10.569 Synthesis of Polymers
Prof. Paula Hammond

Lecture 3: Step Growth Polymerization, Types of Monomers, Kinetics and Equilibrium Considerations, Closed vs. Open Systems

---

Kinetics of Step Growth Polymerization (Chapter 2)

A + B → polymer + byproduct

$Rp =$ rate of polymerization

$$Rp = \frac{-d[M]}{dt} = \frac{-d[a]}{dt} = \frac{-d[b]}{dt} = k[a][b]$$

Assume r =1, where r is the stoichiometric ratio. $r = \frac{a}{b}$

$$[a] = [b]$$

Terminology $\overline{p_n}$ varies with t → $\overline{p_n} = \frac{[a]_o}{[a]}$

(X_n) p. 50

$$\frac{-d[a]}{dt} = k[a]^2$$

$$\frac{-d[a]}{[a]^2} = kt$$

$$\frac{1}{[a]} - \frac{1}{[a]_o} = kt$$

$$\frac{[a]_o}{[a]} - 1 = [a]_o kt$$

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

in book, $\pi = p$ (p. 46)

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

$$\boxed{[a_o]kt = \frac{1}{1-\pi} - 1 = \overline{p_n} - 1}$$

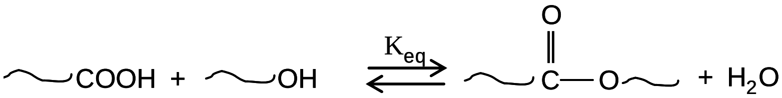
Notes:

1. $[M] \propto \frac{1}{t}$ as time ↑, concentration of monomer ↓
2. $\overline{p_n}$ increases linearly with time

$a + b \underset{k_r}{\overset{k_f}{\rightleftharpoons}} c + d$	$k_f >> k_r$
	LeChatlier's Principle: remove water
	To drive reaction forward

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 course materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date

Making esters:



$$\sim COOH + \sim OH \underset{}{\overset{K_{eq}}{\rightleftarrows}} \sim \overset{\overset{O}{\|}}{C} - O \sim + H_2O$$

Ester can hydrolyze with water and
go backwards (reverse rxn) → drug delivery

$$K_{eq} = \frac{-[COO]- \quad [H_2O]}{[COOH][OH]}$$

Assume at $t = 0$: $[M] = [M]_o$

Put in terms of π:

$$-[COO]- \quad = \pi[COOH]_o = \pi[OH]_o = \pi[M]_o$$

$$[OH] = \qquad \text{“} \qquad \text{“}$$

$$[COOH] \;= [OH] = [M]_o - \pi[M]_o = [M]_o (1 - \pi)$$

$$K = \frac{(\pi[M]_o)^2}{[M]_o^2 (1 - \pi)^2}$$

$$K = \frac{\pi^2}{(1 - \pi)^2}$$

$$\boxed{\pi = \frac{K^{\frac{1}{2}}}{1 + K^{\frac{1}{2}}}}$$

In closed system, limited by K (reaction constant).

That also means rxn and polymer limited by K.

$$\overline{p_n} = \frac{1}{1 - \pi} = 1 + K^{\frac{1}{2}}$$

where $\overline{p_n}$ is the # average degree of polymerization (# of units in polymer)

Polyesterification: K: 1 ~ 10
$\overline{p_n}$ ~ 2 - 5 monomers

Polyamidation: K: 100 – 1000
$\overline{p_n}$: 10 - 40

In between: removing some of the water

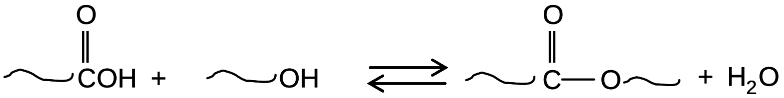
Open Driven System

Removing byproduct

- H_2O by temperature, low pressure, or N_2 blowing of water
- Acid like HCl, base neutralization

$[H_2O] \leftrightarrow MW(\overline{p_n})$ How H_2O affects $\overline{p_n}$

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 course materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date



$$\sim COOH + \sim OH \rightleftharpoons \sim C(=O)-O\sim + H_2O$$

$$K = \frac{[-COO-][H_2O]}{[COOH][OH]} = \frac{\pi[H_2O]}{[M]_o(1-\pi)^2}$$

$$K = \frac{1}{1-\pi}\cdot\frac{\pi}{1-\pi}\cdot\frac{[H_2O]_{eq}}{[M]_o}$$

$$\overline{p_n} = \frac{1}{1-\pi}$$

$$\frac{\pi}{1-\pi} = \frac{1}{1-\pi} - \frac{1-\pi}{1-\pi} = \frac{1}{1-\pi} - 1 = \overline{p_n} - 1$$

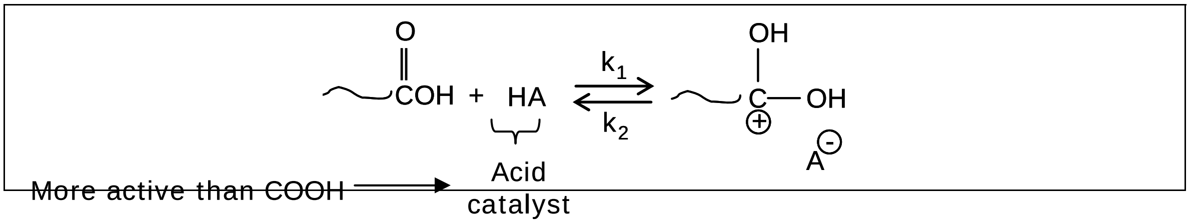
$$K = \overline{p_n}\cdot\left(\overline{p_n} - 1\right)\frac{[H_2O]_{eq}}{[M]_o}$$

$$[H_2O]_{eq} = \frac{[M]_o K}{\overline{p_n}\left(\overline{p_n} - 1\right)}$$

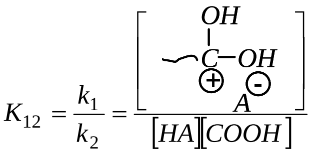
only get down to a certain water concentration

→ solve for best $\overline{p_n}$ possible

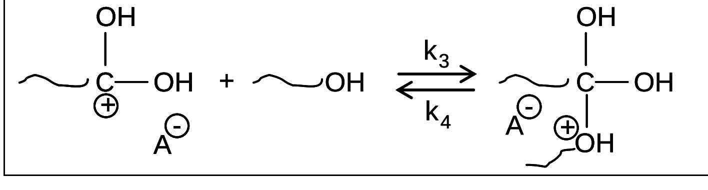
Polyesterification Using Acid Catalysis



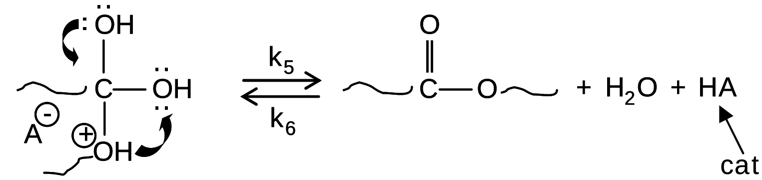
More active than COOH ⟶ $\underbrace{HA}$ Acid catalyst



$$K_{12} = \frac{k_1}{k_2} = \frac{\left[\sim \overset{OH}{\overset{|}{C}}{}^{\oplus}-OH \; A^{\ominus}\right]}{[HA][COOH]}$$

	Slow step (rate-determining step)

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 course materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date



catalyst regeneration

$$R_p = \frac{-d[COOH]}{dt}$$ Rate of disappearance of carboxylic monomer

R_p	$= k_3\left[C^+(OH)_2\right][OH]$	(from previous page)
	$= k_3K_{12}[HA][COOH][OH]$	
	$\underbrace{\qquad\qquad}$	
	From equilibrium expression	[HA] is constant because it's regenerated.

$$R_p = \frac{-d[COOH]}{dt} = k'[COOH][OH] \quad \text{where } k' = k_3K_{12}[HA] \text{ constant}$$

Self-catalyzed: [HA] = [COOH]

$$R_p = \frac{-d[COOH]}{dt} = k''[COOH]^2[OH] \quad \text{where } k'' = k_3K_{12}$$

$$R_p = \frac{-d[M]}{dt} = k''[M]^3$$ separate and integrate

$$2k''t = \frac{1}{[M]^2} - \frac{1}{[M]_o^2}$$

$$[M] = [M]_o(1-\pi)$$

$$\left(\overline{p_n}\right)^2 = \frac{1}{(1-\pi)^2} = 2[M]_o^2\,k't + 1$$

Much slower because of time-dependence ($\sqrt{t}$)
That's why people add acid to drive reaction.

High Temperature

- increase k
- remove byproduct (evaporate H_2O)

Bulk or mass conditions (no solvent)

- $[M]_o$ is maximum
- no need to separate product

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 course materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date

- viscosity η low until high π
- direct processing

Use solvent

- monomers are not miscible with each other but miscible with solvent
- allow high T
- dilute viscous media (carrier for viscous media)
  - → improves processing
- improves heat and mass transfer

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 course materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date