Chapter 4

Radical Polymerization

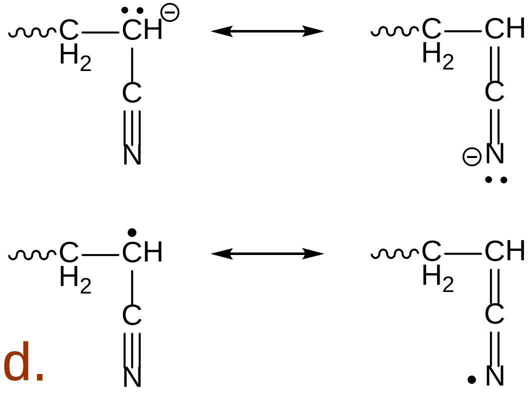
Chain polym’n

- step vs chain polym’n
  - step ~ growth by reaction of functional groups
  - chain ~ growth by addition of monomer to active center

- I → R* → RM* → RMM* → --- → RM_n* → RM_{n+1}*
  - I ~ initiator [開始劑]
  - * ~ active center [活性點]
    - * = • (free-radical) ~ radical polym’n
    - * = + (cation) ~ cationic polym’n Chapter 5
    - * = – (anion) ~ anionic polym’n Chapter 5
    - * = coordination site ~ coordination polym’n Chapter 6
  - M ~ monomer [單量體, 單位體]

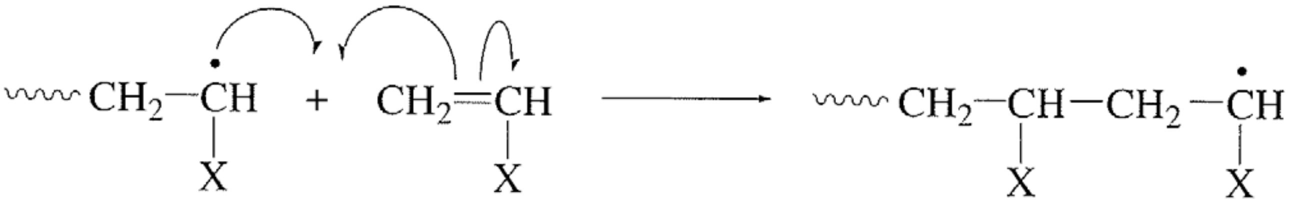
Monomers for chain polym’n

- monomer ~ unsaturated compound with either
  - double bond (C=C, C=O)
  - ring ~ ring-opening polym’n Chapter 7
- polymerizability of monomer Table 5.1 p124
  - C=O by ionic only
  - CH(X)=CH(Y) ~ hardly polymerize ← steric hindrance
  - CH_2=C(X)(Y) ~ can polymerize
  - vinyl monomers CH_2=CH(X)
    - with e⁻ donating X ~ cationic or radical
    - with e⁻ withdrawing X ~ anionic or radical
    - ✓ Most C=C monomers can be radical-polymerized.



Radical polym’n

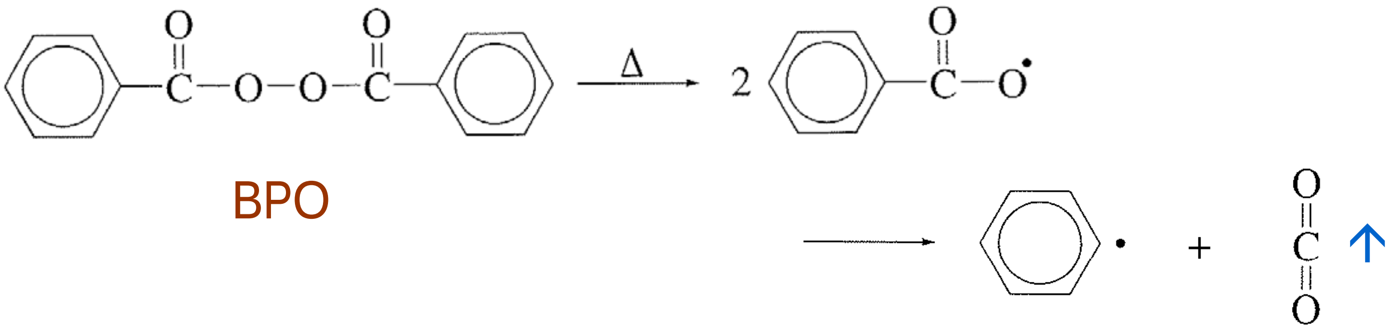
- two types of radical polym’n
  - (conventional) free-radical polym’n
  - (newer) living radical polym’n Section 4.5



- mechanism of free-radical polym’n
  - initiation $I \rightarrow R\bullet \rightarrow RM\bullet$
  - propagation $RM\bullet \rightarrow RMM\bullet \rightarrow --- \rightarrow RM_n\bullet$
  - termination $RM_n\bullet + RM_m\bullet \rightarrow RM_{n+m}R$ or $RM_n + RM_m$
  - chain transfer $RM_n\bullet + TA \rightarrow RM_nT + A\bullet$

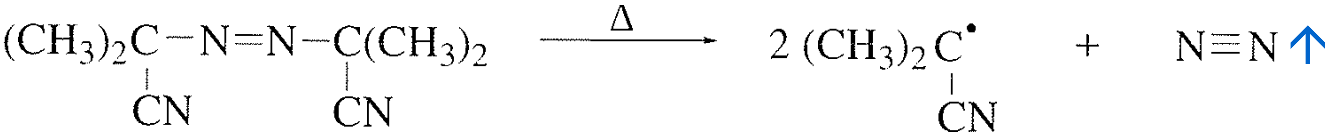
Initiation

- 2 steps I → R• → RM•
- 1st step ~ formation of radical
  - homolysis of initiator
    - thermal initiators ~ containing peroxide or azo linkage
      - thermolysis at (usually) 50 – 100 ºC Table 4.2 p86



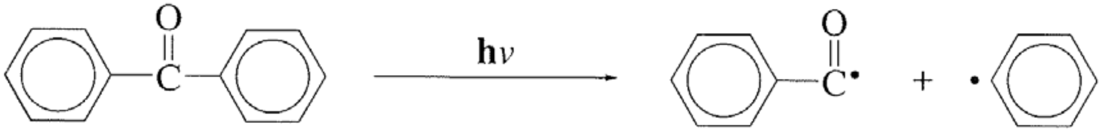
BPO

AIBN

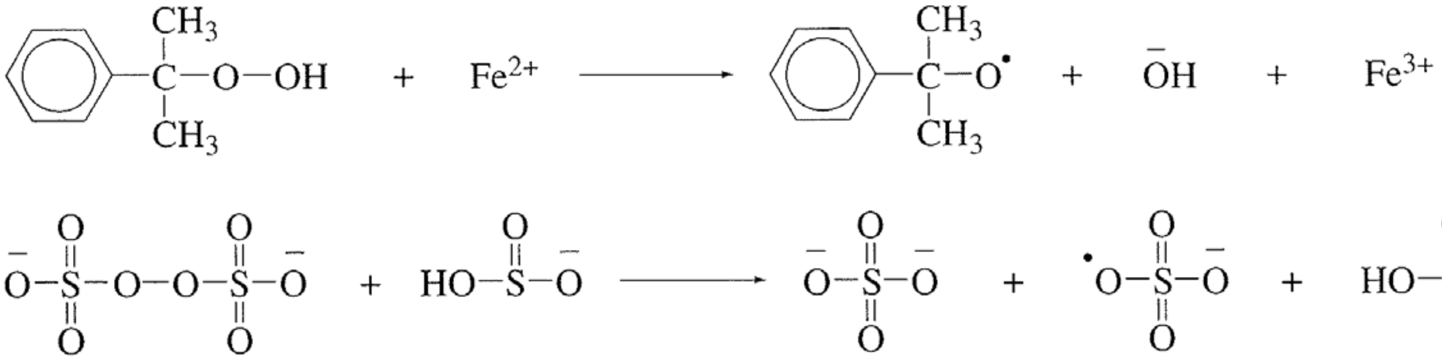


$$(CH_3)_2\underset{\large CN}{C}-N{=}N-\underset{\large CN}{C}(CH_3)_2 \xrightarrow{\Delta} 2\,(CH_3)_2\underset{\large CN}{C}^{\bullet} + N{\equiv}N\uparrow$$

- photochemical initiators ~ UV sensitive
  - photolysis ~ time- and space-controllable

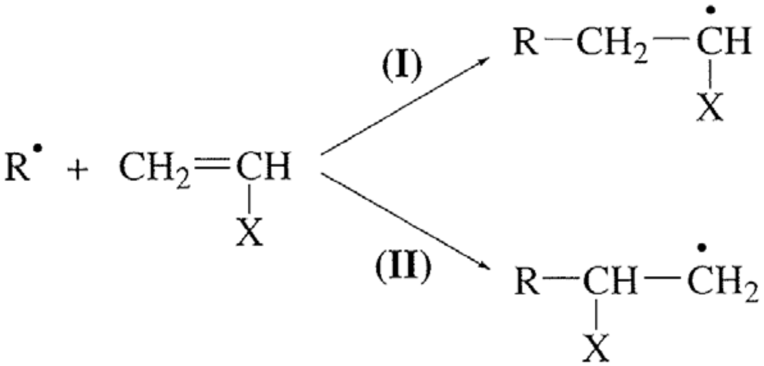


- redox initiation
  - redox = reduction + oxidation ← oxidant + reductant



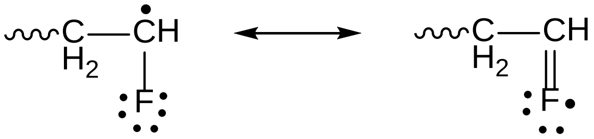
  - fast, at variety of Temp, in aqueous medium
    - useful for low Temp polym’n and/or emulsion polym’n   Section 4.4.4

- 2nd step ~ addition of one monomer
  - much faster than 1st step
  - Not all R• initiate, since R• reacts with
    - other R• within the cage ~ ‘cage effect’
    - other R• or polymer radical → termination
    - solvent, polymer, initiator → chain transfer
    - monomer → initiation
    - initiator efficiency, f ~ 0.3 < f < 0.8 < 1
  - mode



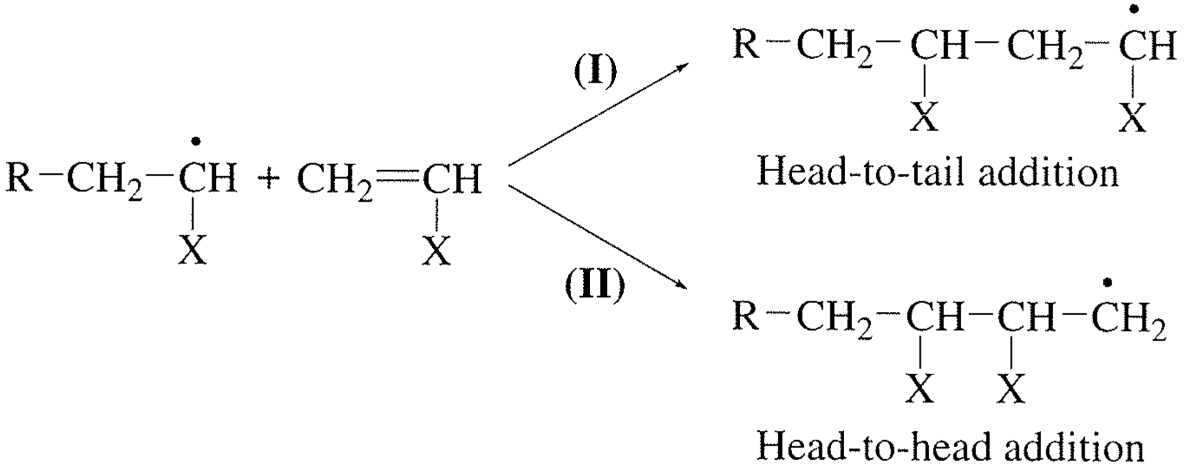
predominant ← steric + mesomeric

mesomeric = resonance



Propagation

- addition of M to growing •
- mode



Head-to-tail addition

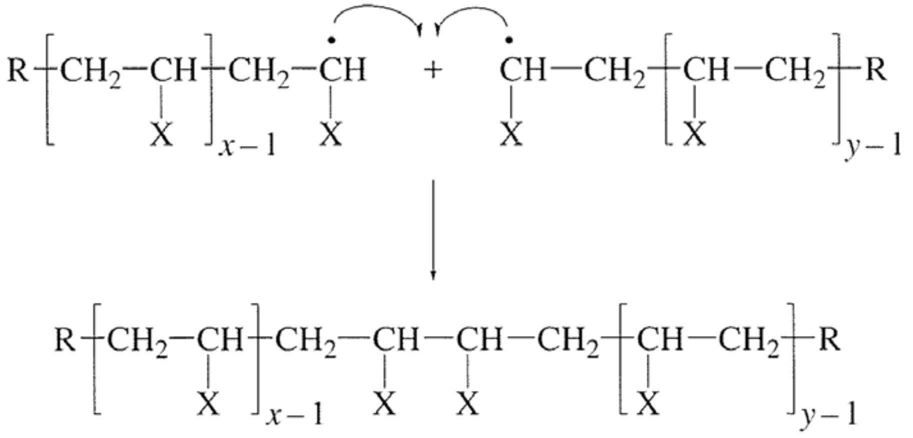
Head-to-head addition

predominant

- head-to-tail configuration favored by > 98%
  - proved by analysis
  - may be < 98% for very small X with little mesomeric effect like F
    - PVF ~ 90%; PVDF ~ 95%
    - PVA > 98%

Termination

- disappearance of radical → polym’n stops
- two modes
  - combination [coupling]
    - one dead polymer
    - (x+y)-mer

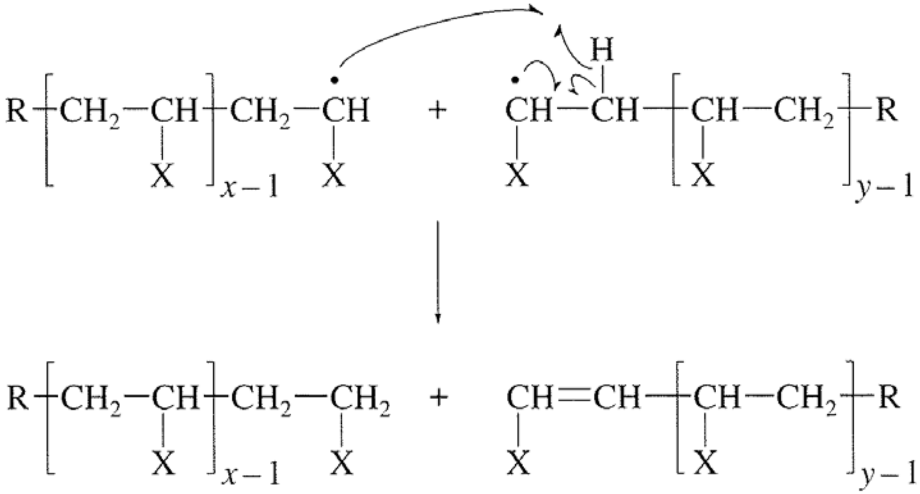


$$\mathrm{R}\!\left[\mathrm{CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}}\right]_{x-1}\!\mathrm{CH_2{-}}\underset{\mathrm{X}}{\dot{\mathrm{C}}\mathrm{H}} + \underset{\mathrm{X}}{\dot{\mathrm{C}}\mathrm{H}}\mathrm{{-}CH_2}\!\left[\underset{\mathrm{X}}{\mathrm{CH}}\mathrm{{-}CH_2}\right]_{y-1}\!\mathrm{R}$$

$$\downarrow$$

$$\mathrm{R}\!\left[\mathrm{CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}}\right]_{x-1}\!\mathrm{CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}}\mathrm{{-}}\underset{\mathrm{X}}{\mathrm{CH}}\mathrm{{-}CH_2}\!\left[\underset{\mathrm{X}}{\mathrm{CH}}\mathrm{{-}CH_2}\right]_{y-1}\!\mathrm{R}$$

  - disproportionation
    - two dead polymers
    - x-mer + y-mer

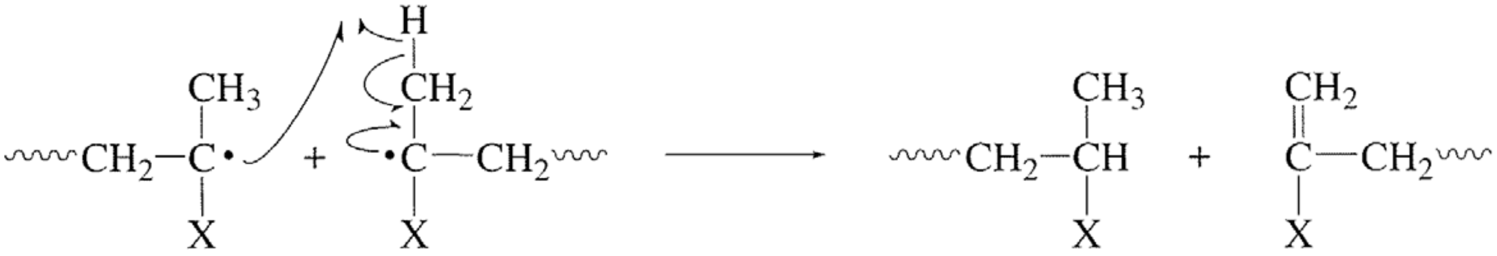


$$\mathrm{R}\!\left[\mathrm{CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}}\right]_{x-1}\!\mathrm{CH_2{-}}\underset{\mathrm{X}}{\dot{\mathrm{C}}\mathrm{H}} + \underset{\mathrm{X}}{\dot{\mathrm{C}}\mathrm{H}}\mathrm{{-}}\overset{\mathrm{H}}{\mathrm{CH}}\!\left[\underset{\mathrm{X}}{\mathrm{CH}}\mathrm{{-}CH_2}\right]_{y-1}\!\mathrm{R}$$

$$\downarrow$$

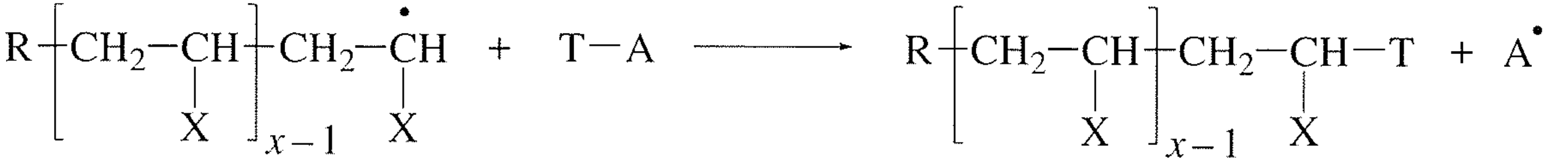
$$\mathrm{R}\!\left[\mathrm{CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}}\right]_{x-1}\!\mathrm{CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH_2}} + \underset{\mathrm{X}}{\mathrm{CH}}\mathrm{{=}CH}\!\left[\underset{\mathrm{X}}{\mathrm{CH}}\mathrm{{-}CH_2}\right]_{y-1}\!\mathrm{R}$$

- Combination requires low E_a.
  - usually favored, esp at low Temp
- Mode highly dep on type of monomer.
  - vinyl monomers favor combination
    - eg PS
  - α-methylvinyl monomers favor disproportionation
    - eg PMMA
    - additional C-H’s



Chain transfer

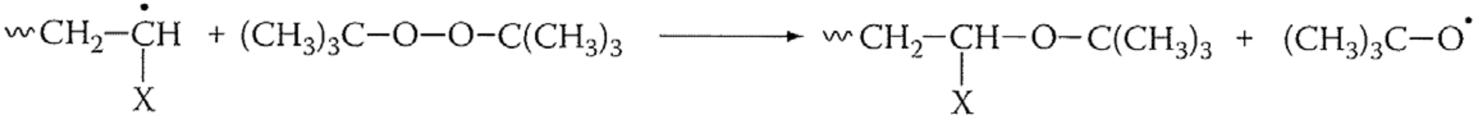
- transfer of kinetic chain to other molecule
  - transfer of active center from active chain



$$\mathrm{R}\left[\mathrm{CH_2}-\underset{\underset{\mathrm{X}}{|}}{\mathrm{CH}}\right]_{x-1}\mathrm{CH_2}-\underset{\underset{\mathrm{X}}{|}}{\overset{\bullet}{\mathrm{C}}\mathrm{H}} + \mathrm{T}-\mathrm{A} \longrightarrow \mathrm{R}\left[\mathrm{CH_2}-\underset{\underset{\mathrm{X}}{|}}{\mathrm{CH}}\right]_{x-1}\mathrm{CH_2}-\underset{\underset{\mathrm{X}}{|}}{\mathrm{CH}}-\mathrm{T} + \mathrm{A}^{\bullet}$$

  - abstraction of T (typically H) from other molecule
  - A•, if reactive, may initiate a new kinetic chain.
- Other molecule can be initiator, monomer, solvent, chain transfer agent, or polymer.
- CT lowers MM.
  - # of chains per # of initiations ↑
  - except for CT to polymer

- CT to initiator

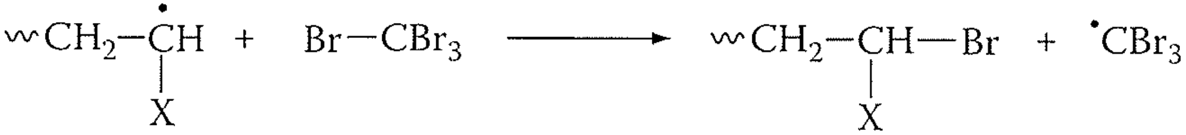


$$\sim CH_2-\underset{\underset{X}{|}}{\dot{C}H} + (CH_3)_3C-O-O-C(CH_3)_3 \longrightarrow \sim CH_2-\underset{\underset{X}{|}}{CH}-O-C(CH_3)_3 + (CH_3)_3C-O^{\bullet}$$

- CT to solvent

- CT to chain transfer agent
  - CTA ~ add to control MM

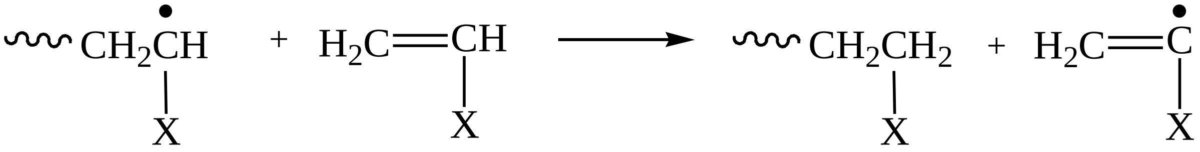
Fig 4.1 p67



$$\sim CH_2-\underset{\underset{X}{|}}{\dot{C}H} + Br-CBr_3 \longrightarrow \sim CH_2-\underset{\underset{X}{|}}{CH}-Br + {}^{\bullet}CBr_3$$

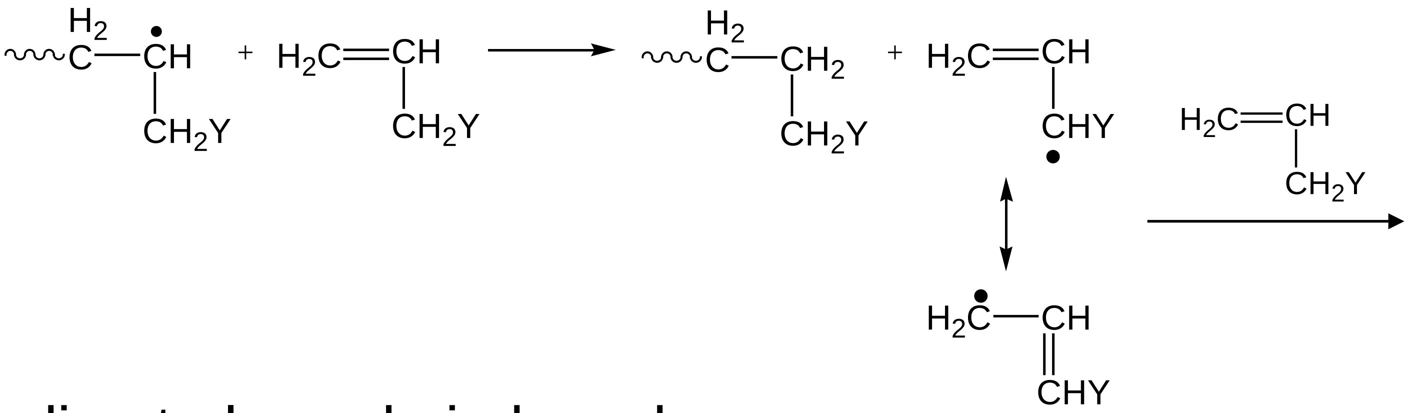
  - What if using CTA as solvent?
    - telomerization [popcorn polym’n]
    - telomer - telogen

- CT to monomer



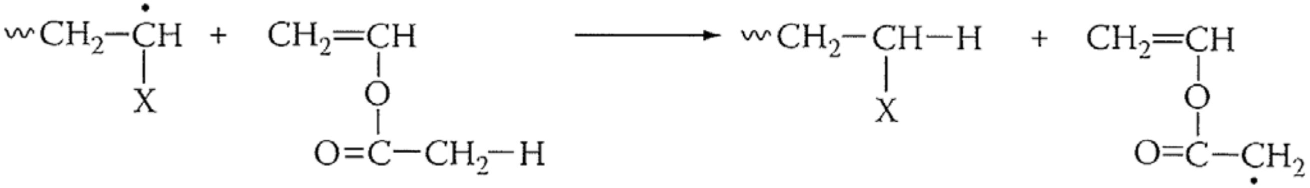
  - not popular ← vinylic H not reactive

- autoinhibition [degradative CT to monomer]

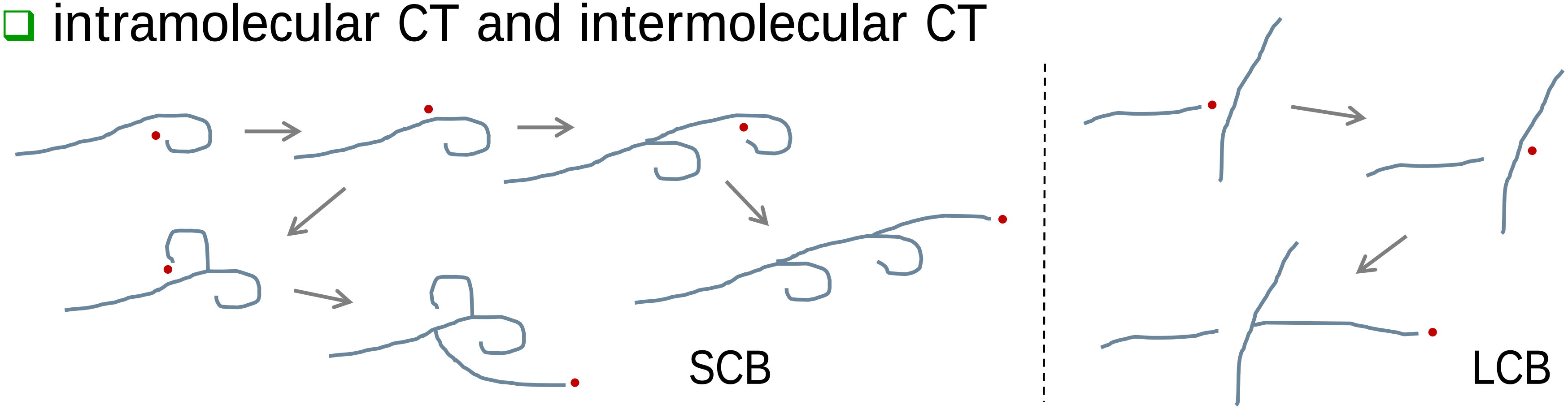


no initiation

- leading to long-chain branch

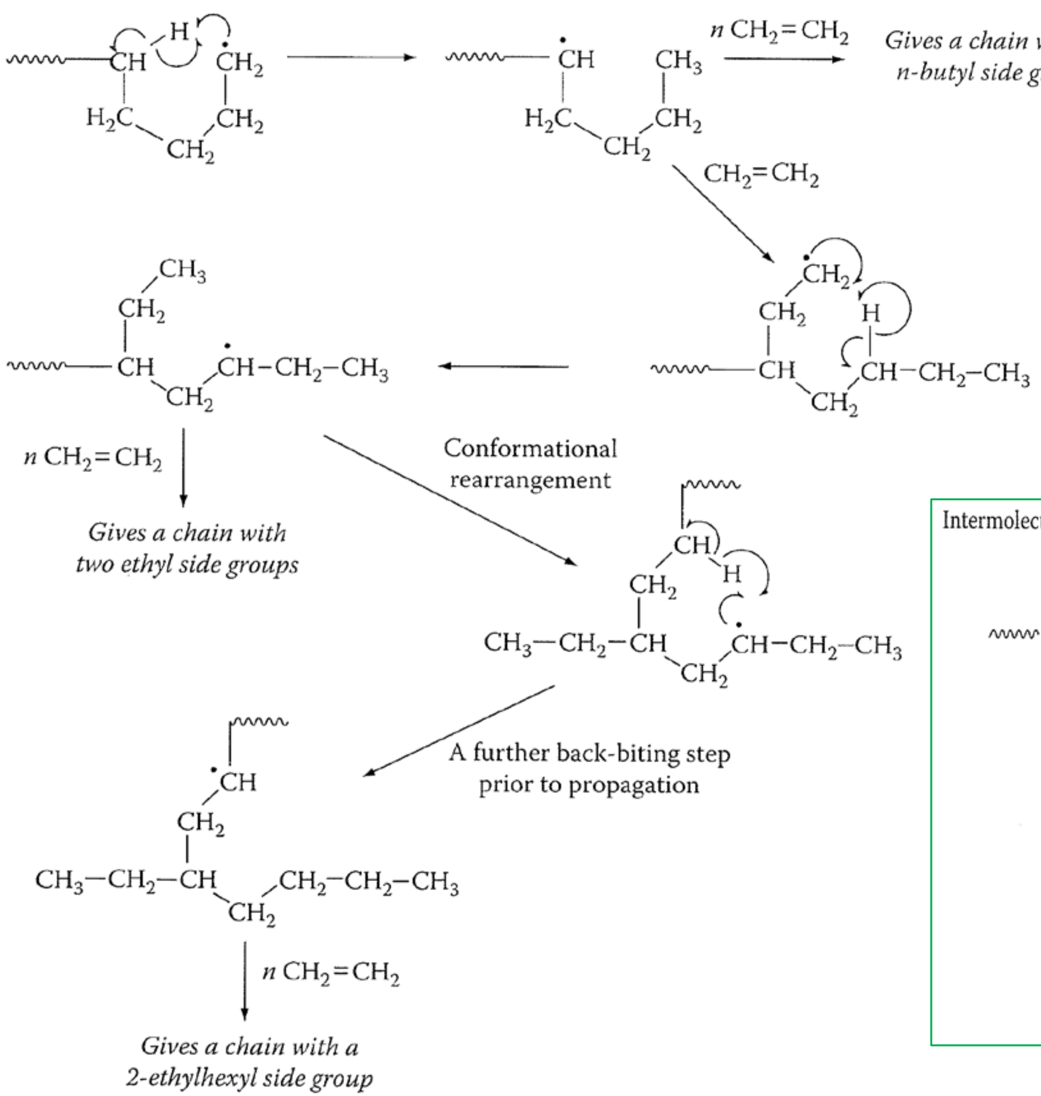


- CT to polymer → branching
  - intramolecular CT and intermolecular CT



  - MM not change (both), PDI increases (intermol)
  - Radical polym’n of ethylene gives LDPE. Fig 4.2 p69
    - intramol CT [back-biting] → short-chain branching
      - butyl, ethyl, ethylhexyl branches
    - intermol CT → long-chain branching
    - lower crystallinity [low density], lower mp, and lower shear-rate sensitivity than HDPE

Intramolecular chain transfer to polymer (termed *back-biting*)



Gives a chain with a n-butyl side group

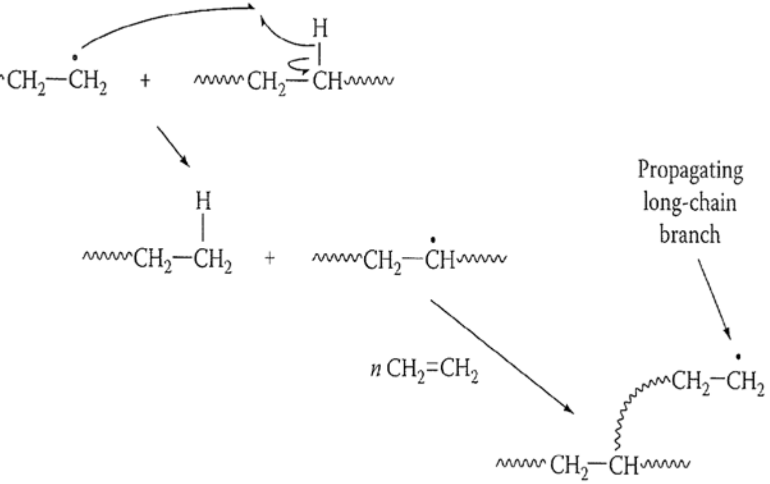
Conformational rearrangement

Gives a chain with two ethyl side groups

A further back-biting step prior to propagation

Gives a chain with a 2-ethylhexyl side group

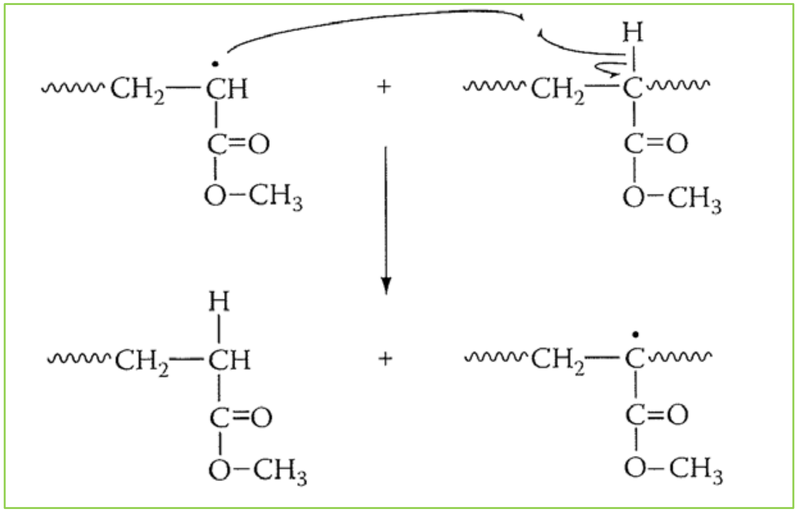
Intermolecular chain transfer to polymer

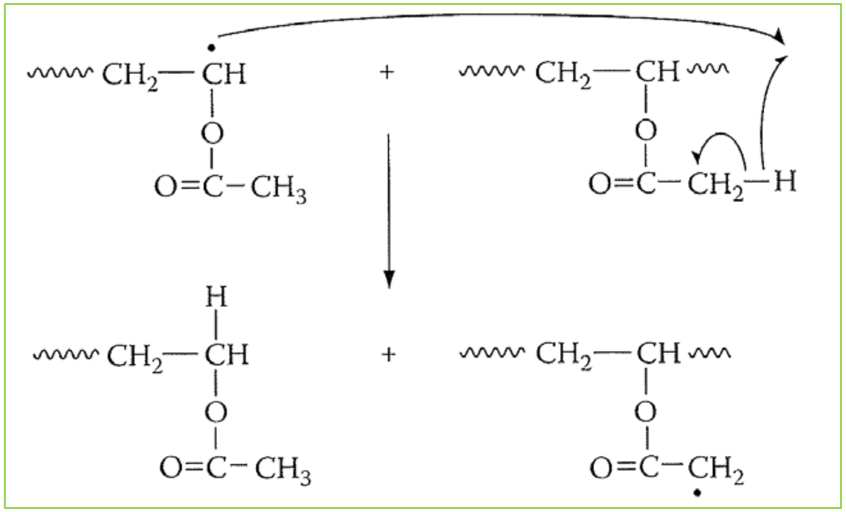


Propagating long-chain branch

❑ CT to polymer (cont’d)

- ❑ PMA vs PVAc Read p68 and see Fig 4.3 & 4.4 p70





- ❑ polymer from 1,2-disubs vinyl monomers [CH_2=CXY]
  - no 3° backbone H → negligible CT to polymer
- ❑ polymer from 1,3-diene Section 4.6.2.2

Kinetics: rate of free-radical polym'n

- initiation

$$I \xrightarrow{\text{Slow}} n\,R^\bullet$$

$$R^\bullet + M \xrightarrow{\text{Fast}} RM_1^\bullet$$

$$R_i = \frac{d[R^\bullet]}{dt}$$

- propagation

$$M_i^\bullet + M \longrightarrow M_{i+1}^\bullet$$

$$R_p = -\frac{d[M]}{dt} = k_p[M_1^\bullet][M] + k_p[M_2^\bullet][M] + \ldots + k_p[M_i^\bullet][M] + \ldots \quad = k_p[M][M^\bullet]$$

- termination

$$[M^\bullet] = \sum_{i=1}^{\infty}[M_i^\bullet]$$

$$M_i^\bullet + M_j^\bullet \xrightarrow{k_{tc}} P_{i+j}$$

$$M_i^\bullet + M_j^\bullet \xrightarrow{k_{td}} P_i + P_j$$

$$R_t = -\frac{d[M^\bullet]}{dt} = 2k_{tc}[M^\bullet][M^\bullet] + 2k_{td}[M^\bullet][M^\bullet] = 2k_t[M^\bullet]^2$$

$$k_t = k_{tc} + k_{td}$$

- steady-state condition [approximation]
  - $R_i = R_t$ → $$\boxed{[\mathrm{M}^\bullet] = \left(\frac{R_\mathrm{i}}{2k_\mathrm{t}}\right)^{1/2}}$$
  - true in early stage, except for very early stage

- rate of polym'n = rate of propagation

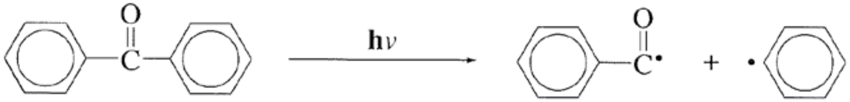
$$R_\mathrm{p} = k_\mathrm{p}[\mathrm{M}][\mathrm{M}^\bullet] = k_\mathrm{p}\left(\frac{R_\mathrm{i}}{2k_\mathrm{t}}\right)^{1/2}[\mathrm{M}]$$

- thermolysis of initiator $\mathrm{I} \xrightarrow{k_\mathrm{d}} 2\,\mathrm{R}^\bullet$ $R_\mathrm{i} = 2fk_\mathrm{d}[\mathrm{I}]$

$$\boxed{R_\mathrm{p} = k_p\left(\frac{fk_\mathrm{d}}{k_\mathrm{t}}\right)^{1/2}[\mathrm{M}][\mathrm{I}]^{1/2}}$$

- photoinitiation $\mathrm{I} \xrightarrow{h\nu} 2\mathrm{R}^{\bullet}$

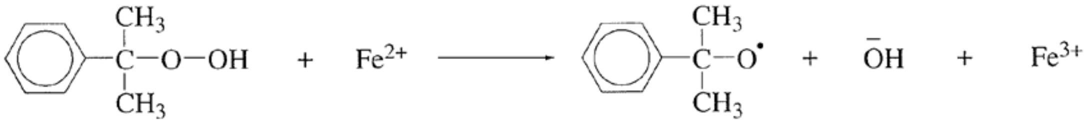
$$R_\mathrm{i} = 2\phi\varepsilon I_\mathrm{o}[\mathrm{I}]$$



$$R_\mathrm{p} = k_\mathrm{p}\left(\frac{\phi\varepsilon I_\mathrm{o}}{k_\mathrm{t}}\right)^{1/2}[\mathrm{M}][\mathrm{I}]^{1/2}$$

I_o is the intensity of the incident light
ε is the molar absorptivity of the initiator
ϕ is the quantum yield (i.e. the photochemical equivalent of initiator efficiency).

- redox initiation



$$R_\mathrm{i} = fk_\mathrm{r}[\mathrm{CumOOH}][\mathrm{Fe}^{2+}]$$

$$R_\mathrm{p} = k_\mathrm{p}\left(\frac{fk_\mathrm{r}}{2k_\mathrm{t}}\right)^{1/2}[\mathrm{M}][\mathrm{CumOOH}]^{1/2}[\mathrm{Fe}^{2+}]^{1/2}$$

Kinetics: molar mass

$$\bar{x}_n = \frac{\text{Moles of monomer consumed in unit time}}{\text{Moles of polymer formed in unit time}}$$

- assuming no chain transfer, $(x_n)_0$

$$(\bar{x}_n)_0 = \frac{k_p[M][M^\bullet]}{k_{tc}[M^\bullet]^2 + 2k_{td}[M^\bullet]^2}$$

$$= \frac{k_p[M]}{(1+q)k_t^{1/2}(R_i/2)^{1/2}}$$

← $q = k_{td}/k_t$ and $[M^\bullet] = \left(\frac{R_i}{2k_t}\right)^{1/2}$ (s-s approx)

  - thermolysis of initiator

$$\boxed{(\bar{x}_n)_0 = \frac{k_p[M]}{(1+q)(fk_dk_t)^{1/2}[I]^{1/2}}}$$

  - photoinitiation

$$(\bar{x}_n)_0 = \frac{k_p[M]}{(1+q)(\phi \varepsilon I_o k_t)^{1/2}[I]^{1/2}}$$

  - redox initiation

$$(\bar{x}_n)_0 = \frac{2^{1/2}k_p[M]}{(1+q)(fk_rk_t)^{1/2}[\text{CumOOH}]^{1/2}[\text{Fe}^{2+}]^{1/2}}$$

- kinetic chain length, ν
  - ν = # repeat units/radical = R_p/R_t

$$\nu = \frac{k_p[\mathrm{M}^\bullet][\mathrm{M}]}{2k_t[\mathrm{M}^\bullet]^2} = \frac{k_p[\mathrm{M}]}{2k_t^{1/2}(R_i/2)^{1/2}}$$

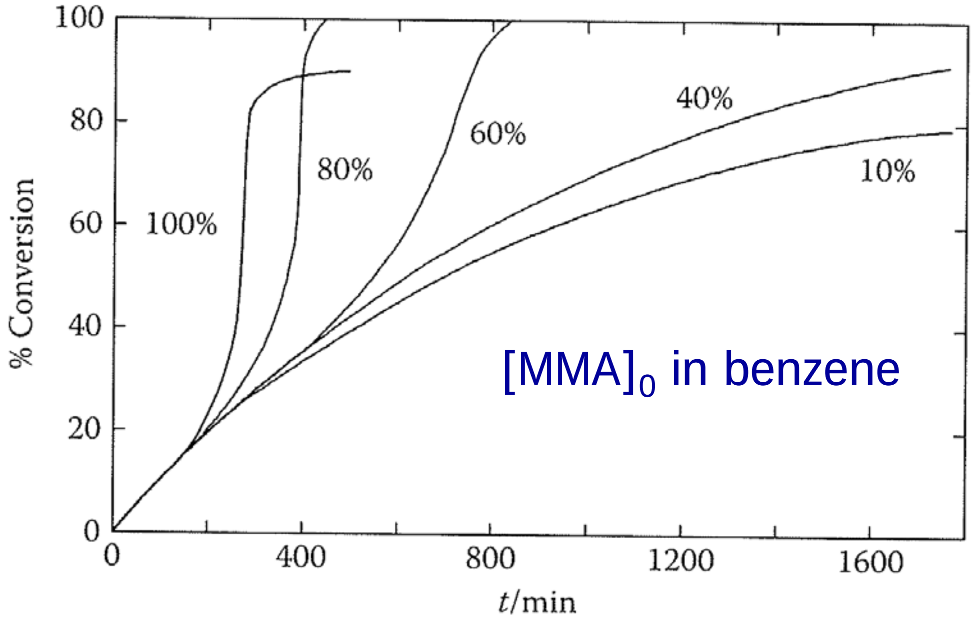
$$(\bar{x}_n)_0 = \left(\frac{2}{1+q}\right)\nu$$

- R_p and MM

$$\boxed{R_p \propto [\mathrm{M}][\mathrm{I}]^{1/2} \quad \text{and} \quad (\bar{x}_n)_0 \propto [\mathrm{M}][\mathrm{I}]^{-1/2}}$$

  - [I] ↑ → R_p ↑ and MM ↓ ~ trade-off in R_p and MM
  - instantaneous equations ~ change with conversion

Diffusion-controlled kinetics



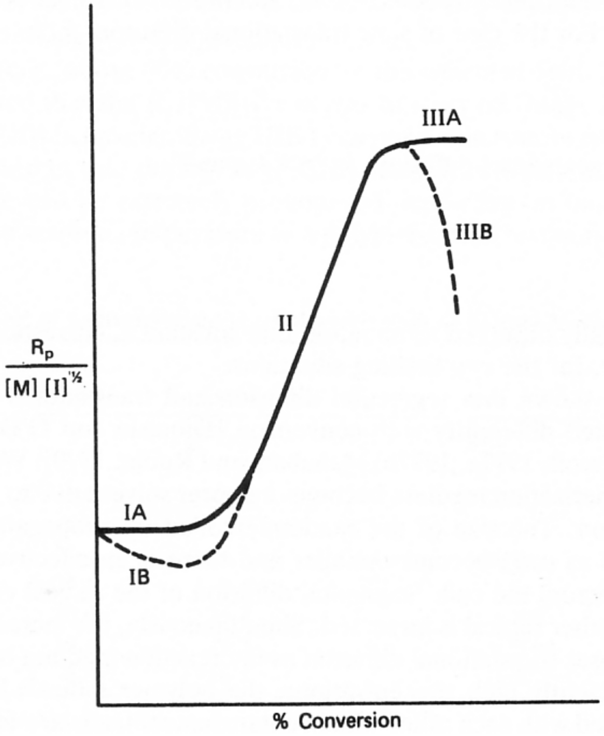
$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[M][I]^{1/2}$$

Fig 4.5 p77

conv vs time at various $[M]_0$

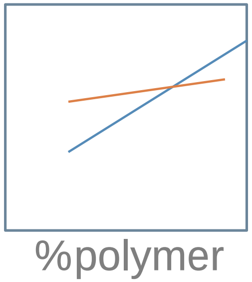
- s-s approx valid only at conversion < 15-20%
  - at higher conversion,
    - $[I] \downarrow$ and $[M] \downarrow \rightarrow R_p \downarrow$
    - actually, $R_p \uparrow$
    - become diffusion-controlled

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



R_p vs conv
Odian pp282-287

- IA ~ steady-state
- IB ~ [M] ↓ → R_p ↓ ~ may or may not occur
- II ~ autoacceleration
  - viscosity ↑ → diffusion of polymer • ↓ → k_t ↓
  - k_p and k_d not changed (← small monomer)
  - R_p ↑, x_n ↑ → viscosity ↑ → heat diffusion ↓ → Temp ↑ → R_p ↑
  - AA, gel effect, Trommsdorff-Norrish effect
- IIIA ~ at higher conv (>50%), k_p also affected
  - R_p levels off
- IIIB ~ glass effect
  - T_g of mixture [M-plasticized polymer] becomes higher than polym’n Temp
  - R_p decreases to stop



MM with chain transfer

$$M_i^\bullet + T{-}A \longrightarrow M_i{-}T + A^\bullet$$

$$A^\bullet + M \xrightarrow{k_r} AM_1^\bullet$$

- When $k_r < k_i$ → R_p ↓ and x_n ↓

<cf> autoinhibition

- When $k_r \approx k_i$ → only x_n ↓

$$\bar{x}_n = \frac{k_p[M][M^\bullet]}{k_{tc}[M^\bullet]^2 + 2k_{td}[M^\bullet]^2 + k_{trM}[M^\bullet][M] + k_{trI}[M^\bullet][I] + k_{trS}[M^\bullet][S]}$$

$$\frac{1}{\bar{x}_n} = \frac{(1+q)k_t^{1/2}(R_i/2)^{1/2}}{k_p[M]} + \frac{k_{trM}}{k_p} + \frac{k_{trI}[I]}{k_p[M]} + \frac{k_{trS}[S]}{k_p[M]}$$

$$\boxed{\frac{1}{\bar{x}_n} = \frac{1}{(\bar{x}_n)_0} + C_M + C_I\frac{[I]}{[M]} + C_S\frac{[S]}{[M]}}$$

Mayo(-Walling) Eqn

Mayo(-Lewis) Eqn ~ copolym’n

- C ~ chain transfer constant

Table 4.1 p79

C’s for radical polym’n of ST

Compound	Bond Cleaved (T–A)	Transfer Constant, C_{TA} $(=k_{trTA}/k_p)$
Styrene	$H—C(Ph){=}CH_2$	7×10^{-5}
Benzoyl peroxide	$PhCOO—OOCPh$	5×10^{-2}
Benzene	$H—Ph$	2×10^{-6}
Toluene	$H—CH_2Ph$	12×10^{-6}
Chloroform	$H—CCl_3$	5×10^{-5}
Carbon tetrachloride	$Cl—CCl_3$	1×10^{-2}
Carbon tetrabromide	$Br—CBr_3$	2
Dodecyl mercaptan	$H—SC_{12}H_{25}$	15

- C_M ~ small, little effect on x_n
- C_I ~ larger than C_M, but lower effect on x_n
- C_S or C_{CTA} ~ dep on bond strength <cf> telomerization

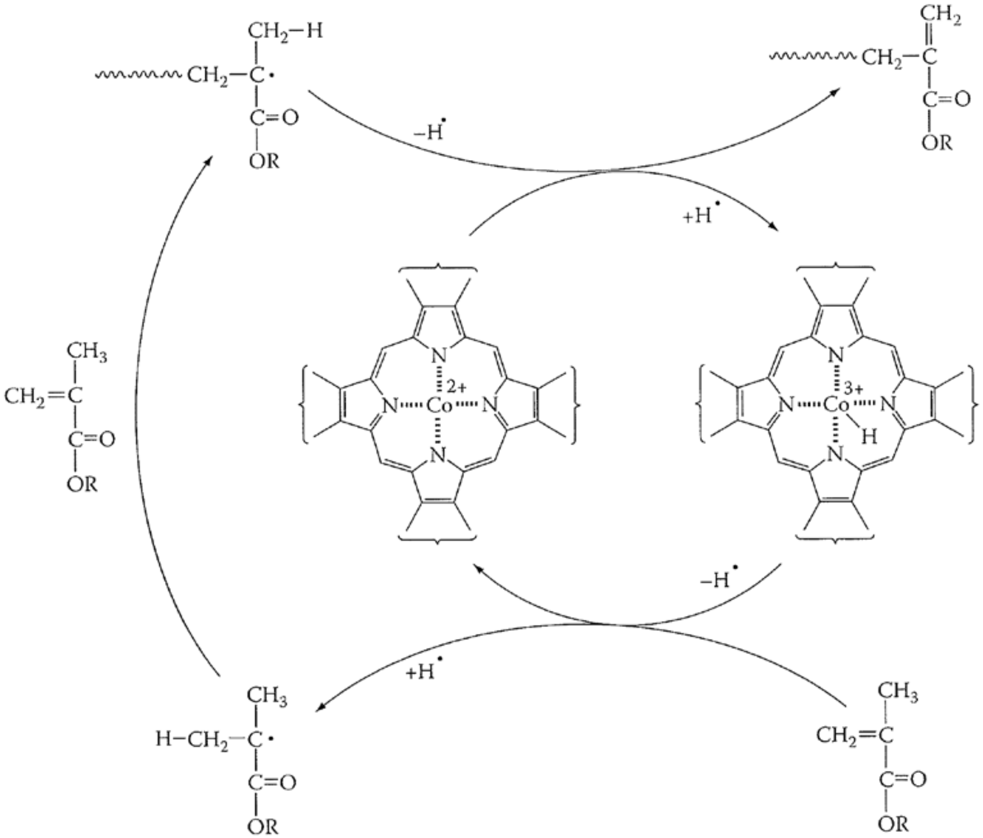
Catalytic chain transfer

- special type of chain transfer to monomer
  - Co(II) abstracts H• from growing radical
  - Co(III) gives H• to monomer
- very effective [high C]
  - for monomer with α-methyl
  - resulting C=C end group
    - macro(mono)mer
  - with controlled MM

$$(\bar{x}_n)_{CCT} = 2 + \frac{k_p[M][M^\bullet]}{k_{CCT}[M^\bullet][Co(II)]}$$

$$(\bar{x}_n)_{CCT} = 2 + \frac{[M]}{C_{CCT}[Co(II)]}$$

p80



Inhibition and retardation

- substance reacts with radical, and
  - does not reinitiate ~ inhibitor
  - slowly reinitiate ~ retarder
- O_2

$$\sim CH_2-\underset{X}{\underset{|}{\dot{C}H}} + O=O \longrightarrow \sim CH_2-\underset{X}{\underset{|}{CH}}-O-\dot{O}$$

  - harmful in polym'n awa in use
- Inhibition and retardation differs only in degree.
  - eg, quinone ~ inhibitor for ST, retarder for MMA

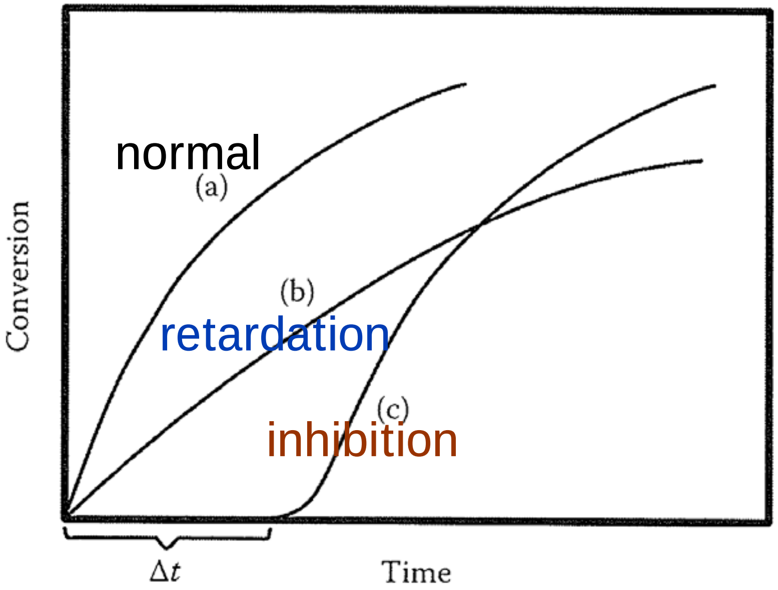
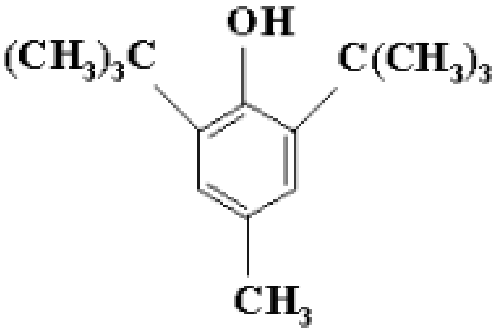
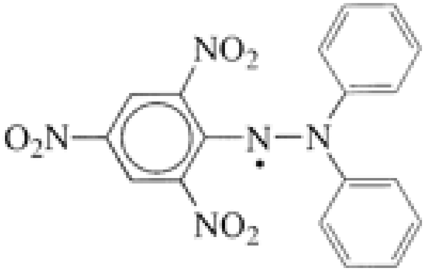


Fig 4.7 p81

- may be added deliberately
    - for transportation, storage
    - remove before or feed more initiator in polym’n
- quinone, hindered phenol, radical scavenger





<cf> autoinhibition

Molar mass distribution

- MMD and its prediction much more complex than step polym'n ← modes of polymer formation; parameters change with conv

- ☐ At low conversion, ([M], [I], k's constant)
  - [M] and [I] decrease a little, actually. Problem 4.1

- ☐ β ~ probability of growth of a radical
  - $\beta = R_p / (R_p + R_t + R_{CT})$
  - same to p in step polym'n

- ☐ termination by disproportionation
  - probability of i-mer, $P(i) = (1-\beta)\beta^{(i-1)}$
  - $\boxed{x_n = 1/(1 - \beta)}$
  - $x_w = (1 + \beta)/(1 - \beta)$
  - PDI or D, $\boxed{\bar{M}_w / \bar{M}_n = 1 + \beta}$
  - PDI → 2 when β → 1 $[R_p >> R_t, R_{CT}]$

$$\beta = \frac{N_0 - N}{N_0}$$

$$N = N_0(1 - \beta)$$

for polymer fraction only, not for whole mixture!!

- low conv (cont’d)
  - termination by combination
    - (j-mer)• + (i – j-mer)• → (i-mer)

$$P(j) = (1-\beta)\beta^{(j-1)}$$

$$P(i-j) = (1-\beta)\beta^{(i-j-1)}$$

$$\xrightarrow[\text{(i – 1) ways}]{} \quad P(i) = (i-1)(1-\beta)^2\beta^{(i-2)}$$

$$\bar{M}_n = \sum P(i)M_i = M_0(1-\beta)^2\sum i(i-1)\beta^{(i-2)}$$

$M_i = i\ M_0$

$$\boxed{\bar{M}_n = \frac{2M_0}{(1-\beta)}}$$

$$\sum_{i=1}^{\infty} i(i-1)\beta^{(i-2)} = 2(1-\beta)^{-3}$$

- 2 propagating chains terminated by 1 combination

$$\beta = \frac{N_0 - 2N}{N_0} \qquad N = \frac{N_0(1-\beta)}{2}$$

- weight fraction, w_i

w_i = i N_i / N_0 = i N P(i) / N_0

$$w_i = \left(\frac{1}{2}\right) i(i-1)(1-\beta)^3 \beta^{(i-2)}$$

$$\boxed{\begin{aligned} & w_x = \frac{N_x(x\bar{M}_0)}{N_0\bar{M}_0} = \frac{xN_x}{N_0} \quad \text{eqn 3.11 p35} \\ & P(i) = (i-1)(1-\beta)^2 \beta^{(i-2)} \\ & N = \frac{N_0(1-\beta)}{2} \end{aligned}}$$

$$\bar{M}_w = \sum w_i M_i = \left(\frac{1}{2}\right) M_0 (1-\beta)^3 \sum i^2 (i-1) \beta^{(i-2)}$$

M_i = i M_0

$$\boxed{\bar{M}_w = \frac{M_0(2+\beta)}{(1-\beta)}}$$

$$\sum_{i=1}^{\infty} i^2(i-1)\beta^{(i-2)} = 2(2+\beta)(1-\beta)^{-4}$$

- PDI, $\boxed{\bar{M}_w / \bar{M}_n = (2+\beta)/2}$
- PDI → 1.5 when β → 1 [R_p >> R_t, R_{CT}]
- smaller PDI than disproportionation

- At higher conversion, MMD gets much broader.
  - [I] decrease faster than [M] does.

    $$(\bar{x}_n)_0 = \frac{k_p[M]}{(1+q)(fk_dk_t)^{1/2}[I]^{1/2}}$$

    - larger molecule at later stage
    - PDI ~ 3 - 5
    - may be controlled by multiple charge of I
  - autoacceleration
    - PDI ~ 5 - 10
  - CT to polymer
    - PDI ~ 20 - 50

- Hard to control AA and CT to polymer
  - avoid bulk polym’n or stop at low conversion

Determination of kinetic parameters

- R_p
  - separation of reaction product
    - step polym'n ~ distillation of small molecules
    - chain polym'n ~ isolation of polymer (ppt in nonsolvent)
  - chemical or spectroscopic analysis
    - step ~ disappearance of functional group
    - chain ~ disappearance of double bond
  - dilatometry
    - monitoring volume change

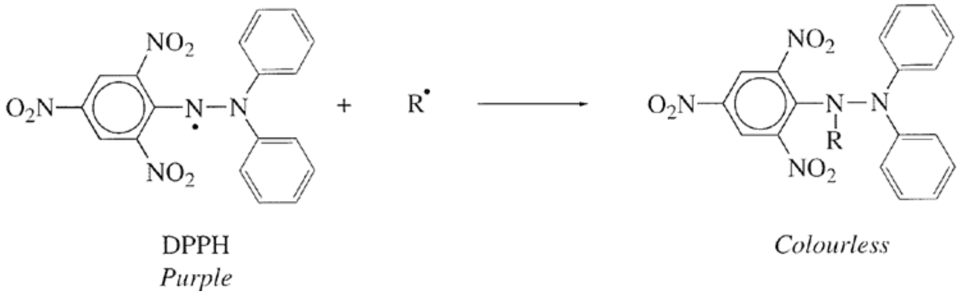
$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[M][I]^{1/2}$$

$$(\bar{x}_n)_0 = \frac{k_p[M]}{(1+q)(fk_d k_t)^{1/2}[I]^{1/2}}$$

- k_d
  - [I] by spectroscopy
  - Table 4.2 p86
- f ← f k_d
  - using radical scavenger
    - color change by UV/vis
  - end-group analysis
    - low conc’n in polymer
  - 0.3 < f < 0.8

$$I \xrightarrow{k_d} 2\,R^{\bullet}$$

$$-\frac{d[I]}{dt} = k_d[I]$$



$$-\frac{d[DPPH]}{dt} = 2fk_d[I] = R_i$$

- k_p and k_t
  - from $k_p/k_t^{1/2}$ and k_p/k_t
  - $k_p/k_t^{1/2}$
    - using $[M]_0$ and $[I]_0$ knowing R_p and f k_d
    - at s-s (low conv)

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

  - k_p/k_t
    - τ, avg life-time of radical

$$\tau = \frac{\text{concentration of active centres}}{\text{rate of loss of active centres}} = \frac{[M^\bullet]}{2k_t[M^\bullet]^2} = \frac{1}{2k_t[M^\bullet]} = \frac{k_p[M]}{2k_t R_p}$$

$$R_p = k_p[M][M^\bullet]$$

    - τ measured using
      'rotating sector method' ~ photopolym'n with on/off
    - $0.1 < \tau < 10$ sec

Odian pp263-267

- k_p and k_t separately by using pulsed-laser polym'n p87-88
  - initiation/termination by short pulse (10 ns) laser
  - MM of the product measured
- chain transfer constants

$$\frac{1}{\bar{x}_n} = \frac{(1+q)k_t^{1/2}(R_i/2)^{1/2}}{k_p[\mathrm{M}]} + \frac{k_{\mathrm{trM}}}{k_p} + \frac{k_{\mathrm{trI}}[\mathrm{I}]}{k_p[\mathrm{M}]} + \frac{k_{\mathrm{trS}}[\mathrm{S}]}{k_p[\mathrm{M}]} = \frac{1}{(\bar{x}_n)_0} + C_{\mathrm{M}} + C_{\mathrm{I}}\frac{[\mathrm{I}]}{[\mathrm{M}]} + C_{\mathrm{S}}\frac{[\mathrm{S}]}{[\mathrm{M}]}$$

- one by one. pp78-79
  - C_I (AIBN) ≈ 0
    - plot $1/x_n$ vs $[\mathrm{I}]_0^{1/2}/[\mathrm{M}]$ → C_M
  - with other I → C_I
  - with S → C_S

$$\boxed{(\bar{x}_n)_0 = \frac{k_p[\mathrm{M}]}{(1+q)(fk_dk_t)^{1/2}[\mathrm{I}]^{1/2}}}$$

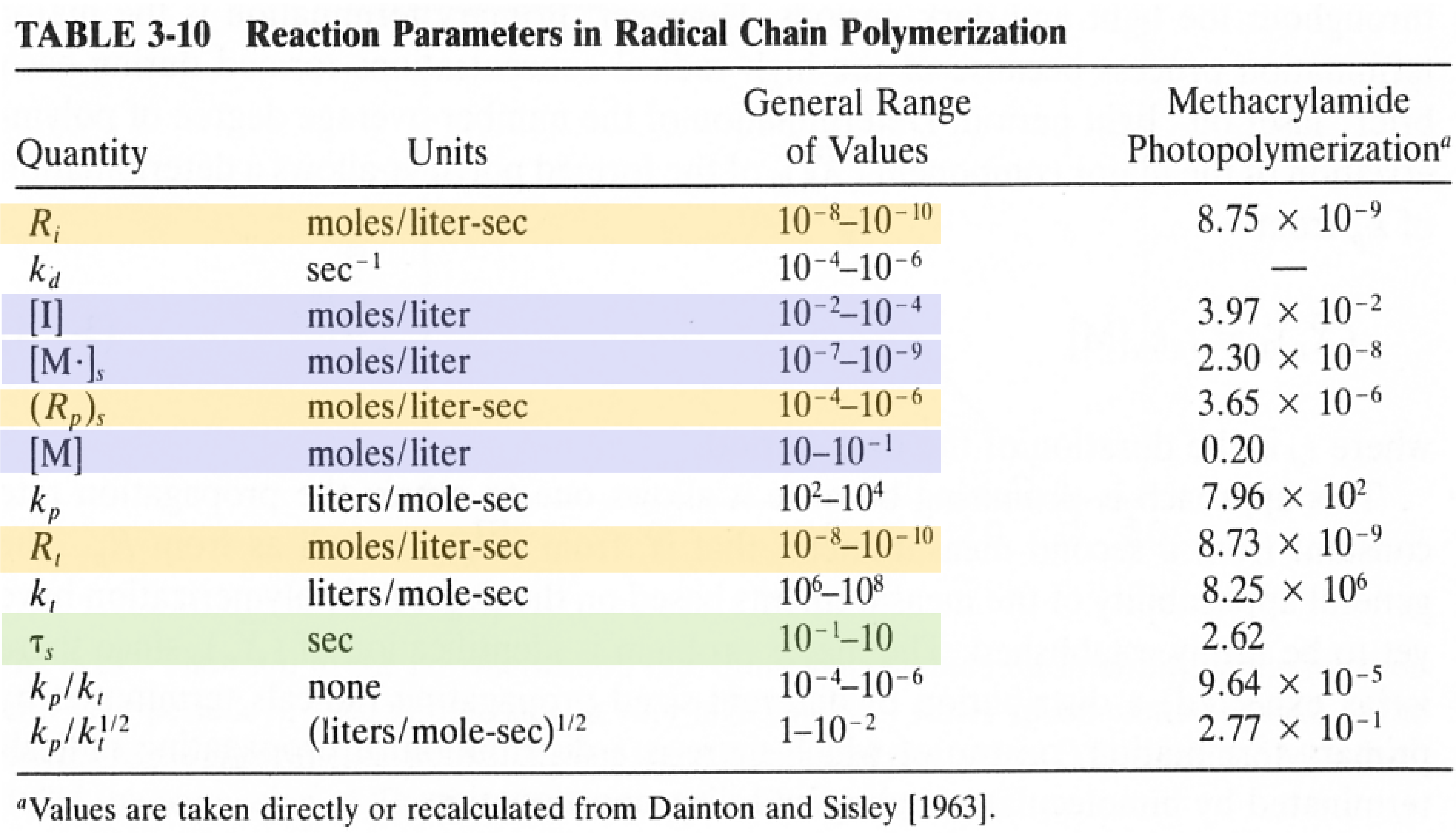


TABLE 3-10 Reaction Parameters in Radical Chain Polymerization

Quantity	Units	General Range of Values	Methacrylamide Photopolymerization[a]
R_i	moles/liter-sec	10^{-8}–10^{-10}	8.75×10^{-9}
k_d	sec^{-1}	10^{-4}–10^{-6}	—
[I]	moles/liter	10^{-2}–10^{-4}	3.97×10^{-2}
$[M\cdot]_s$	moles/liter	10^{-7}–10^{-9}	2.30×10^{-8}
$(R_p)_s$	moles/liter-sec	10^{-4}–10^{-6}	3.65×10^{-6}
[M]	moles/liter	10–10^{-1}	0.20
k_p	liters/mole-sec	10^{2}–10^{4}	7.96×10^{2}
R_t	moles/liter-sec	10^{-8}–10^{-10}	8.73×10^{-9}
k_t	liters/mole-sec	10^{6}–10^{8}	8.25×10^{6}
τ_s	sec	10^{-1}–10	2.62
k_p/k_t	none	10^{-4}–10^{-6}	9.64×10^{-5}
$k_p/k_t^{1/2}$	$(\text{liters/mole-sec})^{1/2}$	1–10^{-2}	2.77×10^{-1}

[a] Values are taken directly or recalculated from Dainton and Sisley [1963].

Odian p269

Effect of Rxn Temp ~ Activation energy

$$R_p = k_p \left(\frac{f k_d}{k_t} \right)^{1/2} [\mathrm{M}][\mathrm{I}]^{1/2} \qquad (\bar{x}_n)_0 = \frac{k_p[\mathrm{M}]}{(1+q)(f k_d k_t)^{1/2}[\mathrm{I}]^{1/2}}$$

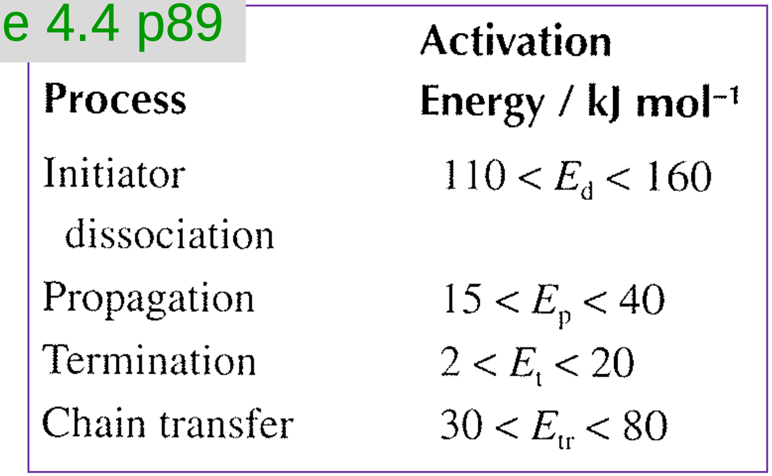
$$k_d = A_d \exp(-E_d/\mathbf{R}T)$$

$$k_p = A_p \exp(-E_p/\mathbf{R}T)$$

$$k_t = A_t \exp(-E_t/\mathbf{R}T)$$

$$k_{tr} = A_{tr} \exp(-E_{tr}/\mathbf{R}T)$$

Table 4.4 p89



Process	**Activation Energy / kJ mol⁻¹**
Initiator dissociation	$110 < E_d < 160$
Propagation	$15 < E_p < 40$
Termination	$2 < E_t < 20$
Chain transfer	$30 < E_{tr} < 80$

$$\frac{\mathrm{d}\{\ln R_p\}}{\mathrm{d}T} = \frac{(2E_p + E_d) - E_t}{2\mathbf{R}T^2}$$

> 0 ~ As T up, R_p up.

$$\frac{\mathrm{d}\{\ln(\bar{x}_n)_0\}}{\mathrm{d}T} = \frac{2E_p - (E_d + E_t)}{2\mathbf{R}T^2}$$

< 0 ~ As T up, x_n down.

- As T up, [M•] up, and $[\mathrm{M}\bullet]^2$ up more rapidly. (p89) **?**

$$\boxed{R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[M][I]^{1/2} \qquad (\bar{x}_n)_0 = \frac{k_p[M]}{(1+q)(fk_dk_t)^{1/2}[I]^{1/2}}}$$

- photopolym’n
  - $E_d = 0$

$$\frac{d\{\ln R_p\}}{dT} = \frac{(2E_p + E_d) - E_t}{2\mathbf{R}T^2}$$ > 0, but small ~ lower effect

$$\frac{d\{\ln(\bar{x}_n)_0\}}{dT} = \frac{2E_p - (E_d + E_t)}{2\mathbf{R}T^2}$$ > 0 ~ As T up, x_n up! (p89)

  - Actually, may not. ← Photoinitiators are thermally decomposed.
- chain transfer

$$\frac{d\{\ln C_{tr}\}}{dT} = \frac{E_{tr} - E_p}{\mathbf{R}T^2}$$ > 0 ~ As T up, C up, and x_n down.

Equilibrium thermodynamics

- Polym'n – depolym'n is an equili rxn

$$M_i^{\bullet} + M \rightleftharpoons M_{i+1}^{\bullet} \qquad \Delta G_p^{o} = -\mathbf{R}T\ln\{K_p\}$$

- $\Delta G = \Delta H - T\Delta S$
  - $\Delta H_p < 0$ (–50 ~ –100 kJ/mol)
    - H(formation of σ bond) > H(breaking π bond)
  - $\Delta S_p < 0$ (–100 ~ –120 J/mol K)
    - loss in DOF by decreased number of molecules
    - disfavors polym'n
  - $|\Delta H_p|$ must be > $|T\Delta S_p|$ for polymerization.
    - T must be lower than T_c.

- ceiling Temp T_c

$$M_i^{\bullet} + M \rightleftharpoons M_{i+1}^{\bullet}$$

$$\Delta G_p^o = -\mathbf{R}T \ln\{K_p\}$$

$$\ln\{[M]_{eq}\} = \frac{\Delta H_p^o}{\mathbf{R}T} - \frac{\Delta S_p^o}{\mathbf{R}}$$

$$\boxed{T_c = \frac{\Delta H_p^o}{\Delta S_p^o + \mathbf{R}\ln\{[M]_{bulk}\}}}$$

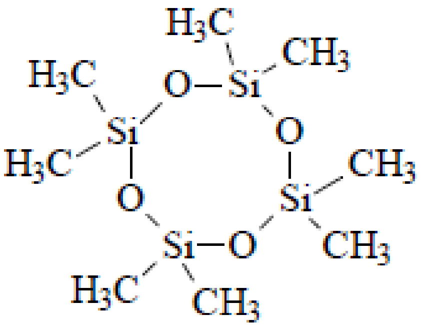
$$\Delta G = \Delta G^0 + RT \ln K = 0$$

$$K_p = \frac{[M^{\bullet}]_{eq}}{[M^{\bullet}]_{eq}[M]_{eq}} = [M]_{eq}^{-1}$$

$$\Delta G_p^o = \Delta H_p^o - T\Delta S_p^o$$

- T_c largely depends on ΔH ← ΔS similar
  - ΔH depends on structure Table 4.5 p90
    - low T_c for 1,1-disubstituted monomers ← small ΔH due to steric
  - critical in carbonyl polym’n (ionic polym’n)

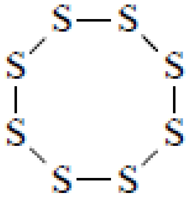
- Floor Temp
  - $\Delta S_p > 0$ and $\Delta H_p > 0$ (both very small)



octamethylcyclotetrasiloxane (OMCTS)

$\Delta H_p \sim 0$

$\Delta S_p = 6.7$ J/mole°K



elemental sulfur

$\Delta H_p = 13.5$ kJ/mole

$\Delta S_p = 31$ J/mole°K

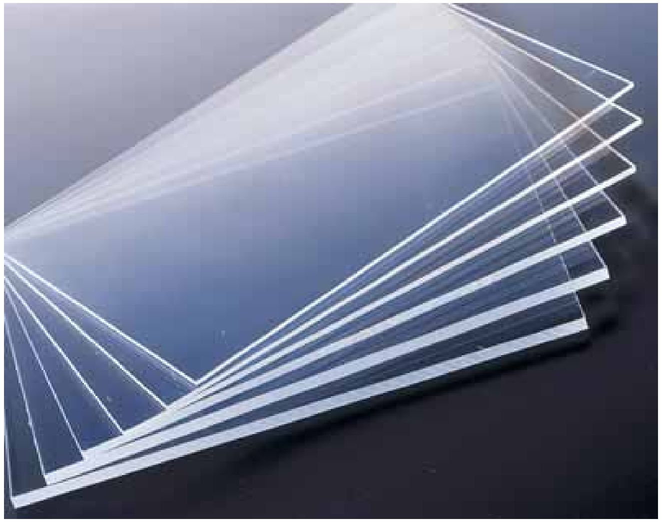
- depolym’n vs thermal stability vs heat resistance
  - T_g vs HDT (or VSP)

Radical polym’n processes

- 4 types of process
  - bulk, solution, suspension polym’n ~ same kinetics
  - emulsion polym’n ~ somewhat different
- bulk polym’n
  - simple and pure
    - [M] fixed at max
    - [I] and Temp controlled to compromise R_p and MM
  - problems at high conversion
    - heat, shrinkage, and autoacceleration
    - stop at low conversion → recovery of monomer needed
  - polymer may not be soluble in monomer ~ ppt polym’n
    - eg, PVC; vs suspension

$$R_{\mathrm{p}} \propto [\mathrm{M}][\mathrm{I}]^{1/2} \quad \text{and} \quad (\bar{x}_{\mathrm{n}})_0 \propto [\mathrm{M}][\mathrm{I}]^{-1/2}$$

- bulk polym’n (cont’d)
  - 2-stage polym’n for PMMA (large) sheet
    - 1st to a low conversion → viscous solution
    - 2nd in a sheet mold
      - taking care of heat and shrinkage problems
      - taking care (actually taking advantage) of autoacceleration
    - Alternatively, polymer + monomer in the cast [mold]
    - ‘cast polym’n’
    - Plexiglas® (cell casting)

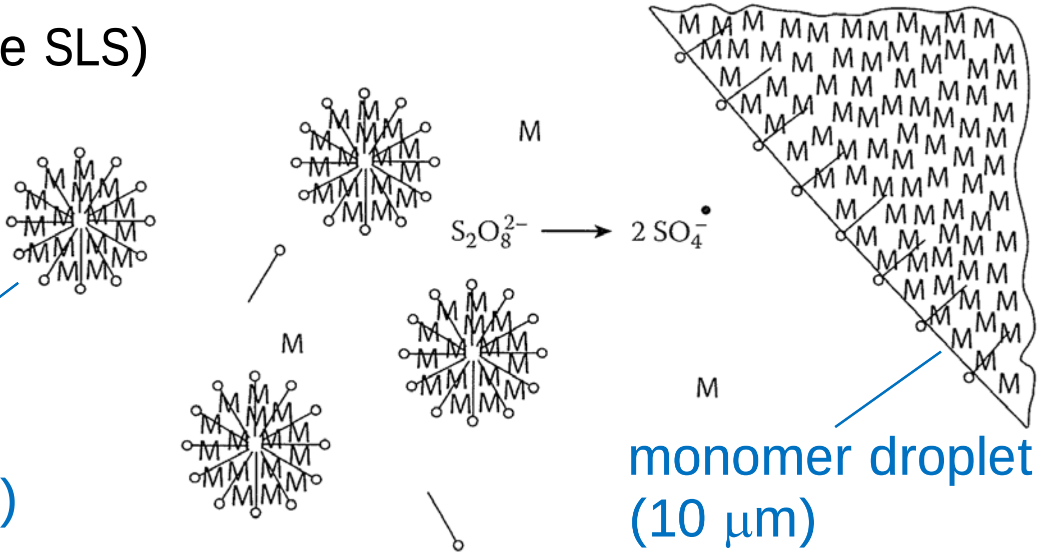


- solution polym’n
  - use of solvent that dissolve M, I, and polymer
    - no heat and autoacceleration problem
    - low rate of polym’n ← low [M]
    - CT to solvent
  - isolation of polymer needed
    - evaporation of solvent or precipitation in non-solvent
  - useful only for polymer used as solution (paint, adhesive)

- suspension polym’n
  - M+I suspended in (heated) water to form droplets
    - with vigorous stirring → determine size (.05 – 2 mm)
    - with dispersion stabilizer (water-soluble polymer like PVA) and surfactant
  - bulk polym’n in droplet
    - problems of bulk polym’n resolved
    - droplet → bead ~ ‘bead polym’n’
  - commonly used industrially
    - for many polymers esp for PVC
    - not for low-T_g polymers
  - What if monomer and/or polymer water soluble?
    - inverse suspension polym’n, eg acrylamide [PAM]

Emulsion polymerization

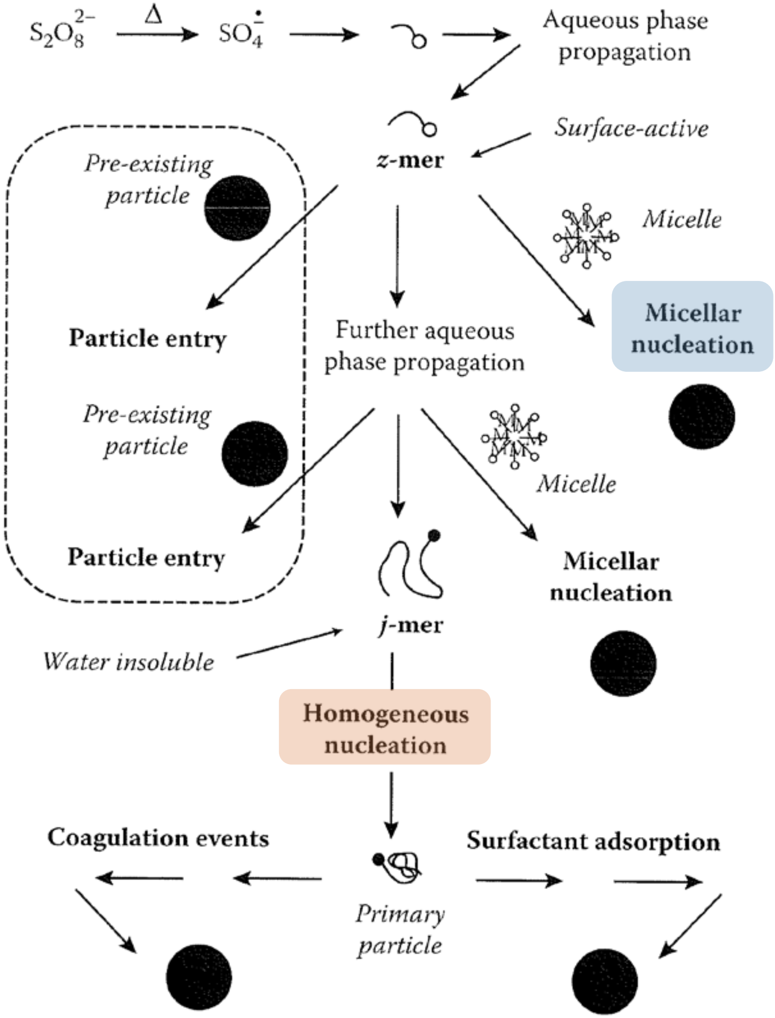
- emulsion = colloidal dispersion
  - particle size < few μm (suspension < few mm)
  - monomer micelles in water
  - polym'n to form latex (= polymer particles in water)
- recipe
  - water-insoluble M
  - water-soluble I ~ usually redox (like persulfate)
  - surfactant [emulsifier] (like SLS)
  - water
- 3 phases



monomer-swollen
micelle (10 nm)
(when conc'n > CMC)

monomer droplet
(10 μm)

- mechanism
  - Interval I: particle nucleation
    - I → R• → oligomer radical [O•]
    - micellar nucleation (z-mer)
      - O• into micelle and polym’n
      - M from droplet thru aq phase
      - surfactant from inactive micelle
    - homogeneous nucleation (j-mer)
      - less water-insoluble M
      - to form primary particle



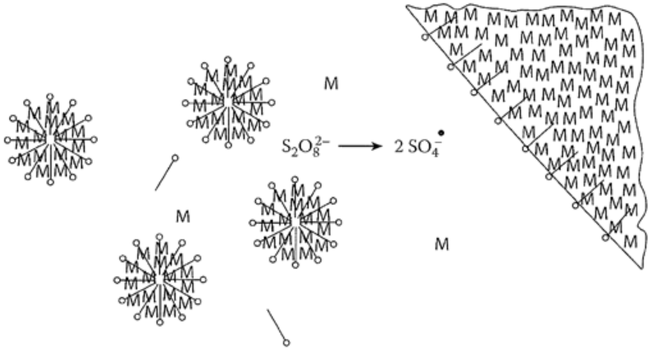
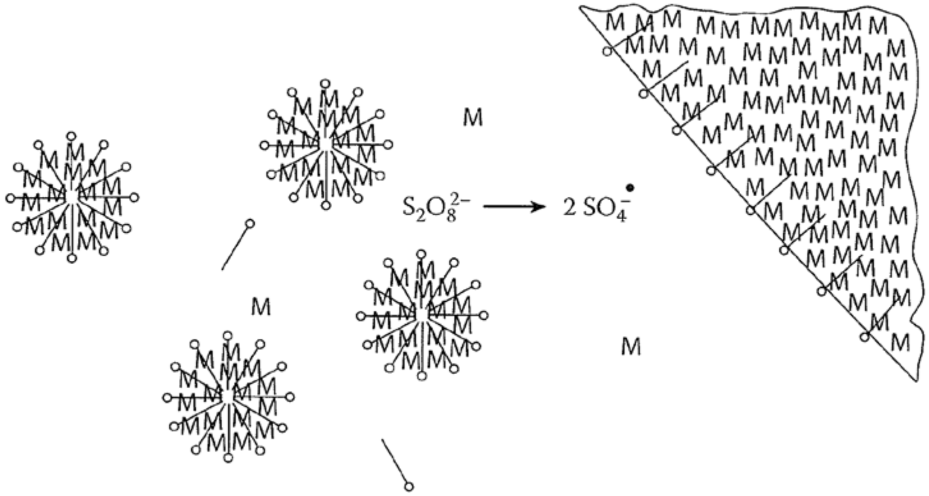


Fig 4.9 p95

- mechanism (cont’d)
  - Interval II: particle growth
    - polym’n in the particles
    - M from droplet through aq phase
    - radical from aq phase: repeat initiation/termination
  - Interval III: completion
    - no more monomer droplet
    - polym’n of residual M
    - autoacceleration may occur



Emulsion Kinetics ~ Smith-Ewart theory

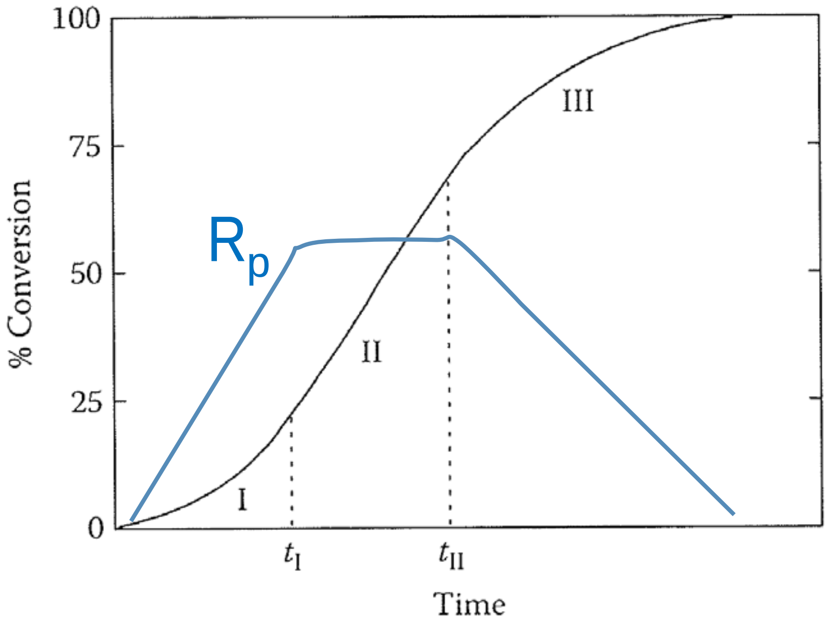
- rate of emulsion polym'n

$$R_p = k_p[\mathrm{M}]_p(\bar{n}/\mathbf{N}_A)N_p = \frac{k_p[\mathrm{M}]_p N_p}{2\mathbf{N}_A}$$

  - N_p ~ # of particles [active micelles at the end of interval I]
  - n ~ avg # of radicals/particle → 0.5
  - $[M]_p$ ~ monomer conc'n in a particle

- at Interval I, N_p ↑ → R_p ↑
- at Interval II, R_p constant
  - [M] constant
- at Interval III, $[M]_p$ ↓ → R_p ↓

Fig 4.10 p96



- MM

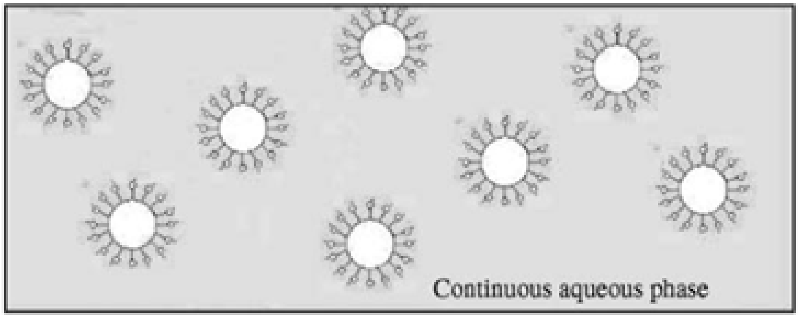
$$\bar{x}_n = k_p[\mathrm{M}]_p(N_p/\rho_i\mathbf{N}_A)$$

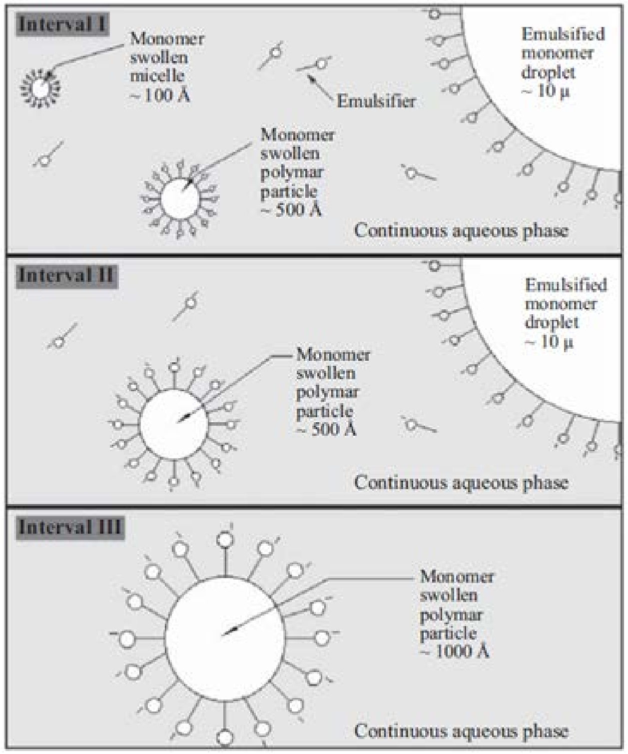
$$R_p = \frac{k_p[\mathrm{M}]_p N_p}{2\mathbf{N}_A}$$

  - ρ = molar rate of radical formation from initiator
- possible to enhance R_p and MM at the same time.
  - by increasing N_p ← increasing conc'n of surfactant
  - reason ~ compartmentalization
- applications of emulsion polym'n
  - water-borne paints, adhesives, coatings
  - core-shell particles
- water soluble monomers? inverse emulsion polym'n

Mini-emulsion polym’n

- start with small (~100 nm) monomer droplet
  → polymer part’l
- compared to macroemulsion;
  - high shear
  - costabilizer ~ highly water-insoluble
    - like $C_{16}H_{34}$ or oligomer
    - osmotic P against Ostwald ripening
- applications
  - water-insoluble additives
  - in-situ polym’n in droplet
    - eg, epoxy latex





Microgel

- micron-size crosslinked polymer
- temperature-sensitive microgel
  - water-insoluble at polym’n Temp > LCST ~ deswell
  - water-soluble at lower Temp < LCST ~ swell
  - eg, pNIPAAm ~ useful in drug delivery

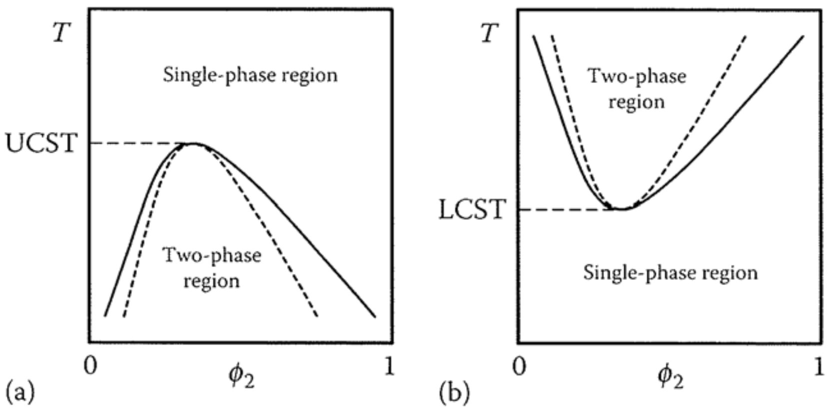
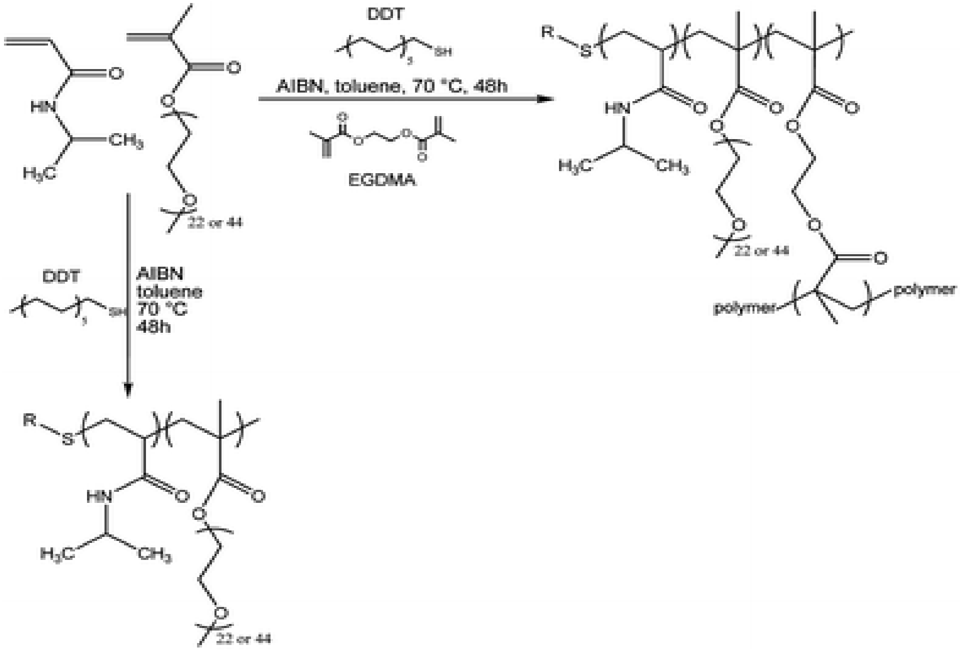


Fig 14.2 p321



LIVING RADICAL POLYMERIZATIONS

- living polym’n
  - polym’n with <u>no</u> termination
  - originally in anionic polym’n
    - for limited monomers
  - gives low PDI
  - enables (block) copolymer structure control
- living radical polym’n
  - became available very recently
  - <u>not</u> truly living, though
    - termination reduced, <u>not</u> absent
    - quasi- or pseudo-living
  - living radical polym’n = controlled radical polym’n
    = reversible-deactivation radical polym’n (IUPAC)

Two types of strategies

(a) Strategy 1: reversible end-capping of a chain radical

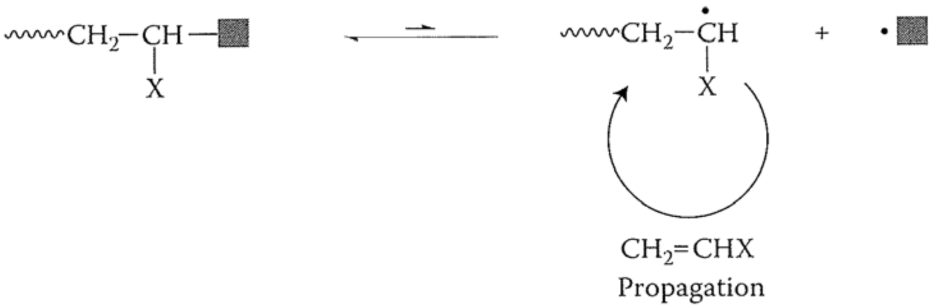
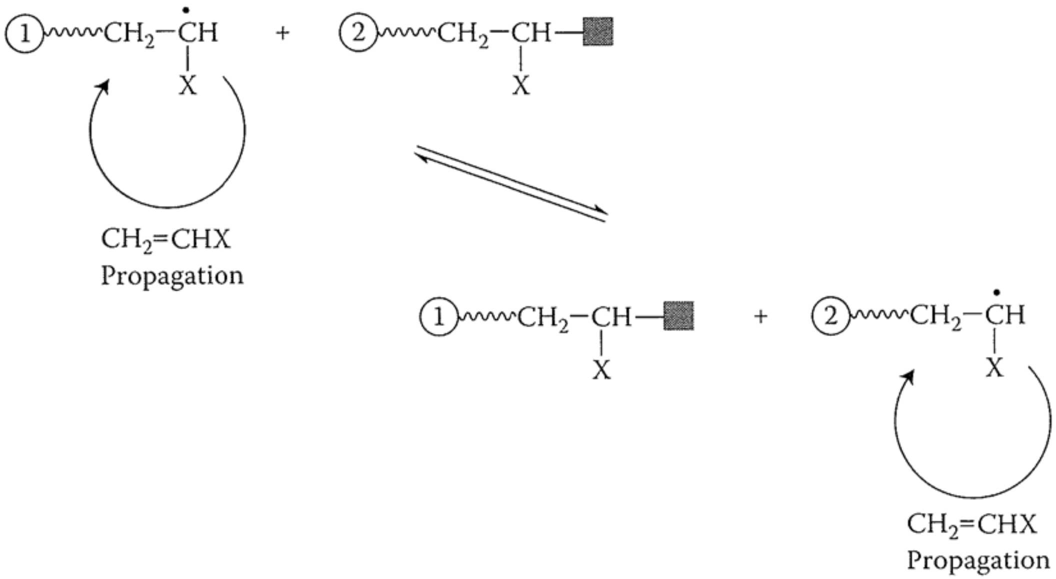


Fig 4.11 p100

(b) Strategy 2: rapid exchange of an end-capped radical with a free chain radical



S1. reversible end-capping

- very low [M•]
- very low R_t ($\propto$ $[M\bullet]^2$)
- low R_p also

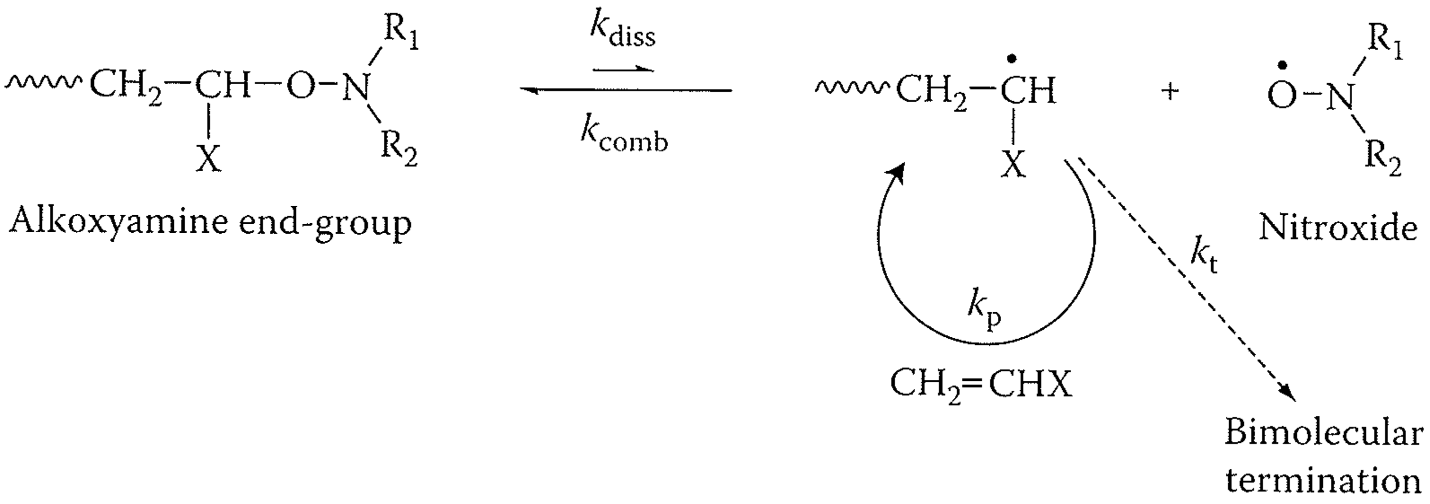
S2. reversible CT

- [M•] similar to conventional
- R_p also similar
- R_t very low

- quasi-living radicals
  - very effective and fast activation-deactivation
  - very short (transient) life-time $t_{rad} \sim .01 - .1$ ms
    - conventional $\tau \sim .1 - 10$ s
  - gives short chain/period
    - $x = k_p [M] t_{rad} \sim .02 - 35$ repeat unit/period p100
- termination suppressed
  - MM increase linearly with conversion
  - narrow MMD
  - block copolymer can be prepared

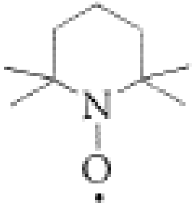
NMP

- nitroxide-mediated radical polym’n



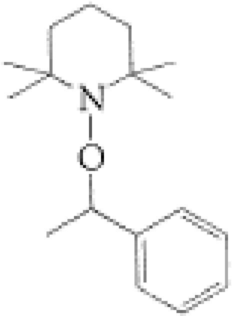
- living-like polym’n possible due to
  - stable nitroxide ~ no self rxn ~ ‘persistent radical’
  - weak C-O bond
  - small K → most chains dormant → very low [M•] → negligible termination
  - equal chance to growth, no AA → low PDI

- developments
  - ST polym’n with TEMPO at 125 ºC
    - with conventional initiator
    - ‘stable-free-radical(-mediated) polym’n (SFRP)’
  - ST, acrylates, dienes at lower Temp
    - with TIPNO, SGI
  - use of monomer-alkoxyamine as initiator
    - better control of [M•]
    - current standard

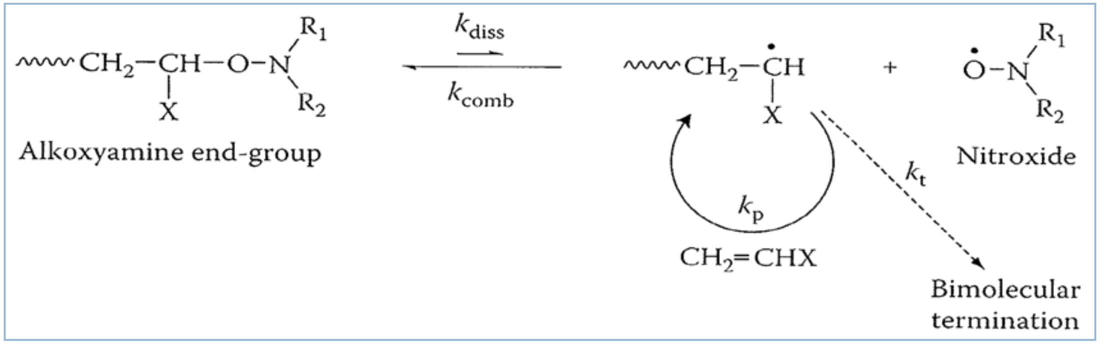


TEMPO

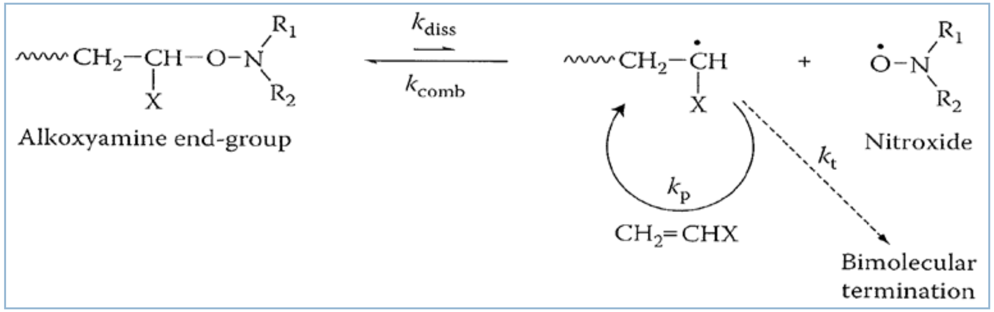
Fig 4.13 p102



Styryl-TEMPO



- kinetics of NMP



$$K_{NMP} = \frac{[M^\bullet][R_1R_2NO^\bullet]}{[P-ONR_1R_2]}$$

$$[M^\bullet] = \frac{K_{NMP}[R_3-ONR_1R_2]_0}{[R_1R_2NO^\bullet]_0}$$

$$R_p = -\frac{d[M]}{dt} = K_{NMP}k_p[M]\left(\frac{[R_3-ONR_1R_2]_0}{[R_1R_2NO^\bullet]_0}\right) \leftarrow R_p = k_p[M][M^\bullet]$$

↘

$$\ln\left(\frac{[M]_0}{[M]_t}\right) = K_{NMP}k_p\left(\frac{[R_3-ONR_1R_2]_0}{[R_1R_2NO^\bullet]_0}\right)t \leftarrow \int_{[M]_0}^{[M]_t}\frac{d[M]}{[M]} = -K_{NMP}k_p\left(\frac{[R_3-ONR_1R_2]_0}{[R_1R_2NO^\bullet]_0}\right)\int_0^t dt$$

- plot linear only in early stage; positive curvature later
  - ‘persistent radical effect (PRE)’
  - termination → [M•] ↓, (relative) [NO•] ↑ → termination ↓

- modified kinetics

$$[M^\bullet] = \left(\frac{K_{NMP}[R_3-ONR_1R_2]_0}{3k_t} \right)^{1/3} t^{-1/3}$$

$$R_p = -\frac{d[M]}{dt} = k_p[M]\left(\frac{K_{NMP}[R_3-ONR_1R_2]_0}{3k_t} \right)^{1/3} t^{-1/3}$$

$$\ln\left(\frac{[M]_0}{[M]_t} \right) = \frac{3k_p}{2}\left(\frac{K_{NMP}[R_3-ONR_1R_2]_0}{3k_t} \right)^{1/3} t^{2/3}$$

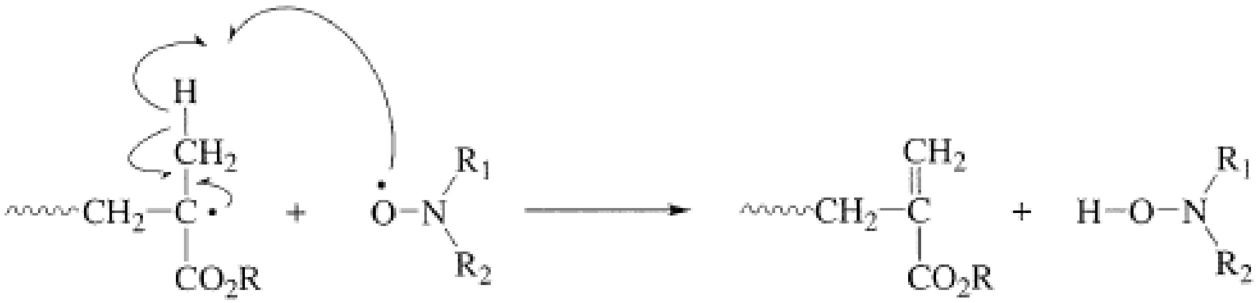
~ linear

  - AA possible, but not critical ($k_t^{-1/3}$)
- MM in NMP

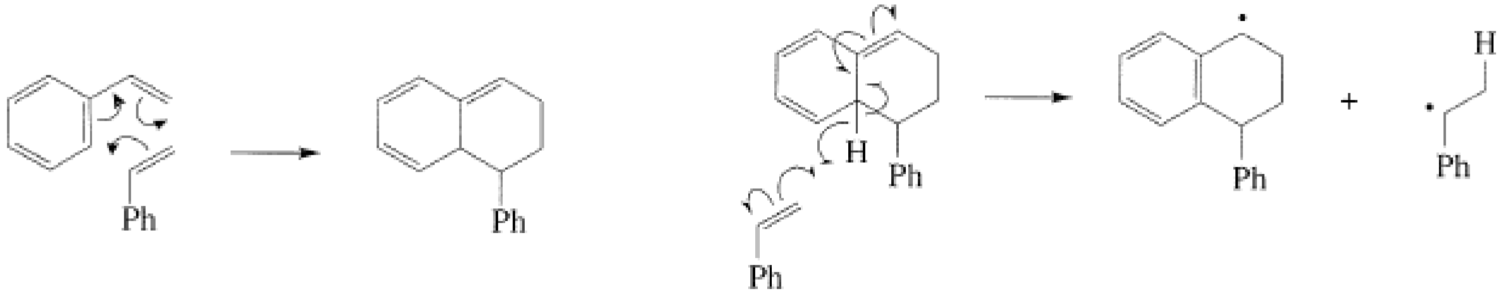
$$\boxed{\bar{x}_n = \frac{c[M]_0}{[R_3-ONR_1R_2]_0}}$$

  - c ~ (fractional monomer) conversion
- PDI? should be ≈1; actually 1.1 - 1.3

side reactions in NMP



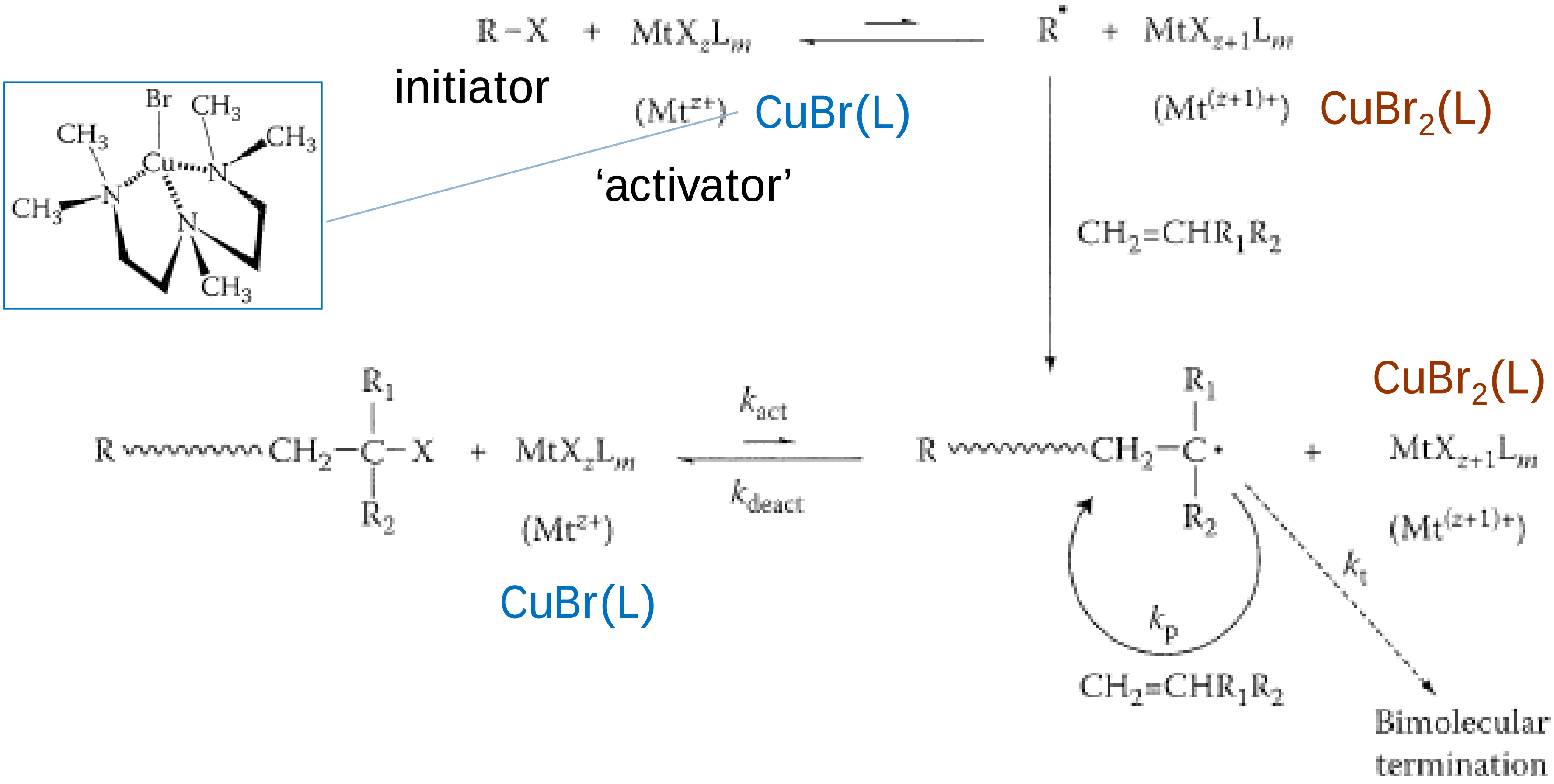
- serious in MMA ~ NMP not for MMA yet



- purely thermal (self) initiation of ST (at 80 ºC)
- Practically, compensate ‘persistent radical effect’

ATRP

- atom-transfer radical polymerization
  - by Krzysztof Matyjaszewski



initiator

CuBr(L)

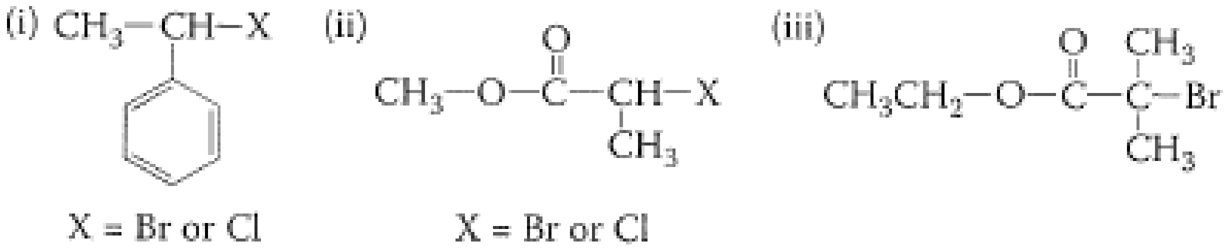
‘activator’

CuBr$_2$(L)

CuBr$_2$(L)

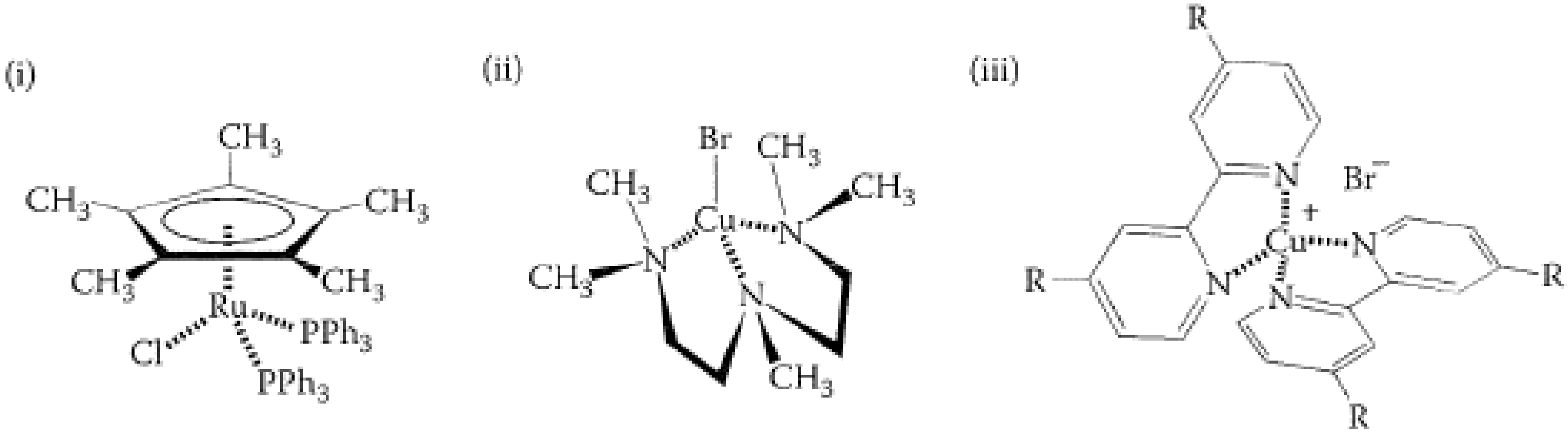
CuBr(L)

- initiators



  - resembles monomer structure ~ slightly larger activity

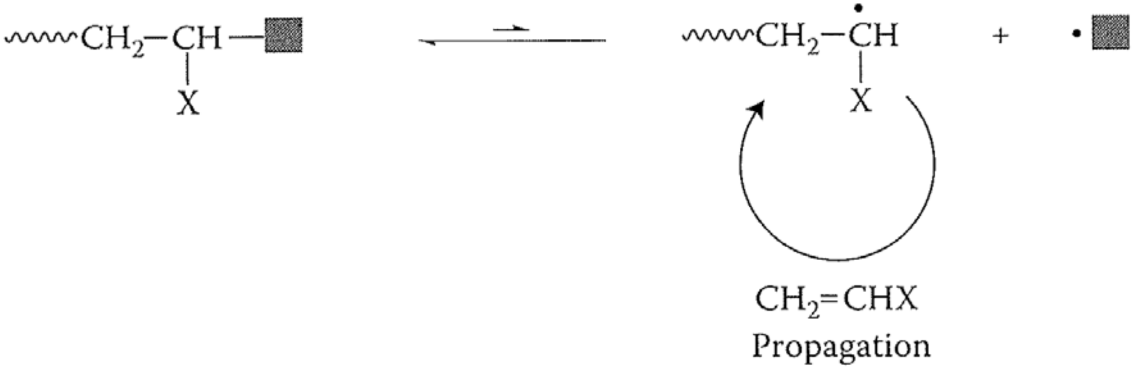
- activators



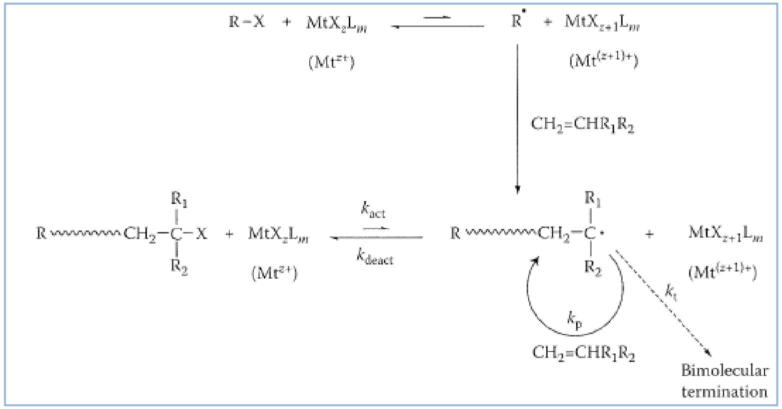
  - Cu dominant

- features similar as NMP
  - chain growth through repeated ‘activation-propagation-deactivation’
  - fast activation-deactivation reactions
  - small K, most chains dormant, low [M•]
  - low R_t, low R_p
  - low PDI, radicals live for 2nd monomer

(a) Strategy 1: reversible end-capping of a chain radical



- ❑ Kinetics of ATRP



$$K_{\mathrm{ATRP}} = \frac{[\mathrm{M}^\bullet][\mathrm{Mt}^{(z+1)+}\mathrm{L}_m]}{[\mathrm{RX}][\mathrm{Mt}^{z+}\mathrm{L}_m]}$$

$$[\mathrm{M}^\bullet] = K_{\mathrm{ATRP}}[\mathrm{RX}]\left\{\frac{[\mathrm{Mt}^{z+}\mathrm{L}_m]}{[\mathrm{Mt}^{(z+1)+}\mathrm{L}_m]}\right\}$$

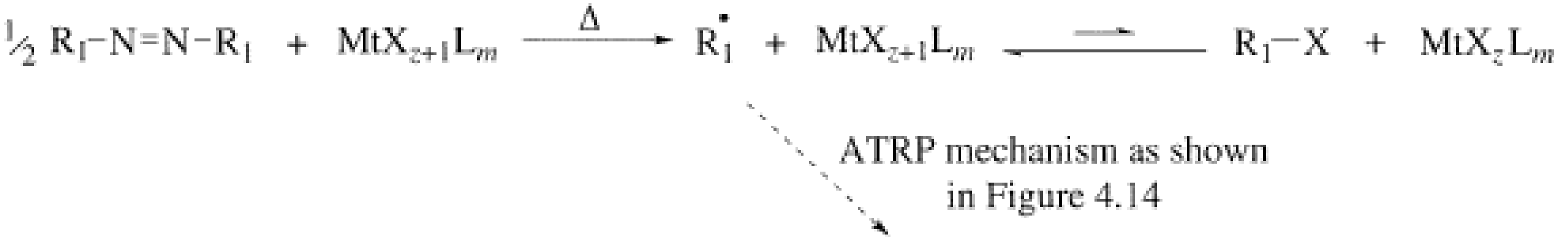
$$R_p = -\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = K_{\mathrm{ATRP}}k_p[\mathrm{M}][\mathrm{RX}]\left\{\frac{[\mathrm{Mt}^{z+}\mathrm{L}_m]}{[\mathrm{Mt}^{(z+1)+}\mathrm{L}_m]}\right\}$$

- ❑ Like NMP, 1st order
  - also be modified by ‘persistent radical effect’
- ❑ Unlike NMP, [activator]/[deactivator] controls kinetics.

$$\bar{X}_n = \frac{c[\mathrm{M}]_0}{[\mathrm{RX}]_0}$$

- ❑ PDI? should be ≈1; actually 1.1 - 1.2

- Compared to NMP, ATRP
  - is for more monomers
    - styrenics, (meth)acrylates, --- even E, VAc ~ still developing
    - Acidic H (like in AA) should be ionized or protected.
  - has more choice of initiators, activators, and deactivators
  - is better controllable
    - reverse ATRP, SR&NI, ICAR, AGET, ARGET



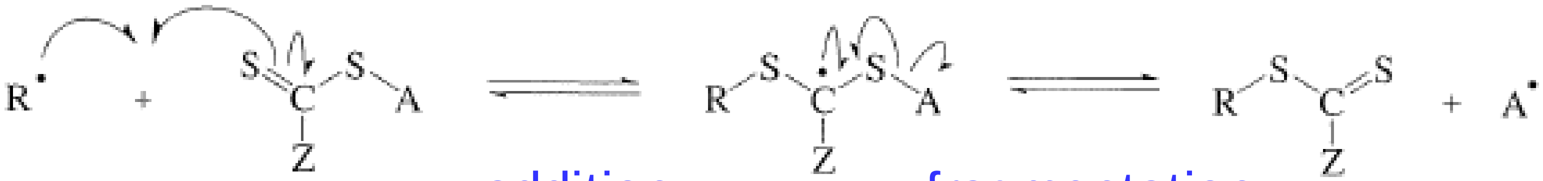
$$\tfrac{1}{2}\, R_1{-}N{=}N{-}R_1 + MtX_{z+1}L_m \xrightarrow{\Delta} R_1^{\bullet} + MtX_{z+1}L_m \rightleftharpoons R_1{-}X + MtX_zL_m$$

ATRP mechanism as shown in Figure 4.14

    - to control K, R_p, MM, MMD
  - use metal ~ should be removed

RAFT

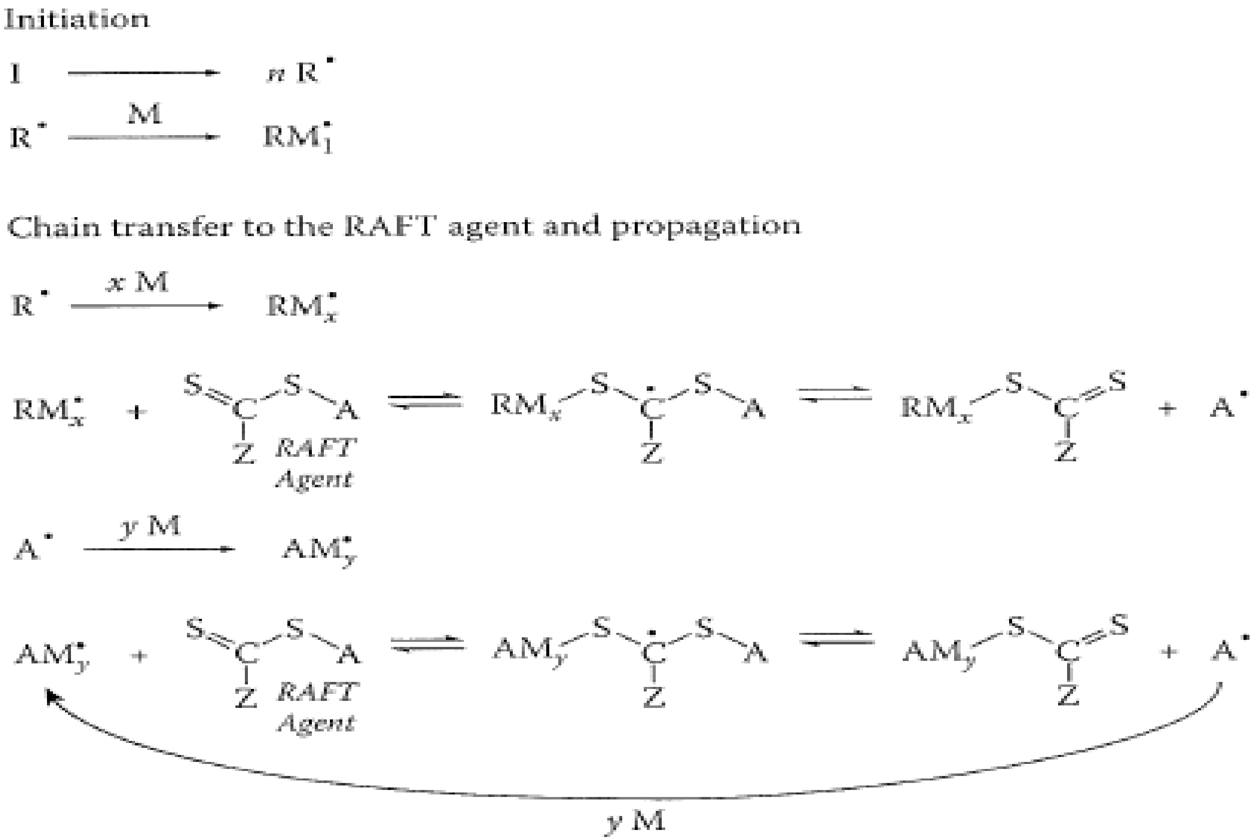
- reversible addition-fragmentation chain transfer radical polym’n
  - in (otherwise normal) radical polym’n
  - use of very effective CT agent [RAFT agent]



addition fragmentation

- C_{CTA} ~ as high as 1000
- A• and R• of similar reactivity

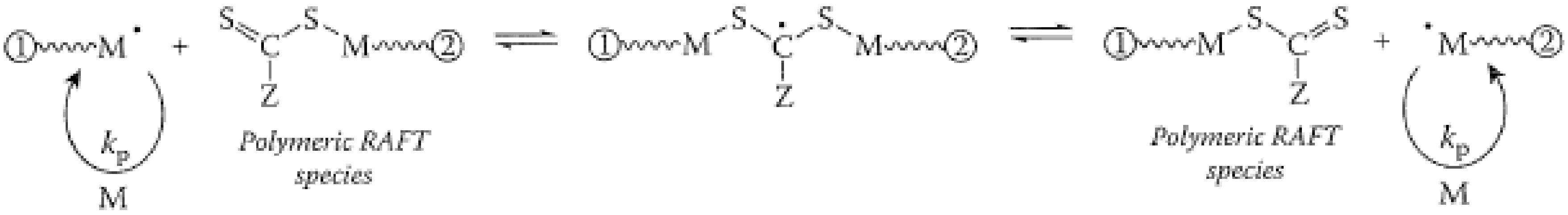
- RAFT mechanism



- use $[RAFT]_0 >> [I]_0$ (like 10-fold)
- all chains with RAFT end-group → no termination

mechanism (cont'd)

Chain transfer to polymeric RAFT species and propagation



- fast and effective A-F → living-like

MM

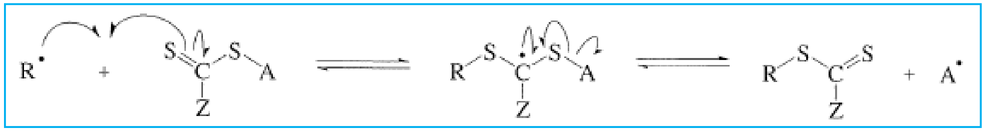
$$\bar{x}_n = \frac{c[\mathrm{M}]_0}{[\mathrm{RAFT}]_0}$$

- all chains with RAFT end-group and living-like
- narrow MMD by that all chains grows equal rate

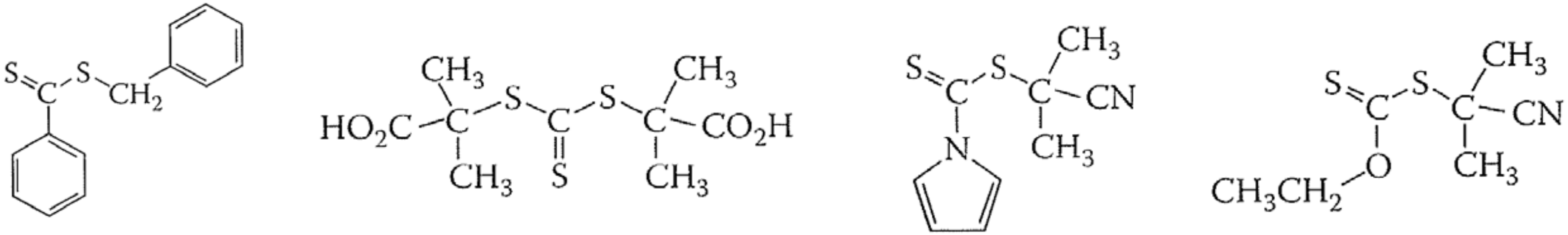
- kinetics
  - R_p should be the same to conventional radical polym’n.
  - Actually, slower. Probably due to
    - ~~radical formation by thermal initiator only~~
    - ~~$[RAFT]_0 >> [I]_0$~~
    - stable adduct radical → slow fragmentation → [M•] ↓
    - termination by rxn of adduct radical and other radical → [M•] ↓

- Compared to NMP and ATRP, RAFT
  - is much faster
  - is for much more versatile monomers
  - color

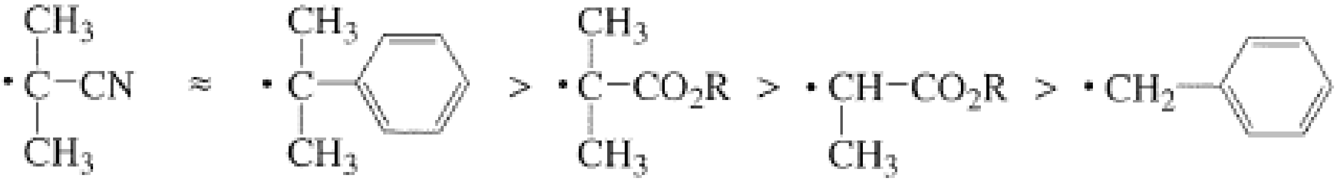
- RAFT agents Fig 4.18 p112



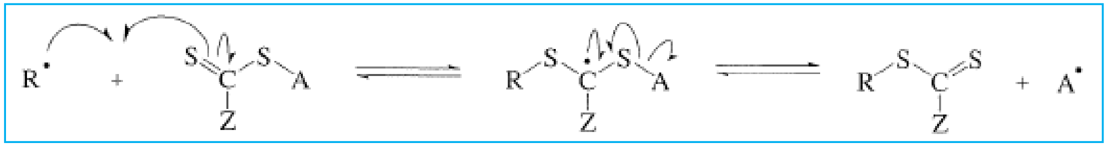
  - adduct stability (Z)



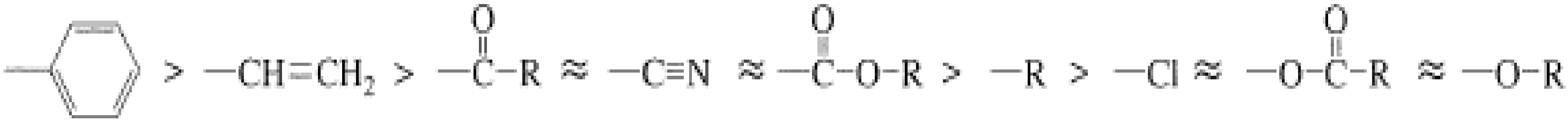
    - stabilizing radical ~ reactive
    - thiobenzoate > thiocarbonate > thiocarbamate > xanthate
  - leaving radical stability (A)
    - stable radical ~ better leaving ~ reactive



❑ RAFT agents (cont'd)

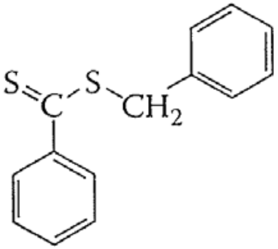


- more reactive RAFT agent for more reactive monomer
  - monomer reactivity ↔ its radical stability
    - important in copolymerization Chapt 9
  - reactive monomer ~ stable radical ~ need reactive RAFT agent



p212

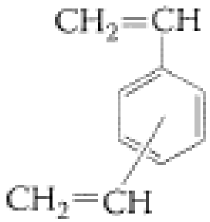
- for PS



Non-linear radical polym’n

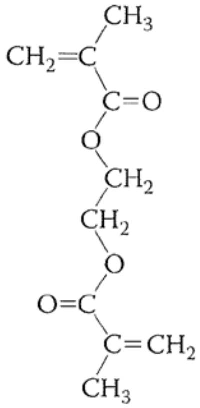
- with crosslinking monomers
  - Degree of Xlinking depends on content of Z.
  - monomers Fig 4.20

(i) DVB

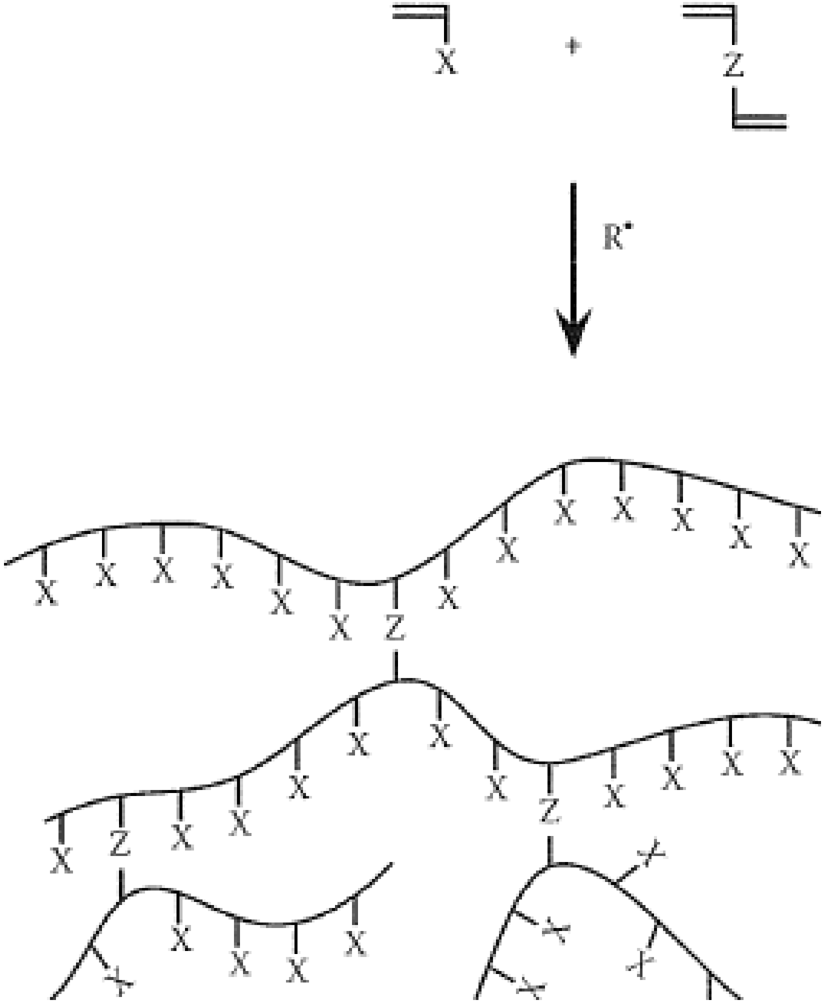


- for PS
- gel for GPC
- ion-exchange resin $-SO_3^{(-)}$
- bead for protein synthesis

(ii) (EG)DMA

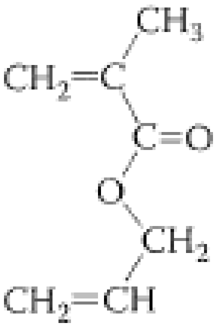


- for acrylates
- ‘hydrogels’
  - hydrophilic network
  - soft lenses



(iv) graft-linking monomer

- with different reactivity
- to graft copolymer
- for core-shell particles



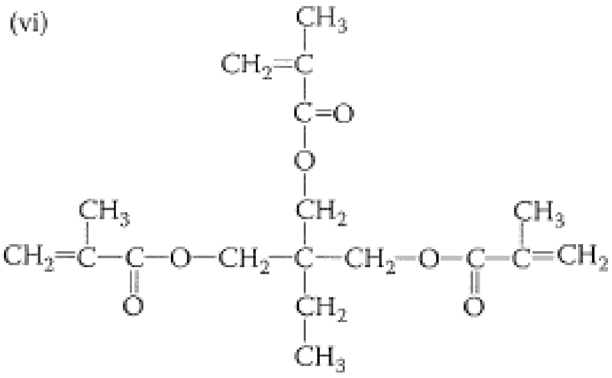
(v) bis-GMA

- for dental material

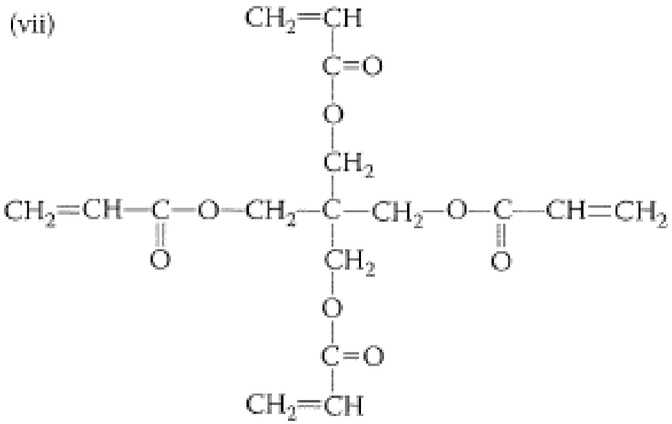
(vi,vii)

- for higher Xlinking density

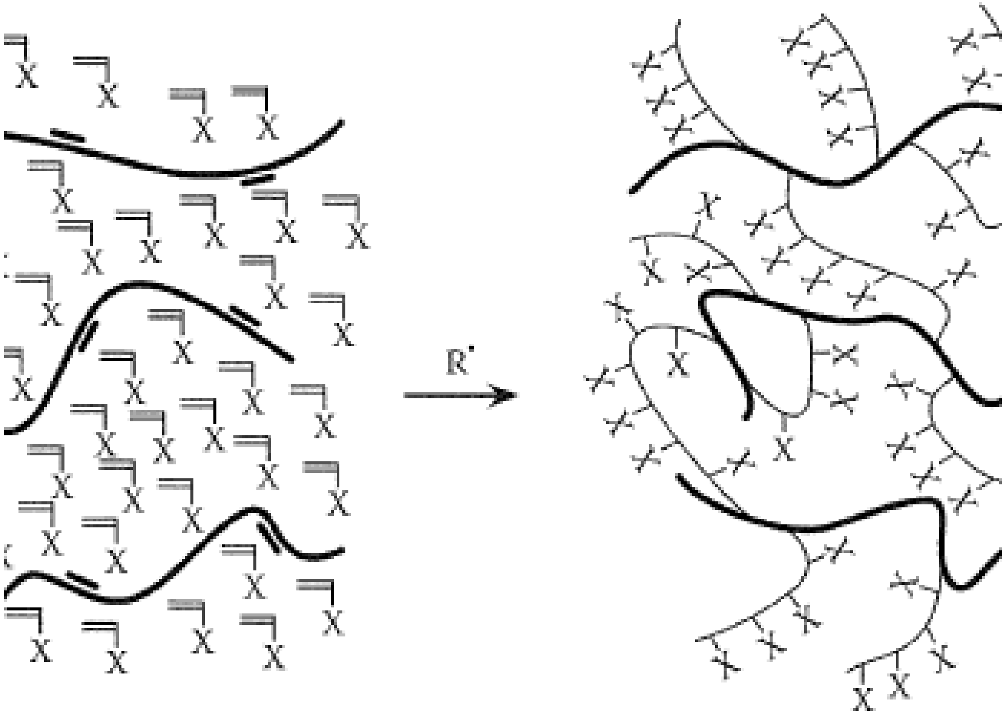
(vi)



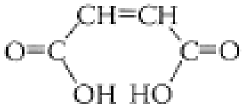
(vii)



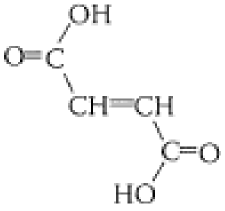
- with unsaturated polymers
  - unsaturated polyester
    - diol + diacid + unsat’d diacid → unsat’d prepolymer
    - prepolymer + styrene + initiator → crosslinking
    - useful for composite



(viii)



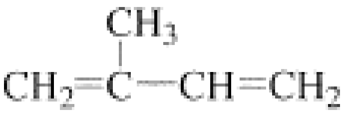
(ix)



in (1,3-)diene polym’n Chapt 6

$CH_2{=}CH{-}CH{=}CH_2$

Butadiene



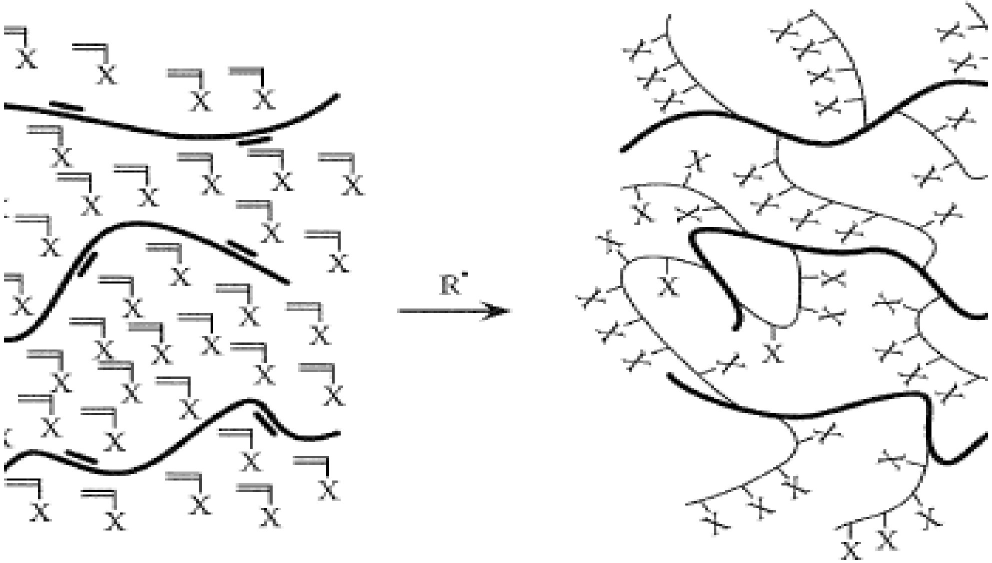
$CH_2{=}C(CH_3){-}CH{=}CH_2$

Isoprene

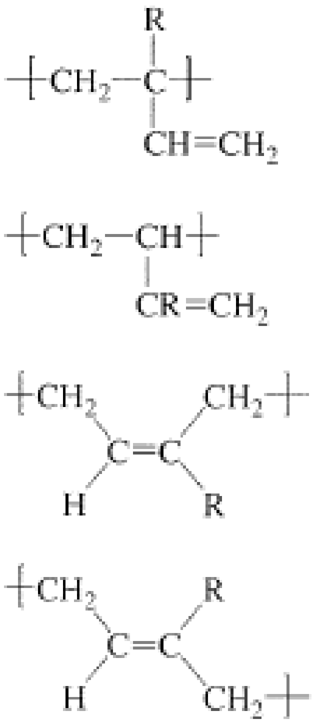
$CH_2{=}C(Cl){-}CH{=}CH_2$

Chloroprene

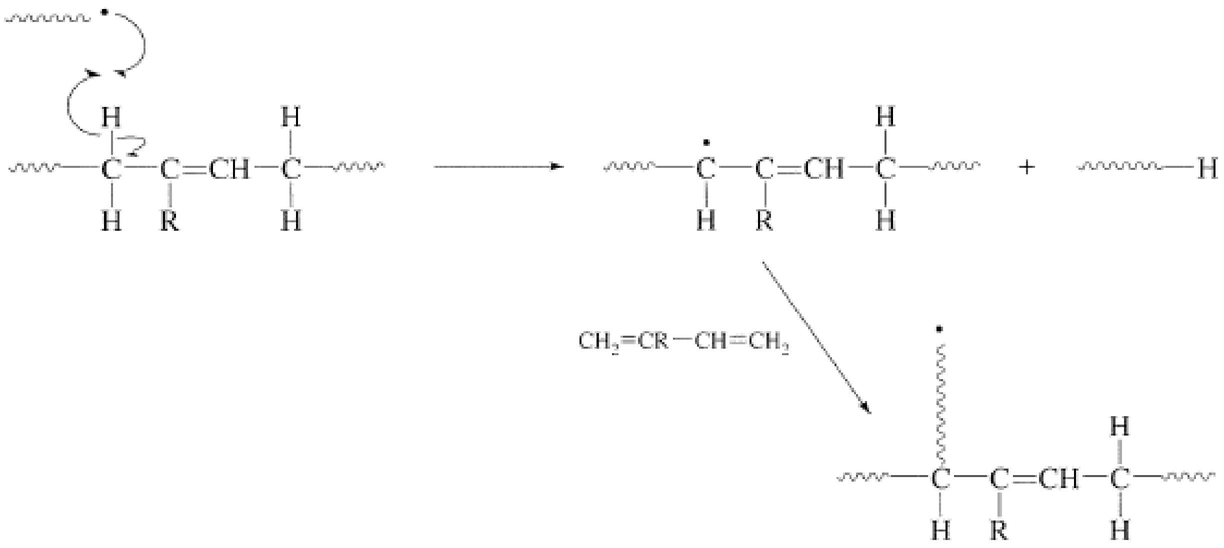
- copolymerization of double bonds
  - along the chain ~ from 1,4-polym’n
  - at side group ~ from 1,2- (or 3,4-)polym’n



Repeat Unit Structure



- in diene polym’n (cont’d)
  - CT to polymer
    - abstraction of allylic H (4 H’s/ru)



- uncontrollable?
  - by conversion or CT agent