HIGH POLYMERS

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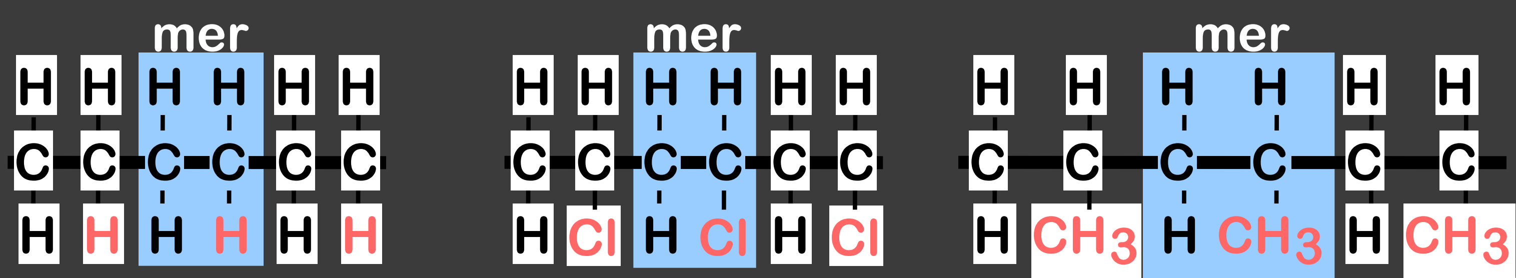
DEFINITION

The word *polymer* is derived from the two greek words

poly and *mers*

many *parts or units*

e.g.



Polyethylene (PE) Polyvinyl chloride (PVC) Polypropylene (PP)

Polymers are macro molecules formed by linking smaller molecules repeatedly, called *monomers*.

Examples:

Polyethylene is formed by linking a large number of ethylene molecules

Ethylene

polyethylene

polystyrene is formed by linking styrene molecules

styrene

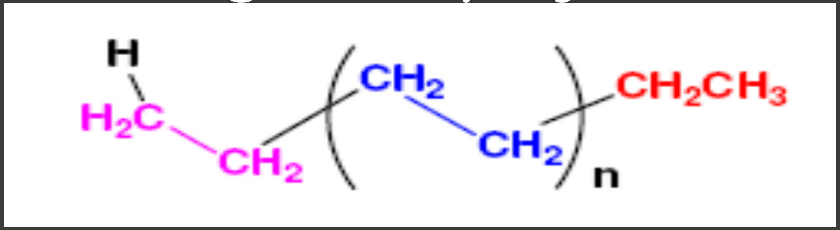
polystyrene

Classification of Polymers

Polymers can be classified in several ways, based on

- origin
- Structure
- methods of formation
- response to heat
- properties (or applications)

The number of repeating units (n) in the chain is known as the degree of polymerization.



Polymers with high degree of polymerization are called high polymers and these have very high molecular weights (10^4 to 10^6).

Polymers with low degree of polymerization are called Oligomers.

Based on the origin

Polymers can be classified as:

- ✓Natural polymers
- ✓synthetic polymers

Natural polymers are those which are obtained naturally
e.g., Cellulose, Silk, Starch, RNA, DNA, Proteins etc.,

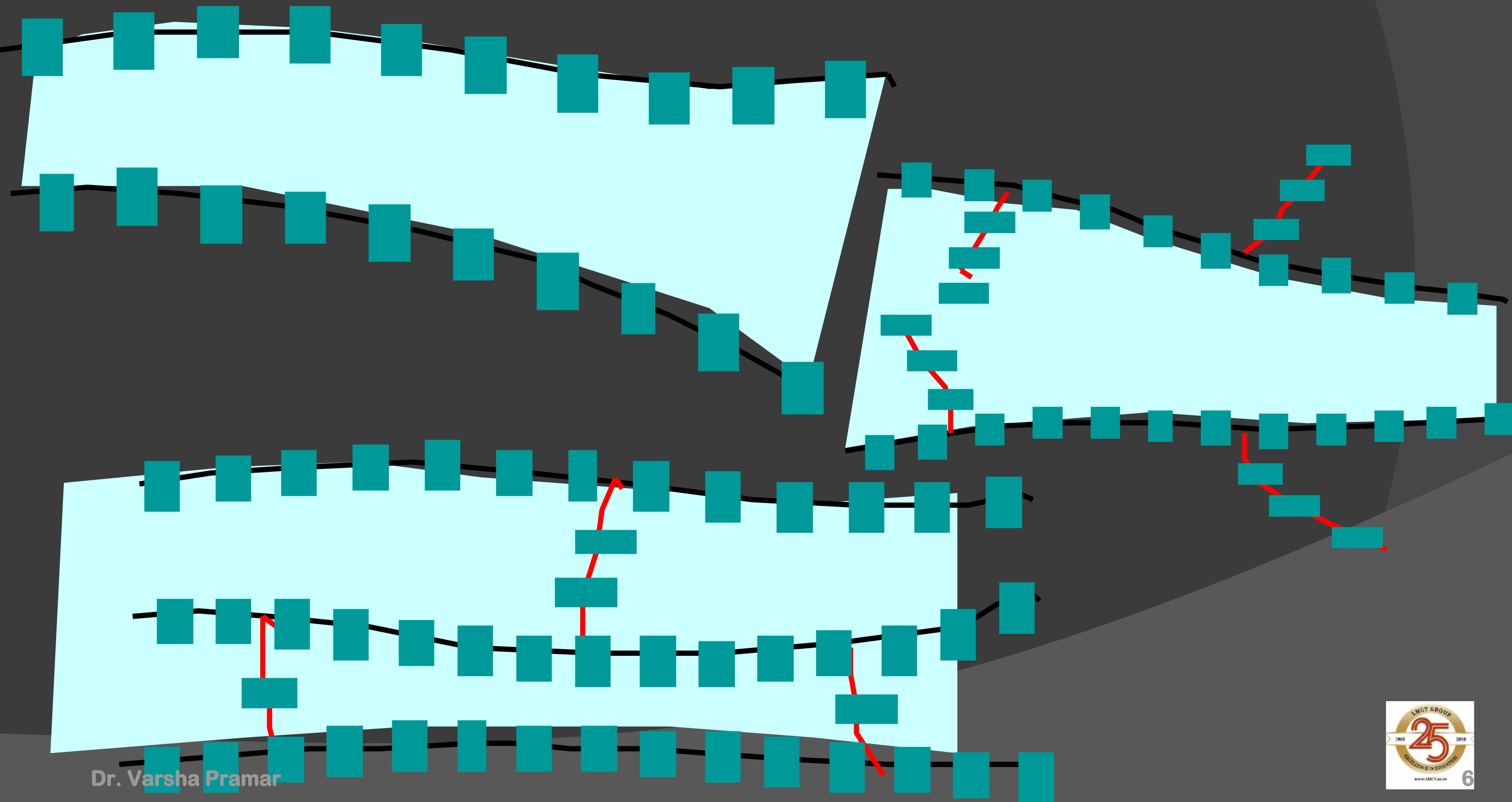
Synthetic polymers are those which are made by man
e.g., polyethylene, polystyrene, PVC, polyester, etc.,

semi-synthetic polymers which are chemically modified natural polymers
e.g., cellulose acetate, cellulose nitrate, halogenated rubbers etc.,

Based on the molecular structure

Polymers can be classified as:

- Linear
- Branched
- Cross-linked



Based on the method of formation

- Addition polymers
- Condensation polymers

Addition polymers are formed by self-addition of monomers The molecular mass of a polymer is an integral multiple of the molecular mass of a monomer

Condensation polymers are formed by condensation reaction

i.e., reaction between two or more monomer molecules with the elimination of simple molecules like water, ammonia, HCl etc.,

Based on the response to heat

- Thermo softening
- Thermosetting

Thermosoftening or thermoplastics

Soften on heating and can be converted into any shape and can retain its shape on cooling

Thermosetting polymers

Under go chemical change on heating and convert themselves into an infusible mass

Based on the properties or applications

- Plastics
- Elastomers
- Fibers
- Resins

Plastics

The polymers, which are soft enough at some temperature to be moulded into a desired shape and hardened on cooling so that they can retain that shape.

e.g., polystyrene, polyvinylchloride, polymethylmethacrylate etc.,

Elastomers

The polymers in which the structural units are either zig-zag or in helical chains. They undergo elastic changes when subjected to an external force but readily regain their original shape when the force is withdrawn.

e.g., natural rubber, synthetic rubbers, silicone rubbers etc.,

Fibers

In these polymers, the molecular chains are arranged parallel to each other in a spiral or helical pattern and the molecular length is at least 100 times its diameter.

e.g., nylons, terylene, etc.,

Resins

These polymers have a glossy appearance.

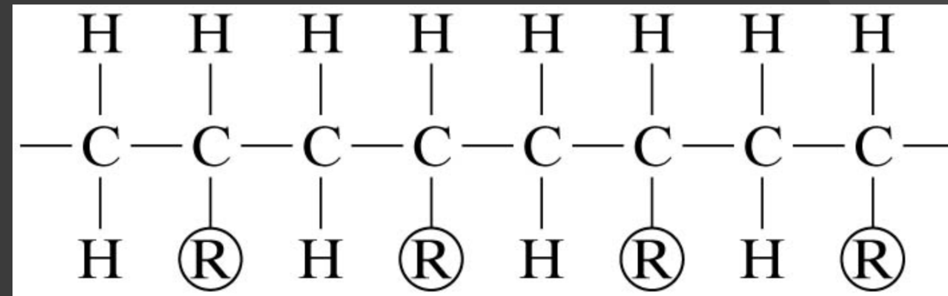
These constitutes the major essential part of the plastics.

These suffers the polymerization reactions and impart different properties to plastics.

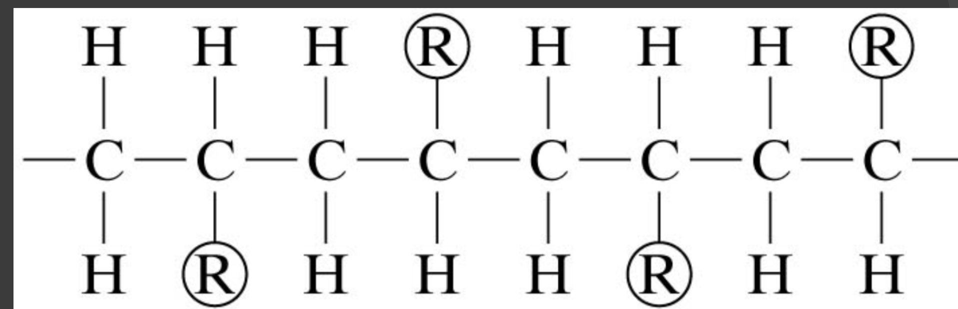
e.g., polysulphide sealants, epoxy adhesives, etc.,

Stereo regular polymers (or) Tacticity of Polymers

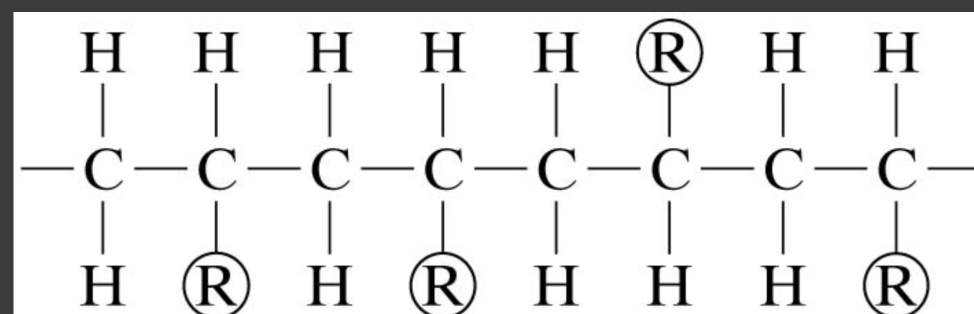
Isotactic
On one side



Syndiotactic
Alternating sides



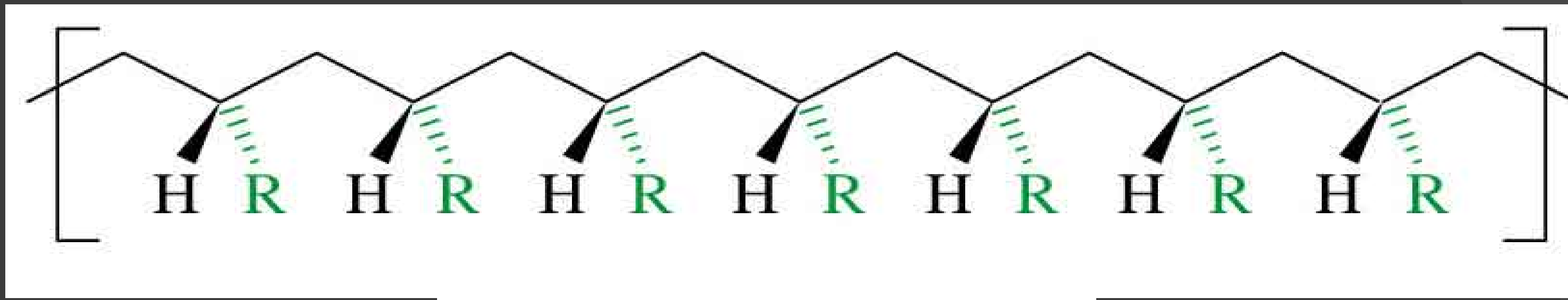
Atactic
Randomly placed



Conversion from one stereoisomerism to another is not possible by simple rotation about single chain bond; bonds must be severed first, then reformed!

An isotactic polymer

(side groups on the same side of the backbone)

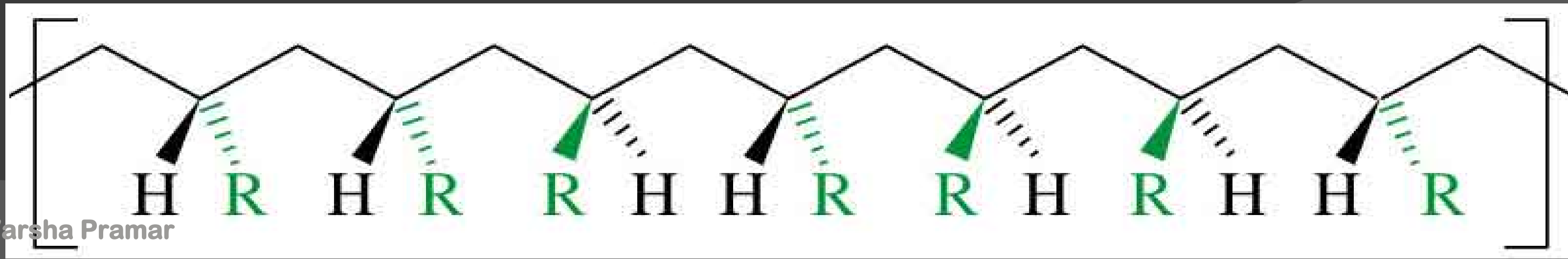


A syndiotactic polymer

(side groups on alternating sides of the backbone)

An atactic polymer

(side groups on random sides of the backbone)



Types of Polymerisation

Polymerisation occurs basically in two different modes.

- ✓ **Addition (chain growth) polymerization**
- ✓ **Condensation (step growth) polymerization**

✓ Addition

- monomers react through stages of initiation, propagation, and termination
- initiators such as free radicals, cations, anions opens the double bond of the monomer
- monomer becomes active and bonds with other such monomers
- rapid chain reaction propagates
- reaction is terminated by another free radical or another polymer

✓ Condensation

Two monomers react to establish a covalent bond,a small molecule, such as water, HCl, methanol or CO_2 is released. The reaction continues until one type reactant is used up

DISTINGUISHING FEATURES OF ADDITION AND CONDENSATION POLYMERISATION

ADDITION	CONDENSATION
Monomers undergo self addition to each other without loss of by products	Monomers undergo intermolecular condensation with continuous elimination of by products such as H_2O, NH_3, HCl, etc.,
It follows chain mechanism	It follows step mechanism
Unsaturated vinyl compounds undergo addition polymeristion	Monomers containing the functional groups (-OH, -COOH, $-NH_2$, ….) undergo this polymerization
Monomers are linked together through C – C covalent linkages	Covalent linkages are through their functional groups
High polymers are formed fast	The reaction is slow and the polymer molecular weight increases steadily throughout the reaction
Linear polymers are produced with or without branching	Linear or cross linked polymers are produced
e.g., polystryrene, plexiglass, PVC, etc.,	e.g., nylons, terylene, PF resins, etc.,

Free Radical Polymerization

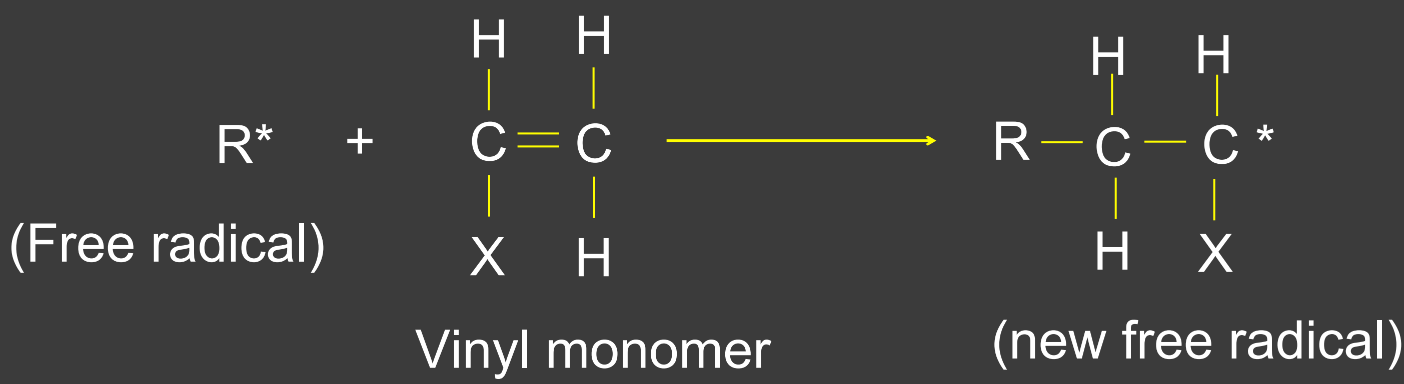
- Addition polymerization can be explained on the basis of free radical mechanism.

It involves three stages

- (i) Initiation
- (ii) Propagation
- (iii) termination

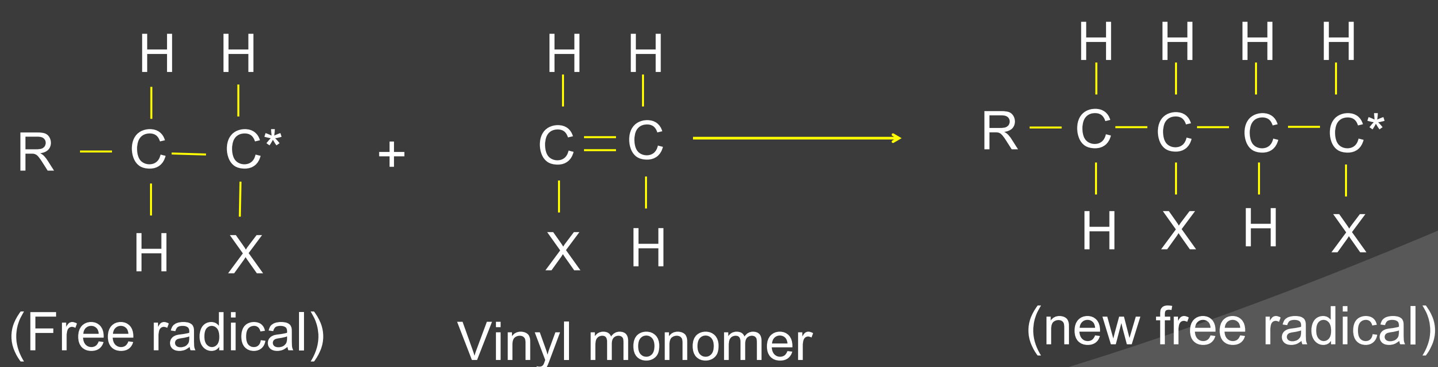
- Initiation

$$\underset{\text{(Initiator)}}{I} \xrightarrow[\text{u.v.light}]{\Delta \text{ or}} \underset{\text{(Free radical)}}{R^*}$$



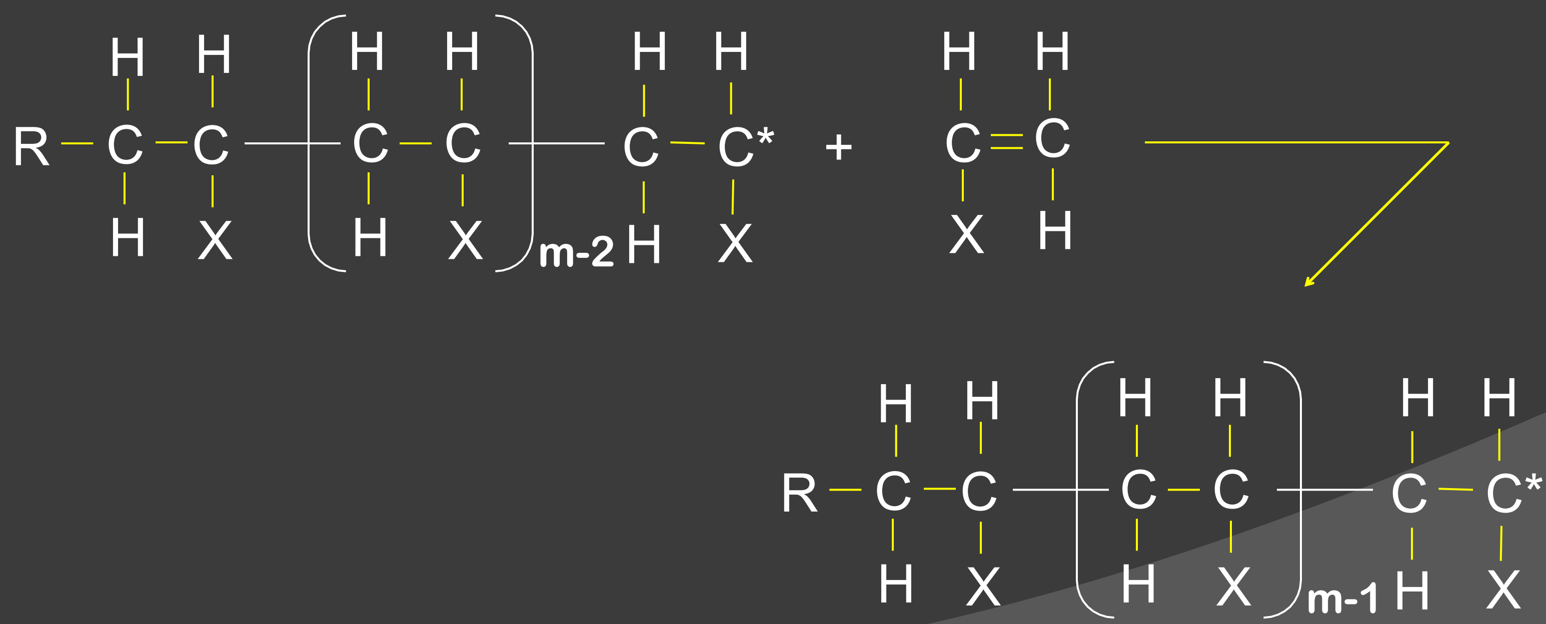
Propagation

The new free radicals attack monomer molecules further in quick succession leading to chain propagation



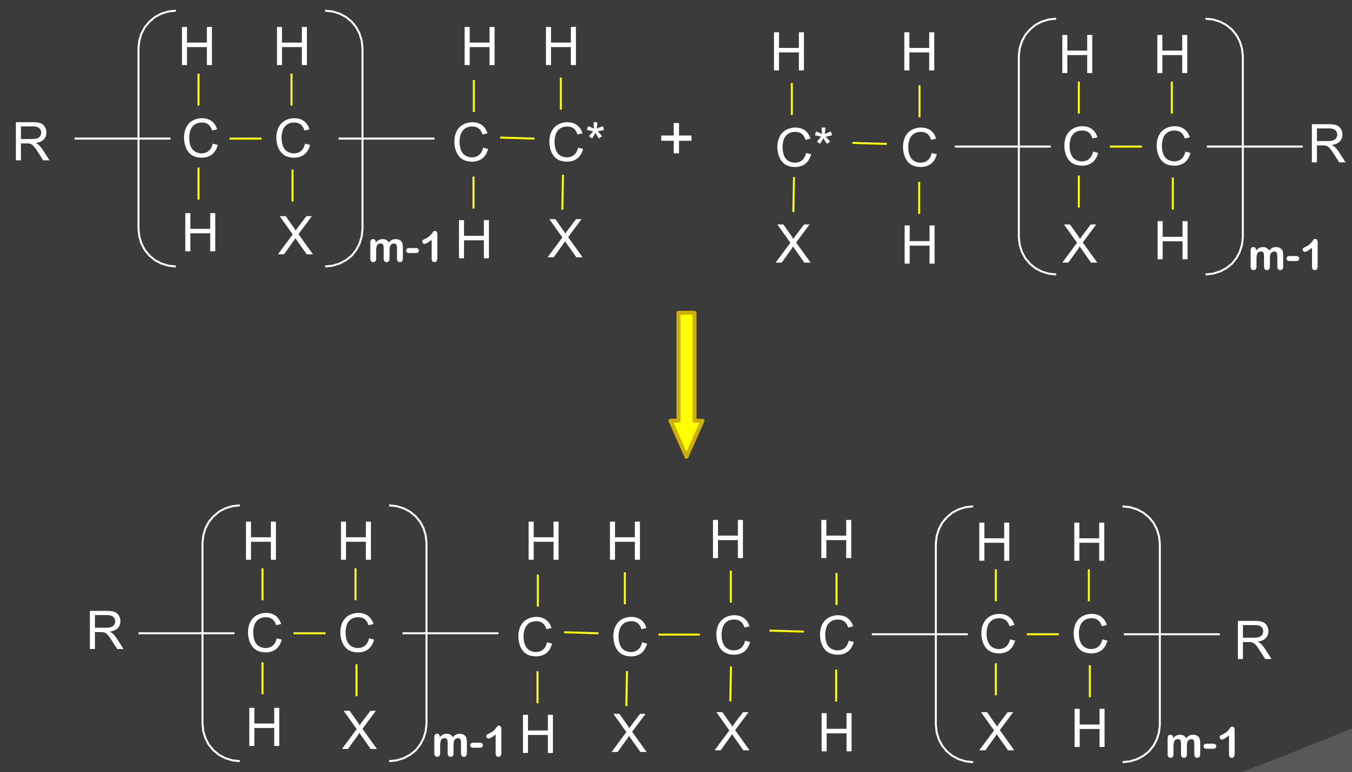
(new free radical) Vinyl monomer (another new free radical)

at *m*th stage,



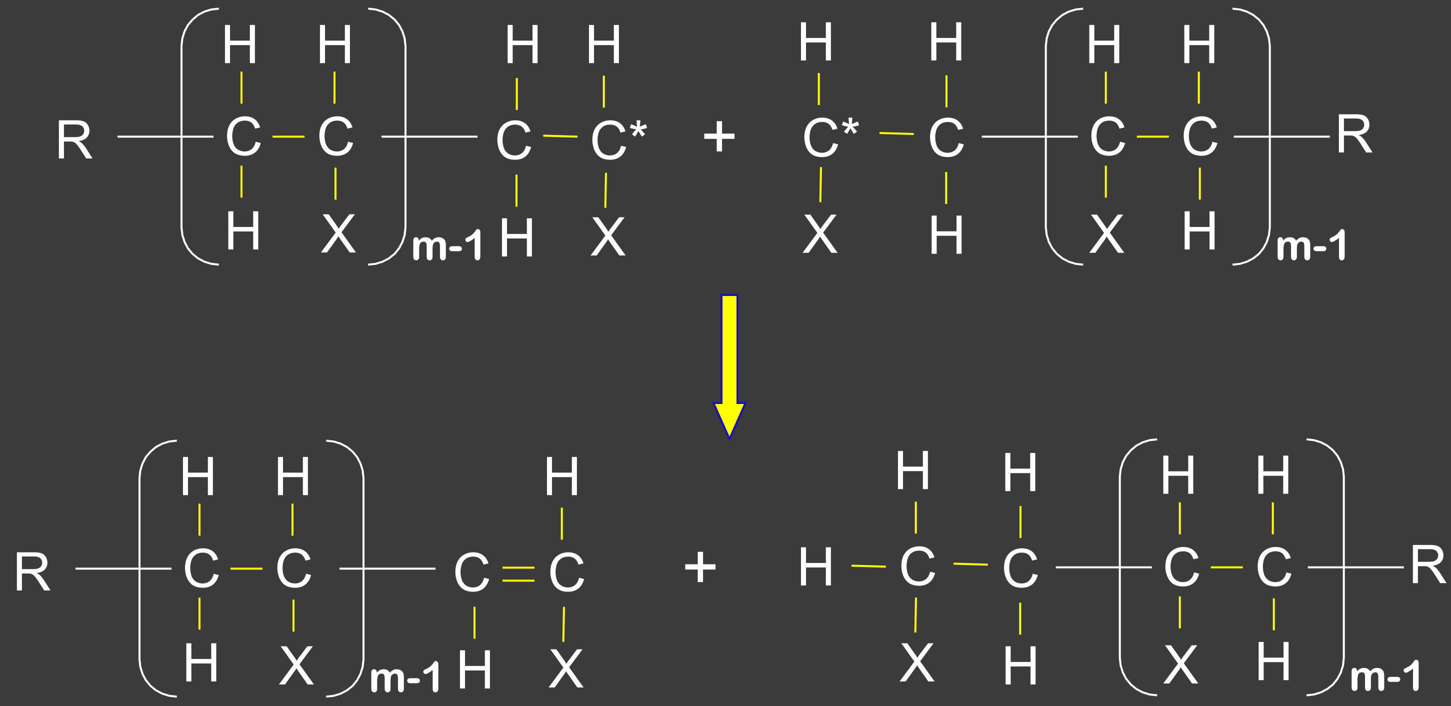
At some stage this chain propagation is terminated when the free adicals combine either by *coupling* (combining) of the two radicals or by *disproportionation*

coupling



saturated highpolymer (dead polymer)

disproportionation



unsaturated oligomer
(dead polymer)

saturated oligomer
(dead polymer)

Coordination or Ziegler-Natta Polymerization

Ziegler and Natta discovered that in the presence of a combination of a transition-metal halide (like $TiCl_4$, $ZeBr_2$, $TiCl_2$ etc.) with a organo-metallic compounds [like $(CH_3)_3Al$] steriospecific polymerization is carried out.

Initiation:

$$Cat\text{-}R' + CH_2{=}CHR \rightarrow Cat\text{-}CH_2\text{-}CHR\text{-}R'$$

Propagation:

$$Cat\text{-}CH_2\text{-}CHR\text{-}R' + nCH_2{=}CHR' \rightarrow Cat\text{-}CH_2\text{-}\underset{R}{\underset{|}{C}}\text{-}\left[CH_2\text{-}\underset{R'}{\underset{|}{CH}}\right]_n\text{-}R'$$

Termination:

$$Cat\text{-}CH_2\text{-}\underset{R}{\underset{|}{C}}\text{-}\left[CH_2\text{-}\underset{R'}{\underset{|}{CH}}\right]_n\text{-}R' + HX \rightarrow Cat\text{-}X + CH_3\text{-}\underset{R}{\underset{|}{C}}\text{-}\left[CH_2\text{-}\underset{R'}{\underset{|}{CH}}\right]_n\text{-}R'$$

Ziegler-Nata polymerization is used to prepare polypropylene, polyethylene, polydiene etc. The importance of this method lies in the fact that stereospecific polymers are obtained.

Plastic

The term plastic is given to organic materials of high molecular weight, which can be moulded into any desired form, when subjected to heat and pressure in the presence of catalyst.

In recent years plastic have attained great importance in every walt of our life, due to their certain properties like:

- ✓Lightness in weight
- ✓Good thermal and electrical insulation
- ✓Corrosion resistance
- ✓Easy workability
- ✓Adhesiveness
- ✓Low fabrication cost into desired shaped products
- ✓Decorative surface effects
- ✓Easy moulding
- ✓Chemical inertness
- ✓Transparency
- ✓Ability to take verity of color shade
- ✓Good shock absorption capacity

Important Thermoplastic Resins

- Polyethylene (PE) is obtained by polymerization of ethylene. The gas is first liquefied under high pressure (up to 1500 atm) and then pump into heated pressure vessel at 150-250°C.
- By using free radical initiator, low density polyethylene is obtained while by using ionic catalyst high density polythene is obtained.

$$nCH_2{=}CH_2 \xrightarrow{\text{Polymerization}} \left[CH_2{-}CH_2 \right]_n$$

- Properties: Polyethylene is a rigid, waxy, white, non-polar material, exhibiting considerable chemical resistance to strong acids, alkalies at room temperature. It is also good insulator of electricity.
- Uses: For making insulator parts, bottle caps, flexible bottles, kitchen and domestic appliance, toyes, sheets for packing materials, pipes, wires and cables coating, bags for packing etc.

- Polyvinyl chloride (PVC) is obtained by heating a water emulsion of vinyl chloride in presence of a small amount of benzyl peroxide in an autoclave under pressure.

$$nCHCl{=}CH_2 \xrightarrow{\text{Polymerization}} -\!\!\left[CHCl\text{-}CH_2\right]_n\!\!-$$

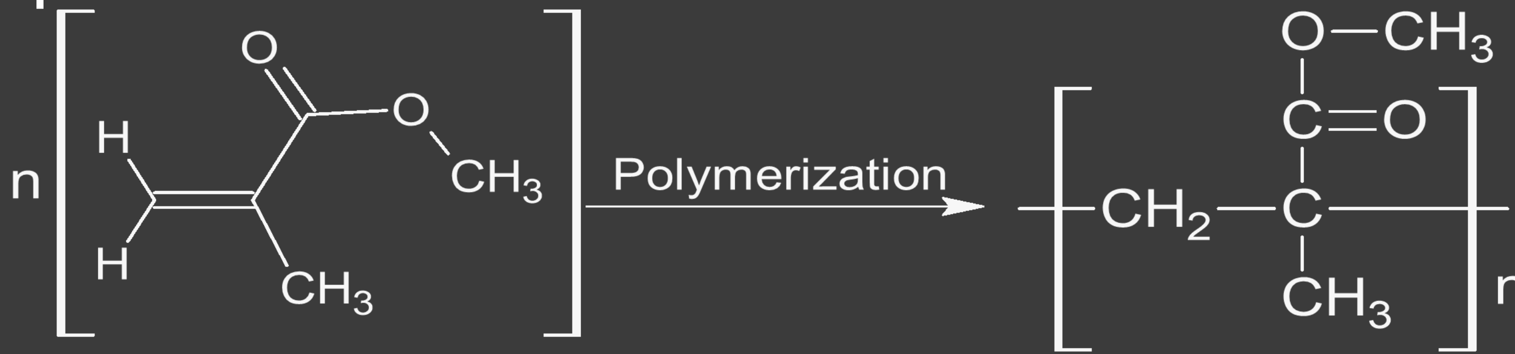
- Properties: PVC is colorless, odorless, non-flammable and chemically inert powder, resistant to light, atmospheric oxygen, inorganic acids and alkalis, but soluble in hot chlorinated hydrocarbons such as ethyl chloride. Pure resin posses a high softening point (148°C). PVC is most widely used synthetic plastic.
- Uses: Rigid PVC or un-plasticized PVC have superior chemical resistance and high rigidity, but is brittle. It used for making sheets, tank linings, light fitting, safety helmets, tyres, mudguards etc.
- Plasticized PVC (obtained by adding plasticizers such as dibutyl pthalate) is used for making continuous sheets, rain coat, table cloths, electric cable insulation, toys etc

- Poly tetrafluoro ethylene (TEFLON) is obtained by polymerization of water-emulsion of tetrafluoro ethylene, under pressure in presence of benzoyl peroxide as catalyst.

$$nCF_2{=}CF_2 \xrightarrow{\text{Polymerization}} \left[CF_2\text{-}CF_2 \right]_n$$

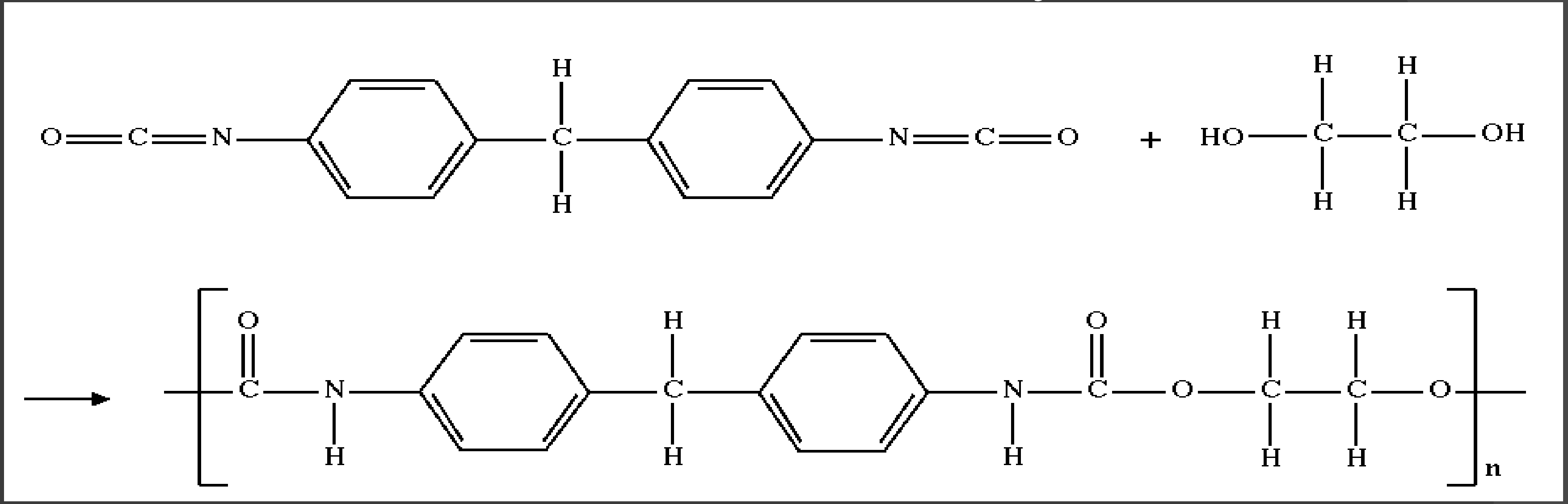
- Properties: Due to presence of highly electronegative fluorine atom and the regular configuration polytetrafluoroethylene molecules results in very strong attractive force between the chains. These strong attractive force give the material extreem toughness, high softening point (350°C), high chemical resistance towards all chemicals.
- Uses: As insulating material for motors, transformers, cables, wires etc, packing, pump parts, tank linings, chemical carrying pipes and non-sticking stop-cocks.

- Polymethyl methylacrylate is obtained by polymerization of Polymethyl methylacrylate in presence of acetyl peroxide or hydrogen peroxide.



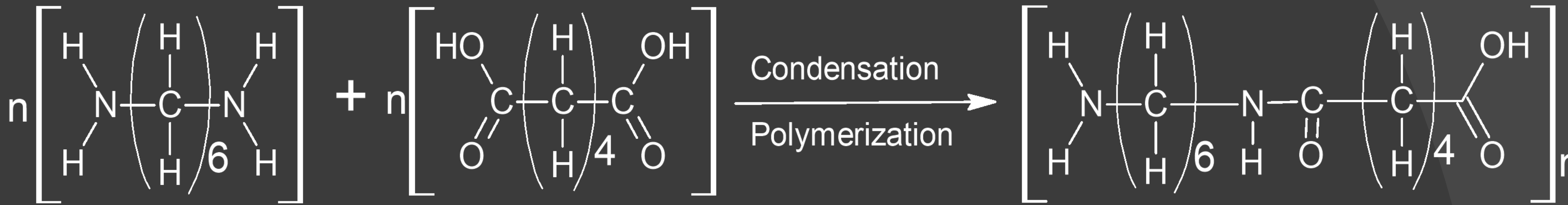
- Properties: it is hard, fairly rigid material with a high softening point of about 130-140°C, but it becomes rubber like at temperature above 65°C. it has low chemical resistance to hot acids and alkalies.
- Use: For making lenses, bone splints, artificial eye, jewelery, wind screen, TV screen etc.

- Polyurethanes are obtained by treating diisocynate and diol. For example *Perlon-U* is obtained by the reaction of 1,4-butane diol with 1,6-hexane diisocynate.

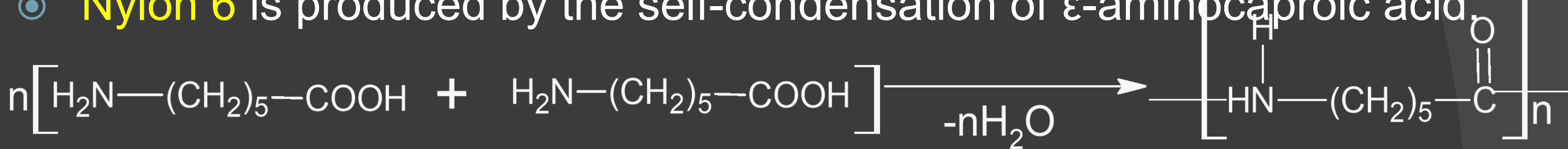


- Properties: Polyurethanes are less stable than nylons at elevated temperature. They are characterized by excellent resistant to abrasion and solvents.
- Use: Polyurathens are used as coating, films, adhesives and elastomers. Polyurethane fibers are used for garments and swim-suit. They also find use as a leather substitute.

- Nylon-6,6 is obtained by polymerization of adipic acid with hexamethylene diamine.



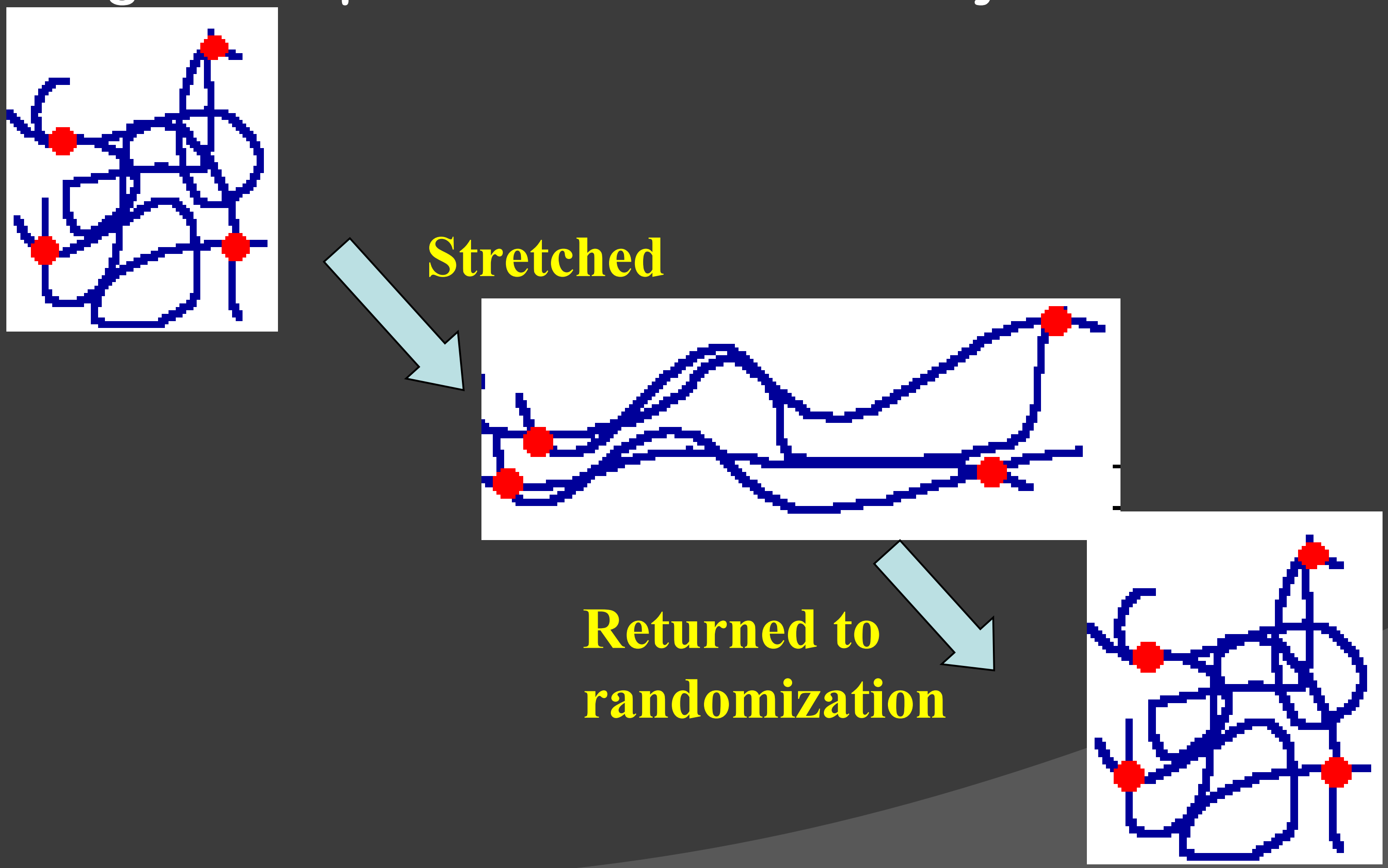
- Nylon 6 is produced by the self-condensation of ε-aminocaproic acid.



- Properties: They are translucent, whitish, horny, high melting polymers. They posses high temperature stability and good abrasion resistance. They are insoluble in common organic solvent and soluble in phenol and formic acid. Nylon fibres have good strength. They are very flexible and retain origional shape after use.
- Use: Nylon-6:6 is primarily used for fiber, which find use in making socks, shoes, under-garments, dresses, carpets etc. Nylon-6 is mainly used for moulding purpose for gears, bearings, electrical mountaining etc. Nylon bearing and gears work quitely without any lubrication. They are also used for making filaments for rope, bristles for toothbrushes.

ELASTOMERS

Elastomer is defined as a long chain polymer which under stress undergoes elongation by several times and regains its original shape when the stress is fully released.

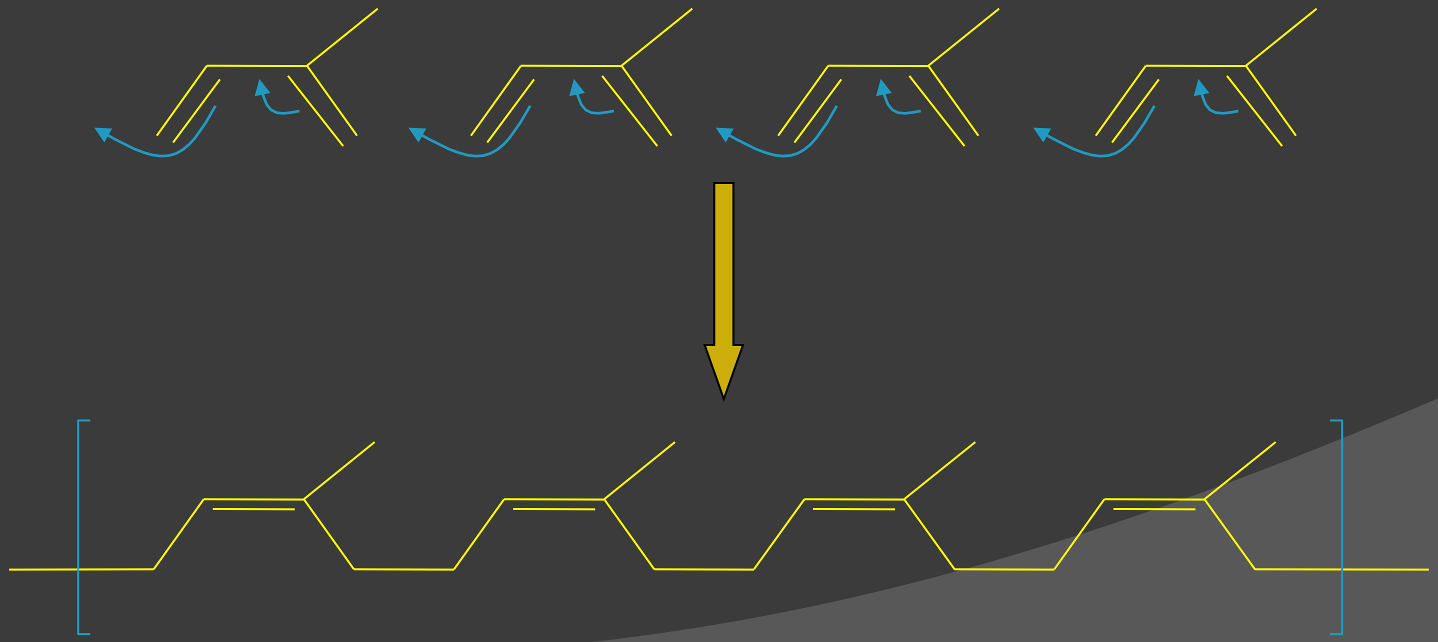


- ✓ Elastomers are high polymers, which have elastic properties in excess of 300 %.
- ✓ The elastic deformation in an elastomer arises due to the fact that the molecule is not a straight chained in the unstressed condition and is in the form of a coil.
- ✓ Hence, it can be stretched like a spring Hence, it can be stretched like a spring So, the unstretched rubber is in an amorphous state.
- ✓ As stretching is done, the macromolecules get partially aligned with respect to another, thereby causing Crystallization.
- ✓ Consequently, stiffening of material (due to increased attractive forces between these molecules) taking place.
- ✓ On releasing the deforming stress, the chains get reverted
- ✓ back to their original coiled state and the material again
- ✓ becomes amorphous

Natural rubber is an addition polymer formed from the monomer called isoprene i.e., 2-methyl-1,3-butadiene.

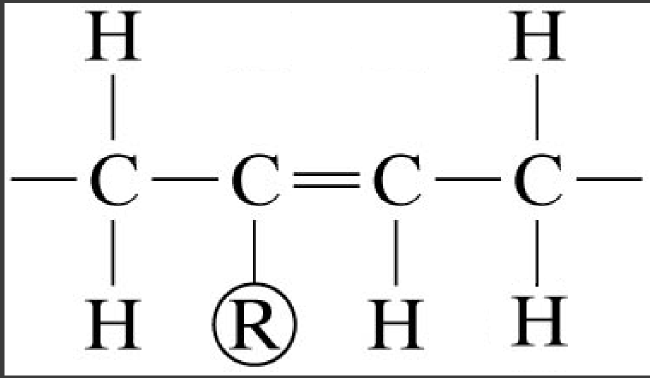
The average D.P. (n) of rubber is around 5000.

Addition between molecules of isoprene takes place by 1,4 addition and one double bond shifts between 2nd and 3rd positions.

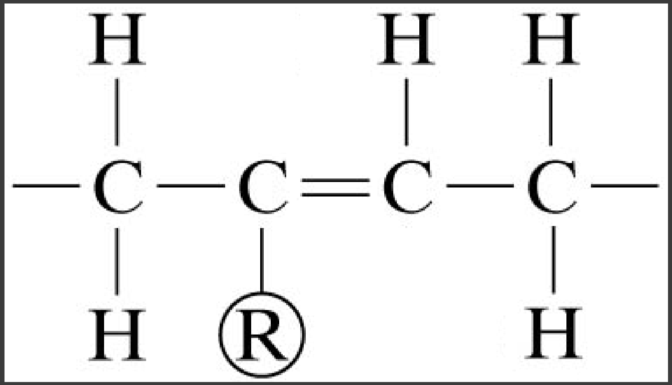


As each isoprene unit contains C = C bond, polyisoprene exists in two isomeric forms

viz., *cis* and *trans*



Cis-polyisoprene



trans-polyisoprene

where R= CH_3

Natural rubber contains the *cis* isomer while the gutta percha contains the *trans* isomer

- Natural rubber consists of basic material latex, which is a dispersion of isoprene.
- During the treatment, these isoprene molecules polymerize to form long-coiled chains of *cis*-polyisoprene.
- The mol. wt. of raw rubber is about 100,000 – 150,000.
- Natural rubber is made from the saps of a wide range of plants like *havea brasillians* and *guayule*, found in tropical countries (such as Indonesia, Malaysia, Thailand, Ceylon, India, South America, etc.,)
- The rubber latex (or milky liquid rubber) is obtained by making incisions in the bark of the rubber trees and allowing the saps to flow out into small vessels.
- Tapping is, usually done at intervals of about six months.
- The latex is emptied into buckets and transferred to a factory for treatment.

✓ Gutta Percha is *trans*-polyisoprene and is obtained from the mature leaves of *dichopsis gutta* and *palagum gutta* trees (belonging to *sapetaceae* family).

✓ These trees are grown mostly in Broneo, Malaya and Sumatra.

✓ Gutta percha may be recovered by solvent extraction Alternatively, the mature leaves are ground carefully; treat with water at about 70 ^{o}C for half an hour and poured into cold water, then the gutta percha floats on water surface and can be easily removed.

Deficiencies of natural rubber

- Natural rubber is addition product of isoprene units and still contains a large number of double bonded carbon atoms.
- Hence it exhibits a large number of deficiencies.
- At low temp. it is hard and brittle but as the temperature rises it becomes soft and sticky.
- It gets oxidized easily in air and produces bad smell even if kept as such for a few days.
- It is soluble in many organic solvents.
- It absorbs large quantities of water.
- Its chemical resistivity is low and is attacked by acids, alkalies, oxidizing and reducing agents.
- Its tensile strength, abrasion resistance wear and tear resistances are low.
- It has little durability.
- When stretched to a great extent, it suffers permanent deformation, because of the sliding or slippage of some molecular chains over each other.
- Synthetic rubbers have slightly modified structures from natural rubber they exhibit properties that are more conducive for their technical uses.

A comparative account of the properties of Natural and Synthetic rubbers

Property	Natural rubber	Synthetic rubber
Tensile strength	Low (only 200 kg/cm^2)	High
Chemical resistivity	Low – gets oxidized even in air	High – not oxidized in air
Action of heat	Cold condition it is hard and brittle, at higher temp.s soft and sticky	Withstand effect of heat over a range of temperature.
With organic solvents	Swells and dissolves	Do not swell and dissolve
Ageing	Undergoes quickly	Resists ageing
Elasticity	On increased stress undergoes permanent deformation.	Has high elasticity.

Vulcanization of rubber

This process was discovered accidentally by Goodyear when he dropped rubber and sulfur on a hot stove. To improve the properties of rubber, it is compoundedwith some chemicals like sulphur, hydrogen sulphide, benzoyl chloride etc., It is known as vulcanisation of rubber.

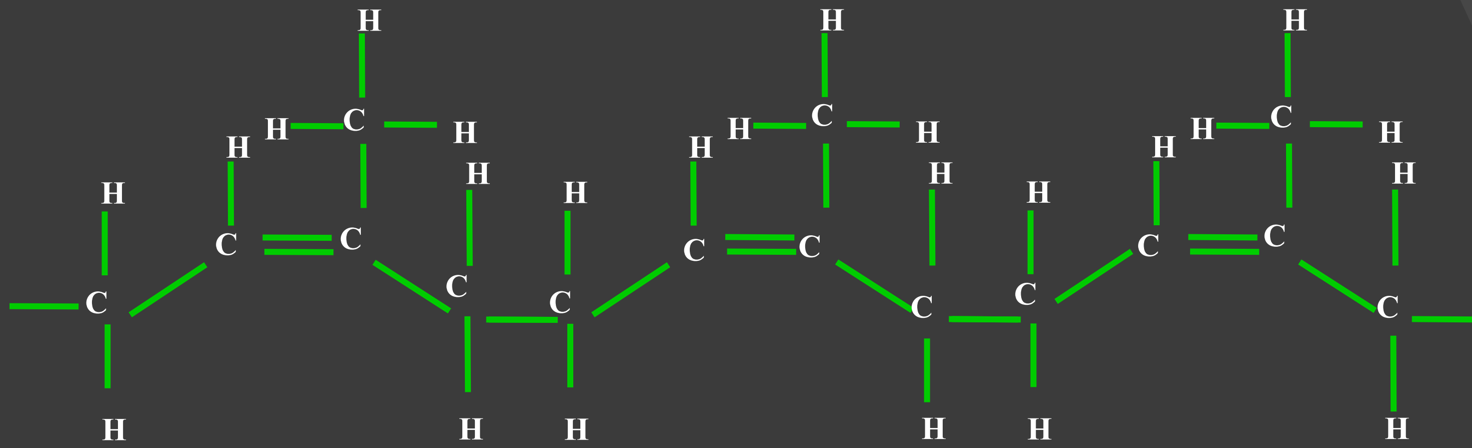
The process consists of heating the raw rubber with sulphur at 100 – 140 ^{o}C.

The added sulphur combines chemically at the double bonds of different rubber springs.

Thus this process serves to stiffen the material by a sort of anchoring and consequently, preventing the intermolecular movement of rubber springs.

The extent of stiffness of vulcanized rubber depends on the amount of sulphur added.

e.g., a tyre rubber may contain 3 to 5% sulphur, but a battery case rubber may contain as much as 30% sulphur



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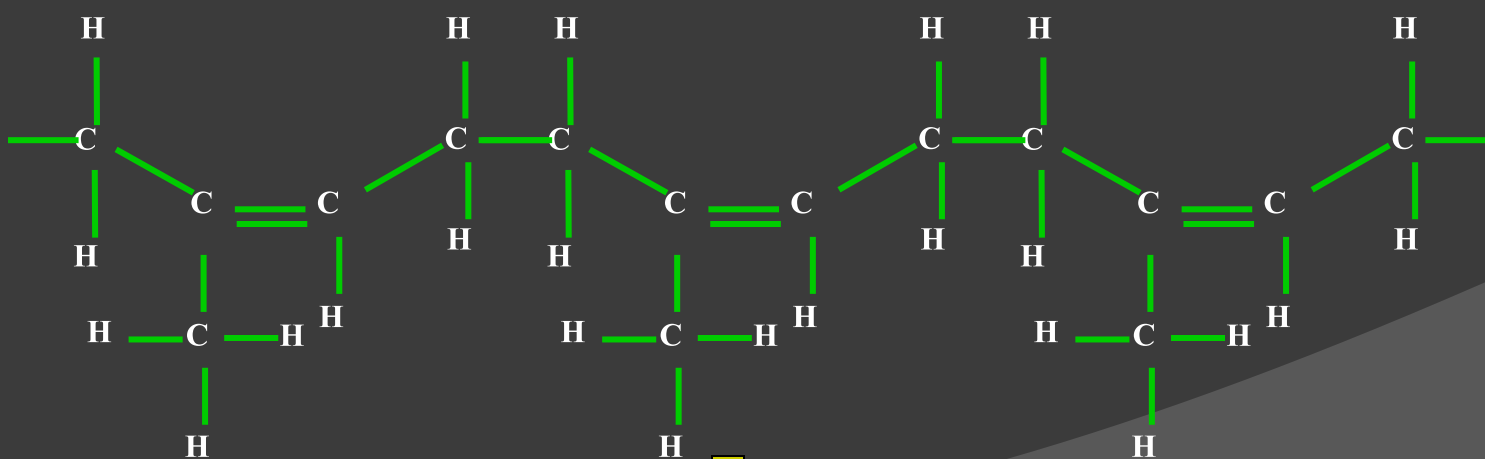
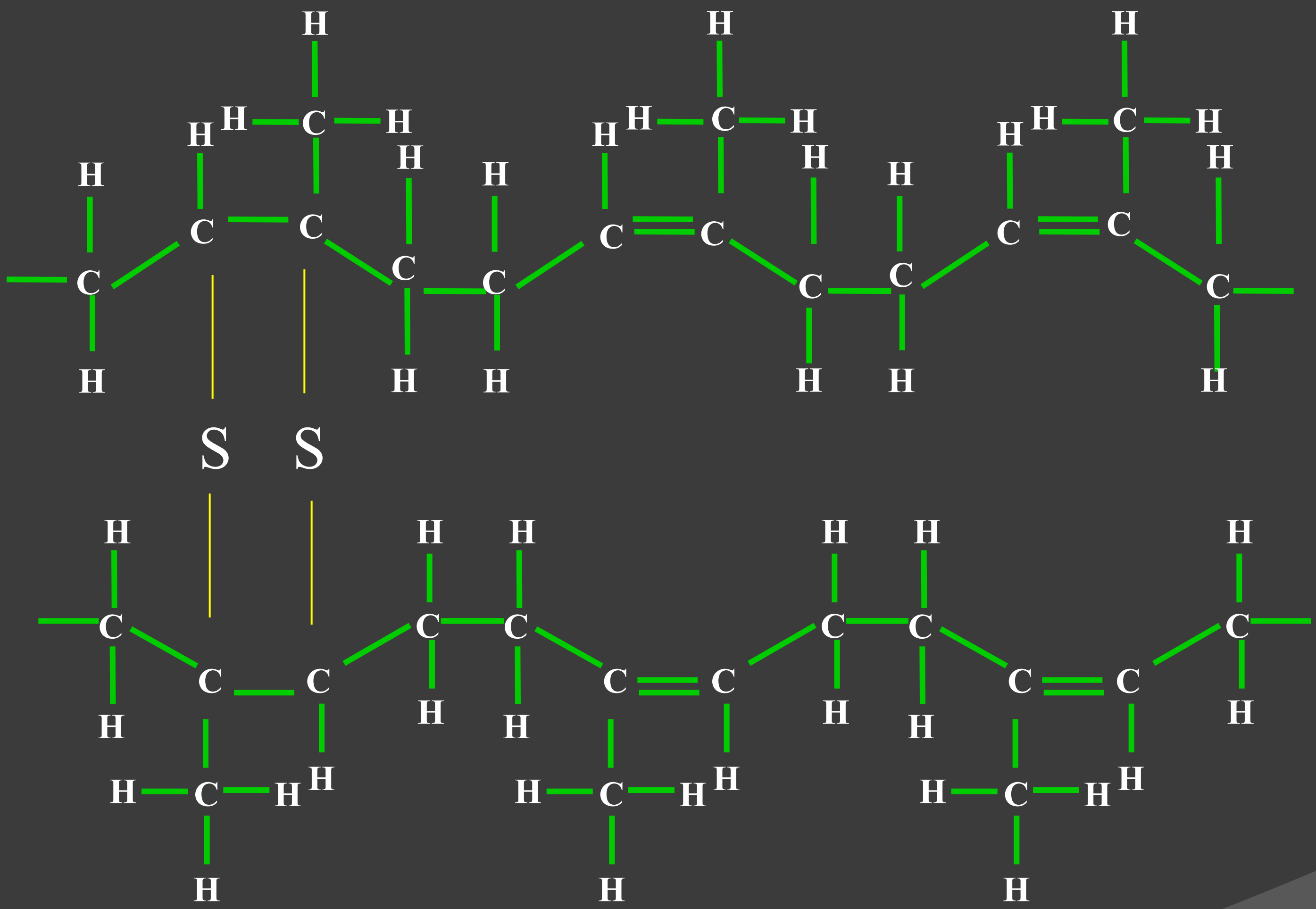




Advantages of vulcanization

Vulcanized rubber

- ✓ has good tensile strength and extensibility, when a tensile force is applied, can bear a load of 2000 kg/cm^2 before it breaks.
- ✓ has excellent resilience. i.e., article made from it returns to the original shape, when the deforming load is removed.
- ✓ possesses low water-absorption tendency.
- ✓ has higher resistance to oxidation and to abrasion.
- ✓ has much higher resistance to wear and tear as compared to raw rubber.
- ✓ is better a electrical insulator, although it tends to absorb small amounts of water.
- ✓ is resistant to organic solvents (such as petrol, benzene, and carbon tetrachloride), fats and oils. However, it swells in these liquids.
- ✓ is very easy to manipulate the vulcanized rubber to produce the desired shape articles.
- ✓ has useful temperature range of - 40 to 100 ^{o}C.
- ✓ has low elasticity and is depending on the extent of vulcanization. e.g., vulcanite (32% Sulphur) has practically no elasticity.

Compounding of rubber

Compounding is mixing of the raw rubber (synthetic or natural) with other substances so as to impart the specific properties to the product, which are suitable for a particular job.

Besides rubber, the following materials may be incorporated.

Softners and ***plasticizers***

These are added to give the rubber greater tenacity and adhesion. Important materials are vegetable oils, waxes, stearic acid, rosin, etc.

Vulcanizing agents

The main substance added is sulphur. Depending on the nature of the product required, the % of sulphur added varies between 0.15 and 32.0%.

Many other vulcanizing agents are now-a-days added to rubber, among them are sulphur monochloride, hydrogen sulphide, benzoyl chloride, trinitrobenzene and alkylphenol sulphides.

Accelerators

These materials drastically shorten the time required for vulcanization. The most used accelerators are 2-mercaptol, benzothiozole and zinc alkyl zanthate.

Antioxidants

Natural rubber has a tendency to perish, due to oxidation. For this reason, anti oxidation materials, such as complex amines like phenyl naphthylamine and phosphates are added.

Reinforcing fillers

These are added to give strength and rigidity to the rubber products.

Common reinforcing fillers are carbon black, zinc oxide, calcium carbonate and magnesium carbonate.

Coloring matter

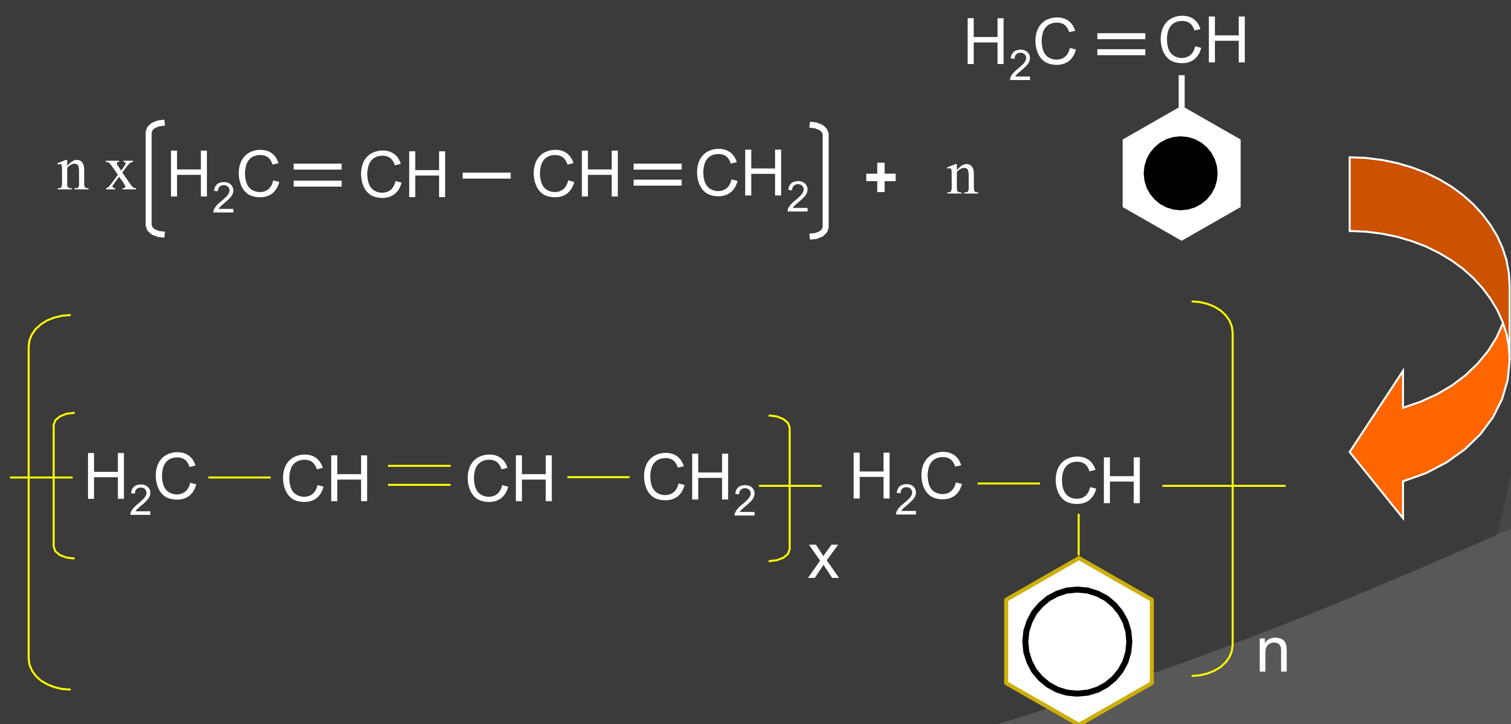
These are added to give the desired color to the rubber product.

for white color (titanium dioxide), Green (chromium oxide), red (ferric oxide), yellow (lead chromate).

Styrene rubber (GR-S or Buna-S or SBR)

Preparation

This is produced by copolymerization of butadiene (about 75% by wt.) and styrene (about 25% by wt.)



Properties

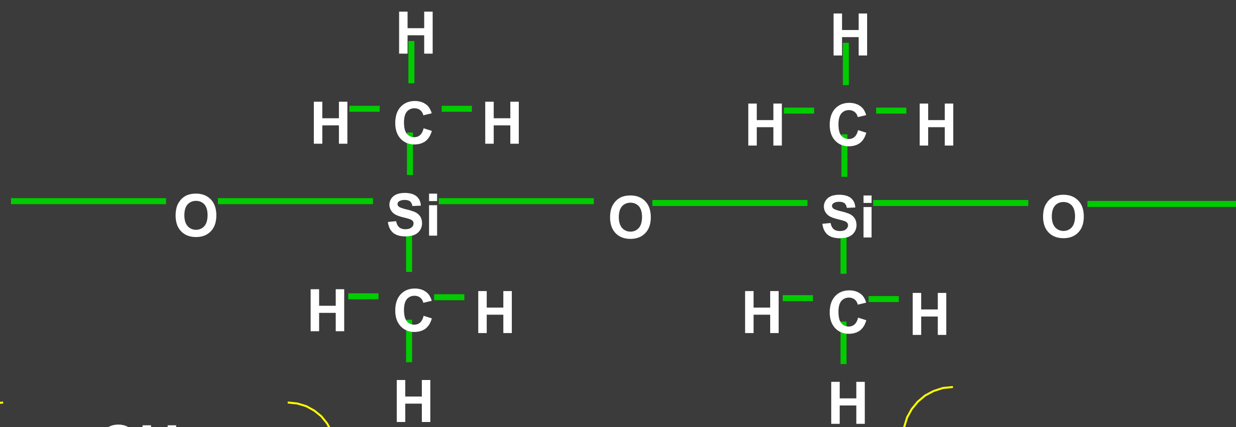
- It possess high abrasion-resistance
- It possess high load-bearing capacity and resilience
- It gets readily oxidized, especially in presence of traces of ozone present in the atmosphere
- It swells in oils and solvents
- It can be vulcanized in the same way as natural rubber either by sulphur or sulphur monochloride, However, it equires less sulphur, but more accelerators for ulcanization
- Styrene rubber resembles natural rubber in processing characteristics as well as the quality of the finished roducts

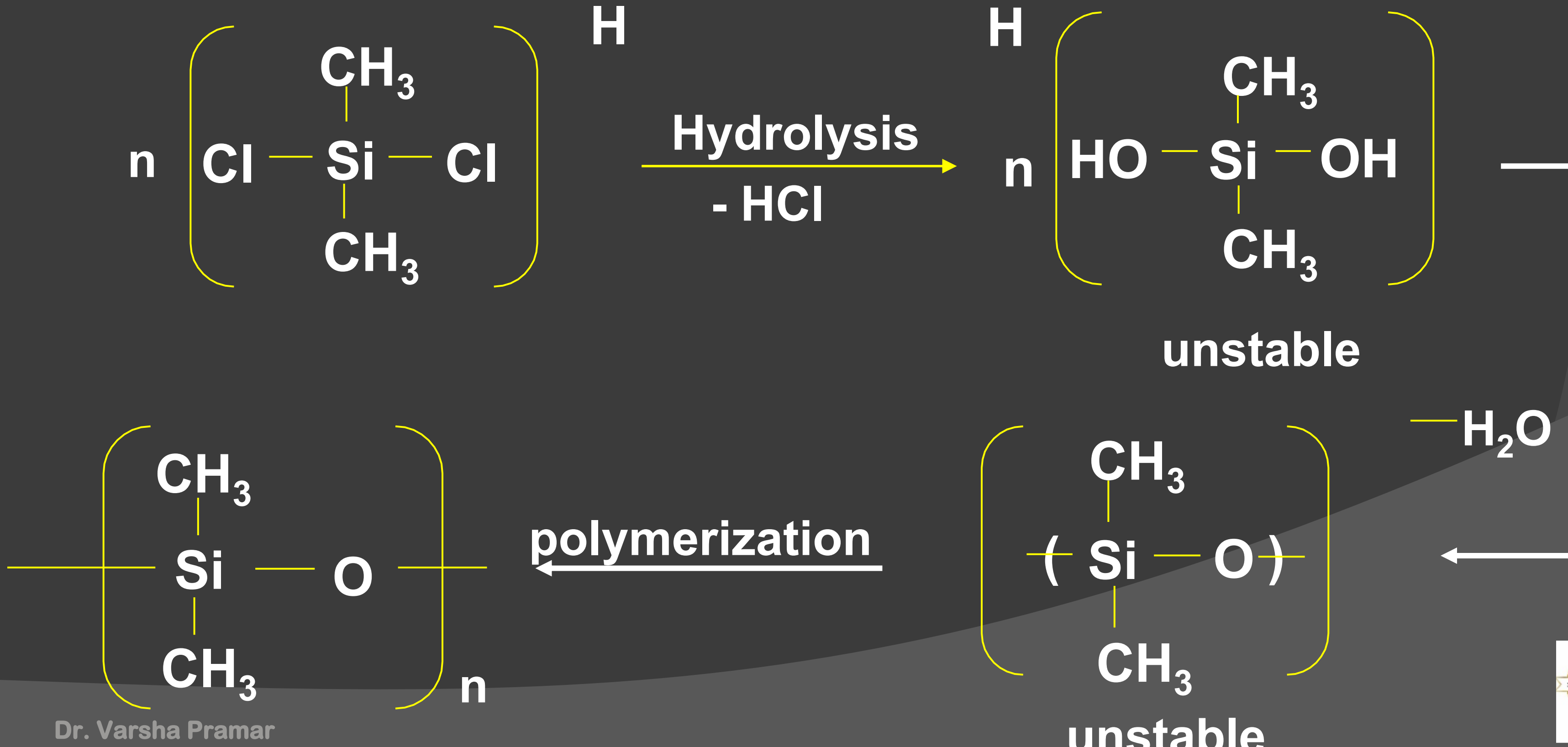
Uses

It is used for the manufacture of motor tyres, floor tiles, shoe soles, gaskets, wire and cable insulations, carpet backing, adhesives, tank-lining etc.

Silicone rubber

Silicone resins contain alternate silicone – oxygen structure, which has organic radicals attached to silicone atoms

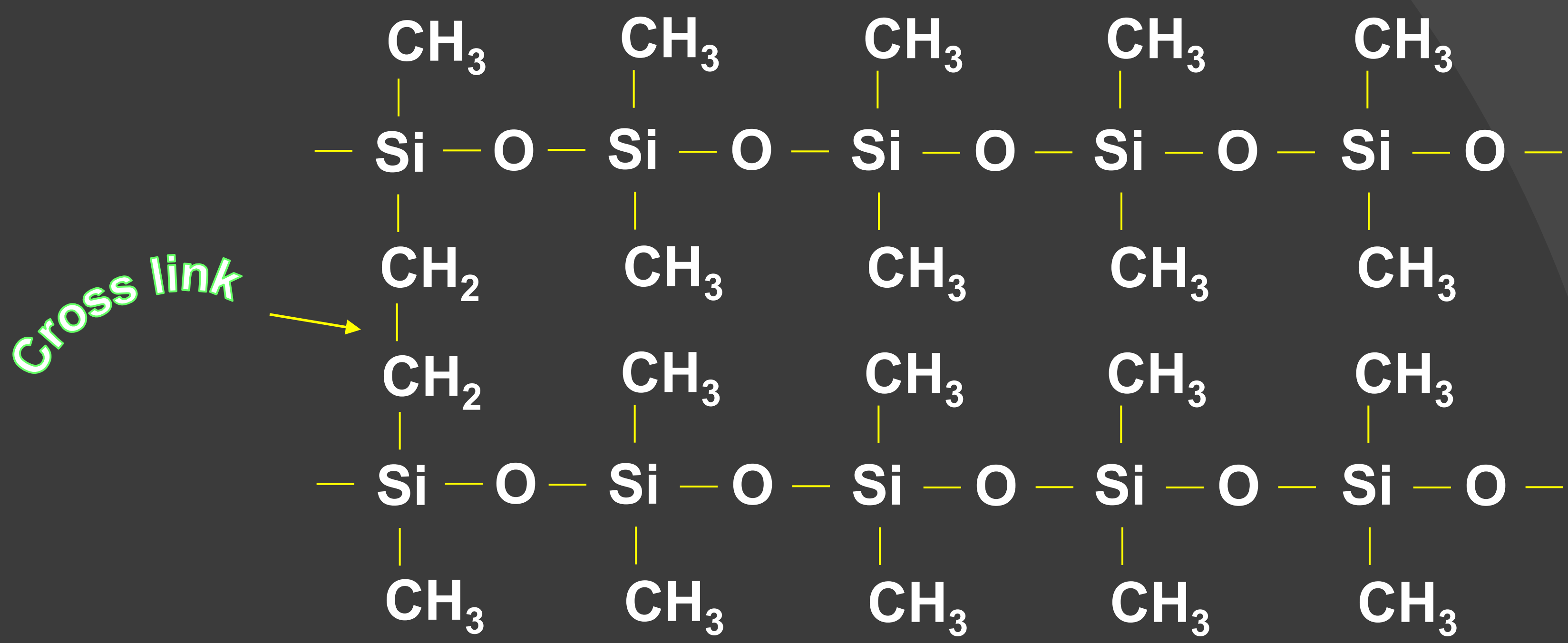




Vulcanized silicone rubbers are obtained by mixing high molecular weight linear dimethyl silicone polymers with filler.

The fillers are either a finely divided silicon dioxide or a peroxide.

It may also contain the curing agents, Peroxide causes the formation of dimethyl bridge (cross link) between methyl groups of adjacent chains.



Properties

They possess exceptional resistance to prolonged exposure to sun light, weathering, most of the common oils, boiling water, dilute acids and alkalies.

They remain flexible in the temp. range of 90 – 250 ^{O}C, hence, find use in making tyres of fighter aircrafts, since they prevent damage on landing. Ordinary rubber tyre becomes brittle and hence disintegrates.

silicone rubber at very high temp. s (as in case of fibers) decomposes; leaving behind the non-conducting silica (SiO_2) instead of carbon tar.

Uses

- ✓ As a sealing material in search-lights and an aircraft engines.
- ✓ For manufacture of tyres for fighter aircrafts.
- ✓ For insulating the electrical wiring in ships.
- ✓ In making lubricants, paints and protective coatings for fabric finishing and water proofing.
- ✓ as adhesive in electronics industry
- ✓ For making insulation for washing machines and electric blankets for iron board covers.
- ✓ For making artificial heart valves, transfusion tubing and padding for plastic surgery.
- ✓ For making boots for use at very low temp., since they are less affected by temperature variation. e.g., Neil Armstrong used silicone rubber boots when he walked on the moon.