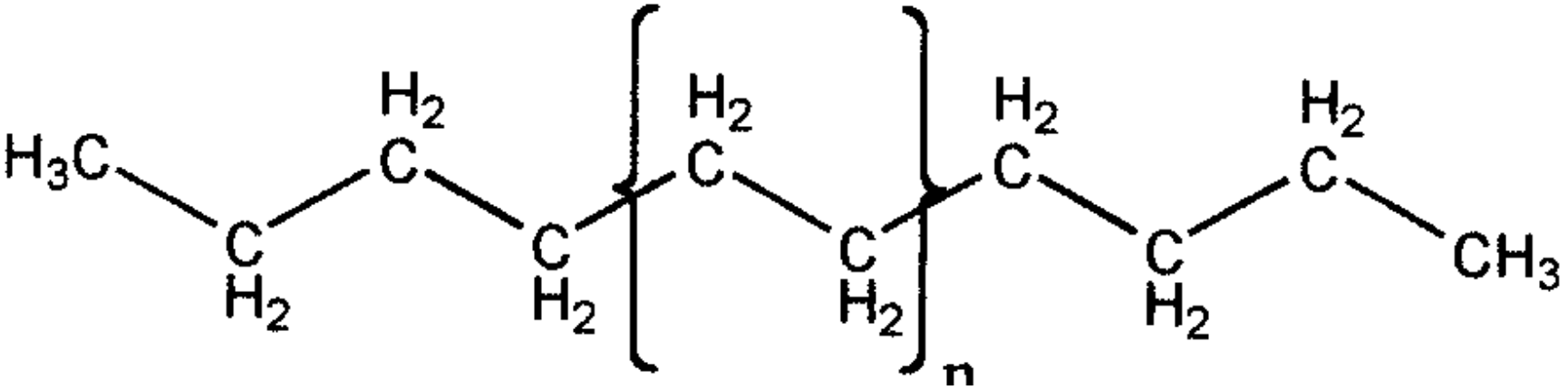
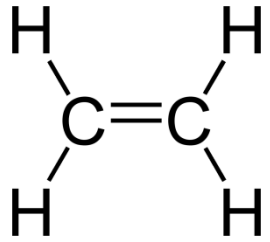
Polyethylene



Monomer:
Ethylene



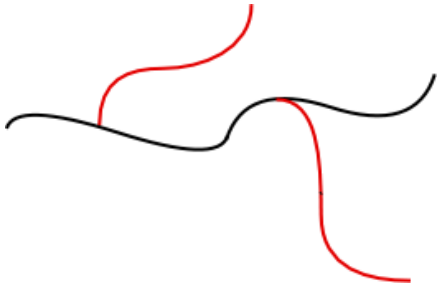
- **High Density Polyethylene (HDPE)**
- **Low Density Polyethylene (LDPE)**
- Linear Low Density Polyethylene (LLDPE)

Low Density Polyethylene (LDPE)

- High degree of short and long chain branching
- Density - 0.910–0.940 g/cm^3
- Lower tensile strength and increased ductility
- Free radical polymerization
- Plastic bags and film wrap

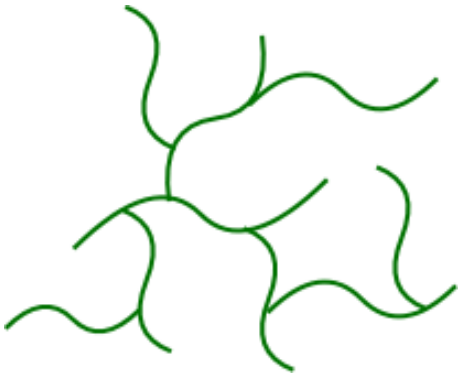
High Density Polyethylene (HDPE)

- Low degrees of branching (essentially linear)
- Density > 0.940 g/cm^3
- High tensile strength
- Various catalysts (ZN, Metallocene)
- Milk jugs, detergent bottles, garbage containers and water pipes



Long chain branching (HDPE)

Short chain branching (LLDPE)



Hyperbranched (LDPE)

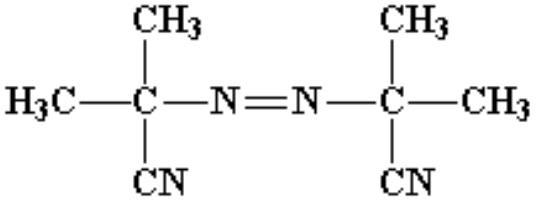
Timeline of Polyethylene

- **1898**
  - Synthesized by accident while heating diazomethane (Called Poly-"methylene" due to repeating $-CH_2$ group)

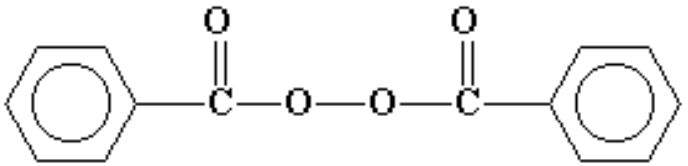
- **1930-35**
  - First polymerization of ethylene at Imperial Chemical Industries.
  - Advent of the **free radical process** to produce LDPE

Free Radical Polymerization

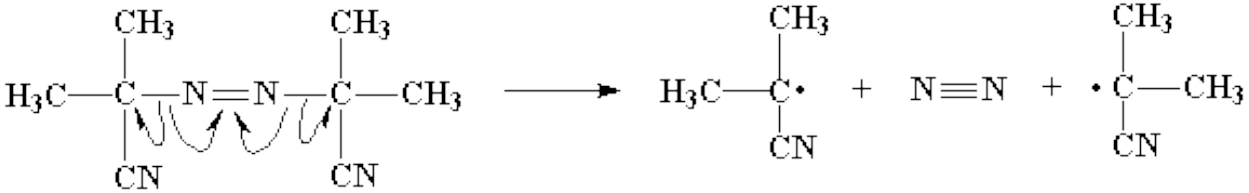
1. INITIATION (You need Initiators)



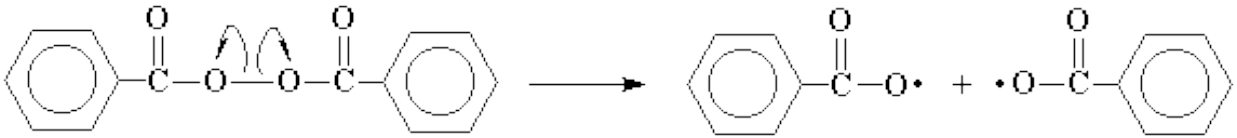
2-2'-azo-*bis*-isobutyrylnitrile
(AIBN)



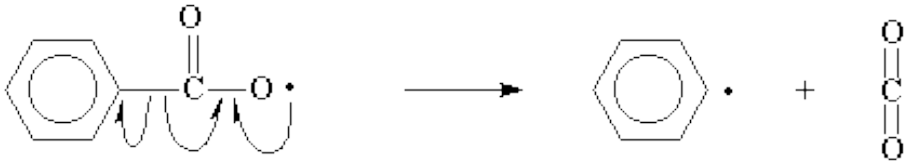
benzoyl peroxide



AIBN



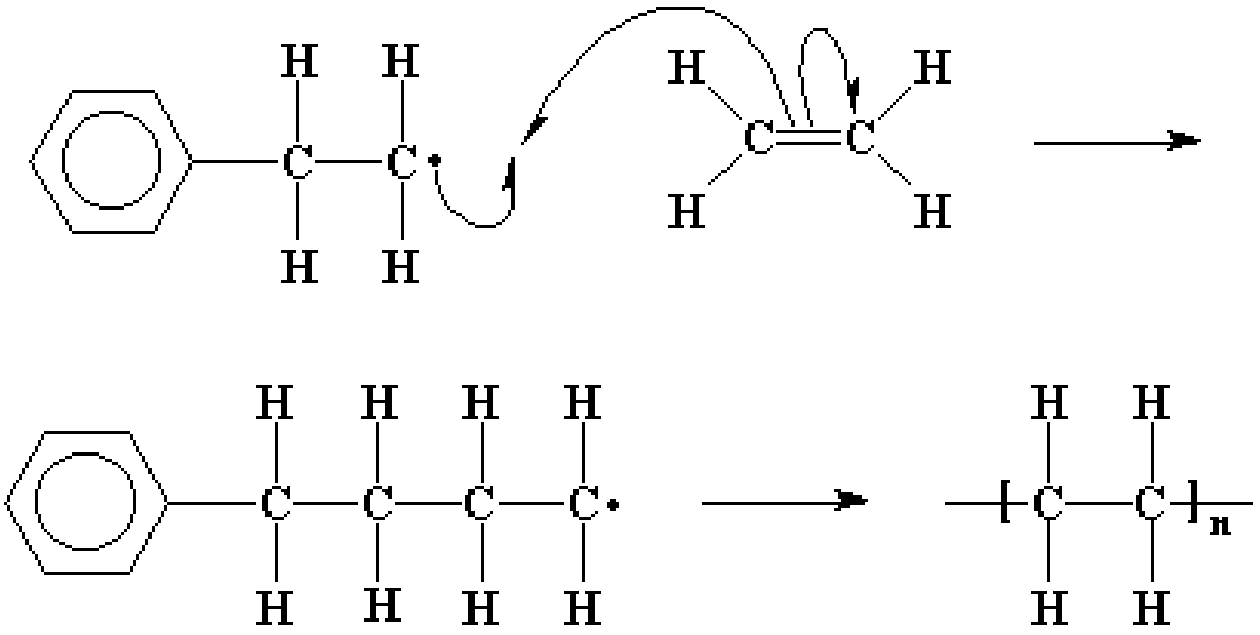
Benzoyl Peroxide



Free Radical Polymerization

2. PROPAGATION

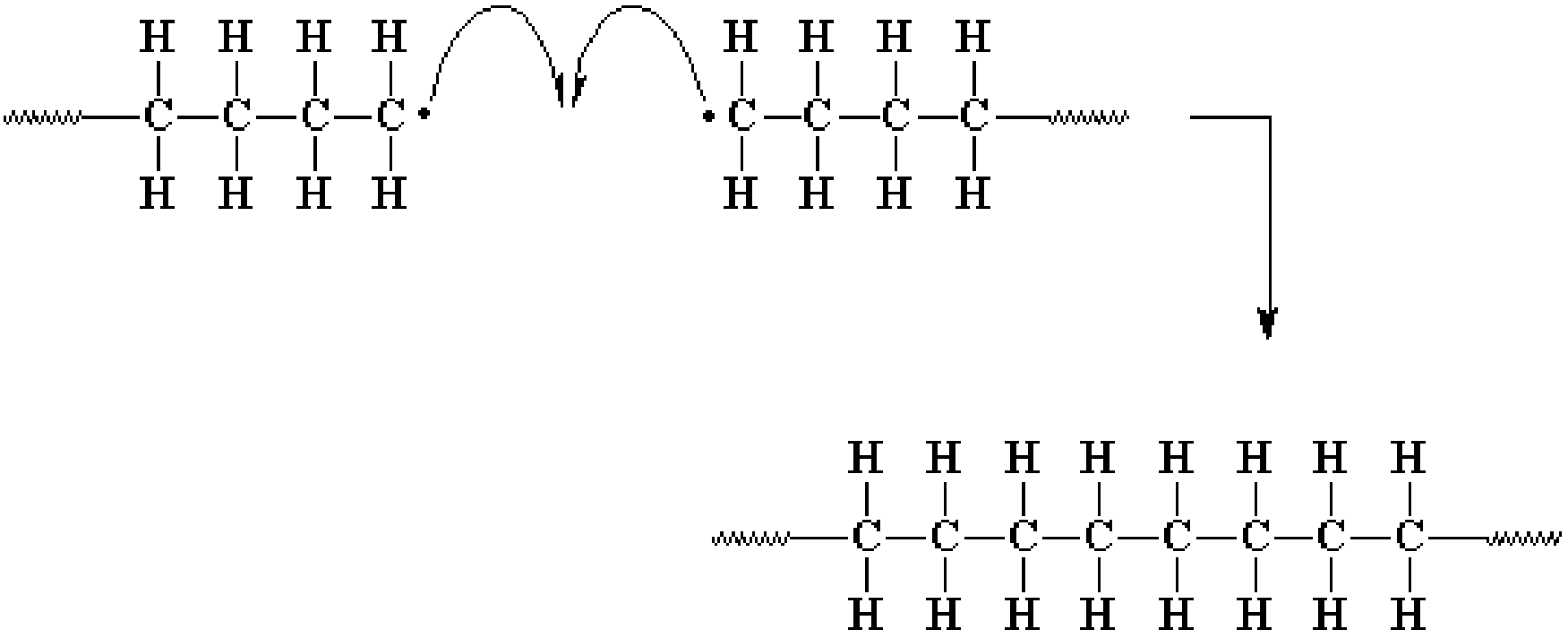
High pressure is needed during the propagation step in order to bring the ethylene monomer closer to the free radicals



Free Radical Polymerization

3. TERMINATION (Many ways)

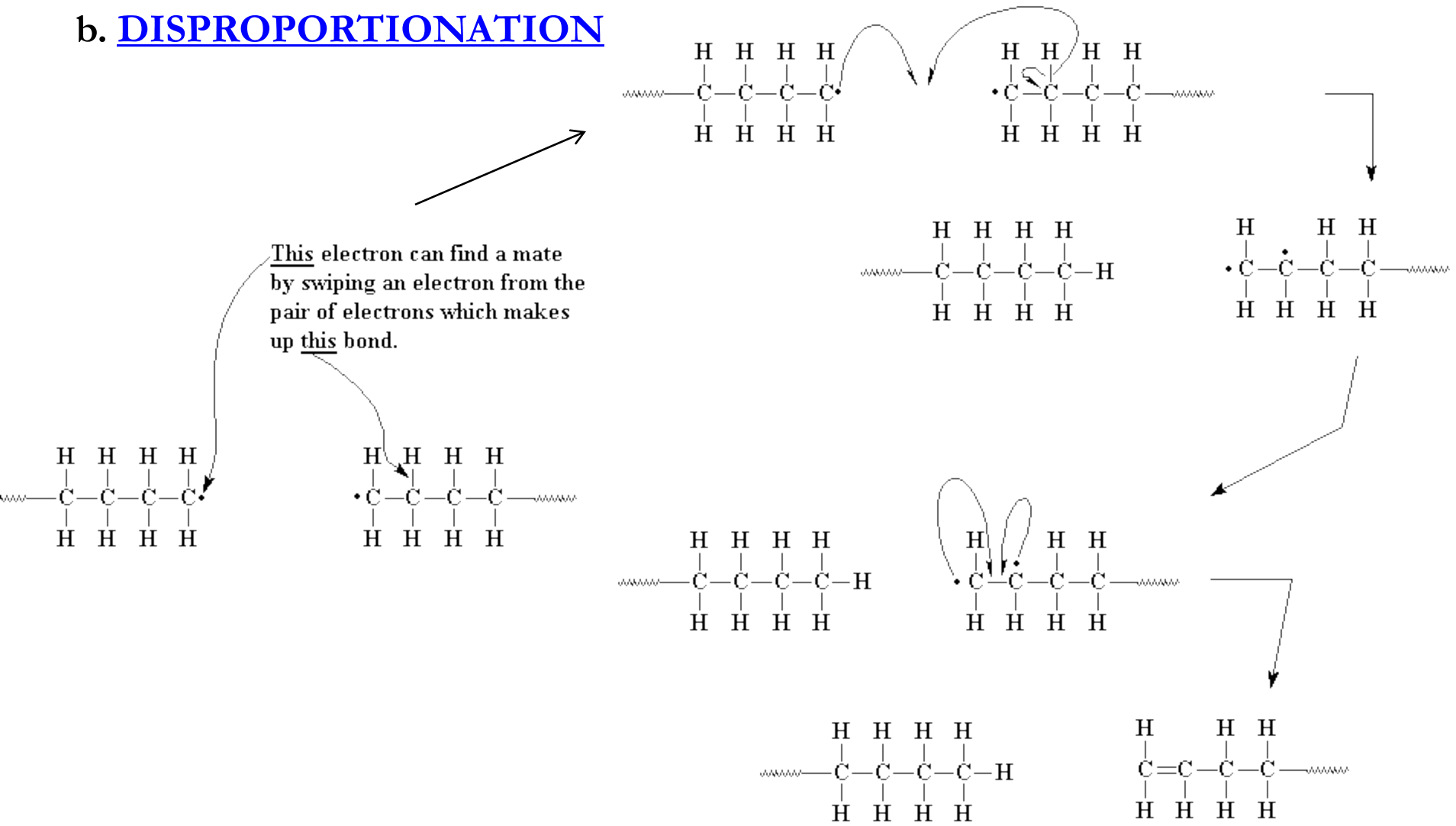
a. COUPLING



Free Radical Polymerization

3. TERMINATION (Many ways)

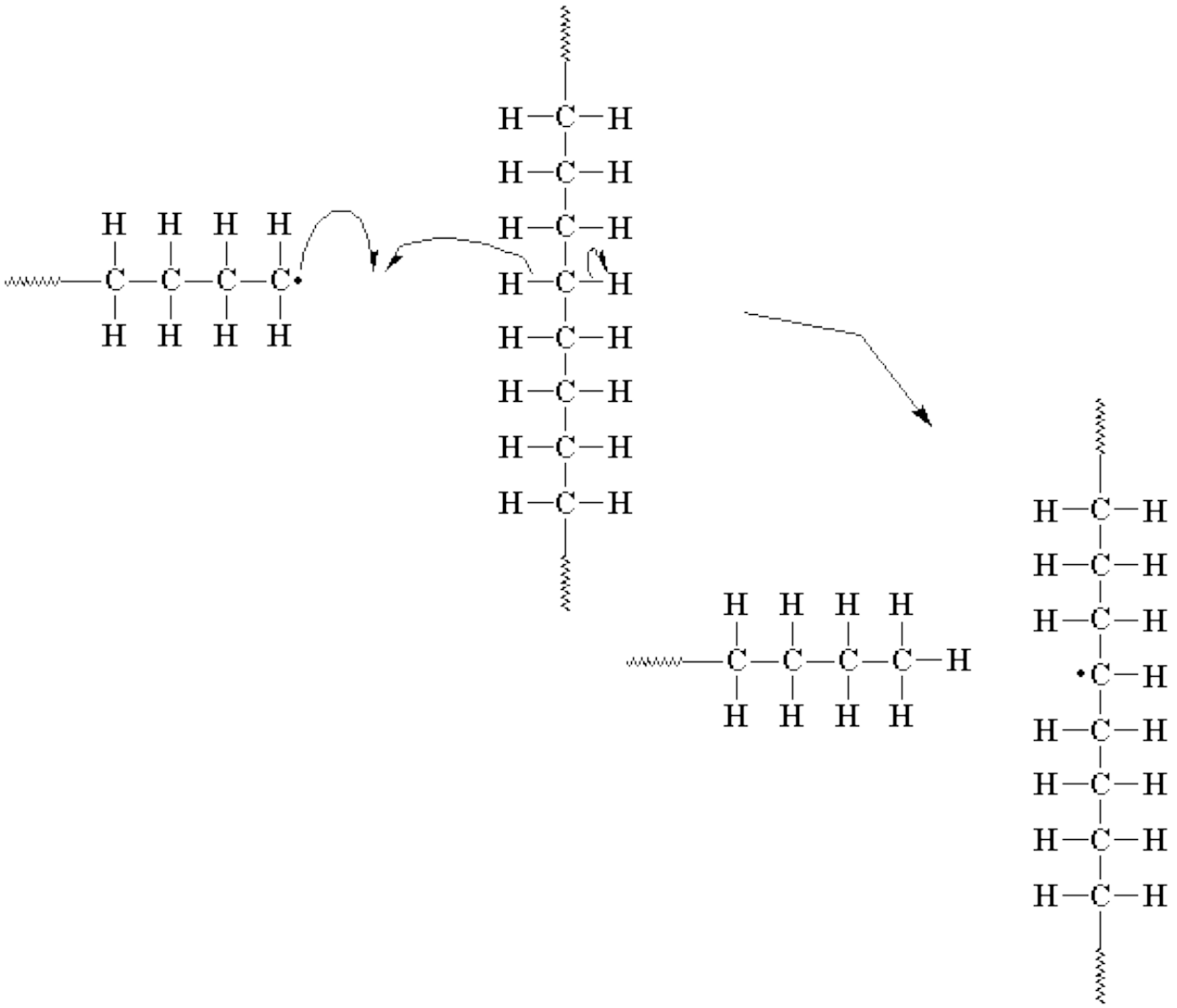
b. DISPROPORTIONATION



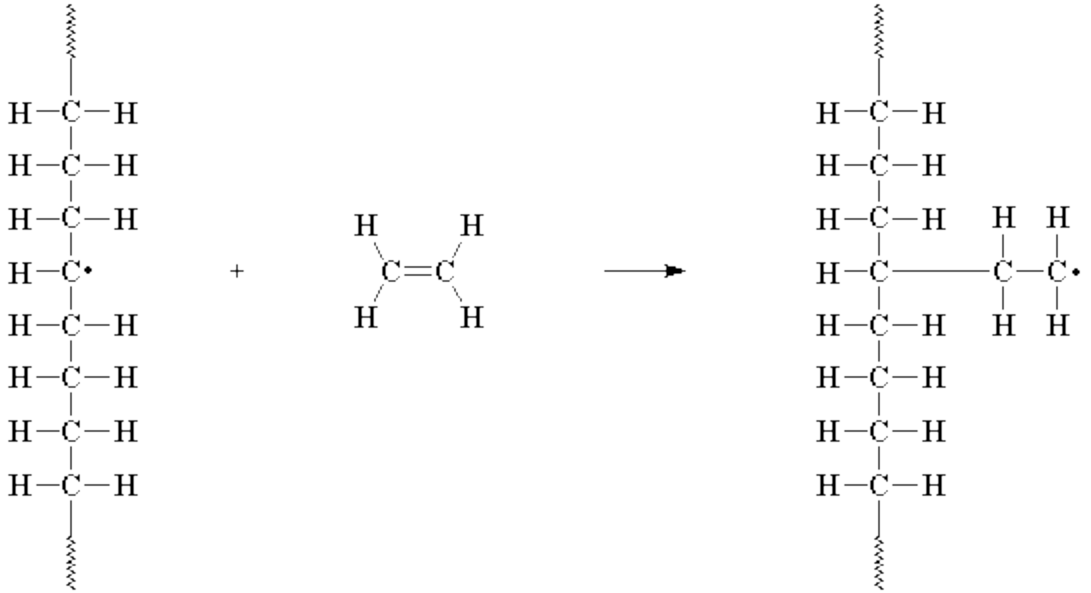
Free Radical Polymerization

3. TERMINATION (Many ways)

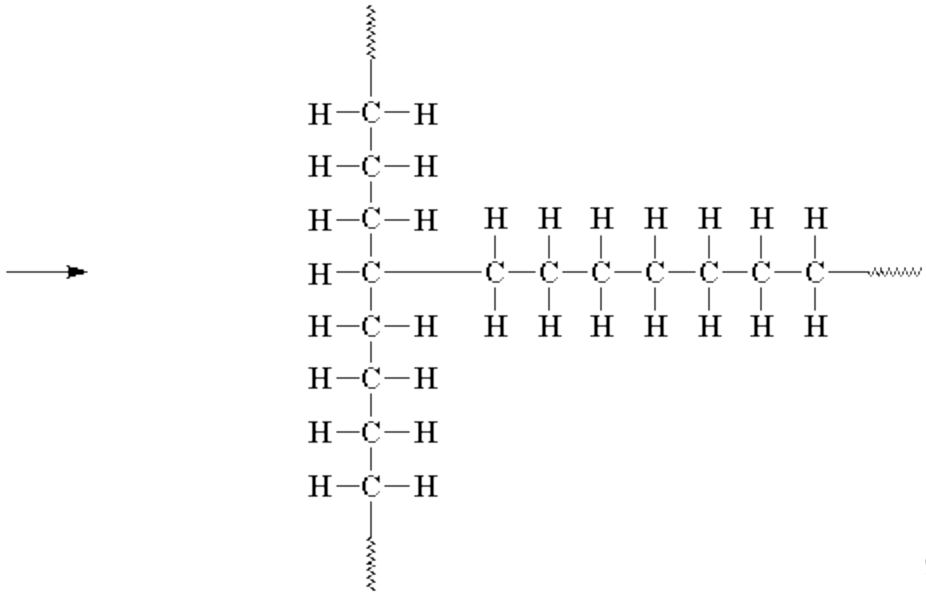
c. CHAIN TRANSFER (Hydrogen Abstraction)

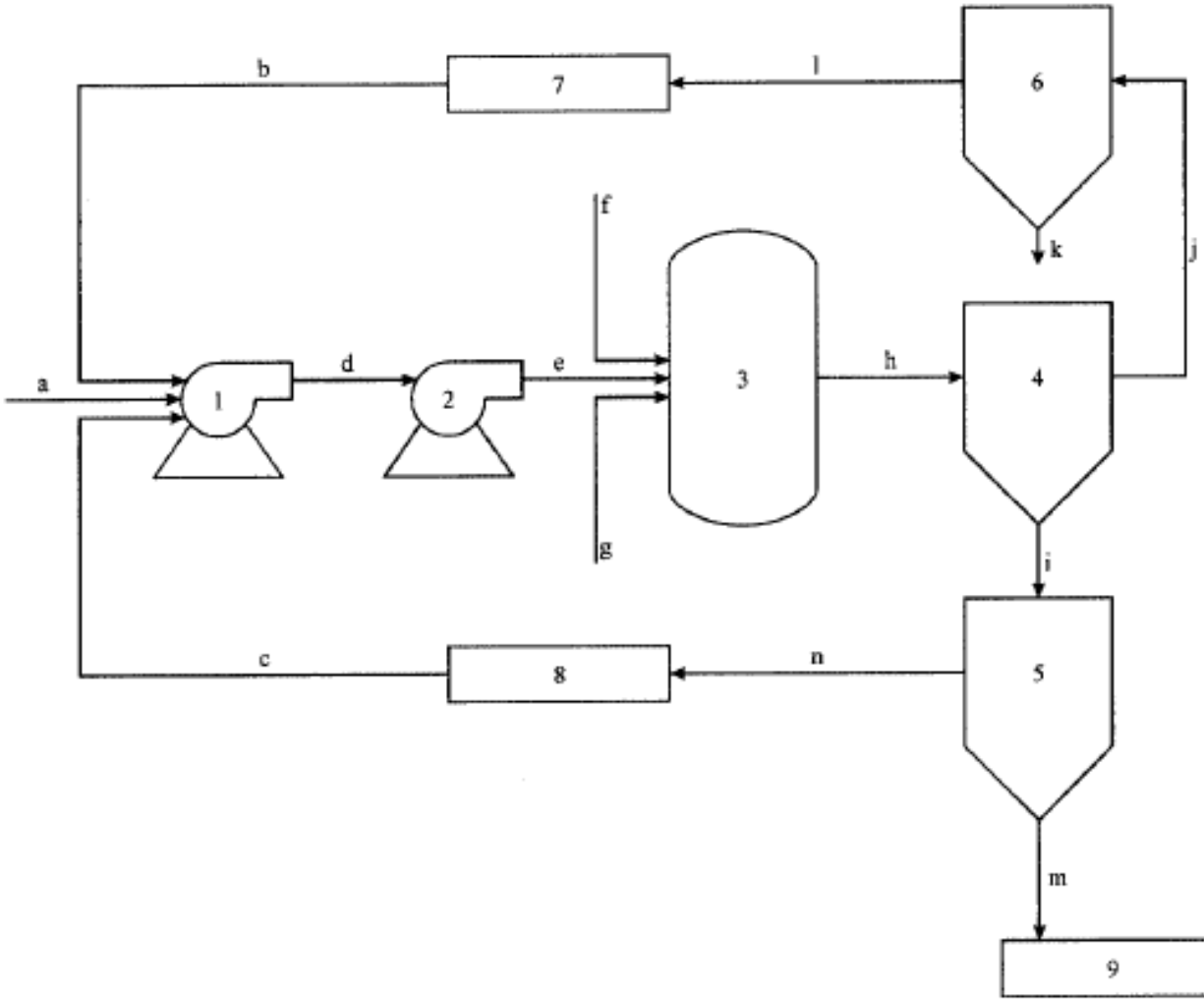


Free Radical Polymerization



SIDE REACTIONS
(Causes Branching)





Disadvantages

1. Uncontrolled Process
   - Structure, Molecular weight
2. Requires high pressure
3. Reactions are highly exothermic
4. Inefficient process (20% ethylene polymerized)

Figure 2 Schematic representation of high pressure polymerization of ethylene. 1, Primary compressor; 2, secondary compressor; 3, reactor; 4, high pressure separator; 5, low pressure separator; 6, low pressure separator; 7,8, coolers; 9, extruder. a, Fresh ethylene; b,c, recycled ethylene; d, intermediate pressure ethylene; e, high pressure ethylene; f, catalyst; g, chain transfer agent; h, ethylene, oils, waxes, and polyethylene; i, ethylene and polyethylene; j, ethylene, oils, and waxes; k, oils and waxes; l, ethylene recycle; m, polyethylene; n, ethylene recycle; o, LDPE pellets.

Timeline of Polyethylene

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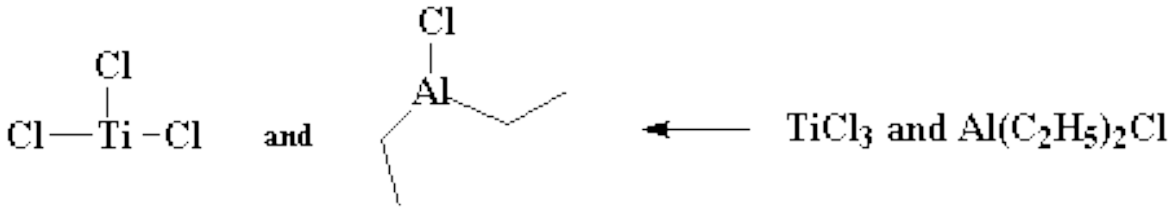
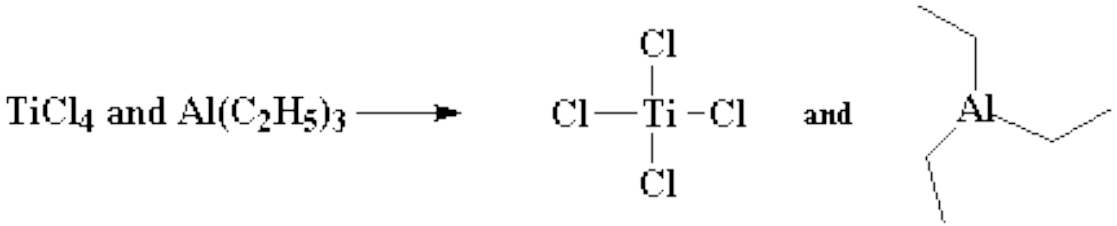
- **1930-35**
  - First polymerization of ethylene at Imperial Chemical Industries.
  - Advent of the **free radical process** to produce LDPE

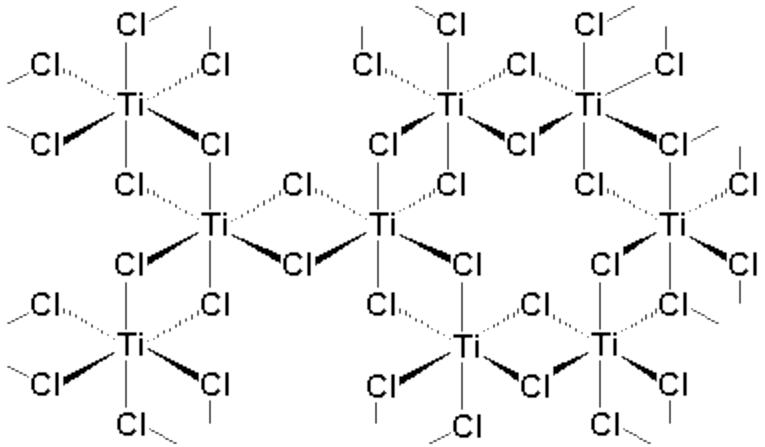
- **1950's**
  - Ziegler-Natta Catalyst (Inorganic Catalyst for HDPE)

Zieglar-Natta Catalyst



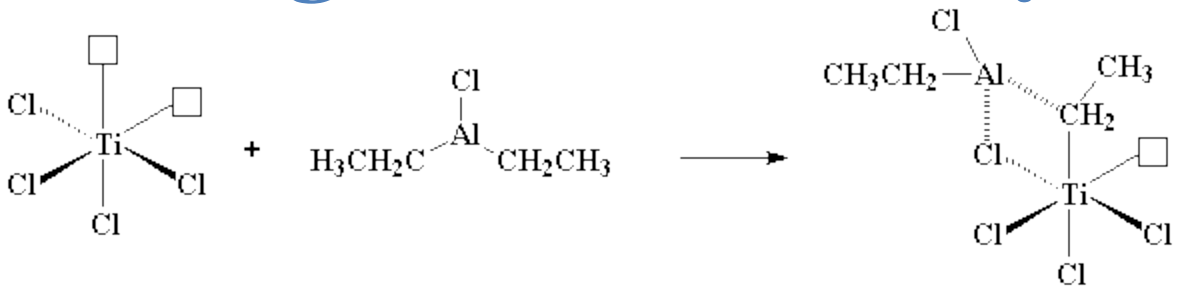
These are two sets of Zieglar-Natta catalyst/co-catalsyt systems. Either way, we have four chlorine atoms.

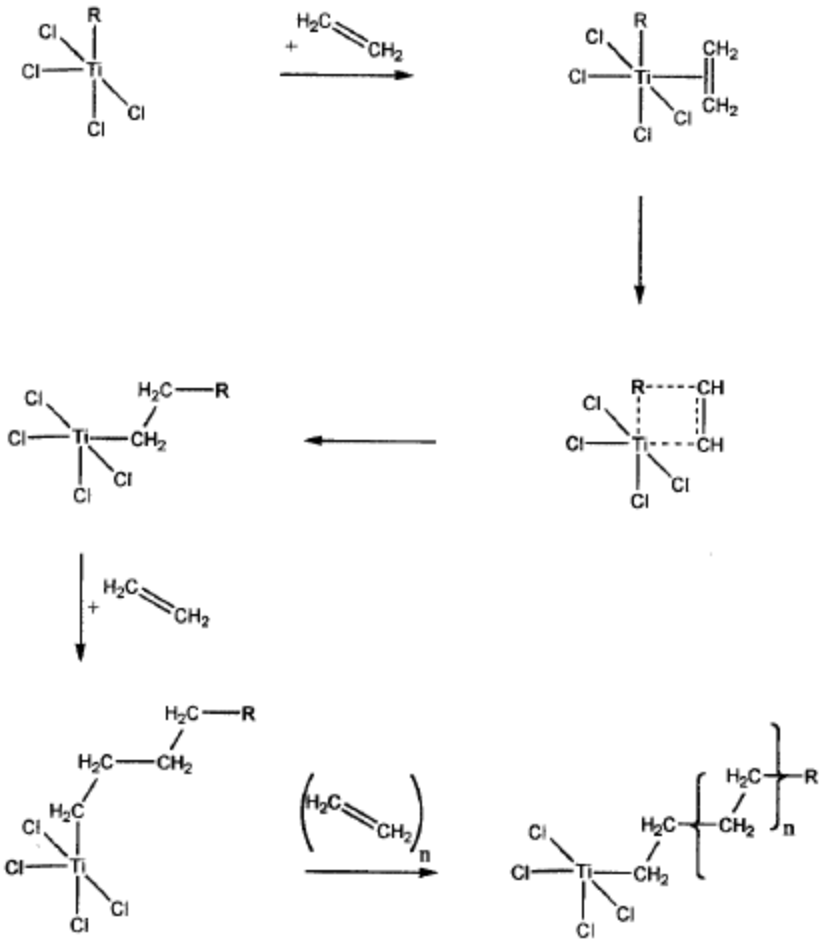




a crystal of α-$TiCl_3$

Zieglar-Natta Catalyst





[Mechanism]

Timeline of Polyethylene

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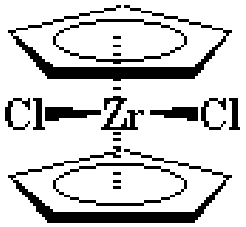
  - Advent of the **free radical process** to produce LDPE
- **1950's**
  - Ziegler-Natta Catalyst (Inorganic Catalyst for HDPE)
- **1970's**
  - Metallocene Catalyst (Organic-Inorganic Hybrid Catalyst for HDPE)

Metallocene Catalyst



bis-chlorozirconocene

Zirconium Sandwich
The Bread is Cyclopentadiene
The Filling is Zr bonded to Chlorine

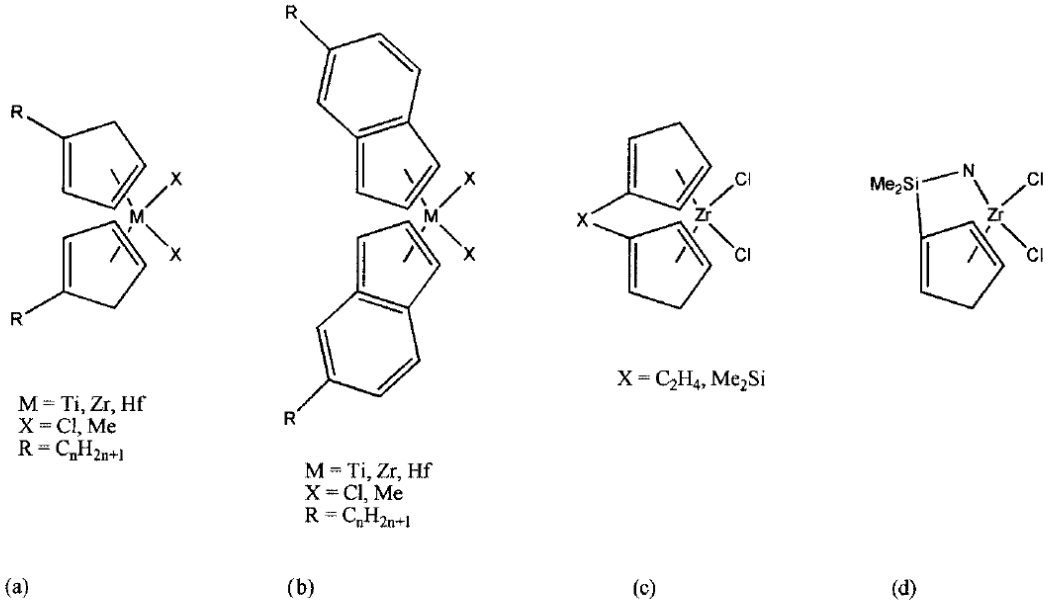


Figure 5 Structure of gneric metallocene catalyst and examples of specific catalyst molecules. (a) Generic metallocene structure; (b) generic metallocene with indenyl substituents; (c) bridged metallocene; (d) ''constrained geometry catalyst.''

Timeline of Polyethylene

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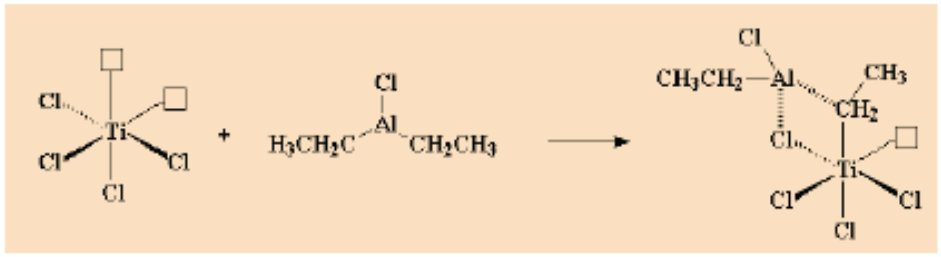
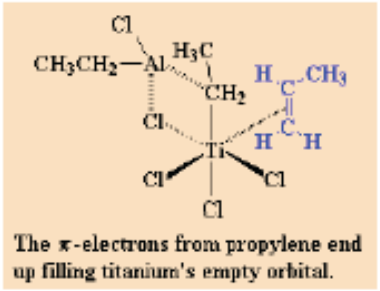
✓ **What is next ?**

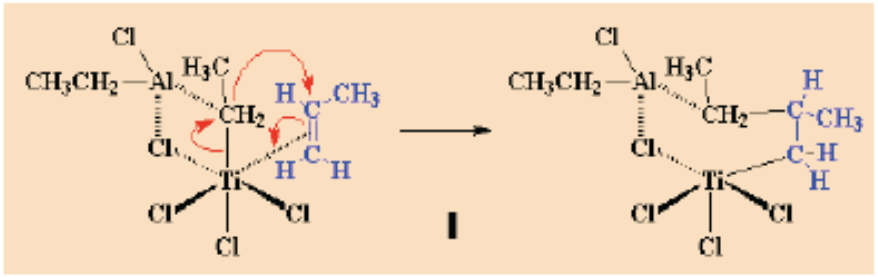
- **Organic Routes (biological enzymatic reactions)**

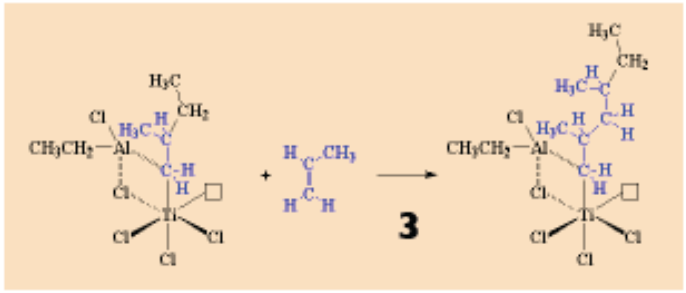
Zieglar-Natta Catalyst

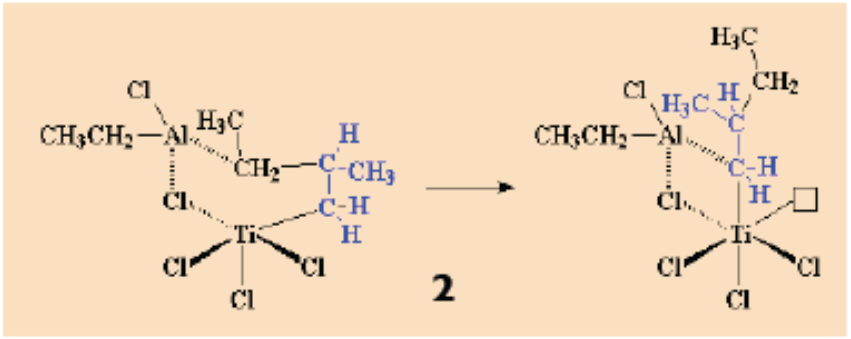
Ziegler-Natta Catalysts (Heterogeneous Catalysts)











[Mechanism]