CLASS-XII

BRUSH UP for NEET/JEE 2020

Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 8

Polymers | Chemistry in Everyday Life

Polymers

POLYMERS

- The process of formation of a bigger molecule from any simpler molecules through mutual bonding is called polymerisation. The simpler molecules undergoing polymerisation are known as monomers and the bigger molecule formed is called a polymer.

$$n\mathrm{CH_2=CH_2} \xrightarrow{\text{Polymerisation}} \text{-}(\mathrm{CH_2-CH_2})\text{-}_n$$

Ethene (Monomer) — Polythene (Polymer)

- **Homopolymers :** Polymers made up of only one type of monomers *e.g.*, polythene, polypropylene.

$$n\mathrm{CH_3-CH=CH_2} \xrightarrow{\text{Polymerisation}} \text{-}(\mathrm{CH(CH_3)-CH_2})\text{-}_n$$

Propylene — Polypropylene

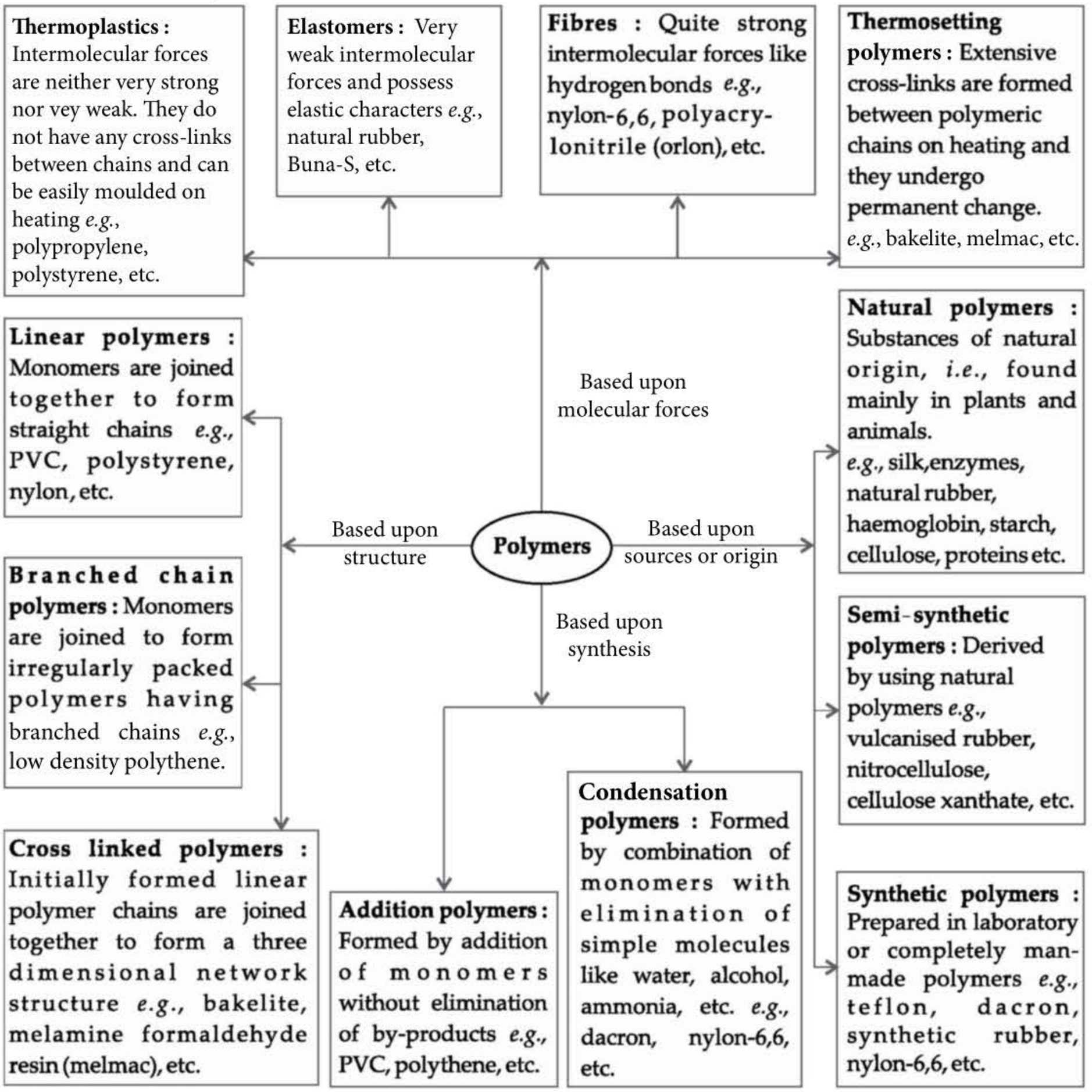
- **Copolymers :** Polymers made up of two or more types of monomers *e.g.*, nylon 6,6. The process of formation of copolymer is called copolymerisation.

$$n\mathrm{NH_2(CH_2)_6NH_2} + n\mathrm{HOOC(CH_2)_4COOH} \xrightarrow[-\mathrm{H_2O}]{\text{Polymerisation}} \text{-}\mathrm{NH(CH_2)_6NHCO(CH_2)_4CO}\text{-}_n$$

Hexamethylene-diamine (monomer) — Adipic acid (monomer) → Nylon 6, 6 (Polymer)

- Copolymers have better physical and mechanical properties, which can be changed by varying the amount of each monomer.

Classification of Polymers



Types of Polymerisation Reaction

- **Addition polymerisation :** In addition polymerisation, the unsaturated monomeric molecules undergo repeated addition reactions in the presence of catalysts like O_2, organic peroxides. Some examples of addition polymers are polythene from ethylene, polypropylene from propylene, polyisoprene from isoprene. etc.

(i) $n CH_2=CH(Cl) \longrightarrow +CH_2-CH(Cl)+_n$

Vinyl chloride — Polyvinyl chloride

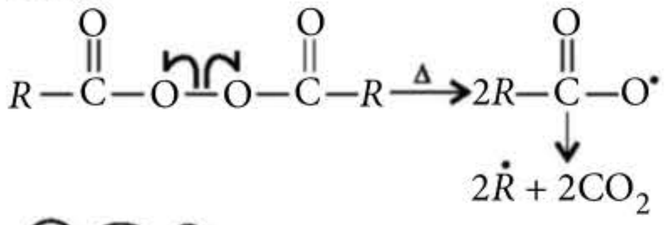
(ii) $n CH_2=C(CH_3)-CH=CH_2 \rightarrow +CH_2-C(CH_3)=CH-CH_2+_n$

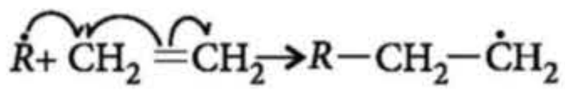
Isoprene — Polyisoprene (Natural rubber)

Mechanism of Addition Polymerisation or Chain Growth Polymerisation

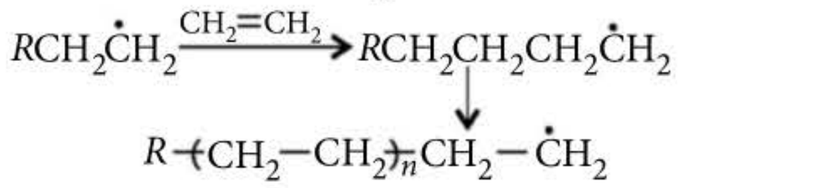
- **Free radical addition polymerisation :** This is initiated by adding a substance which generate free radicals called an initiator *e.g.*, benzoyl peroxide.
  - **Chain initiation :** Peroxide molecules break up and generate free radicals which act as initiators and react with monomer molecules

and generate a larger free radical or growing chain.



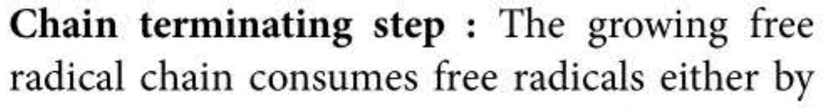


– **Chain propagating step :** The free radical thus formed adds to the double bond of the monomer to form larger free radical.

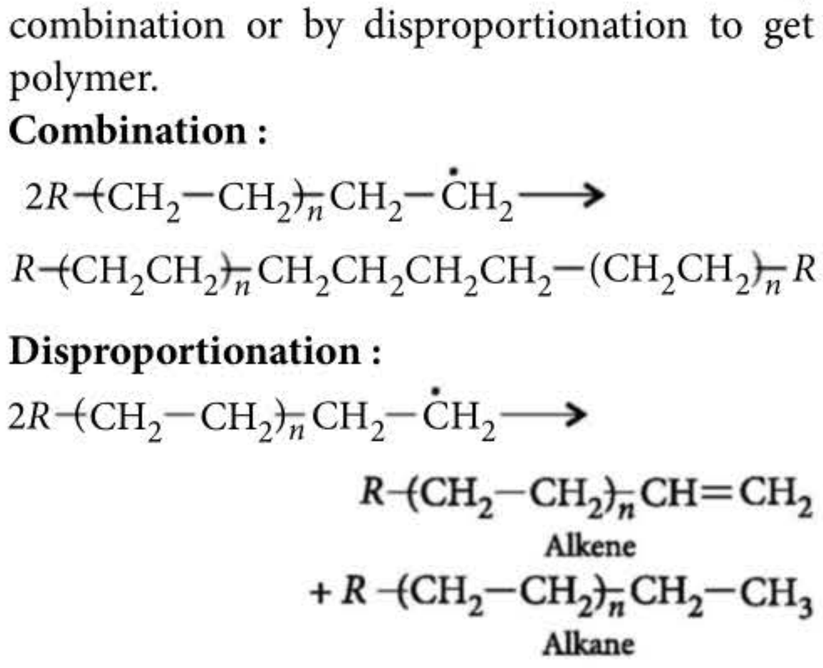


– **Chain terminating step :** The growing free radical chain consumes free radicals either by combination or by disproportionation to get polymer.

Combination :



Disproportionation :



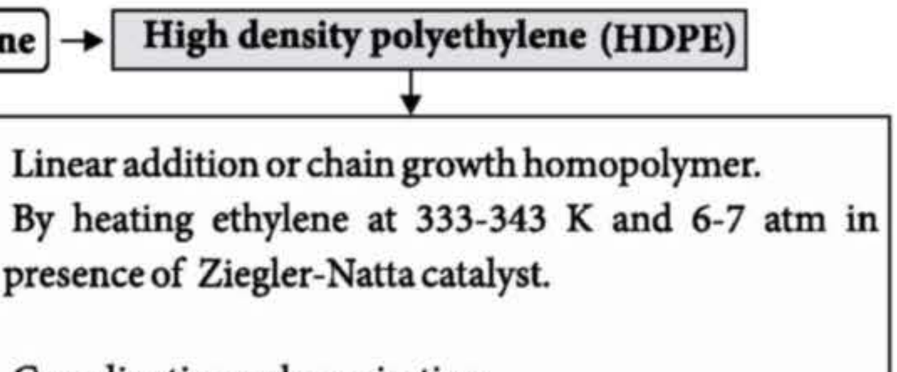
- **Cationic addition polymerisation :** Initiated by the use of strong Lewis acids such as HF, $AlCl_3$, H_2SO_4, etc.

e.g., Polystyrene, polyvinyl ether etc.

- **Anionic addition polymerisation :** Initiated by strong bases such as $NaNH_2$, C_4H_9Li and Grignard reagent, etc.

e.g., Polyacrylonitrile, polyvinyl chloride, etc.

- **Condensation or step growth polymerisation :** Condensation polymerisation normally takes place by condensation of monomeric molecules. For example, terylene is formed by removal of water molecules from ethylene glycol and terephthalic acid molecules.



Some other examples of condensation polymerisation are :

(i) Adipic acid + hexamethylenediamine → Nylon 6, 6 + H_2O

(ii) Phenol + formaldehyde → Bakelite + H_2O

(iii) Urea + formaldehyde → Urea – formaldehyde resin + H_2O

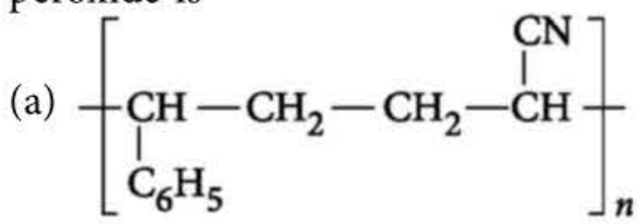
Types of Polythene

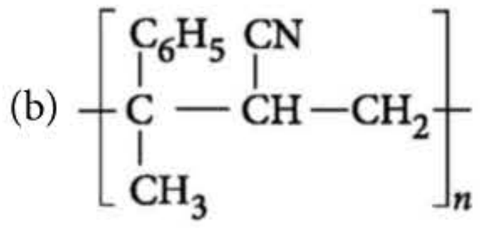
Polyethylene

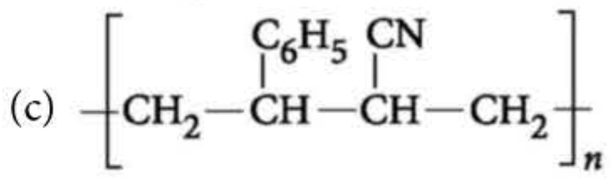
Low density polyethylene (LDPE)	High density polyethylene (HDPE)
– Addition or chain growth homopolymer.	– Linear addition or chain growth homopolymer.
– By heating ethylene under high pressure (1000-2000 atm) at temperature of 350-570 K in presence of traces of oxygen or peroxide.	– By heating ethylene at 333-343 K and 6-7 atm in presence of Ziegler-Natta catalyst.
– Free radical addition polymerisation.	– Coordination polymerisation
– Highly branched polymer.	– Linear molecules, closely packed.
– Low density (0.92 g/cm^3) , low melting point (384 K)	– High density (0.97 g/cm^3), high melting point (403 K).
– Transparent	– Translucent
– Chemically inert, tough but flexible, moderate tensile strength.	– Chemically inert, quite harder, greater tensile strength.
– Used for packaging, insulation and manufacturing squeeze bottles, pipes, toys, etc.	– Used for manufacturing containers, housewares, pipes, etc.

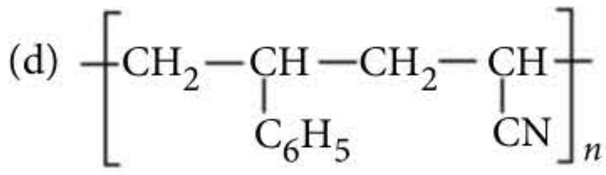
Peep Into Previous Years

1. The copolymer formed by addition polymerization of styrene and acrylonitrile in the presence of peroxide is

(a) 

(b) 

(c) 

(d) 

(JEE Main Online 2018)

2. Regarding cross-linked or network polymers, which of the following statements is incorrect?

(a) They contain covalent bonds between various linear polymer chains.

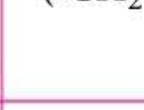
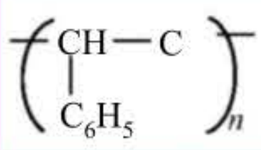
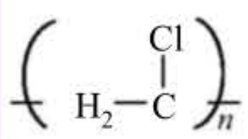
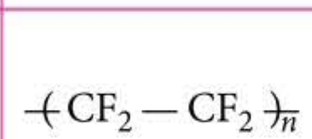
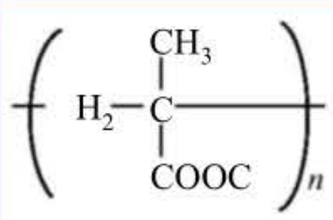
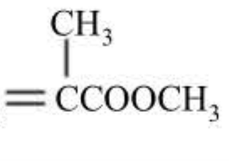
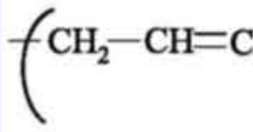
(b) They are formed from bi- and tri-functional monomers.

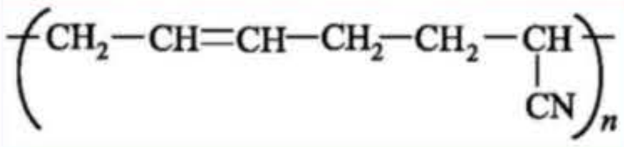
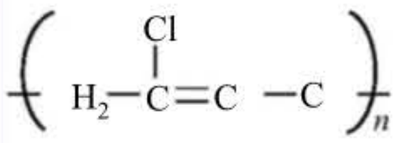
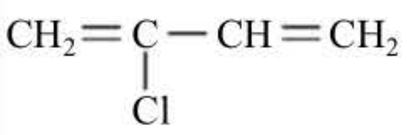
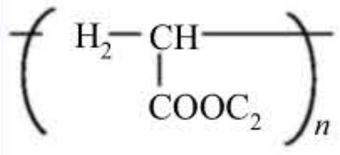
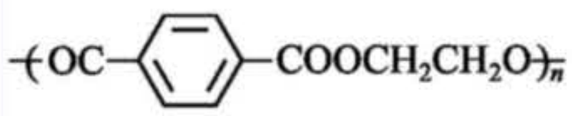
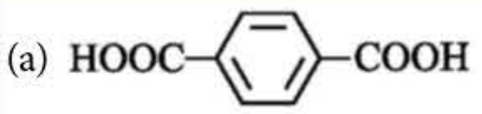
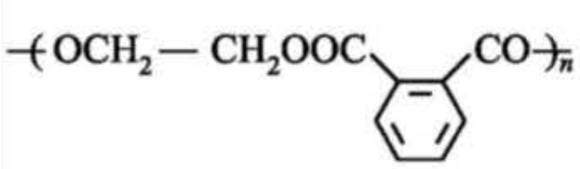
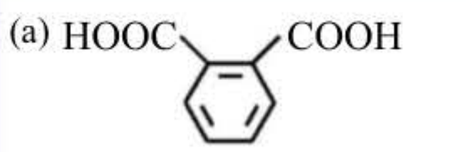
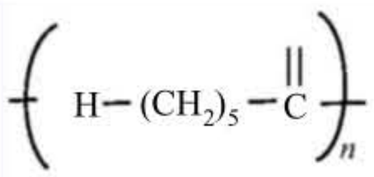
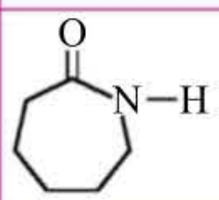
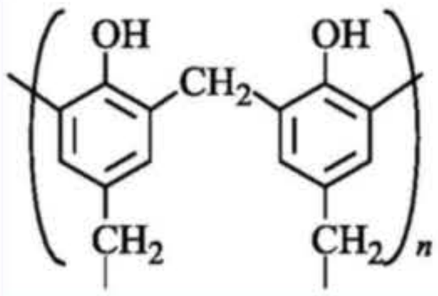
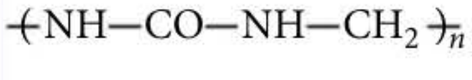
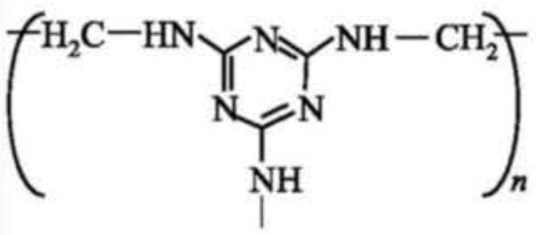
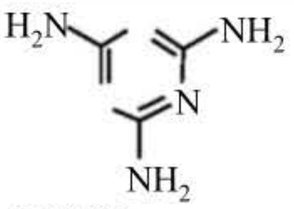
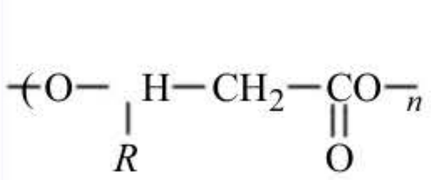
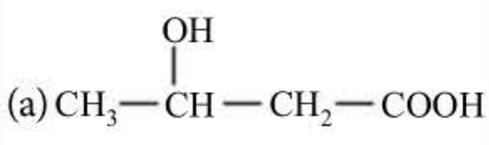
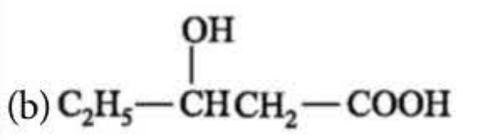
(c) Examples are bakelite and melamine.

(d) They contain strong covalent bonds in their polymer chains.

(NEET 2018)

Some Commercially Important Polymers

Name of polymer	Structure	Monomer	Uses
Polyethylene		$CH_2=CH_2$	Used as insulator, anticorrosive, packing material, household and laboratory wares.
Polystyrene		$C_6H_5-CH=CH_2$	Used as insulator, wrapping material, manufacture of toys and household articles.
Polyvinyl chloride		$CH_2=CHCl$	Manufacture of raincoats, hand bags, vinyl flooring and leather clothes.
Polytetrafluoro ethylene (PTFE) or Teflon		$CF_2=CF_2$	As lubricant, insulator and making cooking wares.
Poly methyl methacrylate (PMMA) or Plexiglass			Used as substitute of glass and for making decorative materials.
Polyacrylonitrile (Orlon)		$CH_2=CHCN$	In making synthetic fibres and synthetic wool.
Styrene butadiene rubber (SBR or Buna-S)		(a) $CH_2=CH-CH=CH_2$ (b) $C_6H_5-CH=CH_2$	In making automobile tyres and footwears.

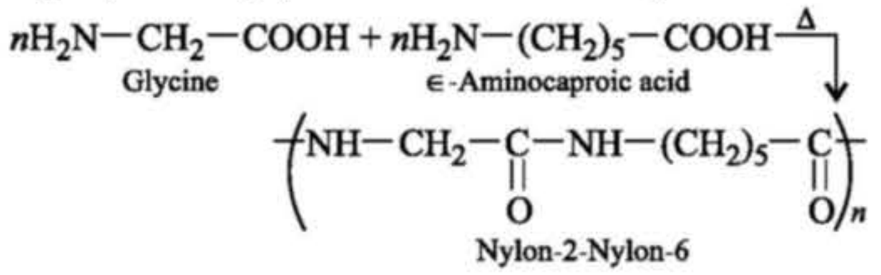
Nitrile rubber (Buna – N)		(a) $CH_2=CH-CH=CH_2$ (b) $H_2C=CH-CN$	In making oil seals, hoses and tank linings.
Neoprene			Used as insulator, in making conveyor belts and printing rollers.
Polyethyl acrylate		$CH_2=CH-COOC_2H_5$	In making films, house pipes and finishing fabrics.
Terylene (Dacron)		(a)  (b) $HO-CH_2-CH_2-OH$	For making films, house pipes and finishing fabrics.
Glyptal		(a)  (b) $HO-CH_2-CH_2-OH$	As binding material in preparation of mixed plastics and paints.
Nylon-6			In making fibres, plastics, tyre cords and ropes.
Nylon-6, 6	$+NH(CH_2)_6NHCO(CH_2)_4CO+_n$	(a) $HOOC-(CH_2)_4-COOH$ (b) $H_2N-(CH_2)_6-NH_2$	In making brushes, synthetic fibres, parachutes, ropes and carpets.
Bakelite		(a) HCHO (b) C_6H_5OH	For making gears, protective coating and electrical fittings.
Urea-formaldehyde resin		(a) HCHO (b) NH_2CONH_2	For making unbreakable cups and laminated sheets.
Melamine-formaldehyde resin		(a)  (b) HCHO	In making non-breakable plastic crockery *i.e.*, unbreakable cups and plates.
Poly-β-hydroxy butyrate-co-β-hydroxy valerate (PHBV)	 $R = CH_3-$, C_2H_5-	(a)  (b) 	As packaging, orthopaedic devices and in controlled drug release.

Rubber

- **Natural rubber :**
  - It is obtained as latex from rubber tree.
  - It is highly elastic.
  - It is *cis*-1,4-Polyisoprene.
  - All *trans* configuration occurs as *Gutta-Percha*, which is non-elastic.
- **Synthetic rubber :**
  - It is obtained by polymerizing certain organic compounds which may have properties similar to rubber and some additional desirable properties.
  - Most of these polymers are derived from butadiene derivatives. For example, neoprene, Buna-S, Buna-N, thiokol, polyurethane rubber etc.
  - **Neoprene or polychloroprene :** Prepared by free radical polymerisation in presence of O_2 or peroxides. It has greater stability to aerial oxidation and it is resistant to action of vegetables or mineral oils.
  - **Buna-S :** Prepared by free radical copolymerisation of 1, 3-butadiene and styrene. It is very tough, possesses high abrasion resistance, high load bearing capacity.
  - **Buna-N :** Prepared by copolymerisation of 1, 3-butadiene and acrylonitrile in the presence of a peroxide catalyst.
  - **Thiokol :** Prepared by copolymerisation of ethylenedichloride with sodium tetrasulphide in presence of magnesium hydroxide.
- **Vulcanization of rubber :** It is a process of treating natural rubber with sulphur and an appropriate additive at a temperature range of 373 to 415 K, to modify its properties.
  - On vulcanization sulphur forms cross-links at the reactive sites of the double bonds and gives mechanical strength to the rubber.
  - The extent of hardness or toughness, however, depends upon the amount of sulphur added. Thus, about 5% sulphur is used for making tyre rubber, 20-25% sulphur for making ebonite and 30% sulphur for making battery case rubber.

Biodegradable Polymers

- Biopolymers disintegrate by enzymatic hydrolysis and to some extent by oxidation and hence are biodegradable.
- Synthetic polymers are non-biodegradable and hence create disposal problem. To overcome this, biodegradable synthetic polymers have been developed.
- **Poly-β-hydroxybutyrate-co-β-hydroxyvalerate (PHBV) :** It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid connected with ester linkages.
  - Used in speciality packaging, orthopaedic devices and in controlled drug release.
- **Dextron :** A copolymer of glycollic acid and lactic acid (90 : 10) was the first biodegradable polyester used for stitching of wounds.
- **Nylon-2-Nylon-6 :** It is a step-growth polyamide copolymer of glycine and ∈-amino caproic acid.



Nylon-2-Nylon-6

Molecular Mass of Polymers

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

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

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

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

$$\bar{M}_n = \frac{\text{Total weight of the molecules}}{\text{Total number of molecules}}$$

$$\bar{M}_n = \frac{n_1M_1 + n_2M_2 + n_3M_3 + ...}{n_1 + n_2 + n_3 + ...}$$

$$\bar{M}_n = \frac{\Sigma n_i M_i}{\Sigma n_i}$$

$\bar{M}_n$ is generally determined by osmotic pressure method.

(b) Weight average molecular weight ($\bar{M}_w$)

$$\bar{M}_w = \frac{w_1M_1 + w_2M_2 + w_3M_3 + ...}{w_1 + w_2 + w_3 + ...}$$

[weight (w) = no. of moles (n) × molecular weight (M)]

$\bar{M}_w$ is generally determined by the light scattering method.

PDI (Polydispersity Index)

The ratio of the $\bar{M}_w$ and $\bar{M}_n$ is called PDI

$$\text{PDI} = \frac{\bar{M}_w}{\bar{M}_n}$$

In natural polymers, which are generally mono-dispersed, the P.D.I. is unity ($\bar{M}_w = \bar{M}_n$).
In synthetic polymers, which are poly-dispersed, P.D.I. is greater than unity because $\bar{M}_w$ is always higher than $\bar{M}_n$.

Peep Into Previous Years

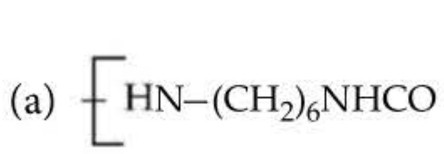
3. The biodegradable polymer is
(a) buna-S (b) nylon-6,6
(c) nylon-2-nylon 6 (d) nylon-6.

(NEET 2019)

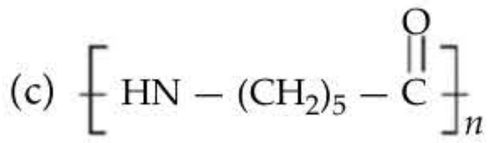
4. Choose the correct option(s) from the following
(a) Teflon is prepared by heating tetrafluoroethene in presence of a persulphate catalyst at high pressure.
(b) Natural rubber is polyisoprene containing *trans* alkene units.
(c) Nylon-6 has amide linkages.
(d) Cellulose has only α-*D*-glucose units that are joined by glycosidic linkages.

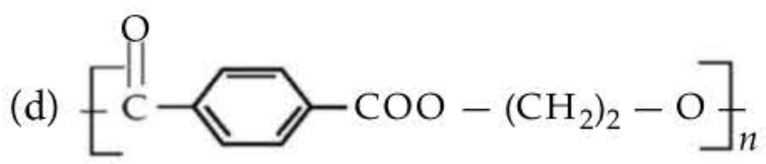
(JEE Advanced 2019)

5. Which of the following is a biodegradable polymer?

(a) 

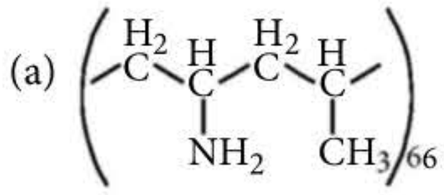
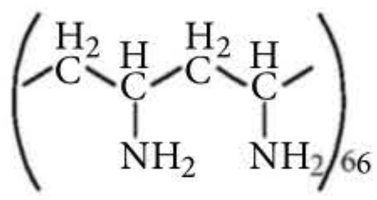
(b) 

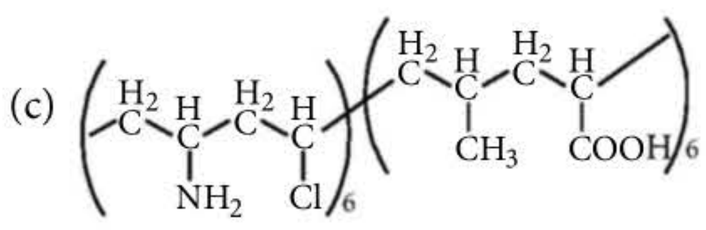
(c) 

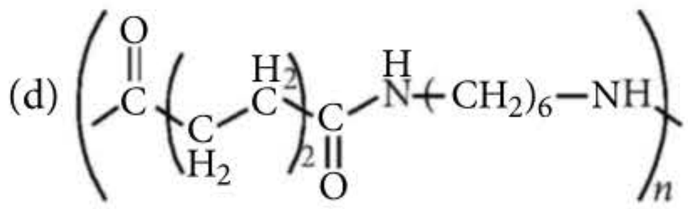
(d) 

(JEE Main Online 2017)

6. Which one of the following structures represents nylon 6, 6 polymer?

(a)  (b) 

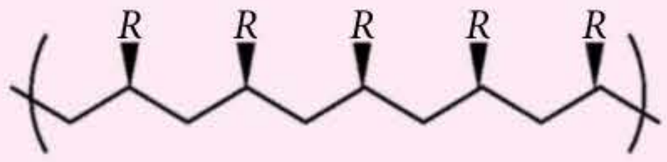
(c) 

(d) 

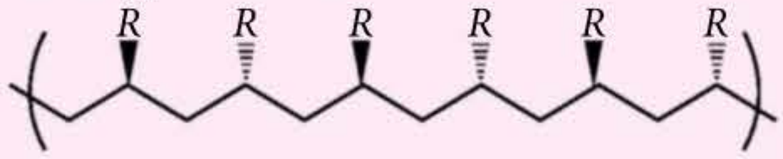
(NEET-II 2016)

Points For Extra Scoring

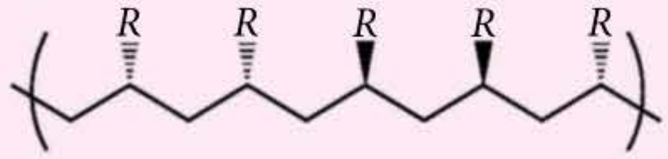
- **Coordination Polymerisation :** It is the process in which the polymerisation occurs through formation of coordination complex.
- **Isotactic** (meaning-same order) : In this type of arrangement all the methyl groups of propylene lie on the same side.



- **Syndiotactic** (meaning-alternating order) : In this case the methyl groups alternate regularly on the opposite side of chain.



- **Atactic** (meaning-no order) : In this type of arrangement no particular order is followed.



- **Polyurethanes**. These are the condensation polymers of toluene-2, 4-diisocyanate and ethylene glycol.
- **Ebonite :** It is a highly vulcanised rubber having about 20–30% of sulphur.
- **Kevlar :** It is a polyamide obtained by condensation copolymerisation and used in making light weight bullet-proof vests.
- **Nomex :** A condensation polyamide used in protective clothing for fire resistance.
- **Lexan :** A condensation copolymerisation polycarbonate (polyester) with unusually high impact strength, used for making bullet proof windows and safety helmets.
- **Rayon (artificial silk) :** It is chemically similar to cotton but shines like silk. Artificial silk is a polysaccharide while natural silk is a protein (polyamide).