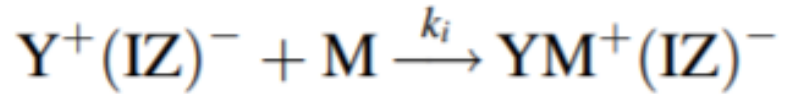# Kinetics of Cationic Polymerization

The initiation process of cationic polymerization can be generalized as

$$I + ZY \overset{K}{\rightleftharpoons} Y^+(IZ)^-$$

$$Y^+(IZ)^- + M \overset{k_i}{\longrightarrow} YM^+(IZ)^-$$

$$YM^+(IZ)^- + M \overset{k_p}{\longrightarrow} YMM^+(IZ)^-$$
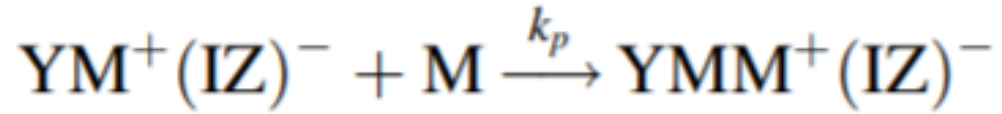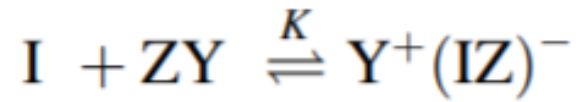
Termination occurs due to a combination of the propagating center with the counterion.

$$YM^+(IZ)^- \overset{k_t}{\longrightarrow} YMIZ$$
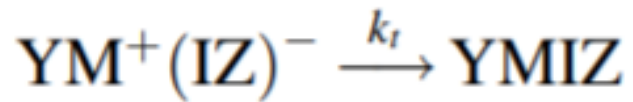
The overall kinetics depends on the mode of termination in a particular system. If the termination is exclusively due to the combination of propagating center with counterion, one can follow the rate expression used in the radical polymerization basis on the steady-state conditions. The rates of initiation, propagation, and termination are given by

$$R_i = K k_i [\text{I}][\text{ZY}][\text{M}]$$

$$R_p = k_p [\text{YM}^+(\text{IZ})^-][\text{M}]$$

$$R_t = k_t [\text{YM}^+(\text{IZ})^-]$$

At steady state $R_i = R_t$, then

$$[\text{YM}^+(\text{IZ})^-] = \frac{K k_i [\text{I}][\text{ZY}][\text{M}]}{k_t}$$

Combining Eq. 8.36 and Eq. 8.38 yields the rate of polymerization as

$$R_p = \frac{R_i k_p [\text{M}]}{k_t} = \frac{K k_i k_p [\text{I}][\text{ZY}][\text{M}]^2}{k_t} \tag{8.39}$$

The number-average degree of polymerization is obtained as the propagation rate divided by the termination rate:

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{k_p [\text{M}]}{k_t} \tag{8.40}$$

Similar to radical polymerization, chain transfer reactions are also involved in cationic polymerization such as chain transfer to monomer, spontaneous termination, and chain transfer to chain transfer agent S. In addition to combination with the counterion, if there are chain transfer reactions present, the concentration of the propagating species remains unchanged, and the polymerization rate is again

$$\bar{X}_n = \frac{R_p}{R_t + R_{ts} + R_{tr,M} + R_{tr,S}} \tag{8.41}$$

The rate of spontaneous termination (R_{ts}) and the two transfer reactions ($R_{tr,M}$ and $R_{tr,S}$) are given by

$$R_{ts} = k_{ts}[\text{YM}^+(\text{IZ})^-] \tag{8.42}$$

$$R_{tr,M} = k_{tr,M}[\text{YM}^+(\text{IZ})^-][\text{M}] \tag{8.43}$$

$$R_{tr,S} = k_{tr,S}[\text{YM}^+(\text{IZ})^-][\text{S}] \tag{8.44}$$

Combining Eq. 8.41 with Eqs. 8.36, 8.37, 8.42 to 8.44 yields

$$\bar{X}_n = \frac{k_p[\text{M}]}{k_t + k_{ts} + k_{tr,M}[\text{M}] + k_{tr,S}[\text{S}]} \tag{8.45}$$

or

$$\frac{1}{\bar{X}_n} = \frac{k_t}{k_p[\text{M}]} + \frac{k_{ts}}{k_p[\text{M}]} + C_M + C_S\frac{[\text{S}]}{[\text{M}]} \tag{8.46}$$

When chain transfer to S terminates the kinetic chain, the polymerization rate is decreased and is given by

$$R_p = \frac{Kk_ik_p[\text{I}][\text{ZY}][\text{M}]^2}{k_t + k_{tr,S}[\text{S}]}$$

$$R_i = k_1[\text{I}][\text{ZY}]$$

The polymerization rate expressions will then be modified by replacing Kki with k1, and there will be one order lower dependence of Rp on [M]. The degree of polymerization is unchanged and still described.

The expressions for Rp in cationic polymerization point out a very significant difference between cationic polymerization and radical polymerization. Radical polymerization shows a half-order dependence of Rp on Ri, while cationic polymerizations show a first-order dependence of Rp on Ri. The difference is a consequence of their different modes of termination. Termination is second order in the propagating species in radical polymerization but only first order in cationic polymerization.

In the absence of any chain transfer, the kinetic chain length m, is equal to DP and is expressed as.

$$\bar{v} = \overline{DP} = \frac{R_p}{R_t} = \frac{k_p[\text{M}][\text{M}^+]}{k_t[\text{M}^+]} = \frac{k_p[\text{M}]}{k_t}$$

If the chain transfer is the predominant mechanism for controlling chain growth, then.

$$\bar{v} = \overline{DP} = \frac{R_p}{R_{tr}} = \frac{k_p[\text{M}][\text{M}^+]}{k_{tr}[\text{M}][\text{M}^+]} = \frac{k_p}{k_{tr}}$$

Consider the situation where one polymer molecule is produced from each kinetic chain. This is the case for termination by disproportionation or chain transfer or a combination of the two, but without combination. The molecular weight distribution is similar to the linear step polymerization as shown. One difference in the use of the equation for radical chain polymerizations compared to step polymerization is the redefinition of p as the probability that a propagating radical will continue to propagate instead of terminating. The value of p is given as the rate of propagation divided by the sum of the rates of all reactions that a pr rgo.

$$\bar{X}_w/\bar{X}_n = (1 + p)$$

$$p = R_p/(R_p + R_i + R_{tr})$$

For the cationic polymerization, the PDI can be determined by Eq. 8.49. It has a limit of 2 (at low conversion). For rapid initiation, PDI will be narrow. For very slow termination and transfer reaction, PDI will be close to 1.

The existence of chain transfer reactions, PDI will be between 1 and 2, mostly larger than 2 depending on the chain transfer reactions and their rates relative to propagation. At high conversion, the concentration of propagating centers, monomer, and transfer agent as well as rate constants change, and the PDI increases.

Anionic Polymerization

In anionic vinyl polymerization, the propagating chain is a carbanion which is formed by initiator undergoing nucleophilic addition to monomer. Monomers having substituent groups capable of stabilizing a carbanion through resonance or induction are most susceptible to anionic polymerization. Examples of such groups are nitro, cyano, carboxyl, vinyl, and phenyl..

The existence of chain transfer reactions, PDI will be between 1 and 2, mostly larger than 2 depending on the chain transfer reactions and their rates relative to propagation. At high conversion, the concentration of propagating centers, monomer, and transfer agent as well as rate constants change, and the PDI increases.

$$Nu^- \ + \ H_2C{=}CHR \longrightarrow Nu{-}CH_2{-}\overset{-}{C}H{-}R$$
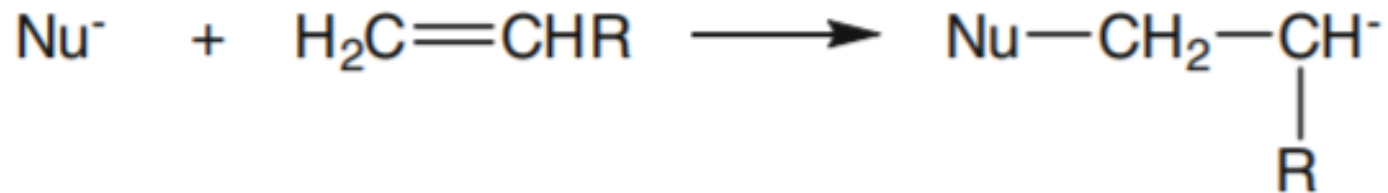
Reaction Mechanisms of Anionic Polymerization

The anionic polymerization is the same as other chain polymerizations which involve three reaction steps: (1) initiation, (2) propagation, and (3) termination, using the base or nucleophile as an initiator, e.g., NaNH2, LiN(C2H5)2, alkoxides, hydroxides, cyanides, phosphines, amines, and organometallics compounds such as n-C4H9Li and C6H5–MgBr.
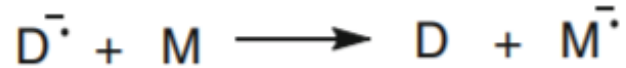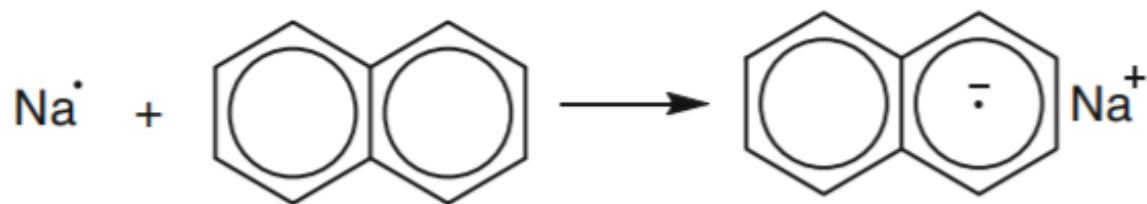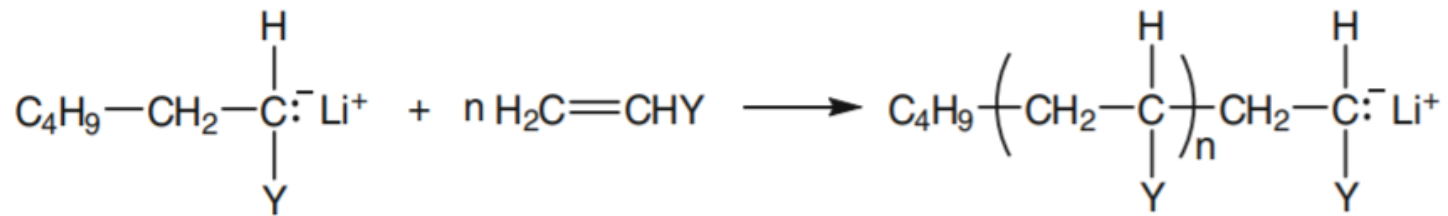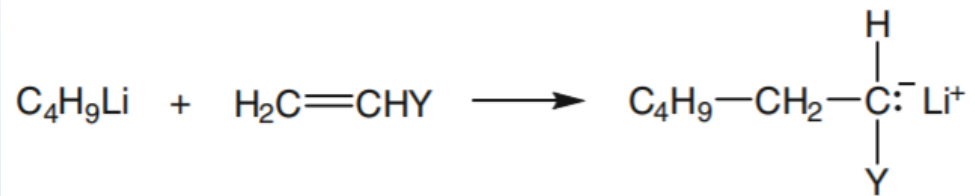
Many anionic polymerizations, such as styrene, 1,3-butadiene, nonpolar monomer have no termination reaction (reacts with counterion). By adding proton donor such as water or alcohol to the living polymers, the living chain can be terminated. The hydroxide ion is usually not

Kinetics of Anionic Polymerization with Termination

The kinetic and mechanistic aspects of anionic polymerization are better understood than those of cationic polymerization. In the case of the potassium amide initiated polymerization in liquid ammonia, initiation involves dissociation followed by addition of amide ion to monomer.
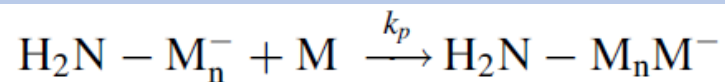
$$KNH_2 \overset{K}{\rightleftharpoons} K^+ + NH_2^-$$

$$NH_2^- + M \xrightarrow{k_i} H_2N - M^-$$
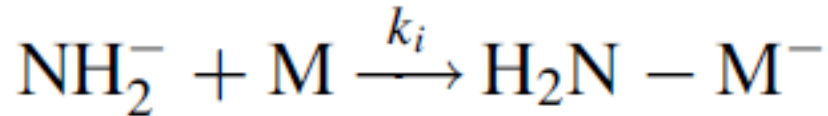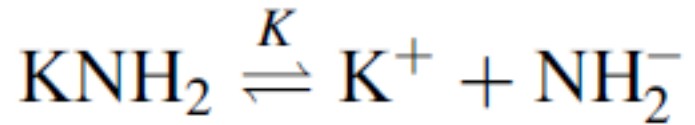
Because the second step is slow relative to the first step,

$$R_i = k_i[H_2N:^-][M]$$

$$R_i = k_i K[M][KNH_2]/[K^+]$$

Propagation proceeds according to

$$H_2N - M_n^- + M \xrightarrow{k_p} H_2N - M_nM^-$$

$$R_p = k_p[M][M^-]$$

REF: Lecture Notes In Chemistry 82 Principles of Polymer Design and Synthesis, Springer

The chain transfers to solvent (NH3) results that an anion produces without termination.

$$H_2N - M_n^- + NH_3 \xrightarrow{k_{tr,NH_3}} H_2N - M_n - H + NH_2^-$$

$$H_2N - M_n^- + H_2O \xrightarrow{k_{tr,H_2O}} H_2N - M_n - H + OH^-$$

$$\bar{X}_n = p[M]_o / [I]_o$$
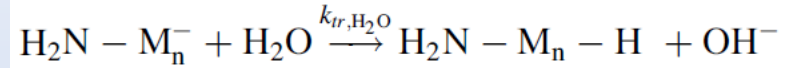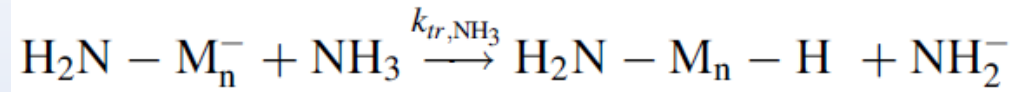
The transfer rates for solvent and impurities can be expressed

$$R_{tr,NH_3} = k_{tr,NH_3}[M^-][NH_3]$$

$$R_{tr,H_2O} = k_{tr,H_2O}[M^-][H_2O]$$

Assuming a steady state whereby $R_i = R_t$, and combining

$$R_P = K k_i k_p [M]^2 [KNH_2] / k_{tr,H_2O}[K^+][H_2O]$$