

### Lecture 13: Thermodynamics of Free Radical Polymerizations, Ceiling T's, Tromsdorff Effect, Instantaneous P<sub>n</sub>

#### Thermodynamics (Continued)

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

$$\Delta G = \Delta G^\circ + RT \ln K_{eq} \quad \text{in general}$$

but at equilibrium:

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

$$\text{so } \Delta H^\circ - T_c \Delta S^\circ = -RT_c \ln \frac{1}{[M]_c} \quad \text{at equilibrium}$$

where  $[M]_c$  = ceiling monomer con'c

Solve for T<sub>c</sub>:

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

$$[M]_c = \frac{[M]_{eq}}{[M]_s} \quad \leftarrow \text{Equilibrium}$$

$$\leftarrow \text{S.S. in mol/L (standard state in mol/L)}$$

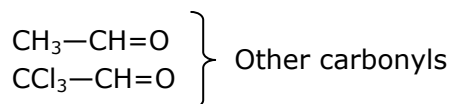
$[M]_s^p \Rightarrow$  bulk concentration of monomer or 1 mol/L (depending on who's defining it)

We will use 1 mol/L

#### Susceptible polymers for "unzipping"

Carbonyl: CH<sub>2</sub>=O

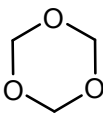
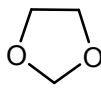
e.g.  $-(CH_2-O)-$  unzips to form formaldehyde



Cyclics:

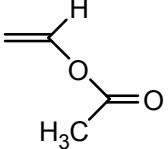
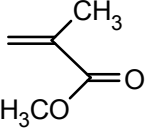
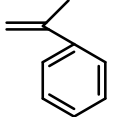


THF



trioxane

unzips via  $-(\overset{H_2}{C}-O)_n$  as well

Monomer	$[M]_c$ @ 25°C (mol/L)	$T_c$ (pure monomer) (°C)
Vinyl acetate	$1 \times 10^{-9}$	~ 400°C or higher
		
Methyl methacrylate (MMA)	$1 \times 10^{-3}$	220°C
		
$\alpha$ -methyl styrene	2.2	61°C
		

## Polydispersity Index (PDI) for Free Radical Polymerization

$$\nu = \frac{R_p}{R_t} = \frac{k_p[M]}{k_t[M\cdot]} = (\text{for thermally diss. initiator}) = \frac{k_p[M]}{(2k_d f k_t [I])^{\frac{1}{2}}}$$

$$\overline{p_n} = 2a\nu$$

### Statistical Approach

$p$  = probability of growth of polymer chain  
= "propagation probability"

$$p = \frac{k_p[M]}{k_p[M] + 2k_t[M\cdot]} = \frac{R_p}{R_p + R_t (+ R_{tr})}$$

if needed (for chain transfer)

$1-p$  = probability of chain termination

$$1-p = \frac{2k_t[M\cdot]}{k_p[M] + 2k_t[M\cdot]}$$

$X_i$  = number fraction of radicals having reached degree of polymerization =  $i$

$$X_i = p^{(i-1)}(1-p)$$

for chain end

$$\bar{p}_n = \frac{\sum_{i=1}^{\infty} iXi}{\sum_{i=1}^{\infty} Xi} = \sum_{i=1}^{\infty} iXi = (1-p) \sum_{i=1}^{\infty} ip^{(i-1)} \quad \text{apply series definition}$$

↑  
1.0

$$\Rightarrow \left[ \bar{p}_n = \frac{1}{1-p} \right] \quad \left. \vphantom{\bar{p}_n} \right\} \text{ here } p \neq \pi \text{ as in step growth}$$

$$\text{now } p = \frac{R_p}{R_p + R_t}$$

$$\bar{p}_n = \frac{1}{1-p} = \frac{R_p + R_t}{R_t}$$

as  $p \rightarrow 1.0$  (i.e.  $R_p \gg R_t$ )

$$\Rightarrow \bar{p}_n \rightarrow \nu$$

$$\Rightarrow \bar{p}_n \rightarrow \frac{R_p}{R_t}$$

$$\bar{p}_w = \frac{\sum i^2 Xi}{\sum iXi} = \frac{\sum i^2 Xi}{\bar{p}_n} \quad \text{apply series defn}$$

weight fraction

$$\Rightarrow \left[ \bar{p}_w = \frac{1+p}{1-p} \right]$$

PDI:  $z = 1+p$  } disproportionation

$$\left. \begin{array}{l} \text{as } p \rightarrow 1.0 \\ z \rightarrow 2.0 \end{array} \right\}$$

This all assumes termination by disproportionation  
If we assume coupling, account for  $\sim X \cdot + \cdot Y \sim$

$$\Rightarrow \bar{p}_n = \frac{2}{1-p}$$

$$\bar{p}_w = \frac{2+p}{1-p}$$

$$z = \frac{\bar{p}_w}{\bar{p}_n} = \frac{2+p}{2}$$

$$\left. \begin{array}{l} \text{as } p \rightarrow 1.0 \\ z \rightarrow 3/2 \end{array} \right\}$$

## Instantaneous vs. Integrated Rate Expressions

$$R_p = k_p \left( \frac{fk_d}{k_t} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}} [M] = -\frac{d[M]}{dt} \quad \text{instantaneous expression}$$

Express things in terms of  $\pi$  (monomer conversion)

$$\pi = \frac{[M]_o - [M]}{[M]_o} = 1 - \frac{[M]}{[M]_o}$$

$$\frac{d\pi}{dt} = -\frac{1}{[M]_o} \frac{d[M]}{dt}$$

$$\frac{d\pi}{dt} = k_p \left( \frac{fk_d}{k_t} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}} [1 - \pi]$$

integrate assuming a constant  $[I] = [I]_o$ .

$$\pi(t) = 1 - \exp \left[ -k_p \left( \frac{fk_d}{k_t} \right)^{\frac{1}{2}} [I]_o^{\frac{1}{2}} t \right]$$

so applies to batch polymer  $[M] \downarrow$   
but  $[I]$  constant  $\Rightarrow$  e.g. early stages of polymer

If  $[I]$  is not held constant:

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

$$[I] = [I]_o \exp(-k_d t)$$

$$\frac{d\pi}{dt} = k_p \left( \frac{fk_d}{k_t} \right)^{\frac{1}{2}} [I]_o^{\frac{1}{2}} \exp\left(-\frac{k_d t}{2}\right) (1 - \pi)$$

Integrate from  $t=0$  to  $t$ :

$$\pi_t = 1 - \exp \left\{ \left( \frac{2k_p}{k_d} \right) \left( \frac{fk_d}{k_t} \right)^{\frac{1}{2}} [I]_o^{\frac{1}{2}} \left[ \exp\left(-\frac{k_d t}{2}\right) - 1 \right] \right\}$$

global expression: time of conv  $\rightarrow$  conv at that time

