

# POLYMERS

## CHAPTER 15

### INTRODUCTION

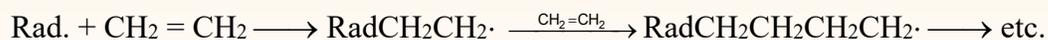
Polymers can be called as macromolecules. Macromolecules can be considered as an association of small molecules to give a big molecule. Macromolecules can be man-made, too. The first syntheses were aimed at making substitutes for the natural macromolecules, rubber and silk; but a vast technology has grown up that now produces hundreds of substances that have no natural counterparts. Synthetic macromolecular compounds include: **elastomers**, which have the particular kind of elasticity characteristic of rubber; **fibers**, long, thin and threadlike, with the great strength along the fiber that characterizes cotton, wool, and silk; and **plastics**, which can be extruded as sheets or pipes, painted on surfaces, or molded to form countless objects. We wear these manmade materials, eat and drink from them, sleep between them, sit and stand on them; turn knobs, pull switches, and grasp handles made of them; with their help we hear sounds and see sights remote from us in time and space; we live in houses and move about in vehicles that are increasingly made of them.

### **Polymers and polymerization**

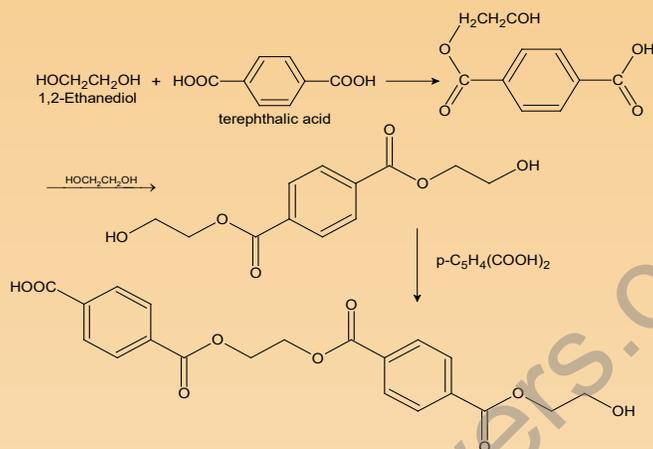
Macromolecules, both natural and man-made, owe their great size to the fact that they are polymers (Greek: many parts); that is, each one is made up of a great many simpler units — identical to each other or at least chemically similar — joined together in a regular way. They are formed by a process we touched on earlier: **polymerization**, the joining together of many small molecules to form very large molecules. The simple compounds from which polymers are made are called monomers.

Polymers are formed in two general ways.

(a) **In chain-reaction polymerization**, there is a series of reactions each of which consumes a reactive particle and produces another, similar particle; each individual reaction thus depends upon the previous one. The reactive particles can be free radicals, cations, or anions. A typical example is the polymerization of ethylene. Here the chain-carrying particles are free radicals, each of which adds to a monomer molecule to form a new, bigger free radical.

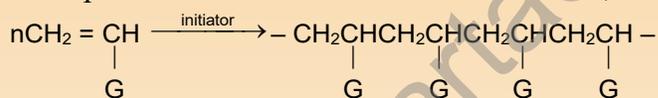


**(b) In step reaction polymerization**, there is a series of reactions each of which is essentially independent of the preceding one; a polymer is formed simply because the monomer happens to undergo reaction at more than one functional group. A diol, for example, reacts with a dicarboxylic acid to form an ester; but each moiety of the simple ester still contains a group that can react to generate another ester linkage and hence a larger molecule, which itself can react further, and so on.

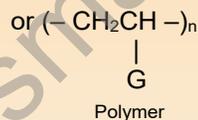


Terylene or Dacron

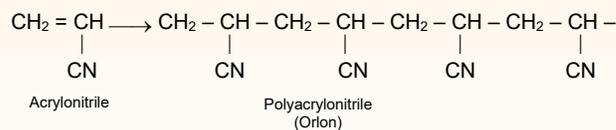
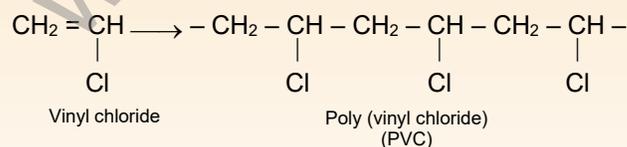
**(c) Free-radical vinyl polymerization:** In we discussed briefly the polymerization of ethylene and substituted ethylenes under conditions where free radicals are generated — typically in the presence of small amounts of an initiator, such as a peroxide.

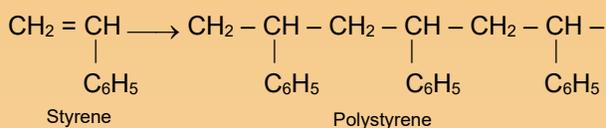


Vinyl monomer

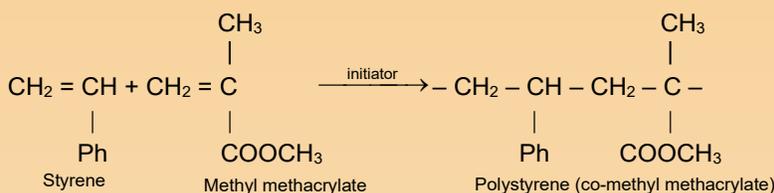


Reaction occurs at the doubly bonded carbons — the vinyl groups — and is called *vinyl polymerization*. A wide variety of unsaturated monomers may be used, to yield polymers with different *pendant groups* (G) attached to the polymer backbone. For example.





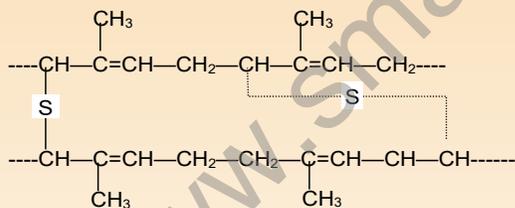
(d) Copolymerization: So far, we have discussed only polymerization of a single monomeric compound to form a *homopolymer*, a polymer made up — except, of course, at the two ends of the long molecule — of identical units. Now, if a mixture of two (or more) monomers is allowed to undergo polymerization, there is obtained a copolymer a polymer that contains two (or more) kinds of monomeric units in the same molecule. For example:



### Some Important Polymers:

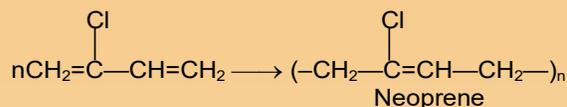
(a) **Natural Rubber:** Natural rubber is an addition polymer of isoprene (2-methyl-1,3-butadiene). Rubber has an average chain length of 5000 monomer units of isoprene.

The rubber in which the arrangement of carbon chain is trans with respect to the double bond is known as *Gutta Percha* and this is the natural rubber obtained from bark of various trees. Natural rubber is sticky material. This disadvantage is removed by 'VULCANISATION' which involves addition of Sulphur to rubber and heating the mixture. Sulphur forms short chains of Sulphur atoms that link two hydrocarbon (isoprene) units together.



When tension is applied the chains can strengthen out but they cannot slip over each other because of Sulphur bridges. Thus, rubber can be stretched only to a certain extent and hydrocarbon chains have the tendency to regain their shape when tension is removed. Vulcanized rubber is thus stronger and less sticky than the natural rubber.

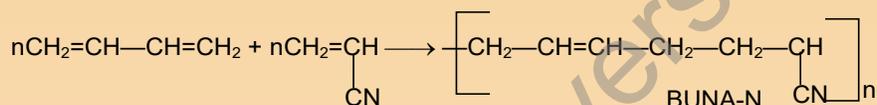
(b) **Synthetic rubber:** (Polychloroprene) or Neoprene) It is obtained by free radical polymerization of chloroprene in



It is a thermoplastic and need not to be vulcanised. It is a good general-purpose rubber and superior to natural rubber as it is resistant to the reaction of air, heat, light chemicals, alkalis and acids below 50% strength. It is used for making transmission belts, printing rolls and flexible tubing employed for conveyance of oil and petrol.

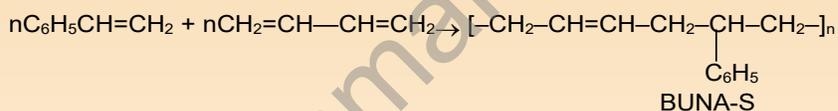
(c) **Buna rubbers:** Butadiene polymerases in the presence of sodium to give a rubber substitute viz. BuNa. It is of two types

(i) Buna - N or GRA: it is synthetic rubber obtained by copolymerization of one part of acryl nitrile and two parts of butadiene.



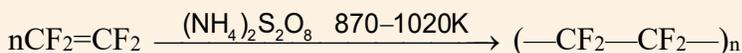
It is more rigid responds less to heat and very resistant to swelling action of petrol, oils and other organic solvents.

(ii) Buna -S or GRS (General purpose Styrene rubber): It is a copolymer of three moles of butadiene and one mole of styrene and is an elastomer. It is obtained as a result of free radical copolymerisation of its monomers.



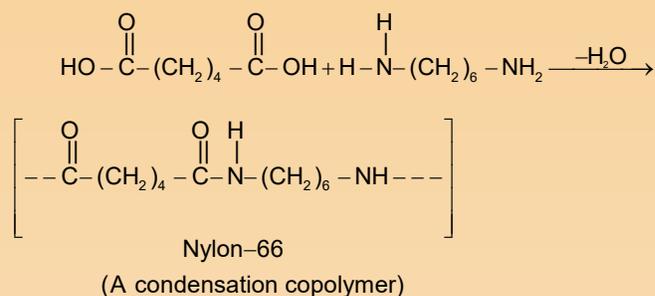
It is generally compounded with carbon black and vulcanised with Sulphur. It is extremely resistant to wear and tear and finds use in manufacture of tires and other mechanical rubber goods.

(d) **Teflon:** It is polymer of tetrafluoroethylene ( $\text{F}_2\text{C}=\text{CF}_2$ ) which on polymerization gives Telfon.



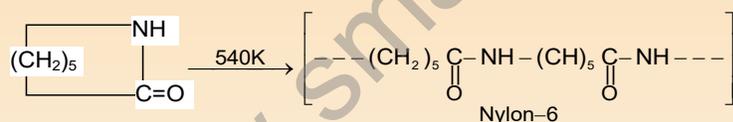
It is thermoplastic polymer with a high softening point (600K). It is very tough and difficult to work. It is inert to most chemicals except fluorine and molten alkali metals. It withstands high temperatures. Its electrical properties make it an ideal insulating material for high frequency installation.

- (e) **Nylon-66:** It is a polymer resin. It is a condensation polymer formed by reaction between adipic acid and hexamethylene diamine. Both monomer units consist of 6 carbon atoms and therefore named nylon -66.



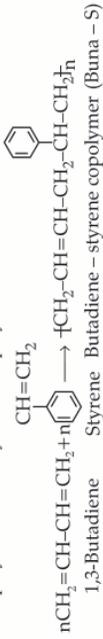
It is thermoplastic polymer when extruded above its melting point (536 K) through spinneret, it gives nylon fiber which is extremely tough and resistant to friction. It possesses greater tensile strength, elasticity and luster than any natural fiber. It is chemically inert and is fabricated into sheet, bristles and textile fibers.

- (f) **Nylon 6 or Parolin - L:** A polyamide is prepared by prolonged heating of caprolactam at 530 - 540 K.



The fiber is practically identical to Nylon in properties

The polymers made by addition polymerisation from two different monomers are known as copolymers.

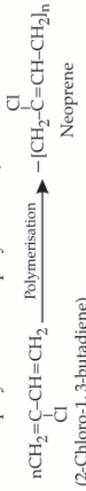


**Types:**

(i) **Natural rubber:** obtained from rubber latex.

It is a polymer of isoprene.

(ii) **Synthetic rubber:** Any vulcanizable rubber. These are homopolymers and copolymer of 1,3 butadiene derivatives.



• Expressed as an average.

• Determined by chemical and physical methods.

Contain functional groups similar to biopolymers (PHBV, Nylon 2– nylon 6)

Those polymers which do not degrade in environment and accumulate in the form of waste, e.g., polystyrene, polystyrene, etc. They consist of long chains of carbon and hydrogen atoms joined by strong interatomic bonding making it hard for microbes to break the bonds and digest them.

**Copolymerization:** A mixture of more than one monomeric species undergoes polymerization

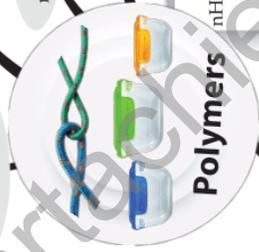
Rubber

Molecular mass of polymers

Biodegradable polymers

Non-Biodegradable polymers

Very large molecules having high molecular mass



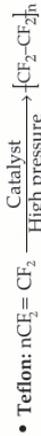
## Polymers

Preparation

• **Polyethene**

Low density : Polymerization of ethene under 1000–2000 atm at 350–570 K + catalyst

High density : Addition polymerization of ethene in a hydrocarbon solvent at 333–343 K and 6–7 atm + catalyst.



(i) **Natural polymers:** Found in plants and animals. (Proteins, rubber)

(ii) **Semi-synthetic polymers:** (Cellulose derivatives)

(iii) **Synthetic polymers:** Man-made. (Polythene, Buna –S)

Classification Based on origin

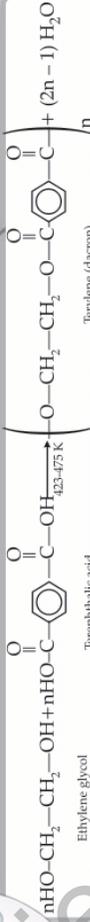
Initial Step of free radical polymerization

Polyesters

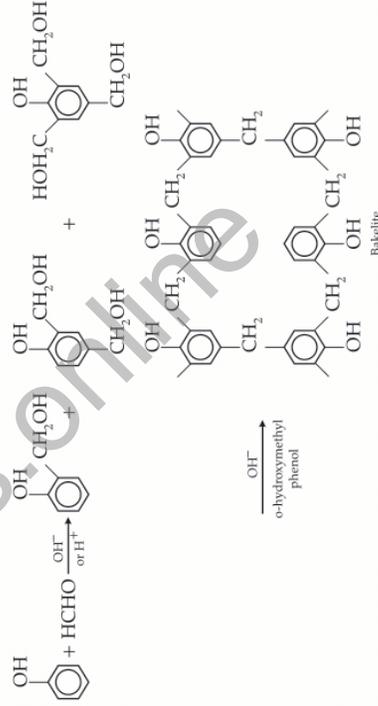
Polymers having large number of ester linkages



Examples



• **Phenol-formaldehyde resin (Bakelite):** It is heat resistant thermosetting plastic.



## PRACTICE QUESTIONS

- What is the molecular mass range of the polymer?  
(a)  $10^{10} - 10^{15}u$  (b)  $10^3 - 10^7u$   
(c)  $10^6 - 10^{18}u$  (d)  $10^1 - 10^3u$
- To which polymer category do cellulose derivatives belong?  
(a) Synthetic polymers (b) Semi-synthetic polymers  
(c) Natural polymers (d) Branched polymers
- What type of polymer is Buna-S?  
(a) Natural polymer (b) Synthetic polymer  
(c) Semi-synthetic polymer (d) None of the above
- Is PVC a:  
(a) Linear polymer (b) Branched polymer  
(c) Cross-linked polymer (d) None of the above
- What does HDP stand for?  
(a) High density polyethylene (b) High density polythene  
(c) High density polypropene (d) High density polypropylene
- What is the term for polymers that contain linear chains with some branches?  
(a) Network polymers (b) Branched polymers  
(c) Linear polymers (d) Cross-linked polymers
- Which of the following is an example of a network polymer?  
(a) HDP (b) Bakelite (c) LDP (d) Polyvinyl chloride

8. Buna-S is a copolymer of:

- (a) Ethene and styrene
- (b) 1,3-butadiene and ethene
- (c) 1,3-butadiene and styrene
- (d) Ethene and propene

9. What are rubber-like solids with elastic properties called?

- (a) Elastomers
- (b) Fibers
- (c) Thermosetting polymers
- (d) Thermoplastic polymers

10. Which polymer contains strong intermolecular forces, such as hydrogen bonding?

- (a) Polystyrene
- (b) Nylon-6,6
- (c) Teflon
- (d) Natural rubber

11. What is the repeated addition of the same monomer molecules with double or triple bonds known as?

- (a) Copolymer
- (b) Elastomer
- (c) Homopolymer
- (d) Fiber

12. How is low-density polythene obtained?

- (a) Electrophilic addition
- (b) Free radical addition
- (c) Nucleophilic addition
- (d) Nucleophilic substitution

13. Why is LDP used in the insulation of electricity wires and manufacture of flexible pipes?

- (a) It is chemically inert.
- (b) It is tough and flexible.
- (c) It is a poor conductor of electricity.
- (d) All of the above

14. What type of polythene is chemically inert, tough, and hard?

- (a) HDP
- (b) LDP
- (c) Both (a) and (b)
- (d) None of these

15. What is the commercial name of polyacrylonitrile?

- (a) Orlon (acrilan)
- (b) Dacron
- (c) Bakelite
- (d) Melamine

16. Nylon belongs to which polymer category?

- (a) Polyester
- (b) Polysaccharide
- (c) Polyamide
- (d) Polythene

17. What type of polymer is represented by the given chemical formula?



- (a) Homopolymer
- (b) Condensation polymer
- (c) Addition polymer
- (d) Thermosetting polymer

18. What are the monomers of dacron a polyester?

- (a) Ethylene glycol
- (b) Terephthalic acid
- (c) Caprolactam
- (d) Both (a) and (b)

19. How is bakelite prepared?

- (a) Electrophilic addition and dehydration
- (b) Condensation and elimination
- (c) Nucleophilic addition and dehydration
- (d) Electrophilic substitution and dehydration

20. Which of the following polymers is phenol formaldehyde resin?

- (a) Teflon
- (b) Bakelite
- (c) Melamine
- (d) Buna-N

21. In natural rubber, what do the cross-links introduced between the chains help with?

- (a) Make the rubber soft
- (b) Retract to the original position after the force is released
- (c) Make the rubber hard
- (d) None of the above

22. What is the monomer of neoprene?

- (a)  $\text{CH}_2=\text{CHC}(\text{CH}_3)=\text{CH}_2$
- (b)  $\text{CH}_2=\text{CHCH}_2\text{CH}_2=\text{CH}_2$
- (c)  $\text{CH}_2=\text{CClCH}_2\text{CH}_2=\text{CH}_2$
- (d)  $\text{CH}_2=\text{CHCH}=\text{CHCH}_2\text{CH}_2$

23. Which polymer has chiral monomers?

- (a) PHBV
- (b) Buna-N
- (c) Nylon-6,6
- (d) Neoprene

24. Which biodegradable polymer can be produced from glycine and amino caproic acid?

- (a) Nylon-2-nylon-6
- (b) PHBV
- (c) Buna-N
- (d) Nylon-6,6



31. Polymer obtained by condensation polymerization is

- (A) Polythene (B) Teflon  
(C) Phenol - formaldehyde (D) Nitrile rubber

32. Which is an example of thermosetting polymer?

- (A) Polythene (B) PVC  
(C) Neoprene (D) Bakelite

33. The catalyst used in the manufacture of polyethylene by Ziegler method is

- (A) Titanium tetrachloride and triphenyl aluminum  
(B) Titanium tetrachloride and triethylaluminium  
(C) Titanium dioxide  
(D) Titanium isopropoxide

34.  $\text{Fructose} + n\text{Pb}(\text{CH}_3\text{COO})_4 \xrightarrow{\Delta} \text{Products}$   
(1 mole)

The value of 'n' in the above reaction is

- (A) 2 (B) 4  
(C) 5 (D) 6

35. Ebonite is

- (A) natural rubber (B) Synthetic rubber  
(C) Highly vulcanized rubber (D) Polypropene

36. Which of the following polymers do not involve cross linkages?

- (A) Meimac (B) Bakelite  
(C) Polyethene (D) Vulcanized rubber

37. Polymer which has amide linkage is

- (A) Nylon - 66 (B) Terylene  
(C) Teflon (D) Bakelite

38. Glyptal polymer is obtained from glycerol by reacting with

- (A) Malonic acid (B) Phthalic acid  
(C) Maleic acid (D) Acetic acid

39. Capri lactic acid is a monomer of

- (A) Nylon - 6 (B) Nylon - 66  
(C) Dacron (D) Neoprene

40. Terylene is condensation polymer of ethylene glycol and

- (A) Benzoic acid (B) Phthalic acid  
(C) Salicylic acid (D) Terephthalic acid

41. Teflon, polystyrene and neoprene are all

- (A) Copolymers (B) Condensation polymers  
(C) Homopolymers (D) Monomers

42. The catalyst used for the polymerization of olefins is

- (A) Ziegler- Natta catalyst (B) Wilkinson's catalyst  
(C) Pd- catalyst (D) Zeise's salt complex  
(E) Zeolite

43. The monomer of Teflon is

- (A) ethane (B) difluoro, dichloromethane  
(C) tetrachloroethene (D) tetrafluoroethylene

44. Which of the following is a polyamide molecule?

- (A) Terylene (B) Rayon  
(C) Nylon -6 (D) Polystyrene

45. Which of the following is/are acrylic acid polymers?

- (B) PMMA (B) PMAA  
(C) PEAA (D) all of these

### HINTS ANS SOLUTIONS

1. Answer: (c)  $10^6 - 10^{18} u$

Explanation: The molecular mass of polymers typically falls within the range of)  $10^6$  to  $10^{18}$  atomic mass units (u), which includes a wide variety of polymer sizes.

2. Answer: (b) Semi-synthetic polymers

Explanation: Cellulose derivatives are derived from natural cellulose but undergo chemical modifications to create new materials. Hence, they belong to the category of semi-synthetic polymers.

3. Answer: (b) Synthetic polymer

Explanation: Buna-S is a synthetic polymer, specifically a copolymer of 1,3-butadiene and styrene.

4. Answer: (a) Linear polymer

Explanation: PVC (Polyvinyl chloride) is primarily a linear polymer with occasional branching, making it predominantly a linear polymer.

5. Answer: (d) High density polypropylene

Explanation: HDP stands for High-Density Polypropylene.

6. Answer: (b) Branched polymers

Explanation: Polymers containing linear chains with some branches are referred to as branched polymers.

7. Answer: (b) Bakelite

Explanation: Bakelite is an example of a network polymer.

8. Answer: (c) 1,3-butadiene and styrene

Explanation: Buna-S is a copolymer of 1,3-butadiene and styrene.

9. Answer: (a) Elastomers

Explanation: Rubber-like solids with elastic properties are called elastomers.

10. Answer: (b) Nylon-6,6

Explanation: Nylon-6,6 exhibits strong intermolecular forces, including hydrogen bonding.

11. Answer: (c) Homopolymer

Explanation: The repeated addition of the same monomer molecules with double or triple bonds is known as a homopolymer.

12. Answer: (b) Free radical addition

Explanation: Low-density polyethylene (LDPE) is obtained through free radical addition polymerization.

13. Answer: (b) It is tough and flexible.

Explanation: LDPE is used in the insulation of electricity wires and the manufacture of flexible pipes because it is tough and flexible.

14. Answer: (a) HDP

Explanation: High-Density Polyethylene (HDP) is chemically inert, tough, and hard.

15. Answer: (a) Orlon (acrilan)

Explanation: The commercial name of polyacrylonitrile is Orlon or Acrilan.

16. Answer: (c) Polyamide

Explanation: Nylon is an example of a polyamide.

17. Answer: (b) Condensation polymers

Explanation: The given chemical formula represents a condensation polymer.

18. Answer: (d) Both (a) and (b)

Explanation: Dacron is a polyester, and its monomers include ethylene glycol and terephthalic acid.

19. Answer: (b) Condensation and elimination

Explanation: Bakelite is prepared through condensation and elimination reactions.

20. Answer: (b) Bakelite

Explanation: Phenol formaldehyde resin is commonly known as Bakelite.

21. Answer: (b) Retract to the original position after the force is released

Explanation: Cross-links in natural rubber help it return to its original shape after deformation.

22. Answer: (c)  $\text{CH}_2=\text{CClCH}_2\text{CH}_2=\text{CH}_2$

Explanation: The monomer of neoprene is chloroprene, which has the chemical formula  $\text{CH}_2=\text{CClCH}_2\text{CH}_2=\text{CH}_2$ .

23. Answer: (a) PHBV

Explanation: PHBV (Polyhydroxybutyrate-co-hydroxyvalerate) has chiral monomers.

24. Answer: (b) PHBV

Explanation: PHBV is a biodegradable polymer that can be produced from glycine and amino caproic acid.

25. Answer: (a) Bakelite

Explanation: Bakelite is commonly used for making combs, electrical switches, handles of utensils, and computer discs.

26. Answer: (A) PVC and (C) Teflon

Explanation: PVC (Polyvinyl chloride) and Teflon (Polytetrafluoroethylene) are both addition polymers. They are formed by the addition of monomer units without the elimination of any small molecules.

27. Answer: (C) Adipic acid and hexamethylene diamine

Explanation: Nylon-6,6 is formed by heating adipic acid and hexamethylene diamine through a condensation polymerization process.

28. Answer: (C) Ethylene glycol and terephthalic acid

Explanation: Terylene (Dacron) is a condensation polymer formed from the reaction of ethylene glycol and terephthalic acid.

29. Answer: (B) Addition polymer

Explanation: Polystyrene is an addition polymer, as it is formed by the polymerization of styrene monomers without eliminating any small molecules.

30. Answer: (B) Elastomer

Explanation: Elastomers have the strongest intermolecular forces among the given options. They are known for their elasticity and flexibility.

31. Answer: (C) Phenol-formaldehyde

Explanation: Phenol-formaldehyde is obtained by condensation polymerization.

32. Answer: (D) Bakelite

Explanation: Bakelite is an example of a thermosetting polymer. It undergoes irreversible cross-linking when heated, forming a hard and rigid structure.

33. Answer: (B) Titanium tetrachloride and triethylaluminium

Explanation: The Ziegler-Natta catalyst used in the manufacture of polyethylene consists of titanium tetrachloride and triethylaluminium.

34. Answer: (C) 5

Explanation: In the given reaction, the value of 'n' is 5.

35. Answer: (C) Highly vulcanized rubber

Explanation: Ebonite is a type of rubber that has undergone extensive vulcanization, making it highly resistant to electrical conductivity and chemical corrosion.

36. Answer: (C) Polyethylene

Explanation: Polyethylene (polyethene) does not involve cross-linkages and is a linear polymer.

37. Answer: (A) Nylon-66

Explanation: Nylon-66 is a polyamide polymer and contains amide linkages.

38. Answer: (B) Phthalic acid

Explanation: Glyptal polymer is obtained from glycerol by reacting it with phthalic acid.

39. Answer: (A) Nylon-6

Explanation: Caprolactic acid is a monomer of Nylon-6.

40. Answer: (D) Terephthalic acid

Explanation: Terylene is a condensation polymer of ethylene glycol and terephthalic acid.

41. Answer: (C) Homopolymers

Explanation: Teflon, polystyrene, and neoprene are all homopolymers, meaning they are composed of a single type of monomer.

42. Answer: (A) Ziegler-Natta catalyst

Explanation: The catalyst used for the polymerization of olefins is typically the Ziegler-Natta catalyst.

43. Answer: (D) Tetrafluoroethylene

Explanation: The monomer of Teflon is tetrafluoroethylene.

44. Answer: (C) Nylon-6

Explanation: Nylon-6 is a polyamide molecule.

45. Answer: (A) PMMA and (B) PMAA

Explanation: PMMA (Poly (methyl methacrylate)) and PMAA (Poly (methacrylic acid)) are both acrylic acid polymers. They are derived from acrylic acid monomers.