

Polymerisation (A Level)

A-Level Chemistry 9701 · Topic 35 revision notes

Everything from the 3 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Condensation polymerisation

2. Polymer deductions

3. Degradable polymers

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1 Condensation polymerisation

Syllabus 35.1

In **condensation polymerisation** monomers join with the loss of a **small molecule** at every link: H_2O when a carboxylic acid is used, HCl when an acyl chloride is used. Each monomer needs **two reactive groups**. A **diol** plus a **dicarboxylic acid** (or diacyl dichloride) gives a **polyester**, for example PET (Terylene) from ethane-1,2-diol and benzene-1,4-dicarboxylic acid; a single **hydroxycarboxylic acid** such as lactic acid can also polymerise on its own, giving poly(lactic acid). A **diamine** plus a dicarboxylic acid or diacyl dichloride gives a **polyamide**, for example nylon-6,6 from hexane-1,6-diamine and hexanedioic acid, or Kevlar from aromatic monomers. **Proteins** are natural polyamides made from amino acids, joined by peptide (amide) links. The **repeat unit** contains one of each monomer residue, so its M_r is the sum of the monomers minus the small molecules lost: $116 + 146 - 2(18) = 226$ for nylon-6,6.

polyester: ester link $-\text{CO}-\text{O}-$



PET (Terylene): repeat unit M_r 192

polyamide: amide link $-\text{CO}-\text{NH}-$



nylon-6,6: repeat unit M_r 226

Fig. 1: forming PET (a polyester) and nylon-6,6 (a polyamide)

Two reactive ends, one small molecule per link.

- ✓ **Diol + diacid** (or diacyl dichloride): polyester, $-\text{COO}-$.
- ✓ **Diamine + diacid** (or diacyl dichloride): polyamide, $-\text{CONH}-$.
- ✓ **Lost:** H_2O from COOH , HCl from COCl .
- ✓ **Repeat unit M_r** = monomers – small molecules lost.

Watch out!

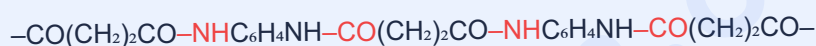
In a condensation polymer the repeat unit contains **one residue of each monomer** and the links **inside** the chain: do not leave H on the N end and OH on the C=O end of a repeat unit. Every link releases one small molecule, so forming n repeat units of nylon-6,6 releases about **$2n$** H_2O , not n . With a **diacyl dichloride** the molecule lost is **HCl**, not water.

2 Polymer deductions

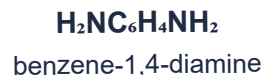
Syllabus 35.2

To deduce monomers from a **condensation polymer**, find each **ester** ($-\text{COO}-$) or **amide** ($-\text{CONH}-$) link, break the $\text{C}-\text{O}$ or $\text{C}-\text{N}$ bond, and add back **OH to the carbonyl carbon** and **H to the O or N** (or Cl to the carbonyl carbon if a diacyl dichloride is asked for). An **addition polymer** has a backbone of carbon atoms only; its monomer is found by taking a two-carbon repeat unit and putting back the **$\text{C}=\text{C}$** . A monomer with a $\text{C}=\text{C}$ bond undergoes **addition**; monomers with **two reactive groups** (OH , NH_2 , COOH , COCl) undergo **condensation**. Properties follow from the intermolecular forces between chains: the $\text{N}-\text{H}$ and $\text{C}=\text{O}$ groups of **polyamides** form **hydrogen bonds between chains**, which makes nylon and Kevlar strong and high-melting.

find the link, cut it, add back water



1. break every amide $\text{C}-\text{N}$ bond (shown in red)
2. add OH to each $\text{C}=\text{O}$ end and H to each N end



addition polymer: $\text{C}-\text{C}$ backbone only, no O or N in the chain
condensation polymer: ester or amide links within the chain

Fig. 1: working back from a polyamide chain to its two monomers

Find the link, cut it, add back water.

- ✓ **C-C backbone only:** addition; restore the C=C.
- ✓ **-COO- or -CONH- in the chain:** condensation.
- ✓ **Cut:** OH back on C=O, H back on O or N.
- ✓ **Polyamides** hydrogen bond chain to chain.

Watch out!

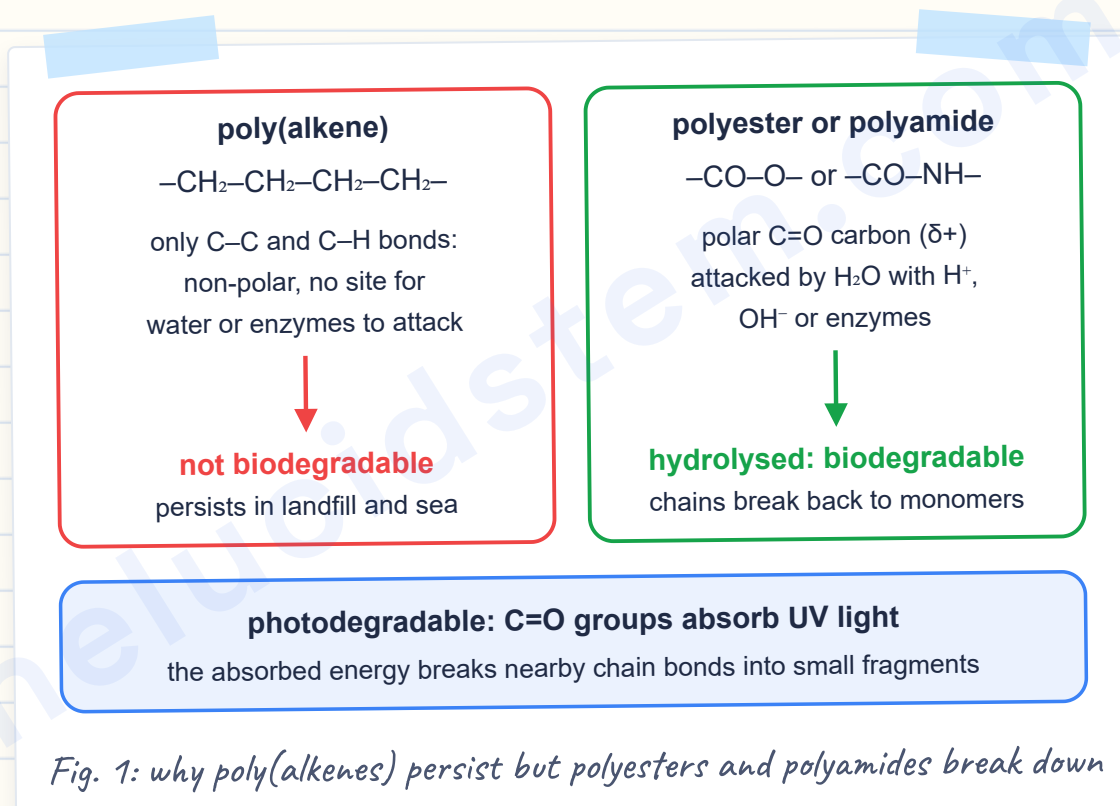
When cutting an amide link, the C=O stays with the **acid** monomer and the N-H with the **amine**: do not split the C=O away from its carbon. A polymer with a C-C backbone and side groups such as -CN or -COOCH₃ is still an **addition** polymer, even if the side group is an ester. Polyesters cannot hydrogen bond chain to chain, because they have **no H on O or N**.

3 Degradable polymers

Syllabus 35.3

Poly(alkenes) such as poly(ethene) contain only strong, non-polar C-C and C-H bonds, so they are **chemically inert** and **non-biodegradable**: they persist in landfill and the oceans.

Polyesters and **polyamides** contain polar C=O groups in their ester and amide links, so they can be **hydrolysed** by hot aqueous **acid**, **alkali** or by **enzymes** in microorganisms; they are **biodegradable**. Acid hydrolysis gives the free acid and the alcohol or the ammonium salt of the amine; alkaline hydrolysis gives the carboxylate salt and the alcohol or free amine. **Photodegradable** polymers contain **C=O groups** that absorb ultraviolet radiation; the energy breaks nearby bonds in the chain so the polymer crumbles. Burning plastics releases CO₂ and can release toxic gases such as HCl from PVC.



Hydrolysis at the link, or UV at the C=O.

- ✓ **Poly(alkenes)**: non-polar C-C backbone, inert, non-biodegradable.
- ✓ **Polyesters, polyamides**: hydrolysed by acid, alkali or enzymes.
- ✓ **Acid** gives COOH (and NH_3^+); **alkali** gives COO^- (and NH_2).
- ✓ **Photodegradable**: C=O absorbs UV.

Watch out!

Poly(alkenes) are **not** biodegradable because their C-C and C-H bonds are non-polar and strong, not because they are "too big". Biodegradable and photodegradable are different: one needs **hydrolysis** (water, acid, alkali or enzymes) at ester or amide links, the other needs **UV light** absorbed by C=O groups. In alkaline hydrolysis the acid monomer appears as its **carboxylate salt**, and in acid hydrolysis of a polyamide the amine appears as its **ammonium salt**.