

POLYMERS

Poly (many) and mer (unit).

Polymers are made up large in called monomers by a process called polymerisation. Is haemoglobin is a polymer or substance?

No, it is not made by repeating unit.

All macromolecules are not polymers but all polymers are macromolecules.

Macromolecules :- A very large molecule such as proteins, carbohydrates, lipids etc which are formed by small repeating unit are called macromolecules.

Classification of polymers

on the basis of origin

- natural : from plant source, from animal
- synthetic / man made polymers (mainly from base)

from plant source :- cellulose, cotton, jute

from animal source :- wool, silk.

synthetic :- polythene, polystyrene

- semi synthetic : cellulose nitrate, rayon

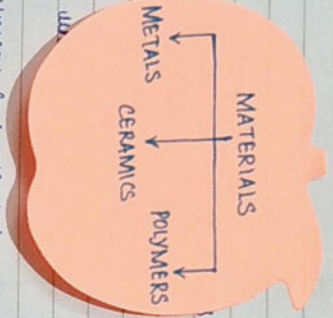
From **lignin** based **cellulose** called **lygno-cellulose** is obtained.

cellulose mixed with NaOH a salt is made. NaOH salt dissolves

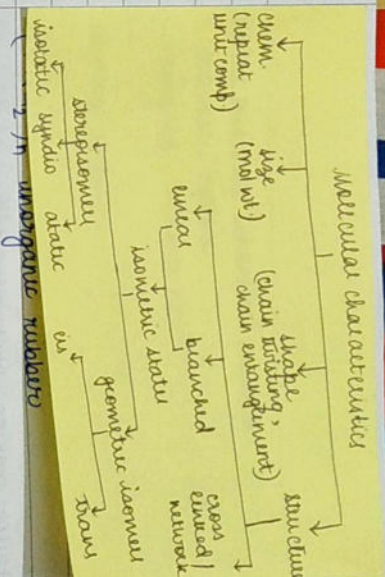
CO₂ is given yellow colour viscous salt and process is called xanthation. The yellow colour viscous salt reacts with NaOH

(by further addition) by a process called spinning to

obtain precipitated cellulose called rayon.



Pen down



on the basis of types of monomers

- addition
- straight chain

on the basis of type of chain

- linear
- branched
- cross linked

on the basis of applications

- plastic
- rubber
- fibre
- film
- coating
- foam

(Si must be in main chain) (periodic)

POLYMERS

Poly (many) and mer (unit).

Polymers are made up large unit of repeating units called monomers by a process of polymerization.

Is haemoglobin is a polymer though it is a biological substance?

No, it is not made by repeating units.

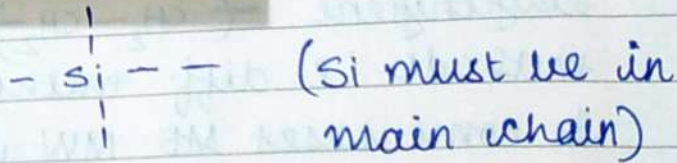


All macromolecules are not polymers but all polymers are macromolecules.

Macromolecules :- A very large molecule such as proteins, carbohydrates, lipids etc which are termed as smaller

- on the basis of chemical nature

- organic: cotton
- inorganic: silicone



Natural rubber $\xrightarrow{\text{Tree}}$ Polyisoprene (organic)

$(\text{PNCI}_2)_n$ inorganic rubber

- on the basis of types of rxns

- addition
- straight chain

• what can be the
rational to prepare
polymer properties do not
change high & low density
polymers are exception.
• diff prop due to diff chain
length & structure.

length of structure. It can be determined from diffraction experiments. It is made to prepare ethylene ($\text{CH}_2=\text{CH}_2$). It is used for all polymers in 1×10^5 some time 1×10^4 etc. But it will diff. no diff. spere. But in case of NaOH MW does not change remains 40. Similarly CH_3OH (MW = 46) remains constant.

- Polymers has tailored making properties. as per need we can utilise its properties.

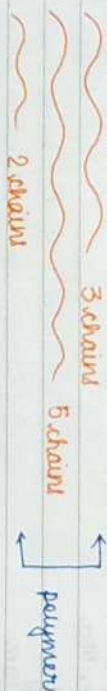
Let's polymers should average properly? Explain with examples
 the polymers :- we use average no. = \overline{M}_n

average MW = \overline{MW}

But in NaOH / NaCl / $\text{C}_2\text{H}_5\text{OH}$ etc. we use only MW of small molecules etc.

The polymers are may get diff. MW (because of diff. amt. not in case of NaCl, NaOH, C_2H_5OH etc).

size and length of polymers are diff. but in case NaCl etc. are same.



in properties can be represented by statistical average value in diff. size and length. But for other molecules are considered unique properties.

Molecular characteristics

21/12/2020

chemistry (repeat unit composition)

big (molecular weight)

shape (chain, twisting, entanglement etc)

structure (linear, branched, crosslink, network)

Showerie statue

Statische Stabilität → Statische Instabilität

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graph TD
    A[Copolymers] --> B[Stereotactic]
    A --> C[Syndiotactic]
    B --> D[Isotactic]
    B --> E[Dyotactic]
    C --> F[Heterotactic]
    D --> G[Isotactic]
    D --> H[Syndiotactic]
    E --> I[Dyotactic]
    E --> J[Syndiotactic]
    F --> K[Heterotactic]
    F --> L[Syndiotactic]
    
```

n. Monomers \longrightarrow Polymers

Can C_2H_6 / C_2H_5OH be considered as monomers?

No. 4 lacks specific characteristics of monomers.

$$\text{CH}_2=\text{CH}_2, \quad \begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad | \\ \text{OH} \quad \text{OH} \end{array} \rightarrow \text{MEMBERS}$$

Memorize characteristics

$\text{CH}_2 = \text{CH}_2 \longrightarrow$ polyethylene (unsaturation)

$$\begin{array}{l} \text{CH}_3\text{-CH}_2 \longrightarrow \text{X} \\ \text{CH}_3\text{-OH} \longrightarrow \text{Y} \end{array}$$

2015/01/17

$$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH} + \text{HOOC}-(\text{CH}_2)_n-\text{COOH}$$

polyester

$2\text{HS}^-\text{OH} + \text{CH}_3\text{COOH} \longrightarrow \text{CH}_3\text{COO}^-\text{HS}^-\text{OH}$ **X** polymer on both sides

$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$ [less / more active sites]

 $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$
$$\text{CH}_2 \equiv \text{CH}_2 \quad (2\text{C}-2\text{e}^- \text{ bond}) - \text{shared paired } e^-$$

π bond weaker than σ bond.

$$\text{OH} - \text{CH}_2 - \text{CH}_2 - \text{OH} \quad \text{COOH} - \text{CH} = \text{CH} - \text{COOH}$$

two func. groups forms two active sites

characteristic of active site is called functionality / average functionality (f_{av}).

For monomers, two functionality (min) is required

How does polymer differ from other materials?

- Polyethylene $\text{-(CH}_2\text{-CH}_2\text{)-}$ can be obtained from diffⁿ methods i.e. diff. methods to prepare ethylene ($\text{CH}_2=\text{CH}_2$). In some cases the MW is 1×10^5 some time 1×10^4 etc. but it remains polyethylene. In case of NaOH MW does not change remains 40. constant.

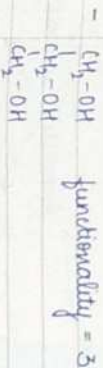
- Polymer has tailored molecular properties. As per need we can utilize its properties.

21-12-2020

Why polymer shows average property? Explain with examples. In polymers :- we use average no. = \overline{M}_n

average MW = \overline{M}_w

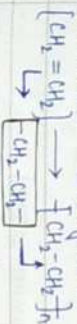
But in NaOH/NaCl $\text{C}_2\text{H}_5\text{OH}$ etc. we use mol^l MW and no. of



If one monomer M_1 functionality is 2 with n_1 moles 1 other functionality of monomer M_2 is 3 with n_2 moles calculate f.w. of polymer formed

$$\text{f.w.} = \frac{\sum_{i=1}^n n_i \cdot f_i}{\sum_{i=1}^n n_i} = \frac{2n_1 + 3n_2}{n_1 + n_2}$$

Monomer \rightarrow polymer repeat unit composition



n numbers of repeating units.
 \hookrightarrow degree of polymerization $(\overline{DP}) = \text{no. of repeating in a polymer.}$ $(\overline{DP}_n) / n$



$$\text{M.W.} = \frac{\text{molecular mass of monomer}}{28 \times 100} \times \overline{DP} \quad \text{f.w. of monomer}$$

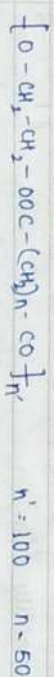
instead of this

molecular mass of each repeating unit

$$\text{M.W.} = \text{molecular mass of each repeating unit} \times \overline{DP}$$



\downarrow condensation



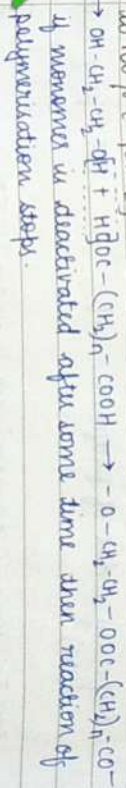
$$\text{M.W.} = 5128 \times 100$$

$$= 512800$$

$$\overline{M}_n = \frac{\sum_{i=1}^n n_i \cdot M_i}{\sum_{i=1}^n n_i}$$

then long the unit monomer this characteristic

$$P < 1 \text{ i.e. ext.}$$



\overline{M}_n (avg. mol wt) = $\frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$
 \overline{M}_n (no. avg. mol wt) \rightarrow based on relative property of polymer
 $\overline{M}_n = \frac{\sum_{i=1}^n n_i \cdot M_i}{\sum_{i=1}^n n_i}$
 $n \rightarrow$ no. of molecules
 $m \rightarrow$ molecular wt.

Carothers relation

$$\text{By using f.w., } \overline{DP} \leq P$$

satisfies most of the monomers so later called Carothers equation.

only relation not derived

Carothers - equation

Case I: when f.w. = 2 (general case)

$$P = \frac{1}{1 - \overline{DP}}$$

$$\overline{DP} = \frac{1}{1 - P}$$

for polymer chains are uniform

$$\overline{M}_n = M_0 \times \overline{DP}$$

M_0 = molecular weight of a structural unit of polymer / molecular wt. of a limiting unit.

$$\overline{M}_n = \frac{1}{1 - P}$$

$$\overline{M}_n = \frac{M_0}{1 - P}$$

28-10-2020

28-12-2020

$$\overline{M}_n = \frac{\sum_{i=1}^n n_i m_i}{\sum_{i=1}^n n_i}$$

How long this repetition occurs?
until monomers are deactivated.

This characteristic is called extent of polymerisation (P).
P < 1 i.e. extent of polymerisation (in general case) is not equal to 100%. [∴ fav = 2]



Carother's relation.

By using fav, D.P. & P

$$\frac{2}{\text{fav} - \frac{2}{\text{fav} \cdot \overline{DP}}} = P$$

satisfies most of the monomers
so later called Carother equation.
Only relation not derived.

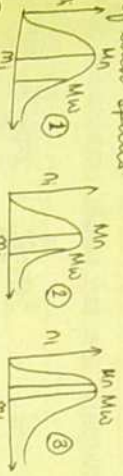
Carother :- organic chemist.

Case I : when fav = 2 (general cases)

$$P = 1 - \frac{1}{\overline{DP}}$$

MOLECULAR WEIGHT DISTRIBUTION

distribution relation b/w no of molecules & molecular mass of each species



(A) $PDI \geq 1$ (polydispersity index)

The PDI of 1 is highest because of broader range of molecular wt distribution which means high molecular mass material influence M_w more than they influence M_n and it is further in sample 2. M_w & M_n are close to each other. PDI is same for all samples. We have to observe the variation of M_w & M_n which can be found with the help of graph. These graphs can be used to get all types of avg. molecular weight.

$\frac{1}{DP}$ tends to 0 (very small value)

$$P \cdot \frac{2}{DP} \left[\frac{1 - \frac{1}{DP}}{DP} \right] < 1$$

$\frac{DP \cdot W}{M_n}$ no avg. degree of polymerization

Here $P < 1$ i.e. point where polymerization stops

Case III: If $DP \rightarrow \infty$ i.e. $DP \gg \gg$ (very large) $\frac{1}{DP} \rightarrow$ negligible i.e. 0

$$P \cdot \frac{2}{DP} \left[\frac{1 - \frac{1}{DP}}{DP} \right] \approx \frac{2}{DP} \left[\frac{1}{DP} \right] \text{ critical extent of polymerization}$$

$P \cdot \frac{2}{DP}$ limiting extent of polymerization

Pe / P_{gel}

Q: When does the above situation occur?

mainly polymers are linear, branched, cross linked etc.

when polymers are cross linked then $DP \rightarrow \infty$ i.e. gel formation

$M_w \geq M_n$

avg. molecular wt. determined by young measurement

PDI - polydispersity index

increases



Pen down

28-12-2020

$\frac{M_w}{M_n} \geq 1$

PDI (dispersity index) can have some ratio by different values of M_w & M_n .

This ratio means dispersity index. $PDI = \frac{M_w}{M_n}$. $PDI = 1$ indicates monodispersity. $PDI > 1$ indicates polydispersity. $PDI < 1$ is not possible.

Monodispersity means dispersity index = 1. $PDI > 1$ indicates polydispersity. $PDI < 1$ is not possible.

$1 - P = 1 - 0.9 = 0.1$

If $P = 90\%$ what is DP value for this polymer?

$$DP = \frac{1}{1 - P} = \frac{1}{1 - 0.9} = \frac{1}{0.1} = 10$$

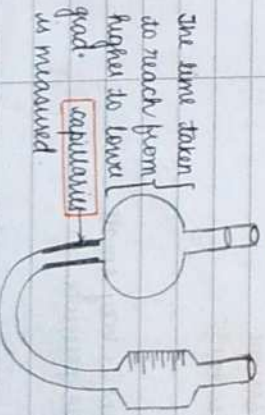
M_v viscosity avg. molecular weight

$$M_v = \left(\frac{\sum_{i=1}^n \eta_i M_i^2}{\sum_{i=1}^n \eta_i M_i} \right)^{1/2}$$

without using η_i, M_i to find out M_v we need viscosity of polymer. \therefore which means polymer need to be dissolved by any suitable solvent (hydrocarbon, polar or non-polar).

$0 < \alpha < 1$

To measure viscosity we need a viscometer, which is called Ostwald viscometer. Ostwald viscometer may be two arm or three arm type.



All molecular chains are not uniform

$$\overline{M}_w \geq \overline{M}_n$$

$$\therefore \overline{M}_w = \frac{\sum_{i=1}^n w_i^2 M_i}{\sum_{i=1}^n w_i} = \frac{\sum_{i=1}^n n_i M_i^2}{\sum_{i=1}^n n_i M_i}$$

$$\overline{M}_w = \overline{M}_n (1 + P)$$

$$\frac{\overline{M}_w}{\overline{M}_n} = 1 + P$$

Dispersity index of poly
(PDI)



Pen down

PDI = poly dispersity index

Case II: Means in case there's eqn if value of \overline{DP} increases exponentially [such as 100, 1000, etc.] then

$\frac{1}{\overline{DP}}$ tends to 0 (very small value)

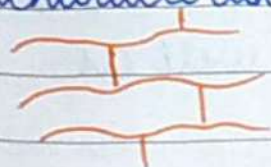
$$P \cdot \frac{2}{\overline{DP}} \left[1 - \frac{1}{\overline{DP}} \right] < 1$$

\overline{DP} is avg. degree of polymerisation.

here $P < 1$ i.e. point where polymerisation stops.

Case III: If $\overline{DP} \rightarrow \infty$ i.e. $\overline{DP} \gg \gg$ (very large)
 $\frac{1}{\overline{DP}} \rightarrow$ negligible i.e. 0

More crosslinking make polymers brittle. Hence undesirable characteristic of polymers.



CROSS LINKING

28-12-21

Q If $p = 50\%$ what is D.P. value for this polymer?

$$D.P. = \frac{1}{1-p} = \frac{1}{1-0.5} = \frac{1}{0.5} = 2$$

If $p = 90\%$ what is D.P. value for this polymer?

$$D.P. = \frac{1}{1-p} = \frac{1}{1-0.9} = \frac{1}{0.1} = 10$$



Pen down

\overline{M}_v viscosity avg. molecular weight.
(BASIS OF AVG. WT.)

$$\overline{M}_v = \left(\frac{\sum_{i=1}^n n_i m_i^{1+\alpha}}{\sum_{i=1}^n n_i} \right)^{1/\alpha}$$

without using n_i, m_i to find out \overline{M}_v

we need viscosity of polymer \therefore which means polymer need to be dissolved by any suitable solvents (hydrocarbon, polar or non polar).

$$0 < \alpha < 1$$

To measure viscosity we need a viscometer, which is called

- $\overline{M}_w, \overline{M}_n, \overline{M}_z$ can be obtained by GPC (gel permeation chromatography)
- \overline{M}_w right scattering instrument
- \overline{M}_n ultracentrifugation
- \overline{M}_z size exclusion chromatography
- molecular wt. distribution of a material

(to analyze a polymer) \downarrow
 you can use simple $\eta(\eta)$ with sample as well as

- r - radius of capillary tube
- l - length of capillary tube
- t - time taken from one graduation to another
- v - volume of solⁿ
- ρ - density
- P - pressure exerted by solution on manometer

NOW we have taken 2 solutions
 polymer solution (SOLUTE + SOLVENT)

polymer solⁿ in which polymer is dissolved
 [small quan]
 [large quan]

polymer $\rightarrow 0.1\% w/v, 0.2\% w/v, \dots, 0.5\% w/v \rightarrow$ thin solutions
 if we make thick solⁿ (of heavy polymers or having large conc of polymer) it may choke the capillary tube so dilute polymer is used.

$0.1\% w/v \rightarrow 0.1g \rightarrow 100ml$ solvent
 $100mg \rightarrow 100ml$ solvent

$\eta \propto \Delta P$ ΔP is very small.

ie diff in both cases is very small.
 osmometer is used to find osmotic pressure



Pen down

$$\eta_{\text{polymer sol}^n} = \frac{\pi r^4 \Delta P t}{8 L V}$$

$$\eta_{\text{solvent}} = \frac{\pi r^4 \Delta P t}{8 L V} = \eta_0$$

$$\text{relative viscosity} = \frac{\eta_{\text{polymer}}}{\eta_0} = \frac{t}{t_0}$$

time taken for polymer solⁿ > time taken for pure solvent

$$\text{specific viscosity } (\eta_{sp}) = \eta_{rel} - 1$$

$$\text{reduced viscosity} = \frac{\eta_{sp}}{c} \quad c \rightarrow \text{conc of polymer sol}^n$$

inherent viscosity = $\ln \eta_{rel}$ can give qualitative idea about polymer i.e. molecular wt. [ONLY IDEAL]

$$\text{inherent viscosity} \rightarrow \eta_{int} \cdot [\eta] = \ln \eta_{rel} \quad c \rightarrow 0 \quad \left[\frac{\eta_{sp}}{c} \right]$$

limiting viscosity when $c \rightarrow 0$, the solution process is called infinitesimal dilution

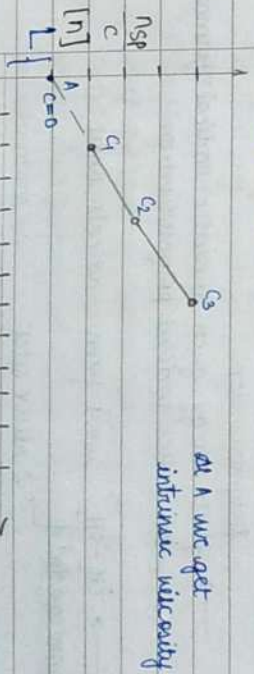
i.e. time taken will be approx same for solvent and polymer solution i.e. $\eta_{rel} = 1, \eta_{sp} = 0$

gives exact idea about molecular wt. by following Mark-Hauser-Sakurada (MHS) eqⁿ.

$$[\eta] = K(\overline{M}_v)^a \quad \text{MARK EQUATION}$$

\propto same as taken in \overline{M}_v

K & a are constⁿ



if η constant of two polymers are given i.e. 0.9 & 1.2 find out polymer with higher \overline{M}_w ?
 1.2

POISEUILLE EQUATION

From Poiseuille's equation we make viscosity (η) into simple terms and find polymer solution viscosity as well as solvent viscosity.

$$\eta = \frac{\pi R^4 t \rho h}{8LV} = \frac{\pi R^4 t \Delta P}{8LV}$$

$$\boxed{\eta \propto t \Delta P}$$

R - radius of capillary tube
 L - length of capillary tube
 t - time taken for solution to flow
 V - volume of solution
 ρ - density
 P - pressure exerted by solution on viscometer

NOW we have taken 2 solutions
polymer solution (SOLUTE + SOLVENT)
↓
polymer ↓
↓
solvent

polymer ↓
solvent

polymer is dissolved

[small quantity]

[large quantity]

Molecular weight distribution (MWD)

* \bar{M}_0 could be used as to find the monomer or info. that initiator monomer is used in repeating unit are not same

\bar{M}_2 (1) - it info. that initiator monomer is used in repeating unit are not same

$\bar{M}_2 > \bar{M}_w > \bar{M}_v > \bar{M}_n$

$$\bar{M} = \frac{\sum_{i=1}^n n_i M_i^a}{\sum_{i=1}^n n_i M_i^{a-1}}$$

general eqⁿ

when $a = 1$, \bar{M}_n

$a = 2$, \bar{M}_w

$a = 3$, \bar{M}_z

\therefore only \bar{M}_v can't be represented

CH-01-2021 Chain polymerization reaction / addition polymerization /

Radical polymerization / cationic polymerization / anionic polymerization

chain monomers $\xrightarrow{\text{found}}$ chain polymer

saturation / functionality = 2

ethylene $\text{CH}_2=\text{CH}_2$

acetylene $\text{CH}\equiv\text{CH}$ func. = 3 = fav

$\text{CH}_2=\text{CH}_2 \rightarrow \text{-(CH}_2\text{-CH}_2\text{)}_n$ although structure is like this but it is like this, it's only added

& addition polymerization

$\rightarrow \text{CH}_2\text{-CH}_2$ initiated using radicals hence radical polymerization

\rightarrow photo energy given initiates radical formation

-env hence radical polymerization

$\text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_2\text{-CH}_2$ won't form radicals until

initiators are added \rightarrow 2 active sites



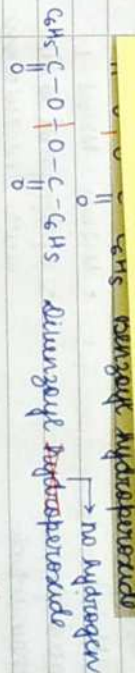
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functionality - no of bonding sites in a monomer. The (=) in ethene can be considered as site for two free valencies where functionality is two linear polymers are formed.

linear - branched - cross-linked

HDPE - LDPE - polybuta

no hydrogen



functional group linkage

$\text{R}-\text{R} \rightarrow 2\text{R}^\cdot$ (initiator)

once initiator attacks the monomer molecule, π bond \uparrow π bonding (2C-2e bonding) and switches 1e from monomer so 1 radical becomes started 1 monomer radical in initiated

$\text{R}^\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{R}-\text{CH}_2-\text{CH}_2^\cdot$ monomer activated

$\text{R}-\text{CH}_2-\text{CH}_2^\cdot + \text{CH}_2=\text{CH}_2 \rightarrow \text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2^\cdot$

STEP-II PROPAGATION

initiated molecule attacks another molecule and so on. In this way a long chain is formed. But under certain conditions it will stop which is called termination.

STEP-III TERMINATION

coupling termination / combination termination

disproportionation termination

coupling termination

when two propagated chain combine together called coupling / combination rxn.

$\sim\text{CH}_2^\cdot + \cdot\text{CH}_2\sim \rightarrow \sim\text{CH}_2-\text{CH}_2\sim$

* If ions are formed by initiator instead of radicals it is called ionic polymerization [cationic anionic polymerization]

* Free sulphuric acid help to form radicals

fluorescent light

04-01-2021

\bar{M}_z (Sedimentation average)

$$\bar{M}_z > \bar{M}_w > \bar{M}_v > \bar{M}_n$$

$$\bar{M}_z = \frac{\sum_{i=1}^n n_i m_i^3}{\sum_{i=1}^n n_i m_i^2}$$

longer chains sediment faster than shorter chains because of same no. of repeating units and \bar{M}_w when medium chain and at last small chain.

$$\bar{M}^a = \frac{\sum_{i=1}^n n_i m_i^a}{\sum_{i=1}^n n_i m_i^{a-1}}$$

Pen down

general eqⁿ

- when $a = 1, \bar{M}_n$
- $a = 2, \bar{M}_w$
- $a = 3, \bar{M}_z$

\therefore only \bar{M}_v can't be represented

Molecular weight distribution

04-01-2021 Chain polymerization reaction / addition polymerisation / Radical polymerisation / Photo polymerisation

STEP-I Initiators (R-R)

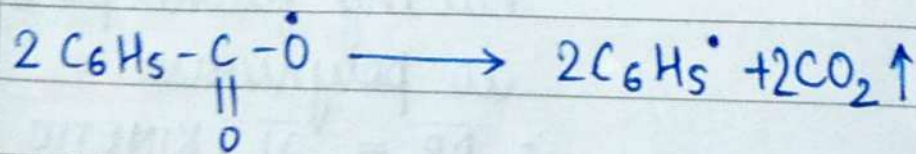
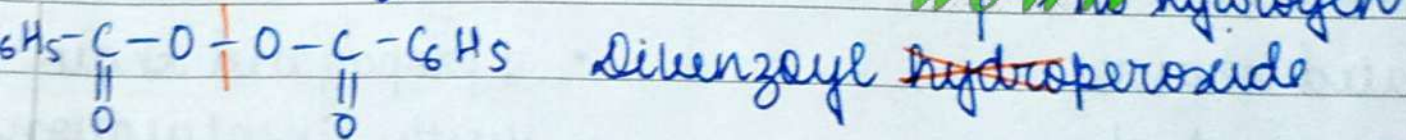
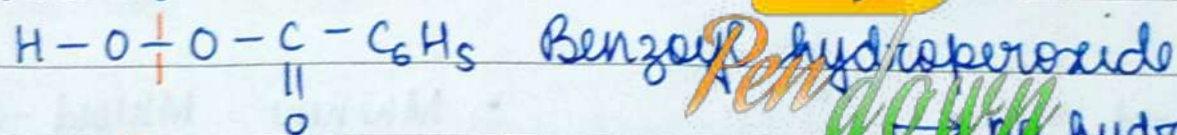
characteristics (R-R are weak bonded)

• free sulphates
also help to form
radicals

- HO-OH (hydrogen peroxide)

↳ peroxide linkage - weak link

Hence, black container is used for H_2O_2 otherwise light will break it.



Benzoyl oxy linkage

• if ions are formed by
initiators instead of radicals
it is called ionic polymeris-
-ation [cation/ anionic]

disproportion termination

In disproportion termination one propagated chain is sufficient as one H atom is abstracted



Coupling termination

MW_{max} = 2 MW₀ old

- 2 propagated chain forms 1 chain which is dead.

$$\overline{DP} = 2 \overline{DP}$$

Chain monomers

- $\text{CH}_2=\text{CH}_2$ can be written in general form $\text{CH}_2=\text{CHR}$ any group.
- $\text{CH}_2=\text{CH}-$ [VINYL GROUP]

Polymers formed using vinyl group called - vinyl

- ethylene** $\text{CH}_2=\text{CH}_2 \longrightarrow \text{-(CH}_2\text{-CH}_2\text{)}_n$ polyethylene
- commodity polymer as used for various purposes.
- $\text{CH}_2=\text{CH}_2 \longrightarrow \text{-(CH}_2\text{-CH-)}_n$

propylene

polypropylene

little polymer than polyethylene (in mesquite nut, fibre purposes)

coloured graded polypropylene - Bi-oxalate orientated polypropylene (BOPP)

- coloured plastic - (BOPP)

disproportion termination

MW_{max} = MW₀ old - 1

- 1 propagated chain with unsaturation having further possibility to polymerise

$$\overline{DP} = \overline{DP} \text{ [KINETIC]}$$



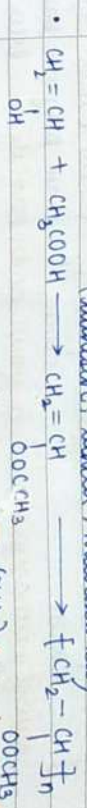
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vinyl alcohol

poly vinyl alcohol (PVA)

(adhesive, binder, matrices etc)



vinyl acetate

(PVAc) polyvinyl acetate

(linked through) (plastics in markets, used for manufacturing of poly vinyl acetate)

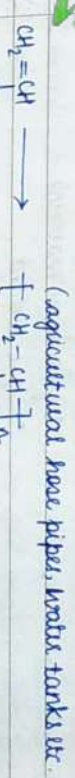
In industrial poly vinyl alcohol is not made from vinyl alcohol but from poly vinyl acetate



vinyl chloride

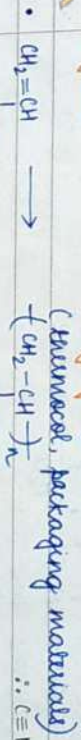
polyvinyl chloride (PVC)

aldehyde



styrene

polystyrene (PS)

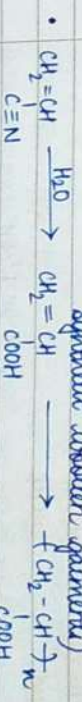


(styrofoam, packaging materials)

acrylonitrile

polyacrylonitrile (PAN)

(garment which looks like cotton, synthetic woolen garment)



acrylic acid

polyacrylic acid

highly susceptible to water (used as a matrix)



poly(methyl acrylate)



poly(methyl methacrylate) (linked through C-C)



poly(vinylidene fluoride) (PVDF)

also called (PIEXIGLASS)

Such material are used as piezoelectric material



polytetrafluoroethylene / teflon

highly stable

inert material

Such material are used as piezoelectric material



condensation / step polymerization

If we extend this to polycondensation



dicarboxylic acid

bi-ol



↓



step by step polymerization

2n-1 → more of water molecules liberated

the remaining functional groups which are not polymerized (ie do not take part in polymerization) are called end groups



when we take equimolar quantities (ie stoichiometric balance has been maintained) [F₁ - R - F₂]



stoichiometric ratio-1

Stoichiometry is NOT maintained



1.01 mole

excess

remains in excess

- so end groups will be -COOH & -COOH (not -OH)

- will match with function-ality of monomers in excess



1 mole

excess

remains in excess

both end groups altered

When stoichiometric ratio / feed ratio

sum of monomers > (M₁)

if M₂ = 10 M₁ = 10⁻¹

so, n = $\frac{\text{excess amount}}{\text{limiting amount}} = \frac{M_2}{M_1} = \frac{10}{10^{-1}}$

excess amount

limiting amount

[OH] → end group

for equimolar case $\bar{D.P.} = \frac{1}{1-P}$ [STOICHIOMETRIC]

if feed ratio < 1 $\bar{D.P.} = \frac{1+Y}{1+Y-2XP}$ [NON-STOICHIOMETRIC]

If we have monomers M_1 & M_2 then there are impurities present which will drastically affect D.P. value and chain length will be reduced. So D.P. value increases.

$$\bar{D.P.} = \frac{1 + N_1}{1 + N_1 + N_2}$$

No

Ni = % of impurity
No = % of purity

for 100% pure

$$\bar{D.P.} = \frac{1 + 0}{1 + 0} = \frac{1}{1-P}$$

for 2% impurities

$$\bar{D.P.} = \frac{1 + 2/98}{(1-P) + 2/98}$$

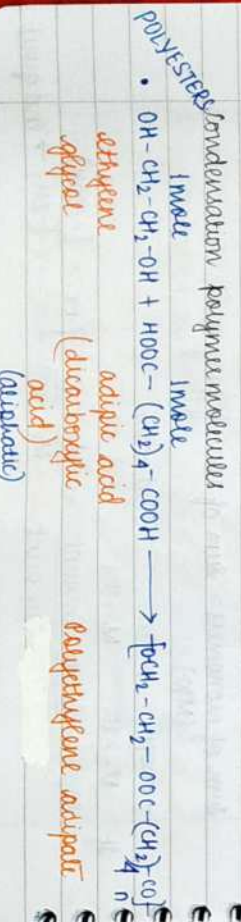
if P = 98%
 $\bar{D.P.} = 25.25$

b.p. due to impurities

In condensation rxn.

$$\bar{D.P.} = \frac{1+Y}{1+Y-2XP}$$

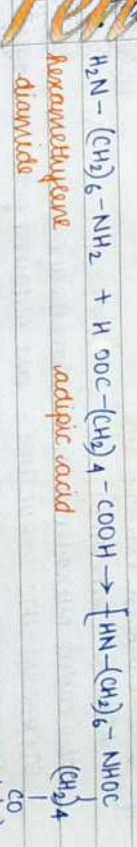
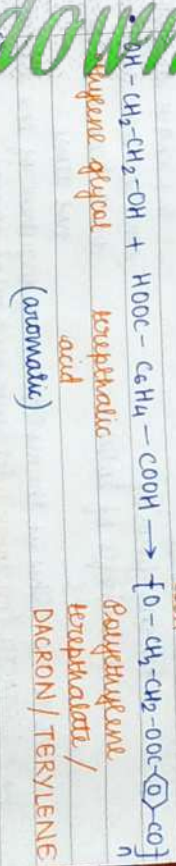
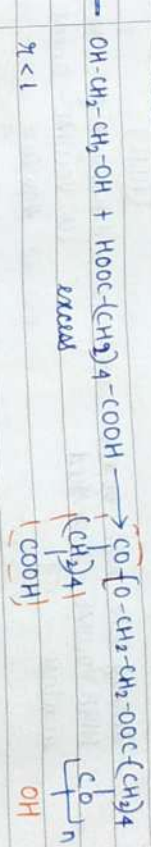
if P = 1 then $\bar{D.P.} = \frac{1+Y}{1-Y}$



20 MW of polyethylene adipate if n = 50 then

$$M = [C_{10}H_{18}O_4 - COO(CH_2)_4COO]_{50}H$$

$$= 1+17 + 50 \times 158 = 7918$$



- we can make 6,12 etc on basis of positioning.
- we can take aromatic - aromatic, aliphatic - aliphatic, aromatic - aliphatic.
- linear - fully aromatic polyamide
- highly branched in case of dendritic
- light weight



4) we take polyethylene



as per their structure concerned.

• LOW DENSITY POLYETHYLENE (LDPE)

- density low, high volume
HIGH VOLUME - branched structure



→ for fiber manufacture - we use LDPE due to branched structure

substance having polarity i.e. transfer of substance

* Structure diff. so property also diff.
• HIGH DENSITY POLYETHYLENE (HDPE)

- density high, low vol.
LOW VOLUME - linear structure



TACTICITY (this is the molecular arrangement of)
• ISOTACTIC (on same side) into molecular chain)
• SYNDIOTACTIC (on opp side)
• ATACTIC (randomly)

also called microstructure or stereospecific structure
STEREOSPECIFIC STRUCTURES are obtained from controlled polymerization i.e. Ziegler Natta catalyst method.
Ziegler Natta catalyst methods gives us either isotactic or syndiotactic.

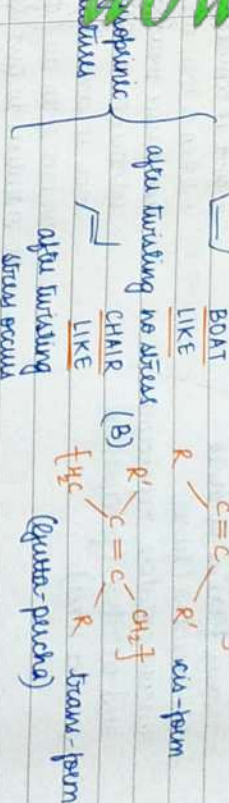
- all synthetic polymers discussed so far comes under non-biodegradable substances.
- Natural polymers are biodegradable.
- Non-biodegradable can be made biodegradable but it isn't the cost effective.
- so we go for combination of natural & synthetic to reduce harm to environment.

structural basis, polymers divided into -
• thermosetting
• thermoplastic
• highly cross link

Polymers basically distinguished as plastic, rubber & fiber
mostly synthetic polymers comes under plastic.

→ Natural Rubber (Elastomer) (NR)

from rubber tree - chemical methods
we collect latex (from stem)
(A) $-(CH_2-CH=CH-CH_2-)_n-$ (polyisoprene structure)



the form, natural rubber - used in tyre industries mostly used

(NEOPRENE)

If methyl group replaced by chlorine groups or any other group we get synthetic rubber.
Used to use synthetic rubber is because of limited availability of natural rubber.

synthetic rubber - neoprene, BUNA-S, BUNA-N, ABS (acrylonitrile butadiene styrene), BS (butadiene styrene) etc.

By diff. copolymerization we can get different synthetic rubber.

Natural rubber + Sulphur $\xrightarrow{\text{vulcanization}}$ Vulcanized rubber (cross-linked)

(= bonds between spins)

- If we use 32% or more % of S in natural rubber then it forms highly cross-linked structure called ebonite which is brittle as well.

FIBRES

Thick solution
natural polymers are dissolved in solvent it passes through some sieves and what found is called spinnings and process spinning is of two types:-

- wet spinning
- viscous fibre is obtained like cellulose (gum)
- viscous cellulose - precipitated cellulose (precipitated in wet cond)

• dry spinning
• speed the and pass spinnings once it contact with it starts to give us fibre. (in that environment)

Give molecular wt. data for some polymers are tabulated below

Sample (a) \bar{M}_n (b) \bar{M}_w (c) If it is known that the material D.P. is 477, find out the molecular wt of the monomers.

Mol. wt. range

\bar{X}_n (mole frac)

\bar{w}_i

8000 - 20000	0.05	0.02
20000 - 32000	0.15	0.08
32000 - 44000	0.21	0.17
44000 - 56000	0.28	0.29
56000 - 68000	0.18	0.23
68000 - 80000	0.10	0.16
80000 - 92000	0.03	0.05

Pen down

$$\begin{aligned} \bar{M}_n &= 141,000 & \bar{M}_n &= 14000 \times 0.05 + 26100 \times 0.15 + 50100 \times 0.18 + 74100 \times 0.10 + 86100 \times 0.03 \\ \bar{M}_2 &= 261,000 & & \\ \bar{M}_3 &= 351,000 & & \\ \bar{M}_4 &= 501,000 & & \\ \bar{M}_5 &= 621,000 & & \\ \bar{M}_6 &= 741,000 & & \\ \bar{M}_7 &= 861,000 & & \\ \bar{M}_w &= 0.02 \times 14000 + 0.08 \times 26100 + 0.17 \times 50100 + 0.29 \times 74100 + 0.23 \times 86100 + 0.16 \times 14000 + 0.05 \times 86100 \\ &= 280 + 2080 + 6460 + 14500 + 14260 + 11840 + 4300 \\ &= 53720 \end{aligned}$$

$$\begin{aligned} \bar{D.P.}_w &= 477 \\ \bar{M}_n \cdot \bar{D.P.} \times \bar{M}_0 &= 477 \times 100 \\ \bar{M}_0 &= \frac{477 \times 100}{477} = 100.041 \approx 100 \end{aligned}$$