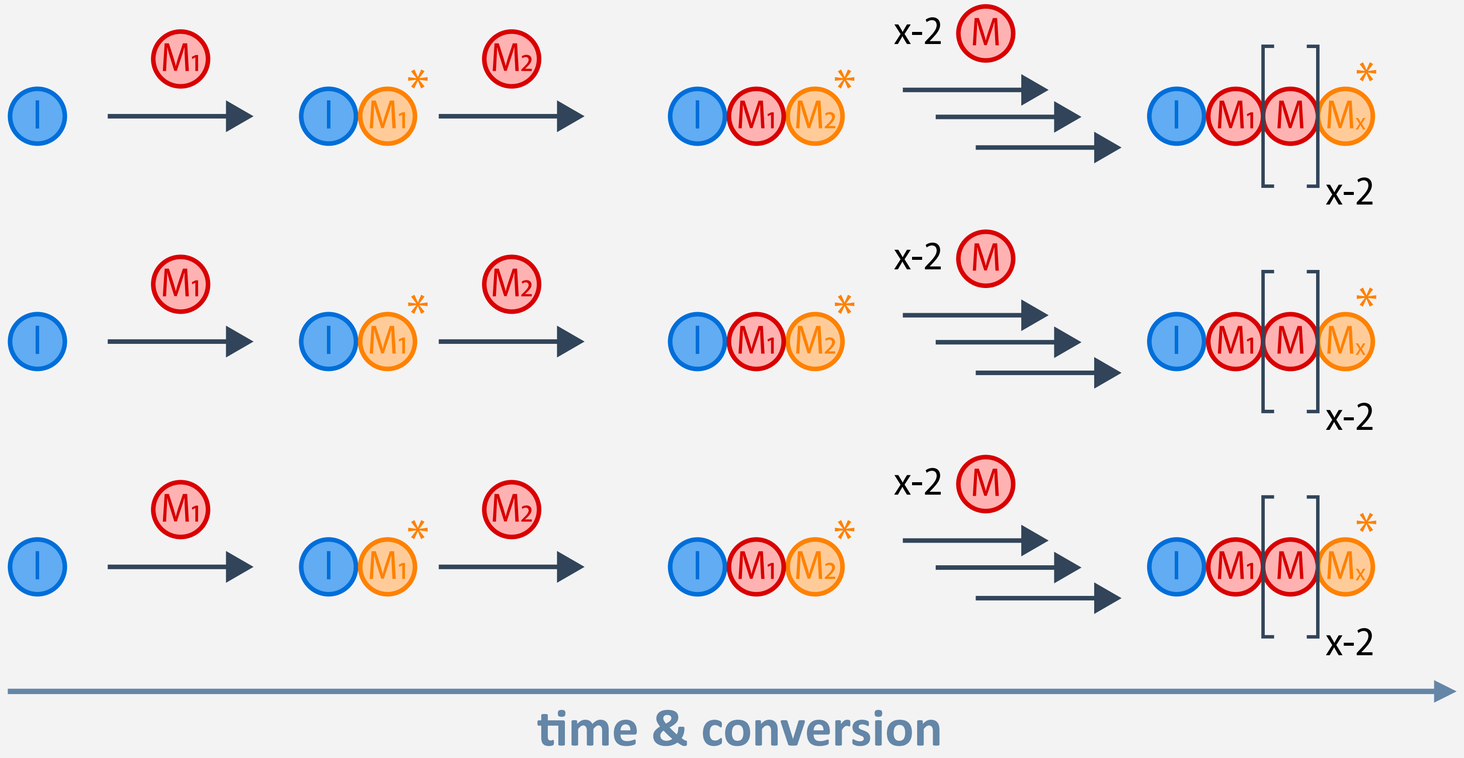
5.4 Living and Controlled Polymerizations

The Living Nature

- absence of termination (no mechanism & strong electronic repulsion between active chain ends!)

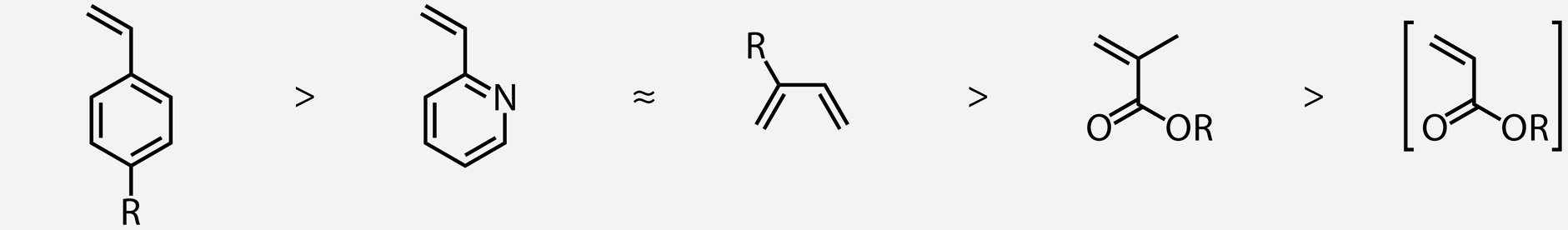


- polymers are all initiated fast and at approximately the same time; origin of (small) dispersity
- chain ends remain active after full monomer consumption (absence of impurities!)
- the polymerization can be continued with an additional feedstock of monomers (same or different)

Living Anionic Polymerization

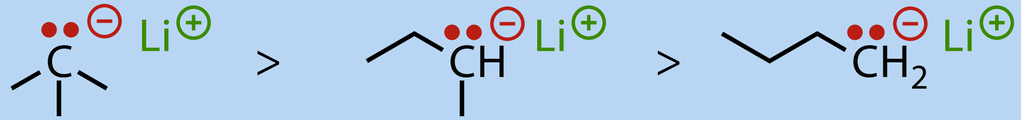
Vinyl Monomers and Initiators

- monomers with possibility for anion delocalisation, ideally with electron-withdrawing side groups



styrene derivatives (R = H, Me, COOR') | 2-vinylpyridine | butadiene (R = H) isoprene (R = Me) | methacrylates (R = Me, Bu, tBu) | acrylates (R = Me, Bu, tBu)

- initiators are organoalkaline compounds or alkaline metals



t-BuLi *tert.*-butyl lithium | s-BuLi *sec.*-butyl lithium | n-BuLi butyl lithium

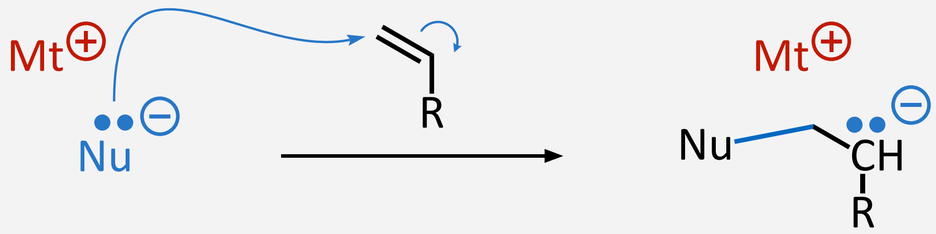
strong nucleophiles for monodirectional chain growth

KNaph potassium naphthalide | K, Na, Li alkaline metals

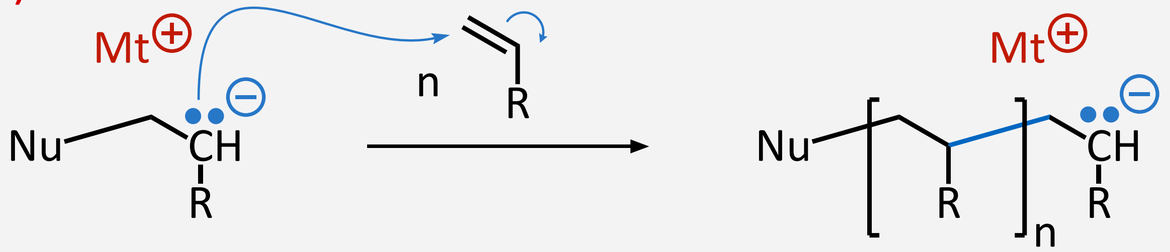
single-electron transfer agents for bidirectional growth

Living Anionic Polymerization of Vinyl Monomers

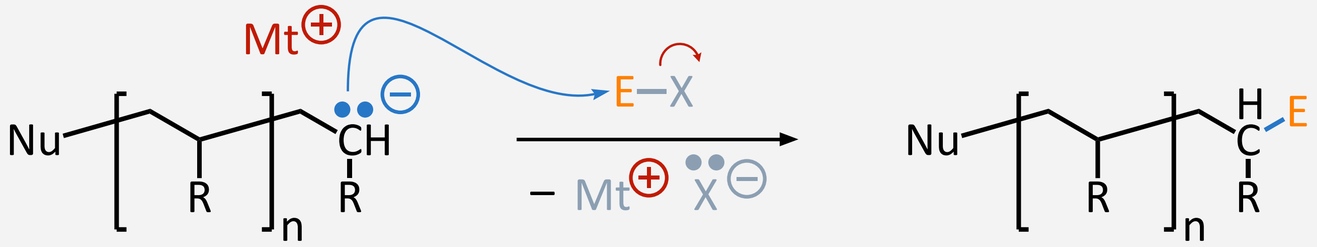
- initiation (very fast)



- propagation (chain growth)

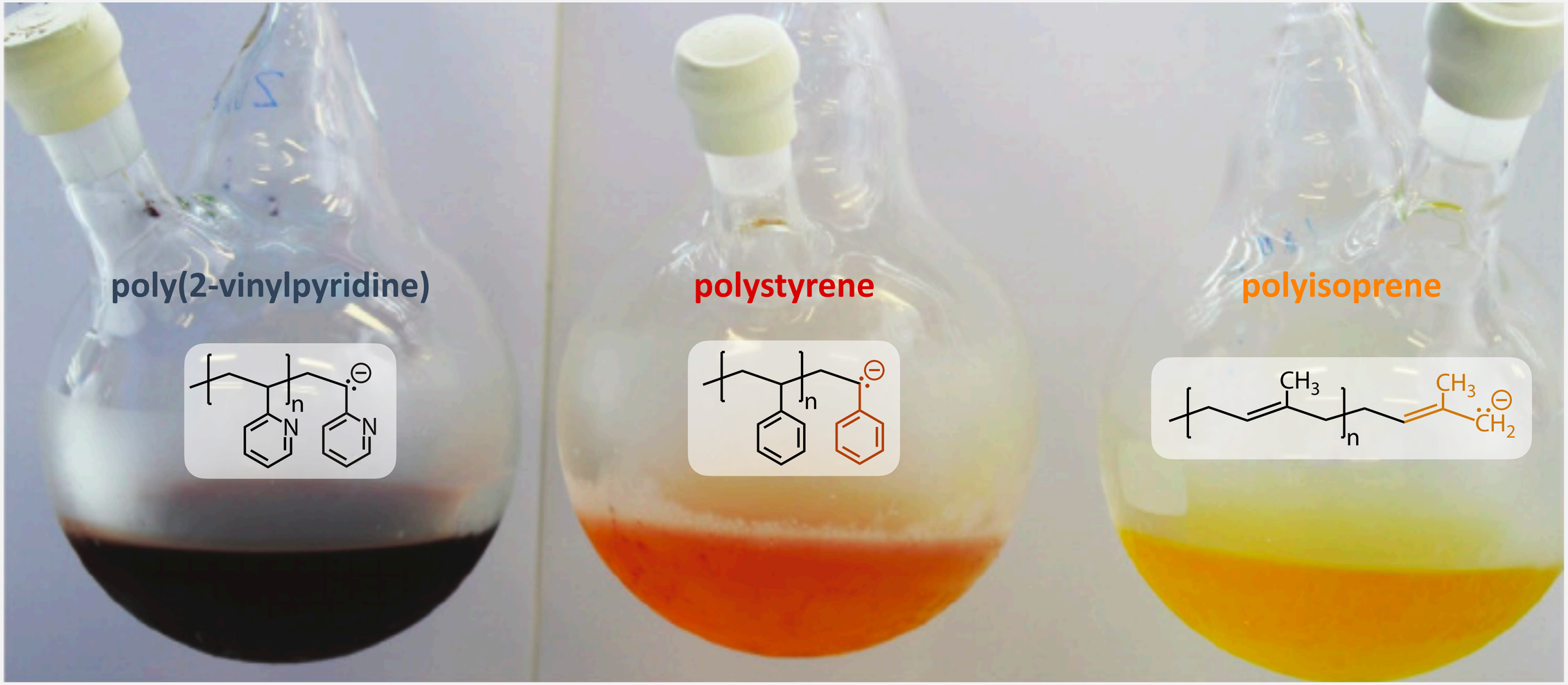


- quenching



- **anionic polymerisations of vinyl monomers are initiated by strong nucleophiles**
- **termination reactions are absent, except for inadvertent electrophilic impurities (H_2O, CO_2)**
- **electrophiles serve as quenching reagents, deliberately end the reaction, introduce end groups**

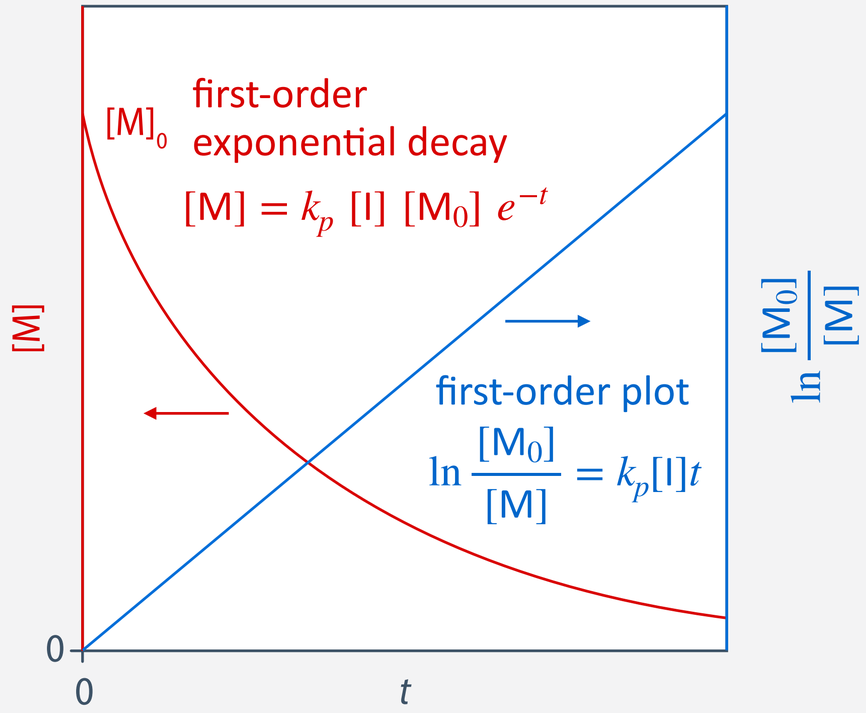
Living Anionic Polymerization of Vinyl Monomers



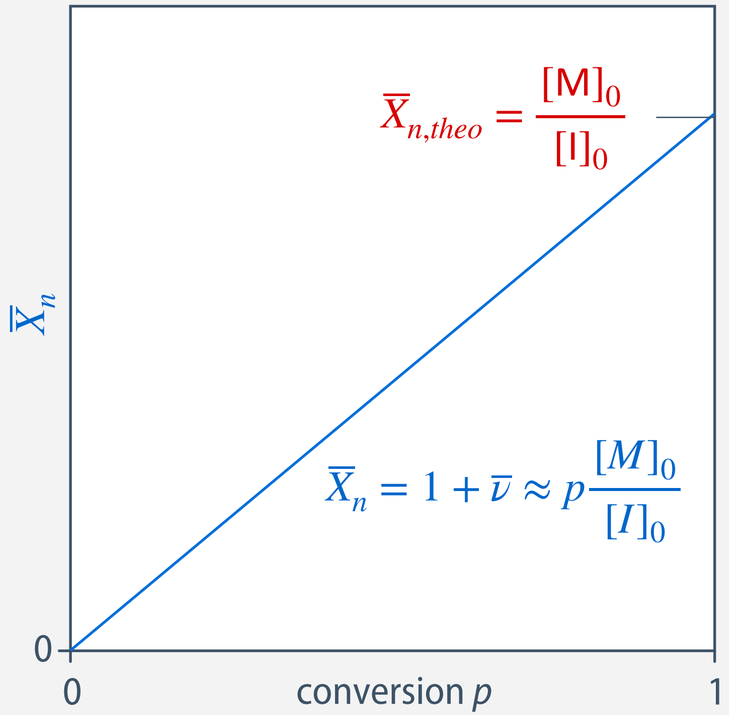
- appearance of color is an evidence of the presence and non-terminating character of living chains

Criteria for the Experimental Verification of Living Polymerizations

conversion over time



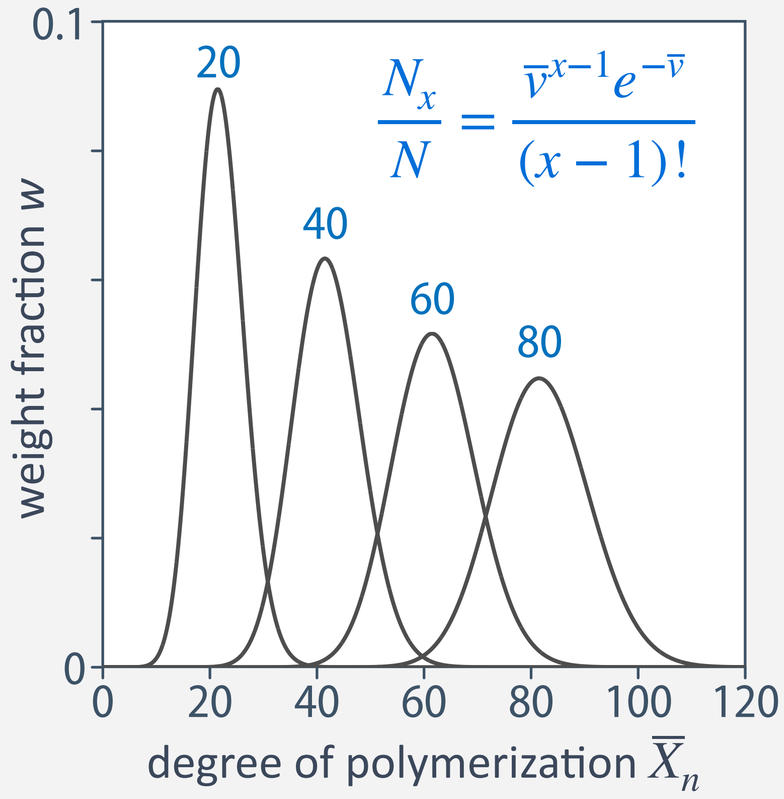
molar mass over conversion

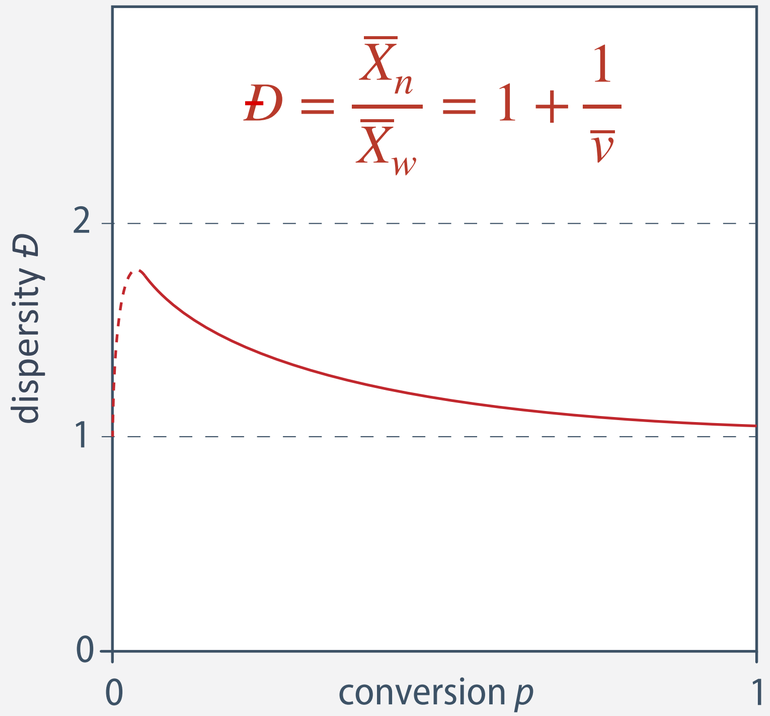


- conversion over time plot: polymerization reaction is **first order** in monomer concentration
- molar mass over conversion plot: number-average molar mass $\overline{X}_n = 1 + \overline{\nu}$ linear with conversion
- molar mass control: final number-average molar mass depends on monomer/initiator ratio

The Poisson Distribution of the Molar Mass

- **kinetic analysis leads to a Poisson distribution for the molar mass distribution:**

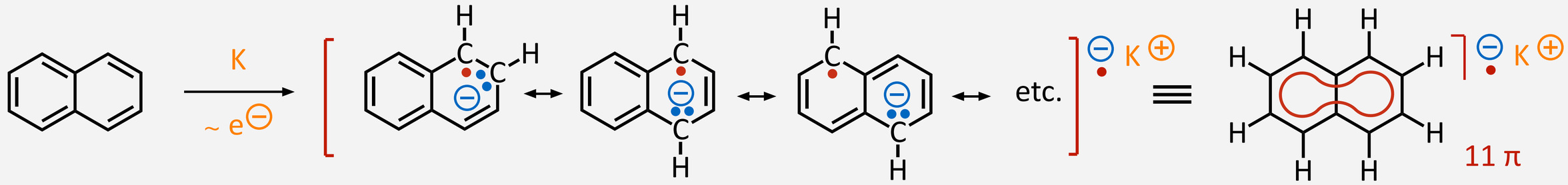




- **number-average degree of polymerization $\overline{X}_n \approx p \frac{[M]_0}{[I]_0}$ controlled by monomer/initiator ratio**

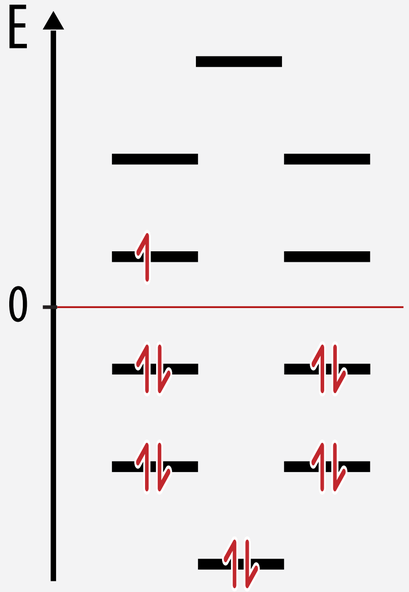
Bidirectional Polymerization with Alkaline Metals and Naphthalides

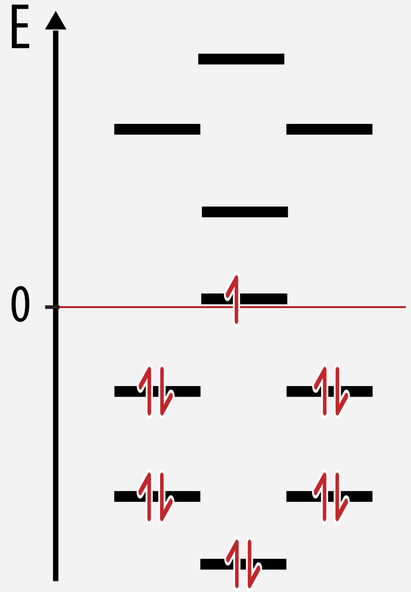
- alkaline metals reduce naphthalene by single-electron transfer (SET)



naphthalene

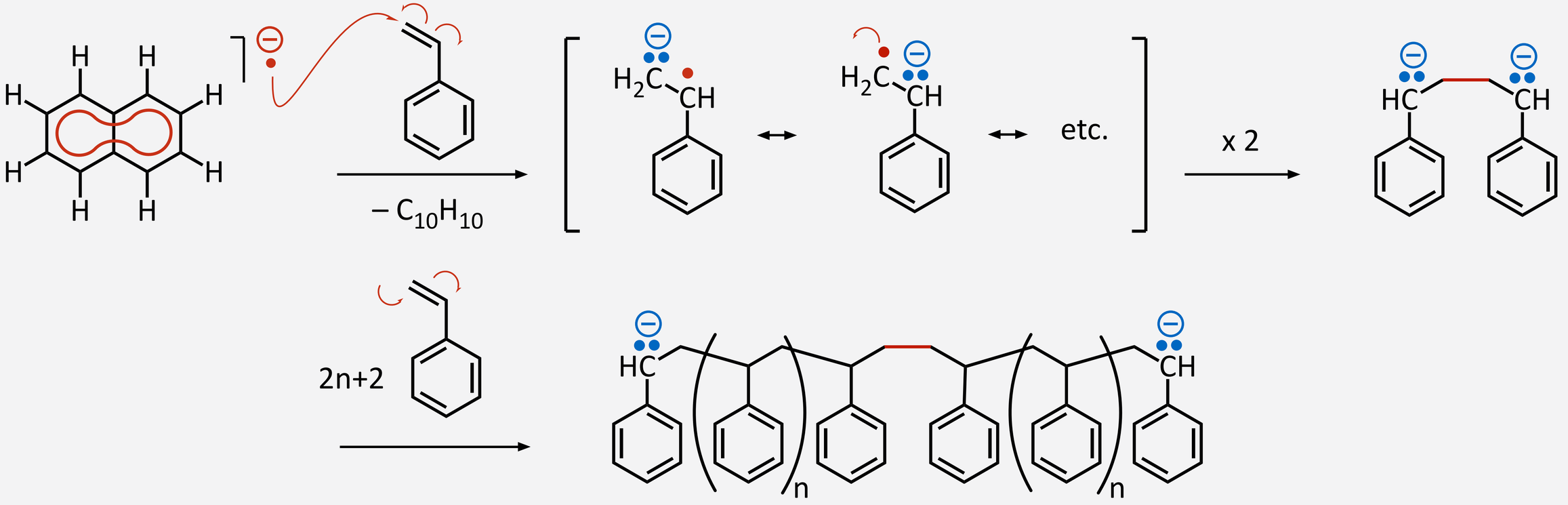
naphthalide



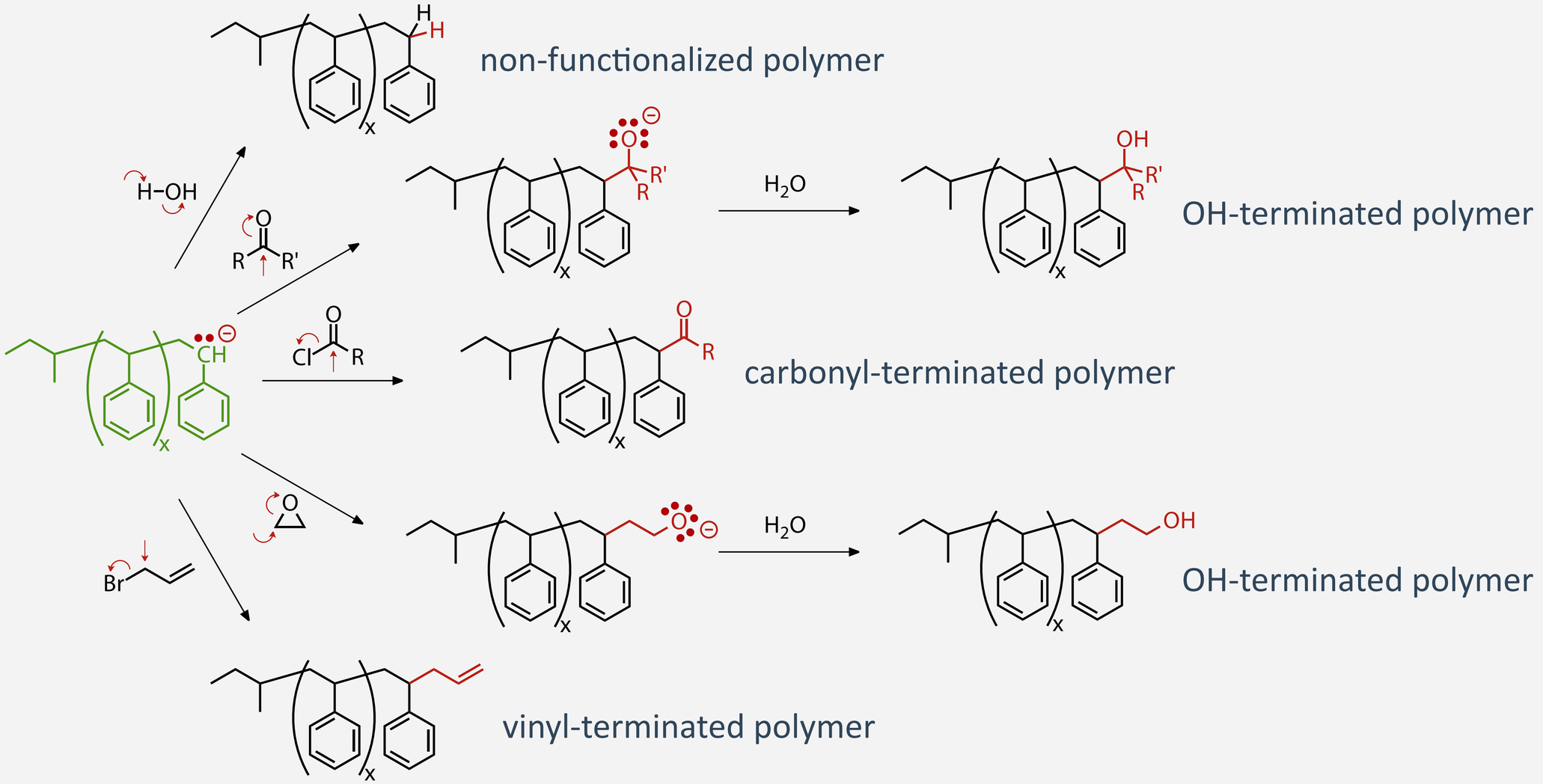


Bidirectional Polymerization with Alkaline Metals and Naphthalides

- SET from KNaph to a monomer results in dimerization, dianion initiator starts bidirectional chain growth



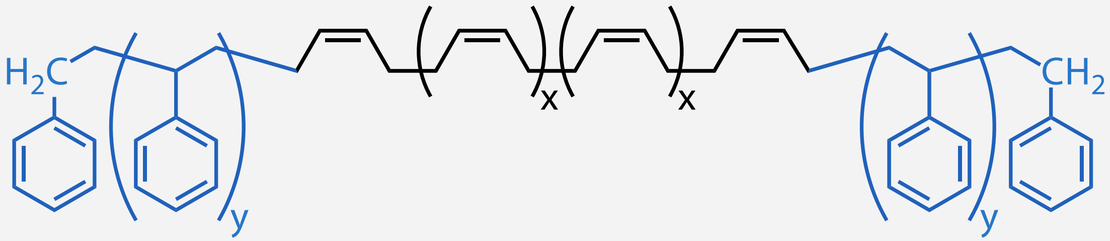
Quenching Reagents and Telechelics



- **the living chain end is a strong nucleophile, end groups can be introduced by S_N and S_{AE} reactions**

Thermoplastic Elastomers from BAB Triblock Copolymers

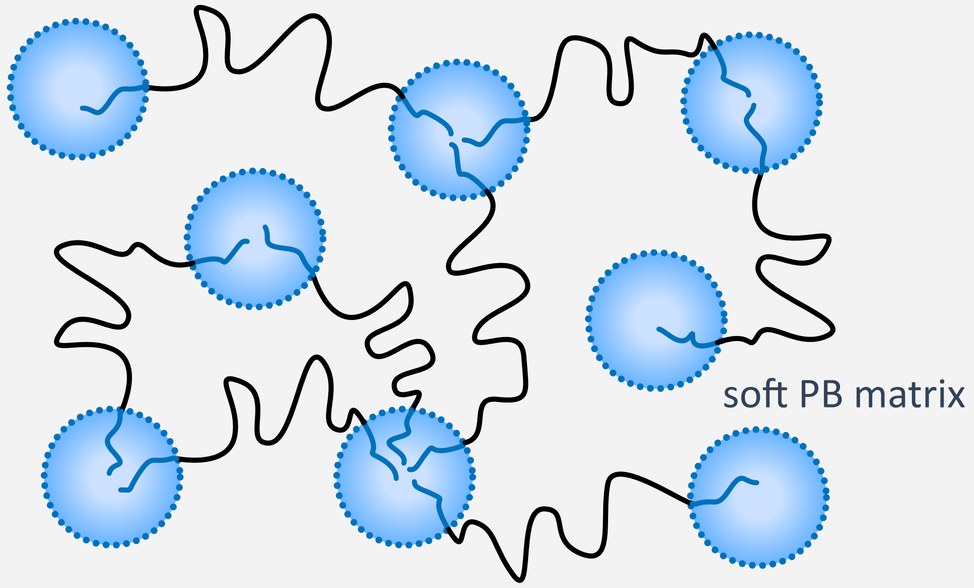
- SBCs (styrene-butadiene block copolymers) are relevant elastomer materials (like some TPUs)



T_g ≈ 100°C **T_g ≈ –60°C** **T_g ≈ 100°C**

SBS rubber (Kraton™, BASF)

poly(styrene-*block*-butadiene-*block*-styrene)



glassy, hard, physical cross-links

∅ 10^{-8}–10^{-7} m

- **phase segregation (demixing) of different polymer segments in bulk material**
- **hard PS domains serve as physical cross-links: they melt above their T_g (reprocessable materials)**