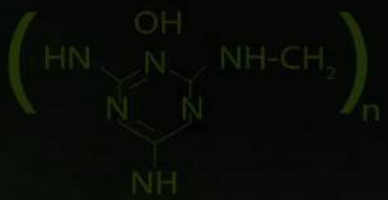
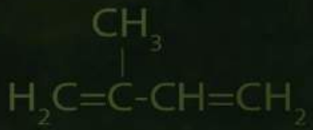




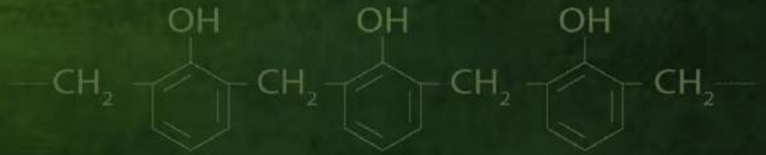
$H_2C{=}\overset{CH_3}{C}{-}CH{=}CH_2$

Welcome to

Aakash

+ BYJU'S LIVE

Polymers



Polymers

- Introduction
- Classification
- Types of polymerisation
- Rubber
- Biodegradable polymers
- Commercial importance

Polymer

Greek words

Poly + mer

Many

Unit/part

Macromolecules

Very large molecules having **high** molecular mass.

$10^3 - 10^7$u

Polymerisation

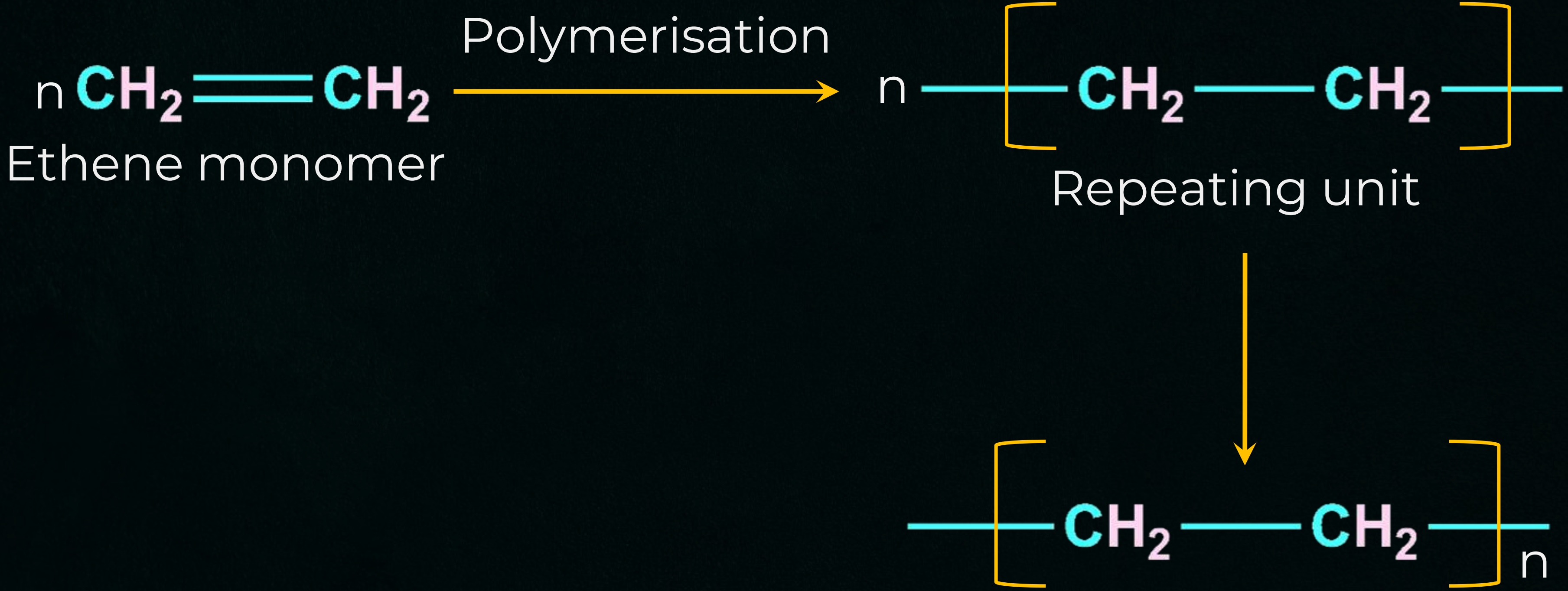
Polymers are formed by the **joining** of **repeating structural units** on a large scale.

The process of formation of the **polymers** from the respective **monomers** that are linked by a **covalent bond**.

Polymerisation

Formation of **polythene** from **ethene**

Example



$$n\,CH_2{=}CH_2 \xrightarrow{\text{Polymerisation}} n\,\left[-CH_2-CH_2-\right]$$

Ethene monomer

Repeating unit

$$\downarrow$$

$$\left[-CH_2-CH_2-\right]_n$$

Polythene polymer

Classification of Polymers

Classification of polymers on the basis of

- Source
- Structure
- Mode of polymerisation
- Molecular forces
- Growth polymerisation

Classification Based on Source

Polymers

- Natural
- Semi-Synthetic
- Synthetic

Natural Polymers

Polymers that are derived from **plants** and **animals**

Example

Proteins, **cellulose**, **starch**, **natural rubber,** and more

Semi-Synthetic Polymers

Polymers that are derived from both **petroleum** and **natural products**

Rayon, **cellulose nitrate**, and more

Cellulose acetate

Cellulose nitrate was used as film negatives.

Synthetic Polymers

Polymers that are **man–made** or derived from **petroleum oil**

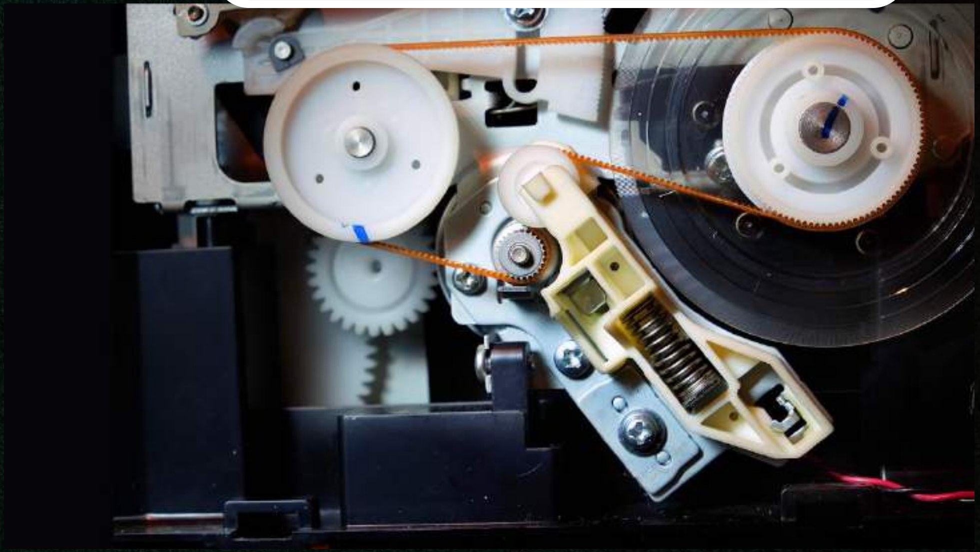
Examples

Plastic ---> Polythene

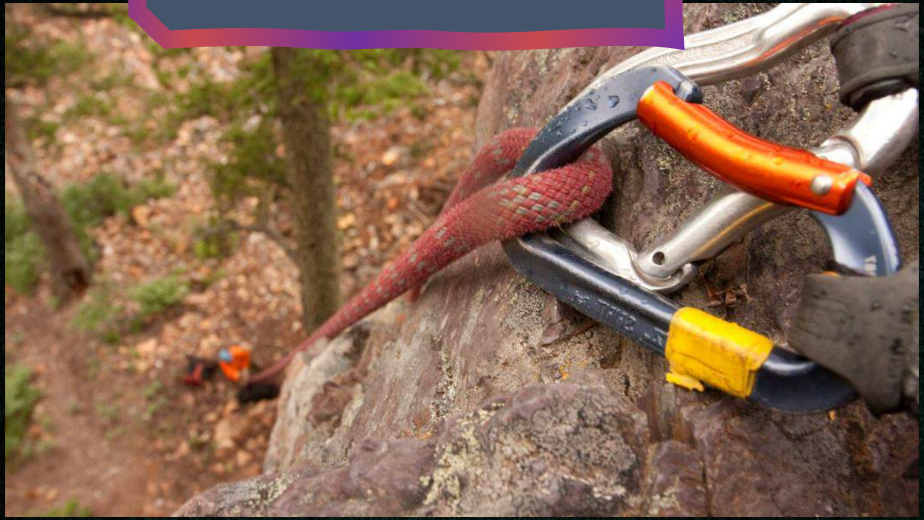
Synthetic fibre ---> Nylon 6,6

Synthetic rubber ---> Buna–S

Computer Machinery



Nylon 6,6



Buna-S

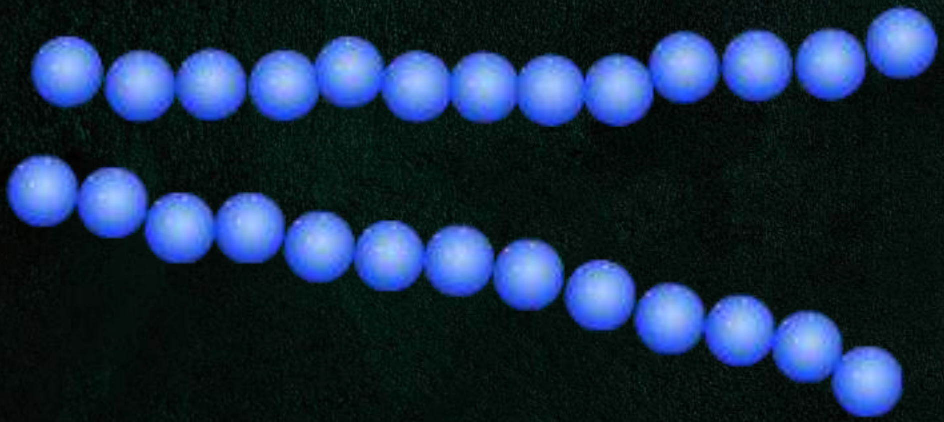
Classification Based on Structure

Polymers

- Linear
- Branched
- Cross-linked

Linear Polymers

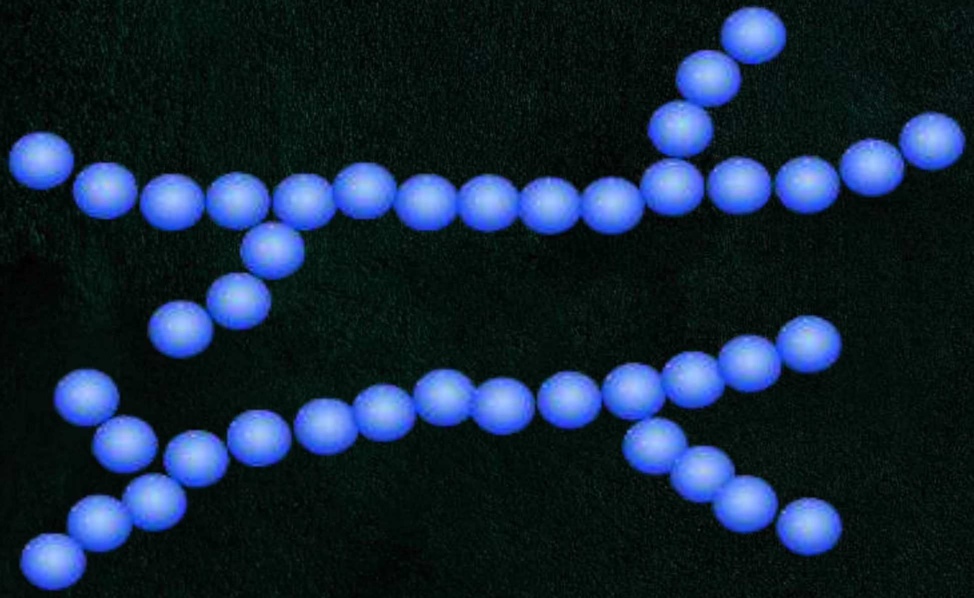
Ex: High-density **polythene, Polyvinyl chloride (PVC),** and more.



Polymer consisting of **long** and **straight chains**

Branched-Chain Polymer

Ex: Low density **polythene, polypropylene,** and more



Polymer consisting of **linear chains** having some **branches**

Cross-linked or Network Polymers

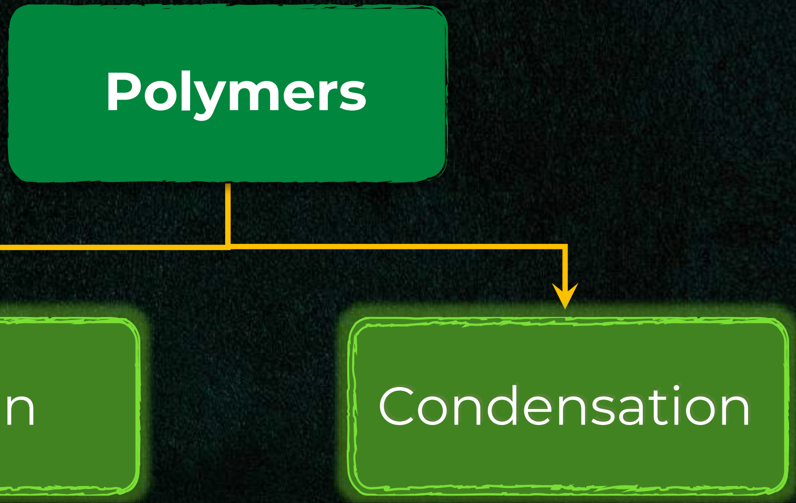
Ex: **Bakelite, Melamine**, and more

They are formed from **bifunctional** and **trifunctional** monomers.

3° amide

They contain **strong covalent bonds** between various linear chains.

Classification Based on Mode of Polymerisation

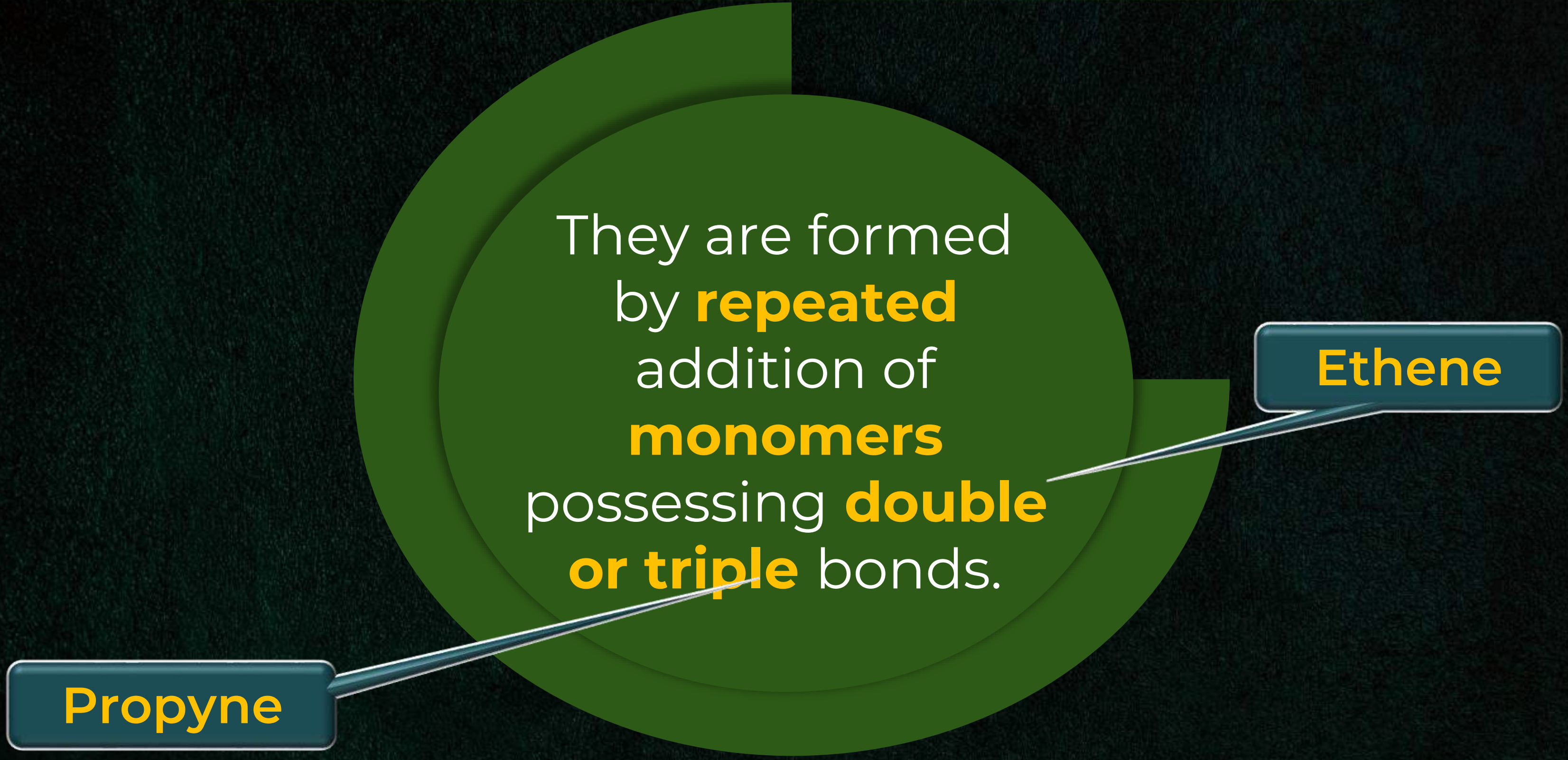


Polymers

Addition

Condensation

Addition Polymers



They are formed by **repeated** addition of **monomers** possessing **double or triple** bonds.

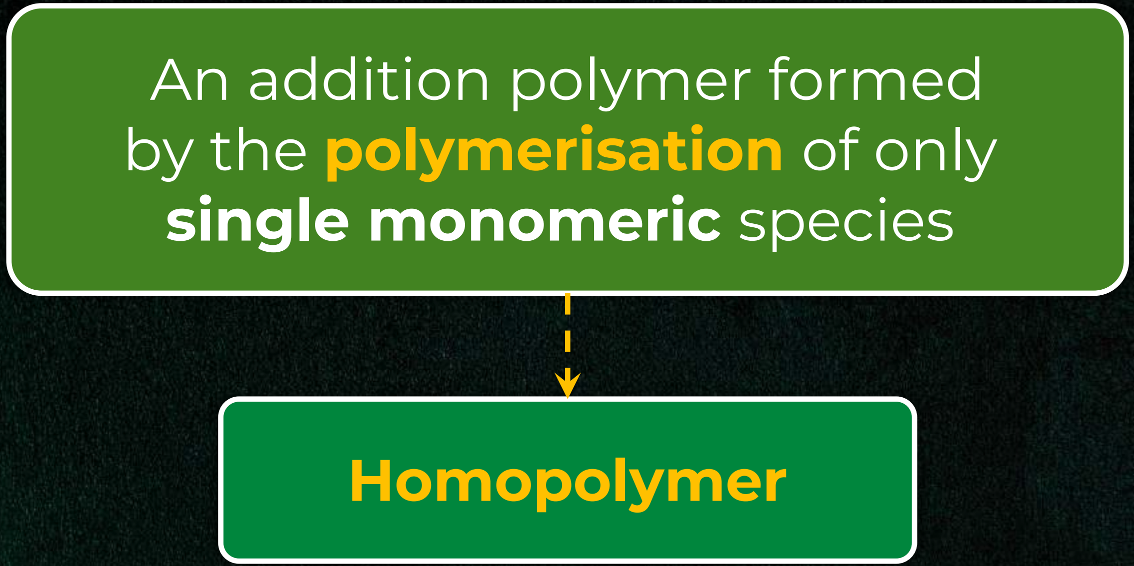
Ethene

Propyne

Formation of **polythene** from **ethene**

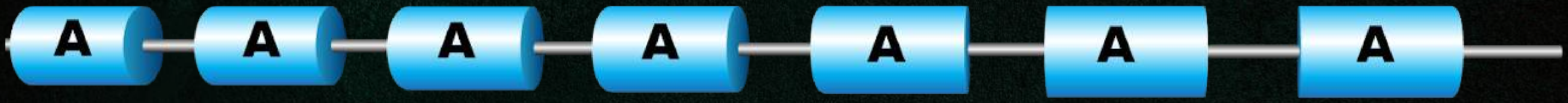
No part from the monomer units are lost during polymerisation; they are simply added.

Types of Addition Polymers - Homopolymers



An addition polymer formed by the **polymerisation** of only **single monomeric** species

Homopolymer



EXAMPLE

Homopolymers

Formation of **polythene** from **ethene**

$$n\,CH_2{=}CH_2 \longrightarrow \left[\!-CH_2-CH_2-\right]_n$$

Ethene

Polythene

Homopolymer

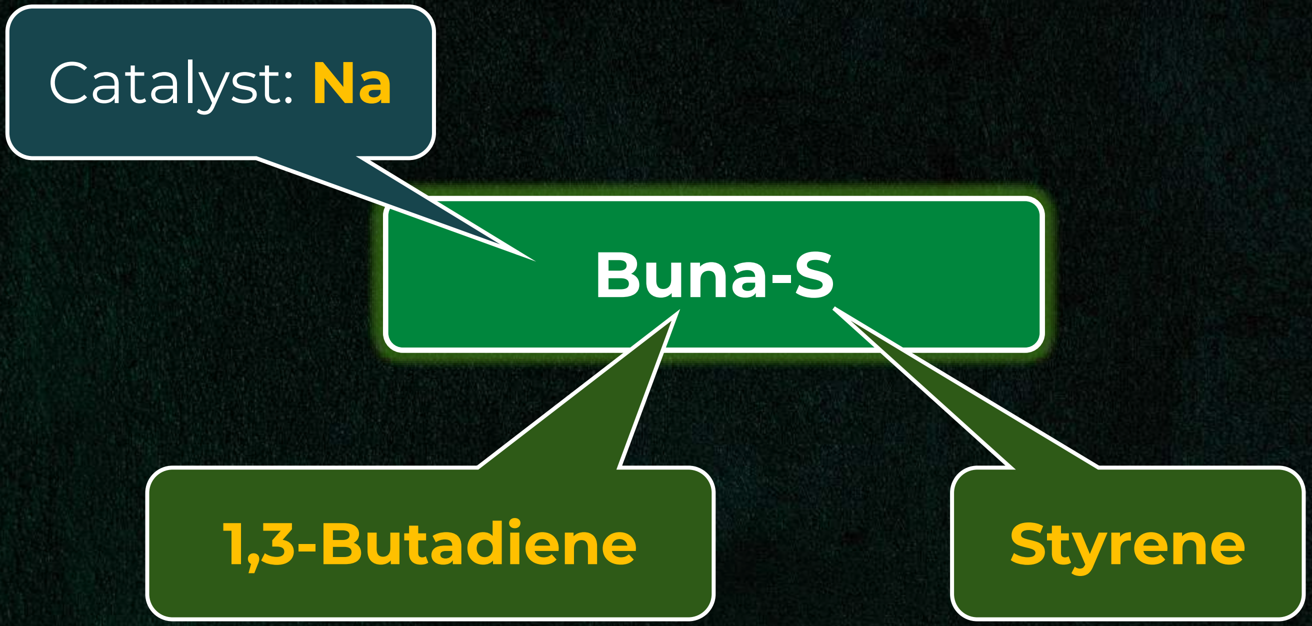
Types of Addition Polymers - Copolymers

Addition polymers formed by **polymerisation** of **two different** monomers

Copolymers

Examples: Buna-S, Buna-N, and more

Buna - S



Catalyst: **Na**

Buna-S

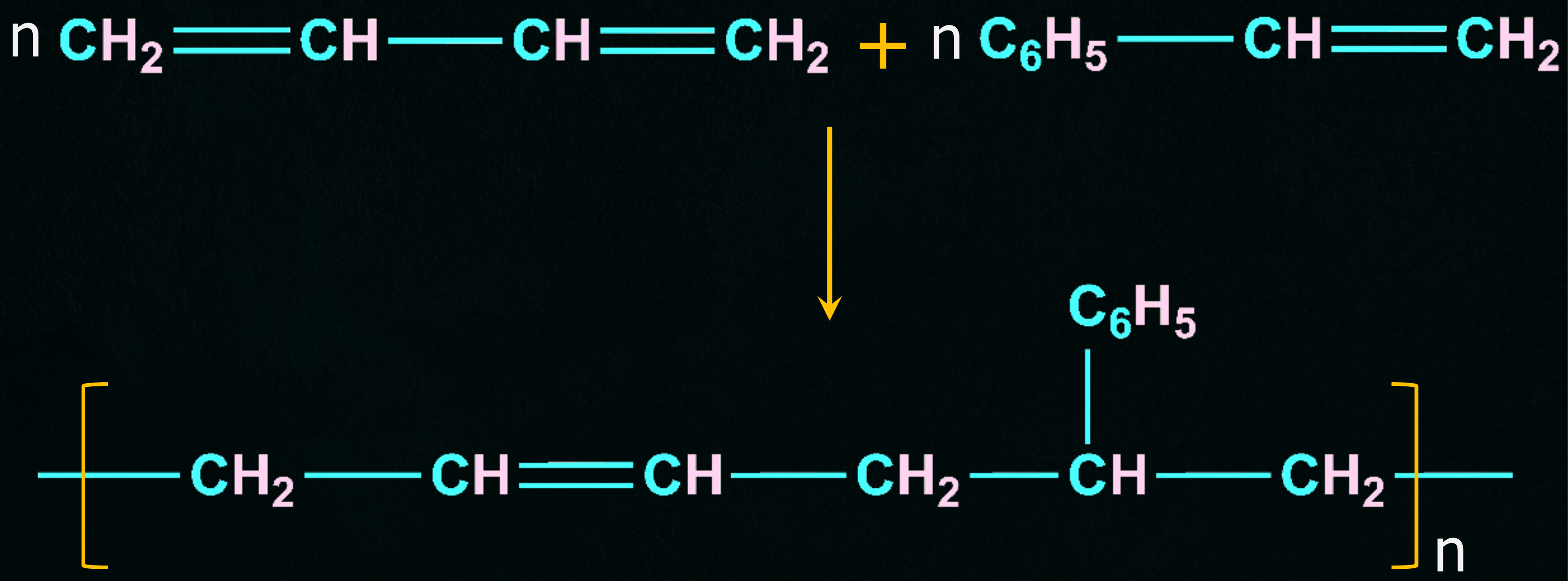
1,3-Butadiene

Styrene

The two different type of monomers (1,3-Butadiene and Styrene) react and form this copolymer.

Buna - S

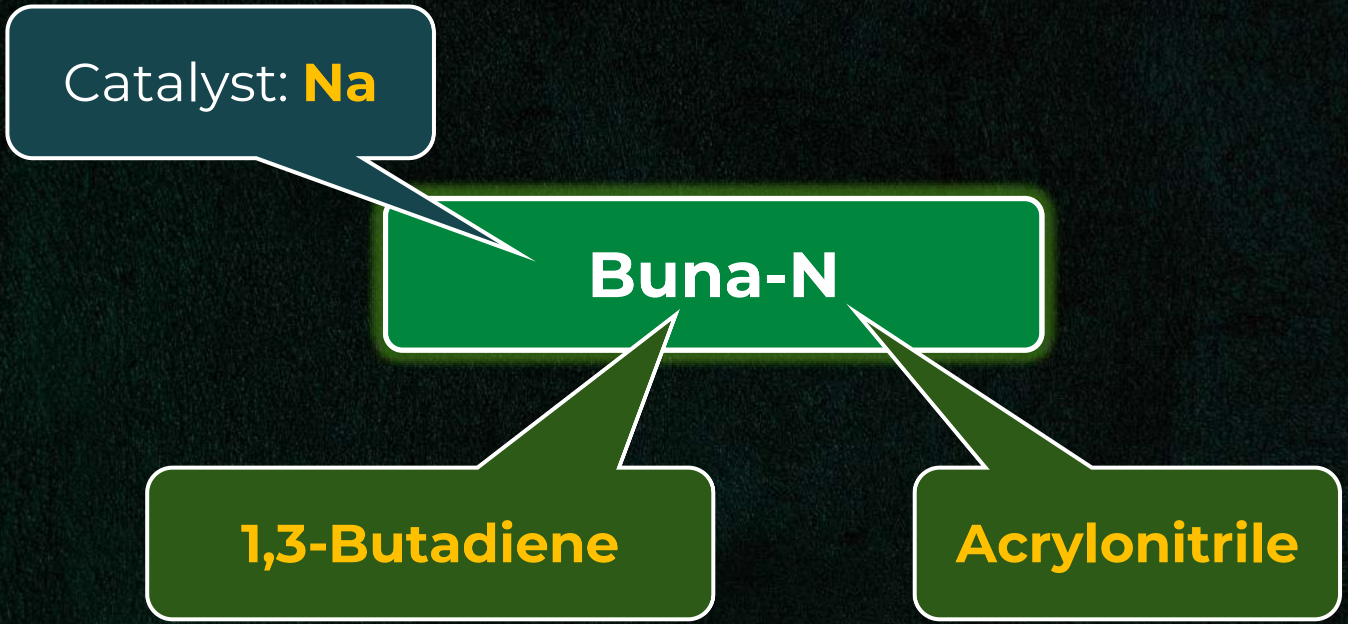
Reaction



$$n\,CH_2{=}CH{-}CH{=}CH_2 + n\,C_6H_5{-}CH{=}CH_2 \longrightarrow \left[-CH_2-CH{=}CH-CH_2-\overset{\overset{\displaystyle C_6H_5}{|}}{CH}-CH_2-\right]_n$$

Butadiene-styrene copolymer (**Buna-S**)

Buna - N



Catalyst: **Na**

Buna-N

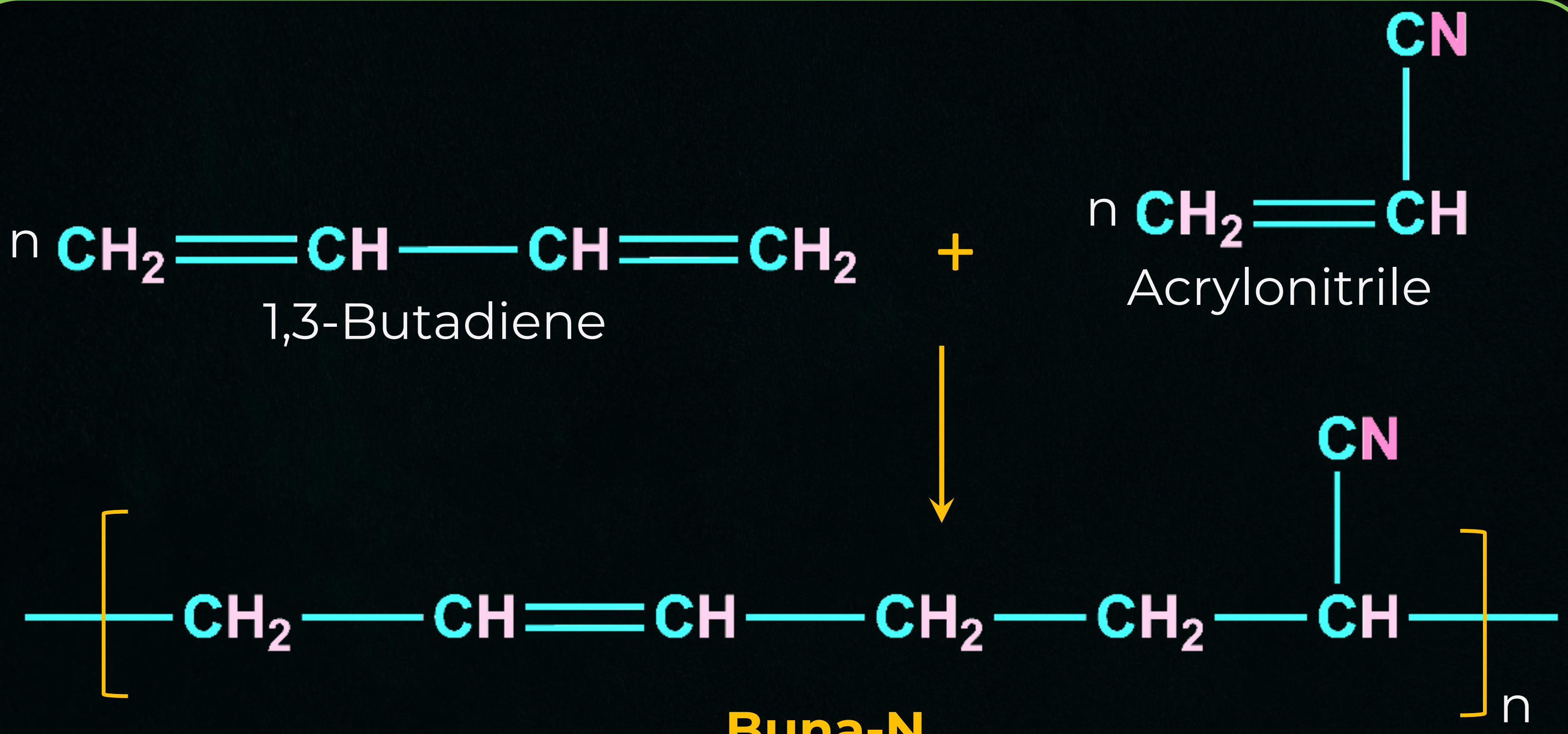
1,3-Butadiene

Acrylonitrile

The two different type of monomers (1,3-Butadiene and Acrylonitrile) react and form this copolymer.

Buna - N

Reaction



$$n\,CH_2{=}CH{-}CH{=}CH_2 + n\,CH_2{=}\overset{\overset{\displaystyle CN}{|}}{CH} \longrightarrow \left[{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle CN}{|}}{CH}{-} \right]_n$$

1,3-Butadiene

Acrylonitrile

Buna-N

Uses of Buna – S and Buna - N

Copolymer	Uses
Buna-S	Auto tyres, floor tiles, footwear components, and more
Buna-N	Oil seals, tank lining, and more

Condensation Polymers

They are formed by **repeated condensation** reactions between two different **bifunctional** or **trifunctional** monomeric units.

Water, HCl, and more

Generally, in condensation reactions, the **elimination of small molecules** takes place.

EXAMPLE

Condensation Polymers

Nylon 6,6

Hexamethylene diamine

Adipic acid

The two different type of monomers (Hexamethylene diamine and Adipic acid) react and form this copolymer.

$$n\ H_2N(CH_2)_6NH_2 \quad + \quad n\ HOOC(CH_2)_4COOH$$

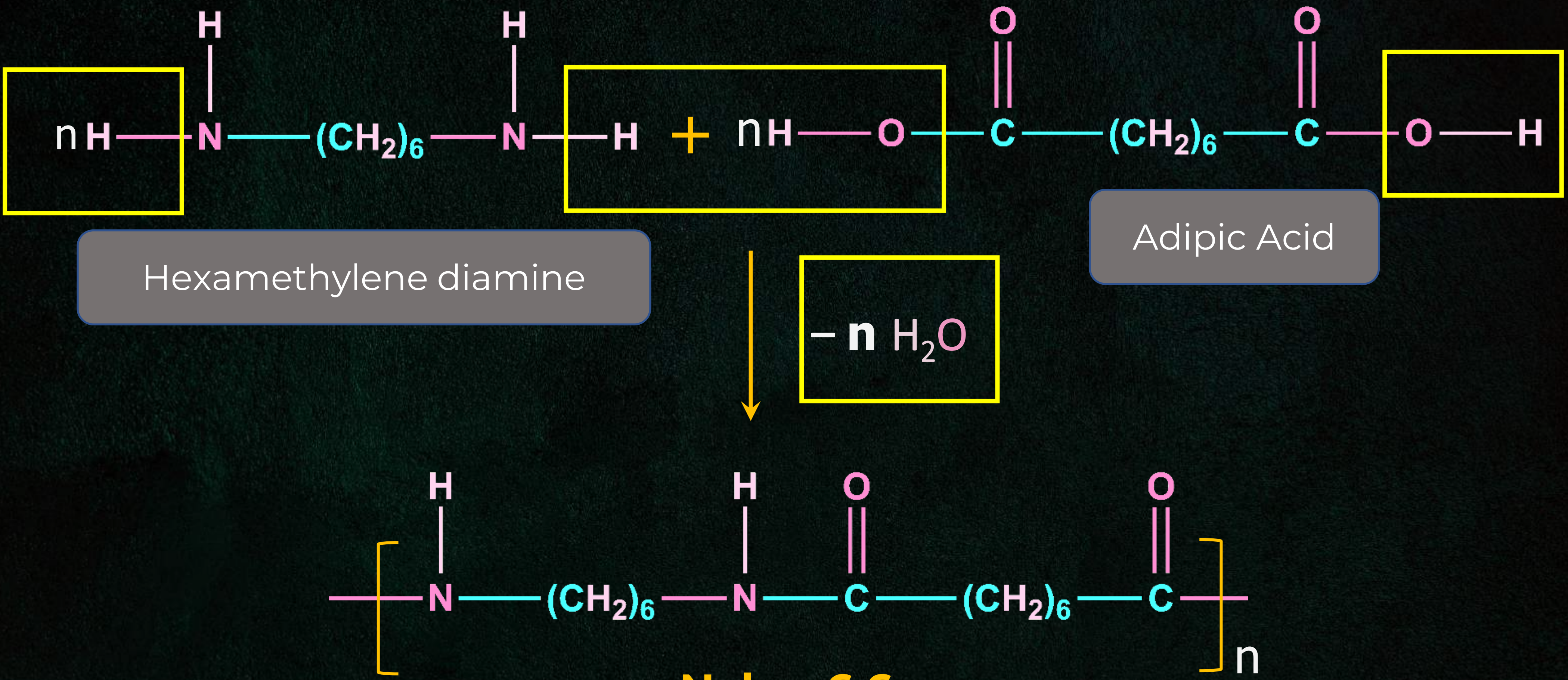
$$\downarrow$$

$$-\!\!\left[\ NH(CH_2)_6NHCO(CH_2)_4CO\ \right]\!\!-_n$$

$$+$$

$$n\ H_2O$$

Condensation Polymers



$$n\,\mathrm{H{-}\overset{\displaystyle H}{\overset{|}{N}}{-}(CH_2)_6{-}\overset{\displaystyle H}{\overset{|}{N}}{-}H} + n\,\mathrm{H{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}(CH_2)_6{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}H}$$

Hexamethylene diamine

Adipic Acid

$$\downarrow\ -\,n\,H_2O$$

$$\left[\mathrm{\overset{\displaystyle H}{\overset{|}{N}}{-}(CH_2)_6{-}\overset{\displaystyle H}{\overset{|}{N}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}(CH_2)_6{-}\overset{\displaystyle O}{\overset{\|}{C}}}\right]_n$$

Nylon 6,6

Classification Based on Molecular Forces

The mechanical properties of polymer- like **tensile strength, elasticity, toughness**, etc., are governed by

Intermolecular forces like Van der Waals forces and hydrogen bonds

Binds the **polymer chain**

Polymers

- Elastomer
- Fibres
- Thermoplastic
- Thermosetting

Elastomers

The polymer chains are held together by the **weakest intermolecular forces**.

Permit **stretching**

This forms a few **crosslinks** between the chains that help the polymer to **retract** to its **original position** after the force is released.

Buna-S, Buna-N, Neoprene, and more

A synthetic rubber

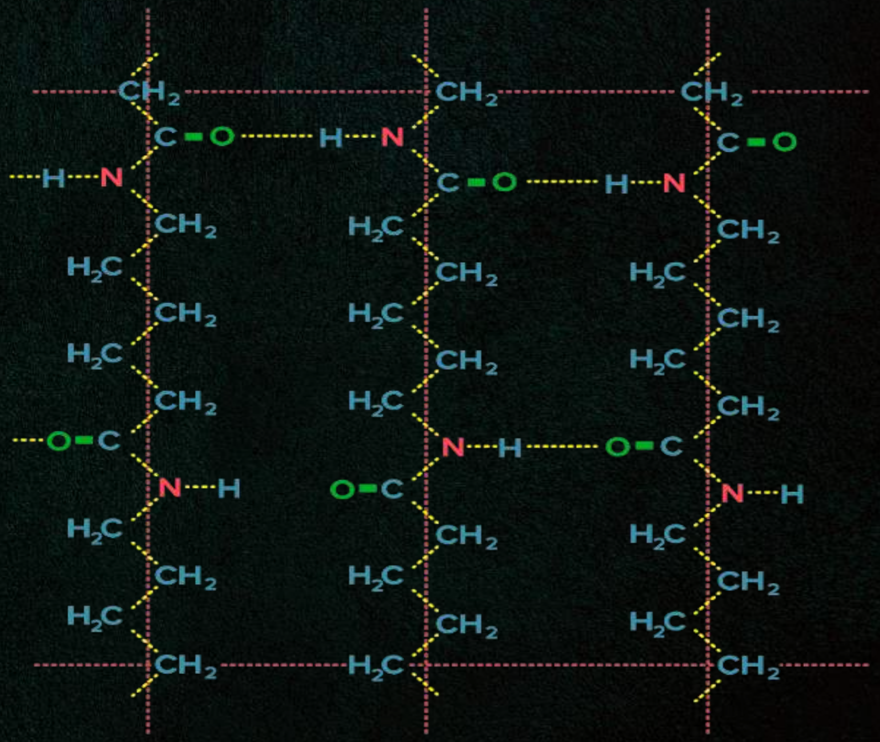
Fibres

They are thread-forming solids that possess **high tensile strength** and **modulus.**

Hydrogen bonding

Strong intermolecular forces present.

Nylon 6,6, terylene and more

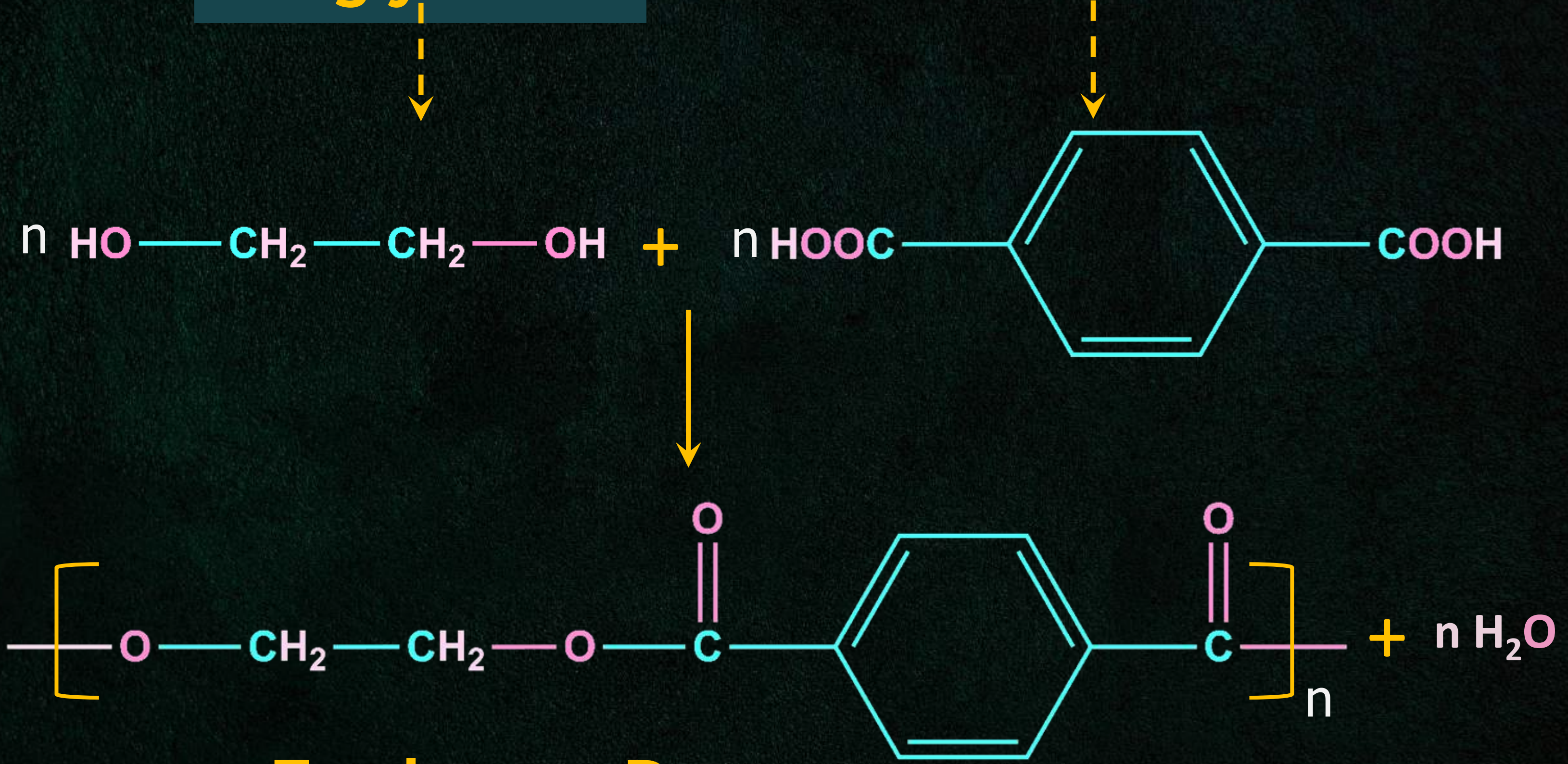


Terylene

Monomers

Ethylene glycol

Terephthalic acid



Terylene or Dacron

Thermoplastic Polymers

Linear or **slightly branched** long-chain molecules

Capable of repeatedly being **soft** on **heating** and **hard on cooling**.

Polythene, polystyrene, polyvinyl chloride(PVC) and more

In **thermoplastics**, the intermolecular forces of attraction are intermediate between **elastomers** and **fibres.**

Fibres > **Thermoplastics** > **Elastomers**

Decreasing order of force of attraction

Thermosetting Polymers

They are cross-linked
or heavily branched polymers.

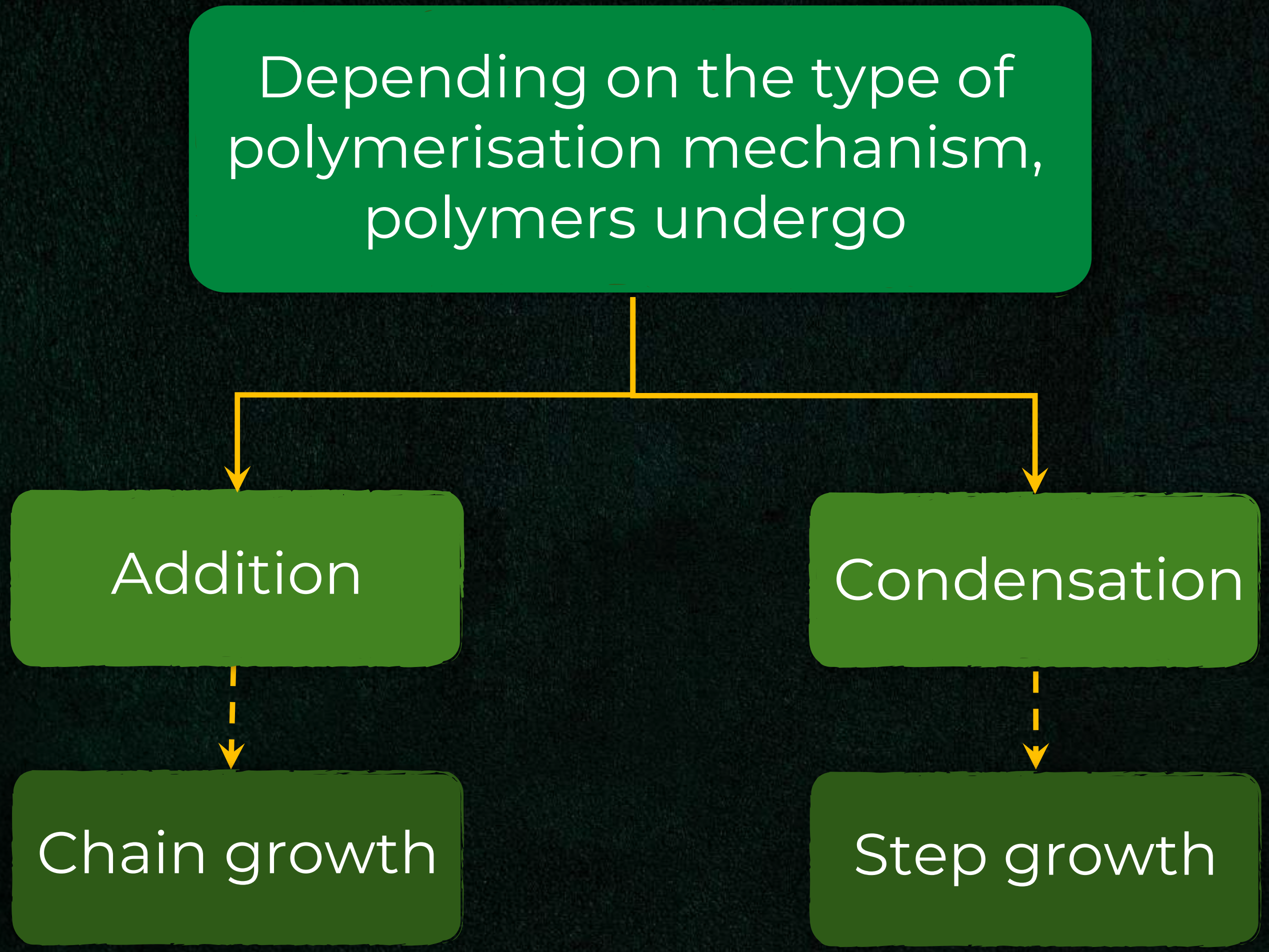
On heating, they undergoes extensive cross-linking in moulds and again become **infusible.**

Cannot be used

Bakelite, Urea-formaldehyde resins, and more

Thermoplastic	Thermosetting
It contains **long-chain linear polymers** and are held together by weak **van der Waals forces.**	It contains a **3D network** structure constructed with **strong covalent** bonds.
It usually becomes **soft** on **heating** and **hard** on **cooling.**	It does **not** become **soft** on **heating.**
It is **expensive.**	It is **less expensive.**
It is **soluble** in **organic** solvents.	It is **insoluble** in **organic solvents.**
It is usually **soft, weak,** and **less brittle** in nature.	It is usually **hard, strong,** and **more brittle** in nature.
It can be **remoulded.**	It **cannot** be **remoulded.**

Growth Polymerisation



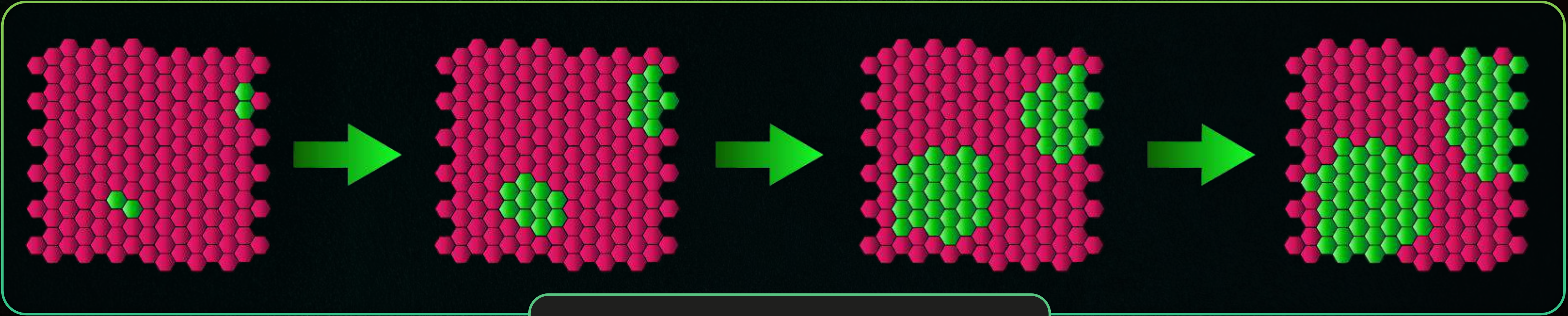
Depending on the type of polymerisation mechanism, polymers undergo

Addition

Chain growth

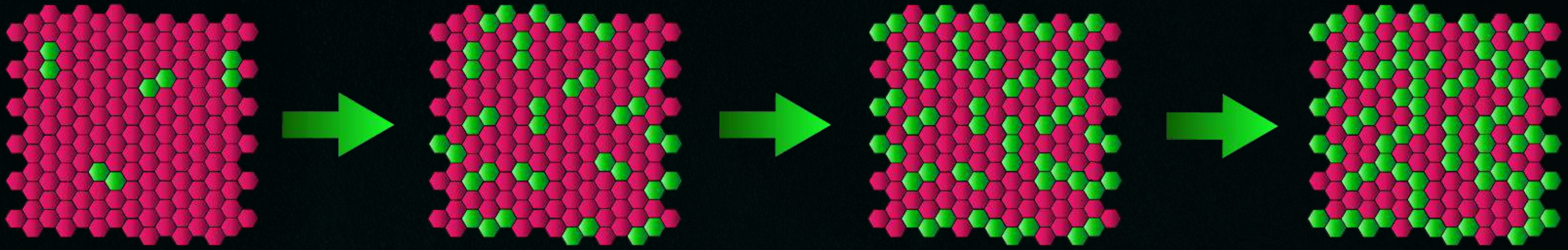
Condensation

Step growth



Chain Growth

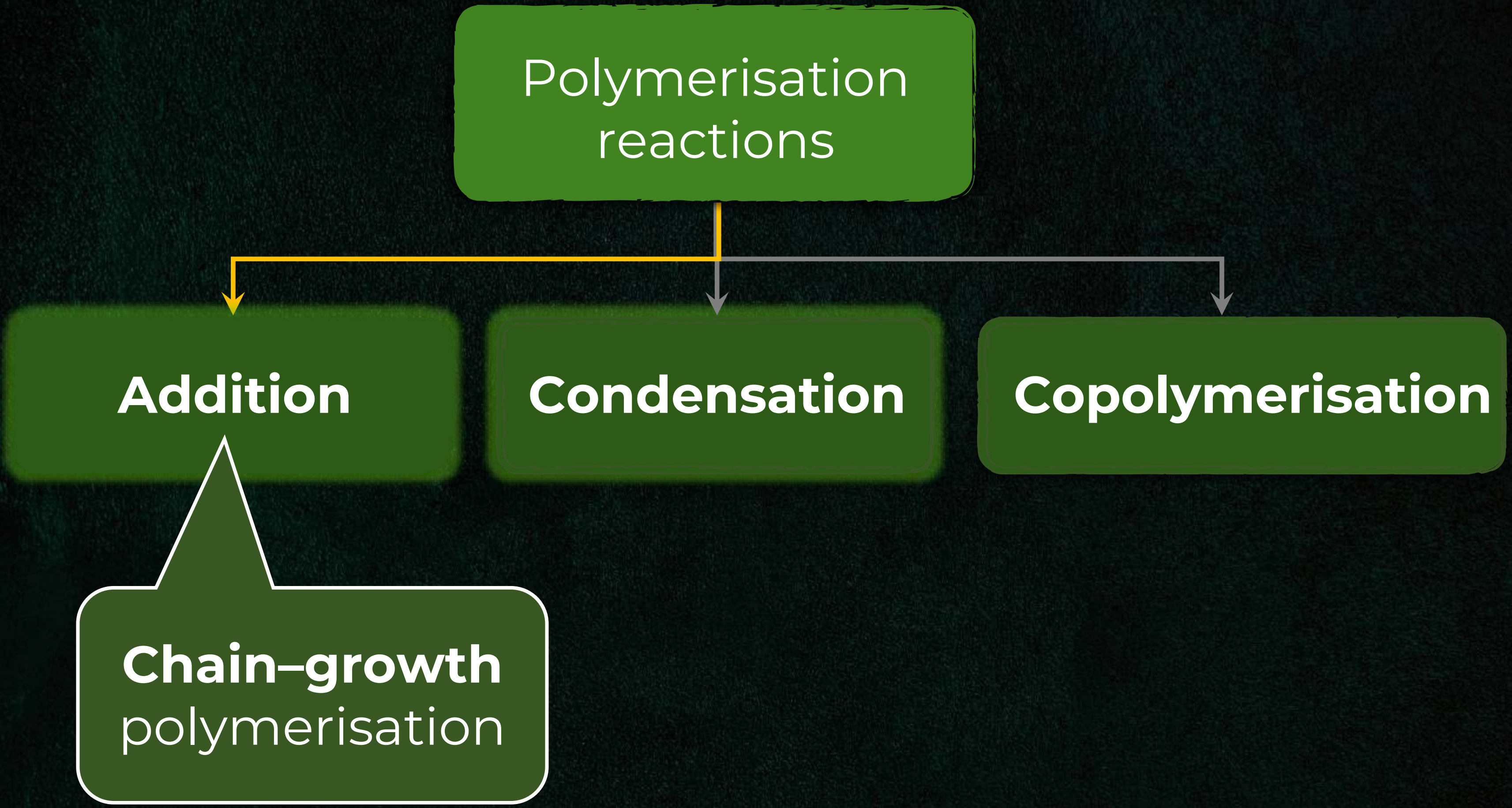
In this type of polymerisation, the molecules of the same monomer or different monomers add together on a large scale to form a polymer. The monomers used are unsaturated compounds. For example, alkenes, alkadienes and their derivatives. This mode of polymerisation leads to an increase in chain length, and chain growth can take place through the formation of either free radicals or ionic species. However, the free radical governed addition or chain-growth polymerisation is the most common mode.



Step Growth

The product of each step is again a bifunctional species, and the sequence of condensation goes on. Since each step produces a distinct functionalised species and is independent of each other, this process is also known as step-growth polymerisation.

Types of Polymerisation Reactions



Polymerisation reactions

Addition

Condensation

Copolymerisation

Chain–growth polymerisation

Addition Polymerisation

The molecules of same **monomer** or **different monomers** add together

This mode leads to an **increase** in the chain length.

Example

Polymerisation of **ethene** to **polythene**

$$n\,CH_2{=}CH_2 \xrightarrow[\text{peroxide}]{\text{Benzoyl}} \left[-CH_2-CH_2-\right]_n$$

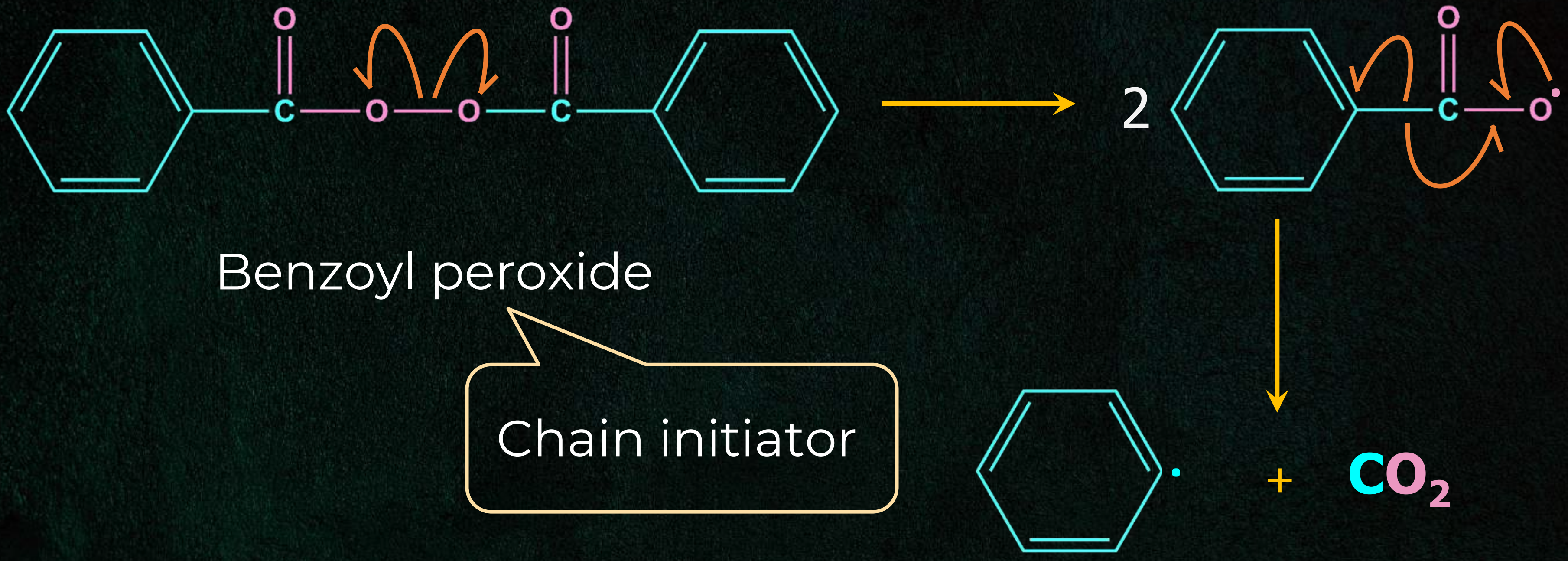
Mechanism of Addition Polymerisation

The mechanism of addition polymerisation involves **three steps.**

Generally, in addition polymerisation, an **increase in chain** length is **governed** by **free radical mechanism**.

Step 1	Chain initiation
Step 2	Chain propagation
Step 3	Chain termination

Chain Initiation



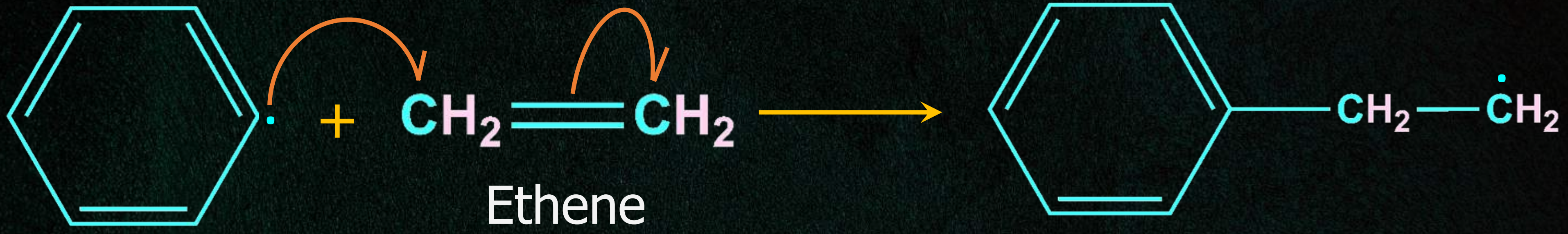
Benzoyl peroxide

Chain initiator

Phenyl free radical

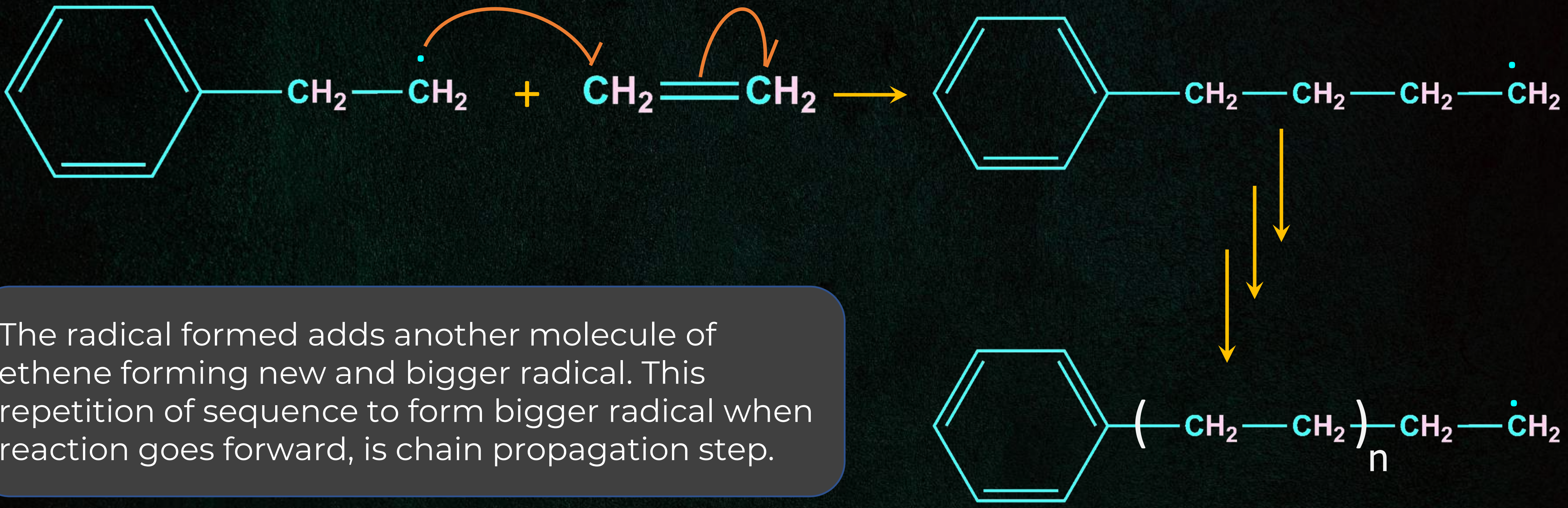
The process starts with generation of phenyl radical from benzoyl peroxide

Chain Initiation



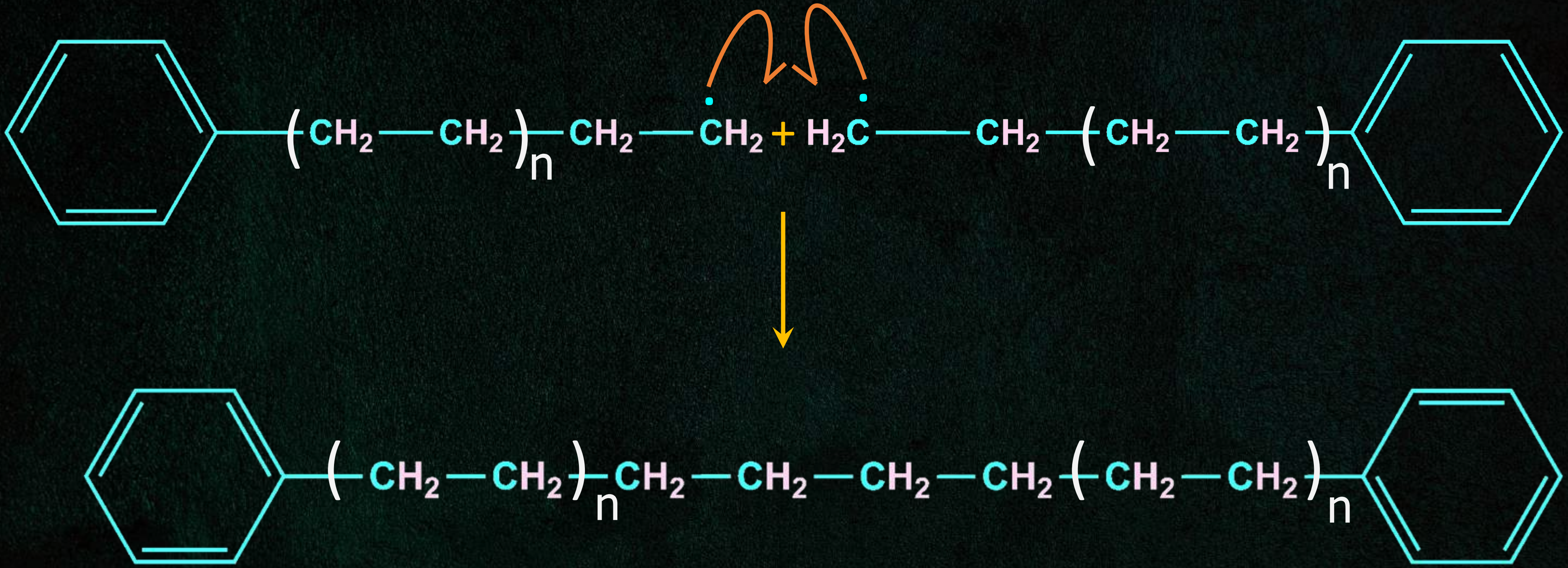
Here, phenyl radical formed adds to the ethene double bond and thus generating a new and larger radical.

Chain Propagation



The radical formed adds another molecule of ethene forming new and bigger radical. This repetition of sequence to form bigger radical when reaction goes forward, is chain propagation step.

Chain Termination



At certain stage, the two radicals combine with each other to form the polymeric product. It is the chain terminating step.

Addition Polymers

Addition polymers

- Polythene
  - Low density
  - High density
- Polytetrafluoroethene
- Polyacrylonitrile

Low Density Polythene (LDP)

It is obtained by the polymerisation of ethane under **certain conditions (**High pressure **1000–2000 atm,** Temperature **350–570 K**) in the presence of **O2** or a **peroxide initiator**.

Reaction

$$n\,CH_2{=}CH_2 \xrightarrow[1000\text{–}2000\ \text{atm}]{O_2,\ 350\text{–}570\ \text{K}} \left[-CH_2-CH_2- \right]_n$$

LDP

Reaction occurs by **free radical mechanism.**

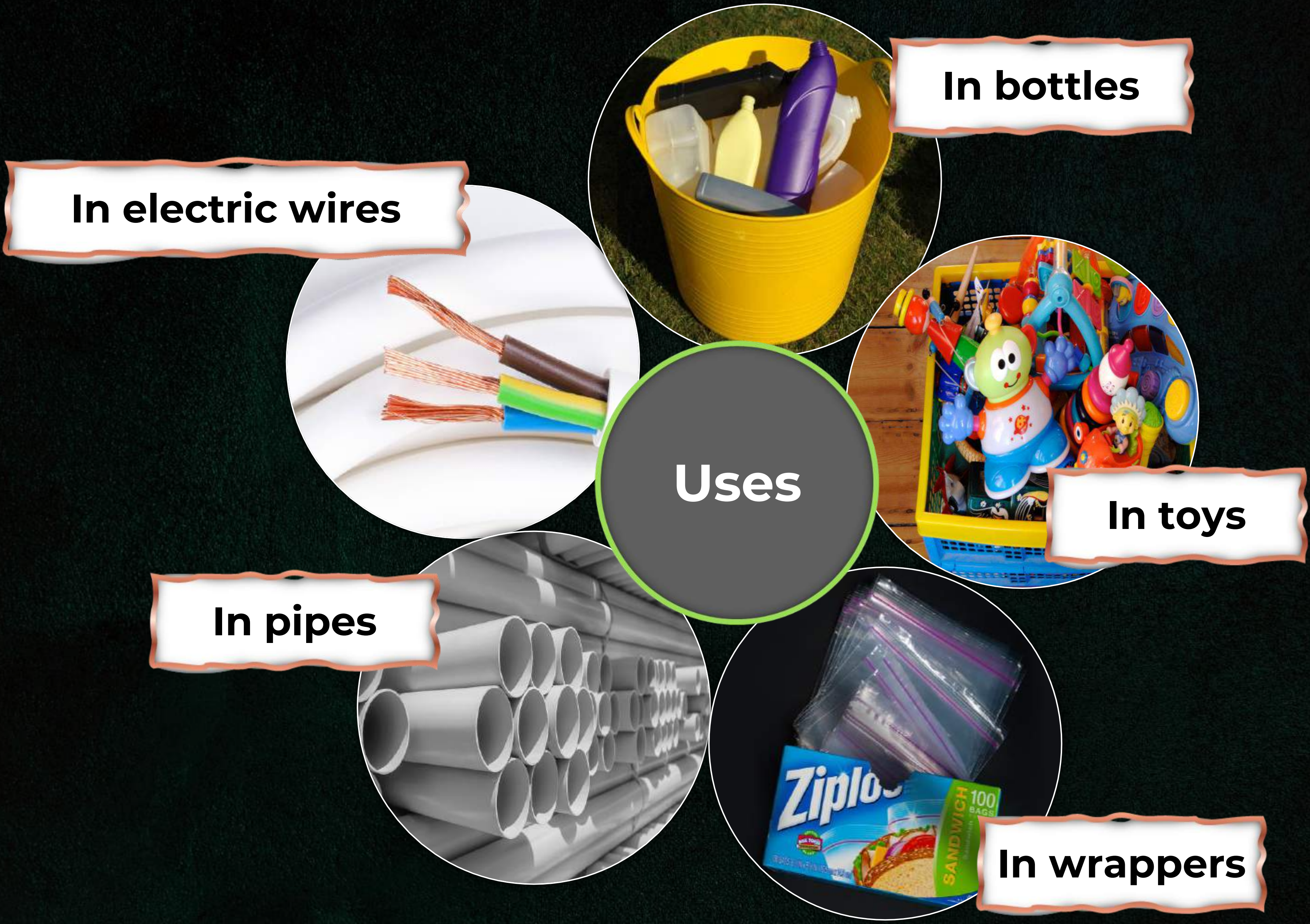
Characteristics of LDP

01 Chemically **inert**

02 **Tough**

03 **Flexible**

04 **Poor** conductor of **electricity**



Uses

In bottles

In electric wires

In toys

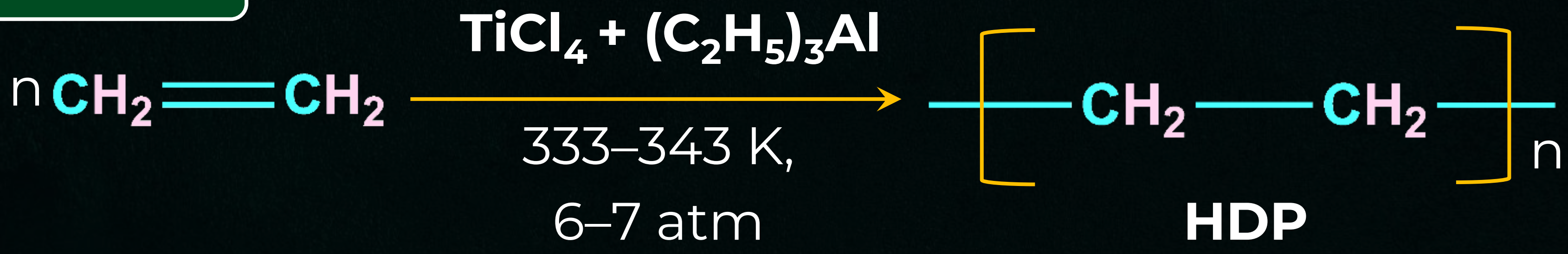
In pipes

In wrappers

High Density Polythene (HDP)

It is obtained by the addition polymerisation of **ethene** in a **hydrocarbon** solvent in the presence of a **catalyst (Ziegler–Natta catalyst)**.

Reaction



$$n\,CH_2{=}CH_2 \xrightarrow[\text{333–343 K, 6–7 atm}]{TiCl_4 + (C_2H_5)_3Al} \left[-CH_2-CH_2-\right]_n$$

HDP

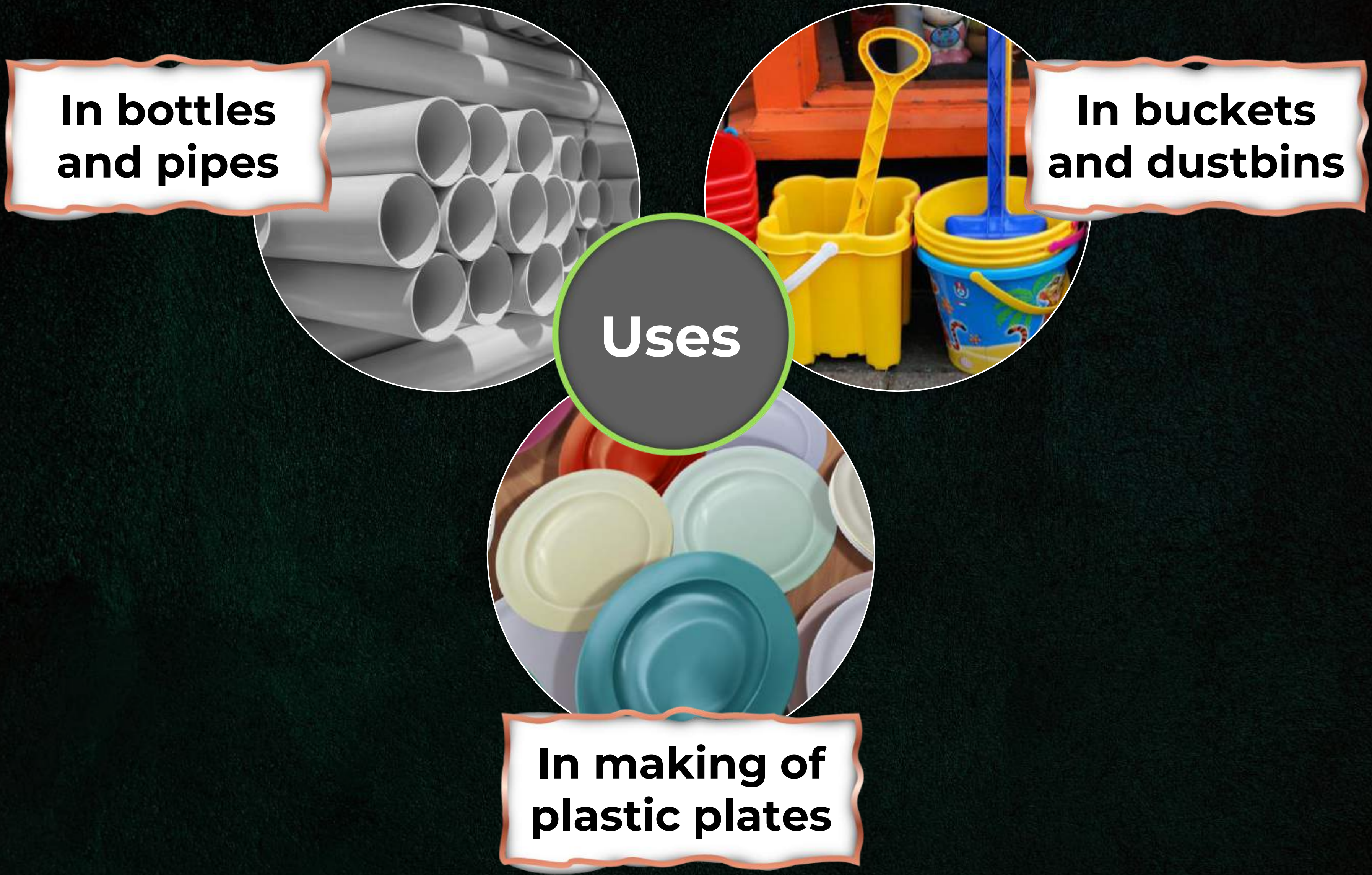
Low temperature and **pressure** is required.

Characteristics of HDP

01 Highly **dense**

02 Chemically **inert**

03 **Tougher** and **harder**



Uses

In bottles and pipes

In buckets and dustbins

In making of plastic plates

Teflon

It is manufactured by heating **tetrafluoroethene** with any **free radical** or **persulphate catalyst.**

At high **pressure**

Reaction

$$n\,CF_2{=}CF_2 \xrightarrow[\text{High pressure}]{\text{Persulphate}} \left[-CF_2-CF_2- \right]_n$$

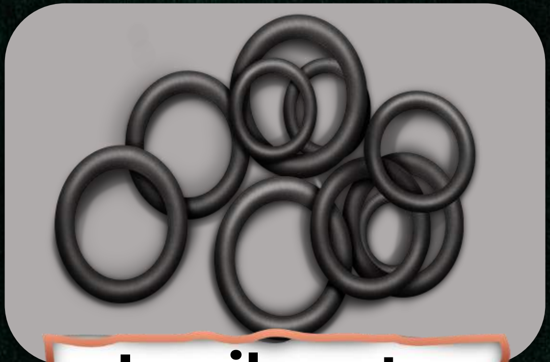
Teflon

Characteristics and Uses of Teflon

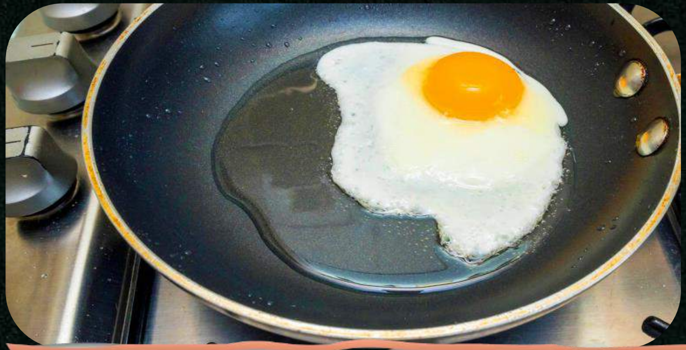
01 Chemically **inert**

02 Resistant to attack by **corrosive agents**

Uses



In oil seats and gaskets



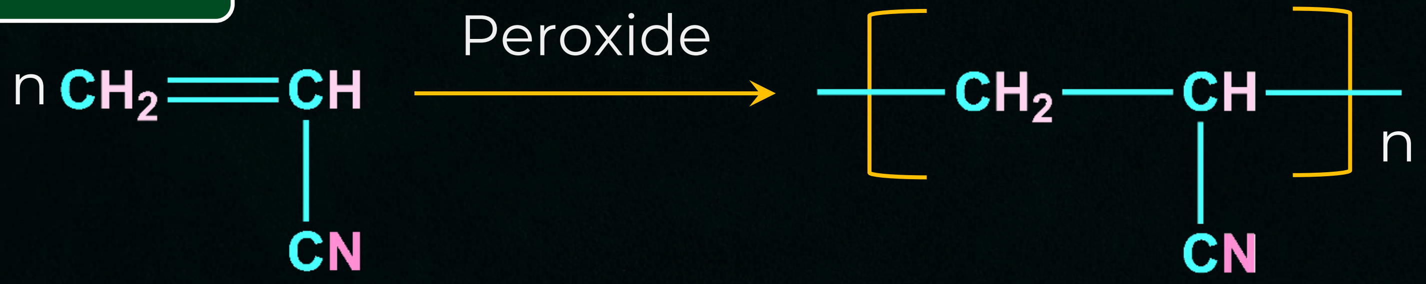
As surface coating on non-stick utensils

Polyacrylonitrile

It is obtained by the **addition** polymerisation of **acrylonitrile** in the presence of a **catalyst**.

Peroxide

Reaction



$$n\,CH_2=\underset{\underset{CN}{|}}{CH} \xrightarrow{\text{Peroxide}} -\left[CH_2-\underset{\underset{CN}{|}}{CH} \right]_n-$$

Polyacrylonitrile (PAN)

Condensation Polymerisation

Generally, it involves repetitive **condensation** between two **bifunctional** groups with **loss** of simple molecules.

H_2O, ROH, and HCl

The product of each step is again, a **bifunctional** species. Thus, the sequence goes on.

Step growth

Polyamides

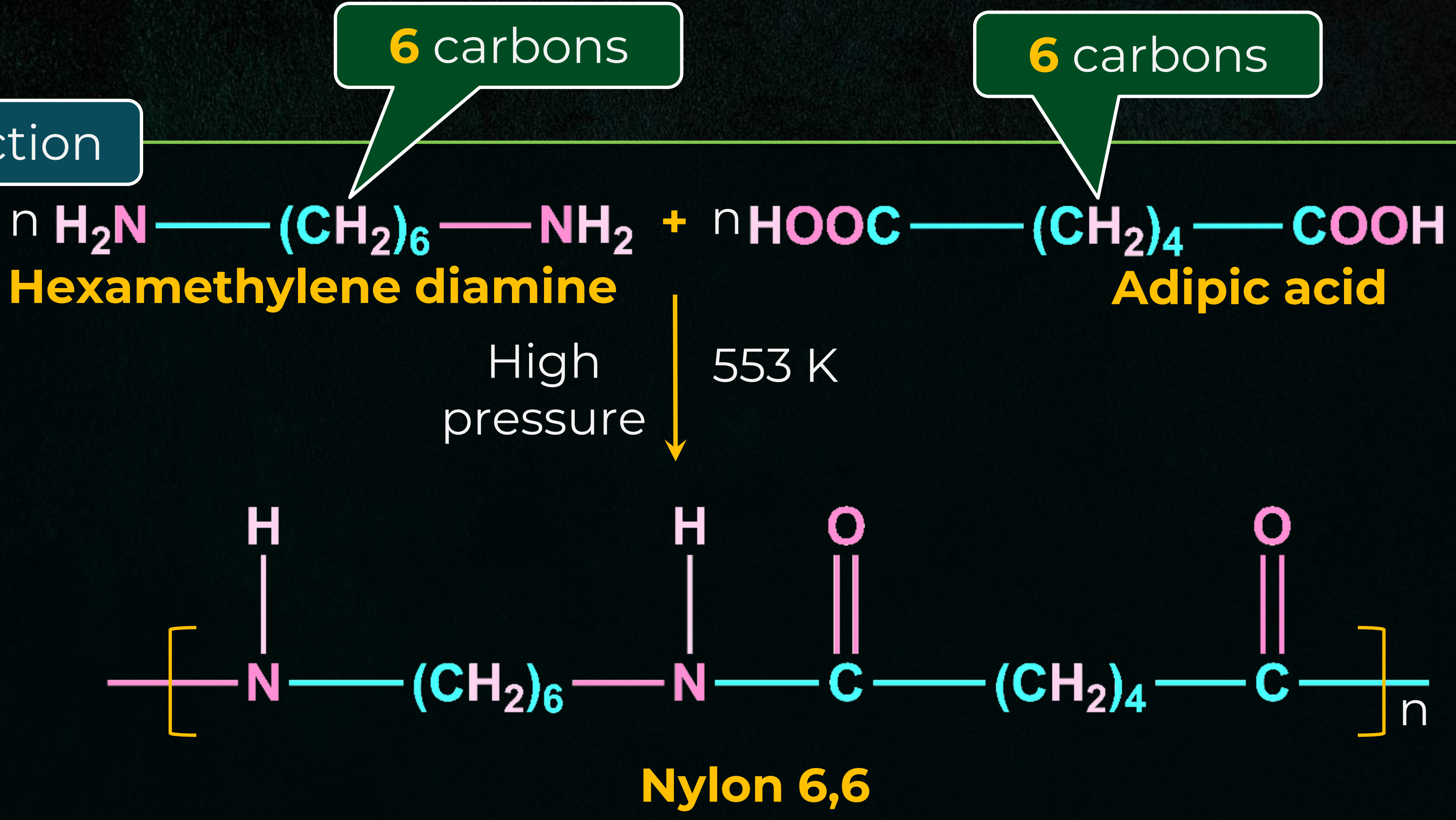
Generally, it is prepared by the condensation polymerisation of **diamines** with **dicarboxylic acids**.

They possess **amide linkages** and are an important class of **synthetic fibres.**

Nylons

Nylon 6,6

Reaction



6 carbons

6 carbons

$$n\,H_2N-(CH_2)_6-NH_2 + n\,HOOC-(CH_2)_4-COOH \xrightarrow[\text{553 K}]{\text{High pressure}} \left[-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$$

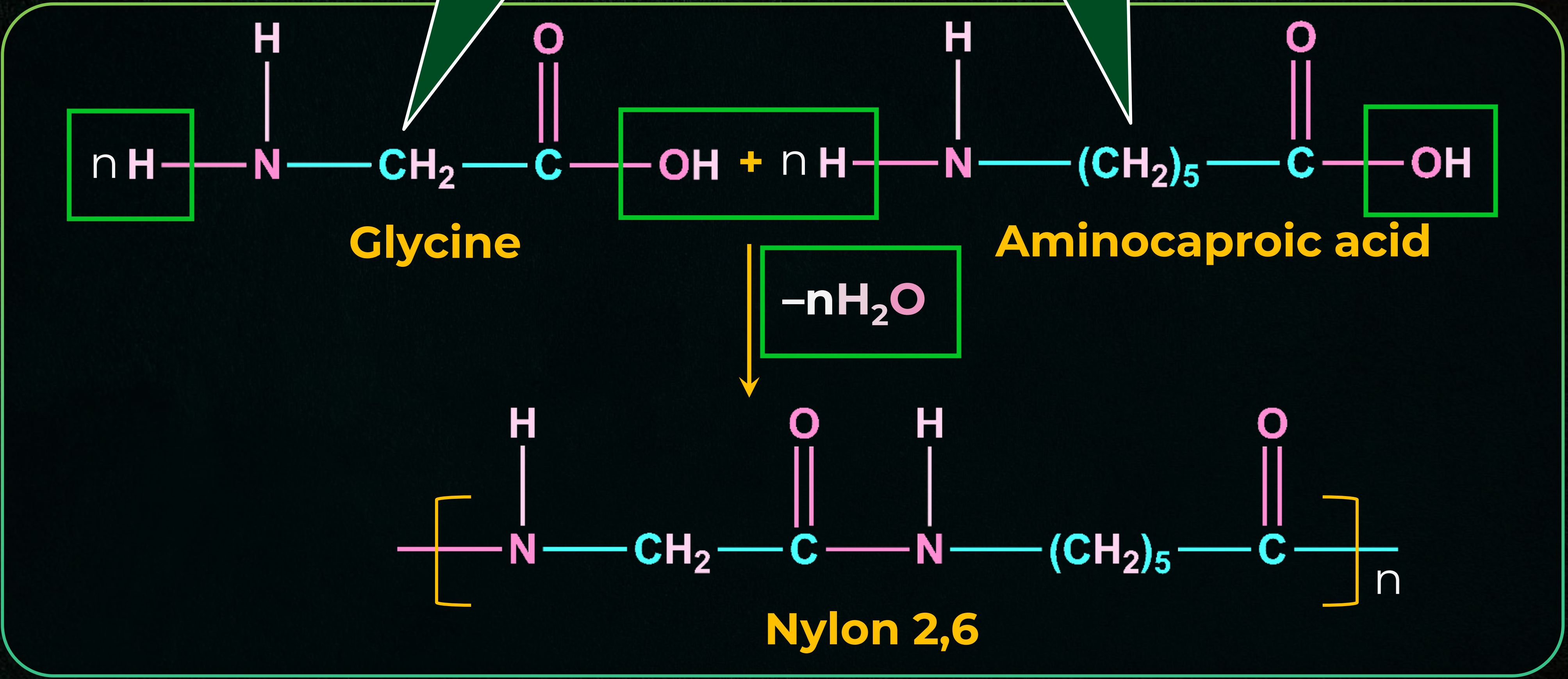
Hexamethylene diamine

Adipic acid

Nylon 6,6

Nylon 2,6

Reaction



$$n\,H-\overset{H}{\overset{|}{N}}-CH_2-\overset{O}{\overset{\|}{C}}-OH + n\,H-\overset{H}{\overset{|}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{-nH_2O} \left[-\overset{H}{\overset{|}{N}}-CH_2-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-\right]_n$$

2 carbons

6 carbons

Glycine

Aminocaproic acid

$-nH_2O$

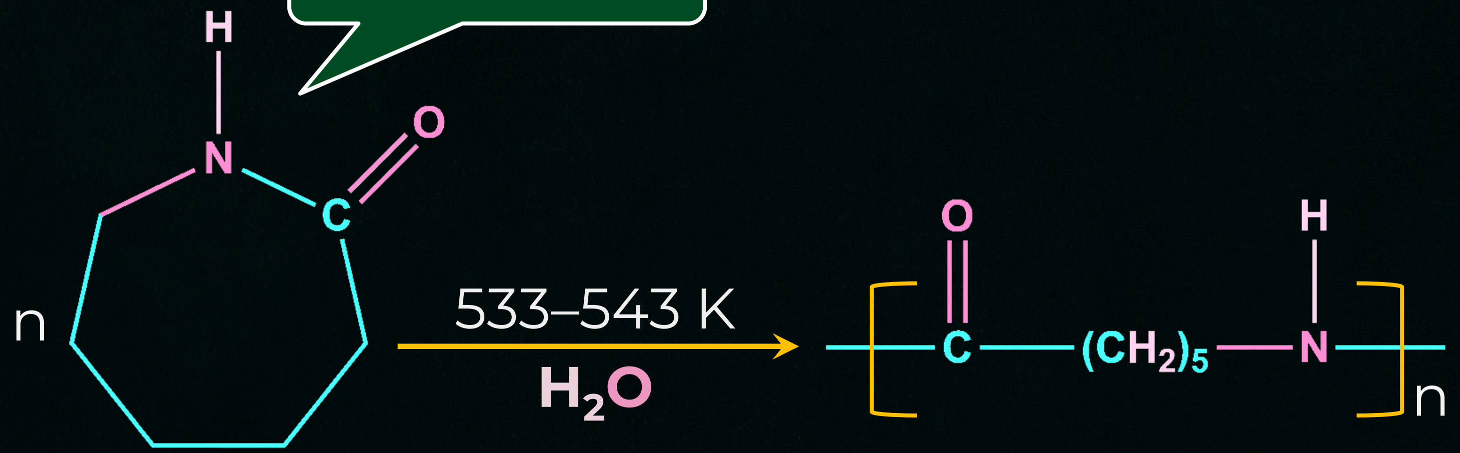
Nylon 2,6

Nylon 6

It is obtained by heating **caprolactum** with **water** at a high temperature

Reaction

6 carbons



Caprolactam

Nylon 6

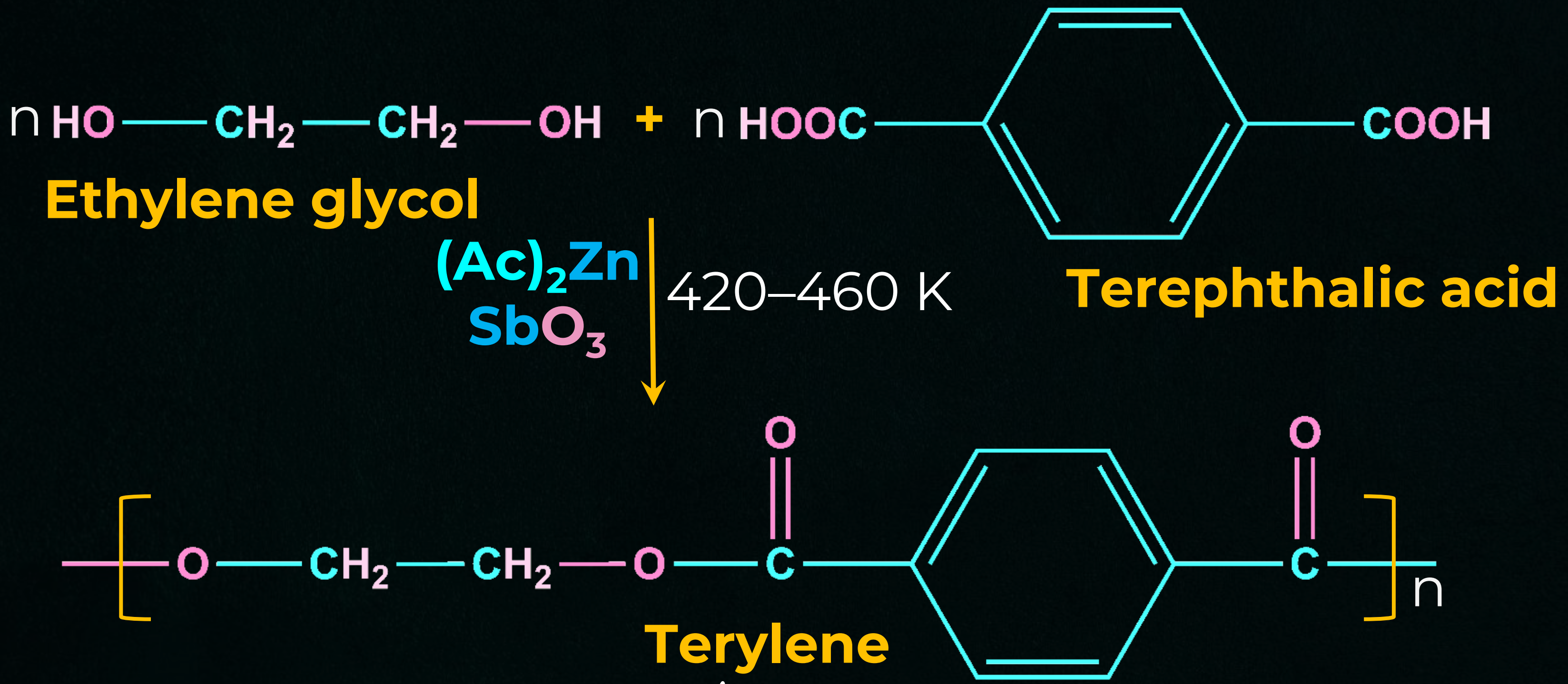
Polyester

Polycondensation products of **dicarboxylic acids** and **diols**.

Examples: **Dacron** or **Terylene**

It is manufactured by heating a mixture of **ethylene glycol** and **terephthalic acid** at 420 to 460 K in the presence of **zinc acetate-antimony trioxide catalyst.**

Dacron/Terylene



Crease resistant

Uses

- In footwear
- Water repellent
- In woollen fibres
- In safety helmets

Phenol-Formaldehyde Polymer

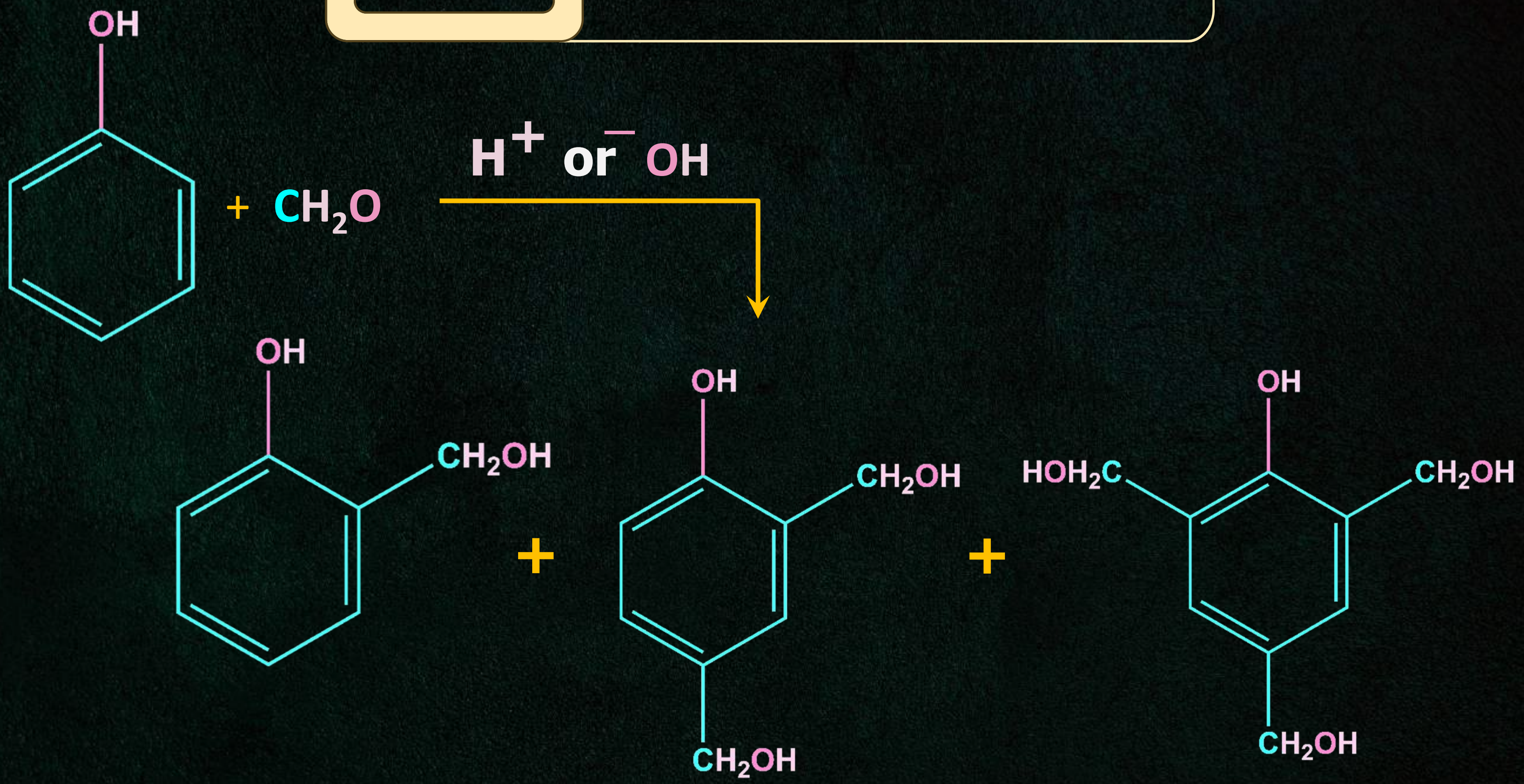
It is obtained by the condensation reaction of **phenol** with **formaldehyde.**

In the presence of an **acid** or a **base catalyst**

Phenol-Formaldehyde Polymer

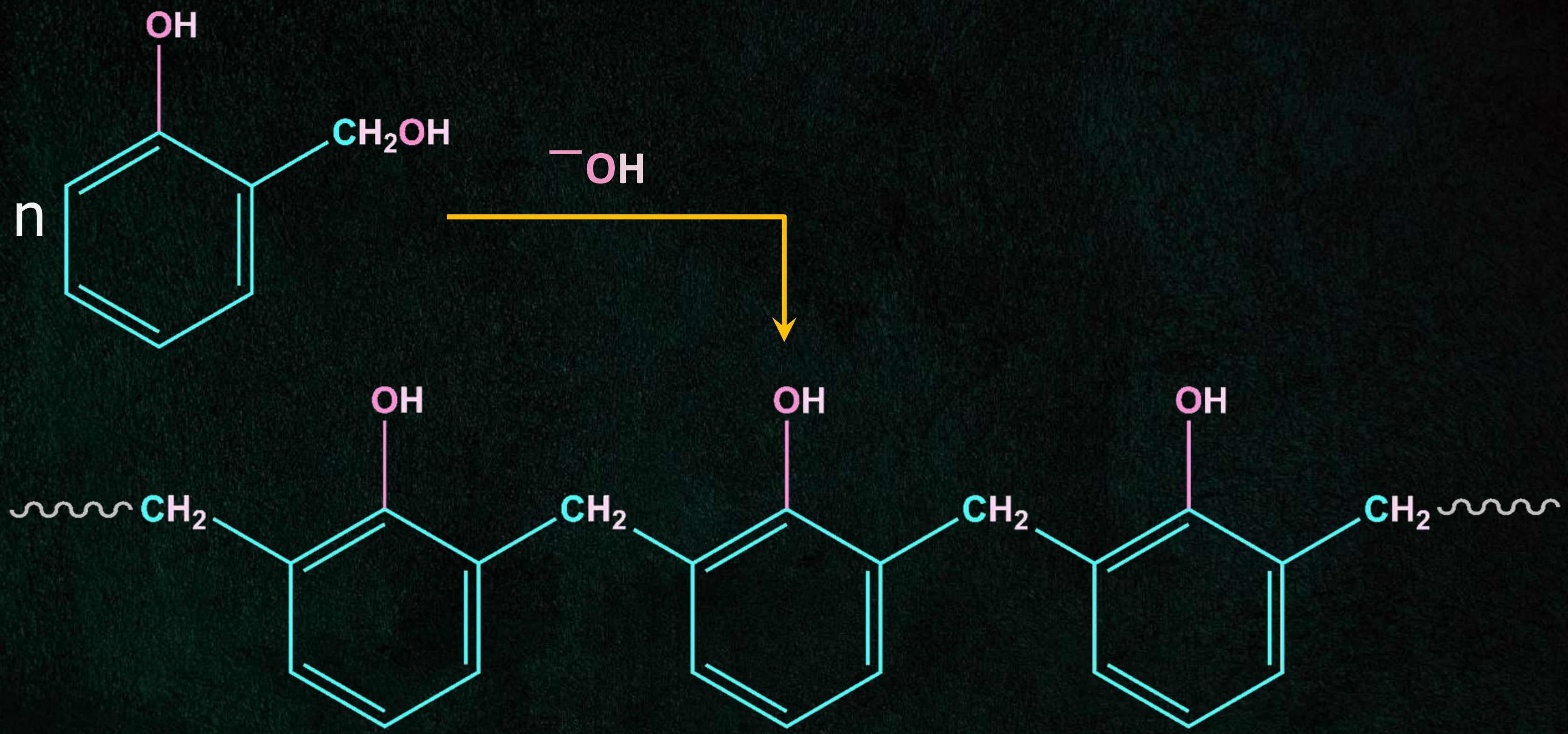
Preparation

Step 1 Formation of **novolac**



o-Hydroxymethyl phenol derivatives

Phenol-Formaldehyde Polymer



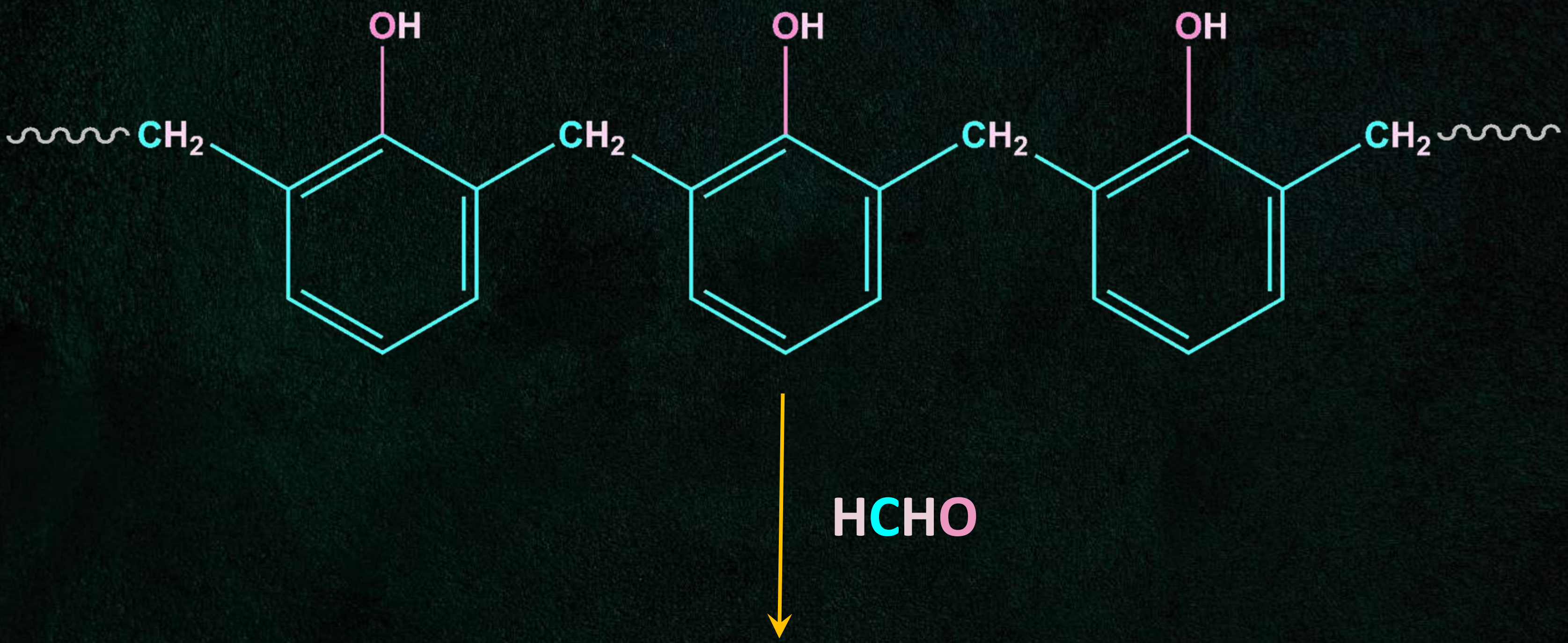
Novolac

Used in **paints**

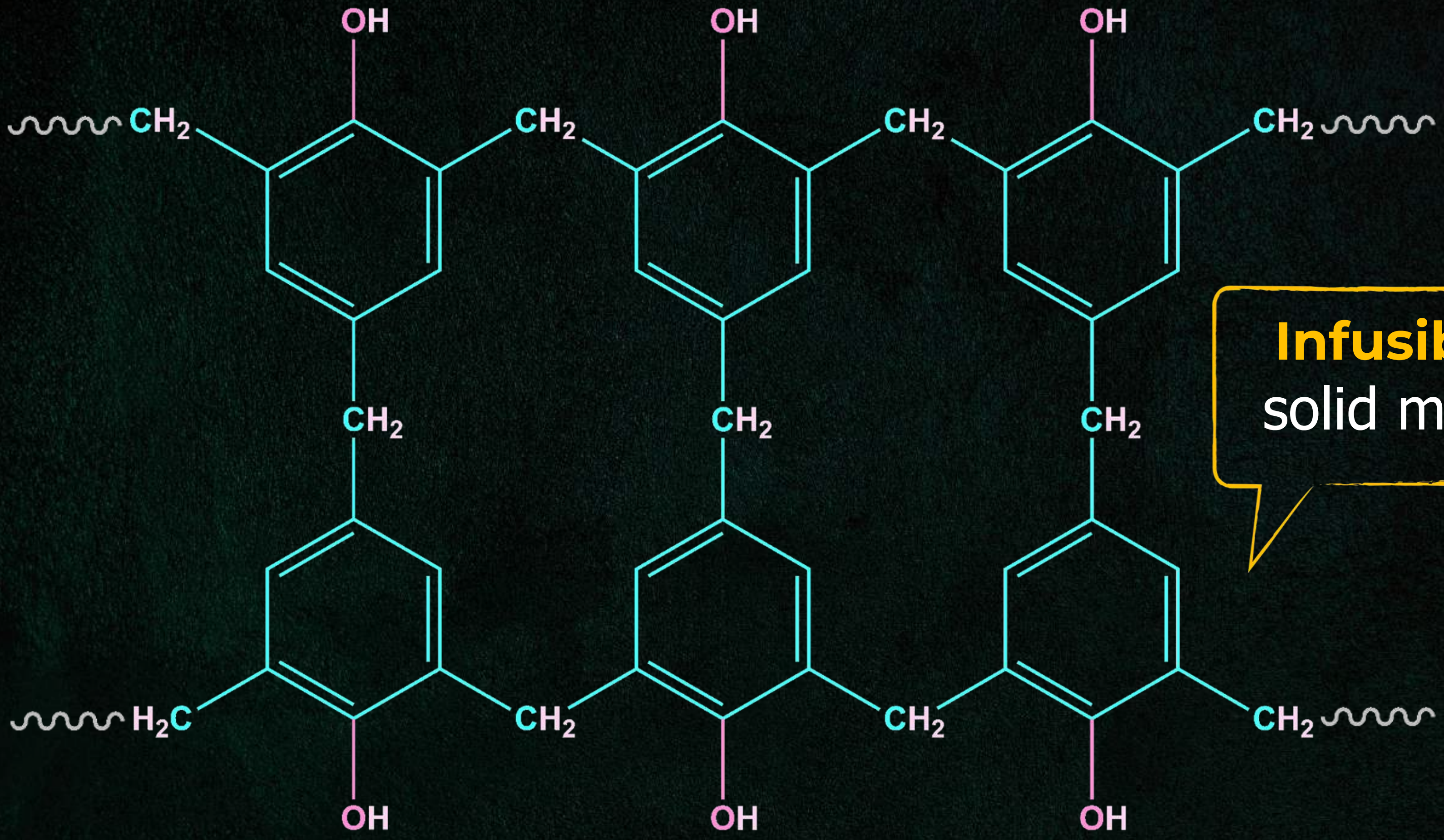
Phenol-Formaldehyde Polymer

Step 2

Novolac, on heating with HCHO, undergoes crosslinking to form **Bakelite.**



Phenol-Formaldehyde Polymer

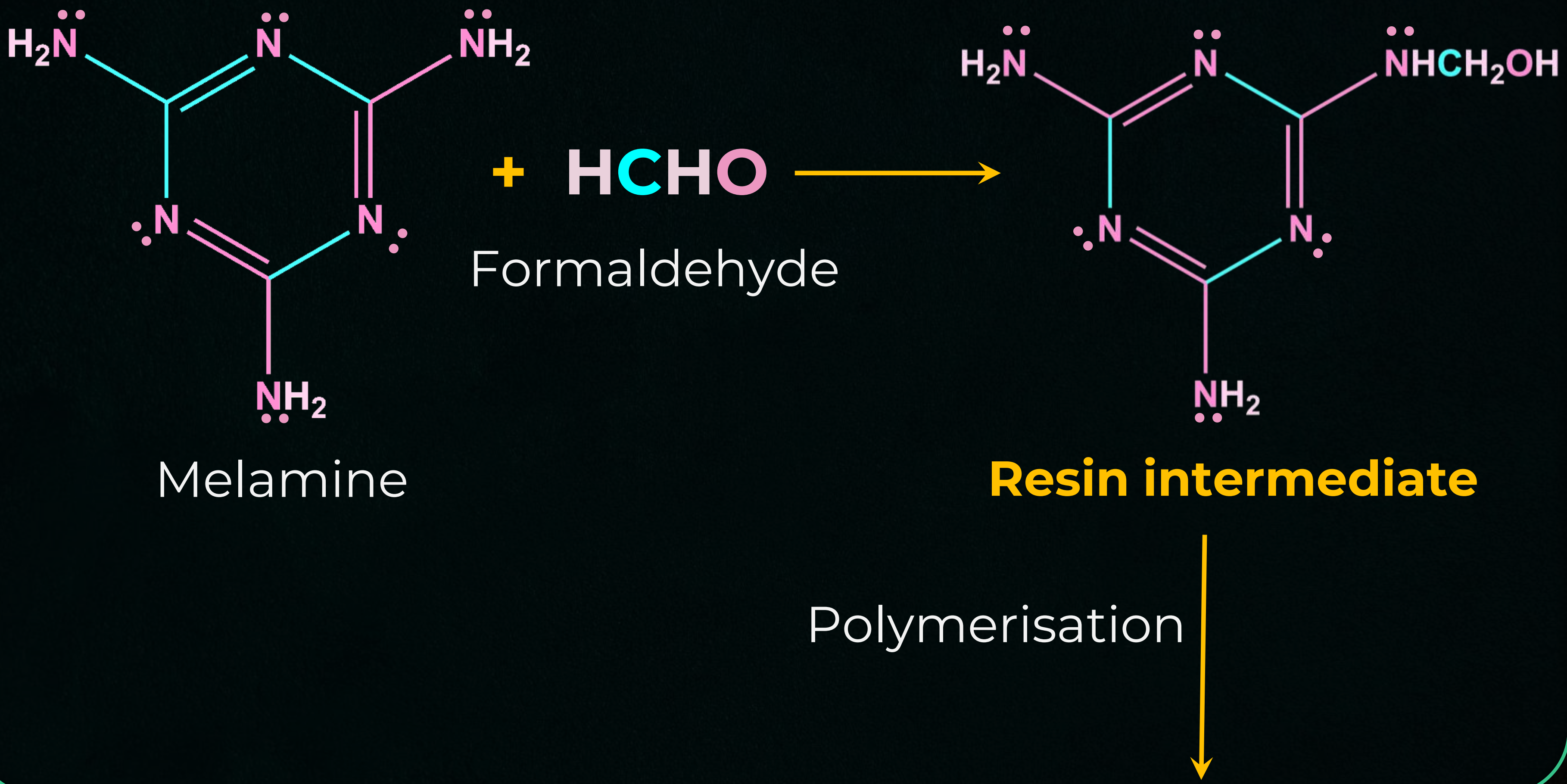


Infusible solid mass

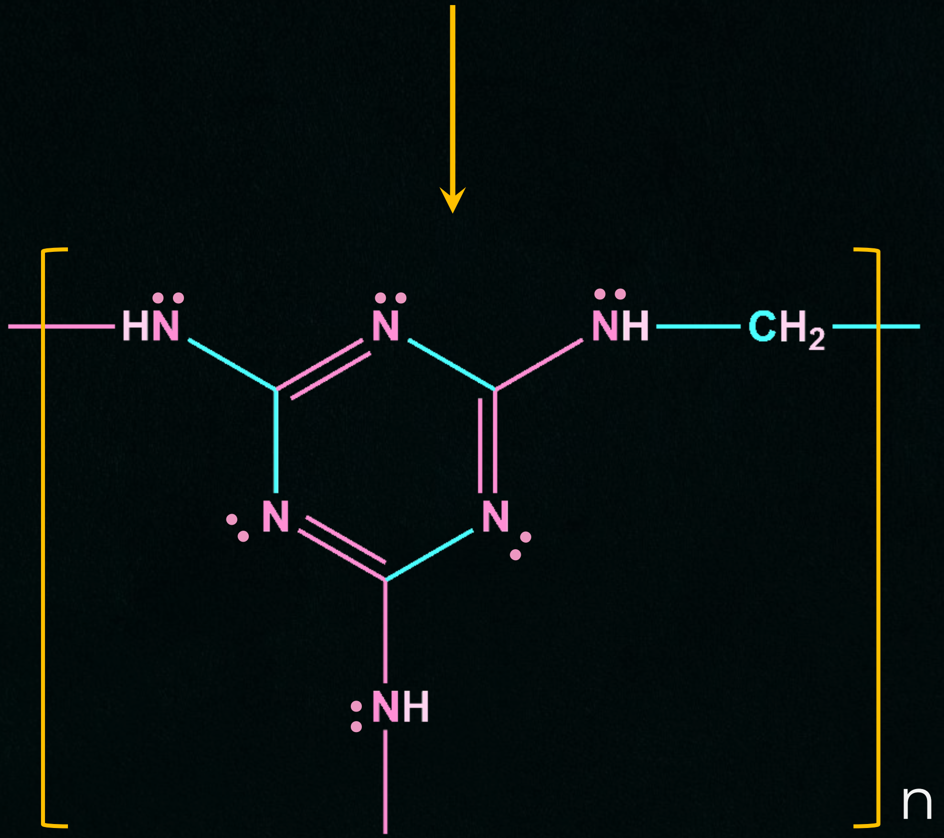
Bakelite

Melamine-Formaldehyde Polymer

It is formed by the condensation polymerisation of **melamine** and **formaldehyde**.



Melamine-Formaldehyde Polymer



Melamine–formaldehyde polymer

Used in Making of Unbreakable Crockery

Types of Polymerisation Reactions

Polymerisation reactions

- Addition
- Condensation
- Copolymerisation

Made by **chain growth** as well as **step growth**

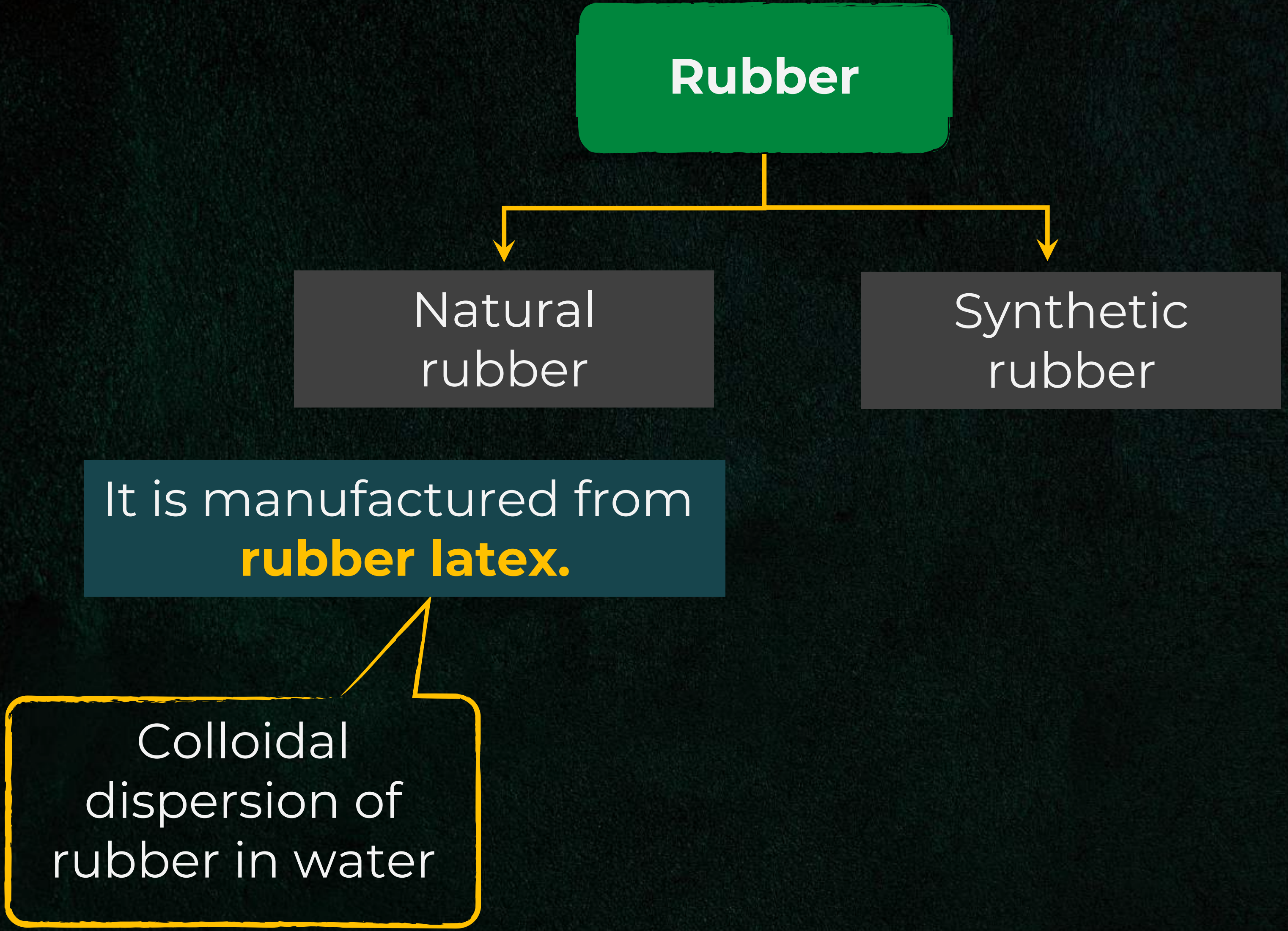
Copolymerisation

Polymerization reaction in which **more than one monomeric** species are allowed to polymerize.

Example

Buna-S

Rubber



Rubber

Natural rubber

Synthetic rubber

It is manufactured from **rubber latex.**

Colloidal dispersion of rubber in water

Natural Rubber

It is a **linear** polymer of **isoprene.**

2-Methyl-1,3-butadiene

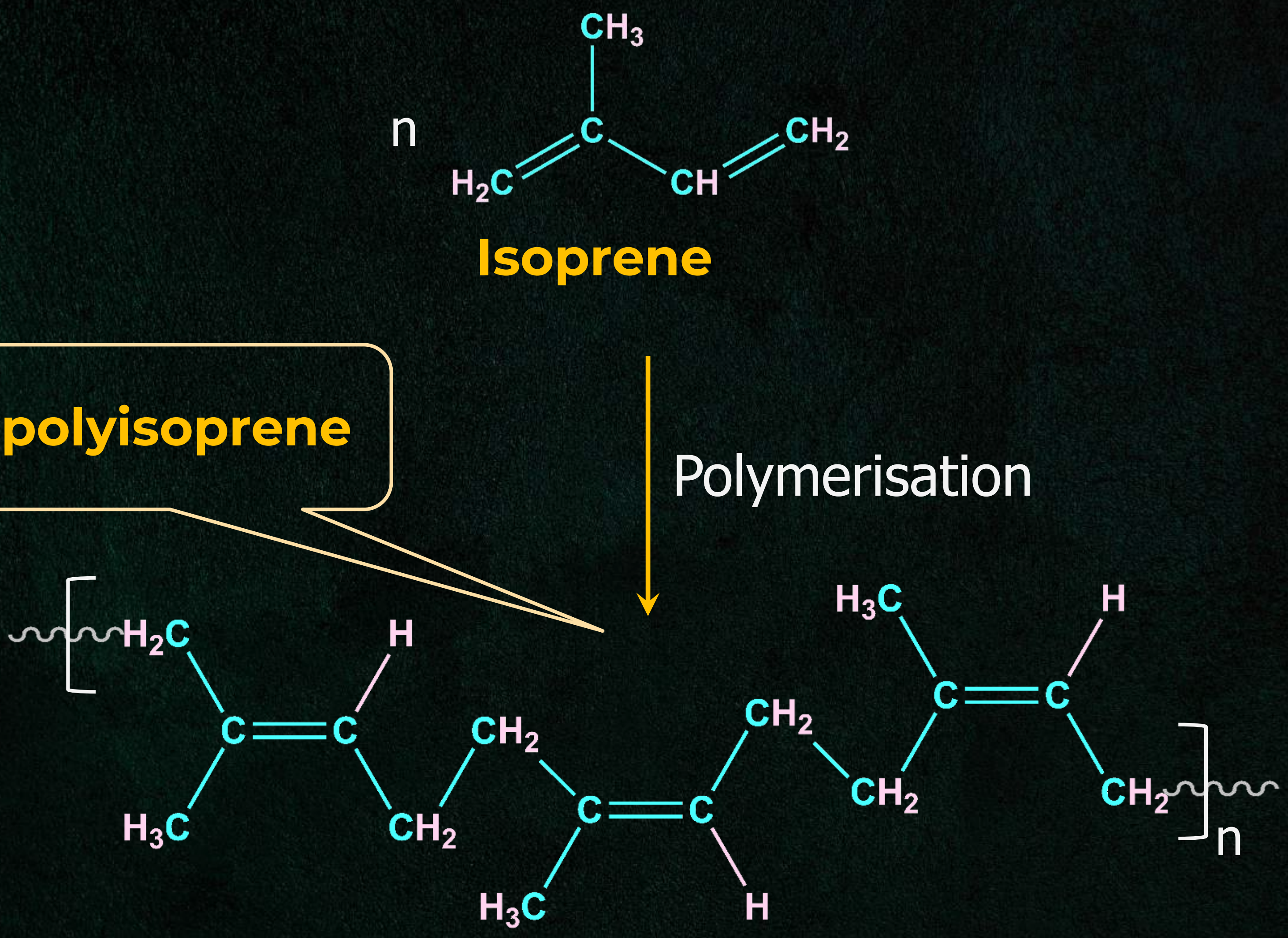
Also known as **cis-1,4-polyisoprene**

Cis-polyisoprene consists of chains held together by weak **van der Waals interaction.**

And due to its coiled structure, it can be stretched like **spring.**

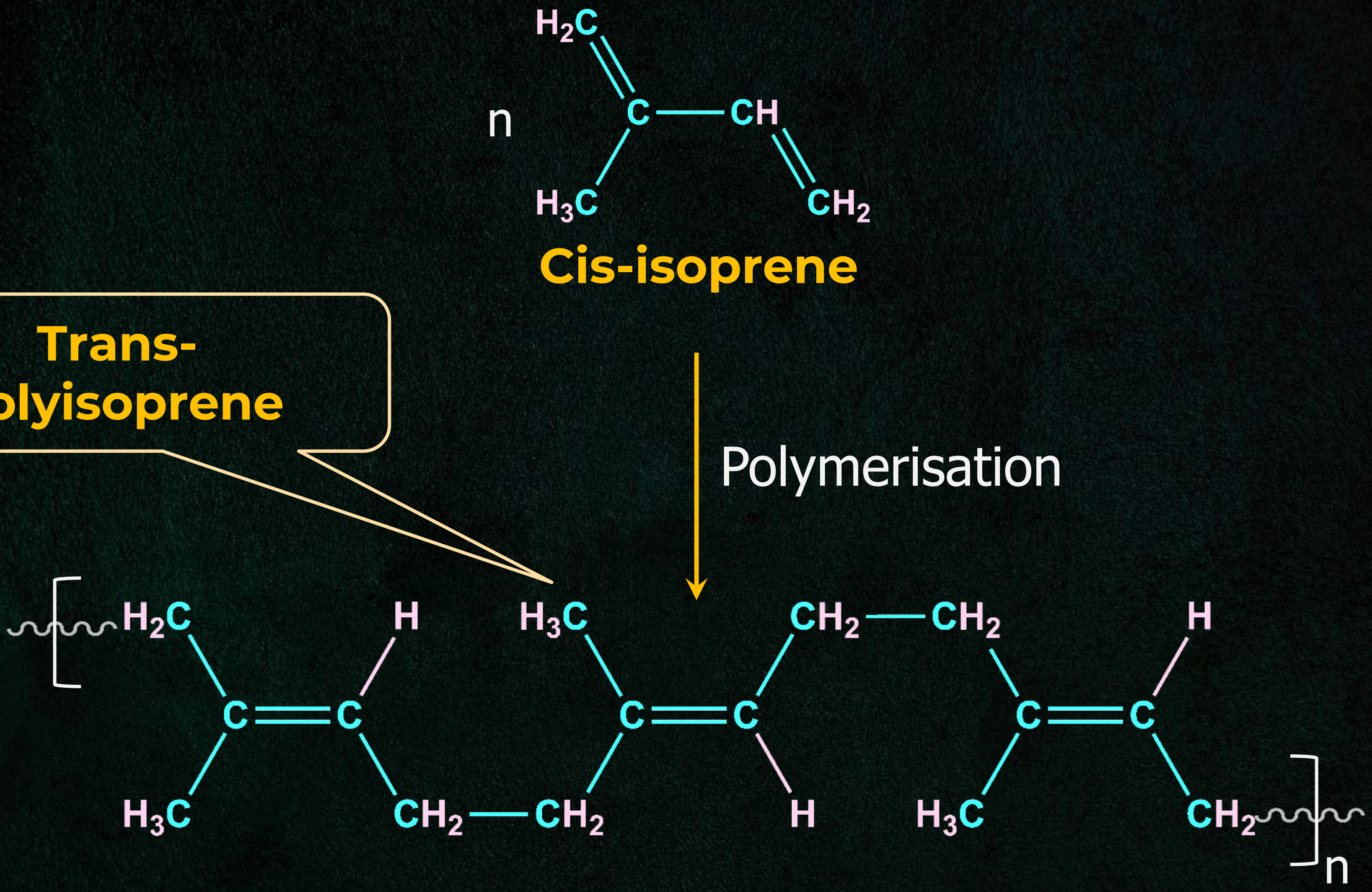
Elastic properties

Natural Rubber



Natural rubber

Gutta–Percha



Cis-isoprene

Polymerisation

Trans-polyisoprene

Gutta–percha

Gutta–Percha

Gutta–percha is **trans–isomer** of **polyisoprene.**

It is used to fill a teeth to prevent **reinfection.**

Natural rubber becomes **soft** at **high temperature** and **brittle** at **low temperature**.

> 335 K

< 283 K

Properties of Rubber

1. Soluble in **non-polar** solvents
2. Non-resistant to attack by **oxidising agents**
3. Shows **high** water absorption capacity

Vulcanisation

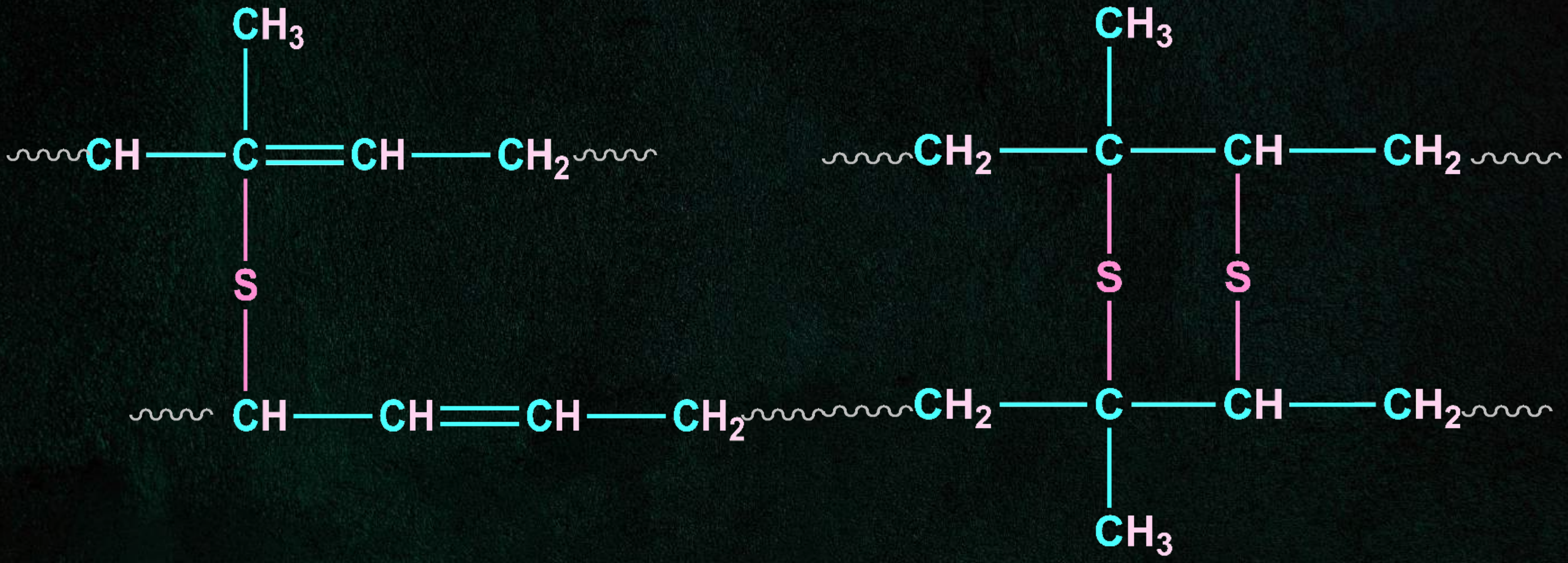
It involves heating a mixture of raw **rubber** with **sulphur** in a **temperature range**.

373–415 K

And **sulphur** forms **cross-links** at the reactive sites of double bonds.

Rubber stiffens

Structure of Vulcanised Rubber



Points to Remember

In the manufacture of **rubber tyres**

5% of **sulphur** is used as crosslinking agent.

Rubber

It is any **vulcanisable** rubber-like **polymer** that is capable of getting stretched to **twice** its **length**.

However, it returns to its **original shape** and **size** once the external force is released.

Examples: **Buna-N**, **Neoprene**

Neoprene

It is formed from polymerisation of chloroprene.

$$n\ CH_2{=}\overset{\overset{\displaystyle Cl}{|}}{C}-CH{=}CH_2 \xrightarrow{\text{Polymerisation}} \left[CH_2-\overset{\overset{\displaystyle Cl}{|}}{C}{=}CH-CH_2 \right]_n$$

Chloroprene

Neoprene

Resistant to **vegetable** and **mineral oils**

Uses

In gaskets

In hoses

In diving suits clothing

Biodegradable Polymer

Polymers that **undergo environmental degradation** and do **not** accumulates as **solid waste**

These polymers contain functional groups that are similar to functional groups present in **biopolymers.**

Proteins, carbohydrates, and more

Nylon 2,6

PHBV

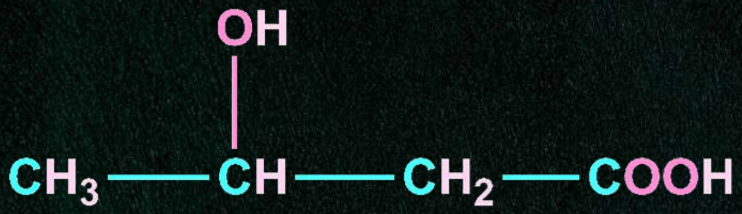
PHBV

3-Hydroxybutanoic acid

Poly-β-hydroxybutyrate-Co-β-hydroxyvalerate (PHBV)

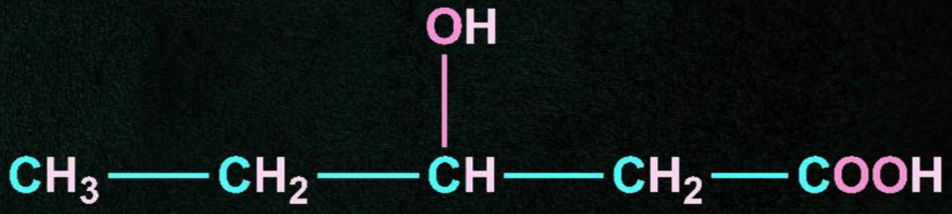
3-Hydroxypentanoic acid

PHBV



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-COOH$$

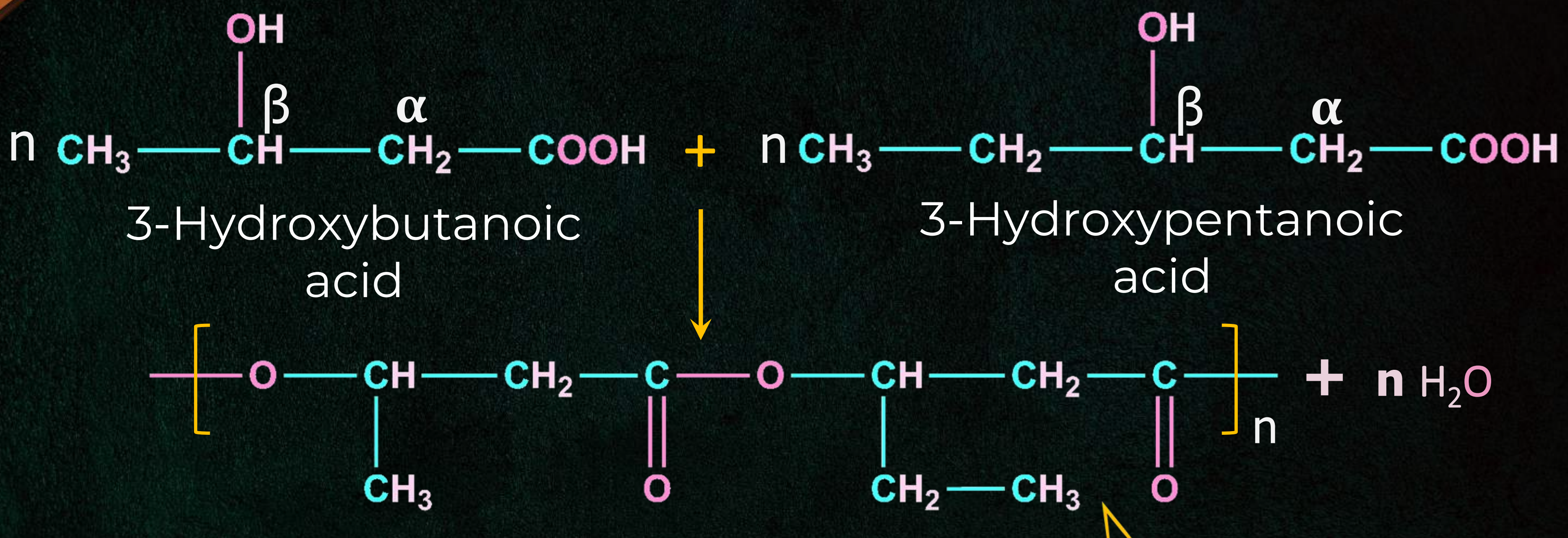
It is obtained by copolymerisation of **3-hydroxybutanoic acid** and **3-hydroxypentanoic acid.**



$$CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-COOH$$

PHBV

Reaction



$$n\ CH_3-\overset{\overset{OH}{|}\ \beta}{CH}-\overset{\alpha}{CH_2}-COOH + n\ CH_3-CH_2-\overset{\overset{OH}{|}\ \beta}{CH}-\overset{\alpha}{CH_2}-COOH$$

3-Hydroxybutanoic acid

3-Hydroxypentanoic acid

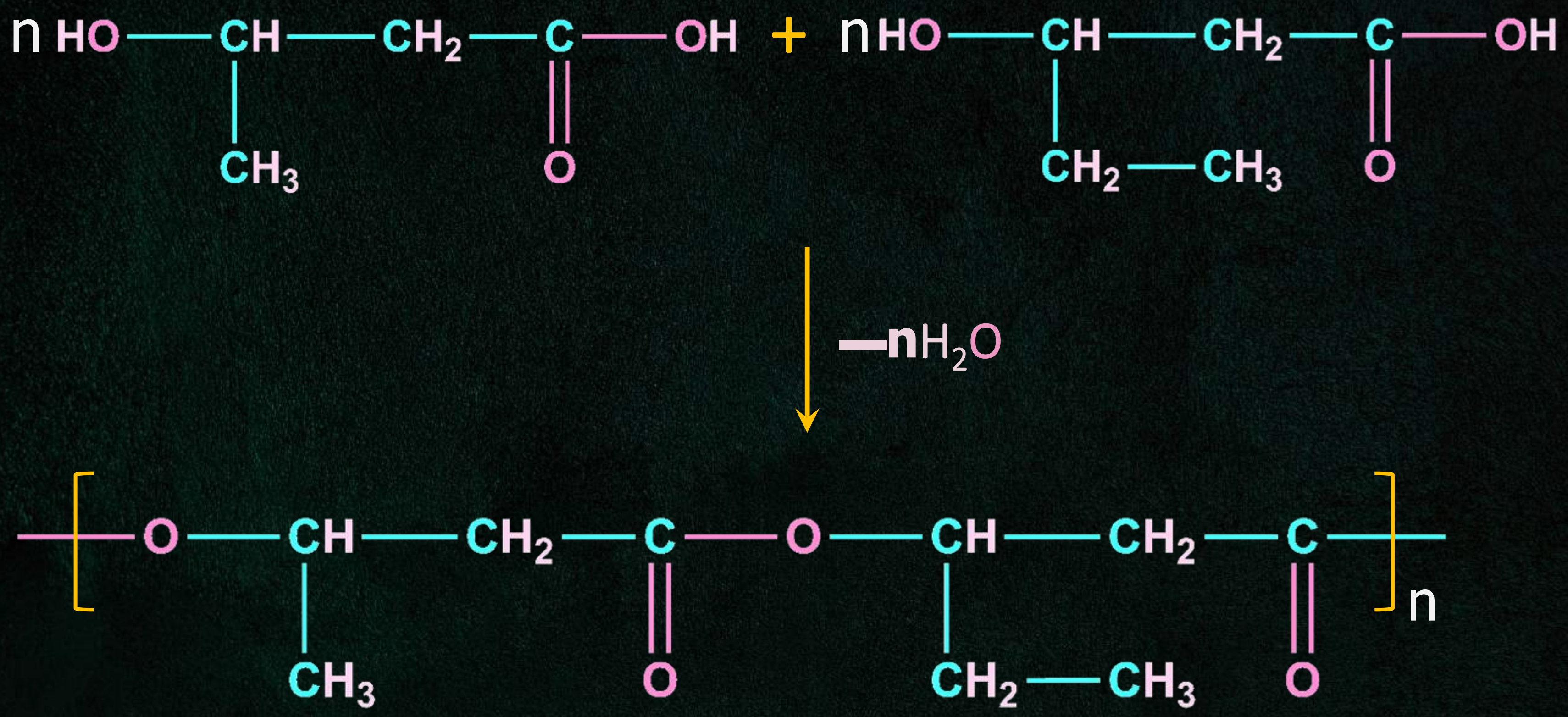
$$\downarrow$$

$$\left[-O-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{CH_2-CH_3}{|}}{CH}-CH_2-\underset{\underset{O}{\|}}{C}-\right]_n + n\ H_2O$$

PHBV

Undergoes **bacterial degradation**

PHBV



$$n\,HO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-OH + n\,HO-\underset{\displaystyle CH_2-CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-OH \xrightarrow{-nH_2O} \left[-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-O-\underset{\displaystyle CH_2-CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-\right]_n$$

Uses of PHBV

1. **Packaging**
2. **Orthopaedic** devices
3. **Controlled** release of **drug**

Polymers Used in Daily Life

Polymers

- Polypropene
- Polystyrene
- Polyvinyl chloride
- Urea-formaldehyde resin
- Glyptal

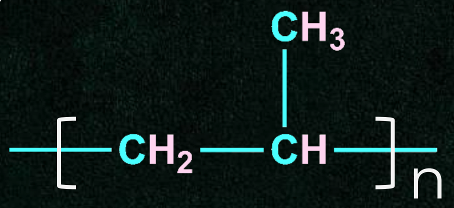
Polypropene

Polypropene

Monomer

Propene

Structure

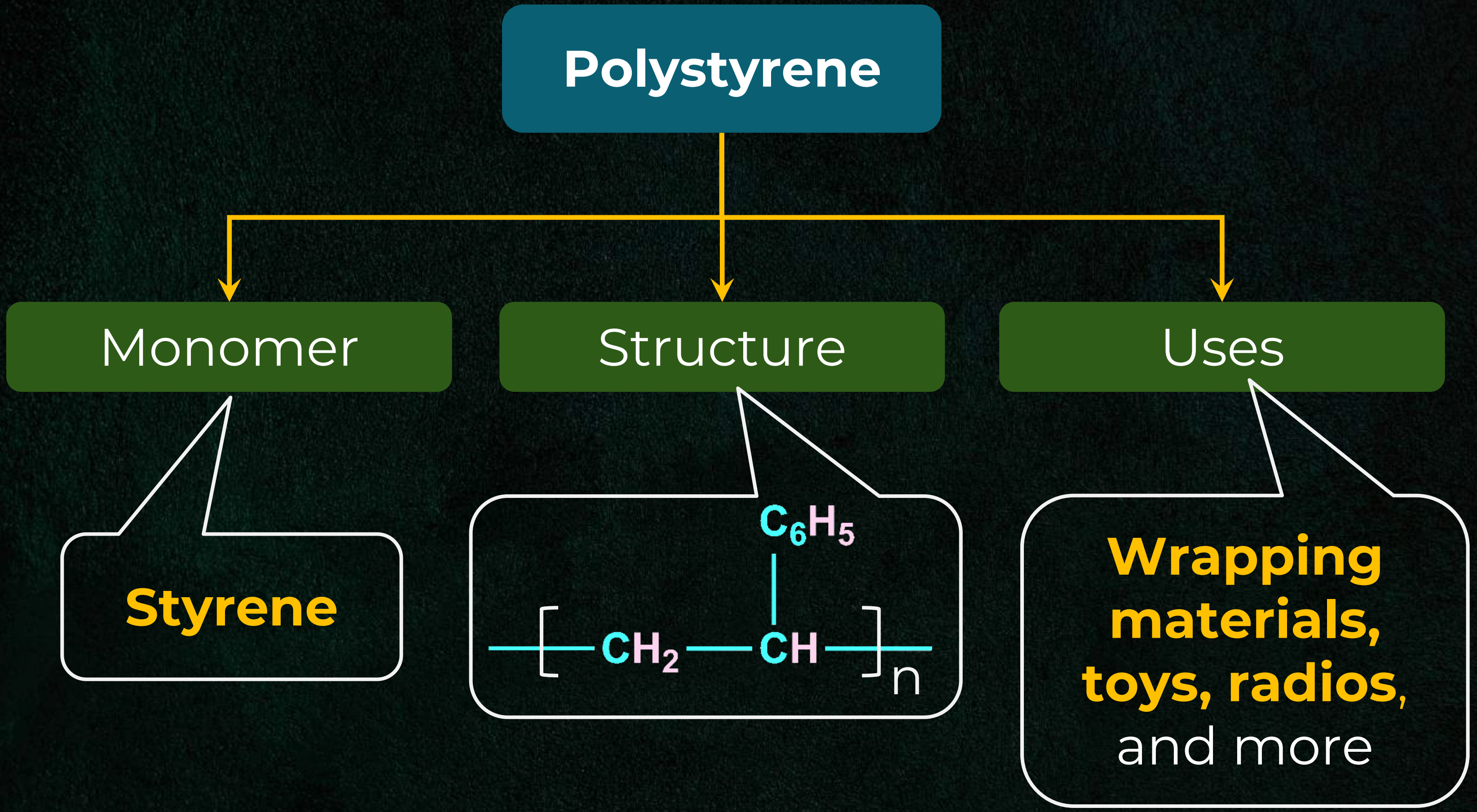


$$\left[-\mathrm{CH_2} - \overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{CH}} - \right]_n$$

Uses

Ropes, toys, pipes, and more

Polystyrene



Polystyrene

Monomer

Styrene

Structure

$$\left[\, CH_2 - \underset{}{\overset{\overset{\displaystyle C_6H_5}{|}}{CH}} \,\right]_n$$

Uses

Wrapping materials, toys, radios, and more

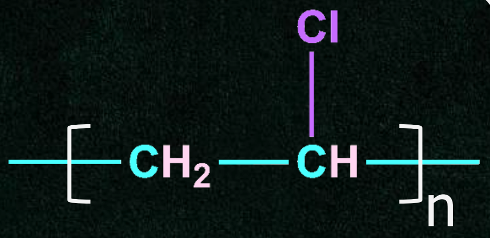
Polyvinyl Chloride (PVC)

Polyvinyl chloride

Monomer

Vinyl chloride

Structure



$$-\!\!\left[\mathrm{CH_2}-\underset{}{\overset{\mathrm{Cl}}{\overset{|}{\mathrm{CH}}}}\right]_n\!\!-$$

Uses

Raincoats, handbags, water pipes, and more

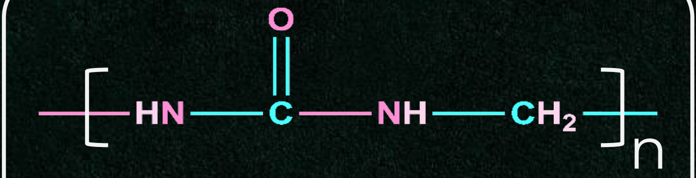
Urea-Formaldehyde Resin

Urea-formaldehyde resin

Monomer

(i) **Urea**
(ii) **Formaldehyde**

Structure



$$\left[-HN-\overset{\overset{O}{\|}}{C}-NH-CH_2-\right]_n$$

Uses

Unbreakable cups and **laminated sheets**

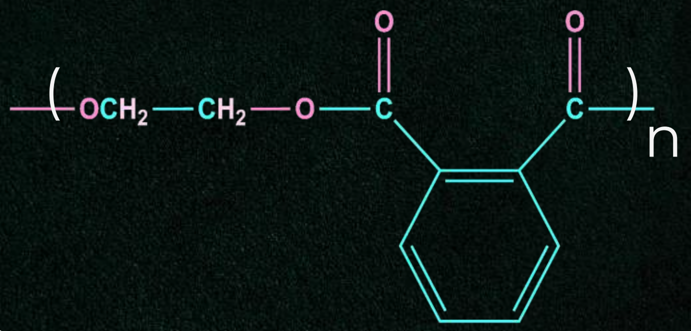
Glyptal

Glyptal

Monomer

(i) **Ethylene glycol**
(ii) **Phthalic acid**

Structure



Uses

Paints
and
lacquers