

Inorganic polymer

Ferdowsi University of Mashhad

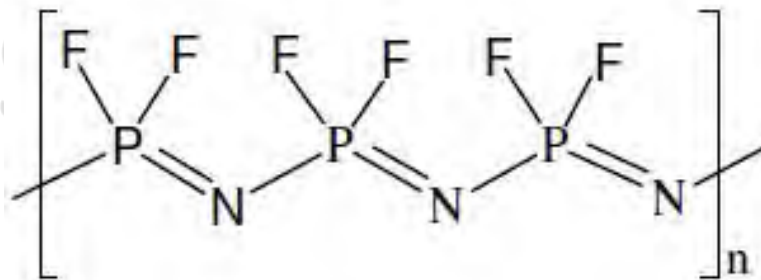
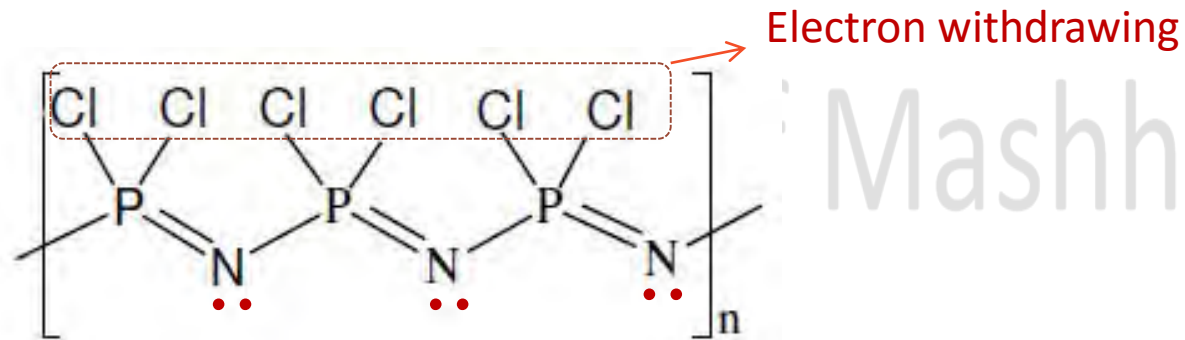
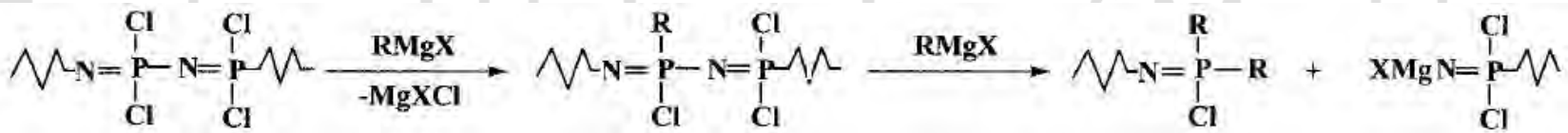
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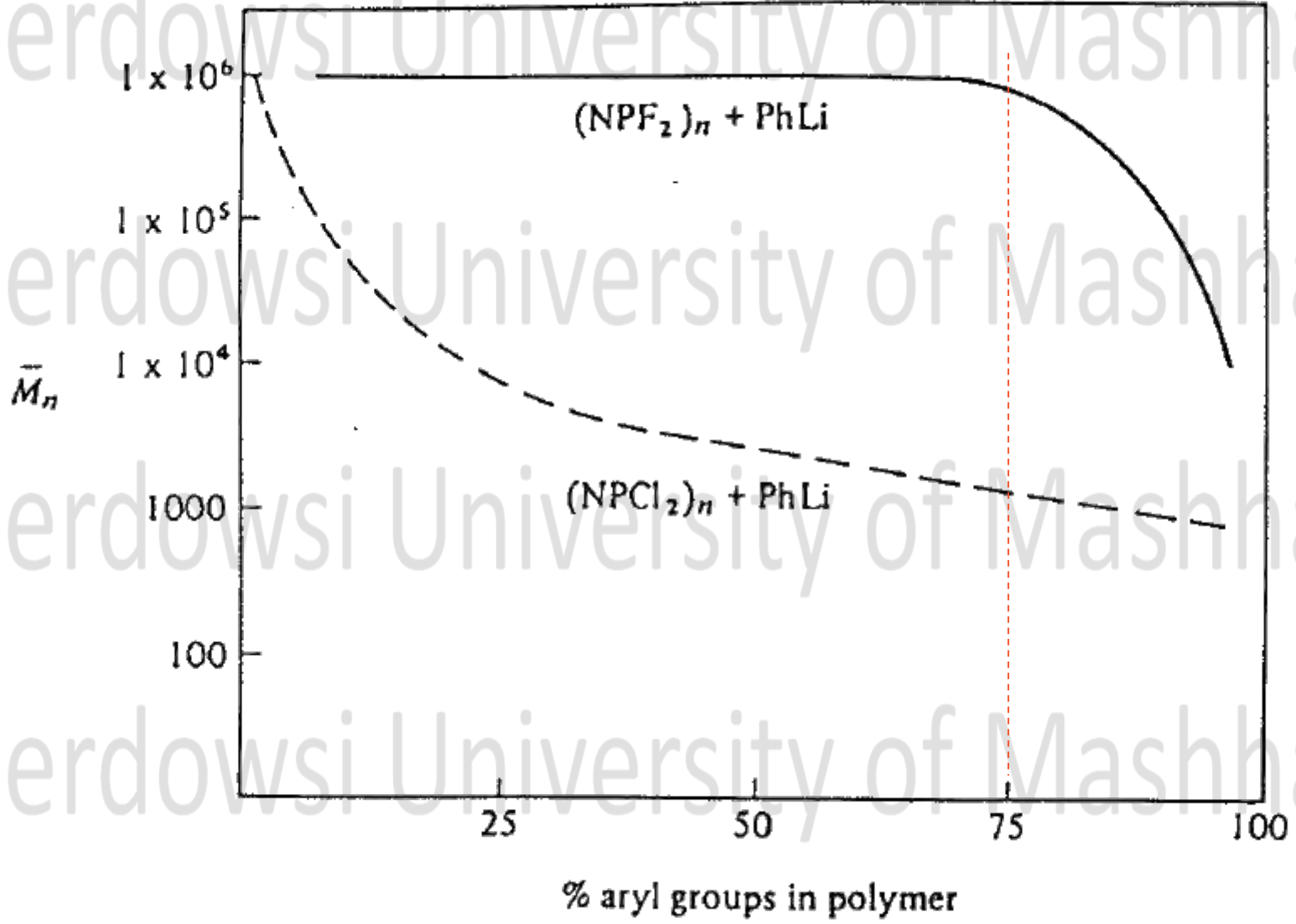


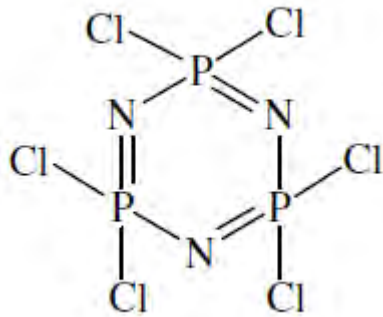
Grignard reagents

Organolithium reagents

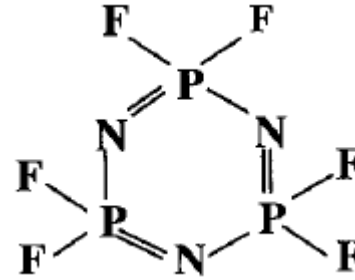
organometallic nucleophiles



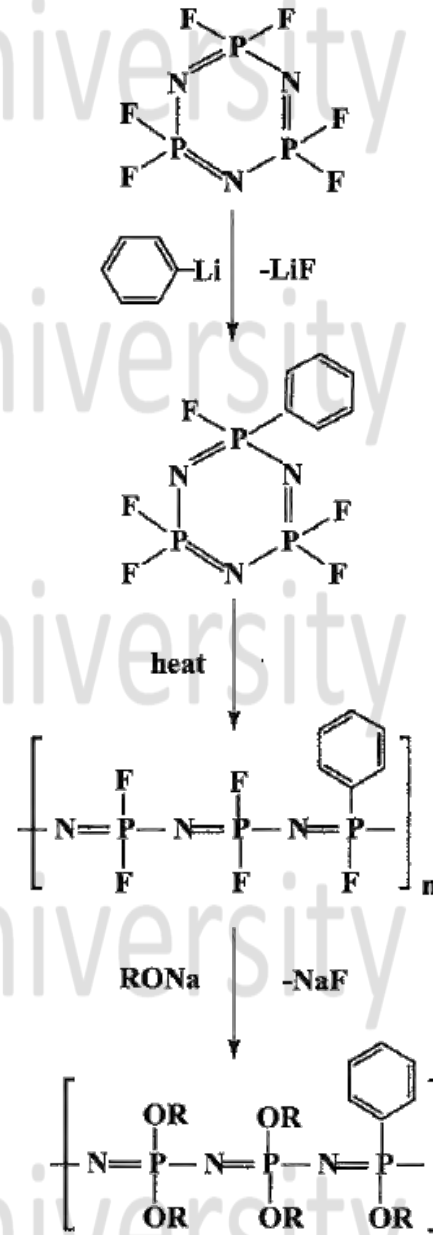




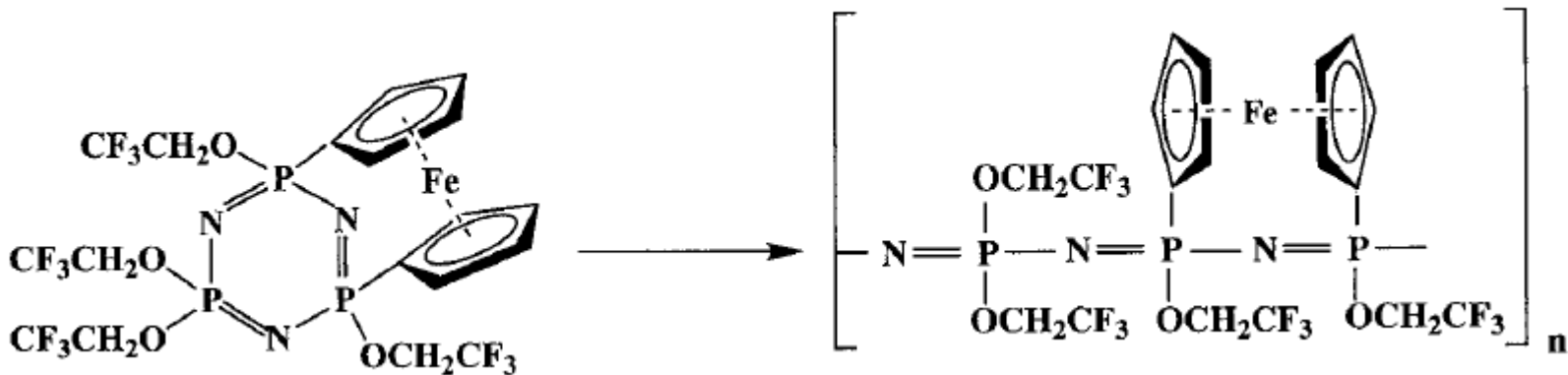
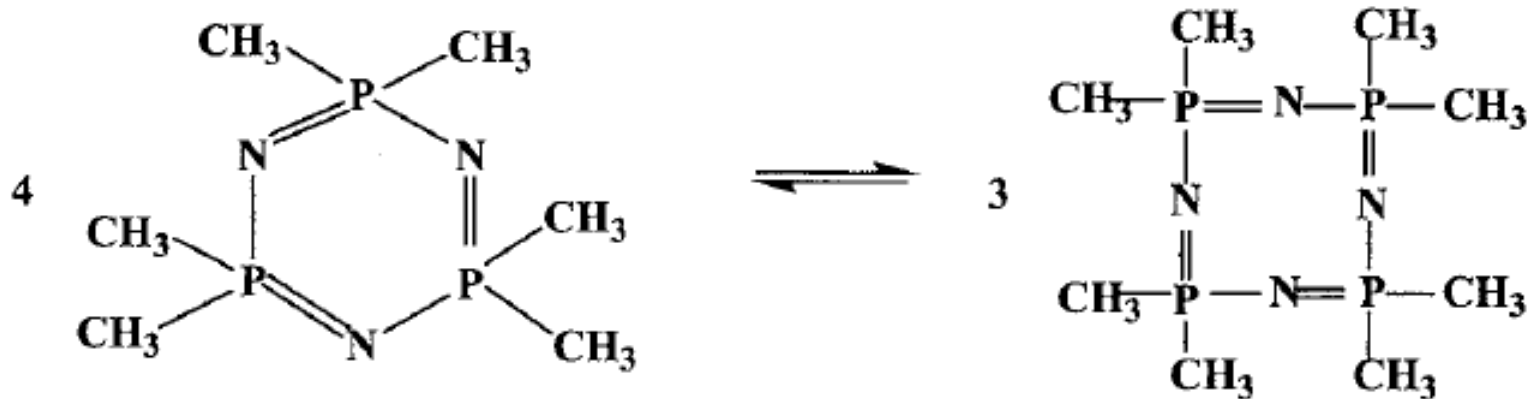
sodium fluoride

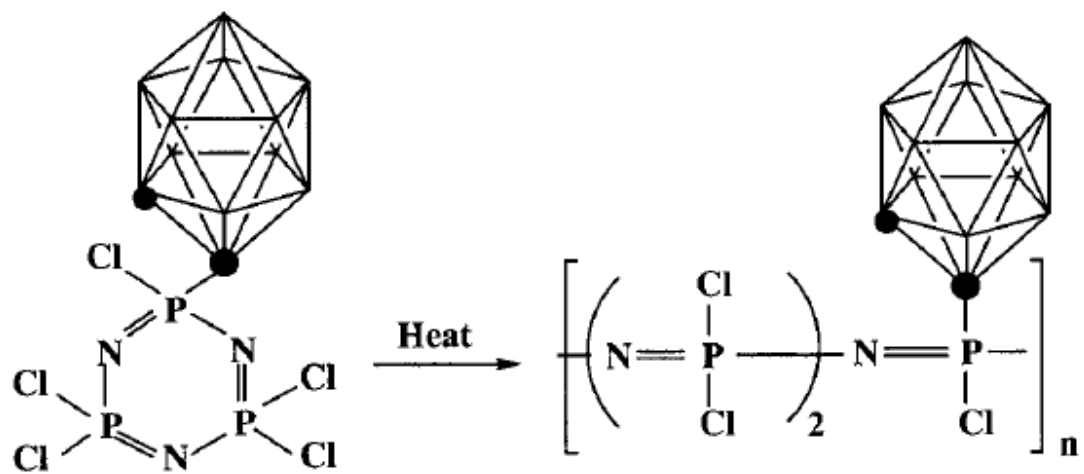
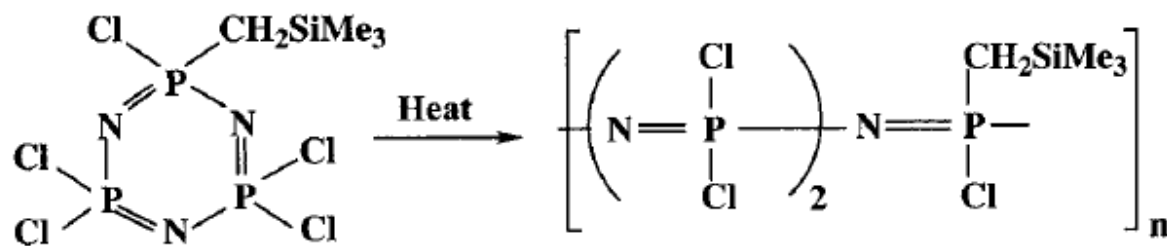
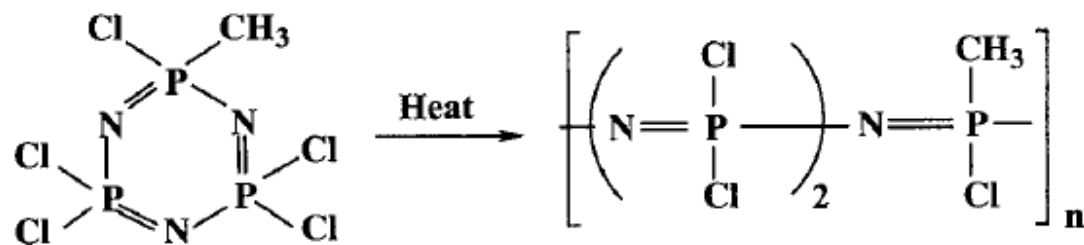


insolubility just in fluorocarbon



Polymerization of Organo- or Organometallo-Substituted Cyclic Phosphazenes





Mechanism of Ring-Opening Polymerizations

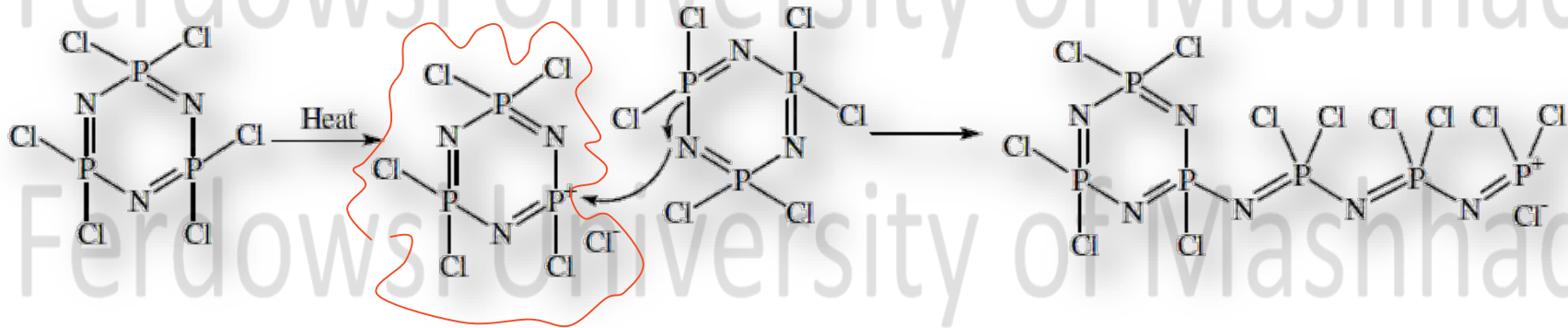


Need to several halogen atoms attached to the ring phosphorus atoms

ionic conductivity of molten $(\text{NPCI}_2)_3$

catalytic effect of impurity

Different temperature required for the polymerization of $(\text{NPF}_2)_3$ (350 °C) and $(\text{NPCI}_2)_3$



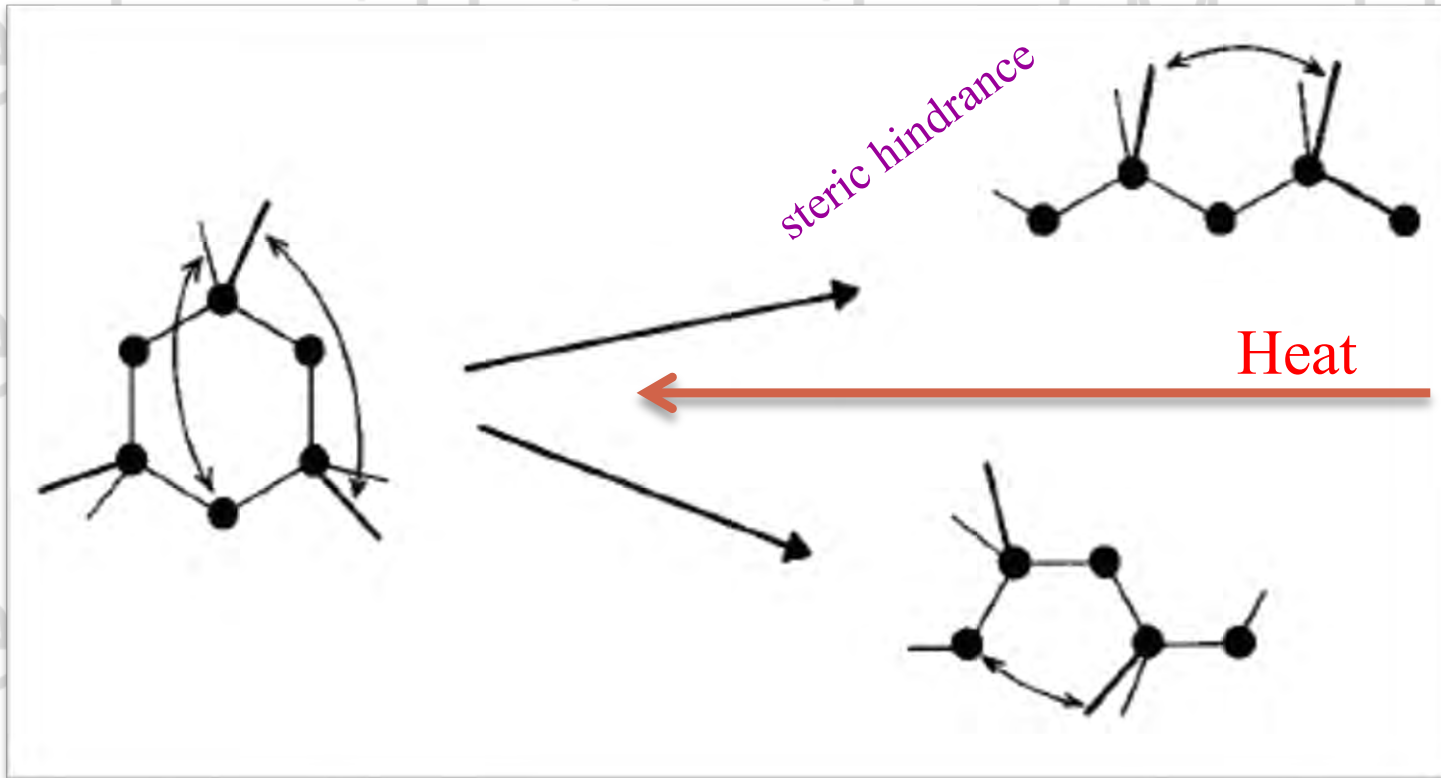
phosphazanium ion

Traces of water catalyze the reaction

Boron trichloride as a commercial catalyst \rightarrow BaCl^4^-

cleave temperature $\text{P-F} > \text{P-Cl}$

The mechanism would also explain why replacement of all the halogen atoms in $(\text{NPCl}_2)_3$ or $(\text{NPF}_2)_3$ by organic groups blocks the polymerization process, since it would be exceedingly difficult to induce the thermal ionization of a methyl or phenyl group from phosphorus.



ceiling temperature

$[\text{NP}(\text{OPh})_2]_n$ kinetically stability / thermodynamically instability

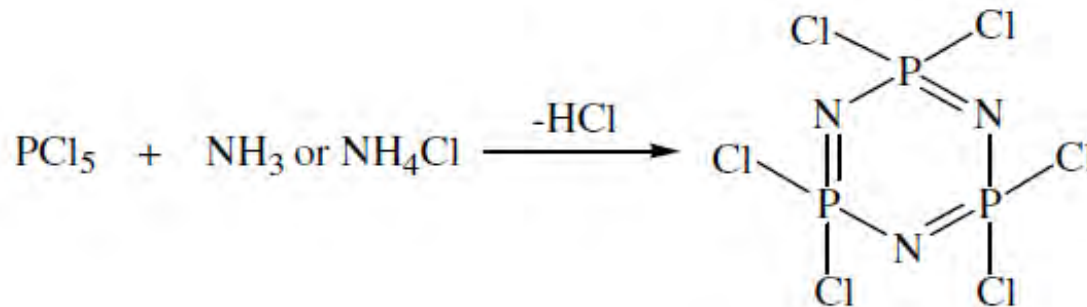
Condensation polymerizations that yield Poly(dichlorophosphazene)

Condensation of PCl_5 with Ammonia

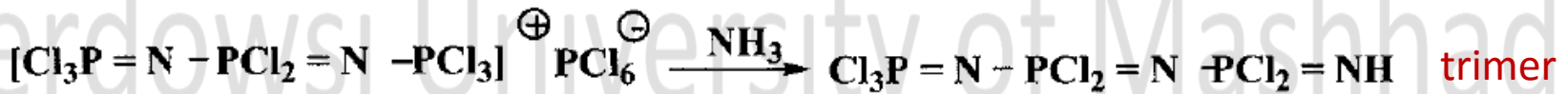
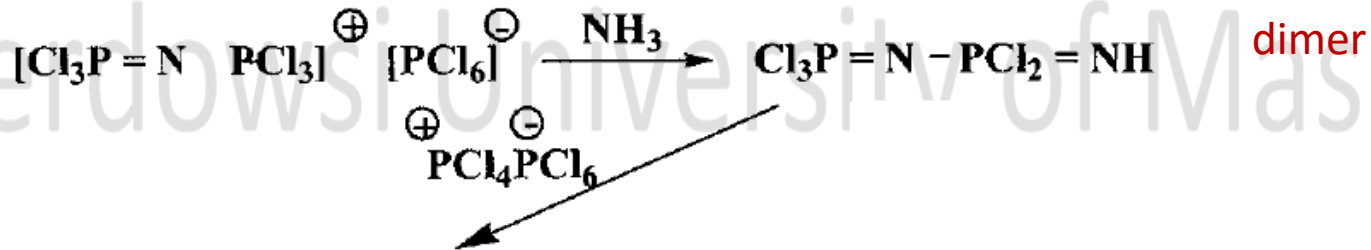
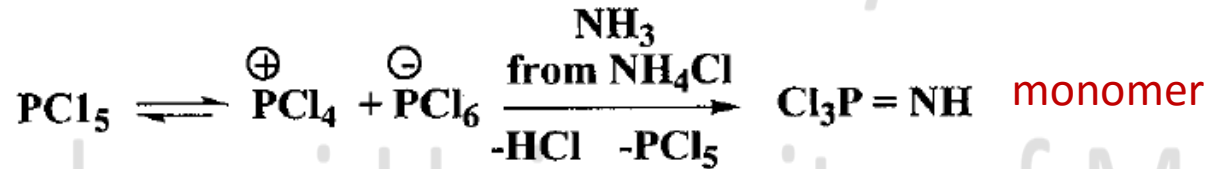
Condensation Reactions of $\text{OCl}_2\text{PN}=\text{PCl}_3$

Living Cationic Polymerization of $\text{Me}_3\text{SiN}=\text{Cl}_3$

Condensation of PCl_5 with Ammonia



Condensation of PCl_5 with Ammonia...



etc

tetramer

Condensation Reactions of $OCl_2PN=PCl_3$

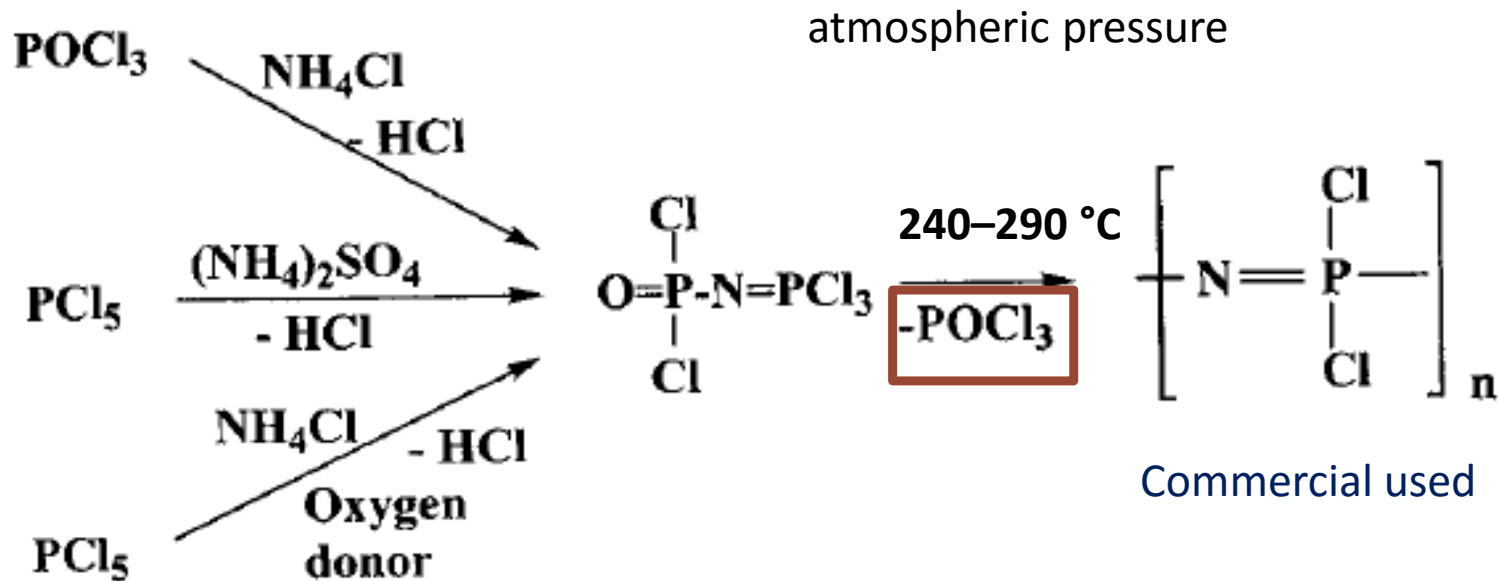
De Jaeger

PCl_5 and ammonium sulfate

phosphoroyl chloride and ammonium chloride

PCl_3 and ammonium chloride

Condensation Reactions of $OCl_2PN=PCL_3...$



low cost method Advantages

broad molecular weight distributions
 lower molecular weight polymers than $(NPCl_2)_3$

Disadvantages

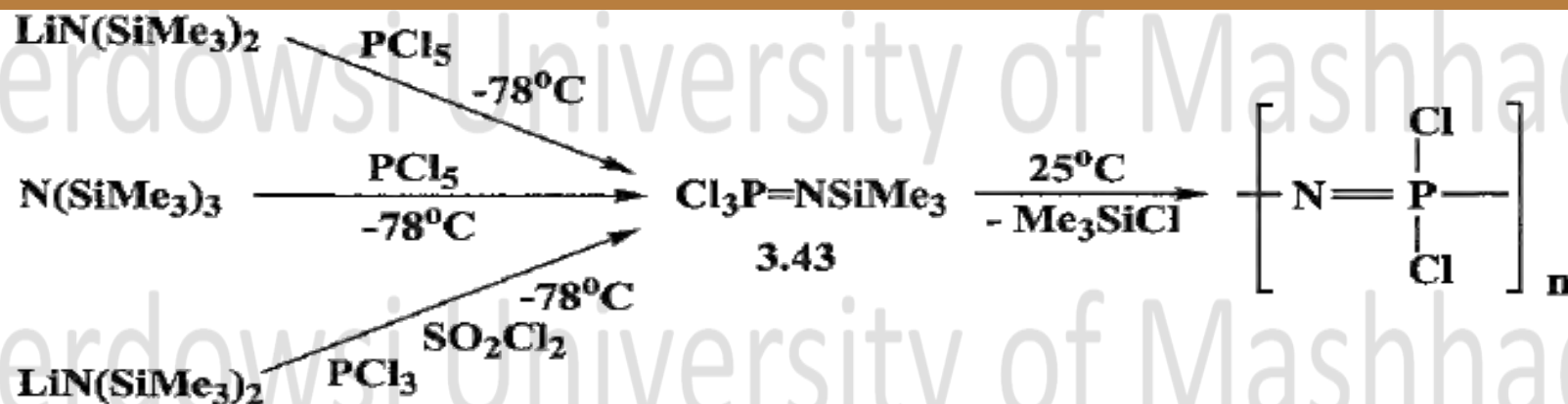
Living Cationic Polymerization of $\text{Me}_3\text{SiN}=\text{Cl}_3$

Allcock Manners

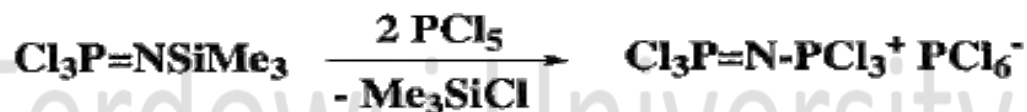
$\text{Me}_3\text{SiN}=\text{PCl}_3$ *N*-silylphosphoranimine(monomer)

bulk or solution phase polymerizations at room temperature in the presence of small amounts of Lewis acids as initiators

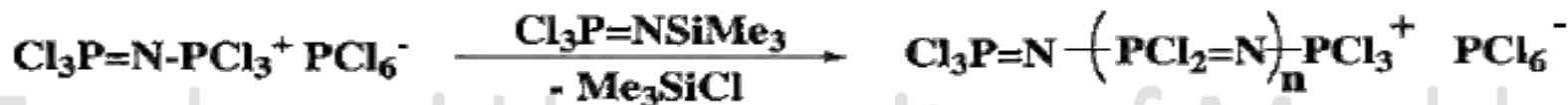
Expensive



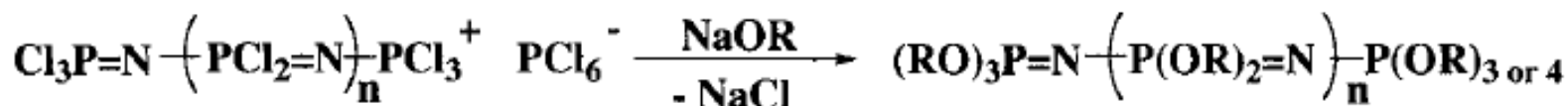
Initiation



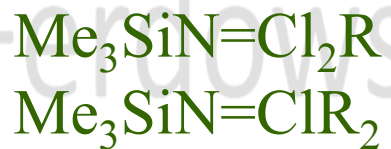
Chain Growth



Halogen Replacement



Condensation Polymerization of Organic Substituted Phosphoranimines



N-silylphosphoranimine(monomer)