Polymerisation (A Level)

Condensation polymers (polyesters and polyamides), deducing repeat units and monomers, predicting the type of polymerisation, and biodegradable and photodegradable polymers.

35.1 Condensation polymerisation

In **condensation polymerisation** monomers with two functional groups join, and a **small molecule (usually water, or HCl)** is lost at each link. The polymer has a **different empirical formula** from the monomers.

Polyesters

An **ester link** (–COO–) forms between a carboxylic acid group and an alcohol.

- From a **diol and a dicarboxylic acid** (or a **dioyl chloride**, which loses HCl instead of water and reacts faster).
- From a **hydroxycarboxylic acid** (one monomer with –OH and –COOH).

$$n\,HOCH_2CH_2OH + n\,HOOC{-}C_6H_4{-}COOH \rightarrow [{-}OCH_2CH_2O{-}CO{-}C_6H_4{-}CO{-}]_n + 2n\,H_2O$$

This gives a polyester (such as Terylene or PET, from ethane-1,2-diol and benzene-1,4-dicarboxylic acid).

Polyamides

An **amide (peptide) link** (–CONH–) forms between a carboxylic acid group and an amine.

- From a **diamine and a dicarboxylic acid** (or a dioyl chloride): nylon-6,6 from 1,6-diaminohexane and hexanedioic acid (or hexanedioyl chloride).
- From an **aminocarboxylic acid** (one monomer with $–NH_2$ and –COOH).
- From **amino acids**, which give proteins (polypeptides).

$$n\,H_2N(CH_2)_6NH_2 + n\,HOOC(CH_2)_4COOH \rightarrow [{-}NH(CH_2)_6NHCO(CH_2)_4CO{-}]_n + 2n\,H_2O$$

With the dioyl chloride, $2n$ HCl is released instead of water.

Repeat units and monomers

- **Repeat unit:** write the two monomers joined, remove the small molecule, and put the **ester or amide link in the middle**. For the polymer, the repeat unit contains **one residue of each monomer** (for two different monomers).

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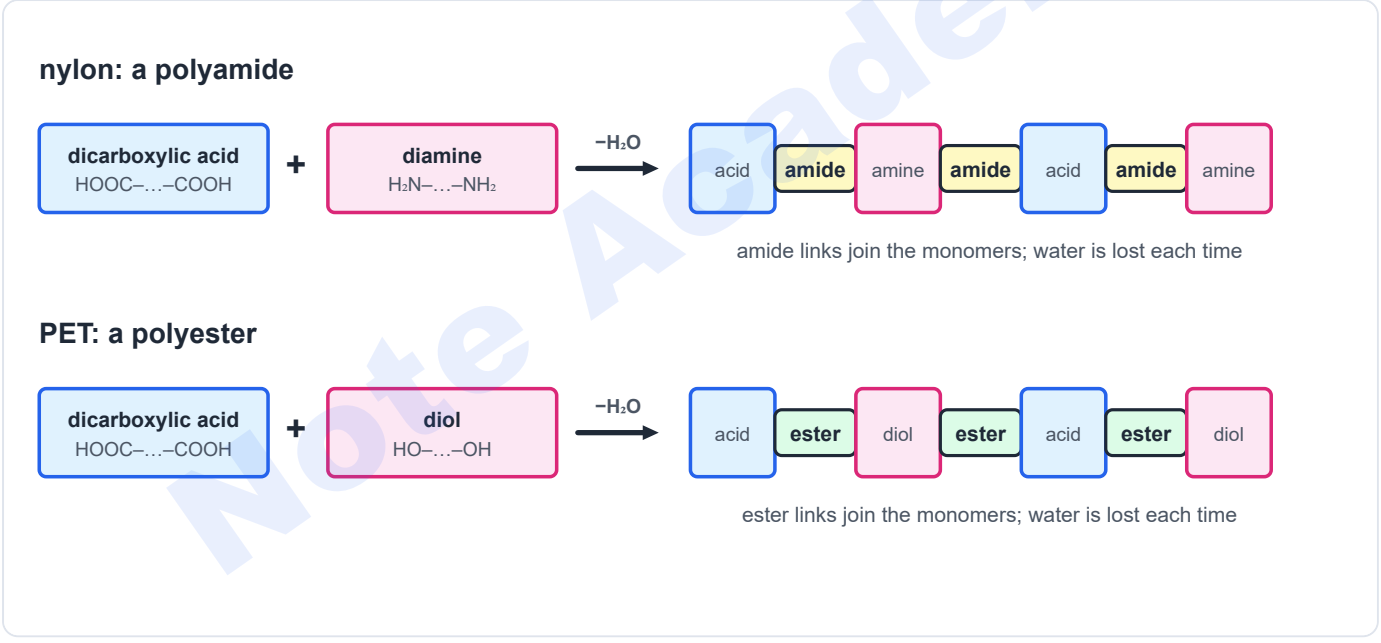
- **Finding monomers** from a section of polymer: **break the ester or amide links** (–CO–O– or –CO–NH–) and **add back** OH to the carbonyl carbon and H to the O or N: the acid and the alcohol (or amine) are recovered. For a chain with identical repeating units, check whether there is **one monomer or two**.

> **TRY IT**
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> A section of polymer is $-NH(CH_2)_5CO-NH(CH_2)_5CO-$. Name the monomer.

Hydrolysing the amide link gives $H_2N(CH_2)_5COOH$, **6-aminohexanoic acid** (an aminocarboxylic acid), one monomer used.

Functional-group count controls chain growth

A monofunctional acid plus a monofunctional alcohol makes a small ester. To grow a long linear polyester, monomers need two compatible reactive sites overall: a diacid plus diol, or a hydroxy acid containing one of each. Both ends can continue reacting after the first link forms. A molecule with only one useful site can terminate a chain rather than sustain its growth.



Worked example: $HOCH_2COOH$ can self-condense into a polyester with a $-OCH_2CO-$ residue. The same molecule contributes both alcohol and acid functionality. By contrast, CH_3COOH alone cannot form that ordinary polyester because it lacks an alcohol end for repeated ester formation.

The displayed $2n$ small-molecule equations are conventional idealised repeat-unit equations that omit end-group details. For an actual finite linear chain made from N separate molecules, forming one chain requires $N-1$ links. In a chain from n diacids plus n diols, this gives $2n-1$ water losses if both end groups are retained explicitly. State the representation being used before applying an exact end-group calculation.

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A linear chain forms from ten hydroxy-acid molecules with no branching or ring closure. How many ester links and waters are formed?

Answer: Nine ester links and nine waters. There are ten residues but only nine joins between them.

Recovering monomers by cleaving the right bond

For an ester link, cut between carbonyl carbon and oxygen, then add OH to the carbonyl fragment and H to the oxygen fragment. For an amide link, cut C(O)–N and add OH to the carbonyl side and H to nitrogen. This reproduces neutral acid/alcohol or acid/amine structures before considering the hydrolysis medium.

Worked example: $-OCH_2CH_2OCO(CH_2)_4CO-$ contains a diol-derived $-OCH_2CH_2O-$ fragment and a diacid-derived $-CO(CH_2)_4CO-$ fragment. The monomers are ethane-1,2-diol and hexanedioic acid. The two carbonyl carbons count towards the diacid's six carbons, so it is not a four-carbon acid.

For a polyamide $-NH(CH_2)_6NHCO(CH_2)_4CO-$, hydrolysis recovers a six-carbon diamine and a six-carbon diacid. Cutting an ordinary C–C bond instead of the amide link would invent different monomers. When only one monomer is used, recognise that the same residue contains both ends of the original amino/hydroxy acid.

TRY IT

What neutral monomer corresponds to the repeat residue $-NHCH(CH_3)CO-$?

Answer: $H_2NCH(CH_3)COOH$, 2-aminopropanoic acid. Restore H at nitrogen and OH at the carbonyl carbon; retain the methyl side chain.

35.2 Predicting the type of polymerisation

- **Addition** if the monomer has a **C=C** double bond and the polymer has a **carbon-only backbone** with no other product.
- **Condensation** if the monomers have **two functional groups** (two –COOH, –OH, $–NH_2$, –COCl groups, or one of each) and a **small molecule** is released.

To decide from a section of polymer, look for **ester** (–COO–) or **amide** (–CONH–) links in the backbone: those show condensation. A backbone of **only C–C bonds** shows addition.

Distinguish backbone links from pendant groups

For familiar syllabus cases, carbon-only addition backbones and ester/amide condensation backbones are useful patterns. However, a pendant ester group does not make an addition backbone into a polyester:

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ask whether hydrolysis of that ester would actually break the main chain. Likewise, the mere presence of nitrogen somewhere in a substituent does not establish a polyamide link.

Worked reasoning: an alkene monomer bearing an ester side group can polymerise through C=C, retaining the ester as a pendant group. It is still an addition polymer from that pathway. A diol and diacid instead form a chain through ester bonds and release water. Identify both the reactive monomer sites and the final backbone connectivity.

> TRY IT
>
> Why does a molecule containing one COOH group not automatically make a condensation polymer?

Answer: It needs additional compatible functionality to continue growth at both ends. With only one acid group and no other reactive site, it generally makes a finite small-molecule derivative or caps a chain.

35.3 Degradable polymers

- **Poly(alkenes)** are **chemically inert** (strong, non-polar C–C and C–H bonds), so they are very difficult to biodegrade and persist in the environment.
- Some polymers can be **degraded by light** (photodegradable), when the bonds absorb ultraviolet radiation, and these can be designed with light-sensitive groups.
- **Polyesters and polyamides** contain links susceptible to hydrolysis, providing a possible route to degradation. This does **not** guarantee rapid biodegradation in ordinary environmental conditions. Link accessibility, crystallinity, temperature, water and available enzymes matter; many nylons and polyesters persist for long periods despite being hydrolysable under stronger laboratory conditions.

Hydrolysis can cleave ester or amide backbone links in the condensation polymers studied here. Ordinary poly(alkene) C–C backbones lack those hydrolysable links; hydrolysing a pendant group would not by itself cut that main chain.

Hydrolysis products depend on the conditions

Acidic hydrolysis of a polyester gives carboxylic acids and alcohols; alkaline hydrolysis gives carboxylates and alcohols. Polyamide acid hydrolysis gives acids and protonated amine/ammonium groups, while alkali gives carboxylates and amines. A later acid/base work-up changes ionic forms without changing the recovered carbon skeletons.

Worked example: complete alkaline hydrolysis of a PET residue supplies ethane-1,2-diol and benzene-1,4-dicarboxylate salt. Acidifying then gives benzene-1,4-dicarboxylic acid. Do not draw free COOH groups as the predominant products while excess hydroxide remains.

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Photodegradation starts when absorbed light initiates bond-breaking chemistry. It can reduce chain length without fully converting material into harmless small molecules. Biodegradation requires biological processing under appropriate conditions; mechanical fragmentation is different again. A responsible chemical comparison specifies the pathway instead of using “degradable” as an undefined guarantee.

> **TRY IT**
>
> Why can a polymer be hydrolysable in hot acid but persist in cold seawater?

Answer: Hydrolysis rate depends on conditions and access to the links. Low temperature, lack of catalysis and a resistant physical structure can make environmental breakdown very slow even when a laboratory reaction is possible.

Chapter check: count both functional ends, cleave the actual backbone link, include end-group corrections when required and distinguish chemical susceptibility from measured degradation rate.

References and further reading

Scope follows section 35 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide’s Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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