Polymerization

A process of making the monomer molecules react together in a chemical reaction and produce three-dimensional networks or polymer chains is called polymerization.

Types of polymerization

Based on the mode of polymerization of polymers, there are two types of polymerization. They are addition polymerization and condensation polymerization.

Condensation polymerization

The formation of condensation polymers occurs by the repeated condensation reaction between two different tri-functional or bi-functional monomeric units. In this type of reaction, small molecules such as alcohol, water, hydrogen chloride, etc. are eliminated. Some examples are nylon 6, nylon 6, 6, terylene (dacron), etc. Formation of nylon 6, 6 occurs due to the condensation of ($C_6H_{16}N_2$) hexamethylene diamine with ($C_6H_{10}O_4$) adipic acid.

Addition polymerization

The formation of addition polymers occurs by the repeated addition of monomer molecules which possess triple or double bonds. For example, the formation of ($(C_3H_6)_n$) polypropene from (C_3H_6) propene, and ($(C_2H_4)_n$) polythene from (C_2H_4) ethene.

- Homopolymers – The formation of addition polymers due to the polymerization of single polymeric species is called homopolymer. For example, polythene ($(C_2H_4)_n$).
- Copolymers – The formation of addition polymers which occur due to by addition polymerisation from two different monomers is called copolymer. For example, Buna-N, Buna-S, etc.

Polymerization techniques

1. Addition polymerization:
    - Bulk polymerization
    - Solution polymerization

- Suspension polymerization
- Emulsion polymerization

2. Condensation polymerization:
   - Melt polycondensation
   - Solution polycondensation

Addition Polymerisation

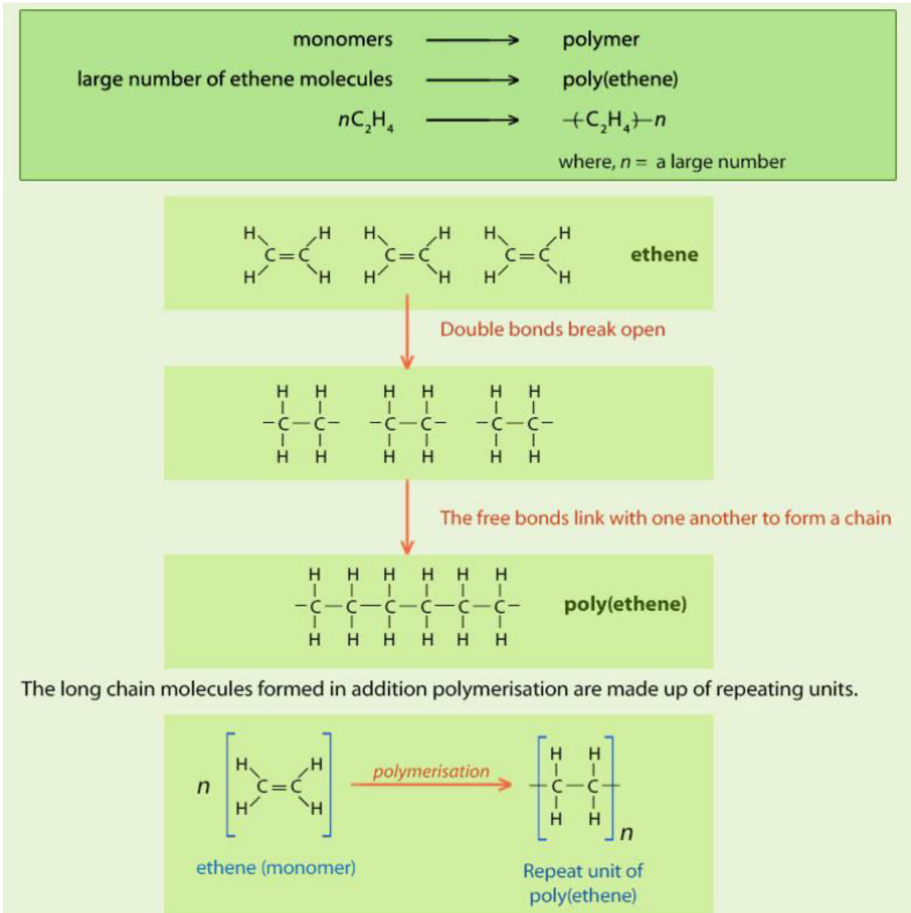
Addition polymerisation involves addition reactions in which a large number of small molecules (monomers) join together to form very large molecules (polymers).

In addition polymerisation the monomers have at least one double bond between carbon atoms. Alkenes are particularly useful monomers as they contain double bonds and can be made to undergo addition reactions amongst themselves.

Addition reactions involving alkenes are reactions in which the carbon-carbon double bond is converted to a single bond and atoms or group of atoms are added to each of the two carbon atoms.

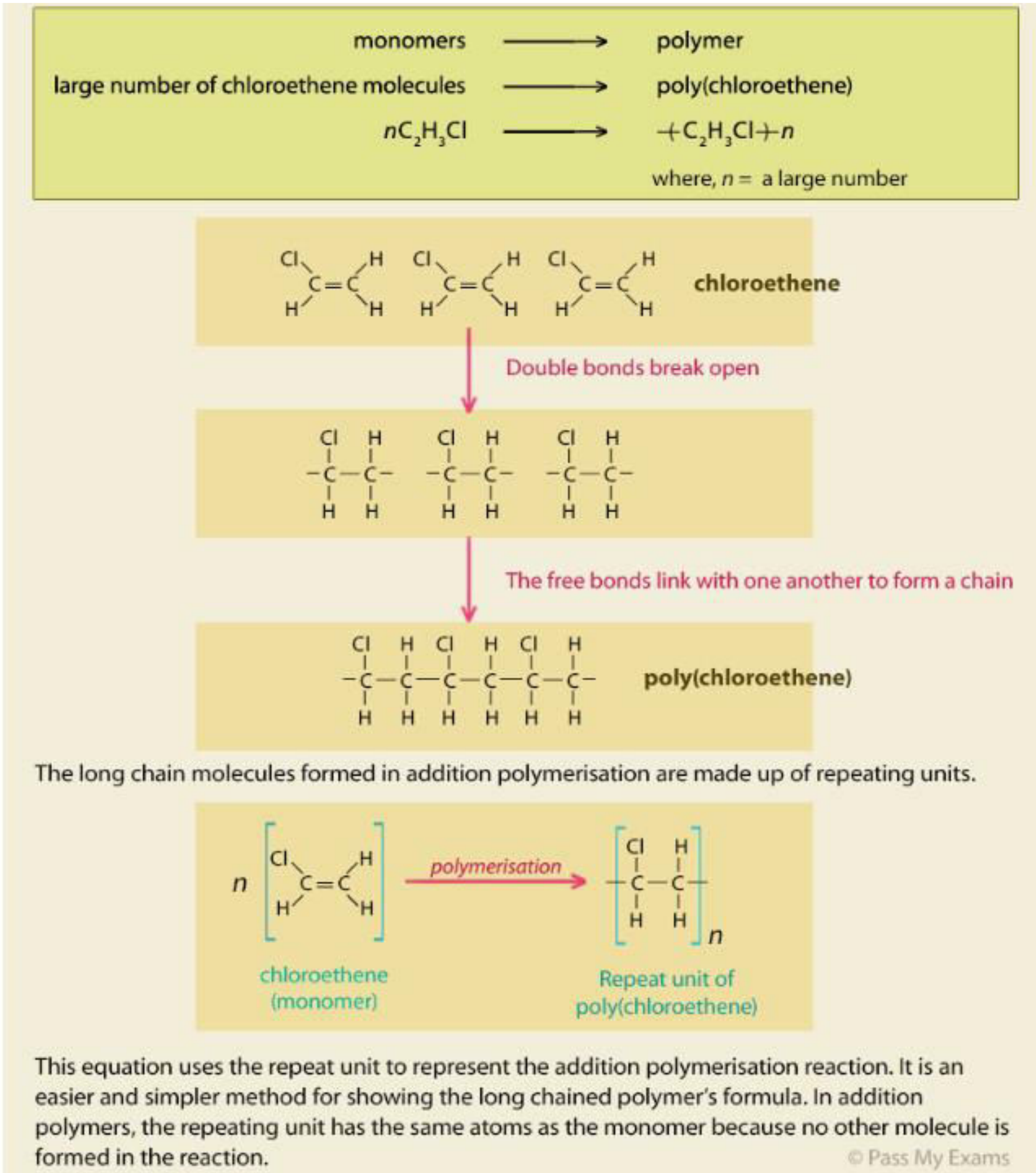
Example 1 – Poly(ethene)

Poly(ethene) or **polythene** is one of the most commonly used synthetic polymers. It is produced by the addition polymerisation of small ethene molecules which are the monomers in the reaction.



Example 2 – PVC

Poly(chloroethene) also known as **poly vinyl chloride (PVC)**
Chloroethene (vinyl chloride) undergoes addition polymerisation to form poly(chloroethene) which is more commonly known by the initials of its old name, poly-vinyl chloride (PVC).

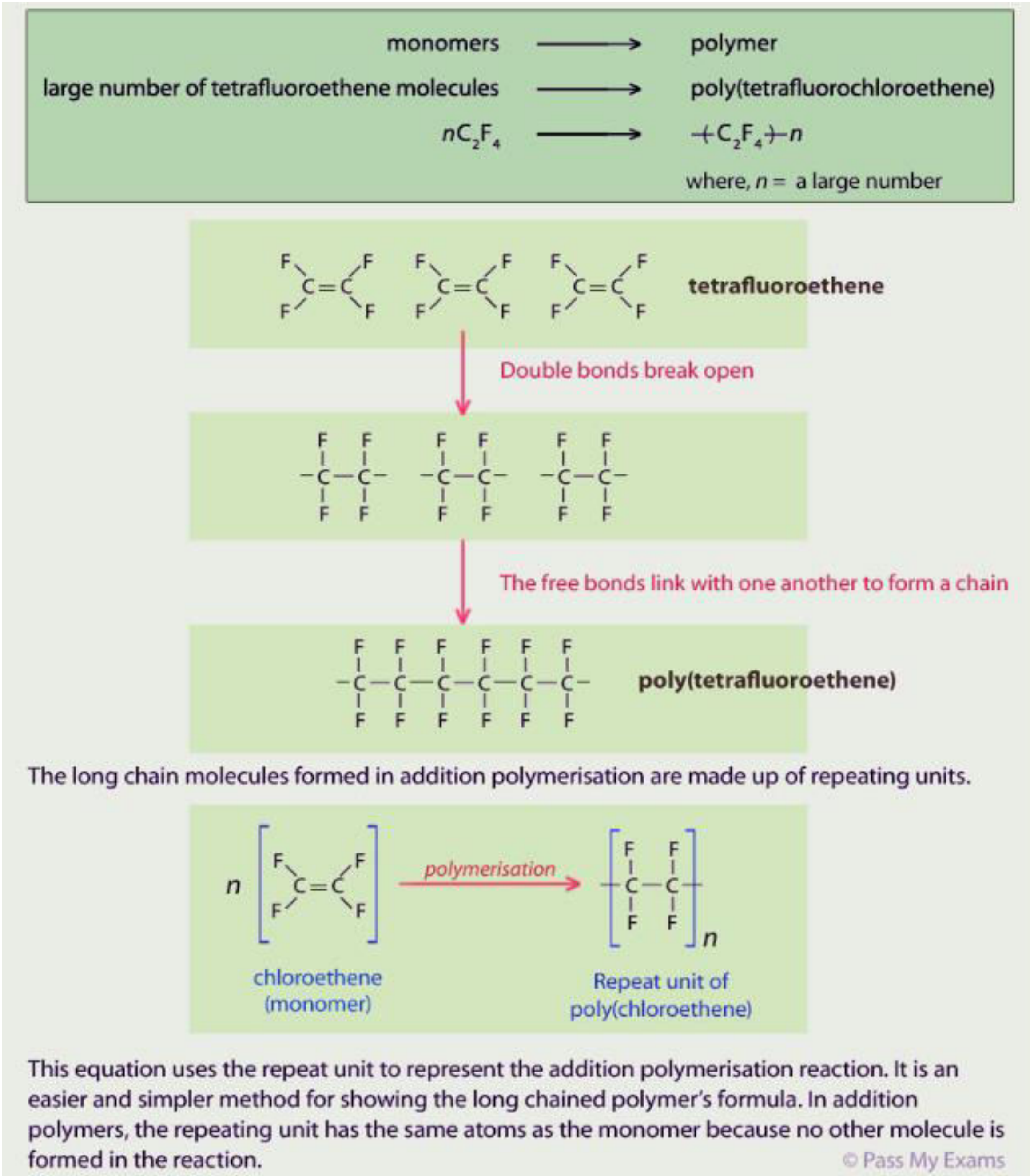


Poly(chloroethene) or PVC is a fairly strong material due to considerable intermolecular forces produced by the polar C – Cl bond. It is also a versatile material which is water and fire resistant. These properties mean it has a lot uses and is a major product produced by the chemical industry. On its own, poly(chloroethene) is a fairly rigid plastic, but additives called plasticisers are added to it to make more softer and flexible. Poly(chloroethene) or PVC has numerous uses from water pipes, guttering, window and door profiles, fabric coatings, electrical wire and cable insulation, furniture etc.

Example 3 – Poly(tetrafluoroethene) PTFE

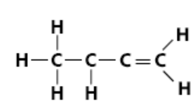
Tetrafluoroethene undergoes addition polymerisation to form poly(tetrafluoroethene) which is also known under the brand names of **Teflon** or **Fluon**.
Tetrafluoroethene is ethene molecule in which all the hydrogen atoms have been replaced by fluorine atoms (4 fluorine atoms to an ethene molecule, giving the name tetrafluoroethene). Structurally, PTFE is the same as poly(ethene) except that the hydrogen atoms are replaced by fluorine atoms.

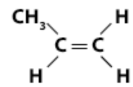
Poly(tetrafluoroethene) is very resistant to chemical attack. The fluorine atoms act as a shield for the carbon chain in the polymer preventing anything from reacting with it. This chemical resistant property makes it useful in the chemical and food industry as a coating material. Vessels and pipes can be coated with PTFE to make them resistant to chemicals that might attack and corrode them. PTFE also has non-stick properties and this property has been used to great success in non-stick kitchen utensils.

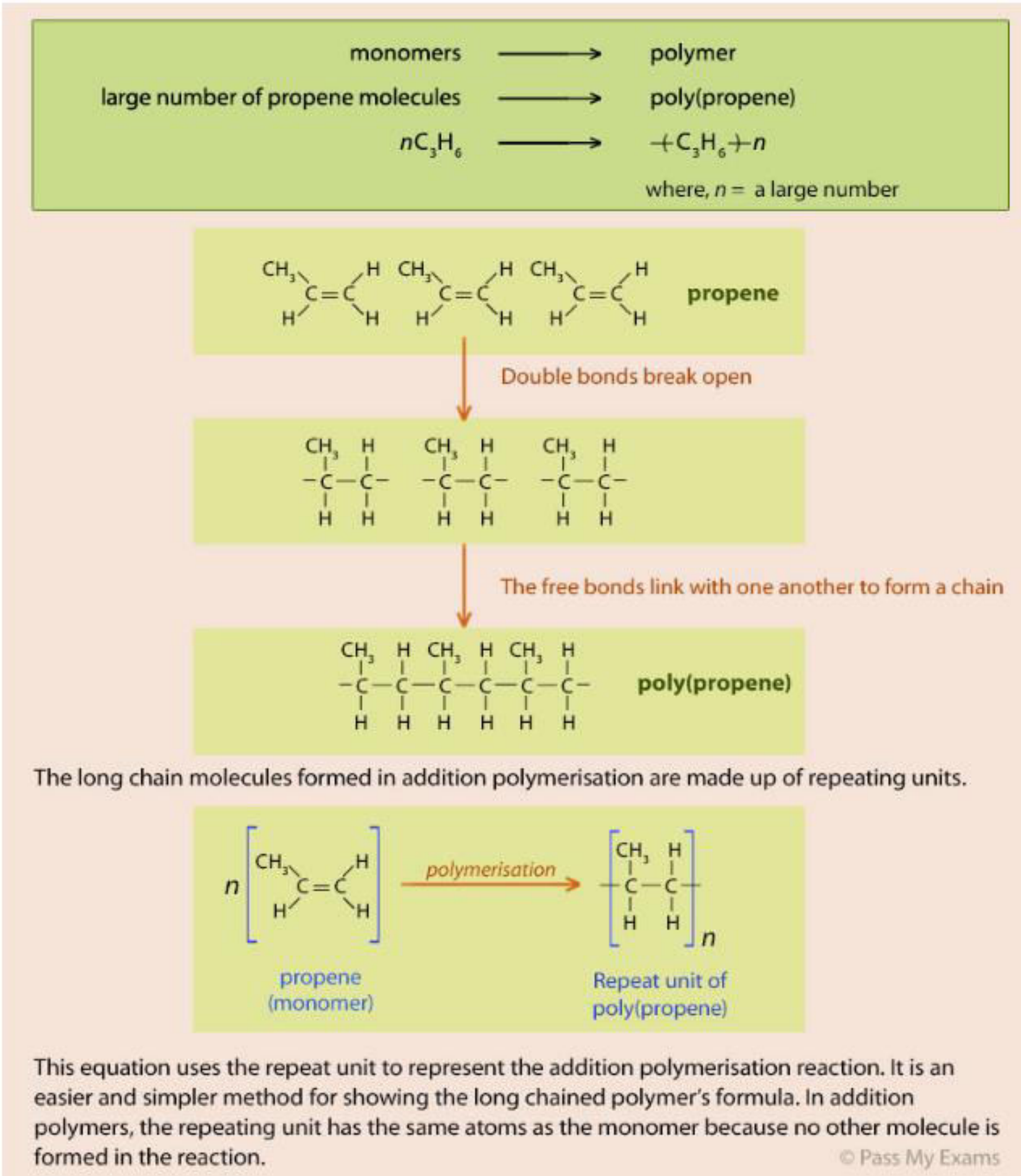


Example 4 – Poly(propene) (polypropylene)

Propene is an alkene readily available from petroleum. It can undergo addition polymerisation to produce poly(propene).

Propene has the molecular formula C_3H_6 and the structural formula: 

In order to represent the polymerisation the propene monomer is redrawn as below to make it easier to represent it as a repeat unit: 

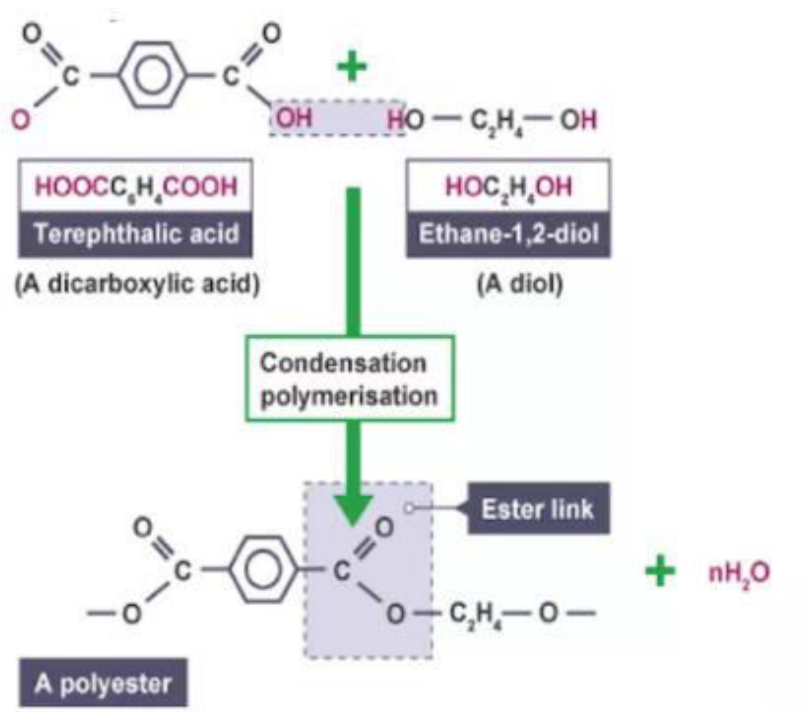


Condensation Polymerisation

Polyester: A condensation polymer formed by the reaction between a dicarboxylic acid with a dialcohol. Both monomers must have two functional groups.

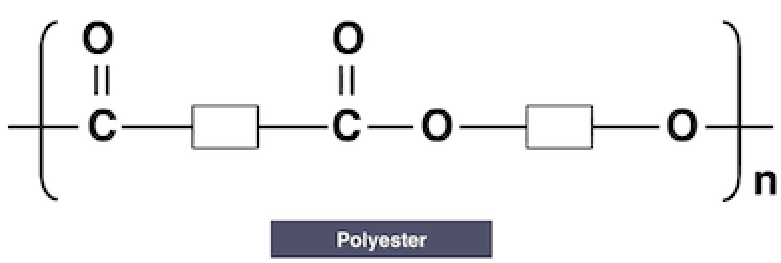
Condensation polymerisation: A reaction in which two different types of monomer join together to produce a polymer and expel a small molecule such as water.

Example:



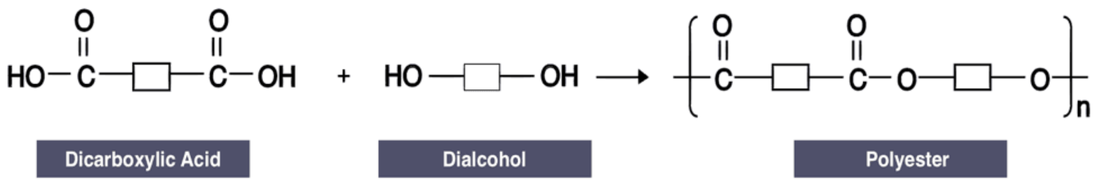
The condensation polymerisation between terephthalic acid and ethane -1,2 diol

Polyester Structural & Displayed Formula



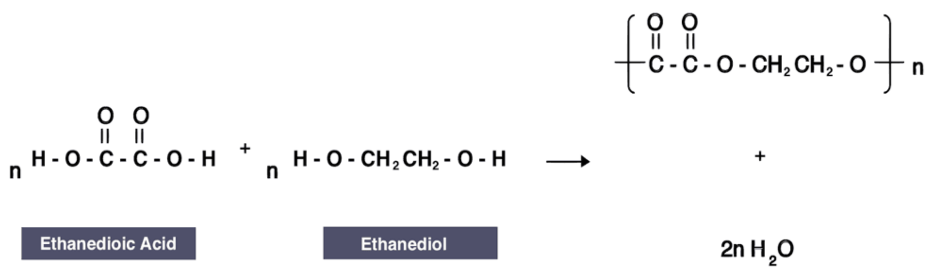
The basic structure of a polyester, the box represents any group of atoms

Equation:



Equation of condensation polymerisation of dicarboxylic acid and dialcohol to form a polyester

Reaction of Ethanedioc Acid and 1,2-Ethanediol



Equation of the reaction between ethanedioc acid and 1,2-ethanediol

Biodegradable Biopolyesters

The biodegradation of a bottle made of biopolyesters

- Biopolyesters are a specific type of polymer that is able to biodegrade naturally in the environment after their intended purpose.
- The polymers are synthetically made, consisting of ester, amide and ether functional groups which gives them the characteristic of being biodegradable.

[Complete reference material/notes on polymerization]

Synthetic Polymers

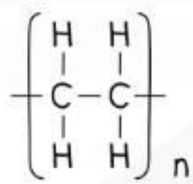
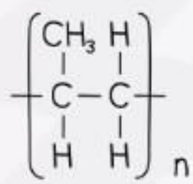
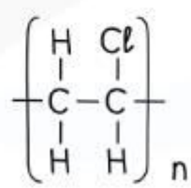
Plastics & Man-Made Fibres

Plastics, nylon and terylene

- These are **synthetic** polymers with many uses
- Nylon is a copolymer used to produce **clothing**, **fabrics**, **nets** and **ropes**
- Terylene is a polyester made from monomers which are joined together by **ester links**
- Terylene is used extensively in the **textile** industry and is often mixed with cotton to produce **clothing**
- Synthetic polymerisation also produces plastics that have many different uses in today's society

Uses of plastics

Uses of plastics

POLYMER	REPEAT UNIT	USES
POLY(ETHENE) I.e. POLYTHENE		PLASTIC BAGS (LOW DENSITY POLYTHENE) PLASTIC BOTTLES (HIGH DENSITY POLYTHENE)
POLY(PROPENE)		FOOD PACKAGING ROPES CARPETS
POLY(CHLOROETHENE) I.e. PVC		PLASTIC SHEETS ARTIFICIAL LEATHER DRAINPIPES AND GUTTERS INSULATION ON WIRES

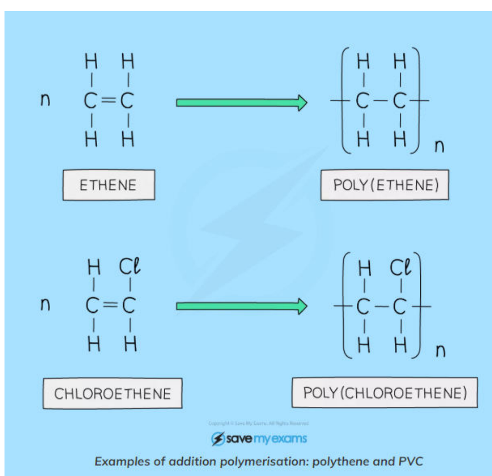
Non-biodegradable plastics

- These are plastics which do not degrade over time or take a very long time to degrade, and cause significant pollution problems
- In particular plastic waste has been spilling over into the **seas** and **oceans** and is causing huge disruptions to marine life
- In landfills waste polymers take up valuable space as they are non-biodegradable so microorganisms cannot break them down. This causes the landfill sites to quickly fill up
- Polymers release a lot of heat energy when **incinerated** and produce **carbon dioxide** which is a greenhouse gas that contributes to climate change
- If incinerated by incomplete combustion, **carbon monoxide** will be produced which is a toxic gas that reduces the capacity of the blood to carry oxygen
- Polymers can be recycled but different polymers must be separated from each other which is a difficult and expensive process

Addition & Condensation Polymers & Deducing Structures

Addition polymerisation

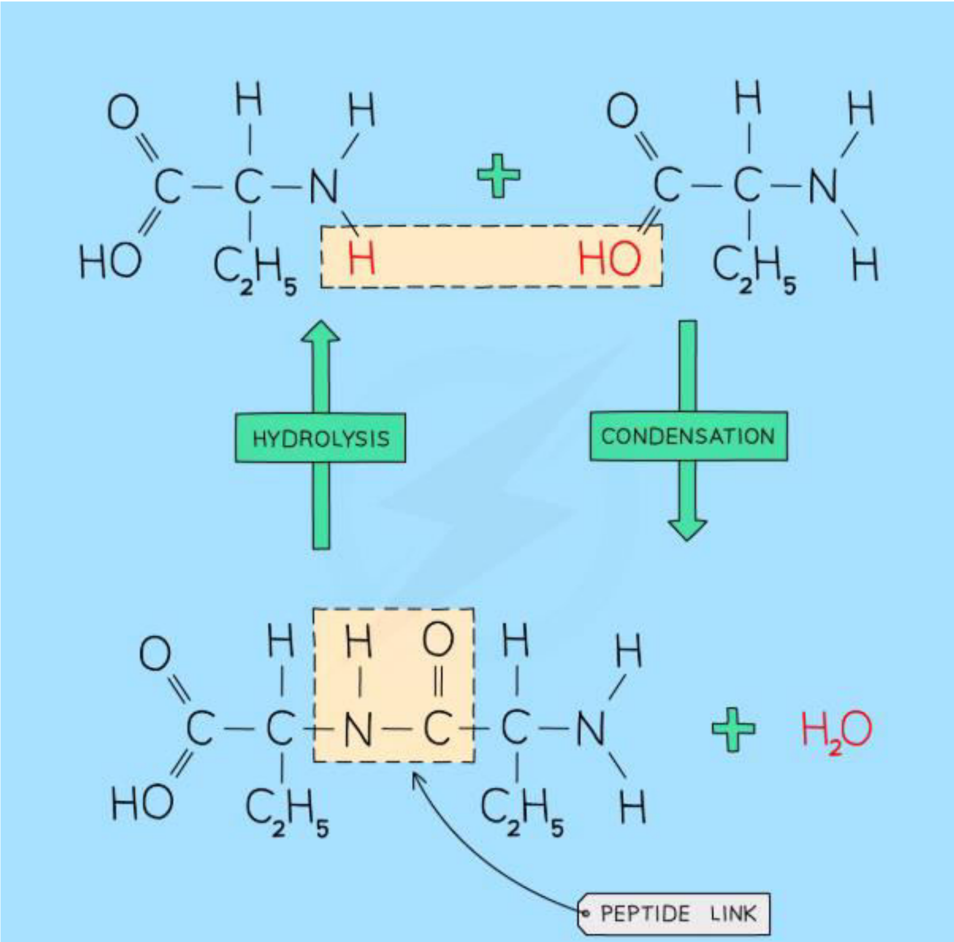
- Addition polymers are formed by the joining up of many monomers and only occurs in monomers that contain C=C bonds
- **One** of the bonds in each C=C bond breaks and forms a bond with the adjacent monomer with the polymer being formed containing single bonds only
- Many polymers can be made by the addition of alkene monomers
- Others are made from alkene monomers with different atoms attached to the monomer such as chlorine or a hydroxyl group
- The name of the polymer is deduced by putting the name of the **monomer** in brackets and adding poly- as the **prefix**
- For example if propene is the alkene monomer used, then the name is **polypropene**



Examples of addition polymerisation: polythene and PVC

Condensation polymerisation

- Condensation polymers are formed when monomer molecules are linked together with the **removal** of a small molecule, usually **water**
- Condensation polymerisation usually involves **two different monomers**, each one having a **functional** group on **each end**
- Hydrolysing (adding water) to the compound in acidic conditions usually reverses the reaction and produces the monomers by rupturing the peptide link



Condensation produces the polyamide which is ruptured at the link by hydrolysis in the reverse reaction

Deducing the monomer from the polymer

- Polymer molecules are very large compared with most other molecules
- **Repeat units** are used when displaying the formula:
- Change the double bond in the monomer to a **single bond** in the repeat unit
- Add a bond to each end of the repeat unit

- The bonds on either side of the polymer must **extend** outside the brackets (these are called extension or continuation bonds)
- A small subscript **n** is written on the bottom right-hand side to indicate a large number of repeat units

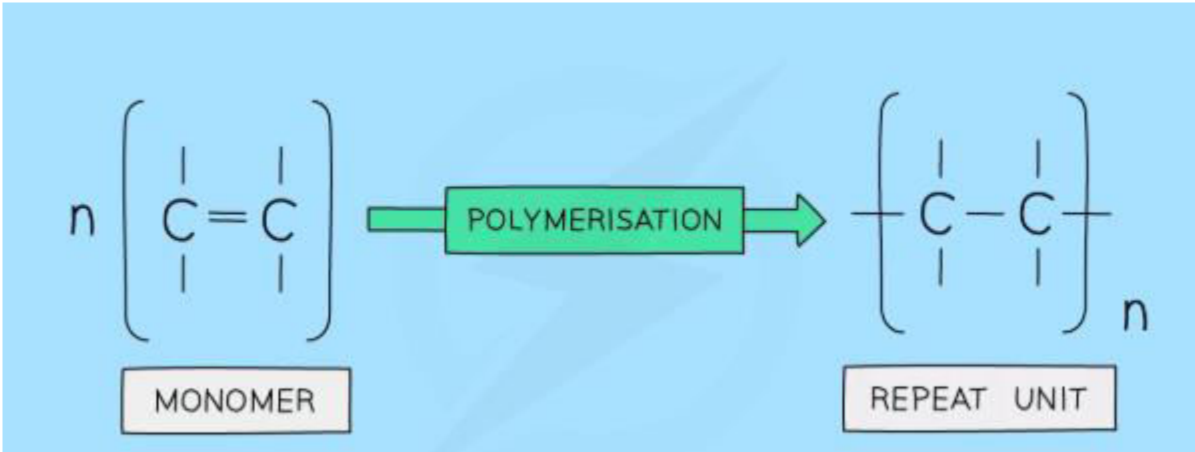


Diagram showing the concept of drawing a repeat unit of a monomer

Deducing the polymer from the monomer

- Identify the repeating unit in the polymer
- Change the single bond in the repeat unit to a **double bond** in the monomer
- Remove the bond from each end of the repeat unit and the subscript **n**

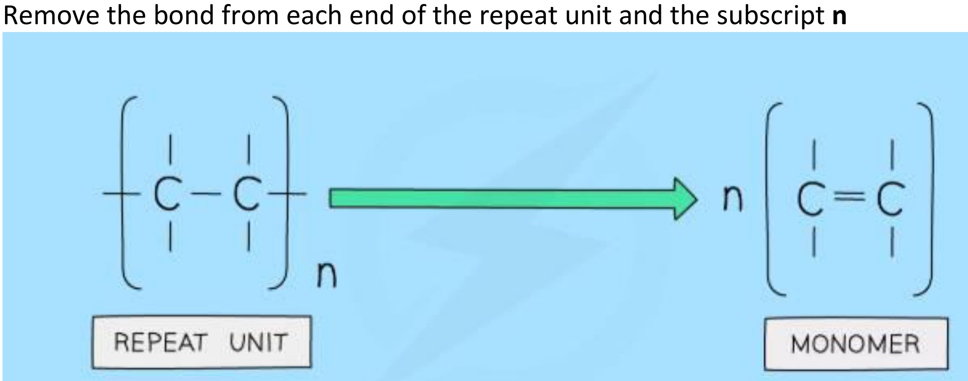
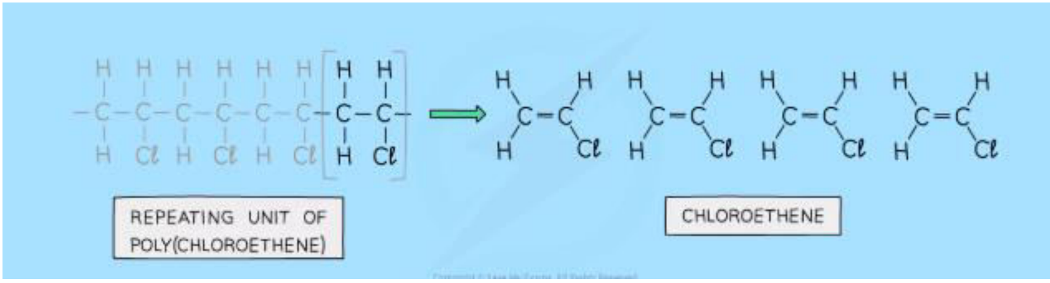


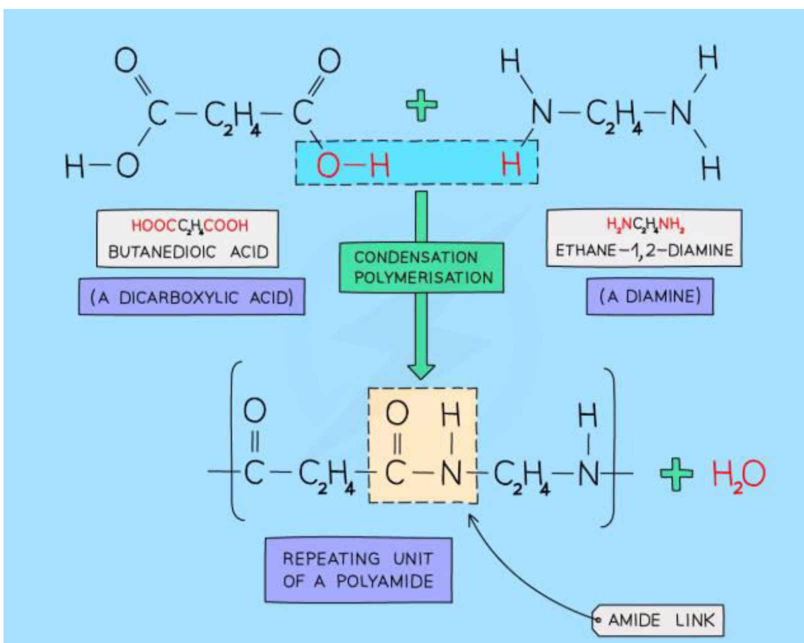
Diagram showing how to deduce the structure of a monomer from a repeat unit



Example: Deducing the structure of chloroethene from a repeat unit of Poly(chloroethene)

Formation of nylon

- Nylon is a polyamide made from **dicarboxylic** acid monomers (a carboxylic with a -COOH group at **either** end) and **diamines** (an amine with an -NH_2 group at **either** end)
- Each -COOH group reacts with another -NH_2 group on another monomer
- An amide linkage is formed with the subsequent loss of **one** water molecule per link



The condensation reaction in which the polyamide Nylon is produced

Formation of terylene

- Terylene is a **polyester** made from **dicarboxylic** acid monomers (a carboxylic with a -COOH group at **either** end) and **diols** (an alcohol with an -OH group at **either** end)
- Each -COOH group reacts with another -OH group on another monomer
- An ester linkage is formed with the subsequent loss of **one** water molecule per link