Chem Factsheet

www.curriculum-press.co.uk Number 259

Addition vs. Condensation Polymerisation

To succeed in this topic, you should be familiar with simple organic nomenclature and some simple organic mechanisms.

After working through this Factsheet you will:
- Know about the two main types of reaction involved in polymer formation.
- Know about polymer nomenclature.
- Know about some of the differences in properties and uses of addition and condensation polymers.

Polymer molecules are long chain molecules formed by the joining together of large numbers of small molecules (monomers).

A polymer is a substance composed of polymer molecules.

Some biological macromolecules (very large molecules) are polymers, e.g. proteins and carbohydrates.

Polymers can be classified in a variety of ways, e.g. natural or synthetic; homopolymers (one type of monomer) and copolymers (more than one type of monomer); thermoplastic or thermosetting; and addition or condensation.

The focus of this Factsheet will be on addition and condensation, which refers to the type of polymerisation reaction involved in the formation of the polymer. This will lead into other comparisons through a consideration of the contrasting properties of addition and condensation polymers.

Addition Polymers

This class of polymers is so named as they are formed by addition reactions between the monomer molecules. The monomers are usually unsaturated (although addition polymerisation of cyclic monomers is also possible). Addition polymers are usually homopolymers, but can also be copolymers such as butyl rubber. Addition polymers are typified by the polyalkenes, for example poly(ethene).

UK A-Level syllabuses do not require knowledge of the mechanism associated with addition polymerisation but, unlike more familiar reactions of alkenes, it involves free-radicals.

Production of poly(ethene): an addition polymer

In the production of low-density poly(ethene), a small amount of oxygen is introduced into the reaction mixture (as an initiator) and reacts with some of the ethene to form free-radicals, R•. When a radical reacts with an ethene molecule, a longer radical is produced. This gives a chain reaction (propagation steps) that continues until two radicals combine in a termination reaction. This is why the polymer molecules are of varying lengths.

$R\bullet + CH_2{=}CH_2 \rightarrow RCH_2CH_2\bullet$ (propagation)

$RCH_2CH_2\bullet + CH_2{=}CH_2 \rightarrow RCH_2CH_2CH_2CH_2\bullet$ (propagation)

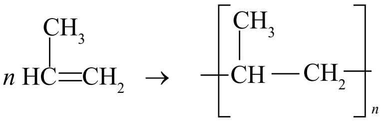
$R(CH_2CH_2)_x\bullet + R(CH_2CH_2)_y\bullet \rightarrow R(CH_2CH_2)_x(CH_2CH_2)_yR$

The commonest examples of addition polymers are those derived from simple alkenes, or monomers derived from alkenes.

The usual way to represent a polymerisation reaction is by showing a large, unspecified number, *n*, of monomer molecules combining to form the polymer chain. The polymer molecule is represented by the 'repeat unit' (sometimes 'repeating unit') of the polymer.

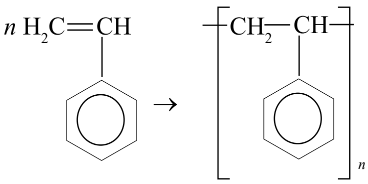
$n\,H_2C{=}CH_2 \rightarrow -\!\!\left[CH_2-CH_2\right]\!\!-_n$

ethene → poly(ethene)

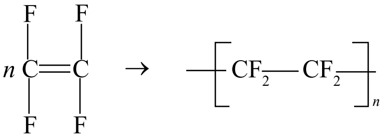


$n\,HC(CH_3){=}CH_2 \rightarrow -\!\!\left[CH(CH_3)-CH_2\right]\!\!-_n$

propene → poly(propene)



phenylethene → poly(phenylethene)
(or styrene → poly(styrene))



$n\,CF_2{=}CF_2 \rightarrow -\!\!\left[CF_2-CF_2\right]\!\!-_n$

tetrafluoroethene → poly(tetrafluoroethene) (PTFE)

In each case the repeat unit represents the simplest repeating portion of the polymer chain, derived from the monomer. As shown, the formal IUPAC naming system for polymers is simply to use the prefix 'poly' before the monomer name, in brackets. Common names are often derived by abbreviating the IUPAC name, e.g. polythene, polypropylene, polystyrene.

Simple addition polymers are usually thermoplastic, meaning that they can be heated, softened, remoulded into a different shape and then solidify on cooling, without decomposing. This simply involves providing enough energy to overcome the weak intermolecular forces between the polymer chains.

Chemically, addition polymers tend to be very inert, which can be explained by:

- The high strength of the C–C and C–H bonds, which makes the activation energy for any reaction high.
- The lack of polarity of the C–C and C–H bonds, which means they are not susceptible to attack by nucleophilic or electrophilic species.

A problem that arises from the chemical inertness of such polymers is that they are non-biodegradable, which causes problems when it comes to disposal. There are three main possibilities for the disposal of a polymer after use:

- Landfill – the non-biodegradable nature means that the polymers will not break down so take up a lot of space, creating problems with the amount of space needed for landfill sites.
- Incineration – under carefully controlled conditions this has potential as a source of energy for electricity generation. However, burning polymers creates potential problems through the possible production of harmful by-products, such as dioxins, and significant amounts of carbon dioxide.
- Recycling – an attractive option as it conserves non-renewable resources and uses less energy than manufacturing new polymers from their original raw materials. However, there are problems associated with the collection and sorting of used polymers, as they are seldom used in a pure state but are mixed with a wide variety of other materials, including paints and dyestuffs.

Condensation Polymers

In this case, when the monomers combine to form a polymer chain, small molecules (often water) are lost in the process. This means that, unlike for an addition polymer, the polymer does not have the same empirical formula as the monomer.

The two most common types of synthetic condensation polymers are:
- Polyesters – in which the monomers are linked by ester groups.
- Polyamides – in which the monomers are linked by amide groups.

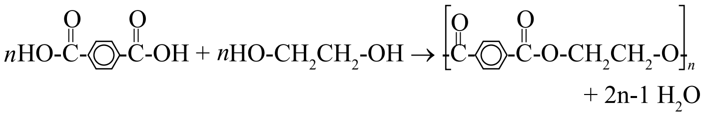
Biological polymers are condensation polymers, e.g., proteins consist of amino acid monomers linked by amide (peptide) groups and carbohydrates are formed by condensation reactions between simple sugar (monosaccharide) monomers.

Many condensation polymers are copolymers and are made of two or more distinct monomers.

Polyesters

The most widely used polyester is commonly known as PET (polyethylene terephthalate), which can be produced in the form of fibres (Terylene) with the fibres mainly orientated in one direction, sheets, with the fibres in two directions, or for packaging (such as drinks bottles), with the fibres arranged in three directions, which gives great strength.

The PET polymer molecules are produced from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.



$$n\mathrm{HO{-}\overset{O}{\overset{\|}{C}}{-}C_6H_4{-}\overset{O}{\overset{\|}{C}}{-}OH} + n\mathrm{HO{-}CH_2CH_2{-}OH} \rightarrow \left[\mathrm{\overset{O}{\overset{\|}{C}}{-}C_6H_4{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2CH_2{-}O}\right]_n + 2n\text{-}1\ \mathrm{H_2O}$$

Polyamides

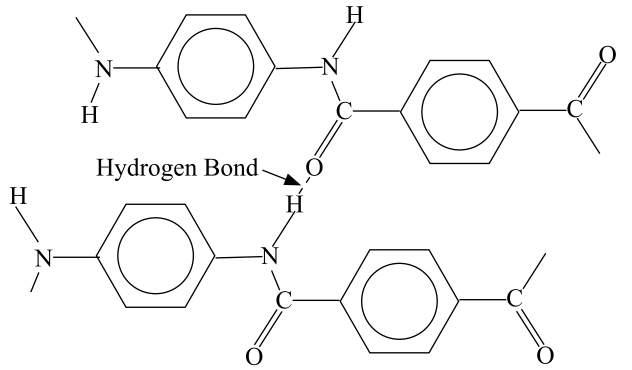
The best-known aliphatic polyamide is probably Nylon, of which there are numerous forms – based on the number of carbon atoms in the repeat unit. e.g.

Nylon-6 $\left[\mathrm{HN{-}(CH_2)_5{-}CO}\right]$

Nylon-6,6 $\left[\mathrm{HN{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_4{-}CO}\right]$

The monomers are typically a dicarboxylic acid (or diacyl chloride) and a diamine.

A well-known example of an aromatic polyamide is Kevlar, which gains a lot of its strength from the hydrogen-bonding between adjacent polymer chains.



A key difference between addition polymers and most condensation polymers is that the condensation polymers are biodegradeable. This is due to the polarity of the ester or amide linkages in the chains, which allows for hydrolysis reactions, especially involving nucleophilic attack.

This property means that condensation polymers pose much less of a pollution hazard than addition polymers.

An example of an application of this difference is in the use of a poly(lactic acid), PLA, derived from cornstarch, being used for supermarket carrier bags as an alternative to poly(ethene).

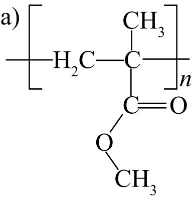
Quick Comparison

Addition polymer	**Condensation polymer**
Commonly made from alkene monomers	Commonly made from diamines, diols, dicarboxylic acids, diacyl chlorides or amino acids
Single product formed	Small molecules, e.g. water or HCl, released
100% atom economy	<100% atom economy
Typically homopolymers	Typically copolymers
Require harsh conditions for production	Reaction conditions general milder
Many produced via a free radical mechanism	Produced via an addition-elimination mechanism
Non-biodegradable	Biodegrade slowly via hydrolysis
Produced from non-renewable petroleum-based feedstock	Can be produced from renewable feedstock

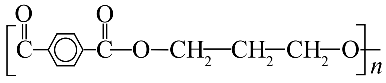
Sample Questions

1. Explain why addition polymers are non-biodegradable but condensation polymers will undergo biodegradation.
2. Explain why the atom economy for a condensation polymerisation reaction is not 100%.
3. Given the repeat unit, deduce the identity of the monomer(s) of the following polymers:

(a)



(b)



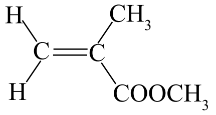
$$\left[\mathrm{\overset{O}{\overset{\|}{C}}{-}C_6H_4{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_2{-}CH_2{-}O}\right]_n$$

polytrimethylene terephthalate (PTT)

Answers

1. Addition polymers have a backbone made of strong, non-polar C—C bonds which are chemically inert.
   Condensation polymers have amide or ester linkages which are polar in nature and can undergo hydrolysis with nucleophile, such as water.

2. An atom economy of 100% implies all atoms in the reactants end up in the desired products.
   Atoms are lost during condensation polymerisation as small molecules such as water or hydrogen chloride, reducing the atom economy.

(a)


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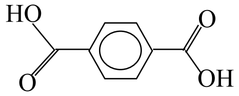

and $HO—CH_2—CH_2—CH_2—OH$

propane-1,3-diol (PDO)

*Acknowledgements: This **Chem Factsheet** was researched and written by **Tony Tooth** and published in January 2017 by **Curriculum Press**, Bank House, 105 King Street, Wellington, TF1 1NU. Chem Factsheets may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.* ***ISSN 1351-5136***