

POLYMERS AND POLYPEPTIDES

- The term POLYMER simply means a structure built from many parts. Polymers are generally large chains made from smaller carbon containing units that become linked under appropriate conditions of temperature, pressure and the presence of certain initiator substances or energy input.
- A polypeptide is a type of natural polymer made from amino acids and is the basis of the proteins in most life forms on the planet.

CLASSIFICATION:

► Plastics can be divided into four basic categories: -

- **Thermoplastics** such as polyethylene, which soften on heating and harden again on cooling (e.g. Milk bottles).
- **Thermosetting plastics** or resins are plastics which cannot be melted and re-moulded when heated (e.g. printed circuit boards and fibre glass resin)
- **Elastomers** or rubbers (e.g. Car tyres, rubber-bands, tennis balls)
- **Natural polymers** such as cellulose, lignin and protein, which provide the mechanical basis for most plant and animal life (e.g. wood, straw and silk).

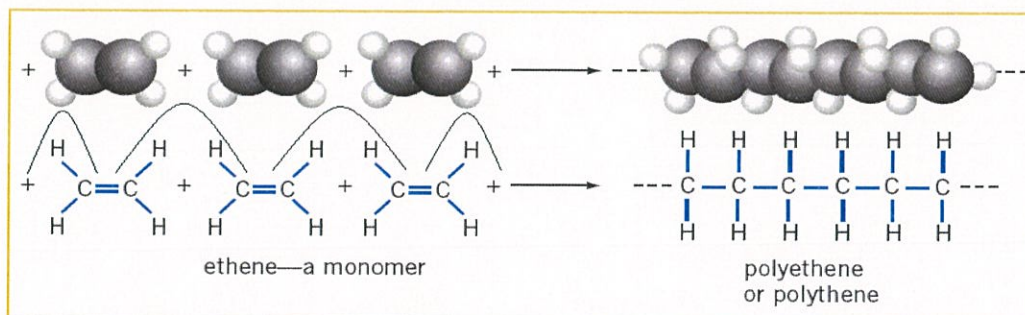
POLYMERISATION PROCESSES:

► There are two major types of polymerisation reaction, **ADDITION** and **CONDENSATION**.

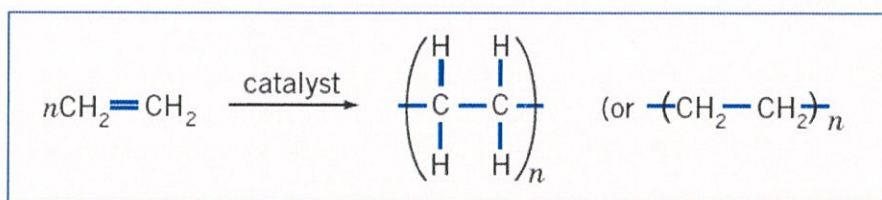
ADDITION:

► Addition polymerisation is where large numbers of the same MONOMER, containing a double bond, are linked or joined together and the polymer is produced without any other products. The double bonded segment of the monomer molecule is known as a VINYL unit.

- The vinyl unit has a sigma bond (α) and a pie bond (π) and under conditions of excitation the pie bond electrons can jump into a zone between two approaching monomer units forming a new covalent bond (α) that act as a link between the two.

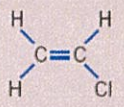
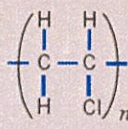
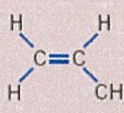
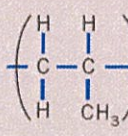
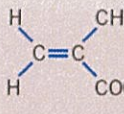
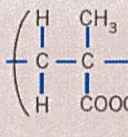
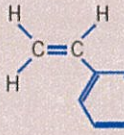
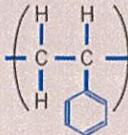


Formation of polyethene from ethene by addition polymerisation

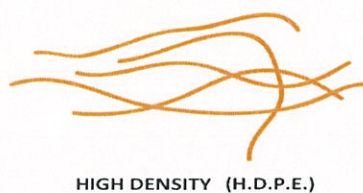
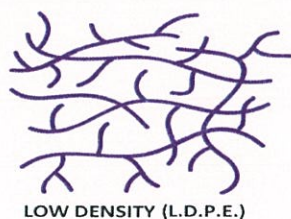


- By substituting hydrogen on the vinyl unit with other groups, the structure of the monomer and hence polymer can be varied almost infinitely, producing desired properties beneficial for intended use.

COMMERCIALLY IMPORTANT ADDITION POLYMERS

Polymer	Formula and name of monomer	Formula of polymer	Examples of uses
Poly(vinyl chloride), PVC	 Vinyl chloride (chloroethene)		Pipes, cable insulation, water tanks
Polypropene	 Propylene (propene)		Rope, carpet, plastic parts for cars
Poly(methyl methacrylate)	 Methyl methacrylate (methyl 2-methylpropen-2-ate)		Plexiglass, paints
Polystyrene	 Styrene (phenylethene)		Insulation, packaging

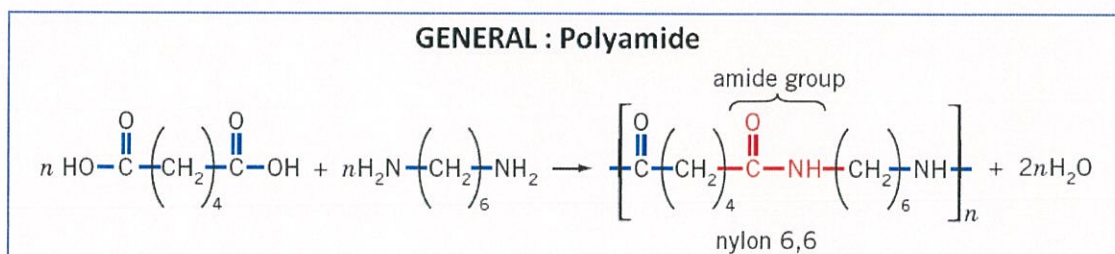
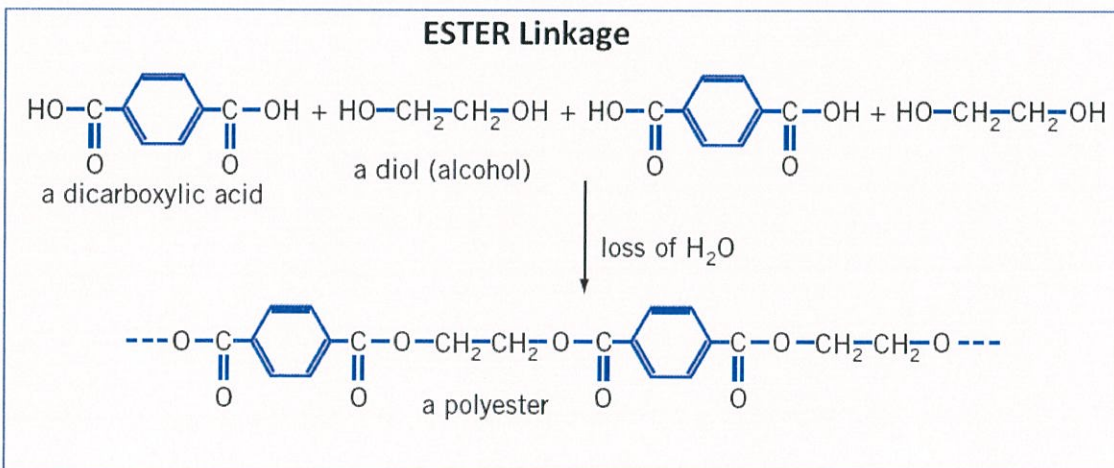
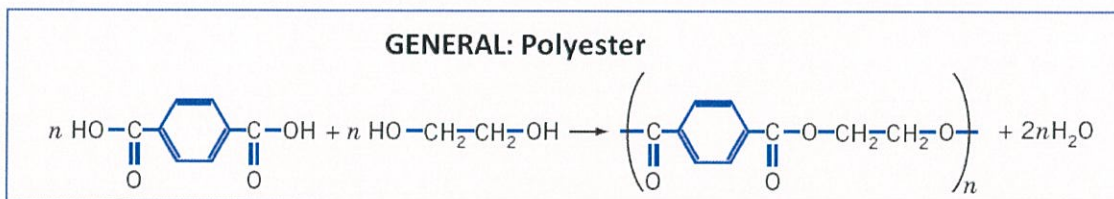
- Depending on the conditions chosen and the particular reaction catalyst, polymer chains can be made to form in a linear fashion or a branched fashion. The presence or absence of branching effects how well the polymer chains can “fit together” and how effective the dispersion forces between them will be. The different polymers formed in this way are known as HIGH DENSITY or LOW DENSITY.



CONDENSATION:

► Condensation polymerisation usually involves two different monomers fusing together. The molecules of at least one but generally both monomers contain two reactive sites that allow them to link together in a continuous fashion. Chemical interaction of these monomers produces a polymer and molecules of such simple substances as water, ammonia or hydrogen chloride.

- The fact that *two different monomers* are used and linked in an alternating fashion and that there are *by-products* in these reactions, sets them apart from addition polymerisation.
- The basis for the linkage in this type of polymer is generally an **ESTER** linkage or an **AMIDE** linkage. An ester linkage is formed if the monomers are a **diol** and a **dioic acid**. Amide links form in a condensation reaction between **diamines** and **dioic acids**.





Condensation Polymers – Investigating Polymers Series

During the Program

1. What is a polymer?

2. Two ways of linking monomers are by:

3. Give three reasons why the condensation reaction is different to the addition reaction?

4. Comparing Kevlar with polystyrene, why does Kevlar have a higher melting point even though the monomers are about the same size?

5. What is a co-polymer?

6. What happens to the molecular particles when a substance melts?

7. How is a thermoplastic useful in industry?



Worksheet

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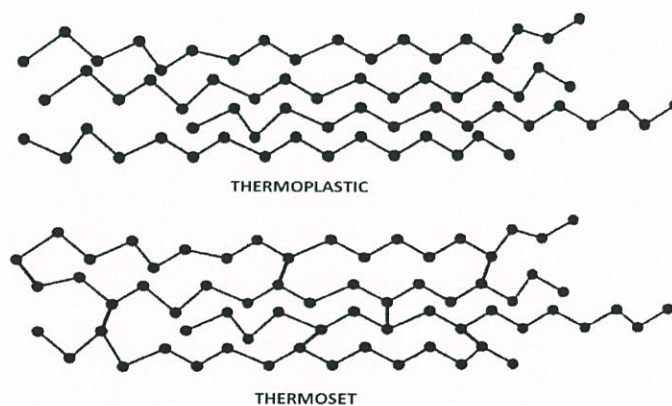
THERMOPLASTICS AND THERMOSETS:

► THERMOPLASTICS (thermo softening) have the main characteristic that they become soft when heated. This can be an advantage as they are easy to mould and when cooled they retain their shape.

- Thermoplastic polymers are made of linear chains that become free to move when heated as their dispersion force interactions are relatively weak and can be overcome. Eg: Glad Wrap.

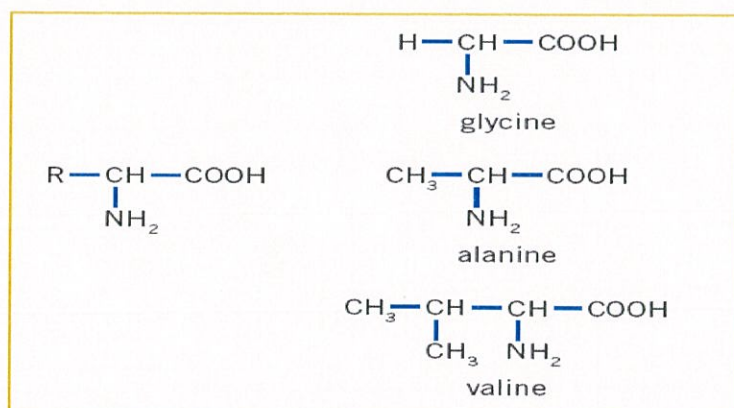
► THERMOSETS have the main characteristic that they do not soften on heating. These polymers are made of networks with "cross-linking" between the chains of molecules.

- The movement of chains across each other is prevented by the cross links and they remain rigid as a result, even when heated. Eg: Araldite Glue.



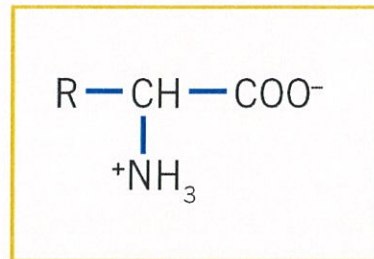
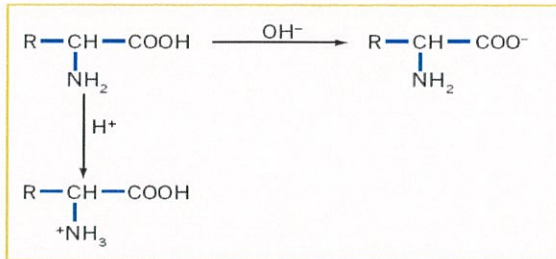
POLYPEPTIDES:

► Polypeptides are the protein molecules that make up our flesh and blood. They are polymers of a group of molecules known as **amino acids**. As the name suggests an amino acid is both an amine and a carboxylic acid, it has one of each functional group at either end and provides the capacity for continued amide links at each point. There are 20 amino acids that are used to construct human proteins.

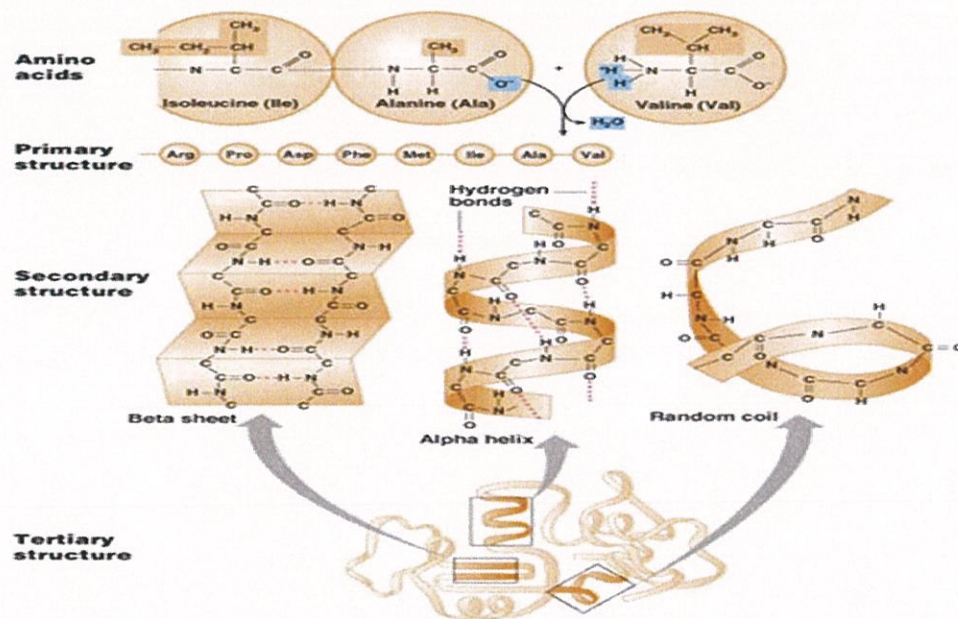
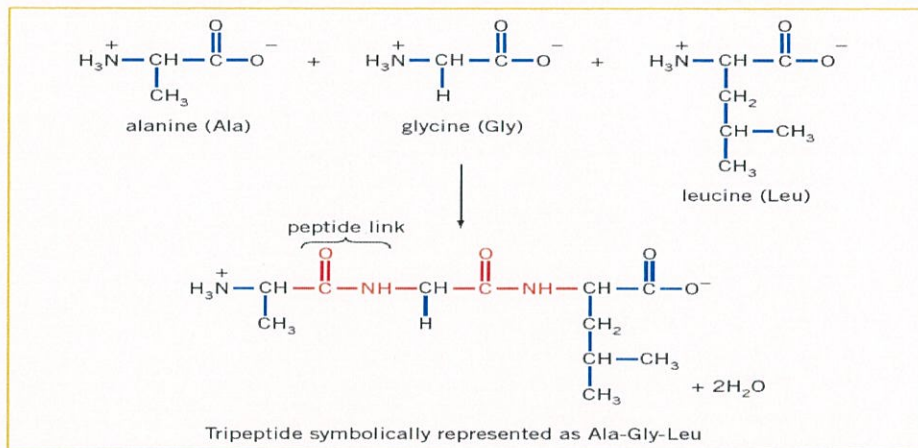


α -amino acids are specifically those that have the amino group attached to the carbon atom next to the carboxylic acid functional group!

- Having an acidic functional group at one end and a basic group at the other the amino acids can react with both acid and base and are described as being AMPHOTERIC. In neutral solution such as that encountered in biological systems they exist in ionic forms with charges at both ends; ions such as these are known as ZWITTERIONS.



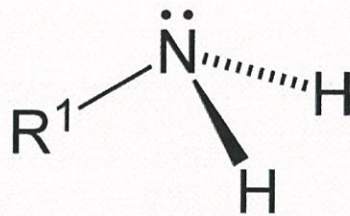
- These zwitterions condense to form the protein polymer. The precise order in which the amino acids are linked to produce a protein will vary its properties. Parts of the protein chain have a basis for intermolecular force interactions such as hydrogen bonding and this leads to them coiling up in specific patterns to produce a unique secondary structure.



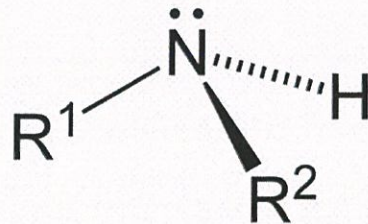
AMINE CLASSIFICATION:

► Amines are derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl (carbon containing) group.

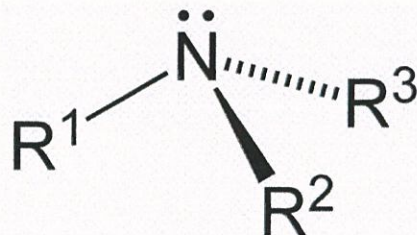
► It should be noted that α -amino acids are also **PRIMARY AMINES**. The classification of 1° , 2° and 3° amines is not the same as that for the alcohols. The classification is based on the number of carbon chains connected to the "Nitrogen" atom rather than to the carbon atom attached to the NH_2 group, as would be the case with alcohols.



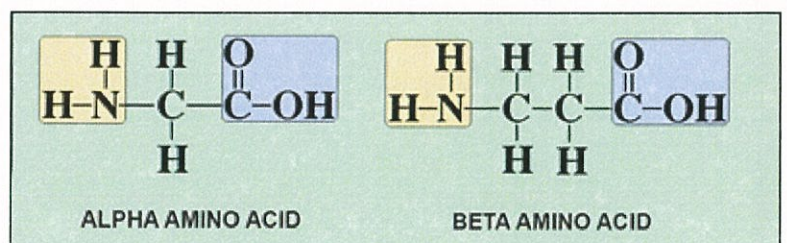
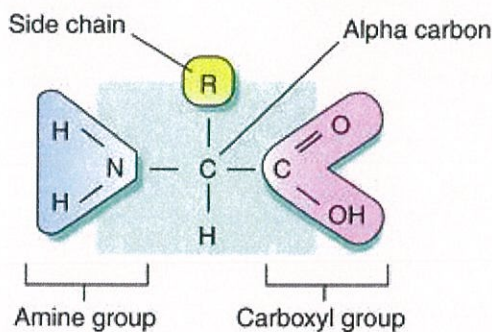
1°
Amine



2°
Amine



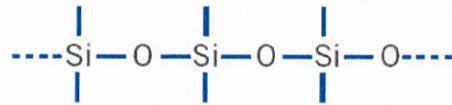
3°
Amine



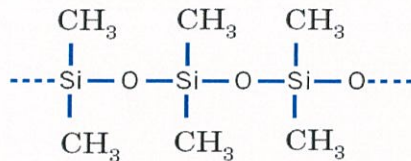
SILICONES (Silicon Based):

► Carbon is the basis of the polymers that we have encountered up till now but **SILICON**, another group IV element, may also form unique polymers with the involvement of oxygen.

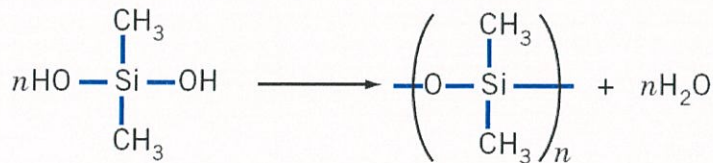
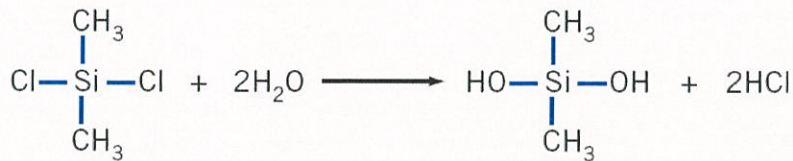
• Silicon is found most commonly in nature as a covalent network with oxygen in the various quartz minerals. A slight modification to this structure can see a host of very different properties. Silicones are built on a “backbone” of silicon and oxygen:



• The remaining bonding positions are often taken up with methyl groups:



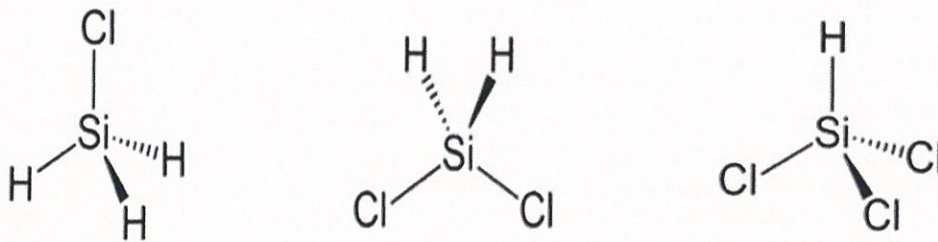
• **Silicones** are made by reacting **CHLOROSILANES** with water to form **silanols** which immediately react to form the polymer chains.



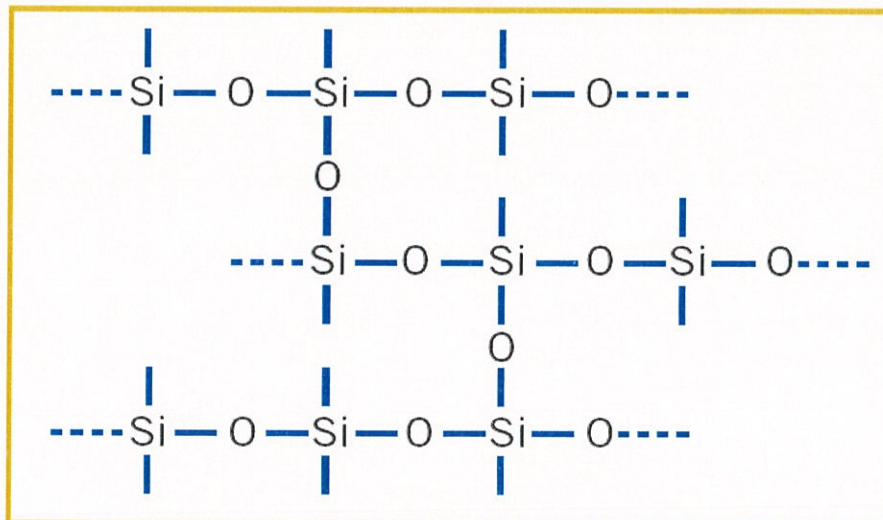
• Silicones have a range of useful properties:

- 1) Excellent electrical insulators
- 2) Good lubricants
- 3) Stable to extremes of temperature
- 4) Water repellent
- 5) Non-toxic
- 6) Chemically unreactive
- 7) Flexible
- 8) Non-stick

- A major difference between carbon based polymers and silicones is that the latter is more often liquid and retains liquid properties over a wide range of temperatures.
- Carbon based polymers often have a basis for hydrogen bonding intermolecular force interactions between parts of their chains (polyesters and polyamides). Hydrogen bonding is not possible with most silicones as they lack the carbonyl carbons and the presence of nitrogen in their structure. Their properties are governed by dispersion forces and dipole-dipole interactions.
- Dispersion forces depend on the number of electrons and the size of the molecule. The *silicon – oxygen* bond is much longer than a *carbon - carbon* bond. The electrons in the “backbone” are more spread having a greater volume and weaker dispersion forces as a result.
- The use of different structures of silane can encourage long chain formation or “cross-linking”.



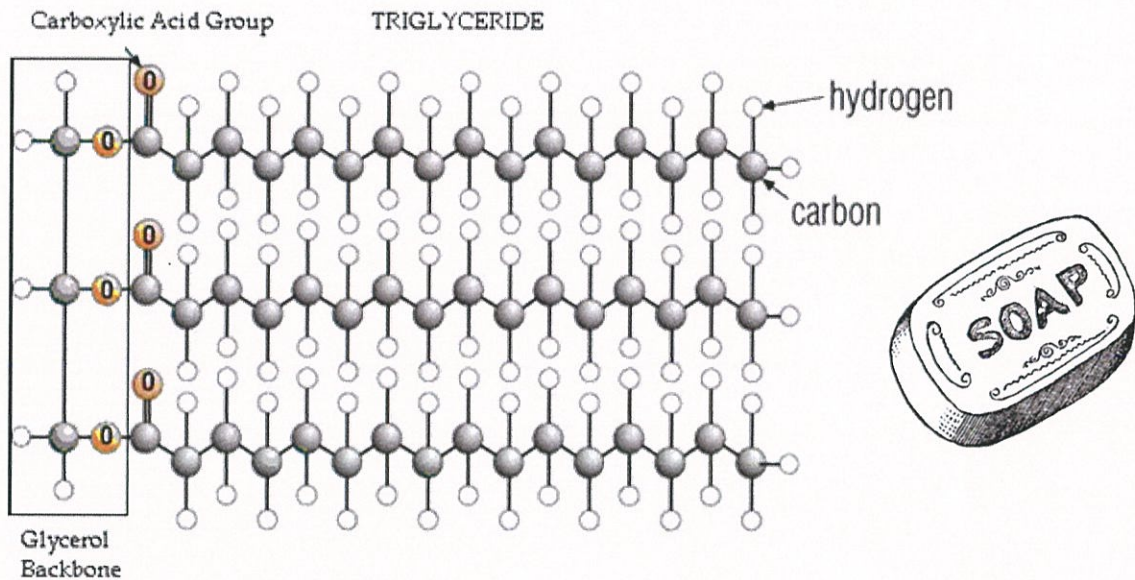
- Trichlorosilanes encourage “cross-linking” which makes the silicones more rigid and as a result they are often used as rubbers or resins. They are better insulators and have better thermal stability than their carbon based counterparts.



SOAPS AND DETERGENTS

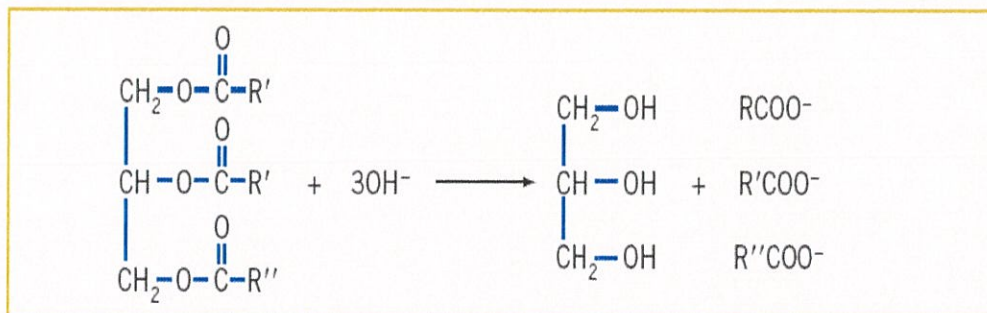
- Both soaps and detergents are long chain organic molecules with POLAR and NON-POLAR parts that enable them to be effective as cleaning agents. The difference between the two is the source of the hydrocarbons used in their preparation.

SOAPS:

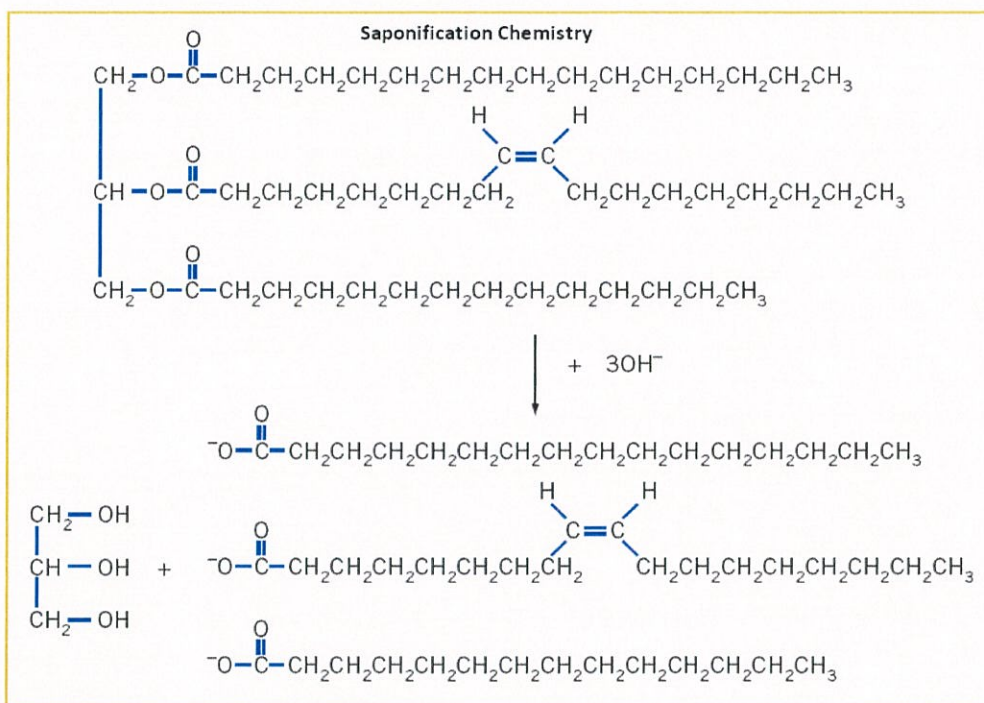


- Soaps are made from natural sources of **TRIGLYCERIDE** such as plant oils or animal fats. A triglyceride is a complex aggregate of 3 long chain **FATTY ACIDS** joined with a **GLYCEROL** molecule as a "backbone". The fatty acids **ESTERIFY** with the glycerol to form an ester linkage as shown below:

- It is the ester link that is broken in soap formation. This is achieved by boiling the fat or oil in a concentrated caustic solution, generally Sodium Hydroxide. The ester link is broken and the sodium ion forms a salt with the fatty acid while regenerating the Glycerol molecule in a reaction known as **SAPONIFICATION**.



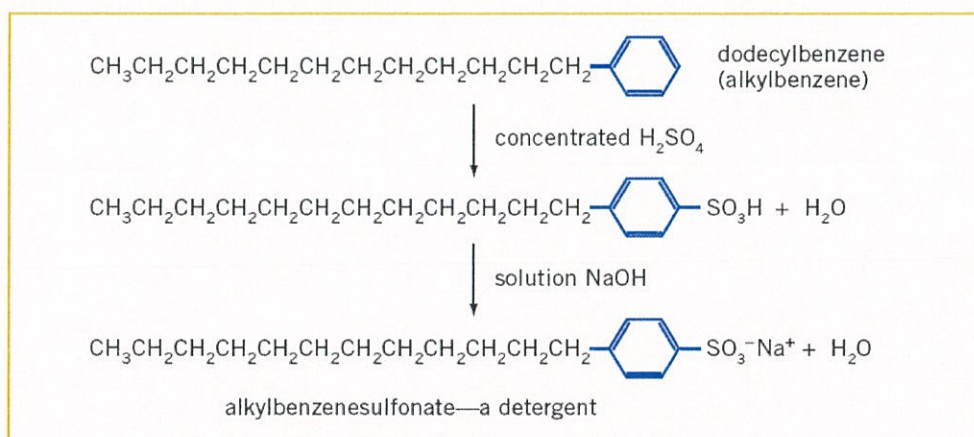
SAPONIFICATION CHEMISTRY :



- The length of the carbon chain can vary from one type of soap to another, but they all function in a similar way.

DETERGENTS:

- The preparation of a detergent differs in that the source of the hydrocarbon is generally from CRUDE OIL. For this reason they are manmade or synthetic by nature, where as soaps are from natural sources.
- Detergents are largely *Alkyl benzene Sulphonates*, which are produced from the sulphonation of alkyl benzenes produced from the reaction of benzene and alkanes obtained from crude oil.

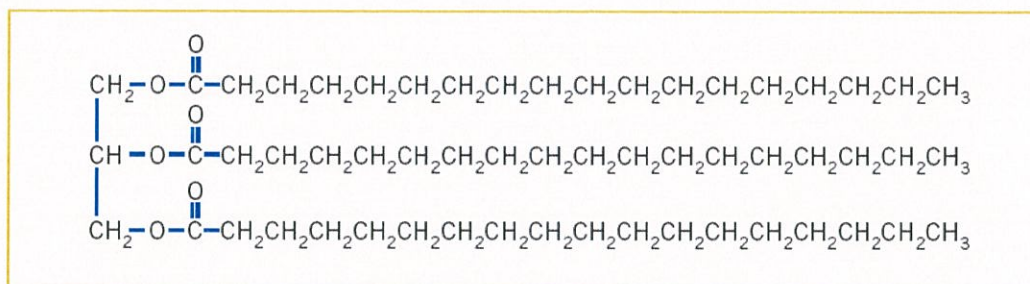


Formation of an alkylbenzenesulfonate detergent

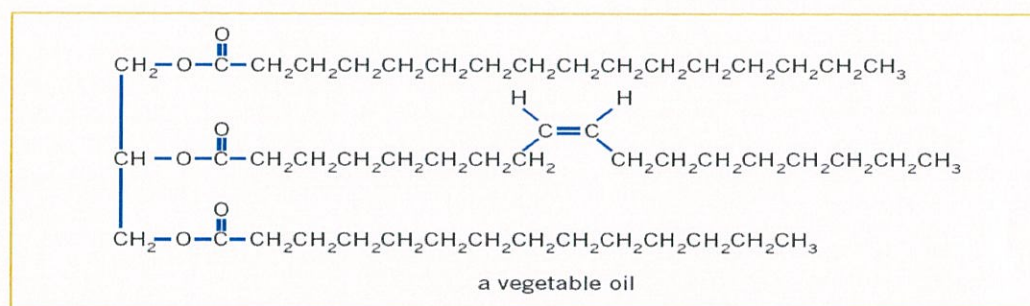


TYPES OF TRIGLYCERIDE :

- Animal triglycerides are generally **saturated** meaning that they have only single carbon – carbon bonds. Vegetable oils on the other hand are often **unsaturated** in that they have one or more carbon–carbon double bonds as part of their non-polar carbon chains. Vegetable oils are often referred to as *unsaturated fats*.



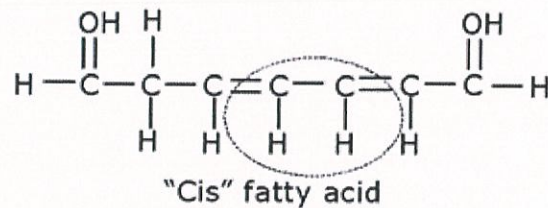
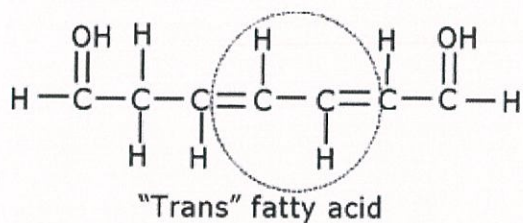
An example of a fat, glyceryl tristearate



A triglyceride with an unsaturated hydrocarbon chain

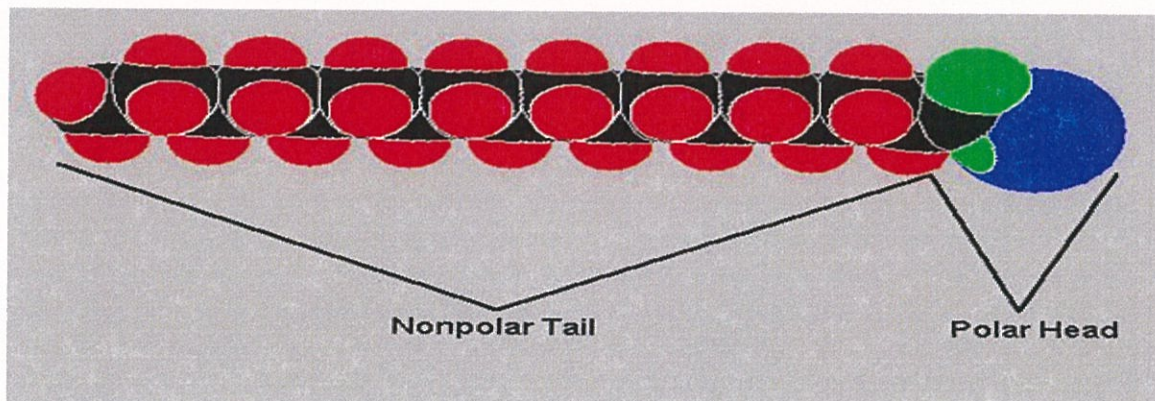
- Saturated animal fats are **solid** at room temperature as the dispersion forces between the straight chain triglycerides are quite effective. The efficacy of a dispersion force interaction often depends on how “close” one molecule can get to another and long saturated chains allow for good proximity.
- Unsaturated vegetable oils are liquid at room temperature as when double bonds are present in one or more of the chains it disrupts the symmetrical shape of the molecule. Neighbouring molecules are unable to approach as closely and so their dispersion forces are less effective.
- Geometric isomerism about any of the double bonds in an unsaturated vegetable oil can also influence its melting and boiling point. Where the unsaturated regions have “cis” isomerism, as in the example above, it makes the molecules even less likely to be able to pack together effectively. The “trans” isomer may be slightly more able to do so and thus dispersion forces may be marginally more effective.

- Vegetable oils are more reactive as the double bonds present may undergo addition reactions or even oxidation of the double bond which can render the oil "rancid" ruining their taste and producing a foul odour.
- Manufacturers of margarines often try to reduce the degree of unsaturation in their product by controlled "hydrogenation" of some of the double bonds in the fatty acids. This increases the efficacy of the dispersion forces and so the margarine will be a soft solid at room temperature. Not all double bonds are hydrogenated so there may well still be multiple regions within each fatty acid making the margarine "polyunsaturated". During the hydrogenation process the amount of the "trans" isomers in the product is reduced as there is some evidence linking "*TRANS FATS*" to health issues associated with the type of cholesterol produced by the body and heart disease.

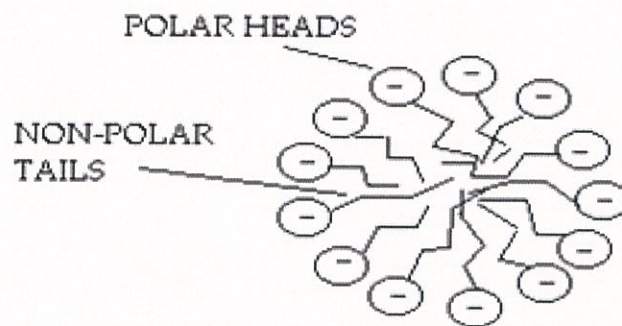


CHEMISTRY AND CLEANSING PROPERTIES:

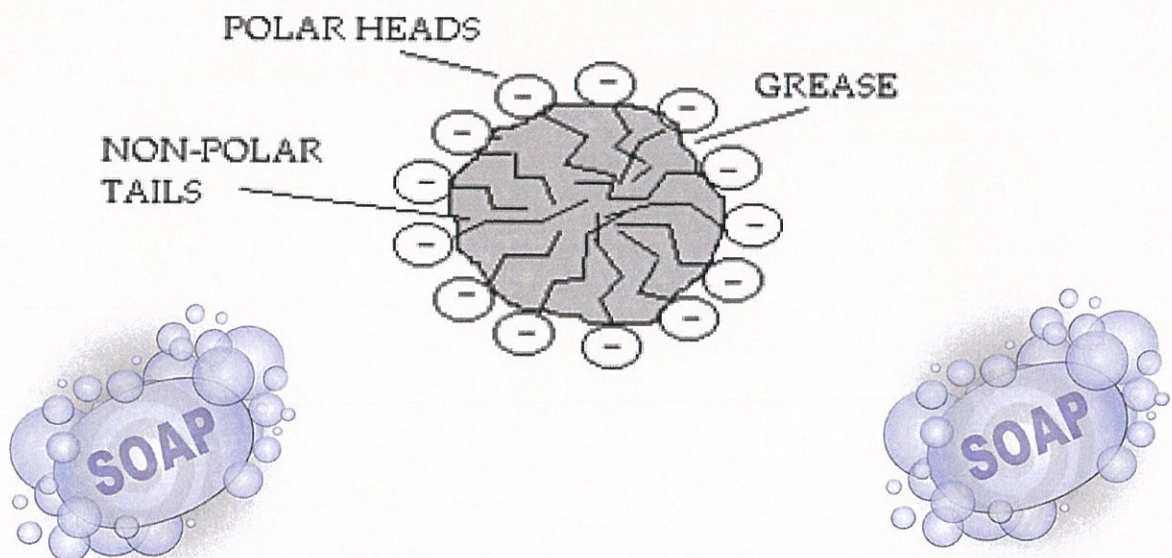
- When placed in water the sodium or potassium salts of the fatty acids dissociate to leave a sodium /potassium ion and a soap anion in the solution.
- The chemistry of soaps and detergents is very similar, as both possess the characteristic POLAR and NON-POLAR parts in their **ANIONS** that allow them to be water soluble despite the length of the hydrocarbon portions. The anions are said to have a POLAR "HEAD" and a NON-POLAR "TAIL".



- It is the way that these anions arrange themselves that is the key to understanding how they can be soluble in water. The polar heads are said to be "HYDROPHILLIC" (Water Loving) while the non-polar tails are said to be "HYDROPHOBIC" (Water Hating). By arranging themselves in units known as "MICELLES" ,where the head points outwards to provide a link with the water, while the tails point inward (dissolving in the tails of other anions) forming a sphere, they are able to dissolve. Micelles once formed have no tendency to join up again as they repel each other because of the charge on their heads.

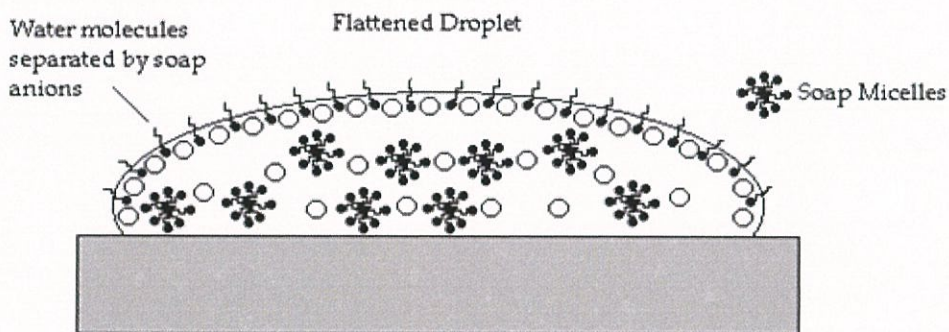


- These soap or detergent micelles (they form the same way), present in the water; allow it to cleanse objects with greasy residues of an organic nature. The action of the water alone is sufficient to dissolve ionic salts but not grease. Micelles bring about cleansing by coating any grease globules with the polar heads of the micelles that wash over their surfaces, as the non-polar tails dissolve very well in the grease. The grease globule becomes like a **very large** micelle in that it is coated in charge and now has an affinity for the water in which it becomes suspended. Once again these grease globules will have no tendency to re-form larger lumps of grease due to the charge on their surface



SURFACTANT PROPERTIES:

- Both soaps and detergents are examples of "Surface Active Agents" as they modify the surface properties of the water in which they are dissolved. They interfere with the water molecules at the surface as the "tails" of the anions are pushed through the surface. These surface anions can not form full micelles unlike those below the surface. The tails act to separate the surface molecules of water from each other.
- The increased separation of surface water molecules lowers the SURFACE TENSION as the water molecules' intermolecular forces have to act over bigger distances and thus their effects are lessened.
- Lowering of the surface tension leads to flatter drops, as the COHESIVE forces are less and an INCREASED SURFACE AREA in contact with the surface on which the droplet is placed. Thus a greater area of the surface is in contact with the water and so we say that the "WETTING PROPERTIES" of the water have been increased. Soaps and detergents act in this way as "wetting agents".



DISADVANTAGES:

- Soaps are not effective in "HARD WATER" as the high concentration of Ca^{2+} or Mg^{2+} ions leads to the formation of precipitates with the soap anions. The solid precipitates float to the top to form a layer of "SCUM". This reduces the amount of micelles in the water and hence its ability to cleanse or lather. Detergent ions have the advantage that they do not precipitate out in hard water and can continue to be effective.
- Detergent molecules, being synthetic, may not always be BIODEGRADABLE whereas soaps being natural products generally are.

