Chapter 8. Vinyl Polymerization with Complex Coordination Catalysts

8.2. Heterogeneous Ziegler-Natta Polymerization

8.2.1. Heterogeneous Catalysts

Ziegler-Natta Catalyst: a combination of

Catalyst: **Transition metal compound (IV – VIII)**

Halide or oxyhalide of Ti, V, Cr, Mo, Fe, Co

Alkoxy, acetylacetonyl, cyclopentadienyl, phenyl

Cocatalyst: **Organometallic compound (I –III)**

Al, Li, Zn, Sn, Cd, Be, Mg

Hydride, akyl, aryl

TABLE 8.1 Commercially Available Polymers Synthesized with Complex Coordination Catalysts

Polymer	Principal stereochemistry	Typical uses
Plastics		
Polyethylene, high density (HDPE)	–	Bottles, drums, pipe, conduit, sheet, film, wire and cable insulation
Polyethylene, ultrahigh molecular weight (UHMWPE)	–	Surgical prostheses, machine parts, heavy-duty liners
Polypropylene	Isotactic	Automobile and appliance parts, rope, cordage, webbing, carpeting, film
Poly(1-butene)	Isotactic	Film, pipe
Poly(4-methyl-1-pentene)	Isotactic	Packaging, metal, supplies, lighting
Polystyrene	Syndiotactic	Specialty plastics
1,4-Polybutandiene	trans	Metal can coating, potting compounds for transformers
1,4-Polyisoprene	trans	Golf ball covers, orthopedic devices
Etheylene-1-alkene copolymer(linear low density polyethylene, LLDPE)	–	Blending with LDPE, packaging film, bottles
Ethylene-propylene block copolymers polyallomers)	Iosotactic	Food packaging, automotive trim, toys, bottles, film, heat-sterilizable containers
Polydicyclopenetadiene	–	Reaction injection molding (RIM) structural plastics

Polymer	Principal Stereochemisty	Typical Uses
Elastomers		
1,4-Polybutadiene	cis	Tires, conveyer belts, wire and cable insulation, footware
1,4-Polyisoprene	cis	Tires, footware, adhesives, coated fabrics
Poly(1-octenylene) (polyoctenamer)	trans	Blending with other elastomers
Poly(1,3-cyclo-pentenylenevinylene) (norbornene polymer)	trans	Molding compounds, engine mounts, car bumper guards
Polypropylene (amorphous)	–	Asphalt blends, sealants, adhesives, cable coatings
Ethyleme-propylene copolymer (EPM,EPR)	–	Impact modifier for polypropylene, car bumper guards
Ethylene-propylene-diene copolymer (EPDM)	–	Wire and cable insulation, weather stripping, tire side walls, hose, seals

The most important Z-N catalyst

Mixing $TiCl_4$ + AlR_3 in a dry, inert solvent in the absence of O_2 at low T

Maximum activity after aging periods of 1 –2 hrs

Exchange reactions

$$\left(\begin{array}{l} AlR_3 + TiCl_4 \rightarrow AlR_2Cl + TiRCl_3 \\ AlR_2Cl + TiCl_4 \rightarrow AlRCl_2 + TiRCl_3 \\ AlR_3 + TiRCl_3 \rightarrow AlR_2Cl + TiR_2Cl_2 \end{array}\right.$$

Reduction of Ti via homolytic cleavage

$$\left(\begin{array}{l} TiRCl_3 \rightarrow TiCl_3 + R\bullet \\ TiR_2Cl_2 \rightarrow TiRCl_2 + R\bullet \\ TiRCl_2 \rightarrow TiCl_2 + R\bullet \\ TiRCl_3 \rightarrow TiCl_2 + RCl \end{array}\right.$$

$TiCl_3$ may be formed by the equation

$$TiCl_4 + TiCl_2 \rightleftarrows 2\ TiCl_3$$

Radicals formed are removed by combination, disproportionation, or reaction with solvent.

Direct use of $TiCl_3$ → Better activity

$\alpha, \beta, \gamma, \delta$ **crystalline forms**

α, γ, δ **: close-packed layered cystal structure**

β : **linear structure → Much more atactic polymer**

Stereoregularity is very much dependent on surface characteristic of the catalyst.

TABLE 8.2 Variation of Polypropylene Isotacticity with Catalyst

Catalyst	Stereoregularity(%)
$AlEt_3$ + $TiCl_4$	35
$AlEt_3$ + β—$TiCl_3$	45
$AlEt_3$ + α−$TiCl_3$	85
$AlEt_3$ + $ZrCl_4$	55
$AlEt_3$ + VCl_3	73
$AlEt_3$ + $TiCl_4$ + P, As, or Sb compounds	35
$AlEt_2X$ + $TiCl_3$	90−99
AlEtX2 + γ−$TiCl_3$ + amine	99

- **Efficiency of heterogeneous catalyst can be improved significantly by impregnating the catalyst on a solid support such as $MgCl_2$ or MgO.**

e.g., $TiCl_3$ – AlR_3 : 50 – 200 g PE per g of catalyst per hr per atm of ethylene

$MgCl_2$ – supported catalyst : 7000 g

High-mileage catalyst

∵ Support maximizes the number of active sites on the catalyst surface

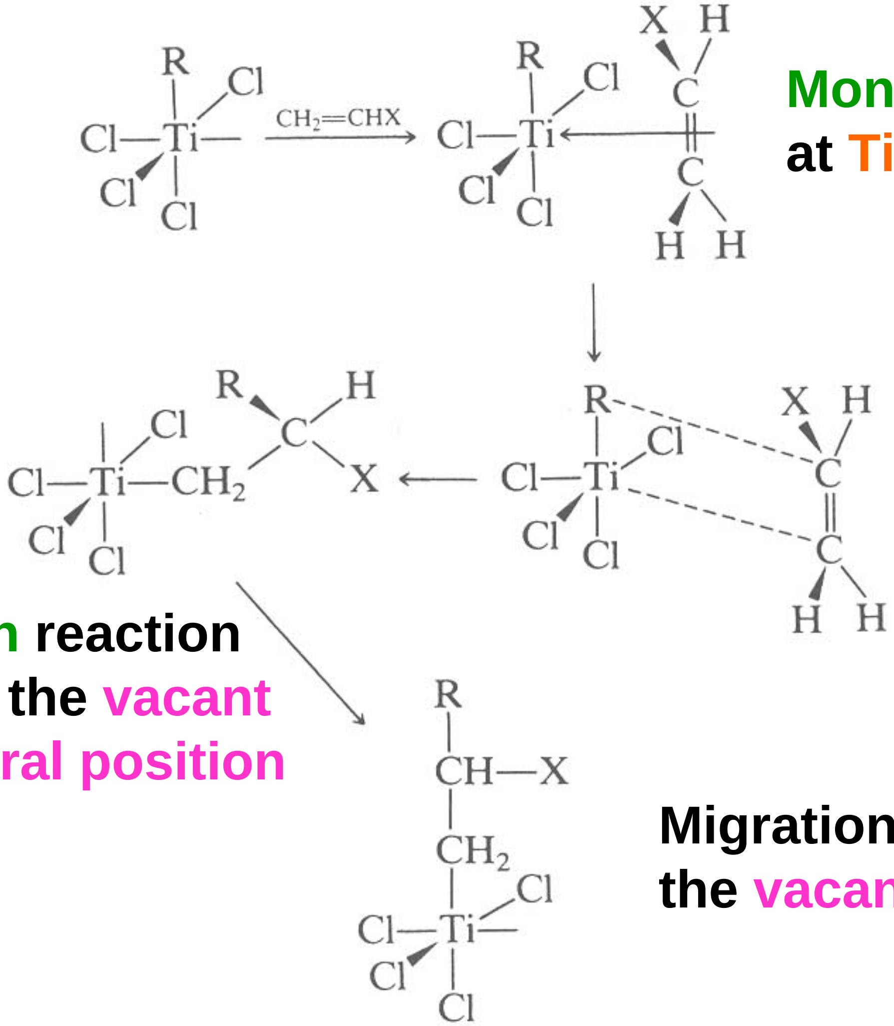
8.2.2 Mechanisms and Reactivity in Heterogeneous Polymerization

- Monometallic mechanism

surface

Ti

Vacant site



Monomer is complexed at Ti atom on the catalyst surface

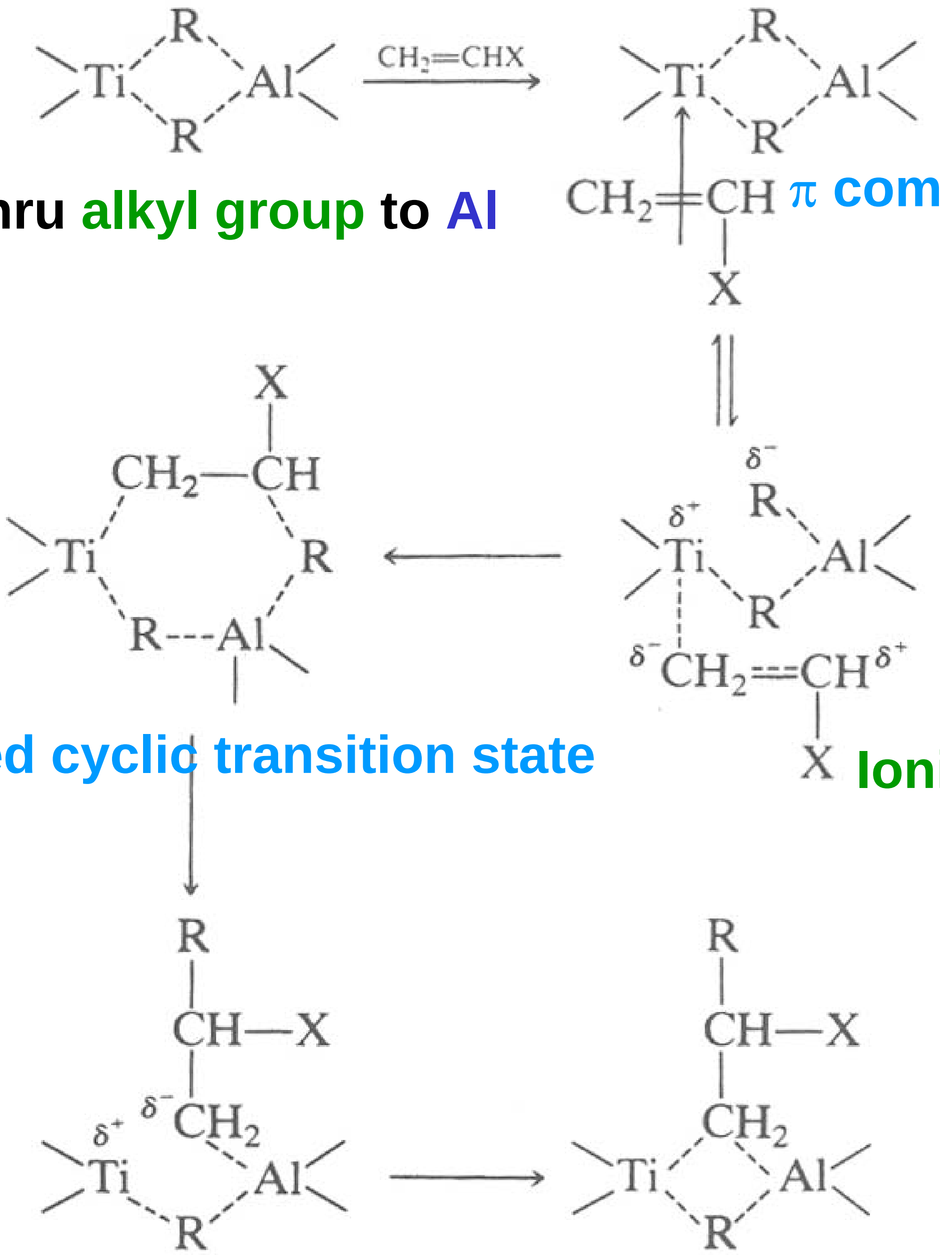
Four-center intermediate

Insertion reaction

Shifting the vacant octahedral position

Migration of the chain to reestablish the vacant site on the surface

• Bimetallic mechanism



Ti is bridged thru alkyl group to Al

π complex of monomer to Ti

Ionization of Ti-alkyl bond

Six-membered cyclic transition state

insertion

- Reactivity of monomers

Decreases with increasing steric hindrance about the double bond

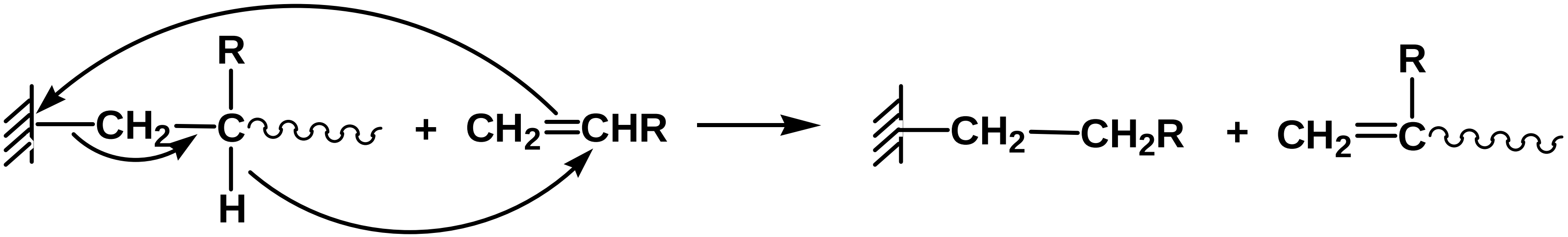
$CH_2 = CH_2$ > $CH_2 = CH – CH_3$ > $CH_2 = CH – CH_2CH_3$

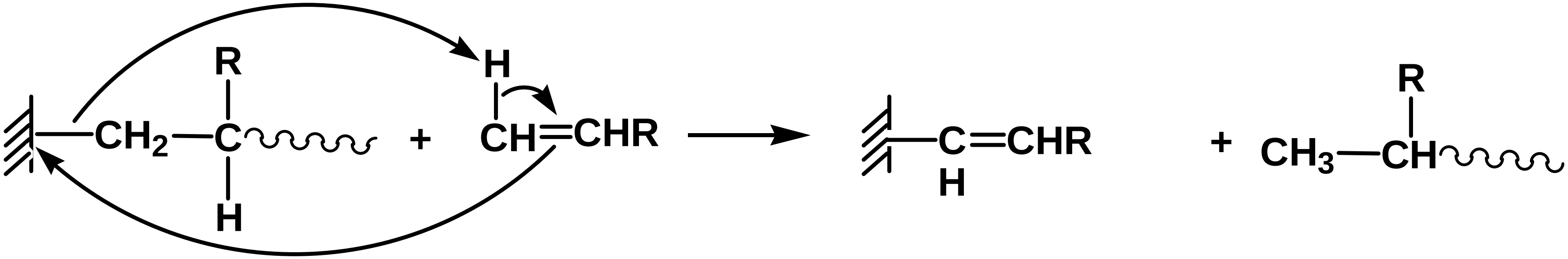
> $CH_2 = CH – CH(CH_3)_2$ > $CH_2 = CH – CH(CH_2CH_3)_2$

> $CH_2 = CH – C(CH_3)_3$

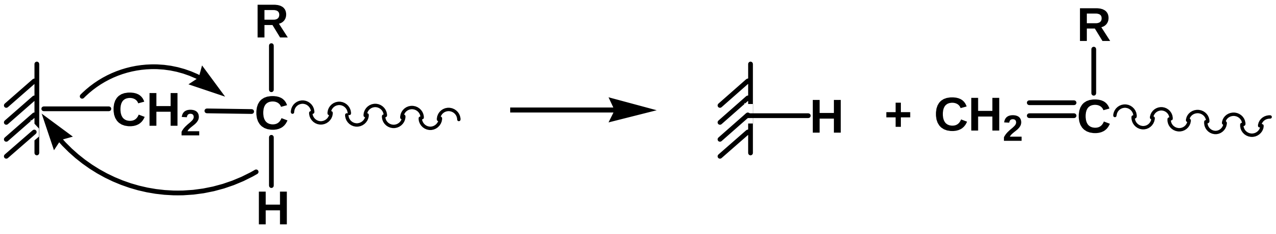
- **Termination**

1) Chain transfer to monomer

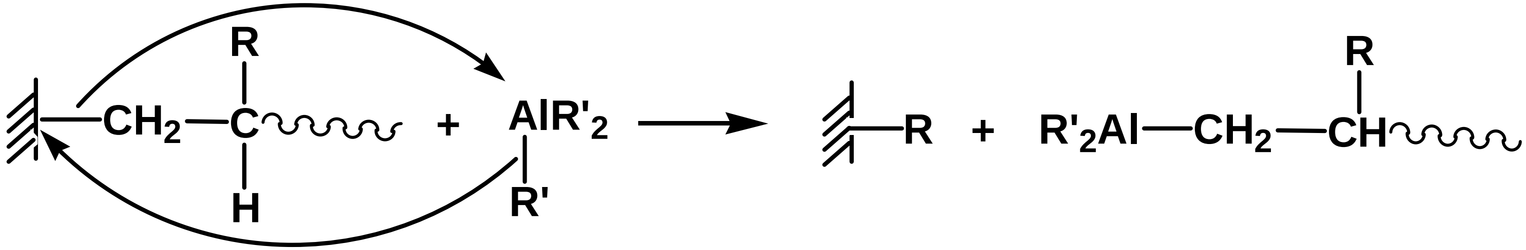




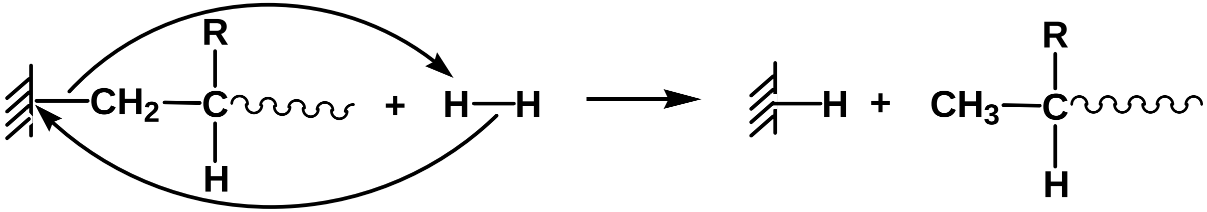
2) Internal hydride transfer



3) Chain transfer to cocatalyst



4) Chain transfer to added H_2

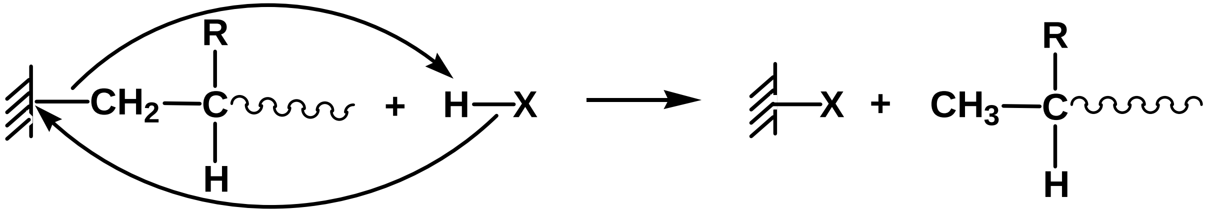


H_2 chain transfer agent for controlling M.W.

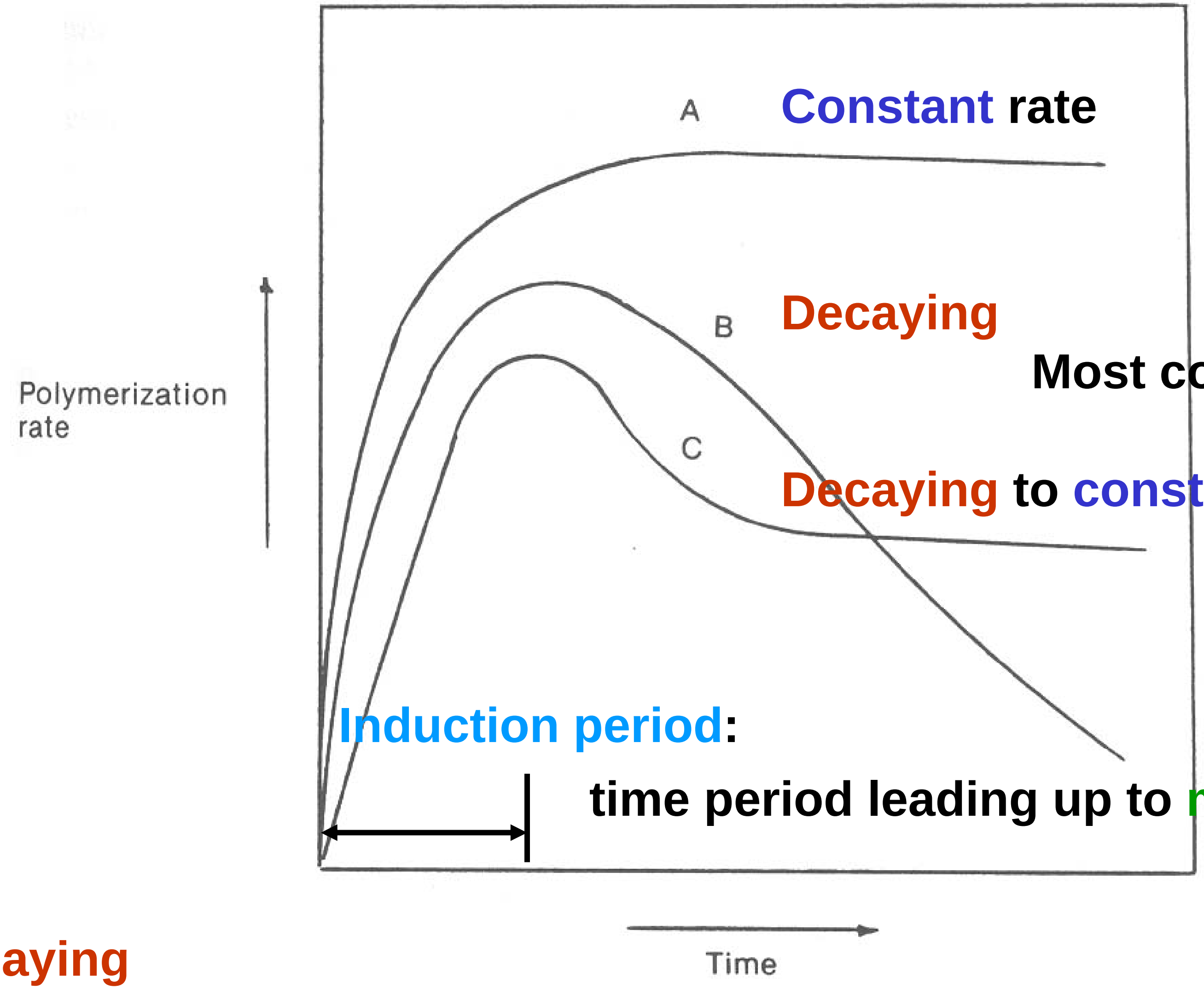
Clean reaction, no residue, low cost

W/o chain transfer agent, too high M.W.

5) True termination with HX



- **Types of Polymerization Rate Curves**



Constant rate

Decaying

Most common

Decaying to constant

Induction period:

time period leading up to maximum rate

Decaying

∵ Structural changes reduce # or activity of active centers
Encapsulation of active centers by polymer prevents approach by monomer

- M.W. distribution

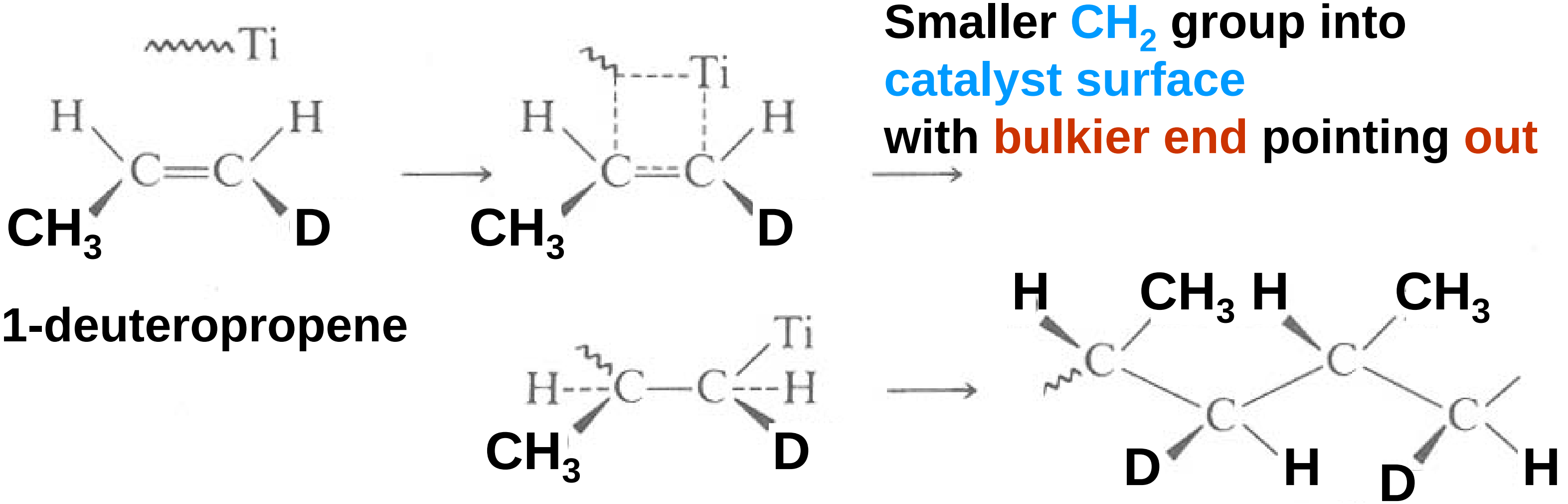
  Broad for insoluble catalyst

  ∵ Decay of catalyst activity or
  presence of sites of variable activity

  Narrow for soluble catalyst

8.2.3 Stereochemistry of Heterogeneous Polymerization

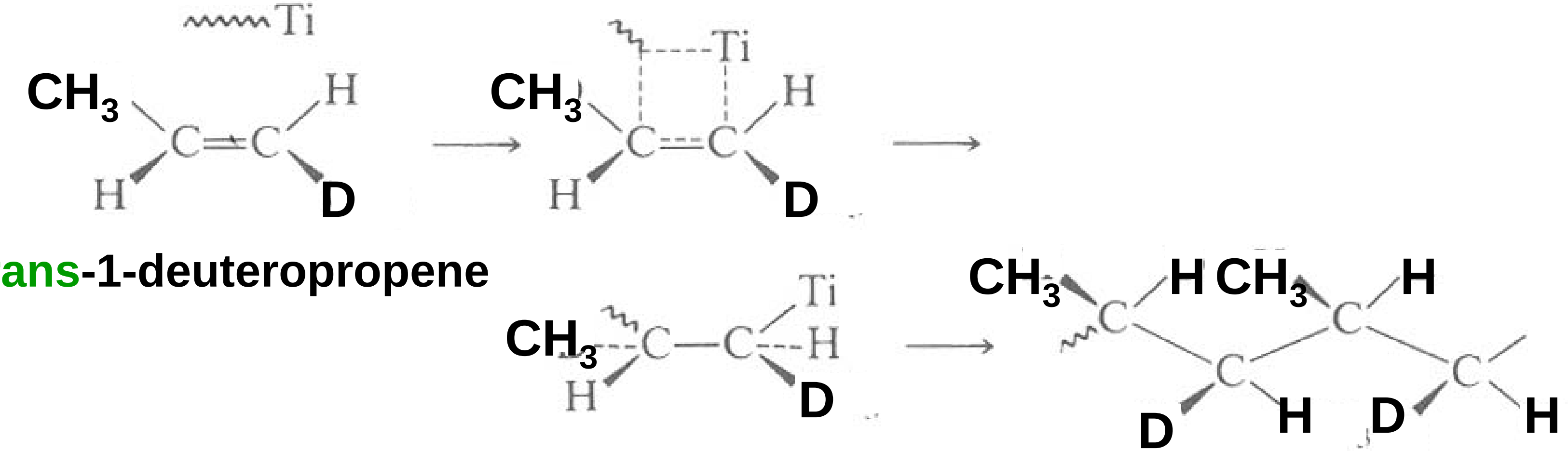
Smaller CH_2 group into catalyst surface with bulkier end pointing out



Cis-1-deuteropropene

Cis addition to double bond

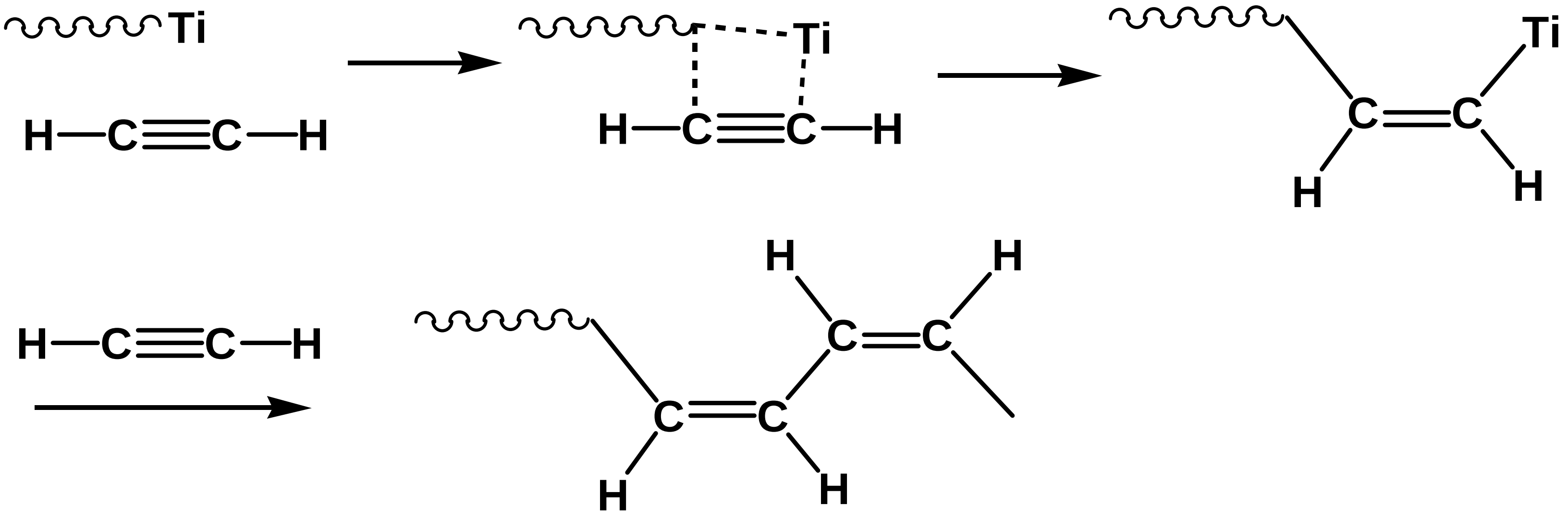
Erythro-Diisotactic



Trans-1-deuteropropene

Threo-Diisotactic

- **Polyacetylene**

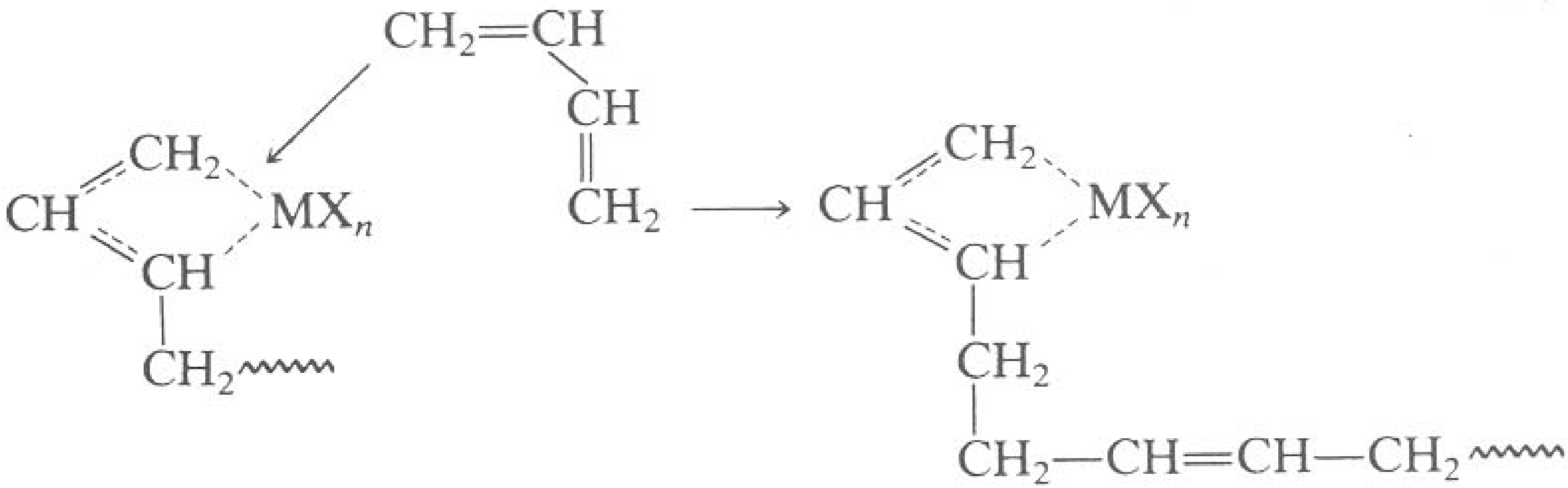


cis-polyacetylene at – 78^{o}C

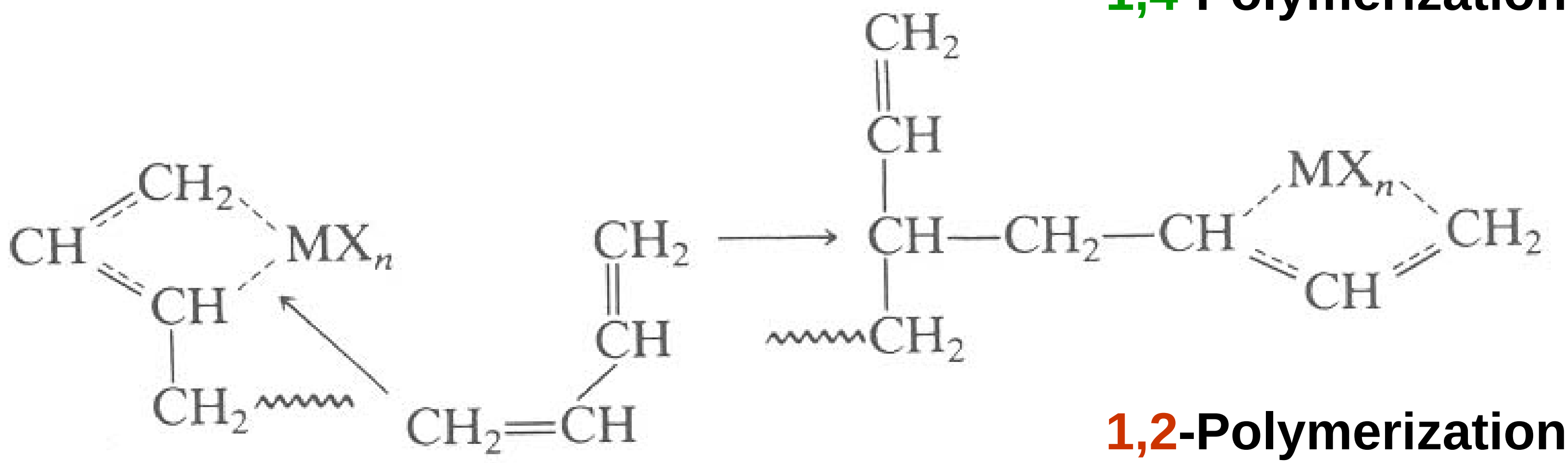
At 150^{o}C trans-polyacetylene

Initially formed cis polymer $\xrightarrow{\text{Thermal isomerization}}$ trans polymer

8.2.4 Polymerization of Dienes



1,4-Polymerization



1,2-Polymerization

1,3-BD → Cis-1,4, trans-1,4, isotactic 1,2, syndiotactic 1,2

TABLE 8.3

1,3-isoprene → Cis-1,4, trans-1,4, ~~1,2,~~ 3,4

TABLE 8.4

No 1,2 polymer observed

∵ More hindered

Table 8.3 Catalysts for Stereospecific Polymerization of Butadiene

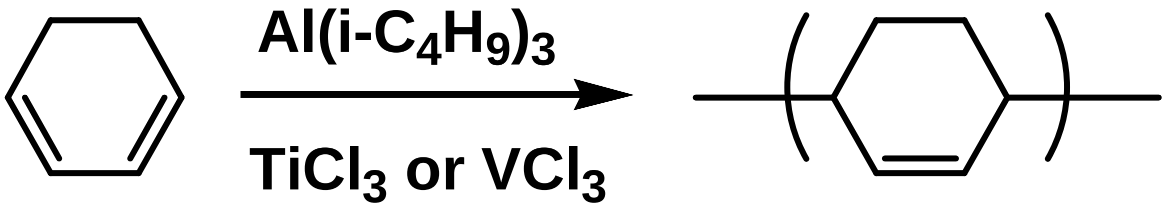
Catalyst	Yield(%)	Polymer structure	Ref. no.
$R_3Al + VCl_4$	97–98	trans–1,4	2
$R_3Al + VCl_3$	99	trans–1,4	2
$R_3Al + VOCl_3$	97–98	trans–1,4	2
$R_3Al + TiI_4$	93–94	cis–1,4	2
$R_2AlCl + CoCl_2$	96–97	cis–1,4	2
$R_3Al + Ti(OC_6H_9)_4$	90–100	1,2	13
$Et_3Al + Cr(C_6H_5CN)_6$			
Al/Cr = 2	~100	st–1,2	14
Al/Cr = 10	~100	it–1,2	14

Table 8.4 Catalysts for Stereospecific Polymerization of Isoprene

Table 4

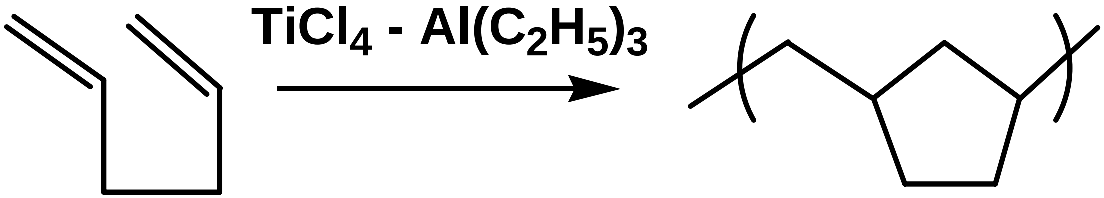
Catalyst	Yield(%)	Polymer structure	Ref.No.
$R_3Al + \alpha-TiCl_3$	91	trans−1,4	15
$Et_3Al + VCl_3$	99	trans−1,4	14
$Et_3Al + TiCl_4$			
Al/Ti < 1	95	trans−1,4	14
Al/Ti > 1	96	cis−1,4	14
$Et_3 + Ti(OR)_4$	95	3,4	14

Conjugated cyclic dienes



1,3-cyclohexadiene

Nonconjugated cyclic dienes



1,5-hexadiene

8.3 Homogeneous Ziegler-Natta Polymerization

8.3.1 Metallocene Catalysts

- The earliest Metallocene Catalysts

$Cp_2TiCl_2 + R_2AlCl$

Cp = cyclopentadiene

Low catalytic activity toward ethylene

Unreactive toward propylene

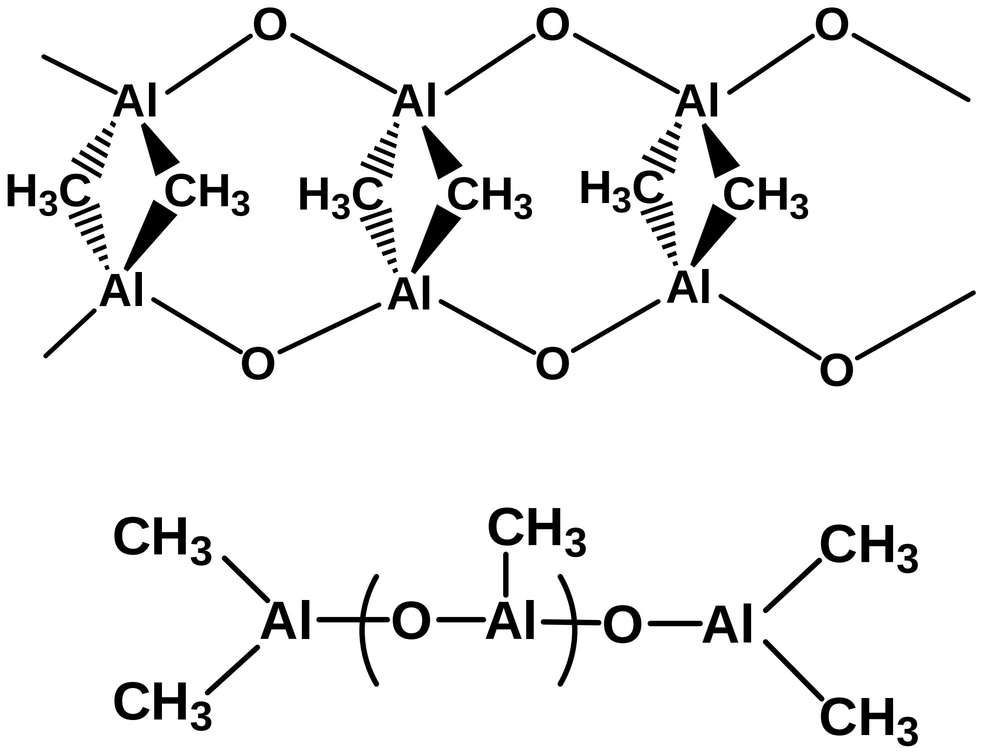
Addition of water increased the activity substantially.

∵ Reaction between the water and the alkylaluminum cocatalyst to form complex alkylaluminoxane

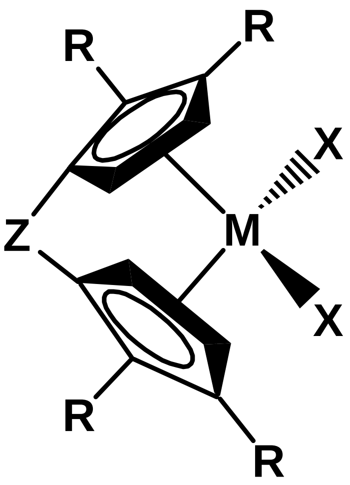
MAO (methylaluminoxane) Formed by hydrolysis of $AlMe_3$

M.W. = 1000 ~ 1500

Two proposed structures



Metallocenes

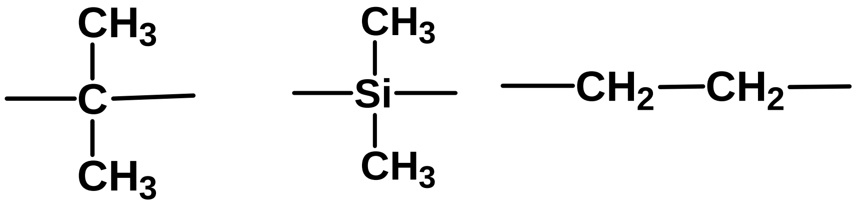


M = transition metal; **Zr, Ti, Hf**

X = **Cl, alkyl**

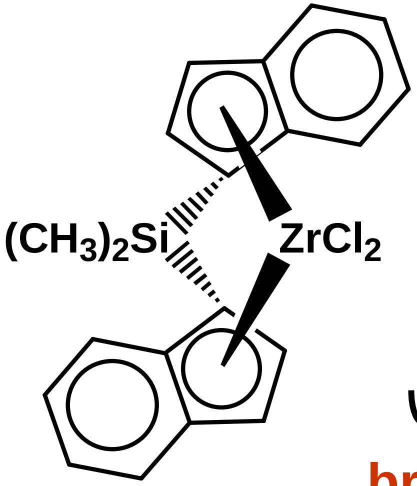
R = H, alkyl

Z = optional **bridging group**

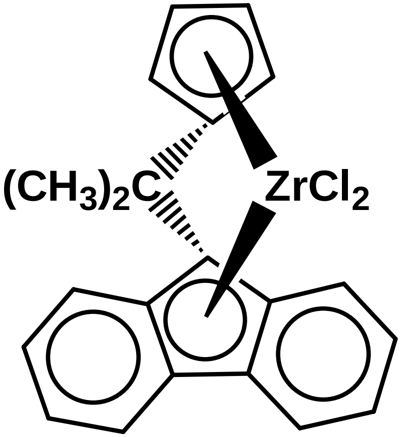


Ligand = **Cp, fused ring**

Examples



$\underbrace{Me_2Si}_{\text{bridge}}\underbrace{(Ind)_2}_{\text{ligands}}ZrCl_2$



$\underbrace{Me_2C}_{\text{bridge}}\underbrace{(Flu)(Cp)}_{\text{ligands}}\ ZrCl_2$

Ind = indene

Flu = fluorene

8.3.2 Mechanism and Reactivity with Metallocene Catalysts

- **Metallocene**

  Well-defined molecular structure

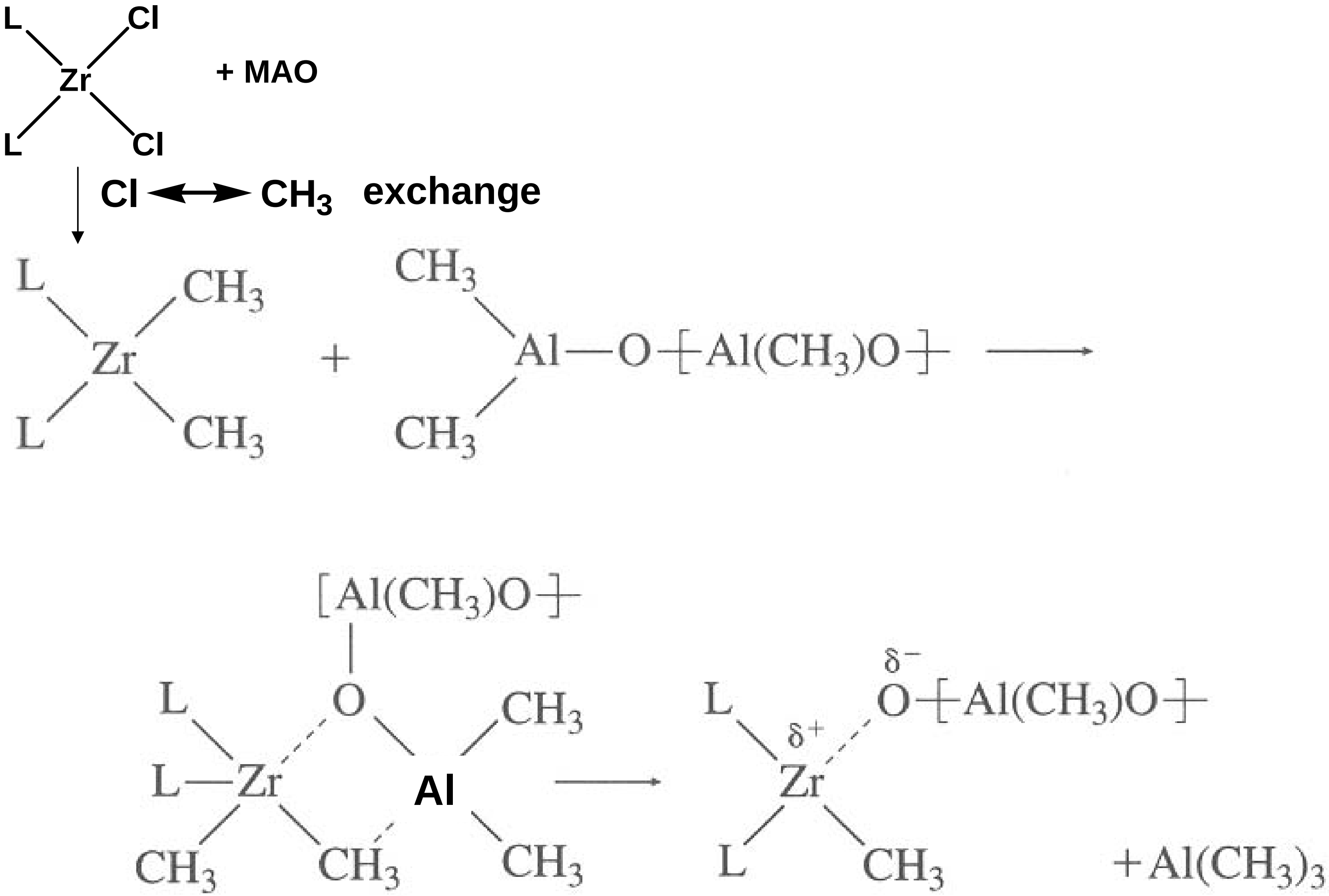
  Single-site catalyst

  (polymerization occurs at one position in the molecule, the transition metal atom)

- **Heterogeneous Z-N catalyst**

  Multiple active sites

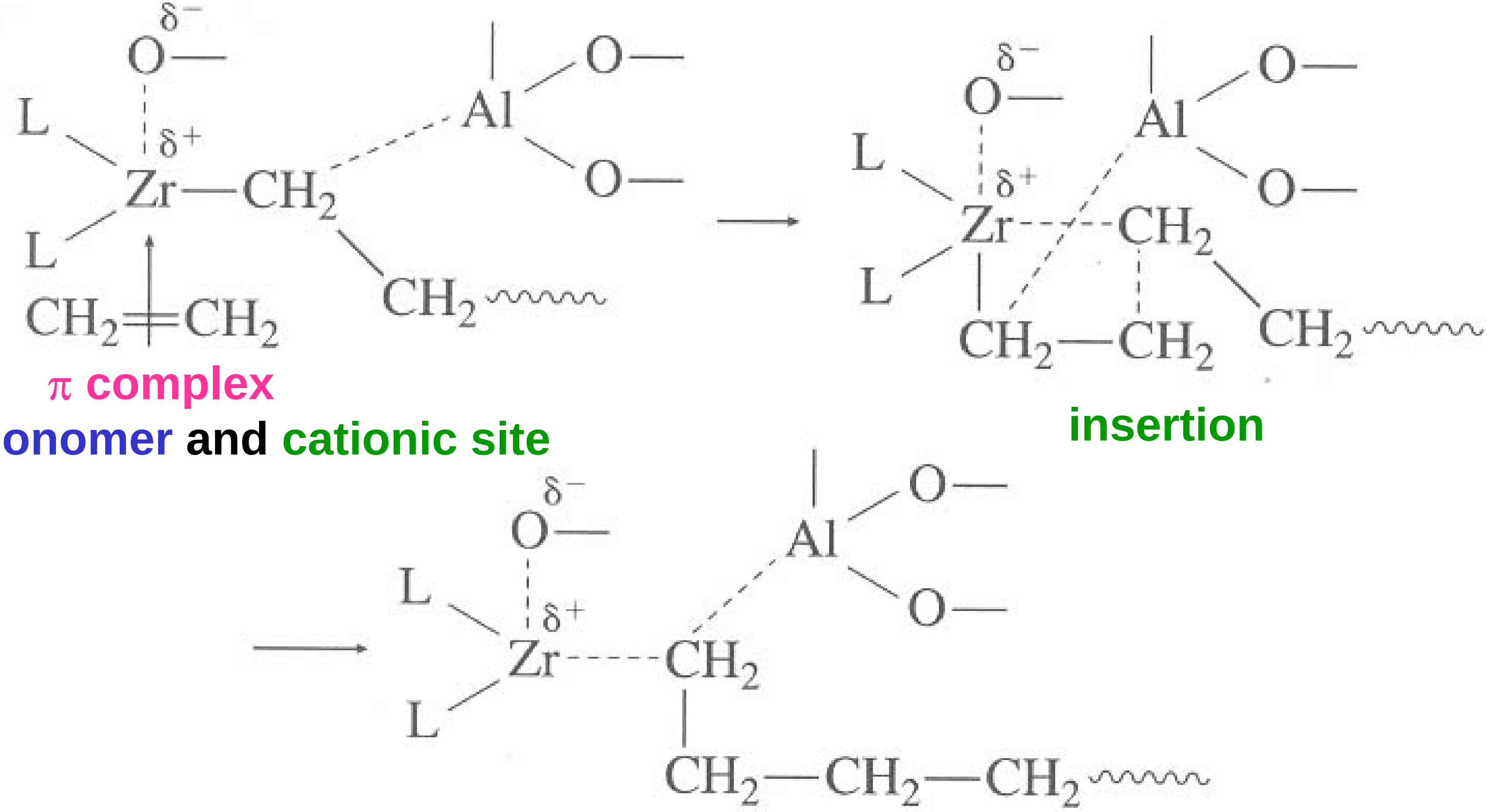
- **Formation of active site**



Active species

Cationic in nature

• Polymerization mechanism



π complex

Monomer and cationic site

insertion

- **Narrower MWD**

$$\frac{\overline{M}_w}{\overline{M}_n} = \begin{cases} 2 \sim 2.5 \text{ for metallocene : single site} \\ 5 \sim 6 \text{ for heterogeneous catalyst : sites of variable activity} \end{cases}$$

M.W. ↓ as

- **T↑**
- **Catalyst conc ↑**
- **Addition of H_2**

- **Activity: 10 ~ 100 times higher than Z-N catalyst**

1. **Order of activity Zr > Ti > Hf**

2. **Alkyl groups on Cp ring increase catalyst activity if they are not too bulky**

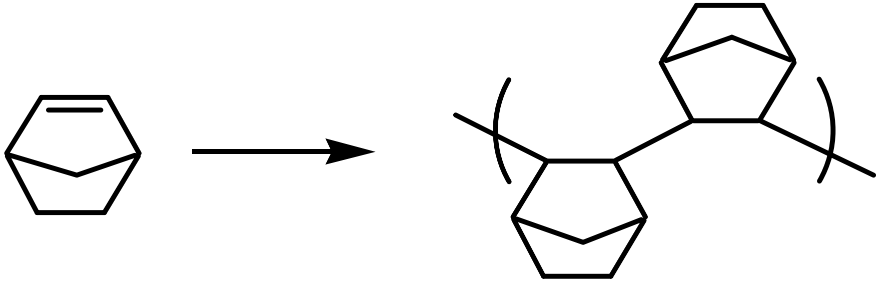
   Bulky alkyl groups and e$^-$ withdrawing groups decrease activity.

3. **Bulky bridging groups → decrease activity**

4. **MAO affords much higher activities than ethyl- or higher alkylaluminoxane cocatalysts**

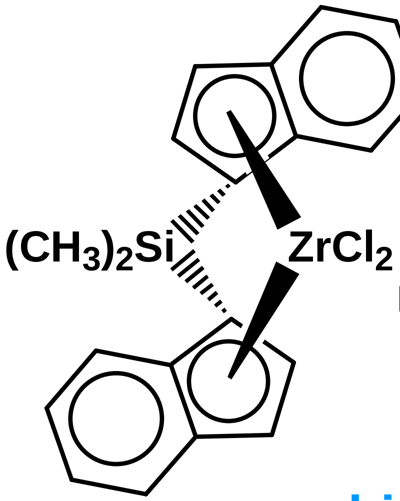
- **Metallocene catalysts**

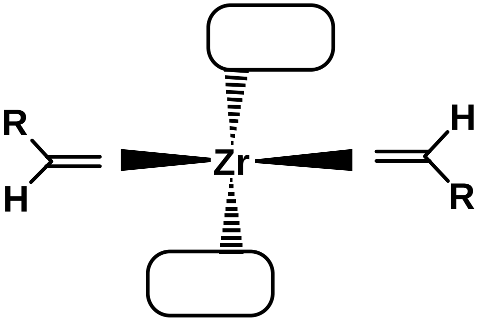
Capable of polymerizing strained cycloalkenes (cyclobutene, norbornene) through the double bond to yield crystalline, high-melting stereoregular polymers.



c.f. Z-N Catalyst : ring-opening polymerization of cycloalkene monomers is more common.

8.3.3 Stereochemistry of Metallocene Catalyzed Polymerization

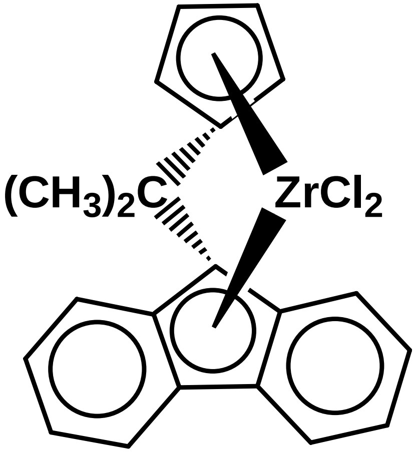


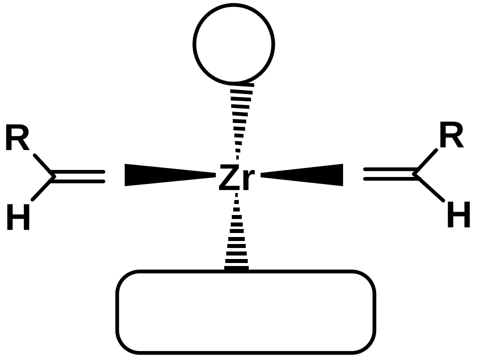


chiral

⇩

Isotactic polymer





achiral

⇩

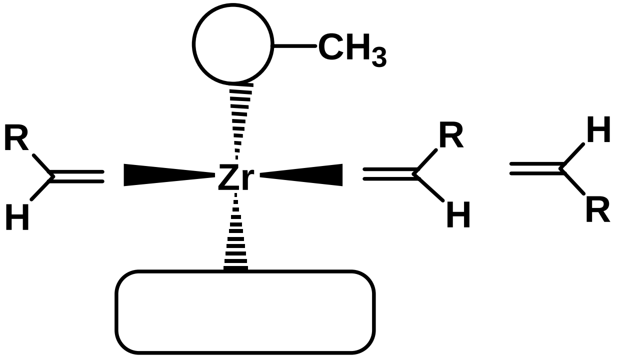
Syndiotactic polymer

Substitution of a methyl group on Cp ring

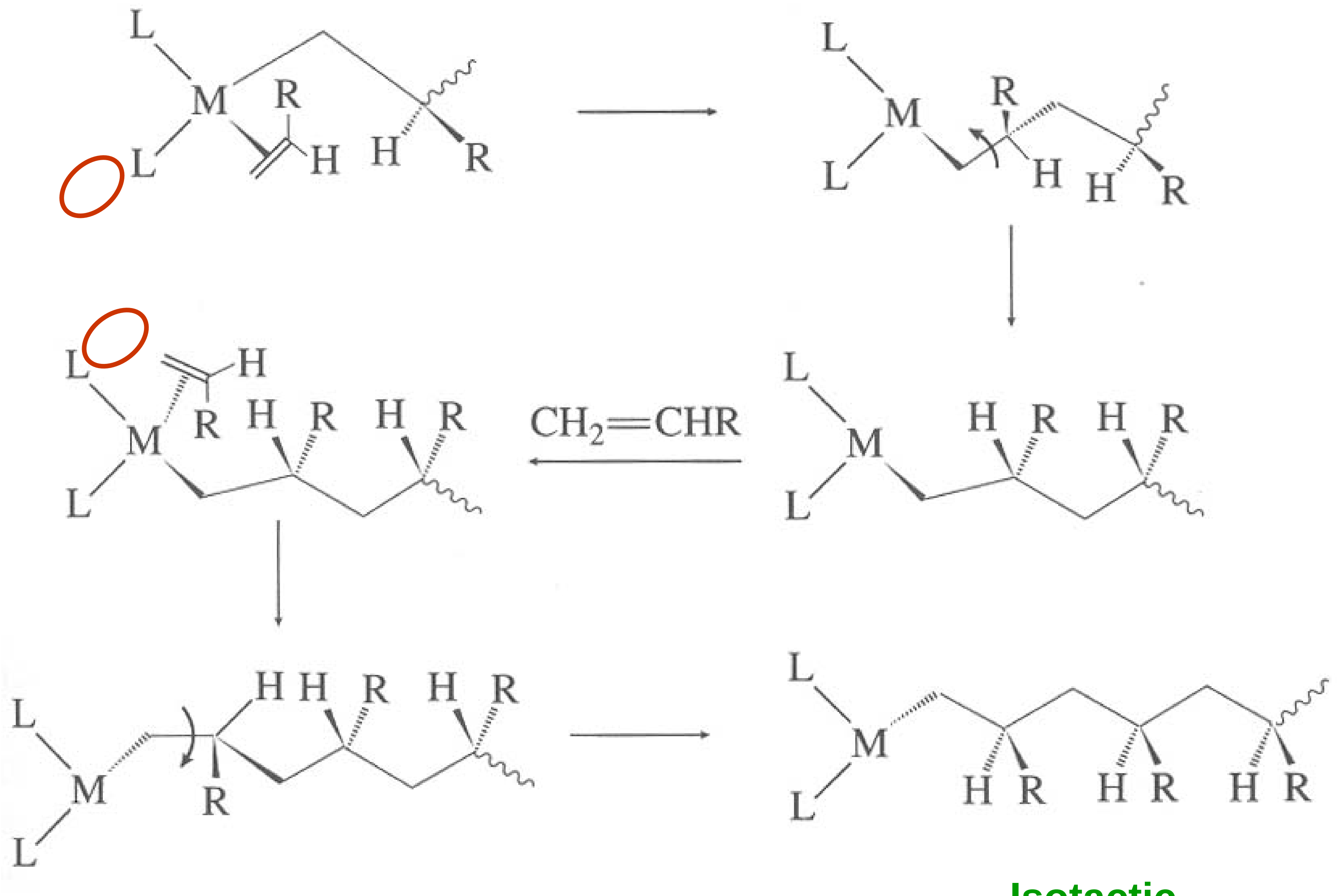
⇩

Hemiisotactic PP

(alternate methyls isotactic, the others atactic)

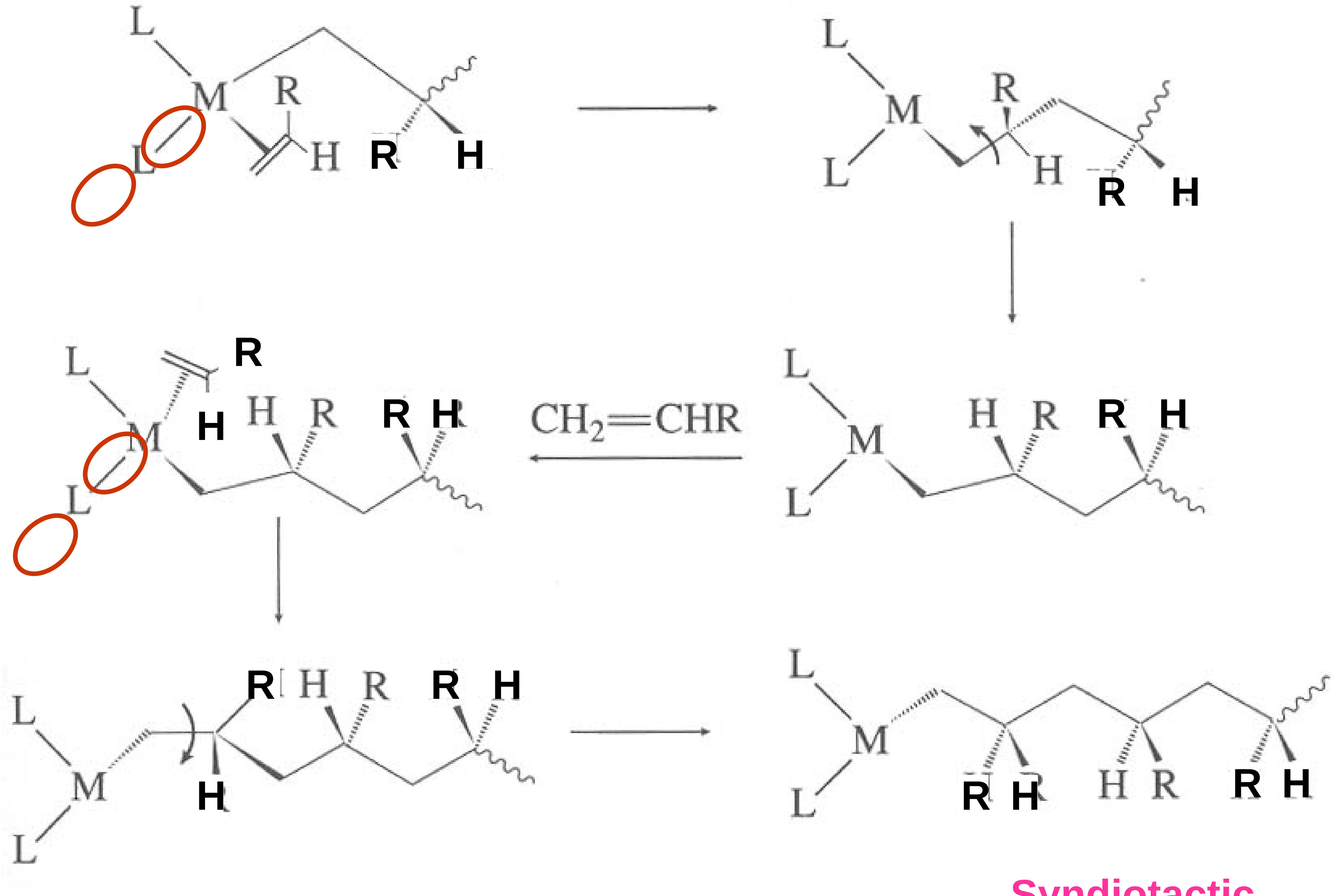


Scheme 8.5 Isotactic placement



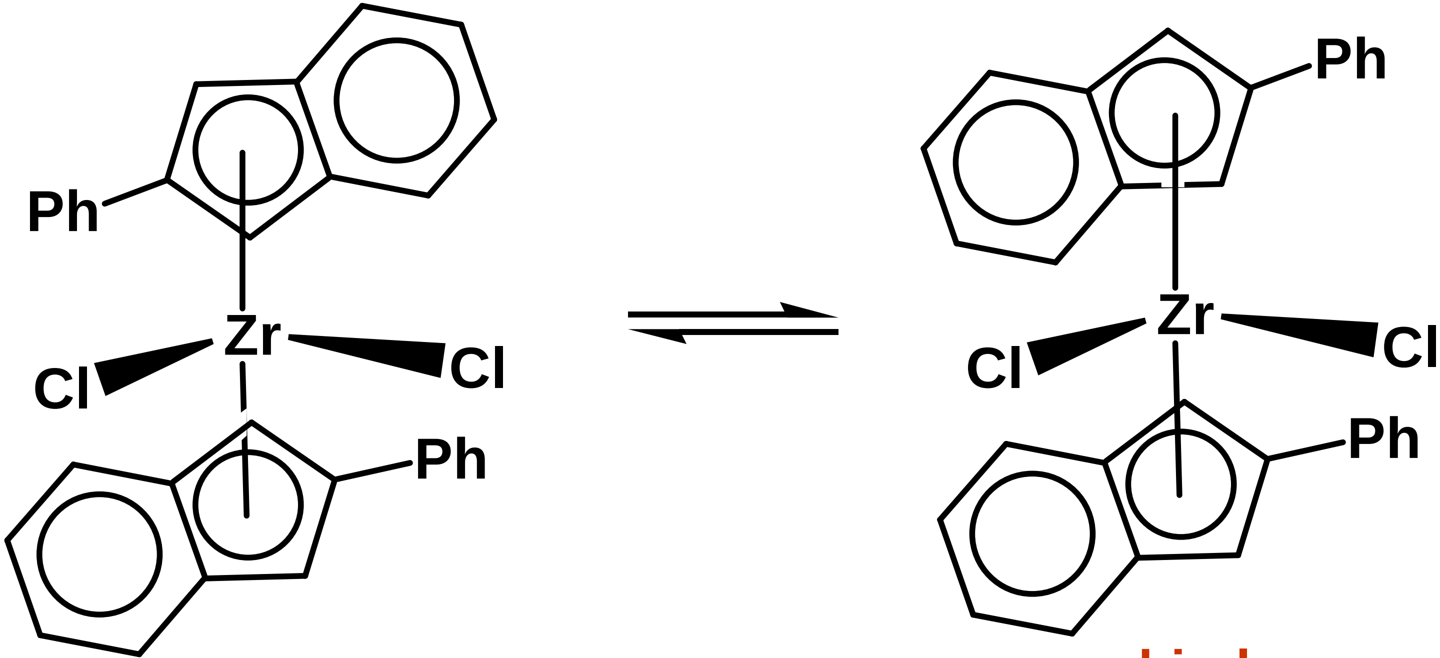
Isotactic

Syndiotactic placement



Syndiotactic

Rotate between chiral and achiral geometries



chiral

Isotactic blocks

crystalline

achiral

Atactic blocks

amorphous

Stereoblock copolymer: elastomeric properties

Thermoplastic elastomers from a single monomer in a one-pot synthesis

8.4 Z-N Copolymerization

LLDPE: ethylene + 1-alkene

EPM, EPR: ethylene + propylene (60:40)

EPDM: ethylene + propylene + diene monomer

↓

crosslinking

diene monomers

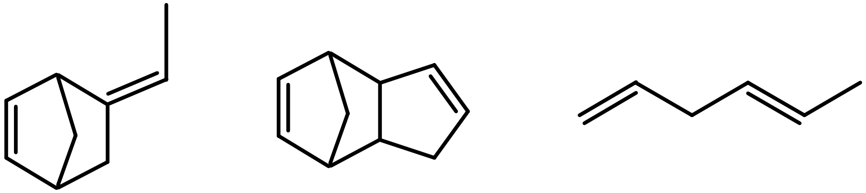


Table 8.5 Reactivity Ratios in Z-N Copolymerization

Monomer 1	Monomer 2	catalyst	r_1	r_2
Heterogeneous				
Ethylene	Propylene	$TiCl_3/AlR_3$	15.72	0.110
Ethylene	Propylene	VCl_3/AlR_3	5.61	0.145
Ethylene	1-Butene	VCl_3/AlR_3	26.90	0.043
Propylene	1-Butene	VCl_3/AlR_3	4.04	0.252
Homogeneous				
Ethylene	Propylene	Cp_2ZrMe_2	31	0.005
Ethylene	Propylene	$[Z(Ind)_2]ZrCl_2$	6.6	0.06
Ethylene	1-Butene	Cp_2ZrMe_2	55	0.017
Ethylene	1-Hexene	Cp_2ZrMe_2	69	0.02

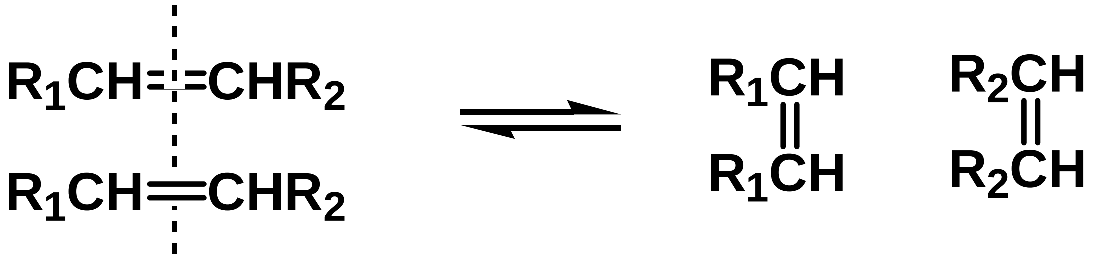
Ethylene is much more reactive than higher alkenes with both heterogeneous and homogeneous catalysis.

In most instances, r_1r_2 is close to unity.

8.7 Metathesis Polymerization

Greek meta + tithemi
(change) (place)

Olefin metathesis: double bond redistribution reaction of alkenes

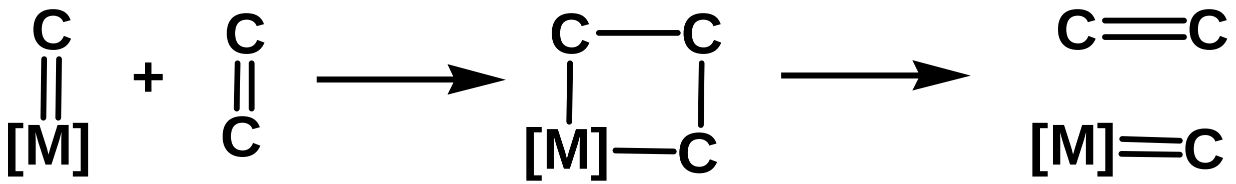


Transalkylidenation = Cleavage of double bonds

Catalysts by reaction of WCl_6 with alcohol and $C_2H_5AlCl_2$

Other transition metals : Ru, Mo, Re, Ti

Double bond redistribution



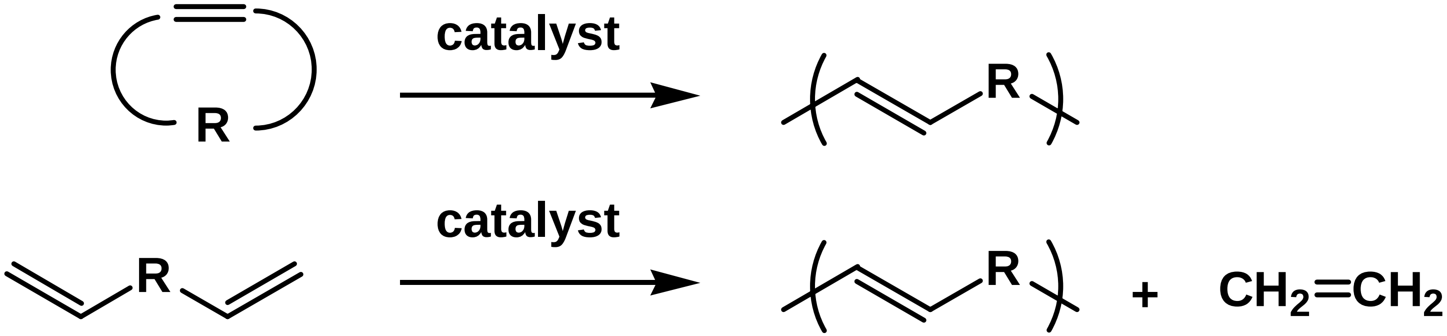
Metal carbene alkene metallacyclobutane

[M] = metal with ligands

Stable metal carbenes such as $(C_6H_5)_2C=W(CO)_5$ are known to initiate metathesis polymerization.

Synthesis of polymers by olefin metathesis

To make polymers containing precisely spaced carbon-carbon double bonds in the backbone from either cycloalkenes or acyclic dienes

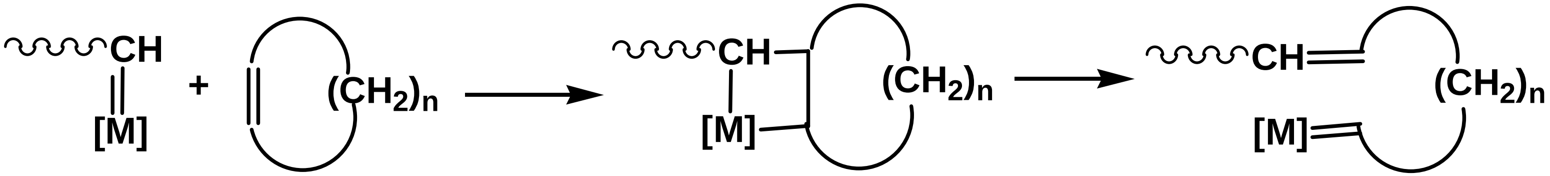


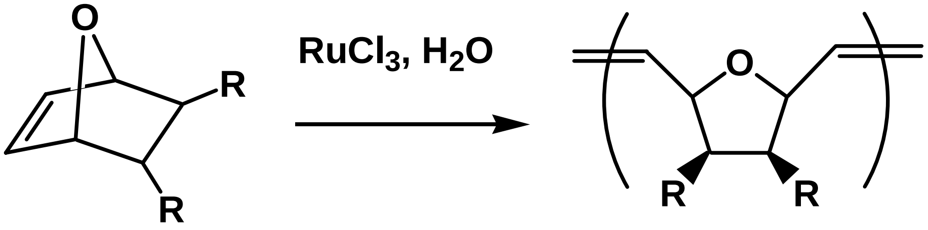
Primarily trans

Living polymers

High M.W. (> 10^5) + low M.W. oligomers

8.7.1 Ring-Opening Metathesis Polymerization (ROMP)

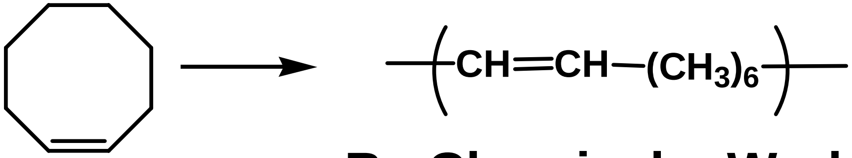




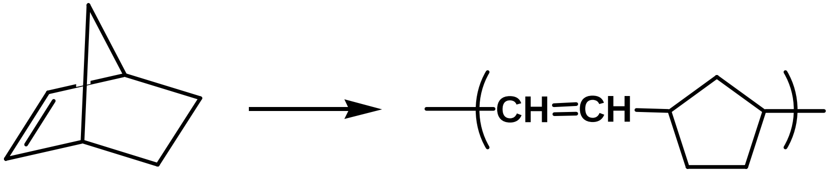
M.W. > 10^6

In aqueous solution

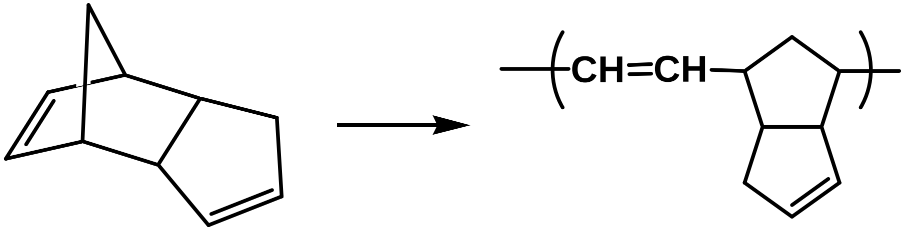
Commercial polymers



By Chemische Werke Huls in Germany (tradename: Vestenamer)

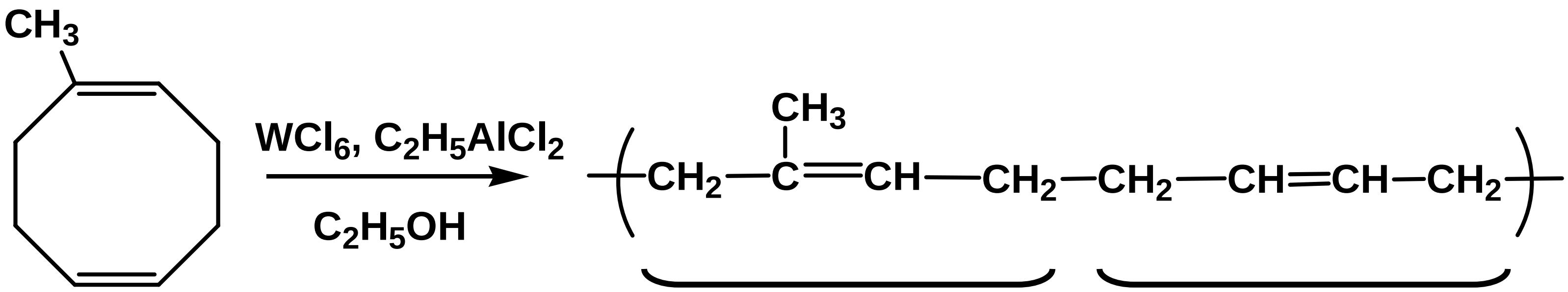


By CdF Chemie in France (tradename: Norsorex)



By Hercules in U.S. (tradename: Metton)

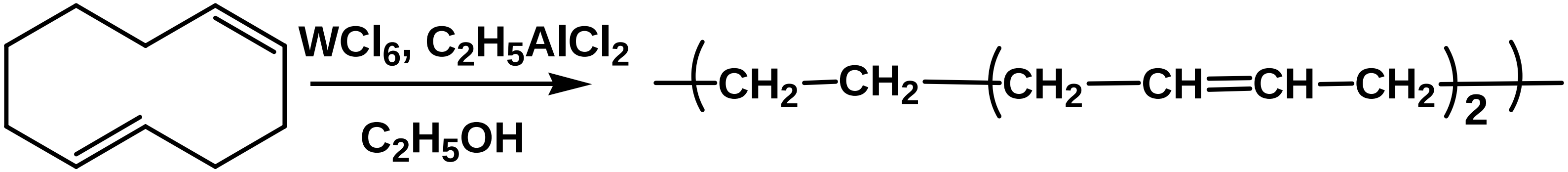
Cyclic Polyenes



$$\xrightarrow[C_2H_5OH]{WCl_6,\ C_2H_5AlCl_2}$$

$$-\!\left(\underbrace{CH_2-\overset{CH_3}{C}=CH-CH_2}-\underbrace{CH_2-CH=CH-CH_2}\right)\!-$$

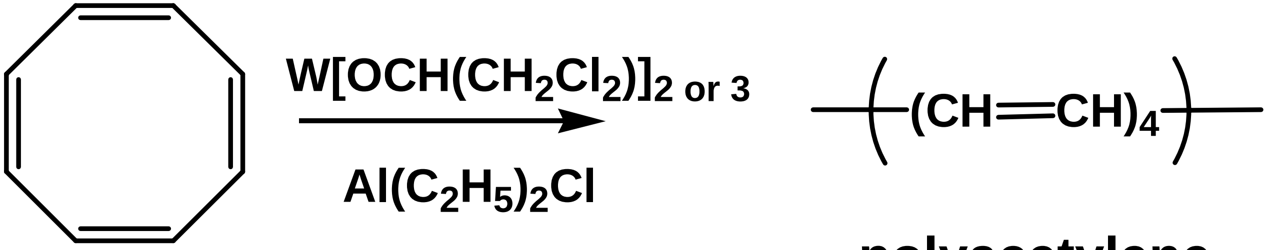
Alternating copolymer of isoprene & butadiene



$$\xrightarrow[C_2H_5OH]{WCl_6,\ C_2H_5AlCl_2}$$

$$-\!\left(CH_2-CH_2-\left(CH_2-CH=CH-CH_2\right)_2\right)\!-$$

1:2 polymer of ethylene & butadiene



$$\xrightarrow[Al(C_2H_5)_2Cl]{W[OCH(CH_2Cl_2)]_{2\text{ or }3}}$$

$$-\!\left((CH=CH)_4\right)\!-$$

polyacetylene

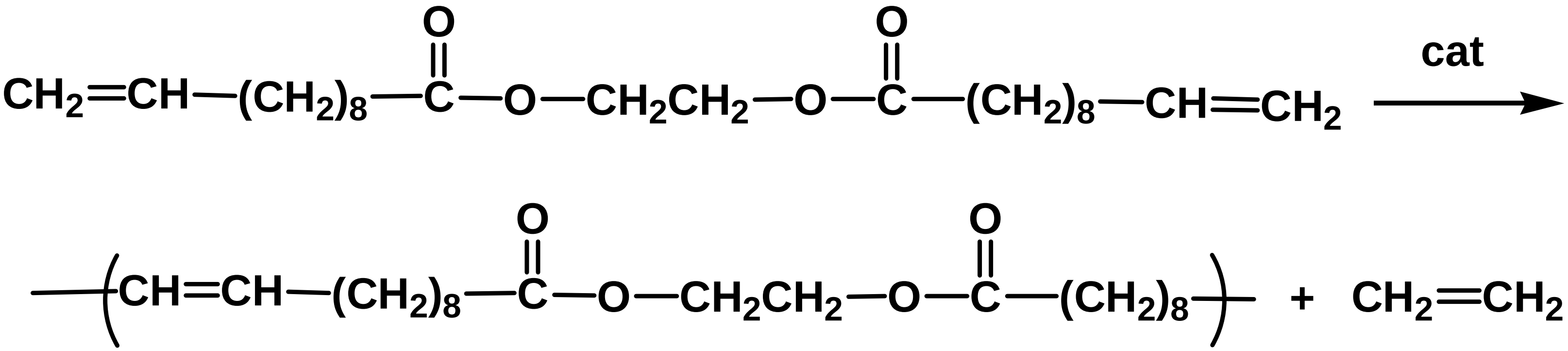
(primarily trans)

8.7.2 Acyclic Diene Metathesis Polymerization (ADMET)

$$CH_2{=}CH{-}(CH_2)_6{-}CH{=}CH_2 \xrightarrow{\text{cat}} {-}\!\left(CH{=}CH{-}(CH_2)_6\right)\!{-} \; + \; CH_2{=}CH_2$$

Must be removed
to obtain high-M-W polymer

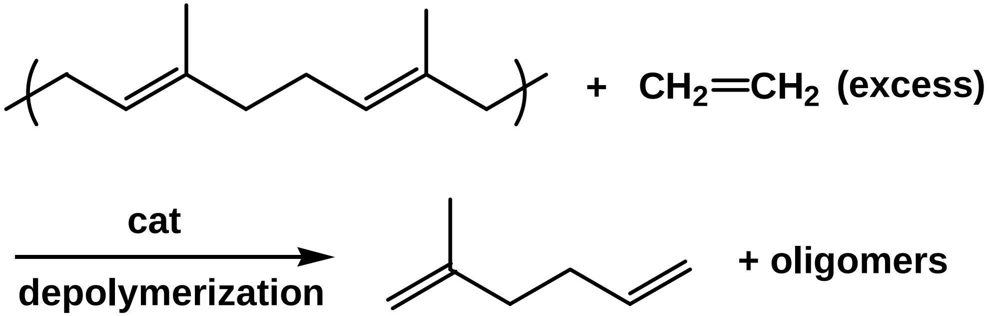
ADMET Useful for synthesis of functionalized polymers



$$CH_2{=}CH{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_8{-}CH{=}CH_2 \xrightarrow{\text{cat}}$$

$${-}\!\left(CH{=}CH{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_8\right)\!{-} \; + \; CH_2{=}CH_2$$

Metathesis reactions: eqm processes



For degrading scrap rubber into potentially useful products.