

Chapter 6



Stereochemistry and Coordination Polymerization

Isomerism in polymers

Ch 6 Sl 2

□ structural isomers

- $[\text{CH}_2\text{CH}_2\text{O}]_n$ and $[\text{CH}_2\text{CH}(\text{OH})]_n$
- 1,2-PBD and 1,4-PBD
- head-to-tail and head-to-head

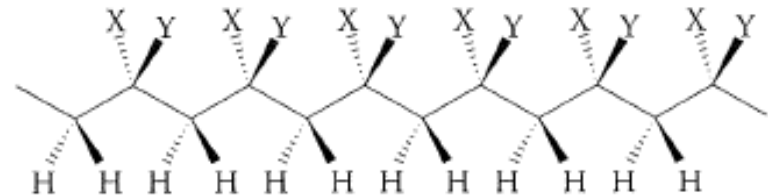
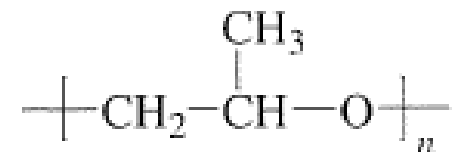
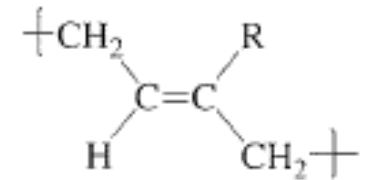
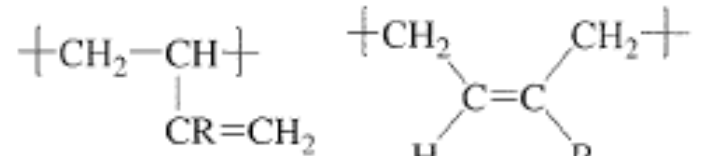
□ stereoisomers

□ geometric isomers

- cis-1,4-PBD & trans-1,4-PBD

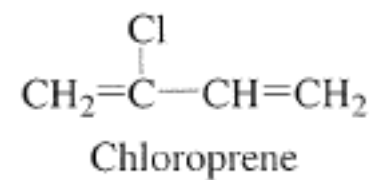
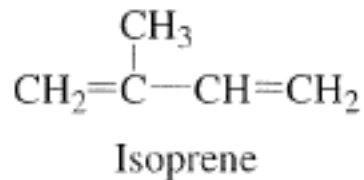
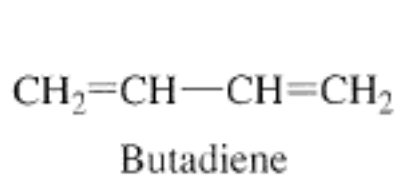
□ optical isomers

- polypropylene glycol ~ optically active
- vinyl polymers
 - have chiral carbon but not optically active
 - tacticity



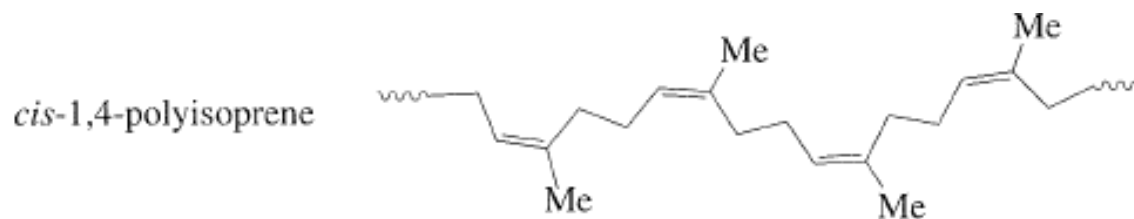
Isomerism in diene polym'n

□ 1,3-dienes

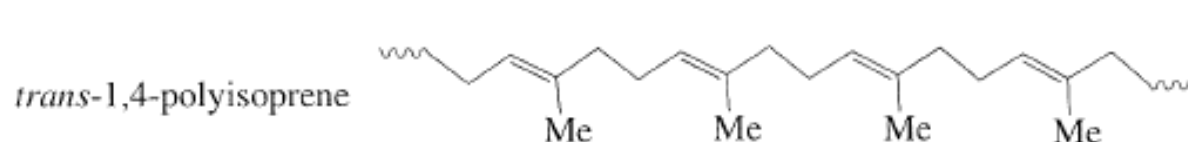


- can be polymerized by radical, cationic, and anionic
- to rubbers ~ BR, IR, CR

□ Natural rubbers ~ 1,4-PIP



Hevea
rubbery
→ vulcanization



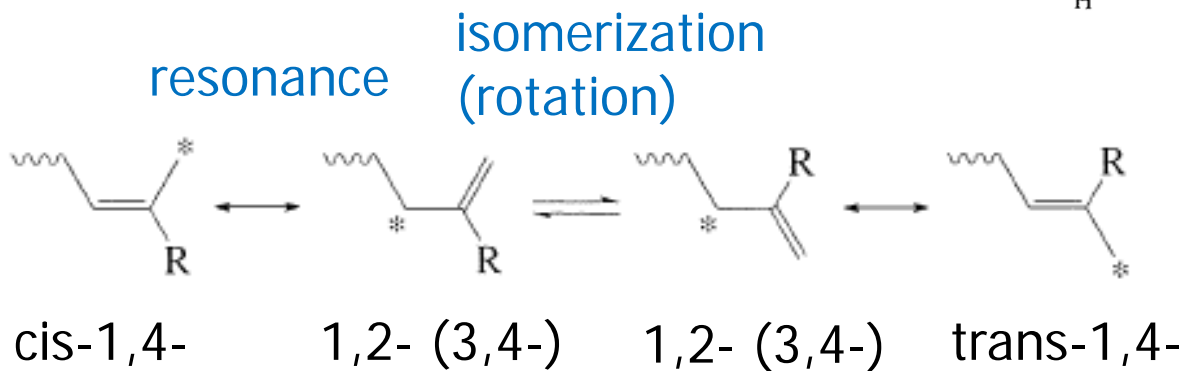
Gutta-percha
crystallizable
→ rigid

□ polym'n of 1,3-dienes

Table 6.1 p151

TABLE 6.1
Basic Modes for Addition of 1,3-Dienes ($\text{CH}_2=\text{CR}-\text{CH}=\text{CH}_2$) to a Growing Polymer Chain (M_n^*)^a

Mode of Addition	Product of Addition	Repeat Unit Structure
1,2-addition	$\text{M}_n-\text{CH}_2-\overset{\text{R}}{\underset{\text{CH}=\text{CH}_2}{\text{C}}^*}$	$\left[\text{CH}_2-\overset{\text{R}}{\underset{\text{CH}=\text{CH}_2}{\text{C}}} \right]$
3,4-addition	$\text{M}_n-\text{CH}_2-\overset{*}{\underset{\text{CR}=\text{CH}_2}{\text{CH}}}$	$\left[\text{CH}_2-\overset{\text{CH}}{\underset{\text{CR}=\text{CH}_2}{\text{}}} \right]$
<i>cis</i> -1,4-addition	$\text{M}_n-\text{CH}_2-\overset{*}{\underset{\text{H}}{\text{C}}}=\overset{\text{CH}_2}{\underset{\text{R}}{\text{C}}}$	$\left[\text{CH}_2-\overset{\text{CH}_2}{\underset{\text{H}}{\text{C}}}=\overset{\text{R}}{\underset{\text{C}}} \right]$
<i>trans</i> -1,4-addition	$\text{M}_n-\text{CH}_2-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\overset{\text{R}}{\underset{*}{\text{C}}}\text{CH}_2$	$\left[\text{CH}_2-\overset{\text{R}}{\underset{\text{H}}{\text{C}}}=\overset{\text{CH}_2}{\underset{\text{C}}} \right]$



□ radical polym'n

Table 6.2 p151

Monomer	Polymerization Conditions	<i>cis</i> -1,4	<i>trans</i> -1,4	1,2	3,4
Butadiene	Free radical at -20 °C	0.06	0.77	0.17	—
Butadiene	Free radical at 100 °C	0.28	0.51	0.21	—
Isoprene	Free radical at -20 °C	0.01	0.90	0.05	0.04
Isoprene	Free radical at 100 °C	0.23	0.66	0.05	0.06

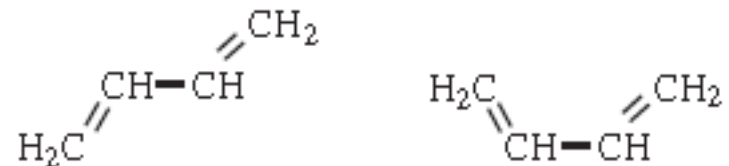


□ 1,4- > 1,2- (& 3,4-)

- lower steric hindrance at C4
 - more pronounced in isoprene (Me on C2)
- more stable product (disubstituted vs monosubstituted alkene)

□ trans > cis

- stability of monomer and polymer
- more pronounced at lower Temp

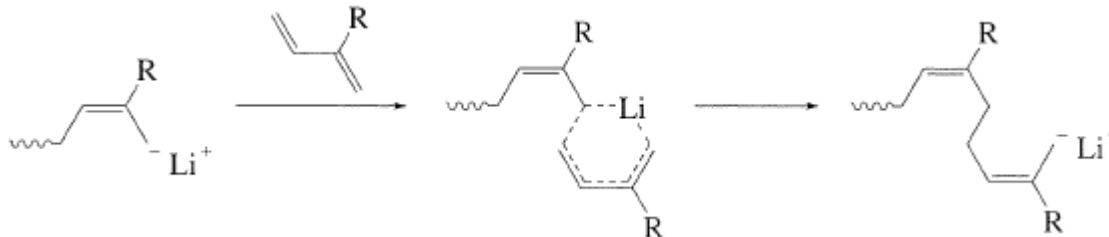


□ anionic polym'n

Monomer	Polymerization Conditions	<i>cis</i> -1,4	<i>trans</i> -1,4	1,2	3,4
Butadiene	Anionic in hexane with Li ⁺ counter-ion at 20 °C	0.68	0.28	0.04	—
Butadiene	Anionic in diethyl ether with Li ⁺ counter-ion at 0 °C	0.08	0.17	0.75	—
Isoprene	Anionic in cyclohexane with Li ⁺ counter-ion at 30 °C	0.94	0.01	0.00	0.05
Isoprene	Anionic in diethyl ether with Li ⁺ counter-ion at 20 °C	← 0.35 →		0.13	0.52

□ in non-polar solvent with Li⁺

- *cis*-1,4- > *trans*-1,4 > 1,2- (& 3,4-)



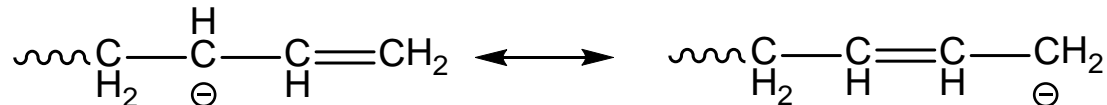
- small Li in nonpolar → coordinates *cis* and stable (1°) carbanion
- pronounced for isoprene ← isomerization [rotation] slow

□ anionic polym'n (cont'd)

Monomer	Polymerization Conditions	<i>cis</i> -1,4	<i>trans</i> -1,4	1,2	3,4
Butadiene	Anionic in hexane with Li ⁺ counter-ion at 20 °C	0.68	0.28	0.04	—
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Isoprene	Anionic in diethyl ether with Li ⁺ counter-ion at 20 °C	← 0.35 →		0.13	0.52

□ with other Mt⁺ or in polar solvent

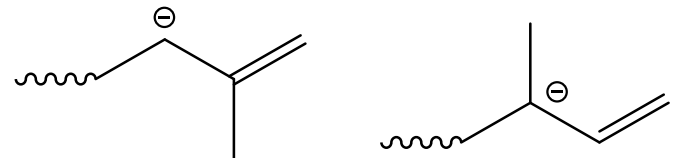
- 1,2- (& 3,4-) > 1,4-



- resonance weak → (-) localized on C2

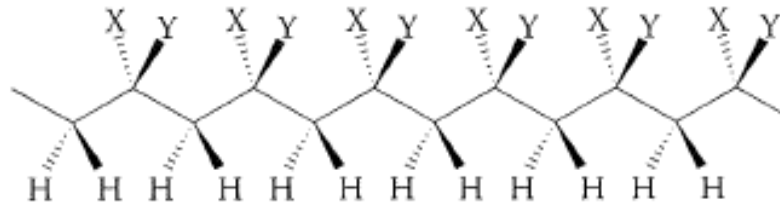
- 3,4- > 1,2-

- 3,4- better accessible

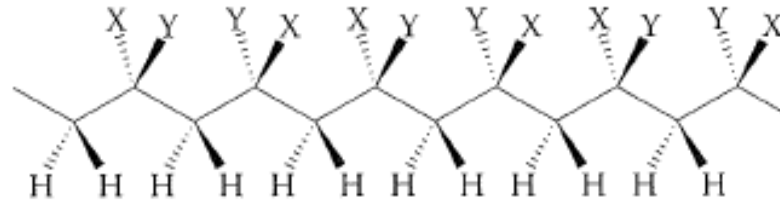


Tacticity

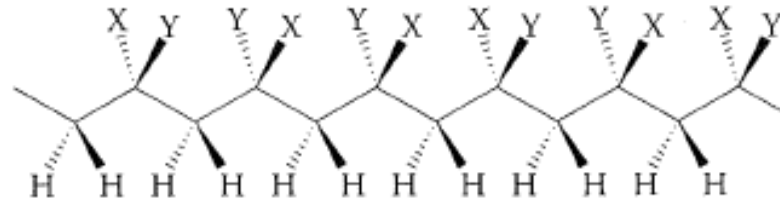
Isotactic



Syndiotactic



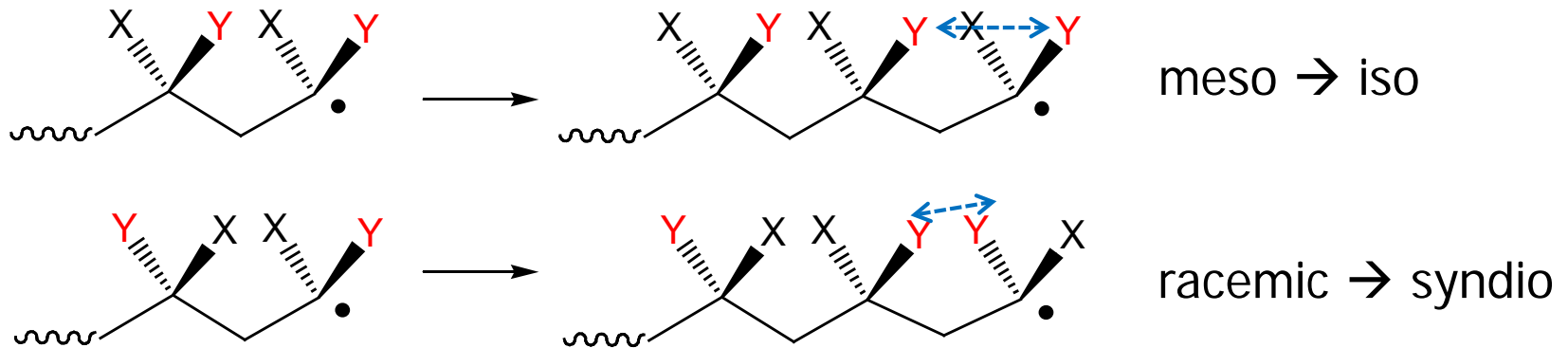
Atactic



- ❑ isotactic, syndiotactic chains
 - crystallizable → thermomechanical property
 - isotactic index (II) ~ wt% insoluble (PP) in boiling heptane
- ❑ ditacticity ~ $\text{CHX}=\text{CHY}$

Stereoregulation in chain polym'n

□ in radical polym'n

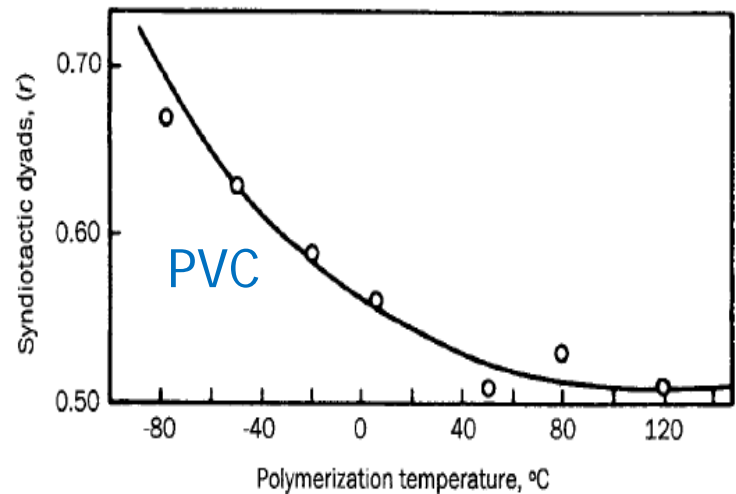


□ 'chain-end control'

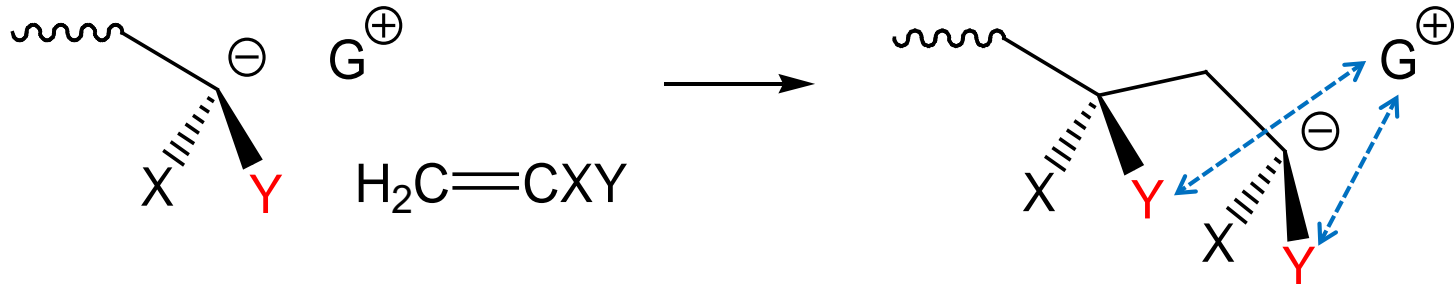
- racemic \rightarrow syndiotactic favored
- ΔH not that high \rightarrow atactic

□ depends on

- Temp \uparrow \rightarrow atactic
- size of Y \uparrow \rightarrow racemic \uparrow
 - PMMA $\sim (r) = .73$ at 100°C



□ in ionic polym'n



□ 'catalyst-site control'

- meso \rightarrow isotactic favored

□ depends on solvent, counter-ion, substituent

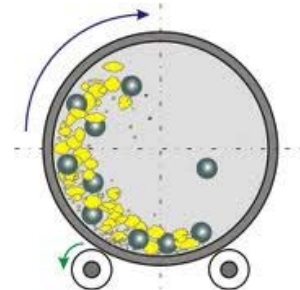
- polarity of solvent $\downarrow \rightarrow$ tightly-bound G \rightarrow meso \uparrow
- size of G $\downarrow \rightarrow$ tightly-bound G \rightarrow meso \uparrow
- polarity of Y $\uparrow \rightarrow$ more coordinating power \rightarrow meso \uparrow

- ❑ for non-polar monomers
 - ❑ ethylene, propylene, 1-butene, etc
 - ❑ no resonance stabilization of propagating radical
 - need high pressure and Temp ~ LDPE
 - ❑ with weak e⁻ donating substituents
 - anionic impossible
 - cationic not facile
 - ❑ → coordination polym'n necessary
- ❑ coordination polym'n gives
 - ❑ stereoregular poly(α -olefin)
 - ❑ unbranched polyethylene

Ziegler-Natta coordination polym'n

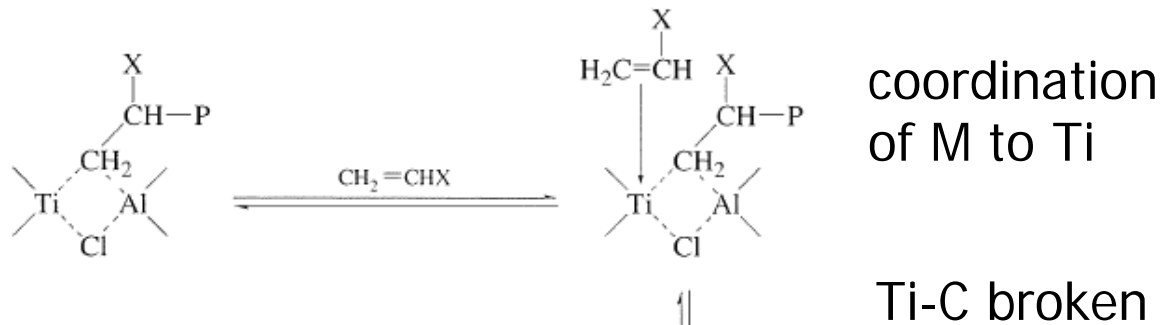
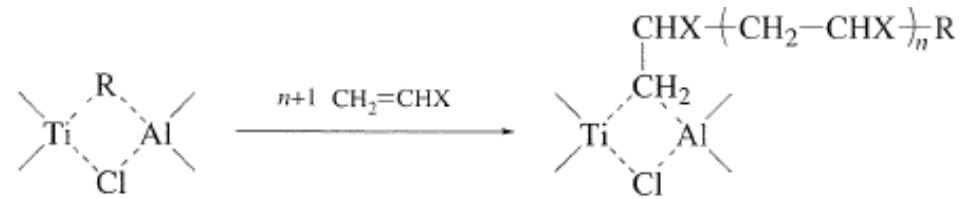
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- ❑ **Phillips** catalyst, CrO_3 (before ZN catalyst)
 - ❑ produced HDPE, not stereoregular PP
- ❑ **Ziegler-Natta** catalyst
 - ❑ group IV – VIII transition metal halide (like TiCl_3) + group I – III metal alkyl (like AlEt_3)
 - ❑ heterogeneous (insoluble) catalysts popular
 - gives stereospecific (isotactic) polymer
 - ball-milling for surface area
 - homogeneous (soluble) catalysts ~ no stereo control
 - with some exceptions, like VCl_4 for sPP
 - ❑ can be supported on Lewis base like MgCl_2

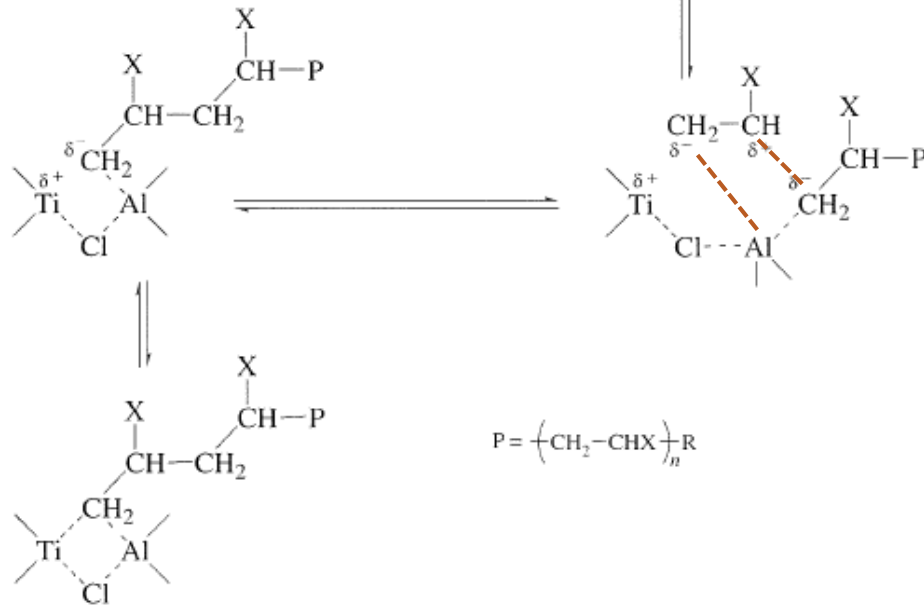


Mechanism of ZN polym'n

- bimetallic mechanism
- proposed by Natta



M insertion betw Al-C



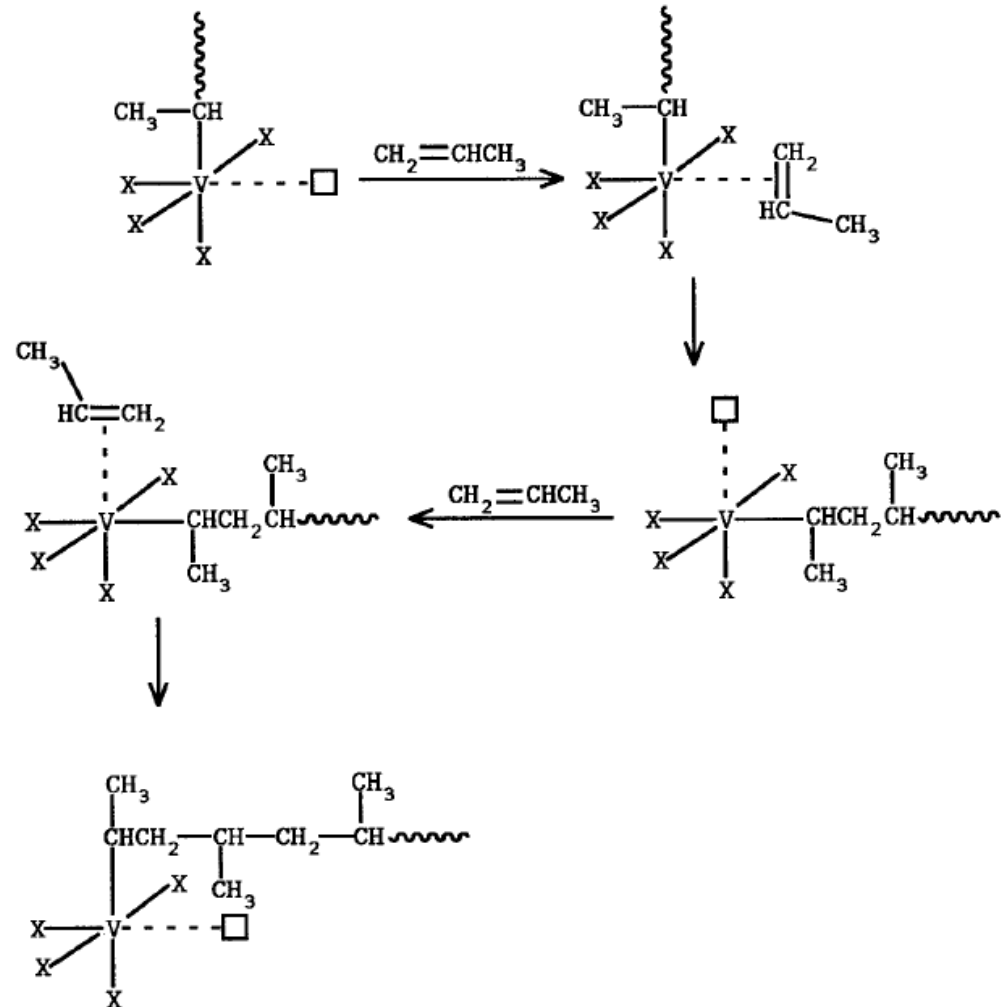
□ syndioselectivity by VCl_4 to produce sPP

□ catalyst-site control?

- differently coordinating □

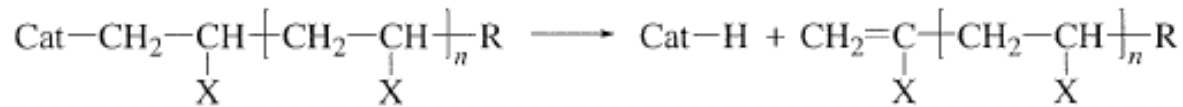
□ chain-end control?

- homogeneous (VCl_4 soluble)
- cat prevent rotation

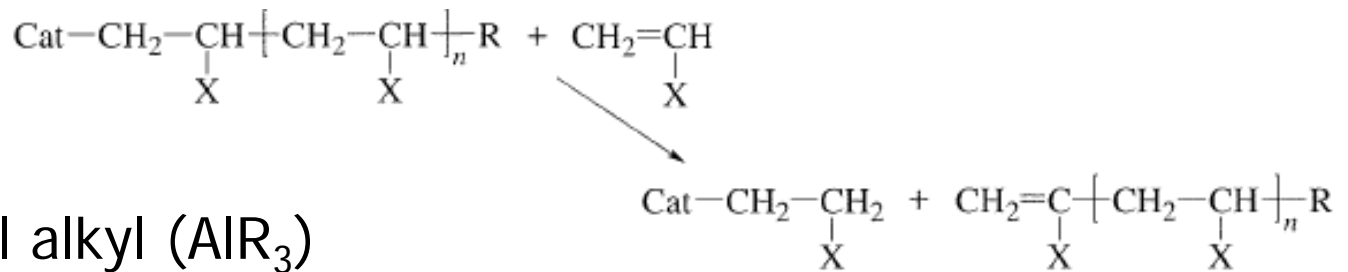


□ termination

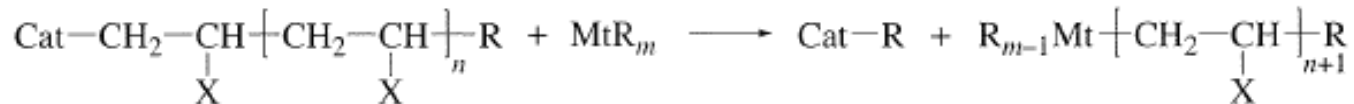
□ internal (β -)hydride transfer



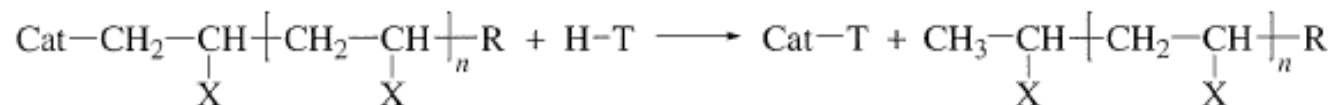
□ CT to M



□ CT to metal alkyl (AlR_3)



□ CT to active H comp'd like H_2 ~ MM control



Kinetics of ZN polym'n

□ R_p

k_p is the rate coefficient for propagation

$$R_p = k_p C_p^* \theta_M$$

C_p^* is the concentration of active catalyst sites

θ_M is the fraction of these sites at which monomer is adsorbed.

not $[M]$ ← heterogeneous

□ MM

$$\bar{x}_n = \frac{k_p C_p^* \theta_M}{k_{ht} C_p^* + k_{trM} C_p^* \theta_M + k_{trA} C_p^* \theta_A + k_{trH_2} C_p^* \theta_{H_2}}$$

$$\frac{1}{\bar{x}_n} = \frac{k_{ht}}{k_p \theta_M} + \frac{k_{trM}}{k_p} + \frac{k_{trA} \theta_A}{k_p \theta_M} + \frac{k_{trH_2} \theta_{H_2}}{k_p \theta_M}$$

□ MMD

□ broad distrib'n ← 'multi-site' catalyst ← heterogeneous

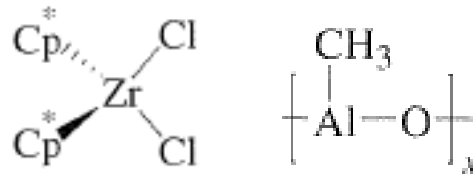
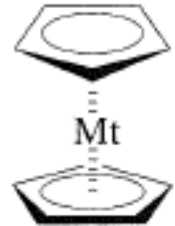
□ $5 < PDI < 30$

Practical considerations in ZN polym'n Ch 6 Sl 18

- ❑ ZN coordination polym'n requires
 - ❑ dry condition and inert solvent like heptane, cx
 - ❑ removal of atactic polymer
- ❑ As Temp up, rate up and stereospecificity down.
- ❑ processes
 - ❑ solution ~ at high T > 100 °C ~ polymer soluble
 - ❑ slurry ~ at 50 < T < 100 °C ~ polymer ppt
 - ❑ gas-phase ~ dispersion of cat in gaseous M
- ❑ ZN polym'n for HDPE, iPP (sPP), and
 - ❑ LLDPE ~ copolymers of E + α -olefins (hexane, octane)
 - ❑ 'synthetic natural rubber' ~ cis-1,4-PIP
 - ❑ not for polar monomers ~ other reaction or atactic polymer

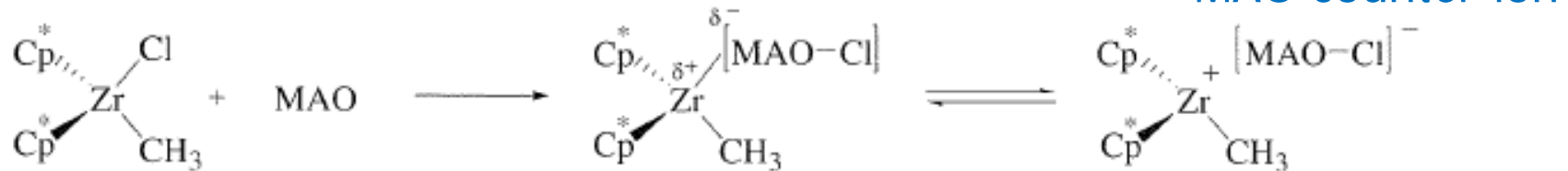
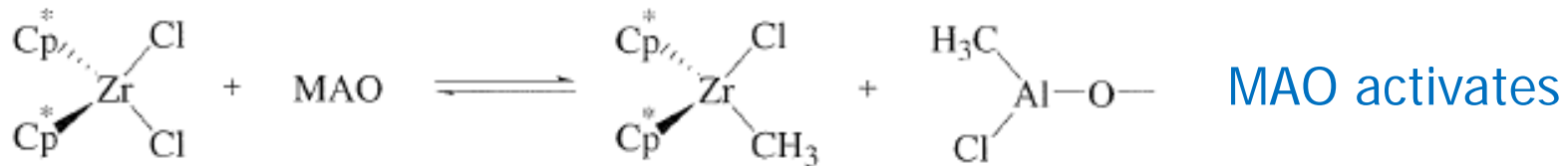
Metallocene coordination polym'n

- ❑ metallocene ~ metal sandwiched by Cp
- ❑ metallocene catalyst
 - ❑ metallocene derivatives + cocatalyst [activator]
 - ❑ first and most popular
 - Kaminsky catalyst



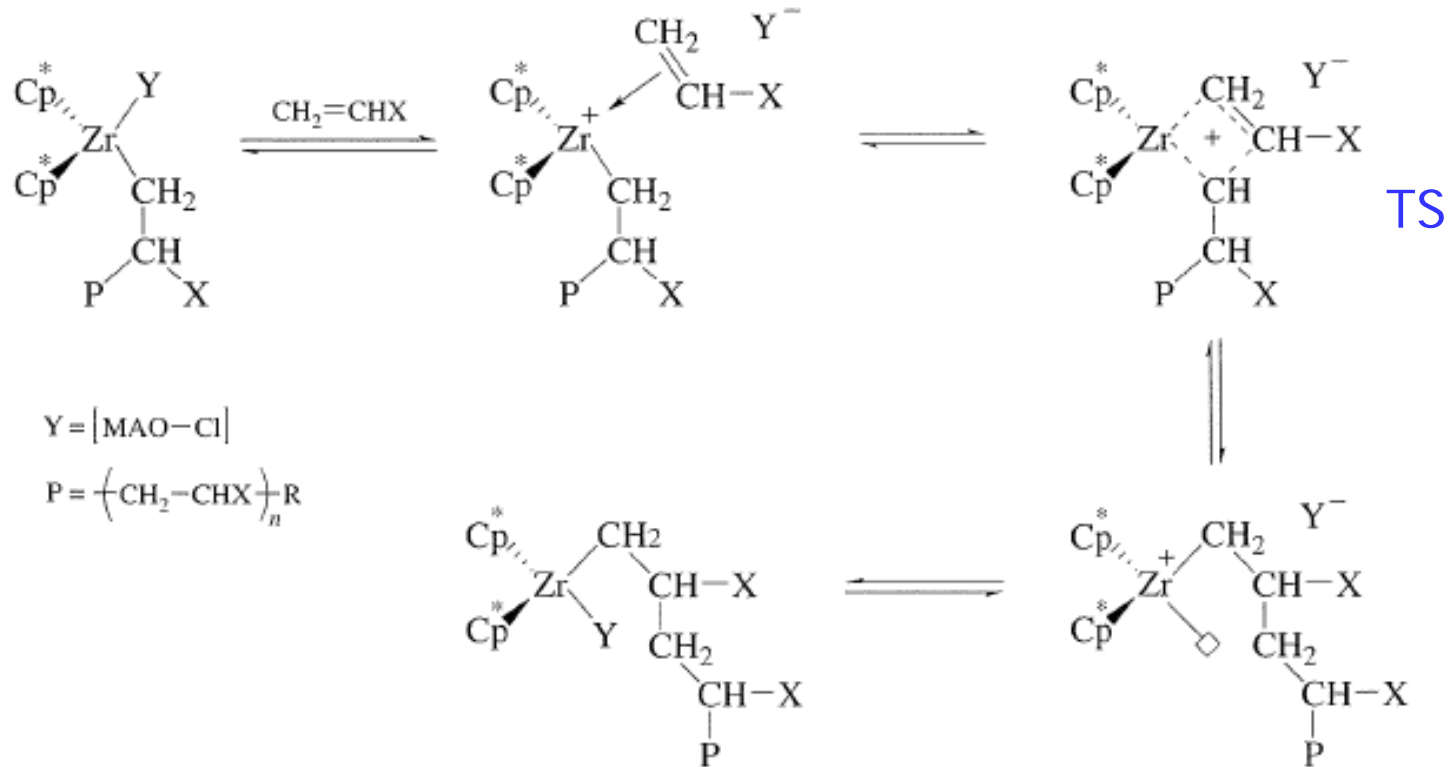
MAO
(in large xs)

❑ mechanism



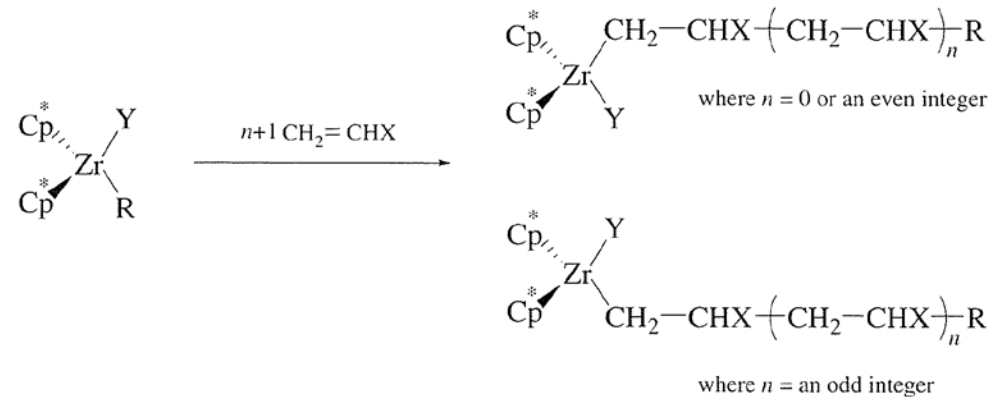
MAO deactivates, re-activates, ---

□ mechanism (cont'd)



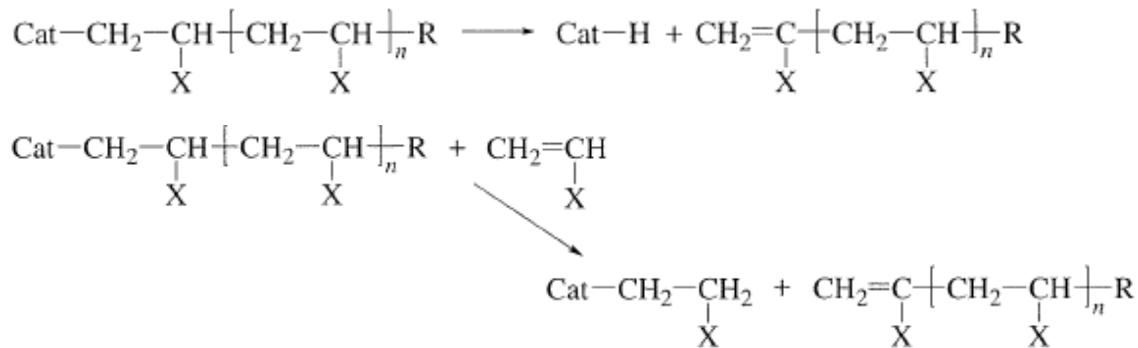
- homogeneous in nonpolar solvent
- primary addition to cationic active site
- no back migration [flip-back] p161

■ alternating insertion



□ no termination (like ZN).

□ Hydride transfer and CT to monomer occur (like ZN).



■ Polymer with = can participate in polym'n. → long-chain branch

■ with more open (high activity, low selectivity) catalyst

■ not in ZN polym'n

Kinetics of metallocene polym'n

□ R_p

$R_p = k_p C_p^* [M]$ ← homogeneous
 C_p^* is the concentration of active catalyst sites

□ Typically, $R_p \propto [M]^{1-2}$

$$R_p = k_p^{\text{slow}} C_p [M] + k_p^{\text{fast}} C_p [M]^2$$

w/o + w/ close second monomer

□ higher activity than ZN catalysts ← homogeneous

□ MM

$$\frac{1}{\bar{x}_n} = \frac{k_{hi}}{k_p [M]} + \frac{k_{trM}}{k_p} + \frac{k_{trH_2} [H_2]}{k_p [M]}$$

□ MMD

□ homogeneous 'single-site catalyst' → narrower MMD

□ $2 < PDI < 5$

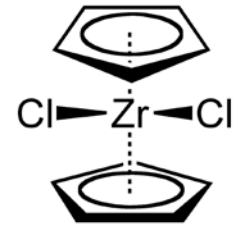
Stereoregular control in metallocene

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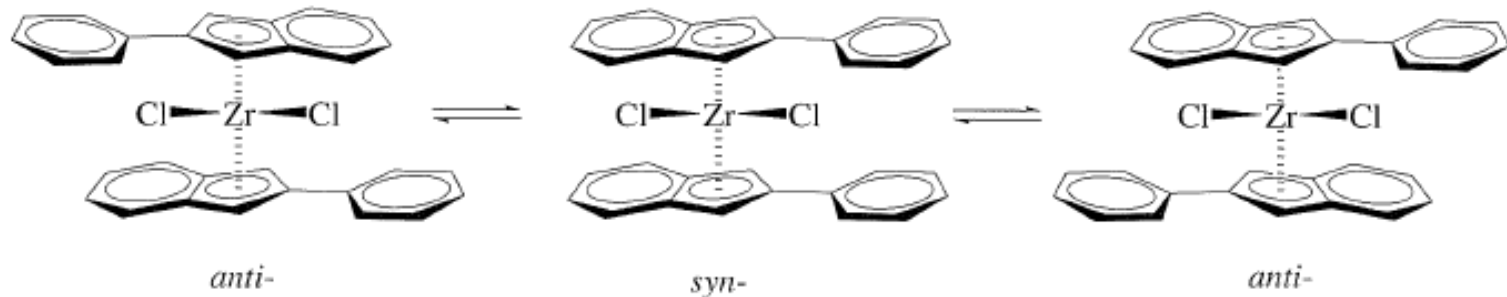
- stereoregular control given by selective active site

- homogeneous catalyst

- $\text{Cp}^*_2\text{ZrCl}_2 + \text{MAO} \sim$ gives atactic \leftarrow rotating Cp^*



- oscillating metallocenes



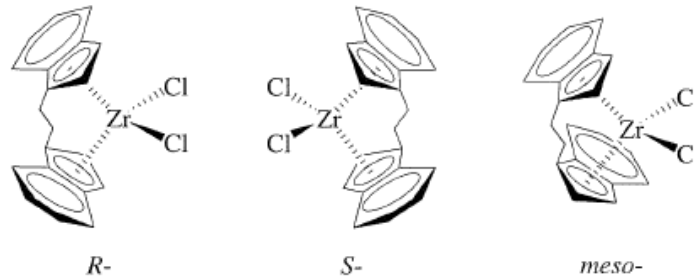
- slow equilibrium \rightarrow **stereoblock** polymer

- isotactic-*b*-atactic \sim a TPO

- As Temp up, block length down.

□ **ansa**-metallocene

□ **bridged**



□ *R*-, *S*- give isotactic and meso- atactic? **not that simple**

□ stereochemistry depends on

Odian pp666-674

■ **symmetry** in the catalyst (c_1 , c_2 , --)

■ chiral (→ stereoregular) or achiral (→ atactic)

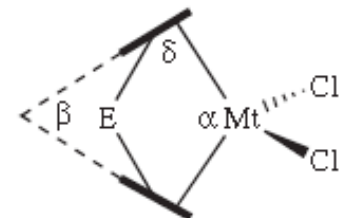
■ catalyst-site control or chain-end control

■ homotopic (→ iso), enantiotopic (→ syndio), diastereotopic

■ bridge structure

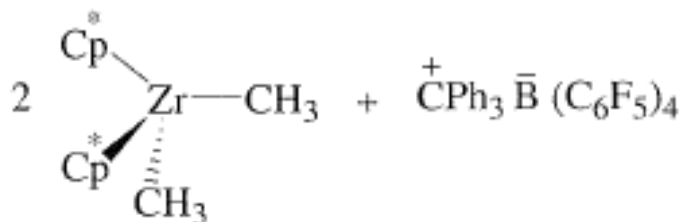
■ short bridge → open → high activity, low selectivity

■ catalyst structure

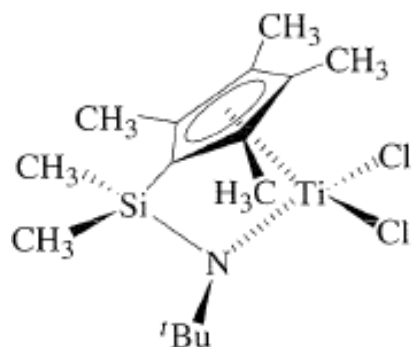


Some other metallocene catalysts

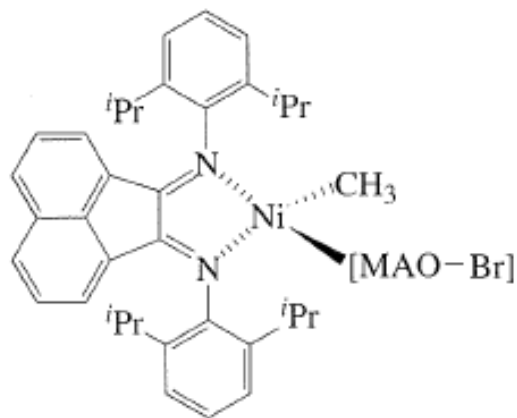
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borane instead of MAO
more robust and hydrolysis-resistant



one Cp + one amino
'constrained geometry catalyst (CGC)'
more open → PE with LCB



diimino complex with Ni, Pd, ---
no Cp
more tolerant to polar groups →
copolymerization of E and MMA, AN, ST, ---

Practical considerations in metallocene

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- ❑ Metallocene polym'n is
 - ❑ originally for homogeneous (HC) solution process
 - ❑ more frequently run heterogeneous ← practical
 - using (MAO + metallocene) supported on silica or alumina
 - behaves 'single-site catalyst'
 - lower activity w/ less termination
 - much less use of MAO
 - ❑ more useful for PE and PE copolymers
 - higher activity
 - LLDPE w/ more even distrib'n of α -olefin
 - PE with polar monomer, eg poly(E-co-ST)
 - poly(α -olefin) with iso-syndio control, eg sPP