Chapter 4

Ionic and Coordination Polymerization

Coordination polymerization;

Complex formation between the transition metal and π-electrons in the monomer

Stereoregular Polymer

Isotactic Polymer

Syndiotactic Polymer

Atactic Polymer or Heterotactic Polymer

No regular sequence

Anionic and Coordination Polymerization

Initiators for *ionic* polymerization

Organic radical anion; sodium naphthalate

Water should be excluded

Initiator vs. Catalyst ?

1. **Transfer electron to (or from) monomer**
2. **Initiate monomer polymerization directly (involved in polymer structure)**

Monomers for anionic polymerization

Electron withdrawing substituent group

A typical experimental procedure for anionic polymerization

Polymerization under vacuum or a inert atmosphere!

The mechanism for anionic polymerization

1. Initiation

2. Propagation

3. No chain transfer and no chain branching at low temperature

4. Termination; Possible with only termination reagent

Without termination reagent, Living polymers

Living Polymers

The mechanism for anionic polymerization using sodium or sodium naphthalate

1. Initiation

2. Dimerization

Naphthalene is recovered; catalyst

3. propagation

+ Monomer

Copolymerization

possible in living polymerization, then block copolymers can be made

Electron withdrawing power vs. copolymerization ability

Ziegler-Natta Catalysts

Ethylene reacts with aluminum alkyls under a high pressure produce organometallic oligomer or polymer with low molecular weight

Addition of ethylene to the mixture of aluminum alkyls and "cocatalysts" of $TiCl_4$ or VCl_4 under at atmospheric pressure and RT produce high molecular weight polymers with stereoregularity

Nobel prize in 1963 !

General features of the reaction

1. The *successive* addition of solutions of $TiCl_4$ and triisobutylaluminum in decahydronaphthalene to decahydronaphthalene under dry N_2 atmosphere, then a black-brown suspended precipitated is formed; preparation of catalysts.
2. Heated to 185 °C for 40 min; color changed to deep violate.

1,2 Aging process

3. The mixture is cooled and cyclohexan is added, then additional triisobutylaluminum is added; purple-black suspension
4. Ethylene gas is bubbled; heat is evolved in this polymerization
5. Cooled using ice bath, then poured into isopropanol to yield the polymer precipitated (product)

Stereoregular polymers are obtained !

Compositions of the catalysts

Two components

1. A transition metal compounds from group 4 (Ti)-10

2. An organometallic compound from group 1,2, or 13 (Al) metal.

For example; $TiCl_3$ or $TiCl_4$ and aluminum trialkyls

The reduced transition metal having unfilled ligand sites is believed to act as the catalysts

The polymerization mechanism

Possible complex structure

d_{xy} with π-antibonding

d_{x2-y2} with π-bonding

Two possible mechanisms

1. monometallic

2. bimetallic

The monometallic mechanism

Alternating insertion

Insertion at the same site

The bimetallic mechanism

Diene and cycloolefin can be polymerization by Z-N catalysts or π-allyl complexes

Mechanism ?

Ring-Opening Metathesis Polymerization (ROMP)

Methathesis reaction

ROMP

Monomers for ROMP

from cyclobutenes to cyclooctenes, and higher ring systemes with some ring strains

Catalysts for ROMP

WCl_6, $WOCl_4$, MoO_3, Ruthenium, or Rhenium halides

(+) cocatalysts (organometallic compounds)

Possible mechanism for ROMP

Cationic Polymerization

Initiators for cationic polymerization

Lewis acids function as catalysts with cocatalysts such as water

Monomers for cationic polymerization

conaining electron-donating groups

Experimental conditions for cationic polymerization

The mechanism of cationic polymerization

1. Initiation

2. Propagation

3. Chain transfer; important at RT (not living system)

4. Termination

loss of proton to X^- or very small amount of water

Living carbocationic polymerization

Initiator; tertiary ester with borontrihalide; mechanism is not clear

Reversible termination in living carbocationic polymerization

X = halide, Y = complexing agent (Lewis acid)

Cationic polymerization of Aldehydes

If only Lewis acid without cocatalyst is used;
pseudocyclic propagation