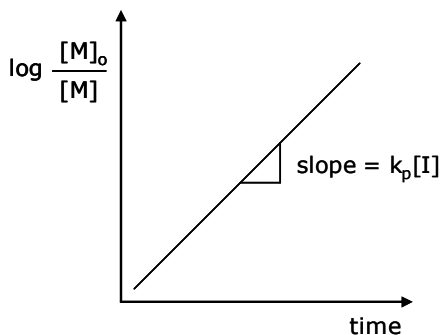## *Living Polymerization*

$$R_p = -\frac{d[M]}{dt} = k_p[M^-][M]$$

$$[M^-] \cong [I]_o \quad \text{(assumes all initiator is active and available)}$$

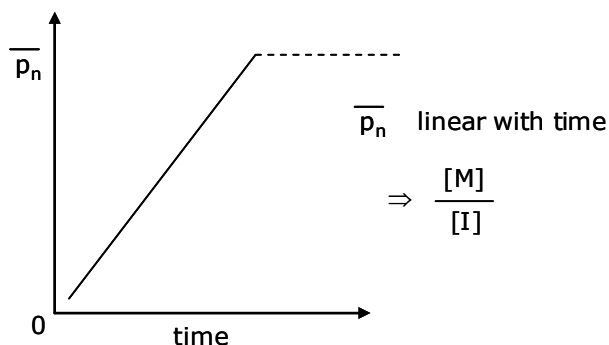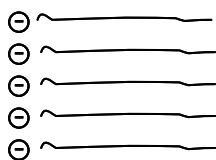$$\Rightarrow \quad R_p = k_p[M][I]_o$$

$$\Rightarrow \quad \ln\frac{[M]_o}{[M]} = k_p[M^-]t = \underbrace{k_p[I]}t$$
$$\text{constant}$$

$$\overline{p_n} = \frac{[M]}{[I]} = \frac{\pi[M]_o}{[I]}$$

polymer grows at exactly
the same rate (monomer
initiated at exactly the
same time)

$\overline{p_n}$ linear with time

$$\Rightarrow \quad \frac{[M]}{[I]}$$

$\therefore$ for complete conversion $\quad \overline{p_n} = \dfrac{[M]_o}{[I]}$

PDI: $\quad \dfrac{\overline{M_w}}{\overline{M_n}} = 1 + \dfrac{v}{(v+1)^2}$ $\qquad$ (not real PDI, but for statistical purposes)

Where ν = kinetic chain length

$\Rightarrow$ as $\nu\uparrow$, $\dfrac{\overline{M_w}}{\overline{M_n}} \rightarrow 1$

$\Rightarrow$ predicts PDI $\sim 1.01 \rightarrow 1.001$

Poisson distribution instead of Gaussian distribution
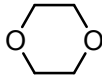
Solvent Characteristics
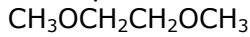
Most common solvents
pentane
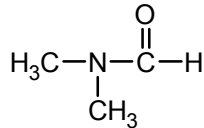hexane
cyclohexane
benzene
dioxane

increasing polarity

1,2 dimethoxyethane
$CH_3OCH_2CH_2OCH_3$
tetrahydrofuran

dimethyl formamide

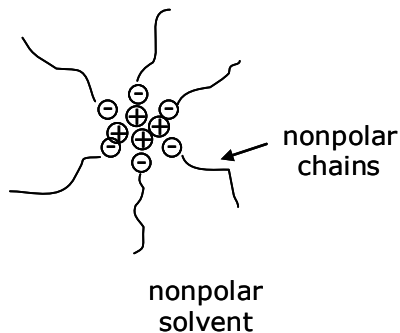$H_3C-N-\overset{\overset{\displaystyle O}{\|}}{C}-H$
$\quad\quad\;\; |$
$\quad\quad\; CH_3$

• solvent must solvate monomer + polymer
$\quad\Rightarrow$ function of polarity

• important solvent effects in anionic polymerization

   - rate of polymerization highly dependent on accessibility
   of ⌒‾‾‾‾$^\ominus$ (propagating anion)
   - association effects
   - degree of counterion/ion dissociation

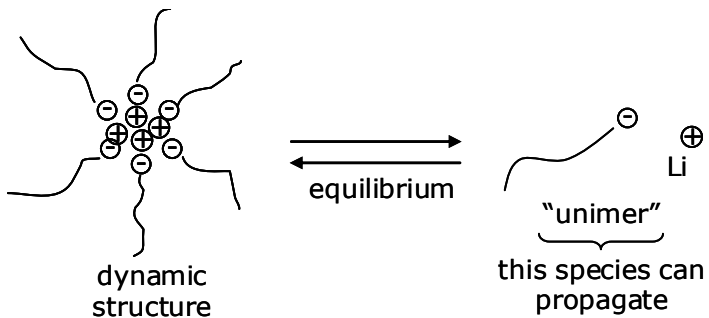## 1. Association Effects:

Low dielectric (nonpolar) solvents are poor environments for ions:
Possible to form micelle-like aggregates:

nonpolar chains

nonpolar solvent

aggregation probabilities $\uparrow$
as polarity of solvent $\downarrow$
and as counterion size $\downarrow$

dependency on concentration:
as conc $\uparrow$, agg $\uparrow$

dynamic structure — equilibrium — "unimer" — this species can propagate

$\{M^-\}_n \xleftrightarrow{K_e} nM^-$ let n = # of chains per aggregate

bracket denotes   (assume all aggregates have same number of chains)
aggregate

$$K_e = \frac{[M^-]^n}{[\{M^-\}_n]} \quad \text{equilibrium constant}$$

$$[M^-] = K_e^{1/n}[\{M^-\}_n]^{1/n}$$

$$R_p = -\frac{d[M]}{dt} = k_p K_e^{1/n}[M][\{M^-\}_n]^{1/n}$$

see 1/n dependency in rate of propagation
with respect to [M⁻]

$$[\{M^-\}_n] \propto [M^-] = [I]$$

can assume $[I] \sim [\{M^-\}_n]$

$$\Rightarrow R_p \cong k_p K_e^{1/n}[M][I]^{1/n}$$

If aggregation number is 2, (n=2)

$$R_p = k_p K_e^{1/2}[M][\{M^-\}_2]^{1/2}$$
$$\cong k_p K_e^{1/2}[M][I]^{1/2} \quad \text{aggregate form}$$

2. Degrees of dissociation of counterion and chain

(happens much more frequently)
different degrees of dissociation:
    Free ions:

Na

ions are fully dissociated from
negative charge

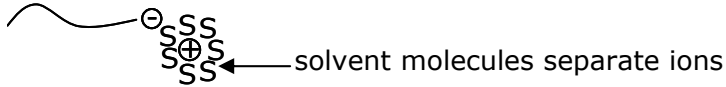$\Rightarrow$ assume full availability of charge to react with monomer

Versus … 2 types of ion pairs

a) unsolvated ion pairs (tight pairs)

"contact ion pairs"

b) solvent separated ion pairs (loose ion-ion connections)

solvent molecules separate ions

thin layer of solvent that separates counterion from + charge

reaction rates of species are going to be different

$k_{p-} \Rightarrow$ rate constant for free ions

$k_{pI} \Rightarrow$ rate constant for all ion pairs
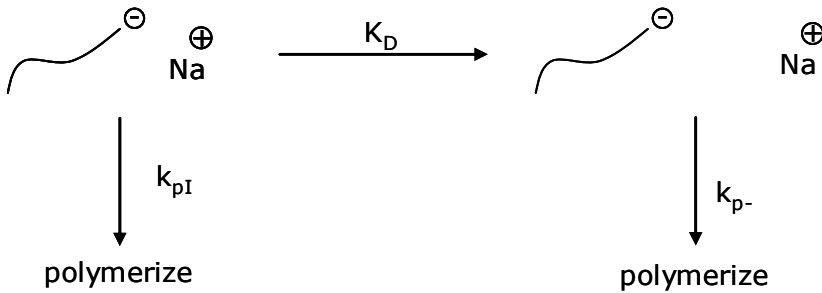
and $k_{pI} = y k_{pII} + (1-y) k p_c$

parallel sign

k_{pII} = solvent separated pair

y = fraction of solvent separated pair

Equilibrium between free and dissociated ion pairs:

Dissociated rate constant

$$K_D = \frac{[\frown \ominus][Na^{\oplus}]}{[\frown \ominus Na^{\oplus}]}$$

$\Rightarrow$ assume $[Na^{\oplus}] = [\frown \ominus]$
(no addition of NaCl that drives up $[Na^+]$)

$$K_D = \frac{[\ominus]^2}{[\ominus Na^\oplus]}$$

Given that $[M^-]$ = concentration of all ionic sites (free and associated)

$$\alpha \equiv \frac{\text{\# of dissociated (free) ions}}{\text{all ions}}$$

$$K_D = \frac{\alpha^2 [M^-]^2}{(1-\alpha)[M^-]} = \frac{\alpha^2 [M^-]}{1-\alpha}$$

solve for α:

$$\alpha \cong \left(\frac{K_D}{[M^-]}\right)^{1/2} \qquad \text{assuming that } \alpha = \text{small}$$

$$\rightarrow \text{ neglect } 1-\alpha \text{ term in denominator}$$

$$k_p = \alpha k_{p-} + (1-\alpha)k_{pI}$$

$$\Rightarrow R_P = -\frac{d[M]}{dt} = \left[k_{pI} + \left(\frac{K_D}{[M^-]}\right)^{1/2}(k_{p-} - k_{pI})\right][M^-][M]$$

$$\updownarrow$$

$$[I]$$