Chem 466

Lecture 13

02/27/2014

- Exam II in one week, next Thursday 03/06/2014

V. Chain-growth Addition Polymerizations

(A) General overview

initiation — propagation — termination

$$i^* \xrightarrow[k_i]{m} i-R^* \xrightarrow[k_p]{m} i-R-R^* \xrightarrow[k_p]{n\,m} i\text{-}(R)_{n+1}\text{-}R^* \xrightarrow[k_t]{t} i\text{-}(R)_{n+2}\text{-}t$$

$$i-R^* \xrightarrow[k_{rt'}]{rt} i-R-rt \qquad i-R-R^* \xrightarrow[k_{rt}]{rt} i-R-R-rt \qquad i\text{-}(R)_{n+1}\text{-}R^* \xrightarrow[k_{-rt}]{rt} i\text{-}(R)_{n+1}\text{-}R-rt$$

$*rt$ — initiator having a reactive site — e.g. radical, anion, cation (but also e.g. Yokozawa, just a highly reactive electrophile)

rt = reversible termination are possible — controlled polyms

k_i = rate constant of initiation

k_p = rate constant for propagation

k_t = rate constant for irreversible termination

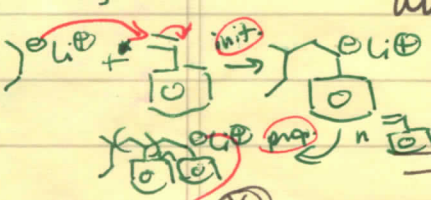
k_{rt} = rate constant for reversible termination

k_{-rt} = rate constant for active end regeneration

$k_{rt'} + k_{-rt'}$ = rate constants for rt + −rt of initiator

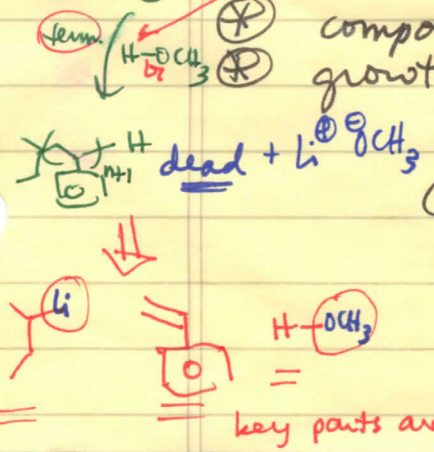
- an initiator is required
- monomers undergo rxn w/ ~~grow~~ initiator or w/ growing poly chain end (no m+m rxn)
- most often involves add'n to an unsaturated group (ring, dbl. bond, triple bond) (Yokozawa's systems are exceptions)

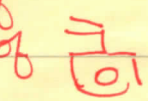
e.g.

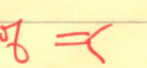


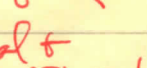
⟹ addition polym.

- composition of monomer ⟹ repeat unit (usually no condensate except for Yokozawa)
- growth continues until
  (a) monomer is exhausted
  (b) termination occurs
  — irreversible termination gives dead chains
  — reversible termination gives



shown in lecture examples of anionic polym of 

cationic polym of 

traditional radical + controlled (NMRP) polym of 

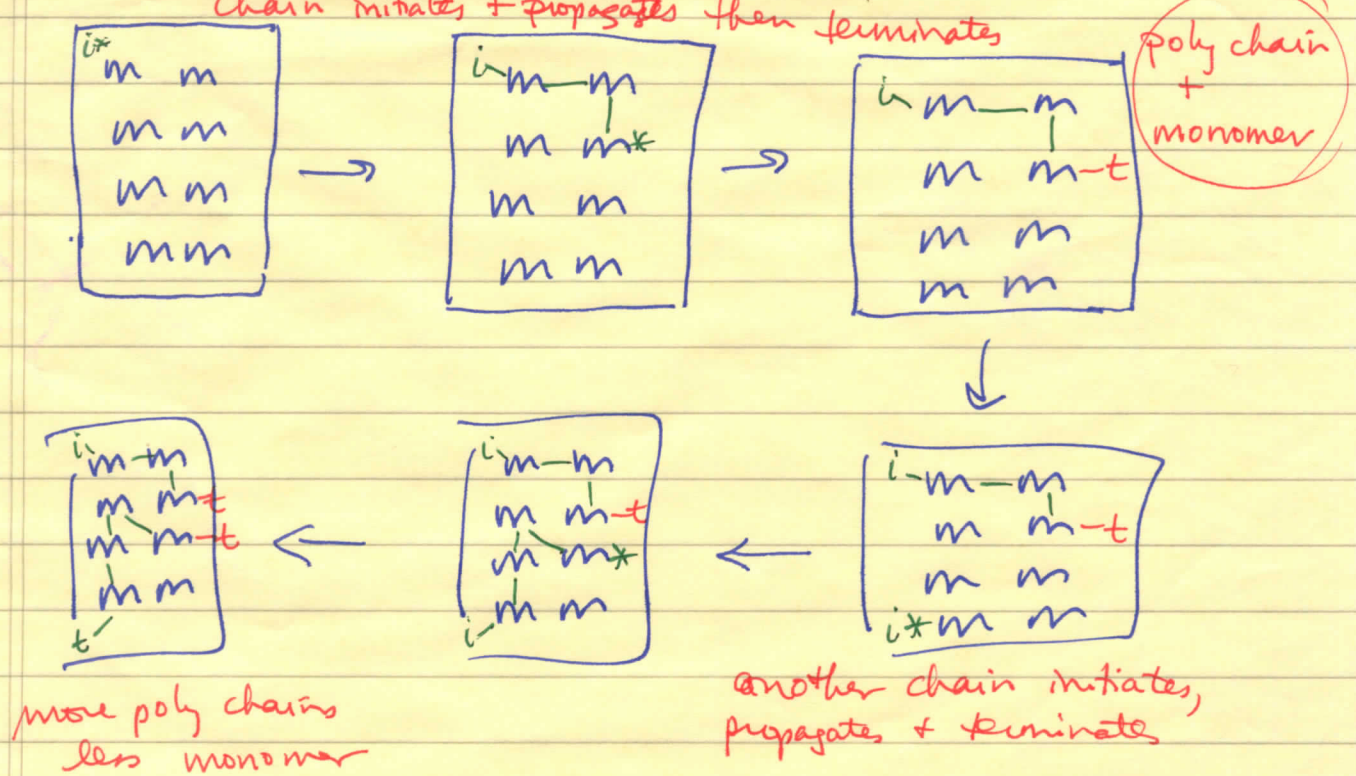
controlled polym.

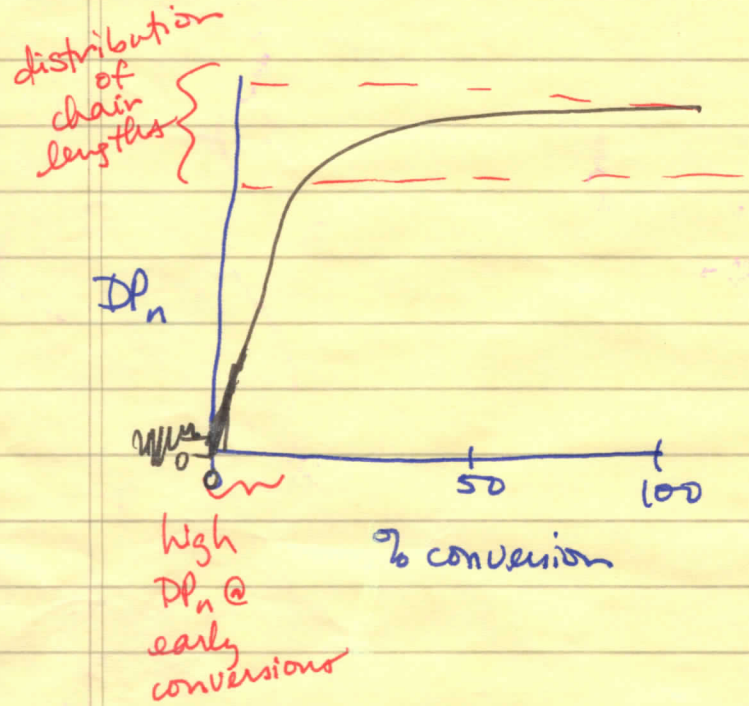
— controlled polym. is possible w/ anionic, cationic, neutral + radical reactive species

⊕ a chain initiates, consumes monomer (propagates), and then terminates (irreversibly or reversibly)

For traditional radical chain-growth, addition polym: (the focus of text Chapter 3)

chain initiates + propagates then terminates

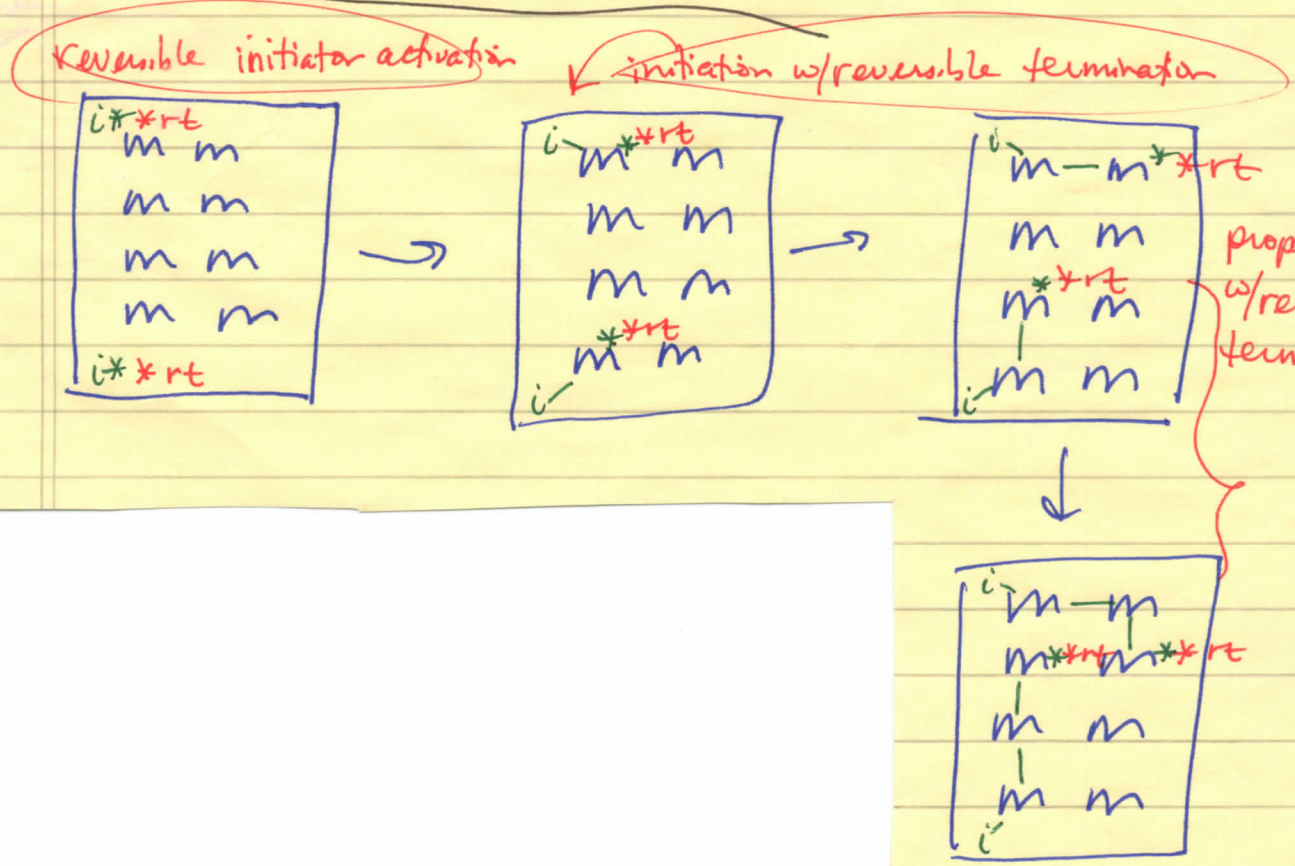


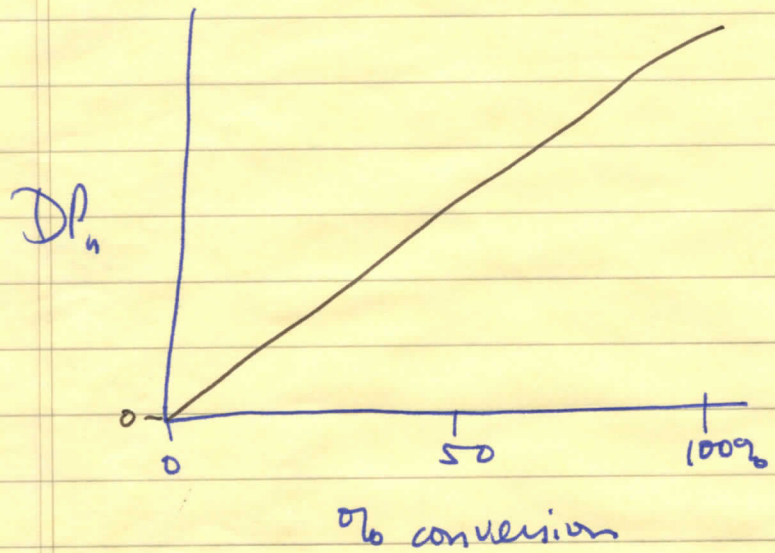


$k_i \sim k_p > k_t$

+ new initiators are generated at times throughout the polym.

For controlled ("living") polyms.:





$$k_i \geq k_p < k_{rt}$$

chains initiate at same time, then propagate + undergo fast reversible termination (to cap reactive chain end + have ~~most chains~~ chains spend most time in dormant state to avoid irreversible termination rxns)

e.g. w/ controlled radical polym.

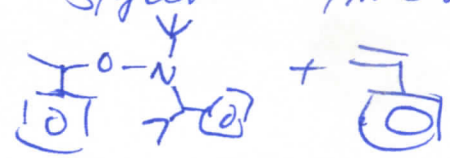
or $$k_i \geq k_p >>> k_t$$

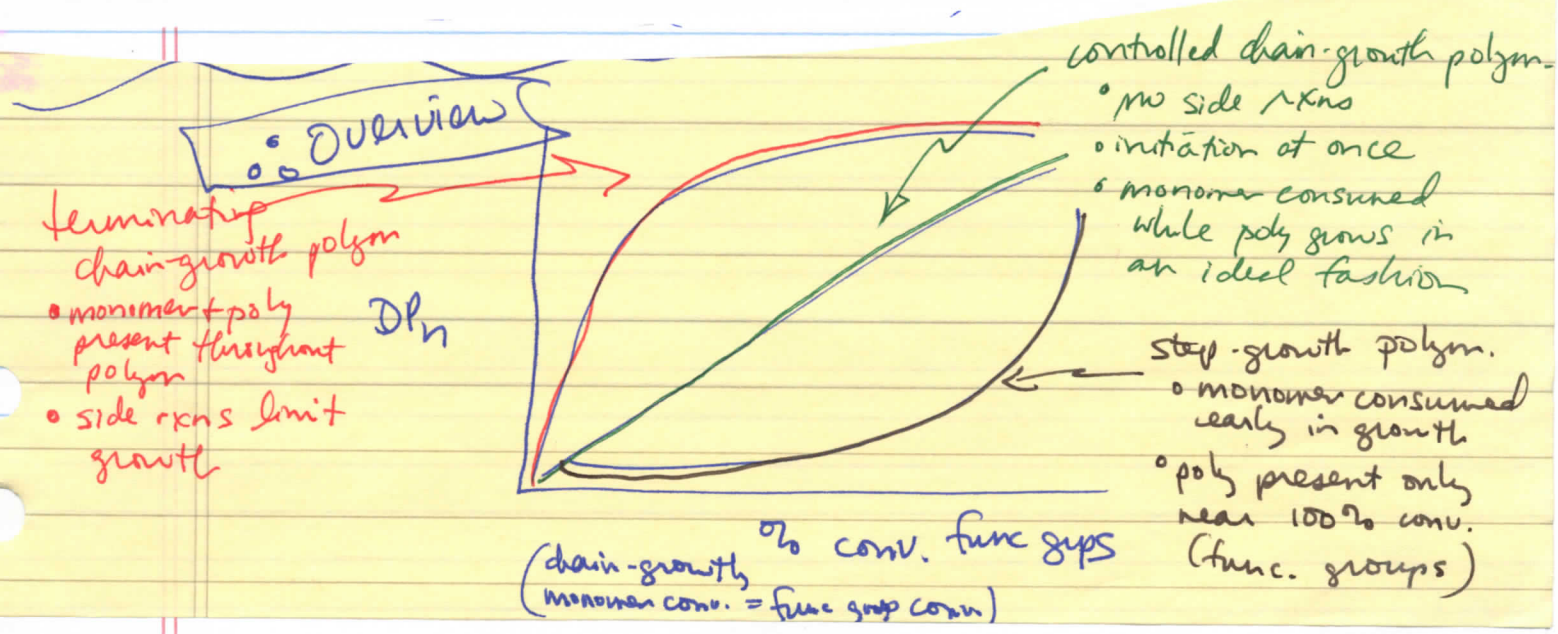
all initiator introduced in a brief time period (so all chains initiate at once) + no irreversible termination

e.g. anionic + cationic polyms (counterions mediate reactivity, but do not "cap" the chain end into a dormant state)

on board

e.g. NMRP of Styrene w/mech





(B) Thermodynamics of Polym

- addition rxns are reversible
- for a polym. to occur, $\Delta G < 0$

$$\Delta G = \Delta H - T\Delta S$$

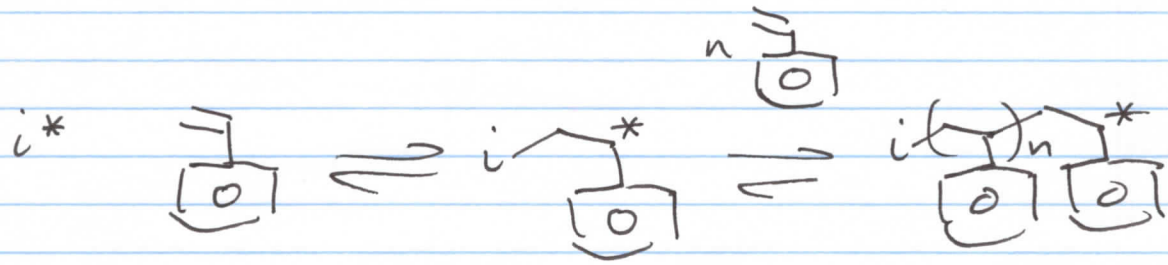
– for chain-growth, addn polyms:

ΔH is -'ve; exothermic; favorable

ΔS is -'ve; exoentropic; disfavorable

loss of translational freedom when linked into poly chain

e.g. for styrene polym.



radical anion or cation

$\Delta H = -73$ kJ/mol "in favor of polym"

$\Delta S = -0.104$ kJ/K·mol "against polym"

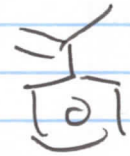
@ 70°C $\Rightarrow \Delta G = -37$ kJ/mol

(remember to convert to K for calc.)

$\therefore$ polym is favorable + will occur

*t (alternatively could be reversible termination)

vs. for α-methylstyrene polym



$\Delta H = -35$ kJ/mol

$\Delta S = -0.104$ kJ/K·mol

@ 70°C $\Rightarrow \Delta G = +3$ kJ/mol

$\therefore$ thermodynamically not possible to polym @ 70°C

styrene $T_c = 429$°C

If we set $\Delta G = 0 \Rightarrow 0 = \Delta H - T_c \Delta S$

$\Rightarrow T_c = \dfrac{\Delta H}{\Delta S}$ = critical temp (ceiling temp) = the upper limit for the temp. @ which polym is thermodynamically favorable

α-methylstyrene $T_c = 64$°C

equil. favors poly @ T<64°C

" " monomer @ T>64°C