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:
  HOOC–R–COOH + HO–R’–OH → HOOC–R–COO–R’–OH + H■O
2. Chain extension:
  HOOC–R–COO–R’–OH + HOOC–R–COOH → HOOC–R–COO–R’–OOC–R–COOH + H■O
3. Repetition of this process forms a long polyester chain with ester linkages (–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:
  Peroxide (RO–OR) decomposes to generate free radicals: RO–OR → 2RO•
  Radical attacks ethylene: RO• + CH■=CH■ → RO–CH■–CH■•

2. Propagation:
  RO–CH■–CH■• + CH■=CH■ → RO–CH■–CH■–CH■–CH■•
  This step repeats, leading to long chain growth.

3. Termination:
  a) Combination: Two chains combine: –CH■–CH■• + •CH■–CH■– → –CH■–CH■–CH■–CH■–
  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■SO■.
CH■=C(CH■)■ + H■ → C■H–C(CH■)■
Propagation occurs via carbocation addition to further monomers.

• Anionic polymerization: Initiated by strong bases or organometallics. Example: Polymerization of styrene using butyl lithium.
C■H■–CH=CH■ + Bu■ → C■H■–CH■–CH■–Bu
Propagation continues via carbanion addition.

Coordination Polymerization:
This type uses transition metal catalysts (e.g., Ziegler–Natta catalyst: TiCl■ + Al(C■H■)■) 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.