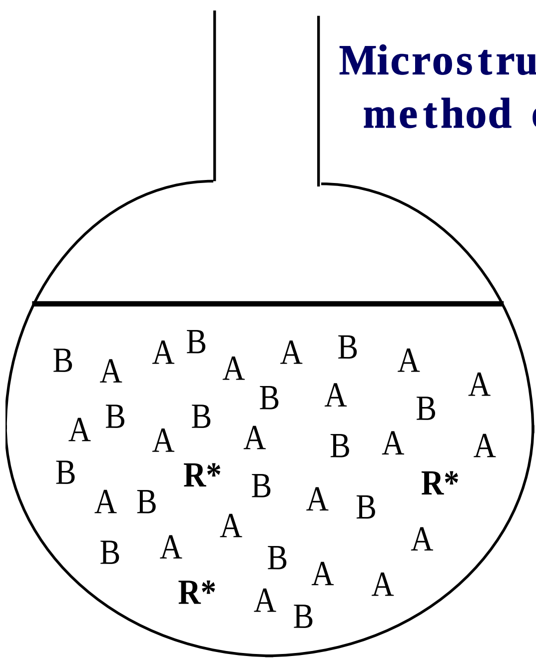
COPOLYMERIZATION

POLYMERIZATION OF TWO OR MORE MONOMERS

Examples:
Poly(ethylene-co-propylene) (EP)
Poly(styrene-co-butadiene) (SBR)
Poly(vinylidine chloride-co-vinyl chloride) (Saran®)



Microstructure depends on method of polymerization

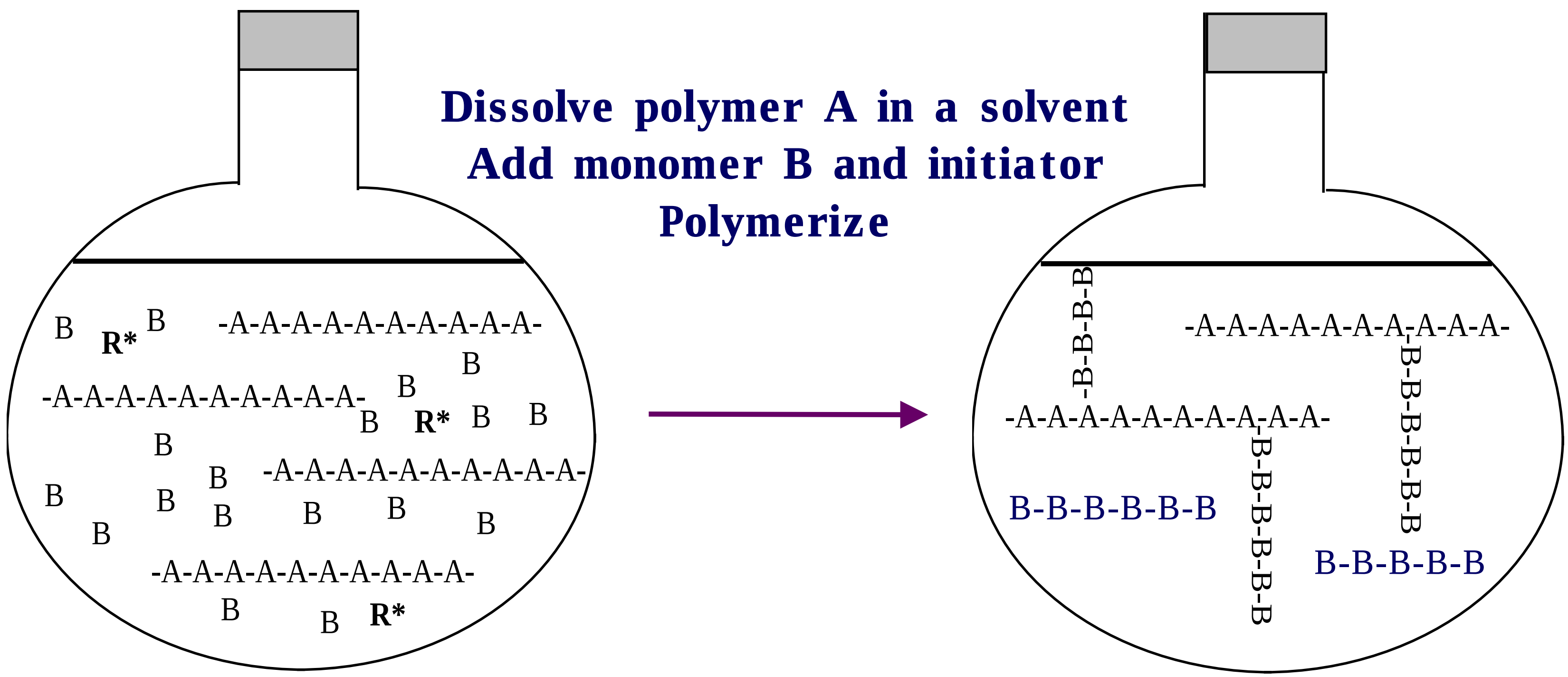
Random Copolymers
-A-B-B-B-A-A-B-A-B-A-A-A-B-A-B-B-

Alternating Copolymers
-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-

Block Copolymers
A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B-B-A-A-A-A-A-A

POST POLYMERIZATION OR HOW TO MAKE A GRAFT COPOLYMER

Examples:
High Impact Polystyrene (HIPS)
Acrylonitrile / Butadiene / Styrene (ABS)



FREE RADICAL COPOLYMERIZATION

ARE "RANDOM" COPOLYMERS REALLY RANDOM ?

$$\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\ A^* \xrightarrow{A} \sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim A\ \text{--}\ A^*$$

$$\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\ A^* \xrightarrow{B} \sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim A\ \text{--}\ B^*$$

$$\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\ B^* \xrightarrow{A} \sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\ B\ \text{--}\ A^*$$

$$\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\ B^* \xrightarrow{B} \sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\ B\ \text{--}B^*$$

DO A's ADD TO A's AS EASILY AS B's ADD TO A's ?
(and vice - versa)

POSSIBLE PRODUCTS

COPOLYMERIZATION OF MONOMERS M_1 AND M_2

- Homopolymers
- Alternating copolymers
- ”Ideal" or truly random copolymers
- Non ideal copolymers - tendency to "blockiness” or alternating

KINETICS OF COPOLYMERIZATION

$$\sim\sim\sim\sim\sim\sim\sim\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim\sim\sim\sim\sim\sim\sim\sim M_1\cdot$$

$$\sim\sim\sim\sim\sim\sim\sim\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim\sim\sim\sim\sim\sim\sim\sim M_2\cdot$$

$$\sim\sim\sim\sim\sim\sim\sim\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim\sim\sim\sim\sim\sim\sim\sim M_1\cdot$$

$$\sim\sim\sim\sim\sim\sim\sim\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim\sim\sim\sim\sim\sim\sim\sim M_2\cdot$$

TENDENCIES

1. BLOCKS AND / OR HOMOPOLYMER
IF $k_{11} > k_{12}$ AND $k_{22} > k_{21}$

2. ALTERNATING IF $k_{12} > k_{11}$ AND $k_{21} > k_{22}$

3. RANDOM COPOLYMERS IF $k_{11} = k_{12}$
AND $k_{22} = k_{21}$

REACTIVITY RATIOS

DEFINE

$$r_1 = \frac{k_{11}}{k_{12}} \qquad r_2 = \frac{k_{22}}{k_{21}}$$

WHAT IF

$r_1 , r_2 >> 1$?

$r_1 , r_2 << 1$?

$r_1 = r_2 = 1$?

$r_1 r_2 = 1$?

KINETICS OF COPOLYMERIZATION

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

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

Divide and eliminate [M]• terms using STEADY STATE ASSUMPTION

- $M_1\cdot$, $M_2\cdot$ generated and consumed at equal rates. we only need focus on one type of radical; e.g. $M_1\cdot$

$$\boxed{k_{12}[M_1\cdot][M_2] = k_{21}[M_2\cdot][M_1]}$$

COPOLYMER EQUATION

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

or

$$\frac{d[M_1]}{d[M_2]} = \frac{(r_1[M_1]/[M_2]+1)}{(r_2[M_2]/[M_1]+1)}$$

remember

$$r_1 = \frac{k_{11}}{k_{12}} \qquad r_2 = \frac{k_{22}}{k_{21}}$$

COPOLYMER EQUATION

It is often more convenient to work in terms of mole fractions.

define :

F_1 = mole fraction of monomer 1 in the polymer at some instant of time

$\mathbf{f_1}$ = mole fraction of monomer 1 in the feed at the same instant of time

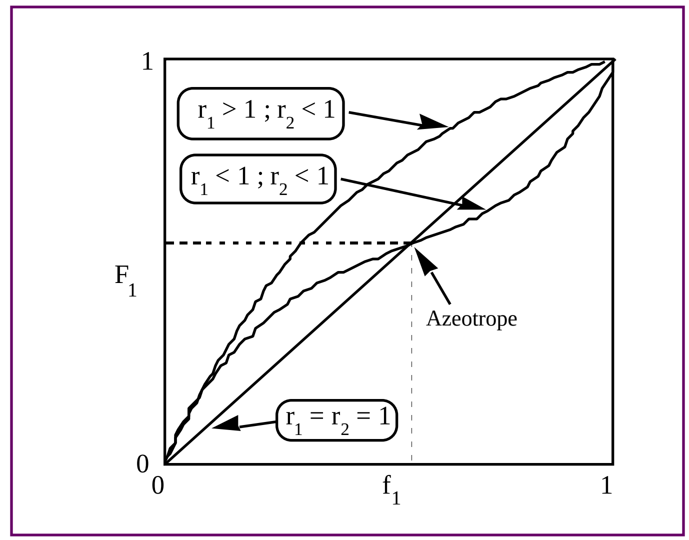
$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]}$$

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]}$$

COPOLYMER EQUATION

$$F_1 = \frac{(r_1 - 1 \;\; f_1) + f_1^{\,2}}{(r_1 + r_2 - 2)f_1^{2} + 2 \; (1 - r_2) \, f_1 + r_2}$$

Note that this equation describes the instantaneous copolymer composition



In a batch copolymerization composition will "drift " with conversion . to treat this properly we need to first do some statistics,but here we will just give a couple of illustrations

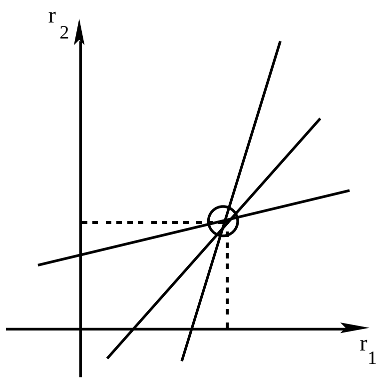
DETERMINATION OF REACTIVITY RATIOS

There are some older methods based on rearrangements of the copolymer equation

LET $\dfrac{[M_1]}{[M_2]} = x$ and $\dfrac{d[M_1]}{d[M_2]} = y$

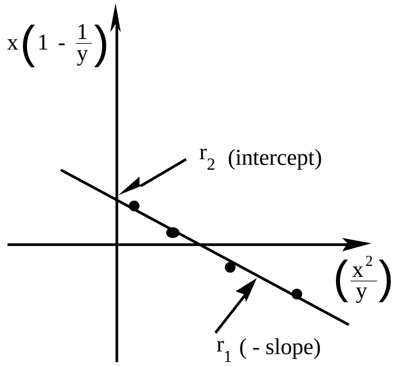
THEN $$y = \frac{1 + r_1 x}{1 + \dfrac{r_2}{x}}$$

$$r_2 = \frac{x(r_1 x + 1)}{y} - x$$



MAYO - LEWIS PLOT

$$x\left(1 - \frac{1}{y}\right) = r_1\left(\frac{x^2}{y}\right) - r_2$$



FINEMAN - ROSS PLOT

DETERMINATION OF REACTIVITY RATIOS

ALSO;

KELEN TUDOS PLOT

Q - e SCHEME

APPLICATION OF PROBABILITY THEORY AND nmr SPECTROSCOPY

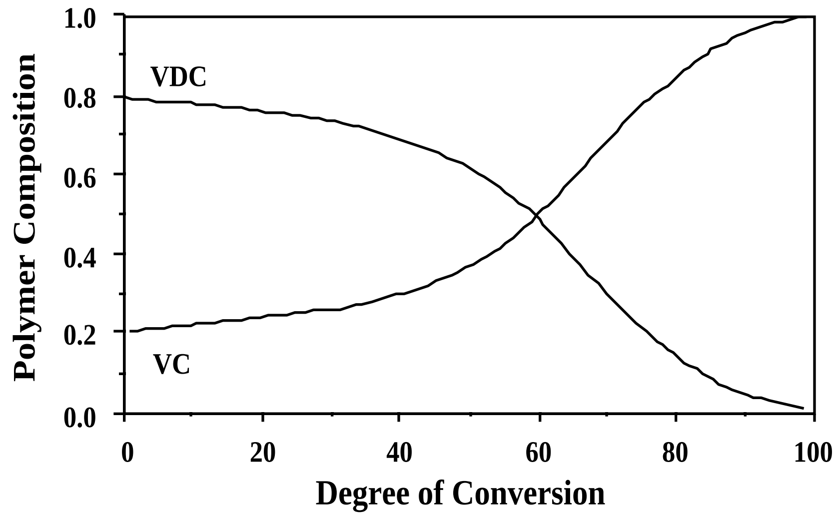
POLYMER SYNTHESIS—COPOLYMERIZATION
THE COPOLYMER EQUATION

$$y = \frac{1 + r_A x}{1 + \frac{r_B}{x}}$$

x = Composition of the Feed = $\frac{[A]}{[B]}$

y = Composition of the Instaneously Formed Polymer = $\frac{P_1[A]}{P_1[B]}$

Copolymer Composition as a Function of Conversion



Compositional variation for vinylidine chloride/vinyl chloride copolymers.