Mechanism of Polymerization — Detailed step-by-step (3 pages)

Introduction
Polymerization is the chemical process where small molecules (monomers) join to form long-chain macromolecules (polymers). Mechanisms are broadly classified into **chain-growth (addition)** and **step-growth (condensation)** polymerizations. This 3-page guide explains common mechanisms step-by-step with reaction sequences, kinetics highlights, and practical control strategies.

1. Chain-growth (Addition) polymerization — Overview
Chain-growth involves rapid monomer addition at an active center. Typical subtypes: free-radical, ionic (anionic & cationic), coordination (Ziegler–Natta / metallocene), and ring-opening.

Free-radical polymerization — Step-by-step
A common example: styrene or methyl methacrylate (MMA). Key stages: **Initiation, Propagation, Termination** and **Chain transfer**. **Initiation**
(a) Initiator decomposition: e.g., AIBN $\rightarrow$ 2 R· (thermolysis) or benzoyl peroxide $\rightarrow$ 2 PhCOO· $\rightarrow$ Ph· + CO_2.
(b) Radical addition to monomer: R· + M $\rightarrow$ M· (monomer radical; active center). **Propagation**
M· + M $\rightarrow$ M–M· $\rightarrow$ M–M–M· ... (chain grows by successive additions). Each step adds one monomer unit to the chain radical. **Termination**
(i) Combination: P· + P· $\rightarrow$ P–P (chains couple).
(ii) Disproportionation: P–CH_2–CH·–R + P–CH·–CH_2–R $\rightarrow$ saturated chain + unsaturated chain (alkene formation via hydrogen transfer). **Chain transfer**
A radical transfers its activity to another species (S–H), terminating growth of one chain and starting another: P· + S–H $\rightarrow$ P–H + S·. Chain-transfer agents (e.g., thiols, halocarbons) reduce molecular weight. **Kinetic highlights**: Rate of polymerization $R_p \approx k_p[M][R\cdot]$, and steady-state radical concentration $[R\cdot] \approx \sqrt{(2 f k_d[I]) / k_t}$, giving $R_p \propto [M]\sqrt{[I]}$ under typical approximations (f = initiator efficiency). Control of molecular weight uses initiator concentration and chain-transfer agents.

2. Ionic polymerizations (Anionic & Cationic)

Anionic polymerization — Step-by-step (e.g., styrene, butadiene, lactones)
1. **Initiation**: strong nucleophile/base (e.g., n-BuLi) attacks monomer: n-BuLi + M $\rightarrow$ Bu–M^- Li^+ (carbanion or alkoxide active center).
2. **Propagation**: Bu–M^- + M $\rightarrow$ Bu–M–M^- ... (chain grows by nucleophilic attack).
3. **Termination**: Often intentionally absent — **living polymerization**. Termination occurs by protonation (H^+ source) or by impurities (water, oxygen).
Notes: Extremely fast and sensitive to impurities; counterion and solvent polarities affect microstructure and stereo-control.

Cationic polymerization — Step-by-step (e.g., isobutylene)
1. **Initiation**: strong acid or Lewis acid forms a carbocation: H^+ + M $\rightarrow$ M–H^+ $\rightarrow$ R^+ (carbocation).
2. **Propagation**: R^+ + M $\rightarrow$ R–M^+ ... (carbocation migrates along chain).
3. **Termination**: Reaction with nucleophiles, counter-ion elimination, or chain transfer to monomer/solvent.
Cationic systems give branching and rearrangements (hydride shift, alkyl shift) as side reactions.

Coordination polymerization (Ziegler–Natta, metallocene) — Stepwise picture
1. **Activation**: Transition-metal catalyst (e.g., $TiCl_4$/$AlEt_3$) forms active site.
2. **Monomer coordination**: ethylene coordinates to the metal center.
3. **Insertion (migratory insertion)**: coordinated monomer inserts into the metal–carbon bond -> chain growth by repeated insertions.
4. **Termination**: β-hydride elimination or chain transfer to aluminum/other ligands.
Outcome: High control of tacticity and molecular weight distribution; used industrially for polyethylene, polypropylene.

Ring-opening polymerization (ROP) — Example mechanisms
ROP converts cyclic monomers (lactones, lactides, epoxides) to linear polymers. Mechanisms can be anionic, cationic, or coordination-controlled.
Example (anionic ROP of ε-caprolactone):
1. Initiation: RO^- (alkoxide) attacks carbonyl carbon, opening the ring to give a new alkoxide chain end.
2. Propagation: Chain alkoxide attacks another monomer ring; the chain grows (–O–C(=O)–$(CH_2)_n$–).
3. Termination: Protonation yields OH-terminated polymer. Many ROPs can be living (control of MW by [M]/[initiator]).

3. Step-growth (Condensation) polymerization — Detailed steps

Step-growth polymerization proceeds by reactions between functional groups of monomers (diols, diacids, diamines, diisocyanates). High molecular weight forms only at very high conversions.

Example: Polyester formation (diacid + diol)

Mechanism (acid-catalyzed esterification):

1. Protonation of carbonyl oxygen of the carboxylic acid (–COOH) increases electrophilicity.
2. Nucleophilic attack by alcohol (–OH) on carbonyl carbon → tetrahedral (hemi-orthoester) intermediate.
3. Proton transfers enable elimination of water ($–H_2O$) from the intermediate.
4. Deprotonation yields the ester linkage (–CO–O–) and regenerates the acid catalyst.

For polyamides (e.g., nylon-6,6), the nucleophile is an amine and the condensation produces amide bonds (–CONH–) with elimination of water (or HCl if acid chloride route used).

Kinetics & Degree of Polymerization (Carothers)

• In step-growth, to achieve high number-average degree of polymerization X_n, conversion p must be close to 1. For stoichiometric A–A + B–B systems:

$$X_n = 1 / (1 – p).$$

E.g., to get $X_n = 100$, $p = 0.99$ (99% conversion).

• Chain-growth systems form high-MW chains early; step-growth requires near-complete conversion for high MW.

Control strategies & Practical tips

• **Purity:** Remove inhibitors, water, oxygen for sensitive systems (ionic, radical). Use inert atmosphere (N_2/Ar).

• **Temperature & Solvent:** Affect kinetics, side reactions, and stereochemistry.

• **Initiator concentration:** For radical polymerization, increasing [I] shortens chain length (more chains started).

• **Chain-transfer agents:** Lower MW and control PDI.

• **Stoichiometry:** In step-growth, small deviations from exact stoichiometry drastically reduce maximum achievable MW.

• **Catalysts:** Acid/base or metal catalysts accelerate specific mechanisms and improve selectivity.

• **Living polymerization methods:** (anionic, controlled radical methods like ATRP, RAFT, NMP) allow narrow PDI and end-group control.

Characterization & Important parameters

• Gel Permeation Chromatography (GPC/SEC) → M_n, M_w, PDI (M_w/M_n).

• NMR → end-group analysis, tacticity, monomer conversion.

• FTIR → functional-group changes (e.g., disappearance of –OH, appearance of ester C=O).

• DSC / TGA → thermal transitions (T_g, T_m) and decomposition data.

Summary (quick comparison)

• Chain-growth: active center adds monomers rapidly; high MW early; MW controlled by initiator & transfer reactions.

• Step-growth: bonds form between functional groups; high MW only at near-complete conversion; stoichiometry crucial.