

Engineering Polymers: Dr. Keshar Prasain

After the completion of this chapter students should be familiar with both organic and inorganic polymers, their preparation and applications. Students also should understand the basic concepts of biodegradable and conducting polymers.

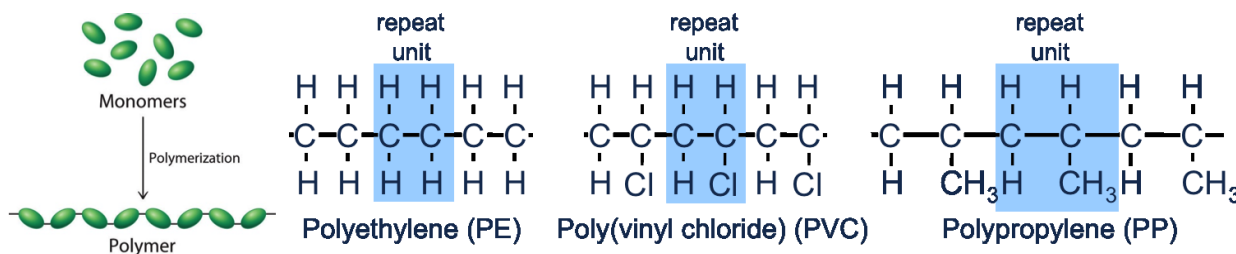
Polymers are macromolecules consisting of several to thousands of repeating units called monomers. Humans have taken advantage of the versatility of polymers for centuries in the form of oils, tars, resins, and gums. However, it was not until the industrial revolution that the modern polymer industry began to develop. In the late 1830s, Charles Goodyear succeeded in producing a useful form of natural rubber through a process known as "vulcanization". Some 40 years later, celluloid (a hard plastic formed from nitrocellulose) was successfully commercialized. Despite these advances, progress in polymer science was slow until the 1930s, when materials such as vinyl, neoprene, polystyrene, and nylon were developed. The introduction of these revolutionary materials began an explosion in polymer research that is still going on today.



Unmatched in the diversity of their properties, polymers such as cotton, wool, rubber, Teflon, and all plastics are used in nearly every industry. Natural and synthetic polymers can be produced with a wide range of stiffness, strength, heat resistance, density, and even price. With continued research into the science and applications of polymers, they are playing an ever increasing role in the society.

Introduction

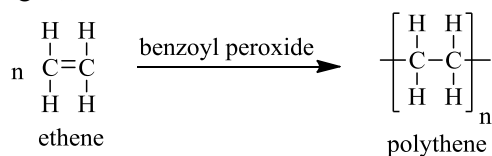
The word polymer is derived from two Greek words; *polos*: many and *merus*: parts (repeating units). Therefore, polymers can be defined as macromolecules (high molecular weight compounds) formed by linking large numbers of repeating units called monomers. For example, polythene is a polymer formed by linking together large number of ethene (C_2H_4) molecules. Ethene is a monomer of polythene (polyethylene). The molecular weight of polymers generally ranges from 5,000 to 200,000 Dalton. The reaction converting monomers to polymers is called polymerization. The number of repeating units (n) in a polymer is called degree of polymerization.



Types of Polymers

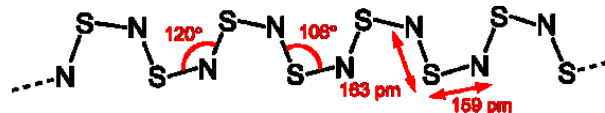
Based on the types of atoms constituting the skeleton of the polymers, polymers are classified into two major types:

A. Organic Polymers: In organic polymers the atoms in the skeleton are mostly carbon. Elements like oxygen, nitrogen, etc., are also found in the skeleton of organic polymers.



B. Inorganic Polymers: In inorganic polymers the skeleton (chain) consists of elements other than carbon.

Example: Polythiazyl (Sulphur based inorganic polymer)



A. Organic Polymers: Organic Polymers can be classified into following types depending on:

i) **Source:** Depending on the source, organic polymers are classified into two major types:

Natural: Examples; starch (polymer of alpha-D Glucose), cellulose (polymer of beta-D Glucose), proteins (polymer of amino acids), natural rubber (polymer of isoprene).

Synthetic Polymers: polythene, Teflon, Bakelite, Kevlar, etc.

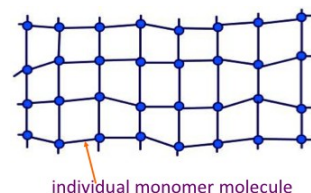
ii) **Methods of synthesis:** Depending on the method of synthesis, polymers are classified into two main types:

Addition Polymers: In addition polymers all the atoms in the monomer are used to form the polymer. Generally alkenes or alkynes form addition polymers. Examples of addition polymers are polythene (polyethylene), polypropylene, polyvinyl chloride (PVC), polytetrafluoroethylene (Teflon), polystyrene, etc.

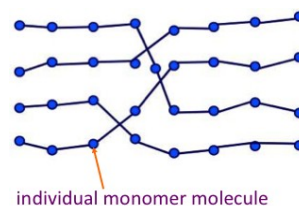
Condensation Polymers: In condensation polymers monomers join up with an expulsion of small molecules like water, ammonia, methanol, etc (all the original atoms are not present in the polymer). Polyamides and polyesters are two important classes of condensation polymers.

iii) **Molecular Force:** Depending on the intermolecular force, organic polymers are classified as:

Thermosetting: Thermosetting plastics are those which are set with heat and have little elasticity. Once set, they cannot be reheated and reformed. They are heated and molded during manufacture. Once cooled, they will not soften again when heated. This breaks the potentially unending cycle that thermoplastic plastics are capable of. If heated too much, they burn. Thermosetting plastics also have lots of long chain molecules, but there are links between them. These cross links prevent the molecules from moving over one another. Melamine, Bakelite, etc are the examples of thermosetting plastics.



Thermoplastic: The majority of common plastics are thermoplastics. Thermoplastics can be heated and reshaped because of the ways in which the molecules are joined together. Reheating and reshaping can be repeated many times (as long as no damage is caused by overheating). Thermoplastic plastics are made of long chains of polymers, which don't cross over very often. When heated, the molecules slip easily over one another. Polyethylene, polystyrene, polyvinyl chloride, etc., are the examples of thermoplastics.



Elastomers: synthetic polymers which can be stretched to three times of its original size are called elastomers. In elastomers the molecules have few or no cross links. The molecules (long chains) are arranged as a spring and can be stretched on applying stretching force. When the stretching force is released, the molecules recoils back to the original form.

Resin: Resin are polymers having strong intermolecular force of attraction due to hydrogen bonding.

Plastics

Plastics are organic materials of high molecular weight, which can be molded into any desired form when subjected to heat and pressure. In recent years, plastics have attained great importance in every part of our life, due to their certain properties like:

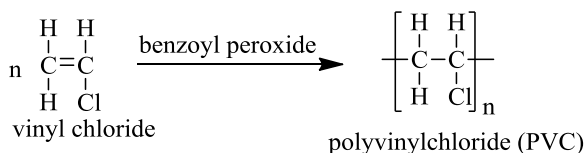
- *Lightness in weight:* Their specific gravity varies from 1 to 2.4.
- *Good thermal and electrical insulation:* They possess very low thermal and electrical conductance. *Corrosion-resistance:* Plastic are highly resistant to corrosion.
- *Easy workability:* Casting, molding, drilling, sawing, machining, etc. of plastics can be easily done.
- *Chemical Inertness:* Plastics are generally inert to the action of lights, oils, acids and dampness.
- *Transparency:* Some plastics are highly transparent and translucent. They can be ground and used as optical lenses.
- *Low softening point:* Most of the plastics have low softening points, even as low as 50°C.

Disadvantages of plastics over metals: High cost, poor ductility, softness, deformation under load, embrittlement at low temperatures, low heat-resistance, etc.

Preparation, properties, and applications of polyurethane, polystyrene, polyvinyl chloride, Teflon, Nylon-6,6, Bakelite, and epoxy resins.

1. Polyvinyl chloride (PVC)

Polyvinyl chloride is obtained by heating a water-emulsion of vinyl chloride in the presence of small amount of benzoyl peroxide in an autoclave under pressure.



Properties: PVC is a colourless, odourless, non-inflammable and chemically inert powder. It is resistant to light, oxygen, inorganic acids and alkalis, but soluble in hot chlorinated hydrocarbons like ethyl chloride. Pure resin possesses a high softening point (148°C) and greater

stiffness as compared to polyethylene. It is the third most widely used synthetic plastic after polythene and polypropylene.

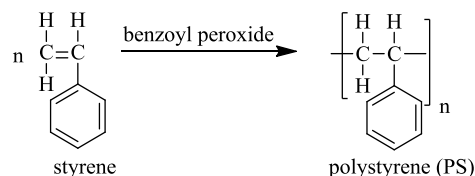
Uses: PVC is used for making sheets, light fittings, safety helmets, cycle and motorcycle mudguards, pipes and pipe-fittings, chemical container, frames for doors and windows, debit and credit cards, etc.

2. Polystyrene

Polystyrene is prepared by polymerization of styrene (dissolved in ethyl benzene) in presence of benzoyl peroxide as initiator (catalyst).

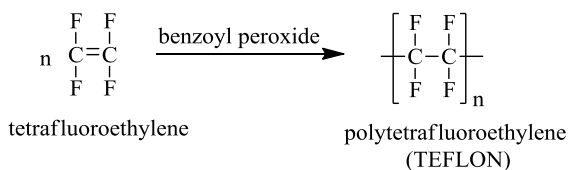
Properties: Polystyrene is a transparent, light, light stable, excellent moisture resistant polymer. It is highly electric insulating, highly resistant to acids and good chemical resistant. It has low softening point of 90-100°C and is brittle. It has a unique property of transmitting light through curved sections.

Uses: Polystyrene is used in protective packaging and containers as styrofoam, toys, disposable food container. They are also used as insulators. They are used in making lenses and disposable cutlery like spoons, forks, plates, trays. They are used in making radio, tv and refrigerator parts, CD cases, etc.



3. Polytetrafluoroethylene (TEFLON or FLUON)

Polytetrafluoroethylene is obtained by polymerization of water-emulsion of tetrafluoroethylene, under pressure in the presence of benzoyl peroxide.



Properties: Due to the presence of highly electronegative fluorine atoms, polymer molecules have very strong attractive force between the different chains. These strong attractive forces give the material extreme toughness, high softening point (350°C), exceptionally high chemical-resistance, and high density (2.1 to 2.3 g/cm³), etc. They have low coefficient of friction.

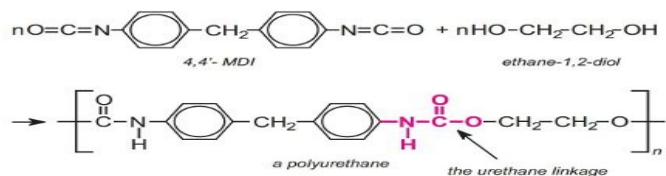
Uses: Teflon is mostly used as insulating materials for cables, wires, transformers, etc. They are used in making gaskets, stop cocks in burettes and pipes for carrying chemicals. They are also used as coating in high quality non-stick cooking pans. They are also used in the making of self lubricating bearings.

4. Polyurethane

Polyurethanes are obtained, commercially by treating diisocyanate and diol. For example when methylene diphenyl diisocyanate (diphenylmethane diisocyanate; MDI) is treated with ethane-1,2-diol we get polyurethane polymers.

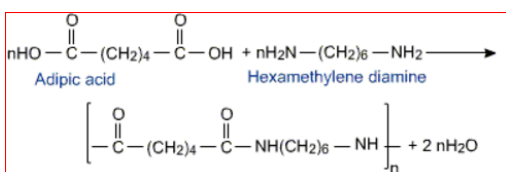
Properties: Polyurethanes are less stable than polyamides (nylons) at high temperature. They are resistant to abrasion and solvents.

Uses: Polyurethanes are used as coatings, films, foams, adhesives and elastomers. Resilient polyurethane fibres (spandex) are used for foundation garments and swim-suits. They also find use as a leather substitute as corfoam. They are used in cast to produce gaskets and seals.



5. Nylon-6,6

Nylon-6,6 is a polyamide and is obtained by polymerization of adipic acid with hexamethylene diamine under nitrogen atmosphere at 200°C.



Properties: Nylons are translucent high melting (160 to 264°C) polymers. They possess high temperature stability and good abrasion-resistance. They have self lubricating property.

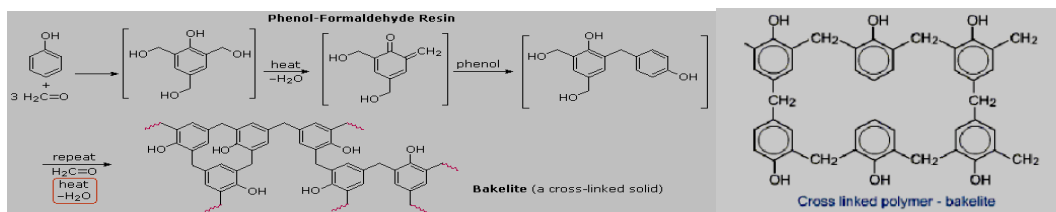
Uses: It is used for ball bearing cages, electro-insulating elements, pipes, profiles and various

machine parts. Other popular applications are: carpet-fibers, apparel, airbags, tyres, zip ties, ropes, conveyor belts, under-garments, dresses, carpets, hoses and the outer layer of turnout blankets.



6. Bakelite

Bakelite is phenol-formaldehyde resin, a condensation polymer formed by polymerization of phenol with formaldehyde. Bakelite is prepared by condensing phenol with formaldehyde in the presence of acidic or alkaline catalyst.

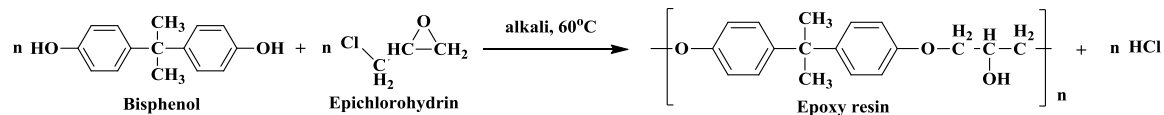


Properties: Bakelite is rigid, hard, scratch-resistant, infusible, water-resistant, insoluble solids, which are resistant to non-oxidizing acids, salts and many organic solvents, but are attacked by alkalis because of the presence of free hydroxyl group in their structures. They possess excellent electrical insulating character.

Uses: Bakelite is used for making electric insulator parts like switches, plugs, switch-boards, heater-handles, etc. Bakelite is also used for making telephone parts, cabinets for radio and television. Bakelite is also used as hydrogen-exchanger resins in water softening, etc.

7. Epoxy resin

Epoxy resins are materials prepared by a polymerization in which one monomer contains epoxy groups.



Properties: Epoxy resins due to the presence of very stable ether linkages, have high resistance to chemicals, water, various solvents, acids, alkalis, etc. The reactive hydroxyl groups are comparatively widely spaced, thereby resulting in high flexibility, but at the same time the presence of cross-links accounts for toughness and heat-resistance of the cured polymers. Moreover, the polar nature of the molecules produces excellent adhesion quality.



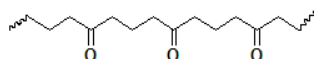
Uses: As surface coatings, adhesives, for skid resistant surfaces for highways, moulds made from epoxy resins are employed for the production of components for aircrafts and automobiles.

Biodegradable Polymers

Why?

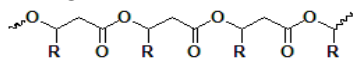
- Because plastic water bottles are shielded from sunlight in landfills, they will not decompose for thousands of years.
- Plastic needs about 450 years just to start decomposing. Then, it takes another 50-80 years to decompose completely.
- 90% of the price you pay for the bottled water goes to the plastic bottle, while the water cost you money. only 10% of the

The polymers which are degraded by micro-organisms within a suitable period so that the polymers and their degraded products do not cause any serious effects on the environment are called biodegradable polymers. For example when ethylene is polymerized in the presence of carbon monoxide, a polyethylene like polymer that contains carbonyl group is produced. This material, which has been used in the production of trash bag undergo degradation upon exposure to UV due to carbonyl group.



PHB and PHV are naturally occurring polyesters produced by certain bacteria.

PHB-PHV copolymer, BIOPOL, has been recently used in the manufacturing of shampoo bottles because it is biodegradable.



R = Me; poly(3-hydroxybutyrate); PHB

R = Et; poly(3-hydroxyvalerate); PHV

Biodegradable polymers are used mainly for medical goods such as:

- Surgical sutures, tissue in growth materials or for controlled drug release devices, plasma substitutes etc.



- ii. The decomposition reactions usually involve hydrolysis (either molecule which can be metabolized by or excreted from the body).
- iii. These are also finding use in agriculture materials (such as films, seed coatings), fast food wrappers, personal hygiene products etc.

Conducting polymers due to pie electron and doping effect

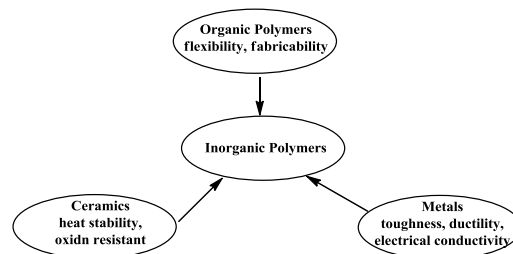
Most organic polymers are insulators. Polyacetylene has conjugated double bonds but is not a conductor; however, by a process called doping, which involves introducing small amounts of electron-donating or electron accepting compounds, it is possible to produce polyacetylene to show conductivity. The purpose of the doping agent is either to remove electrons from the pi system (*p*-doping) or add electrons to the pi system (*n*-doping).



In the above example polyacetylene is *p*-doped. We can think of the positive charge as a defect that can move to the left or to the right along the polymer chain, thus giving rise to conductivity. Applications for conducting organic polymers are beginning to be developed.

B. Inorganic Polymers:

Polymers having skeleton made up of atoms other than carbon are called inorganic polymers. Examples: polyphosphazines, polythiazyl, silicones, chalcogenide glass, etc. Broadly speaking, inorganic polymers are hybrid systems that have advantages of metals, ceramics and organic polymers, while at the same time have minimum disadvantages.

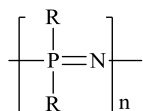


Characteristics of inorganic polymers

- i. They have higher softening point as compared to organic polymers.
- ii. Inorganic polymers with cross-links are usually stiffer, harder and more brittle than organic polymers. The segments between the cross links are usually shorter; therefore, they do not allow intercalation with solvent molecules.
- iii. These polymers have highly polar units, so dissolve in polar solvents.
- iv. They possess lesser tensile strength as compared to organic polymers.

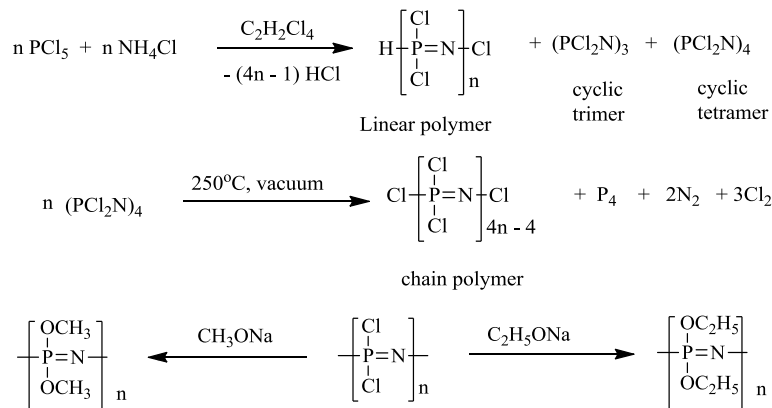
1. Polyphosphazines

Polyphosphazines are inorganic compounds having the following structural formula.



When: R = Cl; Polyphosphonitrilic chlorides
 R = OCH₃; polydimethoxy phosphazines
 R = OC₂H₅; polydiethoxy phosphazines

Preparation: Polyphosphonitrilic chlorides are prepared by treating phosphorus pentachloride and ammonium chloride in 1,1,2,2-tetrachloroethane. The cyclic trimer and tetramer formed during the reaction can be heated in vacuum at 250°C to form linear chain polymers with some cross-linking and limited solubility in inorganic solvents. Polydimethoxy and polydiethoxy phosphazines are prepared by treating polyphosphonitrilic chlorides with sodium methoxide and sodium ethoxide respectively.

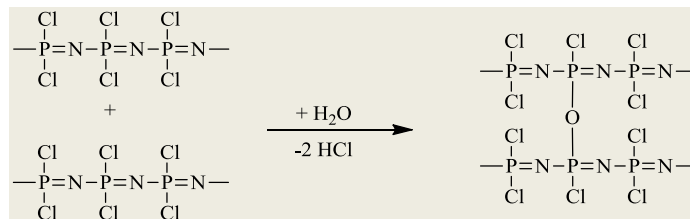


Properties of polyphosphonitrilic chlorides:

- These polymers exhibit high elasticity and can be stretched many times reversibly. They are also called as inorganic polymers.
- Freshly prepared samples are soluble in chloroform, but are insoluble in hexane. However, when the solution is allowed standing, they slowly form gel due to cross-linking.
- Their storage in the absence of air does not cause any change in their elastic properties. However, in the presence of moisture, the polymer becomes brittle due to the formation of oxygen bridges between chains.

Properties of polydimethoxy phosphazines and polydiethoxyphosphazine:

- They are colourless, odourless, transparent and film-forming thermoplastics.
- On heating above 100°C , they slowly form cyclic polymers, $[-\text{P}(\text{OR})_2\text{N}-]_3$ or $[-\text{P}(\text{OR})_2\text{N}-]_4$, where $\text{R} = \text{CH}_3$ or C_2H_5

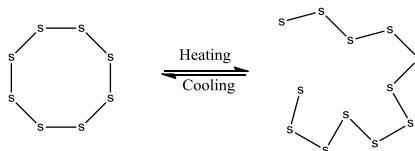


2. Sulphur Based Inorganic Polymer

Sulphur based polymers are classified as following:

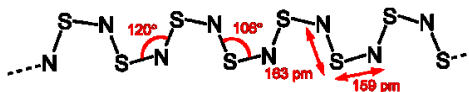
a. Linear chain polymer

i. Polymeric Sulphur (PS): It is prepared by heating rhombic sulphur at 165°C to 168°C following by quenching the molten mass on ice bath. The reaction mixture is washed with carbon disulphide (CS_2) to remove excess of S_8 .

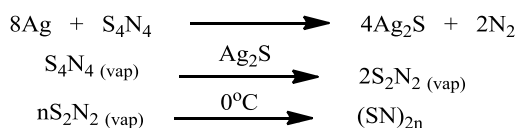


ii. Polymeric Sulphur nitride (SN)_n

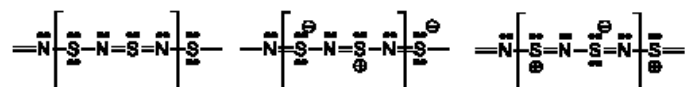
Polythiazyl also known as polymeric sulfur nitride (SN)_n is an electrically conductive gold coloured polymer with metallic luster. It was first discovered around 1910 as the first conductive inorganic polymer.



Polythiazyl is synthesized by the polymerization of the disulfur dinitride (S_2N_2 ; a dimer), which is synthesized from the cyclic alternating tetrasulfur tetranitride (S_4N_4 ; a tetramer) in the presence of hot silver wool as catalyst.



Several resonance structures can be written:

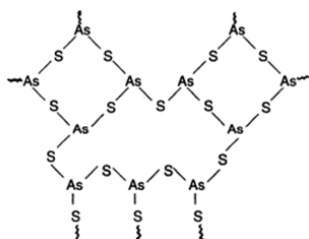


Properties: Its electrical conductivity at room temperature is about $1200 \text{ to } 3700 \Omega^{-1}\text{cm}^{-1}$, which increases 50 - 200 times on lowering the temperature to 4.2 K. At 0.26 K it becomes a superconductor. This is the first discovered non-metallic superconductor.

Uses: Due to its electrical conductivity, polythiazyl is used in LEDs, transistors, battery cathodes, and solar cells.

Chalcogenide Glass

The chalcogenide glasses form a family of amorphous cross linked polymers formed by compounds of chalcogens (ore forming: sulphur, selenium and tellurium) with one or more of polyvalent elements such as arsenic, antimony, bismuth, indium, germanium, phosphorus, tin and thallium. The best known chalcogenide glass is $(As_2S_3)_n$



Chalcogenide glasses are prepared by melt-quenching or passing the chalcogen compounds vapour over the polyvalent elements like arsenic, antimony, indium, germanium, phosphorus, tin and thallium.

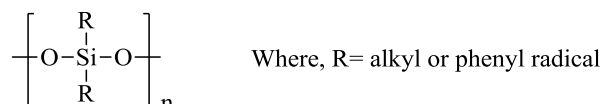
Properties:

- They resemble organic polymers as well as glasses. However, they possess lower softening point, tensile strength and higher refractive indices than borosilicates glasses.
- They are fairly stable to acids, but are attacked by concentrated alkalis.
- They oxidize in air at about 3000°C . Therefore, these polymers can be distilled in vacuum without any decomposition.
- They are deeply coloured and most of them transmit infrared radiations
- Their conductivity changes reversibly from low to high value under applied voltage. This phenomenon is known as switching.

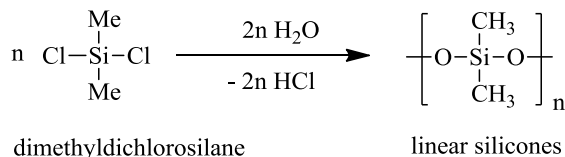
Uses: They are widely used in rewritable optical disks and phase-change memory devices. They are used in infrared detectors, mouldable infrared optics such as lenses, and infrared optical fibers.

3. Silicones

Silicones are inorganic polymers consisting of Si-O bonds in the skeleton. They have a wide variety of commercial uses as fluids, oils, elastomers (rubbers), and resin. They are now produced on a larger scale than any other group of organometallic compounds. Silicones are fairly expensive but have many desirable properties.

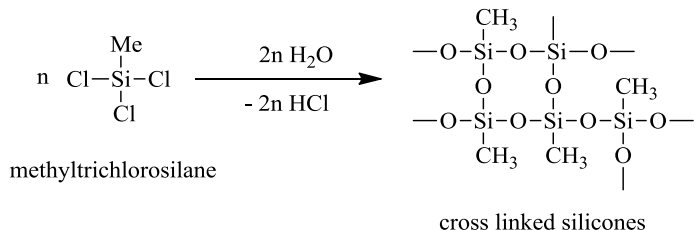


Linear silicones are prepared by the hydrolysis of bifunctional dimethyldichlorosilane $(\text{CH}_3)_2\text{SiCl}_2$ as following:



If some $(\text{CH}_3)_3\text{SiCl}$ (trimethylchlorosilane) is mixed with $(\text{CH}_3)_2\text{SiCl}_2$ and hydrolyzed, the $(\text{CH}_3)_3\text{SiCl}$ will block the end of the straight chain produced by $(\text{CH}_3)_2\text{SiCl}_2$. Therefore, the ratio of $(\text{CH}_3)_2\text{SiCl}_2$ and $(\text{CH}_3)_3\text{SiCl}$ in the reaction mixture will determine the average chain size (chain length).

Extensively crosslinked silicones can be prepared by the hydrolysis of methyltrichlorosilane as following:



Similarly, the ratio of methyltrichlorosilane and dimethyldichlorosilane taken in the reaction mixture determines the extent of cross linking in silicones.

Properties:

- i. Depending on the proportion of various alkyl silicon halides used during the preparation, silicones may be liquid, viscous liquids, semi-solid (grease), rubber and solids.
- ii. Because of the oxygen-silicon bonds (bond dissociation energy = 502kJmol^{-1}), they exhibit outstanding stability at high temperature.
- iii. Because of the presence of alkyl groups surrounding the silicon atoms makes the molecule hydrophobic and gives water repelling tendency of silicones.
- iv. Their physical properties are less affected by the change of temperatures.
- v. They are non-toxic.

Uses:

- i. Straight chain polymers upto 500 units are silicones fluids. They are used as water repellent for treating buildings, glassware and fabrics. They are also included in car and shoe polish. Silicones fluids are non toxic and have low surface tension; therefore, addition of a few parts per million of it greatly reduces foaming in sewage disposal, textile dyeing, beer making and frothing of cooking oil in making potato crisps and chips. Silicone oils are used as dielectric insulating material in high voltage transformers. They are also used in hydraulics fluids.
- ii. Silicone greases are made by mixing silicones oil with lithium stearate soaps and are used as lubricants where high and low temperatures are encountered.
- iii. Silicones rubbers are obtained by mixing long chain silicones with filler like silicon dioxide in the presence of curing agent like peroxide. Rubber has 6000 to 600000 Si units. Silicon rubber is useful because they retain their elasticity from -90°C to $+250^\circ\text{C}$, which is much wider range as compared to natural rubber. They are used in making tyres of aircraft and racing cars, as sealing material in search lights and aircraft engines, in making lubricants, paints and protective coatings. For making boots for the use at very low temperature (Neil Armstrong used silicones rubber boots while walking on the moon).
- iv. Silicones resins are highly cross-linked silicones. They are used in making high voltage insulator, making printed circuit boards and to encapsulate integrated circuits chips and resistors. They are also used as non-stick coatings for pans, moulds for making car tyres etc.

