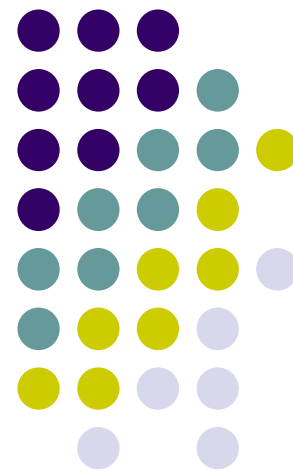


Polymer Chemistry

Dr Bhuse V M, DoC, RCK.

The world would be totally in different place without artificial plastics, elastomers, even in the field of electronics, what would you do without insulation? Lord Todd, President Royal Society, 1980



What are Polymers?

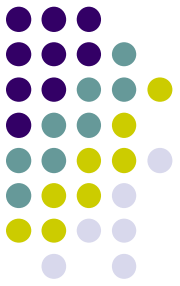
Polymer: derived from Greek words, *Polymeroes*.

poly meaning many

meros meaning part or unit.

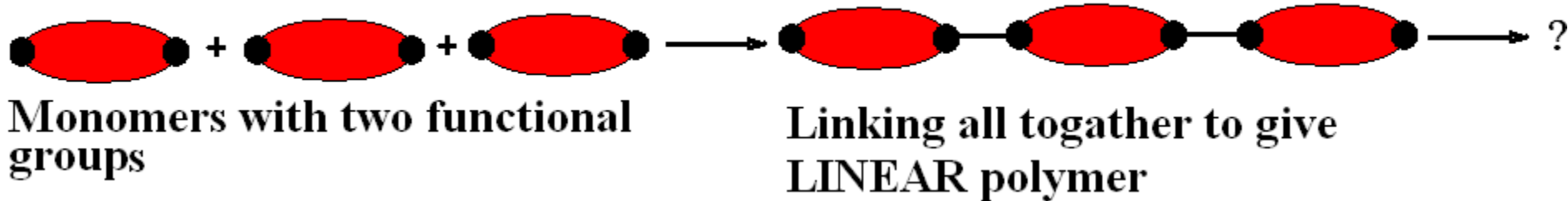
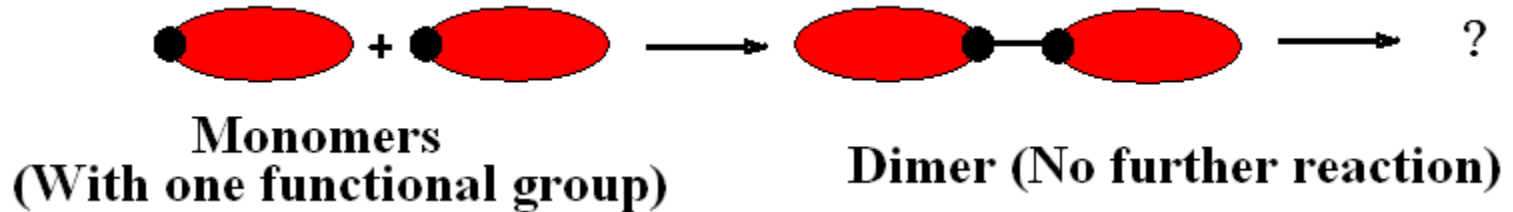
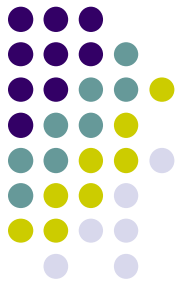
A polymer is thus a substance consisting of many molecular units (called *monomers*)

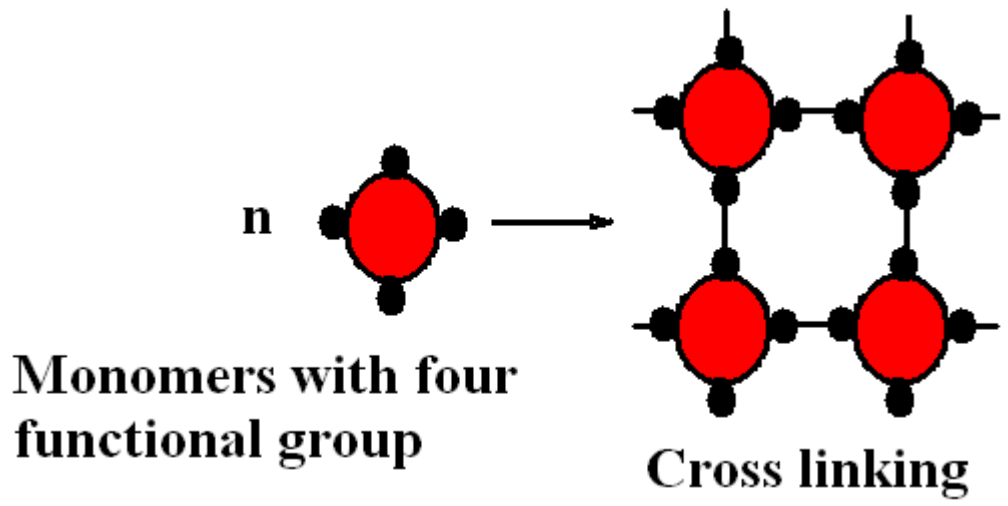
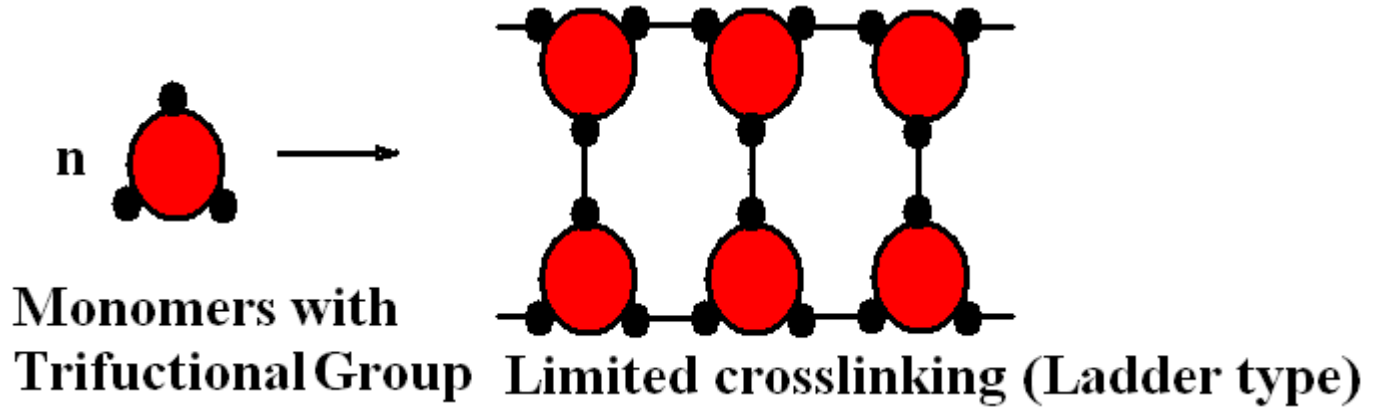
In a polymer, the number of monomers are joined to each other by covalent bonds formed via a chemical reaction.

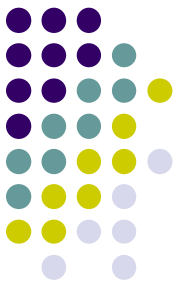


Functionality of Monomer

Bi, Tri, tetra- functional







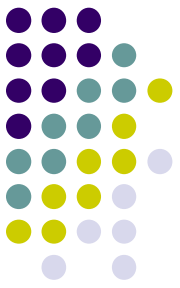
What is Polymer???

linking together of large number of much *smaller molecule* (*Monomers*) may be 100, 1000, tens of thousands or millions of monomers



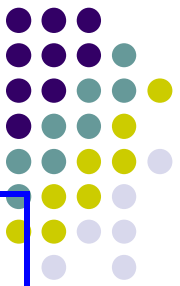
A polymer, in general, has a high molecular weight (usually greater than 1000 amu). The polymers are useful for domestic as well as industrial purposes. The various forms of polymers are plastics, fibers, foams, adhesives, paints, rubbers, aero gels etc.

Definitions

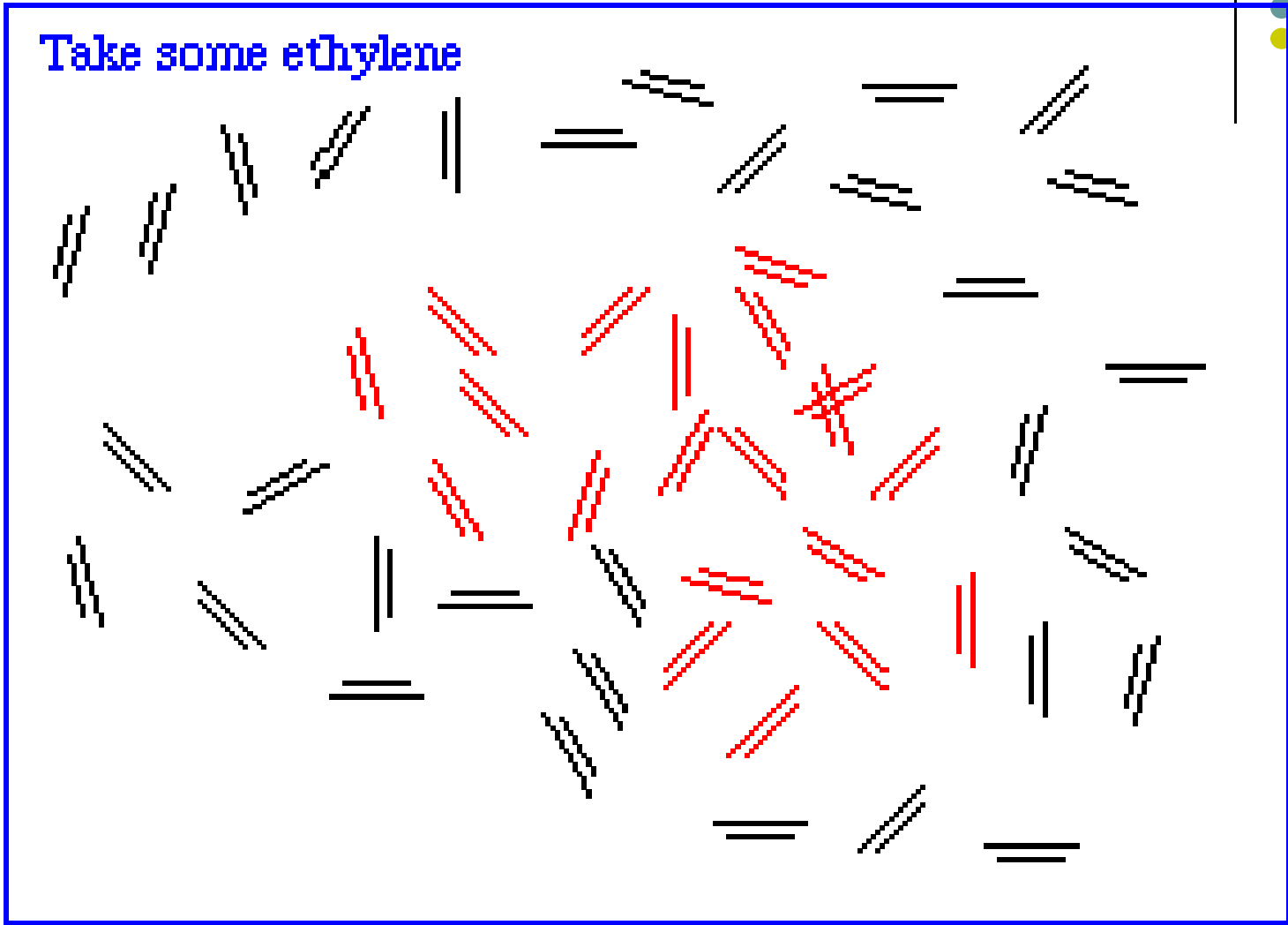


- **Polymer :**
Polymers are macromolecules formed by linking up of large number of smaller molecules (monomers) via chemical reaction.e.g. polythene, PVC, polystyrene etc.
- **Monomer :**
The single repeating unit of polymer is called as monomer.
e.g. ethylene is monomer of polyethylene.
- **Polymerization :**
The process of linking up of large number of smaller molecules (monomers) to form polymer under specific condition of temperature, pressure & catalyst.
- **Degree of Polymerization :**
The total no. of single monomers combined together to form a polymer is known as degree of polymerization.
- Polymers with high degree of polymerization are known as high polymers
While those with comparatively low degree of polymerization are oligopolymers.

Polymerization...

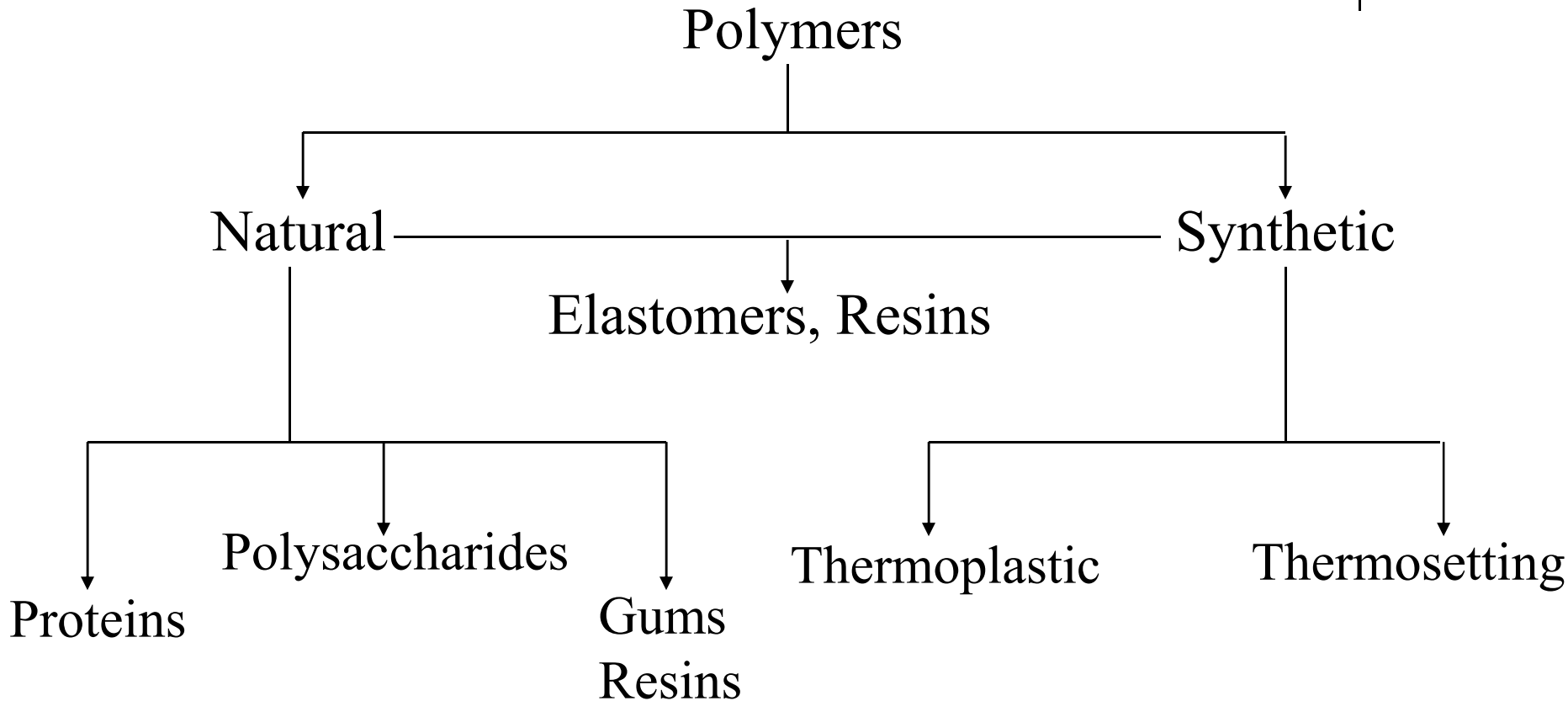
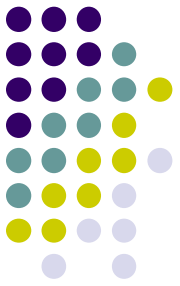


Take some ethylene

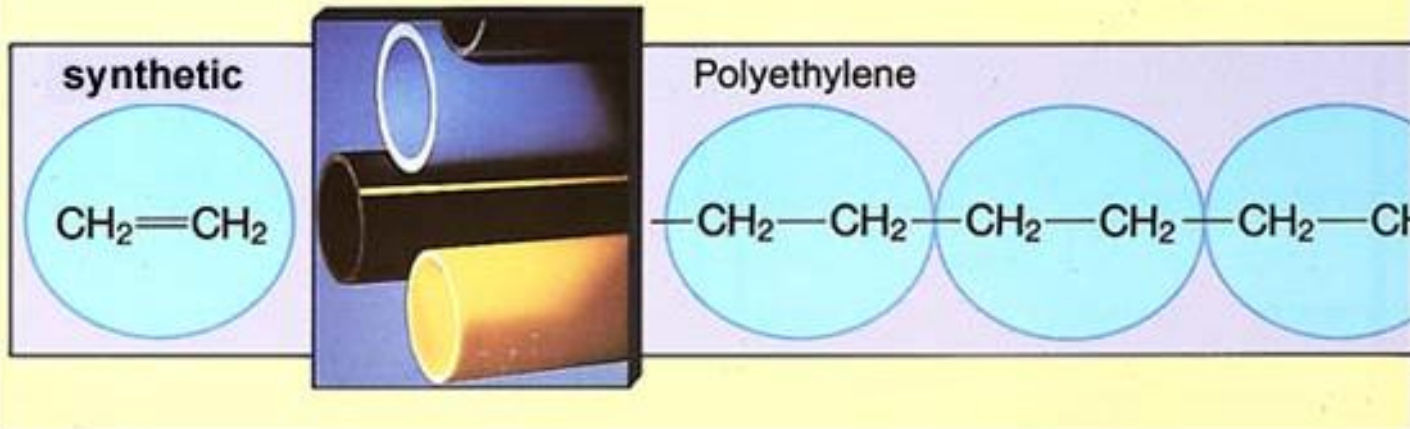
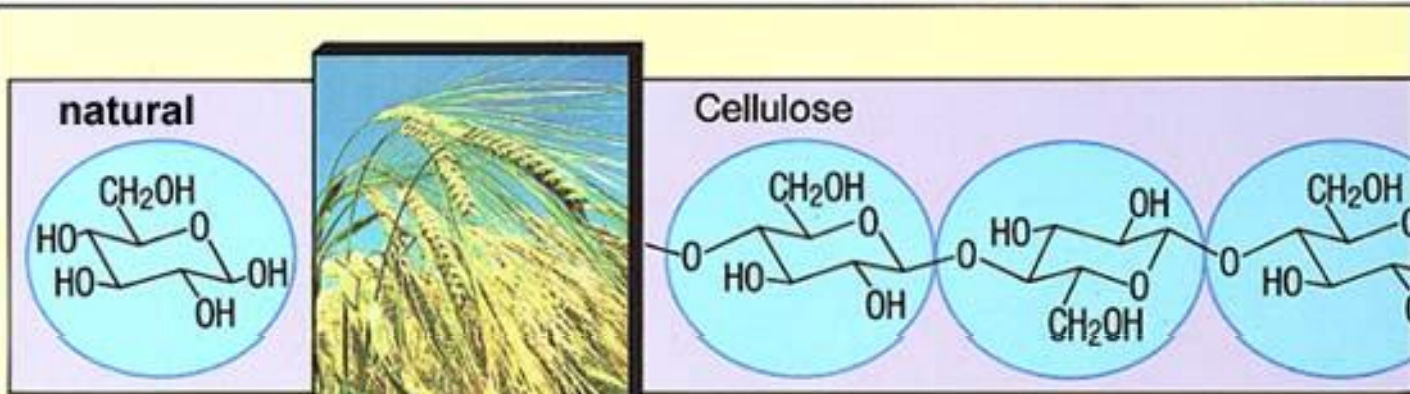
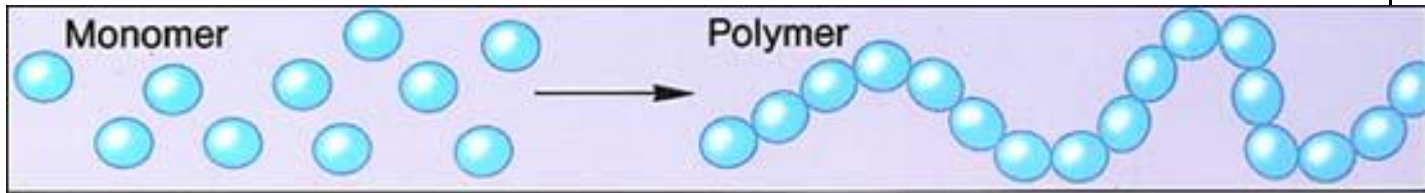
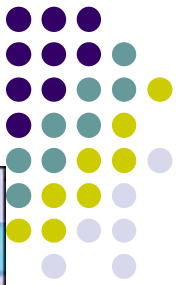


Classification of Polymers

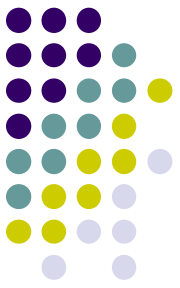
(based on source)



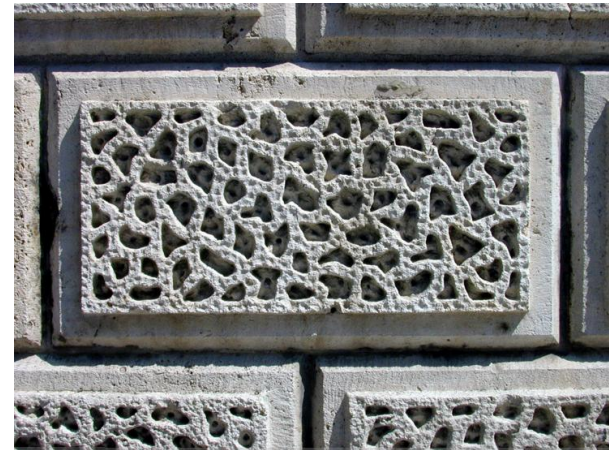
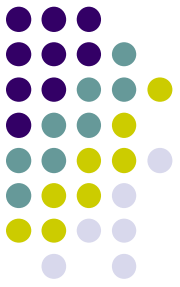
Examples..



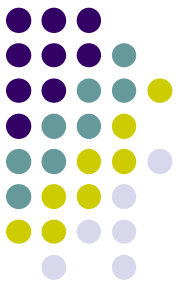
Biopolymers:

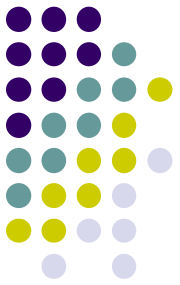


Synthetic Polymers:



Plastics:





Classification

- Organic & Inorganic
- Natural & Synthetic
- Thermoplastic & Thermosets
- Elastomer, Fiber, Resins etc

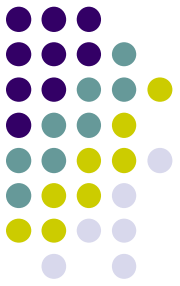
Organic polymers contains framework of covalent C-C bonds to H,O,N,S,Cl,Br,I & some molecular substituents (e.g alkyl group) are linked. The bonding is usually covalent but other type of bonding may be present.

Inorganic polymer contains a framework of nonmetals other than carbon bonds.

- The covalent bond makes the polymer comparatively weaker, non-crystalline, with low specific gravity.
- So they can be easily oxidized, pyrolyzed and can show reactivity towards acids, bases and solvents etc. The existence of poor properties limits its technological applications
- So it is useful to use, '*inorganic*' type *polymers*, which could bear high resistance to heat, oxidation, action of chemicals, solvents etc.



Inorganic Polymers:



Definition: *The polymers containing covalently bonded structural units of nonmetallic atoms like S, N, P, Si, O etc. (other than carbon) and in some cases metals also, are called **inorganic polymers**.*



[Polymerization]

(Based on compositional difference between polymers and monomers)

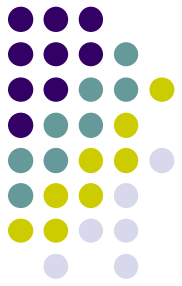
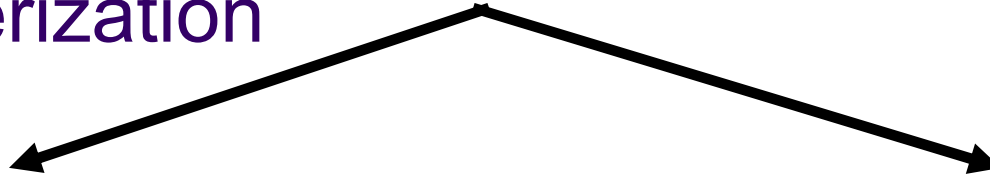
Two type:

1. Condensation / Step Polymers
2. Addition / Chain polymers

a) Require polyfunctional monomers
b) Produce from condensation reaction of organic chemistry with loss of small molecule such as H_2O

a) Formed from monomers without loss of small molecules
b) Repeat unit has same composition as the monomer

Polymerization



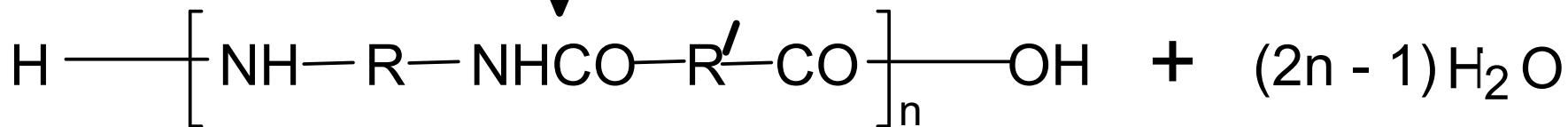
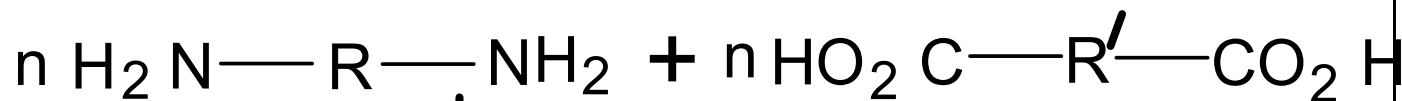
Step Growth

Long reaction time required to get high M.W., M.W. increase throughout the reaction and high M.W. is not obtained until the end of reaction, Monomers disappears much faster as one proceeds slowly to produce dimer, trimer, tetramer and so on

Chain

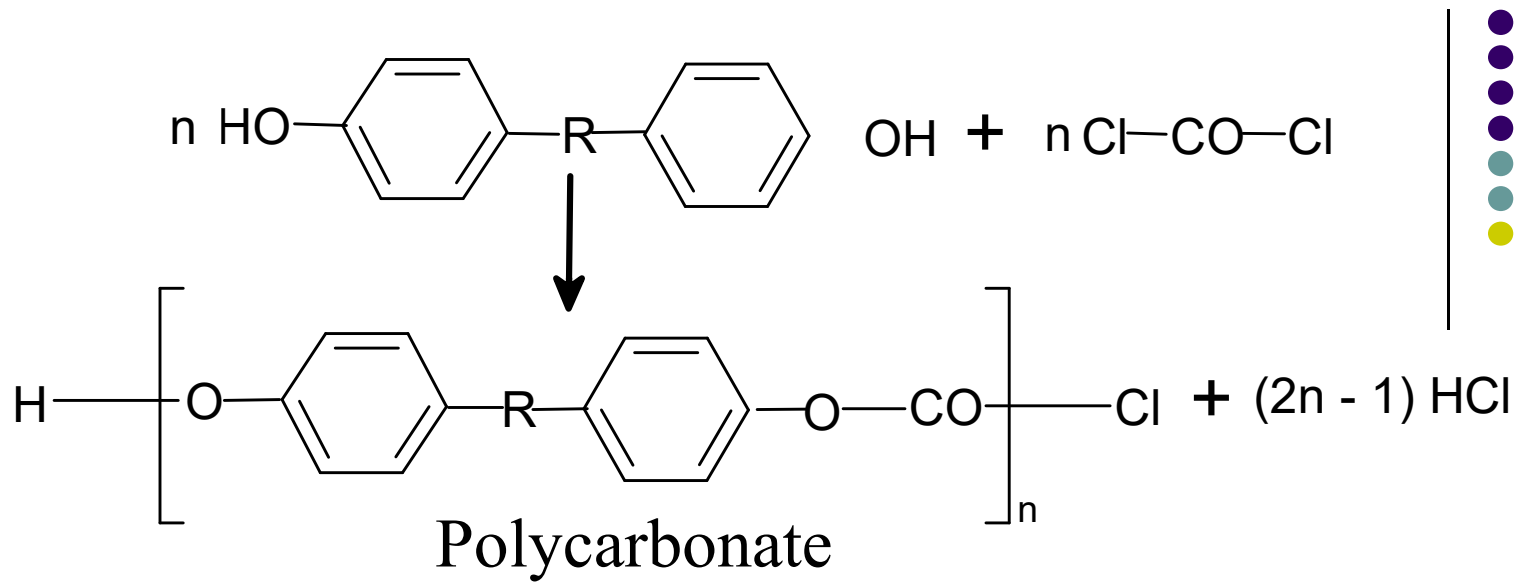
High M.W. polymer is formed immediately, M.W. of the polymer is relatively unchanged during Polymerization, a radical, cation, Anion reaction center produced.

Example for Condensation / Step Polymers

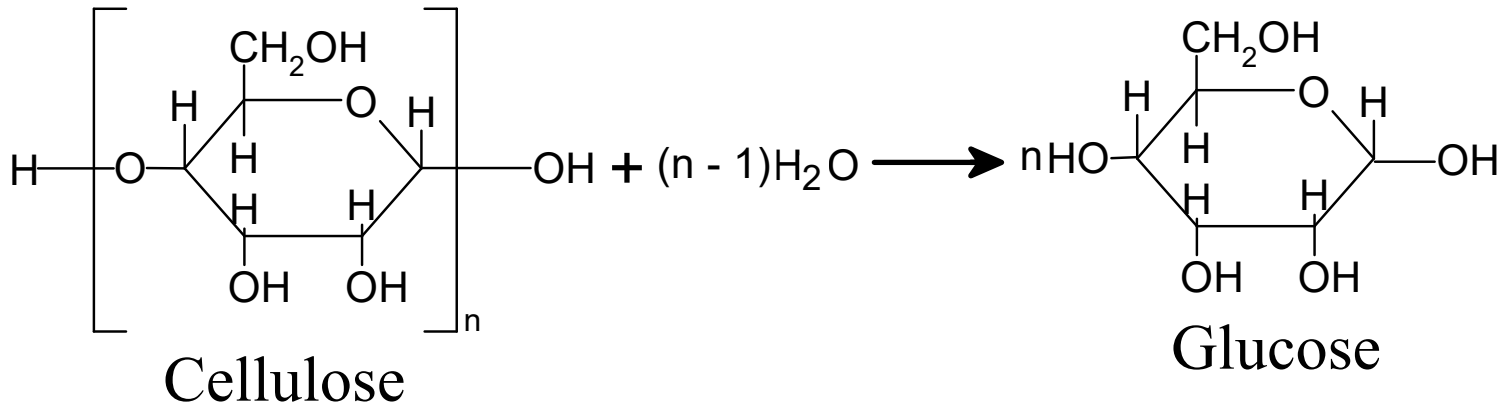


Repeat Unit
Polyamide

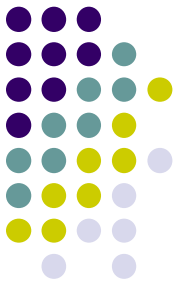




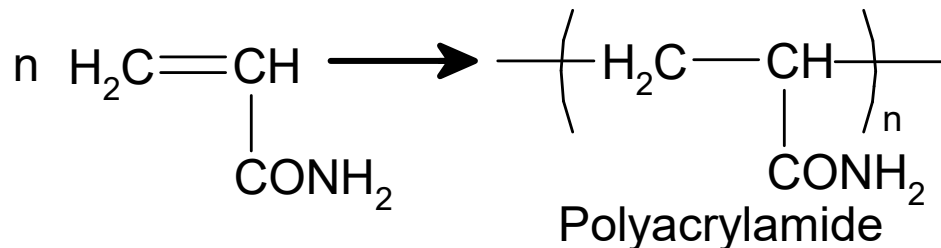
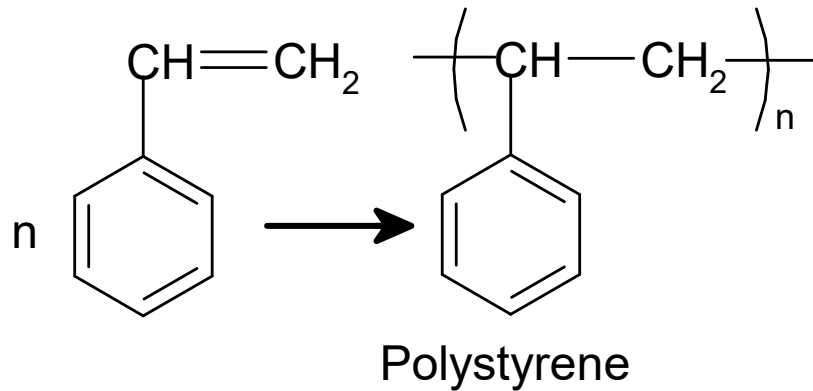
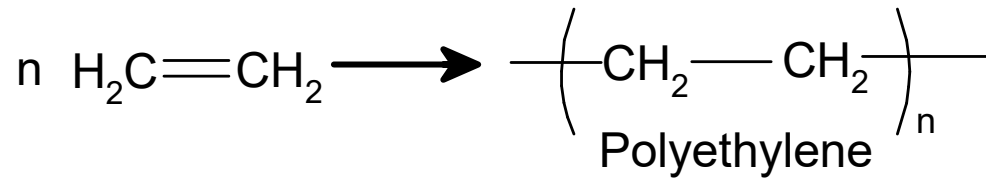
Natural polymers like Cellulose, Starch, wool, silk are also condensation polymers



Example for Addition / Chain Polymers



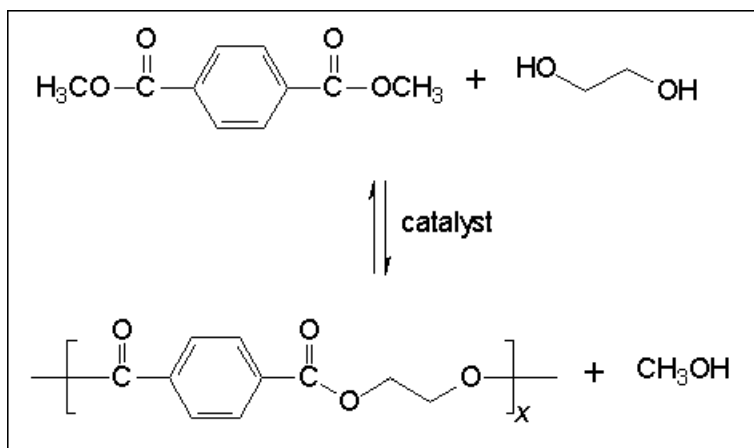
Major examples are monomers having C = C linkage
e.g. $-\text{CH}_2 = \text{CH}$ group (vinyl group)



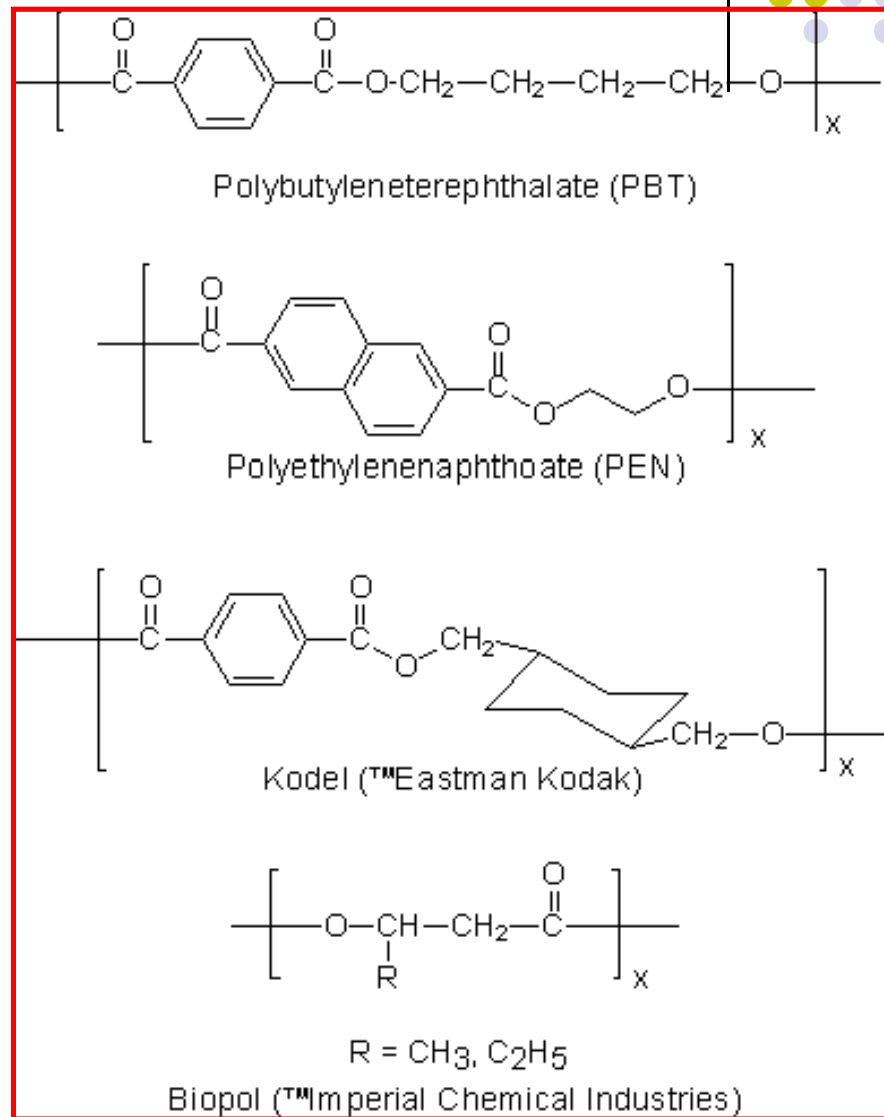
Examples of Step Polymerization



Polyesters

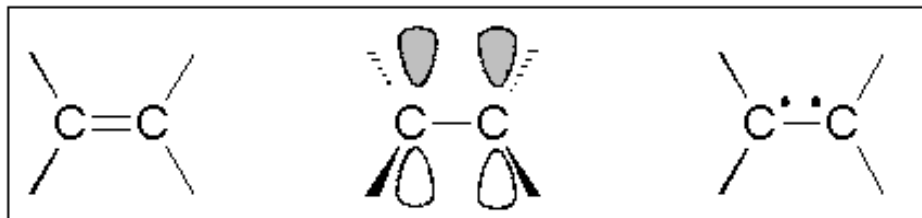


Other commercially important polyesters:



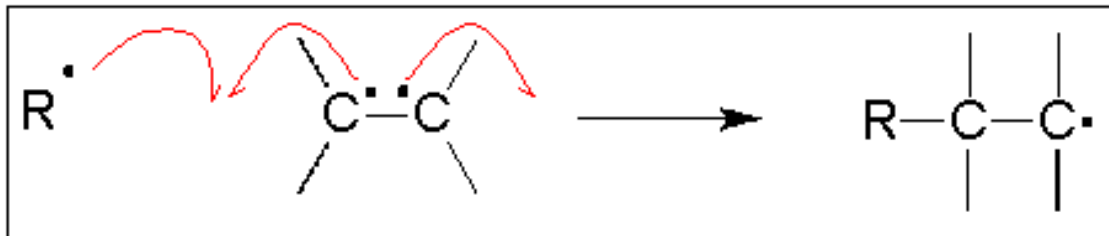
Mechanism of Chain Polymerization

Equivalent views of a carbon-carbon double bond:



The essence of chain polymerizations:

Each addition reproduces the reactive group



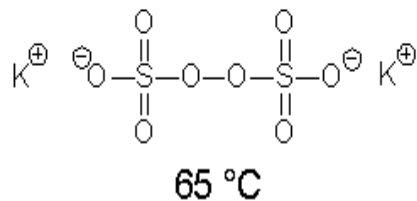
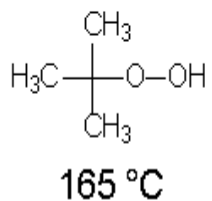
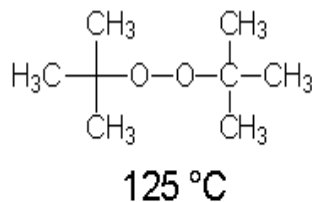
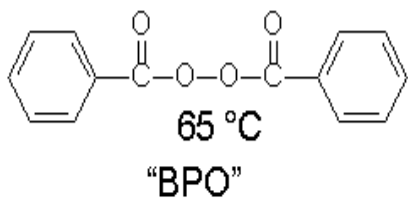
Three components of chain polymerizations:

- Initiation
- Propagation
- Termination (absent for living polymerization)

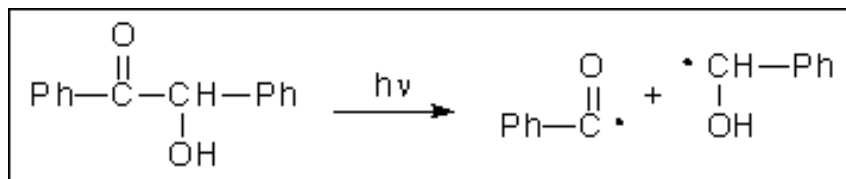


Free Radical Polymerization - Initiation

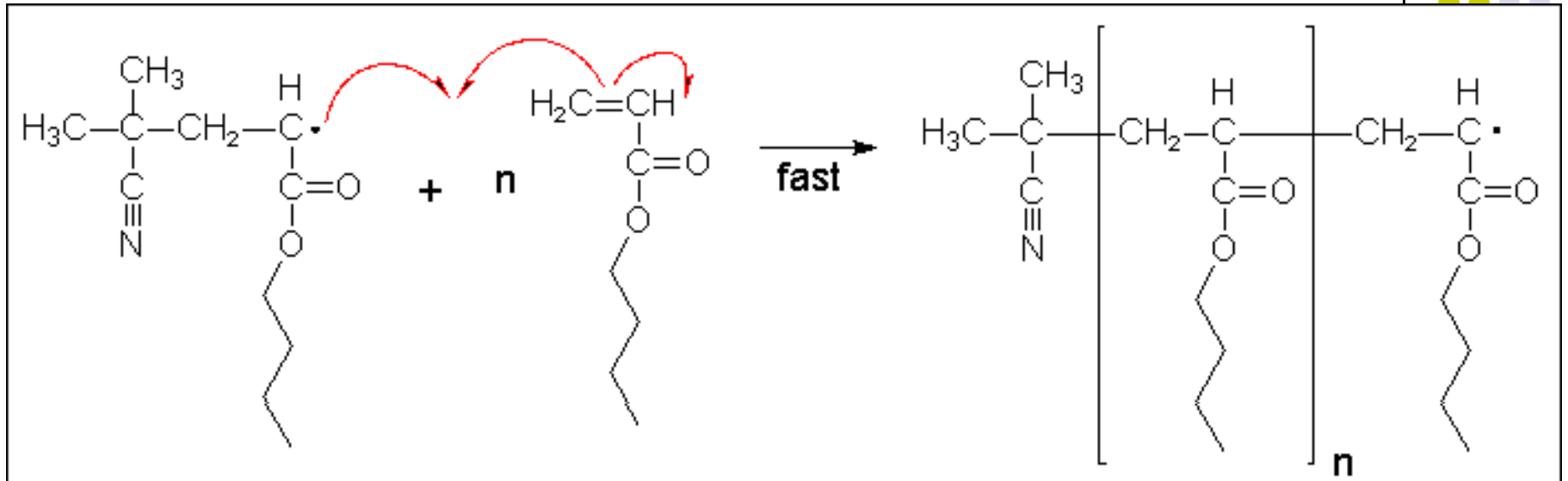
Thermal initiators: Examples: peroxides or azo compounds



Photochemical: Examples:

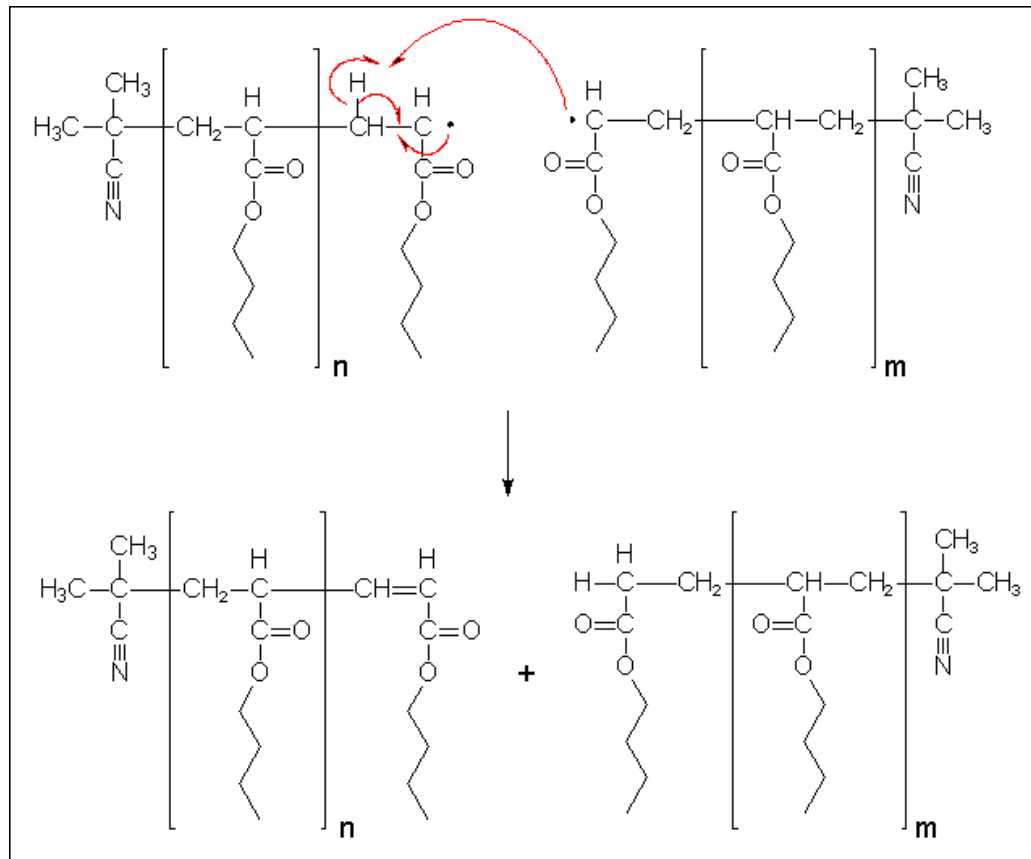


Propagation

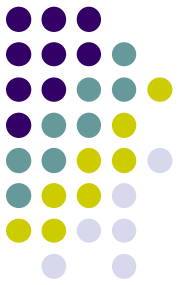


Monomer adds quickly to the small number of growing chains present at any given time

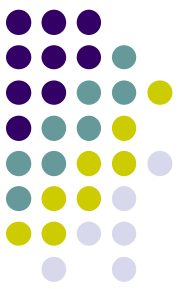
Termination:



Termination is a *bimolecular* process, and occurs when two growing chain ends find each other.

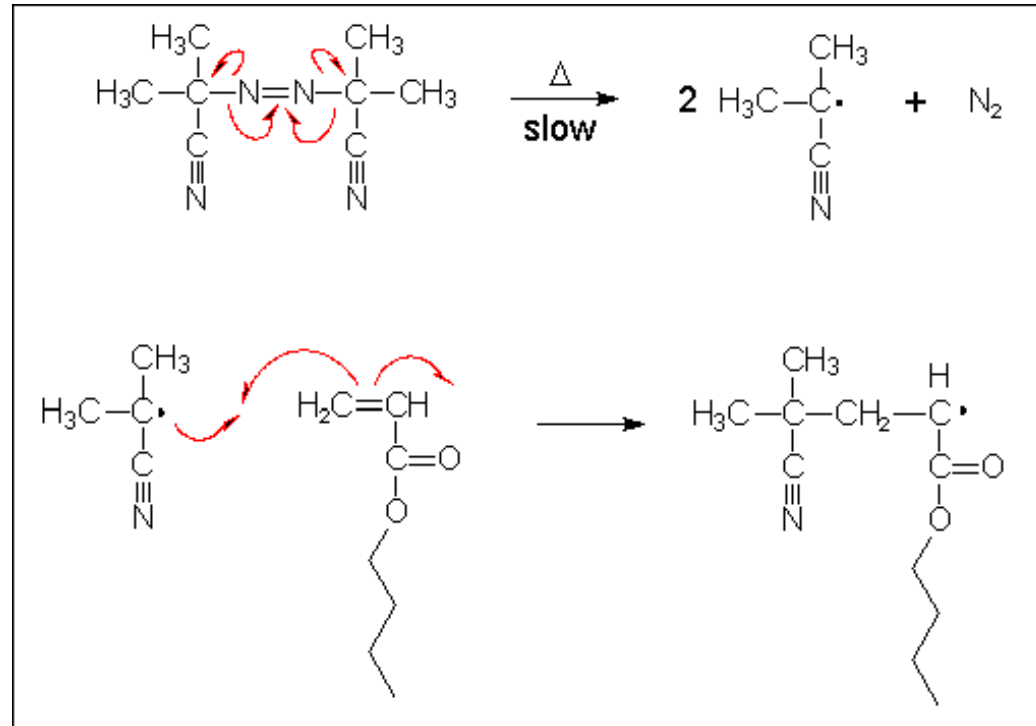


Free Radical Polymerization - Complete Example

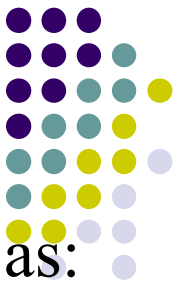


Initiation:

Butyl Acrylate

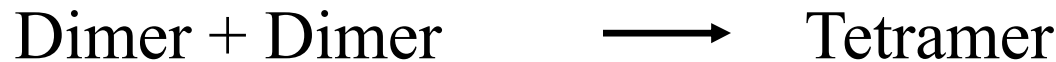


Initiator breaks down smoothly to generate a low, steady-state concentration of radicals



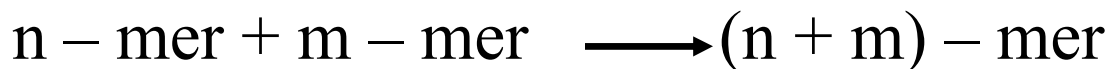
Rates of Step Polymerization

Rates of reaction between molecules of various sizes, such as:



And so on

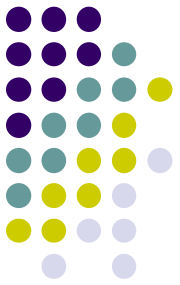
Which can be expressed as the general reaction





Polymer Backbone

- The basic network is called backbone.
- Homoatomic backbone
- Heteroatomic backbone
- Branched backbone
- Ring/Cycloliner / Fused backbone



Different types polymer

-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-

Homopolymer

If the repeat units are different, the result is *copolymer*

-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-

Alternating copolymer

-A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B-

Block copolymer

-A-A-B-A-B-B-A-A-A-B-A-B-B-B-B-A-

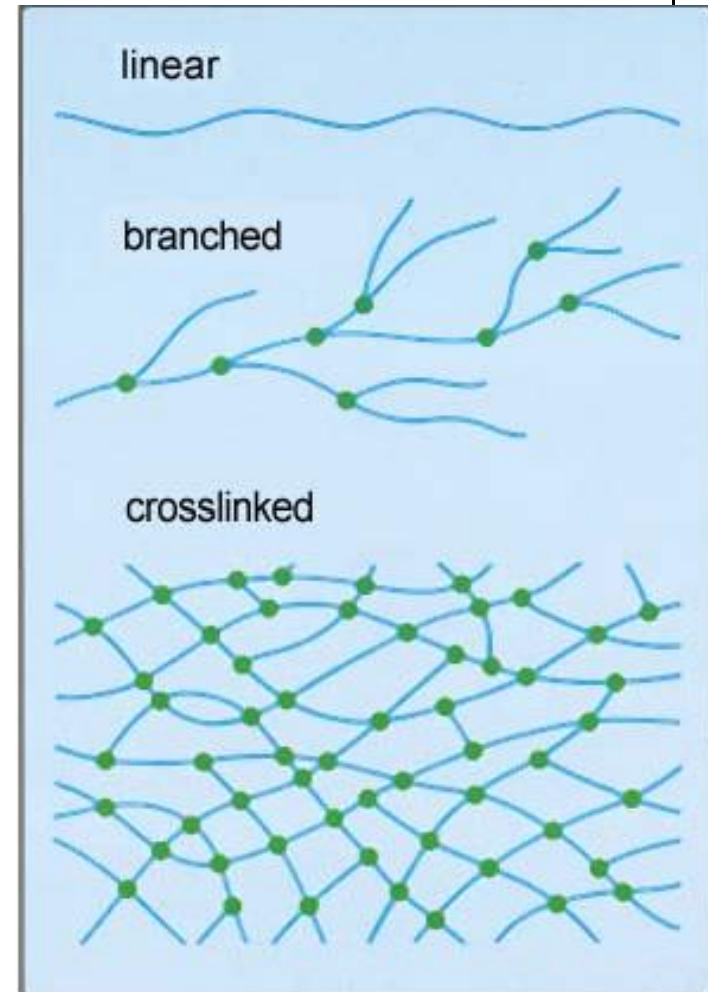
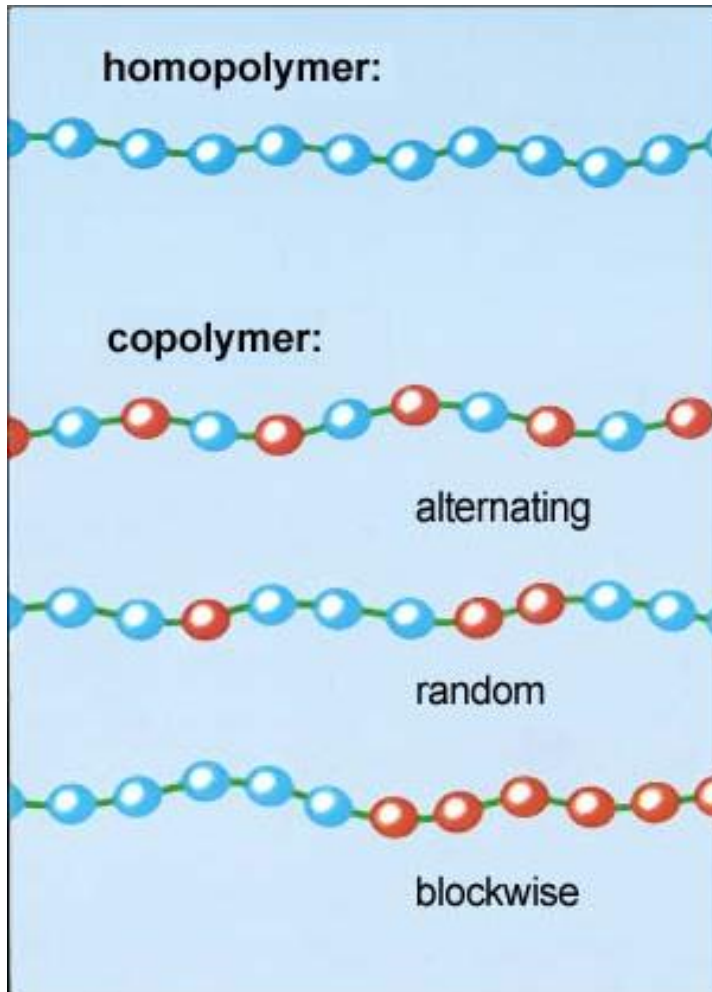
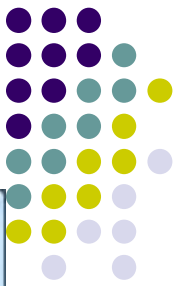
Random copolymer

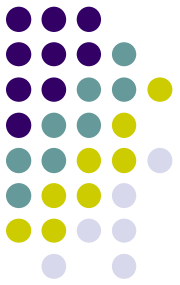
-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-

-B-B-B-B-B-B-B-B-

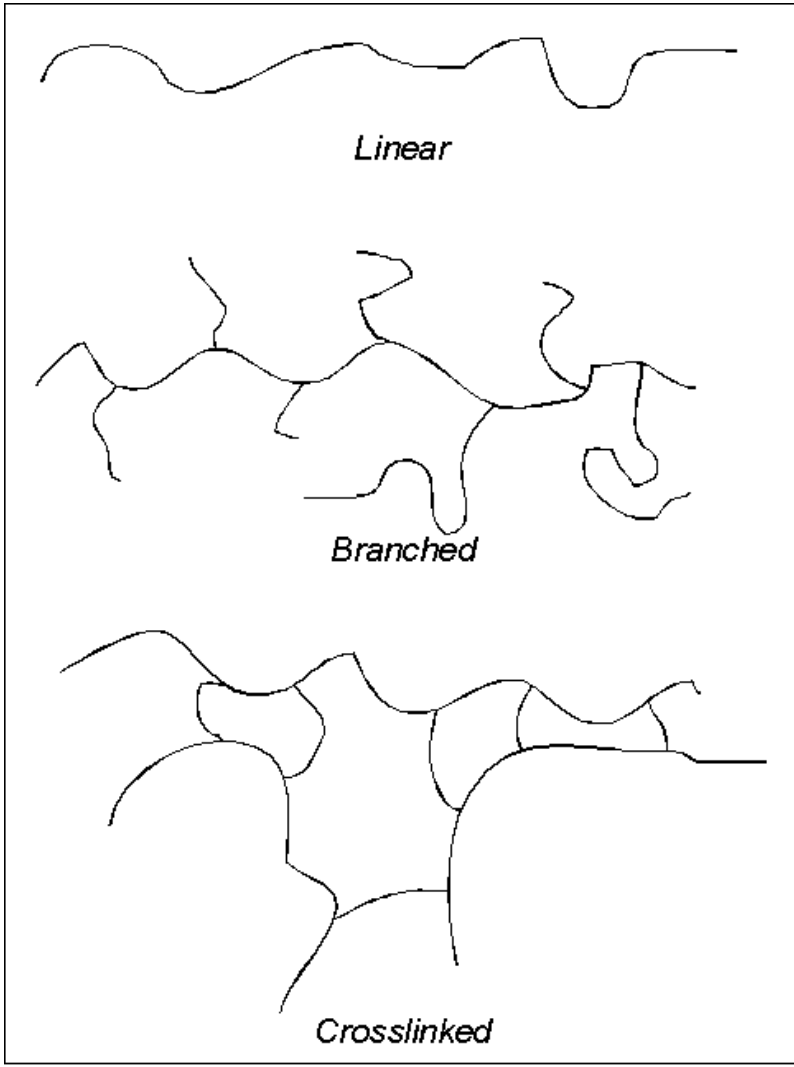
Graft copolymer

Classification





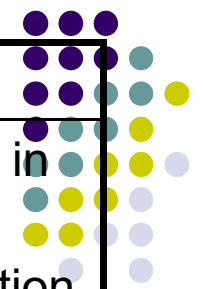
Structure depends on Chain folding





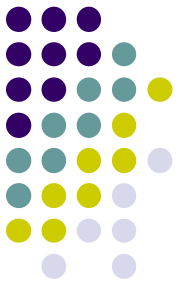
Organic Vs Inorganic

ORGANIC	INORGANIC
<p>1. Their backbone is made up of C atoms only.</p> <p>2. The carbon in backbone may be linked to groups containing C, S, N, O etc.</p> <p>3. The propensity of C to form extensive and stable C-C chains (catenation) results in <i>enormous</i> number of polymers.</p> <p>4. These types of polymers are less stable and are susceptible to pyrolysis and oxidation</p> <p>5. Degree of polymerization is large.</p>	<p>1. Their backbone is made up of nonmetals and metals (except C) e.g Si, Si-O, P-O.</p> <p>2. The nonmetals in backbone may be linked to groups containing C, S, N, O etc.</p> <p>3. Nonmetals other than C show less propensity towards chain formation (catenation), which results in <i>fewer</i> polymers.</p> <p>4. They are stable toward heat and oxidation.</p> <p>5. Degree of polymerization is larger in some compounds.</p>



ORGANIC	INORGANIC
<p>6. Polymers having ring structure in organic polymers are a few.</p> <p>7. They are produced by addition polymerization and condensation polymerization reactions.</p> <p>8. Organic Polymers are used for general purposes.</p> <p>9. Organic polymers are generally not stable beyond 330K.</p> <p>10. They swell or dissolve in organic solvents and have poor weather resistance.</p> <p>11. At low temperatures they lose plasticity and elasticity and become brittle.</p> <p>12. Organic Polymers find applications almost in every need of society.</p>	<p>6. Closed ring structure is common in inorganic polymers.</p> <p>7. They are produced by condensation polymerization only.</p> <p>8. Inorganic Polymers are used for special purposes such as making body parts, special lubricants, space materials etc.</p> <p>9. Inorganic polymers are comparatively more stable than organic polymers.</p> <p>10. They don't dissolve in solvents and are stable towards unusual weather conditions.</p> <p>11. No change in properties even at low temperatures.</p> <p>12. Inorganic Polymers find a limited application.</p>

Classification

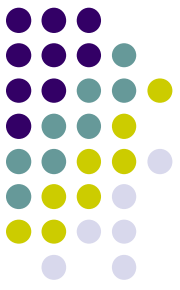


i) Homoatomic Polymers:

They backbone (skeleton) of the same kind of atoms.

ii) Heteroatomic Polymers:

They contain various combinations of nonmetallic atoms like Si-O, P-O, B-N, etc. in the backbone



Homoatomic Polymers:

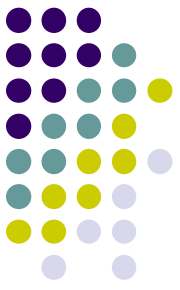
The backbone may be linked to other nonmetals like sulphur, selenium, oxygen, nitrogen or alkyl groups.

- For example: Phosphorus, Sulphur, Selenium etc.

Heteroatomic Polymers:

For examples: silicates, phosphonitrilic polymers etc. Silicates contain skeleton of Si-O atoms with varying degrees of cross linking.

Phosphonitrilic polymers contain P and N atoms linked alternately in the backbone.



Heteroatomic polymers are;

1. Highly stable than homoatomic polymers
2. Stability is due to stronger bonding between unlike atoms.
3. They possess high thermal and chemical stabilities over organic polymers.

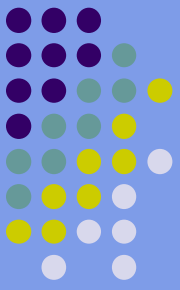


A) Homo-atomic Polymer

Phosphorus Polymers:

A) Polymers with Elemental Phosphorus:

Phosphorus unlike carbon can exhibit catenation (chain forming ability) in many of the hydride and halide compounds with weak P-P bonding.

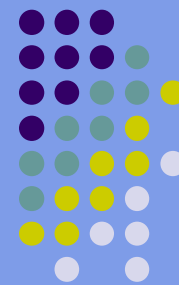


P exhibits three main allotropes;

white, red and black (all polymers)

All may exist either amorphous or crystalline.

Crystalline may exist in hexagonal, cubic, orthorhombic, rhombohedral, triclinic & tetragonal structure.



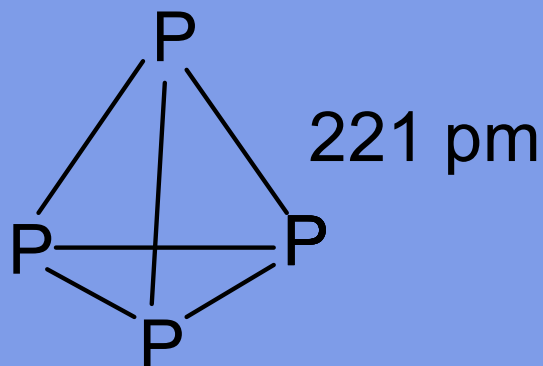
1. A White Modification:

A white modification of P has cubic lattice containing discrete P_4 tetrahedra.

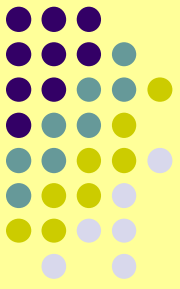
The P-P bond length is 221 pm & PPP angle is 60° .

This common form is stable up to 900°C .

It changes to hexagonal form at -77°C .



Tetrahedron of P_4



2. Red Modification:

Properties: It is amorphous

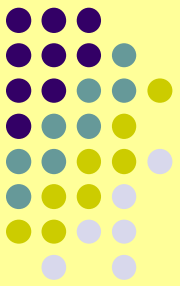
It exhibit high degree of polymerization.

It contains random chains of pyramidal P atoms.

It does not have well defined structure.

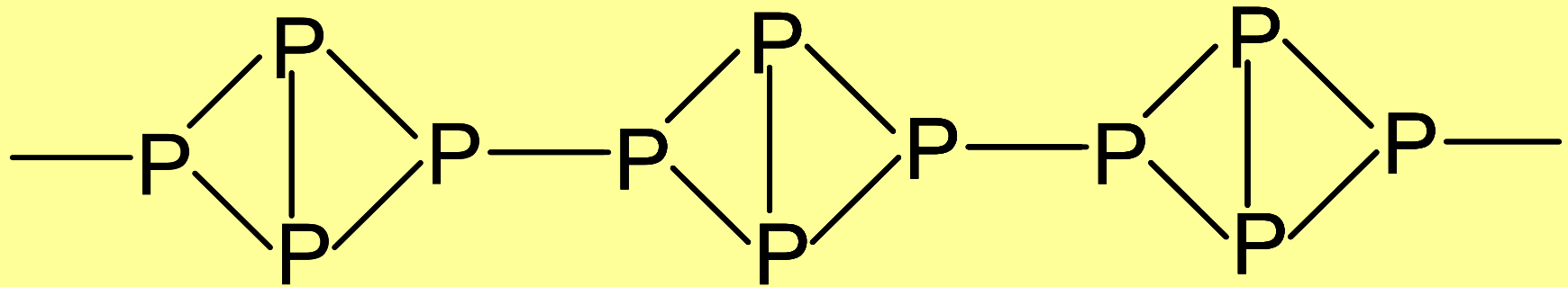
Preparation:

It is produced by heating white P under various specified conditions.



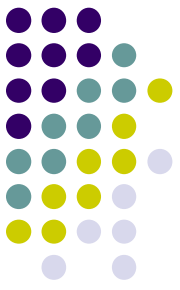
Red Modification: Structure:

Three dimensional network is based on following chain;



P-P-P angle $> 90^{\circ}$

3. The Black Modification:



Properties:

It may be rhombohedral, orthorhombic, cubic etc in structure,

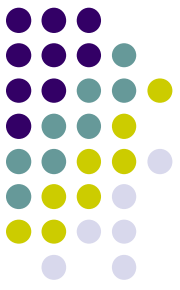
All having layered and puckered structures.

Orthorhombic form is soft, crystalline, flaky consisting of eight Phosphorus atoms in a unit cell.

Black P is semiconductor.

Preparation:

It is produced by heating white or red P at 200- 270⁰C using Hg catalyst.



3. The Black Modification:

Structure:

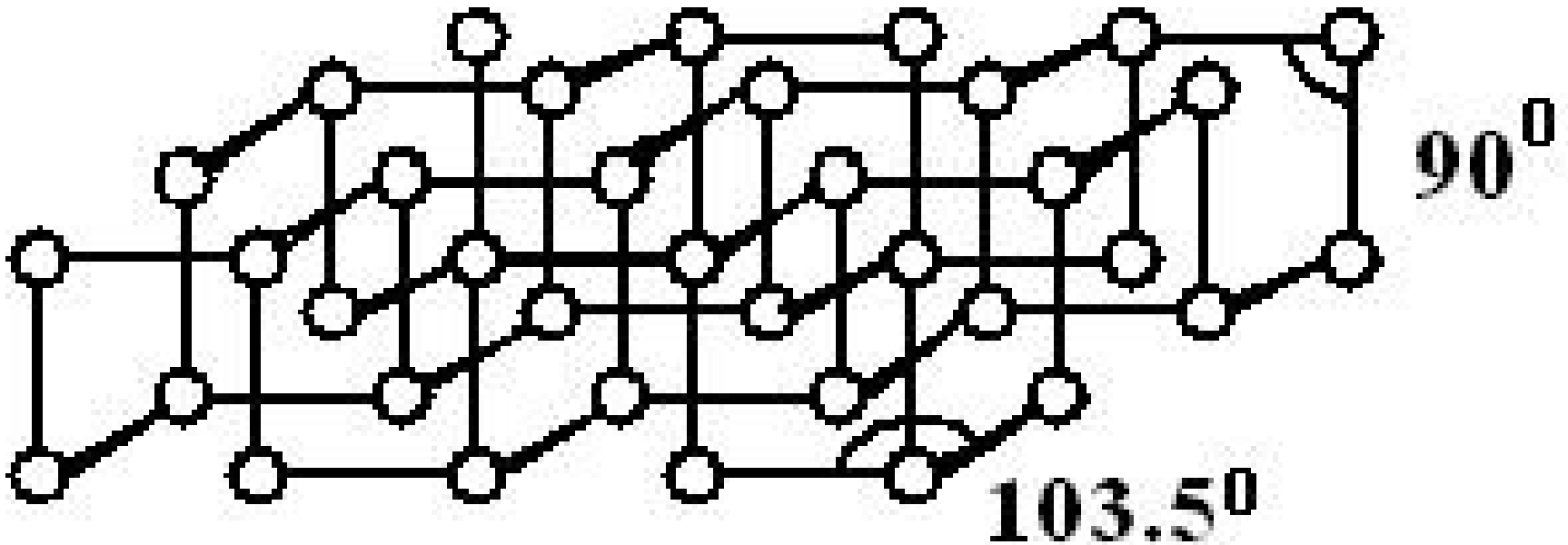
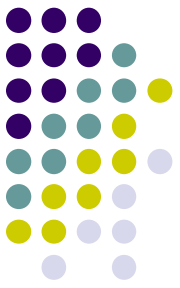
It is composed of corrugated layers made of P atoms each bonded to three neighbouring P atoms.

It can be thought as being in a layer made up of two halves separated by 228 pm (puckered rings).

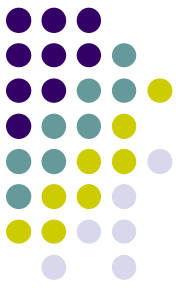
.

3. The Black Modification:

Every P atom exhibits two bond angles, 90° and 103.5° . It exhibits flakiness similar to graphite because of its layer structure.



4. Cyclic Phosphorus Polymer:

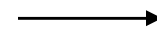


Also called Cyclo-poly (phosphines)

They have closed ring structures with P in backbone.

They are cyclic and stable to heat.

Cyclo-poly (phosphines) have general formula ;



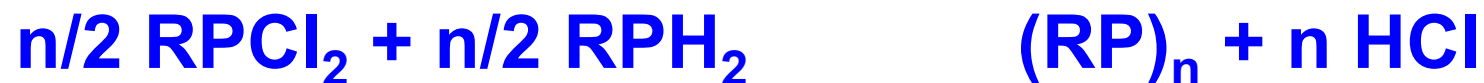
Where $n = 3$ to 6 and $R = \text{Et}, n\text{-Pr}, n\text{-Bu}, n\text{-Oct}, \text{Me}$
etc]

4. Cyclic Phosphorus Polymer:



Preparation:

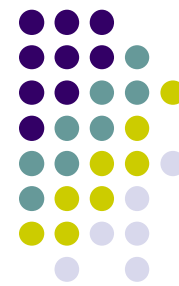
They can be prepared by



The O.S of P is +3 but it $\overrightarrow{\text{can}}$ show +5 also.

Trifluoro-methyl derivatives like $(\text{CF}_3\text{P})_4$ and $(\text{CF}_3\text{P})_5$ can be obtained by condensation of CF_3PCl_2 & CF_3PH_2 .

4. Cyclic Phosphorus contd....:



$(\text{CF}_3\text{P})_4$ & $(\text{CF}_3\text{P})_5$ can be obtained by condensation of CF_3PCl_2 & CF_3PH_2 .

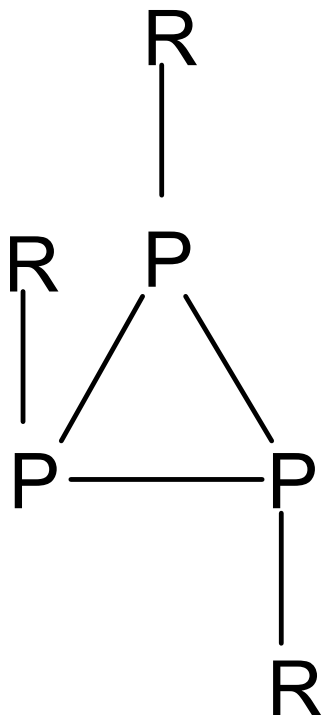
They are cyclic and stable to heat.

A tetramer -stable upto 300°C ,

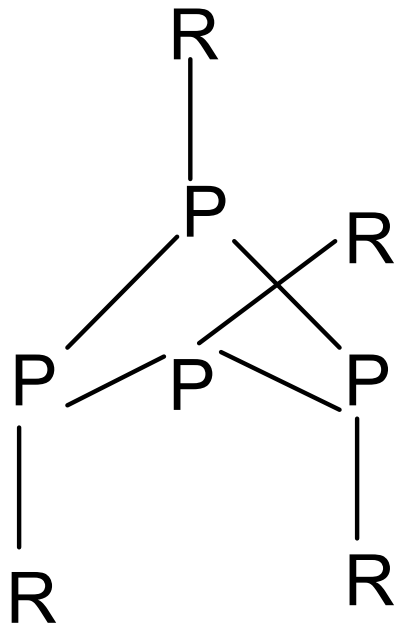
A pentamer is less stable.

CF_3 groups in tetramer are arranged alternatively on opposite side of the ring to minimize nonbonding interaction.

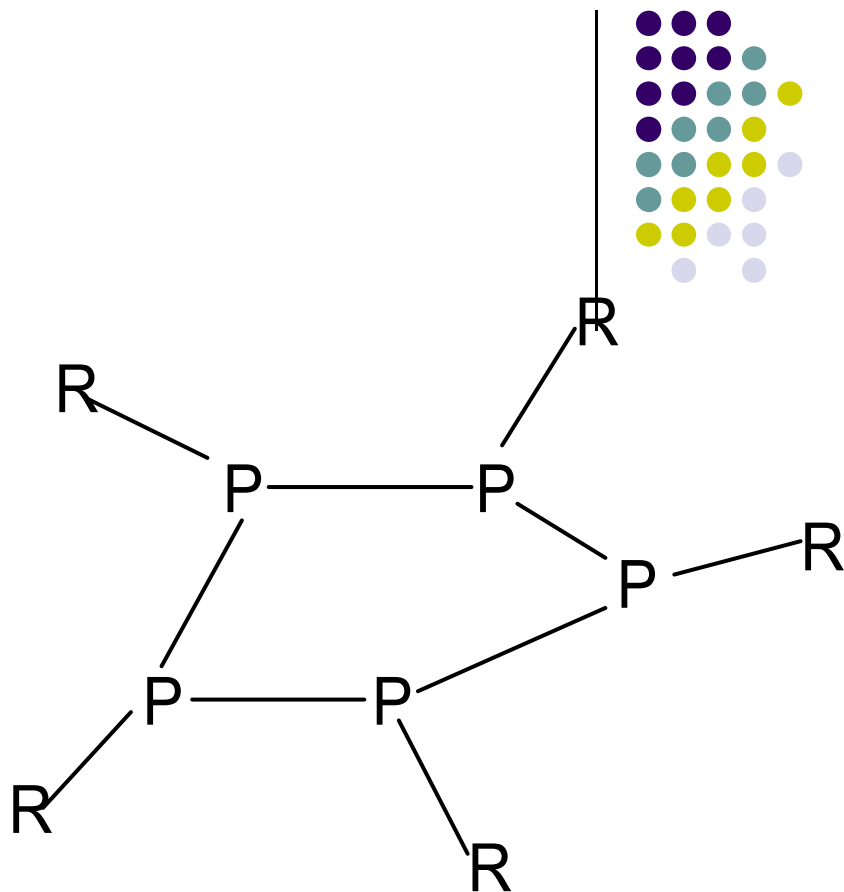
The bonding present is Pi type involving lone pairs of electrons on P atoms and 3d orbital from adjacent P atoms.



Cyclic trimer

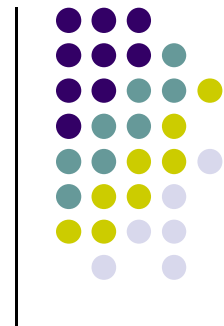
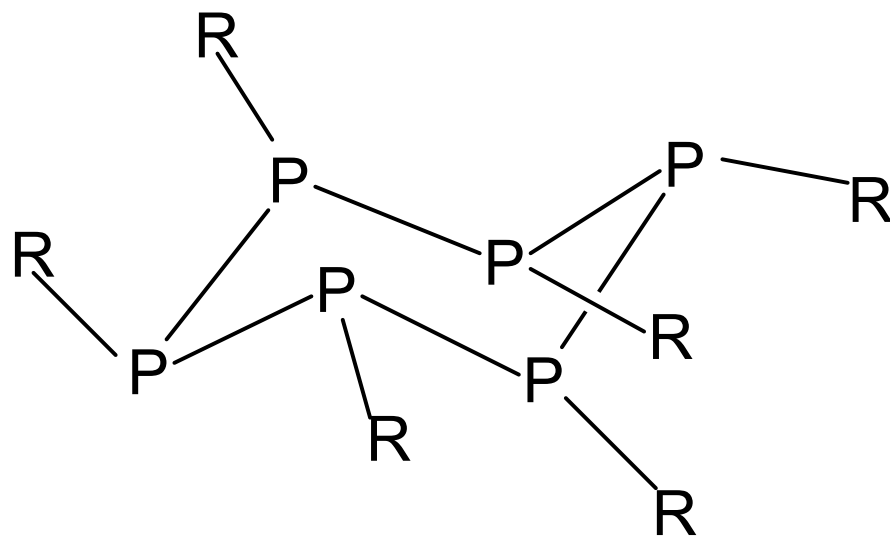


Cyclic tetramer



Cyclic pentamer

Where R is alkyl,
 C_6H_5 for $n = 4 \& 6$
 CF_3, C_6F_5 for $n = 5$;



Cyclic hexamer

Where R is alkyl,
 C_6H_5 for $n = 4 \& 6$
 CF_3, C_6F_5 for $n = 5$;

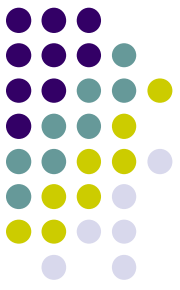
- **Linear molecules like diphosphine (P_2H_6), triphosphine ($H_2P_3H_6$) and tetra phosphine (P_4H_6) are also known.**

However, a linear polymeric molecule having open chain structure becomes increasingly unstable relative to cyclic polymer as number of P atoms in chain increases.



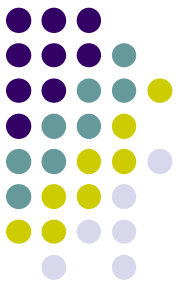
B) Fluorocarbons:

History:



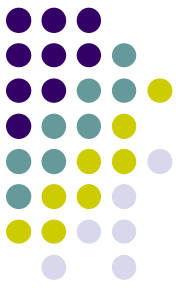
- Poly (chlorotrifluoroethylene) is the first “F” containing polymer prepared in **1934** by **I.G. Farbenindustrie**. However this polymer was of limited value.
- In 1938, Plunkett (USA) reported polytetrafluoro-ethylene which finds a great number of uses.
- First commercial production in **1943** in by **DuePont Co.**
- Up till now a number of technologically important polymers have been investigated and put into use.
- **All fluorine containing polymers have outstanding chemical and thermal resistance due to stronger C-F bonding as compared to analogue organic polymers.**

Fluorocarbon Polymers:



- ***It is homoatomic organic polymer containing fluorine.***
- **Bond Energy:**
- **C-F 480 KJ/Mol,**
- **C-H 416 kJ/Mol,**
- **C-C 347 kJ/Mol**
- **Strong bond energy make this polymer thermally stable and high resistance to chemical attack. This is due to very strong bond between C and F (480 kJ/mole) as compared to).**

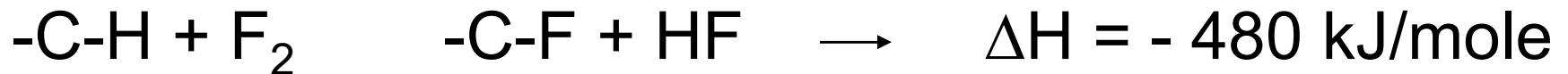
Fluorocarbon Polymers:



- **Preparation:**

By direct fluorination of alkenes or its derivatives. Fluorination is highly exothermic. If the reaction is not controlled, a complete C-C breakdown occur to give simple fluorocarbon and CF_4 . So reactions are always carried out in presence of inert solvent like nitrogen. Another method is to use metal fluoride in place of fluorine.

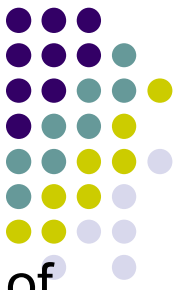
Direct Combination :



Using Metal fluoride :



Poly(vinyl fluoride) and Poly (vinylidene fluoride):



a) Preparation:

Poly (vinyl fluoride) is prepared by free radical polymerization of gaseous vinyl fluoride using catalyst benzoyl peroxide at 85°C. The product obtained is crystalline in nature.

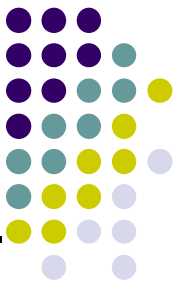


- The monomer vinyl fluoride used in above reaction is usually obtained by reacting HF with acetylene.



- Similarly, poly(*vinilydine fluoride*) can be obtained by polymerization of vinylidene fluoride





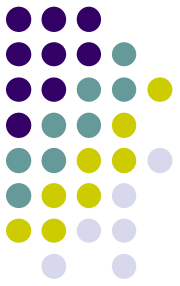
b) Properties:

- They are highly resistant to chemicals and solvents.
- Both are highly crystalline linear polymers without branching.
- The M.P is 200°C and 170°C respectively.
- Both have good thermal stability.
- Both show less permeability to gases.
- Polyvinylidene does not show creep or distortion over a wide range of temperatures.

c) Uses:

- Fluorocarbon polymers are used as protective coatings. The fluorocarbon film of extremely small thickness is even better than conventional paints and coatings.
- As a glazing material over cement mortars in the building industry.

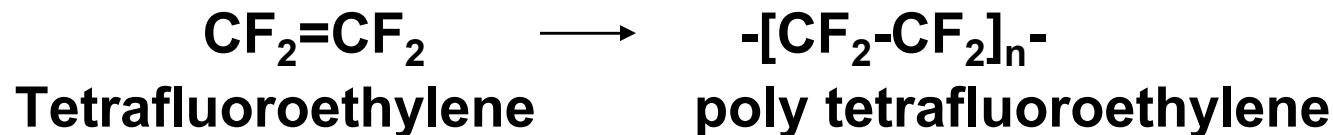
Poly(tetrafluoro ethylene): (Teflon):



a) Preparation:

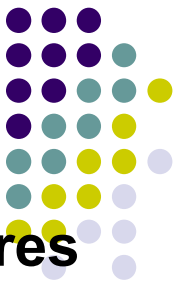
Polymerization of tetrafluoroethylene in presence of Hydrogen peroxide, oxygen, FeSO_4 , persulphate etc. at higher pressure.

The reaction gives a wax like polymer, called poly (tetrafluoroethylene) (abbreviated as PTFE).



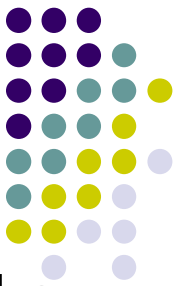
- The commercial name of poly tetrafluoroethylene is *Teflon*. The polymerization reaction accompanies with release of large quantity of heat, it can result in violent explosion.

b) Properties:

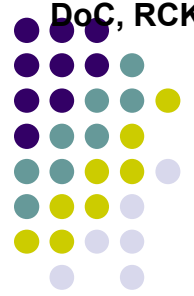


- It is crystalline (crystallinity between 93-98).
- It is linear polymer with no branching (As branching requires breaking of strong C-F bond which is unlikely).
- Its M.P is 327°C , $D = 2.3\text{g/cm}^3$. Its M.Wt is several millions.
- Stable between -100°C - 300°C , but decomposes at 400°C .
- It is resistant to all chemicals & solvents
e.g. strong acids, fuming nitric acid. Corrosive alkalies etc.
- It is attacked by molten alkali metals & their solutions in liquid ammonia. The dissolution is due to formation of metal fluorides.
- It has low dielectric constant (2.0).
- It has low melt-flow rate, so, conventional processing techniques is not used. Therefore a polymer powder is pressed cold to achieve required shape followed by sintering at high temp.
- It can be machined, punched and drilled conveniently.
- It possesses low friction coefficient.
- It has less electrical resistance.

C) Uses:

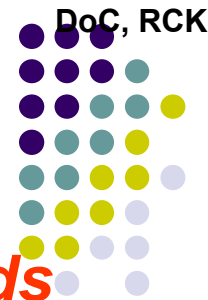


- It is used to make chemical resistance products like pump valves, valve packing, pipes etc.
- It itself acts as a lubricant, so used for making non-lubricated bearings, gun mechanisms, linings for trays in bakeries etc.
- It does not stick to other materials (so called *adhesive*). so used nonstick stop cocks for burettes.
- Used for making fire cloths, fiber belt.
- Used as an insulator for motor, machines, electric parts such as capacitors, coils, wires and cable insulation, and transformer windings etc.
- Used as coating for cooking utensils (called *Teflon coating*)



Hetero-atomic Polymer

Hetero-atomic Polymer

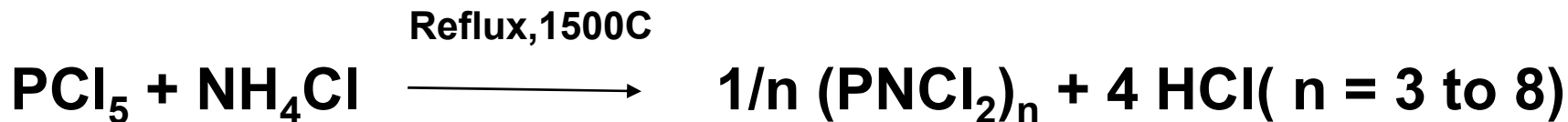


1. PHOSPHONITRILIC POLYMERS:

Phosphonitrilic polymers are linear or cyclic compounds containing unsaturated $-N=P-$ linkages.

A) PREPARATION:

They are obtained by ammonialysis of PCl_5 in a solvent (e.g. s- tetra chloro ethane) at high temp.



The product is cyclic or linear.

It resembles organic nitriles, R-CN, therefore, it is called PHOSPHONITRILE.

Cyclic polymer resembles benzene, therefore also called PHOSPHAZENE.



Mechanism :

It is believed that PCl_5 reacts as $[\text{PCl}_4]^+[\text{PCl}_6]^-$.

The anionic part is attacked by NH_3 with removal of HCl to give $\text{NH}=\text{PCl}_3$



$\text{HN}=\text{PCl}_3$ acts as **nucleophile** towards either itself or PCl_5 .

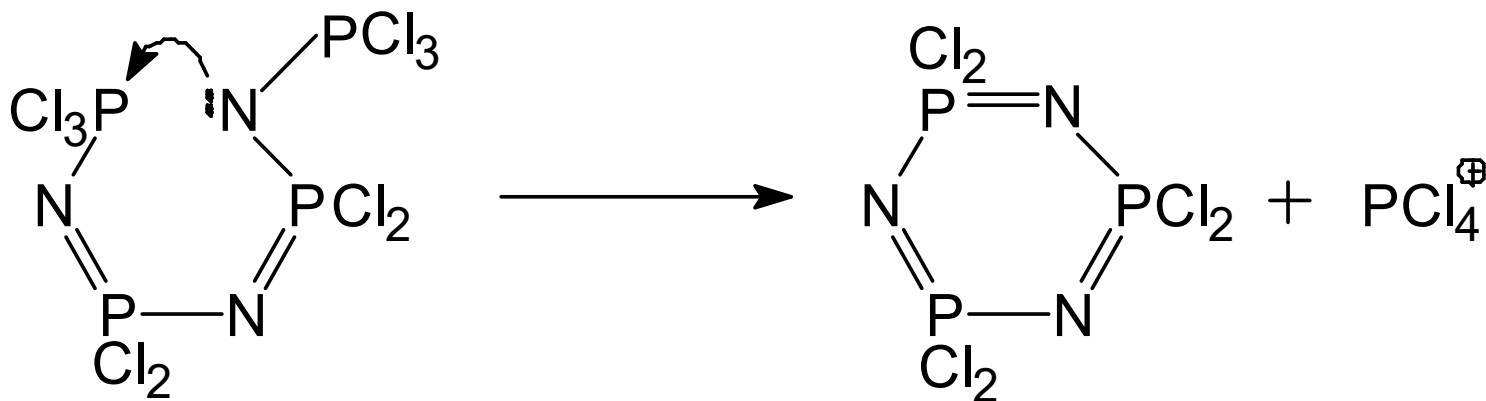


$[\text{Cl}_3\text{P}=\text{N}-\text{PCl}_3]^+[\text{PCl}_6]^-$ is an intermediate. The cationic portion of this further attack on ammonia to produce another linkage.



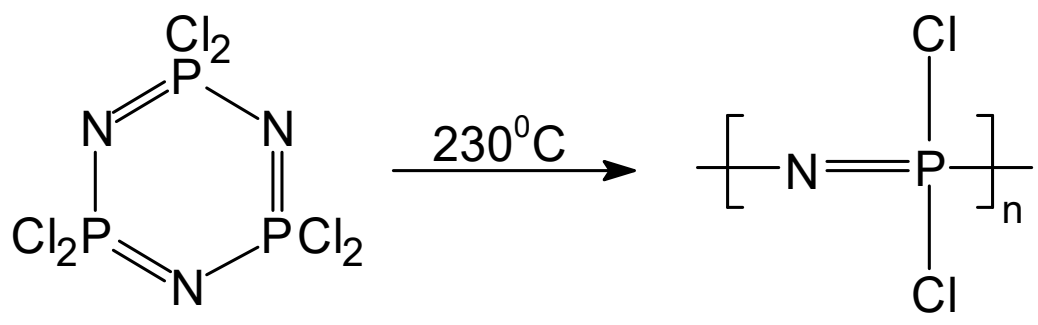
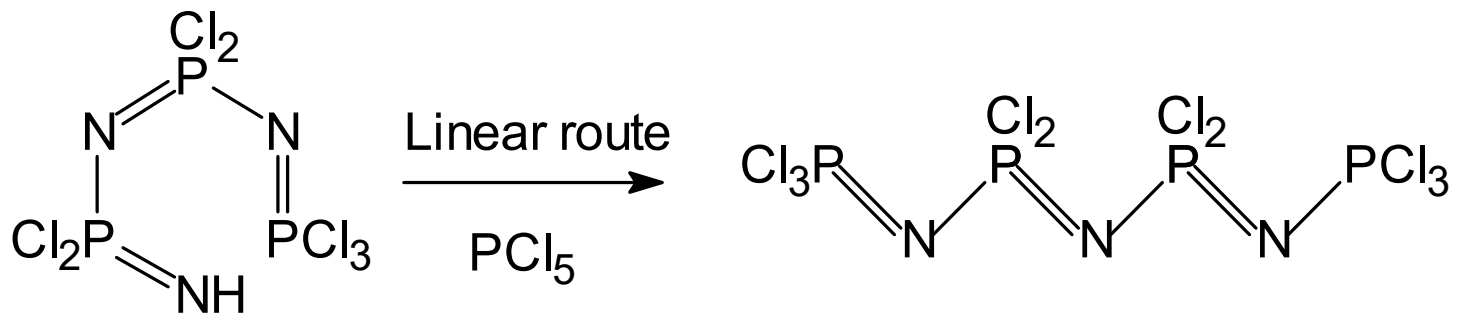
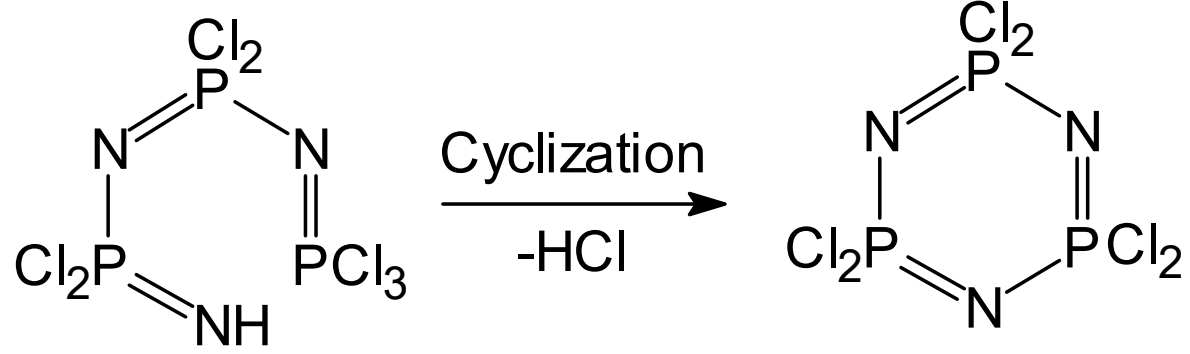
The reaction continues with rise in chain length.

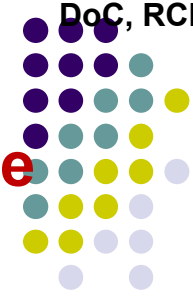
*The linear polymer undergoes cyclization to give cyclic compounds of various ring size.



The products are 80% cyclic & 20% linear.

This proportion can be varied by adjusting reaction conditions. **e.g., if excess PCl₅ is used, linear polymer predominates.** **If it is added slowly to reaction, the polymer is cyclic.**



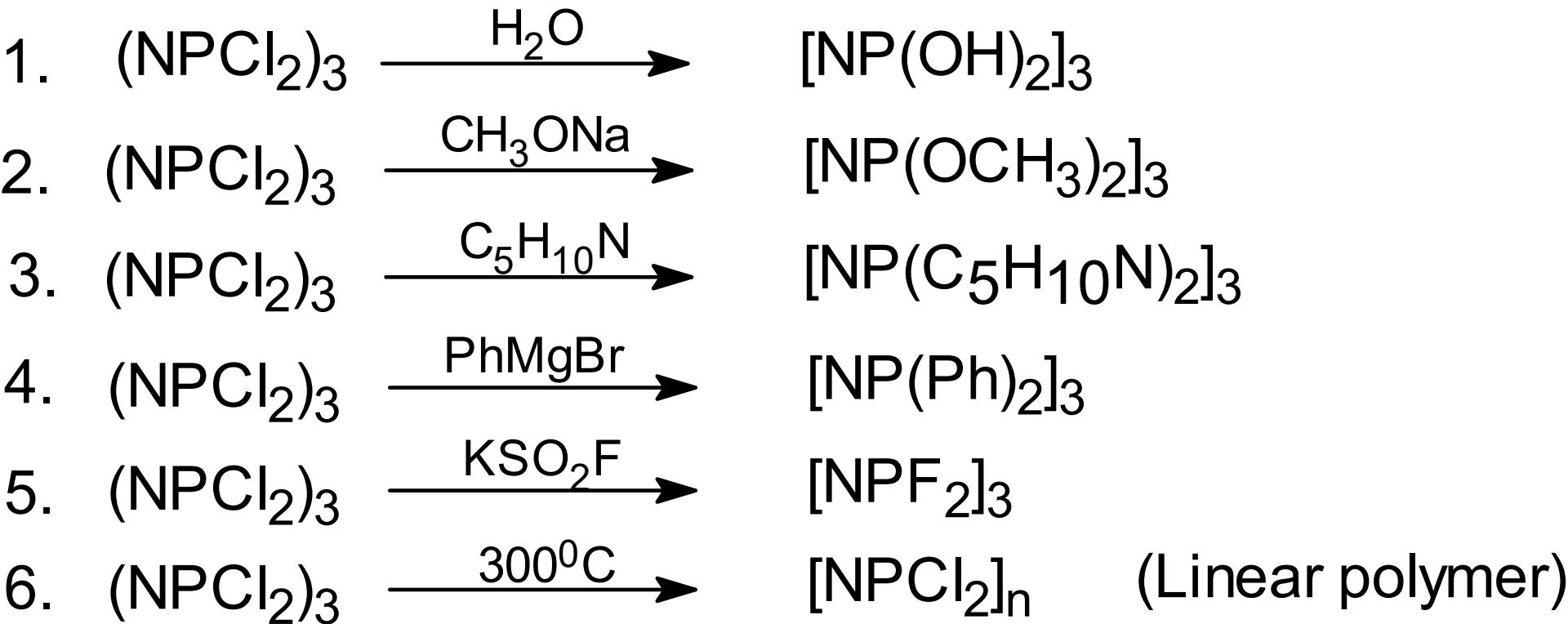


***Cyclic polymers are soluble in petroleum ether while Linear polymer is insoluble. The solution contains dimer to octamer, can be separated by distillation & solvent extraction.**

***They acts as nucleophiles (due to delocalized pi system).**

***This reaction can be used to prepare a no. of salts.**

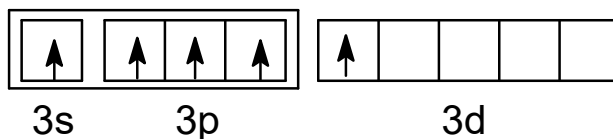
***Using substituted P compounds, other derivatives can be made.**





- **BONDING IN PHOSPHONITRILIC COMPOUNDS:**

- Two models to describe bonding;
- i) Criag & Paddock, ii) Island (Dewar) Model.
- According to Criag and Paddock, bonding in cyclic polymers has alternate P & N atoms.
- *The electronic configuration of P is;
- (GS) P(15): $3s^2, 3p^3, 3d^0$ (ES): $3s^1, 3p^3, 3d^1$

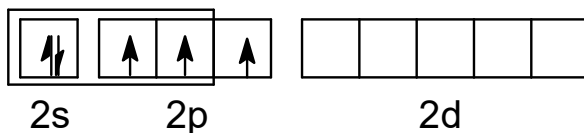


sp^3 , Geometry - Tetrahedral.

P has 4 lobes, directed towards 4 corners of tetrahedron.

***The electronic configuration of N is,**

(GS) N (7): $2p^3$ (E S) N (7): $1s^2, 2s^2, 2p^3$



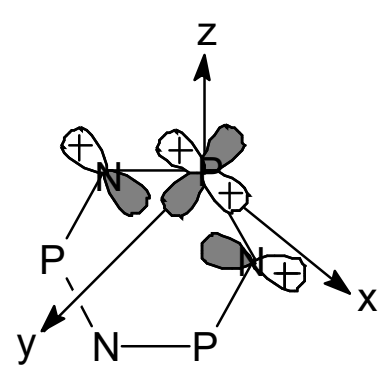
sp^2 , Geometry- Trigonal.



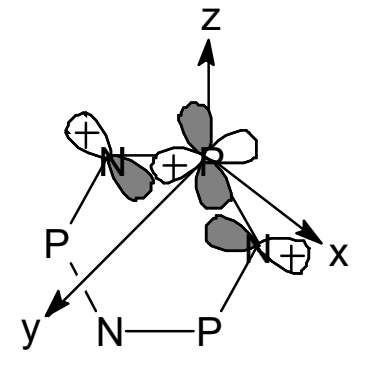
N has 3 lobes in triangular geometry. One of the HO has one lone pair. N atom still has AO(p_z) with an electron.

*Two HOs of P form exocyclic bonds with substituents while two HOs form ring bonds with two adjacent N which use sp^2 HOs, giving a ring with substituents at opposite sides of ring. The remaining HO on N with lone pair (in plane of ring) & p_z AO (unhybridized) with an e^- (in plane \perp to ring) are available for π bonding with $3d$ of P.

Thus, two mutually \perp π systems are present, the first in the ring plane and the second perpendicular to this plane. 1) A π system in the plane of a ring is derived from sp^2 HOs of N and dx^2-y^2 of P atoms. [Fig. 1] [but d_{xy} is also known to contribute in π bonding (Fig. 2)]. The sign of wave functions of combining orbitals is same for both the situations; therefore, the system is called homomorphic system.



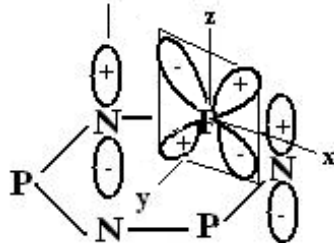
($sp^2(N)-dx^2-y^2$) pi system



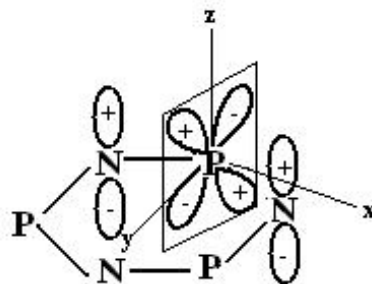
($sp^2(N)-dx-y$) pi system

- 2) A π system in the plane \perp to phosphazene ring is derived from p_z of N and d_{xz} of P. [d_{yz} is also known to contribute in π bonding]. p_z - d_{xz} type of overlap has a node due to sign mismatch of orbital wave function, which reduces the stability (Fig.3). Such system is called heteromorphic system.
- In p_z - d_{xz} , the nodes are introduced between each pairs of d and p orbitals which represent a confinement and thus high energy. However p_z - d_{yz} type of overlap don't have nodal surface (Fig4).

sign mismatch



(p_z - d_{xz}) π system
have a nodal plane



(p_z - d_{yz}) π system
Do not have nodal plane



B) PROPERTIES:

Cyclic polymers are crystalline, A trimeric polymer with bulky groups at N act as elastomers, plastic, films & fiber.

- **It is flexible at low temp .They are water & fire resistant.**
- **Fluoro alkoxy substituted phosphazenes are inert to living tissues.**
- **They have useful optical, electrical and thermal properties.**

C) APPLICATIONS:

- **The commercial applications are not as well established.**
- **Used in making the artificial blood vessels and prosthetic devices.**
- ***As a slow DRA in human body. A slow hydrolysis of phosphazene+drugs/antibiotics/steroids provides drugs to body.**

HETEROATOMIC POLYMERS: SILICONES



Silicones: high m.wt compounds with Si-O linkages (**Siloxane**) & substituents like alkyl, aryl, methoxy, ethoxy, hydroxyl, H at Si atoms.

History:

- Friedal & Craft in 1963 prepared 1st silicone, cyclic tetra ethyl silane. The 1st commercial use- as ignition sealing compound in aircraft (1943).

Nomenclature:

- *Silicon compds* are called **silane**. General formula is $\text{Si}n\text{H}_{2n+2}$. Substituted silanes are named after the parent compound.
e.g. SiH_4 – Silane, $(\text{CH}_3)\text{SiH}_3$ – Methyl silane,
 CH_3SiCl_3 – Methyl trichlorosilane $\text{H}_3\text{Si-SiH}_3$ – Disilane.
- Hydroxy derivative are called **silanol**. The no. of OH groups are named by suffices *ol*, *diol*, *triol* etc.
e.g. $\text{Si}(\text{OH})_4$ - silanetriol.



- **Preparation :**

Preparation involves 2 steps.

STEP: a) Preparation of Intermediates:

Intermediates required - R_3SiCl_4 , R_2SiCl_2 , $RSiCl_3$ etc. $R=Me, Et, Ph, Mo, Eo$.
These are prepared by several methods.

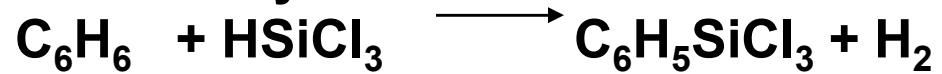
i) Direct method: Methyl chloride is passed over Si containing 10% of Cu
Cu, 300°C



The mixture of is separated by careful fractional distillation.

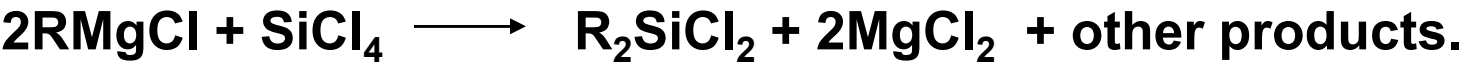
ii) Aromatic Silylation:

Aryl silicone halides are prepared from benzene & trichloro silane using Friedel Craft catalyst.

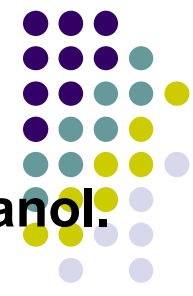


iii) Grignard Reagent Method:

alkyl/ aryl magnesium chlorides react with $SiCl_4$ in ether

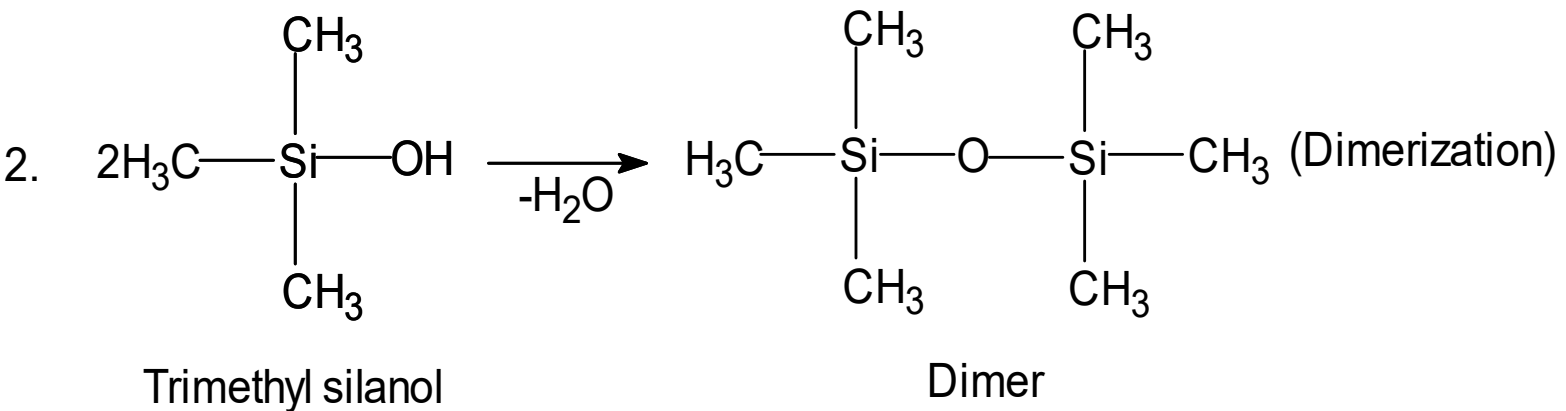
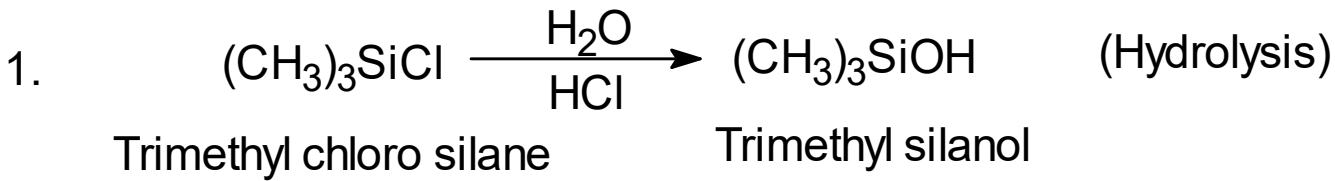


After removing $MgCl_2$, mixture is separated by fractional distillation.

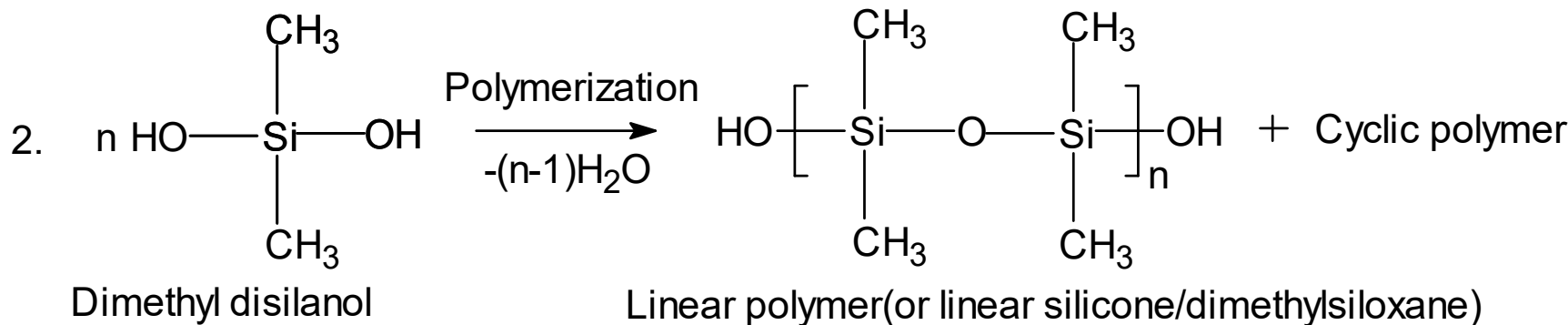
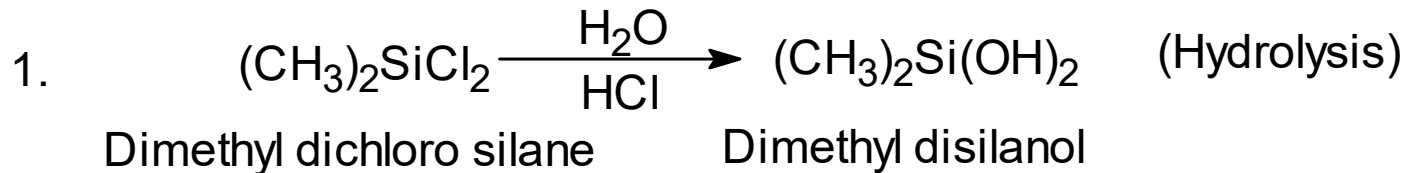


STEP: b) Polymerization of Intermediates:

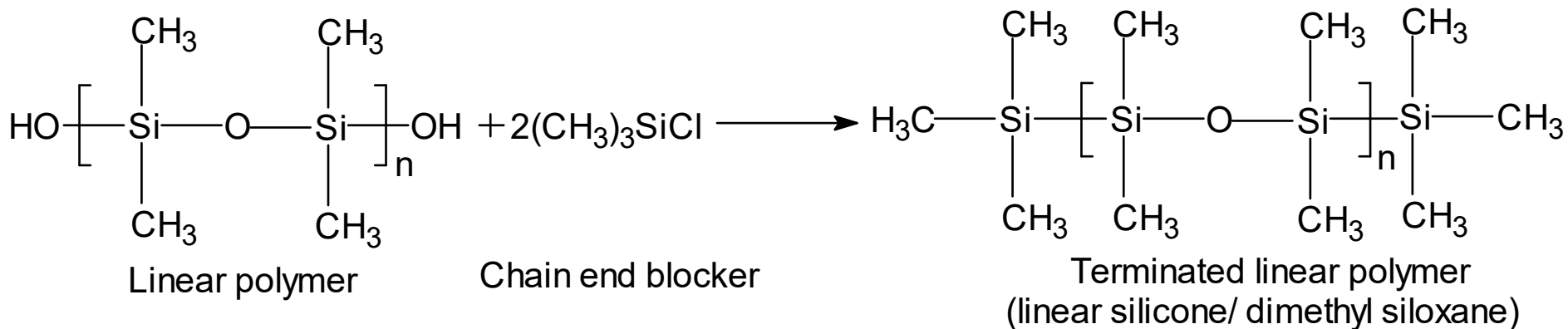
- The hydrolysis of alkyl chloro silane using HCl /NaOH gives silanol. containing 1 to 3 -OH groups, it condense spontaneously to produce polysiloxane.
- The product may be linear/cyclic/cross linked depending on no. of -OH groups & reaction conditions.
- For examples:
- 1) If silane contains 1 Cl, the hydrolysis gives dimer (final product).



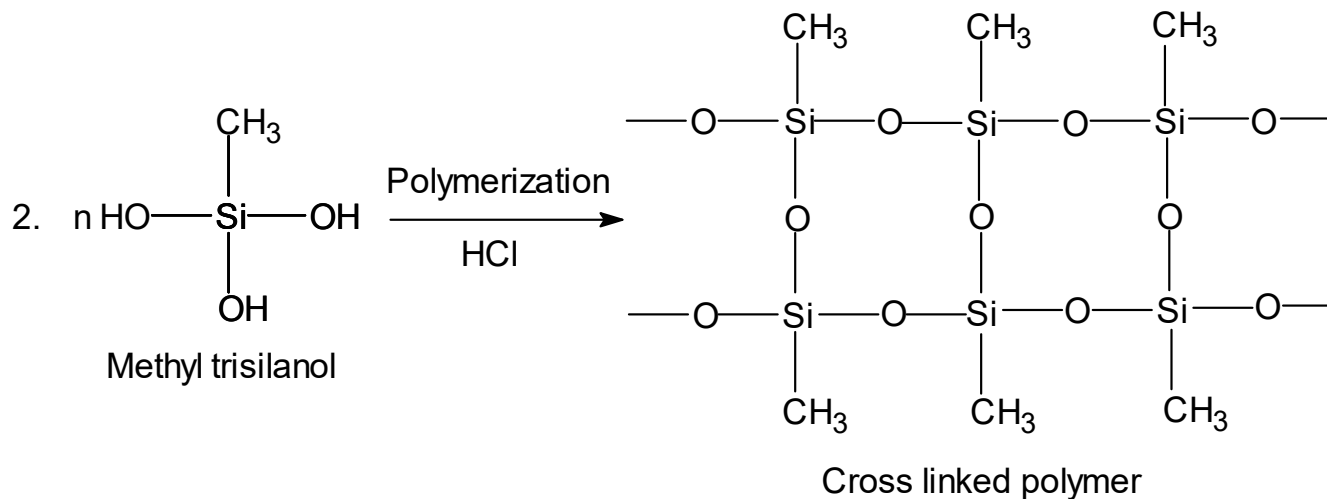
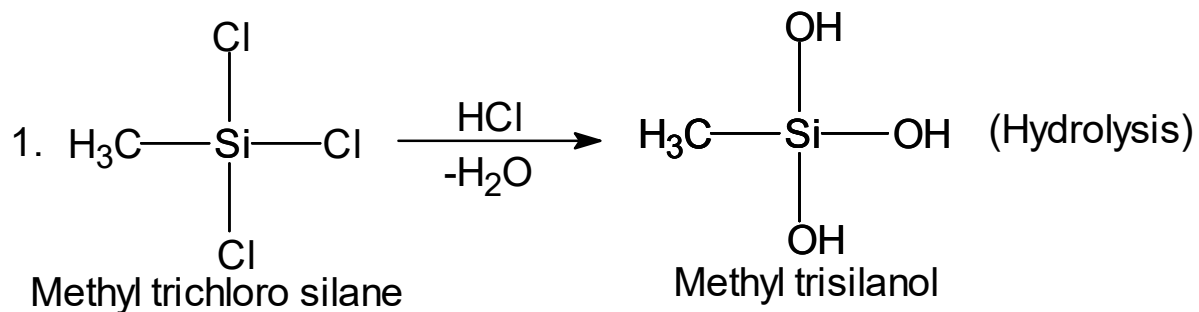
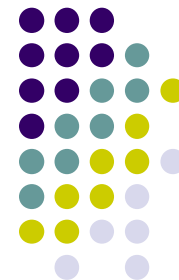
2) If silane has 2 Cl, the final product is linear/cyclic.



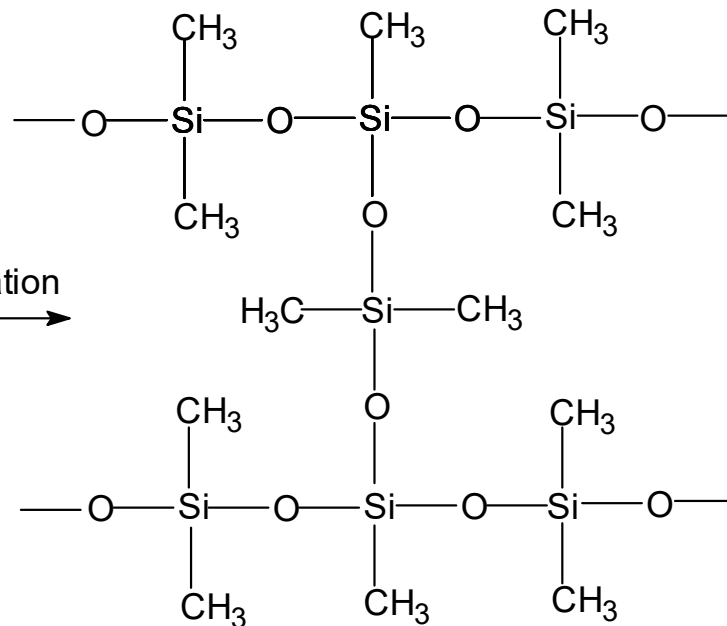
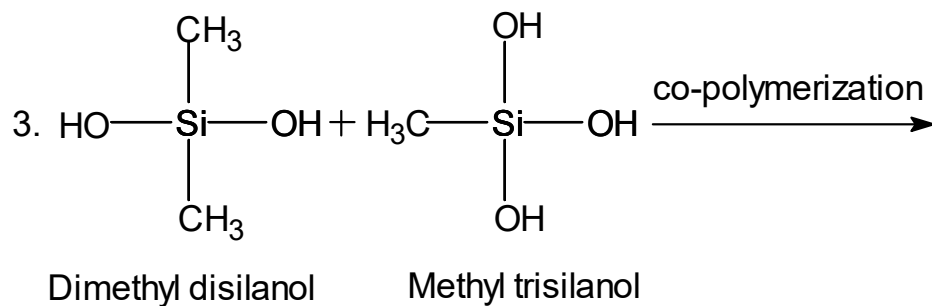
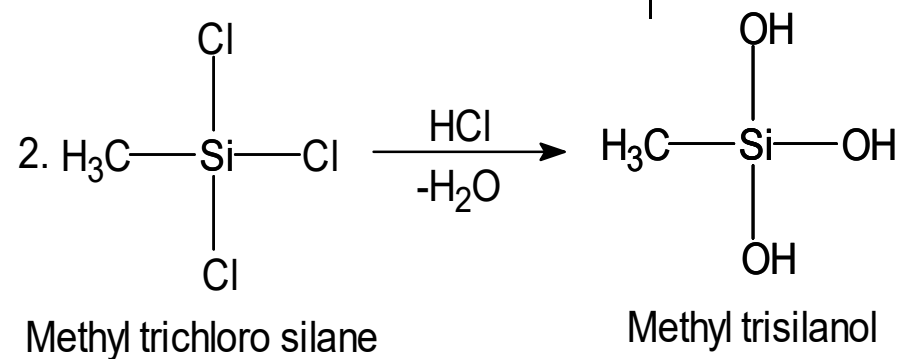
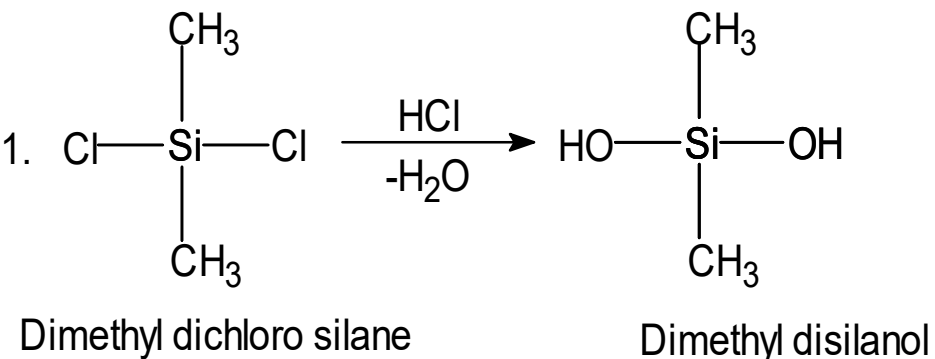
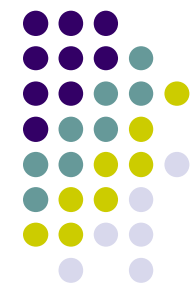
The reaction is ended by neutralizing acid/base or by adding monochlorosilane as *chain end blocker*.



- 3) If silane has 3 Cl the product is cross linked polymer.



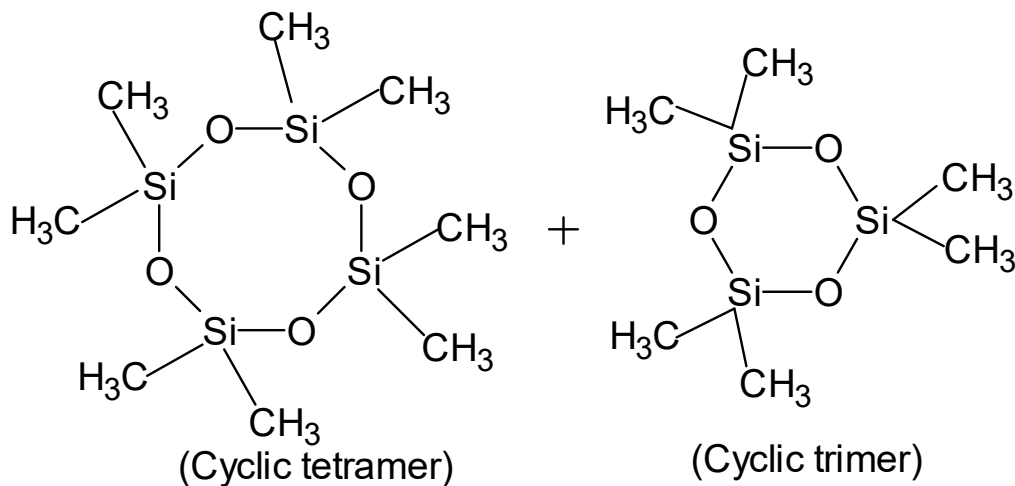
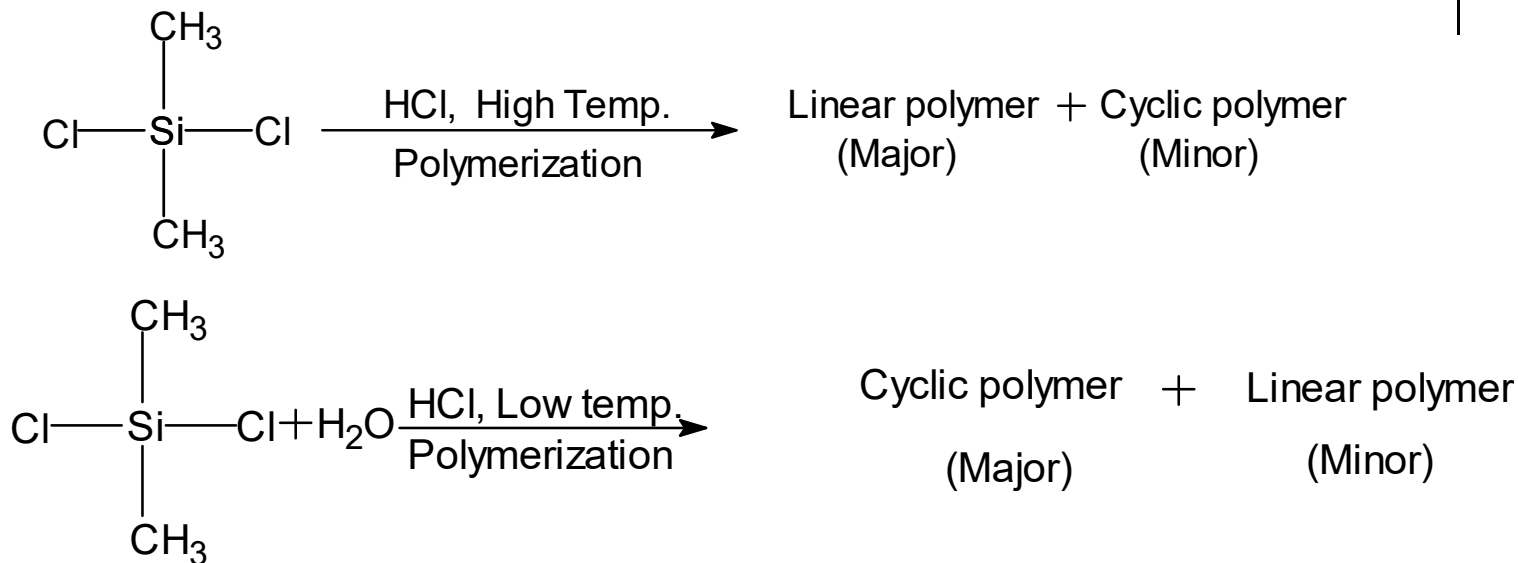
- 4) Siloxane can also be produced by co-hydrolysis of two silane. The hydrolysis produces silanols, which combine with each other at high temp. to give cross linked *ladder* type polymer.



Co-polymer

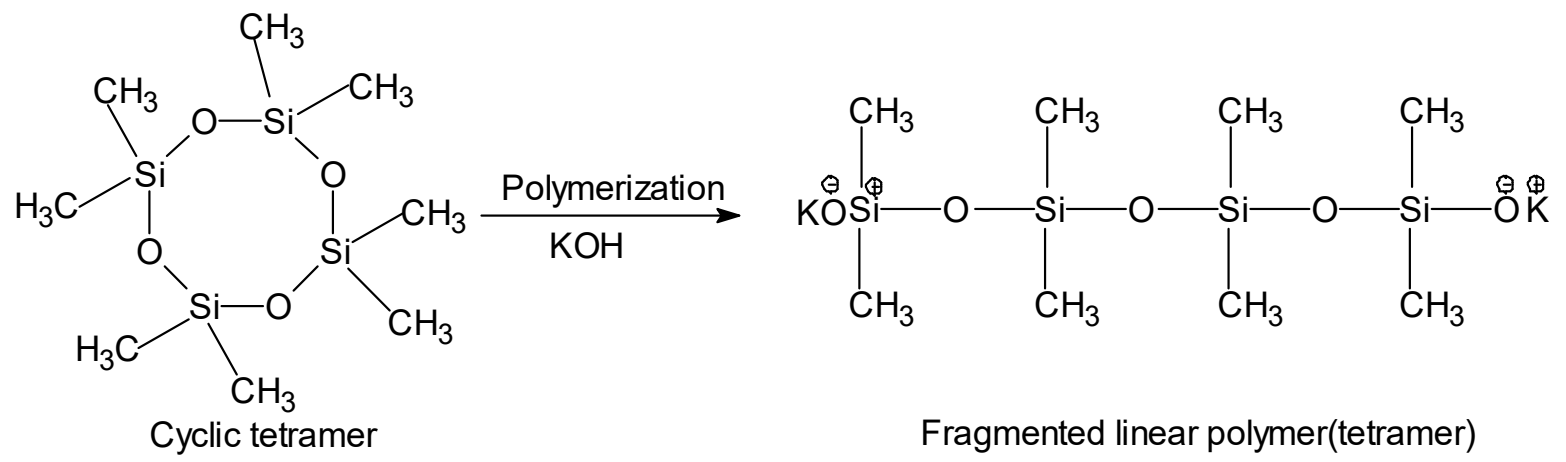


- 5) Dichlorosilane at high temp. gives linear polymer. However at room temp, the product is cyclic polymer, called Silicone fluid.

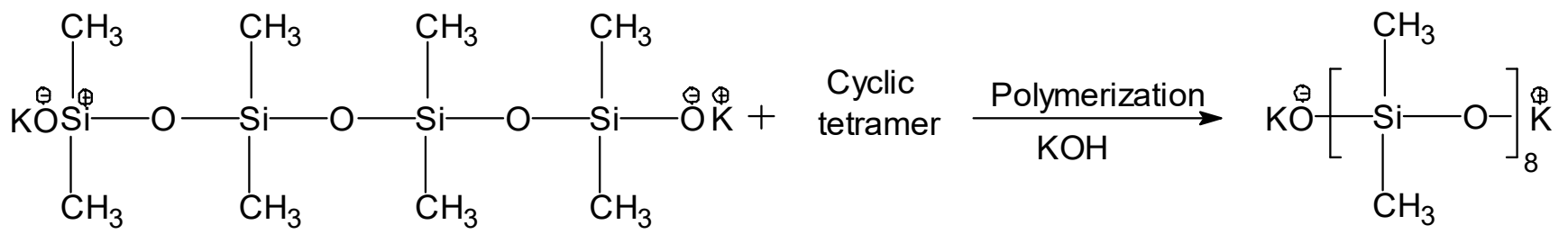


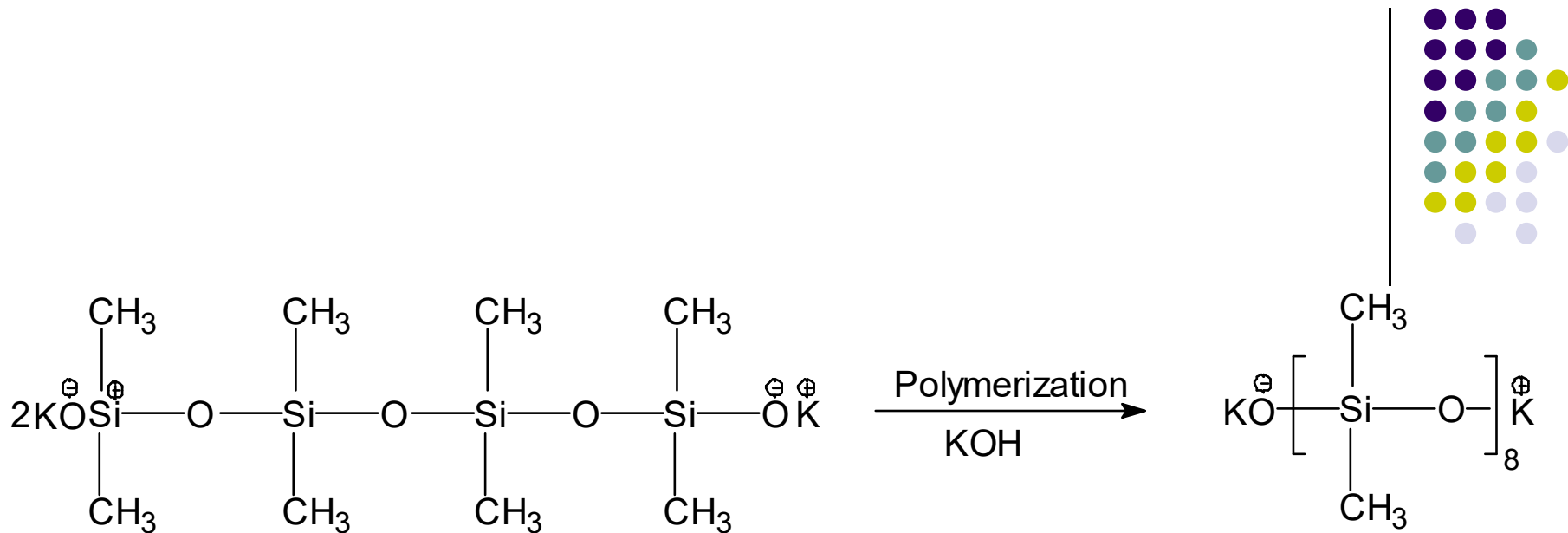


- **Tetramer** is most abundant & stable. **Trimer** and higher ring compounds are unstable due to ring strains.
- The tetramer can be used as starting material for synthesis of polymers. The cleavage of polar Si-O bond gives fragments having negative charge on oxygen.



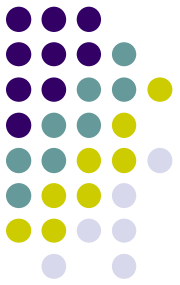
The fragments react with cyclic compds/ other fragments to give high polymer. The fragment- interchange may occur to give different siloxanes.





- **General Properties:**

- All are inert to chemicals, oxidation & stable to heat over -70 to 300° temp.
- excellent water repellent, remains flexible over the wide temp. range.
- shows excellent dielectric properties. possess surface active effects like antifoaming ability, adhesion, polishing and non stickiness, insulators,
- Low m.wt polymers get dissolved in common solvents. The linear siloxanes are fluids, The branched polymers are gummy or resinous materials.

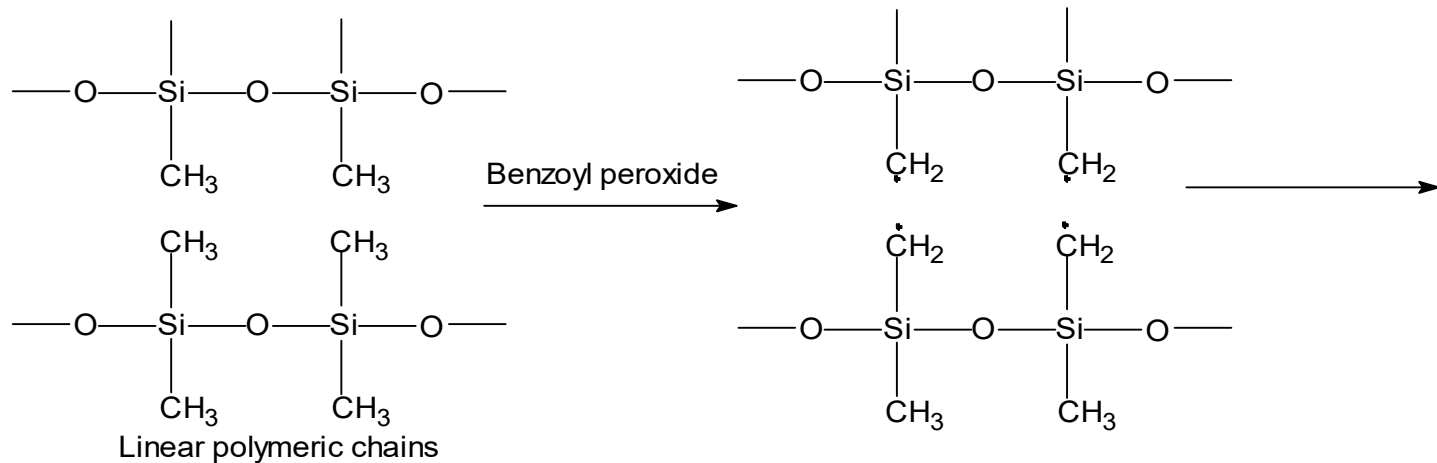


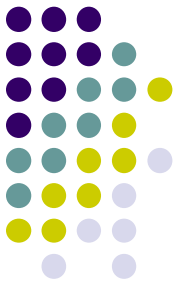
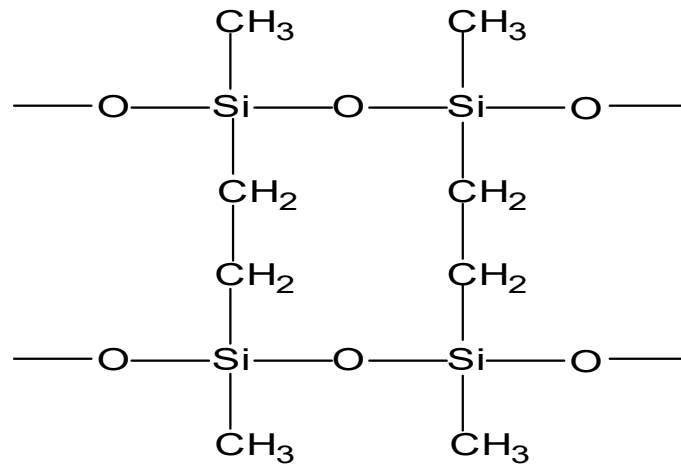
- **TYPES OF SILICONES (SILOXANES):**
- 1. Rubbers, 2. Fluids, 3. Compounds and 4. Resins.

- **a) SILICONE RUBBERS:**

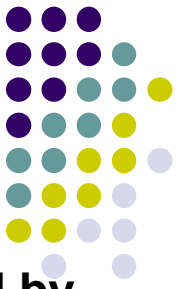
- **i) Preparation:**

- **Silicone rubbers are produced by controlled cross linking of dimethyl silicone with vulcanizer-benzyl peroxide at 1100C. Finally TiO₂, ZnO, FeO, SiO₂ etc. are added as filler, followed by curing at 1500C, in absence of air to give rubbers. The combinations of chain portions occur at active sites which result in ethylene crosslinks.**





- **ii) Properties:** Flexible at -90° to 150°C , good water repellent, resist. to corona discharge, have low TS & elongation
- **iii) Uses:** As heat & chemical resistant coat on glass, fabrics, mats, tubings, belts, gaskets etc., to make compressible pads, mountings, O rings, autoclave seals, nonstick linings etc, as insulator on coils, motors, wires, as space fillers in electrical equipments.



b) SILICONE FLUIDS:

i) Preparation:

Silicone fluids are prepared by hydrolysis of dimethyl dichloro silane in presence of acidic aqueous solution. The low m.wt product is produced by adding tri methyl chloro silane during reaction. The added silane serves as an end site blocker to stop further growth.

ii) Properties:

Fluids have high spreading power so that a thin protective film can be spread over plastics, metals, ceramics etc.

Has high water repellent properties, stable in air upto 1500C, however at high temp. it get crosslinked to produce viscous fluids.

iii) Uses:

Silicone fluids are used to prevent cracking of organic / inorganic powder. A thin coat of polymer on such compounds is helpful.

Used to polish automobiles, cars etc., to treat interior part of a vial for storing aqueous suspension of penicillin.

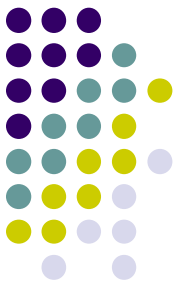
For lining moulds of rubber tyres, plastics, castings etc.

Varying viscosities fluids are used as damping and hydraulic fluids.

As antifoaming agents in petroleum oils.

As fluids for capacitors, transformers since they have excellent water resistance and dielectric properties.

As high temp. bath oils , used for sterilization of dental & surgical instruments.



c) SILICONE COMPOUNDS:

i) Preparation:

The silicon compounds are formulated from dimethyl fluids by adding finely divided silica. Additions of fillers like lithium soaps, carbon etc. give compounds called silicon greases.

ii) Properties:

Consistency varies from free flowing to heavy ointment. The blend retains all properties of dimethyl silicones.

iii) Uses:

- (1) used as water repellent, as sealing agents in aviation type spark plugs, as lubricants, as moisture proof seals, corrosion inhibitors,**
- (ii) As insulators in electrical connections, X- ray equipments, marine engine ignition system, battery cases.**
- (iii) For water proofing, prevention of leather and rubber diaphragms etc.**
- (iv) For lubricating ball bearings, working in chemical and corrosive environments and those under light to moderate loads at low temperatures. Carbon based grease is used as heat resistant grease for conveyor belts and oven doors.**



- **d) SILICONE RESINS:**
- **i) Preparation:**
- **Hydrolysis & condensation silanes under controlled conditions (relative amounts of reactants, additives etc.) followed by adding terminators give resins. Resins are cured at a temp. somewhat higher than at which it is likely to be used.**
- **ii) Properties:**
- **1. high resistant to water and heat.**
- **2. They have excellent adhesion property.**
- **3. Show poor resistance to water vapour due to high vapour permeability.**
- **4. They have no action of strong acids, bases but are easily attacked by aliphatic, aromatic and chlorinated hydrocarbons.**
- **5. Coatings of silicon resins are nontoxic and show non stickiness.**
- **iii) Uses:**
- **1. Used as protective coatings on motors, turbines, boilers, steam pipes, refrigerators & other household equipments.**
- **2. As a water resistant resins, in masonry and concrete.**
- **3. As thermal and electrical insulators, for making firewall structures, high temperature vibration dampers etc.**
- **4. Used to coat the food handling equipments.**