Polymer Chemistry

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SYLLABUS

Polymers and its Applications (4 hrs)

1. Polymers

- Addition, condensation and copolymerization
- Preparation, properties and uses of PVC, Teflon, Silicone Rubber and Neoprene

2. Concept of conducting, & non-conducting, biodegradable & non-biodegradable polymers, examples and their applications

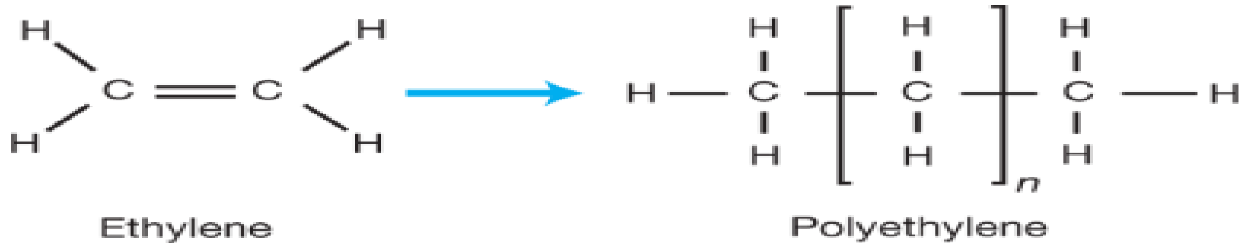
Questions which were asked in board exam

1. What are polymers? Discuss about the mechanism of condensation polymerization taking a suitable example.
2. What is the IUPAC name for a monomer of Teflon? Show the free radical addition mechanism for the preparation of Teflon?
3. Write the preparation, properties and uses of i. Teflon, ii. Polyester and PVC.
4. What is condensation polymerization?
5. Write short notes on silicones.
6. Write the preparation, properties and uses of Teflon and polyvinyl chloride.
7. Write notes on Teflon.

10. Describe the mechanism of condensation and addition polymerization reaction.
11. What is polymerization reaction? Write the different types of polymerization with suitable examples for each Write short notes on – PVC
12. Explain the procedures involved in the preparation of rubber.
13. Explain addition polymerization. How it differs from condensation polymerization?

Introduction

Polymers are compounds of very high molecular weights formed by the combination of a large number of small repeating units. The process by which the simple molecules (monomers) are converted into polymers is called polymerisation. For example, many ethylene molecules combine to form a giant molecule of polythene.



where n = number of monomers in the polymeric chain.

The number of repeating units in a polymeric chain is called 'degree of polymerisation'. In the above example, 'n' is the degree of polymerisation.

Polymers are also called *macromolecules* because of their big size. In fact, the terms polymers and macromolecules are often used synonymously. However, strictly speaking, a polymer contains repeating units (monomers), whereas a macromolecule is a giant molecule that may or may not contain monomer units. For example, chlorophyll and haemoglobin are macromolecules but not polymers.

On the basis of origin On the basis of origin, polymers are of two types:

(a) Natural polymers (b) Synthetic polymers

(a) Natural polymers They are polymers that occur in nature. For example, Examples: Proteins, Nucleic acids, Starch, Cellulose and Natural rubber.

(b) Synthetic polymer It is a polymer that is prepared artificially in the laboratory. For example, polyethylene (PE), polyvinylchloride (PVC), nylon, terylene, bakelite, synthetic rubber, etc.

Mechanism of Polymerisation

There are two types of polymerisation processes:

1. Addition polymerisation or chain polymerisation
2. Condensation polymerisation

Addition Polymerization or Chain Growth Polymerization:

Addition polymerization involves successive addition of monomer units to the growing chain carrying a reactive intermediate such as a free radical, a carbocation or a carbanion.

This type of polymerization is **also called chain growth polymerization** because it takes place in stages leading to increase in chain length and each stage produces a reactive intermediate for use in the next stage of growth of the chain. Depending upon the nature of the reactive species involved, addition polymerization occurs by the following three mechanisms:

(i) Free radical addition polymerization.

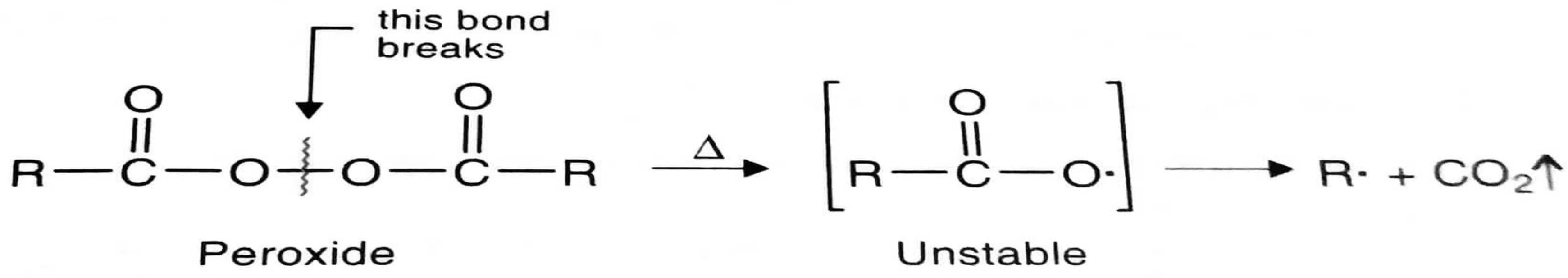
(ii) Cationic polymerization.

(iii) Anionic polymerization.

Free radical addition polymerization:

Free- radical polymerisation is catalysed by organic peroxides or other reagents which decompose to give free radicals. Following steps are involved:

1. **Chain initiation:** Organic peroxides undergo homolytic fission to form free radicals.



2. Chain Propagation: Free radical produced in the above step adds to an alkene molecule to form a new free radical.

$$R\cdot + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}\dot{C}H_2$$

This free radical can attack another alkene molecule and so on.

$$RCH_2\dot{C}H_2 + CH_2{=}CH_2 \longrightarrow RCH_2CH_2CH_2\dot{C}H_2$$

$$RCH_2\dot{C}H_2 + n\,CH_2{=}CH_2 \longrightarrow R(CH_2CH_2)_nCH_2\dot{C}H_2$$

This process is repeated over and over. Hundreds and even thousand of alkene monomers can add one at a time to the growing chain.

(3) **Chain Termination.** The above chain reaction can come to a halt in two ways :

(*a*) **Chain Combination.** Two chains can combine at their propagating sites.

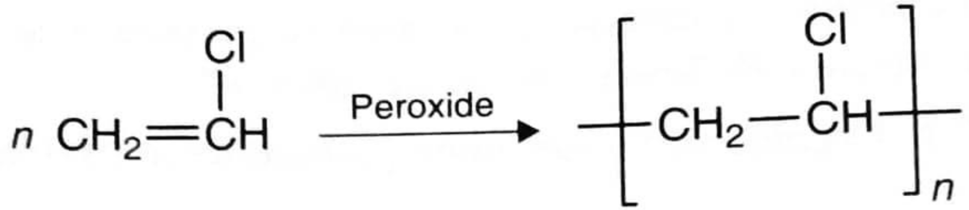
$$2\ R(CH_2CH_2)_nCH_2\dot{C}H_2 \longrightarrow 2\ R(CH_2CH_2)_nCH_2CH_2 : CH_2CH_2(CH_2CH_2)_nR$$

Polyethylene (Polymer)

(*b*) **Disproportionation**. Two chains undergo disproportionation, with one chain being oxidized to an alkene and the other being reduced to an alkane as a result of hydrogen atom transfer.

$$2\ R(CH_2CH_2)_nCH_2\dot{C}H_2 \longrightarrow \underset{\text{Polyethylene (Polymer)}}{2\ R(CH_2CH_2)_nCH{=}CH_2} + \underset{\text{Polyethylene (Polymer)}}{R(CH_2CH_2)_nCH_2CH_3}$$

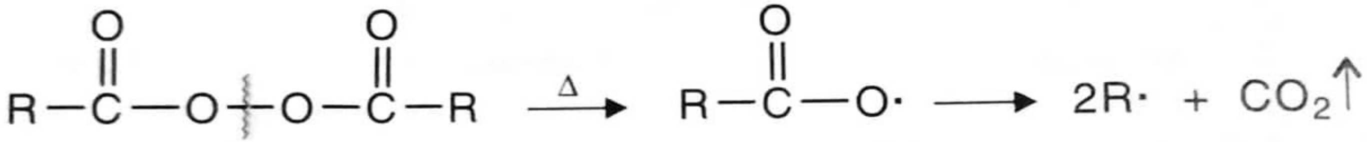
FREE-RADICAL POLYMERIZATION OF VINYL CHLORIDE



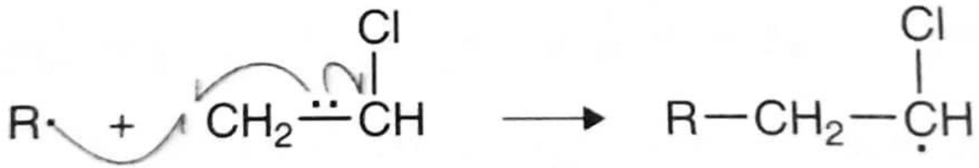
Vinyl chloride   Poly(vinyl chloride)

MECHANISM. Following steps are involved :

(1) **Chain Initiation**. Organic peroxides decompose to form free radicals.

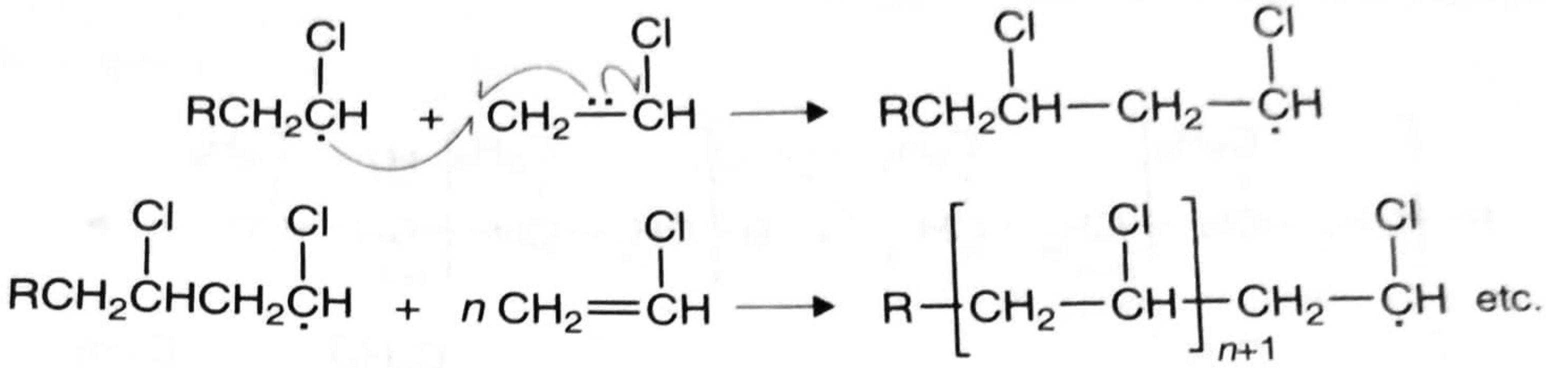


(2) **Chain Propagation.** Free-radical produced in the above step adds to vinyl chloride molecule to form a new free radical.

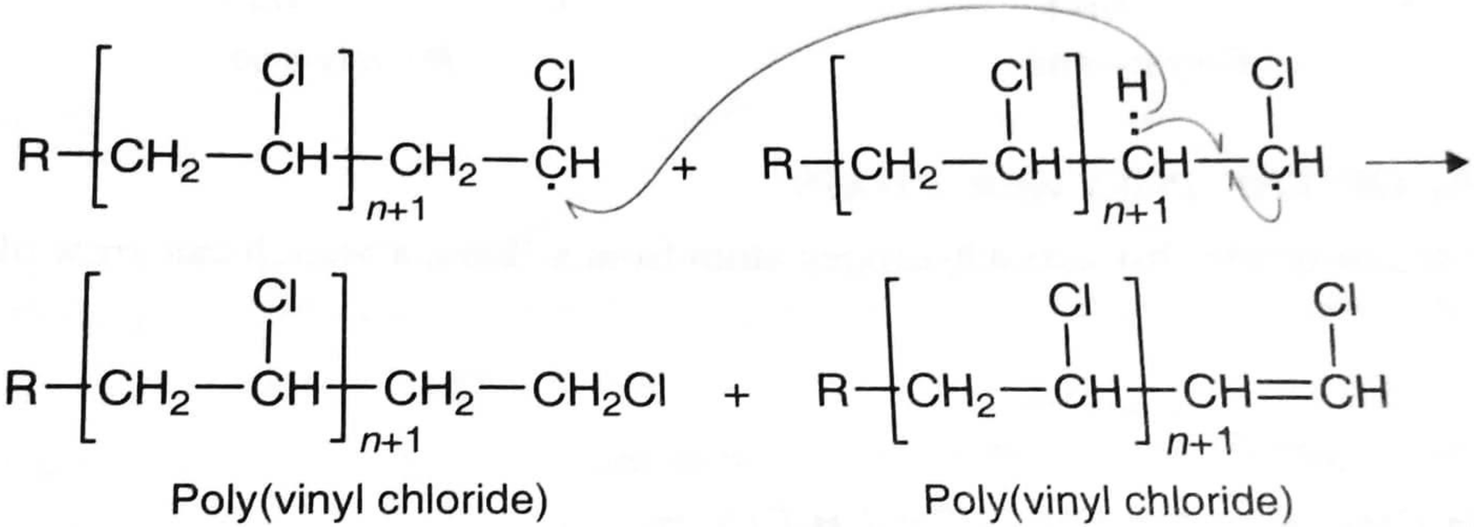


Vinyl chloride

This free radical can attack another molecule and so on.



(3) **Chain Termination**. The chain reaction can be interrupted when the free radicals combine or by disproportionation.



Condensation Polymerization

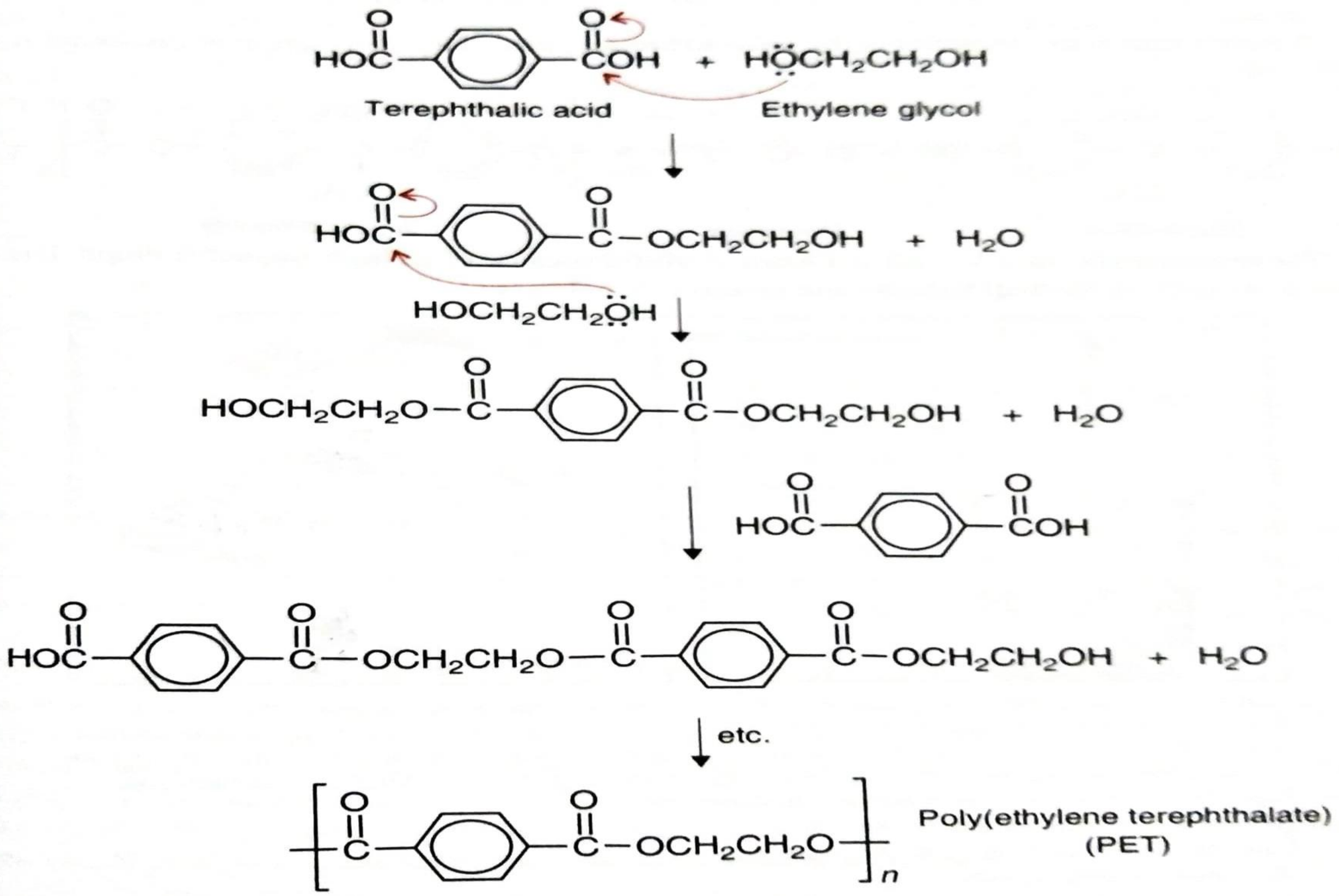
It is a form of a step-growth polymerization where smaller molecules or monomers react with each other to form larger structural units (usually polymers) while releasing by products such as water or methanol molecule. The by products are normally referred to as condensate.

Mechanism:

Polysters:

The polyester is formed from the reaction of terephthalic acid (a diacid) with ethylene glycol (a diol). First, one carboxylic acid group of a diacid molecule and one hydroxyl group of a diol molecule combine to form an ester, with the loss of water.

Then a second diol molecule reacts with the unreacted carboxylic group on the other end of the diacid molecule, or a second diacid molecule reacts with the unreacted hydroxyl group of the diol. Continuation of this process adds a new monomer unit at each step, ultimately producing a polymer. The resulting polyester is called poly(ethylene terephthalate), or PET.

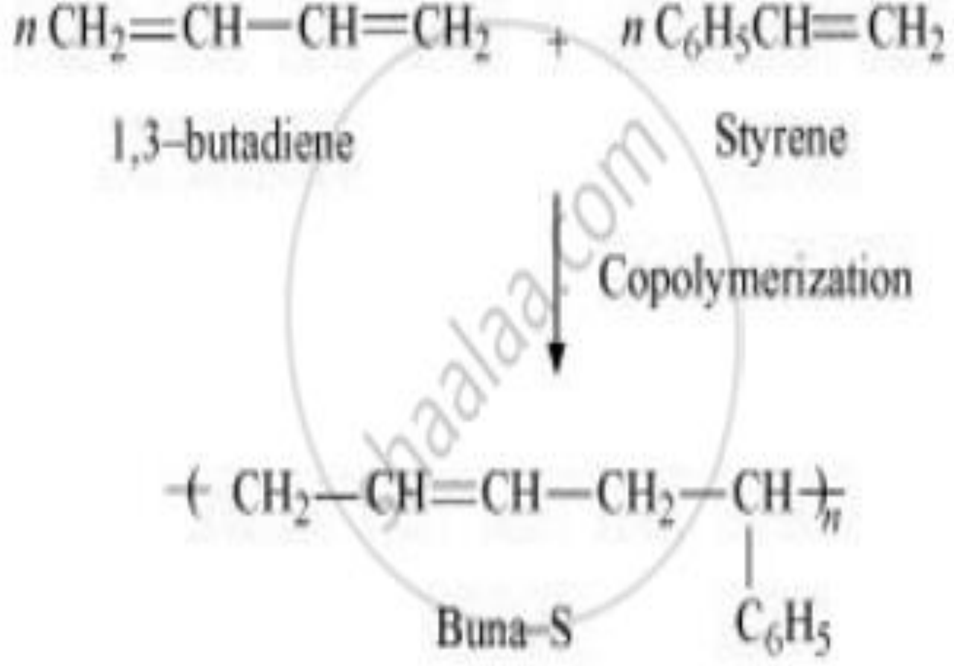

Terephthalic acid
Ethylene glycol
etc.
Poly(ethylene terephthalate)
(PET)

Addition Polymerization	Condensation Polymerization
The polymerization process in which polymers are formed by the addition reaction is called addition polymerization.	The polymerization process in which polymers are formed by the condensation reaction is called condensation polymerization.
Monomers must have either a double bond or triple bond.	Monomers must have two similar or different functional groups.
It results in no by-products.	It results in by-products such as ammonia, water and HCl.
The addition of monomers results in the formation of the polymer.	The condensation reaction between monomers results in the formation of the polymer.
The molecular weight of the resultant polymers is a multiple of the monomer's molecular weight.	The molecular weight of the resultant polymer is not a multiple of the monomer's molecular weight.
Common examples of addition polymerization are PVC, Polyethene, Teflon etc.	Common examples of condensation polymerization are Nylon, Bakelite, Silicon, etc.

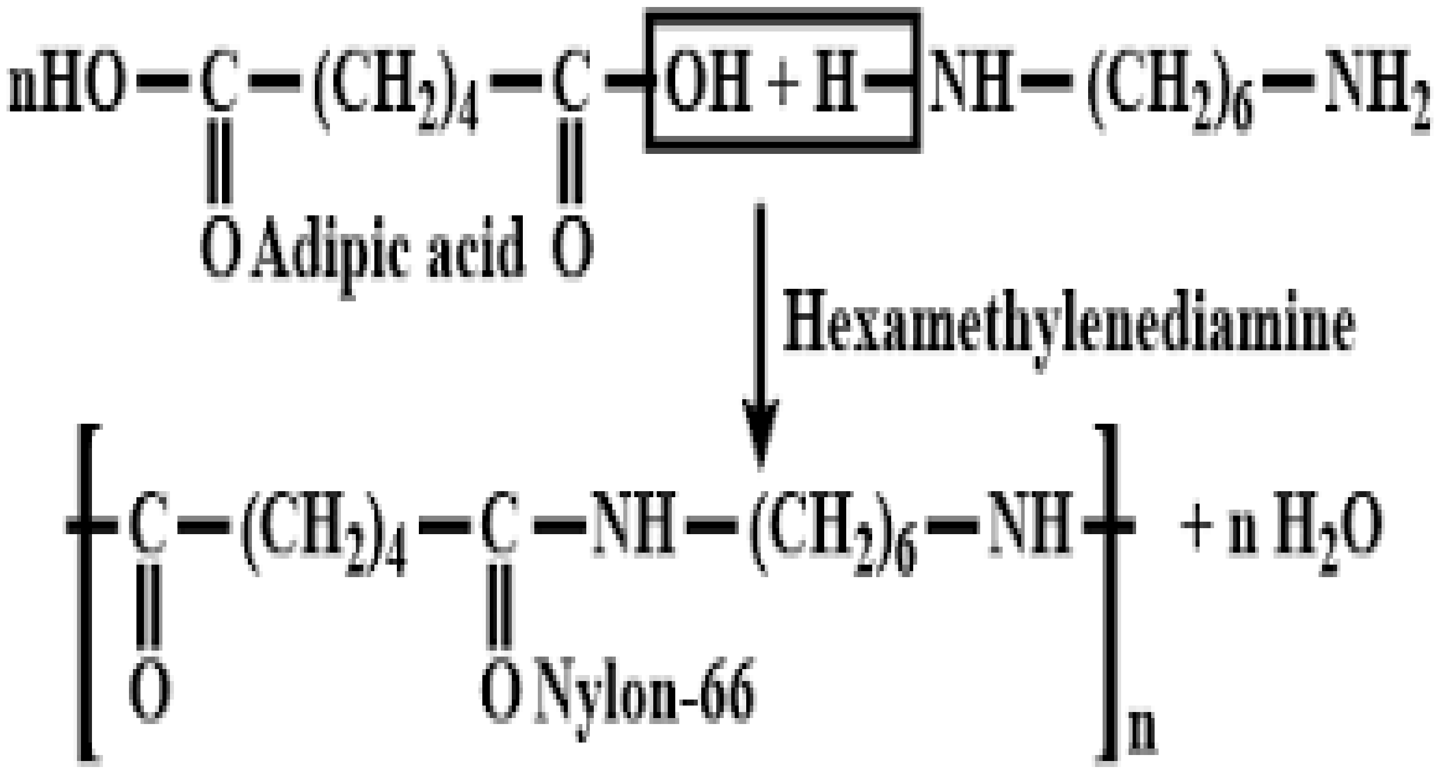
Copolymerization:

- Copolymerization is a process in which two or more different monomers are combined to form a polymer chain. It is a type of polymerization that involves the simultaneous polymerization of multiple monomers.
- During copolymerization, the monomers undergo a chemical reaction, usually through the use of a catalyst or initiator, resulting in the formation of a copolymer. The resulting copolymer contains repeating units from each of the monomers used in the reaction.

Example of copolymerization:



Nylon-6,6

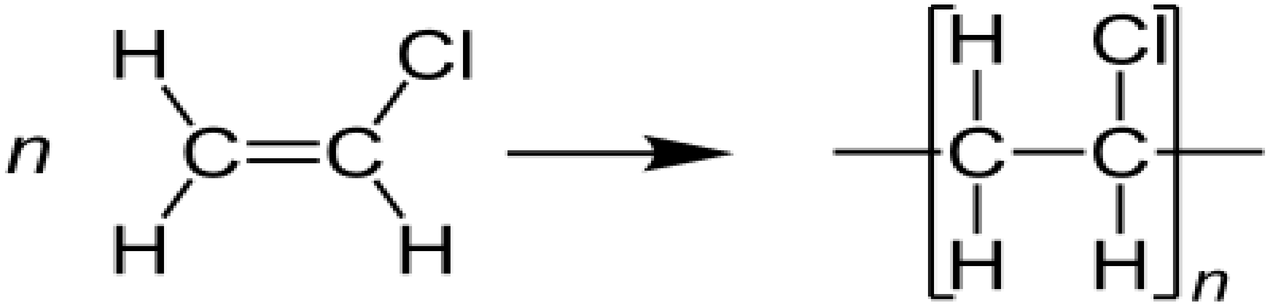

nHO—C—(CH2)4—C—OH + H—NH—(CH2)6—NH2
O Adipic acid O
Hexamethylenediamine
C—(CH2)4—C—NH—(CH2)6—NH
O
O Nylon-66
n
+ n H2O

Preparation of some addition polymers

P.V.C.

Preparation

It is prepared by adding vinyl chloride monomer under high temperature and pressure.



Properties of PVC:

- **Chemical Resistance:** PVC exhibits excellent resistance to many chemicals, including acids, bases, salts, and alcohols. This property makes it useful in applications where exposure to corrosive substances is expected.
- **Durability:** PVC is a durable material with good mechanical strength. It is resistant to impact, weathering, and abrasion, making it suitable for outdoor applications.
- **Flame Resistance:** PVC has inherent flame-retardant properties, which means it is difficult to ignite and self-extinguishes when the source of the flame is removed. This property makes PVC widely used in construction and electrical applications.
- **Electrical Insulation:** PVC is an excellent electrical insulator, making it suitable for insulation on wires and cables. It can withstand a range of temperatures and voltages.

PVC is one of the most widely used polymers globally and finds applications in various industries. Some common uses of PVC include:

1. **Construction:** PVC is extensively used in the construction industry for pipes, fittings, window frames, flooring, roofing membranes, and insulation materials.
2. **Electrical and Electronics:** PVC is used for insulation on wires and cables, as well as in electrical conduits, switch boxes, and connectors.
3. **Automotive:** PVC is used in automotive applications such as dashboards, door panels, seat covers, and wiring insulation.
4. **Packaging:** PVC is used for blister packaging, shrink wrap, and flexible films for food and non-food products.
5. **Healthcare:** PVC is utilized in medical applications such as IV bags, tubing, blood bags, and medical device components.
6. **Consumer Goods:** PVC is used in various consumer products like footwear, inflatable toys, rainwear, and furniture upholstery.
7. **Signage and Graphics:** PVC sheets are commonly used for signs, displays, and printing applications.

Teflon

Preparation

It is prepared by adding number of tetra-floro-ethene monomers using ferrous sulphate ($FeSO_4$) and (H_2O_2) as catalyst at high pressure and controlled temperature.

$$\underset{\text{Tetrafluoroethene}}{n\,CF_2=CF_2} \xrightarrow[\text{High pressure}]{\text{Catalyst}} \underset{\text{Teflon}}{-\!\!\left[CF_2-CF_2\right]_n\!\!-}$$

Properties of Teflon:

1. **Nonstick:** Teflon has an extremely low coefficient of friction, making it highly nonstick. It is resistant to sticking of substances, which allows easy release of food or other materials from cooking surfaces or molds.
2. **Heat Resistance**: Teflon has excellent thermal stability and can withstand high temperatures without significant degradation. It has a melting point of around 327 °C (621 °F) and can withstand continuous use at elevated temperatures.
3. **Chemical Resistance:** Teflon is highly resistant to chemicals and has excellent chemical inertness. It is unaffected by most acids, bases, organic solvents, and other corrosive substances.
4. **Low Friction and Lubricity:** Teflon has a very low coefficient of friction, resulting in low frictional resistance and excellent lubrication properties. It is often used as a dry lubricant or as an additive in lubricating materials.
5. **Electrical Insulation:** Teflon is an excellent electrical insulator, even at high frequencies. It has high dielectric strength and low dielectric loss, making it suitable for insulation in electrical components and wiring.

Uses of Teflon:

1. **Nonstick Cookware:** Teflon coatings are used on cookware such as frying pans and baking sheets to provide a nonstick surface.
2. **Industrial Applications:** Teflon is used in industrial applications where chemical resistance, high temperature resistance, or low friction properties are required. It is used in gaskets, seals, bearings, valves, and linings for chemical processing equipment.
3. **Electrical and Electronics**: Teflon is used in electrical insulation, wiring, and cable applications due to its excellent electrical properties.
4. **Automotive:** Teflon is used in various automotive applications, including fuel hoses, seals, gaskets, and coatings for parts exposed to high temperatures or corrosive fluids.
5. **Medical Applications:** Teflon is used in medical devices and implants due to its biocompatibility and low friction properties.
6. **Coatings and Films:** Teflon coatings and films are used for corrosion resistance, nonstick surfaces, and low-friction applications.
7. **Printing and Packaging:** Teflon is used in printing applications to reduce friction and improve ink flow. It is also used in packaging materials to provide a nonstick surface for easy release.

Silicone (Polymer)

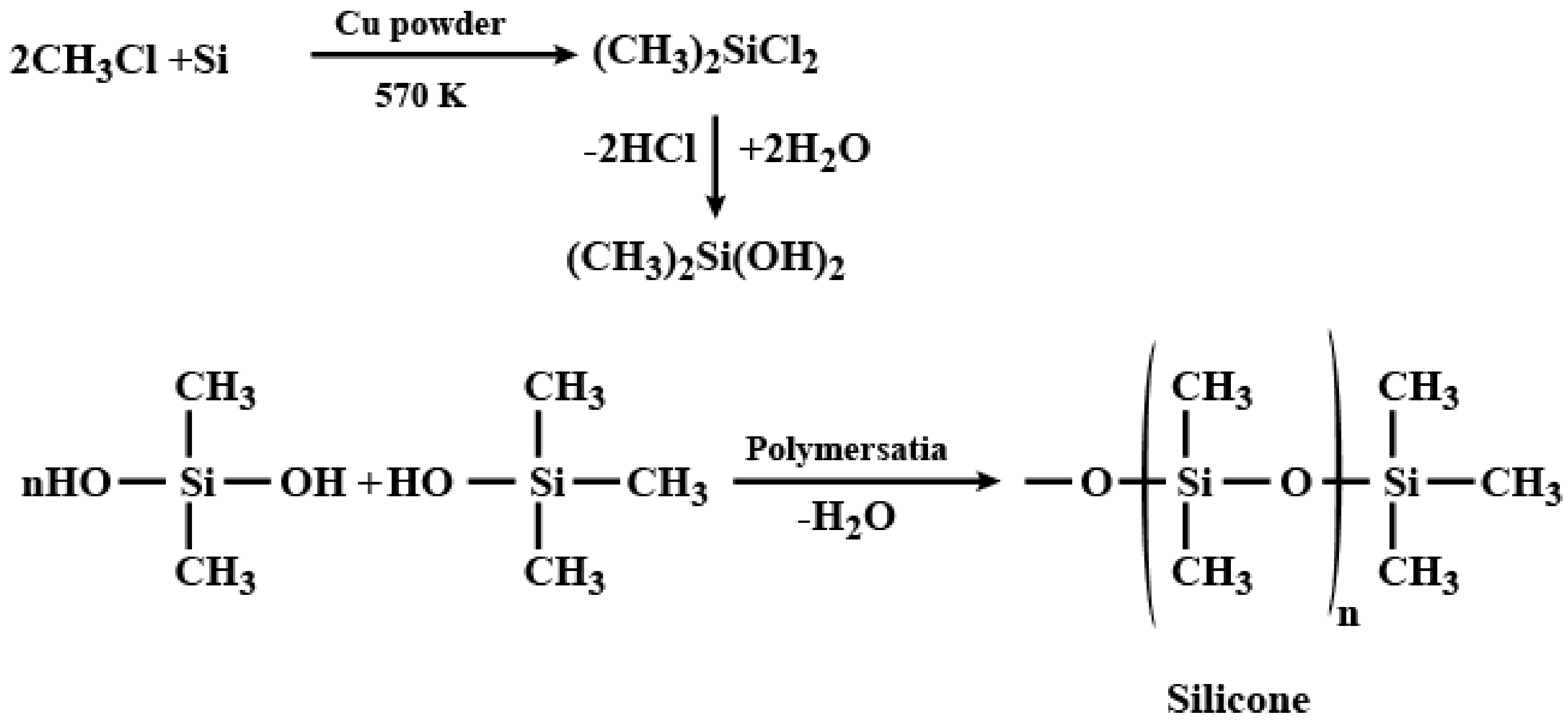
It was first produced by F.S Kipping. Silicone rubber is made from silicone, a synthetic polymer composed of silicon, oxygen, carbon, and hydrogen atoms

Preparation:

Generally silicones are prepared by the hydrolysis of dialkyldichlorosilanes (R_2SiCl_2) or diaryldichlorosilanes Ar_2SiCl_2, which are prepared by passing vapours of RCl or ArCl over silicon at 570 K with copper as a catalyst.

$$2RCl + Si \xrightarrow{Cu\,/\,570\,K} R_2SiCl_2$$

The hydrolysis of dialkylchloro silanes R_2SiCl_2 yields to a straight chain polymer which grown from both the sides.



Properties:

a. They range from oily liquids to rubber like solids.

b. All silicones are water repellent. This property arises due to the presence of organic side groups that surrounds the silicon which makes the molecule looks like an alkane.

c. They are thermal and electrical insulators. Chemically they are inert.

d. Lower silicones are oily liquids whereas higher silicones with long chain structure are waxy solids.

e. The viscosity of silicon oil remains constant and doesn’t change with temperature and they don't thicken during winter

Uses:

a. Silicones are used for low temperature lubrication and in vacuum pumps, high temperature oil baths etc.

b. They are used for making water proofing clothes

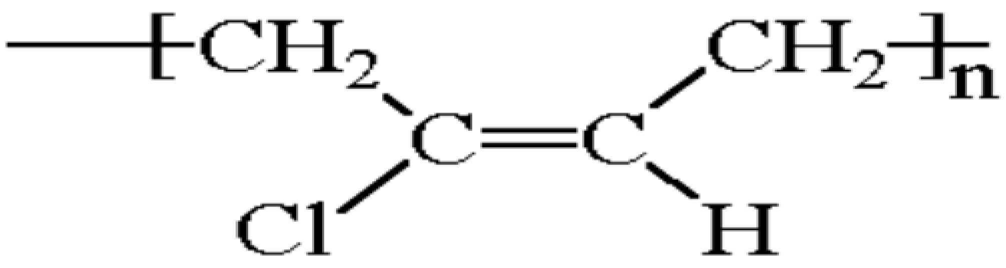
c. They are used as insulting material in electrical motor and other appliances

d. They are mixed with paints and enamels to make them resistant towards high temperature, sunlight, dampness and chemicals.

Neoprene

Neoprene (also known as **polychloroprene**), is a synthetic rubber that is made by polymerization of chloroprene. It is harder and stronger than natural rubber and resistant to water.

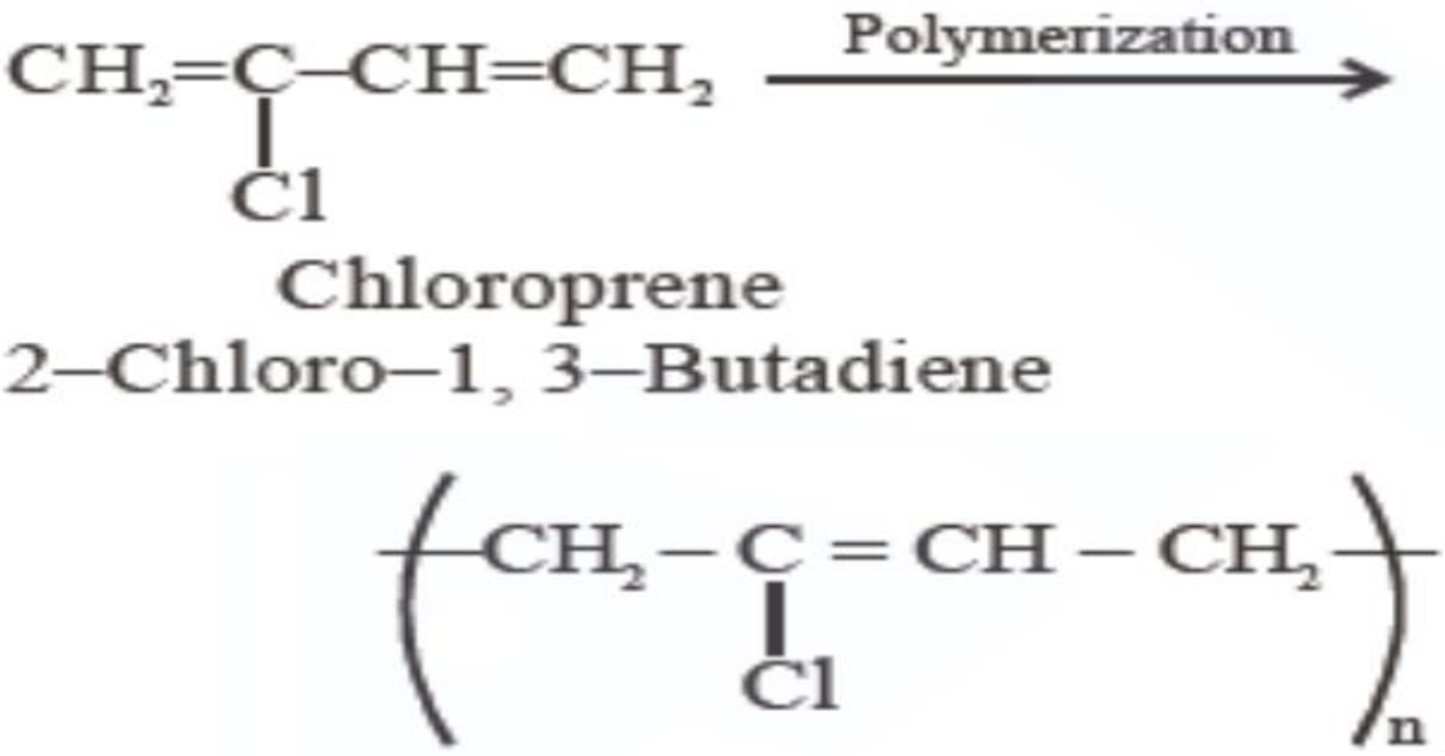
Structure of Neoprene



Preparation of Neoprene

It is prepared by polymerization of chloroprene in which it polymerizes very readily. The reaction occurs by **1,4-addition** of one chloroprene molecule to the other where no specific catalyst is needed but the polymerization is slower in absence of oxygen.

Preparation of Neoprene



Neoprene

Properties of Neoprene

- It has much more oil resistance than natural rubber. It is not oxidized by air.
- It has high tensile strength.
- It has acceptable chemical stability and maintains flexibility over a wide temperatures.
- It is resistant to sun, climate, and ozone determination.

Applications of Neoprene

- It is used as an insulator and for making belts and printing rollers.
- It is used in the manufacture of hoses, gaskets, shoe heels, stoppers, etc.
- During Covid-19, Neoprene is actively used to make face masks having **99.9 %** filtration efficiency.
- It is a popular material in making protective clothing for aqua activities like scuba diving, swimming, etc.