

Chapter 5



Ionic Polymerization

□ Ionic polym'n is

□ specific to monomer Table 5.1 p124

- **cationic** polym'n for $\text{CH}_2=\text{CH}(\text{X})$ with X that donate e^- and/or resonance-stabilize (+) charge
[inductive and/or resonance e^- donating X]
 - $\text{CH}_2=\text{CH}(\text{OR})$, $\text{CH}_2=\text{C}(\text{R}_1)(\text{R}_2)$
 - $\text{CH}_2=\text{CH}(\text{Ph})$, $\text{CH}_2=\text{C}(\text{R})(\text{Ph})$, $\text{CH}_2=\text{CH}(\text{CH}=\text{CH}_2)$, $\text{CH}_2=\text{CH}(\text{CR}=\text{CH}_2)$
 - $\text{CH}_2=\text{CH}(\text{R})$ ~ too-weakly donating with short R (like Me)
- **anionic** ---
 - $\text{CH}_2=\text{CH}(\text{COOR})$, $\text{CH}_2=\text{C}(\text{R})(\text{COOR})$, $\text{CH}_2=\text{CH}(\text{C}\equiv\text{N})$, $\text{CH}_2=\text{C}(\text{R})(\text{C}\equiv\text{N})$
- Both possible for styrenics, dienes
 - weakly inductive-donating
 - resonance-stabilizing both (+) and (-) charge [+M/-M]
- Both not facile for vinyl halides, vinyl esters

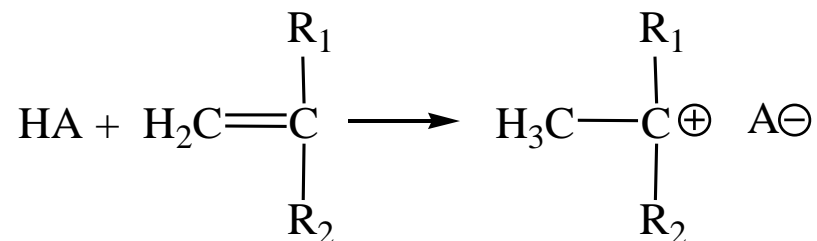
- ❑ Ionic polym'n is (cont'd)
 - ❑ much faster than radical polym'n
 - ← high conc'n of propagating chain
 - ❑ influenced by counter-ion [gegenion]
 - $---C^+ A^-$ or $---C^- M^+$
 - ❑ influenced by solvent
 - $---C^+ A^-$ [contact] $---C^+ //A^-$ [separated] $---C^+ + A^-$ [free]

Cationic polym'n: mechanism

Ch 5 Sl 4

□ initiation

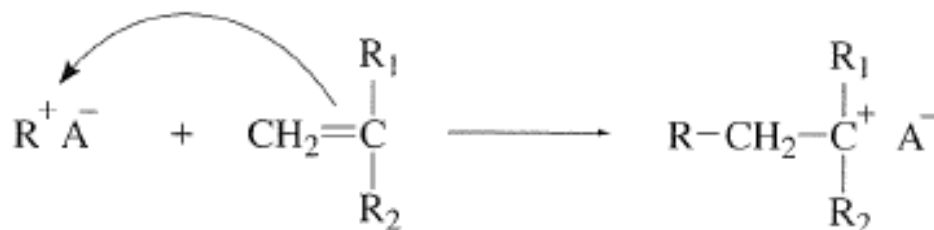
□ with protonic acid, HA



■ not HCl or HBr ← counter-ion [A⁻] too nucleophilic

■ H₂SO₄, HClO₄ popular

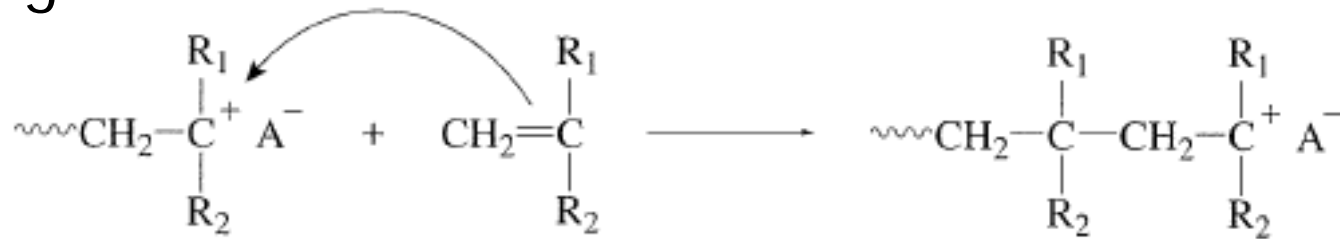
□ with Lewis acid



■ initiator/cocatalyst ~ a misnomer

■ activator/initiator, actually

□ propagation



- head-to-tail
- when C⁺ rearrangement possible → isomerization polym'n

□ termination and chain transfer

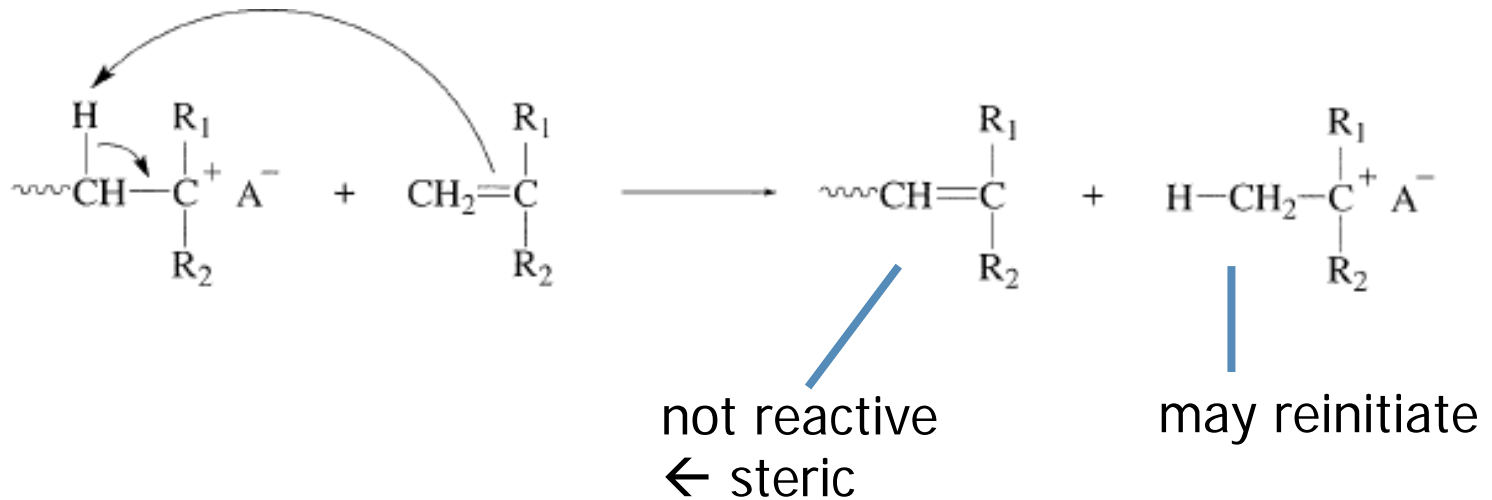
- no bimolecular termination
- ion-pair rearrangement



- chain transfer to counter-ion, spontaneous termination

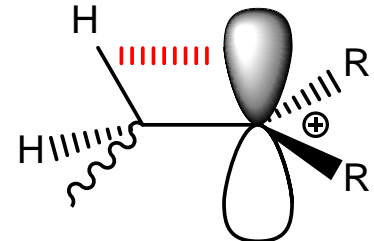
□ termination and chain transfer (cont'd)

□ CT to monomer



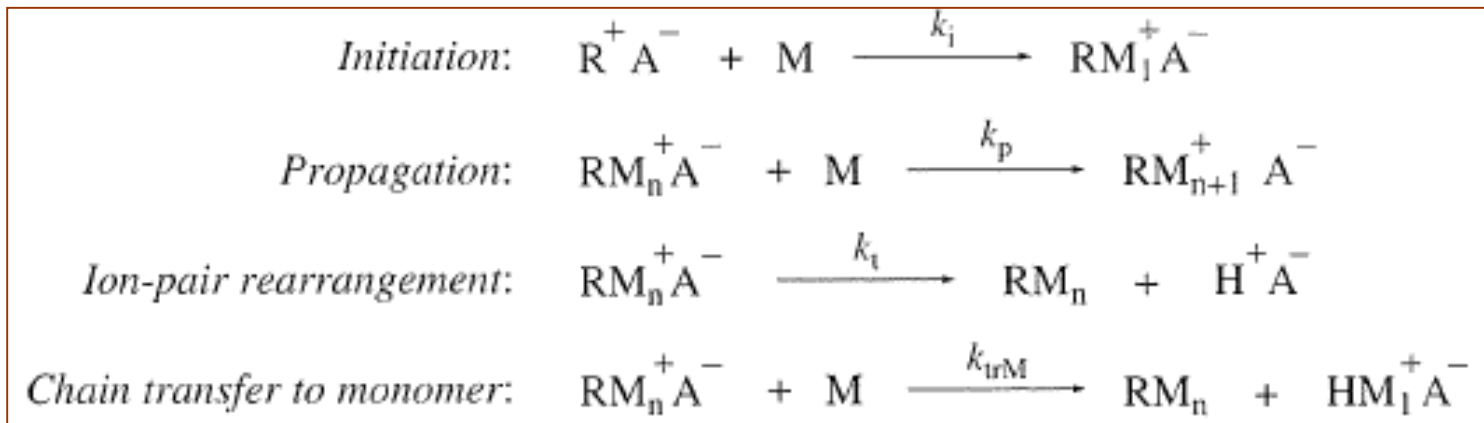
□ CT to solvent, impurity, or polymer also possible

- β -H electrophilic due to hyperconjugation



Kinetics of cationic polym'n

□ rate of polym'n



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

$$[M^+] = \sum_{n=1}^{\infty} [RM_n^+]$$

$$\frac{d[M^+]}{dt} = k_i[R^+ A^-][M] - k_t[M^+] = 0 \quad \leftarrow \text{s-s condition}$$

s-s not achieved in most cases; so fast

$$R_p = \left(\frac{k_i k_p}{k_t} \right) [R^+ A^-][M]^2$$

$$[M^+] = \left(\frac{k_i}{k_t} \right) [R^+ A^-][M]$$

□ R_p (cont'd)

$$R_p = \left(\frac{k_i k_p}{k_t} \right) [R^+ A^-] [M]^2$$

radical polym'n

$$R_p = k_p \left(\frac{f k_d}{k_t} \right)^{1/2} [M] [I]^{1/2}$$

□ 2nd-order on $[M]$

■ when $R^+ A^- + M \xrightarrow{k_i} RM_1^+ A^-$ is RDS. (most cases)

□ If $BF_3 + H_2O \rightleftharpoons H^+(BF_3OH)^-$ is RDS, 1st-order on $[M]$.

□ If transferred active center re-initiate rapidly,

$$[M^+] = [R^+ A^-] \text{ and } R_p = k_p [M] [R^+ A^-].$$

□ X_n $\bar{x}_n = \frac{k_p [M] [M^+]}{k_t [M^+] + k_{trM} [M^+] [M]} \rightarrow \frac{1}{\bar{x}_n} = \frac{k_t}{k_p [M]} + \frac{k_{trM}}{k_p}$

□ If no CT to M, $(\bar{x}_n)_0 = (k_p/k_t)[M]$.

□ effect of Temp

$$\frac{d \ln(R_p)}{dT} = \frac{E_i + E_p - E_t}{RT^2} \quad \text{can be } > 0 \text{ or } < 0$$

- activated C=C by subs $\rightarrow E_i$ and E_p small and $< E_t$

$$\frac{d \ln(\bar{x}_n)_0}{dT} = \frac{E_p - E_t}{RT^2} < 0$$

- As Temp up, x_n down.

$$\frac{d \ln(C_{tr})}{dT} = \frac{E_{tr} - E_p}{RT^2} > 0$$

- As Temp up, C up, and x_n down.

□ Low temperature preferred in cationic polym'n.

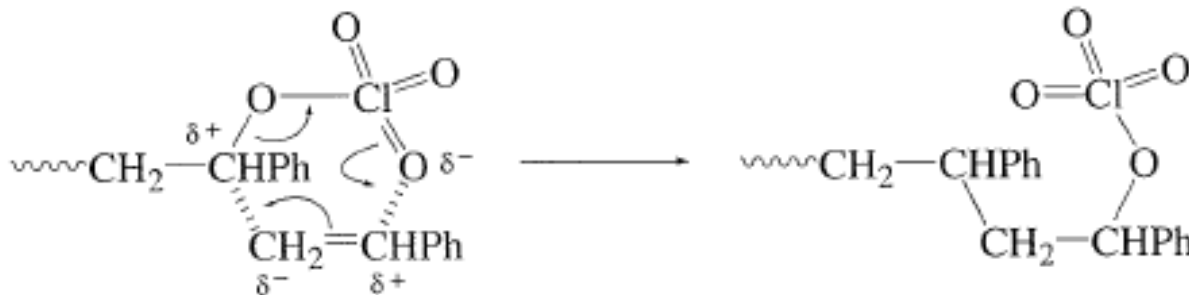
□ effect of solvent and counter-ion



- free ion active center propagates faster
 - higher k_p (by a factor > ten times)
 - lower k_t for ion-pair rearrangement, also
- faster in polar solvent
- faster with larger counter-ion
 - not evident ~ no systematic exp'tal data
 - <cf> anionic polym'n

Pseudocationic polym'n

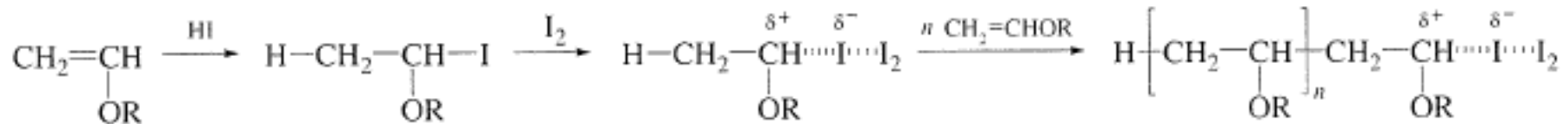
- ❑ In some of cationic polym'n
 - ❑ with protonic acid initiator in less polar solvent
 - eg, ST with HClO_4 and some others
 - ❑ shows **bimodal MMD**.
 - there is another process than ionic propagation
- ❑ pseudocationic (covalent) polym'n



- ❑ slower than ion/ion-pair propagation → lower MM
- ❑ losing popularity ~ ion and ion-pair separately

Living cationic polym'n

- ❑ Cationic polym'n is hardly living-like.
 - ❑ very sensitive to impurity and conditions
 - ❑ CT and rearrangements (← hyperconjugation)
- ❑ living-like may be possible by controlling C---counter ion bond characteristic
 - ❑ betw covalent and ionic (like pseudocationic)



- ❑ x_n should be $[\text{M}]/[\text{I}]$.

Practical considerations in cationic

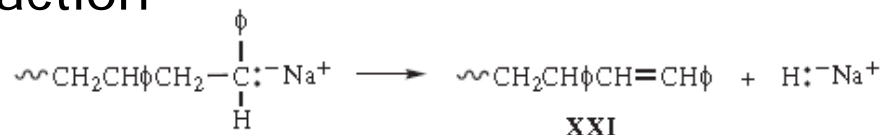
- ❑ Cationic polym'n requires
 - ❑ low rxn Temp ~ often below 0 °C
 - ❑ free from impurities
 - ❑ control of heat ← very fast initiation and propagation
- ❑ butyl rubber
 - ❑ the only commercial polymer by cationic polym'n
 - ❑ isobutylene copolymerized with small amount of isoprene
 - isoprene for (S) vulcanization
 - ❑ with alkyl halide/Lewis acid
 - ❑ at low Temp below 0 °C
 - ❑ MM control by Temp ~ control CT

Anionic polym'n

❑ Virtually all anionic polym'n is **truely living**.

❑ no bimolecular termination

❑ no CT ~ requires H:- ion abstraction



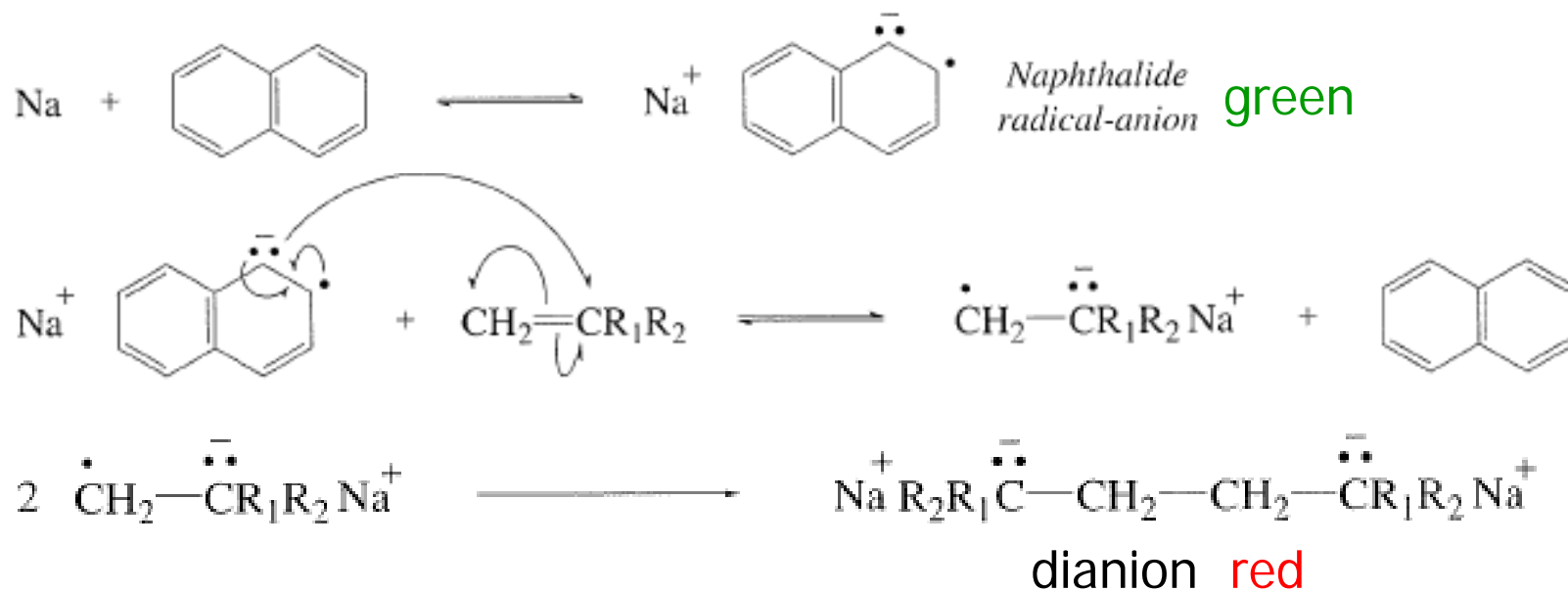
➤ Earlier works were not living [Section 5.3.1 p132](#)

❑ mechanism with basic (organometallic) initiator



❑ in polar solvent like THF ~ for free initiator and ion

□ mechanism with e⁻ transfer initiation



■ in polar solvent like THF

□ propagation

□ No appreciable termination or CT

Kinetics of anionic polym'n

□ R_p

- $k_i > k_p \sim$ initiation completed before propagation

$$R_p = -\frac{d[M]}{dt} = k_p[I]_0[M]$$

- much faster than radical
 - k_p comparable \sim lower in non-polar, higher in polar solvent
 - $[M^-]$ ($= [I]_0$) much higher than $[M\bullet]$

□ MM

$$\bar{x}_n = \frac{cK[M]_0}{[I]_0}$$

$K=1$ for initiation by organometallic compounds

$K=2$ for electron transfer initiation

□ MMD

□ Initially, N initiators (\rightarrow N polymers later)

□ At time t, $N_0, N_1, N_2, \dots, N_x, \dots$

■ $N_x \sim$ # of x-mer

for derivation, pp135-138

$$\frac{dN_x}{dt} = \Phi N_{x-1} - \Phi N_x \quad v = \int_0^t \Phi dt$$

$\Phi \sim$ rate of a monomer addition
 $v \sim$ kinetic chain length, x_n

$$N_x = \frac{Nv^x e^{-v}}{x!} \quad \longrightarrow \quad P(x) = \frac{v^x e^{-v}}{x!} \sim \text{Poisson distribution}$$

$$\bar{M}_n = \sum_{x=1}^{\infty} P(x) M_x \quad \xrightarrow{M_x = xM_0} \quad \bar{M}_n = M_0 e^{-v} \sum_{x=1}^{\infty} \frac{xv^x}{x!} = M_0 v e^{-v} \sum_{x=1}^{\infty} \frac{v^{x-1}}{(x-1)!}$$

$$\bar{M}_n = M_0 v$$

$$\sum_{r=0}^{\infty} v^r / r! = e^v$$

$$w_x = \frac{N_x M_x}{N M_0 v} \longrightarrow w_x = \frac{e^{-v} v^{x-1}}{(x-1)!}$$

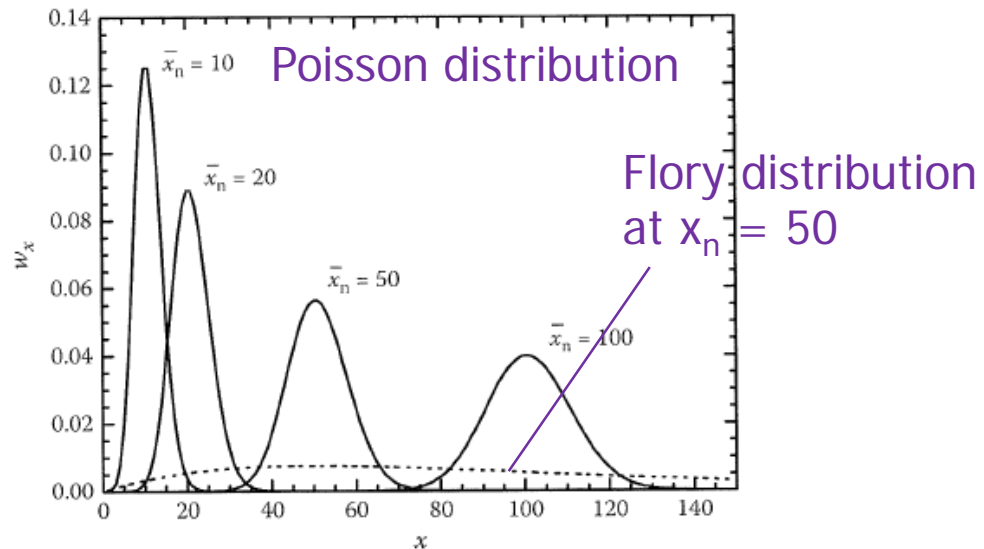
$$\bar{M}_w = \sum_{x=1}^{\infty} w_x M_x \xrightarrow{M_x = x M_0} \bar{M}_w = M_0 e^{-v} \sum_{x=1}^{\infty} \frac{x v^{x-1}}{(x-1)!}$$

$$\bar{M}_w = M_0 (v + 1) \quad \leftarrow \sum_{r=1}^{\infty} r v^{r-1} / (r-1)! = (v+1) e^v$$

$$\frac{\bar{M}_w}{\bar{M}_n} = 1 + \frac{1}{v}$$

□ PDI or D

- theoretically, $D \approx 1.0$
- practically, 1.02 – 1.20



Effect of solvent and counter-ion

□ effect of solvent

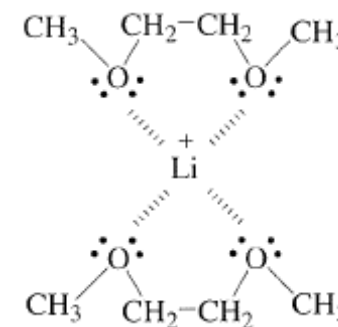
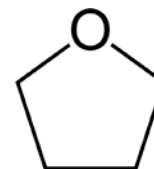
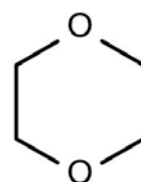
TABLE 5-10 Effect of Solvent on Anionic Polymerization^a of Styrene Odian p424

Solvent	Dielectric Constant (ϵ)	k_p^{app} liters/mole-sec
Benzene	2.2	2
Dioxane	2.2	5
Tetrahydrofuran	7.6	550
1,2-Dimethoxyethane	5.5	3,800

□ polarity [ϵ] of solvent $\uparrow \rightarrow$ fraction of free ion $\uparrow \rightarrow k_p \uparrow$

□ ϵ is not a sole measure ~ solvating power

■ bz vs dioxane; THF vs DME



□ MMD broader in non-polar solvent \leftarrow slow initiation

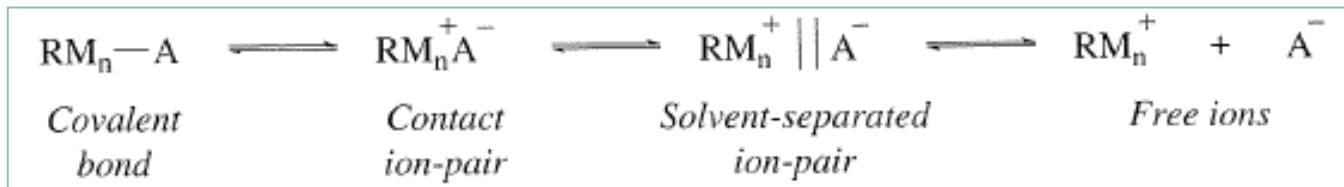
□ effect of counter-ion

□ in polar solvents

- $k_p \sim K^+ < Na^+ < Li^+$
- smaller ions better solvated \sim [free ion] up

□ in non-polar solvents

- $k_p \sim K^+ > Na^+ > Li^+$
- separation of ion governs



□ Energetics \sim complex

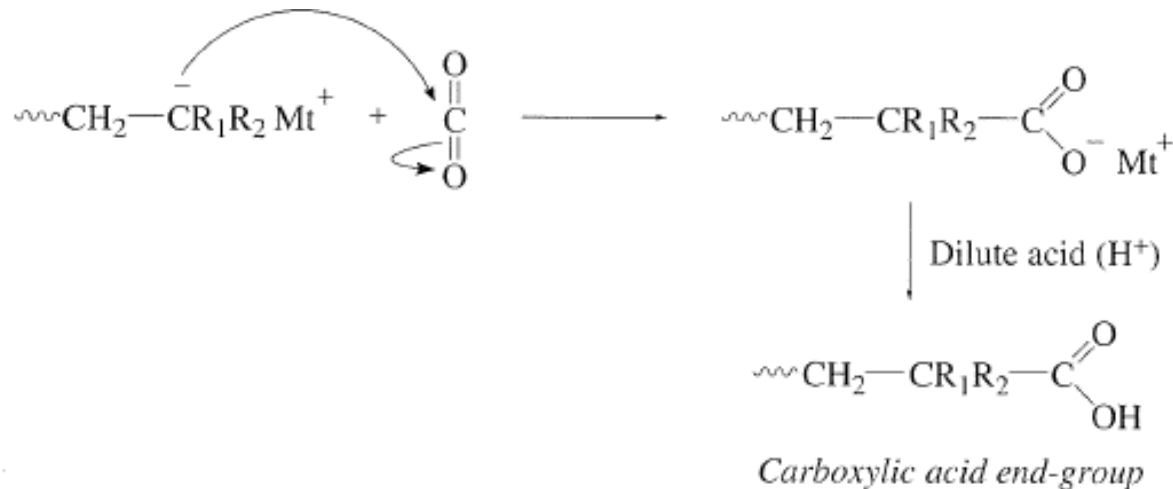
- $E_p > 0 \sim$ small, dependent on solvent and counter-ion

Deactivation/functionaliz'n

- At the end of anionic polym'n
 - addition of proton donor like ROH → deactivation



- functionaliz'n with CO₂, EO, etc [p139](#)

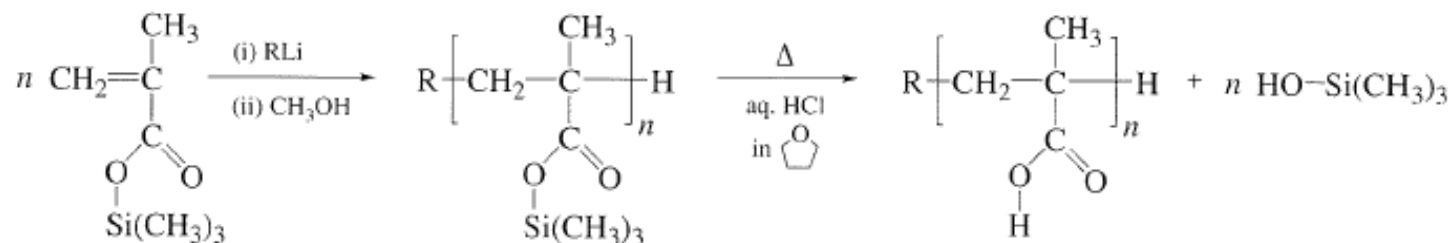


- polymer with functionalized end-group, controlled MM/MMD

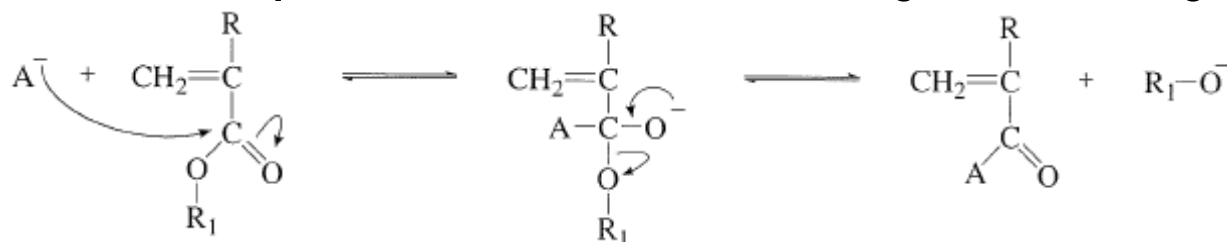
Practical considerations in anionic

Ch 5 SI 22

- ❑ Anionic polym'n requires
 - ❑ highly purified reactants ← reactive active center
 - ❑ inert rxn system ~ high vac, sealed
- ❑ Acidic H in monomer must be protected.



- ❑ side rxn in polar M like (meth)acrylates, acrylonitriles



- ❑ requires polar solvent, bulky initiator, low temperature

□ group transfer polym'n

□ for polar monomers (with C=O or C≡N)

- to avoid side reactions

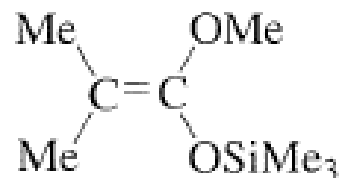
□ initiator ~ silyl ketene acetal

□ catalyst

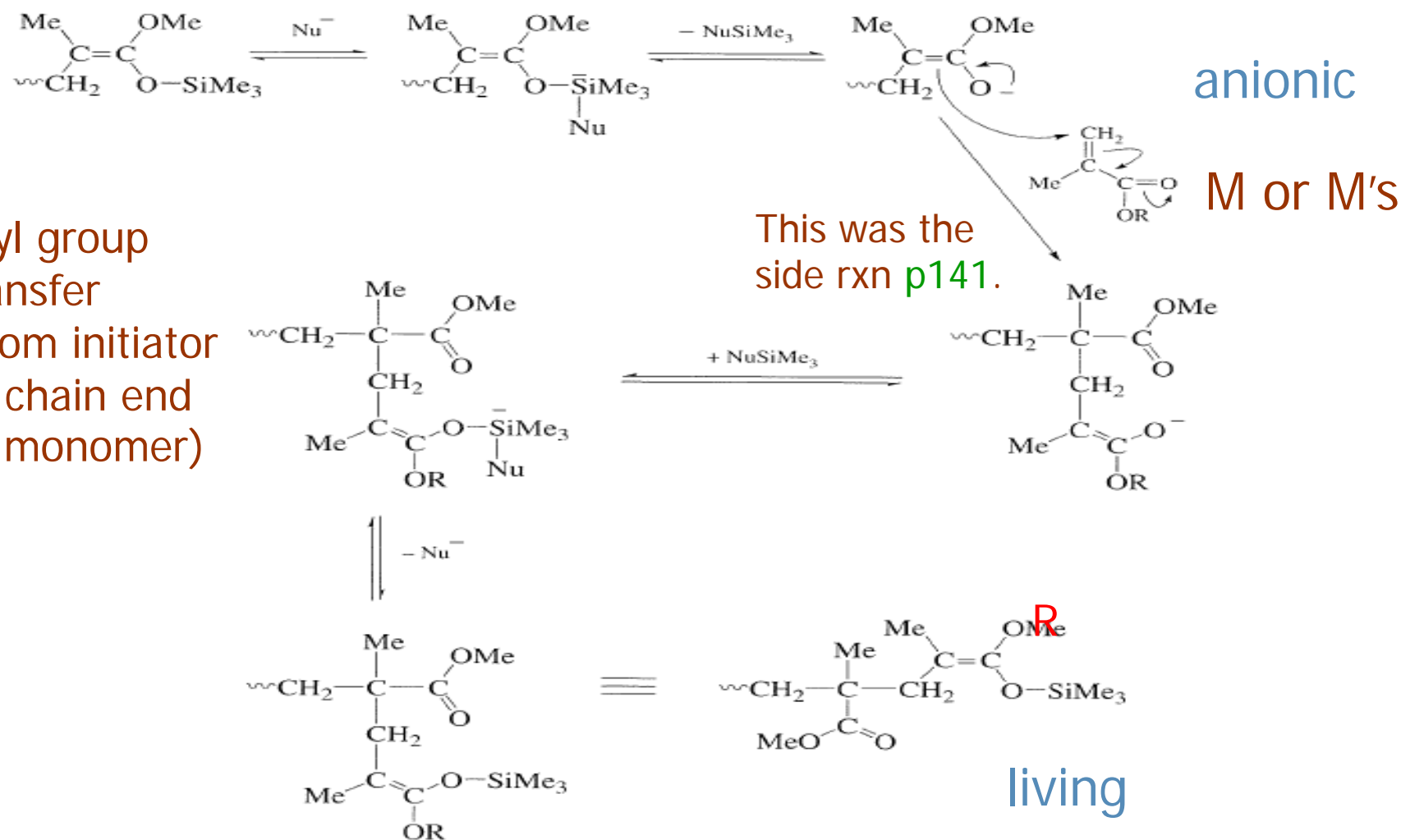
- Nu:⁻ ~ popular ~ HF₂⁻, F⁻, etc
- Lewis acid ~ larger amount needed ~ less popular

□ mechanism

- associative p142 ~ not anionic ~ may be wrong
- dissociative p143 ~ anionic ~ more plausible

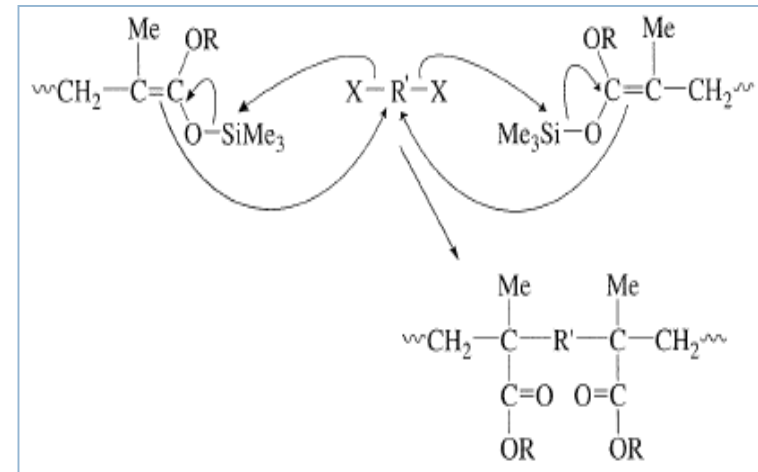
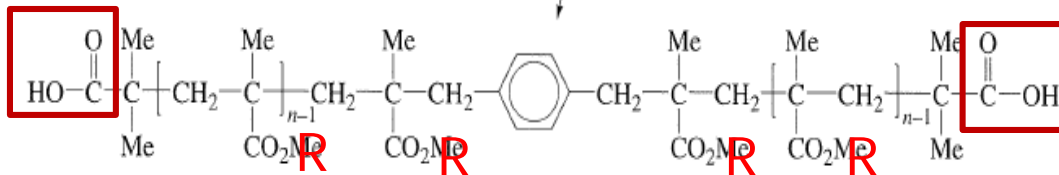
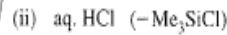
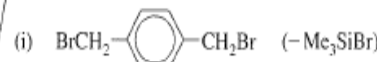
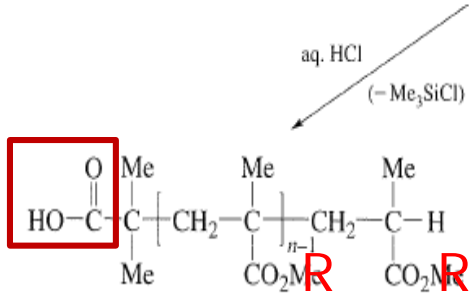
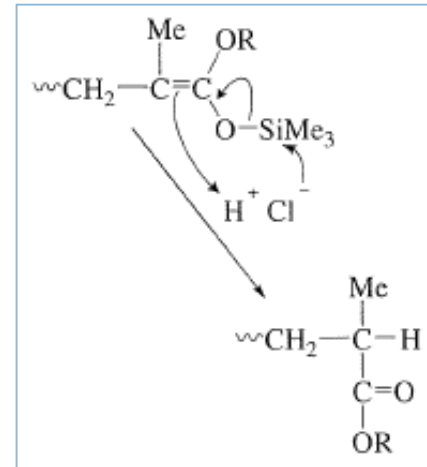
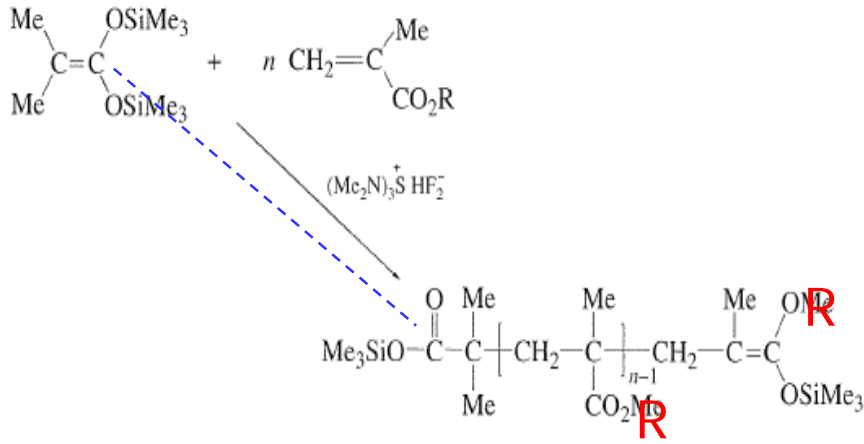


□ mechanism (cont'd)



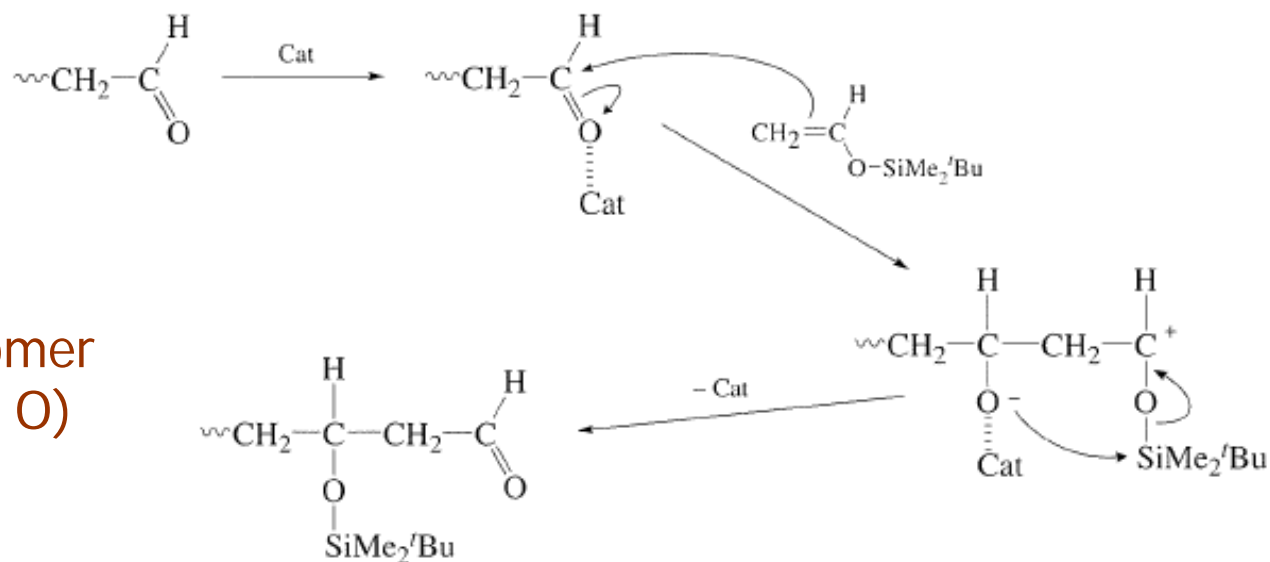
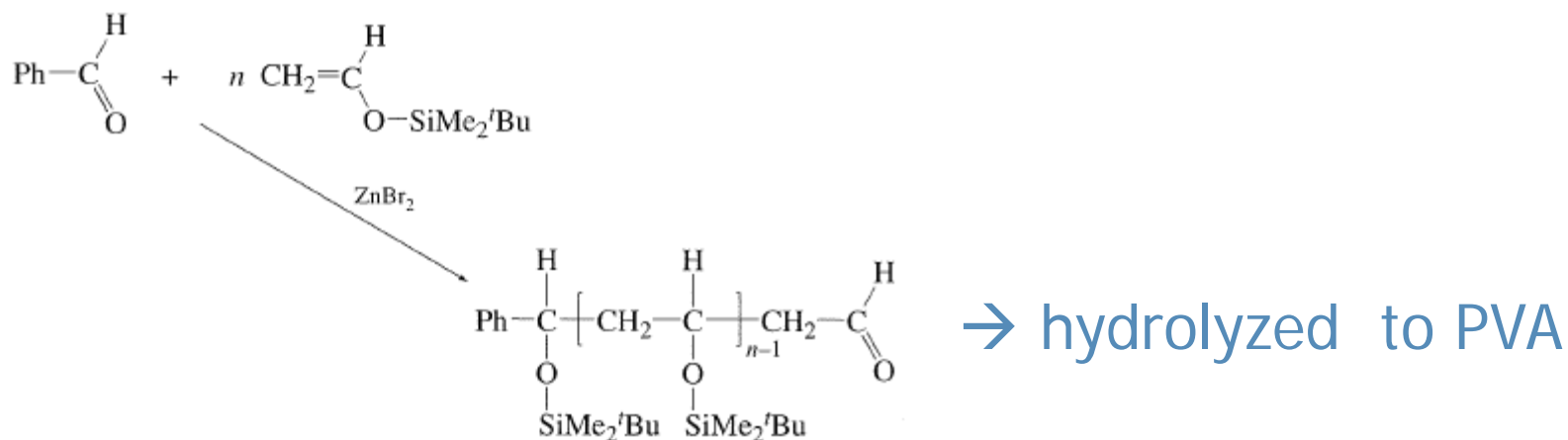
- ❑ GTP is a living anionic polym'n
 - ❑ like anionic, sensitive to impurities like active H
 - dry condition
 - protection needed for monomers with active H
 - ❑ unlike anionic, at high temp (50 - 80 °C)
 - ❑ PDI ~ 1.1 - 1.3
- ❑ side reaction ~ back-biting cyclization p144
- ❑ GTP mainly for
 - ❑ functionalized polymethacrylates with low MM < 50K
 - ❑ GTP of acrylate and (meth)acrylonitrile too fast

functionalization



Aldol GTP

- GTP of silyl vinyl ether using aldehyde initiator

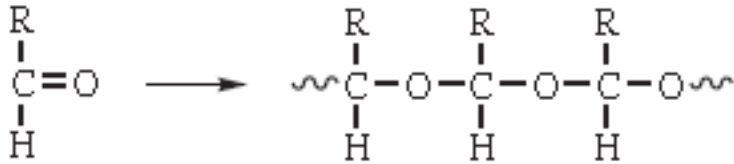


silyl group
transfer
(from monomer
to aldehyde O)

Carbonyl polym'n

Odian p444-449

Ch 5 Sl 28



□ low ceiling temperature

□ due to low ΔH

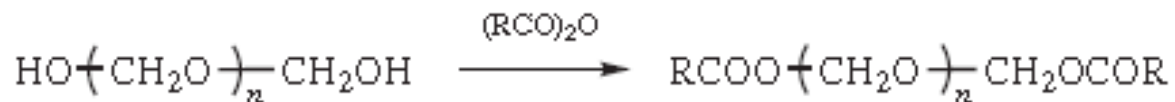
- for R=Me, $\Delta H = 29 \text{ kJ/mol}$
- short and stable C=O

□ anionic polym'n of CH_2O

□ polyformaldehyde [= polyoxymethylene (POM) = polyacetal]

- an engineering plastic with high $T_m = 175 \text{ }^\circ\text{C}$
- mechanical, abrasive, and dimensional stability

□ end-capping for use



Monomer	T_c ($^\circ\text{C}$)
Formaldehyde	119 ^b
Trifluoroacetaldehyde	85
Trichloroacetaldehyde	11
Propanal	-31
Acetaldehyde	-39
Pentanal	-42

Odian p445