CHEMISTRY LEVEL 4C

(CHM 415115)

POLYMER CHEMISTRY

THEORY SUMMARY

&

REVISION QUESTIONS

(CRITERION 7)

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CHEMISTRY (LEVEL 4C)
POLYMER CHEMISTRY

(CRITERION 7)

INTRODUCTION:

Polymers are often described as 'macromolecules', i.e. compounds in which the molecules are extremely big and have M_r values of tens of thousands.
Some of the naturally occurring polymers include:

- Cellulose (a polymer of glucose e.g. cotton, wood,.......)
- Starch (also a polymer of glucose e.g. potatoes, bread, cereals, ...)
- Proteins (polymers of amino acids)

Synthetic polymers, often incorrectly referred to as "plastics" are everywhere around us and are used in practically all walks of life. New polymers with specialised properties are being designed and developed all the time including innovative polymers for use in clothing manufacture, transport vehicles, medicine, sports equipment and the construction industry.

A few familiar examples of synthetic polymers that affect our lives practically every day are:

- Plastic wrap for storage of foods
- Plastic utensils, containers, buckets and bowls
- Non-stick surfaces for pots and pans
- Car components (seats, bumpers, dash boards, tyres, belts, ...)
- Ropes
- Home insulation and packing foams
- Paints and glues
- chairs, desks, kitchen appliances.....
- Boat hulls, yacht sails, ...
- Electrical insulation
- IT equipment etc.....

The term 'plastics' is commonly used in place of 'polymers' although the word plastic is more correctly used to describe the physical property of a material being easily moulded into a given shape.

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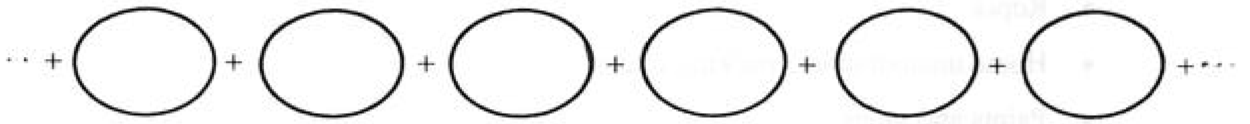
PROPERTIES OF POLYMERS:

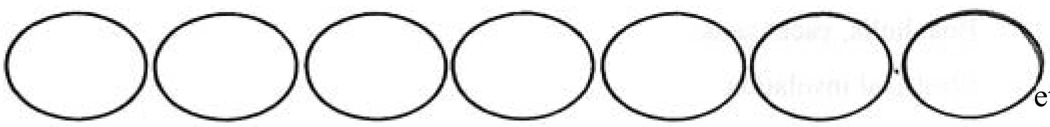
(i) Most but not all polymers are based on molecules involving very long and often branched chains of ***carbon*** atoms. Our emphasis in this unit of study will be on these carbon based polymers.
Remember that carbon's electron configuration is C = 2)4). The four outer (valence) electrons give carbon the capacity to form 4 covalent bonds per atom and thus form four linkages to other atoms including carbon itself.
(ii) The existence of carbon based polymers is due to the fact that carbon is able to form strongly bonded straight and branched chains which may comprise thousands of linked atoms in a stable structure. Carbon's capacity to form stable ring structures leads to further complexity in the possible structures of polymer molecules.
(iii) The main features of carbon based polymers are:

- they are covalent molecular substances.
- they involve the element carbon bonded with (usually) hydrogen and other non-metallic elements such as halogens (F, Cl,……), oxygen, nitrogen, ……
- being covalent molecular compounds, all electrons are localised and thus (most) polymers are non-conductors of electricity.
- the polymer molecules are not all the same size although the average chain length of the molecule plays a key role in determining the properties of the polymer.
- polymer molecules can be thought of as molecular 'chains' formed by joining together simple, small molecules called 'monomers' which are the links that form the chain.
- The chemical process of the joining of monomers to produce the polmer chain is called polymerisation.
- polymerisation involves covalent bond formation between monomer molecules

In the following diagram, each of the ovals represents a small carbon based molecule that we will identify as the **MONOMER**.



These ovals are the individual links that will form the polmer chain as represented below.



etc...

When the polymer forms, the chain linking or propagation process can be effectively controlled so as to determine the average chain length formed.
e.g. 10 million monomer molecules could be used to form various polymer chains of sizes:

200 chains of average size = 50 thousand
500 chains of average size = 20 thousand
1000 chains of average size = 10 thousand etc……….

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TYPES OF POLYMERS:

All polymers have several properties in common due to the characteristic of having such long chains and the corresponding intermolecular (van der Waal's or dispersion) forces that exist between the chains.
Polymers are often classified by their plastic or non-plastic properties when they are heated.
The two broad categories of polymers are:

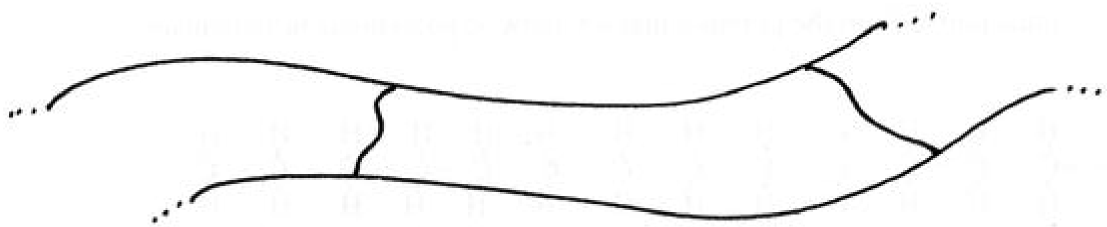
1. THERMOPLASTIC POLYMERS
2. THERMOSETTING POLYMERS

THERMOPLASTIC POLYMERS

These are polymers that when heated, become soft, pliable and often shrink in size.
Typical examples of thermoplastic polymers are cling-wrap, plastic shopping bags and icecream containers. They are typically low melting and flexible.
When these polymers are heated, some of the weak intermolecular forces are broken and the molecules are thus able to move more freely so the polymer becomes soft i.e. "plastic".
The strong covalent bonds within the carbon chains do not break and so the polymer doesn't decompose or break down.
The softening property of thermoplastics when heated enables manufacturers to mould these polymers into various shapes such as bottles, buckets, toys,....
The moulding process is done whilst the polymer is hot and 'plastic' and then when it cools down, the shape of the desired article is fixed.

THERMOSETTING POLYMERS

These are much more rigid polymers that when heated char (turn black) and start to burn.
The bonding in these polymers corresponds more closely to the bonding we encountered in covalent network solids.
Therosetting polymers have strong covalent bonding extending throughout the structure and thus will resist melting when heated.
Further heating eventually causes bonds within the polymer chains to break and hence the polymer decomposes and will char forming a black carbon residue.
This greater strength associated with thermosetting polymers occurs due to there being ***crosslinking*** molecules between the chains as shown below.



Examples of thermosetting polymers are laminates (kitchen bench tops e.g. 'laminex'), knobs on saucepans, ropes, light switches, ...

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POLYMERISATION REACTIONS

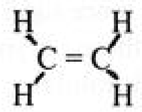
We are now going to see how the ***linking process*** between monomer molecules takes place.
This reaction is called **POLYMERISATION**
The two main types of reactions for making polymers are:

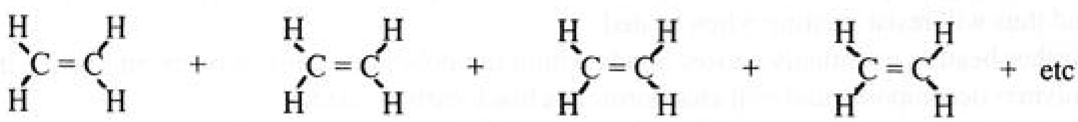
1. ADDITION POLYMERISATION – this is typically the reaction process leading to the formation of **thermoplastic polymers.**
In the year 11 Physical Sciences course, this is the only polymer-isation process that is studied.

2. CONDENSATION POLYMERISATION – this is typically the reaction process leading to the formation of **thermosetting polymers.**
In the year 12 Chemistry course you are expected to be familiar with both reaction types.

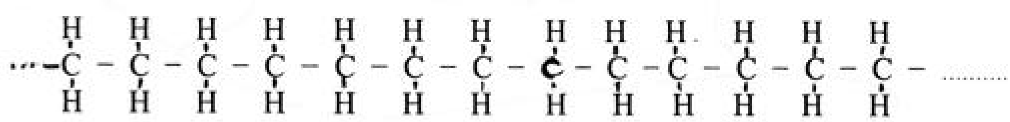
ADDITION POLYMERISATION

This type of polymerisation reaction usually occurs where the monomer unit has (at least) one carbon/carbon double bond; i.e. the monomer is an UNSATURATED hydrocarbon.
The process of chain propagation (lengthening) takes place by way of the carbon/carbon double bond (C=C) being converted to a carbon/carbon single bond.
To start the linking process a catalyst is normally used.
For example consider the monomer ethene (C_2H_4).





When a catalyst is added to start ("initiate") the polymerisation reaction, the monomer units join to form the polymer that we know as polyethene or polythene;   i.e.



The carbon chain in polythene could entail as many as 15 000 carbon atoms!

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TYPES OF POLYTHENE

Depending on the polymerisation conditions of temperature, pressure and type and amount of catalyst, the properties of the final polythene polymer will vary.
e.g.
At 1.0 atmosphere pressure and 300°C using a metal oxide catalyst, the polymer formed has straight chains with no significant level of chain branching occurring.
These chains can pack closely together and give rise to the form of polythene that we call **HIGH DENSITY POLYTHENE**.
This form of polythene is used to make milk and cream containers.

At 2000-3000 atmospheres pressure and around 300°C using oxygen as the catalyst, the polymer formed has branched chains.
These branched chains cannot pack closely together and give rise to the form of polythene that we call **LOW DENSITY POLYTHENE**.
This form of polythene is used to make cling wrap and garbage bags etc.......

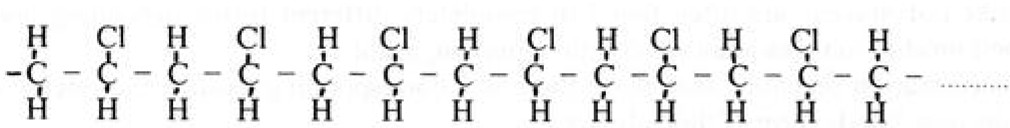
NAMING ADDITION POLYMERS

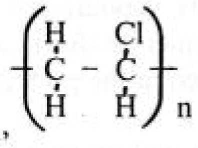
The normal naming procedure for addition polymers is to write "**POLY**" as a prefix and then the monomer's name afterwards with this monomer name sometimes in brackets.
e.g.

MONOMER	POLYMER
ethene	poly(ethene) or polythene
chloroethene	poly(chloroethene) or PVC
tetrafluoroethene	polytetrafluoroethene or TEFLON
styrene	polystyrene
propene	poly(propene) or polypropylene

ADDITION POLYMER REPEAT UNITS

As the structures for polymers involve vast numbers of atoms, it is much easier to represent the polymer molecule using a shorthand which indicates the 'repeat unit' or the structure of the polymer that is repeated throughout the polymer chain.
e.g. the structure for the polymer poly(chloroethene) is:



This can be represented in shorthand by  where n = a large number

This abbreviation is called the 'repeat unit'.

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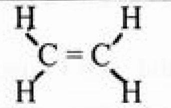
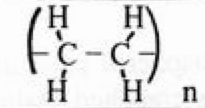
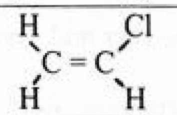
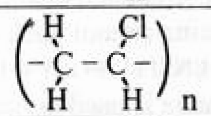
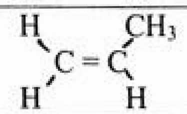
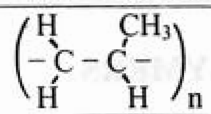
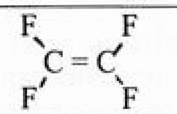
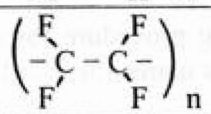
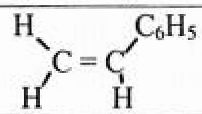
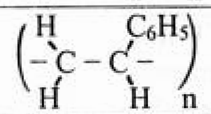
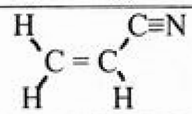
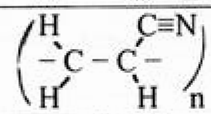
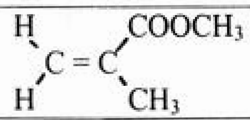
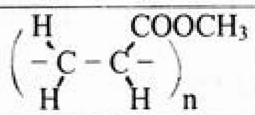
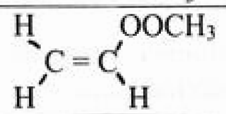
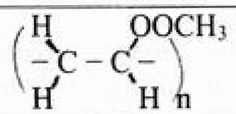
COMMON ADDITION POLYMERS

Although you are not expected to memorise the following polymeric structures, some represent polymers that are commonly encountered in every day life.
In a number of cases, the names for the polymers are the old fashioned names and are not the IUPAC systematic names unfortunately.

MONOMER	MONOMER'S STRUCTURE	POLYMER REPEAT UNIT	POLYMER'S NAME
ethene			polyethene
chloroethene			poly(chloroethene)
propene			poly(propene)
tetrafluoroethene			poly(tetrafluoroethene) "teflon"
styrene			polystyrene
acrylonitrile			polyacrylonitrile
methylmethacrylate			polymethylmethacrylate perspex
vinyl acetate			poly(vinylacetate) PVA

Polymers like polystyrene are often found in completely different forms depending upon whether their production was associated with a foaming agent.
As the polymerisation reaction takes place there is a corresponding exothermic release of energy as the new bonds form in the polymer.
By including a volatile (easily vapourised) compound in with the monomer, the heat of reaction will cause the polymer to form a foam. This occurs with the production of polystyrene foam which is used in the protective packing for cameras, stereo, video and IT equipment.
If ***no*** foaming agent is present, polystyrene forms as a higher density solid as is found with perspex windows and ballpoint (Bic) pen cases.

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COPOLYMERS

Copolymers are made by the combination of more than one monomer. This often results in very different properties for the copolymer compared with the monomers when polymerised individually.
This process is used to manufacture polymers for specific purposes. By using the desired properties of several polymers chemists are able to make polymers that have suitable characteristics for the intended function.

For example, some polymers are hard and some others maybe soft and sticky. By blending certain quantities of these monomers before polymerising, chemists can form a copolymer that has just the desired degree of hardness.

e.g. poly(methyl methacrylate) paints form a hard film whereas poly(butyl acrylate) forms coatings that are soft. Combining these two monomers in a special ratio gives a desired outcome such that many water based acrylic paints are copolymers of poly(methyl methacrylate) and poly(butyl acrylate).

Consider two different monomers **X** and **Y**. These may be combined in the formation of two types of copolymer where the sequence of monomer units is either random or definitely ordered.; i.e.

RANDOM COPOLYMERS

–X–Y–Y–X–X–Y–X–X–X–Y–Y–X–Y–Y–X–X–Y–X–X–X–Y–Y–X–

BLOCK COPOLYMERS

–Y–Y–Y–Y–Y–Y–X–X–X–X–X–X–X–Y–Y–Y–Y–Y–Y–X–X–X–X–

Icecream containers are usually made from poly(propene). To make the lids less brittle at low temperatures involved, they are made from a random copolymer based on the monomers ethene and vinyl acetate.

Telephones and car radiator grills are made from a copolymer based on the three monomers; styrene, acrylonitrile and butadiene.

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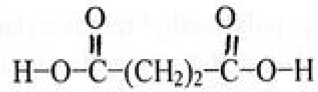
CONDENSATION POLYMERS

Typically, **addition polymers** are formed where there is a **single monomer** molecule which possesses a carbon/carbon double bond (C=C). This carbon/carbon double bond is the key property leading to chain propagation.
However, condensation polymers form chains by a completely different mechanism where there are two monomers which are are bifunctional.
Bifuntional means that the molecule has two functional groups present.

Examples of **BIFUNCTIONAL** molecules that we will consider are those with:

- two **ALCOHOL** groups per molecule e.g. hexan-1,6-diol $H{-}O{-}(CH_2)_6{-}O{-}H$
- two **AMINE** groups per molecule e.g. 1,6-diaminohexane $H_2N{-}(CH_2)_6{-}NH_2$
- two **CARBOXYLIC ACID** groups per molecule e.g. butan-1,4-dioic acid



- amino acids (molecules possessing both a carboxylic acid (COOH) functional group as well as a amine (NH_2) functional group.

As these molecules have effectively two reactive ends to their molecules they can undergo reactions with two other molecules and if these other molecules in turn have two reactive ends, then reactions will lead to a chain propagation process.

A simple analogy is to imagine one of the monomers being a group of girls and the other monomer being a group of boys. Having two hands allows each boy to hold two girls by the hand and similarly each girl can hold two boys' hands forming a chain;

……….−girl−boy−girl−boy−girl−boy−girl−boy−girl−boy−……….

This chain forming process with the girls and boys is only possible because each person has TWO hands!

Condensation polymers form because the ***two reactive sites*** on each molecule can link to two reactive site on the other molecule.
The linking of the monomers usually comes about with the elimination of a small molecule such as water.
This is typically the case in the formation of polyesters, an example of which is shown in the next section.

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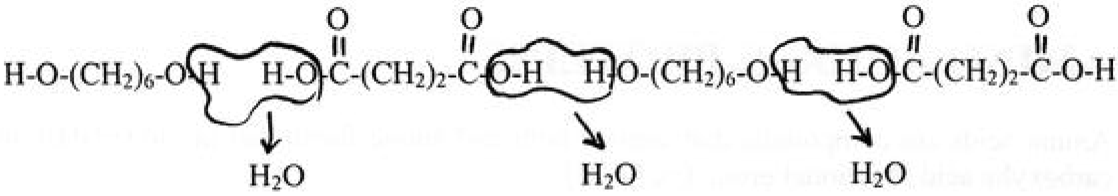
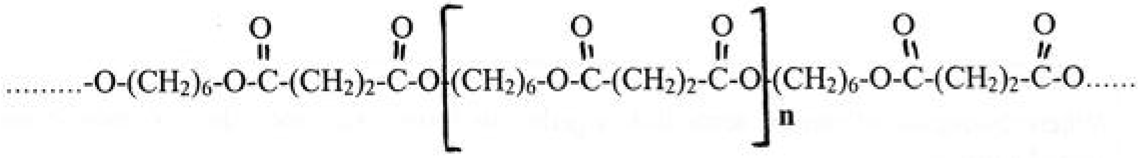
POLYESTERS

The formation of a polyester is associated with the polymer formed between an alcohol with two OH functional groups (i.e. a “diol”) and a carboxylic acid with two COOH groups (i.e. a “dioic acid”)
e.g.
Consider the reaction between hexan-1,6-diol and butan-1,4-dioic acid.



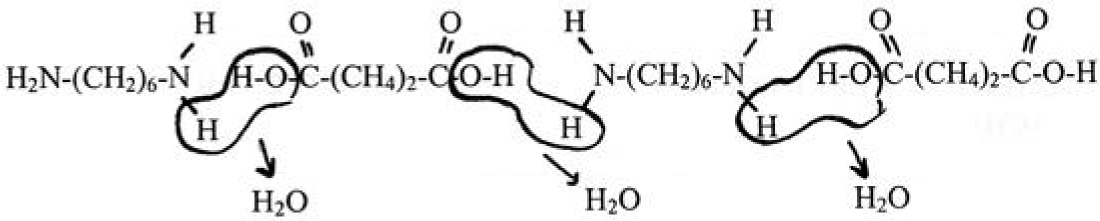
The elimination of water (H_2O) by reaction between the alcohol and carboxylic acid functional groups results in the linkage occurring and the chain growth. This is esterification and thus the polymer formed is described as a **POLYESTER**.
The chain growth will continue to form an extensive molecule with M_r of many thousands.

The chain is best represented by way of its “repeat unit”; i.e.

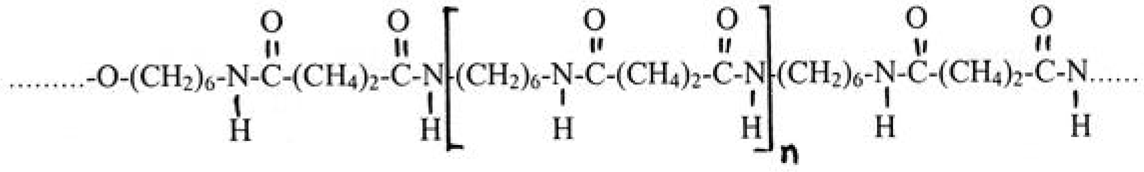


POLYAMIDES

The formation of a polyamide is associated with the polymer formed between an amine with two NH_2 functional groups (i.e. a “diamine”) and a carboxylic acid with two COOH groups (i.e. a “dioic acid”)
e.g. Consider the reaction between hexan-1,6-diamine and hexan-1,6-dioic acid.



The chain is best represented by way of its “repeat unit”; i.e.



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PEPTIDE LINK

The linkage involving the $-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-$ is called a PEPTIDE link!

AMINO ACIDS & PROTEINS

Amino acids are compounds that contain both and amine functional group ($-NH_2$) and a carboxylic acid functional group ($-COOH$).

They are generally of the structure: $H_2N-\underset{R}{\underset{|}{CH}}-COOH$ where R is a carbon based side chain.

The presence of these two functional groups gives amino acids the capacity to form multiple linkages as described in the polyamide section on page 11.

When thousands of amino acids link together to form a polymer, the polymer formed is called a protein.

Proteins are polymers comprised of linkages of thousands of amino acid molecules joined together but there are only 20 amino acids commonly found in nature. Some of the 20 amino acids are shown below together with their structures and abbreviated names.

AMINO ACID	ABBREVIATION	STRUCTURE
glycine	Gly	$H_2N-\underset{H}{\underset{|}{CH}}-COOH$
alanine	Ala	$H_2N-\underset{CH_3}{\underset{|}{CH}}-COOH$

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AMINO ACID	ABBREVIATION	STRUCTURE
valine	Val	$H_2N-CH-COOH$ $CH_3-CH-CH_3$
phenylalanine	Phe	$H_2N-CH-COOH$ $CH_2-C_6H_5$
aspartic acid	Asp	$H_2N-CH-COOH$ CH_2-COOH
lysine	Lys	$H_2N-CH-COOH$ $CH_2-(CH_2)_3-NH_2$
serine	Ser	$H_2N-CH-COOH$ CH_2-OH
glutamic acid	Glu	$H_2N-CH-COOH$ CH_2-CH_2-COOH

By forming peptide links, the amino acids can join to form polymers which are a special group of polyamides called proteins.
Because of the complexity of drawing the protein structures, biochemists often use their abbreviated name to show the sequencing of amino acids in a given protein.

e.g. A section of a protein polymeric molecule could be shown as:

-Ser-Phe-Ala-Gly-Ala-Asp-Lys-Ser-Ala-Glu-Val-Phe-Ala-

In the process of digestion, we take in proteins in our food and they are broken down into the amino acids by a process called hydrolysis in the presence of organic catalysts (enzymes).

These amino acids are then transported in our blood to sites in the body where they are combined in the correct sequence to form the desired protein.
Proteins are of two main types:

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FIBROUS PROTEINS:
These are proteins associated with the structural materials such as:

- KERATIN found in skin, fingernails, horns, hair, feathers,...
- COLLAGEN found in tendons, cartilage, hides,...
- FIBROIN found in silk

GLOBULAR PROTEINS:
These are water soluble proteins e.g. haemoglobin (red blood cells), insulin, myoglobin in muscles, enzymes, antibodies, ...

REVIEW QUESTIONS ON POLYMERS

Q1. How would you test a polymer in the laboratory to determine whether it was a thermoplastic polymer or whether it was a thermosetting polymer?

Q2. What is the effect on the physical properties of a polymer if there is a significant degree of 'cross-linking' between polymer chains? Explain why this occurs.

Q3. Which of the two main categories of polymer would be most suitable for utilising as the handle of an electric kettle? Explain your reasoning.

Q4. The coating on electric cables is commonly made from 'plastics'. What are three desirable properties of these polymers that make them suitable for this purpose?

Q5. Give two examples of (i) thermoplastic polymers (ii) thermosetting polymers.

Q6. If a given monomer has a molar mass of 42, and the addition polymer formed from this monomer has an average molar mass of 28 000, what is the average number of repeat units in each polymeric chain of this polymer? **(667)**

Q7. Consider the monomer 1,2-dichloroethene which is made to undergo addition polymerisation by the action of an initiating catalyst.
Sketch a section of the polymer chain formed and indicate the polymer's repeat unit.

Q8. Sketch three consecutive repeat units for the polymer poly(1-bromoprop-1-ene).

Q9. Photocopying drums are coated with a very thin (0.01 mm) thick layer of a light sensitive addition polymer called poly(vinyl carbazole).
Use the internet or otherwise to find the structure for vinyl carbazole.
What special properties of poly(vinyl carbazole) make it ideal for usage in photocopiers?
Why does a photocopy feel warm when it first comes out of the photocopier?

Q10. Why can ethene act as a monomer but ethane cannot?

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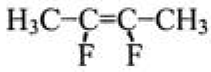
Q11. Draw a section of the polymer chain made from the monomer having the structure:



Q12. Wise sportsmen and sportswomen wear mouthguards if their sport involves contact. When they are custom made, a mouthguard is placed in near boiling water and then moulded to fit the person's mouth. Once it has cooled it retains the desired shape of the person's mouth. Suggest the polymer type employed and the chemistry involved.

Q13. What type of polymers are associated with the building materials used on kitchen benches such as laminex? Why is this type preferred for this purpose?

Q14. Consider a monomer containing two separate carbon/carbon double bonds (C=C) such as butadiene which has the IUPAC name butan-1,3-diene.

$$H_2C = CH - CH = CH_2$$

When this monomer is polymerised, what special bonding properties are likely to occur in the polymer formed?

Q15. About 60% of the rubber used in the world is synthetic rubber made from random copolymerisation of styrene and butadiene.
Representing the styrene as **A** and the butadiene as **B**, sketch a section of the random copolymer that is synthetic rubber.

Q16. Draw the repeat unit for the condensation polymer formed between:
(a) 1,6-diaminohexane and pentan-1,5-dioic acid
(b) butan-1,4-diol and pentan-1,5-dioic acid

Q17. For humans, what are are main sources of dietary protein?

Q18. One of the listed amino acids is glutamic acid. It can be neutralised with sodium hydroxide to form monosodium glutamate (MSG) which was used commonly as a flavour enhancing agent especially in Chinese food.
Write the chemical equation for this neutralisation reaction.

Q19. A given protein has a relative molecular mass (M_r) of approximately 2.25 million. If the average amino acid used to form this protein has a M_r of 135, how many amino acid units are present (approx) in the protein?

Q20. When two amino acids link together they form a dipeptide. Draw the structural formula for the dipeptide formed between:
(i) alanine and valine
(ii) glycine and lysine
(iii) phenylalanine and glutamic acid.