Polymerisation

Addition polymerisation, deducing repeat units and monomers, and the problems of disposing of poly(alkene)s.

20.1 Addition polymerisation

Addition polymerisation joins many unsaturated **monomer** molecules (alkenes) into a long-chain **polymer**, with **no other product**. The C=C bonds open and join, so the polymer has the same empirical formula as the monomer.

$$n\,CH_2{=}CH_2 \rightarrow [-CH_2-CH_2-]_n \qquad n\,CH_2{=}CHCl \rightarrow [-CH_2-CHCl-]_n$$

These are poly(ethene) and poly(chloroethene), PVC. Conditions depend on the monomer and process: catalysts or radical initiators may be used, and some routes use high pressure. One set of conditions does not apply to every addition polymer.

The repeat unit

The **repeat unit** is the smallest group of atoms that repeats along the chain. To write it from a monomer, draw the monomer with the C=C **opened** into a single bond, with the two ends as open bonds (shown with brackets and n). Substituents stay on the same carbon.

For propene $CH_3CH{=}CH_2$ the repeat unit is $-CH(CH_3)-CH_2-$.

Finding the monomer from a section of polymer

1. Find the repeat unit (the carbon backbone is a chain of single bonds, with the pattern repeating, usually every **two** backbone carbons).
2. Put the double bond back between those two carbons and close off the bonds.

> **TRY IT**
>
> A section of polymer is $-CH_2-CHCN-CH_2-CHCN-$. Name the monomer.

The repeat unit is $-CH_2-CHCN-$, so the monomer is $CH_2{=}CHCN$, **propenenitrile** (acrylonitrile).

Properties and disposal of poly(alkene)s

Poly(alkene)s have strong C–C and C–H bonds and are **non-polar**, so they are **chemically inert**. This makes them durable and useful, but they are **non-biodegradable** and persist in landfill and as litter, in the

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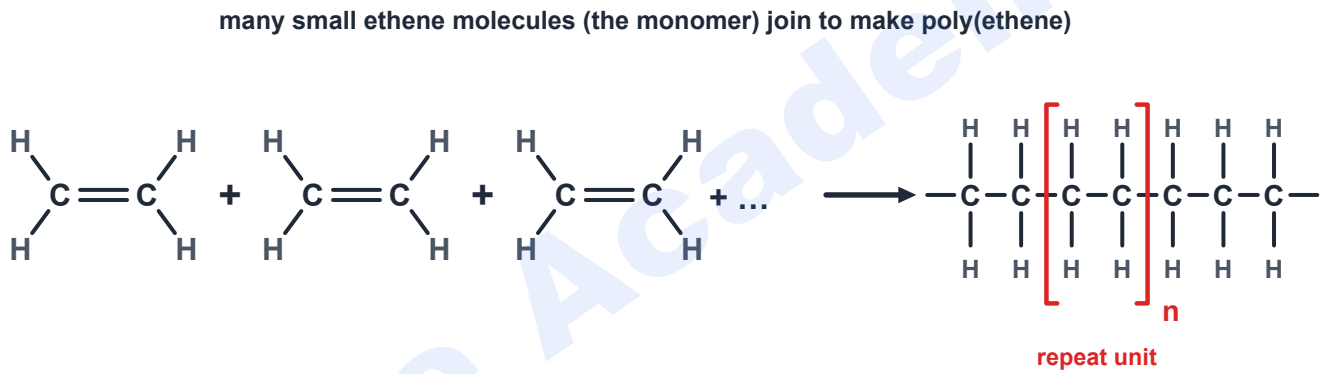
sea in particular.

Disposal problems:

- **Landfill:** takes up space, and the plastic lasts for a very long time.
- **Burning:** gives energy but forms **carbon dioxide** and, from PVC, **toxic gases such as hydrogen chloride** (and carbon monoxide if combustion is incomplete), so the products of burning are **harmful**; scrubbers are needed.
- **Recycling:** possible but requires sorting.

Follow the original double-bond carbons

In a simple alkene monomer, the pi component of C=C is replaced by new sigma links to neighbouring units. The original alkene carbons become adjacent backbone carbons. Their substituents remain attached to the same carbon; they do not all move into the backbone. No small molecule is removed, so all monomer atoms are retained in the repeat unit.



Worked example: $CH_2 = C(CH_3)_2$ gives $-CH_2 - C(CH_3)_2-$ as the repeat unit. Two carbons form the backbone segment and two methyl groups remain branches. A drawing with all four carbons in one backbone line would be a different structure. Draw continuation bonds through the brackets and place n outside.

> **TRY IT**
>
> Give the repeat unit from $CH_2 = CHCH_2CH_3$.

Answer: $-CH_2 - CH(CH_2CH_3)-$. The ethyl substituent stays on the second original alkene carbon. Check that each backbone carbon still has four bonds.

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Recovering the monomer from a chain section

Identify the smallest repeating pattern, isolate the original two backbone carbons and restore C=C between them. Remove the continuation bonds but retain all substituents. Reversing the direction of a repeat-unit drawing does not produce a new monomer if connectivity remains identical.

Worked example: $-CH_2-CH(CH_3)-CH_2-CH(CH_3)-$ contains two propene-derived units. Restoring the double bond in one unit gives $CH_2=CHCH_3$. The branch methyl is not removed during polymerisation, and an alkene product does not retain the repeat unit's two open continuation bonds.

For more complex monomers containing several unsaturated groups, use the supplied structure rather than assuming every addition polymer must have the elementary two-carbon repeat pattern. The familiar pattern is a method for the stated simple alkene cases, not a substitute for reading the question.

> **TRY IT**
>
> A repeat unit is $-CH_2-CCl_2-$. Give the monomer and check valencies.

Answer: $CH_2=CCl_2$. Each carbon has two other single bonds plus the double bond, making four bonds. The chlorines remain on the same carbon.

Quantitative relationships

The repeat-unit molar mass equals the monomer molar mass for addition polymerisation because no small molecule is lost. Approximate degree of polymerisation is chain molar mass divided by repeat-unit molar mass, ignoring end-group corrections. Real samples contain a distribution of chain lengths, so average molar mass does not imply that every chain has exactly the same number of units.

Worked example: a poly(ethene) sample has average molar mass 28,000 g mol^{-1}. A C_2H_4 repeat unit has molar mass 28.0 g mol^{-1}, so there are about 1000 repeat units per average chain. This corresponds to roughly 2000 backbone carbons, because each unit contributes two.

One mole of monomer supplies one mole of repeat units, distributed among chains. It does not supply one mole of whole polymer molecules each containing thousands of units. Distinguish these amounts when combining conversion data with average chain length.

> **TRY IT**
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> A propene-derived polymer has approximate average molar mass 84,000 g mol^{-1}. Estimate the repeat-unit count using monomer molar mass 42.0 g mol^{-1}.

Answer: $84000/42.0=2000$ units. Each unit contains three carbons overall, although only two form the main backbone segment.

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Why structure affects durability and properties

Unsubstituted poly(alkene) backbones have strong, relatively unreactive C–C and C–H bonds and lack readily hydrolysable links. This contributes to persistence. Substituents can introduce polarity, as in PVC, so the statement that **all** addition polymers are non-polar is too broad. The underlying lack of easily broken backbone links remains important.

Long chains interact at many sites, so bulk properties differ substantially from those of a small monomer. Branching and chain arrangement affect packing and intermolecular attractions, influencing flexibility and strength. It is not enough to say "strong bonds make every polymer hard": the particular chain structure and its organisation matter.

Evaluate disposal options rather than listing them

Mechanical recycling needs collection, sorting and processing. Mixed plastics, dyes, additives and contamination can reduce recovery quality. Incineration may recover useful energy but produces carbon dioxide, and chlorine-containing polymers can release acidic gases requiring treatment. Landfill avoids immediate combustion emissions but occupies space and retains persistent material. Fragmentation into smaller pieces is not equivalent to complete biodegradation.

Worked evaluation: a durable cable coating must resist chemical attack during use. Replacing it with a readily hydrolysable material might create one disposal advantage but shorten its service life. A balanced answer considers the use, collection system and actual end-of-life conditions rather than declaring one material universally preferable.

> TRY IT
>
> Why are ester-linked polymers generally more susceptible to hydrolysis than a poly(ethene) backbone?

Answer: Ester groups provide reaction sites that can be cleaved by water under suitable conditions. Poly(ethene) lacks comparable hydrolysable backbone groups. This does not imply every ester-linked polymer disappears rapidly in ordinary seawater.

Chapter check: retain substituents, show continuation bonds and distinguish repeat units from complete chains. Compare these structures with **condensation polymers**.

References and further reading

Scope follows section 20 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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