4. Coordination Polymerisation

This polymerisation requires a catalyst, usually in combination with an "activator".

Principle:



Chain growth within the coordination sphere of a metal centre.

Example: ethylene

1930's: radical polymerisation to give low-density polyethylene branched structure, soft, wide polydispersity
→drastic reaction conditions: 300°C, 2000 atm pressure, initiated by traces of O₂.

1953: <u>Karl Ziegler</u>: Discovery of catalytic route to polyethylene Catalyst: TiCl₄ activated with AlEt₃ → Ziegler catalysts mild conditions: 25 – 50°C, 1 – 10 atm pressure 1955: Giulio Natta: use of Ziegler catalysts to <u>polymerise propene</u> stereoselective: mainly *isotactic polypropene* (i-PP)

1973: Nobel Prize to K. Ziegler and G. Natta

What is happening?

(1) TiCl4 reacts with AIEt₃ under reduction to give small crystallites of [TiCl3]x

→ catalyst is very finely suspended in solution but heterogeneous

(2) On the surface of the crystallites some CI atoms are exchanged for Et:



This is known as the Cossée-Arlman mechanism of polymerisation:

Polymer chain growth proceeds by transfer of a metal-bound alkyl chain to the coordinated monomer.

This process is <u>exothermic</u>:

1 C=C bond \rightarrow 2 C-C single bonds, Δ H \approx 20 kcal/mol

<u>Fast reaction</u>: can give $10^4 - 10^5$ C-C bond formations per second!

Ziegler-PE differs from radical-PE:

- regular, no or very little branching
- better packing of polymer chains: → crystalline, higher density harder, high tensile strength
- narrower polydispersity ($M_w/M_n 5 10$)

Other catalysts for PE:

 $TiCl_3/MgCl_2$ with additives

Cr on silica, probably $Cr(II)/SiO_2$ Phillips catalyst, gives very non-branched PE

Uses: hard materials, drainpipes

Other polyethylenes:

Random copolymers with 1-hexene or 1-octene:

- → side chains make polymer flexible
- Use in films, packaging material

Polyethylene now forms a range of polymers with different properties for different applications;

Most common polymer: world production about 40 million tons / year

Polypropene:

Two sides of monomer are prochiral: stereoselectivity of product depends on mode of monomer coordination to metal centre:



Successive monomer additions from <u>opposite</u> prochiral π -faces gives <u>syndiotactic</u> polymer



This isotactic polymer is the main product. Stereoregular, high melting (163°C).

Used in household goods, fibres. Stretched i-PP has very high tensile strength.

Large volume production: worldwide 25 - 30 million tons / year

The "Metallocene Revolution": Soluble catalysts for ethylene and propylene polymerisations





 C_2 symmetric: isotactic PP





C_s symmetric: syndiotactic PP



"Constraint-geometry catalyst":

high activity for ethylene/alkene copolymerisation

New *<u>"metallocene" catalysts</u> give unprecedented control over*

- polymer stereoregularity,
- molecular weight
- polydispersity
- degree of comonomer incorporation in contrast to classical Ziegler catalysts, comonomer incorporation is uniform and independent of molecular weight.

➔ New ranges of polyolefin materials

Suitable for gas phase and solution processes.

Methyl methacrylate can also be polymerised by a coordination-type mechanism.

Other coordination polymerisations:

CO + alkene



Gives polyketones: $-[CH_2CH_2C(O)]_x$ -Process developed by Shell.

Summary

Polymers provide a wide range of materials without which modern Society would be unthinkable.

We have seen:

- ◆ differences between polymers and small-molecule compounds
- physical characteristics: glass transition, melt transition, molecular weight distribution
- the techniques for polymer characterisation: viscosity, GPC
- number-average and weight-average molecular weights
- ◆ stereo- and regio-regularity

Polymerisation mechanisms:

- Stepwise polymerisations: polyesters, polyamides
- ◆ Kinetics of stepwise polymerisation
- Chain polymerisations:
- Radical
- Cationic
- Anionic
- Coordination: Catalysis