

# The Mayo-Lewis Copolymerization Model

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<http://www-rohan.sdsu.edu/~vadim/mayolewis.pdf>



# Outline

Chemistry

Old Models

New Models



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# Basics

A **polymer** is a large molecule, built up from many small **monomers**. We study the building process.

Consider the polymer as a long necklace.

Note: Branching (non-linear polymers) is possible, but not today.

## Step Polymerization

All monomers and (partial) polymers are simultaneously reactive. (attach two small necklaces)

## Chain Polymerization (our interest today)

A small amount of reactive (partial) polymer absorbs monomers one at a time. (add one bead to a necklace)



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These are classified into types, based on underlying reaction:

**Ionic** (cationic/anionic).

More complex, less common, not today.

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# Radical Chain Polymerization Life Cycle

## Step 1: Radicals are born. (initiator radicals)

Processes used: thermal, redox, photochemical, ionizing radiation, etc.

Very small amount, compared to monomers.

## Step 2..1000: Radicals react with monomers.

radical chain + monomer  $\Rightarrow$  longer radical chain

## Final Step: Radicals die.

Two radical chains react with each other.

Coupling: they become nonradical and merge

Disproportionation: they become nonradical and don't merge



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## Steady-State for Radicals

Radicals are created at a constant rate, and destroyed at a rate proportional to the square of their concentration.

$$\frac{dx}{dt} = a - bx^2; \text{ has solution } x(t) = \sqrt{\frac{a}{b}} \tanh((t + c)\sqrt{ab}).$$

$$\text{As } t \rightarrow \infty, x(t) \rightarrow \sqrt{\frac{a}{b}}.$$

In practice,  $\infty$  is actually quite small.



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# Polymerization Summary

## Molecule Concentrations

Molecule	Initial	In Progress	Final
Monomers	high	decreasing	low
Radicals	none	tiny	none
Polymers	none	increasing	high

We want to understand the rate at which this happens. 'kinetics'

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With one type of polymer, the relevant DE is:

$$\frac{dx}{dt} = -krx$$

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$r$  is the (constant) radical concentration

$k$  is the goal (rate constant)

Too simple for chemists to screw up.

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With two type of monomers, we divide radicals into  $r_x, r_y$  based on last monomer added.

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$k_{yx}, k_{xy} \cong 0$  Block Copolymerization; homogeneous chains

$k_{xx}, k_{yy} \cong 0$  Alternating Copolymerization

$k_{yx} \cong k_{xy} \cong k_{xx} \cong k_{yy}$  Random Copolymerization



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$$\frac{dr_x}{dt} = -\frac{dr_y}{dt} = k_{yx}r_y x - k_{xy}r_x y = 0 \text{ (Mayo, Lewis) BAD IDEA}$$



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# Mayo Lewis Copolymerization Model

Divide  $dx/dt$  by  $dy/dt$ , and use the assumption  $dr_x/dt = 0$

$$\frac{dx}{dy} = \frac{x(k_x x + y)}{y(x + k_y y)} \text{ 'copolymerization equation'}$$

$$k_x = \frac{k_{xx}}{k_{xy}}, k_y = \frac{k_{yy}}{k_{yx}}, \text{ new rate constants}$$

$k_x$  measures the degree to which a radical ending in  $x$  preferentially bonds with  $x$  again. (still meaningful)



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## Using The Copolymerization Equation

$$\frac{dx}{dy} = \frac{x(k_x x + y)}{y(x + k_y y)}$$

Basic use: Take multiple measurements of  $x$ ,  $y$  throughout. Estimate  $\frac{dx}{dy}$  at each paired measurement. With two such, can solve  $2 \times 2$  linear system to find  $k_x$ ,  $k_y$ .

Advanced use: Change variables (e.g. to  $\frac{x}{x+y}$ ,  $\frac{y}{x+y}$ ) and/or manipulate algebraically. Find  $k_x$ ,  $k_y$  through regression. Many variations exist.

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Critical Assumption:  $\frac{dr_x}{dt} = k_{yx} r_y x - k_{xy} r_x y = 0$ .

Note that  $k_{yx}, r_y, k_{xy}, r_x$  are all constants. Hence  $\frac{x}{y} = \alpha$ , for some constant  $\alpha$  independent of  $t$ .

The model collapses;  $x$  and  $y$  must react exactly in their initial proportions. Hence all rate constants are equal ( $x, y$  indistinguishable) 'random model'.



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Can we derive the equation from the starting DEs without the critical assumption?

This has been done (e.g. probabilistic methods).

It doesn't help. The copolymerization equation is equivalent to the critical assumption. It cannot be saved.





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$$\frac{dx}{dt} \cong -k_{xx}r_xX \qquad \frac{dy}{dt} \cong -k_{xy}r_xY$$

$$-k_{xx}r_xX \geq \frac{dx}{dt} \geq -k_{xx}r_xX(1 + \epsilon)$$

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$$k_x \frac{x}{y} \frac{1}{1+\epsilon} \geq \frac{dx}{dy} \geq k_x \frac{x}{y} (1 + \epsilon)$$

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$$-k_{xx}r_xX \geq \frac{dx}{dt} \geq -k_{xx}r_xX(1 + \epsilon)$$

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$$\frac{dx}{dy} \cong k_x \frac{x}{y}$$

Analytic solution:  $\frac{x(t)}{x(0)} = \left( \frac{y(t)}{y(0)} \right)^{k_x}$



# Decoupled Model

Assume vastly more  $r_x$  reactions.

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## Weaknesses of Decoupled Model

$$\frac{dx}{dy} \approx k_x \frac{x}{y}$$

We assumed  $k_{xx}r_x x \gg k_{yx}r_y x$ ,  $k_{xy}r_x y \gg k_{yy}r_y y$ .

We may force  $r_x \gg r_y$  by  $x(0) \gg y(0)$ , hopefully.

However, what if  $k_{xx} \ll k_{yx}$ , or  $k_{xy} \ll k_{yy}$ ?

The error  $\epsilon$  is difficult to determine, and yet has a large effect on the outcome interval.

Need to have  $x(0) \gg y(0)$ .



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## Partially Decoupled Model

Assume extreme relative concentrations of  $x$ ,  $y$  and  $r_x$ ,  $r_y$ :  
 $x \gg y$ ,  $r_x \gg r_y$ . More precisely,  $\frac{y}{x}, \frac{r_y}{r_x} \in [0, \epsilon]$ .

$$\frac{dx}{dt} = r_x x (-k_{xx} - k_{yx} \frac{r_y}{r_x}) = A r_x x \quad A \cong -k_{xx}$$

$$\frac{dy}{dt} = r_x y (-k_{xy} - k_{yy} \frac{r_y}{r_x}) = B r_x y \quad B \cong -k_{xy}$$

$$\frac{dr_x}{dt} = r_x x (-k_{xy} \frac{y}{x} + k_{yx} \frac{r_y}{r_x}) = C r_x x \quad C \cong 0$$

$$-k_{xx} \geq A \geq (-k_{xx} - k_{yx}\epsilon)$$

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## Partially Decoupled Model, II

The system  $\frac{dx}{dt} = Ar_x x$ ,  $\frac{dy}{dt} = Br_x y$ ,  $\frac{dr_x}{dt} = Cr_x x$ ,  
has an analytic solution.

$$x(t) = x(0) \frac{1-\alpha A}{1-\alpha A e^{x(t)(1-\alpha A)Ct}}$$

$$y(t) = y(0) \left( \frac{1-\alpha A}{1-\alpha A e^{x(t)(1-\alpha A)Ct}} \right)^{B/A}$$

$$r_x(t) = \alpha x(0) C \frac{1-\alpha A}{-\alpha A + e^{-x(t)(1-\alpha A)Ct}}$$

$$\frac{x(t)}{x(0)} = \left( \frac{y(t)}{y(0)} \right)^{A/B}$$

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More precisely,  $\frac{x(t)}{x(0)} = \left(\frac{y(t)}{y(0)}\right)^{A/B}$

$$-k_{xx} \geq A \geq (-k_{xx} - k_{yx}\epsilon)$$

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Error Range:

$$\frac{A}{B} - \epsilon k_* \leq k_x \leq \frac{A}{B} (1 + \epsilon k_y k_*)$$

$$k_x = \frac{k_{xx}}{k_{xy}}, k_y = \frac{k_{yy}}{k_{yx}}, k_* = \frac{k_{yx}}{k_{xy}}$$



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## Weaknesses of Partially Decoupled Model

$$\frac{x(t)}{x(0)} \simeq \left( \frac{y(t)}{y(0)} \right)^{k_x}$$

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Error range depends on  $k_y, k_x$ . Can estimate  $k_y$  through dual experiment, but  $k_x$  is a mystery.

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## Future Work

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