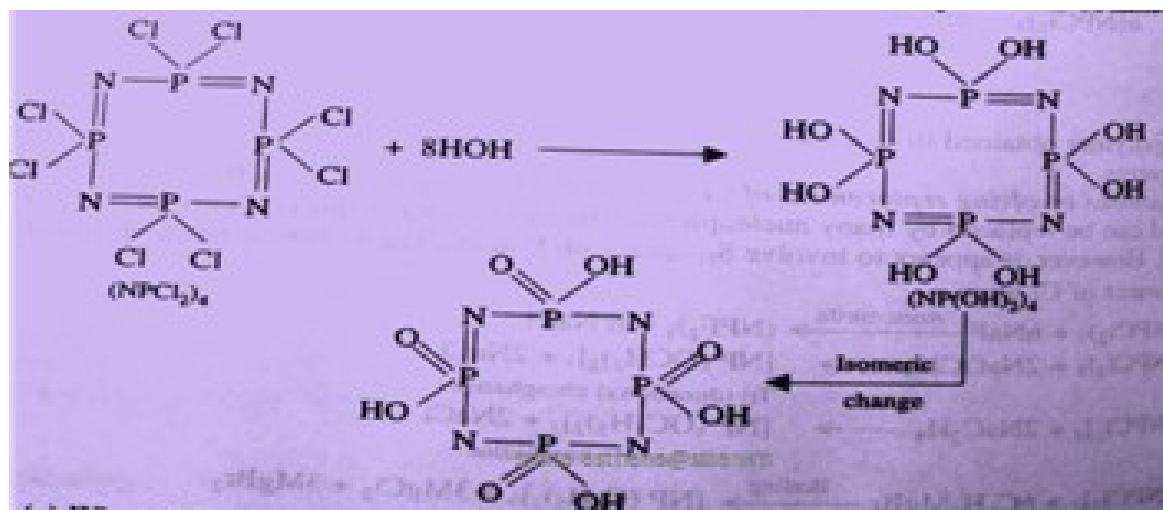
## Properties: Hydrolysis

(a) When  $(\text{NPCl}_2)_3$  reacts with  $\text{H}_2\text{O}$ , all Cl atoms are replaced by OH groups.

# polyphosphazene



(b) Hydrolysis of  $(NPCl_2)_4$  in boiling water is rapid and a stable product is obtained.



## USES OF PHOSPHAZENES:

1. The phosphonitrilic halides are used as rigid plastics, fibers because they are water proof and fire proof and are unaffected by oil and petrol.
2. They are used as catalysts in manufacture of silicones.
3. Thin films of poly( aminophosphazene) are used to cover severe burns because they prevent the loss of body fluids and keep germs out.