Polymer Chemistry

Poly means $\longrightarrow$ Many
mer " $\longrightarrow$ Units(or) parts

Polymers are macromolecules of high molecular weight built up by the linking together of a large number of small, repeated units

Examples: Polyethylene $\left[\underbrace{H_2C=CH_2} \longrightarrow \left[CH_2-CH_2\right]_n \right.$

Polyvinyl Chloride $\left[\underbrace{H_2C=\underset{|}{C}H}_{Cl} \longrightarrow \left[CH_2-\underset{Cl}{\underset{|}{C}H}\right]_n \right.$

Monomer

Degree of Polymerization:

The size of the polymer molecule is decided by the number of repeating unit present in it. The no. of repeating unit(s) in a chain formed in a polymer is known as the "degree of polymerization.

$$n\,[H_2C=CH_2] \longrightarrow [CH_2-CH_2]_n$$

degree of polymerization

n may be 10^4-10^7 (or more)

So, $\boxed{\text{Molecular weight of polymer} = n \times \text{M.W. of the repeating units}}$

Polymerization: A process that combines several monomers or polymeric compound, to form a polymer or polymeric compound, is called Polymerization

P.T.O $\rightarrow$ 1

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classification of Polymers

- Based on sourse
  - Natural Polymer
  - Synthetic Polymer
- Based on Composition
  - Homopolymer
  - Co-polymer
    - Random
    - Alternating
    - Block
    - Graft.
- Based on chemical Composition
  - Organic
  - Inorganic
- Based on structure
  - Linear
  - Branchained
  - Cross-linked
  - Network
- Based on mode of polymerization
  - Additional
  - Condensation
- Based on molecular forces
  - Elastomers
  - Fibres
  - Thermoplastic
  - Thermosetting
- Based on Tacticity
  - Isotactic
  - Syndiotactic
  - Atactic

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1. **Based on sourse:**

(a) **Natural polymer:**

The polymers are isolated from natural material, such as animal, plants, cotton, silk, wool, natural rubber

ex:

$$n\ CH_2=\underset{\displaystyle |}{\overset{CH_3}{C}}-CH_2=CH_2 \longrightarrow \left[CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\right]_n$$

(Isoprene) — natural rubber

2-Methyl-1,3-butadiene

(b) **Synthetic polymer:**

The polymer synthesized from low molecular weight monomer.

ex:

$$n\ H_2C=\underset{Cl}{\underset{|}{CH}} \longrightarrow \left[CH_2-\underset{Cl}{\underset{|}{CH}}\right]_n$$

(Vinyl chloride) — PVC (Polyvinyl chloride)

2. **Based on Composition:**

(a) **Homopolymer:** They ~~have~~ are formed with same monomer units

ex: PVC

(b) **copolymer:** They are formed two or more different monomer units

Ex: 1. **Styrene-butadiene rubber:**

$$\underset{Ph}{\underset{|}{CH_2=CH}} + CH_2=CH-CH=CH_2 \longrightarrow \cdots$$

Styrene — Butadiene

$$\underbrace{\left[CH_2-\underset{Ph}{\underset{|}{CH}}-CH_2-CH=CH-CH_2\right]_n}_{\text{styrene-butadiene rubber}}$$

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Nitrile rubber:

$$CH_2 = \underset{\substack{| \\ CN}}{CH} + CH_2 = CH - CH = CH_2 \longrightarrow \underbrace{-\!\!\left[CH_2 - \underset{\substack{| \\ CN}}{CH}\right.}_{\text{Acrylonitrile Unit}} \underbrace{\left. - CH_2 - CH = CH - CH_2 \right]_n}_{\text{Butadiene Unit}}$$

Acrylonitrile

Copolymer

- Random
- Alternating
- Block
- Graft

Random: These are formed by the random arrangements of polymer

$$A + B \longrightarrow -A-B-A-A-B-B-A-B-B-$$

Alternating: Monomer units in a copolymer molecule are arranged in an alternating manner

$$A + B \longrightarrow -A-B-A-B-A-B-$$

Block: A block copolymer consists of one in which blocks of repeating units of one monomer alternate with blocks of another monomer

$$A + B \longrightarrow [A-A-A-A][B-B-B-B]$$

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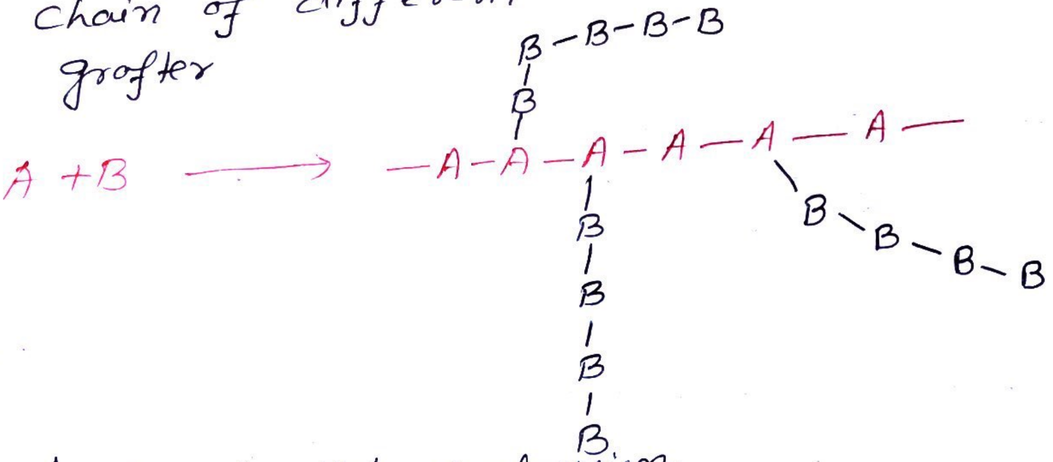
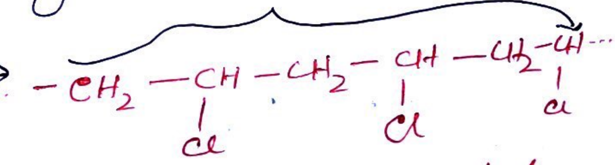
Graft: The copolymer consists of a linear polymer chain of one monomers to which side chain of different monomer has been grafter



③ **Based on chemical Composition**

(a) Organic: A polymer whose backbone chain is essentially made of Carbon atoms

ex: PVC →

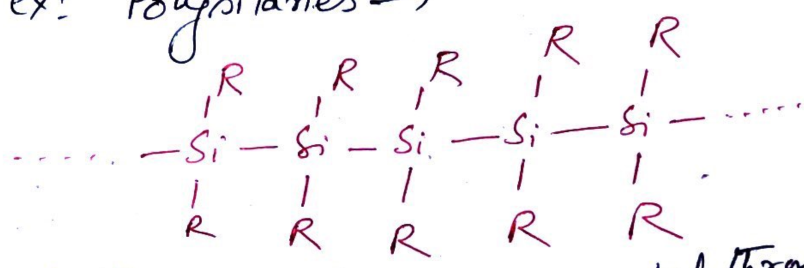


backbones are Connected Through Carbon-Carbon bonds.

(b) Inorganic:

Polymers that are Connected by non Carbon-Carbon bonds are inorganic polymers

ex: Polysilanes →



backbones are connected through Si–Si bonds (i.e. non carbon-Carbon bond)

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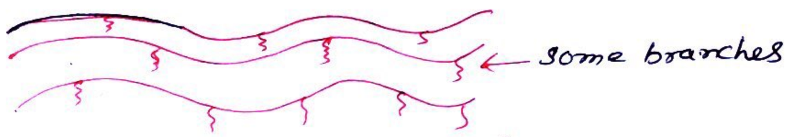
(4) Based on Structure:

- Linear
- Branched-Chain
- Cross-linked
- Network

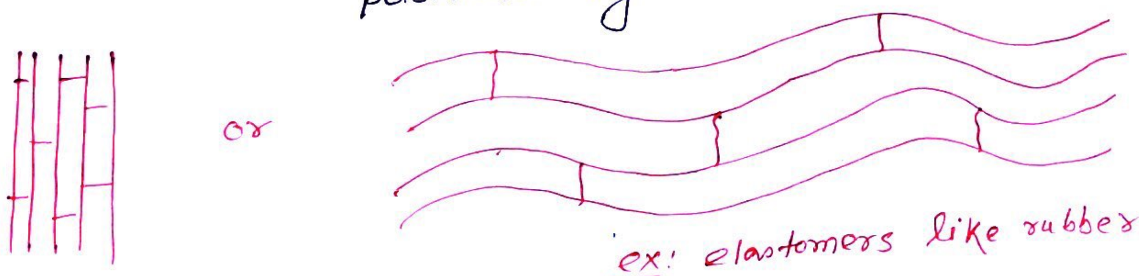
Linear: Here monomeric Units are joined in the form of long & straight chains. ex: nylons, PVC

Branched-Chain: These polymers mainly linear in nature, but also posesses some branches along the chain



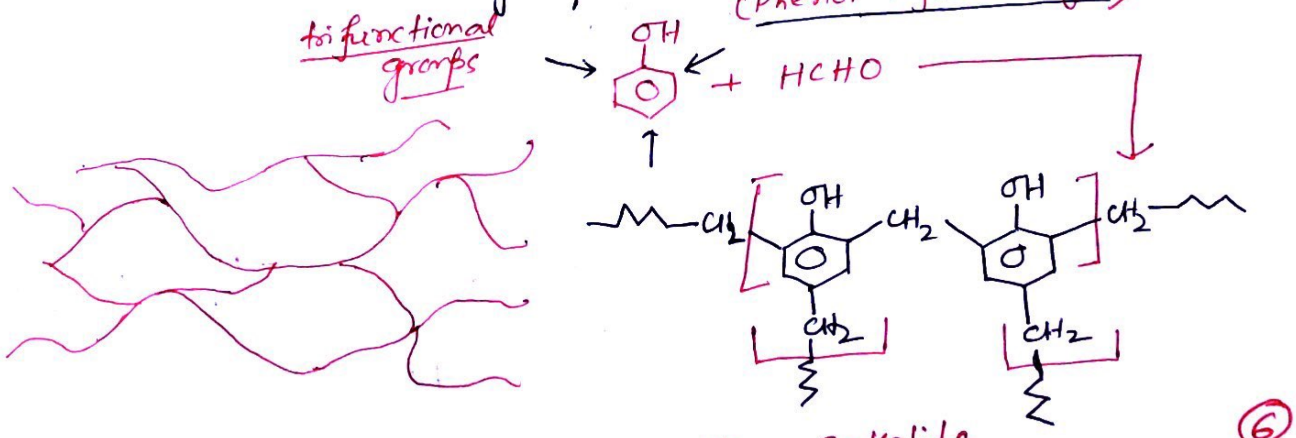
ex: glycogen, amylopectin

Cross-linked polymer: In these polymers, adjacent chains are joined one to another at various positions by covalent bonds:



ex: elastomers like rubber

Network polymers: Monomer units that have trifunctional groups form three dimentional networks. (Phenol + formaldehyde)



ex: Bakelite

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5. Based on mode of polymerization:

(a) Additional Polymerization:

Additional polymerization takes places in compounds conteining reactive double bonds. Chain polymerization is charecterized by a self-addition of the monomer molecules to eachother very rapidly through chain rea^{n}.

$$\underset{\text{Styrene}}{H_2C=\underset{\displaystyle Ph}{CH}} \longrightarrow \underset{\text{Polystyrene}}{\left[CH_2-\underset{\displaystyle Ph}{CH}\right]_n}$$

(b) Condensation: This type of polymerization was brought about by monomers containing two or more reactive functional groups conteining with each other to form condensation polymer & also a loss of small molecule like (H_2O, NH_3, HCl, etc.)

ex: Nylon 6:6

$$\underset{\text{(Hexamethylenediamine)}}{H_2N(CH_2)_6NH_2} + \underset{\text{(Adipic acid)}}{HO_2C(CH_2)_4CO_2H}$$

* Functional groups present here are
$-NH_2$ &
$-CO_2H$

$$\Big\downarrow -H_2O$$

* removal of small molecule (H_2O)

$$-\Big[\underbrace{HN-(CH_2)_6-NH}_{\text{Hexamethylene diamine unit}}-\underbrace{\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}}_{\text{Adipic acid unit.}}\Big]_n$$

Nylon 6:6

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Distinguish between Additional & Condensation Polymer

Additional Polymer	Condensation polymer
1. Only growth rea^n adds repeating Units one at a time to the chain	1. Only two molecular species present can react.
2. Reaction initiats with the help of an initiators	2. No need of initiators
3. Reations are very fast. Three step involves ↳ initiation, Propagation, Termination	3. Reac^n is very slow. No such steps are involbed.
4. Loss of small molecule(s) like H_2O, HCl, NH_3, etc are not formed	4. Loss of small molecule(s) like H_2O, HCl, etc are formed
5. Ex: PE, PVC, Teflon etc.	6. Nylon 6:6, Nylon 6, Polyester, etc.

(6) Based on molecular forces

- Elastomers
- Fibres
- Thermoplastic
- Thermoselling

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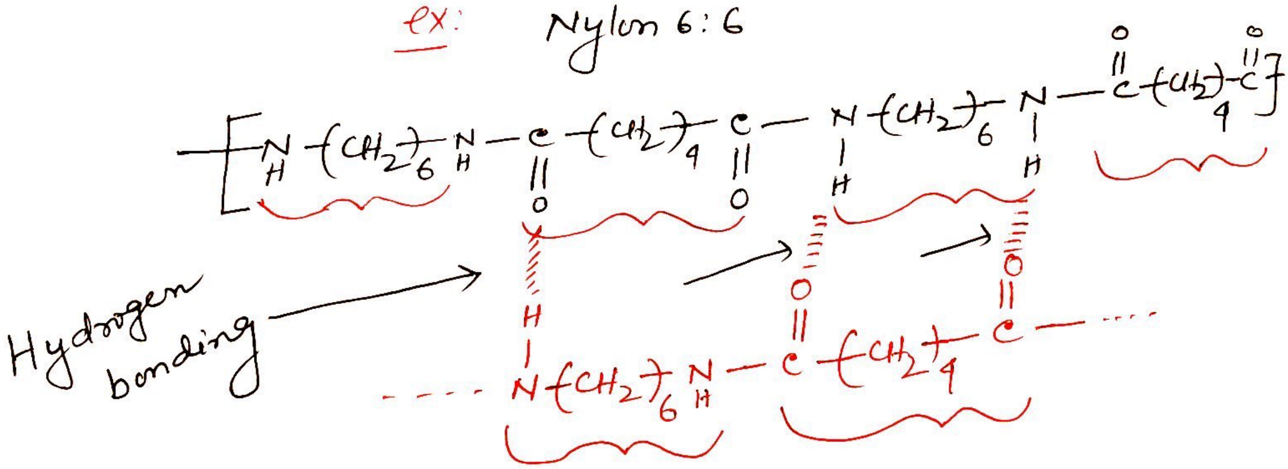
(a) Elastomers:

These are rubber-like solids with elastic properties, In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. This weak binding forces permit the polymer to be stretched out and it return back to it's orginal position when forces are released

ex: Natural rubber

(b) Fibres: Polymers whose chains are held by strong hydrogen forces, They are crystalline in nature, high tensile strength & high modulus

ex: Nylon 6:6



(c) Thermoplastic: They are linear or slighly branched long chain molecules capables of ~~repeating~~ repeatedly softening on heating & hardening on cooling.

These polymers posesses intra molecular forces of attraction in between elastomers & fibres

ex: PVC

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(d) Thermosetting:

These polymers are network structure with heavily branched molecules, which on heating undergo extensive cross-linking in moulds & again becomes infusible. They can't be reused or resoftened

ex: Bakelite

Distinguish between Thermoplastic & Thermosetting polymer

Thermoplastic	Thermosetting
1. They soften on heating	1. They do not soften on heating, On pro-longed heating, they burn
2. They consist of long-chain linear macromolecules	2. They consist of three-dimentional network structure
3. They are formed mosty by additional polymerization	3. They are formed mostly by condensation polymer
4. They are usually soft	4. usually strong & hard
5. They can be reused	5. They can't be reused
6. They are soluble in organic solvents	6. They are insoluble in all organic solvents due to strong bonds connected to eachother & presence of heavily cross-linking

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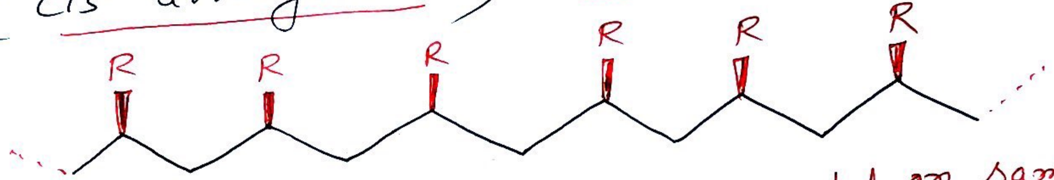
⑦ Based on Tacticity

Three dimensional arrangement of the monomer(s) unit in the main chain of a polymer is Known as Tacticity

- Isotactic
- Syndiotactic
- Atactic

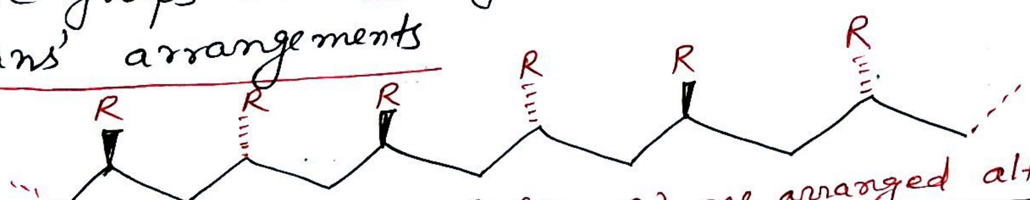
ⓐ Isotactic :

In these polymer, all side gronps lie on the same side of the chain arrangements ('cis' arrangements) ex: Natural rubber



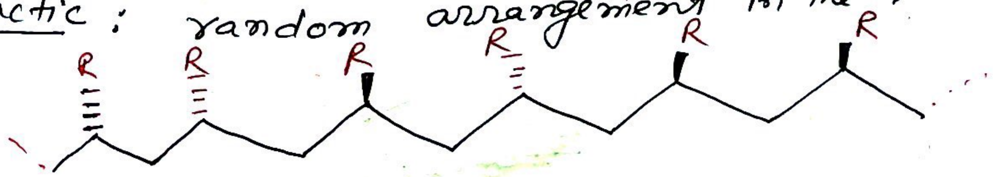
↳ Here side gronps (ie. –R) located on same side or in 'cis' arrangement.

ⓑ ~~Isotactic~~, Syndiotactic : In This polymer, side gronps are arranged alternatingly (ie. 'trans' arrangements



↳ Here side gronps (ie. -R) are arranged alternatingly One is above the plane (R) & onother is bellow the plane (R) ex: Gutta-percha

ⓒ Atactic : random arrangement in the side chains



ex: Polyprofylene

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Mechanism of Additional Polymerization

In additional Polymerization, free radical, Carbonium ions (~~carbocati~~ cationic or anionic) & Complex Catalyst), acts as active Centres. Hence, Polymerization may occur in the following

(i) Free radical
(ii) Ionic (Cationic and anionic)
(iii) Co-ordination (Complex Catalyst)

Each process except Co-ordination polymerization Consists of the following steps

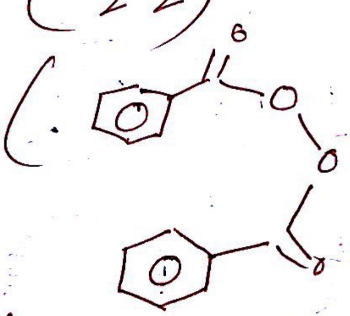
(a) Initiation
(b) Propagation
(c) Termination

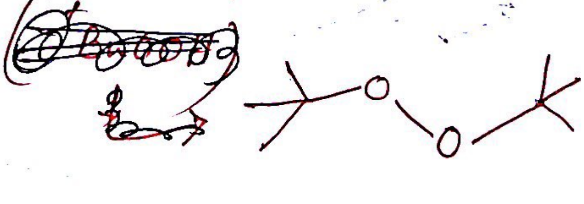
Free radical Polymerization:

The process involved ~~with~~ in the presence of ~~free~~ radical initiators.

Examples are as follows:

Hydrogen peroxide (H_2O_2)

Benzoyl peroxide 

^{t}Butyl peroxide 

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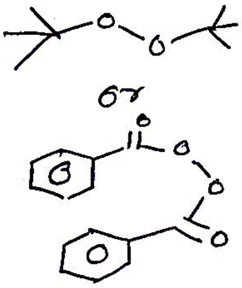
Initiation :

First step, Production of free radicals by initiators

$$In \longrightarrow 2R^{\cdot} \text{ (free radical)}$$

ex: In (H_2O_2, ~~[illegible]~~



2nd Step :

Addition of free radicals to a monomer

$$\underbrace{\underset{\underset{Y}{|}}{H_2C = CH}}_{\text{(Monomer)}} + R^{\cdot} \text{ (Initiator radical)} \longrightarrow \underset{\underset{Y}{|}}{R - CH_2 - \dot{C}H}$$

~~Simply~~ It Can be Considered as M

It can be Considered as $M_1^{\cdot}$

$$\text{so, } \quad R^{\cdot} + M \longrightarrow M_1^{\cdot}$$

Propagation : Consists of the growth $M_1^{\cdot}$ by additions of large numers (hundreds or Thousands or more)

monomer

$$M_1^{\cdot} + M \longrightarrow M_2^{\cdot}$$

$$M_2^{\cdot} + M \longrightarrow M_3^{\cdot} \text{ ...... so on}$$

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

$$M_{n+1}^{\cdot} + M \longrightarrow M_x^{*}$$

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Termination :

At some point, the propagating polymer chain stops growing & terminated by coupling & disproportionation method.

$$M_x^* \longrightarrow M_x$$

M_x ↳ Inactive polymer molecules

M_x^* ↓ Activated growing polymer chain

Ionic polymerization ;

Example of cationic initiators are as follows ⟶ BF_3

H_2SO_4

$AlCl_3$

Example of anionic initiators are as follows ⟶ KNH_2

Co-ordination polymerization

Catalyst used here is

Ziegler - Natta Catalyst

Two italian scientist (Ziegler & Natta) shared the Nobel prize for Chemistry in 1963 using Zeigler - Natta Catalyst to polymerize non-polar monomers.

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Zeiglar- Natta Catalyst :

The mixture of titanium halides & trialkyl aluminium is Known as Zeigler-Natta Catalyst)

$$\underbrace{(TiCl_3 + R_3Al)}_{\text{Zeigler-Natta Catalyst.}}$$

List of Few Polymers & their monomeric units

Name	Monomer(s)		Polymer
1. Polythene(PE)	$H_2C=CH_2$	$\longrightarrow$	$-[CH_2-CH_2]_n-$
2. Polyvinyl chloride (PVC)	$H_2C=CH(Cl)$	$\dashrightarrow$	$-[CH_2-CH(Cl)]_n-$
3. Polystyrene (PS)	$H_2C=CH(Ph)$	$\dashrightarrow$	$-[CH_2-CH(Ph)]_n-$
4. Polymethyl ~~methyl~~ methacrylate (PMMA) or Lucite or Plexiglass	$H_2C=C(CH_3)(CO_2Me)$	$\dashrightarrow$	$-[CH_2-C(CH_3)(CO_2Me)]_n-$
5. Polypropylene(PP)	$CH_2=CH(CH_3)$	$\dashrightarrow$	$-[CH_2-CH(CH_3)]_n-$
6. Polytetrafluoroethylene / Teflon	$F_2C=CF_2$	$\dashrightarrow$	$-[CF_2-CF_2]_n-$
7. Natural Rubber	$H_2C=C(CH_3)-CH=CH_2$ (Isoprene) or 2-Methyl-1,3-butadiene		$-[CH_2-C(CH_3)=CH-CH_2]_n-$

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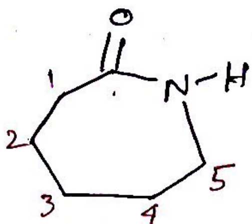
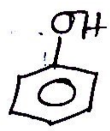
Name	Monomer	Polymer
8. Nylon 6:6	$H_2N-(CH_2)_6-NH_2$ (Hexamethylene diamine) + $HO_2C-(CH_2)_4-CO_2H$ (Adipic acid)	$\dashrightarrow$ $\left[\underbrace{\underset{H}{N}-(CH_2)_6-\underset{H}{N}}_{\text{Hexamethyldiamine unit}}-\underbrace{\overset{O}{\overset{\parallel}{C}}-(CH_2)_4-\overset{O}{\overset{\parallel}{C}}}_{\text{Adipic ā unit}}\right]_n$
9. Nylon 6	 Caprolactum	$\dashrightarrow$ $\left[\overset{O}{\overset{\parallel}{C}}-(CH_2)_5-\overset{H}{N}\right]_n$
10. Bakelite	 Phenol + HCHO formaldehyde	$\dashrightarrow$ Bakelite (see it in previous page)
11. Styrene-Butadiene rubber (Buna-S)	$CH_2=CH-CH=CH_2$ (Butadiene) + $CH_2=\underset{Ph}{CH}$ (Styrene)	$\dashrightarrow$ $\left[\underbrace{CH_2-CH=CH-CH_2}_{\text{Butadiene unit}}-\underbrace{CH_2-\underset{Ph}{CH}}_{\text{Styrene unit}}\right]_n$
12. Nitrile Rubber (Buna-N)	$CH_2=CH-CH=CH_2$ (Butadiene) + $CH_2=\underset{CN}{CH}$ (Acrylonitrile)	$\left[\underbrace{CH_2-CH=CH-CH_2}_{\text{Butadiene unit}}-\underbrace{CH_2-\underset{CN}{CH}}_{\text{Acrylonitrile unit}}\right]_n$

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Comodity polymers:

Plastics That are used in high volume & wide range of applications, such as film for packaging, photographic, clothing, beverage & trash containers & a varity of household products

Such plastics exhibit relatively low mechanical properties & are of low cost

ex: PE, PP, PS, PVC, PMMA etc.

Few polymers & Their synthesis, properties & applications

Polythene(PE):

Synthesis: Polythene is the most widely used plastic of ethylene, making use of O_2 as initiator.

$$n\ CH_2=CH_2 \xrightarrow{\text{Polymerization}} -[CH_2-CH_2]_n$$

* LDPE (Low-density polythene)

It is prepared under very high pressure of 1,000 – 5,000 atm. & temp of 80°c – 250°c, O_2 as initiators

$$n\ CH_2=CH_2 \xrightarrow[\substack{80^\circ C - 250^\circ C \\ \& \\ O_2 \text{ as initiators}}]{1{,}000-5000\ atm} LDPE$$

* HDPE (High-density polythene)

It is polymerized under low temp at 60°c in presence of Ziegler-Natta Catalyst ($TiCl_3 + AlR_3$)

$$n\ CH_2=CH_2 \xrightarrow[60^\circ C]{(TiCl_3 + AlR_3)} HDPE$$

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Properties:

(i) It is regid, waxy, white non-polar material, exhibiting considerable registance to strong acid, alkalis at room temperature

(ii) It is a good insulator of electricity

(iii) Due to its highly symmetrical chain structure PE crystallise very easily. The degree of crystallinity vary from 40% to 95%

(iv) HDPE is completely linear, has better chemical-resistance, high softening point & greater rigidity than LDPE.

Type	Density (gm/cc)	crystallinity	softening point (K)	Tensile strength (atm)
1. LDPE →	0.91 – 0.92 →	55% →	360 →	85-136
2. HDPE →	0.91 - 0.96 →	80% →	400 →	204-313

Applications:

1. LDPE: It is used in making films & sheets. Pipes of LDPE are used for agricultural irrigations & domestic waterline connections. It is used for making wires & cable wires

2. HDPE: It is used in manufacture of toys, insulator, bottle caps, kitchen & domestic articles.

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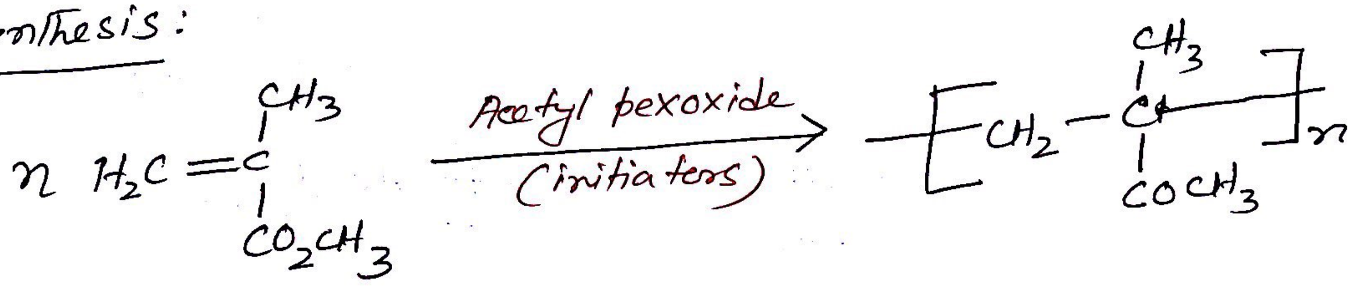
PMMA (Polymethyl methacrylate, or Lucite or plexiglass):

Synthesis:



Properties:

(1) It is hard, fairly rigid with high softening point 130-140°C, But it becomes rubber like at temperature above 65°C

(2) It has low chemical resistance to hot acids & alkalis

(3) It has high optical transparency, high resistance to sunlight

Applications:

It is used in making -

(i) lenses
(ii) aircraft light fixtures
(iii) bomber noses
(iv) cockpit canopies
(v) artificial eyes
(vi) Adhesives
(vii) jewellery
(viii) wind screen
(ix) TV screen etc.

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Polypropylene : (PP)

Synthesis : PP is obtained by polymerizing propylene in presence of Zeiglar-NaHa Catalyst (~~$AlCl_3 + A$~~ $AlR_3 + TiCl_3$)

$$n\ CH_2 = \underset{CH_3}{\underset{|}{CH}} \longrightarrow -\!\!\left[CH_2 - \underset{CH_3}{\underset{|}{CH}} \right]_n$$

Properties : (1) PP is highly crystalline polymer ($mp \to 160°C - 170°C$)

(2) It possesses better hardness, strength & stiffness than PE

(3) PP is more resistant than PE

Uses : It is used in making

(a) ropes
(b) carpets
(c) furniture
(d) blankets
(e) hand bags
(f) water pipes
(g) washing-machines parts
(h) sterilized hospital equipments etc.
~~(i)~~
~~(j)~~

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PVC (Polyvinyl Chloride):

Synthesis: $n \; CH_2 = \underset{\substack{| \\ Cl}}{CH} \xrightarrow[\text{Hydrogen peroxide}]{\text{benzoyl peroxide or}} -\!\!\left[CH_2 - \underset{\substack{| \\ Cl}}{CH} \right]_n$

Properties:

(1) PVC is colourless, odourless, chemically inert

(2) It is registant to light, O_2, acids & alkali

(3) It is soluble in hot chlorinated solvents

(4) PVS possesses high softening point, great stiffness & rigidity, but it is brittle

Applications: It is used in making

(a) light fittings
(b) safety helmets
(c) refrigerator components
(d) tyres
(e) cycle & motorcycle mudguard
(f) rain coats
(g) table cloths
(h) curtains etc.

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Polystyrene (PS):

Synthesis:

$$n\ CH_2=\underset{\large Ph}{\underset{|}{CH}} \xrightarrow{\text{benzoyl peroxide}} -\!\!\left[CH_2-\underset{\large Ph}{\underset{|}{CH}}\right]_n$$

Properties: (i) PS is transparent, light-Stable & moisture-resistant

(ii) PS is highly electric insulating

(iii) PS is highly resistant to acids

(iv) PS is less softening & is brittle

Applications:

It is used in making

(a) Toys
(b) combs
(c) buttons
(d) radio & television parts
(e) refrigerator parts
(f) electric insulator
(g) food Container
(h) food packaging
(i) Umbrella handles.

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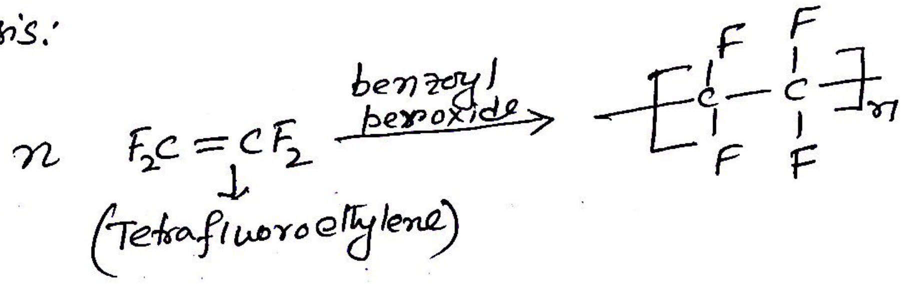
Polytetrafluoroethylene [Teflon]:

Synthesis:



properties:

(1) It has twisted & zigzag structure with fluorine atoms

* (2) Due to the presence of highly electronegative F-atoms, they are very strong attractive forces between diff. chains

(3) The strong attractive forces gives the polymer extreme toughness, high softening point, exceptionally high chemical resistance towards all chemicals,

(4) Teflon has high density., ~~and~~

Applications:

It is used in making

1. coating glass fibres
2. asbestors fibres
3. non-sticking frying pan
4. chemical-Carrying pipes
5. pump parts
6. tank lining.

Q: 1. Why teflon is highly chemically resistant?

Ans: (*)

2. Teflon is an additional polymer, but it behave some what like a thermosetting polymer — why?

Ans (*)

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Nylon:

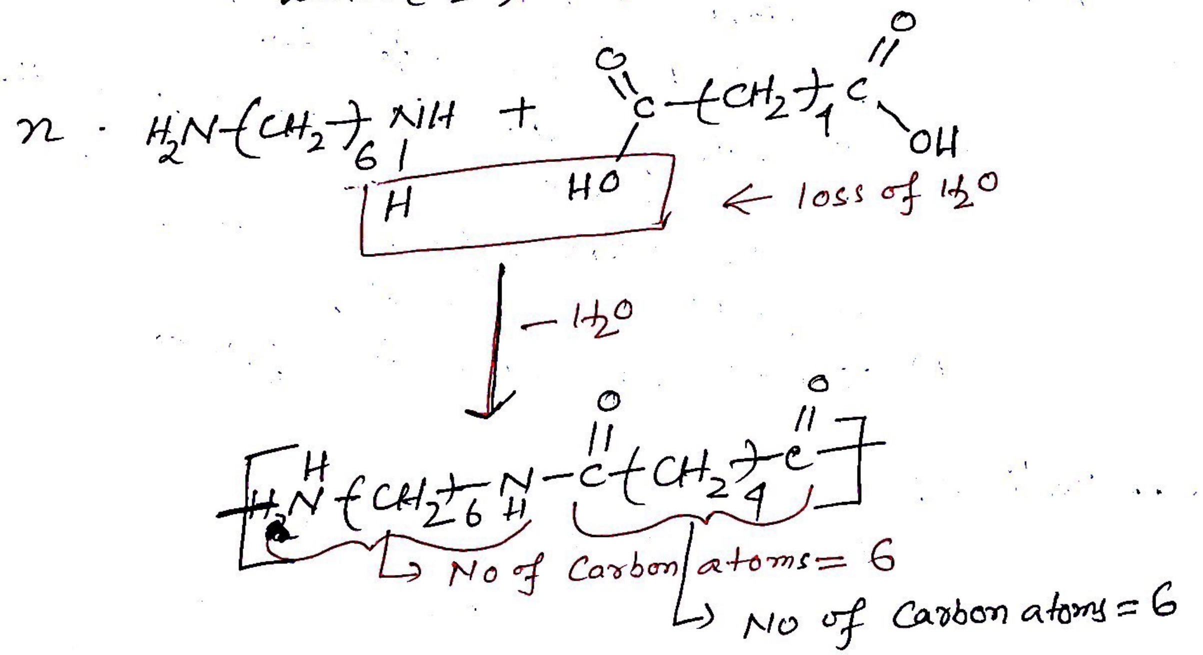
Examples: Nylon 6:6, Nylon 6:10, Nylon 6,11 etc.

This number denotes the number of carbon atoms of one monomer

This number denotes the number of Carbon atoms of other monomer

Ex: Nylon 6:6

Preparation: It is synthesized by Condensation polymerization process with a loss of water(H_2O) molecule.



So, it is Called Nylon 6:6

Properties:
(1) They are light & high melting
(2) Insoluble in common solvents
(3) flexible & retain original shape easily

Uses: (1) It is used in making socks, undergarments, dresses, carpets, ropes → (use of Nylon 66)
(2) used for making gears, bearing, electrical mounting (Use of Nylon 6:11)

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Synthetic Rubber : [Buna-S & Buna-R]

Landmark discovery of synthetic rubber is the greatest achievement in polymer industry (Buna-S)

** Due to better performances properties of synthetic rubber, natural rubber failed to give stiff competition

Advantages → They can be produced bulk amount
→ Economically benificial
→ superior to natural rubber in certain cases
→ diverse applications
→ highly resistant & high tensile strength
→ higher flexibility & high temp stability

Buna-S (Styrene-butadiene rubber)

Synthesis: It is a copolymer of 25% of styrene (by weight) & 75% of butadiene (")

$$\underset{\substack{\text{(butadiene)}\\ 75\%}}{n\,CH_2=CH-CH=CH_2} + \underset{\substack{\text{(Styrene)}\\ 25\%}}{n\,CH_2=\underset{C_6H_5}{\underset{|}{CH}}} \xrightarrow{\text{peroxide initiators}} \underbrace{-[CH_2-CH=CH-CH_2-CH_2-\underset{Ph}{\underset{|}{CH}}]_n}_{\text{Buna-S}}$$

Properties: (1) High load bearing capacity
(2) highly resistant
(3) It swells in oils & solvents
(4) It can be vulcanized in same way as natural rubber, but it require less sulphur (S)

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Uses:

(1) It is used for manufacture of motor tyre (cycle, motor, scooter types)

(2) It is used for floor tiles, shoe soles, footwear, cable insulator, carpet etc.

Buna-N (Butadiene-acrylonitrile or Nitrile rubber)

Synthesis:

$$n\, CH_2=CH-CH=CH_2 + n\, CH_2=\underset{\large CN}{\underset{|}{CH}}$$

1,3-butadiene   Acrylonitrile

$$\downarrow$$

$$-\!\!\left[\underbrace{CH_2-CH=CH-CH_2}-\overbrace{CH_2-\underset{\large CN}{\underset{|}{CH}}}\right]\!\!-_n$$

Buna-N

Properties: (1) excellent resistant to heat, sunlight, oils, acids & salts, but less resistant to alkali than natural rubber due to the presence of $-CN$ group

(2) As the proportion of acrylonitrile increased, the resilience to acids, salts, oils & solvents increases, but the low temperatures resilience suffers

Uses: They are extensively used for

(a) fuel tanks
(b) gasoline hoses
(c) high-altitude craft components
(d) Adhesives
(e) latex
(f) printing rollers
(g) leather
(h) textile

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Vulcanization:

To improve the properties of rubber, It is heated with some compound e.g. sulphur at 100°C – 140°C — This process is called <u>vulcanization</u>

ex:

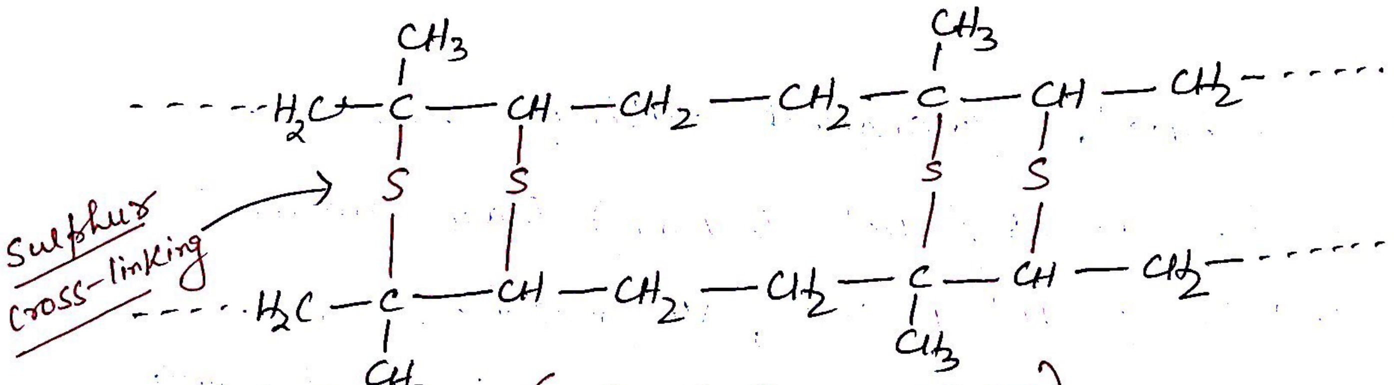
$$H_2C = \underset{|}{\overset{CH_3}{C}} - CH = CH_2 \longrightarrow \left[CH_2 - \overset{CH_3}{\overset{|}{C}} = CH - CH_2 \right]_n$$

(isoprene) natural rubber

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

(natural rubber)
repeating units of isoprene in natural rubber

$\Big\downarrow$ heat at 100°C – 140°C



(vulkanized rubber)

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The following properties are changed when it is vulcanized

Properties	Natural rubber	Vulcanized rubber
1. Tensile strength →	200 Kg/Cm² →	2000 Kg/Cm²
2. Useful temp rang →	10°C – 60°C →	–40°C – 100°C
3. resistance to organic solvents →	poor →	large
4. resistance to moisture oxidation →	poor →	very good
5. Elasticity →	very high →	Low

As compared, vulcanized rubber has more temp. ranges (–40°c to 100°c) Than natural rubber (10°C to 60°C), Vulcanized rubber has more tensile strength Than natural rubber (~ 10 times more) & also vulcanized rubber is more resistant to organic solvents & higher resistant to oxidation Than natural rubber —— That's why, Natural rubber needs vulcanization.

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Biopolymers

What is biopolymers?

Biopolymers are macromolecules that occur in nature from plants, bacteria, or other natural sources that are long chains linked through chemical bond. They are often degradable through microbial process:

ex: cellulose, proteins, starch, etc.

Explain the importance of biopolymers?

(1) Biopolymers have the potentials to produce fewer green house gases & produce fewer toxic pollutants
(2) They may also be recycle
(3) They reduce waste stream

→ That's why, Biopolymers is increasingly altnetive in sustainable development

Examples of Biopolymers

(1) Polylactic acid (PLA): produced from fermantation using sugar from corn
(2) Triglycerides: produced from soyabean
(3) Starch: Found in corn, potatoes, wheat etc.
(4) Collagen: Found in mammals, used in capsules for drug

Classification of Biopolymer

- Carbohydrates (Polysaccharides)
- Protein (Polyamide)
- Nucleic acid (Polynucleotides)
- Natural rubber (Polyisoprene)

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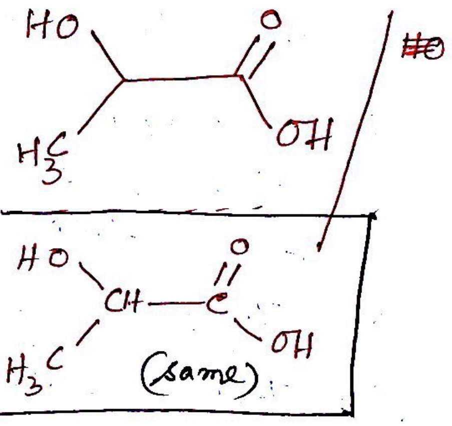
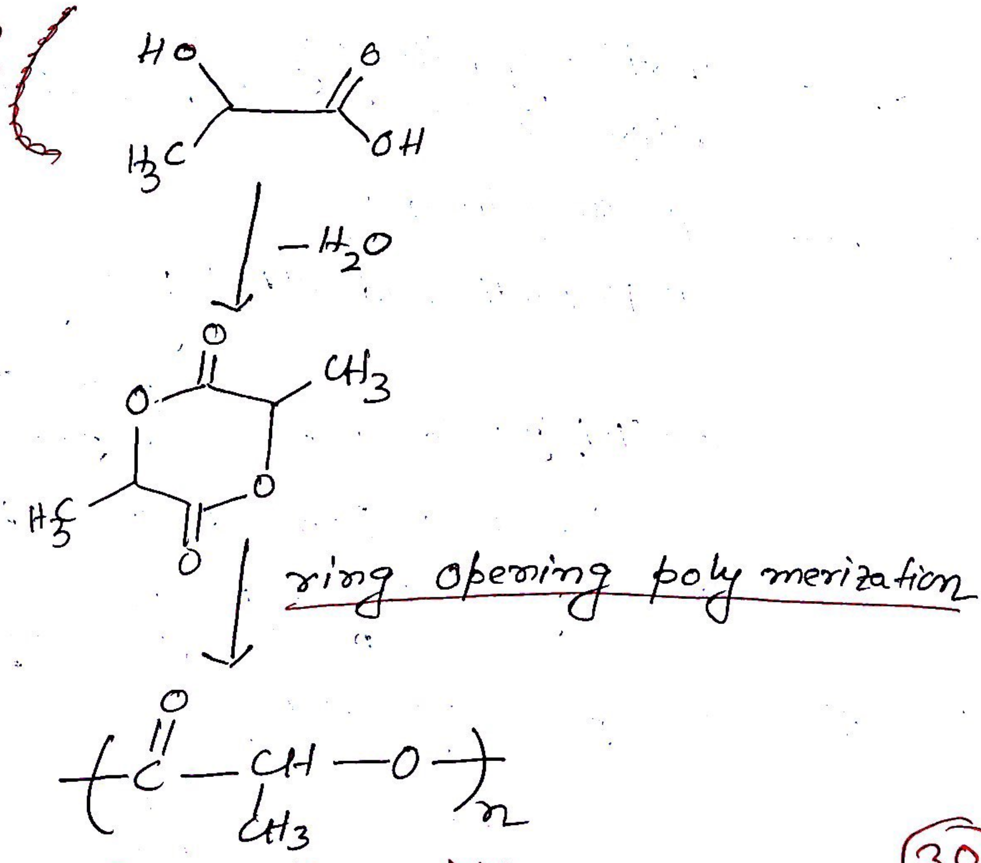
Polylactic acid (PLA)

Synthesis: PLA is derived by means of fermentation process using sugar from corn, followed by either ring-opening polymerization or by condensation polymerization of lactic acid

CORN $\xrightarrow{\text{Fermentation}}$ Lactic acid



Lactic acid:



(Polylactic acid)

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Property:

(1) PLA is thermoplastic aliphatic polyester

(2) PLA is one of the most important biocompatible & biodegradable polymers

(3) It has good mechanical properties & processability

(4) It is soluble in chlorinated solvents

(5) PLA exists in amorphous glassy polymer to highly crystalline having m.p. of 130°c–180°c

Uses: It is used in textile industries, automotive & clinical users & also used to produce disposable packaging

Q: 1. What are biopolymers?

2. Explain why biopolymers are increasingly attractive in sustainable developement

3. What is PLA? How can PLA be prepared?

4. What are the properties & applications of PLA

5. Give few examples of biopolymers.

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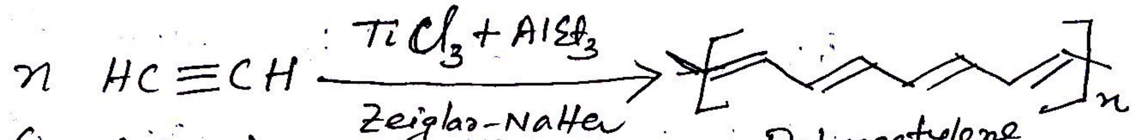
Conducting Polymers:

A polymer which can conduct electricity is called conducting polymer.

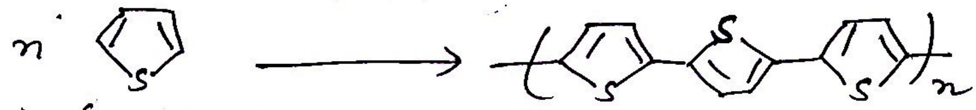
In general, polymers are found to be insulators. Infact, electricity wires are coated with polymers because of its insulating properties.

Examples:

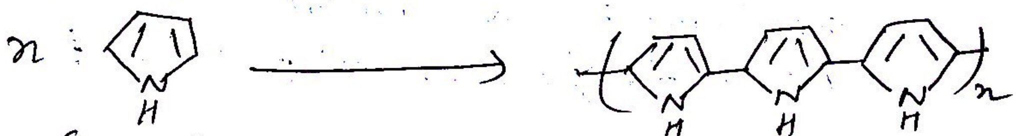
1. 

$n\ HC \equiv CH \xrightarrow[\text{Zeiglar-Natter Catalyst}]{TiCl_3 + AlEt_3}$ Polyacetylene

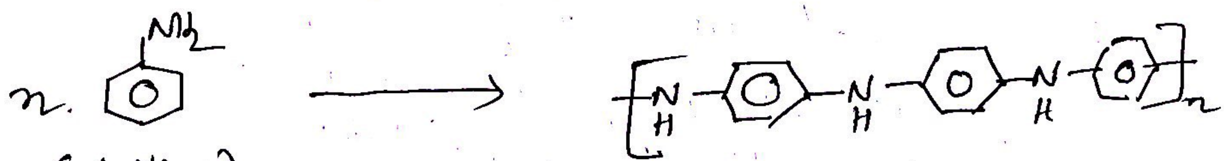
(Acetylene)

2. 

(Thiophene) — PolyThiophene

3. 

(Pyrrole) — Polypyrrole

4. 

(Aniline) — Polyaniline

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** Reasons for Conducting nature of These polymer *

(a) Conducting polymers having π-electrons in backbone

(b) Doped Conducting polymers

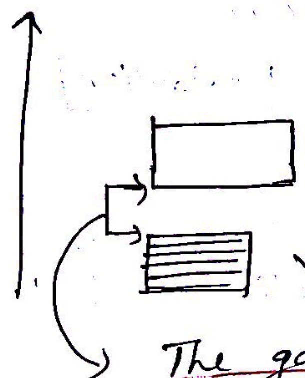
(a) Conducting polymers having π-electrons in backbone

Such polymers contain conjugated π-e^-'s (consequitive presence of double bonds) increases their Conductivity to a large extent

(Polyacetylene)

consequitive presence of double bonds i.e. actually conjugated π-electrons.

This is because, overlaping of conjugated π-electrons of polyacetylene results the narrow band gap between Valance band (VB) & Conduction band (CB); thus increases the Conductivity



E

CB (Lowest unoccupied band)

VB (Highest occupied band)

The gap is narrow due to the presence of consequitive double bonds (π-e^-'s)

If band gap (between VB & CB) is narrow, the e^-'s from VB are excited to jump from VB to CB, thus giving rise to conductivity.

If band gap is too wide, the substance is insulator

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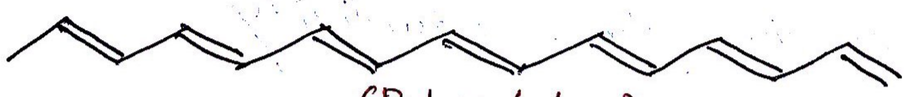
(b) Doped Conducting polymers :

(1) p-doping
(2) N-doping

p-doping : It is done by oxidation process by treating with lewis acids (e.g. $FeCl_3$) or Iodine in CCl_4

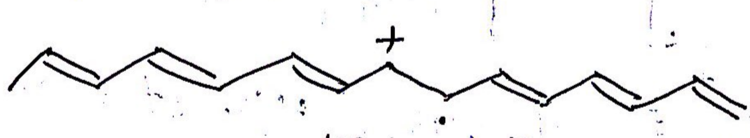
This oxidation process [basically, removal of an electron from the polymer pi-back bone] leads to the formation of delocalised radical ion [called radical cation] — polaron. A second oxidation of this polaron, followed by radical combination forms two +ve charges carrier on each chain, which are mobile.

Thus this delocalized +ve charge are current carriers for conduction.



(Polyacetylene)

$-e^-$ ↓ $FeCl_3$ [oxidation]



radical cation or Polaron

$-e^-$ ↓ 2^{nd} oxidation

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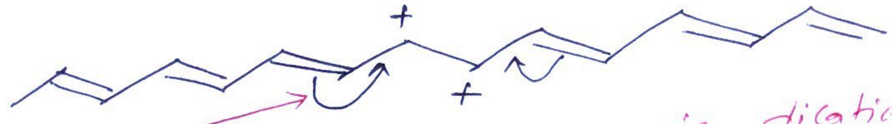


mobile π electrons

form two +ve charge ie. dication

(p-doped polyacetylene)

movement of +ve charges on polymeric back bone, Thus, increases the conductivity

N-doping:

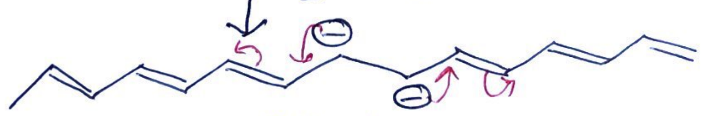
It is done by reduction process by treating with Sodium Naphthalide $[Na^{+}(C_{10}H_8)^{-}]$ $Na^{+}(C_{10}H_8)^{-}$

This reduction process [Addition of an e^- to polymer backbone] leads to the formation of polaron ie. radical anion. A second reduction by $Na^{+}(C_{10}H_8)^{-}$ can also add one more e^- to the back bone; Thus forming dianion. These two e^-s present in the polymer backbone is responsible for conduction.

$+e^-$ $Na^{+}C_{10}H_8^{-}$

radical anion or polaron

2^{nd} reduction



(dianion)

(n-doped polyacetylene) movements of -ve changes on polymeric back bone, Thus increases the Conductivity

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Properties of conducting polymer:

(1) Highly reactive & redox active material
(2) Show Conductivity
(3) Ability to store a charge
(4) Absorption of visible light to coloured products
(5) Poor stability

Applications:

(1) It is used in commercial rechargeable batteries
(2) It is used as sensors — gas sensor, radiation sensor, humidity sensor, biosensor etc.
(3) Used in light-emitting diode
(4) Used in fuel cells
(5) Used in information storage devices

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Molecular weight of a polymer :⇒

Polymers are polydisperse. In other words, polymers are mixtures of molecules of different molecular masses —— These are three types

1. Number-average molecular mass ($\bar{M}_n$)
2. Weight-average molecular Mass ($\bar{M}_w$)
3. Viscosity-average Molecular Mass ($\bar{M}_v$)

$\bar{M}_n$: It is defined as the total mass (w) of all the molecules in polymer sample devided by the total number of molecules present.

$$\boxed{\bar{M}_n = \frac{w}{\sum N_i} = \frac{\sum N_i M_i}{\sum N_i}} = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}{N_1 + N_2 + N_3 + \cdots}$$

N_i = number of molecules in polymer of Mass M_i
N_1 = " " " " of " M_1
N_2 = " " " " " " M_2
- - - - -

$\bar{M}_n$ is determined by measurement of colligative properties (such as, freezing point depression, boiling point elevation etc.)

$\bar{M}_n$ is the good index of physical properties of polymer, such as impact & tensile strength, but not a good index of other properties, such as flow

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$\overline{M}_w$:

$$\overline{M}_w = \frac{\sum W_i M_i}{\sum W_i}$$; where W_i is the weight fraction of molecules of mass M_i

It can be defined as, $\overline{M}_w = \frac{\sum C_i M_i}{\sum C_i}$

C_i is the weight concentration of mass M_i

It is known that $\boxed{C_i = N_i M_i}$

N_i is the number of molecules of Mass M_i

$$\text{so, } \boxed{\overline{M}_w = \frac{\sum C_i M_i}{\sum C_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}}$$

$$\overline{M}_w = \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2 + \text{-----}}{N_1 M_1 + N_2 M_2 + N_3 M_3 + \text{-----}}$$

$\overline{M}_w$ can be determined from light-scattering techniques.

$\overline{M}_v$:

$$\overline{M}_v = \frac{\sum W_i M_i^a}{\sum W_i} = \left(\frac{\sum N_i M_i^{a+1}}{\sum N_i M_i}\right)^{1/a}$$

a = Constant

Polydispersity index or molecular Mass distribution:

PDI = Polydispersity index

$$PDI = \frac{\overline{M}_w}{\overline{M}_n}$$

— This can be calculated using the weight average molecular weight devided by the number average molecular weight

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If, PDI > 1 i.e. $\bar{M}_w > \bar{M}_n$

↳ The polymer is polydisperse

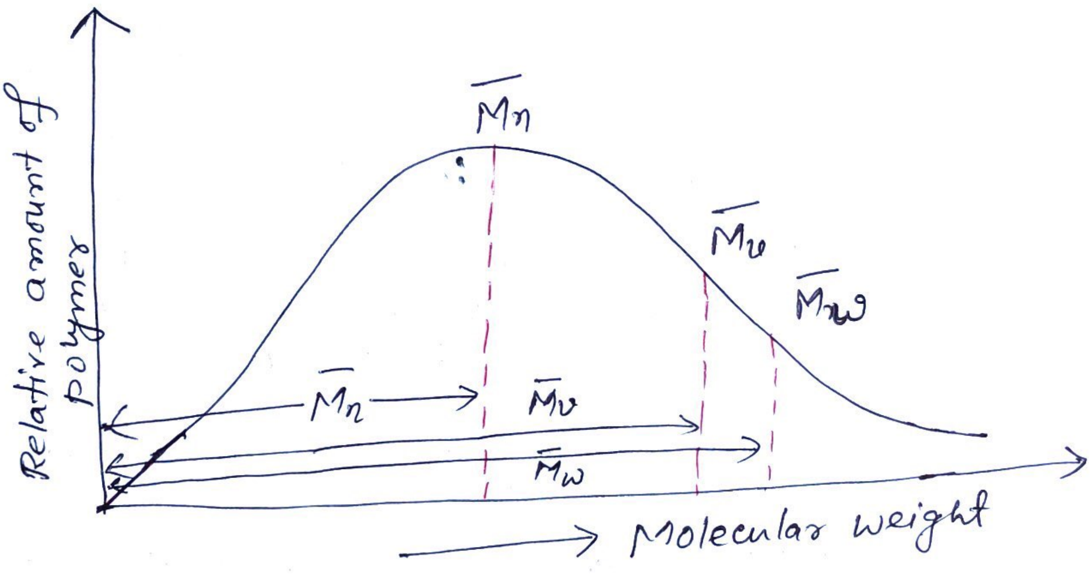
If PDI = 1 i.e. $\bar{M}_w = \bar{M}_n$

↳ The polymer is monodispers

Q: How does the polydispersity index indicate the polydispersity or/and monodispersity of a polymer?

Ans: PDI > 1 i.e. $\bar{M}_w > \bar{M}_n$; polydisperse
PDI = 1 i.e. $\bar{M}_w = \bar{M}_n$; Monodisperse

* Distribution of molecular masses' curve for polymer



so, $\bar{M}_w > \bar{M}_v > \bar{M}_n$

Polydisperse: A polymer material is called polydisperse, That means, its chain lengths vary over a wide range of molecular masses

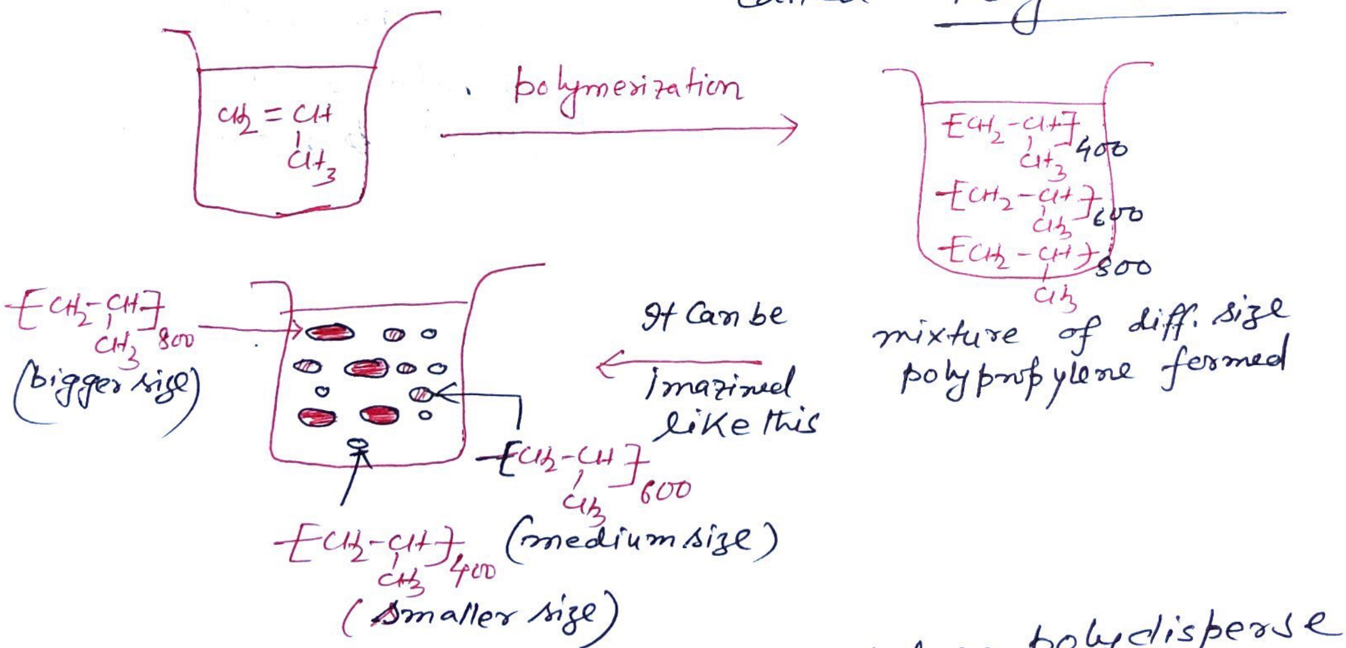
Monodisperse: A polymer is often referred to monodisperse, when a uniform composed of polymer molecules of same mass

Example: ⇒

If we want to synthesize polymer ~~of~~ from its ~~molecular~~ monomer of polypropylene, the polymers are formed with different ~~sis~~ chain size polypropylene (i.e. different degree of polymerization)

$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{CH}} \longrightarrow \left[CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}\right]_{400} + \left[CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}\right]_{600} + \left[CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}\right]_{800}$$

⟶ Here, polypropylene is formed with a different chain size polymer having three different degree of polymerization. So, This polypropylene is called <u>Polydisperse</u>



SO, The polymer sample is treated as <u>polydisperse</u>

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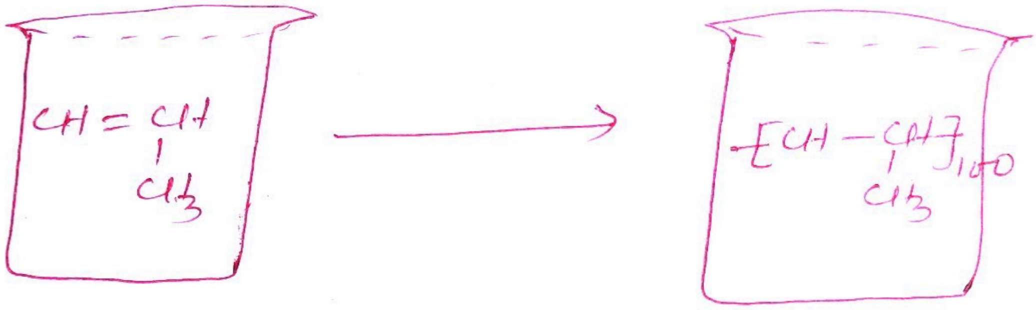
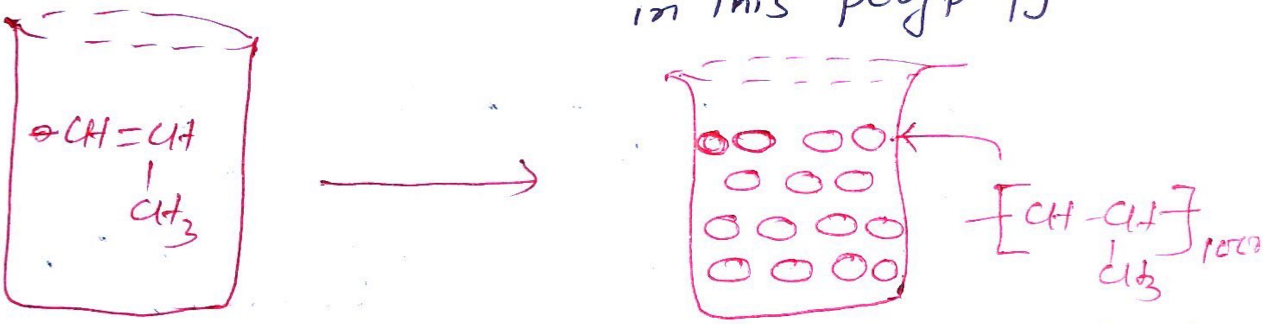
If,

$$CH = \underset{\displaystyle CH_3}{\underset{|}{CH}} \xrightarrow{\text{polymerization}} \left[CH - \underset{\displaystyle CH_3}{\underset{|}{CH}} \right]_{1000}$$



Here, only one ~~si~~ size of chain is present in this polypropylene



all the polymer molecules have same size, so The polymer sample is called monodisperse

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Q:1 Calculate the number average & weight-average molecular masses of polypropylene with the following composition

I $-[CH_2-CH(CH_3)]_{400}- \longrightarrow 25\%$

II $-[CH_2-CH(CH_3)]_{800}- \longrightarrow 35\%$

III $-[CH_2-CH(CH_3)]_{600}- \longrightarrow 40\%$

given that at mass of $C=12$; $H=1$

Ans: Mass of repeating unit $-(CH_2-CH(CH_3))- = 12\times3+6\times1 = 42$

No of repeating (n) in polymer (degree of polymerization)	400 in I	800 in II	600 in III
Molecular weight $(M_i) = 42\times n$	$42\times400 = 16,300$	$42\times800 = 32,600$	$600\times42 = 25,200$
No. of molecules in 100%	25	35	40

$$\text{So, } \bar{M}_n = \frac{\sum N_iM_i}{\sum N_i} = \frac{25\times16,300+35\times32,600+40\times25,200}{25+35+40}$$

$$= 25,565$$

$$\bar{M}_w = \frac{\sum N_iM_i^2}{\sum N_iM_i} = \frac{25\times16300^2+35\times32600^2+40\times25200^2}{25\times16300+35\times32600+40\times25,200}$$

$$= 27084$$

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Functionality of a monomer:

A functionality of a monomer is defined as the number of binding sites that monomer.

Examples

1. The number of reactive functional group represent in a monomer

Functionality

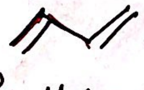
ex: $H_2N-(CH_2)_6-NH_2 \longrightarrow$ 2 (two $-NH_2$ gr. present)

$HO_2C-(CH_2)_4-CO_2H \longrightarrow$ 2 (Two $-CO_2H$ gr. present)

2. The number of Hydrogen that can be added to monomer

ex: $CH_2=CH_2 \dashrightarrow CH_3-CH_3$; Functionality = 2

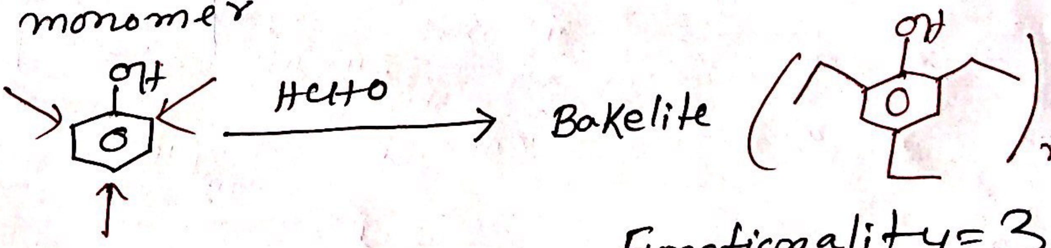
$HC\equiv CH \dashrightarrow CH_3-CH_3$; Functionality = 4



$\longrightarrow H_3C-CH_2-CH_2-CH_3$;

$H_2C=CH-CH=CH_2$ (1,3-dibutadiene) Functionality = 4

3. The number of replacable atom present in a monomer



Functionality = 3

Books Recomended

1. Engineering chemistry by K. Sesha Maheswaramma & Mridula Chugh
2. Engineering chemistry by Shashi Chawla
3. Engineering chemistry by Jain and Jain

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