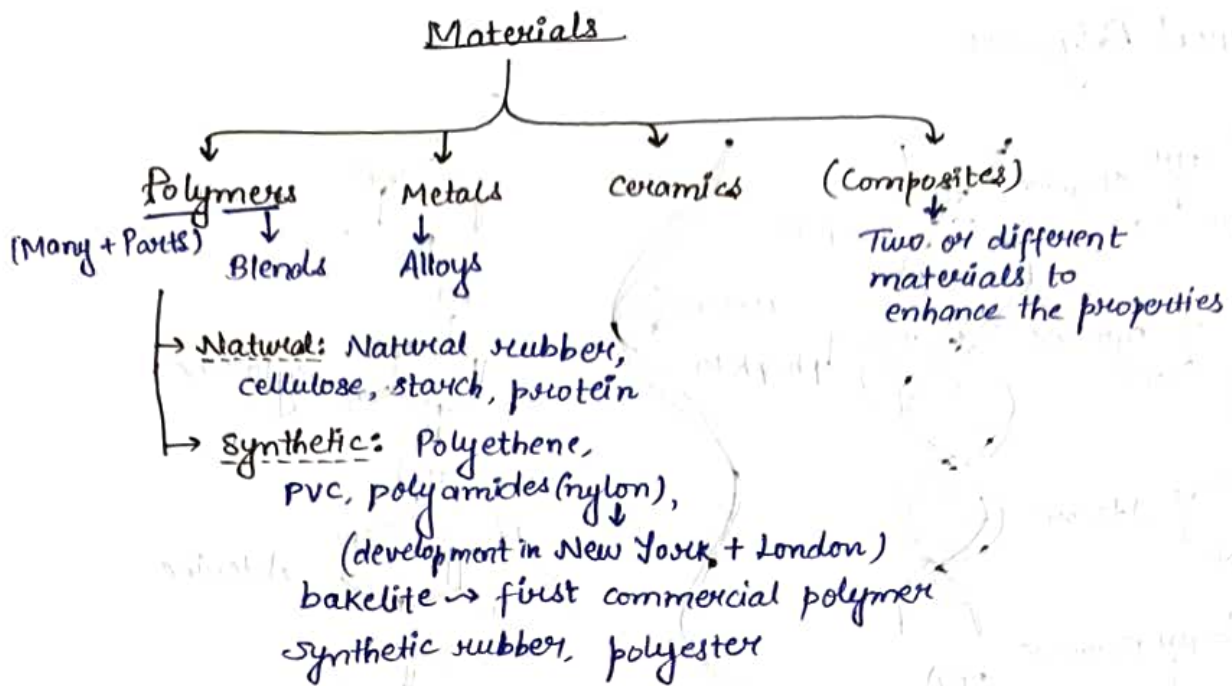
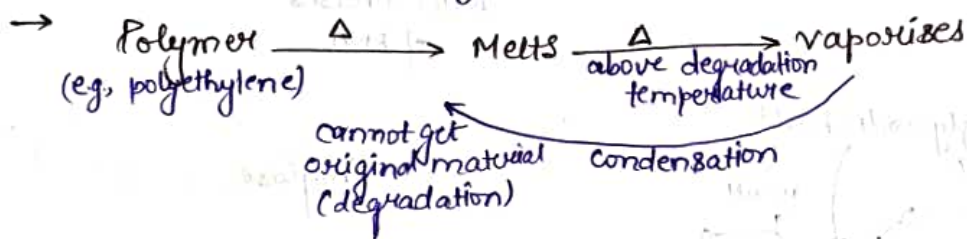


बहुलक विज्ञानम्
POLYMER SCIENCE



Mastication: Reducing molecular weight

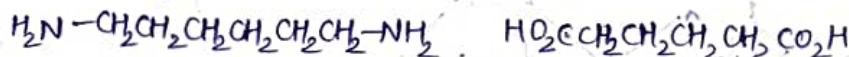
Smart polymers: changes properties based on stimuli.



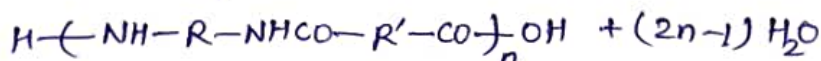
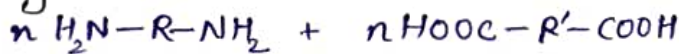
Examples

① Nylon

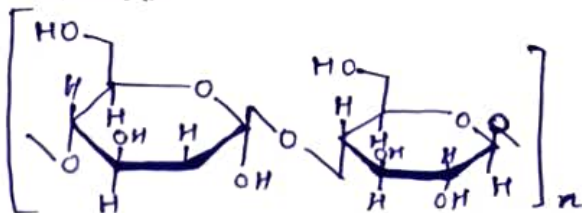
hexamethylenediamine + Adipic acid



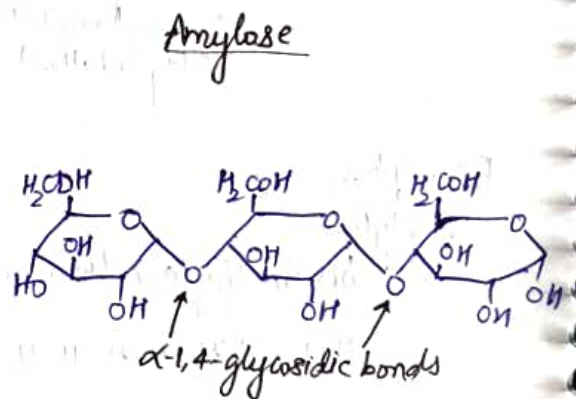
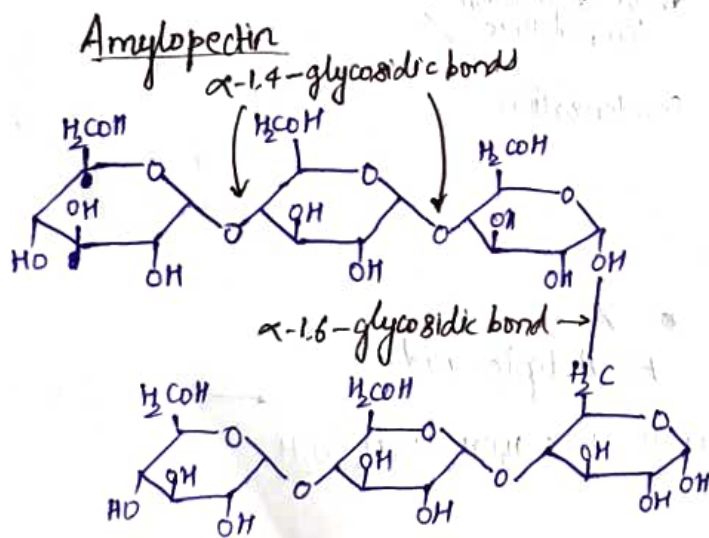
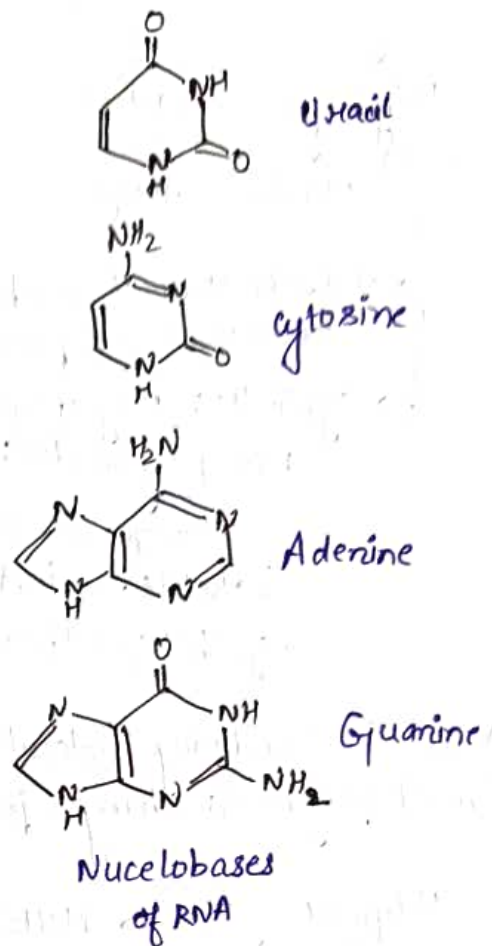
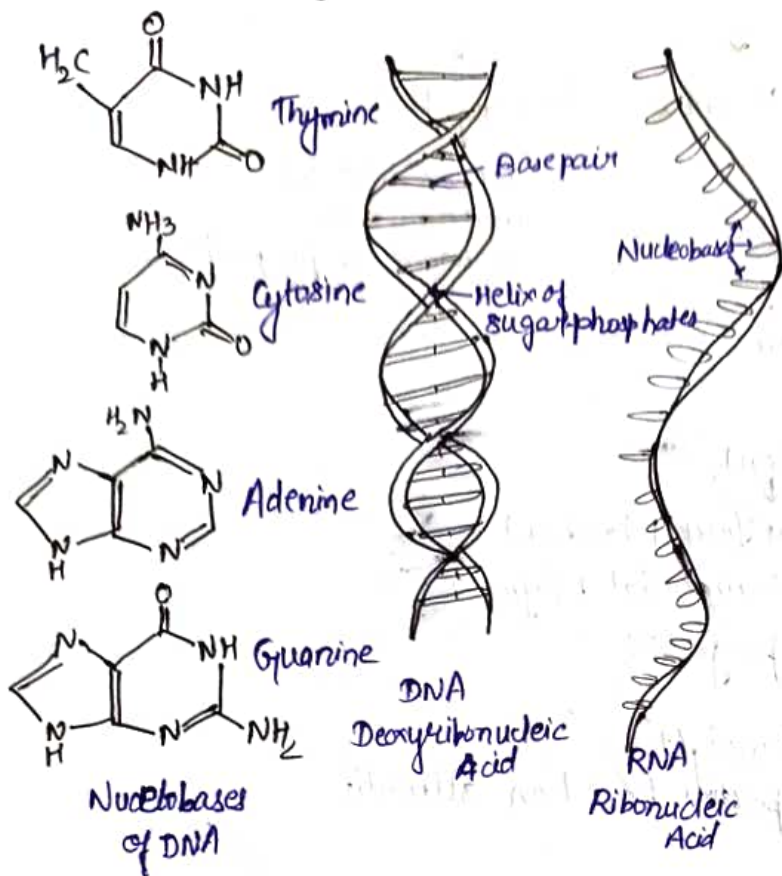
② Polyamides



③ cellulose

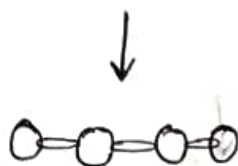
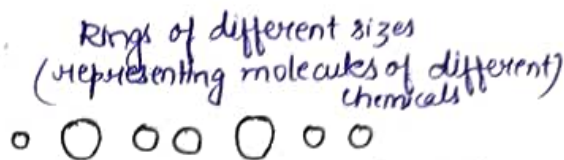
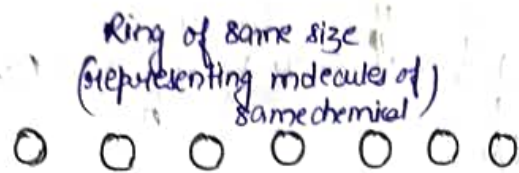


④ Natural Polymers



Structure

- Physically-associated aggregates of small molecules
- Very large molecules containing long sequences of simple chemical units linked together by covalent bonds.
- Macromolecules
- Functional, biomedical, optical, electronic, smart



Chains made of interlinked rings
(representing polymer molecules)

butadiene + butadiene + ... + butadiene → polybutadiene
(4,000 times)

CLASSIFICATION

Basis

① Thermal properties

Types

Thermoplastic
Thermosets

② Mechanical properties

Fibre
Plastic
Elastomers

③ Structure

Linear
Branched
Cross-linked

④ origin

Synthetic
Natural

⑤ Mechanism of reaction
(polymerisation)

step
chain

⑥ Composition
classified by
Carothers [1929]

Condensation
(e.g., polyamides,
nylon-6,6)

Addition

composition difference b/w polymers & repeated units

no composition diff. b/w polymers & repeated units

Polymers

Thermoplastics

Elastomers

Thermosets

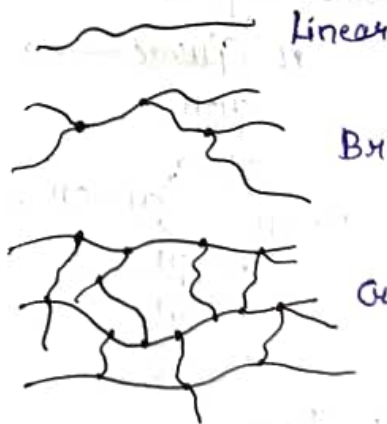
crystalline

Amorphous

Linear

Branched

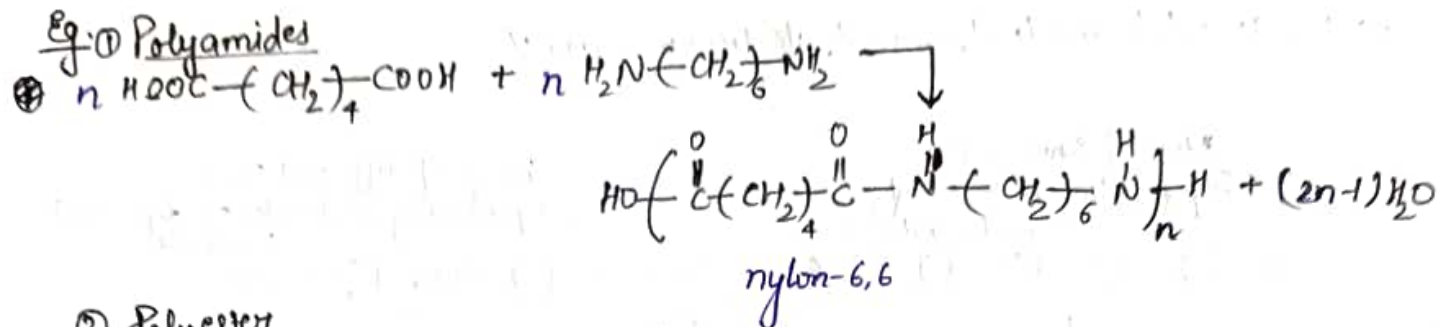
Crosslinked



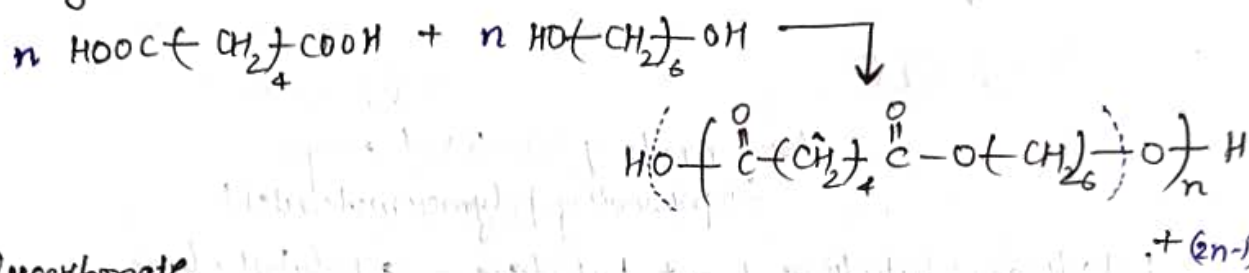
Condensation Polymers

- Composition difference between the monomers and the polymer repeat unit.
- Elimination of small molecules.

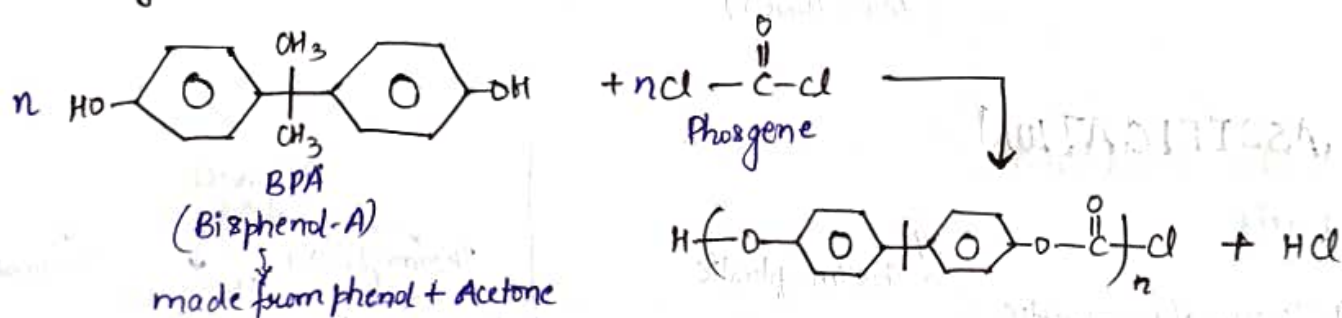
Ex. ① Polyamides



② Polyester

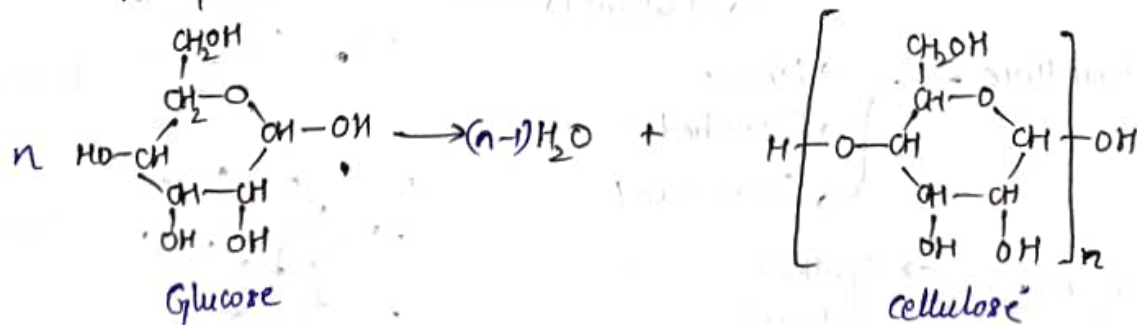
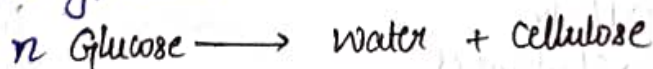


③ Polycarbonate

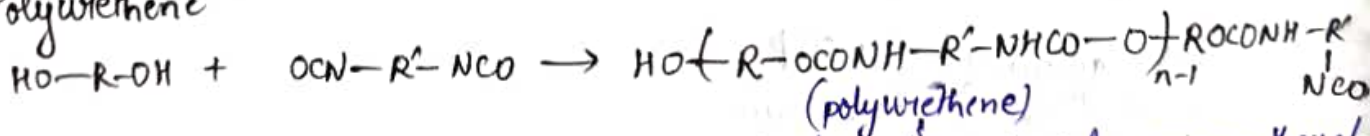


④ cellulose

cellulose
Hypothetically, cellulose is considered to be condensation polymer of glucose

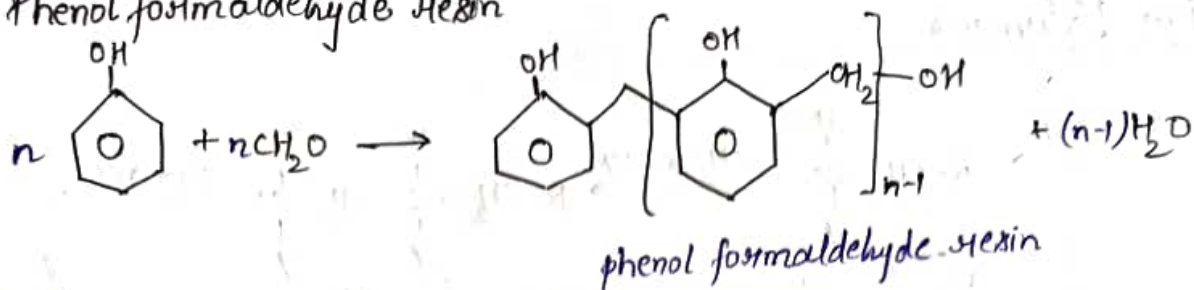


⑤ Polyethylene



considered as condensation polymer even though there's no composition diff. b/w monomer & repeat units b/c it contains functional group which is not there in monomer

⑥ Phenol formaldehyde resin



Polystyrene → used to make thermocol

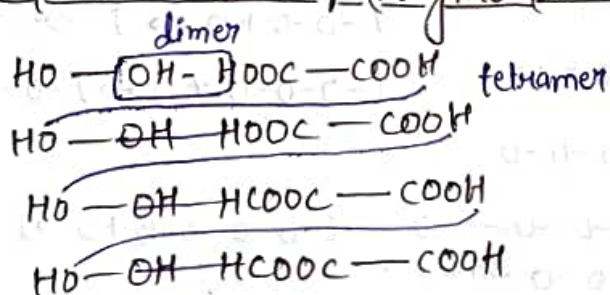
polypropylene → used to make plastic chairs

→ A polymer is classified as a condensation polymer if

- Synthesis involves the elimination of small molecules.
- contains functional groups as part of the polymer chain
- Repeating units lack certain atoms that are present in the (hypothetical) monomer to which it can be degraded.

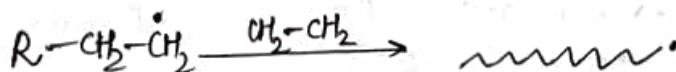
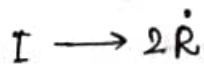
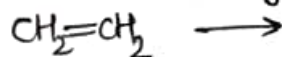
↳ If a polymer does not fulfil any of these requirements, it is classified as an addition polymer.

Step Growth and Step Polymerisation → Analogous to condensation polymer



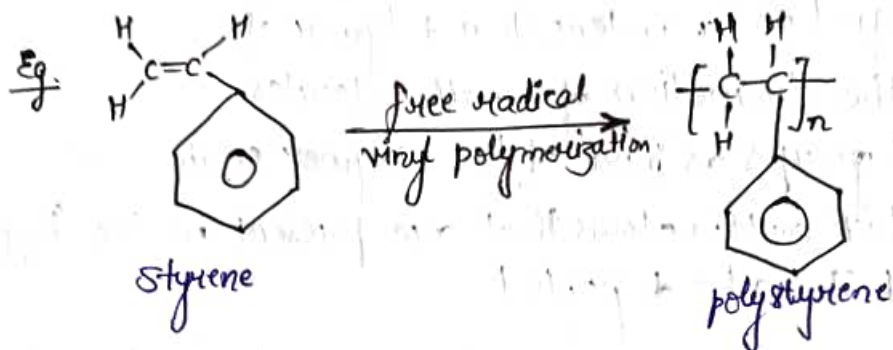
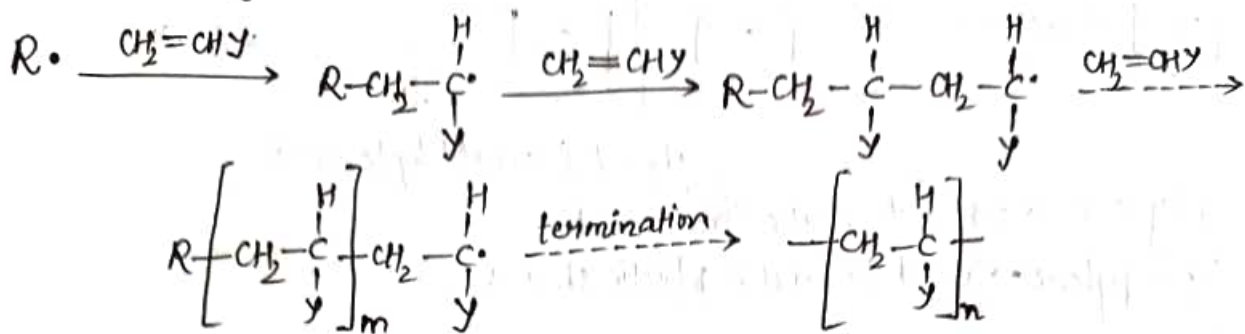
step-①: Dimers form
step-②: Tetramers form

Chain Growth Polymerisation

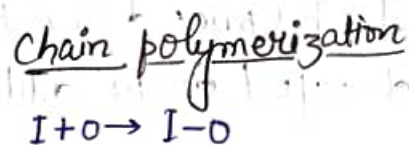
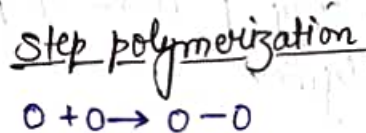


- Chain growth → very fast
- Observation of mixture, we'll get:
 - high chain polymer
 - unreacted monomer
 - unreacted initiator.

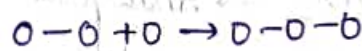
Addition Polymers



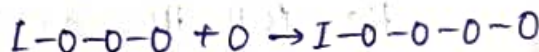
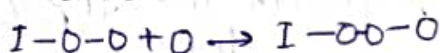
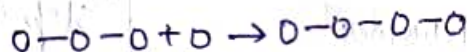
→ Formation of
Dimer



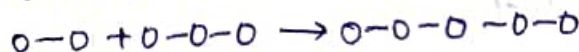
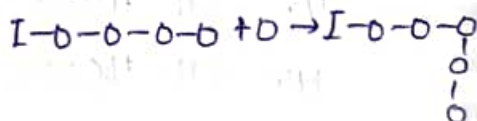
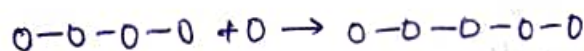
Trimer



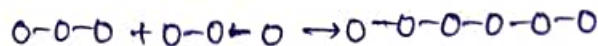
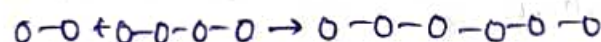
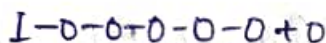
Tetramer



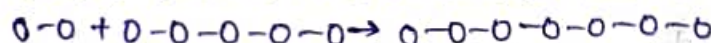
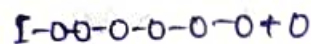
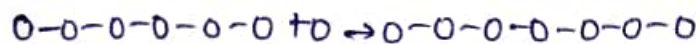
Pentamer



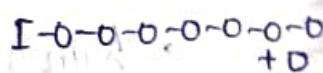
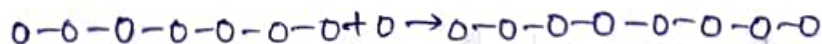
Hexamer



Heptamer



Octomer



I : Initiator species

O : molecule of monomer & repeat unit, - : chemical link

↳ Fundamental differences in reaction mechanism b/w step & chain polymerization

→ The molecular weights of the polymers at any time after the start of the reactions for the two polymerisations are different.

→ Stopped at 0.1%, 1%, 10%, 40%, 90% conversion.

• The continuous increase in the no. of polymer molecules.

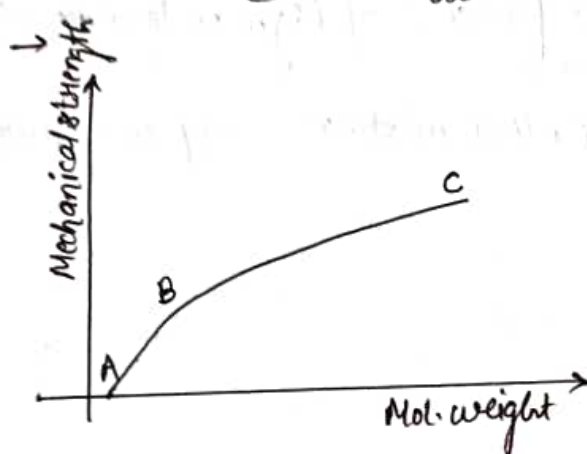
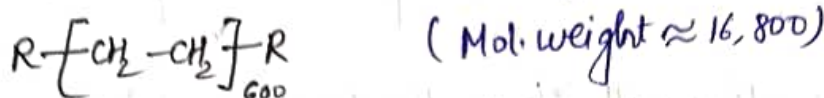
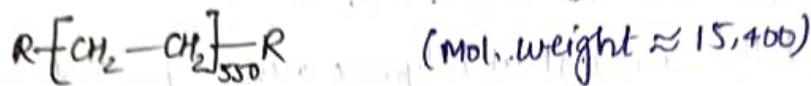
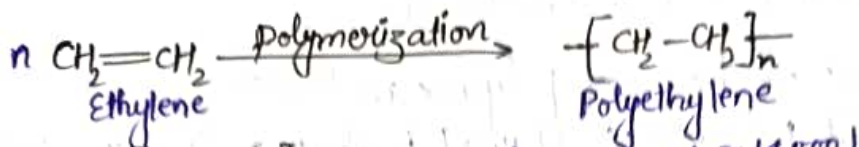
• High molecular-weight polymer is obtained in chain polymerization only near the very end of the reaction (>98% conversion).

• Both polymer size and the amount of polymer are dependent on conversion in step polymerization.

• The chain polymerization will show the presence of high molecular-weight polymer molecules at all percents of conversion.

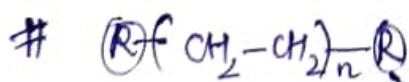
• No intermediate-sized molecules in the reaction mixture — only monomer, high-polymer, and initiator species.

MOLECULAR WEIGHT



- Min.^m polymer mol. weight (A): produce any significant strength.
- Above A: strength increases rapidly with mol. weight until a critical point (B) is reached.
- Mechanical strength increases more slowly above B.
- Reaches a limiting value C.
- B: the min.^m mol. weight for a polymer to begin to exhibit sufficient strength to be useful.
- Most practical applications of polymers require higher molecular weights to obtain higher strengths.
- The min.^m useful mol. weight (B), usually in the range 5-10 K, differs for different polymers.
- Plot shifts to the right as the magnitude of the intermolecular force decreases.
- Polyamides and polyesters, develop sufficient strength to be useful at lower mol. weights than polyethylene.

- Processability increase with mol. weight to a maximum value.
- Decrease with further increase in mol. weight.
- The control of mol. weight is essential for the practical application of a polymerization process.



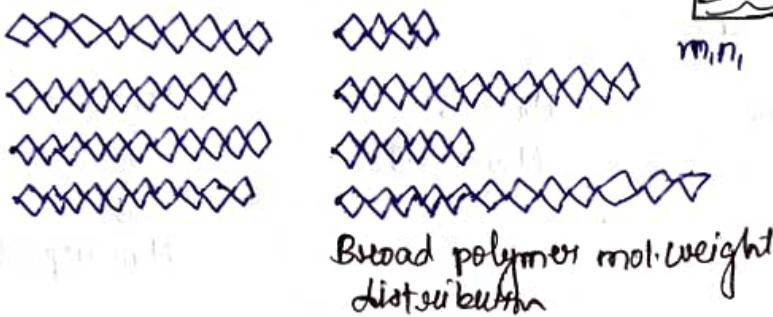
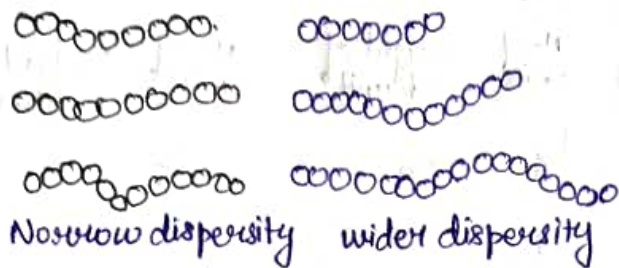
oligomer \rightarrow small polymer mol. wt. of end groups are generally not counted (as they are very small)

\rightarrow polyethylene $<$ polyamide : mechanical strength (bk of H bonding)

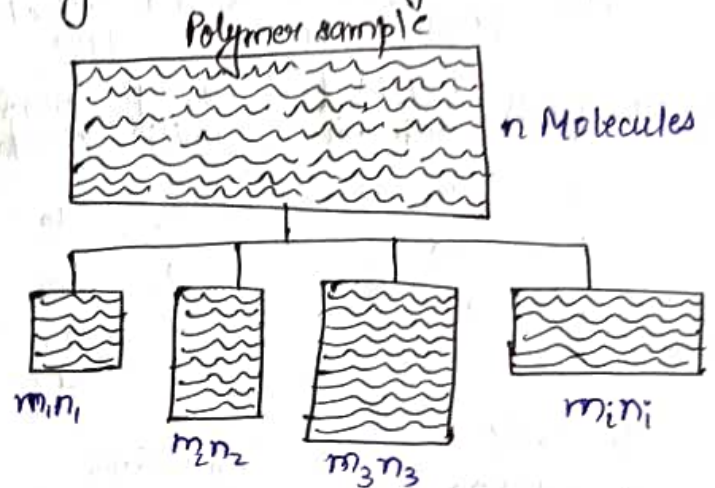
van der Waals force only H-bonding

- Poly dispersed polymer: Polymers in a solution have different chain length.
- ↳ Normally, polymers have polydispersity.
- Mono dispersed polymer: Polymers have same chain length.

Polydispersity



Average molecular weight



→ Number Average Molecular weight (\bar{M}_n):

$$\bar{M}_n = \frac{n_1 m_1 + n_2 m_2 + n_3 m_3 + \dots}{n_1 + n_2 + n_3 + \dots} = \frac{\sum n_i m_i}{\sum n_i}$$

$$= \frac{n_1}{\sum n_i} m_1 + \frac{n_2}{\sum n_i} m_2 + \frac{n_3}{\sum n_i} m_3 + \dots = \sum x_i m_i$$

x_i : no. fraction

m_i : mass of each unit

→ Weight Average Molecular weight (\bar{M}_w):

$$\bar{M}_w = \frac{n_1 m_1}{\sum n_i m_i} \times m_1 + \frac{n_2 m_2}{\sum n_i m_i} \times m_2 + \frac{n_3 m_3}{\sum n_i m_i} \times m_3 + \dots = \frac{\sum n_i m_i^2}{\sum n_i m_i}$$

$$= \sum w_i m_i$$

Eg.	No. of units	weight of each unit
	2	10
	4	20
	6	100
	3	250

$$\bar{M}_n = \frac{2}{15} \times 10 + \frac{4}{15} \times 20 + \frac{6}{15} \times 100 + \frac{3}{15} \times 250$$

$$= \frac{1450}{15} = 96.67$$

$$\text{Total weight} = 1450$$

$$\bar{M}_w = \frac{20}{1450} \times 10 + \frac{80}{1450} \times 20 + \frac{600}{1450} \times 100 + \frac{750}{1450} \times 250 = 171.93$$

Eg	No. of units	Weight of each unit	No. of units	Weight of each unit	No. of units	Weight of each unit	No. of units	Weight of each unit
	2	10	2	10	6	20	15	30
	4	20	4	20	9	30		
	6	100	6	30				
	3	250	3	40				
	$\bar{M}_n = 96.67$		$\bar{M}_n = 26.66$		$\bar{M}_n = 26$		$\bar{M}_n = 30$	
	$\bar{M}_w = 171.93$		$\bar{M}_w = 20$		$\bar{M}_w = 26.92$		$\bar{M}_w = 30$	
	$\Rightarrow \boxed{\bar{M}_w \geq \bar{M}_n}$						\downarrow	Monodispersed

$$\rightarrow \text{Polydispersity Index (PDI)} = \frac{\bar{M}_w}{\bar{M}_n} \geq 1$$

(1, for monodispersed).

Q In a hypothetical polymer sample, 95% of weight is contributed by molecules of mol. wt. 10,000 g/mol. 5% of the weight is contributed by molecules of mol. wt. 100 g/mol. Calculate \bar{M}_n and \bar{M}_w .

Soln:

95% $\rightarrow \bar{M}_w = 10k$

5% $\rightarrow \bar{M}_w = 100$

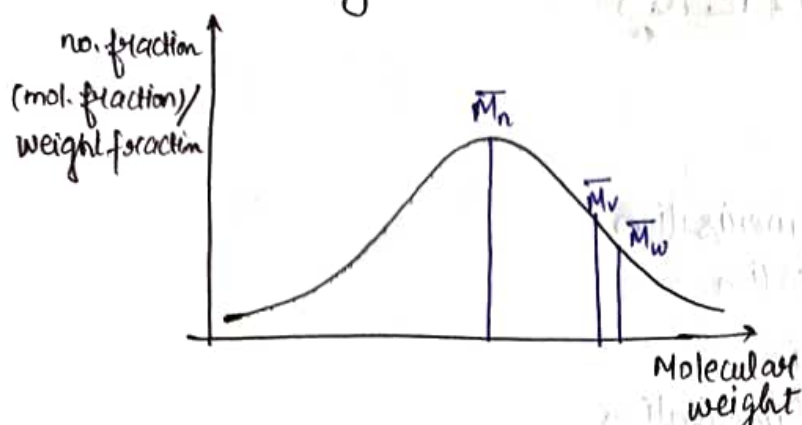
Weight fraction

$$\bar{M}_w = 0.95(10,000) + 0.05(100)$$

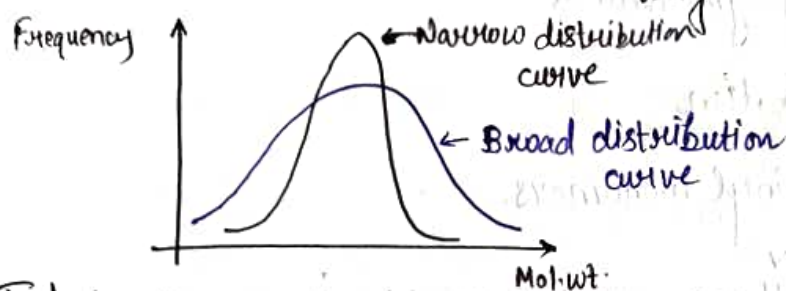
$$= 9505 \text{ g/mol}$$

$$\bar{M}_n = \frac{\frac{95}{10000} \times 10,000 + \frac{5}{100} \times 100}{\frac{95}{10000} + \frac{5}{100}} = \frac{100 \times 10^4}{595} \text{ g/mol}$$

Molecular weight Distribution Curve



\bar{M}_v : viscosity average molecular weight



Techniques:

→ vapour phase osmometry (VPO)

↓ based on
lowering of vapour pressure

→ viscometry

↓ based on
viscosity
↓ depends on
size of polymer chain

Petroleum + ether → petether

→ GPC (also called SEC, size exclusion chromatography)

↓ (Gel permeation chromatography)
based on size, mol. weight fraction separation
↓
gives both \bar{M}_n and \bar{M}_w .

ADDITION POLYMERS

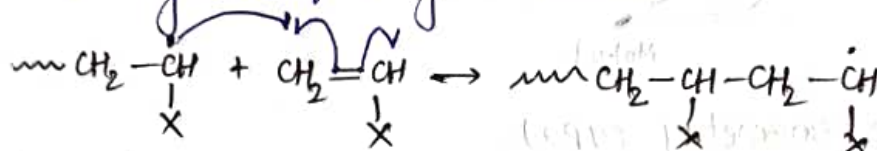
Polymerisation

Addition polymerisation

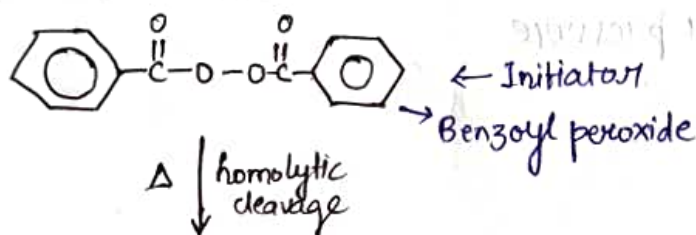
- ① Free radical polymerisation
- ② Ionic polymerisation
 - Anionic
 - Cationic
- ③ Coordination polymerisation

Free Radical Polymerisation

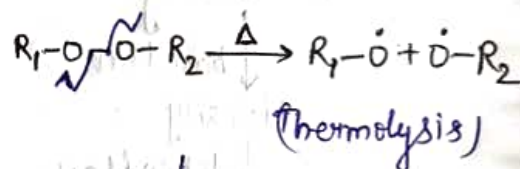
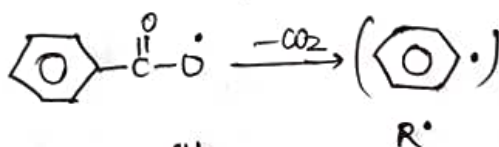
↳ Most widely used for vinyl monomers.



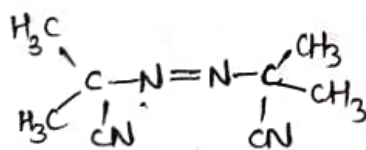
Initiation Initiators:



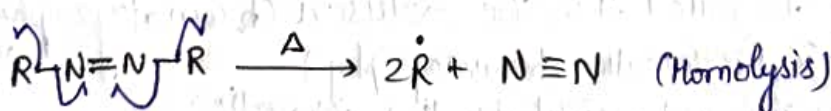
Δ homolytic cleavage



R_1, R_2 : aromatic/alkyl/
H (often $\text{R}_1 = \text{R}_2$)

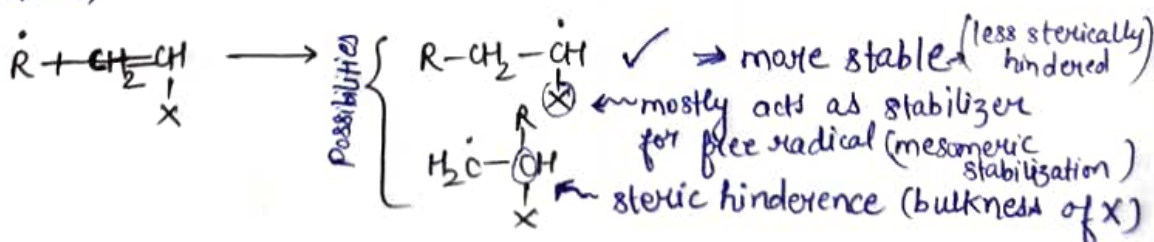
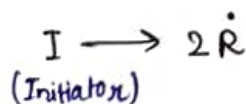


← Azobisisobutyronitrile (AIBN)

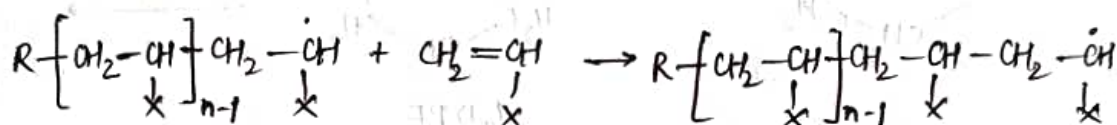
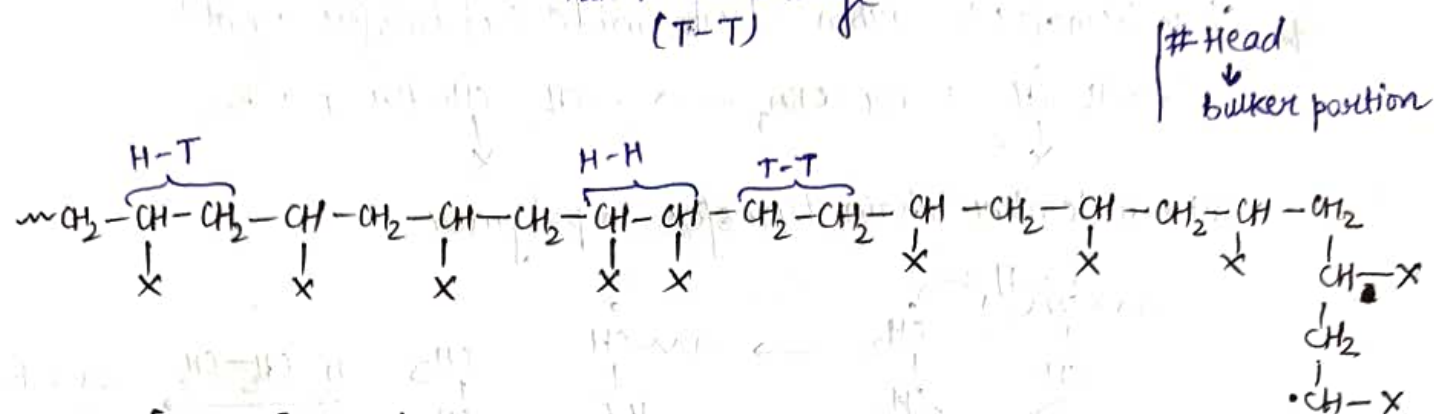
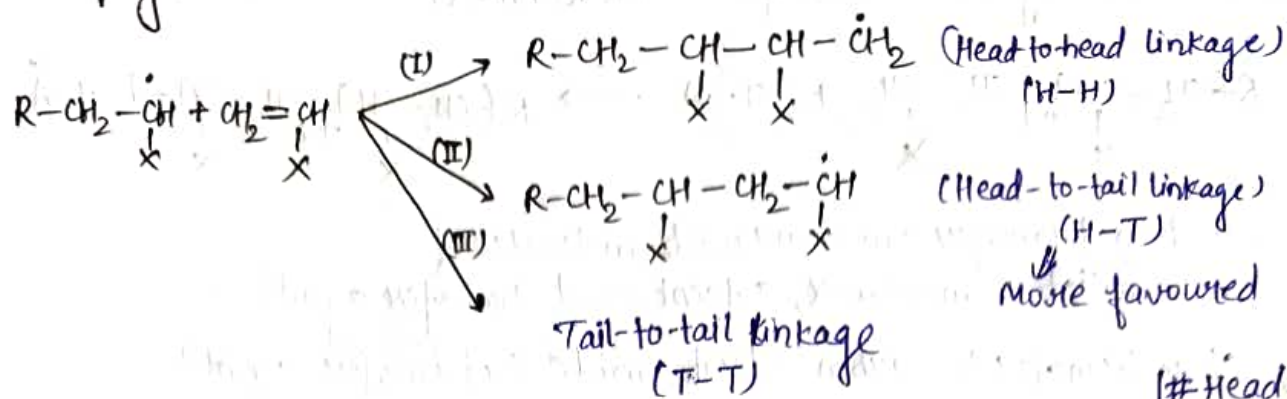


R : aromatic/
alkyl

Initiation: Generation of free radical + Attacking first monomer.

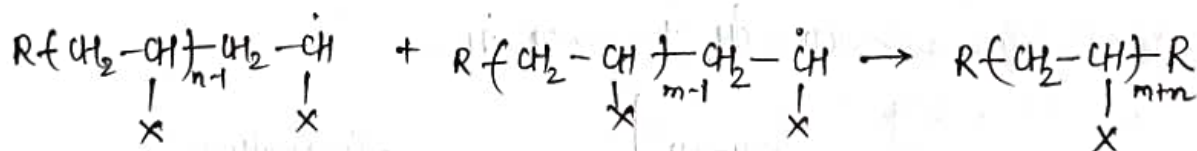
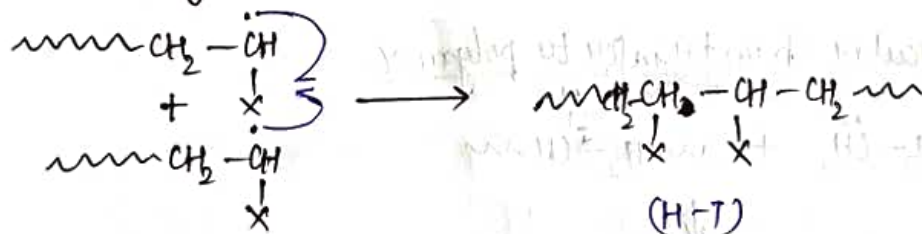


Propagation:

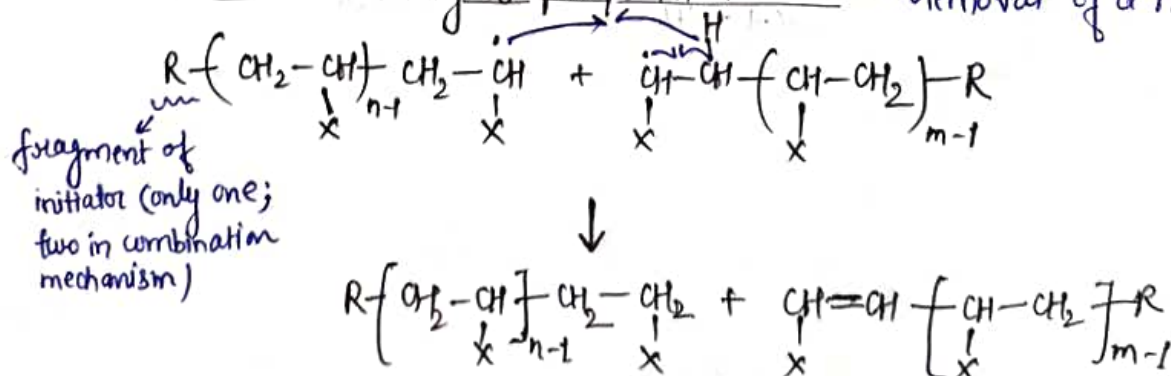


Termination:

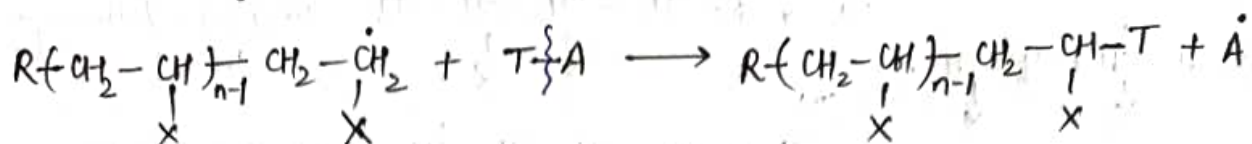
① Termination by couplet/combination (Radical combination)



② Termination by Disproportionation \rightarrow removal of a H

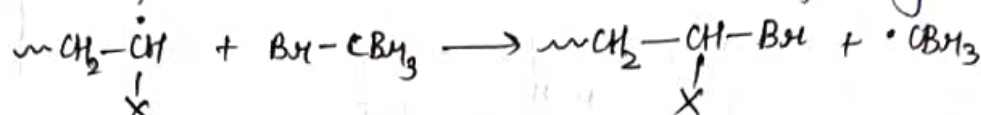


③ Termination by Chain Transfer (Side Reactions)

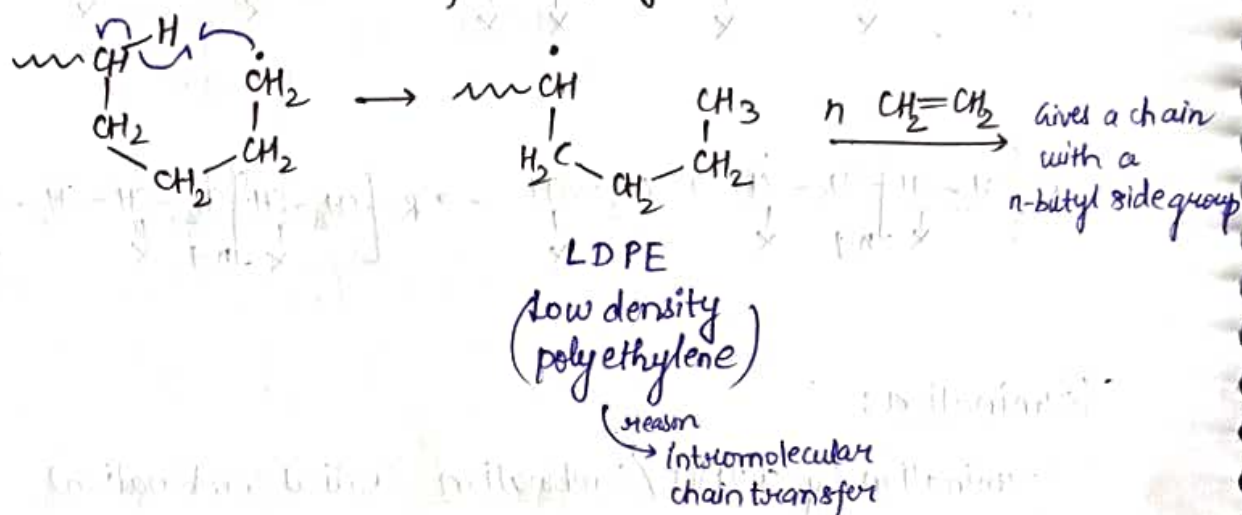


→ chain transfer can occur with molecules of initiator, monomer, solvent and transfer agents.

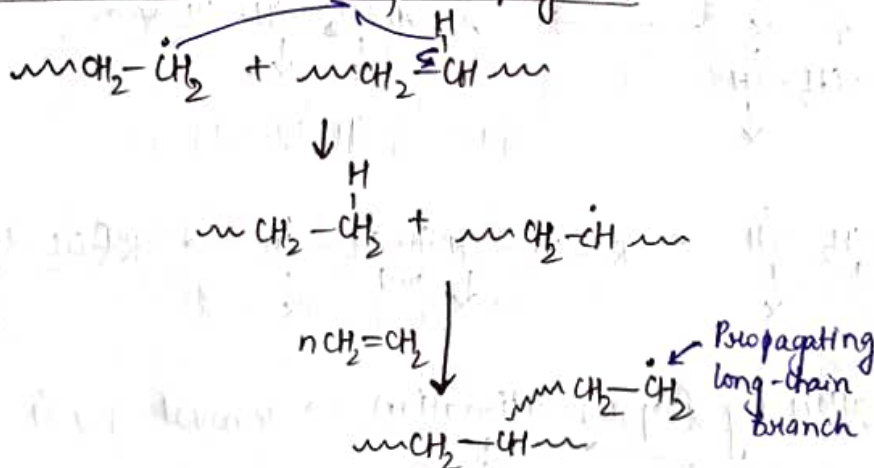
Eg chain transfer to carbon tetrabromide (a transfer agent)

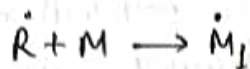
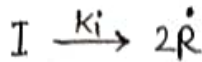
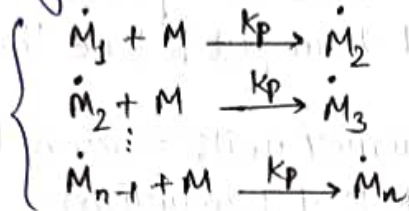


→ Intramolecular chain transfer to polymer

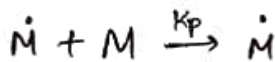
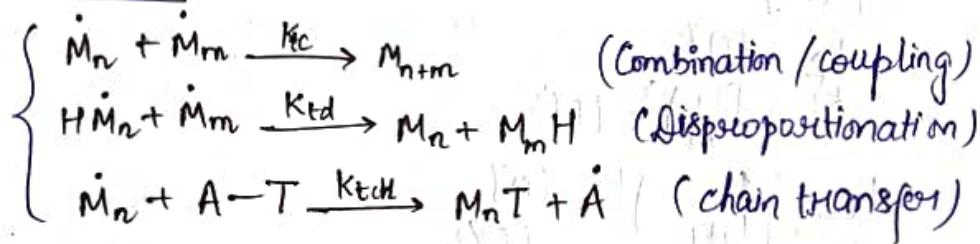


→ Intermolecular chain transfer to polymer



MechanismInitiation:Propagation:

Number like (n-1) is not significant important.

Termination:

$$-\frac{1}{2} \frac{d[\dot{M}]}{dt} = k_t [\dot{M}]^2$$

Rate of polymerisation, $R_p = k_p [\dot{M}] [M]$

$$\left(\frac{d[\dot{M}]}{dt} \right)_{\text{production}} = \frac{d[\dot{R}]}{dt} = 2fk_i [I]$$

f : fraction of initiator radicals which are reacting successfully with monomers
(Initiator efficiency)

$$\left(\frac{d[\dot{M}]}{dt} \right)_{\text{consumption}} = 2k_t [\dot{M}]^2$$

Steady state approximation: $\left(\frac{d[\dot{M}]}{dt} \right)_{\text{production}} = \left(\frac{d[\dot{M}]}{dt} \right)_{\text{consumption}}$

$$\Rightarrow 2fk_i [I] = 2k_t [\dot{M}]^2$$

$$\Rightarrow [\dot{M}] = \left(f \frac{k_i}{k_t} [I] \right)^{1/2}$$

$$\Rightarrow [\dot{M}] = \left(f \frac{k_i}{k_t} \right)^{1/2} [I]^{1/2}$$

$$\therefore R_p = K_p \left(f \frac{K_i}{K_t} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}} [M]$$

- Degree of polymerisation (\bar{X}_n or \bar{D}_p): ^{Average} No. of monomer units incorporated in the polymer chain.
- Kinetic Chain Length (λ): No. of monomer units incorporated in fully grown radical chain just before the termination.
- Rate of polymerisation (R_p): No. of monomer units consumed per unit time. (= Rate of production)

$$\begin{aligned} \lambda &= \frac{\text{Rate of polymerisation}}{\text{Rate of consumption of } [M]} \\ &= \frac{K_p [M][M]}{2K_t [M]^2} \\ &= \frac{1}{2} \frac{K_p}{K_t} \frac{[M]}{\left(f \frac{K_i}{K_t} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}}} \\ &= \frac{K_p}{2} \left(\frac{1}{f K_i K_t} \right)^{\frac{1}{2}} \frac{[M]}{[I]^{\frac{1}{2}}} \end{aligned}$$

$$\therefore \lambda = \frac{K_p}{2} (f K_i K_t)^{-\frac{1}{2}} [I]^{-\frac{1}{2}} [M]$$

$\bar{D}_p = \lambda$, (if termination is by disproportionation)

$\bar{D}_p = 2\lambda$, (if termination is by coupling)
 $= K_p (f K_i K_t)^{-\frac{1}{2}} [I]^{-\frac{1}{2}} [M]$

Mode of Termination: Determination

- a : fraction of chain which are undergone termination by coupling
 $(1-a)$: no. of fraction of chain, undergone disproportionation.
 b : average no. of initiator fragments (R) per polymer chain.
 n : no. of radicals.

Termination by coupling: Two initiator fragments per polymer molecule.

Termination by disproportionation: one initiator fragment per polymer molecule.

$$b = \frac{an + (1-a)n}{\frac{an}{2} + n(1-a)} = \frac{n}{\frac{na}{2} + n(1-a)} = \frac{2}{2-a} \Rightarrow a = \frac{2b-2}{b}$$

$$1-a = \frac{2-b}{b}$$

Q A hypothetical polymer sample has 1.3 initiator fragment per polymer chain. Calculate the % of termination by coupling disproportion.

Soln:

$$1.3 = \frac{2}{2-a} \Rightarrow 2.6 - 1.3a = 2$$

$$\Rightarrow 0.6 = 1.3a$$

$$\Rightarrow a = \frac{6}{13}$$

$$\therefore \% a = \frac{600}{13} \% = 46.15\%$$

10-04-23

Auto acceleration:

Conc. of monomer $\uparrow \Rightarrow$ viscosity of solvent $\uparrow \Rightarrow$ Termination \downarrow
 \Rightarrow large chain formation $\uparrow \Rightarrow$ Polymerisation $\uparrow \Rightarrow$ Temperature \uparrow .

Inhibition and Retardation:

\hookrightarrow Due to environmental factors (heat, light), some initiators can get generated, resulting in unwanted polymerisation of monomers on its own (eg., in transportation).

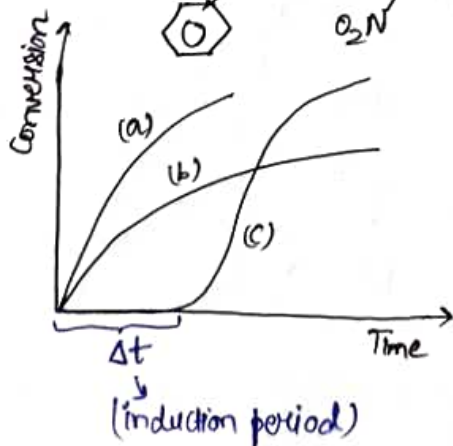
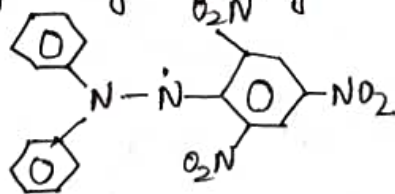
\hookrightarrow can be prevented using inhibitors (poisons)
 \hookrightarrow react with initiators to form stable molecule (kill initiators).

Retarder: React with free-radical active centres causing the rxnⁿ to be less efficient or yields species that slowly reinitiate polymerisation, the rate of polymerisation is reduced.

eg. Nitrobenzene

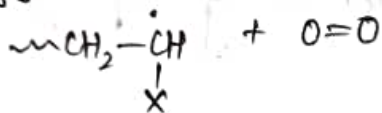
Quinones

Diphenyl picryl hydrazyl (DPPH)



(a): Normal polymerisation
 (b): In presence of a retarder
 (c) In presence of of an inhibitor

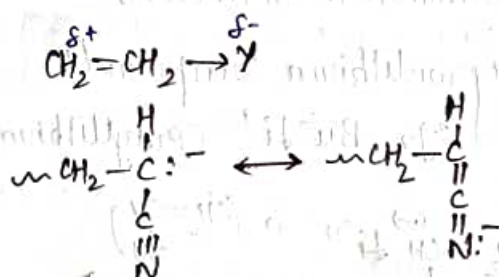
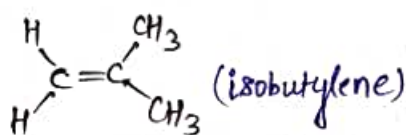
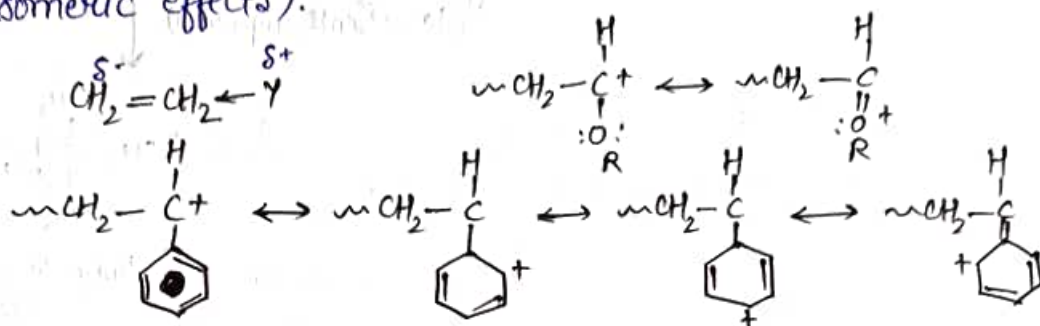
Oxygen:



- Peroxy radical may reinitiate polymerization slowly, or not at all.
- Reinitiation: Chains with weak peroxide ($-\text{O}-\text{O}-$) bonds in the backbone.
- Sites for bond scission leading to premature degradation of the polymer during use.

IONIC POLYMERISATION

- The active centre has an ionic charge.
- Monomer: Specific than radical polymerization.
- Proceed only with monomers that have substituent groups which can stabilize the active centre (e.g., by inductive and/or mesomeric effects).

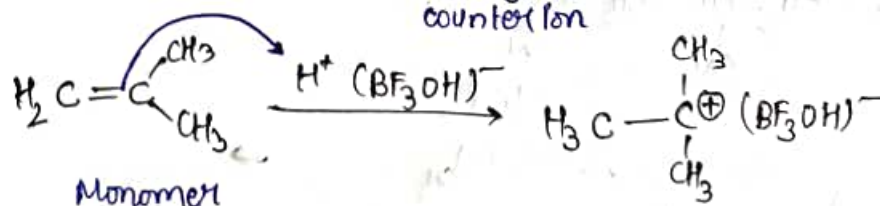
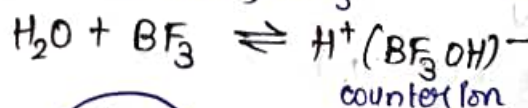


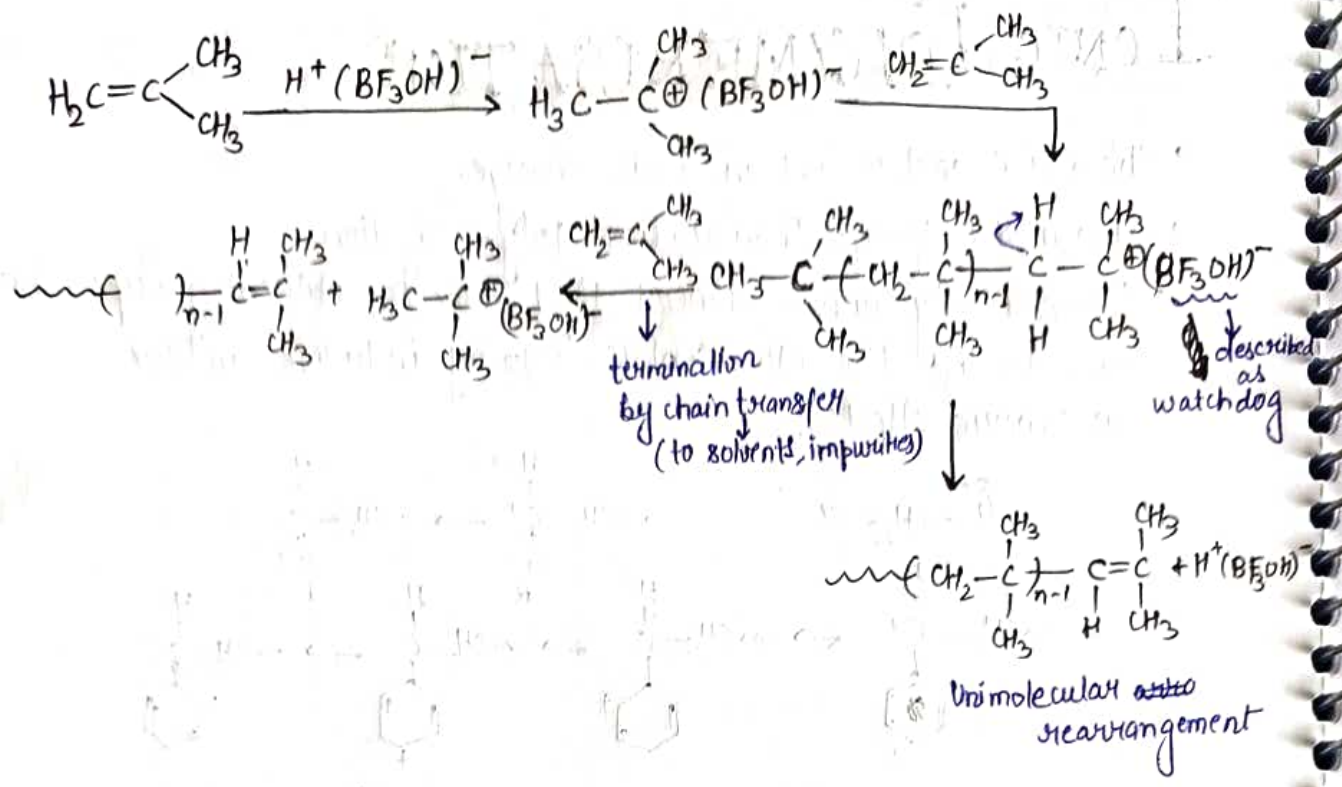
Cationic Polymerisation

- Cationic active centres are created by reaction of monomer with electrophiles (e.g., R^+).

Initiation:

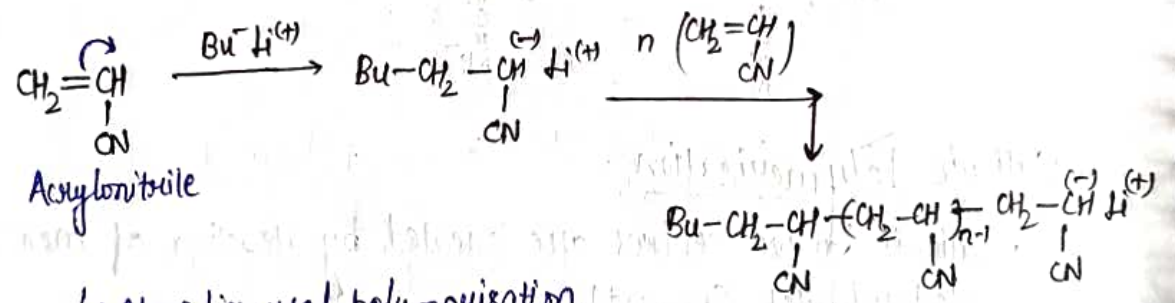
Initiators \rightarrow provide H^+
 e.g., Lewis acids (not strong acids)
 $\hookrightarrow \text{AlCl}_3, \text{BF}_3$.



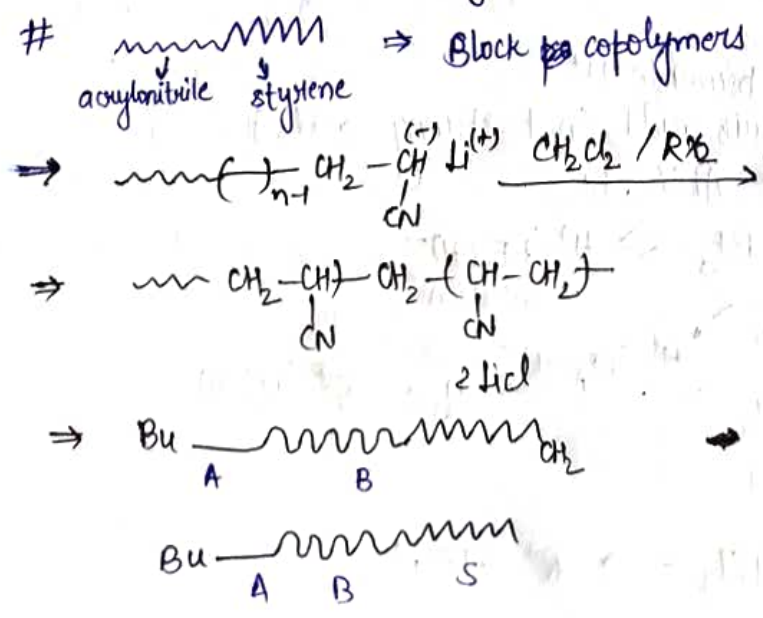


Anionic Polymerisation

- ↳ Living polymerisation (no termination on its own)
- ↳ Most common initiator: Organolithium compounds
eg., Bu^-Li^+ (Butyllithium)



↳ Monodispersed polymerisation



- ↳ Absence of inherent termination process
- ↳ Termination by ion-pair rearrangement does not occur: requires the highly unfavourable elimination of a hydride ion.
- ↳ The counter-ions used have no tendency to combine with the carbanionic active centres to form unreactive covalent bonds.
- ↳ In the absence of chain transfer reactions, the propagating polymer chains retain their active carbanionic end groups.
- ↳ More monomer is added after complete conversion of the initial quantity, the chains grow further by polymerization of the additional monomer and will again remain active.
- ↳ Polymer molecules, which permanently retain their active centres in chain polymerisation and continue to grow so long as monomer is available, are termed as living polymers.

Kinetics:

- ↳ The initiator reacts completely before any of the active centres begin to propagate.
- ↳ All of the initiator species exist in active form free in solution.
- ↳ The rate coefficient ' k_i ' for initiation is very much greater than the rate coefficient ' k_p ' for propagation.
- ↳ The total concentration of propagating carbanionic active centres is equal to the concentration $[I]_0$ of initiator used.
- ↳ Thus, in the absence of termination reactions.

$$R_p = - \frac{d[M]}{dt} = k_p [M] [M^-] \\ = k_p [M] [I]_0$$

$$\rightarrow \bar{X}_n = \frac{[M]_0}{[I]_0}$$

- Q] A 0.16 mol/L solution (3.50 mL) of butyllithium in toluene was added to a solution of styrene (8.40g) in toluene (200 mL). After complete conversion of the styrene, isoprene (28.00g) was added. When the isoprene had completely polymerized, the reaction was completed by addition of dichloromethane in toluene. Evaluate the relevant degrees of polymerization and the corresponding molar masses for the final polymer.

Soln: 3.5 mL 0.16 mol/L BuLi

8.4 g styrene

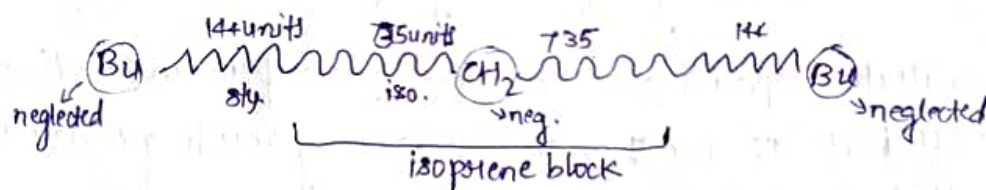
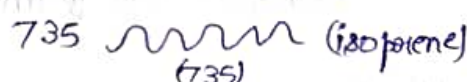
28 g isoprene

5.6×10^{-4} mol [I].

$$[M]_{\text{styrene}} = \frac{8.4}{104} = 0.0807 \text{ mol}$$

$$[M]_{\text{iso}} = \frac{28}{68} = 0.4117 \text{ mol}$$

$$\bar{D}_p = \frac{[M]_0}{[I]_0}$$



$$\text{Mol. mass of final polymer} = 144 \times 104 \times 2 + 735 \times 68 \times 2$$

$$\approx 1 \text{ lakh } 30 \text{ thousands g/mol.}$$

- Q] A sample of polystyrene prepared by bulk polymerisation using radioactive ^{14}C (AIBN).

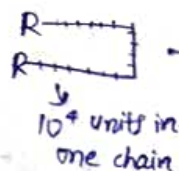
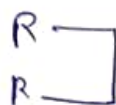
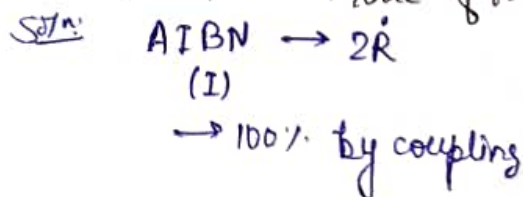
19-04-2023

$$M_n = 1000 \text{ kg/mol} \rightarrow 10^6 \text{ g/mol}$$

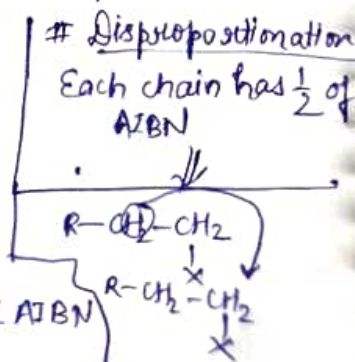
$$\text{PS} = 6 \times 10^5 \text{ counts s}^{-1} \text{ g}^{-1} \rightarrow 6 \times 10^9 \text{ counts s}^{-1} \text{ mol}^{-1}$$

$$\text{AIBN} = 6 \times 10^9 \text{ counts s}^{-1} \text{ mol}^{-1}$$

Calculate the mode of termination assuming no chain transfer.

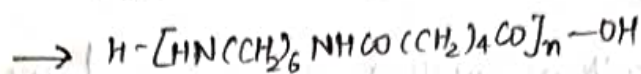
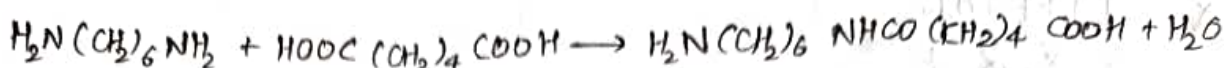


1 chain has 2R
 \downarrow
1 chain has 1 AIBN
 \downarrow
Coupling

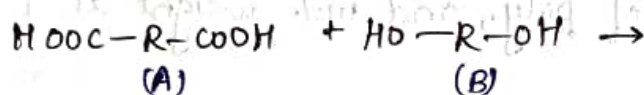


CONDENSATION POLYMERIZATION

(Stepgrowth)



- Formation of a polyester from monomer: $\text{HO}-\text{R}-\text{COOH}$
- Progress can be measured in terms of the concentration of the $-\text{COOH}$ groups in the sample (denoted A).
- These groups gradually disappear as the condensation proceeds.
- The condensation rxn can occur b/w molecules containing any no. of monomer units.
- Chain of many different lengths can grow in the rxn mixture.



$$[\text{A}]_0 = [\text{B}]_0 \quad (\text{2nd order; type-II})$$

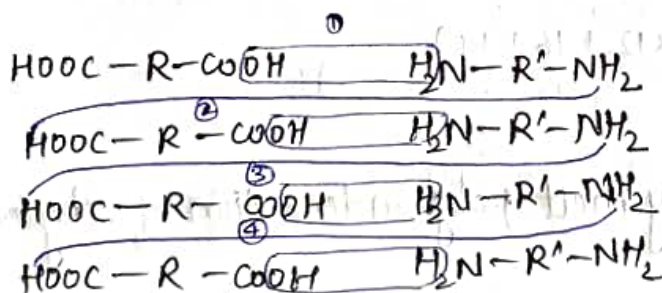
(reduced to type I)

$$\frac{1}{[\text{A}]} - \frac{1}{[\text{A}]_0} = kt$$

$$\text{Extent of polymerization, } P = \frac{[\text{A}]_0 - [\text{A}]}{[\text{A}]_0}$$

↓
fraction of molecules that has been reacted.

24-04-2023



Monomers
(8 moles of $-\text{COOH}$)

Monomers
(8 moles of $-\text{NH}_2$)

$\text{Dp} = 2$ (\because 2 monomers are involved) \rightarrow form dimer

$\text{Dp} \neq$ Repeat units no. \rightarrow for condensation poly.

$[\text{A}]_0 = 8$	$[\text{A}]_0 = 8$	$[\text{A}]_0 = 8$
$[\text{A}] = 4$	$[\text{A}] = 2$	$[\text{A}] = 1$
for ① dimer	② tetramer	③ octamer
		formation steps

①, ②, ③, ④
↓
steps

$$\bar{X}_n = D_p = \frac{[A]_0}{[A]}$$

$$\text{From } \left(\frac{1}{[A]} - \frac{1}{[A]_0} = kt \right),$$

$$\bar{X}_n = 1 + kt[A]_0$$

$$\Rightarrow \bar{X}_n \propto t.$$

$$\boxed{\bar{X}_n = \frac{1}{1-p}} \rightarrow \text{Carothers equation.}$$

$$[A] = \frac{[A]_0}{1 + kt[A]_0}$$

$$\text{For } \bar{X}_n = 100, P = 0.99$$

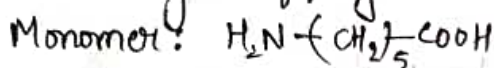
$$\bar{X}_n = 1000, P = 0.999$$

Q1 Consider a polymer formed by step-growth polymerisation.

$$k = 1 \text{ L mol}^{-1} \text{ s}^{-1}$$

$$[A]_0 = 4 \times 10^{-3} \text{ M}$$

Calculate degree of poly., extent of poly., and mol. weight at $t = 1.5 \times 10^4 \text{ s}$.

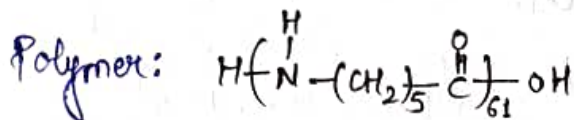


Soln: $\bar{X}_n = 1 + kt[A]_0$

$$= 1 + 1 \times 1.5 \times 10^4 \times 4 \times 10^{-3}$$

$$= 61$$

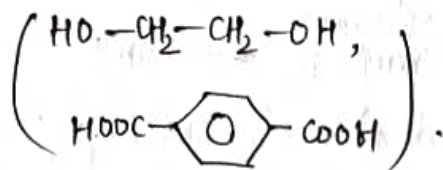
$$\bar{X}_n = \frac{1}{1-p} \Rightarrow 61 = \frac{1}{1-p} \Rightarrow 1-p = \frac{1}{61} \Rightarrow 1 - \frac{1}{61} = p \Rightarrow p = \frac{60}{61}$$



$$\text{Mol. wt.} = 61 \times (11 \times 1 + 6 \times 12 + 16 + 14)$$

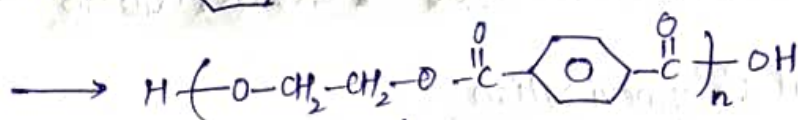
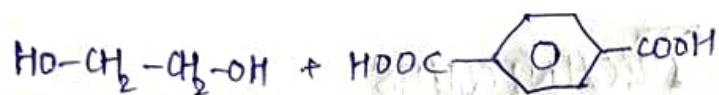
$$= 61 (113)$$

Q2 A polyester was prepared by melt polycondensation of ethylene glycol and terephthalic acid



Analysis of the polymer showed that it contained 5×10^{-5} moles of hydroxyl groups. Find out the no. average molar mass of the polymer, if 1.94 g of ethylene glycol was taken initially for the rxn and the reactants were taken in 1:1 molar ratio.

Soln.



↓
192 = Repeat unit molar weight

$$[A] = 5 \times 10^{-5} \text{ moles}$$

$$\frac{1.94}{62} \times 2 = 0.031 \times 2 = 0.062 = [A]_0$$

$$\bar{X}_n = \frac{[A]_0}{[A]} = 1240$$

↓
No. of monomer

↪ $\frac{1}{2} \times 1240 = \text{No. of Repeat unit}$

$$\bar{M}_n = \left(\frac{1240}{2} \right) \times 192$$

POLYMERISATION TECHNIQUES

Radical Polymerisation

① Bulk Polymerisation

↳ Disadvantages:

conc. of monomer $\uparrow \Rightarrow$ Rate of poly. $\uparrow \Rightarrow$ No control over reaction \uparrow
 \Rightarrow Autoacceleration $\quad \quad \quad \Rightarrow$ viscosity \uparrow

↳ Advantages:

↳ Rate of polymerisation \uparrow , conc. of monomer \uparrow
 ↳ we get a pure polymer with high mol. weight.

The monomer is first partially polymerised to yield a viscous solⁿ which then is poured into a sheet mould where poly. is completed at high T.

polymethylmethacrylate polymer: $(\text{CH}_2 - \overset{\text{CH}_3}{\underset{\text{OCH}_3}{\text{C}}} - \overset{\text{O}}{\text{C}})_n$ (PMMA)

② Solution Polymerisation

↳ used of solvent which dissolves initiator, monomer & polymer.

↳ Advantages: Autoacceleration is prevented (& facilitate good heat transfer).

↳ Disadvantages: Impurity of solvent.

Isolation of polymer requires either evaporation of solvent or precipitation of polymer.

↳ Low mol. mass (due to chain transfer reaction).
 ↳ Rate & degree of poly. \downarrow

③ Suspension Polymerisation (Beads poly./ Pearl Poly.)

↳ Suspend small droplets of monomer and initiator (stⁿ mixture)

↳ Polymers have very low (non-polar) solubility in medium (water). suspended using polar

↳ Thermol is made using this \rightarrow made from EPS (Expanded polystyrene).

Initiator, monomer & polymer \rightarrow insoluble in the suspension medium.

Advantages:

↳ autoaccelⁿ much better controlled.

↳ polymers are easily isolated by filtration or centrifugation

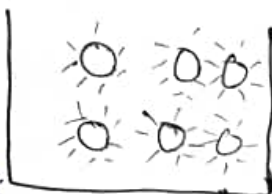
↳ improved heat dissipation. (good heat transfer)

Sodium lauryl sulphate: $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^- \text{Na}^+$

\rightarrow AIBN: hydrophobic

\rightarrow Each droplet is acting like bulk polymer reactor.

\rightarrow directly converts to polymer in bead form.



0.05-0.1mm beads

↳ A solⁿ of initiator in monomer is prepared and then added to the preheated aqueous suspension medium. Poly. T. are limited by the bp. of water (70-90°C)

↳ Droplets of the organic phase are formed and maintained in suspension by vigorous agitation throughout stⁿ, or dispersion stabilizers dissolved in aqueous phase.

↳ Disadvantages: Removal of dispersion stabilizers, polymers are contaminated.

④ Emulsion Polymerisation \rightarrow Use of surfactant above CMC

→ Initiator soluble only in aq. dispersion medium (not in monomer) (critical micelle concentration), unlike in suspension polymerisation.

Dispersion: $\text{CH}_3(\text{CH}_2)_n\text{SO}_4^- \text{Na}^+$

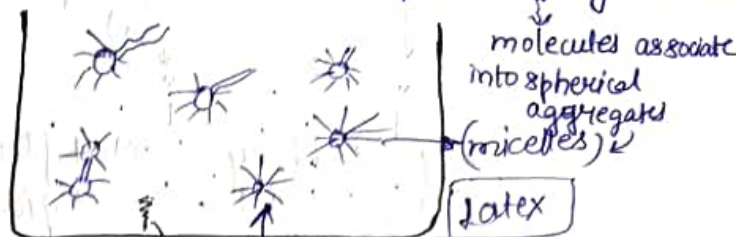
stabilizers

Amphiphilic
Anionic surfactant hydrophobic hydrocarbon chain

$$\text{~~~~~SO}_4^{2-} \text{Na}^+$$

lic : H_2O_2

Hydrophilic : H_2O_2
initiators $K_2S_2O_8$



oligomer droplets
(not monomer)
(not polymer)

unreacted monomers
are present
(reservoir)

go into micelles (reservoir)
↓
propagation starts ~~unag~~
↓
size increases

Freeze drying

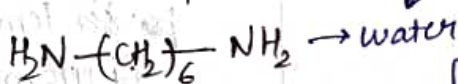
→ Reaction product: Latex is a colloidal-stable dispersion of particulate polymer in water (polymer particles diameters $\sim 0.1-1 \mu\text{m}$).

→ Interfacial polycondensation: Proceed at interface b/w an aq. & an organic medium.

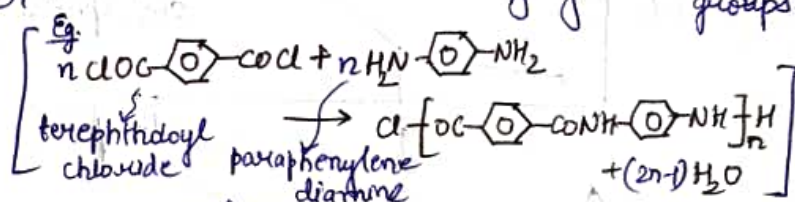


→ very fast $n \log n$

for reactants having highly reactive π groups.



Poly Melt Condensation



→ Used for polymerisation of monomers which have at least one solid component and do not decompose around their m.p.s.

- $T \uparrow$, Inert atmosphere (of N_2 or CO_2) to avoid side rxns. In some cases, rxn is carried out under reduced P. to facilitate removal of the byproduct.
- Polymer ~~is~~ formed is in the solid state.

→ Polymer is formed in the molten state at T_m .

→ eg. polymerisation of polyethylene terephthalate (from dimethyl terephthalate & ethylene glycol), nylon 6,6 preparation.

Solution Polycondensation

→ Reactants are taken as a soln in a suitable inert solvent.

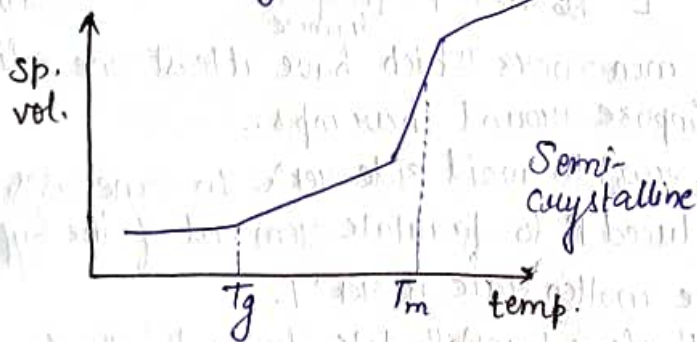
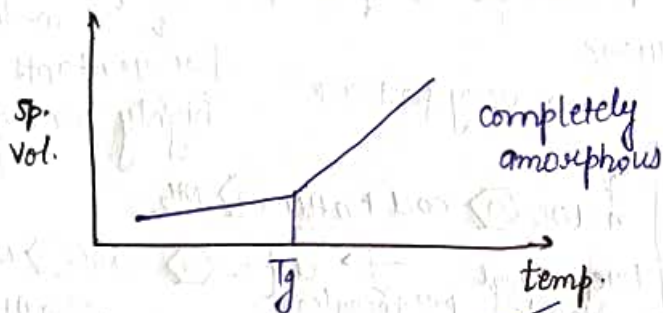
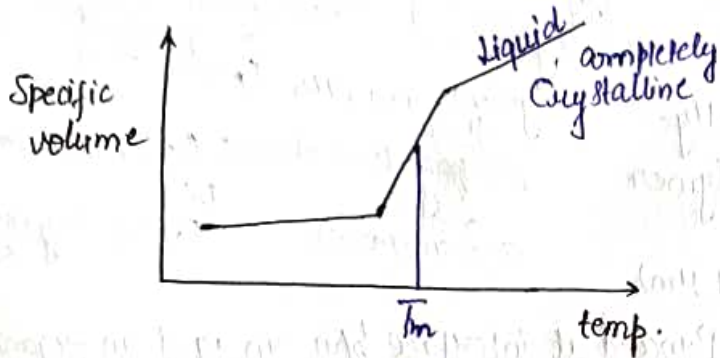
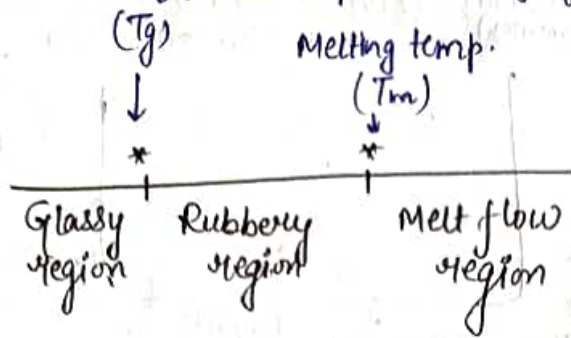
- Reaction at $T \downarrow$ during which heat & mass transfer are easier than in the melt technique.
- The solvent can also serve as an entrapping agent for the byproduct formed, and hence, the removal of the byproduct becomes easy.
- Due to solvent phase transition, the byproduct removal becomes easy.

→ In liquid solvent phase, kinetic probability of chain growth is low and this leads to a reduced rate and a low degree of polymerisation.

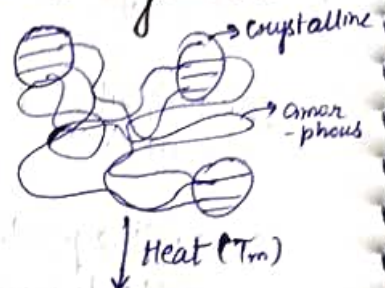
Eg: Liquid polyester resins based on glycols and unsaturated dicarboxylic acid.

CRYSTALLINITY

Glass transition temp. \rightarrow temp. at which amorphous region changes from glassy to rubbery region. Amorphous Crystalline

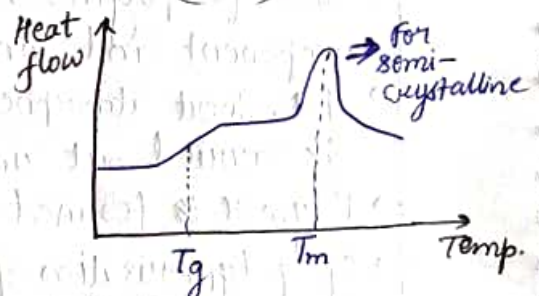


\rightarrow Polymers can be either amorphous or crystalline.
 \rightarrow Generally, they are Semi-crystalline.

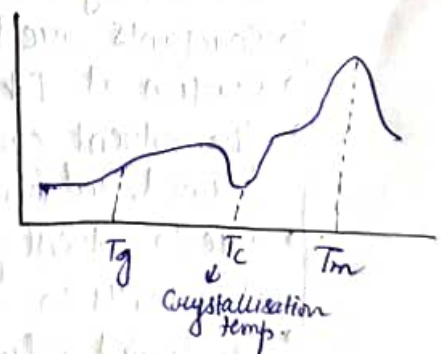


Amorphous region will attain freedom of internal Brownian motion (Glass \rightarrow rubbery)
 After T_m , both amorphous & crystal. get segmental motion.

Technique to find melting temp.:
 Dilurometry \rightarrow not used anymore
 or
 Differential Scannery Calorimetry (DSC)



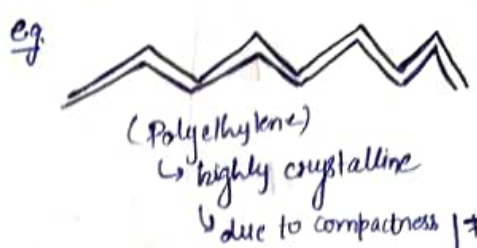
Melting - endothermic
 # Crystallisation - exothermic



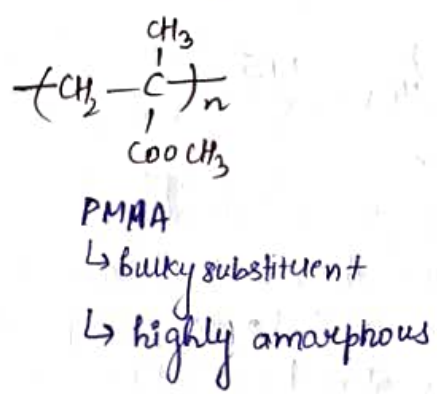
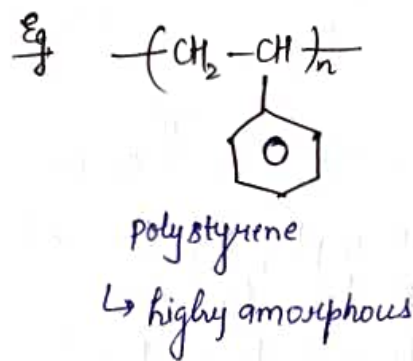
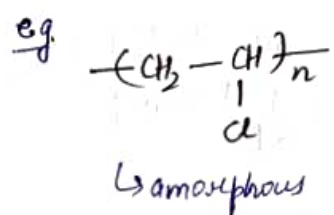
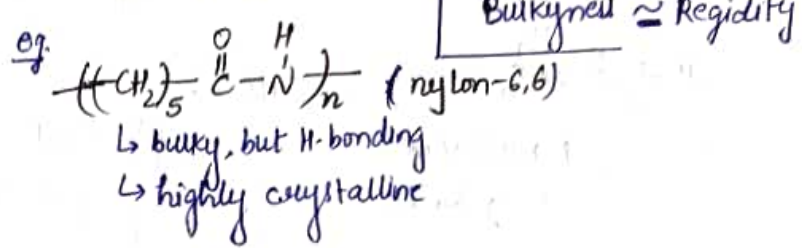
Factors affecting Crystalline nature:

① Intermolecular forces — secondary attractive force (hydrogen bonding) → more crystalline

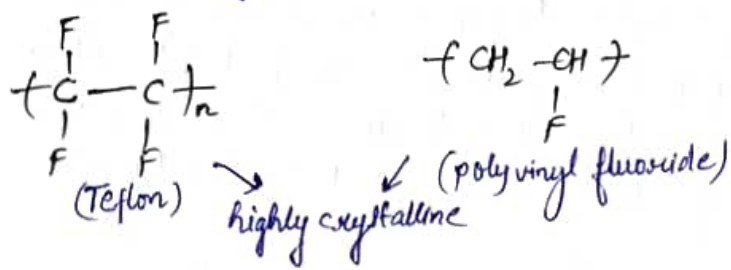
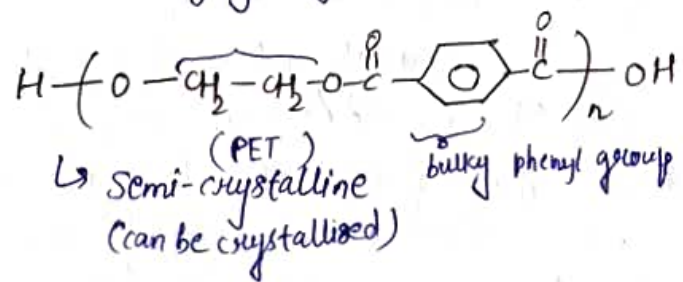
② Bulkiness / compactness
 ↓
 less crystalline more crystalline



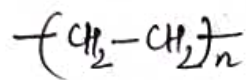
③ Flexibility / Rigidity
 ↓
 high value ⇒ more amorphous
 ⇒ less crystalline



Cellulose
 ↳ amorphous due to theory
 ↳ but, highly crystalline



eg.

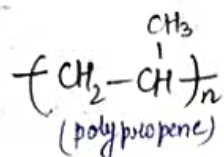


$T_g (^{\circ}\text{C})$

-127

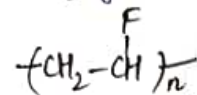
$T_m (^{\circ}\text{C})$

137



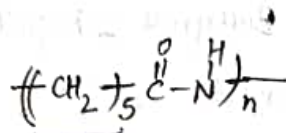
-1

176



41

200



40

223

CH₂ length \uparrow \Rightarrow H-bond \downarrow
 $\Rightarrow T_g, T_m \downarrow$

Nylon-6,6

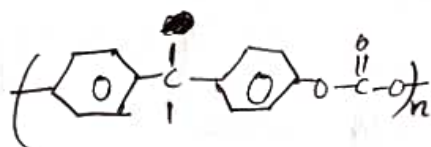
50

265

PET

61

270



145

-

(polycarbonate)
 $\hookrightarrow \text{CD}$

PVC

81

273

Polystyrene
 (PS)

100

250

PMMA

105

220

Polytetrafluoroethylene
 (PTFE)

117

327

\hookrightarrow highly crystalline