

26

POLYMERS

Student Learning Outcomes

[C-12-D-98 to C-12-D-108]

- ⊙ Describe the chemical processes of addition and condensation polymerisation and the differences between them. Examples include.
 - Addition polymers such as poly(ethene) and poly(chloroethene), PVC.
 - Polyesters (from reaction of diol and dicarboxylic or dioyl acid and from hydroxylic acid.
 - Polyamides (from reactions of a diamine and a dicarboxylic acid or dioyl chloride of an amino-carboxylic acid or between amino acids).
- ⊙ Describe the condensation reaction of ammonia or an amine with acyl chloride at room temperature to give an amide.
- ⊙ Explain the chemical processes and properties of PVC and nylon and applications of these polymers in the industry.
- ⊙ Identify the polymer formed, the monomer present in a section of polymer, and classify them as one of the two polymers.
- ⊙ Deduce the repeating unit of a polymer obtained from a given monomer or pair of monomers and identify the monomers present in a given section of a polymer molecule.
- ⊙ Predict the type of polymerisation reaction for a given monomer or pair of monomers.
- ⊙ Recognize that polyesters and polyamide are biodegradable by acidic and alkaline hydrolysis.
- ⊙ Recognize that some polymers can be degraded by the action of light.
- ⊙ Recognize that poly(alkane) is chemically inert and can, therefore, be difficult to biodegrade.
- ⊙ Explain the challenges associated with the disposal of non-degradable polymers.
- ⊙ Outline the use of polymers to create artificial organs in biomedical science.

Polymers are very large molecules made by joining many small molecules called **monomers** through polymerisation.

Organic polymers are modern materials of great significance. They have made our lives easier, more efficient, and highly economical due to their superior properties and affordable costs. Polymers can be observed in our daily lives from shopping bags (poly(ethene)) and clothesline (poly(propene)) to plastic used in

bulletproof vests (Kevlar[®]) and aerospace applications as in **Figure 26.1**. The properties of polymers broadly vary depending on the type and number of monomers in the polymer, and the



Figure 26.1 a) A bulletproof vest made from Kevlar[®] b) poly(propene) rope





Figure 26.2 Various uses of PVC

26.1.2 Condensation Polymerisation

In condensation polymerisation, monomers join together, but each time a new bond forms, a small molecule is eliminated from the monomers. This small molecule is usually water can also be H_2O , HCl or CH_3OH , or NH_3 . Monomers must have at least two reactive functional groups (like $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$) that can react with each other. These groups are on different ends of the monomer(s). Small molecules are always produced as a side product. This typically happens in a "step-by-step" manner as depicted in Figure 26.3.

Condensation polymerisation

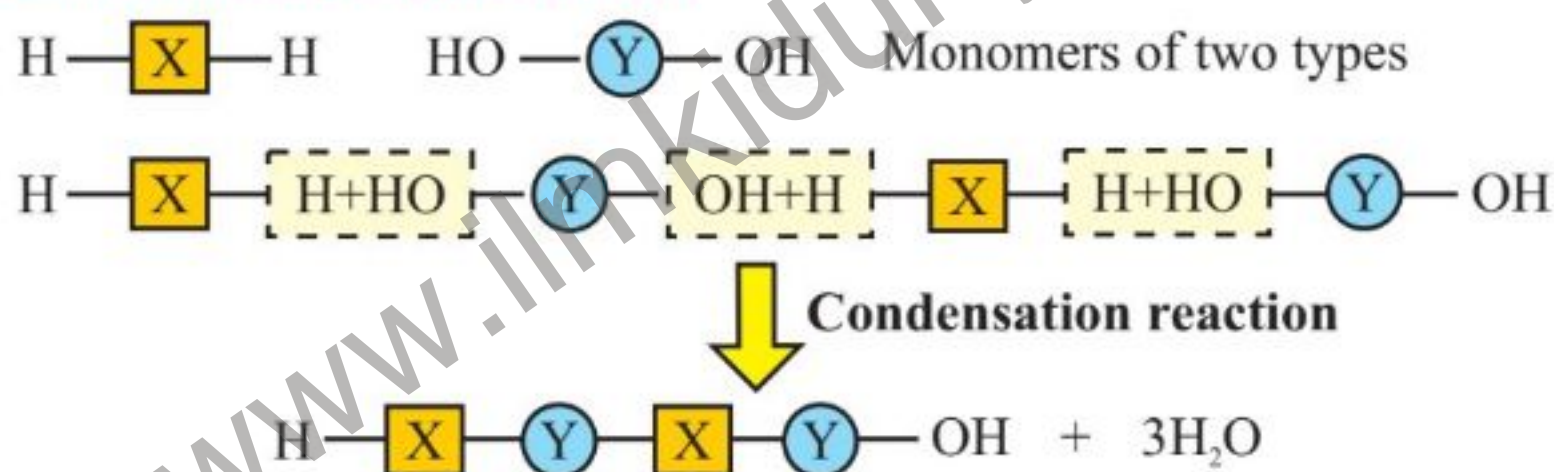
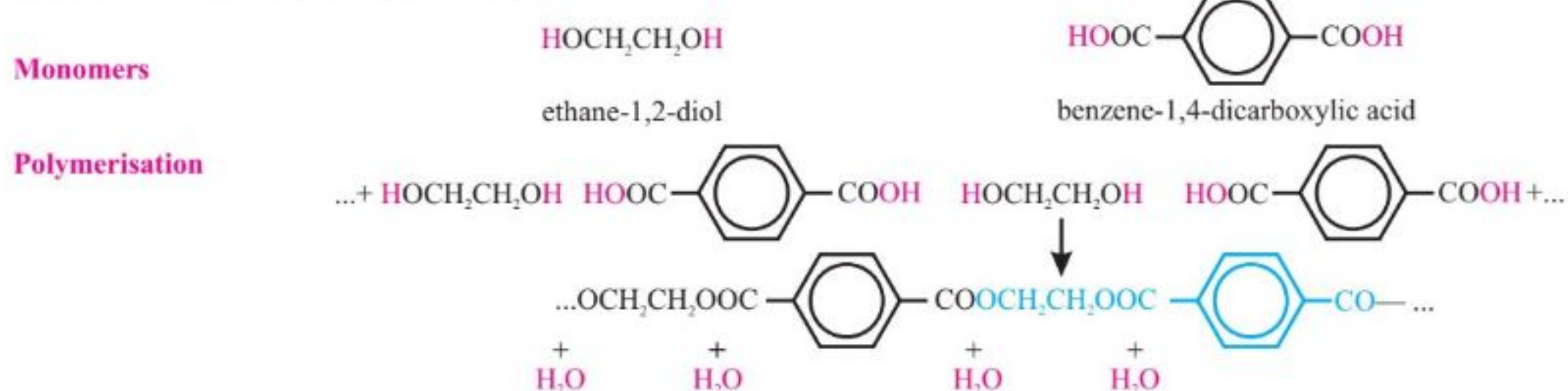


Figure 26.3 Illustration of condensation polymerisation

a) Polyesters

Polyesters have **ester links** $\left[-\overset{\text{O}}{\parallel}{\text{C}} - \text{O} - \right]$ in their backbone. A diol (molecule with two $-\text{OH}$ groups) and a dicarboxylic acid (molecule with two $-\text{COOH}$ groups) as monomers are combined to give polyester. The $-\text{OH}$ from the diol reacts with the $-\text{COOH}$ from the acid. A molecule of water is removed as shown below.



Preparation of Terylene/PET, a polyester from ethane-1,2-diol and Benzene-1,4-dicarboxylic acid.



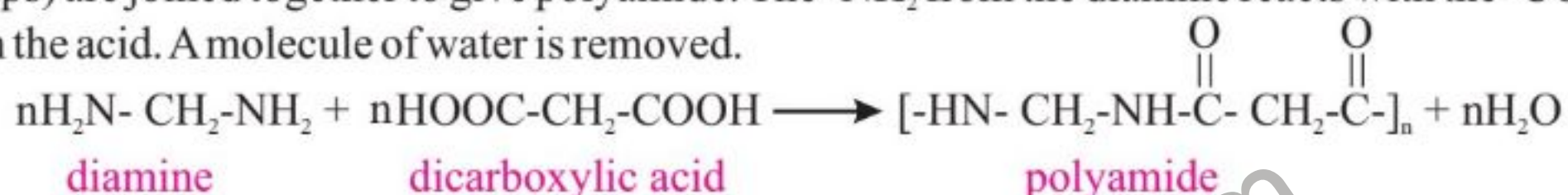
Polyesters have special features, such as high tensile strength, which make them suitable to manufacture fibres. Polyester is used as an alternative to cotton due to its low cost and ability to resist creases. It is also used as a plastic; for example, PETE is used in making plastic bottles for beverages and other food packaging. Polyester is also used as cross links to obtain hard plastics. An example is the glass fibre reinforced cross-linked polyester.

b) Polyamides

Polyamides have **amide links** $\left[-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}- \right]$ in their backbone. They can be prepared from many starting materials.

i) From a Diamine and a Dicarboxylic Acid:

A diamine (molecule with two $-\text{NH}_2$ groups) and a dicarboxylic acid (molecule with two $-\text{COOH}$ groups) are joined together to give polyamide. The $-\text{NH}_2$ from the diamine reacts with the $-\text{COOH}$ from the acid. A molecule of water is removed.



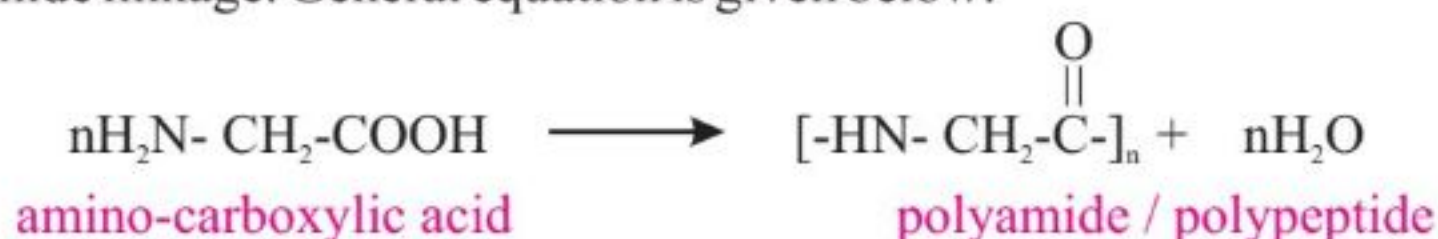
Example: Nylon 6,6 uses hexamethylenediamine and Adipic acid.

ii) From a Diamine and a Diacyl Chloride

A diamine and a diacyl chloride (molecule with two $-\text{COCl}$ groups) as monomers are joined to give polyamide. Diacyl chlorides are more reactive than dicarboxylic acids. The $-\text{NH}_2$ from the diamine reacts with the $-\text{COCl}$ from the diacyl chloride. A molecule of hydrogen chloride (HCl) is removed. General equation is given below:

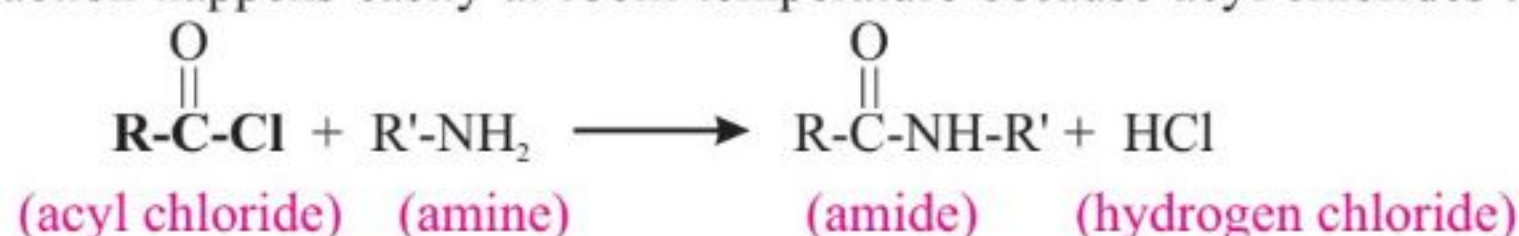


An amino acid is a single monomer that has both an $-\text{NH}_2$ (amino) group and a $-\text{COOH}$ (carboxylic acid) group in one molecule. The $-\text{NH}_2$ group of one amino acid reacts with the $-\text{COOH}$ group of another amino acid removing a water to form a peptide bond. Peptide bond is also a type of amide linkage. General equation is given below:



Proteins are natural polyamides made from amino acids, which will be discussed in Biochemistry (Chapter 27).

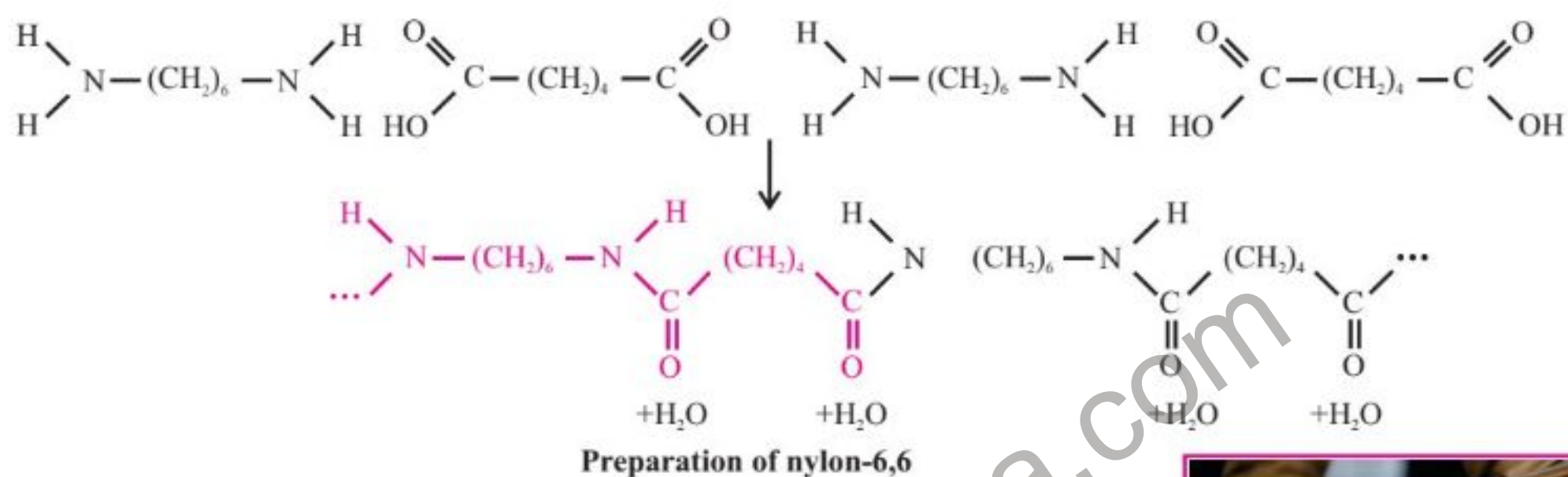
Amide linkage is also formed between acyl chlorides, a very reactive organic compound and an amine, e.g. ammonia, methanamine (CH_3-NH_2), N, N-dimethylamine, $(\text{CH}_3)_2\text{NH}$. When an acyl chloride reacts with ammonia or an amine, a molecule of hydrogen chloride (HCl) gas is removed. This reaction happens easily at room temperature because acyl chlorides are fairly reactive.



26.2 NYLON

Nylon is a type of synthetic polyamide. It is formed by condensation polymerisation, usually from two different monomers (a diamine and a dicarboxylic acid). During the reaction, a small molecule, typically water, is removed. Generally, a diamine ($\text{H}_2\text{N-R-NH}_2$) and a dicarboxylic acid (HOOC-R-COOH) act as monomers.

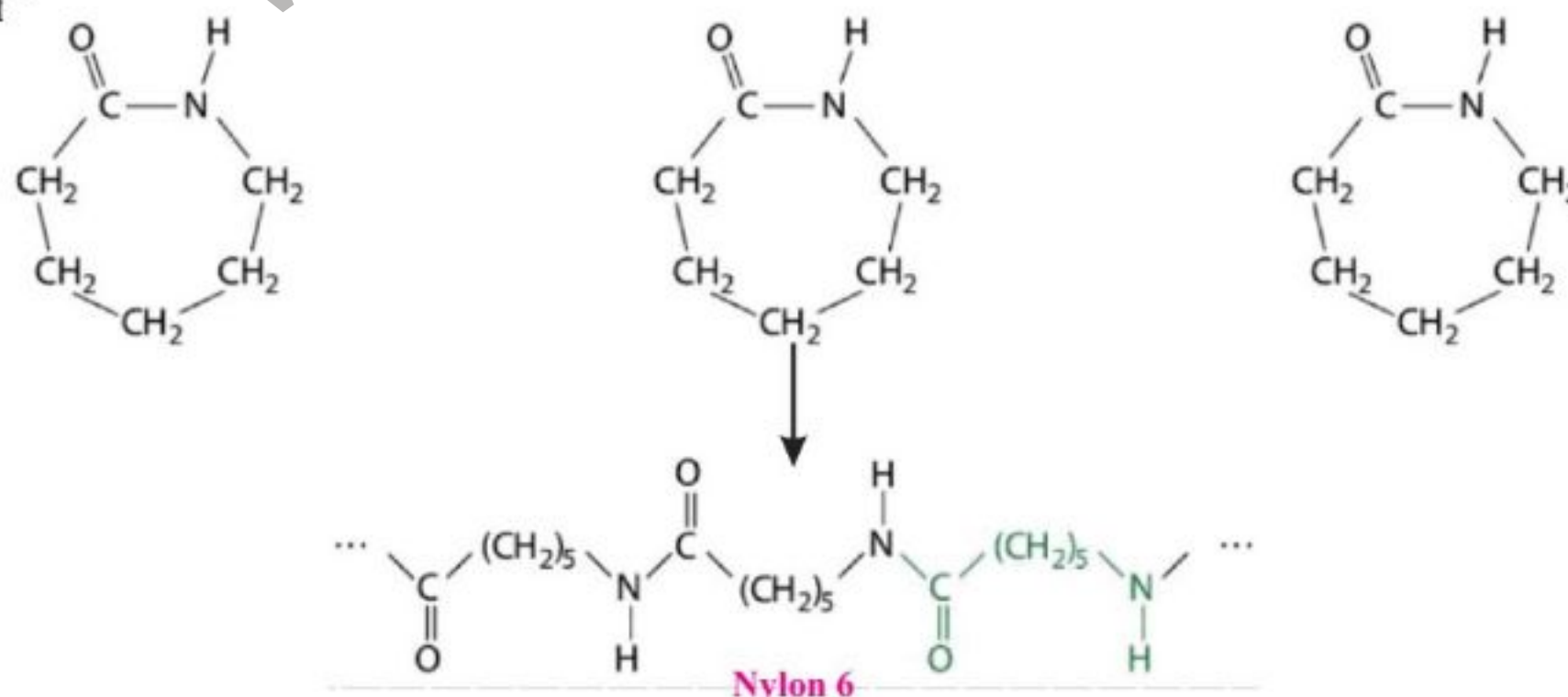
Nylon 6,6 is the most common example of synthetic amides. The formation of Nylon 6,6 involves a polymerisation reaction between 1,6-diaminohexane and 1,4-hexanedioic acid as shown below.



The wheels of this skateboard are made from nylon, due to its hard, smooth, and shock-free nature.



Another type of nylon is nylon-6, which is formed from a single monomer called caprolactam as in the following scheme. It is named nylon-6 because it involves a monomer with six carbon atoms. Caprolactam has a cyclic structure as shown in the following figure. The reaction is not a typical condensation reaction because no small molecule is removed during the reaction. Nevertheless, nylon 6 is classified as a condensation polymer due to the mode of formation of the amide link.

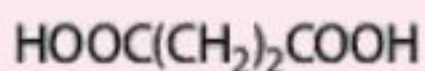
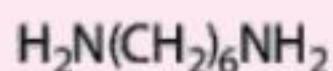
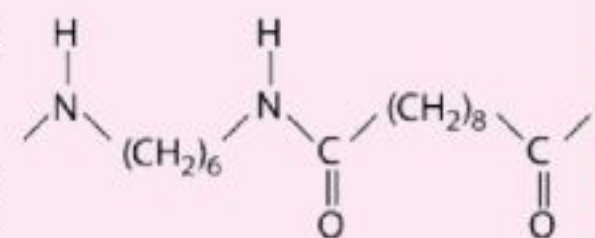


Nylon 6 is a harder material than nylon-6,6 and provides a smoother surface and higher impact resistance (harder to break by hitting). It is easier to mold as its melting point is lower than nylon-6,6. It is mostly used in rollers, skateboard wheels, and power tool handles to avoid shocks.




Quick Check 26.1


- a) The repeating unit of nylon-6, 10 is shown below. Draw the structures of its monomers from this structure.
- b) Monomers of nylon-6,4 are given below. Draw the structure of the repeating unit of the polymer formed from these monomers.



26.2.1 Properties of Nylon

- ✔ Strong and resistant to breaking and can withstand rubbing and wear and tear.
- ✔ Stretchable due to elasticity.
- ✔ Slippery surface, reduces friction.
- ✔ Generally resistant to oils, many solvents, and alkalis.
- ✔ High melting point.

26.2.2 Industrial Applications of Nylon

- ✔ It is used for clothing (stockings, activewear, and swimwear), carpets, and ropes due to its strength and elasticity. Its fabric is used for raincoats, sportswear, and lingerie.
- ✔ Nylon is used for the manufacturing of mechanical parts of automotive industry like gears, bearings, bushings, engine covers, and fuel lines due to its strength, low friction, and heat resistance.
- ✔ Nylon is also used in making of machine parts such as screws, nuts, bolts, and various industrial components where strength and wear resistance are needed.
- ✔ It is also commonly used to make ropes, fishing nets, and lines due to its high tensile strength and resistance to water wear.
- ✔ Consumer goods like zippers, toothbrushes, hairbrushes, and various molded plastic parts are made of nylon.



Figure 26.4 General uses of different types of nylon



26.3 IDENTIFICATION OF THE TYPE OF A POLYMER, REPEAT UNIT AND MONOMERS FROM A POLYMER SECTION

To identify a polymer from a skeletal or structural formula, you must look for the repeating linkage and the monomer units. At this level, only two classes of polymers are under discussion

i. Addition

ii. Condensation.

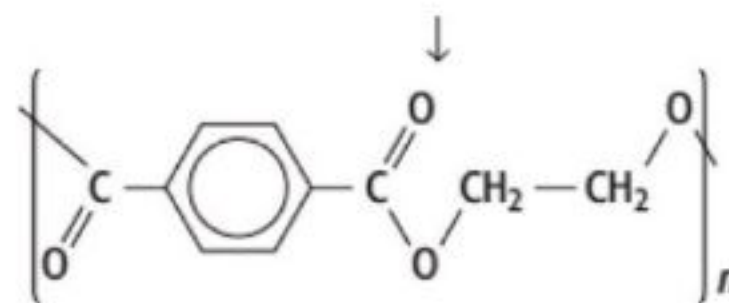
Follow the given steps to identify the type of the polymer by considering the example of poly(ethene)

1. Identifying the Type of Polymer:

- The first thing to check is what atoms make up the main horizontal chain of the polymer, i.e to identify the backbone. .
- If the main chain consists only of carbon atoms (-C-C-C-C-), it is an addition polymer. These are formed from alkenes.
- If the main chain contains oxygen (O) or nitrogen (N) atoms with carbon, it is a condensation polymer (like polyesters or polyamides).

Now, identify the functional linkage. There are again two possibilities:

- If a carbonyl group (C=O) is directly attached next to an oxygen (O). Such polymers are classified as polyesters. For example, PET has an ester linkage in the given section of its structure.



If there is a carbonyl group (C=O) directly next to a nitrogen (N) with a hydrogen (H) attached, it presents an amide or peptide linkage. The polymer is, therefore, classified as a polyamide (e.g., Nylon 6,6 or Kevlar).

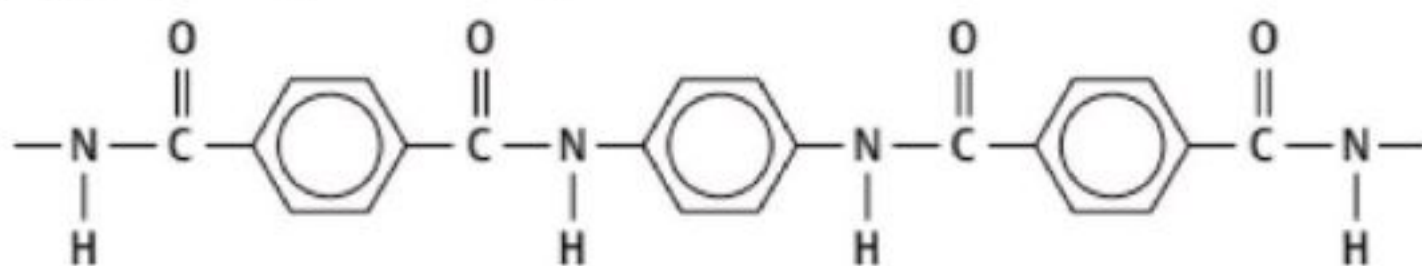


Table 26.1 Identification of the type of a polymer from its section

Functional Groups in the Polymer	Type	Example
Only C-C bonds in the chain	Addition Polymer	Poly(ethene), PVC, PTFE (poly(tetrafluoroethen))
-COO- links	Polyester	Terylene, PLA (poly(lactic acid))

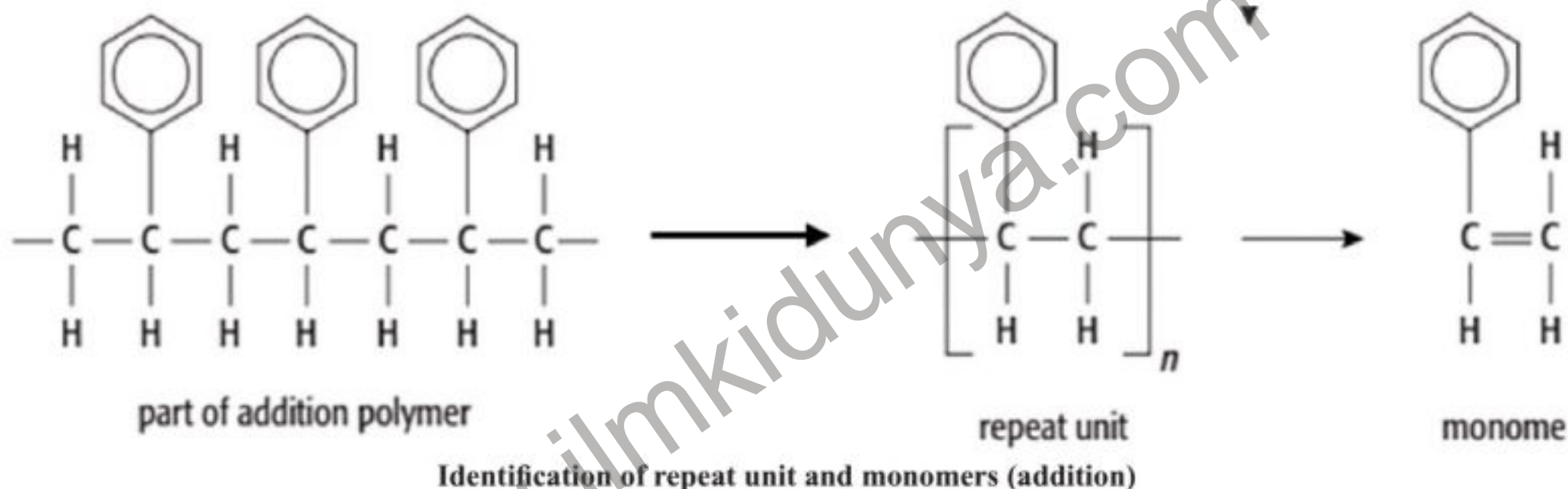


-CONH- links	Polyamide	Nylon-6,6, Kevlar
Benzene rings in the chain	Aromatic Polymer	PET or Kevlar

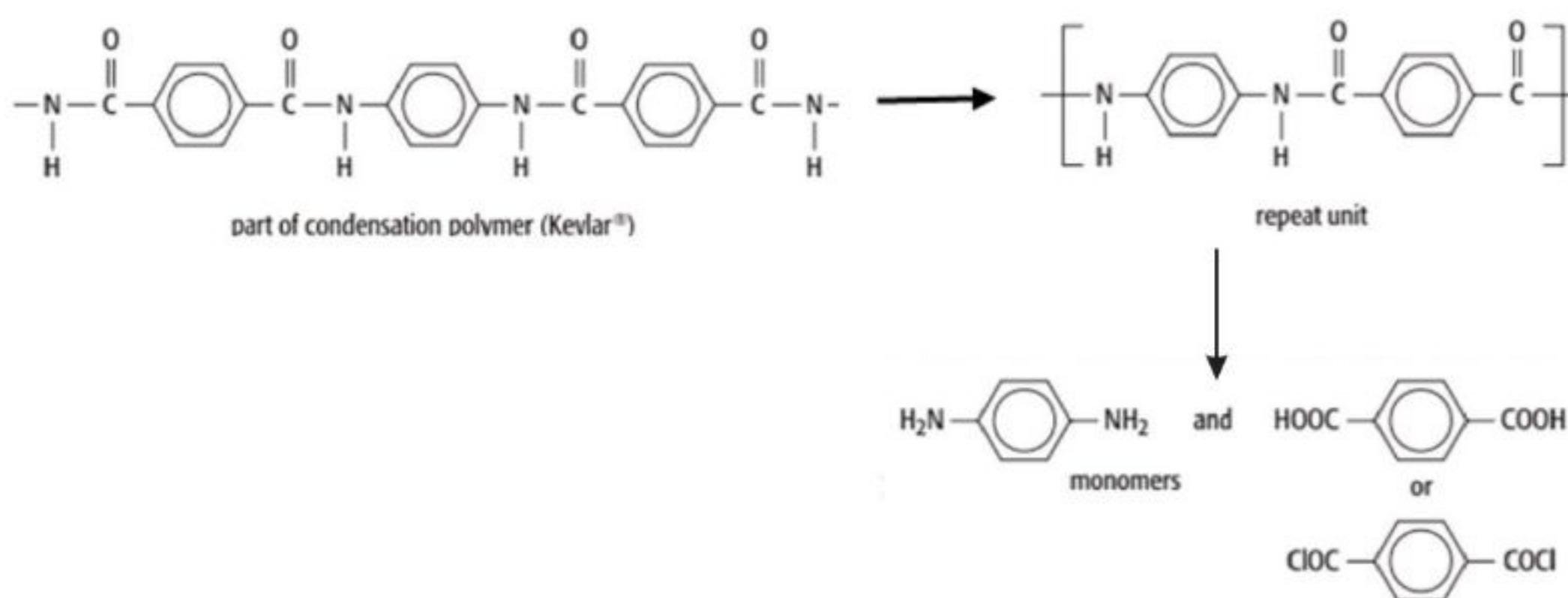
- 2. Determining the "Repeat Unit":** To find the original monomers, one must first identify the smallest section that repeats itself in the section of the polymer.
- To find the repeating pattern, look for where the sequence starts to duplicate itself. Locate such duplicating sections in the backbone.
 - Place brackets around one of these recurring sections and add the subscript n . This section within the brackets is the *repeat unit* of the polymer.

3. Identifying the Monomer(s):

- a) For addition polymers, change the C-C single bond in the repeat unit back into a C=C double bond to find the monomer.



- b) For Condensation polymers: Add water back in. Break the ester or amide bond. Add -OH to the C=O side and -H to the O or N side as given below.

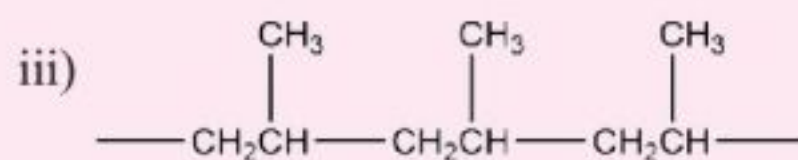
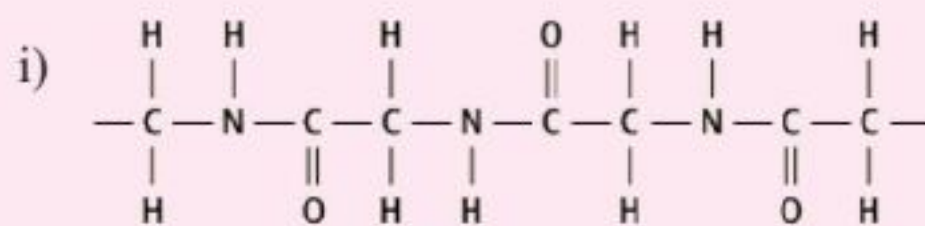


Identification of repeat unit and monomers (addition)



**Quick Check 26.2**

a) Identify the type of polymerisation and monomers forming the following polymer sections.



Polypropylene

26.4 USING MONOMER(S) TO PREDICT THE TYPE OF POLYMERISATION

26.4.1 Addition polymers

When the given monomer(s) contains C=C bonds, addition polymerisation will take place. The examples include ethene, propene, phenyl ethene (styrene). Mostly homopolymers are formed through the addition polymerization, however, sometimes copolymerisation of two different monomers having double bond can also be achieved. Such an example is a copolymer of ethene and propenoic acid (H₂C=CH-COOH).

26.4.2 Condensation polymers

When there are two functional groups available for the formation of a bond or bridging linkage to create the polymeric chains, the condensation polymerisation takes place. Mostly, a small molecule is removed from the two monomers during the formation of the polymer. The two functional group may exist in a single molecule (e.g. lactic acid) or two different molecules, as in the case of nylon 6,6.

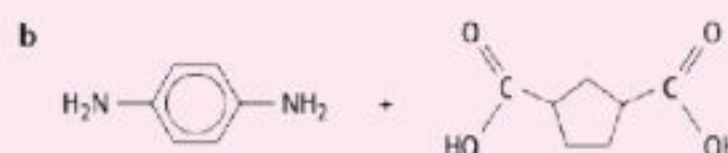
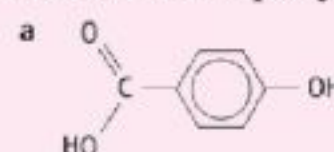
The common functional groups that can undergo condensation polymerisation are:

- amino group (NH₂) and carboxylic (COOH) group (polyamide and H₂O)
- amin group (NH₂) and acyl chlorides (COCl) (polyamide and HCl)
- carboxylic group(COOH) and alcohols (OH) (polyester and H₂O)
- acyl chlorides (COCl) and alcohols (OH) (polyester and HCl).

**Quick Check 26.2**

Give the structures of the polymers formed from the monomers. For each polymer identify the following:

- i. the repeat unit
- ii. the type of linkage present
- iii. the attractive force between the polymer chains.



26.5 CHALLENGE OF NON-DEGRADABLE POLYMERS

Plastic, such as poly(ethene), is the most widely used polymeric material on the globe. Conventional polymers are non-degradable, which means they can be broken down into simpler, non-toxic compounds. Due to this reason, they become an environmental nuisance after their disposal. These polymers become part of water bodies, soil, and natural habitats of living organisms. Therefore, scientists are now developing degradable polymers to cope with this issue. The plastic material is either buried underground or even disposed off in open air in the regions where the municipality system is not good.

- They stay in the environment for a very long time. This means they accumulate in landfills, oceans, and natural landscapes, leading to persistent pollution.
- They take up huge amounts of space in landfills because they do not decompose. As population grows, finding space for more landfills becomes difficult.
- Animals (especially marine life) can mistake plastic waste for food, leading to choking, internal injuries, or starvation. They can also get tangled in plastic debris.
- Over time, large pieces of non-degradable plastics break down into tiny pieces called **microplastics**. These microplastics spread everywhere, polluting soil, water, and even the air. They can enter the food chain and potentially harm human health.

This leads to the need for the development of two major classes of polymers biodegradable and photodegradable polymers.



Figure 26.5 A beach littered with non-degradable poly(alkene) waste

26.5.1 Biodegradable Polymers

The plastic that is naturally decomposed by microorganism into simpler non-toxic compounds when buried for a certain period is called biodegradable plastic. Plastics that contain natural polymers, such as starch, are degraded faster, as bacteria in the soil can attack natural polymers easily. Polyesters and polyamides are more biodegradable than poly(alkene)s because the soil organism can attack them better through hydrolysis into simpler components. Polyamides produce carboxylic acids and amines, whereas polyesters can be decomposed into carboxylic acids and alcohols. For, example, poly(lactic acid) (PLA) can enhance the biodegradability of plastic. **Figure 26.6** shows the degradation of a plastic material containing PLA after a certain period

26.5.2 Photodegradable Plastics

Some functional groups can absorb more energy from the sunlight in the form of UV light. Polymers with such functionalities can be degraded by light and are termed as photodegradable. Some polymers with carbonyl groups in their chains ($C=O$) have been developed due to their



enhanced photosorption. The absorption of the UV light weakens the bonds within the chain and forces between different chains of the polymers. This makes a polymer more biodegradable, thus accelerating its decomposition into less toxic compounds in the natural environment. However, photodegradable plastics cannot be used for longer time and recycling of such polymers is not efficient. Also, the plastic is buried in landfills where no light is available for photodegradability.

Because polyesters and polyamides can biodegrade under these conditions, it means they don't stay in the environment forever like some other plastics. This helps reduce the adverse effects of the plastic pollution. Scientists and engineers can use this knowledge to design materials that break down when they are no longer needed. For example, some medical implants or dissolvable stitches are made from polyesters that slowly break down in the body through hydrolysis.

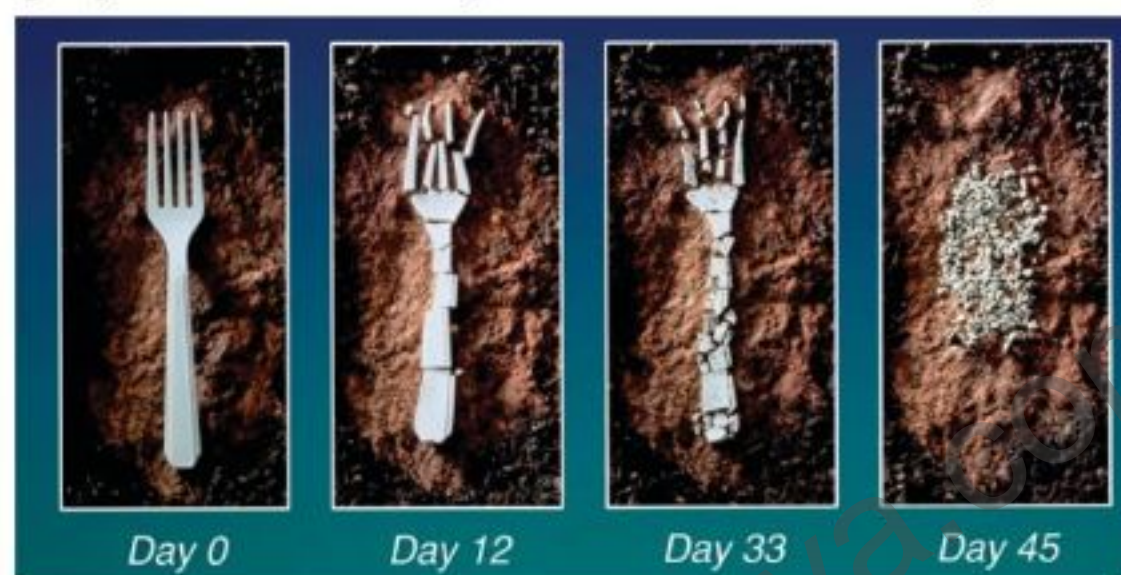


Figure 26.6 Chemists are devising plastics that can be broken down by microorganism in soil or by light

26.6 POLYMERS IN ARTIFICIAL ORGANS

In biomedical science, polymers are very important for creating artificial organs. These are man-made devices designed to replace or support the function of damaged or diseased body parts. Polymers used in the body need to be biocompatible, mechanically suitable, sterilizable, durable and tunable.

They must not harm the body, cause allergies, or be rejected by the immune system.

Their strength, flexibility, or elasticity can be adjusted to match the body part they replace (e.g., flexible for blood vessels, strong for bones). The uses of various polymers in medical science are summarised in **Table 26.2**.

Table 26.2 Polymers in artificial organs

Application	Polymers Used	Key Properties & Functions
Artificial Blood Vessels (Grafts)	Poly(tetrafluoroethylene)(PTFE) and Poly(ethylene terephthalate) (PET)	Smooth surfaces to prevent blood clots; used to replace or bypass blocked vessels.
Artificial Heart Valves	Specialized Polyurethanes and Silicone	Highly flexible and durable; must be resistant to clotting.



Artificial Skin	Collagen (natural) and Polylactic acid (PLA) (synthetic)	Acts as a scaffold for new skin growth; some are designed to dissolve as the wound heals.
Artificial Joints (Hip/Knee)	Ultra-high molecular weight polyethylene (UHMWPE)	Provides a smooth, low-friction surface to allow movement and resist wear.
Artificial Cornea	Poly(methyl methacrylate) (PMMA) and Hydrogels	Must be perfectly clear (transparent) and biocompatible to restore vision.

Exercise

Q1. MULTIPLE CHOICE QUESTIONS

I. Which pair of monomers reacts to form a polyester?

- a) Diamine and dicarboxylic acid b) Diol and dicarboxylic acid
c) Ethene and chloroethene d) Amino-carboxylic acid

II. What small molecule is eliminated when a diamine reacts with a diol chloride?

- a) Water (H₂O) b) Hydrogen chloride (HCl)
c) Ammonia (NH₃) d) Ethene (C₂H₄)

III. How do plasticizers affect PVC?

- a) Make it harder. b) Make it brittle
c) Reduce inter-chain forces, make it flexible
d) Increase melting point and conductivity

IV. What are the two monomers for Nylon 6,6?

- a) Vinyl chloride & Adipic acid b) Hexamethylenediamine & Adipic acid
c) Ethane-1,2-diol & Adipic acid d) Only Hexamethylenediamine

V. A polymer section is shown: [-CH₂-CH(CH₃)-CH₂-CH(CH₃)-]... What is the monomer, and what type of polymer is it?

- a) Propene; Addition b) Propene; Condensation
c) Ethene; Addition d) Ethene; Condensation

VI. Polyesters and polyamides are considered biodegradable because they:

- a) are natural polymers. b) break down in sunlight.
c) have small monomers. d) are hydrolysable ester/amide links.



VII. What are the products of alkaline hydrolysis (saponification) of a polyester?

- a) Carboxylic acid and alcohol b) Carboxylate salt and alcohol
c) Carboxylic acid and amine d) Carboxylate salt and amine

VIII. What are the products of acidic hydrolysis of a polyamide?

- a) Carboxylate salt and amine b) Carboxylic acid and alcohol
c) Carboxylic acid and protonated amine d) Carboxylate salt and protonated amine

IX. What is the primary cause of photodegradation in polymers?

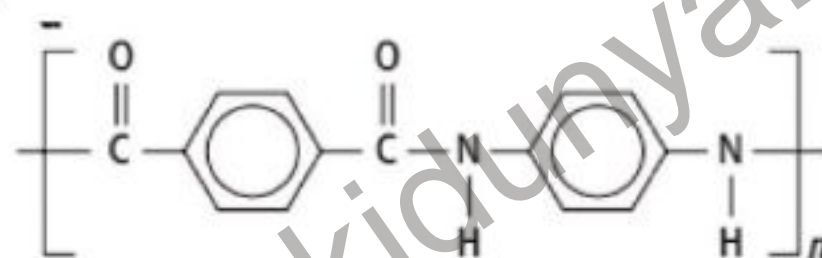
- a) Acidic hydrolysis b) Microorganisms
c) Absorption of UV light d) Alkaline hydrolysis

X. Poly(alkenes) are considered "chemically inert" because they:

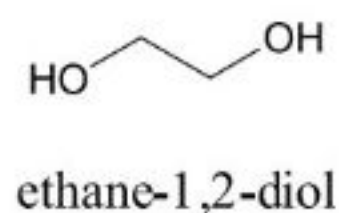
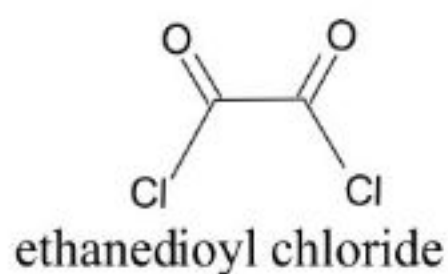
- a) have weak, easily broken bonds. b) have strong C-C and C-H bonds.
c) They react quickly with acids. d) They dissolve in water.

Q2. SHORT ANSWER QUESTIONS

a) Kevlar[®] is a thermally and mechanically very stable but flexible polymer; a section of this polymer is given below:



- Name the characteristic linkage and type of polymerisation in its structure
 - Identify the two functional groups that react to form it.
 - Name the monomers from which it is formed.
- b) Explain why the reaction between an acyl chloride and ammonia is classified as a condensation reaction. Identify the small molecule that is eliminated during this reaction.
- c) For the following monomers:
- Predict the type of the polymer formed.
 - Draw the repeat unit and a section of the expected polymer.
 - Name this polymer systematically.
- d) For Nylon 6,6 (from 1,6-hexanediamine and 1,4-hexandioic acid acid):
- Name the linkage.
 - Name the small molecule eliminated.



- iii) Draw the repeating unit.
- e) For poly(chloroethene) (PVC)
 - i) Name the monomer for PVC
 - ii) Why can it undergo addition polymerization?
- f) State two properties of nylon that make it suitable for ropes and fishing nets.
- g) Give two industrial applications for PVC and two for Nylon.
- h) Draw the repeating unit of the polyester from propan-1,3-diol and benzene-1,4-dicarboxylic acid.
- i) State three distinct environmental problems caused by the disposal of non-degradable polymers.
- j) Name two different polymers used in artificial organs and state the specific application for each.

Q3. CONSTRUCTED RESPONSE QUESTIONS

- a) Describe the chemical role of plasticizers in polyvinyl chloride (PVC) and explain how this modification influences the polymer's industrial applications.
- b) Explain why poly(alkenes) like poly(ethene) pose a greater environmental challenge than polyesters and polyamides. Identify the chemical process that allows the latter to degrade.

DESCRIPTIVE QUESTIONS

- Q.4** Compare and contrast addition and condensation polymerization, giving details of the specific structural requirements for the monomers in each.
- Q.5** Illustrate the formation of two major condensation polymers.
- Q.6** Differentiate between the environmental degradation of poly(alkenes) and polyesters.

