



Polymers

- Polymers consist of long chain molecules made from smaller molecules called monomers
 - \circ ~ The monomers in any polymer might be identical, or they may occur in a repeating pattern
 - \circ \quad The monomers of an organic polymer are linked together by covalent bonds
 - o The properties of a polymer are determined by the properties of its monomers
- The chemical process by which monomers are joined to form polymers is called polymerisation. Polymers may be fabricated by two processes:
 - Addition polymerisation: Result from the addition reactions of monomers containing unsaturated carbon-carbon bonds
 - Each monomer molecule undergoes an addition reaction in which the double bond in the molecule is broken, allowing monomer molecules to join end on end
 - o Condensation polymerisation: Result from reactions between functional groups

Addition Polymerisation

- Alkenes undergo addition reactions in which substances can be added to the carbon-carbon double bond
- In a similar way, alkene monomer molecules can undergo addition reactions with other alkene monomer molecules to produce a polymer
 - The double bond in each alkene monomer is transformed into a single bond, freeing up an unbonded electron pair that then forms a single carbon-carbon bond with another monomer
- E.g. Polyethene (commonly called polyethylene)
 - o Ethene molecules react with other ethene molecules to produce polyethene



• The structure of a polymer can be written in condensed form, with the repeating unit being bracketed and a subscript "n" denoting the number of repeating units





- Depending upon the manufacturing conditions used, polyethene can be produced as:
 - Low density polyethene (LDPE)
 - This form of polyethene has numerous side chains situated along the main chain



- The side chains prevent the molecules from packing efficiently (i.e. amorphous arrangement), thus reducing the strength of its intermolecular dispersion forces
 - Consequently, LDPE has a relatively low melting point, is soft, flexible and fairly weak
- LDPE is used for making thin flexible films that can be used for food wrapping, garbage bags, tank and pond liners, other soft flexible articles (like squeeze bottles, toys and electrical wire), etc
- High density polyethene (HDPE)
 - This form of polyethene has mainly long straight chains with very few side chains



- The more linear shape allows a more efficient regular packing of HDPE molecules (i.e. crystalline structure) and consequently has a stronger interaction by dispersion forces
 - Consequently, HDPE is stronger, more rigid and has a higher melting point than LDPE
- HDPE is used for making food containers, chemical resistant containers (like fuel tanks), pipes, etc
- Using different monomers enables a variety of different addition polymers to be produced. E.g. Polytetrafluroethylene (PTFE, commonly called Teflon)
 - \circ Tetrafluoroethene molecules react with each other to produce PTFE



- The extensive presence of fluorine atoms is PTFE contributes to its greater resistance to chemical attack and chemical stability, due to the higher strength of the C–F bonds in PTFE, as compared to C–H bonds in polyethylene
 - Consequently, PTFE acts as a non-stick, low friction surface
- PTFE is used for frying pains and other cookware, as a solid lubricant, low friction bearings and gears, etc
 - Its resistance to chemical attack and chemical stability allows it to be in contact with foods at high temperatures without 'sticking'



Condensation Polymerisation

- An alcohol molecule reacts with a carboxylic acid molecule to produce a single ester molecule. This esterification reaction is also called a condensation reaction because water is eliminated when the functional groups react
- In a similar way, the functional groups on adjacent monomer molecules can react to produce a polymer, and eliminate water molecules in the process
- E.g. Polyesters
 - o Dicarboxylic acid reacts with diols to produce polyesters
 - A dicarboxylic acid is an acid with a carboxyl group at each end of the molecule
 - A diol is an alcohol with a hydroxyl group at each end of the molecule
 - Ester linkages can then be formed end to end between alternating acid molecules and alcohol molecules, with the removal of a water molecule

 $\underline{HO}OCCH_{2}CH_{2}COOH + \underline{H}OCH_{2}CH_{2}OH + \underline{HO}OCCH_{2}CH_{2}COOH + \longrightarrow$ di-ethanoic acid 1,2-ethanediol

• If we were to depict the dicarboxylic acid with the symbol $\Delta^{--}\Delta$, the diol with the symbol $\mathbb{O}^{--}\mathbb{O}$, and the ester linkage with $\mathbb{O}\Delta$, we could represent the polymerisation reaction like this:

$$\Delta - \Delta + 0 - 0 + \Delta - \Delta + 0 - 0 \longrightarrow \Delta - \Delta - 0 - 0 - \Delta - 0 - 0 + water$$

- The two functional groups on each monomer do not have to be identical. E.g. The monomer may contain a carboxyl group at one end and a hydroxyl group at the other end
 - Ester linkages can be formed between the carboxyl group and the hydroxyl group of adjacent identical monomers
 - If we were to depict such a monomer with the symbol Δ -O, we can represent the reaction as shown below:

$$\Delta - o + \Delta - o + \Delta - o + \Delta - o \longrightarrow \Delta - o \Delta - o \longrightarrow - o + water$$

polyester

- o Polyester molecules have a permanent net dipole around each of the ester groups
 - Consequently, polyester molecules can attract and align by dipole-dipole forces (as well as by dispersion forces). The greater the degree of crystallinity (ordered alignment of molecules) of the polymer, the greater its strength and toughness
 - Polyesters are mixed with natural cotton fibres to produce fabric for clothing, carpet, etc



- E.g. Polyamides
 - \circ \quad Dicarboxylic acids react with diamines to produce polyamides
 - Diamines are monomers with an amide group at each end of the molecule
 - Amide linkages can then be formed end to end between alternating acid molecules and amine molecules, with the removal of a water molecule
 - Polyamide molecules form hydrogen bonds between lone pairs of electrons on the oxygen atom from a carbonyl group of one molecule, and a hydrogen atom from the amine group of another
 - Consequently, polyamide molecules have increased strength and stiffness
 - \circ As with polyesters, polyamides can be converted into strong fibres suitable for weaving into fabric
 - o E.g. Nylon 6,6



- The name nylon 6,6 refers to the number of carbon atoms in the monomers
 - The first "6" refers to 1,6-diaminohexane, which contains 6 carbon atoms
 - The second "6" refers to adipic acid, which also contains 6 carbon atoms
- Nylon fibres is used in fabric for clothing, ropes, carpets, fishing lines, seat belts, bearings, gears, etc
- Kevlar is a variation of nylon 6, 6, where aromatic benzene rings replace the two carbon chain sections of the polyamide
 - This increases the strength and stiffness of the polymer further
 - Kevlar is used for high performance ropes and cables, sail cloth, bulletproof vests, sports gear, etc



Soaps

- Fats and oils are triglycerides, i.e. esters formed between the alcohol glycerol and long-chained carboxylic acids called fatty acid
 - \circ \quad Glycerol is a 3-carbon alcohol with three hydroxyl groups

- o The three fatty acids that are attached to each molecule of glycerol may be identical or may be different
- o E.g. Palmitin

$$CH_{3}(CH_{2})_{14}COO - CH_{2}$$

$$|$$

$$CH_{3}(CH_{2})_{14}COO - CH$$

$$|$$

$$CH_{3}(CH_{2})_{14}COO - CH_{2}$$

- A soap (and glycerol) is produced between the reaction of a fat and a base
 - The process of forming soap is known as **saponification**
 - o Recall that the hydrolysis reaction of esters upon treatment with an acid or a base
 - A reversal of esterification occurs (i.e. the ester is split into its acid and alcohol components)
 - The reaction below is carried out in a basic solution, and the products are the sodium salt of the carboxylic acid and the alcohol

$$\begin{array}{c} O & O \\ || \\ RC - O - R' + Na^+ + OH^- \longrightarrow RC - O^- + Na^+ + R'OH \\ ester & acid & alcohol \end{array}$$

• When triglycerides are hydrolysed with sodium hydroxide, the products are the sodium salts of the fatty acids and glycerol and

$$\begin{array}{c} (\mathrm{CH}_2)_{14}\mathrm{COO}-\mathrm{CH}_2 \\ | \\ (\mathrm{CH}_2)_{14}\mathrm{COO}-\mathrm{CH}+3\,\mathrm{NaOH} \xrightarrow{} 3\,\mathrm{CH}_3(\mathrm{CH}_2)_{14}\mathrm{COONa}+\mathrm{CH}_2(\mathrm{OH})-\mathrm{CH}(\mathrm{OH})-\mathrm{CH}_2\mathrm{OH} \\ | \\ (\mathrm{CH}_2)_{14}\mathrm{COO}-\mathrm{CH}_2 \\ \\ palmitin & sodium palmitate & glycerol \\ (triglyceride) & (soap:\,\mathrm{Na}^+\,\mathrm{salt}\,\mathrm{of}\,\mathrm{fatty}\,\mathrm{acid}) \end{array}$$

These salts of fatty acids between sodium and the stereate ion is more commonly called soap

- The cleaning properties of soap are due to its ability to act as an emulsifying agent. An emulsifying agent or surfactant is a substance that can dissolve two normally immiscible (i.e. non-polar and polar substances) substances together
- The soap has both a:
 - A non-polar part (the long hydrocarbon chain)
 - The non-polar part of the molecule is referred to as the hydrophobic (water-hating) 'tail', also called the lipophilic (lipid loving) 'tail'
 - A polar part (the carboxylic acid anion, COO⁻)
 - The polar part of the soap molecule is often referred to as the hydrophilic (water loving) 'head' because it is soluble in water

non-polar "tail"

polar "head"

Since most greases, oils and stains that are commonly referred to as 'dirt' are non-polar and insoluble in water, the soap molecules rearrange so that the non-polar hydrocarbon tails dissolve (i.e. bury themselves) in the 'dirt', while the polar carboxylic heads dissolve in the water



- o This spherical structure of arrangement of the soap molecules and dirt is called a micelle
- o Consequently, the 'dirt' can be washed away with the soap, by the water, thereby leaving a clean surface

Detergents

- In the presence of ions such as Ca²⁺, Mg²⁺ and Fe²⁺ in hard water, the negatively charged soap ions form an insoluble precipitate, a scum
 - o Consequently, more soap needs to be used for washing in hard water than in 'soft' water, in order to obtain a lather
 - \circ \quad Detergents have been designed to correct this problem associated with soap scum
- Detergents have the same non-polar hydrophobic tail and polar hydrophilic head arrangement as soap, but will not form an insoluble precipitate with the ions in hard water
 - Replacing the carboxylate, COO⁻, with a sulfonate, SO₃⁻, group provided an effective surfactant ion that would not produce a scum in hard water