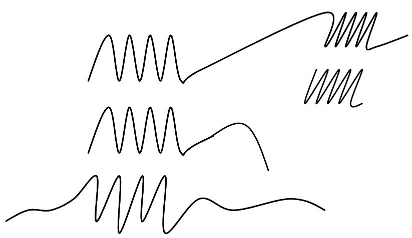
10.569 Synthesis of Polymers
Prof. Paula Hammond
Lecture 16: Ziegler-Natta, Stereochemistry of Polymers

"Precipitation Polymerization"

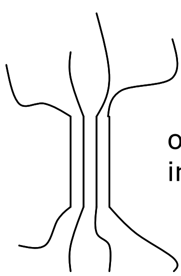
polymer: -semicrystalline
-semicrystalline polymer not soluble in monomer

⇒ crystalline regions insoluble
⇒ amorphous regions remain soluble

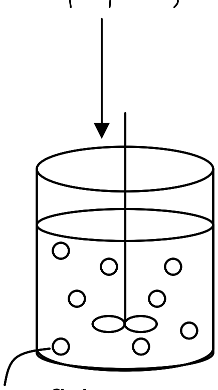
Polymerization in bulk monomer
As # of high MW chains ↑, precipitation occurs



also:

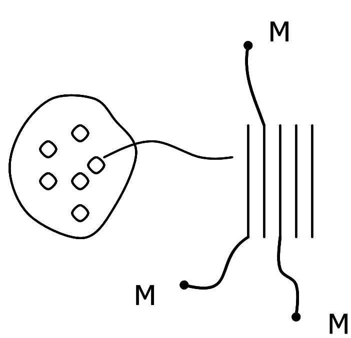


occur in polymer chains with enough irregularity to form short chains



-some active sites remain accessible via diffusion through pores

polymer flakes, particles, etc. are porous



monomer can still diffuse to active sites

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

Kinetics

- ill-defined and complex
- similar to emulsion polymerization
- can have red light/green light effect with free radicals

⇒ gain advantages

→ more temp/heat control
→ low η (can dilute slurry)
→ no surfactant

Common Monomers	$T_{m,crys}$
Vinyl chloride	140 – 200°C
Vinyl fluoride	200 – 230°C
Vinylidene fluoride	200°C
Acrylonitrile	317°C
Tetrafluoroethylene (Teflon)	327°C

Dispersion Polymerization

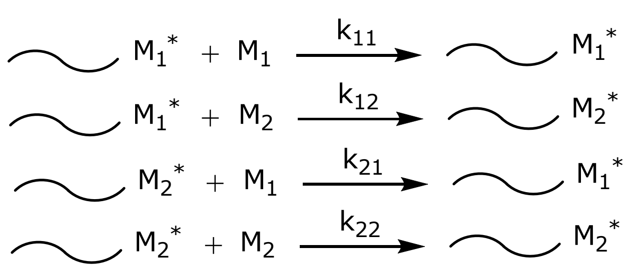
- monomer
- organic solvent (good for monomer, bad for polymer)
- initiator
- particle stabilizer: repel sticky polymers, avoid coalescence

As polymerization occurs, form large solid/semisolid particles of polymer

Random copolymers

Incorporating 2 or more different monomer units in chain growth process (radical, cationic, or anionic polymerizations)

Consider 2 different monomers: 1 and 2



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

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

The ratio of rates of monomers entering polymer chains

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]}$$ (relative rates)

Assume steady state concentration of both $[M_1^*]$ and $[M_2^*]$

$\Rightarrow$ Rate of $M_2^* \rightarrow M_1^*$ = rate of $M_1^* \rightarrow M_2^*$

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2]$$

Simplify and combine with $\frac{d[M_1]}{d[M_2]}$:

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

where $r_1 \equiv \frac{k_{11}}{k_{12}}$ and $r_2 \equiv \frac{k_{22}}{k_{21}}$ (reactivity rates)

reactivity of M_1^* with M_1 versus M_1^* with M_2 } r_1

reactivity of M_2^* with M_2 versus M_2^* with M_1 } r_2

Fraction of each monomer:

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

$\Rightarrow$ expressions for monomer composition

Define:

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

Combine expressions and definitions:

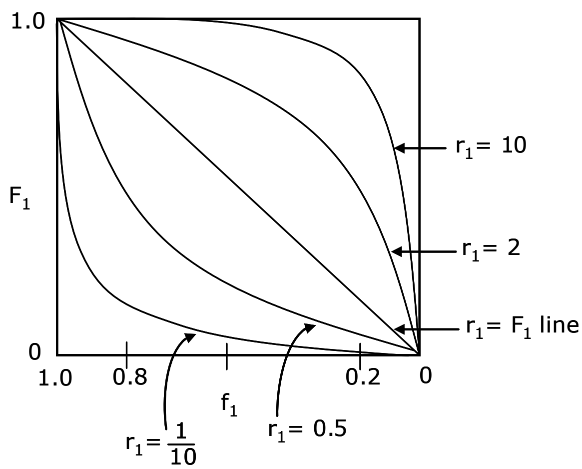
$$\boxed{F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}}$$ copolymer composition equation

Special Cases:

1. "Ideal" copolymerization:

$$\Rightarrow \quad \left.\begin{array}{l} r_1 \cdot r_2 = 1.0 \\ \dfrac{k_{22}}{k_{21}} = \dfrac{k_{12}}{k_{11}} \\ r_2 = \dfrac{1}{r_1} \end{array}\right\}$$

probability of ~M_1^* or ~M_2^* react with M_1 vs M_2 is equal



special case:
$r_1 = r_2 = 1.0$
$\Rightarrow f_1 = F_1$
Bernoullian (random) arrangement of monomers
large r1 $\Rightarrow$ monomers want to react with M_1 much more than M_2

Simplified expression for ideal copolymerizations:

$$F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2} \qquad (r_1 \cdot r_2 = 1.0)$$

2. $r_1 = r_2 = 0$

neither M_1 nor M_2 react with themselves

$$\left.\begin{array}{l} M_1 \rightarrow M_{2*} \\ M_2 \rightarrow M_{1*} \end{array}\right\}$$

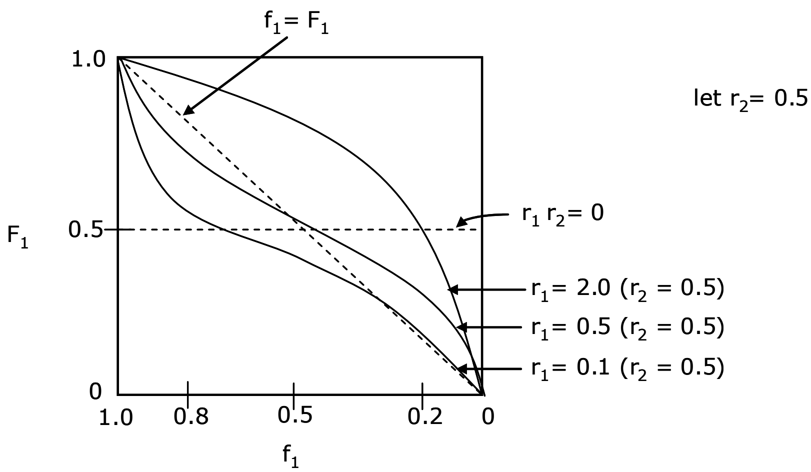
Perfectly alternating composition: $M_1M_2M_1M_2$… (not random at all)

Regardless of f_1: $F_1 = 0.5$

2 extremes:

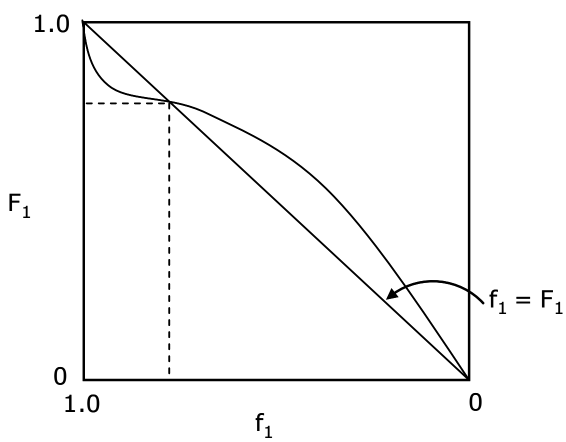
- perfect Bernoullian (random) case: $r_1 = r_2 = 1$
  $r_1 r_2 = 1$
- perfect alternating case: $r_1 = r_2 = 0$
  $r_1 r_2 = 0$

As $r_1 r_2$ product goes from $0 \rightarrow 1.0$, move from random to alternating sequencing:



If $r_1 < 1.0$ and $r_2 < 1.0$

Then induce inflection $\Rightarrow$ form an azeotrope:



at the azeotrope:
$F_1 = f_1$
If you can maintain f1
$\rightarrow$ copolymer comp will not change throughout polymer

Find azeotrope condition:

$$f_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)}$$ azeotrope exists at this monomer composition

- Block polymer: If $r_1 > 1$, $r_2 > 1$

$M_1M_1M_1M_1M_2M_2M_2M_2$

- Consecutive homopolymer if $r_1 >> r_2$

M_1 homopolymerizes $r_1 >> 1$
Then
M_2 homopolymerizes $r_2 << 1$