11.0 APPLIED ORGANIC CHEMISTRY

In this topic, we shall consider the following subtopics:

(a) Fermentation
(b) Soaps and soapless detergents
(c) Polymers and polymerization

11.1 FERMENTATION

Ethanol can be obtained by fermentation of sugars (carbohydrates).

(a) If ethanol is to be prepared from starch;

A source of starch such as maize, rice, potatoes, wheat or sorghum is used. Any of the above sources of starch is squeezed with hot water and filtered to obtain a solution of starch. The aqueous starch solution is heated to about 60°C with malt. Malt is germinated cereal (usually barley but can be any other) that contains an enzyme known as diastase. Diastase hydrolyses starch to maltose.

$$\underset{\text{starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[60^oC]{\text{Diastase}} \underset{\text{maltose}}{nC_{12}H_{22}O_{11}}$$

The liquid is then cooled to 35°C and yeast is added. Yeast contains the enzyme maltase which catalyses the hydrolysis of maltose to glucose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} 2C_6H_{12}O_6$$

Another enzyme in the yeast called Zymase, converts glucose to ethanol.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2CH_3CH_2OH + 2CO_2$$

(b) From Sugar

Molasses containing sugar is mixed with water and yeast and allowed to ferment for several days after which ethanol is obtained. One of the enzymes in yeast called sucrase catalyses the hydrolysis of sucrose in molasses to glucose and frusctose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Sucrase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Another enzyme in yeast called Zymase then catalyses the decomposition of glucose to ethanol and carbon dioxide.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2CH_3CH_2OH + 2CO_2$$

When the concentration of ethanol reaches 12%, it kills the yeast and fermentation stops. This obtained liquor is purified to obtain pure ethanol by distillation. The distillation results into formation of a mixture containing 95% ethanol. Further distillation forms a constant boiling mixture (an azeotropic mixture) whose composition does not change. This mixture is known as rectified spirit. The rectified spirit is stored over quick lime in the laboratory.

Subsequently the mixture is refluxed over quicklime for about 6 hours and then allowed to stand overnight to obtain absolute ethanol which is then distilled off.

In industry, benzene is added to the rectified spirit and then fractionally distilled. Pure ethanol is obtained at 78°C.

Uses of ethanol

(i) Manufacture of ethanol

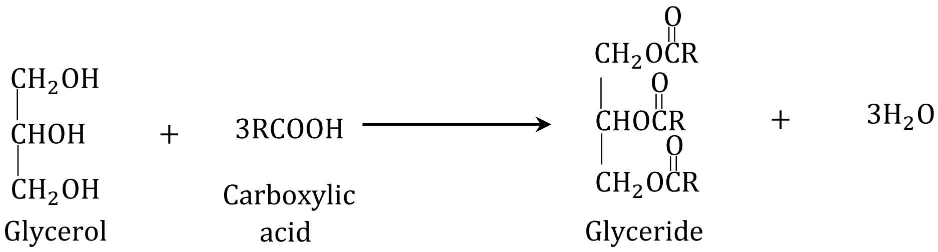
(ii) Manufacture of ethylesters.

(iii) As a solvent for many organic compounds.

11.2 Soaps and soapless detergents

11.2.1 Soap

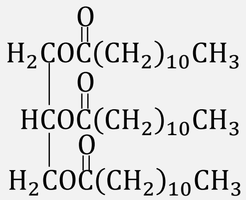
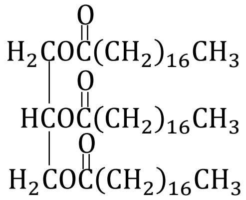
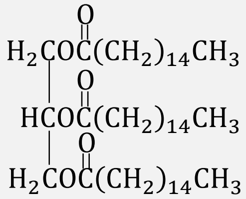
Soap is a sodium or potassium salt of a long chain carboxylic acid. Soaps are obtained from vegetable oils or natural fats known as glycerides. The fats (glycerides) are esters of a triol known as glycerol or propane – 1, 2, 3 – triol and long chain carboxylic acids as shown by the general equation below.



$$\underset{\text{Glycerol}}{\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} + \underset{\text{Carboxylic acid}}{3RCOOH} \longrightarrow \underset{\text{Glyceride}}{\begin{array}{l}CH_2O\overset{O}{\overset{\|}{C}}R\\ |\\ CHO\overset{O}{\overset{\|}{C}}R\\ |\\ CH_2O\overset{O}{\overset{\|}{C}}R\end{array}} + 3H_2O$$

The carboxylic acid used to obtain the glycerides are usually saturated and have an even number of carbon atoms in the range (12-20).

Examples are shown below:

Carboxylic acid	*Formula*	*Glyceride (fat used to form soap)*
Dodecanoic acid (lauric acid) (12 carbon atoms)	$CH_3(CH_2)_{10}COOH$	 $H_2CO\overset{\overset{O}{\Vert}}{C}(CH_2)_{10}CH_3$ $HCO\overset{\overset{O}{\Vert}}{C}(CH_2)_{10}CH_3$ $H_2CO\overset{\overset{O}{\Vert}}{C}(CH_2)_{10}CH_3$
Octadecanoic acid (stearic acid) (18 carbon atoms))	$CH_3(CH_2)_{16}COOH$	 $H_2CO\overset{\overset{O}{\Vert}}{C}(CH_2)_{16}CH_3$ $HCO\overset{\overset{O}{\Vert}}{C}(CH_2)_{16}CH_3$ $H_2CO\overset{\overset{O}{\Vert}}{C}(CH_2)_{16}CH_3$
Hexadecanoic acid (palmitic acid) (16 carbon atoms)	$CH_3(CH_2)_{14}COOH$	 $H_2CO\overset{\overset{O}{\Vert}}{C}(CH_2)_{14}CH_3$ $HCO\overset{\overset{O}{\Vert}}{C}(CH_2)_{14}CH_3$ $H_2CO\overset{\overset{O}{\Vert}}{C}(CH_2)_{14}CH_3$

Any of the fat (glyceride) above or others not shown can be used to make soap. Fats are solids at room temperature and are saturated compounds. They can be obtained from coconut.

However vegetable oils are liquids at room temperature and are highly unsaturated and are usually obtained from plants.

Samples of the oils include cotton seed oil, sim sim oil, groundnut oil, sunflower oil, palm oil and cashew nut oil, e.t.c.

11.2.2 Extraction of Animal Fat and Vegetable Oils

Animal Fat

The animal tissue is heated with water. The fat melts and floats on the surface of the hot water. The molten fat is then skimmed off into a separate container, allowed to cool until it solidifies.

Vegetable Oils

Using groundnut sees;

The dried seeds are roasted and then crushed to obtain a paste. The paste is added to water and the mixture boiled until oil floats on top of the mixture. The oil is then decanted off.

11.2.3 Preparation of Soap

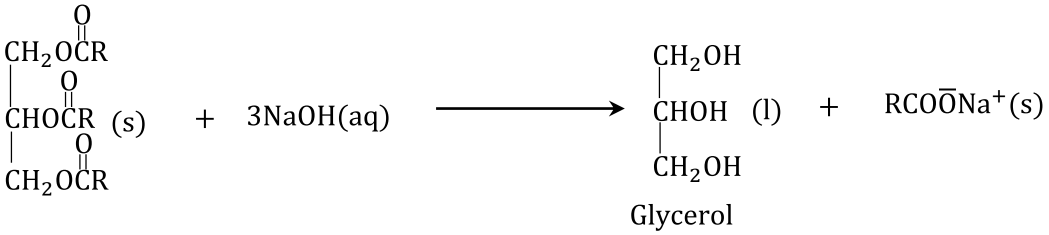
Soap is prepared by the process called saponification.

Procedure

The vegetable oil / animal fat is boiled with concentrated sodium hydroxide solution while stirring until the vegetable oil / fat completely dissolves.

The solution is cooled and concentrated Sodium Chloride (brine) is added to precipitate soap. The soap floats and is skimmed off. It can then be processed into bars or soap powder.

General Equation:



$$\begin{array}{l} CH_2O\overset{O}{\overset{\|}{C}}R \\ | \\ CHO\overset{O}{\overset{\|}{C}}R\ (s) \\ | \\ CH_2O\overset{O}{\overset{\|}{C}}R \end{array} + 3NaOH(aq) \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH\ \ (l) \\ | \\ CH_2OH \end{array} + RCO\bar{O}Na^+(s)$$

Glycerol

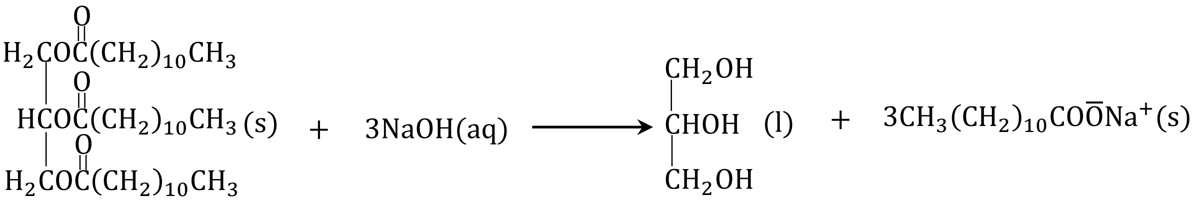
Where R is an alkyl group.

Note:

(a) Glycerol is a valuable bi-product because in the manufacture of nitroglycerin which is a constituent of many explosives. Glycerol is also used in manufacture of glyptal plastics.

(b) Sodium soaps have limited solubility in water and can be obtained as solid cakes. Whereas potassium soaps are more soluble and are used as gels in shampoos and shaving creams.

(c) If the glyceride used is specified then in the equation for the reaction R is specified. For example:



$$\begin{array}{l} H_2CO\overset{O}{\overset{\|}{C}}(CH_2)_{10}CH_3 \\ | \\ HCO\overset{O}{\overset{\|}{C}}(CH_2)_{10}CH_3\,(s) \\ | \\ H_2CO\overset{O}{\overset{\|}{C}}(CH_2)_{10}CH_3 \end{array} + 3NaOH(aq) \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH\ \ (l) \\ | \\ CH_2OH \end{array} + 3CH_3(CH_2)_{10}CO\bar{O}Na^+(s)$$

(d) If the mass of glyceride used is known, then we can calculate the mass of soap formed.

Worked Example

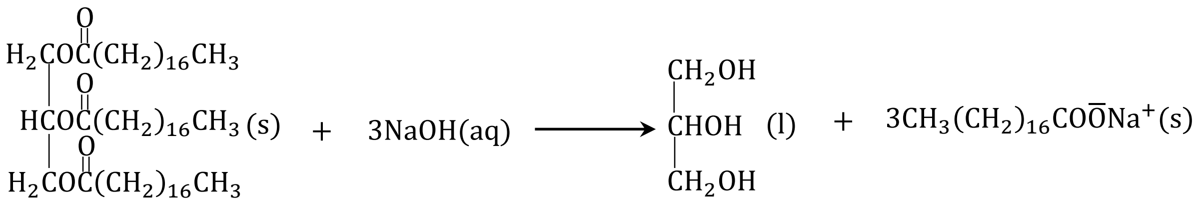
Soap was prepared from 96.65, of a fat mainly derived from octadecanoic acid,

(a) Write equation for the reaction leading to formation of soap.

(b) Calculate the mass of soap formed after complete reaction.

Answer

(a)



$$\begin{array}{l} H_2COC(CH_2)_{16}CH_3 \\ HCOC(CH_2)_{16}CH_3\,(s) \\ H_2COC(CH_2)_{16}CH_3 \end{array} + 3NaOH(aq) \longrightarrow \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array}(l) + 3CH_3(CH_2)_{16}CO\bar{O}Na^+(s)$$

(b)

$$\text{Molar mass of the ester} = (12 \times 19 \times 3) + (16 \times 2 \times 3) + [(37 \times 2) + 36] \times 1$$

$$= 890\text{g}$$

$$\begin{array}{c}\text{Number of moles} \\ \text{of ester used}\end{array} = \frac{96.95}{890} = 0.108933$$

1 mole of ester form 3 moles of soap.

$$0.108933 \text{ moles of ester form } \left(\frac{0.108933 \times 3}{1}\right) \text{ moles of soap}$$

$$= 0.326798 \text{ moles of soap}$$

$$\text{Molar mass of soap}(CH_3(CH_2)_{16}COONa) = (18 \times 12) + (35 \times 1) + (16 \times 2) + (23 \times 1)$$

$$= 306\text{g}$$

$$\text{Mass of soap formed} = 306 \times 0.326798$$

$$= \mathbf{100g}$$

11.2.4 The cleansing action of soap

Soap acts by lowering the surface tension between water an oil / grease or other insoluble material and also emulsifying them.

The soap molecule has both a long chain hydrocarbon chain which is non-polar and hydrophobic and a carboxylate group which is polar and hydrophilic. When soap is added to water, the hydrocarbon chain (alkyl group) is attracted carboxylate group is attracted to the water. This reduces the surface tension between water and the dirt. The oil / grease / dirt particles are removed and suspended in water (emulsified).

Note

(a) Soap is not effectively used in hard water because it forms insoluble calcium or magnesium salts (scum) leading to soap wastage.

$$2RCOONa(aq) + Mg^{2+}(aq) \longrightarrow (RCOO)_2Mg(s) + Na^+(aq)$$

Lather can only be formed when all the magnesium ions or calcium ions are completely precipitated as scum.

(b) Soap is not recommendable for continuous use when washing aluminium utensils. This is because soap is a salt of a strong base and a weak organic acid. Soap therefore undergoes hydrolysis in solution to form a week acid and hydroxide ions.

$$RCOO^-(aq) + H_2O(aq) \rightleftharpoons RCOOH(aq) + \bar{O}H(aq)$$

The hydroxide ions react with aluminium, to form aluminate ions and hydrogen. This causes wearing off of aluminum utensils.

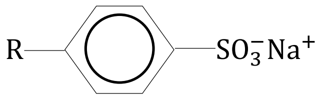
$$2Al(s) + 2\bar{O}H(aq) + 6H_2O(aq) \longrightarrow Al(OH)_4^-(aq) + 3H_2(g)$$

(c) Soaps with longer alkyl chains are more effective than those with shorter alkyl chains. For example sodium octadecanoate ($CH_3(CH_2)_{16}COONa$), also called sodium stearate, is more effective than sodium dodecanoate ($CH_3(CH_2)_{10}COONa$). This is because sodium octadecanoate has a longer non-polar, hydrophobick alkyl chain, which congregates more dirt than that in sodium dodecanoate.

11.2.5 Soapless Detergents

Soapless detergents are sodium salts of alkyl benzene sulphonic acids or sodium salts of long chain alkylhydrogensulphate.

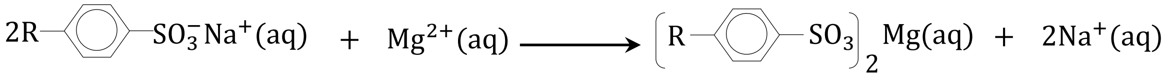
Their general structures are as shown below;



or $RCH_2OSO_3^-Na^+$

Where R is an alkyl group.

Unlike soaps, soapless detergents have the sulphonate group (in alkylbenzene sulphonates) and sulphate group (in alkyl sulphates) instead of the carboxylate group. Therefore detergents are effective even in hardwater because the corresponding magnesium or calcium salts formed are soluble.



$$2RCH_2OSO_3^-Na^+(aq) + Mg^{2+}(aq) \longrightarrow (RCH_2OSO_3)_2Mg(aq) + 2Na^+(aq)$$

Examples of common detergents include: Omo, Nomi, surf, etc.

By JOSEPH JOBS KAYIIRA AND HYPERCHEMIST

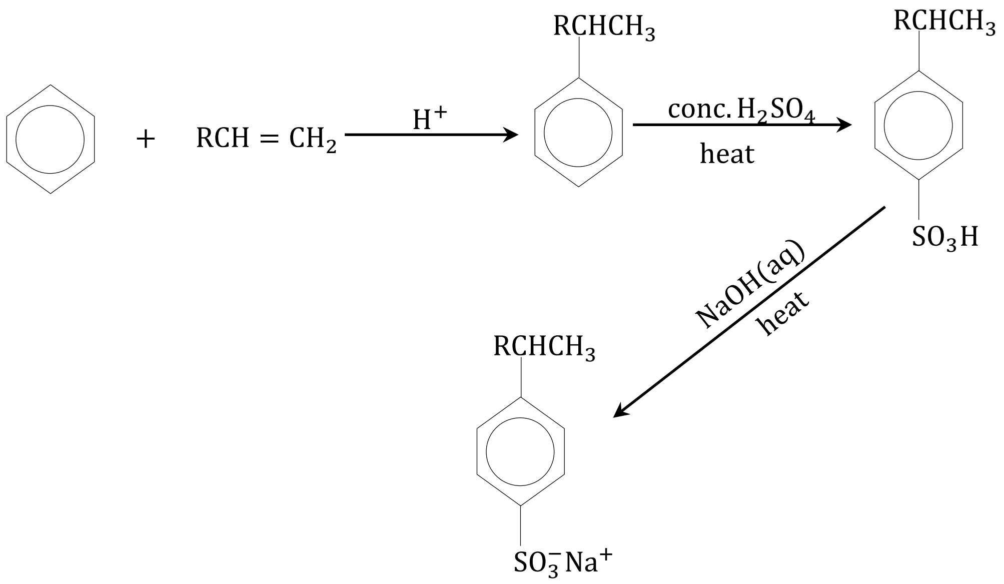
11.2.6 Preparation of Soapless detergents

(a) The most commonly used detergents are sodium salts of alkylbenzene sulphonic acids. These are made from:

(i) Non-branched, alkenes containing $12 - 18$ carbon atoms.

Procedure

Benzene is reacted with a long chain alkene in presence of an acid to form alkylbenzene. The alkylbenzene formed is heated with concentrated suplhuric acid to form an alkylbenzene sulphonic acid which is then heated with sodium hydroxide solution to form a detergent or alkylbenzene sulphonate.



(ii) **From an alcohol**

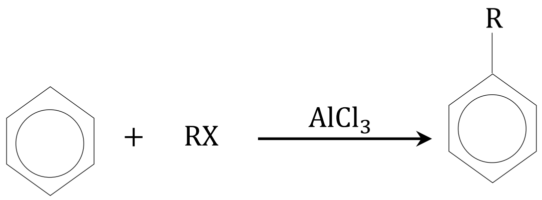
The long chain alcohol is heated with excess concentrated sulphuic acid to form an alkene.

$$RCH_2CH_2OH \xrightarrow[180^oC]{\text{conc. } H_2SO_4} RCH = CH_2$$

The alkene formed is then treated as in procedure (a)(i) above to obtain the detergent.

(iii) **From an alkylhalide**

Benzene is reacted with a long chain alkylhalide in the presence of aluminum chloride to form alkylbenzene. The alkylbenzene is then treated as in (a)(i) above until the alkylbenzene sulphonate is obtained.



(b) Detergents in the form of sodium salts of long chain alkylhydrogen sulphates are prepared by the procedure described below:

They are prepared from long straight chain alcohols.

A long chain alcohol (for example dodecanol) is reacted with cold concentrated sulphuric acid and the mixture stirred to form an alkylhydrogen sulphate (dodecylhydrogen sulphate for dodecanol). The alkylhydrogen sulphate is reacted with sodium hydroxide solution to form a detergent (a sodium alkylsulphate).

$$\begin{tikzcd}
CH_3(CH_2)_{10}CH_2OH \arrow[r, "\text{conc. } H_2SO_4"] & CH_3(CH_2)_{10}CH_2OSO_3H \arrow[d, "NaOH(aq)"] \\
 & CH_3(CH_2)_{10}CH_2OSO_3^-Na^+
\end{tikzcd}$$

Note

Some additives are added to detergents for specific uses. These include:

(i) Sodium sulphate – to increase the bulk of the detergent.

(ii) Inorganic phosphates – react with calcium ions in the dirt to form soluble complex calcium salts.

(iii) Sodium proxoborate – to act as bleaching agent.

11.2.7 The cleansing action of soapless detergents

Soapless detergents act in essentially the same way as soap does.

The soapless detergent molecule has an alkylbenzene group or a long alkyl chain which is non-polar and hydrophobic and a sulphonate group (for alkylbenzenesulphates) that is polar and hydrophilic. When a soapless detergent is added to water, the alkylbenzene group / alkyl chain is attracted to the oil grease/dirt and the sulphonate / sulphate group is attracted to the water. This reduces the surface tension between water and the dirt. The dirt particles are removed and suspended in water (emulsified).

Advantage of soaps over detergents

Soaps are biodegradble whereas the alkylbenzenesulphonates are only slowly biodegradable.

Disadvantage of soap

Soap forms scum with hard water leading to soap wastage.

Advantage of soapless detergents over soaps

Detergents can be used even in hard water because their Calcium and magnesium salts are soluble in water.

Disadvantages of detergents over soap

- Alkylbenzene sulpohonates are only slowly biodegradable hence pollute the environment.
- Detergents also contain inorganic phosphates which are nutrients for algae growth which deprives lakes and rivers of oxygen. This leads to suffocation of aquatic organisms hence death.

11.3 Polymers and Polymerization

A polymer is large molecular mass compound formed by repeatedly joining together many smaller molecules called *monomers*. The monomers are connected by covalent bonds. Polymerization is the process by which many small molecules are repeatedly joined together to form a large molecular mass compound.

There are fundamentally two types of polymerization. They include:

(i) Addition polymerization

(ii) Condensation polymerization.

11.3.1 Addition polymerization

This is the type of polymerization in which very many molecules of an unsaturated monomer join together to form a large molecule which has the same empirical formula as the monomer without loss of small molecules.

Examples of addition polymers include:

(i) Poly (ethene)

(ii) Poly(phenylethene); also called polystyrene

(iii) Poly(propene)

(iv) Poly (chloroethene); also called polyvinylchloride (PVC)

(v) Poly (methyl2-methylpropenoate); also called Perspex.

(vi) Poly (tetrafluroethene); also called PTFE or Teflon or Fluon.

(vii) Natural rubber and synthetic rubbers.

(viii) Poly (propenonitrile); also called Orlon.

Details about structure, preparation, properties and uses f each of the addition polymers are described below:

(i) Poly (ethene)

Poly (ethene) is also called Polythene. Its monomer is ethene $(H_2C = CH_2)$ and the polymer has the structure $-(CH_2CH_2)_n -$.

There are two types of poly (ethene).

(a) Low density poly (ethene)

This type has a low softening point (about 120°C). It is formed by compressing ethene at a high pressure of 1500 atmospheres and a temperature of 200°C in a very small amount of oxygen. This is called the ICI high pressure process.

Equation

$$nH_2C = CH_2 \xrightarrow[1500\text{atm}, 200^{\circ}\text{C}]{O_2 \text{ initiator}} \left[CH_2CH_2 \right]_n$$

Low density poly (ethane) is used;

- As a film for packaging and for coating.
- As a covering for cables.
- For making plastic bags.
- For making toys.

(b) High density polythene

This type has a higher softening point (about 130°C). It is made by passing ethene into an insert solvent (usually an aromatic hydrocarbon) containing a suspension of triethylaluminium and titanium(IV) chloride as catalyst.

A dilute acid is added after polymerization and polyethene filtered off. This is called the Zeigler process.

$$nH_2C = CH_2 \xrightarrow[\text{(ii) dilute acid}]{\substack{\text{(i) } (CH_3CH_2)_3Al + TiCl \\ /\text{Aromatic hdrocarbon}}} \left[CH_2CH_2 \right]_n$$

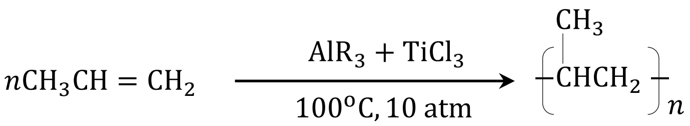
High density poly(ethene) is more rigid than low density poly(ethene) and is used:

- For making kitchen ware, food boxes, bowls and buckets
- Making good quality mouldings including bottles, etc.

(ii) Poly(propene)

Poly(propene) can be used in place of poly(ethene) due to the advantages it has over poly(ethene). It is lighter, tougher and has a higher melting point than polyethene. Poly(propene) has a high tensile strength that enables it to be pulled to make tough fibres.

Poly(propene) is made by propene under pressure into an inert solvent (heptane) which contains a trialkylaluminium and a titanium compound.



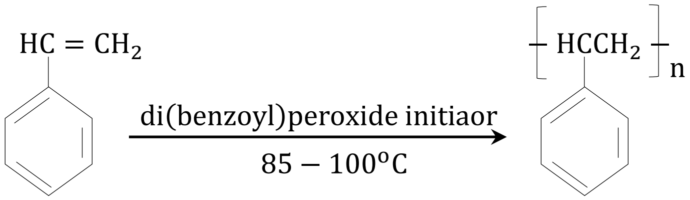
$$n\mathrm{CH_3CH=CH_2}\xrightarrow[100^{\circ}\mathrm{C,\,10\,atm}]{\mathrm{AlR_3+TiCl_3}}\left[\overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{CH}}\mathrm{CH_2}\right]_n$$

The polymer is used for:

- Making ropes, carpets and bottles.
- Making packaging materials.

(iii) Poly(phenylethene)

Poly(phenylethene) is also called polystyrene. It's free radical polymerization is done by using di(benzoyl) peroxide as an initiator at a temperature of 85-100°C

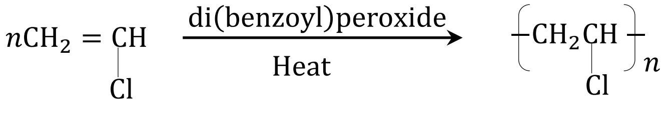


The uses of poly(phenylethene) include:

- Making thermal and electrical insulators
- Making light weight packaging materials
- Making household goods like egg boxes
- Making lining material for refrigerators
- Making theatrical properties
- For decorative purposes etc.

(iv) Poly (chloroethene)

It is altos called polyvinyl chloride (PVC). Poly (chloroethene) is formed by heating chloroethene in an inert solvent with di(benzoyl) peroxide to initiate polymerization.



$$n\mathrm{CH_2=}\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}\xrightarrow[\mathrm{Heat}]{\mathrm{di(benzoyl)peroxide}}\left[\mathrm{CH_2}\underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{CH}}\right]_n$$

PVC is a very tough polymer. A plasticizer is usually added to soften it. The polymer is also easy to colour.

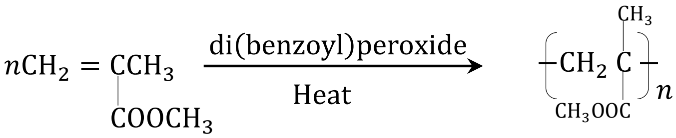
It is also resistant to weathering, fire and chemicals and a good electrical insulator.

Uses of Polyvinyl Chloride (PVC)

- Manufacture of plastic raincoats, curtains, furniture coverings, water piping and guttering, and floor coverings.
- As an insulator for cables.
- Manufacture of artificial leather e.g. car upholstery.
- Making gramophone records, etc.

(v) Poly (methyl 2-methylpropenoate)

This polymers is also called Perspex or Diakon (in its powder form). It is formed in the same way as poly(phenylethene).



$$nCH_2=\underset{\displaystyle COOCH_3}{C}CH_3 \xrightarrow[\text{Heat}]{\text{di(benzoyl)peroxide}} \left[CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3OOC}{C}}\right]_n$$

Perspex is a light, strong and transparent plastic.
It has a variety of uses although most frequently used as replacement for glass.

The uses include:

- Packaging
- Making aeroplane windows, lenses and corrugated roof lights.

(vi) Poly (tetrayluoroethene) – (PTFE)

This is also called Teflon or Fluon. It is made by heating tetrafluolroethene under pressure in the presence of ammonium peroxosulphate as a catalyst.

$$nF_2C=CF_2 \xrightarrow{(NH_4)_2S_2O_8\ cat.} \left[CF_2CF_2\right]_n$$

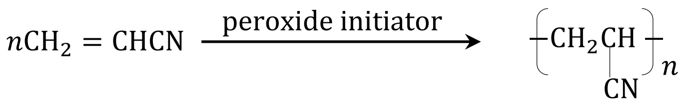
Teflon has a high softening point of 327°C and very stable at temperatures in excess of 400°C. It is also highly resistant to chemicals and has a low coefficient of friction.

Uses of Teflon include:

- Making seals and gaskets.
- Surface coating for cooking equipment.
- Making low friction bearings.

(vii) Poly(properionitrile)

This is also called Polyaerylonitrile or Orlon. The equation for its formation from the monomer (propenonitrile) is as shown below:



$$n\mathrm{CH_2 = CHCN} \xrightarrow{\text{peroxide initiator}} \left[\mathrm{CH_2}\underset{\mathrm{CN}}{\underset{|}{\mathrm{CH}}}\right]_n$$

The polymer is used for making clothes, blankets and carpets.

(viii) Rubber

There are two forms of rubber namely;

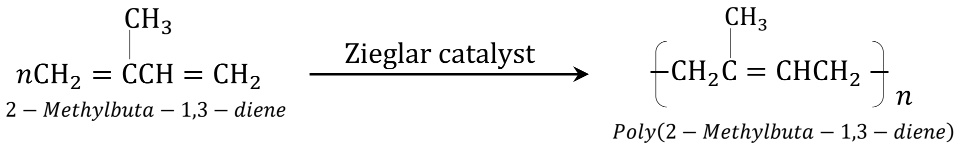
- Natural rubber.
- Artificial / synthetic rubber

(a) Natural rubber

Raw rubber is obtained from latex, which is an emulsion of rubber particles in water found in the bark of many tropical and sub-tropical trees.

The latex extrudes from the bark when the tree is cut. The raw rubber is the coagulated by adding ethanoic acid.

Natural rubber is also called polyisoprene and is a polymer of the monomer whose IUPAC name is 2-Methylbuta-1, 3-diene (also called isoprene).



$$\underset{2-Methylbuta-1,3-diene}{n\mathrm{CH_2 = \overset{\overset{\mathrm{CH_3}}{|}}{C}CH = CH_2}} \xrightarrow{\text{Zieglar catalyst}} \underset{Poly(2-Methylbuta-1,3-diene)}{\left[\mathrm{CH_2\overset{\overset{\mathrm{CH_3}}{|}}{C} = CHCH_2}\right]_n}$$

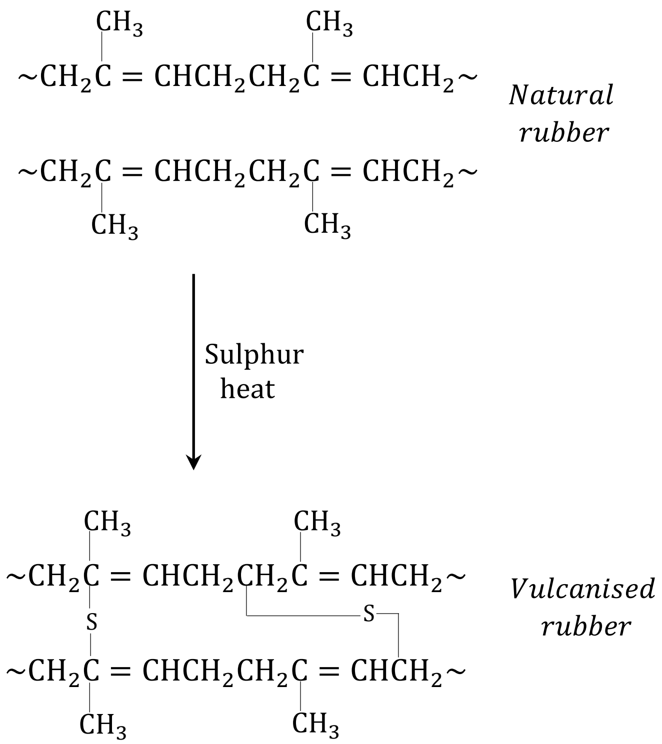
Natural rubber is not strong enough and not an elastic enough material for use. It softens and becomes sticky on heating. On cooling it becomes hard and brittle. These problems can be largely solved by a process called *vulcanization.*

Vulcanization of rubber

The raw rubber is heated with up to 8% sulphur. The sulphur forms cross-linkages between neighbouring polymeric chains of rubber. Accelerators of vulcanization are used to increase the rate of combination and to allow the process take place at a lower temperature.

The accelerators may be organic or inorganic

Illustration



$$\sim CH_2\overset{\overset{\textstyle CH_3}{|}}{C} = CHCH_2CH_2\overset{\overset{\textstyle CH_3}{|}}{C} = CHCH_2\sim \qquad \sim CH_2\underset{\underset{\textstyle CH_3}{|}}{C} = CHCH_2CH_2\underset{\underset{\textstyle CH_3}{|}}{C} = CHCH_2\sim$$

Vulcanized rubber is better for use than natural rubber because;

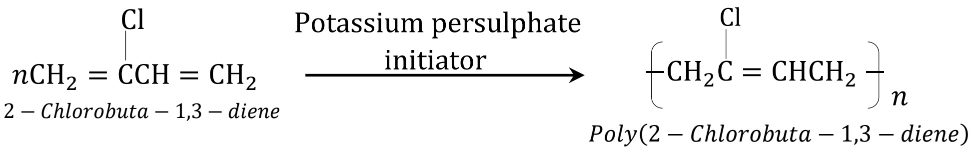
- It has a greater tensile strength.
- It is more durable
- It is more elastic.

(b) Synthetic rubber

Synthetic rubber, also called neoprene is the polymer whose IUPAC name is poly (2-chlorobuta-1, 3-diene), and is made from the monomer 2-chlorobuta-1, 3-diene.

Neoprene rubber is resistant to organic solvents and is strong.

However, it is more expensive to produce than natural rubber. During polymerization, potassium persulphate is used as a catalyst.



$$\underset{2-Chlorobuta-1,3-diene}{nCH_2 = \overset{\overset{\textstyle Cl}{|}}{C}CH = CH_2} \xrightarrow[\text{initiator}]{\text{Potassium persulphate}} \underset{Poly(2-Chlorobuta-1,3-diene)}{\left(CH_2\overset{\overset{\textstyle Cl}{|}}{C} = CHCH_2 \right)_n}$$

Uses of rubber

- Making coverings for underwater cables.
- Making golf balls.
- Making car tyres.

- Making shoe soles.
- Making waterproof boots.
- Making hoses and gaskets etc.

11.4.2 Condensation Polymerization

This is the type of polymerization in very many molecules of two different bifunctional monomers join together to form a large molecule with loss of small molecules such as water, ammonia, methanol, carbon dioxide and hydrogen chloride.

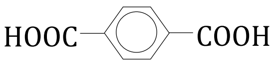
Examples of condensation polymers include:

(i) Terylene; also called Daeron or Fortrel
(ii) Nylon-6, 6
(iii) Nylon-6, 10
(iv) Bakeute
(v) Melamine
(vi) Proteins
(vii) Lipid
(viii) Polyurethanes
(ix) Silicones
(x) Wool

Details about structure, preparation, properties and uses of some of the condensation polymers are described below:

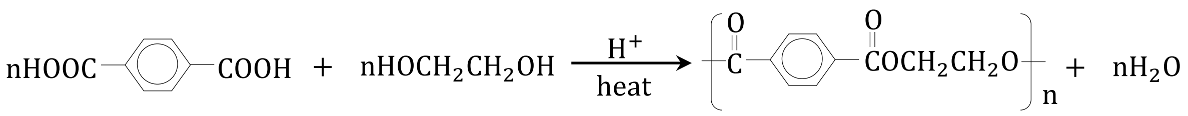
(i) Terylene

Terylene is also known as Daeron or fortrel. It is polyester formed by the interaction between a dicarboxylic acid and a diol. Terylene is formed from two monomers;

(a) Benzene – 1,4 – dicarboxylic acid, 

(b) Ethane – 1,2 – diol, $HOCH_2CH_2OH$

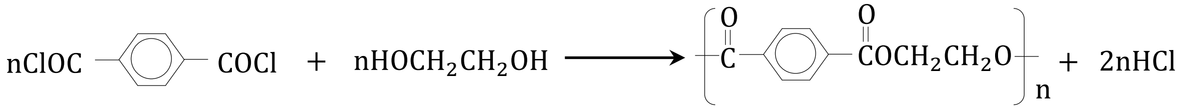
<u>Equation</u>



An acid catalyst is used in the above reaction and water molecules are lost.

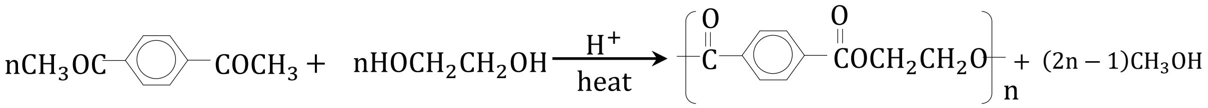
Instead of benzene-1, 4- dicarboxylic acid, Benzene-1, 4-dioyldichloride can be used and ethane-1, 2-diol.

Equation



In this reaction, no catalyst is required. Molecules of hydrogen chloride are lost.

Another method is to use a methyl ester of benzene-1, 4-dicarboxylic acid which is known as Dimethylbenzene -1-4- dicarboxylate and ethane-1, 2-diol. This reaction also requires an acid catalyst.



Methanol molecules are lost.

Polyesters have good thermal and chemical stability although they can be hydrolysed by alkalis. They can make permanent creases in fabrics.

Uses of polyesters e.g. Terylene

- Making clothes
- Making ropes
- Making safety belts

(ii) Nylon-6,6

Nylons belong to a class of polymers called polyamides.

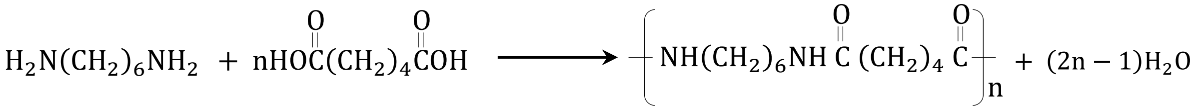
Nylon-6, 6 is called so because it is made from two monomers, each of which has 6 carbon atoms.

The monomers are

(a) Hexane – 1,6 – diamine, $H_2N(CH_2)_6NH_2$

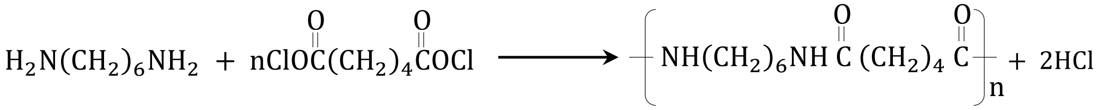
(b) Hexane – 1,6 – dioic acid, $HOOC(CH_2)_4COOH$

Equation



$$H_2N(CH_2)_6NH_2 + nHO\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OH \longrightarrow \left[NH(CH_2)_6NH\,\overset{O}{\overset{\|}{C}}\,(CH_2)_4\,\overset{O}{\overset{\|}{C}} \right]_n + (2n-1)H_2O$$

Similarly, hexane-1, 6-dioyldichloride can be used instead of the dioic acid as monmer.



$$H_2N(CH_2)_6NH_2 + nClO\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OCl \longrightarrow \left[NH(CH_2)_6NH\,\overset{O}{\overset{\|}{C}}\,(CH_2)_4\,\overset{O}{\overset{\|}{C}} \right]_n + 2HCl$$

In this case, hydrogen chloride is eliminated instead of water.

Nylon-6, 6 is greatly versatile and its manufacture is done at a low cost. It is also insoluble in common solvents, has a melting point of 263°C, strong, tough, rigid and resistant to chemical attack.
It is used for:

- Making fishing nets, bottles, ropes and clothing.
- Making sutures, gears, unlubricated bearings and tarpaulins.

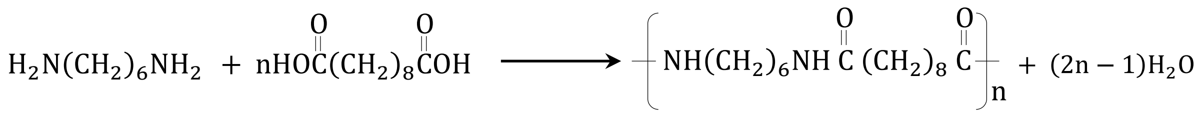
(ii) Nylon-6,10

Nylon-6,10 is called so because it is formed from a diamine with 6 carbon atoms a dioic acid or a dioyldichloride with 10 carbon atoms. Therefore the monomers are;

(a) Hexane – 1,6 – diamine, $H_2N(CH_2)_6NH_2$

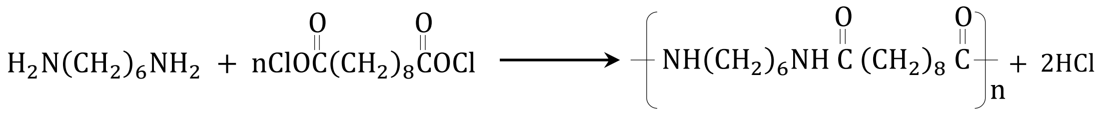
(b) Decane – 1,10 – dioic acid, $HOOC(CH_2)_8COOH$

<u>Equation</u>



$$H_2N(CH_2)_6NH_2 + nHO\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}OH \longrightarrow \left[NH(CH_2)_6NH\,\overset{O}{\overset{\|}{C}}\,(CH_2)_8\,\overset{O}{\overset{\|}{C}} \right]_n + (2n-1)H_2O$$

Similarly, hexane-1, 10-dioyldichloride can be used instead of the dioic acid as monmer.



$$H_2N(CH_2)_6NH_2 + nClO\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}OCl \longrightarrow \left[NH(CH_2)_6NH\,\overset{O}{\overset{\|}{C}}\,(CH_2)_8\,\overset{O}{\overset{\|}{C}} \right]_n + 2HCl$$

In this case, hydrogen chloride is eliminated instead of water.

Nylon-6, 10 has properties similar to Nylon-6, 6. Nylon-6,10 is useful in making synthetic bristles.

(iv) Bakelite

This is a condensation polymer formed from phenol and methanol.
It is used for making switches, electrical plugs, radio cases, fuse holders and doors handles.

11.4.3 Differences between addition and condensation polymerization.

Addition polymerization	*Condensation Polymerization*
Involves one type of monomer	Involves two different types of monomers
All atoms of the monomer form part of the polymer	Some atoms of the monomers are lost in form of small molecules
Empirical formula of polymer is the same as that of monomer	Empirical formula is different from the constituent monomers

Monomers usually contains at least a cabon-carbon double bond	Monomers do not have carbon-carbon double bonds.
Molecular weight of polymer is an integral multiple of the molecular weight of monomer	Molecular weight of the polymer is not an integral multiple of molecular weight of any of the monomers.

11.4.4 Classes of Polymers

Polymers can be classified as natural or synthetic.

(a) Natural Polymers

These are naturally occurring polymers not made by man. Examples are summarized in the table below:

Type of natural polymer	*Examples*	*Monomer(s)*	*Uses*
Addition natural polymers	Natural rubber	2-Methylbuta-1, 3-diene	Making car tyres, shoe sols, golf balls, etc.
Condensation natural polymers	Wool	Amino acids	Making clothings, blankets, woolen carpets etc.
	Cotton	Cellulose	making clothes, bed sheets, paper, etc,
	Silk	Amino acids	Making clothes, beddings, etc.
	Starch	Glucose	Manufacture of ethanol, as animal food, etc.

(b) Synthetic polymers

These are man-made polymers. Examples are summarized in the table below:

Type of artificial polymer	*Examples*	*Monomer(s)*	*Uses*
Addition synthetic polymers	Poly(ethane)	Ethene	Packaging, making plastic bags, buckets, etc.
	Poly (phenylethene) (polystyrene)	Phenylethene	Making packaging materials, egg boxes, etc.
	Poly (chloroethene) (PVC)	Chloroethene	Plastic rain coats, curtains, insulator for cables, etc.

Condensation synthetic polymers	Perspex	Methyl2-methyl – propenoate	Making lenses, aeroplane windows, corrugated rooflights etc.
	Teflon	Tetrafluroethene	Making seals and gaskets etc
	Synthetic rubber	2-Chlorubuta-1, 3-diene	Making car tyres, shoe soles, golf balls, etc.
	Terylene (Daeron)	Ethane-1, 2-diol & Benzene-1, 4-dicarboxylic acid	Making clothes, ropes, safety belts, etc
	Nylon-6, 6	Hexane-1, 6-diamine Hexane-1, 6-dioic acid	Making fishing nets, bottles, ropes, clothings, sutures, etc.
	Nylon 6, 10	Hexane-1, 6-diamine Decane-1, 10-dioic acid	
	Bakelite	Phenol & methanol	Making switches, electrical plugs, fuse holders etc.
	Melamine	Methanal & melamine	Making table ware, plates, etc

11.4.5 Fibres

Some polymers can be classified as fibres. Fibres are polymers which can be made into thin, strong threads that can made into thin, strong threads that can be spun and woven together.

Fibres can also further be classified as natural or synthetic fibres. Example are summarized below. Their uses, properties and monomers from which they are derived have already been discussed.

Natural fibres	*Synthetic fibres*
Wool	Nylon-6, 6
Cotton	Nylon-6, 10
Silk	Poly(propenonitrile)

These fibres are used in the textile industry

11.4.6 Plastics

A plastic is a polymerized organic solid substance of a high molecular mass which at sometime in its manufacture can be shaped to flow.

Plastics can be moulded into required shapes and for manufacture of a wide range of substances.

Plastics are widely used to manufacture many substances because of its properties. These include toughness, resistance to water and corrosion, ease of moulding, colour change and insulation to electricity and heat.

The properties of plastics can be modified by the following substances:

(i) Plasticisers

These compounds for example esters of benzene 1, 2, - dicarboxylic acids with long chain alcohols are added to PVC to make it softer and a more easily worked material.

(ii) Dyes and pigments

These are added to give plastic colour.

(iii) Filler

This increases the bulk of the plastic, making it less expensive without altering its desirable properties.

There are two types of plastics namely; ***thermosoftening plastics*** and **thermosetting plastics.**

(a) Thermosoftening plastics

These are also called thermoplastics. These are plastics which become soft when heated hence can be remoulded. Thermoplastics easily soften on heating because they consist of long polymer chains held by weak intermolecular forces which require only small changes in temperature to overcome. Examples of thermoplastics include:

(i) Poly(ethane)
(ii) Polyvinyl chloride
(iii) Poly (propene)
(iv) Perspex

(b) Thermosetting Plastics

These are also called thermosets. These are plastics which contain a three dimensional network of bonds and are moulded during the polymerization stage of their manufacture and cannot be softened to be remoulded on heating. These polymers require very strong heating to bring about any form of chemical change. This is because the three dimensional structure in them has chains that are cross-linked and held by strong covalent bonds.

Examples of thermosets include:

(i) Bakelite
(ii) Melamine
(iii) Polyurethanes
(iv) Vulcanized rubber
(v) Expoxyresins
(vi) Glyptal resins, etc.

Differences between thermoplastics and thermosets

Thermoplastics	*Thermosets*
Have low melting point	Have high melting
Soften on heating and can be reshaped	Not easily softened on heating hence cannot be reshaped
Polymeric chains held by weak vander waal's forces of attraction	Polymeric chains are held by strong covalent bonds
They have linear polymeric chains	The polymeric chains are cross-linked
Thermoplastics can be recycled	Thermosets cannot be recycled
Are soft and flexible	Are hard and brittle

Effects of Plastics on the environment

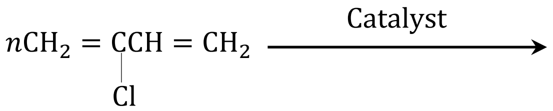
Plastics are non-bio degradable hence their poor disposal to the environment leads environmental pollution. When some plastics are burnt, they form toxic gases like hydrogen chloride from PVC, hydrogen cyanide from poly(propenonitrile). These problems can most effectively be overcome by recycling.

End of topic questions

1. Ethanol can be formed by fermentation of molasses.
   - (a) (i) Name two other raw materials from which ethanol can be produced by fermentation using molasses.
     - (ii) Write equations to show how crude ethanol formed in (a) above.
   - (b) Describe how 100% (absolute) ethanol can be produced from crude ethanol formed in (a) above.
   - (c) Write equation(s) to show each of the following compounds could be obtained from ethanol.
     - (i) Polythene
     - (ii) Ethoxyethane.
2. Vegetable oils have great economic and social importance
   - (a) (i) Explain what is meant by the term vegetable oils.
     - (ii) Name two sources of vegetable oils.
     - (iii) Describe how vegetable oil can be obtained on a large scale from one of the sources you have named in (a) (i) above. (Technical details are not required)
   - (b) (i) State the name given to the reaction leading to the formation of soap from oil.
     - (ii) Write a general equation for the formation of soap from oil.
     - (iii) Outline how soap is manufactured. (Technical details not required).

3. Complete the following equations and give the IUPAC name of the major organic

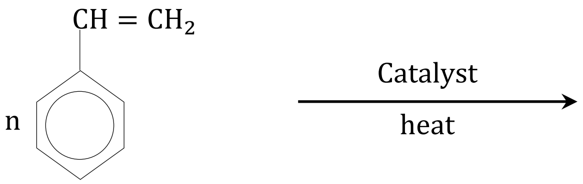
(i)



$$n\mathrm{CH_2 = C(Cl)CH = CH_2} \xrightarrow{\text{Catalyst}}$$

(ii) $n\mathrm{CH_3CH = CH_2} \xrightarrow{\text{Catalyst}}$

(iii)



4. (a) (i) State the main difference between fats and vegetable oils.
   (ii) Name any one source of vegetable oils.
   (b) (i) Define the term soap.
   (ii) State a chemical name of any soap you know.
   (c) (i) Briefly describe how soap can be prepared from any vegetable oil.
   (ii) When 9.5g of an oil derived from $\mathrm{C_{15}H_{31}COOH}$ (hexadecanoic acid) was boiled with sodium hydroxide, soap was formed. Calculate the mass of soap formed.
   (iii) State two uses of the byproduct formed in (iii) above.
   (d) (i) Explain how soap removes dirt from a fabric.
   (ii) State the difference between a soap and a soapless detergent.
   (iii) State one advantage and one disadvantage of a soapless detergent over soap.

5. (a) Distinguish between soap and soapless detergent.
   (b) Using equations only describe how an alkylbenzene sulphonate can be prepared from dedecan-1-ol.
   (c) Briefly explain the cleansing action of a soapless detergent.
   (d) State one:
   (i) advantage of soap over a detergent.
   (ii) disadvantage of soap over detergent.

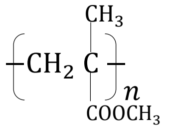
6. Soap was prepared form a fat derived from hexadecanoic acid,
   (i) Explain briefly how soap is formed from the fat.
   (ii) Write the equation leading to formation of soap.
   (iii) Calculate the mass of soap formed.

7. (a) Name any two sources of vegetable oils.
   (b) Describe briefly how vegetable oil can be obtained on a large scale from one of the sources you have named in (a).
   (c) Soap was prepared from 19.0g of oil formed between hexadecanoic acid, and glycerol.

(i) Write equation for the reaction leading to formation of soap.

(ii) Calculate the mass of soap formed.

8. Perspex is a polymer of structure:



$$\left[CH_2 \overset{CH_3}{\underset{COOCH_3}{C}} \right]_n$$

(a) Name the reaction leading to formation of Perspex.

(b) Write the structure and give the IUPAC name of the monomer used to manufacture Perspex.

(c) A solution containing 5.5g of Perspex in 1dm^3 of benzone has an osmotic pressure of 6.796×10^{-2} atmospheres at 25°C. Calculate the:

(i) Molecular mass of perspex.

(ii) Value of n

(iii) State one application of Perspex

9. (a) Explain what is meant by the term "condensation polymerization".

(b) Nylon-6, 10 can be made by reacting Hexane-1, 6-diamine and decane dioyldichloride.

Write the structural formula of:

(i) Hexane-1, 6-diamine

(ii) Decane dioyldichloride

(iii) Nylon-6, 10

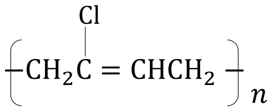
(c) State one use of nylon-6, 10.

10. The osmotic pressure of a solution containing 1.4g of a polymer per 100cm3 of a solution is 1200Nm^{-2} at 25°C.

(a) Calculate the relative molecular mass of the polymer.

(b) If the molecular mass of the monomer is 28, determine the number of monomers in the polymer.

11. (a) Neoprene, is a synthetic polymer which has the following structure



$$\left[CH_2\overset{Cl}{C} = CHCH_2 \right]_n$$

(i) Name the type of polymerization reaction which leads to formation of neoprene.

(ii) Name of the monomer from which neoprene is formed.

(b) When 350g of the monomer was polymerized 9.89 x 10^{-2} moles of neoprene was formed. Calculate the relative molecular mass of neoprene.

(c) State one use of neoprene.

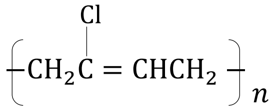
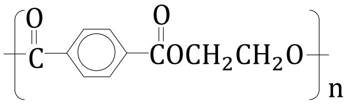
12. (a) Define the term osmotic pressure.

(b) A polysaccharide has the formula ( ). A solution containing $5.00 gdm^{-3}$ of the sugar has an osmotic pressure of $7.12 \times 10^2 Nm^{-2}$ at 20°C. Find the value of n.

(c) State two assumptions made in (b) above.

13. (a) Distinguish between thermoplastics and thermosetting plastics.

(b) For each of the following polymers write the structure(s) of the monomer(s) from which they were synthesized.

Polymer	**Structure of monomer**
 $\left[CH_2\overset{Cl}{\overset{\vert}{C}} = CHCH_2 \right]_n$	
	

(c) A solution containing 1.00g of polyphenylethene in $100 cm^3$ of benzene is found to have an osmotic pressure of 59B at 27°C. Calculate the average relative molecular mass of polyphenylethene.

14. Chloroethene, hexane-1, 6-dioic acid and hexane-1, 6-diamine are monomers for two polymers.

(a) Define the term polymer

(b) Write the structural formulae of:

    (i) Chloroethene

    (ii) Hexane-1, 6-dioic acid

    (iii) Hexane-1, 6-diamine

(c) Write the:

    (i) Structural formula of the polymer and type of polymerization undergone by chloromethane.

    (ii) Name and structural formula of polymer formed from hexane-1, 6-dioic acid and hexane-1, 6-diamine.

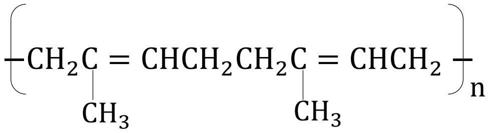
(d) State one use of each of the polymers in (c) above.

(e) Name one natural polymer formed by the same reaction as:

    (i) The polymer in (i) above.

    (ii) The polymer in (ii) above.

15. Natural rubber has the following structure



$$\left[CH_2\underset{\displaystyle CH_3}{\underset{|}{C}} = CHCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}} = CHCH_2 \right]_n$$

(a) Write the structure and name of the monomer of natural rubber.

(b) (i) Name the type of polymerization by which natural rubber is formed.

(ii) Give a reason for your answer in (b) (i) above.

(c) When 135g of the monomer was polymerized, 584 x 10^{-3} moles of natural rubber was formed. Calculate the relative molecular mass of natural rubber.

16. (a) Explain what is meant by the terms:

(i) Addition polymerization

(ii) Condensation polymerization

(b) Natural rubber is a natural polymer formed by addition polymerization. Write the structural formula and name of the monomer of natural rubber.

(c) One stage involved in the processing of rubber is vulcanization.

(i) Describe how vulcanization is carried out.

(ii) What is the effect of vulcanization on the properties of rubber?

(iii) Give one use of rubber.

(d) Write the structural formula and name of the monomer of synthetic rubber.

(e) Polyphenylethene is another polymer formed by addition polymerization.
Write equations to show how polyphenylethene is prepared starting form benzene.

(f) Nylon-6, 6 is also a polymer formed by condensation polymerization.

(i) Write the structural formula(e) and name(s) of the monomer9s0 of nylon6, 6.

(ii) Write the equation leading to formation of nylon-6, 6.

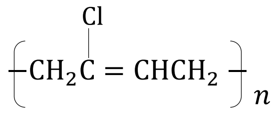
17. (a) Teflon, which is used in making non-stick utensils is an addition polymer whose synthesis is represented by the equation below:

$$nF_2C = CF_2 \xrightarrow[(NH_4)_2S_2O_8\ \text{catalyst}]{H_2O\ \text{under pressure}} \left[CF_2CF_2 \right]_n$$

What is meant by an addition polymer?

(b) 3.0g of Teflon were dissolved in 2 litres of solvent X at 25C. The osmotic pressure of the resultant solution was 247.9Nm^{-2}. Calculate the value of n is the formular of Teflon.

18. (a) Neoprene rubber is a polymer with the structure.



$$\left[CH_2\overset{Cl}{\overset{|}{C}} = CHCH_2 \right]_n$$

(i) Name the type of reaction by which neoprene is formed.

(ii) Write equation leading to formation of neoprene rubber. (Indicate condition(s) for the reaction)

(b) A solution containing 28.76gdm^{-3} of neoprene rubber had an osmotic pressure of 0.23 atmosphere at 27°C. Determine the,

(i) molecular mass of the polymer.

(ii) number of monomers in the formula of the polymer.

19. (a) Soap can be prepared from a vegetable oil or an animal fat.
Briefly describe how an oil can be extracted form a natural source.

(b) (i) Briefly describe how soap is prepared.

(ii) Write the equation for the reaction leading to formation of soap.

(iii) State one advantage and one disadvantage of using soap.

(iv) Briefly explain the cleansing action of soap.

(c) (i) Distinguish between soap and a non-soapy detergent.

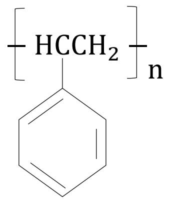
(ii) Starting from duodecan-1-ol, write equations to who how you would prepare a soapless detergent.

(d) (i) Distinguish between addition and condensation polymerization.

(ii) Write equations to show how the polymers, Perspex, Terylene and nylon-6, 6 are formed.

(e) State the difference between thermosetting and themosoftening plastics.

20. The structure of a polymer, G, is,



The osmotic pressure of a solution containing 5.5gdm-3 of G in benzene is 106.39 Pa at 20°C.

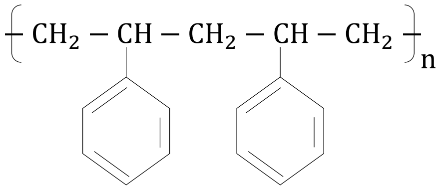
(i) Calculate the relative molecular mass of G.

(ii) Determine the number of monomers that formed polymer G.

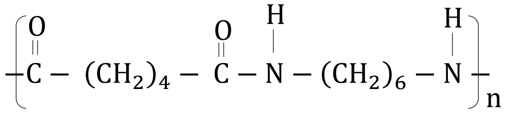
21. (a) Distinguish between addition and condensation polymerization.

(b) The structural formulae of polymers; P, Q, R and S are given below.

P :

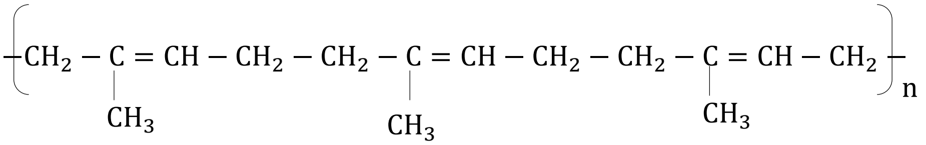


Q :



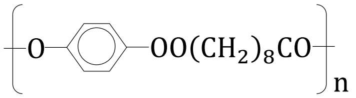
$$\left[\overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}}\right]_n$$

R :



$$\left[CH_2 - \underset{CH_3}{\underset{|}{C}} = CH - CH_2 - CH_2 - \underset{CH_3}{\underset{|}{C}} = CH - CH_2 - CH_2 - \underset{CH_3}{\underset{|}{C}} = CH - CH_2\right]_n$$

S :



In the table below, write the structural formula of the monomer(s) in each case and name the type of polymerization that lead to the formation of each polymer.

	Structural formula of monomer(s)	**Type of polymerization**
P		
Q		
R		
S		

(i) Give use of Q

(ii) R exists as natural rubber. State how it is treated before putting it to industrial use.

22. Nylon-6, 6 is a synthetic polymer made by condensation polymerization.

(a) Explain the terms:

(i) Synthetic polymer

(ii) Condensation polymerization

(b) (i) Write the structure of nylon-6, 6.

(ii) Give one example of a natural polymer formed by the same type of reaction as Nylon-6, 6.

(iii) State the monomer of the polymer given in b (ii) above.

(c) (i) Name one soapless detergent.

(ii) Using available materials, write equations to how how the detergent named in (b) (i) above is prepared.

23. (a) (i) An organic compound Q, consists of 38.7% Carbon, 51.613% oxygen and the rest being hydrogen. The density of Q is 2.7662g per litre at s.t.p. Calculate the empirical formula of Q.

(ii) Determine the molecular formula of Q.

(b) (i) Q is oxidized by nitric acid to form a dioic acid and then carbon dioxide and water.

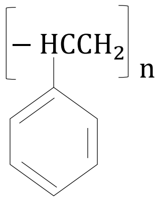
(ii) Explain why Q boils at 197°C but ethanol boils at 75°C.

(c) (i) Q reacts with a dioic acid K to form a polyester. Name K and draw the structure of the polyester.

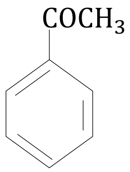
(ii) Name one use of the polyester in (c) (i) above.

24. Write equations to show how the following conversions can be effected.

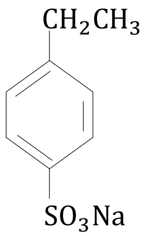
(a)



from

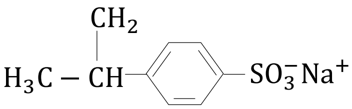


(b)



from ethyne

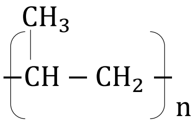
(c)



$H_3C-\overset{CH_2}{\overset{|}{CH}}-C_6H_4-SO_3^-Na^+$ from benzene

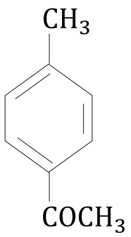
(d) Nylon – 6,6 from Cyclohexanol

(e) Propanol to



$\left[\overset{CH_3}{\overset{|}{CH}} - CH_2 \right]_n$

(f)



to Terylene