2001 Open Paper: Polymerisation of alkenes

Addition polymerisation

Addition polymerisation is a type of reaction in which many monomers react to form a long chain called a polymer, and in which no atomic or molecular species are eliminated.

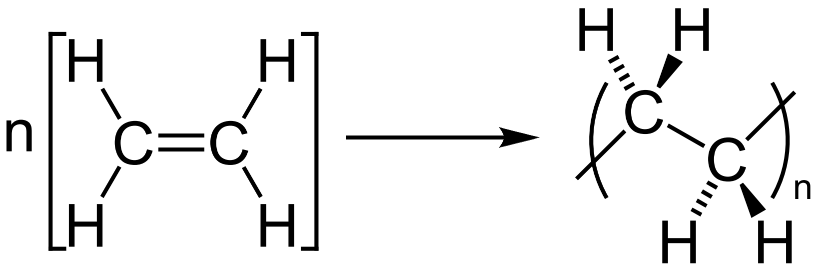

Figure 1: The stoichiometric equation for the formation of poly(ethene) by the polymerisation of ethene.

Ethene is an alkene, an unsaturated hydrocarbon containing a carbon-carbon double bond. The double bond consists of a σ bond and a π bond[1].

In the addition polymerisation of ethene, the double bond opens and becomes a single bond – specifically, the π bond breaks and its two electrons form a σ bond with another ethene molecule.

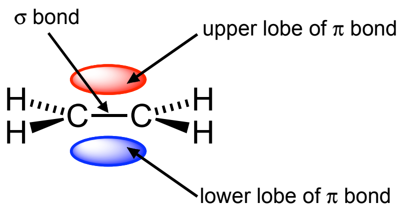

Figure 2: Bonding in ethene

Mechanism of ethene polymerisation to form LDPE

The addition polymerisation of ethene at 75 °C and 1700 atm proceeds via radical intermediates[2]. A radical is an atomic or molecular species containing an unpaired electron, i.e. one not in the same orbital as an electron of opposite spin. The mechanism has three stages: initiation, propagation and termination.

Initiation

Initiation is the formation of radicals from atoms or molecules whose electrons are all paired. Radical initiators generate radicals by undergoing homolytic bond fission. They generally require a weak bond that will easily dissociate into radicals – oxygen or benzoyl peroxide in the early 1930s experiments[3].

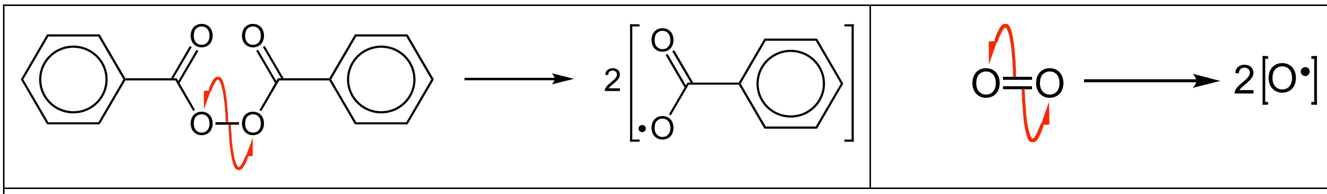

Figure 3: The formation of radicals by homolytic bond fission in radical initiators.
Left: benzoyl peroxide forms benzoyl radicals. **Right:** dioxygen forms atomic oxygen.

The term initiation is also describes the radicalisation of the first ethene molecule in a poly(ethene) chain[2].

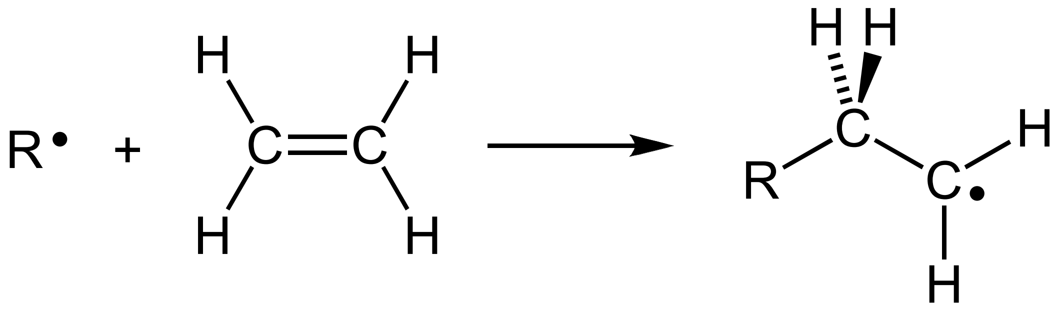

Figure 4: Initiation can also mean the beginning of a poly(ethene) chain by the attack of an initiator radical on an ethene molecule.

Propagation

Propagation is the reaction of radicals with non-radical species.

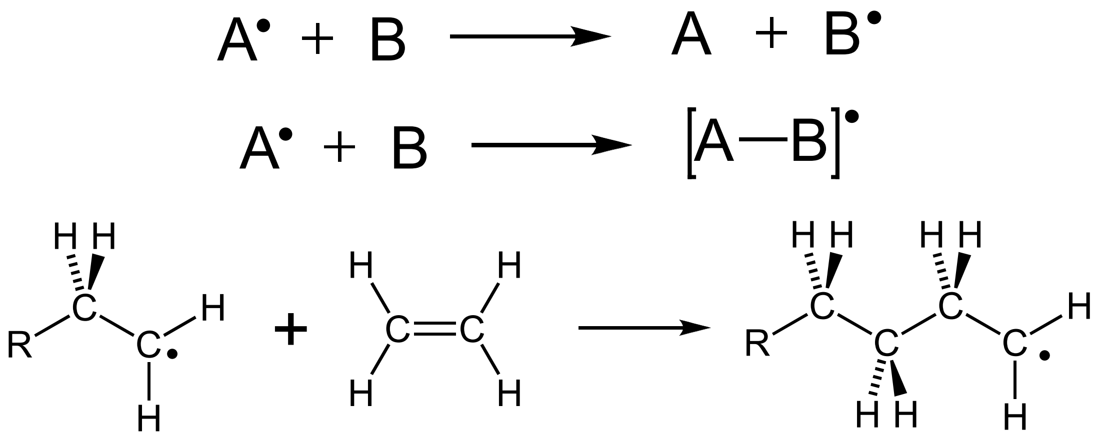

Figure 5: Propagation results in either the radical abstracting an electron from the non-radical (**top**), or the combining of both species to form a new molecular radical (**middle**). In ethene polymerisation, propagation is mostly by the second mechanism, resulting in the poly(ethene) chain growing as ethene molecules add (**bottom**).

Termination

Termination involves two radicals reacting to from a non-radical product. Two unpaired electrons, one from each radical, pair up.

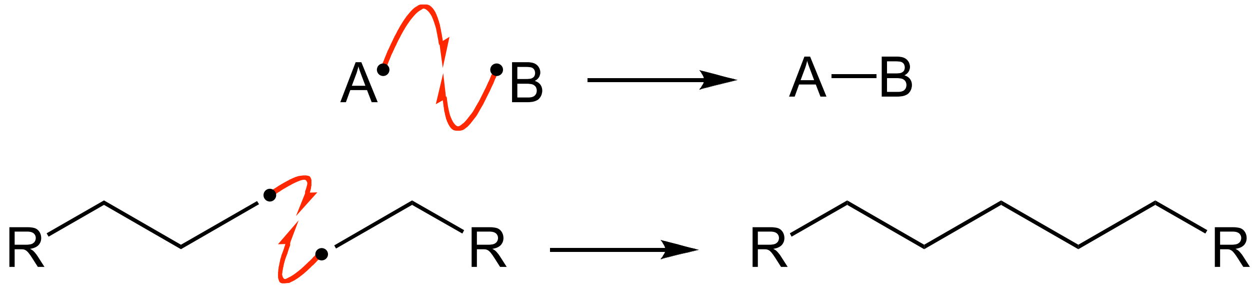

Figure 6: Termination
Top: The general mechanism for radical termination.
Bottom: Termination of radicals in ethene polymerisation completes a poly(ethene) chain.

Effect of chain packing on properties

The closeness of chains in a sample of polymer determines three important characteristics: its density, the strength of its intermolecular forces and the ease with which neighbouring chains can move with respect to each other.

The more closely packed the chains, the higher the density. If chains cannot align closely, e.g. because of branching, the polymer will have a low density.

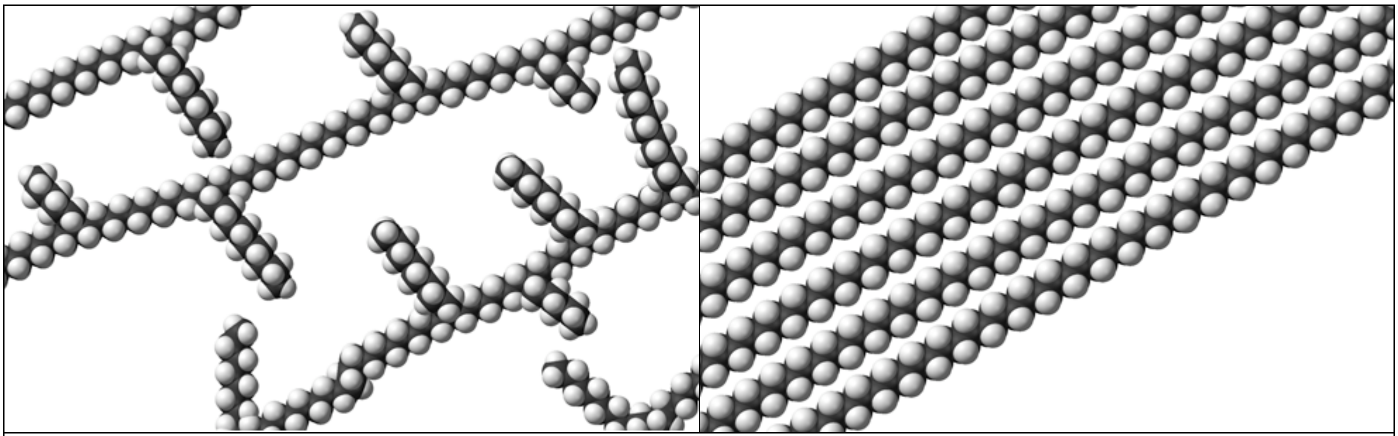

Figure 7: Close packing and density in poly(ethene).
Left: In LDPE, chains cannot align closely so LDPE has a low density.
Right: In HDPE, chains align very closely so HDPE has a high density.

Intermolecular forces are much stronger at close range. The more closely packed the chains, the greater the overall force of attraction between chains. Chains that are far apart, e.g. due to extensive branching, have low intermolecular forces (van der Waals' forces in poly(alkenes)).

The closer the chains are, and therefore the greater the intermolecular forces are, the more difficult the movement of chains with respect to each other is.

LDPE: Low-density poly(ethene)

LDPE is heavily branched and these branches prevent its chains aligning closely. Consequently, LDPE has low density, low tensile strength and a low softening temperature. Its softness and flexibility can, however, be beneficial.

HDPE: High-density poly(ethene)

HDPE, produced by Ziegler-Natta catalysis, has unbranched chains that align closely, leading to high crystallinity, high density, rigidity, hardness, high tensile strength and a high softening temperature.

LLDPE: Linear low-density poly(ethene)

LLDPE has short butyl side chains introduced by copolymerisation with hex-1-ene. These branches limit the crystallinity of LLDPE, rendering it flexible, but because they are short, LLDPE is still crystalline enough to withstand tearing forces. It is cheaper than LDPE because it not manufactured via a high-pressure process but with Ziegler-Natta catalysts.

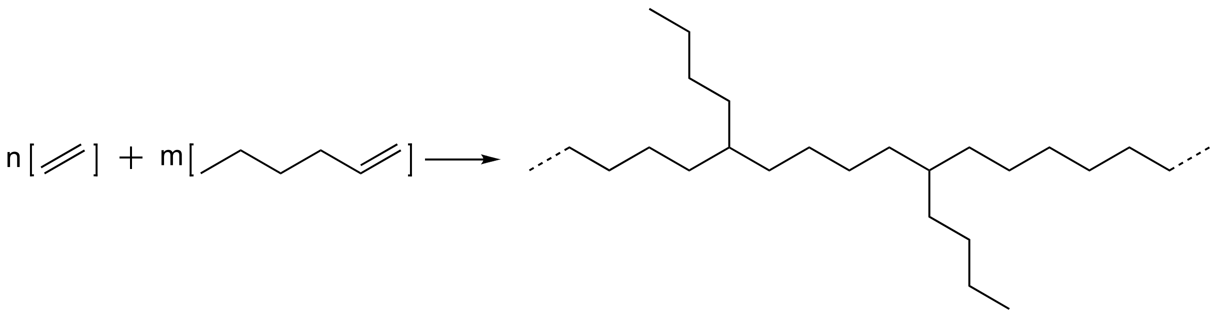

Figure 8: In LLDPE, branching is short and controlled. It is produced by copolymerising ethene with hex-1-ene.

Isotactic poly(propene)

A chain of isotactic poly(propene) has all its methyl groups on one side, so neighbouring chains can align closely. As a consequence, it has a high density, high crystallinity, is rigid and hard, and has a high softening temperature and high tensile strength.

Syndiotactic poly(propene)

In syndiotactic poly(propene), successive methyl groups are on alternate sides of the chain. This regularity allows chains to align closely, in a similar way to the isotactic form. The result is a highly crystalline polymer. It is superior to isotactic poly(propene) in some respects: higher impact strength, greater transparency and greater resistance to γ-rays.

Atactic poly(propene)

In atactic poly(propene), the side of the chain on which a methyl group resides is random – there is no pattern. As such, chains cannot align as closely as they can in the isotactic and syndiotactic forms, resulting in low crystallinity, low density, low softening temperature and low tensile strength. It is soft and flexible.

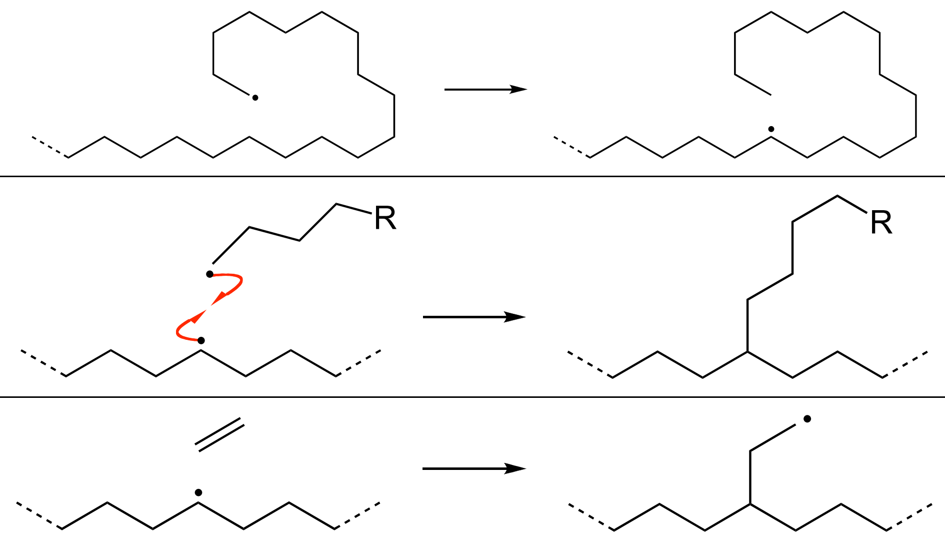

Figure 9: The mechanism of branch formation. Backbiting (propagation, **top**) is the attack of an end-of-chain radical on the chain itself, forming a mid-chain radical, which reacts with another end-of-chain radical (termination, **middle**) or another ethene monomer (propagation, **bottom**), forming a branch.

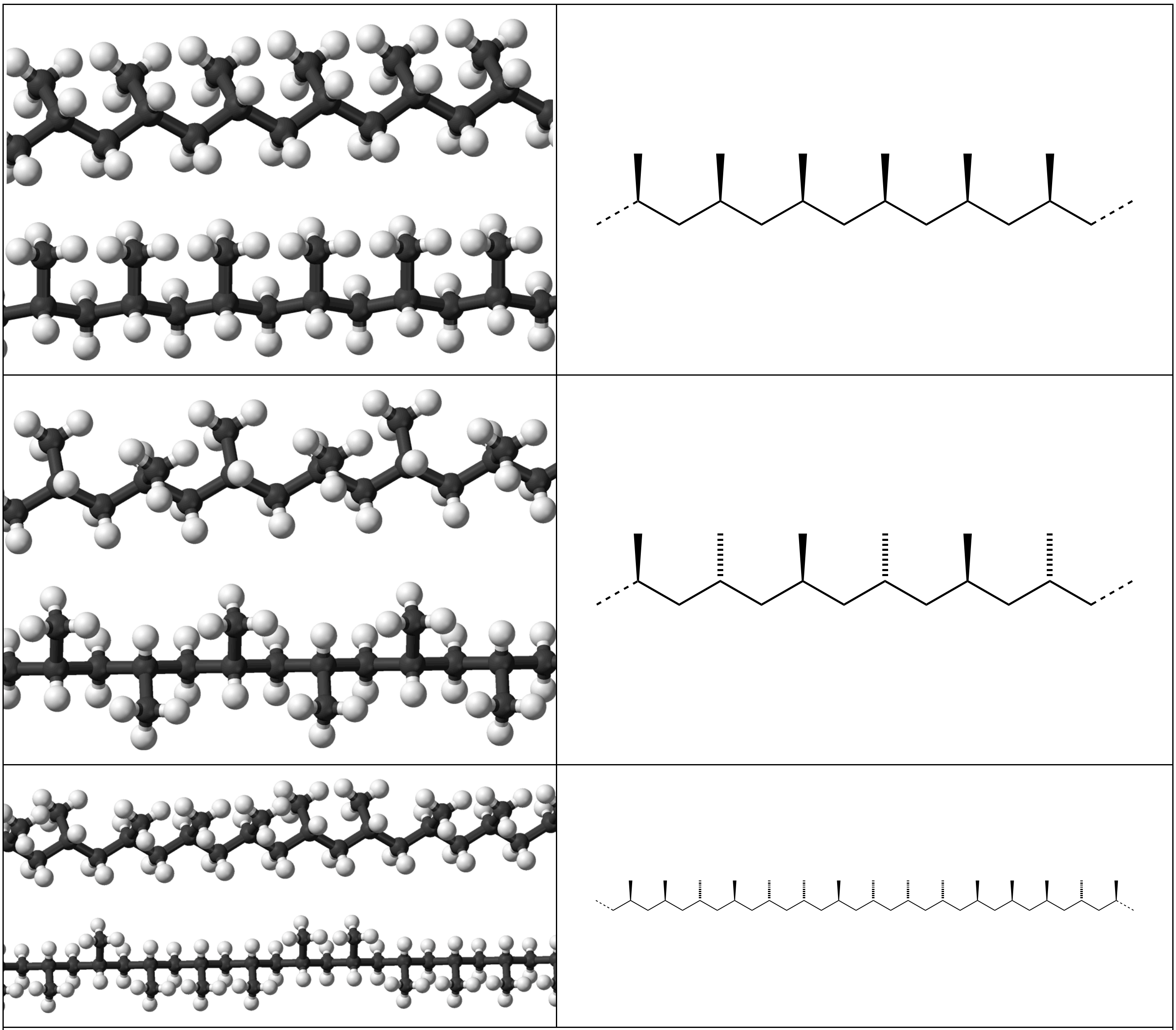

Figure 10: The three different forms of poly(propene).
Left column: ball-and-stick models. **Right column:** skeletal formulae.
Top row: isotactic poly(propene). **Middle row:** syndiotactic poly(propene). **Bottom row:** atactic poly(propene).

Hardening poly(ethene)

The first commercial poly(ethene), LDPE, was too soft and melted at too low a temperature for many purposes, so a stronger and more rigid form was sought.

$$C_2H_4(g) \longrightarrow 2C(s) + 2H_2(g)$$

$$\Delta H = -60 \text{ kJ mol}^{-1}$$

Figure 11: The exothermic decomposition of ethene to its constituent elements (**above**) caused explosions that hampered research into ethene polymerisation.

Chemists found high pressures yielded longer-chain, less waxy poly(ethene), and kept the polymerisation under control by continually adding cold ethene to the reaction vessel.

In the high-pressure, high-temperature Fawcett-Gibson-Perrin process, chains became branched and had variable lengths. Backbiting (see **Figure 9**) could not be controlled, so an entirely different mechanism was required to form unbranched poly(ethene).

Ziegler made real progress in the 1950s when he found trialkylaluminium compounds sometimes catalysed the formation of crystalline poly(ethene). Accidental contamination of the equipment with a nickel compound inhibited the reaction. Further investigation found $TiCl_4$, $ZrCl_4$ and VCl_4 were effective cocatalysts[4]. Ziegler-Natta catalysts have limitations: susceptibility to poisoning by the polymer that halts chain growth and branching caused by a second catalyst particle. Additionally, they only work with small hydrocarbon monomers.

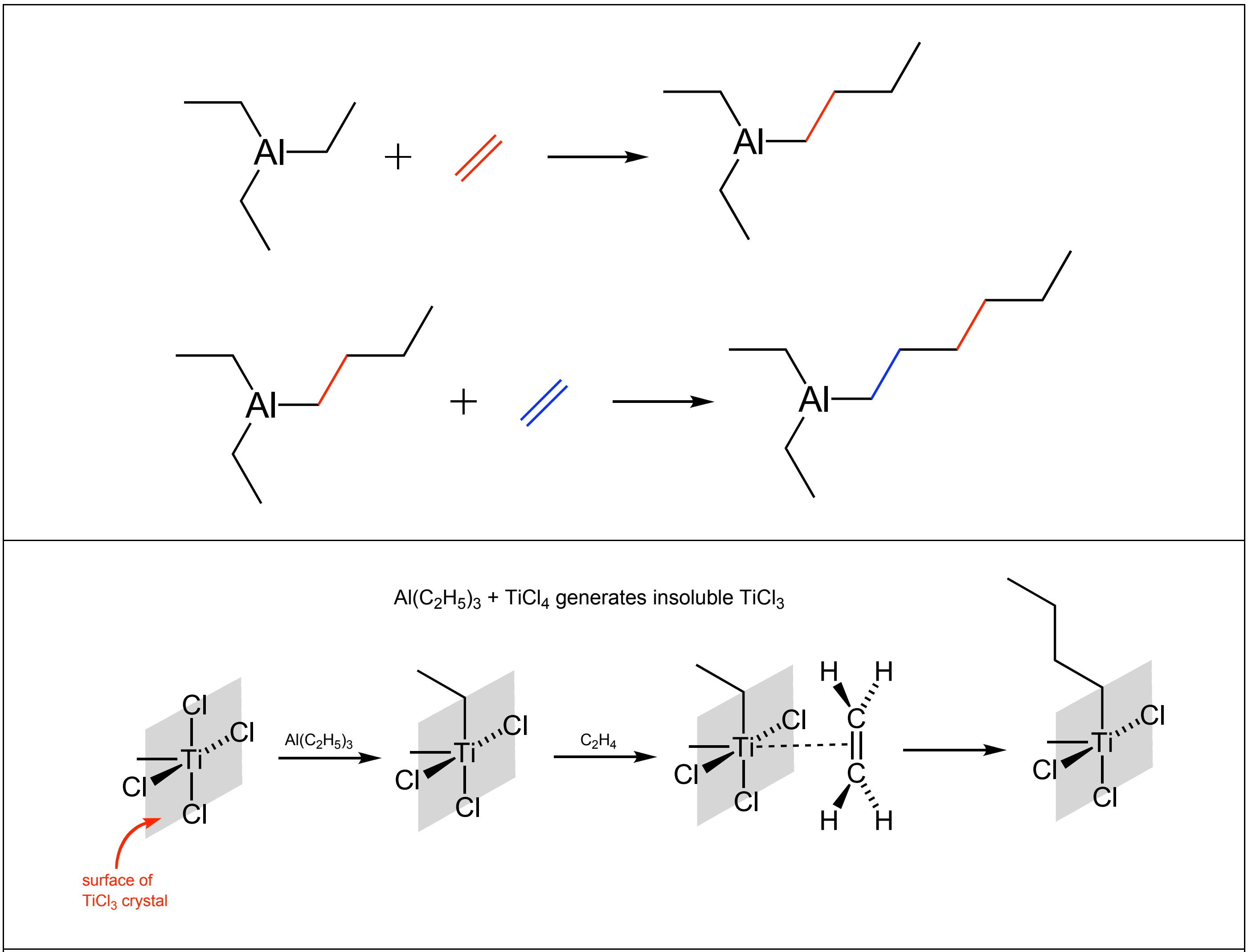

Figure 12: Mechanisms of Ziegler-Natta catalysis

Top: With AlR_3 but not $TiCl_4$, ethene monomers insert between aluminium and an R group bonded to it[5].

Bottom: With both AlR_3 and $TiCl_4$ present, ethene monomers insert at titanium. Some details are still unknown to chemists, but the scheme shown above reflects current academic opinion.

Metallocene catalysts

Metallocenes are compounds in which a metal atom or ion is ‘sandwiched’ between two aromatic ring systems.

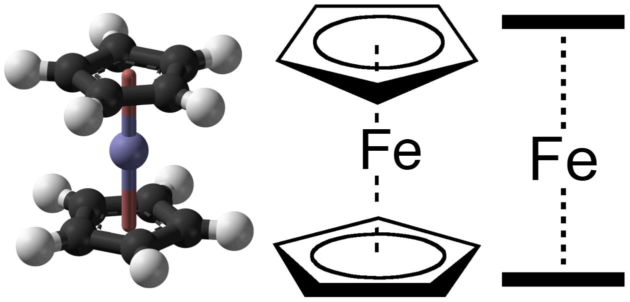

Figure 13a: Ferrocene, $Fe(C_5H_5)_2$, is the prototypical metallocene. It consists of an Fe^{2+} ion sandwiched between two planar cyclopentadienide ($C_5H_5^-$) ions.

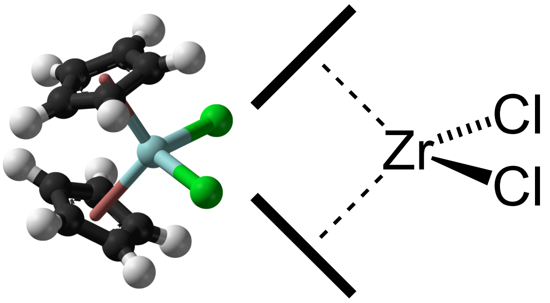

Figure 13b: Metallocenes used as polymerisation catalysts have labile ligands such as chlorine atoms, as in zirconocene dichloride, shown above.

In the seventies and eighties, Kaminsky was investigating Ziegler-Natta-type catalytic systems with $TiCl_4$ replaced by titanocenes. In one experiment, heating triethylaluminium, a titanocene and ethene unexpectedly gave a high yield of poly(ethene).

The apparatus had not been flushed with an inert gas, allowing air to remain in the system. They later deduced that water in that air had reacted with triethylaluminium to generate MAO, a compound that ‘activated’ the titanocene, converting it from a poor catalyst into an excellent one[7].

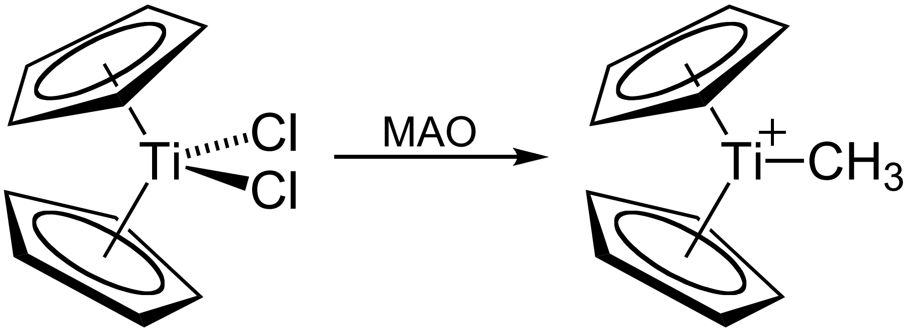

Figure 14: MAO (methylalumoxane) is an activator that replaces labile ligands with methyl groups in certain metallocenes, producing a more effective catalyst. The structure of MAO is uncertain[4,8], but its composition, $[Al(CH_3)O]_n$, is known[9].

The mechanism of metallocene catalysis is similar to that of traditional Ziegler-Natta catalysis as illustrated in **Figure 12**. Successive alkene monomers insert between the growing chain and the metal atom. The difference in metallocenes is the bulky arene ligands (the ‘jaws’ or ‘bread’ of the sandwich!), which restrict the inserting monomers to particular orientations. Different ring systems confer a different stereochemistry on the methyl groups in poly(propene).

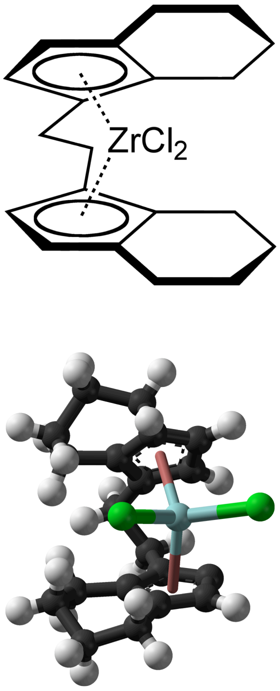	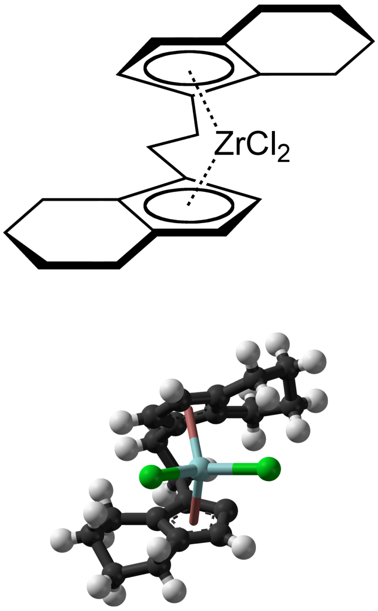	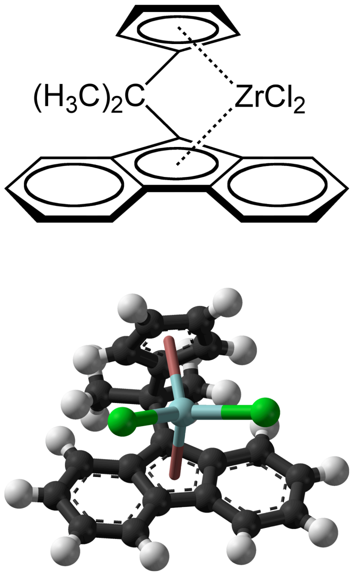
Figure 15a: This zirconocene catalyses the formation of atactic poly(propene), since there is no restriction on the direction of methyl groups.	**Figure 15b:** This zirconocene catalyses the formation of isotactic poly(propene) because its bridged-ring system restricts all methyl groups to one side of the growing polymer chain.	**Figure 15c:** This zirconocene allows the growing chain to flip from side to side, generating the alternating methyl groups required for syndiotactic poly(propene).

Until 1988, metallocene catalysts could only produce the atactic and isotactic forms of poly(propene). Ewen eventually found a bridged arene system that forced the growing polymer chain to flip from side to side as each alkene molecule inserts, generating the elusive and valuable syndiotactic poly(propene)[10].

Main report: 987 words

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Summary

A high-pressure, high-temperature, radical-mediated process produced the first poly(ethene). Uncontrolled branching kept its density low. Ziegler developed the $AlR_3/TiCl_4$ catalyst to produce higher-density crystalline poly(ethene) at low pressure. Natta synthesised three stereochemically different forms of poly(propene). Ewen developed a different zirconocene catalyst to produce each form of poly(propene).

Summary: 48 words