# SYNTHETIC & NATURAL POLYMERS

## Preface

Monomers join together and forms polymers. This topic is a fundamental topic of which applications are wider in organic chemistry.
In this chapter you will learn about various types and varieties of polymers and their formation.

After successful completion of it, you will be able to know about :
(i) Various aspects of classification of polymers.
(ii) Difference between various types of polymers.
(iii) Sketch representation of polymers.
(iv) Important polymers.

This book consists of theoritical & practical explanations of all the concepts involved in thechapter. Each article followed by a ladder of illustration. At the end of the theory part, thereare miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develope bettter understanding of the chapter and to have better grasping level in the class.

Total No.of questions in **Synthetic and natural polymers** are -

| | |
|---|---|
| In Chapter Examples | 05 |
| Solved Examples | 10 |
| **Total No. of questions** | **15** |

## 1. INTRODUCTION

A polymer is a compound of high molecular mass formed by the combination of large number of small molecules and process is called polymerisation. The small molecules which constitute the repeating units in a polymer are called monomer units. These large molecule have relative molecular masses in the range $10^4$ - $10^6$.

**eg.**

$$\underset{\text{ethene}}{nCH_2{=}CH_2} \longrightarrow \underset{\text{polythene.}}{[-CH_2-CH_2-]_n.}$$

Where n is as high as $10^5$. The number of monomers units in a polymer is called the degree of polymerisation.

## 2. CLASSIFICATION OF POLYMERS

Polymers are classified on the following basis-

### 2.1 Classification based on monomers :

(a) **Homopolymer :** The polymer formed from one kind of monomer is called homopolymer.

**eg.** Polyethylene

(b) **Copolymer or mixed polymer :** Polymer formed from more than one kind of monomer units is called copolymer.

**eg.** Buna - S

### 2.2 Classification based upon origin or source :

There are of two types based on source

(a) **Natural polymers** whose source is animal and plants are called natural polymers eg.starch,cellulose, protein etc.

(b) **Synthetic polymers** :- These are man made polymers synthesised in the laboratory from low molecular weight compounds.

eg. Nylon, dacron, bakelite, synthetic rubber, polystyrene etc.

### 2.3 Classification bassed on structure :

These are of three types based on structure –

(i) Linear polymers
(ii) Branched chain polymers
(iii) Cross linked polymers

**(i) Linear polymers :** In which monomer units are linked together to form long straight chains. The polymeric chains are stacked over one another to give a well packed structure. Such polymers have high densities, high tensile strength and high melting points.

**eg. :** Polythene, Nylon and polyesters

**(ii) Branched chain polymers :** In this type of polymers, the monomeric units are linked to constitute long chains (called main chain). There are side chains of different lengths which constitute branches. Branched chain polymers are irregularly packed and they have lower tensile strength and lower melting points as compared to linear polymers.

**eg. :** Amylopectin (Component of starch)

**(iii) Cross linked polymers :** The monomeric units are linked together to constitute a three dimensional network. Cross linked polymers are hard , rigid and brittle because of their network structure.

**eg. :** Bakelite, Formaldehyde resin etc.

### 2.4 Classification based on synthesis :

These are of two types based on synthesis-

(a) **Condensation polymerisation**: In this the monomer (same or different) units link with each other by the elimination of a small molecule (e.g. water, methyl alcohol) as a by-product. The polymer formed is known as condensation polymer. Nylon and terylene are the most common examples.

Since the condensation polymerisation proceeds by a stepwise intermolecular condensation, it is also known as step polymersation and the polymer formed is known as step growth polymer.

(b) **Addition polymerisation** : This involves the self addition of several unsaturated molecules of one or two monomers without loss of any small mulecule to form a single giant molecule. The polymer formed is known as addition polymer. Polythene is the most common example.

**Differences between Addition and Condensation Polymers**

| S.N. | Addition polymers | Condensation polymers |
|---|---|---|
| 1. | Formed by addition reaction. | Formed by condensation process with elimination of small molecules like $H_2O$. |
| 2. | Molecular mass is a whole number multiple of the monomer. | Molecular mass is not whole number multiple of the monomer units. |
| 3. | Generally involve one monomer unit. | Generally involve more than one monomer unit. |
| 4. | Monomers are unsaturated molecules. | Monomer units must have two active functional groups. |
| 5. | They are generally chain growth polymers. | They are generally step growth polymers. |

### 2.5 Classification based on intermolecular forces :

**(a) Elastomers :** These are the polymers having elastic character. The polymer chains in such type of polymers are held together by weakest intermolecular forces. These forces permit the polymer to be stretched under stress but they regain their former shape when the stress is relieved. The elasticity of such polymers can be further modified by introducing few cross links between the chains.

**eg. :** Natural rubber

**(b) Fibres :** These are the polymers which have quite strong interparticle forces such as H-bonds.

**eg. :** Nylon , Dacron etc.

**(c) Thermoplastics :** These are the polymers which can be easily moulded into desired shapes by heating and subsequent cooling to room temperature. The intermolecular forces in thermoplastic polymers are intermediate to those of elastomers and fibres. Thermoplastic polymers soften on heating and become fluids but on cooling they become hard.

**eg. :** Polyethene, Polystyrene

**(d) Thermosetting polymers :** These are the polymers which become hard and infusible on heating. Heating results in excessive cross linking between the chains forming three dimensional network of bonds.

**eg. :** Bakelite, Melamine

## 3. METHOD OF POLYMERISATION

**(a) Addition Polymers :**

(i) A polymer formed by direct addition of repeated monomer's without the elimination of any byproduct molecules.

(ii) In this type, the monomers are unsaturated compounds and are generally derivative of ethene.

(iii) The addition polymers have same empirical formula as their monomers.

**Ex.** Nylon 6, 6, Terylene, bakelite etc.

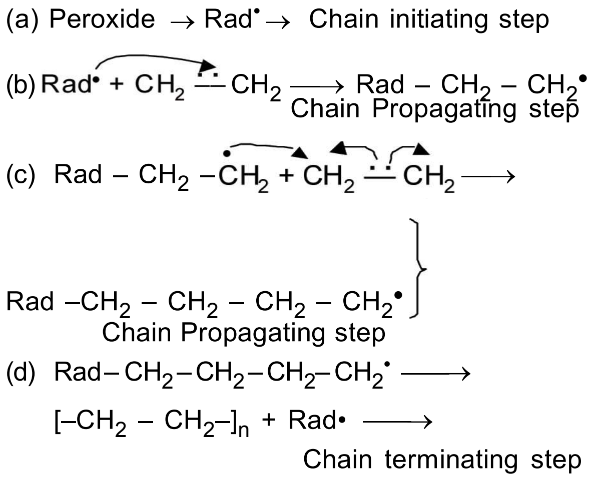
**Chain growth polymerization :**

(i) There is a series of reaction each of which consume a reactive particle and produce another, similar particle, each individual reaction thus depend upon the previous one.

(ii) The reactive particle can be free radical, cations or anions.

(iii) The polymerization start when a molecule of monomers react with an initiator to form an active intermediate.

(iv) This active intermediate is added to another monomer forming another intermediate. In this way chain propagation continue and ultimately a polymer is formed.



(a) Peroxide $\rightarrow$ $Rad^{\bullet}$ $\rightarrow$ Chain initiating step

(b) $Rad^{\bullet} + CH_2 = CH_2 \longrightarrow Rad - CH_2 - CH_2^{\bullet}$

Chain Propagating step

(c) $Rad - CH_2 - CH_2^{\bullet} + CH_2 = CH_2 \longrightarrow$

$Rad - CH_2 - CH_2 - CH_2 - CH_2^{\bullet}$

Chain Propagating step

(d) $Rad - CH_2 - CH_2 - CH_2 - CH_2^{\bullet} \longrightarrow$

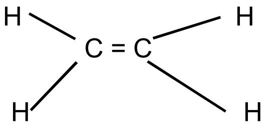
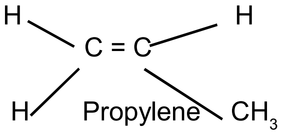
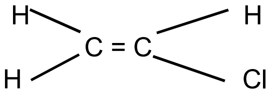
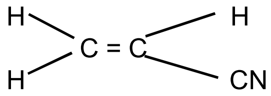
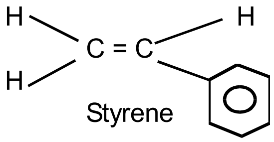
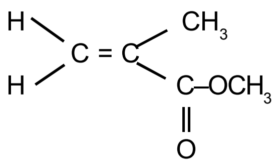
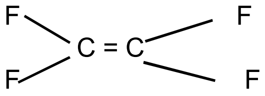
$[-CH_2 - CH_2-]_n + Rad\bullet \longrightarrow$

Chain terminating step

**Example :**

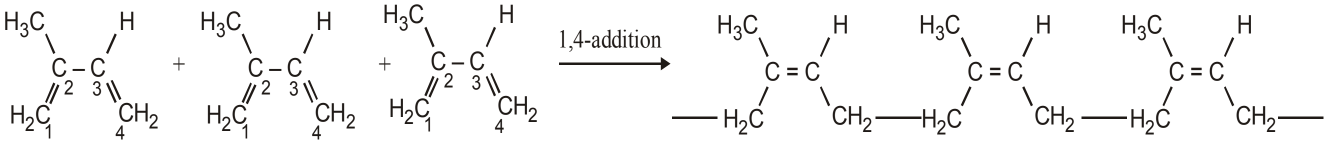
Polyethylene, Polypropylene, PVC, teflon, etc.

### SOME COMMON ADDITION POLYMERS

| Monomer | Polymer | Uses |
|---|---|---|
|  Ethylene | Polythene | Bags , toys. etc |
|  Propylene | Polypro-pylene | Beakers , mill cartons etc. |
|  Vinyl chloride | Polyvinyl chloride (PVC) | Rain coats, pipes,tiles etc. |
|  Acrylonitrile | Poly acrylo-nitrile, (PAN)Orlon | Carpets etc. |
|  Styrene | Polystyrene | Thermocole, Insulating material etc. |
|  Methyl methacrylate | Plexiglass | Transparent objects lenses etc. |
|  Tetrafluoro ethylene | Teflon (PTFE) | Chemical equipment Non stick cookware |

## 4 NATURAL RUBBER

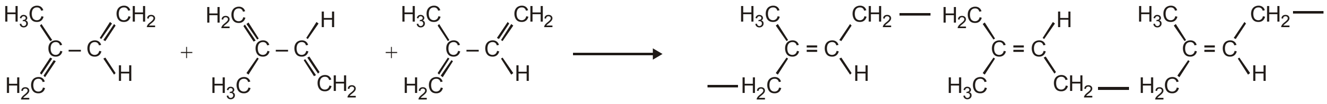
**(a) It is cis Polyisoprene**



Isoprene

cis -polyisoprene (natural rubber)

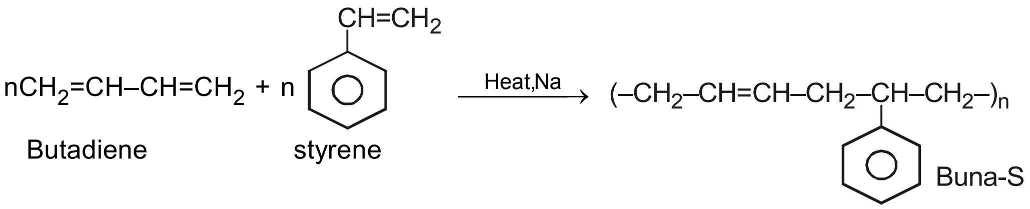
**(b) Gutta percha:**



trans - polyisoprene (gutta percha)

## 5. SYNTHETIC RUBBER

**(i) Buna S :** It is copolymer of 1, 3 butadiene and styrene. It is obtained by the polymerisation of butadiene and styrene in the ratio of 3 : 1 in the presence of sodium



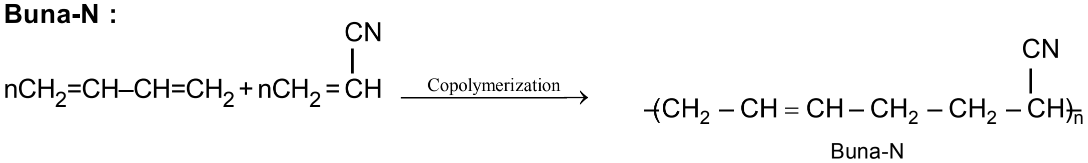
Butadiene

styrene

Buna-S

**Uses :** Buna - S is also vulcanised and used in making tyres for the vehicles. It is also used as rubber soles and in making water proof shoes.

**(ii) Buna-N :**



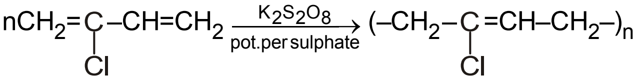
$$nCH_2{=}CH{-}CH{=}CH_2 + nCH_2{=}\overset{\overset{\displaystyle CN}{|}}{C}H \xrightarrow{\text{Copolymerization}} {+}CH_2 - CH = CH - CH_2 - CH_2 - \overset{\overset{\displaystyle CN}{|}}{C}H{+}_n$$

1,3-Butadiene Acrylonitrile

Buna-N

⇒ It is used in making oil seals, tank lining, etc.

**(iii) Neoprene**



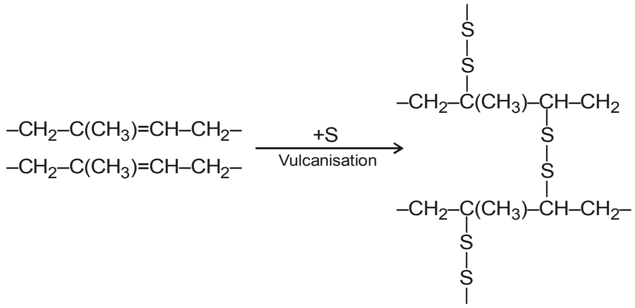
$$nCH_2{=}\underset{\underset{\displaystyle Cl}{|}}{C}{-}CH{=}CH_2 \xrightarrow[\text{pot.per sulphate}]{K_2S_2O_8} ({-}CH_2{-}\underset{\underset{\displaystyle Cl}{|}}{C}{=}CH{-}CH_2{-})_n$$

Chloroprene

Neoprene

**Vulcanisation :**

In vulcanisation rubber is heated (3 hrs) it with sulphur (3-10%) at a temperature of 125-140$^0$C. Rubber hydrocarbon combines with the sulphur atoms to form the sulphur bridges. The resulting product is tough, non-elastic and resistance to heat. It becomes non-abrasive and not affected by chemicals.

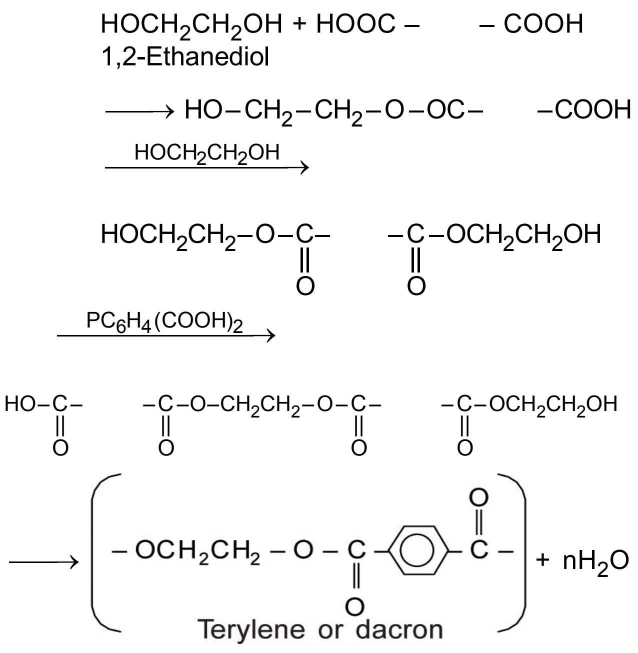


## 6. STEP GROWTH POLYMERISATION

(i) This type of polymerization involve a series of reaction each of which is essentially independent of the proceeding one.

(ii) A polymer is formed simply because the monomer happen to undergo reaction at more than one functional group.

(iii) In the case of polyester, a diol for example, react with a dicarboxylic acid to form an ester but each moiety of the simple ester contain a group that can react to generate another ester linkage and hence a large molecule, which itself can react further, and so on



$$HOCH_2CH_2OH + HOOC-\qquad-COOH$$

1,2-Ethanediol

$$\longrightarrow HO-CH_2-CH_2-O-OC-\qquad-COOH$$

$$\xrightarrow{HOCH_2CH_2OH}$$

$$HOCH_2CH_2-O-\underset{O}{\underset{\|}{C}}-\qquad-\underset{O}{\underset{\|}{C}}-OCH_2CH_2OH$$

$$\xrightarrow{PC_6H_4(COOH)_2}$$

$$HO-\underset{O}{\underset{\|}{C}}-\qquad-\underset{O}{\underset{\|}{C}}-O-CH_2CH_2-O-\underset{O}{\underset{\|}{C}}-\qquad-\underset{O}{\underset{\|}{C}}-OCH_2CH_2OH$$

$$\longrightarrow \left(-OCH_2CH_2-O-\underset{O}{\underset{\|}{C}}-\qquad-\overset{O}{\overset{\|}{C}}-\right) + nH_2O$$

Terylene or dacron

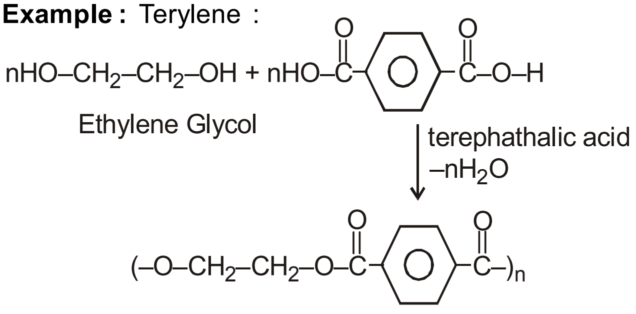
### 6.1 Condensation polymers :

(i) A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecule like - $H_2O$ / $NH_3$ etc..

(ii) In this type, each monomer generally contain two functional group. Ex.Nylon 6, 6, Terylene, bakeliteete

**(a) Polysters :** These are the polymers having ester linkage ( $-\overset{O}{\overset{\|}{C}}-O-$)

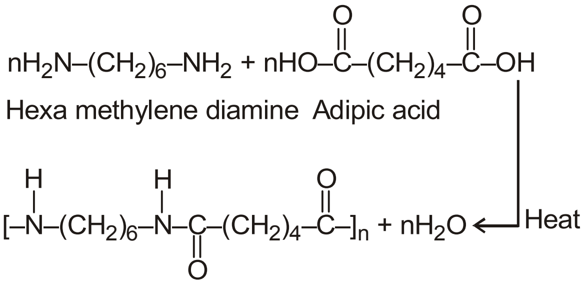
**Example :** Terylene :



terylene

**(b) Polyamides :** Such polymers have amide linkage $(-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-)$ in the chain

**(i) Nylon-66**



$$nH_2N-(CH_2)_6-NH_2 + nHO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH$$

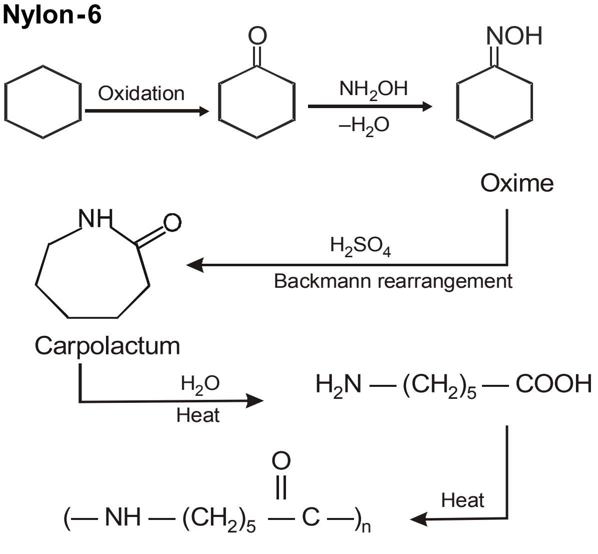
Hexa methylene diamine  Adipic acid

$$[-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\underset{O}{\underset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-]_n + nH_2O \xleftarrow{} \text{Heat}$$

(nylon 66)

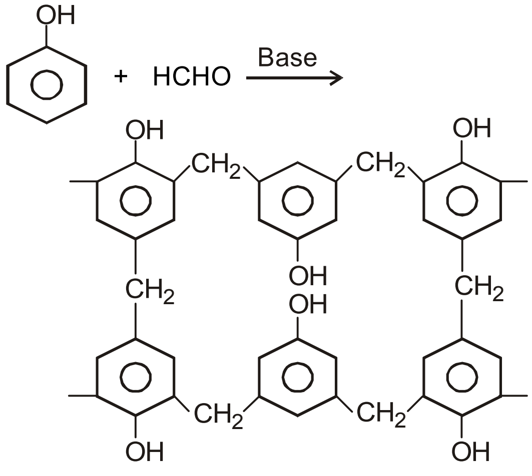
**Uses :** Nylon 66 have high tensile strength so it is used in the manufacture of carpets, textile fibres and bristles for brushes. It is used in making elastic hoisery.

**(ii) Nylon-6**



(Nylon–6)

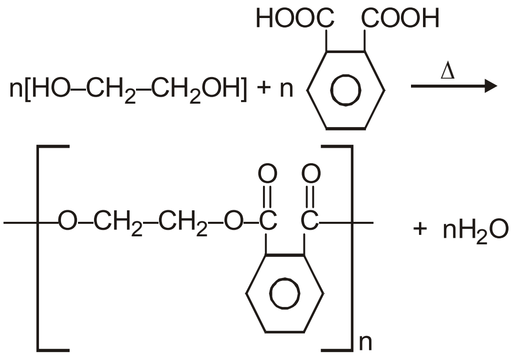
**(c) Phenol-formaldehyde resins( Bakelite)**



Bakelite

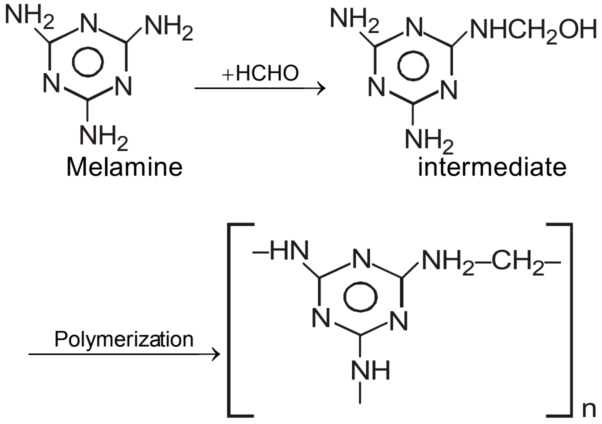
Because bakelite is hard and is a good electrical insulator, it is extensively used on making electrical switches, fuse holders, etc.

**(d) Glyptal or (alkyd resin) :** The most simple glyptal (polyethylene phthalate) formed from the polycondensation of glycol and phthalic acid.



**Uses :** It is used in the manufacture of paints

**(e) Melamine formaldehyde resin :** Melamine formaldehyde resin is formed by the co-polymerisation of melamine and formaldehyde.



**Uses** : It is used for making non breakable plastic crockery i.e cup plates etc.

## 7. MOLECULAR WEIGHT OF POLYMERS

There are two types of average molecular weight in case of polymers.

(a) $\overline{M}_n$ = Number average molecular weight.

(b) $\overline{M}_w$ = Weight average molecular weight.

**(a) Number average molecular weight ($\overline{M}_n$)**

$$(\overline{M}_n) = \frac{\text{Total weight of the molecules}}{\text{Total number of molecules}}$$

**If:** $n_1$ molecules of mol. wt. $M_1$.

$n_2$ molecules of mol. wt. $M_2$.

$n_3$ molecules of mol. wt. $M_3$. Then

$$\overline{M_n} = \frac{n_1M_1 + n_2M_2 + n_3M_3 + - - -}{n_1 + n_2 + n_3 + - - -}$$

$$\overline{M_n} = \frac{\sum_{n_i} M_i}{\sum_{n_i}}$$

**(b) Weight average molecular weight $\overline{M_w}$**

$$\overline{M_w} = \frac{w_1M_1 + w_2M_2 + w_3M_3 + - - -}{w_1 + w_2 + w_3 + - - -}$$

[Weight = no. of molecules × molecular weight]

**Where :** $w_1$ = weight of the molecules of mol. wt. $M_1$

$w_2$ = weight of the molecules of mol. wt. $M_2$

$w_3$ = weight of the molecules of mol. wt. $M_3$

**NOTE :–** Polydispersity index (PDI) is the ratio of weight average mol mass to no. average mol mass

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

For natural polymers PDI = 1 i.e. $\overline{M}_w = \overline{M}_n$

For Synthetic polymers PDI > 1 i.e. $\overline{M}_w > \overline{M}_n$

### Examples based on Polymer theory

**Ex.1** The product of addition polymerization reaction is-

(A) PVC (B) Nylon

(C) Terylene (D) Polyamide

**(Ans. A)**

**Sol.** PVC (polyvinyl chloride) is an addition polymer while nylon, terylene and polyamides are condensation polymers.

**Ex.2** A raw material used in making nylon-6,6 is-

(A) Adipic acid

(B) Butadiene

(C) Ethylene

(D) Methyl methacrylate **(Ans.A)**

**Sol.** Nylon-6,6 is a copolymer of adipic acid [$COOH(CH_2)_4COOH$] and hexamethylene diamine.

**Ex.3** Polymerisation of chloroethylene gives rise to the polymer-

(A) Polyethene (B) PVC

(C) Teflon (D) Nylon **(Ans.B)**

**Sol.** Chloroethylene is $CH_2 = CHCl$ (vinyl chloride) whose polymer will be PVC (polyvinyl chloride).

**Ex.4** Rubber is heated with sulphur and the process is known-

(A) Galvanization (B) Vulcanization

(C) Bessmerization (D) Sulphonation

**(Ans.B)**

**Sol.** It is used for making tyres.

**Ex.5** Monomer of orlon is:

(A) vinyl chloride (B) styrene

(C) propylene (D) acrylonitrile

**(Ans.D)**

**Sol.** Acrylonitrile is $CH_2= CHCN$

# SOLVED EXAMPLES

**Ex.1** Which one is used as a heterogeneous catalyst in the polymerization of ethylene into polyethene-

(A) Walker catalyst

(B) Ziegler-Natta catalyst

(C) Wilkinson's catalyst

(D) Ruthenium catalyst **(Ans.B)**

**Sol.** In the polymerisation of ethylene into polyethylene Zeigler–Natta catalyst (Triethyl aliminium + Titanium tetrachloride) is used as heterogeneous catalyst.

**Ex.2** Natural polymer is-

(A) Polyester (B) Glyptal

(C) Starch (D) Nylon-6 **(Ans.C)**

**Sol.** Starch is natural polymer of D glucose.

**Ex.3** Which is a synthetic rubber-

(A) Buna-S (B) Neoprene

(C) Both the above (D) None **(Ans.C)**

**Sol.** Buna – S and neoprene are synthetic rubber.

**Ex.4** Thermosetts are-

(A) Cross-linked polymers

(B) Do not melt (or soften) on heating

(C) Cross-linking is usually developed at the time of moulding where they harden irreversibly

(D) All **(Ans.D)**

**Sol.** Ex of thermosetts is bakelite

**Ex.5** Di–n–butyl phthalate is-

(A) Plastisizer

(B) Thermoplastic

(C) Polymer

(D) Thermosetting plastic **(Ans.A)**

**Sol.** Di–n–butylphthalate is plastisizer added to PVC to make it soft.

**Ex.6** Natural rubber is-

(A) Trans polyisoprene

(B) Cis polyisoprene

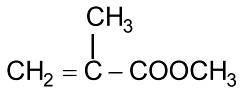
(C) Cis and trans isoprene

(D) None of these **(Ans.B)**

**Sol.** Natural rubber is a homopolymer of cis-isoprene.

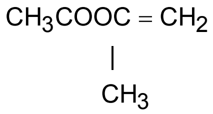
**Ex.7** The structual formula of monomer of poly methymethacrylate (PMMA) is-

(A) $CH_2=CHCOOCH_3$

(B) 

$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-COOCH_3$$

(C) $CH_3COOCH=CH_2$

(D) 

$$CH_3COO\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2$$

**(Ans.B)**

**Sol.** Formula 2nd is of methyl methacrylate, the monomer of PMMA. or Plexiglass.

**Ex.8** Which one of the following compounds is polyester-

(A) Bakelite

(B) Nylon 6,6

(C) Terylene

(D) Rubber

**(Ans.C)**

**Sol.** Terylene is a polyester fibre made up of by the polymerisation of ethylene glycol and pterephthalic acid.

**Ex.9** Nylon is classified as a condensation polymer because-

(A) In its preparation a solid is formed from liquid monomers

(B) Its structure contains the peptide linkage, –CONH–

(C) It can be prepared from aqueous solutions of its monomers

(D) A small molecule is eliminated in its formation from its monomers **(Ans. D)**

**Sol.** Nylon is a condensation polymer because in the reaction of adipic acid with hexamethylene diamine, small molecule $H_2O$ is eliminated in its formation.

**Ex.10** The primary structure of a polypeptide is determined by-

(A) The number of disulphide bonds in the polypeptide

(B) The number of amino acids in the polypeptide

(C) The order of amino acids in the polypeptide

(D) The length of the polypeptide

**(Ans. C)**

**Sol.** The primary structure of a polypeptide is the information of order of different amino acids in that polypeptide.