Chem Factsheet

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Polymers

To succeed in this topic you need to:
- **Be able to recall the features of polymers as represented in this Factsheet.**
- **Have a thorough knowledge of the importance of polymers.**
- **Be able to manipulate structural formulae to show monomer, polymer and repeating units**

After working through this Factsheet, you will:
- **Have revised the chemistry relating to polymers that is required for AS and A2 chemistry modules.**
- **Have a reference paper with you as you start to work through questions about polymers.**

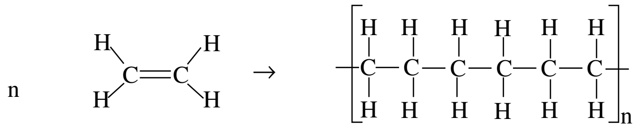
Please check your specification carefully to see which areas of polymer chemistry you need to study.

What are polymers?

Polymers are very large, covalently bonded molecules that are made up of repeating units. Many polymers are synthetic but a great many are natural substances. Avoid using words like 'plastic' in your answers when you actually mean 'synthetic polymers'. The word 'plastic' describes a property of many polymers as well as other substances, which, when a force is applied to them, alter their shape - like 'plasticine' or uncooked pastry.

Addition polymers

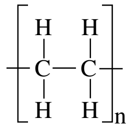
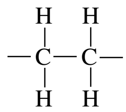
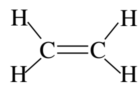
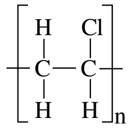
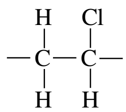
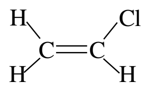
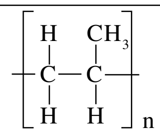
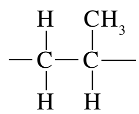
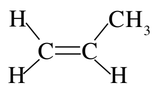
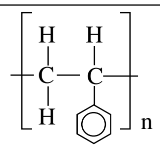
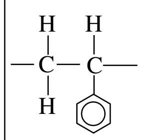
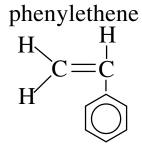
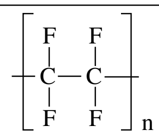
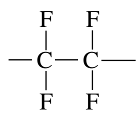
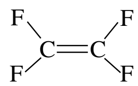
The simplest way that polymers are formed is by a process called addition polymerization. All addition polymers are based on the structure of ethene. In such reactions, the double bond between the carbon atoms becomes a single bond. In most cases this is a **free radical reaction** in which a free radical **initiates** the reaction which is then **propagated,** ending in a **termination** step (see **Factsheet 16** Organic Chemistry II Reactions 1). Free radical reactions are difficult to control and need extreme conditions of pressure and temperature. Catalysts involving transition metals may enable a more controllable reaction to take place. In the case of poly(ethene) the catalyst used is the **Ziegler-Natta catalyst** (which uses titanium chloride in a system with triethylaluminium).



many monomer molecules **one** polymer molecule

(n is a very large number, usually from 100 to 10,000)

The following table gives the names and structures of common addition polymers. As you can see, there is a pattern of structure, all based on the ethene model - **unsaturated** molecules polymerise to form **saturated** molecules.

Addition Polymer	Structure	Repeating Unit	Monomer Structure
poly(ethene) 'polythene'			ethene 
poly(chloroethene) 'PVC'			chloroethene 
poly(propene) 'polypropylene'			propene 
poly(phenylethene) 'polystyrene'			phenylethene 
poly(tetrafluoroethene) 'P.T.F.E' Teflon®			tetrafluoroethene 

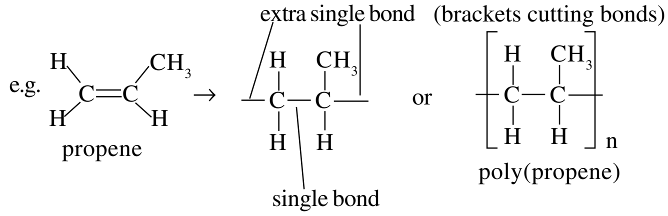
Please note that many polymers go by more than one name - for instance, the IUPAC (International Union of Pure and Applied Chemistry) give official names for poly(ethene), poly(propene) etc., but they also have common names like 'polythene' and 'polystyrene'. In exam answers, use the correct chemical name for any compound that you are discussing. If you mention a polymer and can only think of its common name, use speech marks to show that you recognise that this is not the chemical name. Sometimes polymers are referred to by trade names like Teflon®; if you use these names, use a '®' symbol to show that you recognise this.

> ***Exam Hint:*** *you are sometimes asked to draw polymer structures - do this in the way shown above using brackets, and making sure that lines representing bonds extend through them. The letter 'n' indicates that this unit is repeated for an unstated number of times.*

Often an examination question will ask:

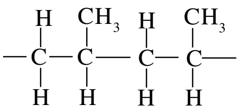
- **Given the structure of the monomer, show the structure of the repeating unit (or the structure of the polymer formed from it).**

1. Rewite the structure of the monomer replacing the C=C with C–C
2. Draw two extra single bonds, one on each C atom



Monomer **Repeating Unit** **Polymer**

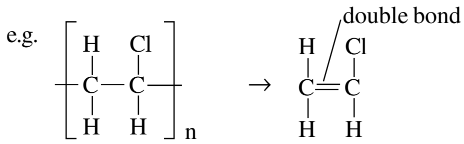
Note that if the question asks for a structure showing two repeating units



- **Given the structural formula of the polymer, draw the structural formula of the monomer from which it has been formed**

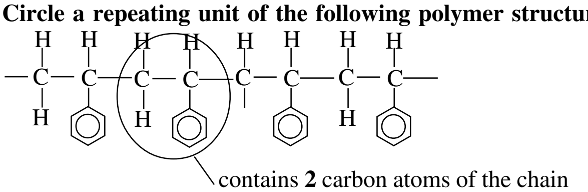
Procedure is the reverse of the above:
Rewrite the structure of the polymer with:

1. A C=C in the place of C–C
2. Eliminate the single bonds extending from the two carbon atoms
3. Eliminate the brackets and the 'n'



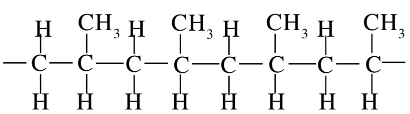
poly(chloroethene) Chloroethene
Polymer **Monomer**

- **Circle a repeating unit of the following polymer structure:**



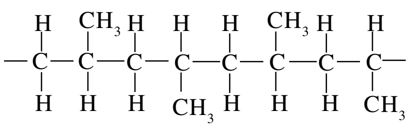
The geometry of polymer chains
With addition polymers it is possible to have different arrangements of groups within the chain. Using poly(propene) as an example (CH_3 is the 'substituent group').

Isotactic form



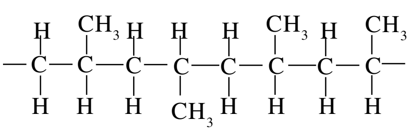
All the methyl (CH_3) groups are above the plane of the molecule.

Syndiotactic form



The methyl groups **alternate** above and below the plane of the molecule.

Atactic form



The methyl groups are **randomly** situated along the chain.
Note that these forms exist with the **larger** substituent groups. If the substituent group is very small then full rotation about the C–C bond can occur.

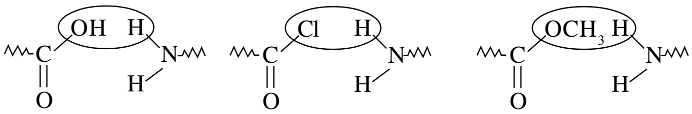
Monomers are saturated molecules, the C=C bonds making them very reactive. The polymers, however, contain all C–C bonds in the chain and are, therefore, very **unreactive**. This inertness contributes to many of their uses **but** gives rise to environmental problems. They are **non-biodegradable** - disposal is difficult

Condensation polymers
Many polymers seem to have a more complex structure than addition polymers and these are usually prepared by adding two molecules via a **condensation reaction**.

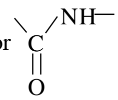
The two monomer molecules both have **two** functional groups. They react alternately, eliminating a simple molecule, to give a polymer chain.

Polyamides

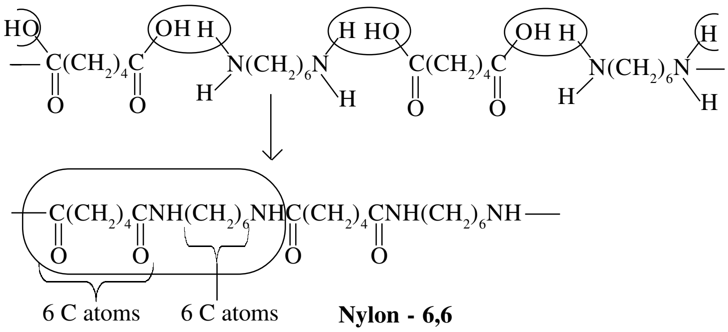
One molecule is a **diamine**
e.g. $H_2N(CH_2)_6NH_2$, hexane-1,6-diamine
The other molecule is a **dicarboxylic acid**.
e.g. $HOOC(CH_2)_4COOH$, hexanedioic acid.
(Note that a diacyl chloride or a dimethyl ester can be used instead).



(carboxylic acid) (acyl chloride) (methyl ester)
H_2O eliminated HCl eliminated CH_3OH eliminated

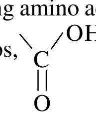
The 'molecules' are linked by –CONH– or 

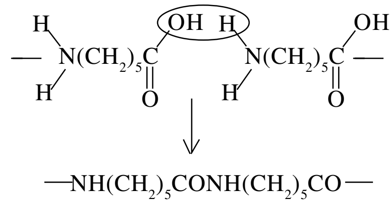
an **amide bond**, or **peptide link**



Repeating unit: $—CO(CH_2)_4CONH(CH_2)_6NH—$

The formula of the polymer is $\left[CO(CH_2)_4CONH(CH_2)_6NH\right]_n$

Condensation polymerisation can take place using amino acids.
Amino acids have two different functional groups,  and $—NH_2$ in the **one** molecule.



Nylon - 6

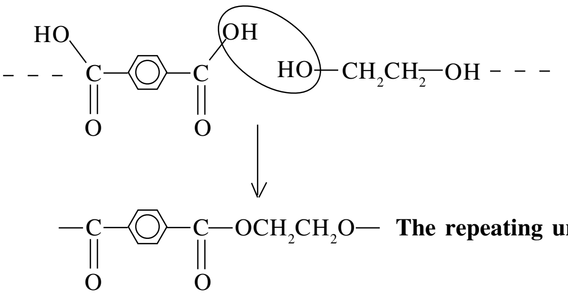
$$n\ H_2N(CH_2)_5COOH \longrightarrow \left[NH(CH_2)_5CO\right]_n + nH_2O$$

6- aminohexanoic acid

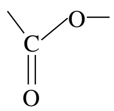
Polyesters

As with polyamides one molecule is a dicarboxylic acid, diacyl chloride or dimethyl ester. The other molecule is a **diol**.

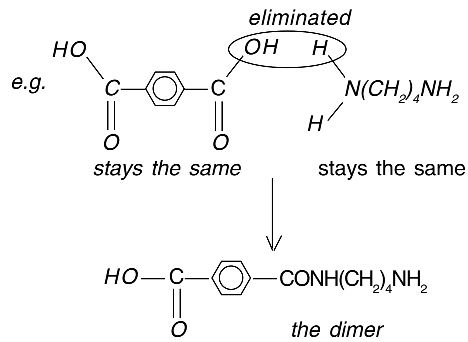
Benzene-1,4-dicarboxylic acid and ethane-1,2-diol react together to form **terylene**. Water is the simple molecule eliminated.



The repeating unit



is the **ester** linkage

> ***Exam Hint*** *: An examination question may give you the structures of the two monomer molecules in a condensation polymerisation reaction and ask you to draw the structure of a* ***dimer****.*
>
> - *Draw the structures side by side with the functional groups adjacent*
> - *Eliminate the simple molecule between them*
> - *The other functional groups do* ***not*** *change.*
>
> 
>

Altering polymers

One way to classify synthetic polymers is by looking at the effect that heat has on them. Polymers which can have their shape altered by heating (and thus can be re-melted and reshaped), are called **thermoplastic** or sometimes **thermosoftening** polymers**.** Other polymers cannot be re-melted and have to be moulded in manufacture; these are called **thermosetting** plastics. The property that makes thermosetting plastics so resistant to heat is usually the presence of covalently bonded **cross-links** between the polymer strands.

Thermoplastic polymers may be forced into moulds under pressure - **injection molding**, or can be forced through small holes, which process is called **extrusion**.

Synthetic polymers in the environment

Many synthetic polymers are very long-lasting and will exist in the environment for perhaps thousands of years. Generally speaking, polymers break down much faster in sunlight, so substances on the surface do not take more than seven to ten years for their structure to start to disintegrate.

The problem of synthetic polymer disposal is partially overcome by **recycling**. The difficulty with this is that many products are made from a mixture of polymers, making them difficult and expensive to recycle. For instance, a bottle may be made of PVC with a poly(propene) cap, a poly(ethene) wad and a paper label.

Another solution being used for poly(ethene) is to add small amounts of starch when the material is being moulded. This has the effect of the individual polymer fibres becoming separated in the environment, with the product eventually breaking down.

50 years ago carrier bags were made of brown paper. Children's toys were made from wood or metal! There was little plastic to be seen! Then came the polymer revolution!

Natural polymers

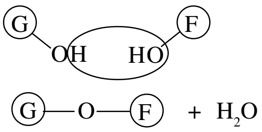
Natural polymers include substances like rubber, oils, cotton, leather, paper, silk and hair. Often these polymers have a complex structure but are made up of proteins, carbohydrates, lipids or, in the case of rubber, an addition polymer. These natural polymers have not been fully replaced by synthetic ones and the properties of materials like leather and cotton have proved difficult to copy.

Carbohydrates

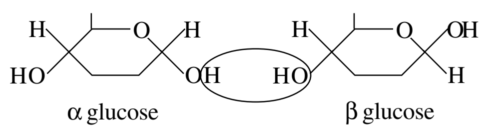
All carbohydrates are produced as a result of **photosynthesis**

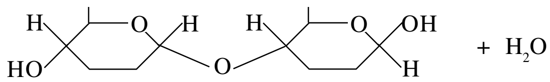
$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O(s) + 6O_2(g)$$

Carbohydrates form polymers by a condensation reaction involving the elimination of water. For instance, in the diagram below a molecule of fructose links to a molecule of glucose with the elimination of one water molecule.



In a different example, but with more detail, we can see that if two glucose molecules join together, water is eliminated. In this way, long polymers of carbohydrate molecules such as starch are built up.





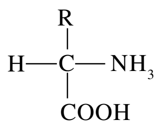
Uses of synthetic polymers

Synthetic polymer	Uses	Advantages and disadvantages
High density poly(ethene)	Milk bottles, buckets, kitchen containers, crates and packing material.	Very strong and easily coloured. Can be recycled with ease. Very long-lasting in the environment.
Low density poly(ethene)	Plastic bags, sheeting, electrical cable insulation, poly-tunnels (greenhouses).	Can be made transparent or opaque. Flexible and easy to manipulate. Can be recycled with ease. Very long-lasting in the environment.
'PVC'	Cable insulation, window frames, cling film.	Is used in a rigid 'unplasticised form 'uPVC' or flexible 'plasticised' form. Very resistant in the environment. Combustion may release toxic gases into the environment.
Polyamide 'nylon'	Clothing ropes and parachutes.	Can form very strong fibres, which are long-lasting under extreme conditions.
Polystyrene	Insulation, packing materials, flowerpots.	Can be used either in its expanded form or compressed. Very difficult to dispose of.
'PTFE'	'Stick-proof' tools and cookwear, coating for clothing.	The unreactivity of this compound makes it very useful, non-toxic and almost indestructible.

Proteins

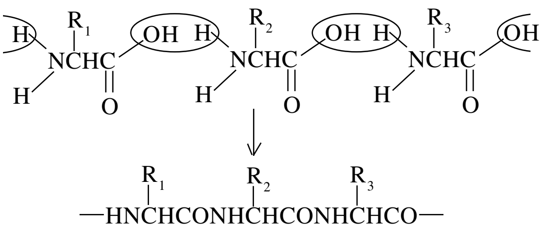
Amino acids build up into polymers by forming peptide links. **Never** refer to a peptide link as a 'peptide bond';

The general structure of an amino acid is:



They are α-amino acids where the $-NH_2$ group is on carbon 2

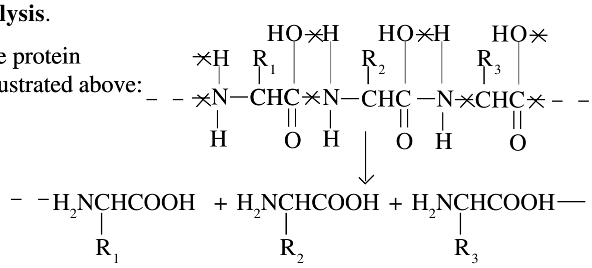
Different amino acid monomers join via the elimination of water molecules.



Hydrolysis

The natural polymers given above are all condensation polymers, formed by the removal of water molecules. Under certain conditions (usually acidic or by the use of an enzyme), the water can be replaced and the polymer broken down into its monomer units again. This is called **hydrolysis**.

e.g. the protein illustrated above:

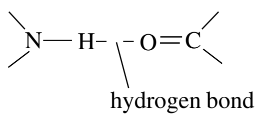


The separate amino acids

Synthetic condensation polymers are also susceptible to hydrolysis to give the original monomers. This means that they are **biodegradeable** and do not create a disposal problem.

Hydrogen bonding

Proteins and synthetic polyamides have hydrogen bonding between the polymer chains. The bonding is between the N–H of one chain with the C=O of another.



Despite individual hydrogen bonds being weak, the accumulative effect along the full lengths of the polymer chains gives an enhanced attraction. Kevlar, a polyamide of benzene1,4-dicarboxylic acid and benzene-1,4-diamine, due to this hydrogen bonding between chains is stronger than steel and is used as replacement steel cord in tyres and bullet proof vests.

Useful websites

You may find it helpful to visit these websites as part of your exam preparation for polymer chemistry.

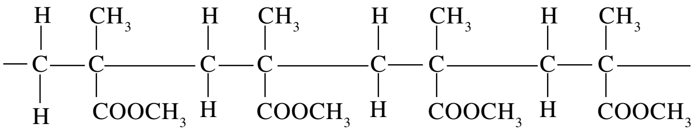
www.chemsoc.org/networks/learnnet/index.htm

www.environment.allinfoabout.com

www.chemsoc.org/networks/learnNet/green.chem.htm

Practise Questions

1. Perspex is a polymer with the following structure



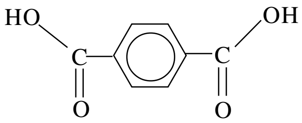
   (a) Circle the repeating unit

   (b) Draw the structural formula of the monomer

   (c) Which type of polymerisation has taken place in its formation?

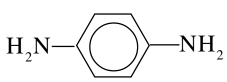
   (d) Why is this polymer non-biodegradeable?

2. Kevlar is a synthetic polyamide formed from the two molecules



benzene-1,4-dicarboxylic acid

and



benzene-1,4-diamine

   (a) Draw the structural formula of the **dimer** formed when the two molecules react.

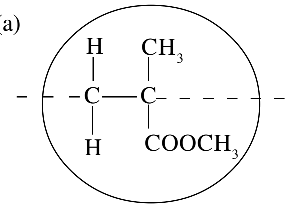
   (b) What type of polymerisation occurs?

   (c) Why is Kelvar:
   (i) so strong

   (ii) biodegradeable?

Answers

1. (a)



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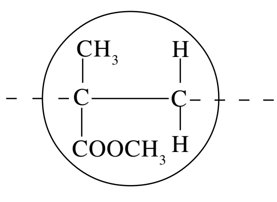
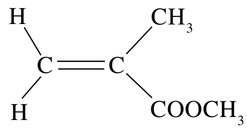


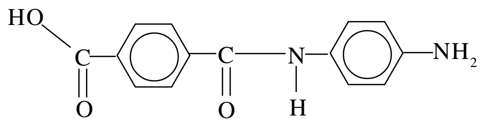
   (b)



   (c) Addition

   (d) The C–C bonds in the polymer chain are unreactive/ inert

2. (a)



   (b) Condensation

   (c) (i) Hydrogen bonding between the polymer chains

   (ii) The amide bond / peptide link can be hydrolysed.

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