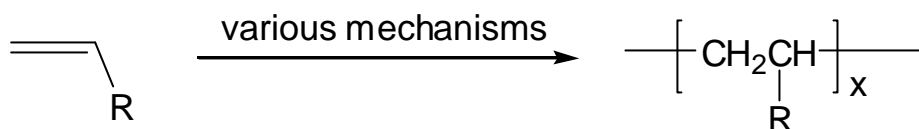# Chain (= Addition) Polymerisation

Generally exothermic process: one C=C bond replaced by two C-C bonds

Bond energy: C=C   611 kJ/mol

C-C   347 kJ/mol (x 2) ➔ ΔE = 83 kJ/mol

Examples: Polyethylene

Polypropylene

Polystyrene

Poly(methylmethacrylate)   "Perspex"

Poly(acrylonitrile)   "Acrylic" fibres

Poly(vinylacetate)   "Acetate" fibres

Poly(vinylchloride)   PVC

Poly(butadiene) and others   Rubber

Addition polymers are some of our most important large-scale ("commodity") polymer materials.

All are made in principle by having one growing "active" end on every chain. Only this is able to add another monomer.
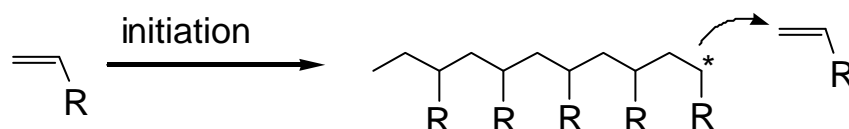

In this way, large molecules are produced rapidly, with excess monomer in solution.

This differs from the step reaction where there are two "active" ends, each growing independently, and all monomer is quickly converted into oligomers.

1. Radical Polymerisation

C=C bond can be attacked by radicals. Easy for monomers $CH_2=CHX$ and $CH_2=C(X)(Y)$: "vinyl" monomers.

Radicals are moieties that arise by the homolytic cleavage of a single bond, to give <u>species with one unpaired electron</u>.

benzoyl peroxide

AIBN = azobis(isobutyronitrile)
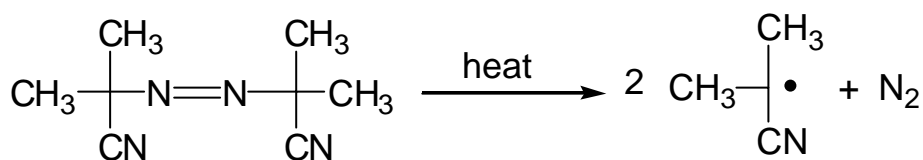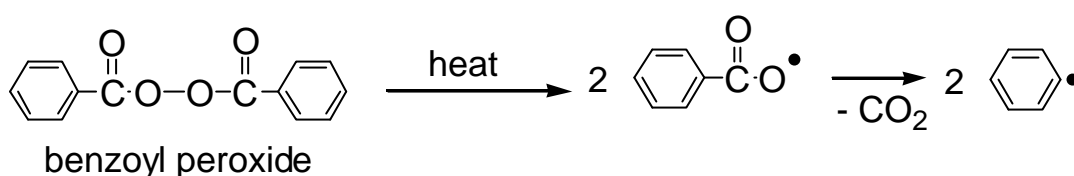
These are consumed in the subsequent radical reaction ➔ *"radical initiators"* (not catalysts).

Three phases:

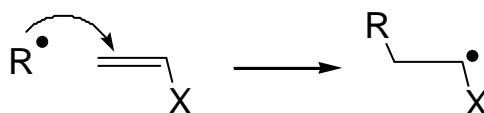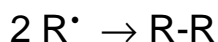**Initiation** **Propagation** **Termination**

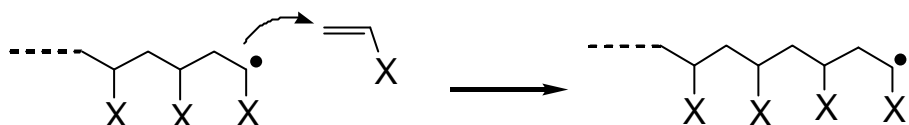<u>Initiation:</u>

Initiator I decomposes to give "free radicals", R˙

R˙ adds to a vinyl monomer to generate a new radical:
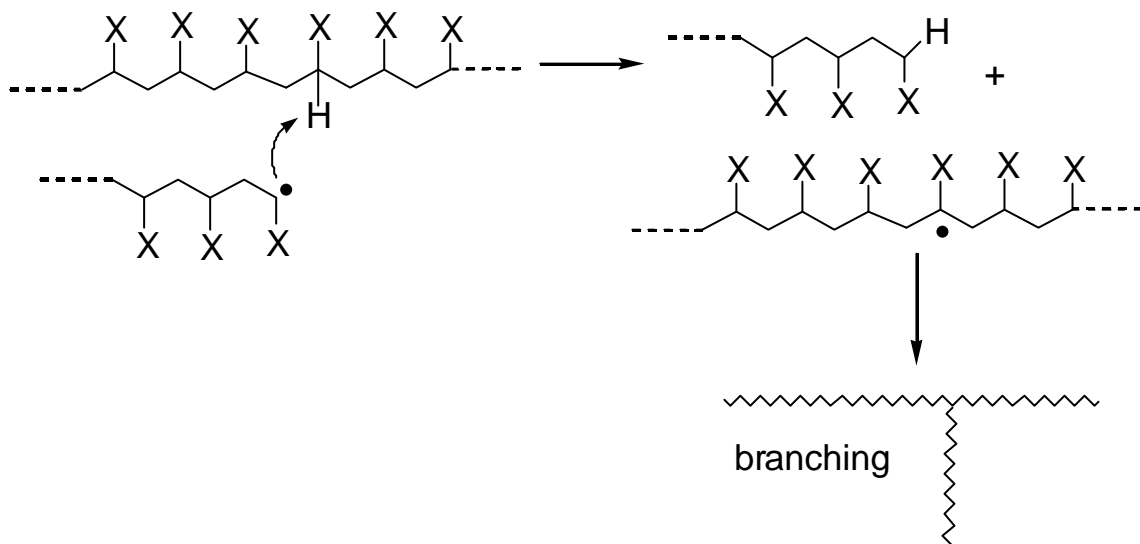
About 60 – 100% of radicals typically generate a polymer chain. This can be lower if *radical recombination* is facile:

$$2 \text{ R}^\bullet \rightarrow \text{R-R}$$

Propagation:

During propagation, chain transfer is possible: one radical centre may attack another polymer chain:
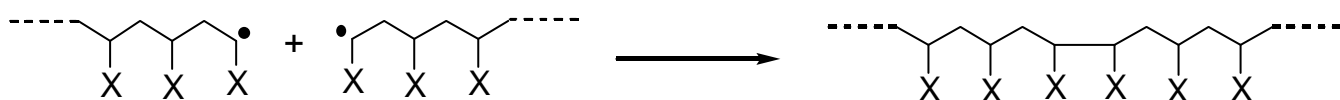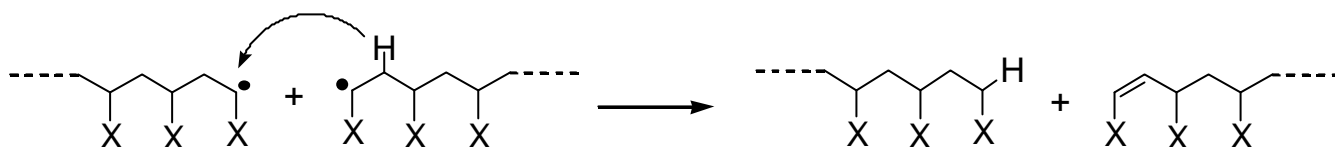

branching

If a radical attacks its own chain, rings may be formed.

Termination:

Theoretically a radical polymerisation could live forever. One radical could consume all monomers.
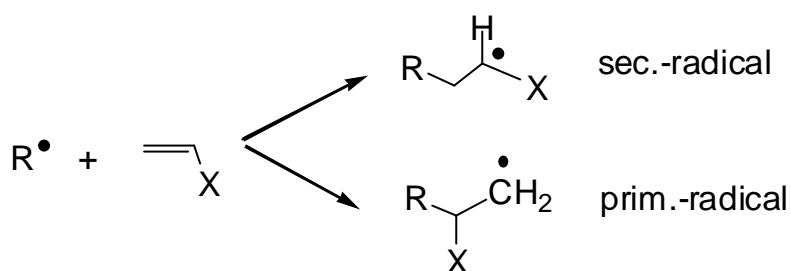
However, termination can occur by *radical combination* or *disproportionation*:

Termination can also occur by attack on the solvent: H-abstraction.

Regioselectivity of radical reactions:

$R^\bullet$ + (alkene with X)

→ sec.-radical

→ prim.-radical

primary radicals are very reactive and unstable. Usually X stabilises a radical, hence secondary radicals are favoured ➜ head-to-tail polymers.

Eamples of radical polymerisations:

Initiated by AIBN etc.:

      Styrene to give atactic polystyrene

      Vinyl chloride to PVC

      Methylmethacrylate to PMMA
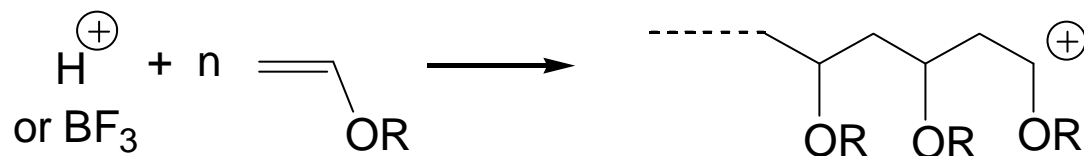
2. Cationic Polymerisation

Chain polymerisations can be initiated <u>ionically</u>. In that case the initiator and the propagating centre is either a **carbocation** (*cationic polymerisation*) or a **carbanion** (*anionic polymerisation*).

Cationic polymerisations can be initiated by H^+ of R^+:
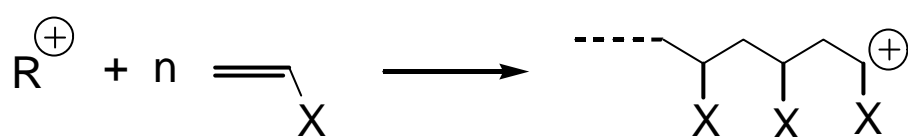
X = electron-donating group

Vinyl ethers are particularly easily polymerised cationically:

Initiation with Lewis acids: BF_3 is often used. Forms hydrate that releases H^+:
$BF_3 \cdot OH_2 \rightarrow H^+ [BF_3(OH)]^-$.

The only large-scale industrial process using cationic polymerisation is the copolymerisation of **isobutene with isoprene to butyl rubber**. Here, an $AlCl_3/H_2O$ catalyst is used as H^+ source. H^+ in highly reactive form adds to isobutene to give a Me_3C^+ cation:
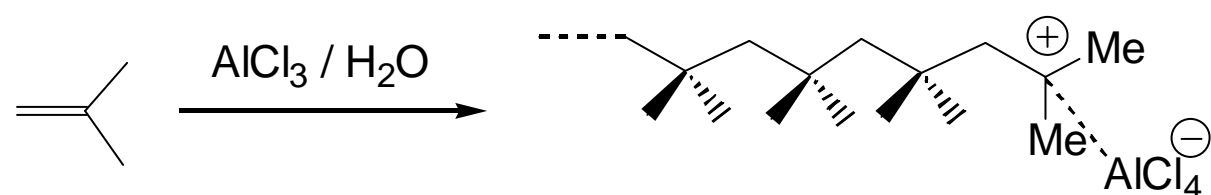
Since the end-CH₃ groups are easily deprotonated, chain transfer is facile:

chain transfer

new polymer
chain
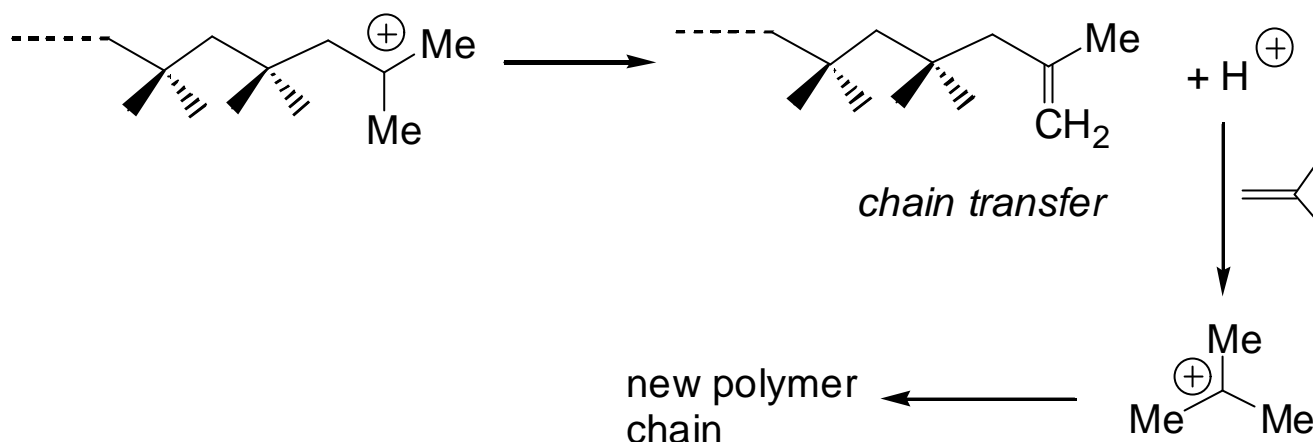
Chain transfer would reduce the molecular weight and give useless products. In order to prevent this, the reaction is carried out at very low temperatures, about -100°C, using CH_3Cl as solvent.
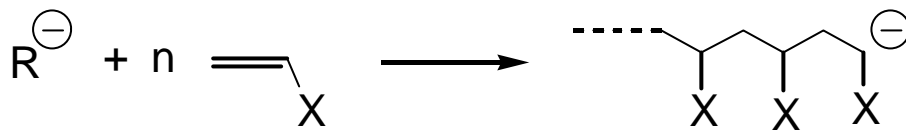
Cationic polymerisations proceed essentially diffusion controlled, without activation barrier. Therefore they proceed <u>rapidly even at very low temperatures</u>.
In fact, yields at higher temperature tend to be poor: deactivating reactions.

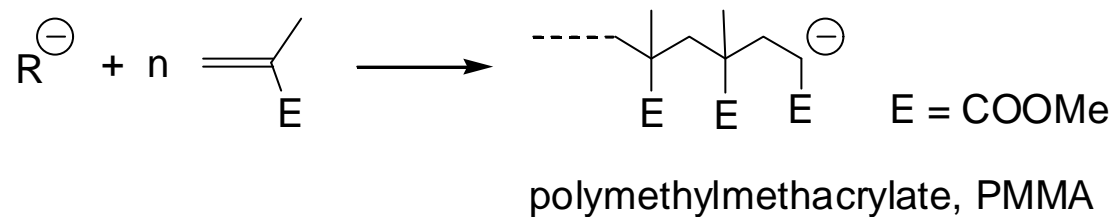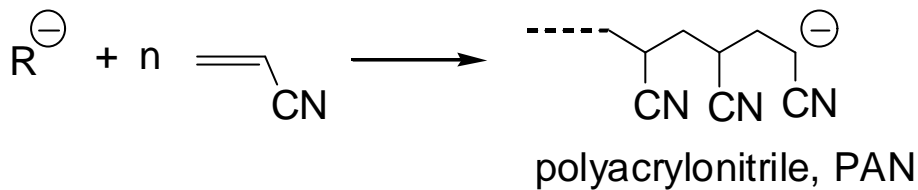Butyl rubber contains about 2% isoprene to give an unsaturated polymer that can be crosslinked.
It is almost impermeable to gases including oxygen: car tyre inner tubes, protection against oxidation.

3. Anionic Polymerisation

R$^{\ominus}$ + n =⟨ (X) ⟶ ⋯⟨X X X⟩$^{\ominus}$

X = electron-withdrawing group

Examples:

R$^{\ominus}$ + n =⟨CN ⟶ ⋯⟨CN CN CN⟩$^{\ominus}$

polyacrylonitrile, PAN

R$^{\ominus}$ + n =⟨E ⟶ ⋯⟨E E E⟩$^{\ominus}$ E = COOMe
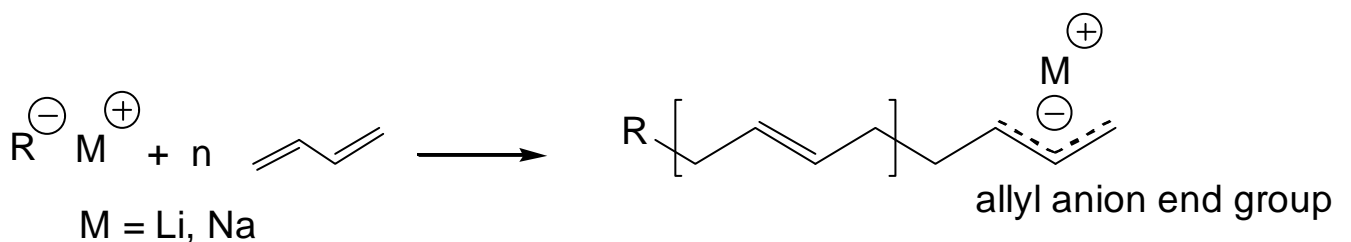
polymethylmethacrylate, PMMA

Anionic polymerisations are initiated e.g. by lithium alkyls.

They tend to be ***living polymerisations***: all centres are reactive, all polymer chains have nearly identical molecular weights
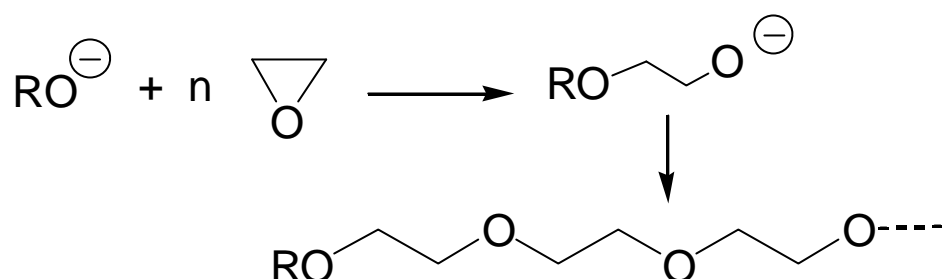➔ very narrow polydispersity: $M_w/M_n \approx 1$

Anionic polymerisation of dienes:

R$^{\ominus}$M$^{\oplus}$ + n ⟨⟩ ⟶ R⟨⟩ M$^{\oplus}$ ⟨⟩$^{\ominus}$

M = Li, Na

allyl anion end group

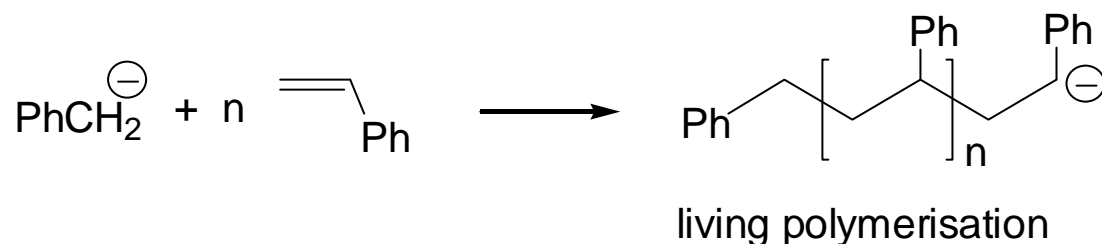Large scale process for butadiene polymerisation.

Ring-opening polymerisation of cyclic monomers

Anionic polymerisation of epoxides:

Anionic polymerisation depends on the nucleophilicity of the initiator:

e.g. Styrene: OH^- inactive, NH_2^- fairly good, $PhCH_2^-$ very effective.

living polymerisation

Differences between radical and ionic polymerisation:

Radical polymerisations: not influenced by nucleophilic or electrophilic impurities. For example, they proceed in <u>water</u> ➔ emulsion polymerisation of vinyl chloride.

Cationic polymerisations: very sensitive to traces of water, H^+ sources
Poisoned by Nu^-: terminated by water, alcohols.

Anionic polymerisations: terminated by electrophiles, killed by water.