Polymerisation

$$X - Y \xrightarrow[\text{fission}]{\text{heterolytic}} \underset{\text{Cation}}{X^{\oplus}} + \underset{\text{anion}}{Y^{\ominus}}$$

$$Y^{\ominus} + \underset{\text{(Monomer)}}{CH_2 = CH_2} \longrightarrow \underset{\text{(Monomer chain initiating species)}}{Y - CH_2 - \overset{\ominus}{C}H_2}$$

Chain Propogation -

$$Y - CH_2 - \overset{\ominus}{C}H_2 + CH_2 = CH_2 \longrightarrow Y - CH_2 - CH_2 - \overset{\ominus}{C}H_2$$

$$Y - [CH_2 - CH_2]_{n-1} CH_2 - \overset{\ominus}{C}H_2 + CH_2 = CH_2 \longrightarrow \underset{\text{(Elongated chain)}}{Y - [CH_2 - CH_2]_n CH_2 - \overset{\ominus}{C}H_2}$$

(iii) Chain Termination -

$$X - Y \xrightarrow[\text{fission}]{\text{heterolytic}} \underset{\text{(cation)}}{X^{\oplus}} + \underset{\text{(anion)}}{Y^{\ominus}}$$

$$X^{\oplus} + \underset{\text{(monomer)}}{CH_2 = CH_2} \longrightarrow \underset{\text{(Initiating species)}}{X - CH_2 - \overset{\oplus}{C}H_2}$$

- Chain Propogation -

$$X - CH_2 - \overset{\oplus}{C}H_2 + CH_2 = CH_2 \longrightarrow X - CH_2 - CH_2 - CH_2 - \overset{\oplus}{C}H_2$$

$$X - [CH_2 - CH_2]_{n-1} CH_2 - \overset{\oplus}{C}H_2 + CH_2 = CH_2 \longrightarrow X - [CH_2 - CH_2]_n CH_2 - \overset{\oplus}{C}H_2$$

Polymer Blends — there is no chemical bond formation

Polymer A + Polymer B → Polymer Blend (different properties)
P_1 P_2

Polymer Blend

Homogenous/Miscible

2 polymer - blended together but Tg is any one

A + B → Blend
T_{gA} T_{gB} T_x

eg - PET
PBT

Heterogenous/ Imiscible

but Tg will be observed as two different Temperature

A + B → Blend
T_{gA} T_{gB} T_{gA} & T_{gB}

Biodegradable Polymers

Degradation of polymers by micro-organism (fungi bacteria)

↓ Depolymerase

Monomer / Dimer

Aerobic (in presence of O_2)

Anaerobic (in absen

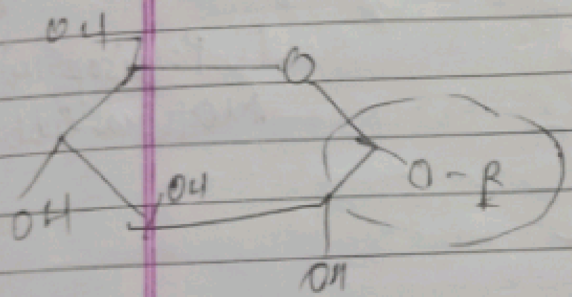
Biodegradable polymers

[derived]

Biomass

Agro polymers

Polysaccharides (glycosidic linkage)



starch, cellulose, nucleic acid

Protein (peptide linkage)

$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-$

silk wool gelatine

(Micro-organism)

Bio polyesters (ester linkage)

$-\overset{O}{\overset{\|}{C}}-O-$

(Polyglycolic acid)

<u>Elastomer</u> – organic polymer having elastic property upto 200 – 300 percent due to coiled structure of polymer

Elastomer

Natural Rubber

e.g. polyisoprene

Synthetic Rubber

- Buna-N
- Buna-S
- Neoprene

Natural Rubber –

Monomer Unit :– Isoprene

$$CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}=CH_2$$ 2 Methyl butadiene

Type of polymer → Homopolymer

Types of Polymerisation → Addition Polymerisation

Synthesis

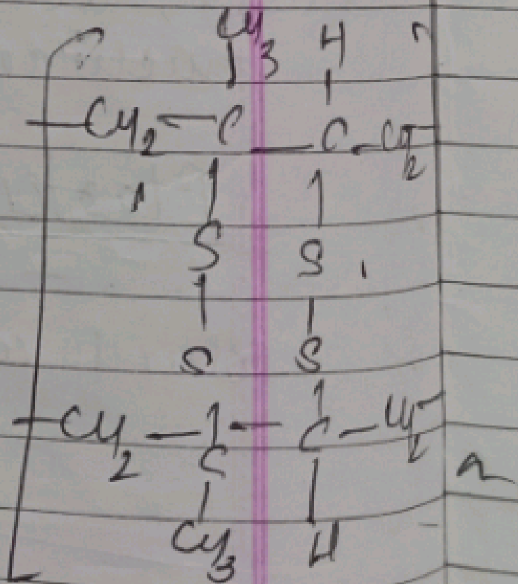
$$n\,CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{H}{\overset{|}{C}}=CH_2 \longrightarrow \left[-CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2-\right]_n$$

Isoprene (Polyisoprene) Natural Rubber

(Vulcanisation) :
compounded with sulphur

$$\left[-CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2-\right]_n$$

$$\left[-CH_2-\underset{CH_3}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-CH_2-\right]_n$$



BUNA-N

Monomer Unit
1) Butadiene . Acrylonitrile

$CH_2=CH-CH=CH_2$ $\quad\quad$ $CH_2=CH(CN)$

Type of polymer – Heteropolymer or Copolymer

Type of polymerisation → Addition

Synthesis

$$nm\ CH_2=CH-CH=CH_2 + n\,CH_2=\underset{\displaystyle CN}{\underset{|}{CH}} \longrightarrow$$

(butadiene) 75%. $\quad$ (acrylo nitrile)

$$-\left[CH_2-CH=CH-CH_2\right]_n-\left(CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}\right)_n-$$

BUNA-N

Good strength
resistivity
low solubility
good insulating property.

Styrene Rubber (Buna-S)

Monomer Unit → 1,3 Butadiene & styrene

$CH_2=CH-CH=CH_2$ $\quad$ $CH_2=$

Type of polymer - Heteropolymer

Type of polymerisation - Addition polymerisation

Synthesis

$nm\ CH_2 = CH - CH = CH_2 + n\ CH_2 = CH$

$\longrightarrow \left[CH_2 - CH = CH - CH_2 - CH \right]_n$

(Buna-S)

(Polystyrene Butadiene)

Like Natural Rubber

Shoe sole, motor tyres, toys, floor tiles, Cables, Carpets, decorative Material

Exam

Nylon 6,6

Terelene

Neoprene -

Monomer Unit - Chloroprene

$CH_2 = \overset{Cl}{\overset{|}{C}} - \overset{H}{\overset{|}{C}} = CH_2$ (2 Chloro 1,3 Butadiene)

Type of polymer - Homopolymer

Type of polymerisation - Addition polymerisation

Synthesis

$$\underset{\text{Chloroprene}}{n\,CH_2 = \overset{Cl}{\overset{|}{C}} - \overset{H}{\overset{|}{C}} = CH_2} \longrightarrow \underset{\text{Neoprene}}{\left[CH_2 - \overset{Cl}{\overset{|}{C}} = \overset{H}{\overset{|}{C}} - CH_2 \right]_n}$$

Properties – It shows resistivity with organic solvents.
good insulating property
good tensile strength

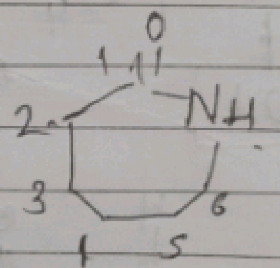
Application – belts, shoe soles, motor pad, coating (corrosion resistance), adhesive

BUNA-S < Natural Rubber < Neoprene < BUNA-N < Vulcanised Rubber

Synthetic Fibres

- having high interparticle force
- high length to width ratio
- Exam Nylon 6,6 – polyamides (amide group) $-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-$
- Terelene – polyesters (ester group) – $(-\overset{O}{\overset{\|}{C}}-O-)$

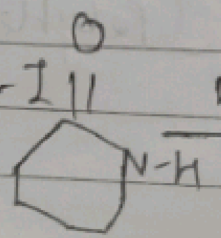
Monomer → Caprolactum (having 6 carbon atom)



Type of polymer – Homopolymer

Types of polymerisation – Condensation polymerisation

Synthesis Step-I



$\xrightarrow[\Delta]{H_2O} H_2N-(CH_2)_6-COOH$

Amino caproic acid

$$\underset{H}{\overset{H}{N}}-(CH_2)_5-\underset{OH}{\overset{O}{\overset{\|}{C}}} + \underset{H}{\overset{H}{N}}-(CH_2)_5-\underset{OH}{\overset{O}{\overset{\|}{C}}} \xrightarrow{-H_2O}$$

$$\left[\overset{H}{N}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right]_n$$

Nylon 6.

Nylon, 66

Monomer – Hexamethylene diamine & Adepic Acid

$$NH_2-(CH_2)_6-NH_2 + \underset{OH}{\overset{O}{\overset{\|}{C}}}-(CH_2)_4-\underset{OH}{\overset{O}{\overset{\|}{C}}}$$

Type of polymer → Heteropolymer / copolymer

Polymerisation → Condensation

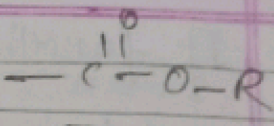
$$\left[\underset{H}{\overset{H}{N}}-(CH_2)_6-\underset{H}{\overset{H}{N}} + \underset{OH}{\overset{O}{\overset{\|}{C}}}-(CH_2)_4-\underset{OH}{\overset{O}{\overset{\|}{C}}}\right] \xrightarrow{-2H_2O}$$

$$\left[\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n$$

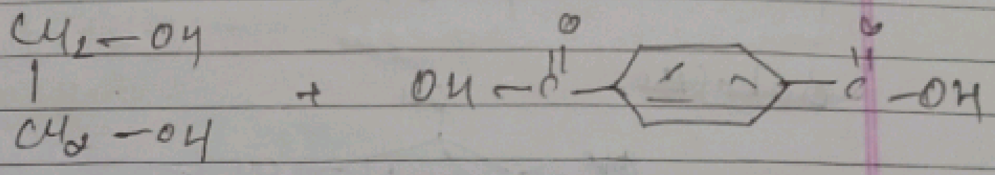
Nylon 6, 6

(PolyHexamethylene Adepate)

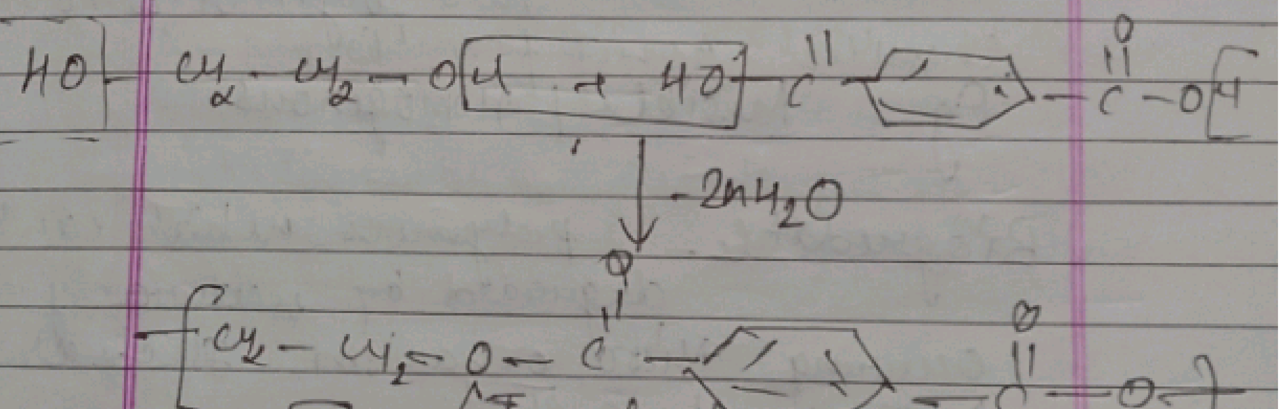
Terelene / Dacron



Monomer → ethylene glycol & Terephthalic acid



Type of polymer – Heteropolymer / Copolymer
polymerisation – Condensation



(Terelene)

[Poly ethylene terephthalate PET]

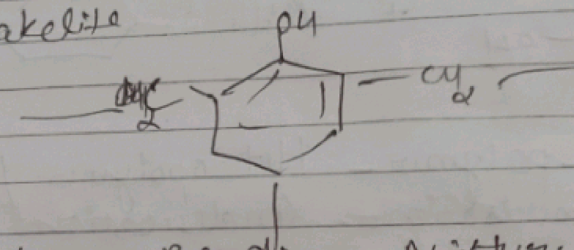
- low moisture absorbing
- having good insulator
- resist to acid, Alkali

If functionality is 2 $\longrightarrow$ linear polymer

$$n\,CH_2 = CH_2 \longrightarrow -[CH_2 - CH_2]_n-$$

functionality - 3 or 4

Bakelite



Polymer Blends → Mixture of Atleast two polymer without chemical bond formation.

Eg - Misible / Homogenous

Biogradable - polymers which can be degraded by naturally occuring Micro-organism, such as bacteria, fungi etc.

Neoprene

$CH_2 = C - CH = CH_2$

2 chloro, 1,3 butadiene

Terelyne.

Ethylene glycol + Thalic acid.

Acrylonitrile — (PAN)

Rigidity.
Toughness

Grignard Carbon is highly basic in nature & react with the acidic protons of polar solvent (such as water) → form alkane

$$R-Mg-X \xrightarrow{H-OH} \underset{(alkane)}{R-H} + Mg\begin{matrix} OH \\ X \end{matrix}$$

[ether has no acidic proton, so it is used in grignard reagent

γ-rays	X-rays	U.V	Visible	IR	Micro waves	Radio waves

VIBGYOR

U.V - VISIBLE Spectroscopy

Introduction →

• Alternate name → Electronic spectroscopy
OR
Ultra-violet Visible spectroscopy

Main function - for identification of number of conjugation in Molecule

$$-C=C-C=C-C=C-$$

single bond (pointing to C–C); double bond (pointing to C=C)

• Presence of single & Multiple bonds at alternate position

Range -

200nm to 800 nm

Vacuum U.V region	U.V region	Visible region

10 nm 200 nm 400nm 800nm

Effect of Range - this technique involves the promotion of electron from Ground level to higher energy level (Electron transition)

U.V. visible spectroscopy → Sample ↑ higher energy level

e^- — Ground

(200 - 800nm)

Types of electronic transition

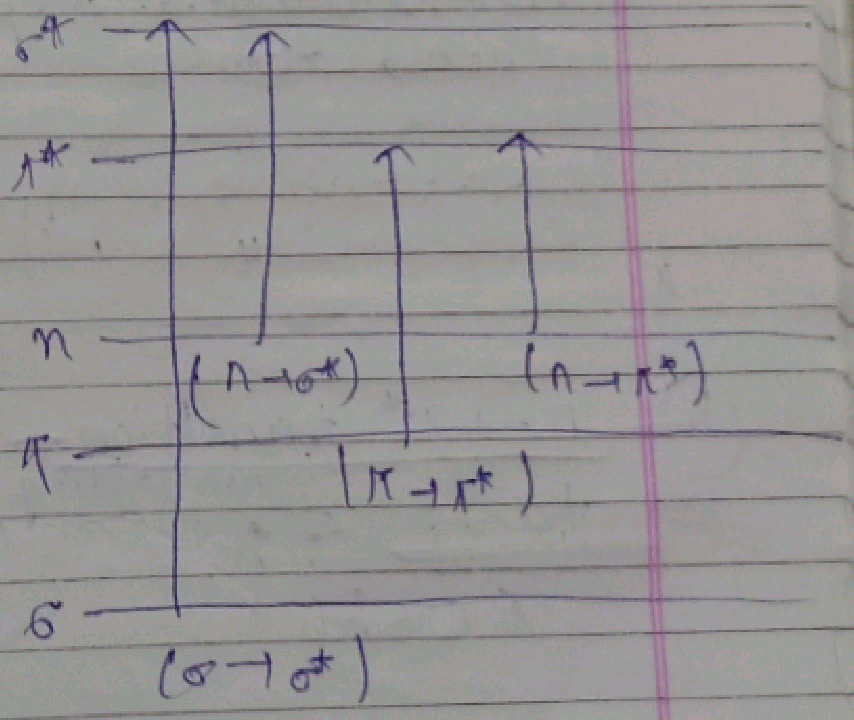
$\sigma \rightarrow \sigma^*$

$n \rightarrow \sigma^*$

$\pi \rightarrow \pi^*$

$n \rightarrow \pi^*$

Increasing energy ↑



Energy sequence →

$$\boxed{\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*}$$

1. **$\sigma \rightarrow \sigma^*$ transition →** Promotion of e^- from bonding σ orbital to antibonding σ^* orbital

where no hetero atom present

2. $n \to \sigma^*$ transition →

Promotion of non bonding e into antibonding σ^* orbital

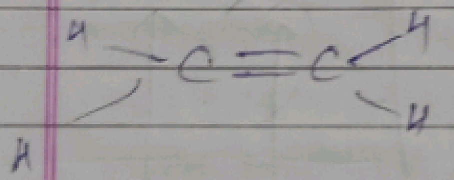
Insaturated compounds having heteroatom

eg CH_3OH, CH_3NH_2

(iii) $\pi \to \pi^*$ transition –

transfer of π electron into antibonding π^* orbital

• In unsaturated compounds with no hetero atom



, $H-C\equiv C-H$

(4) $n \to \pi^*$ transition –

transfer of non-bonding electron (n) into antibonding π orbital

present • In unsaturated compounds having hetero atom

$>C=O$ $>C=S$ $-C\equiv N$

1 In identification of conjugation in the given compound
2 In detection of functional group
3 In distinguishing conjugated & non-conjugated compound
4 In qualitative analysis
5 In determination of various type of isomers.
6 In identification of unknown compound
7 Examination of polynuclear hydrocarbons
8 Identification of a compound in different solvent.
9 In determining the Molecular weight

10 Saturated → Inactive
Unsaturated → Active in U.V. visible Spectrum.

Types of σ, π, n

$\sigma \to \sigma^*$

$\pi \to \pi^*$ Active

$n \to \sigma^*$

$n \to \pi^*$ Active

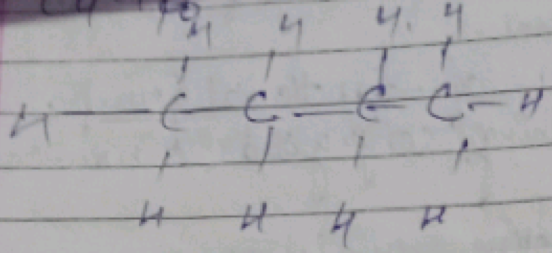
Active Transitions:-

$\pi \to \pi^*$

$n \to \pi^*$

due to presence of π electron or Active Transitions of compound is U.V active compound

C_4H_{10}



Type of electron = σ

∴ transition → σ – σ*

Inactive

Compound is U.V inactive compound

<u>Lambert's law</u> -

When a beam of monochromatic light is passed through a solution, the decrease in intensity of light with the thickness of solution is directly proportional to intensity of incident light

$$\boxed{I = I_0 e^{-kx}}$$

<u>Beer's law</u> – When a beam of monochromatic light is passed through a soln, the decrease in intensity of light with the thickness of soln is ∝ intensity of incident light as well as conc of soln.

• By rearranging Eq (3)

$$\frac{I_r}{I_0} = e^{-kcx}$$

ound

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thickness
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e soln,
with
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ln.

taking log

$$\boxed{\ln\left(\frac{I_x}{I_0}\right) = -kcx}$$

$$-\ln\left(\frac{I_x}{I_0}\right) = kcx$$

$$-\ln T = kcx \qquad T = \frac{I_t}{I_0}$$

$$-\log T = \frac{k}{2.303}cx \qquad \boxed{A = -\log T}$$

$$-\log T = acx$$

$$a = \frac{k}{2.303}$$

$$\boxed{A = acx} \qquad \boxed{A = \varepsilon C_m x}$$

ε → Molar absorptivity

C_m = Molar Concentration

$$\boxed{C_m = \frac{C}{\text{Mol wt}}} \qquad \boxed{A = \text{Absorbance}}$$

Q. $C = 0.01$ gm/L

$A = 0.2$

$x = 1$ cm

$$A = acx \qquad a = \frac{A}{cx} = \frac{0.2}{1\times 0.1}$$

$$\boxed{a = 2}$$

$A = \varepsilon c x$

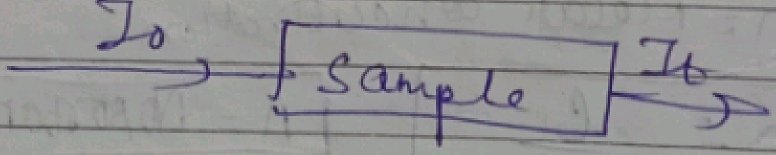
$$\varepsilon = \frac{A}{C_m x}$$

$$C_m = \frac{c}{\text{Mol wt}} = \frac{0.1}{200}$$

$$\varepsilon = \frac{0.2}{\frac{0.1}{200} \times 1} = 400 \text{ lit/mol cm}$$

Molar Absorptivity (ε) = 400 lit / mol cm

<u>Ques</u> A definite wavelength when placed in a cell of 1 cm path length absorbs 20% of the incident light. If the absorptivity of the absorber at this wavelength is 2. find out its concentration.



$x = 1$ cm

$a = 2.0$ (absorptivity)

$I_0 = 100\%$

$I_t = 80\%$

Concentration (c) = ?

According to Lamber's Beer law:

$$A = acx$$

$$A = \log\left(\frac{1}{T}\right) = \log\left(\frac{1}{I_t/I_0}\right)$$

$$\boxed{A = \log\left(\frac{I_0}{I_t}\right)}$$

$$\log\left(\frac{100}{80}\right) = 0.0969$$

$$C = \frac{A}{ax} = \frac{0.0969}{1 \times 2}$$

$$\boxed{C = 0.04845}$$

INFRARED

IR Active Molecules	IR Inactive Molecules
Permanent dipole Moment.	No permanent dipole moment
Change in dipole moment during Molecular Vibration	No change in dipole Moment during Molecular Vibration
$HF, HCl, H_2O, NO_2, PCl_3, ClF_3$	$H_2, N_2, O_2, Cl_2, CH_4, CCl_4, PCl_5, SF_6, CS_2$

$\overleftarrow{O = C} \overrightarrow{= O}$ $\overrightarrow{O = C = O}$

(Symmetric stretching) (Asymmetric stretching)

IR Inactive IR Active

- Finger Print & functional Group Region

functional group Region	Finger Print Region
Range – 400-1300 cm^{-1}	1300 – 667 cm^{-1}
It is useful for identification of functional group of given compound	It is useful for identification of specific compound
Compounds having same functional group, show similar absorption band in this region	Compounds having same functional group show different absorption band in this region.