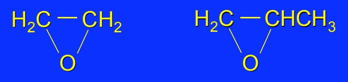
6.19
Epoxidation of Alkenes

Epoxides

are examples of heterocyclic compounds

three-membered rings that contain oxygen

ethylene oxide propylene oxide

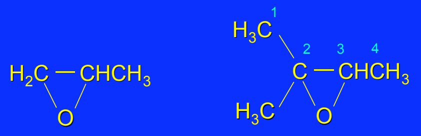


Epoxide Nomenclature

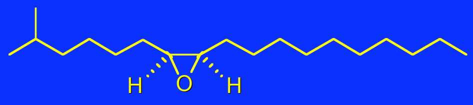
Substitutive nomenclature: named as epoxy-substituted alkanes.

"epoxy" precedes name of alkane

1,2-epoxypropane 2-methyl-2,3-epoxybutane

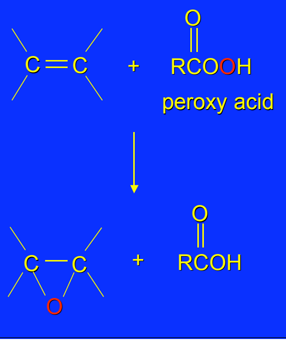


Problem 6.21 Give the IUPAC name, including stereochemistry, for disparlure.

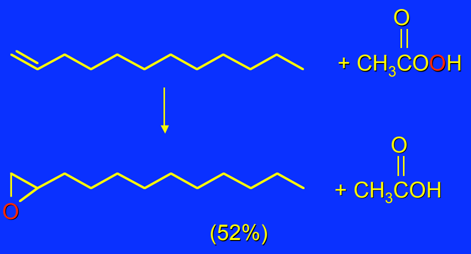


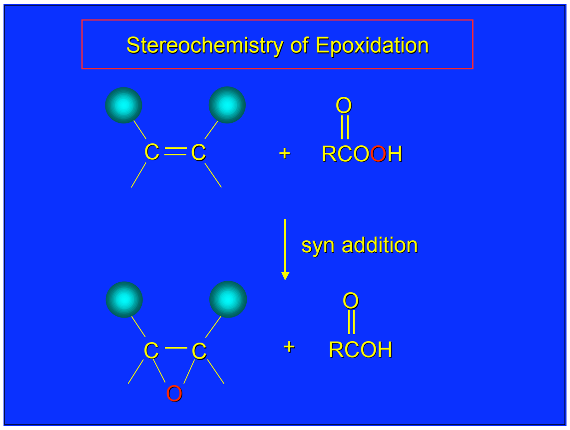
cis-2-Methyl-7,8-epoxyoctadecane

Epoxidation of Alkenes



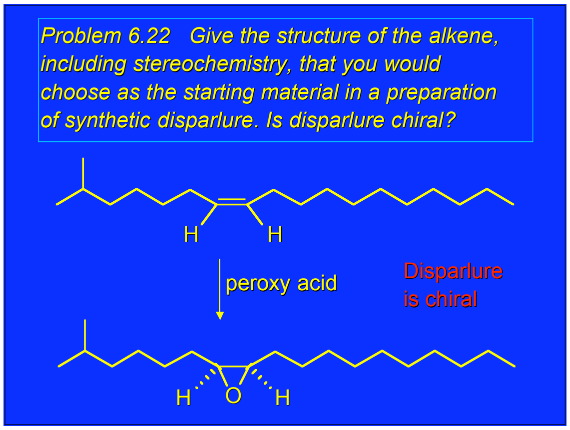
Example





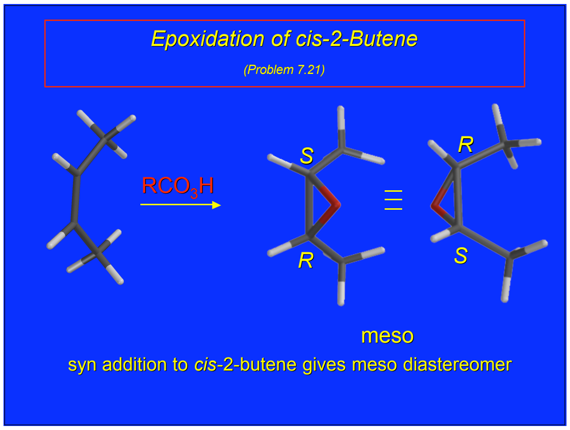
Stereochemistry of Epoxidation

$$C{=}C \quad + \quad R\overset{O}{\overset{\|}{C}}OOH \xrightarrow{\text{syn addition}} \underset{O}{C{-}C} \quad + \quad R\overset{O}{\overset{\|}{C}}OH$$



Problem 6.22 Give the structure of the alkene, including stereochemistry, that you would choose as the starting material in a preparation of synthetic disparlure. Is disparlure chiral?

Disparlure is chiral

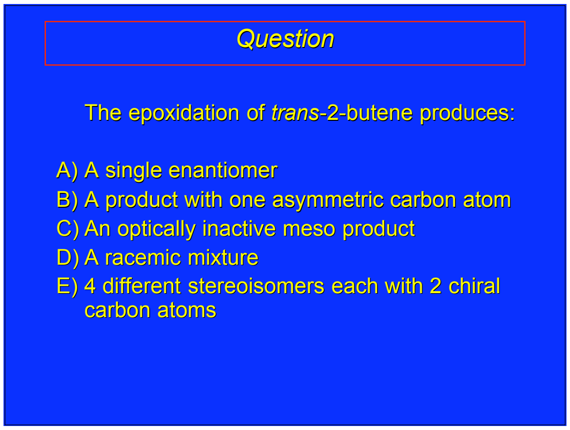


Epoxidation of cis-2-Butene

(Problem 7.21)

meso

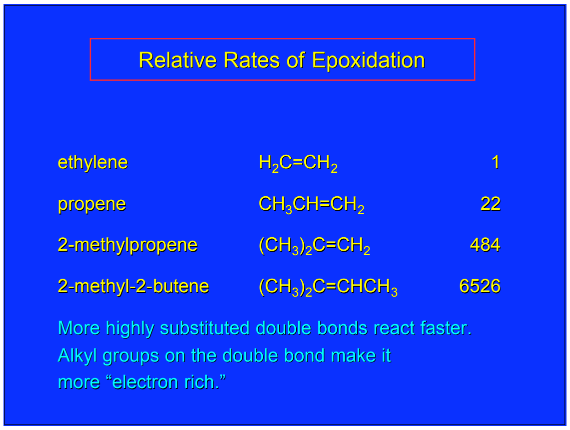
syn addition to *cis*-2-butene gives meso diastereomer



Question

The epoxidation of *trans*-2-butene produces:

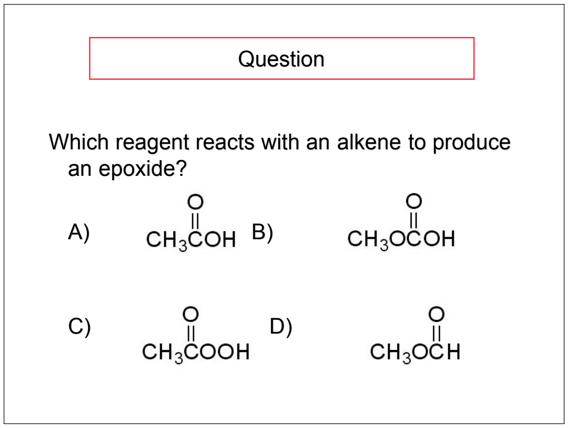
A) A single enantiomer
B) A product with one asymmetric carbon atom
C) An optically inactive meso product
D) A racemic mixture
E) 4 different stereoisomers each with 2 chiral carbon atoms



Relative Rates of Epoxidation

ethylene	$H_2C{=}CH_2$	1
propene	$CH_3CH{=}CH_2$	22
2-methylpropene	$(CH_3)_2C{=}CH_2$	484
2-methyl-2-butene	$(CH_3)_2C{=}CHCH_3$	6526

More highly substituted double bonds react faster. Alkyl groups on the double bond make it more "electron rich."



Question

Which reagent reacts with an alkene to produce an epoxide?

A) $CH_3\overset{O}{\overset{\|}{C}}OH$ B) $CH_3O\overset{O}{\overset{\|}{C}}OH$

C) $CH_3\overset{O}{\overset{\|}{C}}OOH$ D) $CH_3O\overset{O}{\overset{\|}{C}}H$

6.20
Ozonolysis of Alkenes

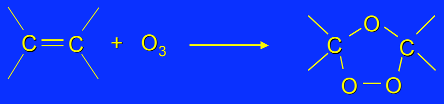
Ozonolysis has both synthetic and analytical applications.

- synthesis of aldehydes and ketones
- identification of substituents on the double bond of an alkene

---

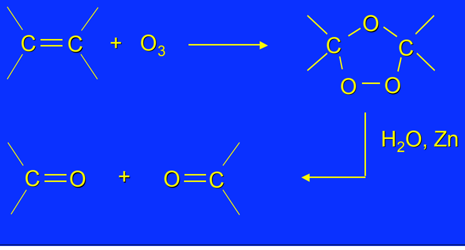
Ozonolysis of Alkenes

First step is the reaction of the alkene with ozone. The product is an *ozonide.*



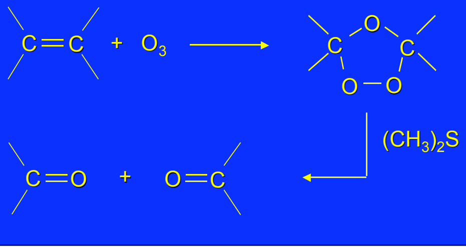
Ozonolysis of Alkenes

Second step is hydrolysis of the ozonide.
Two aldehydes, two ketones, or an aldehyde
and a ketone are formed.

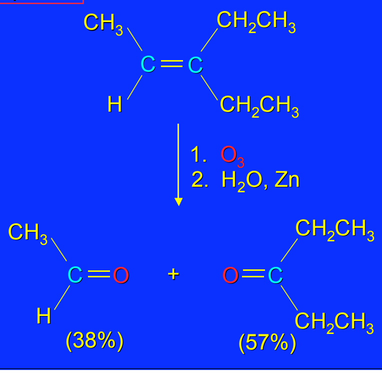


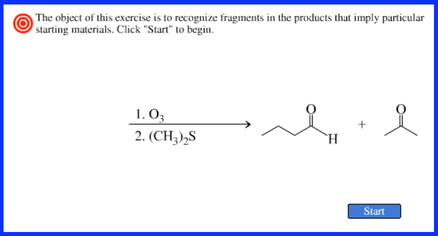
Ozonolysis of Alkenes

As an alternative to hydrolysis, the ozonide can
be treated with dimethyl sulfide.



Example

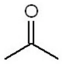


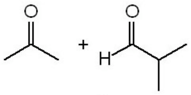


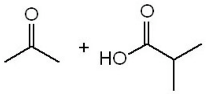
The object of this exercise is to recognize fragments in the products that imply particular starting materials. Click "Start" to begin.

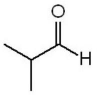
Question

The ozonolysis of 2,4-dimethyl-2-pentene will produce:

A) 

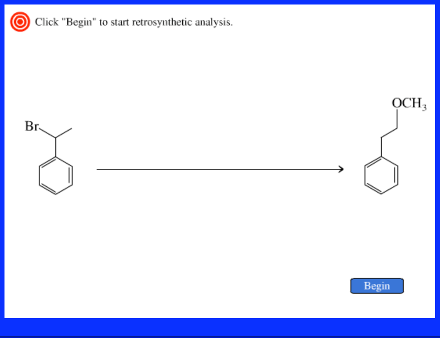
B) 

C) 

D) 

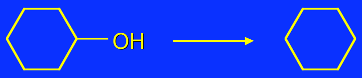
6.21
Introduction to Organic Chemical Synthesis

Retrosynthesis



Click "Begin" to start retrosynthetic analysis.

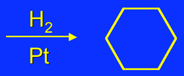
Prepare cyclohexane from cyclohexanol



devise a synthetic plan

- reason backward from the target molecule
- always use reactions that you are sure will work

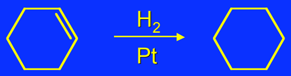
Prepare cyclohexane from cyclohexanol



ask yourself the key question

- "Starting with anything, how can I make cyclohexane in a single step by a reaction I am sure will work?"

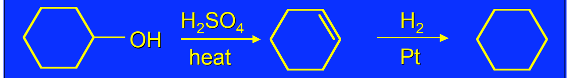
Prepare cyclohexane from cyclohexanol



The only reaction covered so far for preparing alkanes is catalytic hydrogenation of alkenes.

This leads to a new question. "Starting with anything, how can I prepare cyclohexene in a single step by a reaction I am sure will work?"

Prepare cyclohexane from cyclohexanol



Alkenes can be prepared by dehydration of alcohols.

The synthesis is complete.

Question

Which one of the following outlines the best synthesis of *trans*-2-chlorocyclohexanol?

A) Heat a mixture of cyclohexanol and Cl_2 to 400°C.

B) 1. Treat cyclohexene with HCl;
   2. Treat product of reaction 1 with peroxyacetic acid.

C) 1. Hydrogenation of cyclohexene in the presence of Pt;
   2. Treat product of reaction 1 with Cl_2 in H_2O.

D) 1. Treat bromocyclohexane with $KOC(CH_3)_3$ in DMSO;
   2. Treat product of reaction 1 with Cl_2 in water.

Question

Which one of the following is **not stereospecific**?

A) reaction of *cis*-2-butene with peroxyacetic acid

B) hydroboration-oxidation of 1-methylcyclopentene

C) addition of Br_2 to *trans*-2-pentene

D) addition of HBr to *cis*-2-butene in the presence of peroxides

---

Question

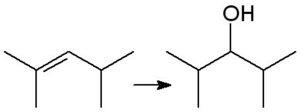
Which combination of reagents is the best choice for carrying out the conversion shown?

A) 50% water - 50% sulfuric acid

B) 1. H_2SO_4
   2. H_2O, heat

C) 1. O_3
   2. H_2O, Zn

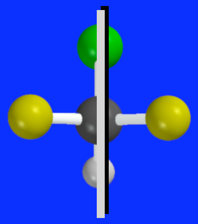
D) 1. BH_3-THF
   2. H_2O_2, NaOH



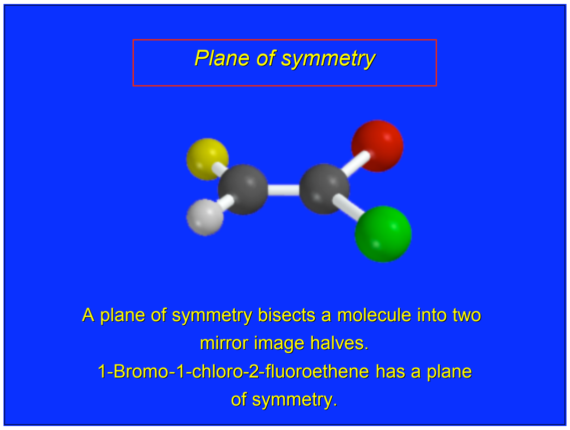
Chirality (continued)

Di-substituted cyclopentanes and cylcohexanes

Plane of symmetry

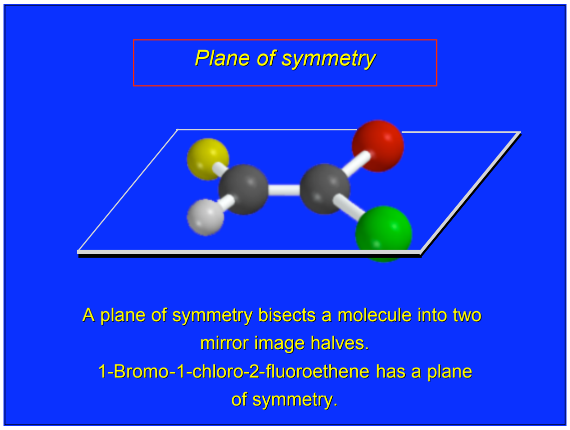


A plane of symmetry bisects a molecule into two mirror image halves. Chlorodifluoromethane has a plane of symmetry.



Plane of symmetry

A plane of symmetry bisects a molecule into two mirror image halves.
1-Bromo-1-chloro-2-fluoroethene has a plane of symmetry.



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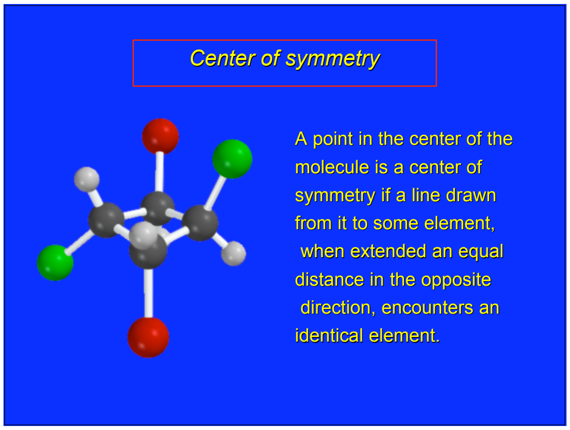
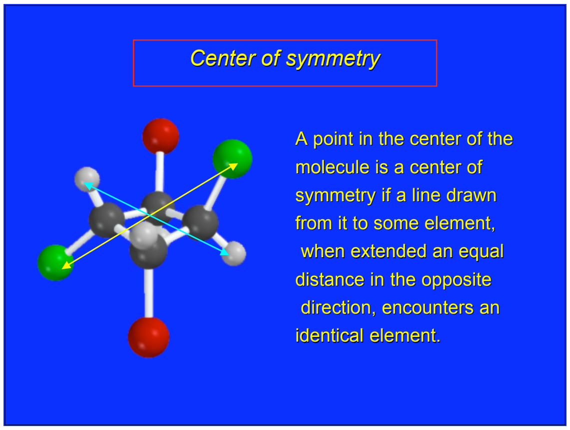


Center of symmetry

A point in the center of the molecule is a center of symmetry if a line drawn from it to some element, when extended an equal distance in the opposite direction, encounters an identical element.



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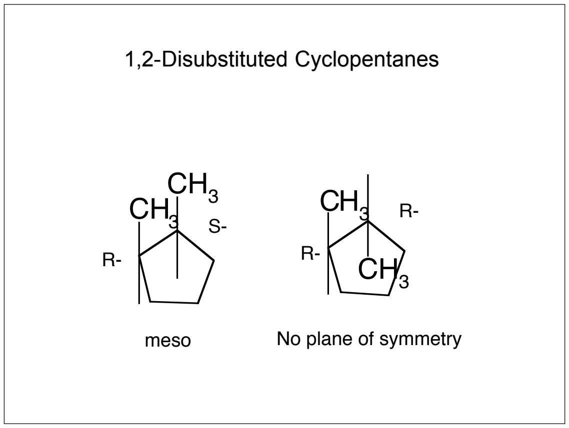
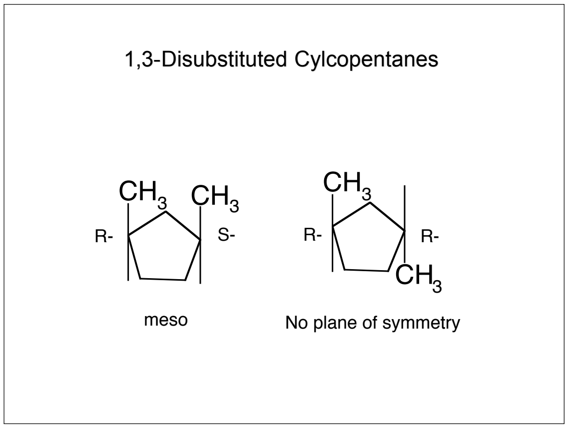


1,2-Disubstituted Cyclopentanes

meso

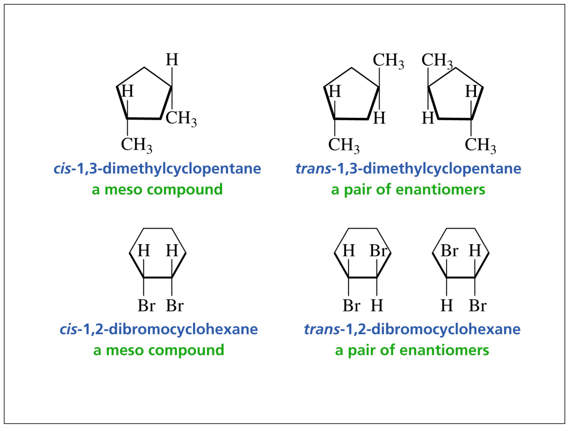
No plane of symmetry



1,3-Disubstituted Cylcopentanes

meso

No plane of symmetry

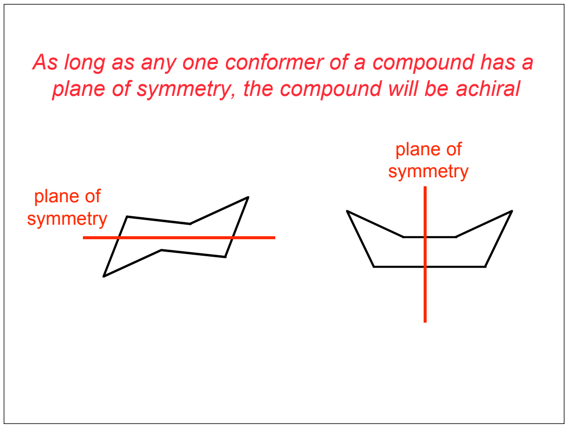


cis-1,3-dimethylcyclopentane
a meso compound

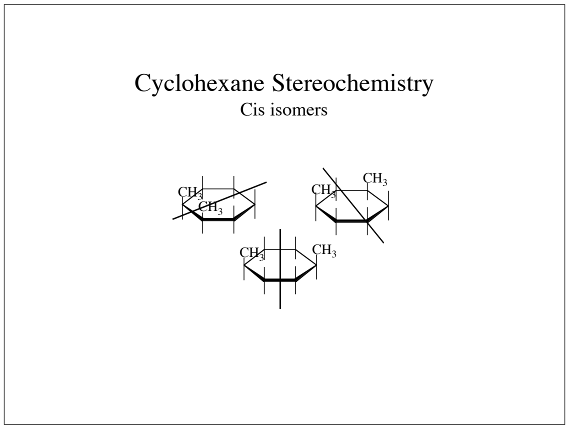
trans-1,3-dimethylcyclopentane
a pair of enantiomers

cis-1,2-dibromocyclohexane
a meso compound

trans-1,2-dibromocyclohexane
a pair of enantiomers

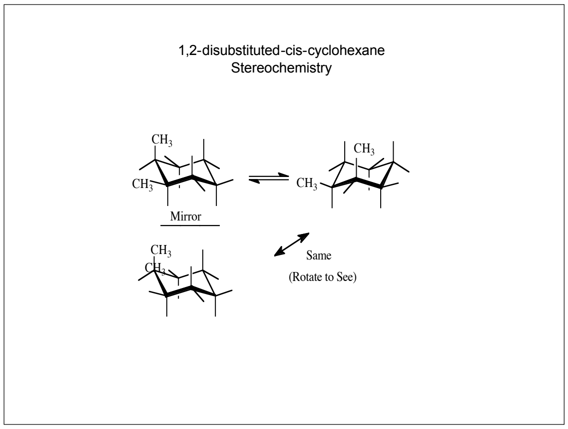


As long as any one conformer of a compound has a plane of symmetry, the compound will be achiral

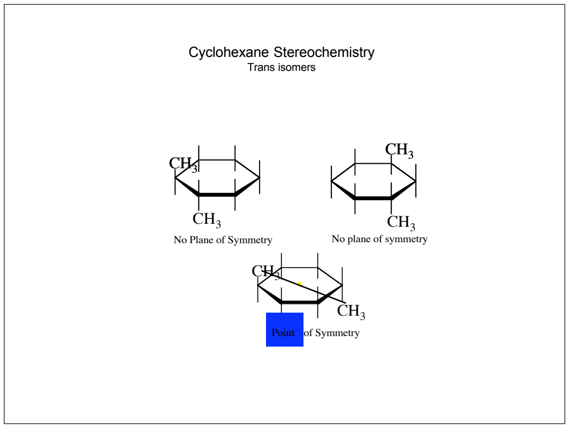


Cyclohexane Stereochemistry

Cis isomers



1,2-disubstituted-cis-cyclohexane
Stereochemistry



Cyclohexane Stereochemistry

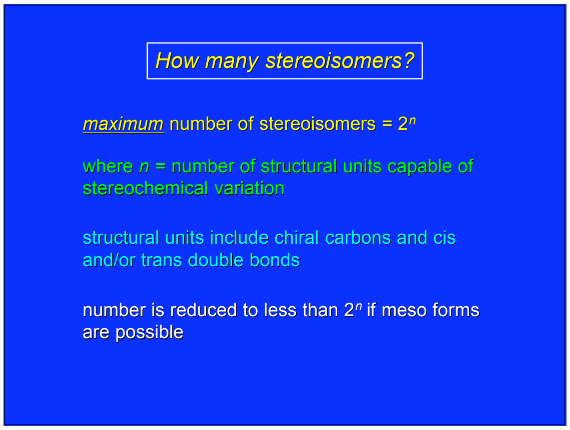
Trans isomers

No Plane of Symmetry

No plane of symmetry

Point of Symmetry

Molecules
with
Multiple chiral carbons
(continued)



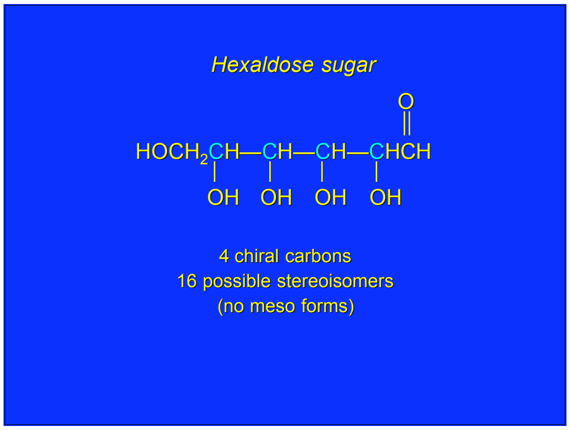
How many stereoisomers?

maximum number of stereoisomers = 2^n

where n = number of structural units capable of stereochemical variation

structural units include chiral carbons and cis and/or trans double bonds

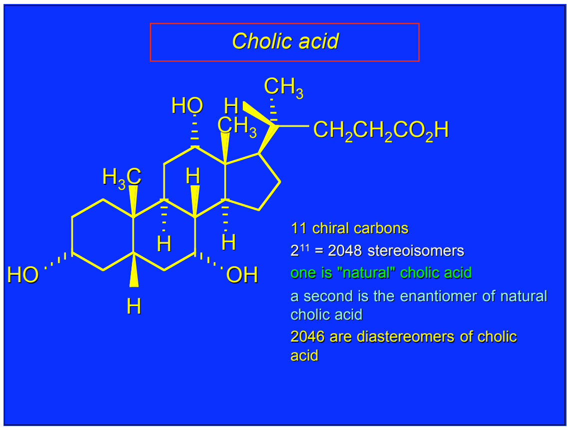
number is reduced to less than 2^n if meso forms are possible



Hexaldose sugar

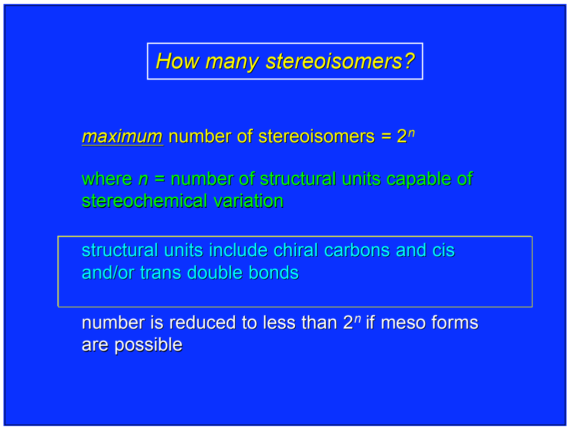
$$\mathrm{HOCH_2\underset{OH}{\underset{|}{C}H}{-}\underset{OH}{\underset{|}{C}H}{-}\underset{OH}{\underset{|}{C}H}{-}\underset{OH}{\underset{|}{C}H}\overset{O}{\overset{\|}{C}}H}$$

4 chiral carbons
16 possible stereoisomers
(no meso forms)



Cholic acid

11 chiral carbons
2^{11} = 2048 stereoisomers
one is "natural" cholic acid
a second is the enantiomer of natural cholic acid
2046 are diastereomers of cholic acid



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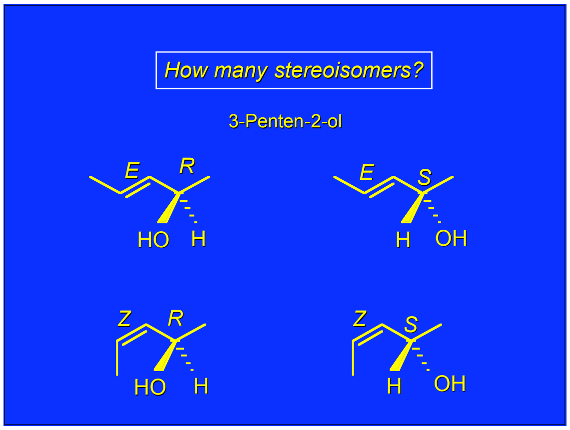
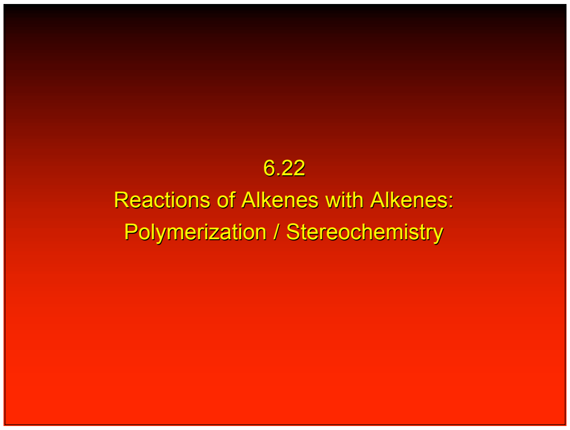
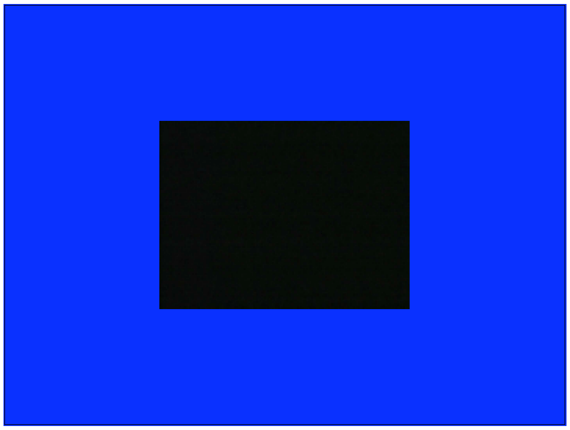


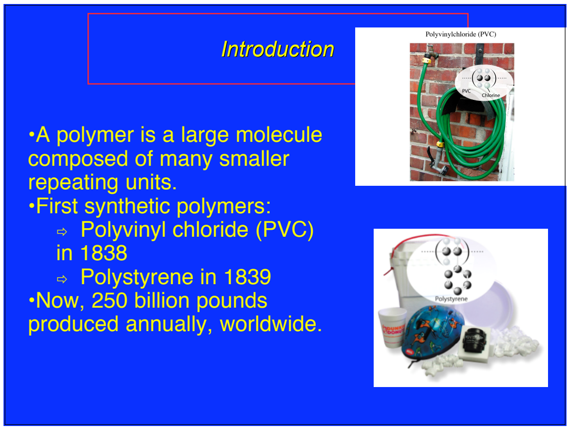
How many stereoisomers?

3-Penten-2-ol



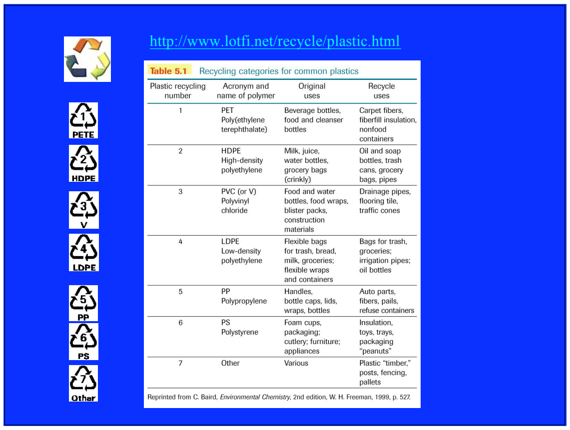
6.22
Reactions of Alkenes with Alkenes:
Polymerization / Stereochemistry





Introduction

- A polymer is a large molecule composed of many smaller repeating units.
- First synthetic polymers:
  - ⇨ Polyvinyl chloride (PVC) in 1838
  - ⇨ Polystyrene in 1839
- Now, 250 billion pounds produced annually, worldwide.

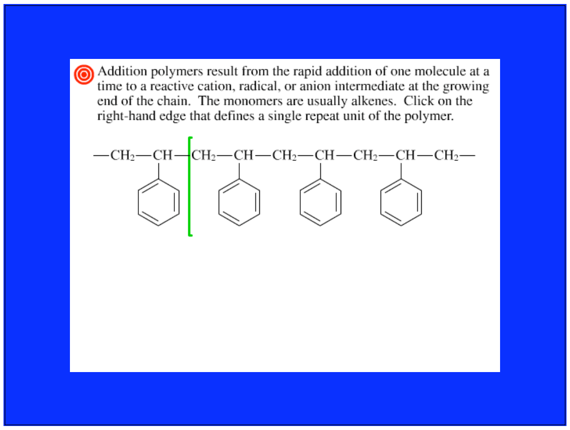


http://www.lotfi.net/recycle/plastic.html

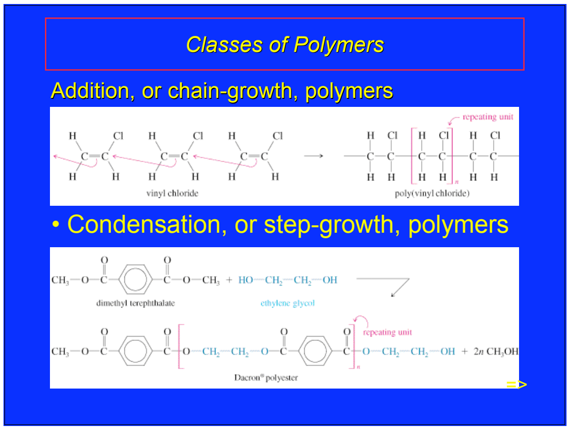
Table 5.1 Recycling categories for common plastics

Plastic recycling number	Acronym and name of polymer	Original uses	Recycle uses
1	PET Poly(ethylene terephthalate)	Beverage bottles, food and cleanser bottles	Carpet fibers, fiberfill insulation, nonfood containers
2	HDPE High-density polyethylene	Milk, juice, water bottles, grocery bags (crinkly)	Oil and soap bottles, trash cans, grocery bags, pipes
3	PVC (or V) Polyvinyl chloride	Food and water bottles, food wraps, blister packs, construction materials	Drainage pipes, flooring tile, traffic cones
4	LDPE Low-density polyethylene	Flexible bags for trash, bread, milk, groceries; flexible wraps and containers	Bags for trash, groceries; irrigation pipes; oil bottles
5	PP Polypropylene	Handles, bottle caps, lids, wraps, bottles	Auto parts, fibers, pails, refuse containers
6	PS Polystyrene	Foam cups, packaging; cutlery; furniture; appliances	Insulation, toys, trays, packaging "peanuts"
7	Other	Various	Plastic "timber," posts, fencing, pallets

Reprinted from C. Baird, *Environmental Chemistry*, 2nd edition, W. H. Freeman, 1999, p. 527.



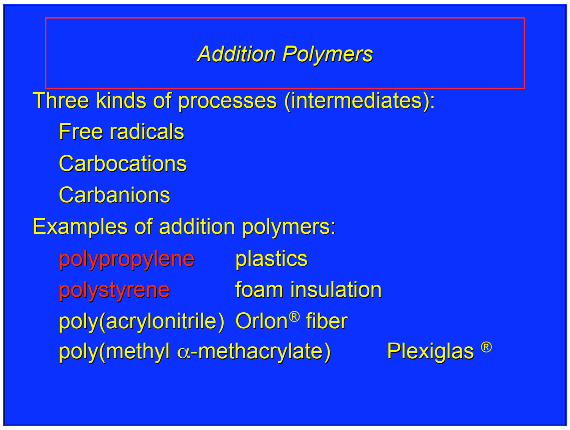
Addition polymers result from the rapid addition of one molecule at a time to a reactive cation, radical, or anion intermediate at the growing end of the chain. The monomers are usually alkenes. Click on the right-hand edge that defines a single repeat unit of the polymer.



Classes of Polymers

Addition, or chain-growth, polymers

- Condensation, or step-growth, polymers



Addition Polymers

Three kinds of processes (intermediates):

Free radicals

Carbocations

Carbanions

Examples of addition polymers:

polypropylene	plastics
polystyrene	foam insulation
poly(acrylonitrile)	Orlon® fiber
poly(methyl α-methacrylate)	Plexiglas ®

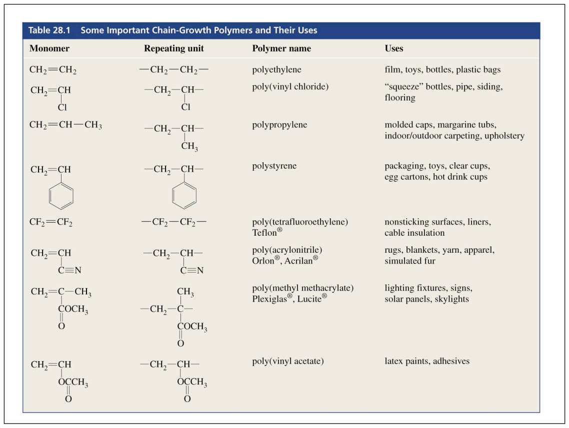
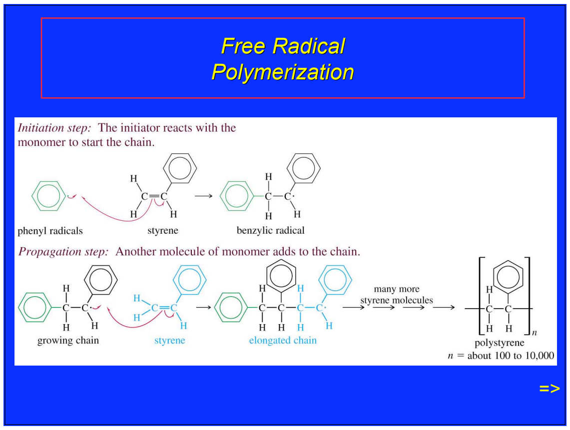


Table 28.1 Some Important Chain-Growth Polymers and Their Uses

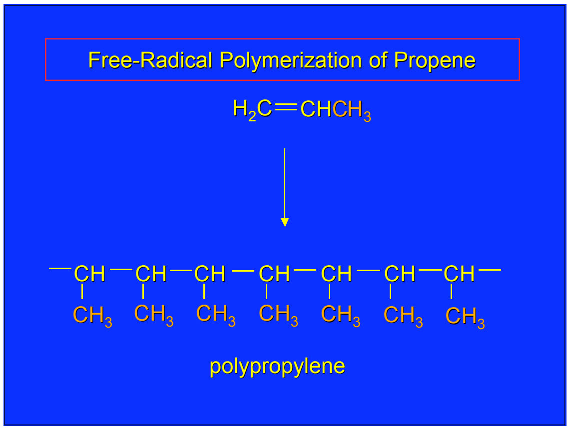
Monomer	Repeating unit	Polymer name	Uses
$CH_2{=}CH_2$	$-CH_2-CH_2-$	polyethylene	film, toys, bottles, plastic bags
$CH_2{=}\underset{\displaystyle Cl}{\underset{\vert}{CH}}$	$-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-$	poly(vinyl chloride)	"squeeze" bottles, pipe, siding, flooring
$CH_2{=}CH-CH_3$	$-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-$	polypropylene	molded caps, margarine tubs, indoor/outdoor carpeting, upholstery
$CH_2{=}\underset{\displaystyle C_6H_5}{\underset{\vert}{CH}}$	$-CH_2-\underset{\displaystyle C_6H_5}{\underset{\vert}{CH}}-$	polystyrene	packaging, toys, clear cups, egg cartons, hot drink cups
$CF_2{=}CF_2$	$-CF_2-CF_2-$	poly(tetrafluoroethylene) Teflon®	nonsticking surfaces, liners, cable insulation
$CH_2{=}\underset{\displaystyle C{\equiv}N}{\underset{\vert}{CH}}$	$-CH_2-\underset{\displaystyle C{\equiv}N}{\underset{\vert}{CH}}-$	poly(acrylonitrile) Orlon®, Acrilan®	rugs, blankets, yarn, apparel, simulated fur
$CH_2{=}\underset{\displaystyle \underset{\displaystyle O}{\overset{\Vert}{C}}OCH_3}{\underset{\vert}{C}}-CH_3$	$-CH_2-\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle \underset{\displaystyle O}{\overset{\Vert}{C}}OCH_3}{\underset{\vert}{C}}}}-$	poly(methyl methacrylate) Plexiglas®, Lucite®	lighting fixtures, signs, solar panels, skylights
$CH_2{=}\underset{\displaystyle O\underset{\displaystyle O}{\overset{\Vert}{C}}CH_3}{\underset{\vert}{CH}}$	$-CH_2-\underset{\displaystyle O\underset{\displaystyle O}{\overset{\Vert}{C}}CH_3}{\underset{\vert}{CH}}-$	poly(vinyl acetate)	latex paints, adhesives



Free Radical Polymerization

Initiation step: The initiator reacts with the monomer to start the chain.

Propagation step: Another molecule of monomer adds to the chain.

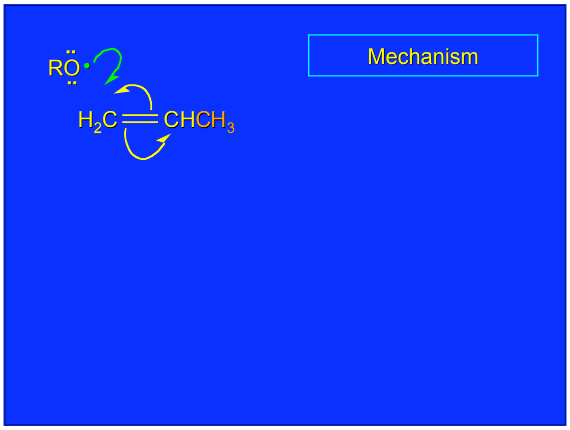


Free-Radical Polymerization of Propene

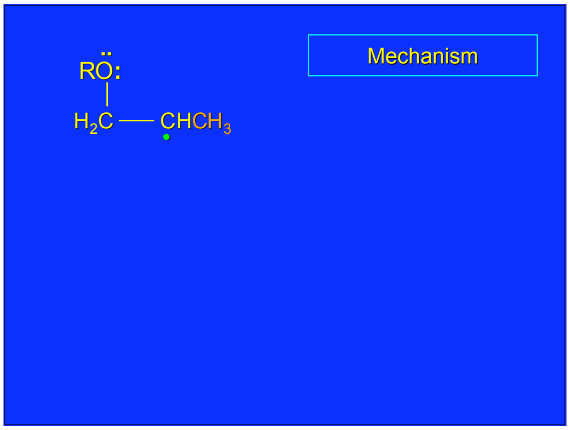
$H_2C{=}CHCH_3$

$$-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-$$

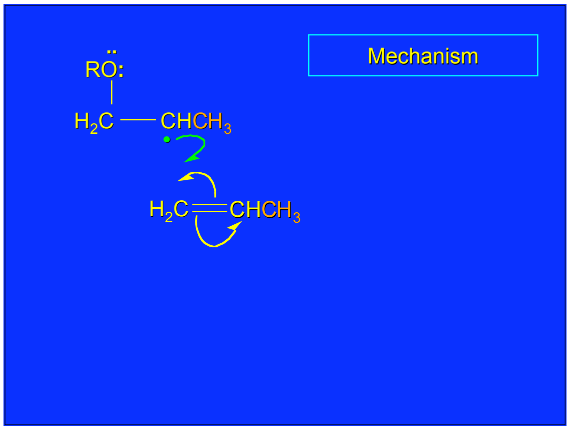
polypropylene



Mechanism

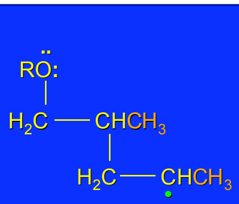


Mechanism

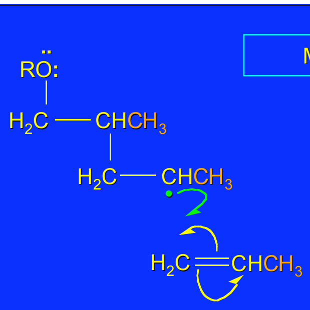


Mechanism

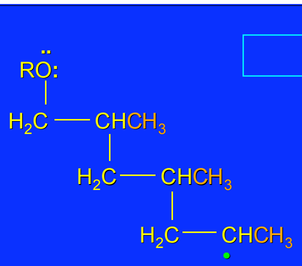
Mechanism



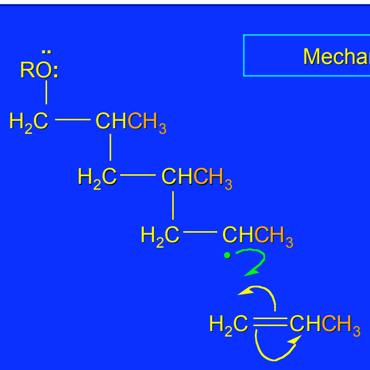
Mechanism



Mechanism



Mechanism



Likewise...

$H_2C{=}CHCl$ → polyvinyl chloride

$H_2C{=}CHC_6H_5$ → polystyrene

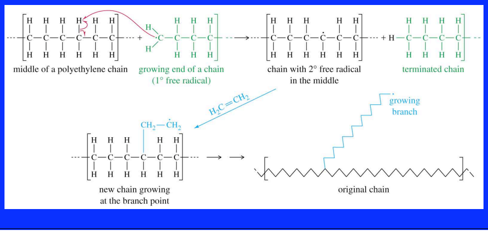
$F_2C{=}CF_2$ → Teflon

Chain Branching

Low-density polyethylene:

soft and flimsy

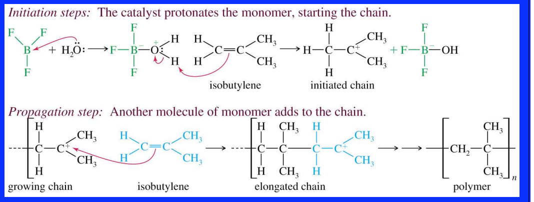
highly branched, amorphous structure



Cationic Polymerization

Alkene is treated with an acid.

Intermediate must be a stable carbocation.



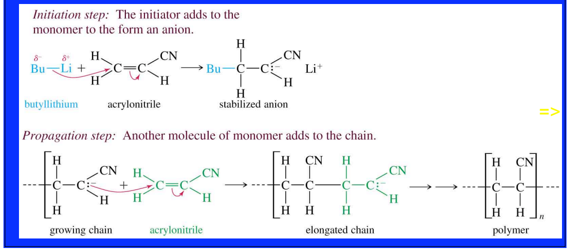
Initiation steps: The catalyst protonates the monomer, starting the chain.

Propagation step: Another molecule of monomer adds to the chain.

Anionic Polymerization

Alkene must have an electron-withdrawing group like C=O, C≡N, or NO_2.

Initiator: Grignard or organolithium reagent.

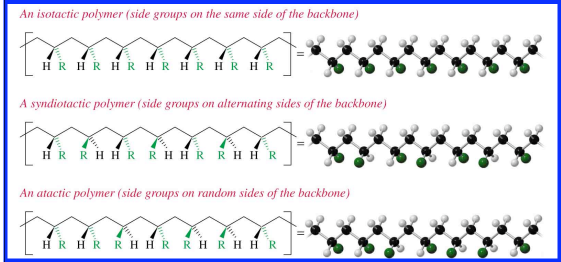


Initiation step: The initiator adds to the monomer to the form an anion.

Propagation step: Another molecule of monomer adds to the chain.

=>

Stereochemistry



An isotactic polymer (side groups on the same side of the backbone)

A syndiotactic polymer (side groups on alternating sides of the backbone)

An atactic polymer (side groups on random sides of the backbone)

=>

Properties of Polymers

Isotactic and syndiotactic polymers are stronger and stiffer due to their regular packing arrangement.

Anionic intermediate usually gives isotactic or syndiotactic polymers.

Free radical polymerization is nearly random, giving branched atactic polymers.

Ziegler-Natta Catalyst

Polymerization is completely stereospecific.

Either isotactic or syndiotactic, depending on catalyst.

Polymer is linear, not branched.

Example of catalyst: solution of $TiCl_4$ mixed with solution of $(CH_3CH_2)_3Al$ and heated for an hour.