

Lecture 12: Free Radical Kinetic Chain Length, MWD, Chain Transfer, Energetics

Energetics

General Equation

$$k = Ae^{\frac{-E}{RT}}$$

$$\ln k = \ln A - \frac{E}{RT}$$

For thermal decomposition of initiator

$$R_p = k_p [M][M \cdot] = k_p \underbrace{\left(\frac{k_d}{k_t}\right)^{\frac{1}{2}}}_{\text{net rate constant}} f^{\frac{1}{2}} [M][I]^{\frac{1}{2}}$$

"fudge factor"

Arrhenius expression:

$$\ln \left[k_p \left(\frac{k_d}{k_t}\right)^{\frac{1}{2}} \right] = \ln \left[A_p \left(\frac{A_d}{A_t}\right)^{\frac{1}{2}} \right] - \frac{\left[E_p + \frac{E_d}{2} - \frac{E_t}{2} \right]}{RT}$$

constant
w.r.t. Temp

E_p = activation energy for propag. step

$\left[E_p + \frac{E_d}{2} - \frac{E_t}{2} \right]$ is activation energy for polymerization

$$E_R = E_p + \frac{E_d}{2} - \frac{E_t}{2}$$

Overall:

$$\ln R_p = \ln \left[A_p \left(\frac{A_d}{A_t}\right)^{\frac{1}{2}} \right] + \ln \left[(f[I])^{\frac{1}{2}} [M] \right] - \frac{E_R}{RT}$$

Sample Values of E_p and E_t in kJ/mol

Monomers	E_p (kJ/mol)	E_t (kJ/mol)
Vinyl chloride	16	17.6
Methyl acrylate	29.7	22.2
Methyl metacrylate	26.4	11.9
Styrene	26.0	8.0

Initiator	E_d (kJ/mol)
AIBN	123.4
Acetyl Peroxide	136
Benzoyl Peroxide	124.3

On Average: $E_p \sim 20 - 30$
 $E_t \sim 10 - 15$
 $E_d \sim 100 - 150$
 $\Rightarrow E_R = E_p + E_d/2 - E_t/2$
 is dominated by E_d
 $E_R \sim 80 - 90$ kJ/mol

Because R_p is a positive number \rightarrow positive activation energy

If $T \uparrow$, $k \uparrow$

e.g. if $T \uparrow \sim 10^\circ\text{C}$, $R_p \uparrow$ by 2-3x

(rate of polymerization increases by 2 or 3 times)

What about $\overline{p_n}$?

(assume no chain transfer)

$$\overline{p_n} = 2av$$

let $a = 1$ (coupling)

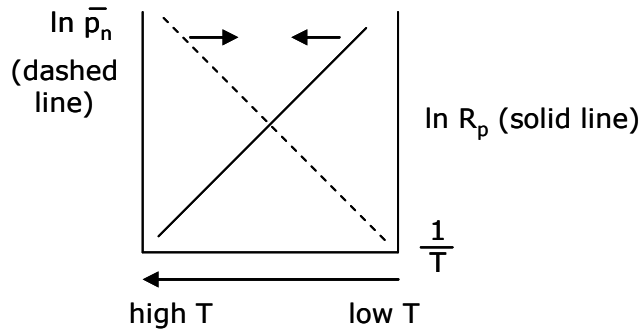
$$\overline{p_n} = 2v = \frac{k_p[M]}{(fk_d k_t [I])^{1/2}}$$

Large value

$$\ln \overline{p_n} = \ln \left[\frac{A_p}{(A_d A_t)^{1/2}} \right] + \ln \left[\frac{[M]}{(f[I])^{1/2}} \right] - \left[\frac{E_p - \frac{E_d}{2} - \frac{E_t}{2}}{RT} \right]$$

\Rightarrow on average, get negative value for [] E term

$$\Rightarrow \left[\frac{E_{p_n}}{RT} \right] \text{ is negative}$$



Thermodynamics

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

should be negative for polymerization to take place

1. $\Delta H \rightarrow$ strongly exothermic rxns

$$\Delta H_p \text{ (enthalpy of propagation)} \rightarrow \sim -160 \text{ to } -60 \text{ kJ/mol}$$

2. $\Delta S \rightarrow$ lose entropy with polymerization

$$\Delta S \rightarrow \sim -90 \text{ to } -120 \text{ J/(mol}\cdot\text{K)}$$

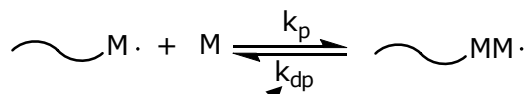
$$\text{or } -0.09 \text{ to } -0.12 \text{ kJ/(mol}\cdot\text{K)}$$

Usually ΔH is much larger than $T\Delta S$ term

\Rightarrow negative ΔG (thermodynamically favorable to polymerize)

At certain Temp range, its possible for $\Delta G \rightarrow 0$

\Rightarrow get near equilibria conditioning



depropagation rate constant

At equilibrium (or near):

$$-\frac{d[M]}{dt} = (k_p[M] - k_{dp})[M\cdot]$$

at equilibrium = 0

$$K_{eq} = \frac{[M_{n+1}\cdot]}{[M_n\cdot][M]} \quad [M_{n+1}\cdot] \text{ and } [M_n\cdot] \text{ approx. equal}$$

$$= \frac{1}{[M]} = \frac{k_p}{k_{dp}}$$

$$[M_{eq}] = \frac{k_{dp}}{k_p} = \frac{1}{K_{eq}}$$

equilibrium monomer concentration at a given temp

Will always define with respect to monomer conc or temperature.

Standard States Defns:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq}$$

$$\Delta G = \Delta G^\circ + RT \ln K_{eq} = 0$$

$$\begin{aligned} \Delta H^\circ - T\Delta S^\circ &= -RT_c \ln \frac{1}{[M]_{eq}} \\ &= RT_c \ln [M]_{eq} \end{aligned}$$

Solve for T:

$$T_c = \frac{\Delta H^\circ}{\Delta S^\circ + R \ln [M]_{eq}}$$

"ceiling temp"

$[M]_{eq}$ defined as ratio:

$$\frac{[M]_e}{[M]_s}$$

← Equilibrium monomer conc

← Standard state monomer conc

= highest T for polymerization to occur

$[M]_s^\circ = 1 \text{ M soln}$
(or bulk conc'n)

$$\Rightarrow \ln \frac{[M]_e}{[M]_s^\circ} = \ln [M]_{eq} = \frac{\Delta H^\circ}{RT_c} - \frac{\Delta S^\circ}{R}$$

determine $[M]_e$ from T

ceiling temperature term when no monomer conc is specified, is usually assuming that $[M]_c = [M]_{bulk}$

	(at 25°C)	
Examples	$[M]_c$ (M)	T_c (assuming bulk monomer)
Vinyl acetate	1×10^{-4}	--
Methyl methacrylate	--	220°C
α -methyl styrene	2.2	61°C