⟹ Free radical Vinyl polymerization

$$n\ CH_2=CH-G \xrightarrow{\text{Initiator}} \sim CH_2-CH(G)-CH_2-CH(G)-CH_2-CH(G)\sim$$

Vinyl monomer

or

$$\left(-CH_2-CH(G)-\right)_n$$

polymer

at the doubly bonded carbons – the vinyl gr – so it is called vinyl polymerization. A wide variety of unsaturated monomer may be used to give polymers with different pendant group (G) attached to the polymer back bone.

(as)

$$CH_2=CH-Cl \longrightarrow \sim CH_2-CH(Cl)-CH_2-CH(Cl)-CH_2-CH(Cl)\sim$$

Vinyl chloride

Poly vinyl chloride (PVC)

$$CH_2=CH-CN \longrightarrow \text{Polyacrylonitrile (Orlon)}$$

acrylonitrile

$$\text{Styrene} \longrightarrow \text{Polystyrene}$$

Polymerization involves addition of free radical to the double bond of the monomer

↳ Addition first of the free radicals generated from the initiator ⟷ & then of the growing polymer molecul. This is Ex of chain reaction -polymerization.

(Process) →

(a) Peroxide → Rad.

(b) Rad. + $CH_2=CH$ (–G) → Rad $CH_2-\dot{C}H$ (–G)

chain initiating step

(c) Rad $CH_2-\dot{C}H$ (–G) + $CH_2=CH$–G → Rad–CH_2-CH(–G)$-CH_2-\dot{C}H$ (–G)

chain propagation step

& then steps like (c) repeated until finally combination or disproportion

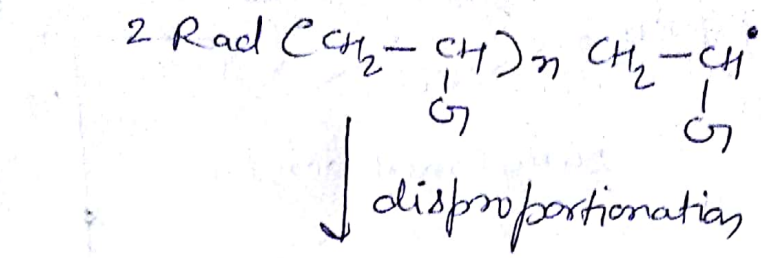
(d) 2 Rad $(CH_2-CH)_n-CH_2-\dot{C}H$ (–G)

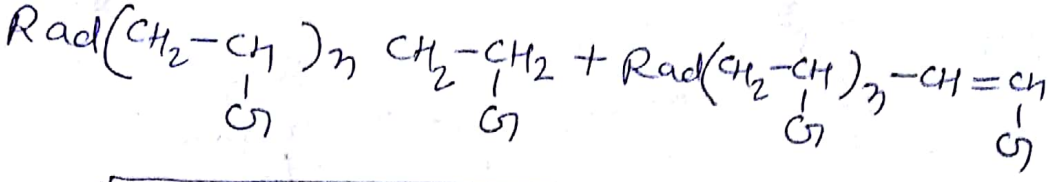
combination ↓

. Rad $(CH_2CH)_n-CH_2-CH-CH-CH_2-CH-CH_2)_n$ Rad (–G)

OR

(e)





(d) & (e) are chain terminating step

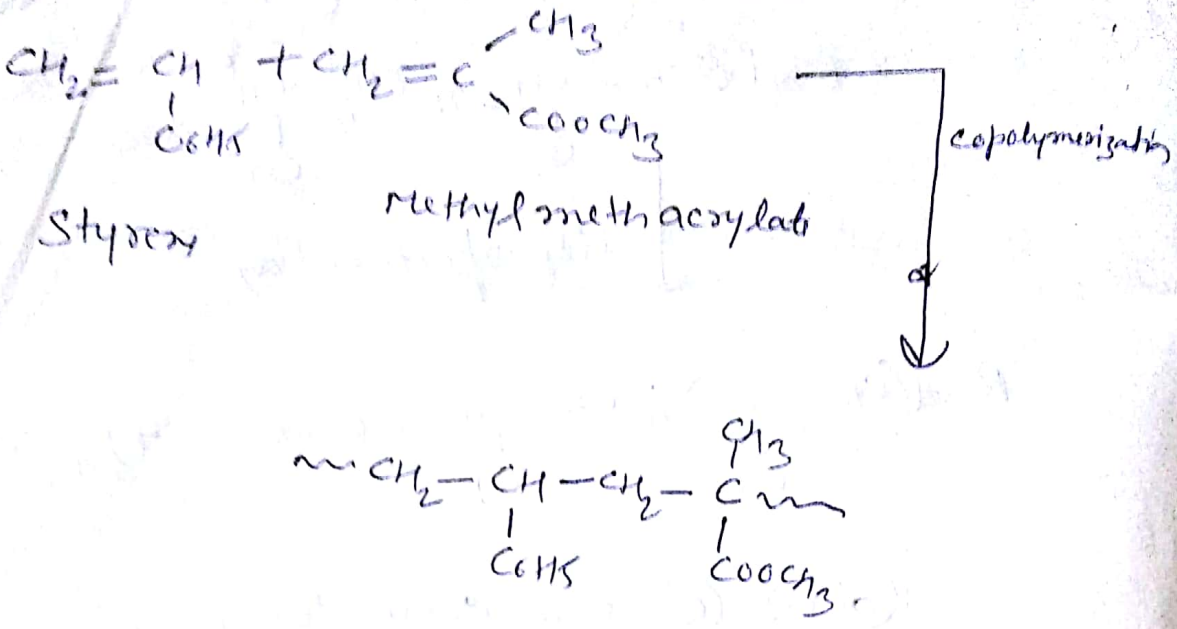
In each step the consumption of a free radical is accompained by the formation of a new, bigger free radical.

Eventually, the reaction chain is terminated by steps that consume but do not form free radicals, combination or disproportionation of two free radicals.

(X) **Copolymerization** →

when two or more different monomers are allowed to polymerize together the product formed is called a copolymer & this process is called copolymerization

(Ex) The polymerization of a mixture of Styrene & methyl methacrylate gives a copolymer called Styrene methacrylate copolymer.



In general, the composition of the copolymer depends not only upon the proportion of the monomers but on their relative reactivity

→ The properties of copolymers are usually quite different from those of homopolymers derived from each of the combining monomers.

→ Acually, copolymers have better physical & mechanical properties

→ Some other polymer के 3-4 को table में

another variant of chain growth poly

⊗ Coordination polymerisation →

generally reaction between dienes & olefins

Dienes & olefins → monomer

↓ catalysed by organo-metallic compds (As Ni, Co, Mo, V, Ti or Rh)

Monomer–catalyst complex

↳ coordination bond used होता है

The propagation process starts at the active centre site when chain growth begins.

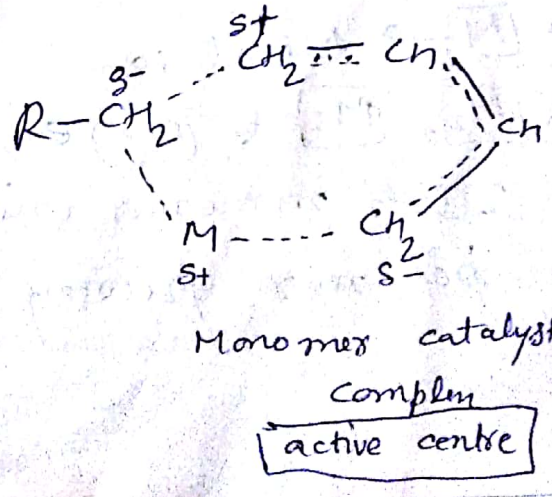
→ This polymerization is also known as Insertion polymerization since monomer molecule is inserted in b/w the metal ion & carbanion.

CH_2-R + $CH_2=CH-CH=CH_2$
CH_2-M

organometallic catalyst

Diene Monomer

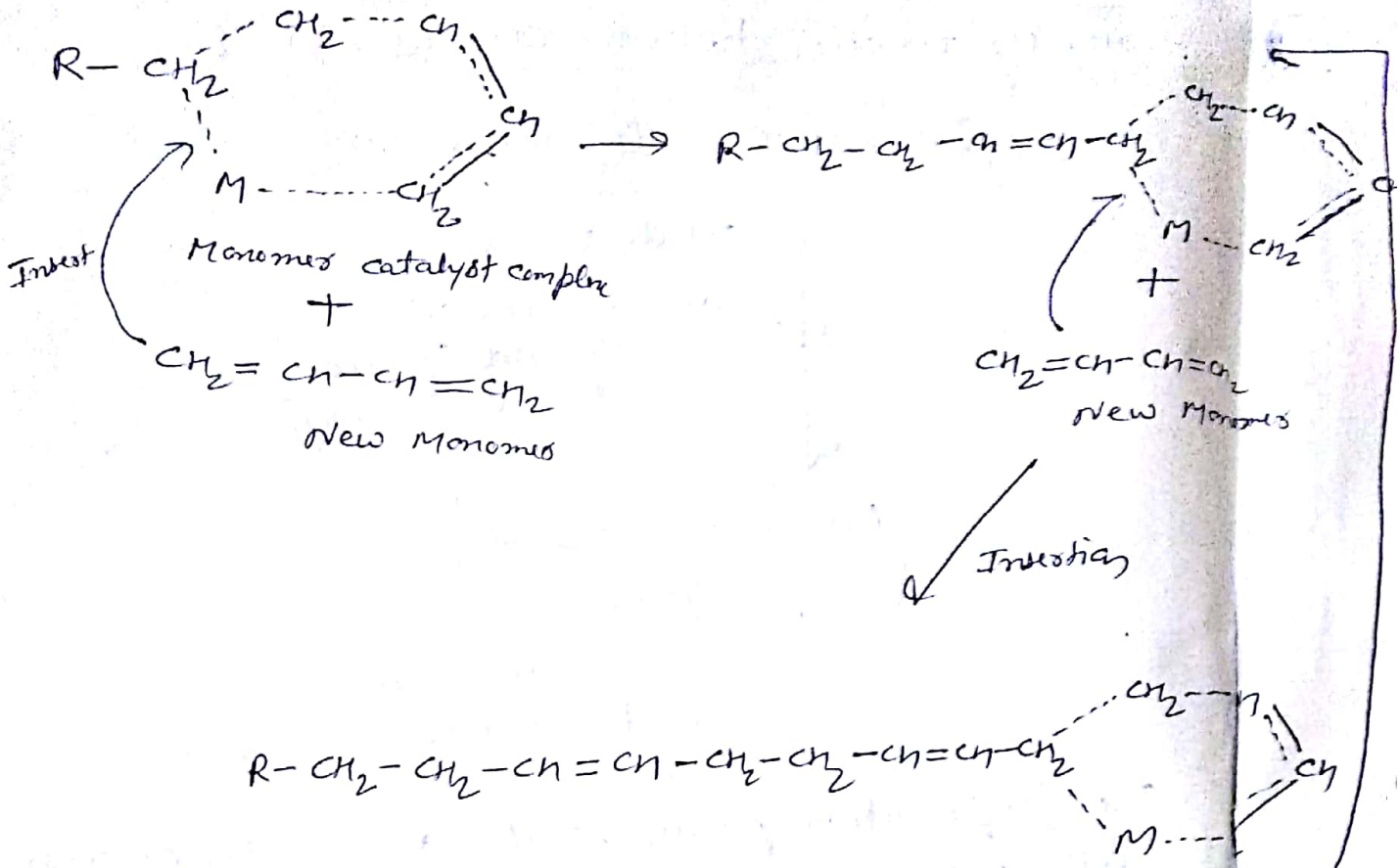
M = Transition metal



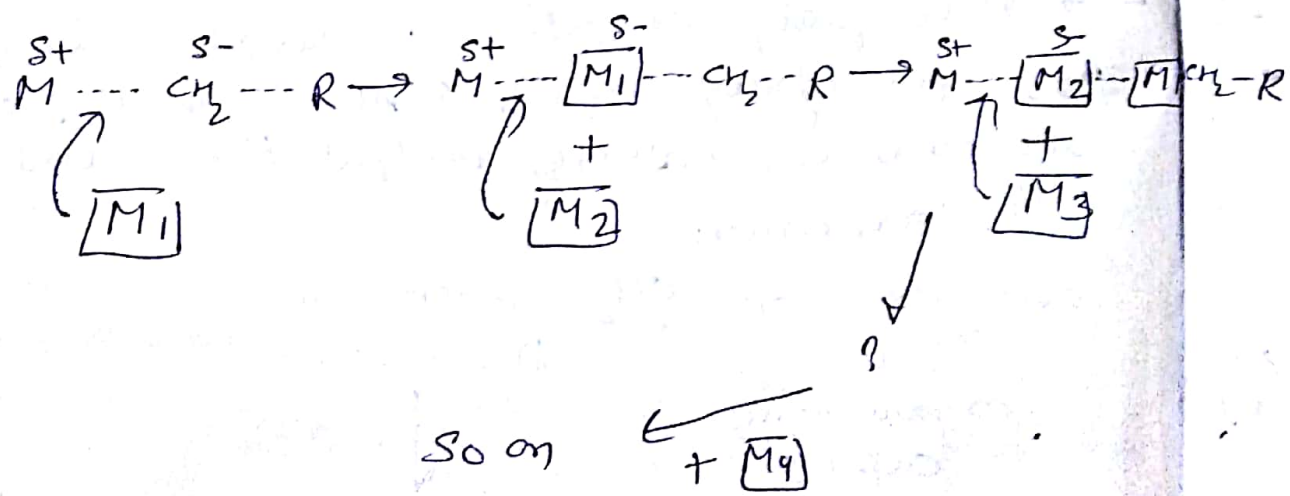
Monomer catalyst complex

active centre

chain propagation process → chain growth begins as—



Insertion may be shown as →



So on

where [M] → Metal ion

[M1], [M2], [M3] & [M4] etc are the Ist, IInd, IIIrd & IVth monomer units which are added to the polymer growing chain.

(Q-7)

So the coordination polymerization is characterised by 3 steps —

(a) $M-R + CH_2=CH(X) \longrightarrow M-CH_2-CH(X)-R$

active centre

[Initiation]

(b) $M-CH_2-CH(X)-R + n\,CH_2=CH(X) \longrightarrow M-CH_2-CH(X)-[CH_2-CH(X)]_n-R$

[Propagation]

(c) ~~Termination~~

$M-CH_2-CH(X)-[CH_2-CH(X)]_n-R + CH_2=CH(X)$

$\downarrow$

$M-CH_2-CH_2 + CH_2=C(X)-[CH_2-CH(X)]_n-R$

Termination by transfer with monomer

M = T.M

→ Glass Transition temp → so clear है कि all amorphous solid & many crystalline polymer के लिए एक temp boundary होती

Glassy state (Brittle plastic)	elastomer Rubbery OR Viscoelastic state (Tough plastics & rubbers)	Viscofluid State (Polymer melts)

Tg — Glass transition temp   Tf — Flow temp

T →

(Change of state with temp in polymeric materials)

Glass transition temp → वो temp, below which a polymer is hard & brittle & above which it is soft

→ The hard, brittle state is → **Glassy state**

→ Soft flexible state is → **Rubbery or visco-elastic state**

viscofluid state → on further heating the polymer, एक highly viscous liquid बन जाता है & flow करने लगता है → this transition takes place at temp ~~place~~ as Tf

Rheology of polymeric materials

→ It is the study of deformation or flow behaviour which is showing by materials

→ low molecular wt solids & liquids show their characteristic flow behaviour acc to Hook's or Newton's equⁿ —

viscosity → friction force of liquid (liquid के यदि particle आपस में attached ie interaction है) → तो viscosity high, यदि interaction नहीं है (ie free है) तो viscosity (zero)

→ It is generally defined as the study of flow. It is the scientific study of How polymeric fluids deform when subjected to external stresses

↳ during deformation a polymer will alter its molecular configuration & at the end of the deformation will return to to equilibrium due to Brownian motion.

↳ Newton's law of viscosity → The shear stress in a flowing fluid is ∝ Rate of shear strain

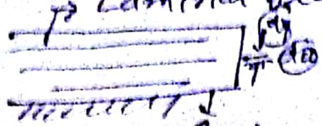
$$\tau \propto \frac{du}{dy}$$ → Rate of shear strain

$$\tau = \mu \frac{du}{dy}$$ where μ = viscosity

↳ वो fluid, which follow Newton's law of viscosity are called Newtonian fluid.

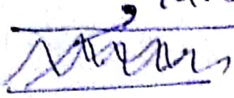
↳ Newtonian fluid वे होते हैं, जिसमें fluids की parallel layers के बीच में shear forces काम करता है

→ Laminar fluid layers की form में flow करता है



Surface

→ Turbulent fluid (zigzag manner में flow करता)



↓ Shear strain

↓ viscosity

Viscosity का अर्थ →

↳ liquid के particle के बीच के interaction or affinity के measurement को ही viscosity

water < Honey < Tooth past → viscosity
(Small) (highly)

↳ Shear stress, force tending to cause deformation of a material by slippage along a pla or planes parallel to the imposed stress

$$\tau = \mu \frac{du}{dy}$$

τ → Shear Strain
μ → Visosity
du → change in velosity
dy → in distance

1

Polyethylene → 2 types

(I) Low density poly ethylene (LDPE)

(Prep) → By heating ethylene at 200°c & a pressure of 1500 atm & in presence of traces of oxygen.

↳ Involves free radical polymerization = इस प्रकार low density polyethylene मिलता है

$$nCH_2=CH_2 \xrightarrow[1500\,atm]{200°C} (CH_2-CH_2)_n$$

↳ इस प्रकार प्राप्त polythene का molecular mass ~ 20,000 & has a branched str. → इसी कारण से प्राप्त poly ethylene की low density (.92) & low M.P (110°c) होता है

(II) High density poly ethylene (HDPE)

prepared by the use of Ziegler-Natta catalyst at 160 under P of 6-7 atm

↳ It is linear chain

↳ " has high density (.97)

↳ " " high M.P (130°c)

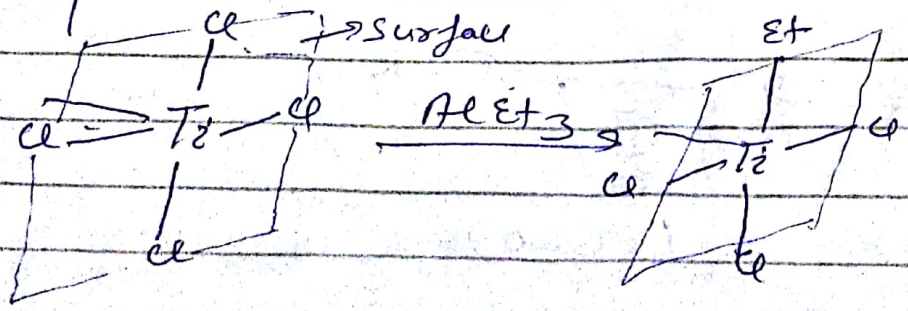
इन दोनों कारणों से इसे high density polyethylene कहते है

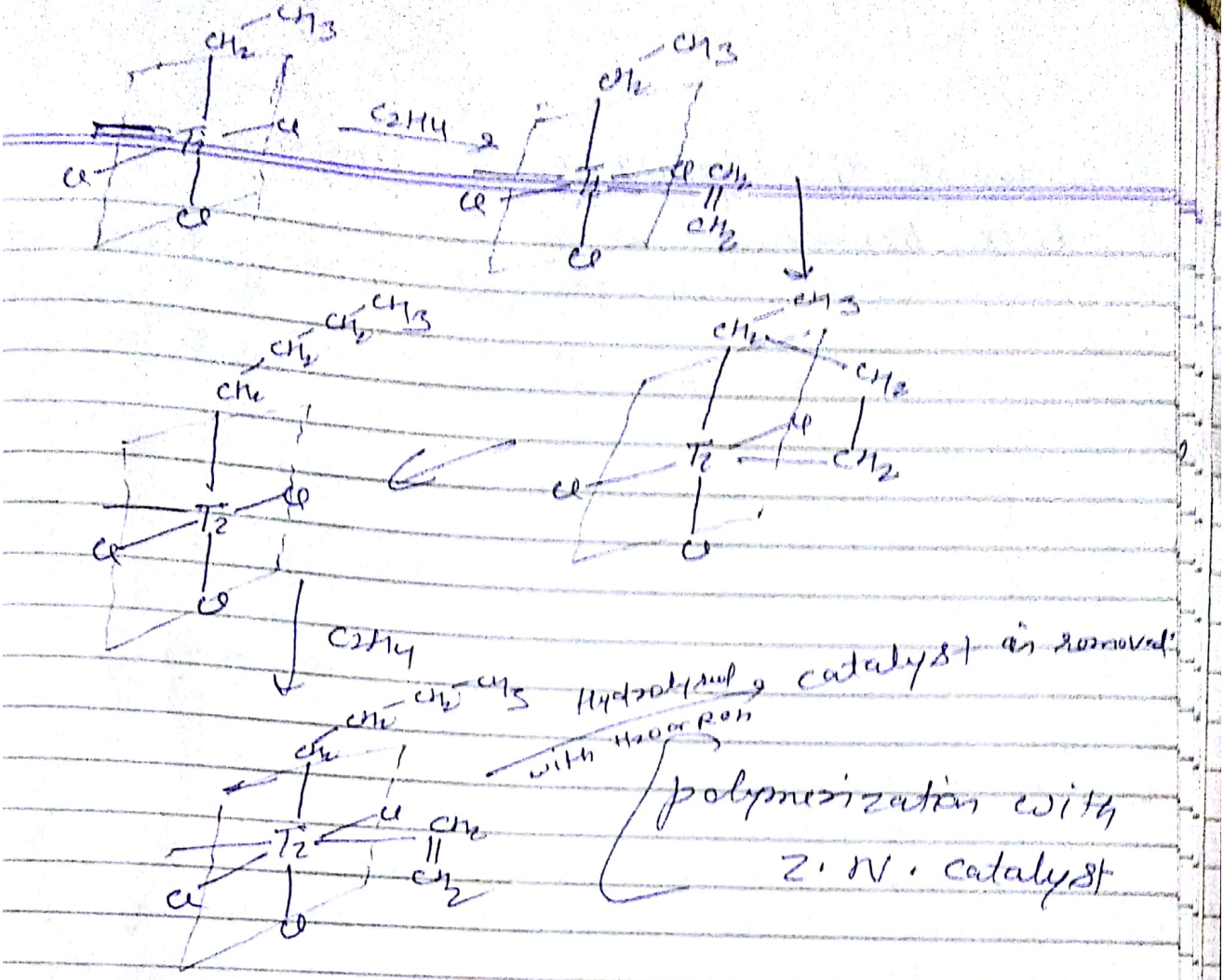
↳ It is translucent polymer

(X) Ziegler–Natta catalysts → Solution say Et_3Al & $TiCl_4$ in a hydrocarbon solvent react exothermically to form a brown solid. This is the important Z.N. catalyst for polymerizing ethene (ethylene) to form polythene.

↳ The $AlCl_3$ / $TiCl_4$ produces stereoregular polymers (that is polymers where the molecules have the same orientation). These are stronger & have higher M.P than atactic or random polymers.

The active species is Ti^{III} & the $AlEt_3$ can reduce $TiCl_4$ to $TiCl_3$ in situ or $TiCl_3$ may be added instead.





Mech → double bond in ethene attaches itself to a vacant site on a Ti atom on the surface of the catalyst. A carbon shift reaction occurs & the ethene migrates & is inserted b/w Ti & C in the Ti–Et bond. This extends the C-chain from 2 to 4 atoms, leaving a vacant site on Ti

↳ $CH_3-CH=CH_2$ के साथ भी reaction हो सकती है

↳ polymerization can be carried out relatively mild conditions from room temp to 93°C & from atm pressure to 100 atm.

↳ This polymer obtained is called high-density polythene & has a density .95–.97 gcm^{-3} & a M.p of 135°C. It has a molecular wt of 20000 – 30000 &.

& consist of straight chain with very little branching.

Degradation

→ degradation means change in properties as lusture & strength either during the fabrication or during the daily usage

↳ degradation means a decrease in molecular wt of polymer as plastic bucket को sun & rain में long time तक छोड़ देने पर strength lusture & strength loss हो जाती है यह polymer के molecular wt में uncontrolled change के कारण होता है

→ Types of degradation → chain end deg.
→ Random deg.

① Chain end deg → chain के end से एक एक monomer release होते रहते है
↳ Reverse of propogation step in chain polymerization → so called depolymerisation
↳ closing of a zip → represent polymerisation
↳ opening of a zip → " depolymerisation

→ chain end degradation से polymer का molecular wt धीरे-2 decrease होता जाता है

$M_n^{\cdot} \longrightarrow M_{n-1} + M$

$M_{n-1}^{\cdot} \rightarrow M_{n-2}^{\cdot} + M$

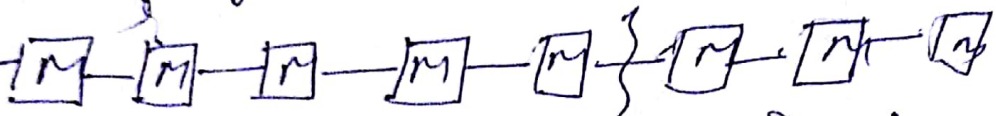
$M_{n-2}^{\cdot} \rightarrow M_{n-3}^{\cdot} + M$ & so on

where $M_n^{\cdot}$, $M_{n-1}^{\cdot}$, $M_{n-2}^{\cdot}$ represent the polymeric chain made up of many monomeric unit

(b) Random degradation

This takes place at any random point along the polymer chain instead of at the end chain

↳ Reverse of polymerisation process

(as) 

↳ यह low molecular wt के fragments में होता है but practically no monomer is liberated.

as degradation of polyester

$$\sim\overset{O}{\overset{\|}{C}}-OR + H_2O \rightarrow \sim\overset{O}{\overset{\|}{C}}-OH + ROH$$

↳ साथ molecular wt में sudden decrease होता है

↳ degradation of polymer may be brought by →

(a) By physical factors → heat, light or mechanical stress

(b) By chemical agents → as O_2, O_3, acid or alkalies.

⟹ Types

(1) Thermal → degradation under the influence of heat.

It may take place either by unzipping or randomly

→ The unzipping mechanism leads to the formation of pure monomer.

→ While random degradation से, a no. of products बनते हैं, जो polymer की size के upar depend करते है)

⟹ Factors affecting the C–C bond Stability → जैसे-2 C–C chain पर substrate की NO बढ़ती जायेगी, polymer की stability बढ़ती जायेगी)

(a)

polyethylene > polypropylene > ...

(Most stable)

↳ But ऐसा always नहीं होता है

(a) (a) PTFE → Polytetrafluoroethylene

↳ यह thermally very stable, since C–F bond की dissociation energy बहुत ज्यादा है)

(b) Presence of aromatic ring → aromatic ring की NO बढ़ने पर thermal Stability बढ़ती है  ....

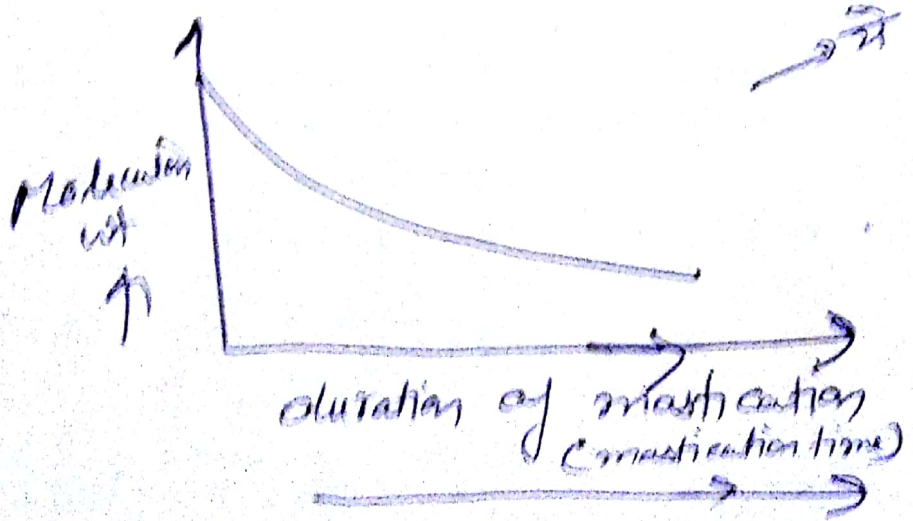
(c) The presence of oxygen atom in the polymeric chain & branching also make polymers susceptible to thermal degradation

(2) Mechanical degradation →

when a polymer as polystyrene is dissolved in a suitable solvents & subjected to vigorous stirring or heating, then it mechanical degs. show करता.

as rubber को ambient temp पर O_2 के atom को Masticate करते हैं, तो थोड़ी degradation नहीं होता है, but O_2 or air की presence में degradation very quickly हो जाता है

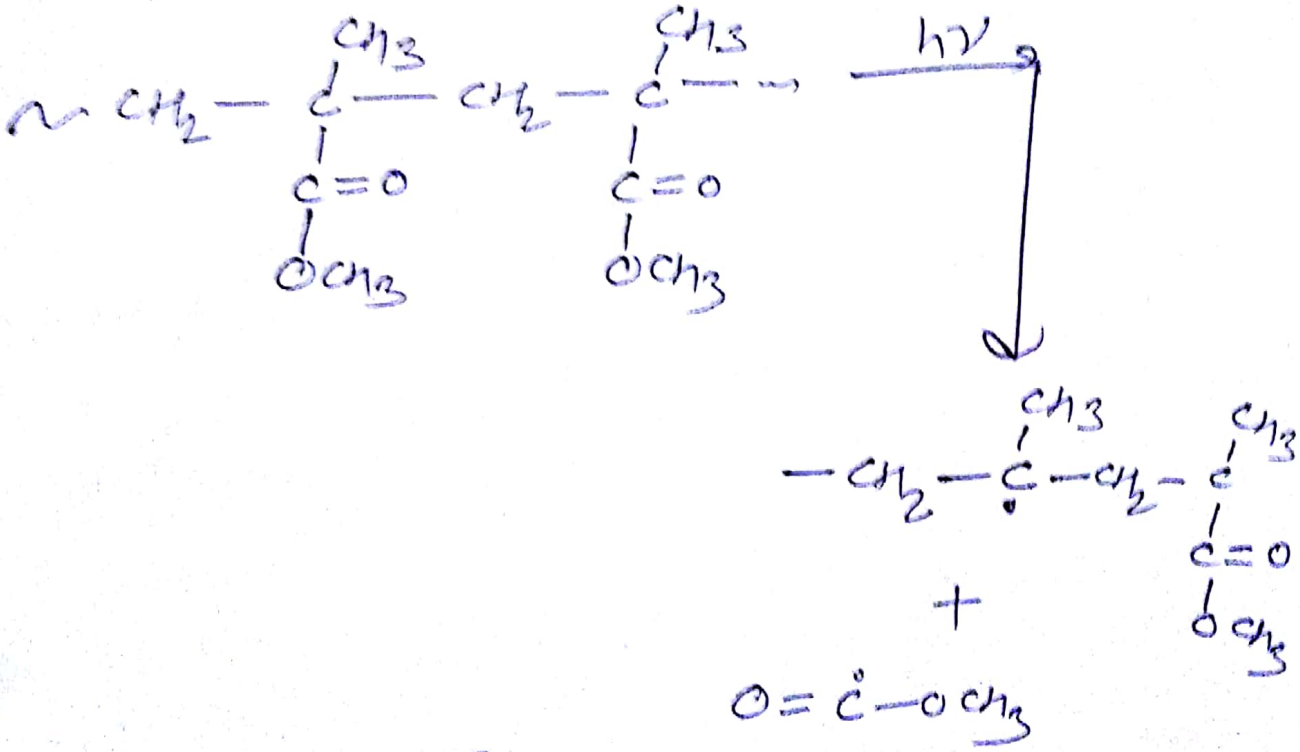
→ Mechanical degradation show करता है



© Photodegradation →

This process brought about by U.V light.
• The yellowing & the embrittlement on storage, of some of the transparent plastics or coloured rubber articles are also due to their interaction with U.V light

as U.V irradiation of polymethylmetha -crylate in molten state.



& so on.

⟹ Use of photostabilisers in photodegradation → polymer को photodegradation से protect करने के लिए plastic में photostabiliser को कुछ मात्रा में मिलाते हैं

as phenyl salicylate (Salol)

↳ ~~photosen~~ photostabiliser U.V radiation को absorb करते हैं & absorb energy को environment में dissipate कर देते हैं

(d) Oxidative degradation →

This usually leads to hardening, discolouration & surface change in the polymer molecule.

↳ This degradation mainly depends on its str.

(e) Degradation by high energy radiation → X-rays, gamma rays, α-, & β rays are well know high energy radiation.

↳ High energy radiation smash a polymer molecule to tiny fragments

↳ Many polymers when exposed to high energy radiation give out gases as H_2, CO_2, CO, CH_4, etc.

as polyethylene & polypropylene

↓ High energy

gives H_2

(21)

(f) Hydrolysis degradation →

polymers with amide, ester & acetal linkage can be easily hydrolysis in the presence of acids & alkalies

(a)

$$\sim NH-\overset{\overset{O}{\|}}{C}\sim \xrightarrow{+H_2O} \sim NH_2 + HOOC\sim$$

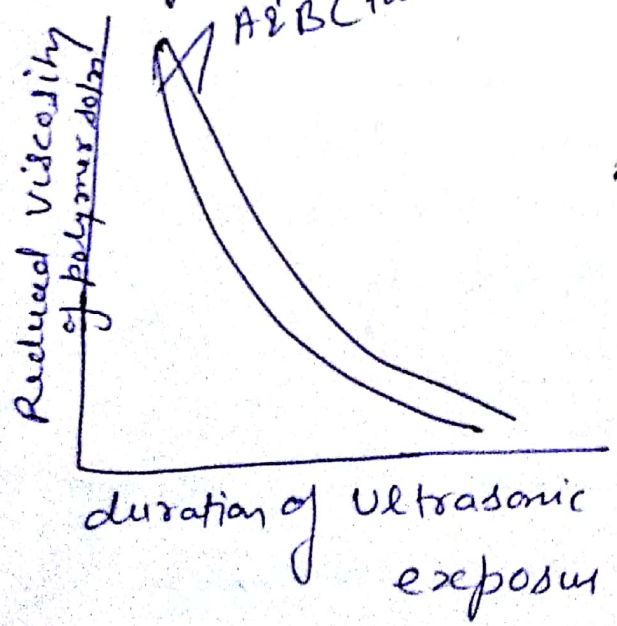
(g) Degradation by Ultrasonic way →

↳ These are of very high frequencies

(~ 20,000 Hz)

↳ dil sol of a high Molecular weigh polymer + Ultrasonic way → degrade → degradation

(A & B Two sample)



पर polymer का molecular wt reduce हो जाता है

The molecular wt is shown in term of reduced viscosity

Epoxy Resins

These form an important & versatile class of cross-linkable polymers made from monomers containing at least two strained ing group called oxiranes. These rings contain one oxygen & two carbon atoms & are attached to a ~~vast~~ large variety of other aliphatic or aromatic organic molecules.

prep →