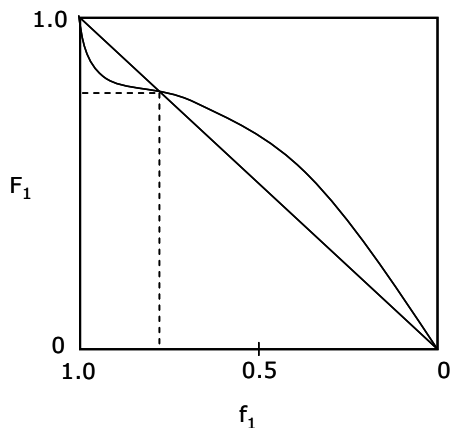


10.569 Synthesis of Polymers
 Prof. Paula Hammond
Lecture 17: Stereoregular Polymerizations

Final comments: copolymerization

Recall azeotrope: occurs $r_1, r_2 < 1$



$\Rightarrow f_1 = F_1$
 monomer comp = final copolymer comp
 - if you have no perturbations, can get same composition throughout full range of π
 - if there is perturbation \rightarrow move further and further away from $f_1 = F_1$

For all copolymerizations in which
 - azeotrope comp
 - perfectly alternating system ($f_1 = F_1$)
 We have unchanged polymer composition

BUT for all other cases (most cases), monomer compositions are continually changing.
 - must create different expressions and integrate to get polymer composition averaged over conversion

Skeist:

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

$$\int_{M_o}^M \frac{dM}{M} = \ln \frac{[M]}{[M]_o} = \int_{(f_1)_o}^{f_1} \frac{df_1}{(F_1 - f_1)}$$

$$\pi = 1 - \frac{[M]}{[M]_o} = 1 - \left[\frac{f_1}{(f_1)_o} \right]^\alpha \left[\frac{f_2}{(f_2)_o} \right]^\beta \left[\frac{(f_1)_o - \delta}{(f_1 - \delta)} \right]^\gamma$$

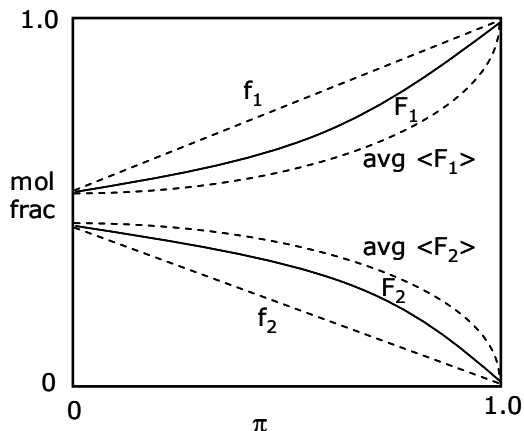
where

$$\alpha = \frac{r_2}{1 - r_2}$$

$$\beta = \frac{r_1}{1 - r_1}$$

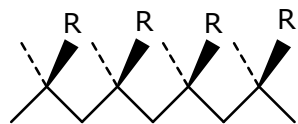
$$\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)}$$

$$\delta = \frac{1 - r_2}{(2 - r_1 - r_2)}$$

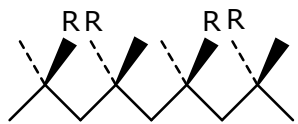


For $r_2 > r_1$
 (M_2 consumed more rapidly)

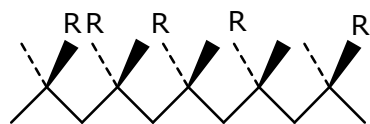
Stereochemistry of polymer chains



isotactic (same side)

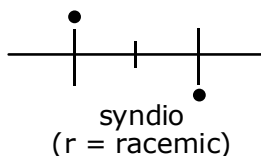
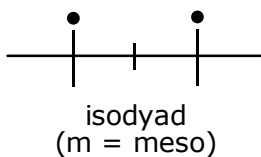


syndiotactic (alternating)



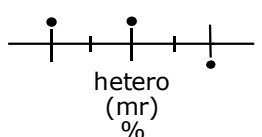
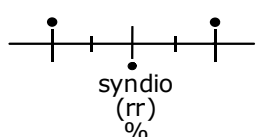
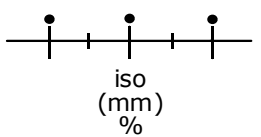
atactic (no sequence, random)

Dyad tacticity

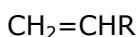


fraction $m + r = 1.0$

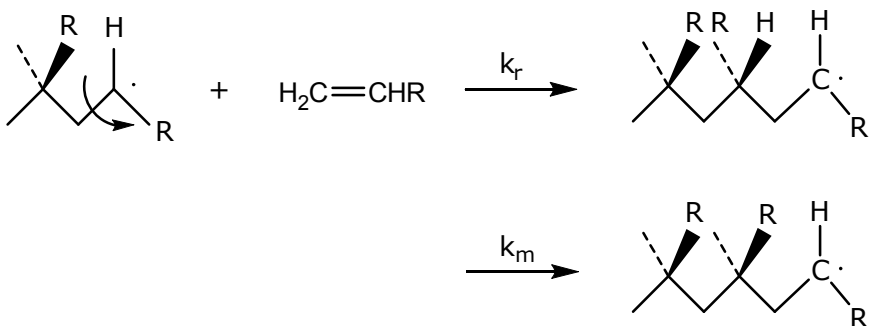
Triad tacticity



$mm + rr + mr = 1$
use percentages = 100%
(use NMR to determine percentage)



In "normal" solution/bulk free radical polymerization



$\frac{k_r}{k_m} \Rightarrow$ determine tacticity

$\frac{k_r}{k_m} \sim 1.0 \Rightarrow$ atactic

$\frac{k_r}{k_m} \ll 1.0 \Rightarrow$ isotactic

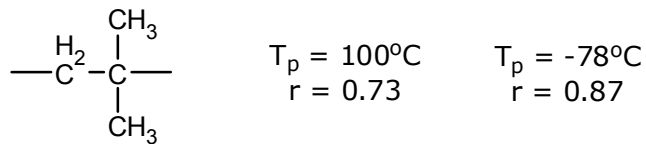
$\frac{k_r}{k_m} \gg 1.0 \Rightarrow$ syndiotactic

Sterics prefer syndiotactic addition.

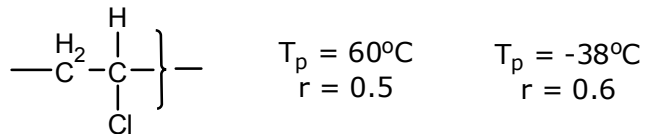
E_a slightly higher for iso addition

As $T \uparrow$ iso fractions \uparrow
 $T \downarrow$ syndio fractions \uparrow

e.g. PMMA:



e.g. PVC

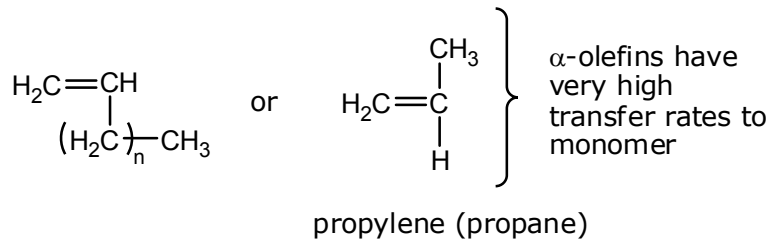


Coordination Polymerization

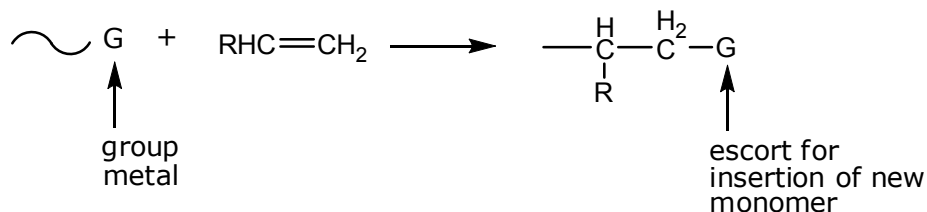
Coordinated catalyst: usually metal/metal halide or oxide complex:
- promote stereospecific + controlled addition of monomer

Ziegler and Natta Nobel Prize, 1963
(Germany) (Italy)

e.g.



Initiator: Group I-III metal (e.g. Al)
+ transition metal (e.g. Ti)

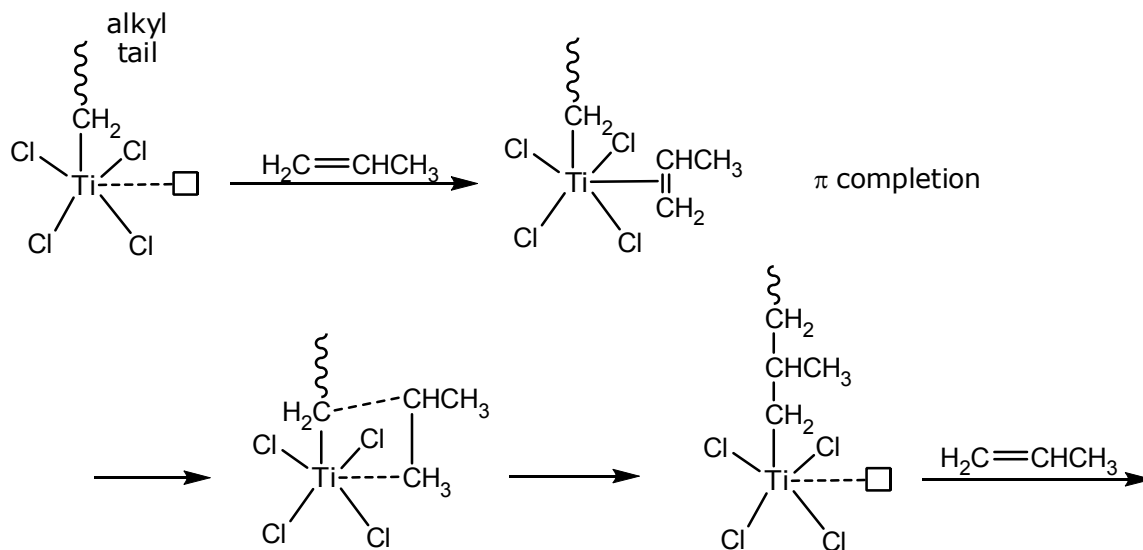


Ziegler-Natta Catalyst

Usually TiCl_4 or TiCl_3

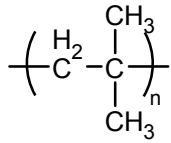
+

$\text{AlR}_3 + \text{AlR}_2\text{Cl}$
R = CH_2CH_3 or $(\text{CH}_2)_n\text{CH}_3$



“Escort” process guides stereochemistry
many of Z-N catalysts
(crys) \Rightarrow isotactic addition
(soluble) \Rightarrow syndiotactic

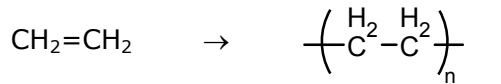
Consider polypropylene



Atactic PP: $T_g \sim -70^\circ\text{C}$
 fully noncrystalline
 liquid-like, paste

Isotactic PP: $T_m = 170^\circ\text{C}$
 highly crystalline
 amorphous region: $T_g \sim -50^\circ\text{C} - -60^\circ\text{C}$
 insoluble

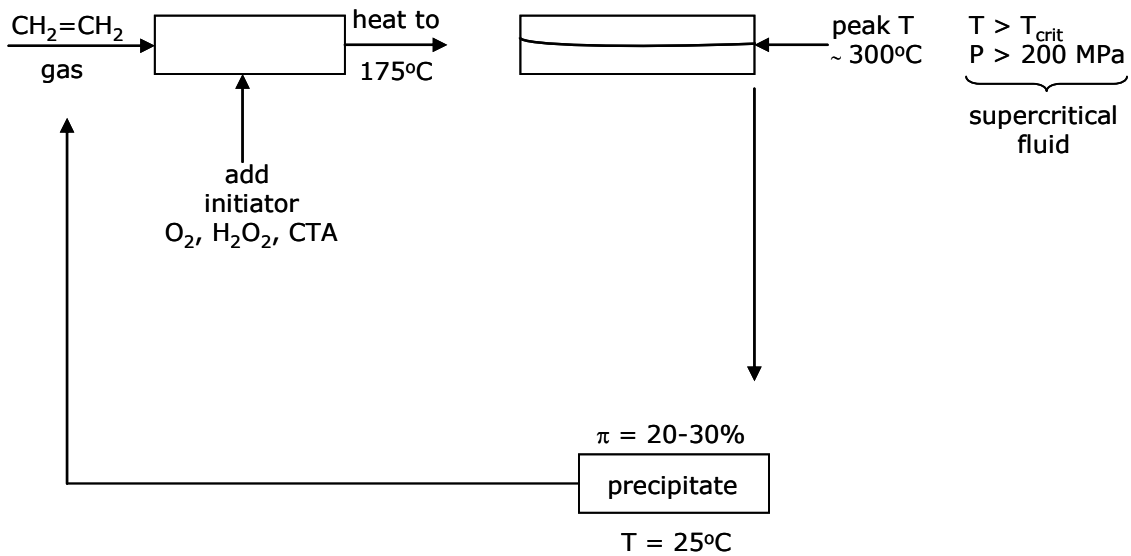
Syndiotactic PP: very crystalline $T_m \sim 130^\circ\text{C}$



regular structure

Traditional free radical polymerization

Tubular Reactors: 2-6 cm in diameter
 0.5 - 1.5 km in length



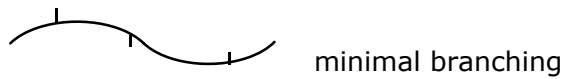
Chain transfer to monomer and polymer:



Branches hinder crystallinity
Low density PE (LDPE)
 $\rho = 0.9 \text{ g/cm}^3$
 $T_g = -120^\circ\text{C}$
 $T_m = 105^\circ\text{C}$

Highly branched,
Irregular length

Z-N catalyst: reduce transfer



High density PE (HDPE)
% crystallinity: 80-90%
 $\rho = 0.94 - 0.96$
 $T_m > 130^\circ\text{C}$