# Lecture 5
# Chain copolymerization

# Copolymerization

- Copolymers involve the use of two or more monomers.
- Copolymers allow us to tailor product properties.

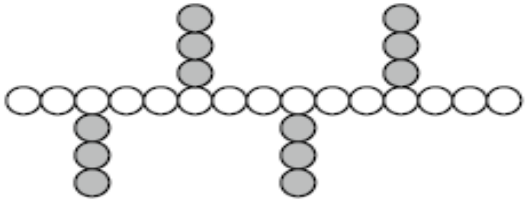
➢ **Types of copolymer**

**Regular copolymer**

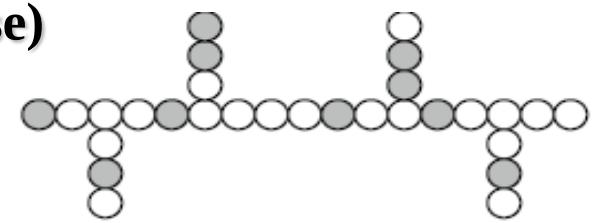
**Random copolymer**

**Block copolymer**

**Graft copolymer**

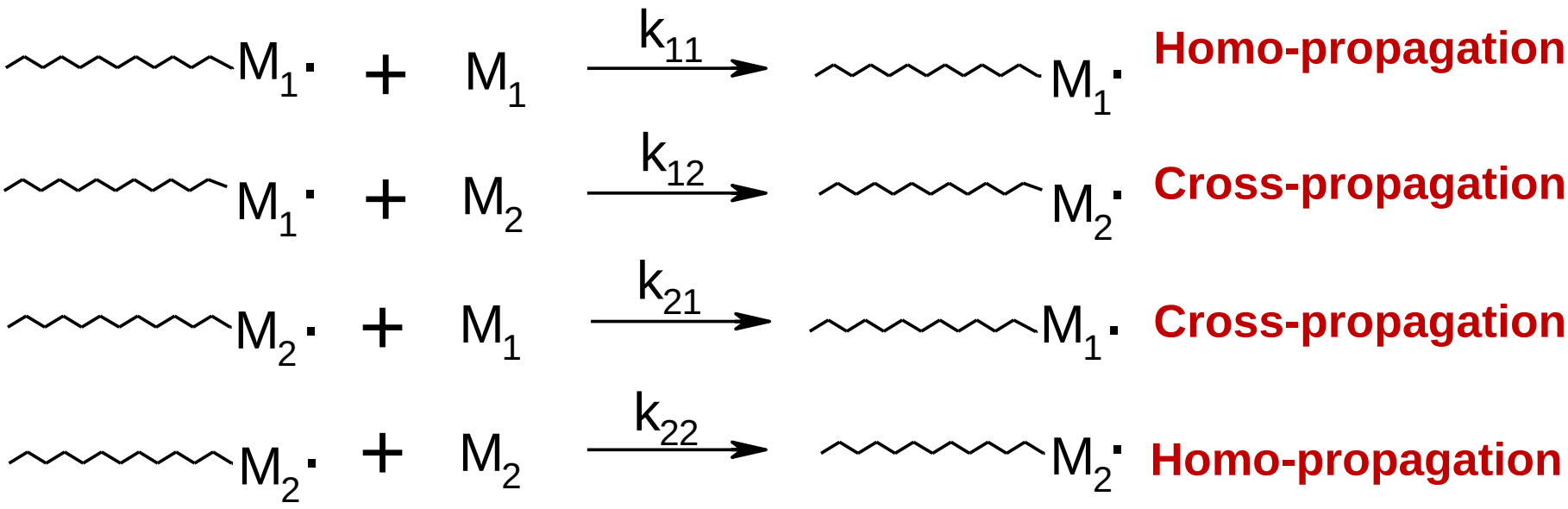


**Actual copolymer (case)**



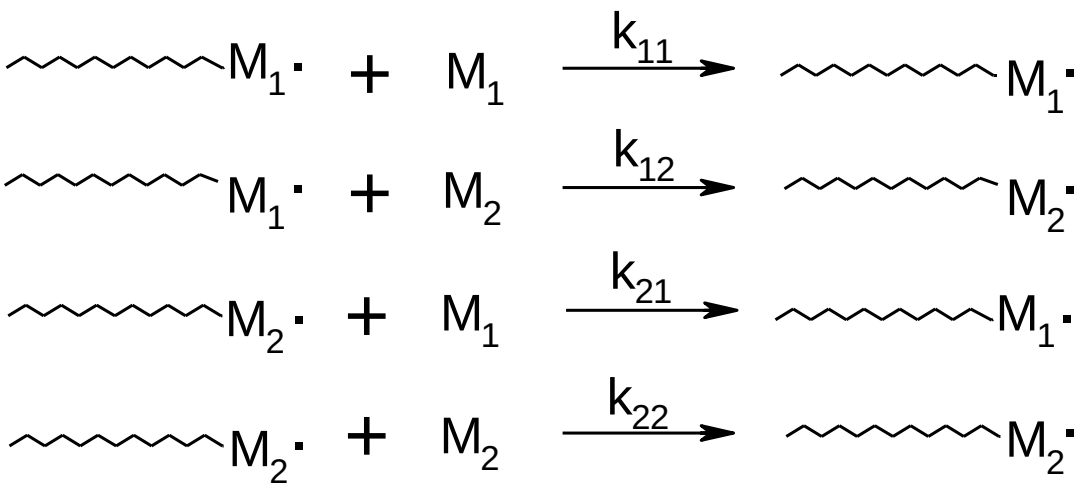
# Copolymerization Kinetics

**Only Binary Case**
**Two Monomers; M1 + M2**




**Terminal Model**

# Copolymerization Kinetics




$R_{p11} = k_{11}[M_1\bullet][M_1]$

$R_{p12} = k_{12}[M_1\bullet][M_2]$

$R_{p21} = k_{21}[M_2\bullet][M_1]$

$R_{p22} = k_{22}[M_2\bullet][M_2]$

**The rate of disappearance of *$M_1$* and *$M_2$* can be expressed as:**

$$-\frac{d[M_1]}{dt} = k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1]$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2]$$

# Copolymerization Kinetics

The ratio of the two rates is then:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{k_{11}[M_1\cdot] + k_{21}[M_2\cdot][M_1]}{k_{12}[M_1\cdot] + k_{21}[M_2\cdot][M_2]} \qquad \text{.....(1)}$$

**Instantaneous ratio of monomers in copolymer**

Assume the Steady State Approximation:

The concentrations of $M_1\bullet$ and $M_2\bullet$ are constant

Therefore: The rate of addition of $M_1\bullet$ to $M_2$ will equal
The rate of addition of $M_2\bullet$ to $M_1$

$$-\frac{d[M_1\cdot]}{dt} = -\frac{d[M_2\cdot]}{dt} = 0$$

$$k_{12}[M_1\cdot][M_2] = k_{21}[M_2\cdot][M_1] \qquad \frac{[M_1\cdot]}{[M_2\cdot]} = \frac{k_{21}[M_1]}{k_{12}[M_2]} \qquad \text{.....(2)}$$

# Copolymer Equation

**From ① and ②**

$$\frac{d[M_1]}{d[M_2]} = \frac{1 + r_1 \dfrac{[M_1]}{[M_2]}}{1 + r_2 \dfrac{[M_2]}{[M_1]}}$$

**where** $r_1 = \dfrac{k_{11}}{k_{12}}$ , $r_2 = \dfrac{k_{22}}{k_{21}}$ ← **monomer reactivity ratio**

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}$$

Copolymer Composition Equation:

**Molar ratio of the monomers in the *copolymer***

**$[M_1]$ and $[M_2]$ Concentrations of the monomers in the *feed***

# Meaning of r & Definition of $f_1$, $F_1$

## Meaning of r

$r_1$ characterizes the reactivity of the 1 radical with respect to the two monomers, 1 and 2

$r_1 > 1$ then homopolymerization growth is preferred

$r_1 = 0$ then only reaction with 2 will occur

**Define $f_1$, $F_1$**

**$f_1$, $f_2$ : mole fractions of monomers in feed**
**$F_1$, $F_2$ : mole fractions of monomers in polymer**

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1 + M_2]} \quad \cdots\cdots ③ \qquad F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \quad \cdots\cdots ④$$

From ③, ④

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad \cdots\cdots ⑤$$

**How come?**

# Ideal Copolymerization

## Ideal Copolymerization

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]}$$

$$= r_1 \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{r_1[M_1]+[M_2]}$$

$$= r_1 \frac{[M_1]}{[M_2]}$$

**where** $r_1 \cdot r_2 = 1 \longrightarrow r_2 = \frac{1}{r_1}$

$$F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2}$$

$$\frac{k_{11}}{k_{12}} \cdot \frac{k_{22}}{k_{21}} = 1$$

$$\frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}}$$

**Most ionic copolymerizations are characterizes by the ideal type of behavior**

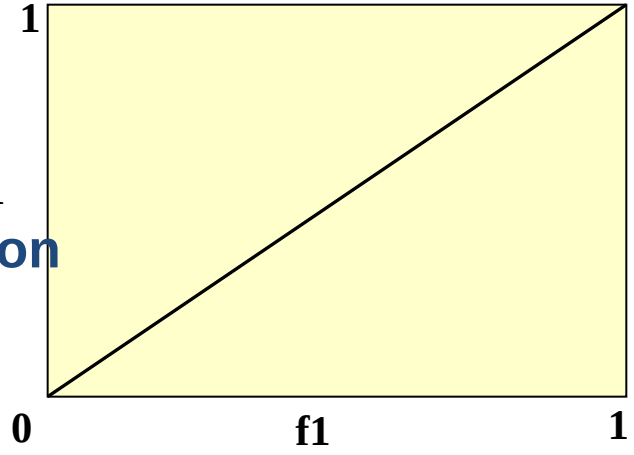
**When** $r_1 = 1 = r_2$ **, the two monomers show equal reactivity toward both propagating species**

$\longrightarrow$ **random copolymer**

# Ideal Copolymerization

$r_1 > 1 \quad r_2 < 1 \quad$ **or** $\quad r_1 < 1 \quad r_2 > 1$

**One of the monomer is more reactive than the other toward both propagating spices. The copolymer will contain a larger proportion of the more reactive monomer in random placement**




$r_1 = r_2 = 1.0$

- Monomers exhibit no preference for homo-propagation vs. cross-propagation
- Truly random copolymer results
- $F_1 = f_1$
- Ethylene / vinyl acetate

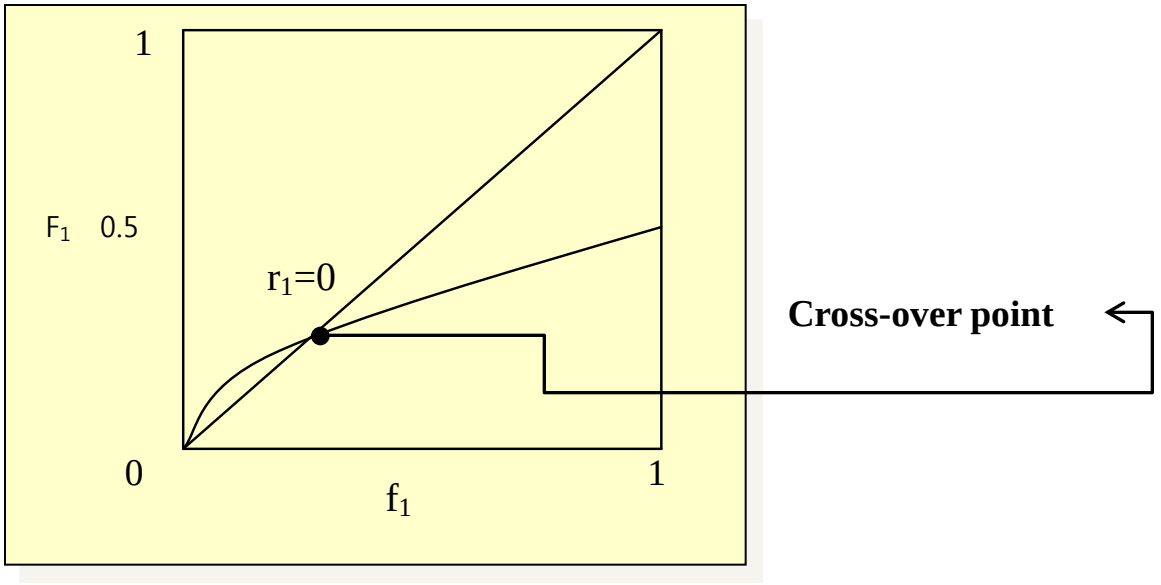
# Alternating Copolymerization

## Alternating Copolymerization

$r_1 = r_2 = 0$

**or**

$r_1 r_2 = 0$




**As $r_1$, $r_2$ approach to zero, alternating tendency can be observed**

**If** $r_1 = r_2 = 0 \rightarrow$ **perfect alternation!**

$$\frac{d[M_1]}{d[M_2]} = 1$$

$$F_1 = 0.5 = \frac{d[M_1]}{d[M_1] + d[M_2]}$$

Styrene / maleic anhydride

**If** $r_1 < 1$ , $r_2 < 1$ $F_1 / f_1$ **plots cross the line representing** $F_1 = f_1$

**If** $r_1 = r_2 = \infty$, **then, become a homopolymer**

# Alternating Copolymerization

**Mean of Cross-over Point**

$$F_1 = f_1$$

**At these crossover points the copolymer and feed compositions are the same and copolymerization occurs without a change in the feed composition**

**Such copolymerizaions are termed Azeotropic copolymeriztions.**

the composition of an azeotropic blend will be constant throughout the polymerization, that is, both the feed and the copolymer composition will not change.

**Condition of Azeotropic copolymeriztion**

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \quad \textbf{and} \quad \frac{[M_1]}{[M_2]} = \frac{(r_2 - 1)}{(r_1 - 1)}$$

$$\because \quad F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]} = \frac{[M_1]}{[M_1] + [M_2]} = f_1$$

# Condition of Azeotropic copolymeriztion

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]}$$

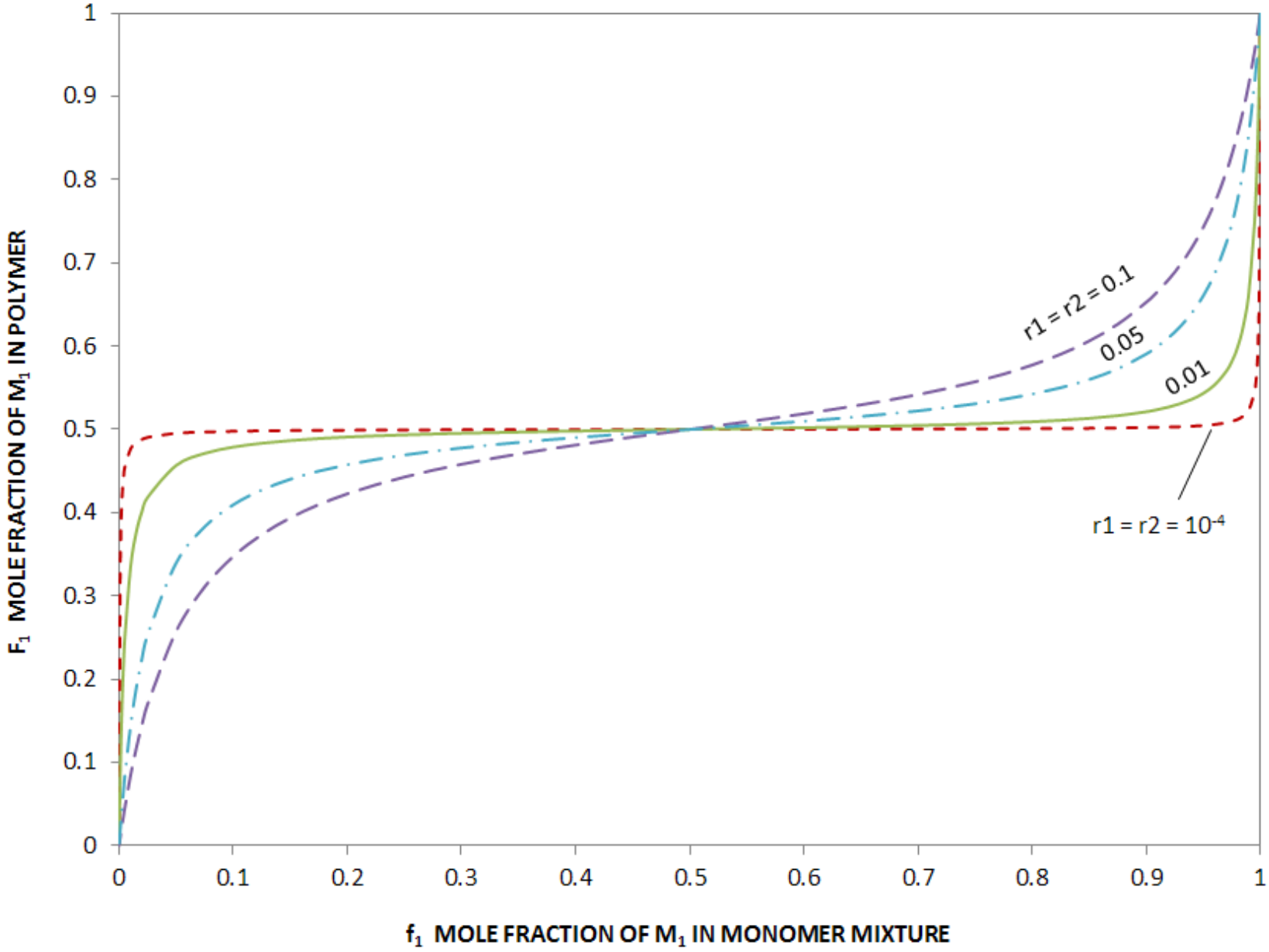
$$r_1[M_1]+[M_2] = [M_1]+r_2[M_2]$$

$$r_1 \frac{[M_1]}{[M_2]} + 1 = \frac{[M_1]}{[M_2]} + r_2$$

$$\frac{[M_1]}{[M_2]} = \frac{r_2 - 1}{r_1 - 1} \qquad f_1 = \frac{[M_1]}{[M_1]+[M_2]}$$

$$\frac{1}{f_1} = 1 + \frac{[M_2]}{[M_1]} = 1 + \frac{r_1 - 1}{r_2 - 1} = \frac{r_2 + r_1 - 2}{r_2 - 1}$$

$$\therefore \quad f_1 = \frac{r_2 - 1}{r_2 + r_1 - 2} = \frac{1 - r_2}{2 - r_1 - r_2}$$


1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
F1 MOLE FRACTION OF M1 IN POLYMER
f1 MOLE FRACTION OF M1 IN MONOMER MIXTURE
r1 = r2 = 0.1
0.05
0.01
r1 = r2 = 10-4

# Experimental Determination of $r_1$ & $r_2$

## Experimental Determination of $r_1$ & $r_2$

### 1.Mayo and Lewis

**rearrange copolymer eq. and can get**

$$r_2 = \frac{[M_1]}{[M_2]} \cdot \left\{ \frac{d[M_2]}{d[M_1]} \left[ 1 + \frac{r_1[M_1]}{[M_2]} \right] - 1 \right\}$$

**monomer comp**

$[M_1]/[M_2]$

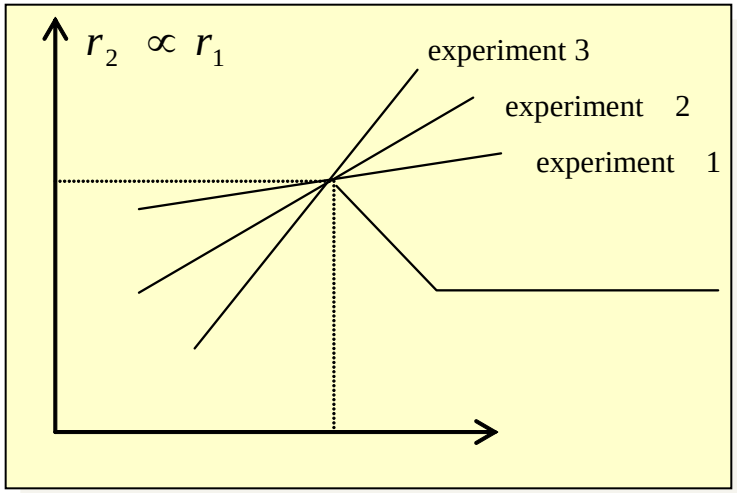
⋮

**copolymer comp.**

$d[M_1]/d[M_2]$

⋮

**then vary $r_1$ value (put) and iterate**




**This Δ is more for smaller, $r_1$, $r_2$ value calculate with accuracy**

For each different monomer composition, a line is generated using arbitrary r1 values. The intersection of these lines is the r1 and r2 for the system. More frequently, the lines do not intersect and the area in which most line intersect can be given as a range of r1and r2 values.

# Experimental Determination of $r_1$ & $r_2$

## 2. Finemann and Ross

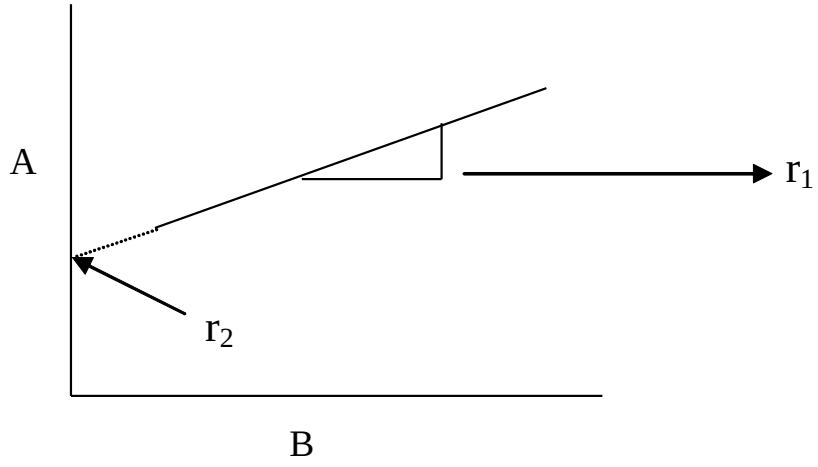
**Recall**

$$F_1 = \frac{r_1 f_1^{\,2} + f_1 f_2}{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}}$$

$$\underbrace{\frac{f_1(1-2F_1)}{F_1(1-f_1)}}_{\mathbf{A}} = r_2 + \underbrace{\frac{f_1^{\,2}(F_1-1)}{F_1(1-f_1)^2}}_{\mathbf{B}} \cdot r_1$$

**A const.** **B const.**

**at low conversion**




**Slope : $r_1$**
**Intersection : $r_2$**