

Mechanism of Polymerization

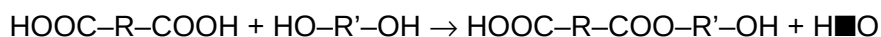
Polymerization is the process of reacting monomer molecules together in a chemical reaction to form polymer chains. The mechanism of polymerization is generally divided into two broad categories: step-growth (condensation) polymerization and chain-growth (addition) polymerization. Each mechanism has distinct reaction steps, intermediates, and resulting polymer structures.

Step-Growth Polymerization:

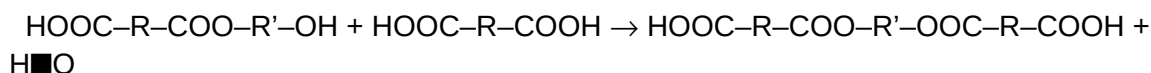
In step-growth polymerization, bi-functional or multi-functional monomers react to form first dimers, then trimers, oligomers, and eventually long-chain polymers. The functional groups react in a stepwise manner, and polymerization occurs throughout the mixture. Typical examples include polyesters, polyamides, and polyurethanes.

Reaction Mechanism Example: Formation of Polyester

1. Reaction between a diacid and a diol:



2. Chain extension:



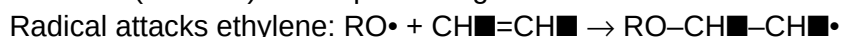
3. Repetition of this process forms a long polyester chain with ester linkages ($-\text{COO}-$).

Chain-Growth Polymerization:

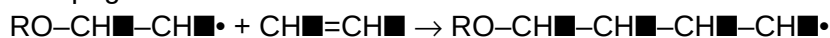
In chain-growth polymerization, unsaturated monomer molecules (such as alkenes) react through a reactive intermediate (free radical, cation, or anion). The reaction occurs in three major steps: initiation, propagation, and termination.

Reaction Mechanism Example: Free Radical Polymerization of Ethylene

1. Initiation:

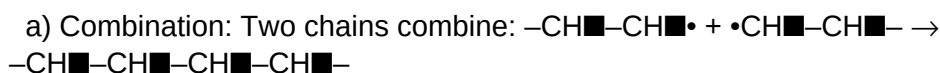


2. Propagation:



This step repeats, leading to long chain growth.

3. Termination:



b) Disproportionation: Hydrogen abstraction stops growth.

Example Polymers: Polyethylene, polystyrene, polyacrylates.

Ionic Polymerization:

This type involves ionic intermediates (cations or anions).

• Cationic polymerization: Initiated by strong acids. Example: Polymerization of isobutene

using H_2SO_4 .



Propagation occurs via carbocation addition to further monomers.

- Anionic polymerization: Initiated by strong bases or organometallics. Example:

Polymerization of styrene using butyl lithium.



Propagation continues via carbanion addition.

Coordination Polymerization:

This type uses transition metal catalysts (e.g., Ziegler–Natta catalyst: $\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$) for polymerization of alkenes.

Example: Polymerization of propylene to isotactic polypropylene.

1. Monomer coordination: Propylene coordinates to metal center.
2. Insertion: Alkyl group migrates to monomer double bond.
3. Chain growth continues in a stereoregular fashion.

Conclusion:

The mechanism of polymerization determines the structure, properties, and application of the resulting polymer. Step-growth leads to condensation polymers like polyesters and nylons, while chain-growth yields addition polymers like polyethylene and polypropylene. Mastery of these mechanisms allows chemists to design materials with tailored properties.