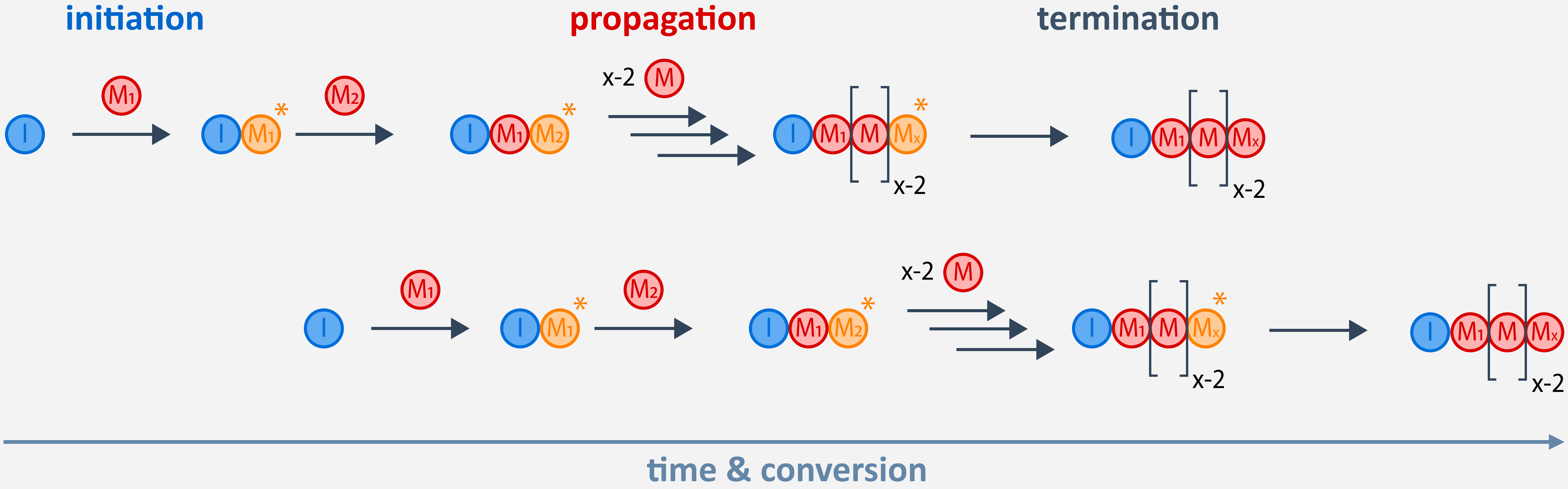
5.3 Chain-Growth Polymerization

Principal Steps of Chain-Growth Polymerizations

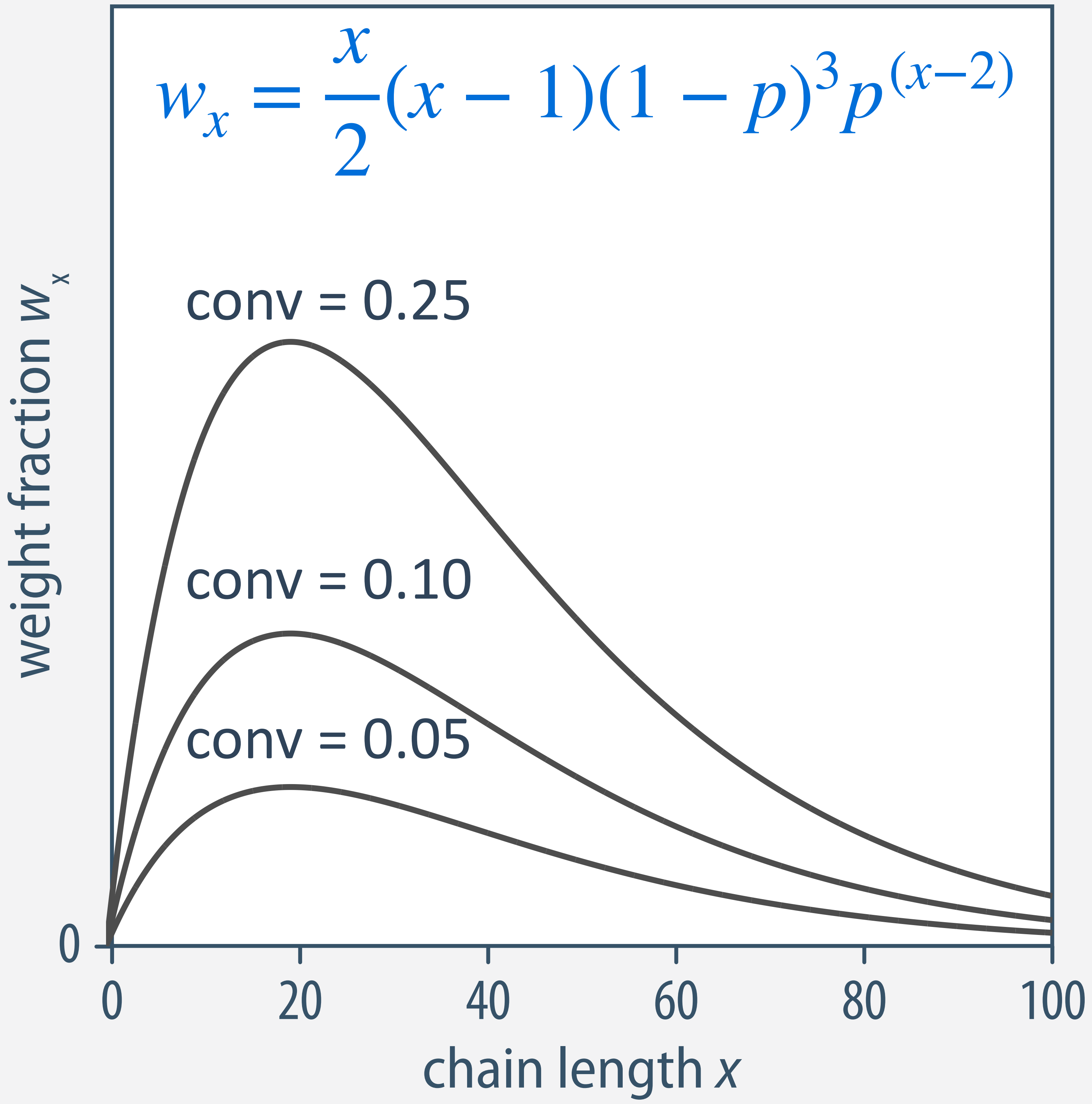
- monomers add rapidly to the active center of a growing chain until that center is deactivated



- **polymerizations require an initiator that attacks a first monomer and creates an active center**
- **during propagation, monomers add consecutively to the active center of a growing polymer chain**
- **initiation continuously occurs during entire polymerization time**
- **termination is a stochastic event, greatly determining the molecular weight distribution**

Molar Mass Distribution in Chain Grwoth Polymerizations

- Flory-Schulz-type distribution is expected (at least, in the low conversion regime)



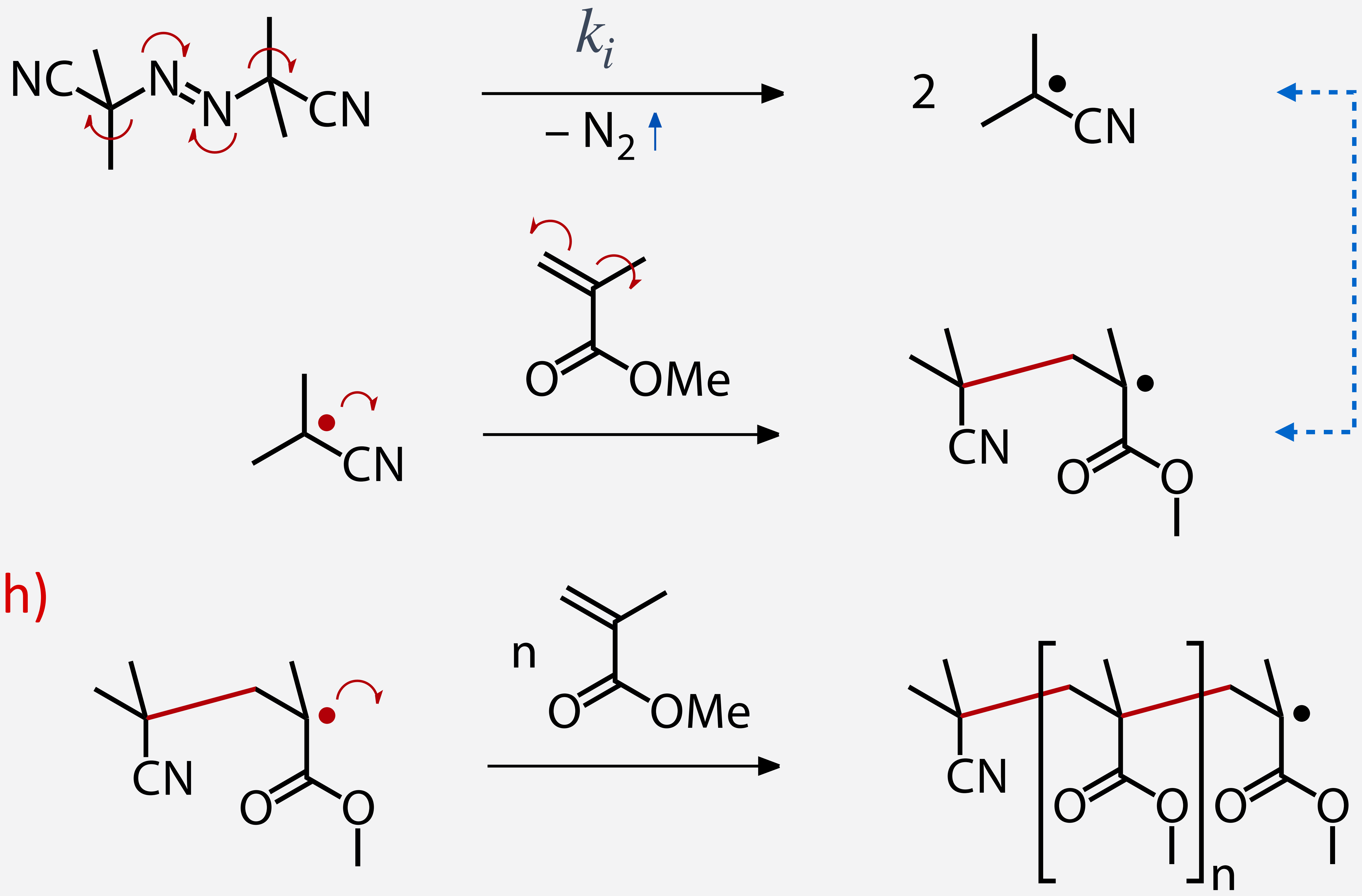
- **high molar mass polymer is formed from the beginning in a free radical polymerization**
- **with increasing time and conversion, the number of each species increases continuously**

EPFL Key concept: see reader “Chain-Growth Polymerizations” 323

Free Radical Polymerizations

Initiation and Propagation in Free Radical Polymerizations

- initiator decomposition (slow)
- initiation (fast)
- propagation (chain growth)



not all generated radicals initiate chains

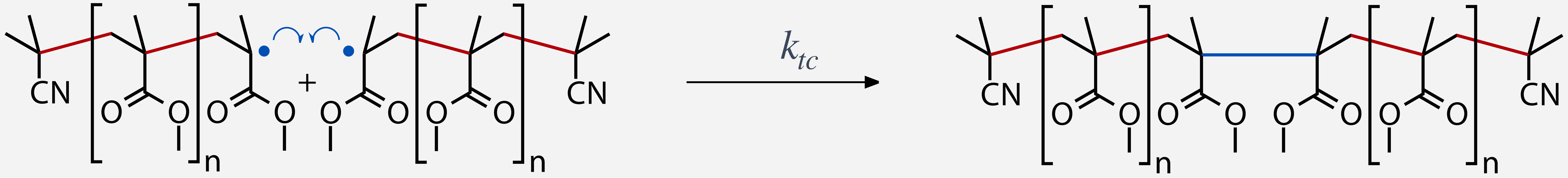
concentrations not identical

efficiency factor *f*

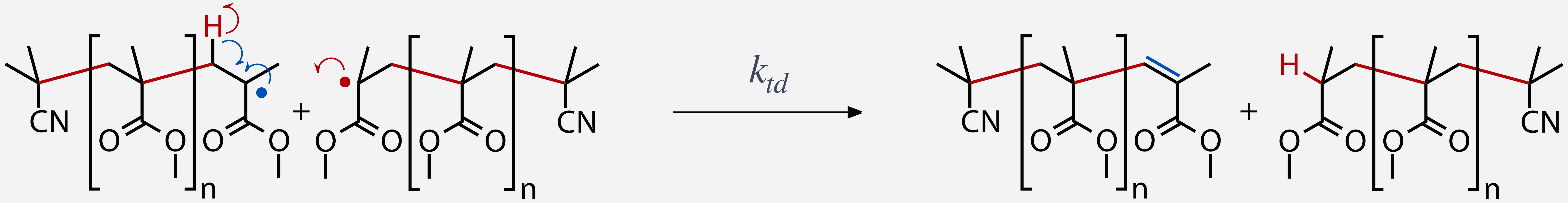
- **reaction with a monomer instead of immediate recombination with efficiency factor *f* ≈ 0.3–0.8**
- **initiator decomposition is a statistical process, occurring slowly throughout polymerization process**
- **radical life time *τ* = 0.1–10 s, about 100–10’000 propagation steps before chain terminates**

Termination Reactions in Radical Polymerizations

- **termination by radical combination**

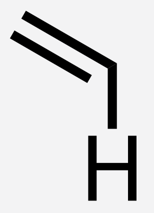


- **termination by disproportionation**

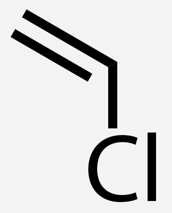


- **termination by combination and disproportionation often occur both and are stochastic processes**

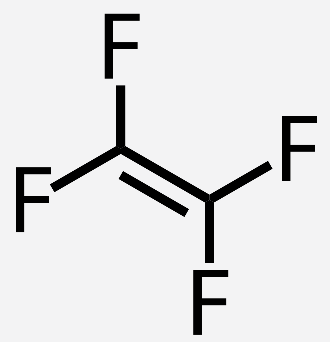
Important Vinyl Monomers in Radical Polymerization



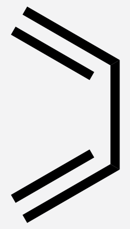
ethene
ethylene (PE)



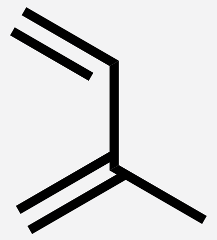
chloroethene
vinyl chloride (PVC)



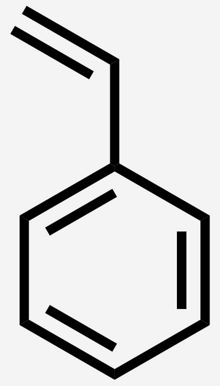
tetrafluoroethene
(PTFE, Teflon)



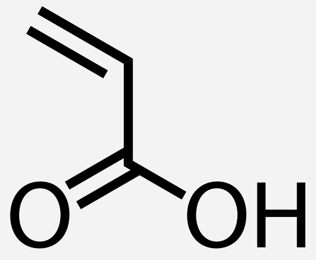
butadiene
(PB)



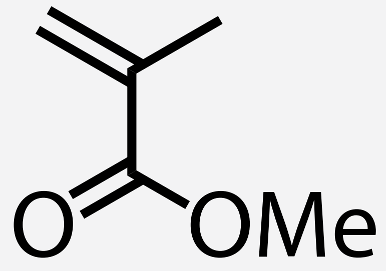
2-methylbutadiene
isoprene (PI)



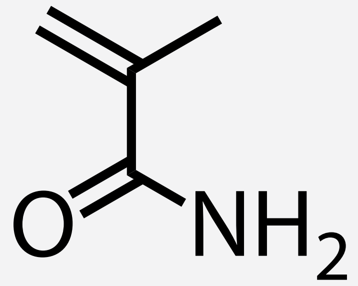
phenylethene
styrene (PS)



propenoic acid
acrylic acid (PAA)



methyl 2-methylpropenoate
methyl methacrylate (PMMA)

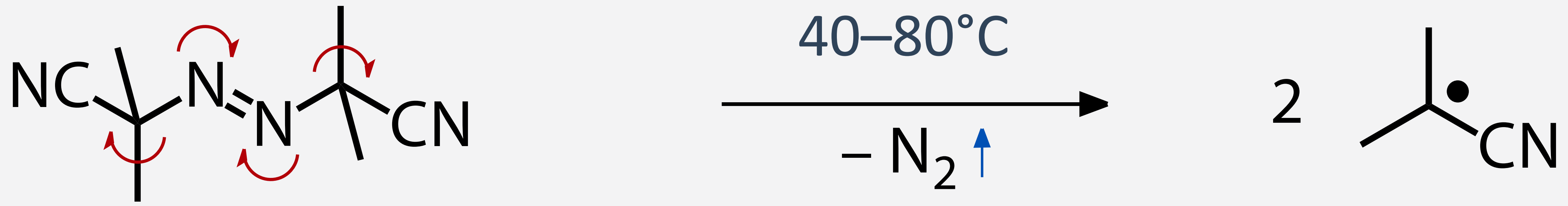


2-methylpropenoic amide
methacrylamide (for PMAAm)

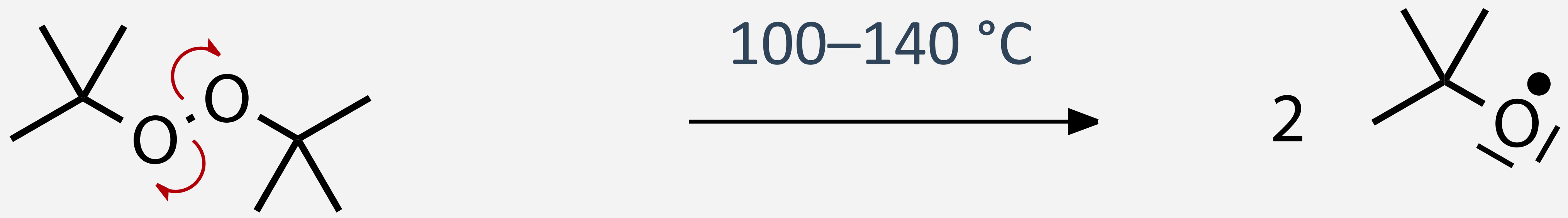
- **vinyl monomers mostly with +M or –M substituents used for technologically relevant polymers**

Examples of Radical Initiators and their Decomposition

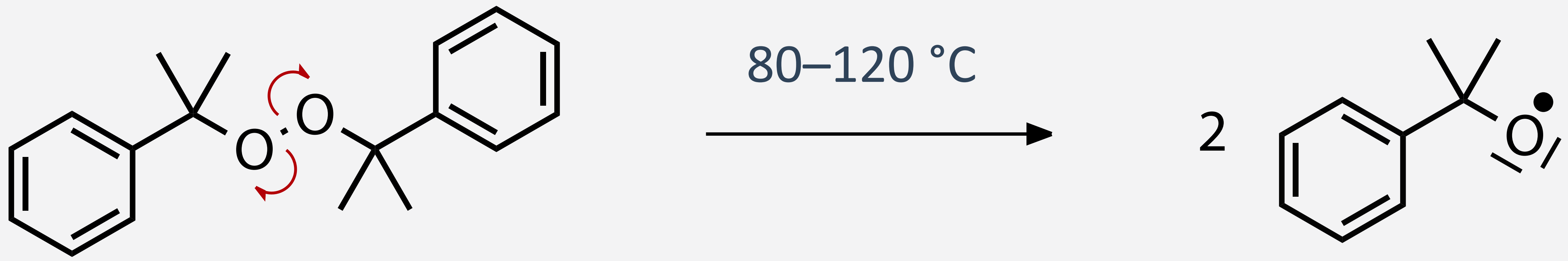
- azobis(isobutyronitrile) (AIBN)



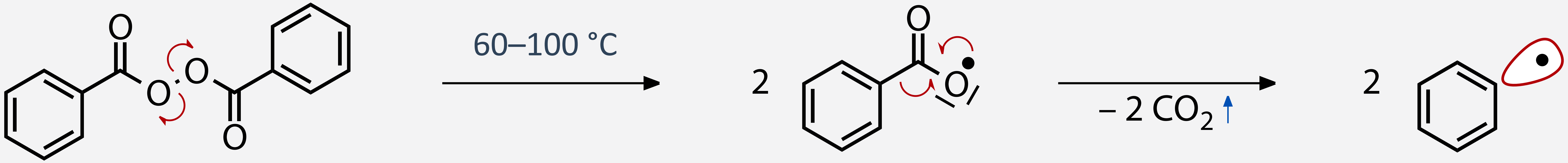
- di(tert.-butyl peroxide) (DTPO)



- dicumyl peroxide (DCPO)



- dibenzoyl peroxide (DBPO)



- **suitable decomposition rates ($k_i = 10^{-7}–10^{-6}$ M s^{-1}) for different temperature regimes**
- **goal is to balance initiation and termination reaction rates to reach “steady state” conditions**

Kinetics of Chain Growth Polymerization

rate of initiation

$$R_i = \frac{d[\mathrm{R}^\bullet]}{dt} = 2fk_i[\mathrm{I}]$$

rate of propagation

$$R_p = -\frac{d[\mathrm{M}]}{dt} = \sum k_p[\mathrm{M}_i^\bullet][\mathrm{M}]$$

rate of termination

$$R_t = -\frac{d[\mathrm{M}^\bullet]}{dt} = 2k_t[\mathrm{M}^\bullet]^2$$

- **steady-state-conditions:** $R_i = R_t$ $\quad R_p = k_p\sqrt{\frac{fk_i}{k_t}}\sqrt{[\mathrm{I}]}[\mathrm{M}]$ $\quad$ with $k_t = k_{tc} + k_{td}$

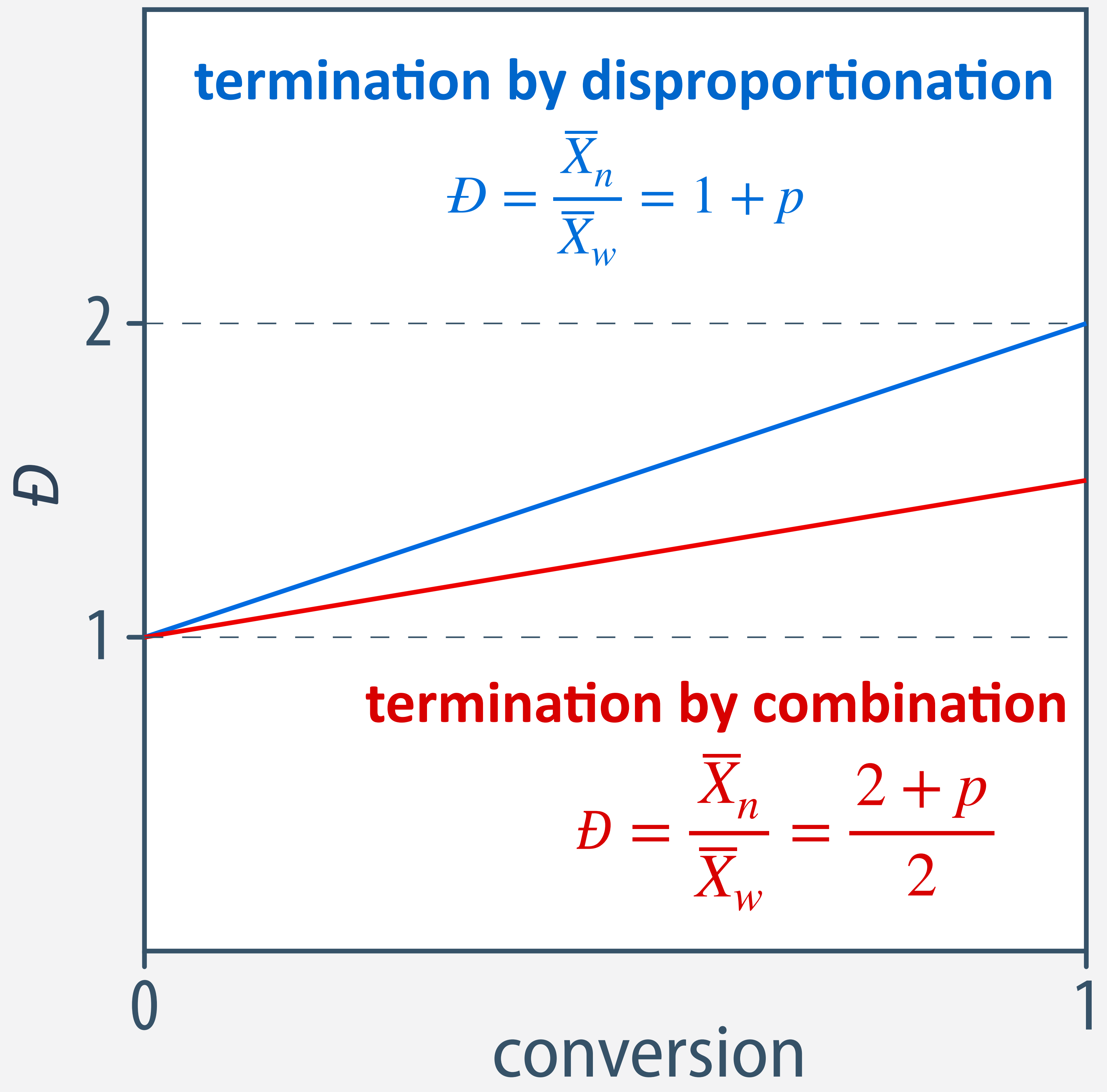
- **kinetic chain length:** $\bar{\nu} = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p[\mathrm{M}]}{2(fk_ik_t[\mathrm{I}])^{1/2}} \propto \frac{[M]}{\sqrt{[\mathrm{I}]}}$

- **steady state conditions required for stable polymerization, results in reaction order 0.5 for initiator**
- **increasing initiator concentration increases polymerization rate but results in decreased molar mass**

see reader “Chain-Growth Polymerizations”

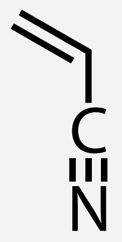
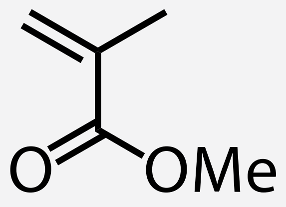
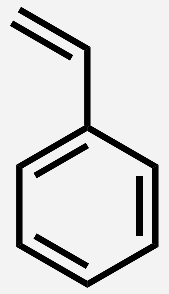
Dispersity in the Low Conversion Regime

- in reality, termination may occur via both pathways
- transfer reactions and side-reactions are not taken into consideration



$$Đ = \frac{\overline{X}_n}{\overline{X}_w} = 1 + p$$

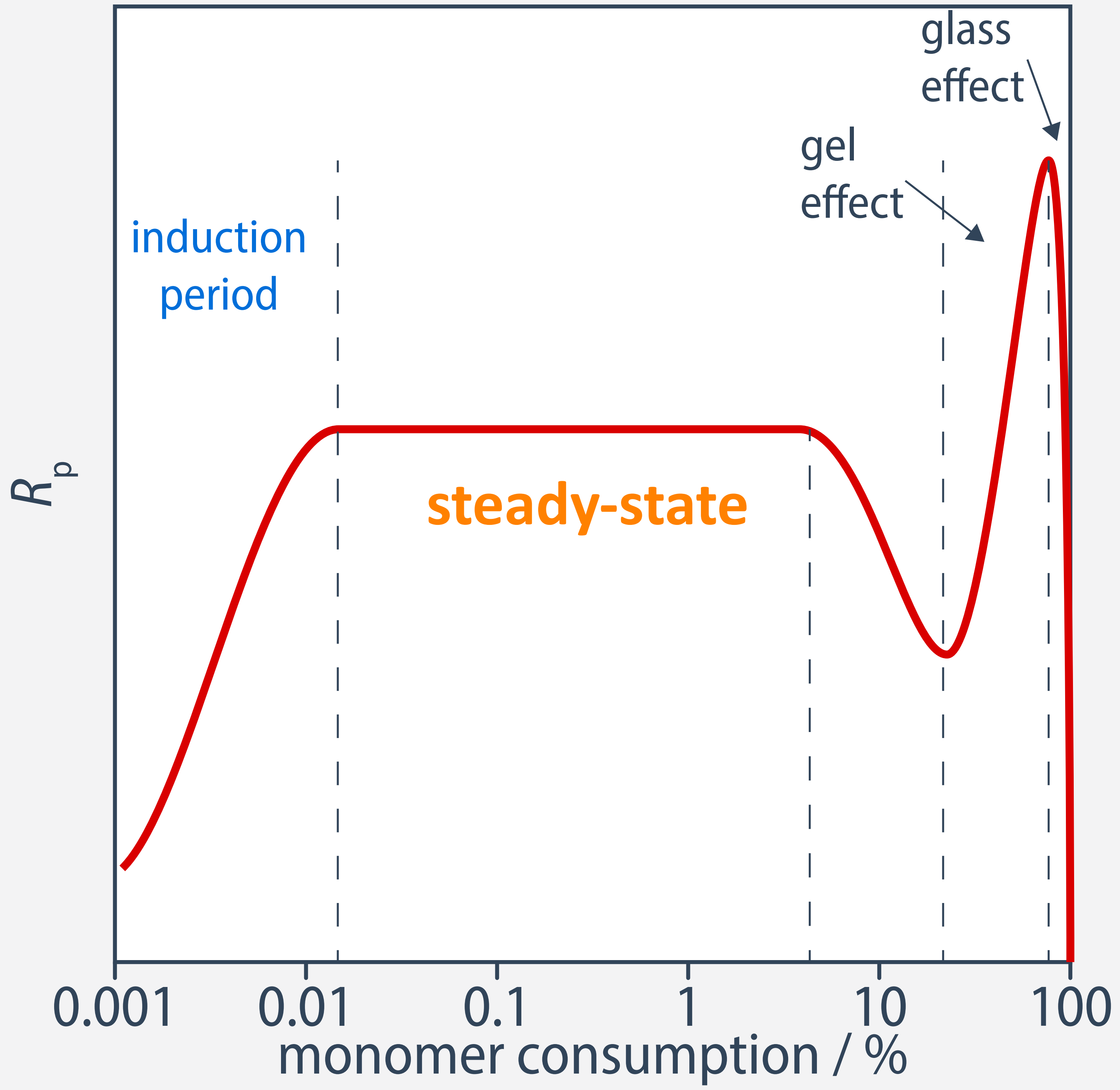
$$Đ = \frac{\overline{X}_n}{\overline{X}_w} = \frac{2 + p}{2}$$

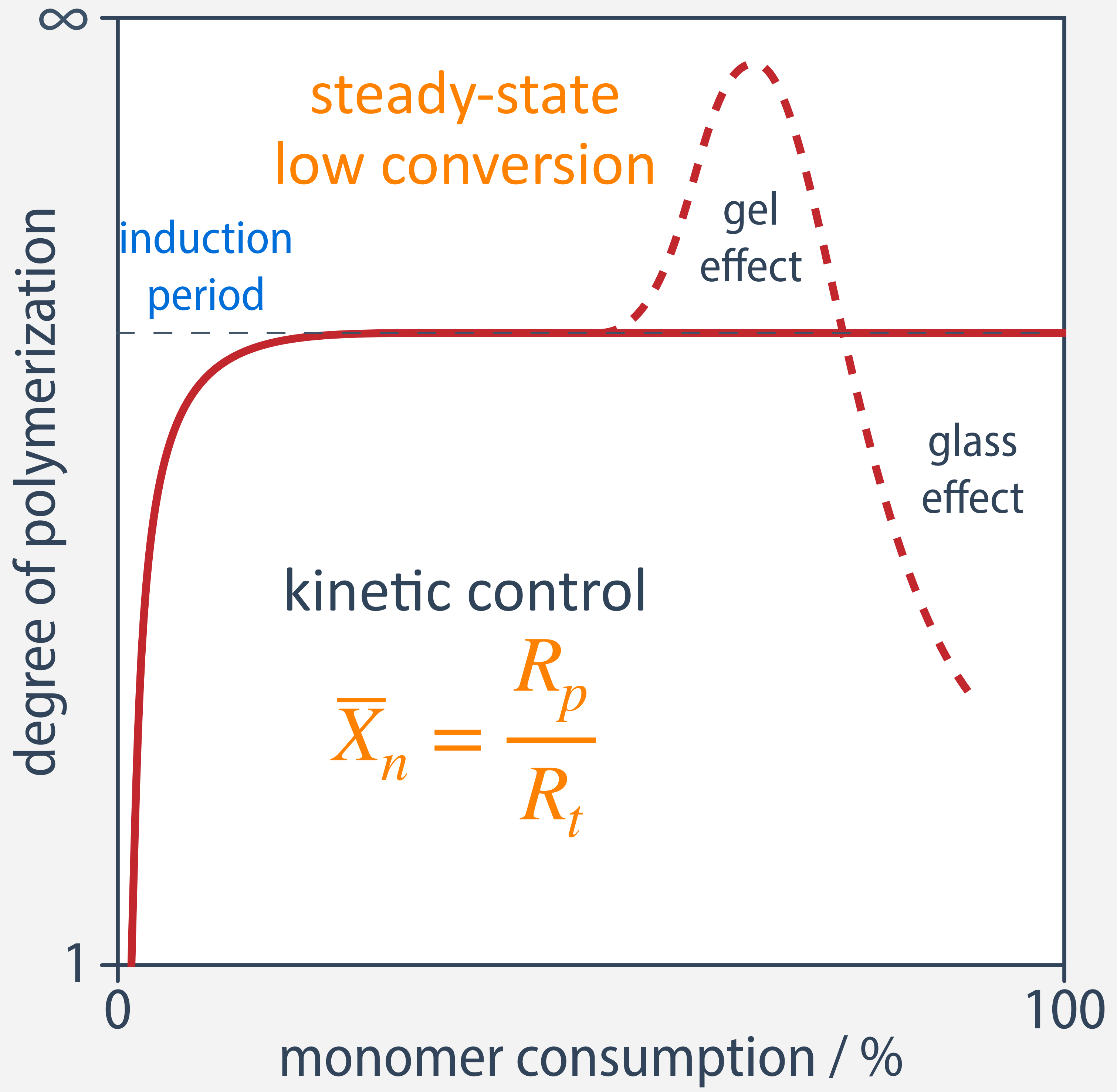
	disproportionation	**combination**
	**0%**	**100%**
	**79%**	**21%**
	**23%**	**77%**

- **molecular weight distribution and dispersity depend on termination mechanism**

High Conversion Effects in Bulk Polymerizations

- **gel effect: diffusion-controlled termination (auto-acceleration of propagation)**
- **glass effect: monomers get trapped, if the matrix becomes increasingly glassy**



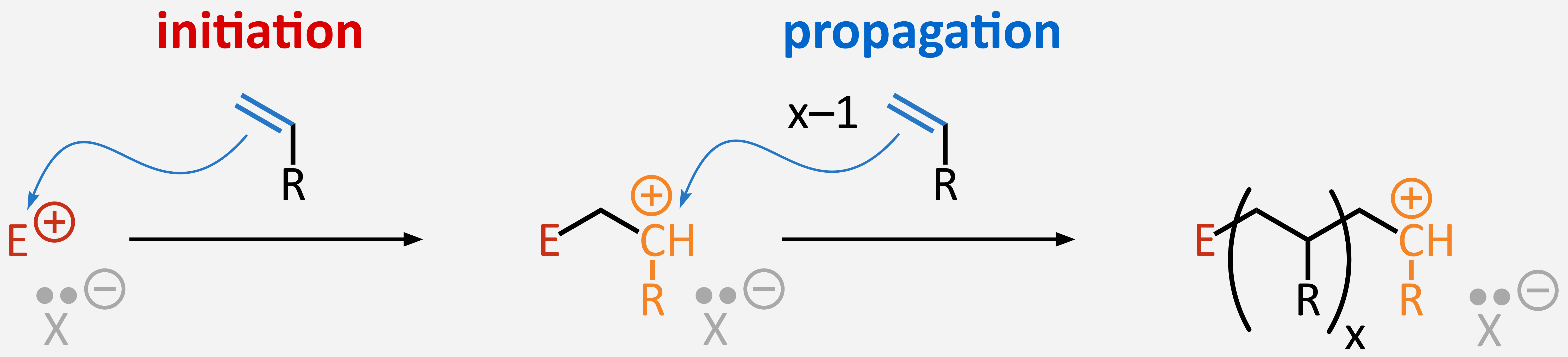


$$\overline{X}_n = \frac{R_p}{R_t}$$

Free Cationic Polymerization

Cationic Polymerization of Vinyl Monomers

- polymerization started by reaction of a vinyl monomer with a strong (cationic) electrophile



- initiation is like the first step in electrophilic addition to a double bond (of the monomer)
- reactive chain end is a (highly electron-deficient, elctrophilic, reactive) carbocationic intermediate
- monomer must have electron-donating residue R to be reactive, but *also* to stabilize chain end
- initiator must be sufficiently strong Lewis or Brønsted acid, hence counterion must be well stabilized
- counterion must be well stabilized / non-nucleophilic *also* to avoid completing the addition reaction
- cabocationic chain end and counterion are close ion pairs in organic solvents (even when not shown)

- **cationic polymerization like first step of electrophilic addition, while avoiding the second step**

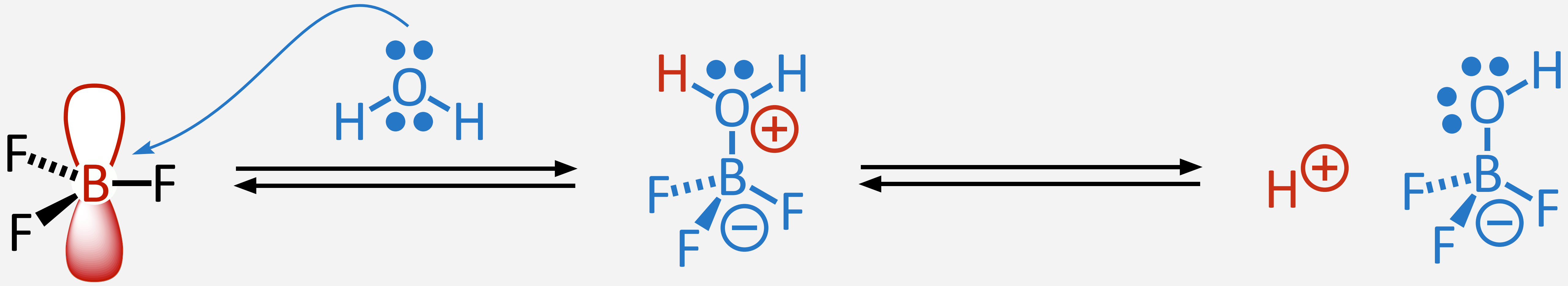
Examples of Initiators for Cationic Polymerization of Vinyl Monomers

- Brønsted acids with large, resonance-stabilized, non-coordinating, non-nucleophilic counterions

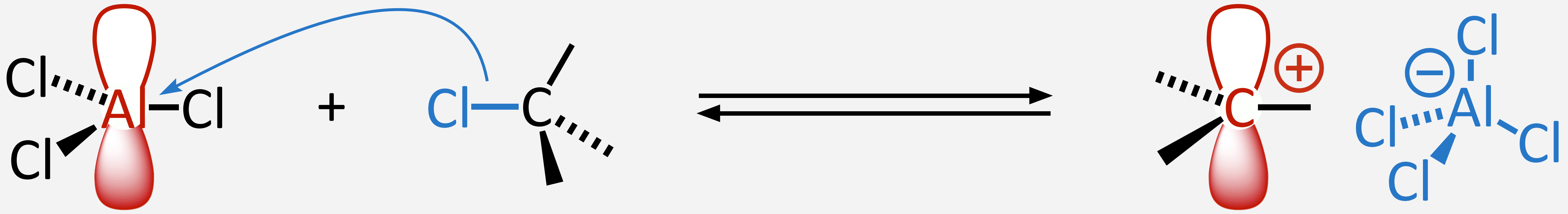
  - hydrogen halogenides are inefficient as initiators
  - halogenide counterions are still too nucleophilic, complete addition to the double bond

- Lewis acids such as halides of metals in high oxidation states (BF_3, BCl_3, $AlCl_3$, $TiCl_4$, $SnCl_4$, $SbCl_5$, $ZnCl_2$)

  - two coinitiators that deliver a proton as the actual initiator

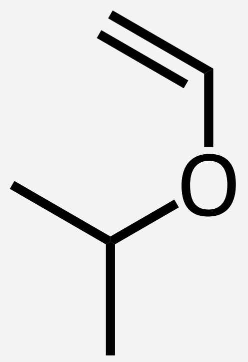


  - two coinitiators, one with a good leaving group that generates a carbocation

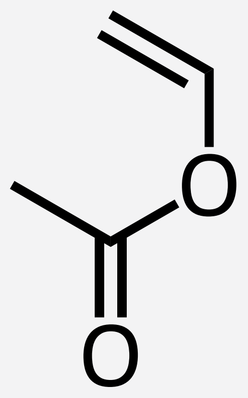


Examples of Monomers for Cationic Polymerization of Vinyl Monomers

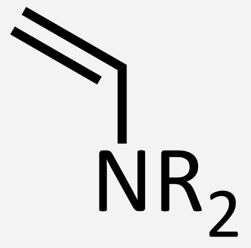
- +M substituents or 1,1-dialkyl substitution (stabilized and polarized by hyperconjugation)



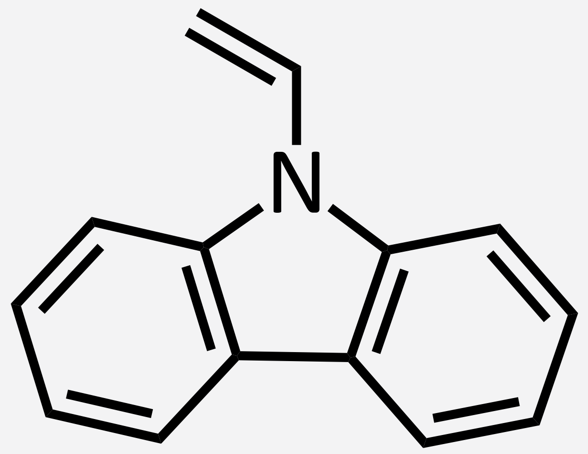
vinyl ethers



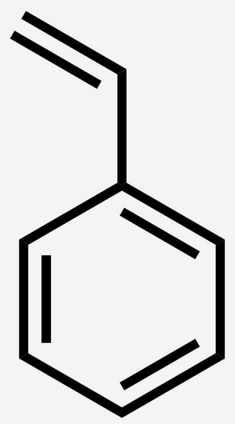
vinyl esters



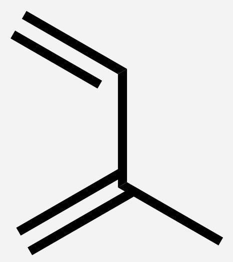
vinyl amines



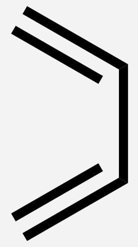
vinyl carbazol



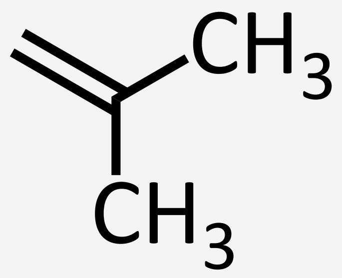
styrene(s)



isoprene
2-methylbutadiene



butadiene

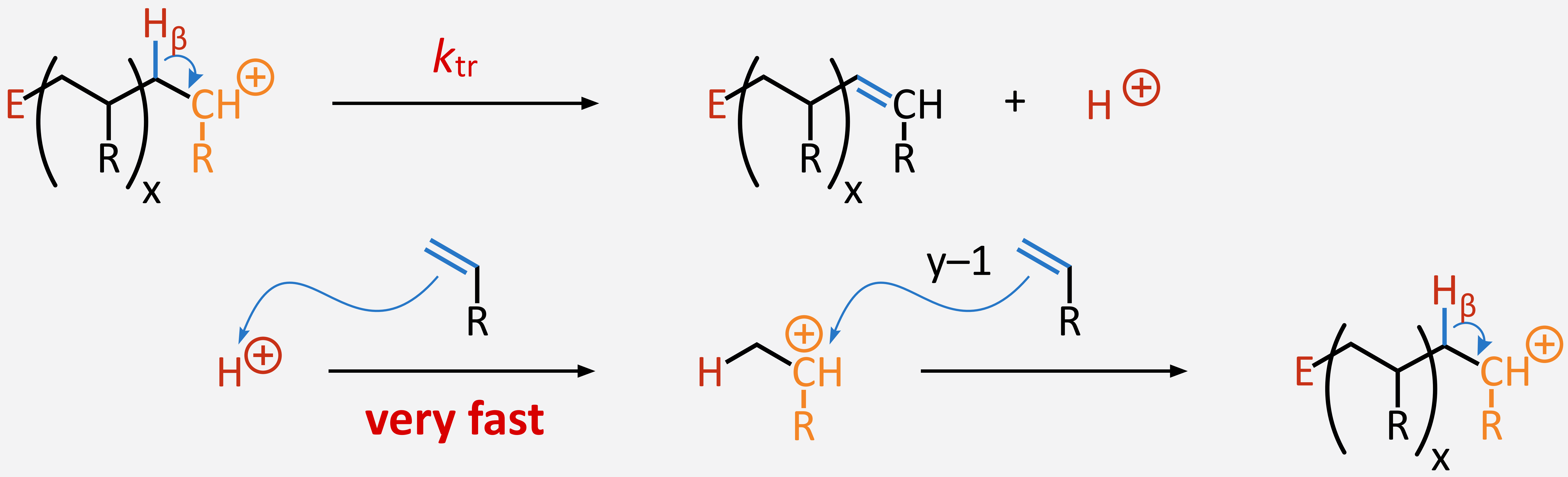


isobutylene
1,1-dimethylethene

- **electron-donating group to increase reactivity towards electrophile and bias for terminal reaction**
- **also necessary to stabilize the carbocationic center on the reactive chain end**

Chain Transfer Reactions

- chain transfer by β-hydrogen transfer to monomer is prevalent mechanism

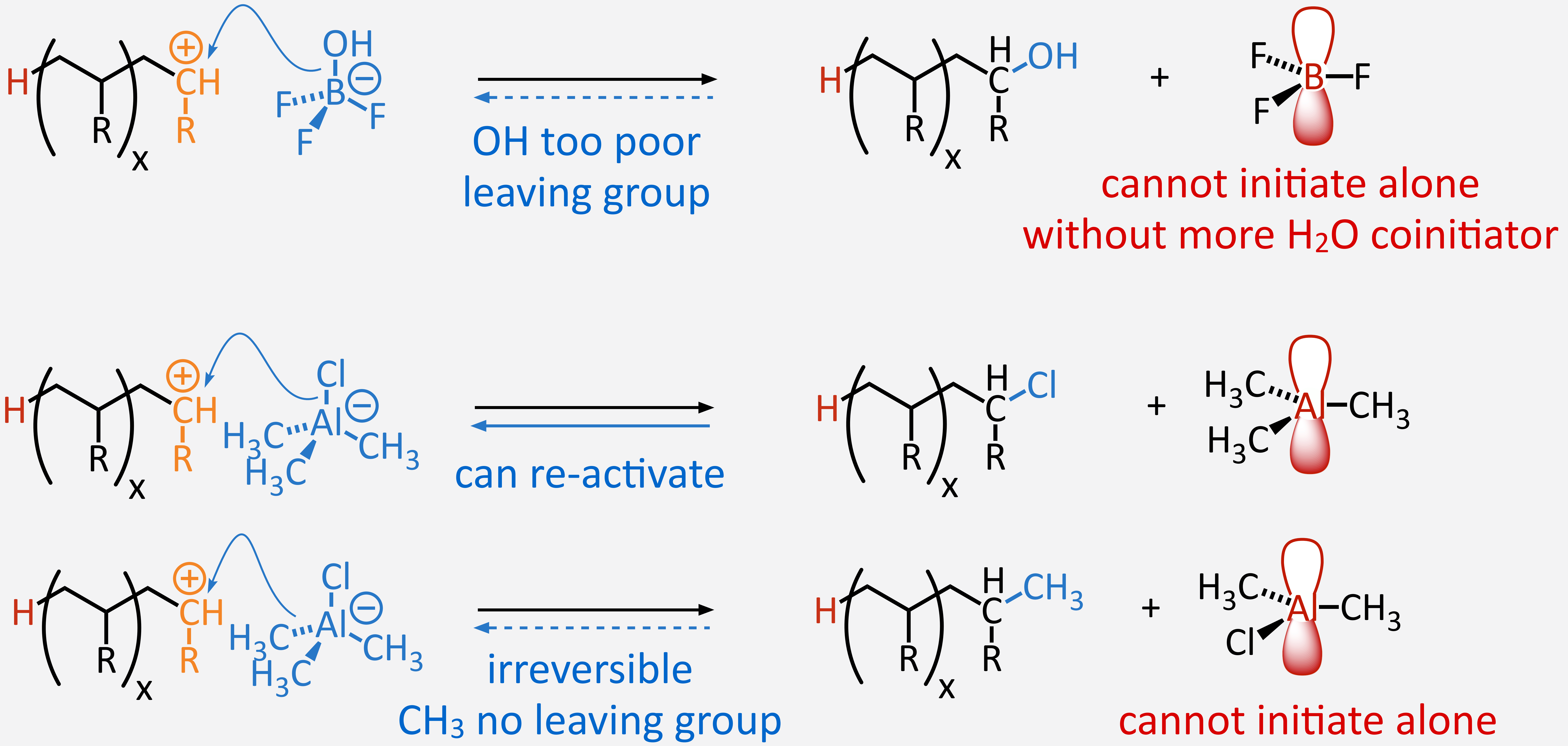


  - individual polymer chain is deactivated but kinetic chain reaction continues
  - both propagation and chain transfer are first order in monomer and in active chain end
  - molar mass determined by kinetics, inverse of chain transfer constant $C_{tr} = k_{tr} / k_p$
  - polymerization typically performed at (very) low temperatures to increase molar mass
  - β-hydrogen transfer results in double bond chain ends; polymerizable hence risk of branching

- **chain transfer to monomer is principal process that limits molar mass and results in Schulz-Flory distribution, especially at reaction temperatures above r. t.**

Termination Reactions

- chain termination is possible by combination with counterion (in some cases)



OH too poor leaving group

cannot initiate alone without more H_2O coinitiator

can re-activate

but

irreversible

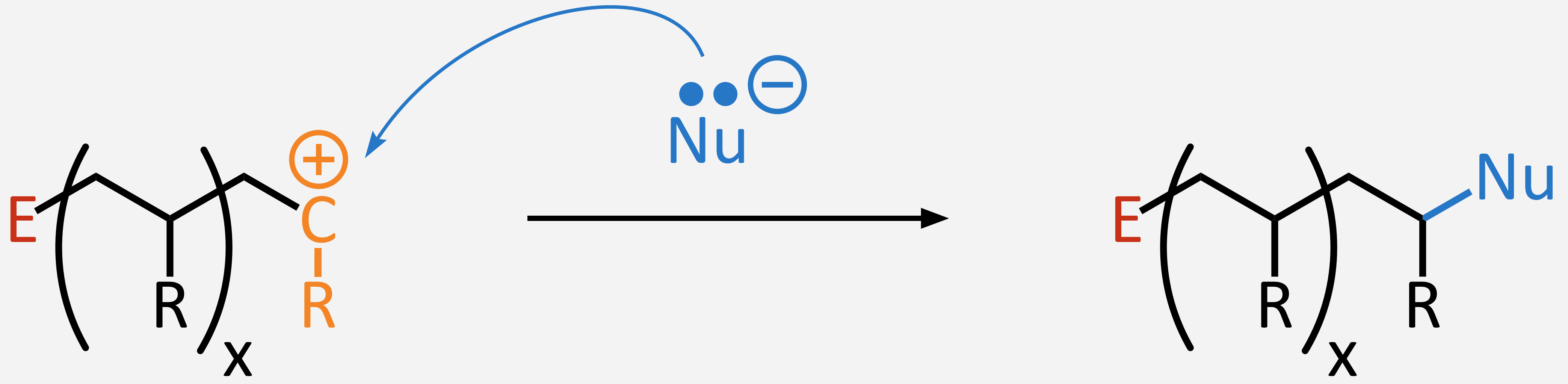
CH_3 no leaving group

cannot initiate alone

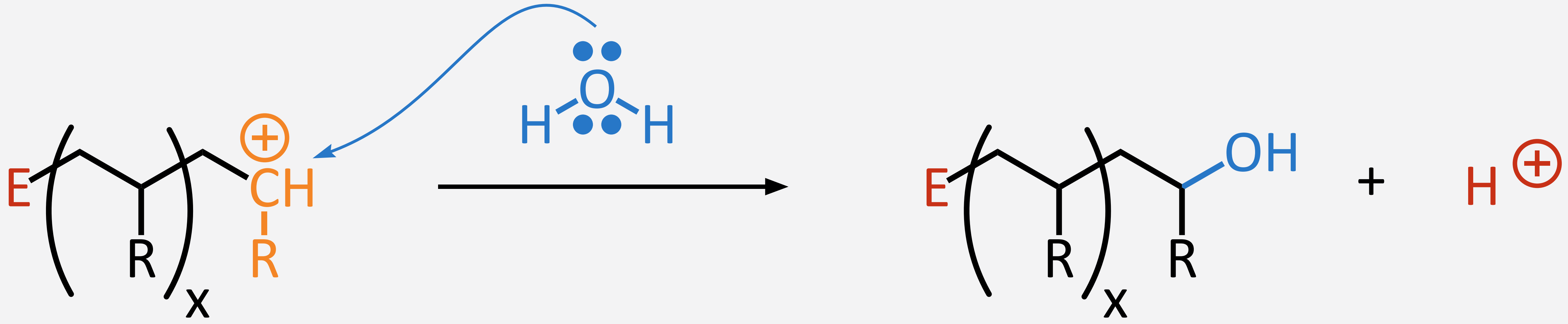
- **different from radical polymerization, terminations are not prevalent in cationic polymerizations**

Quenching

- carbocationic chain end remains reactive intermediate, is “quenched” (deactivated) by nucleophiles



  - strong nucleophiles (anionic, with wekaly acidic counterions) result in irreversible termination
  - weak nucleophiles that release strongly acidic coutnerion for accelerated chain transfer
  - useful to tailor molar mass control

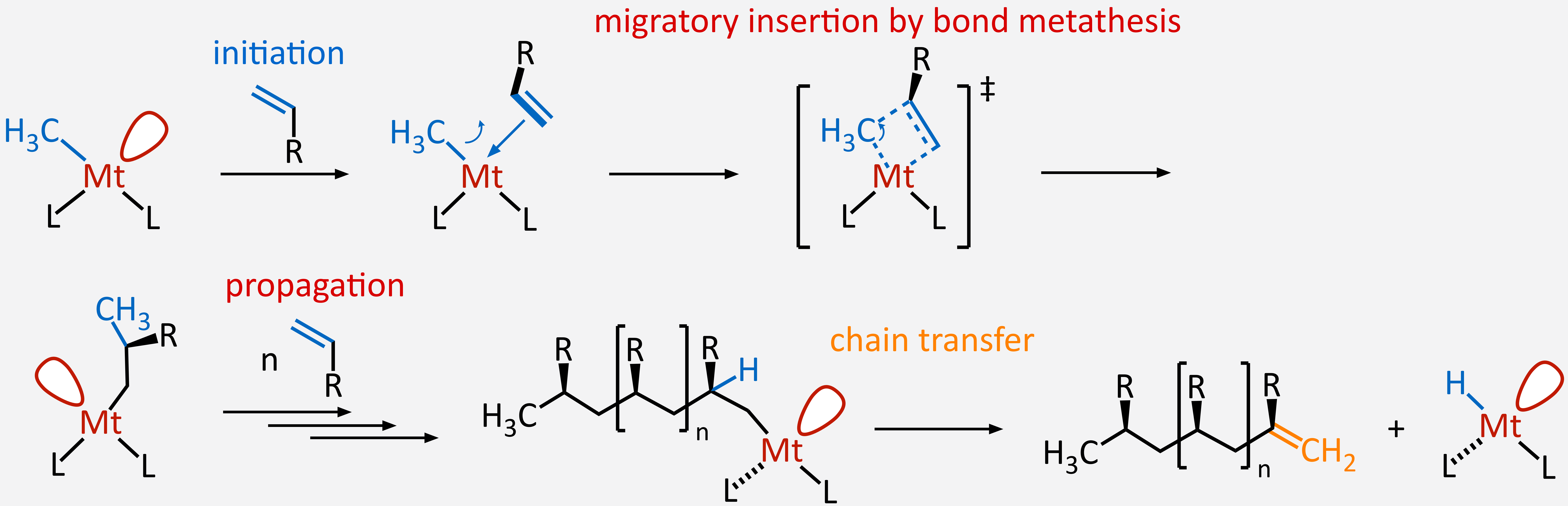


- **quenching generally useless for introducing end groups deliberately because of chain transfer**
- **cationic polymerizations require careful scavenging of inadvertent nucleophiles (including water)**

Coordination Polymerization

Generic Mechanism of Transition-Metal-Catalyzed Coordination Polymerization

- coordination (insertion) polymerization of alkenes by transition metals with empty coordination site

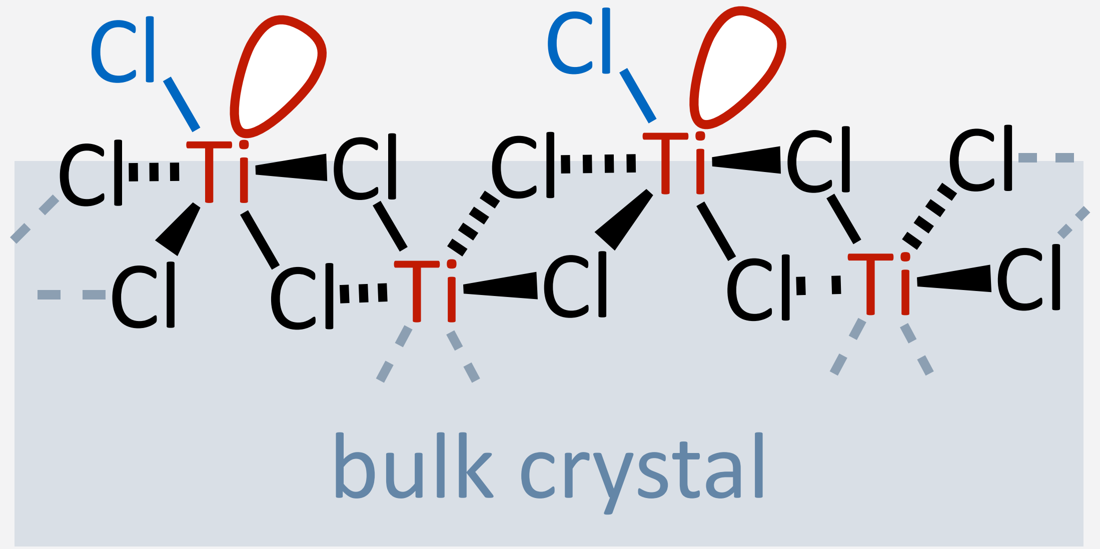


- initiation by first alkene monomer adding as ligand to the vacant coordination site (empty d orbital)
- propagation by migratory insertion of the monomer into Mt–C bond, polymer chain migrates
  - via four-electron, four-membered cyclic transition state
  - finalized by bond metathesis, generating new Mt–C & C–C bonds, reforming empty coordination site
- chain transfer by β-hydrogen elimination from last unit, generates double bond chain end

- typical catalysts are a wide variety of transition metal solids and moelcular organometallic compounds

heterogeneous catalysts

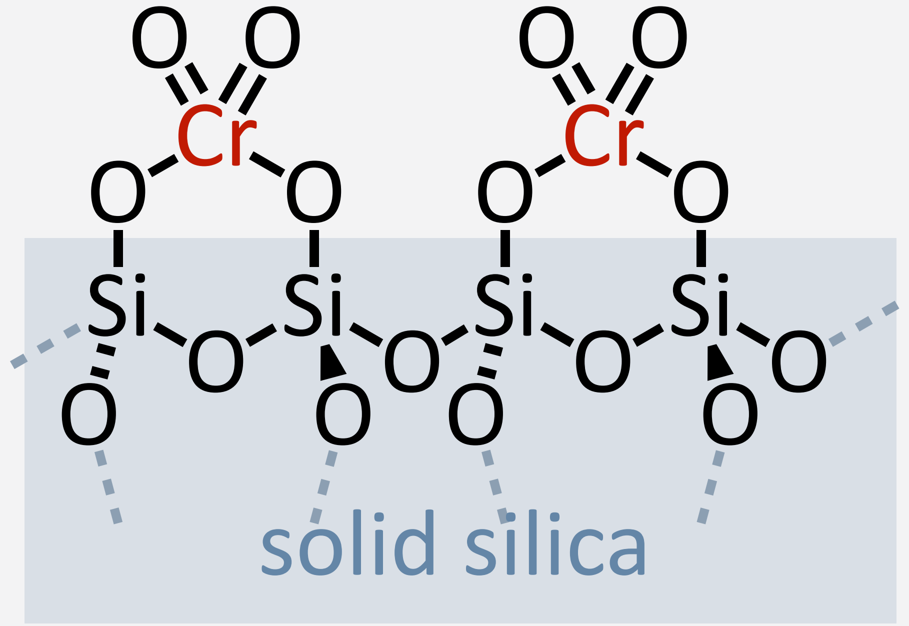
crystal surface



Ziegler-Natta

crystalline $TiCl_3$ particles

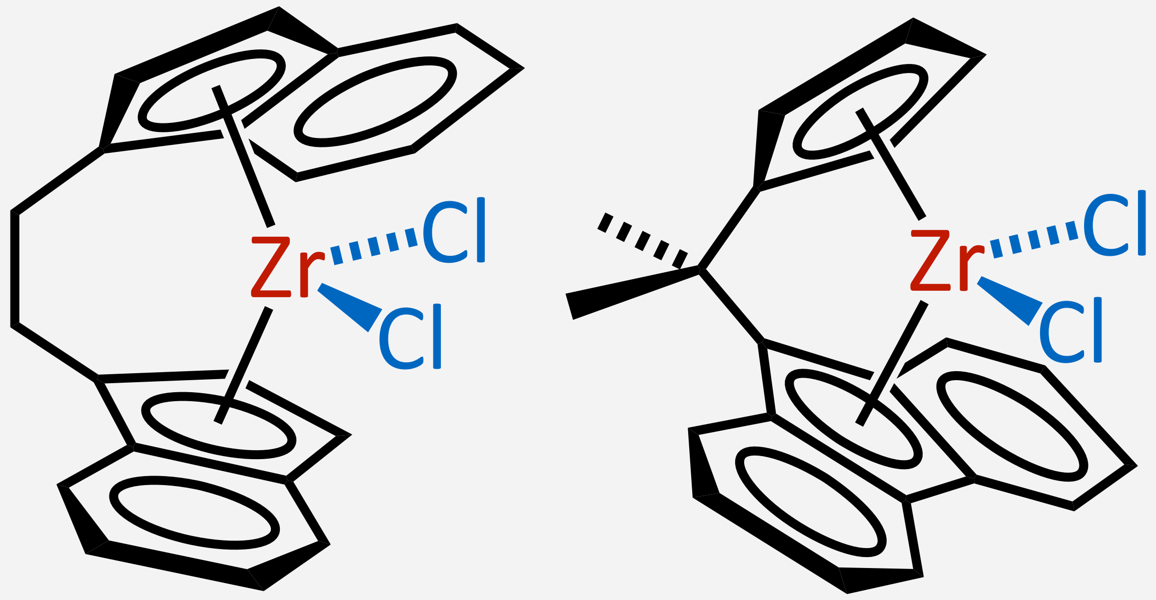
particle surface



Phillips

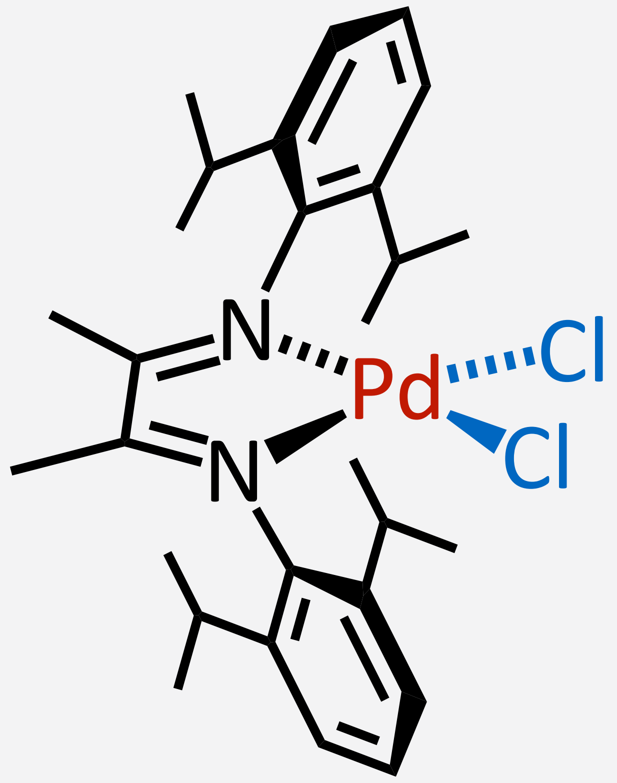
chromium oxide
supported on silica gel

homogeneous catalysts



Brintzinger

Zirconocenes



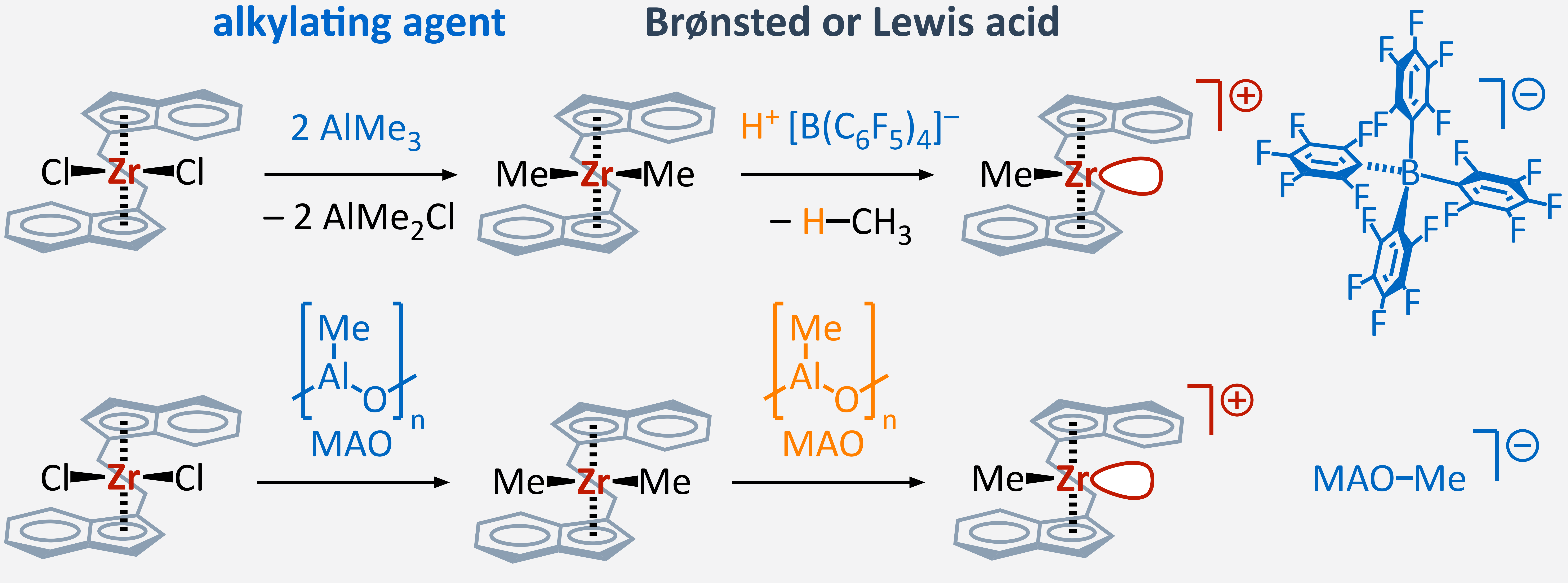
Brookhart

palladium diimines

- **heterogeneous catalysts are solid particles dispersed in reaction medium, only surface is active**
- **homogeneous catatalysts are defined organometallic compounds, in homogeneous solution**

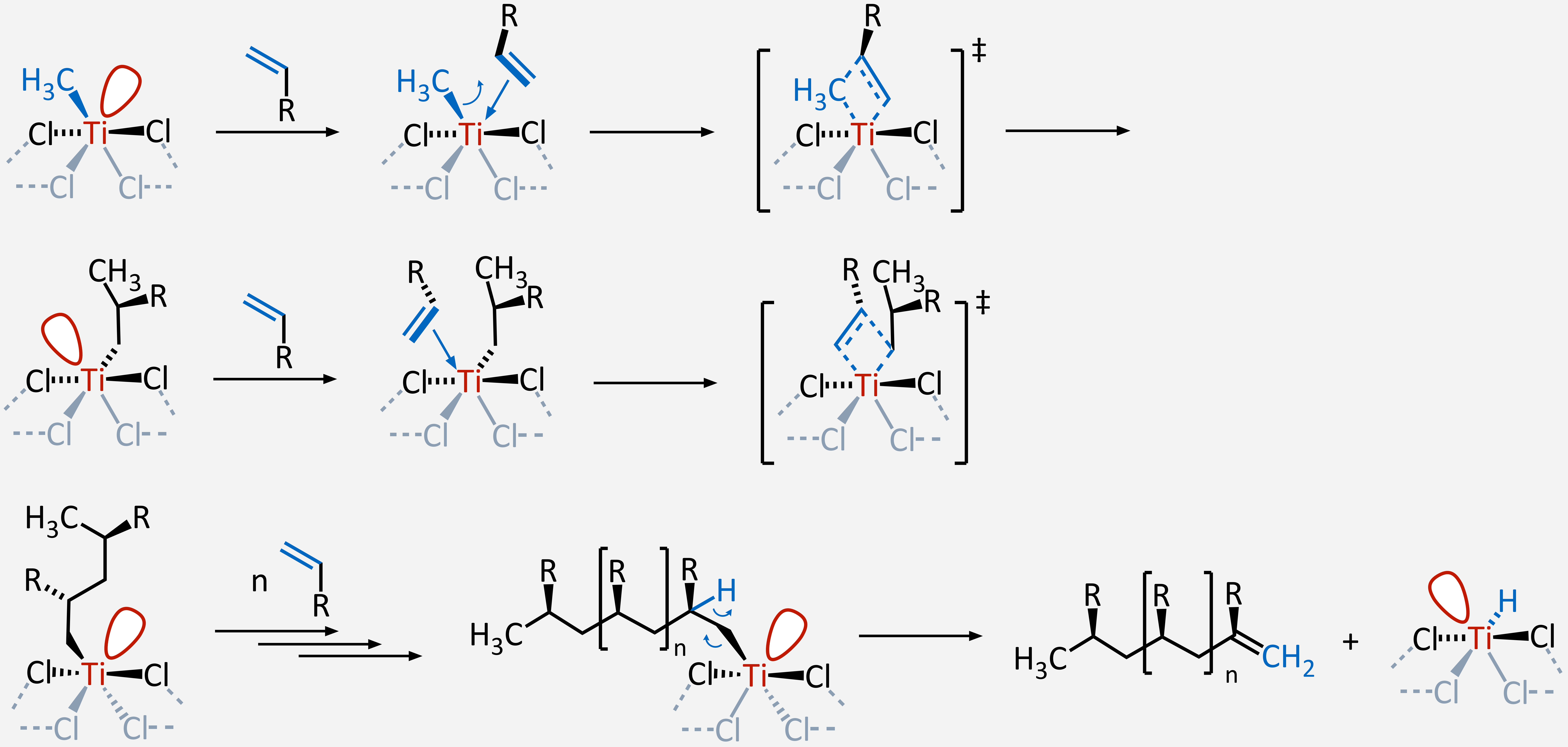
Catalyst Activation

- catalyst activation requires generating an alkylated metal center with a free coordination site



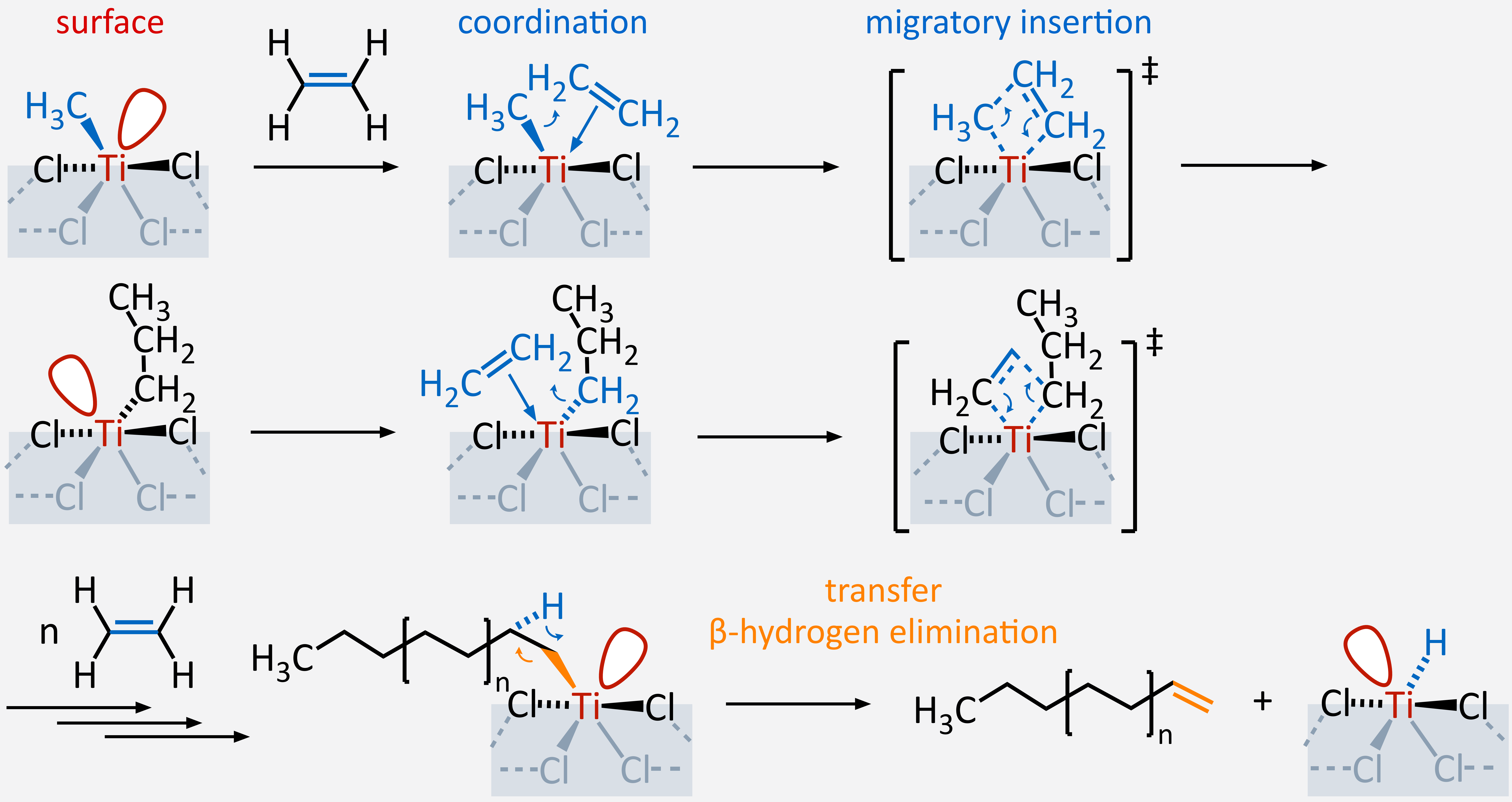
- **alkylation of stable precursors typically achieved with $AlMe_3$ or methylaluminoxide (MAO)**
- **alkylated metal center with a free coordination site is highly electron-deficient species**
- **very strong Lewis/Brønsted acid with weakly coordinating anion required for its formation**
- **MAO (clusters of about 20 Al atoms, unknown structure) does both, common in industrial processes**

Example of a Ziegler-Natta Polymerization via Cossee-Arlman Mechanism



- **migratory insertion means that polymer switches coordination site with every insertion step**

Example of a Ziegler-Natta Polymerization



- Cossee Arlman mechanism: **monomer coordination** to **empty coordination site** on surface metal atom
- **migratory insertion** into Mt–C bond, means that **polymer switches coordination site at every step**
- **chain transfer** generates terminal **double bonds**, can result in branches when polymerized