

CHEM 4210/5210

Chapter 4  
Polymer Isomerism  
and Conformation

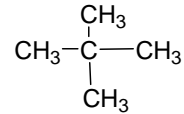
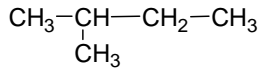
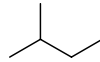
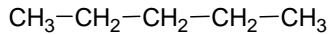
## Types of Isomerism

Same molecular formula , different structure  
3 kinds relevant to macromolecules

- Constitutional – bond connectivity of atoms
- Configurational – 3-D spatial arrangements beyond bond rotation
- Conformational – spatial arrangements due to bond rotation only

# Chain Topology: Straight vs. Branched

- In micromolecules:



- In macromolecules:



Linear



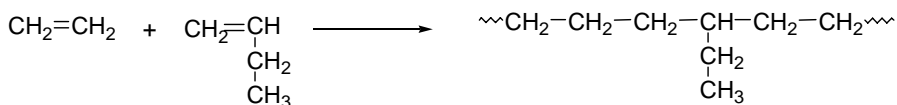
Branched

## Effects of Chain Topology

- Low density polyethylene (LDPE) –
  - high degree of branching, low % crystallinity, low melting point, high flexibility, transparent
- High density polyethylene (HDPE) –
  - little branching with ~ 2% small side chains, high crystallinity, higher melting point, rigid but not brittle, strong, durable, opaque
- Linear low density polyethylene (LLDPE) –
  - ~ 8 % small branches, weaker & more flexible & transparent than HDPE

## Generating Branches

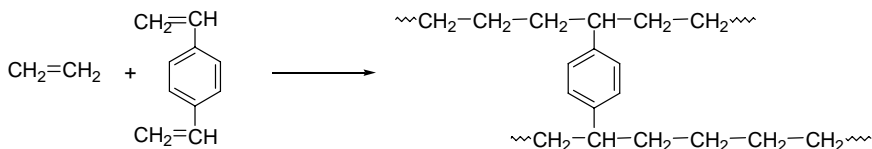
- LDPE is “self-branching”, due to nature of the radical process used.
- In HDPE & LLDPE, special catalysts maintain linear chains.
- Co-polymerization with  $\alpha$ -olefins yields small, controllable branching.



- Increasing the % of  $\alpha$ -olefin increases branching.

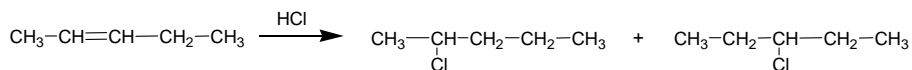
## Generating Branches - 2

- Small amounts of polyfunctional monomers, such as divinylbenzene, also increase branching

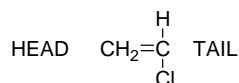


# Positional Isomerism

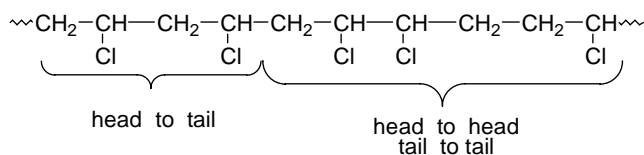
- In small molecules, different positional substitution yields distinct products...



- In addition polymers, monomers can exhibit chemically diverse ends...

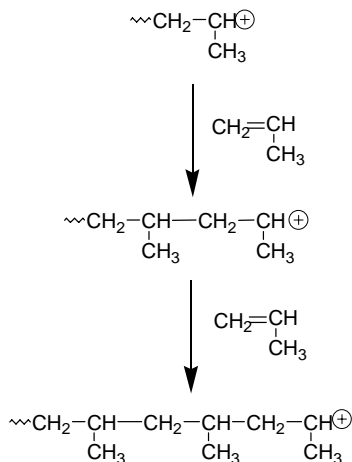


leading to different arrangements of pendant groups on a polymer backbone...



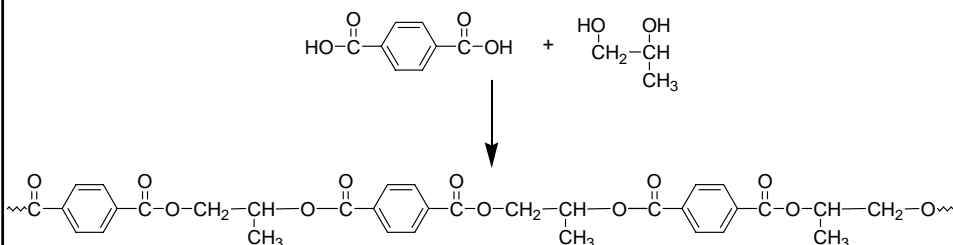
# Addition Polymers

- Vinyl monomers polymerize through an “active center”, a radical, ion, or metal complex.
- Resonance (delocalization) or inductive (electronegativity) stabilization of intermediates almost always leads to a “head to tail” arrangement.
- Tail to tail linkages may be “weak” points which lead to thermal degradation.



## Condensation Polymers

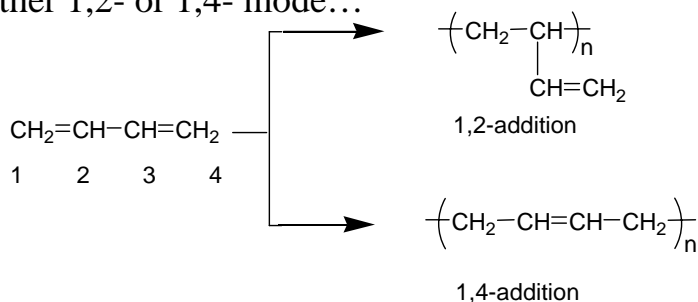
- Use of unsymmetrical monomers can lead to similar isomerism in condensation polymers...



- Due to the nature of this reaction, the arrangement in the polymer will likely be random.

## Diene Additions

- Conjugated dienes can undergo polymerization in either 1,2- or 1,4- mode...

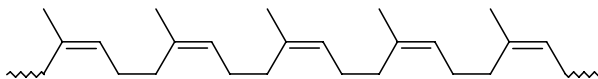


- Substituted dienes, like isoprene, can yield further isomers.
- Mode of addition can be controlled by use of specialized catalysts.

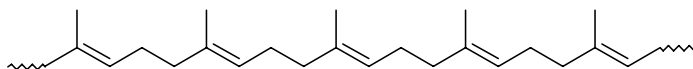
# Geometric Isomerism

- 1,4-diene polymers contain double bonds in the backbone, which may be *cis* or *trans*.

Polyisoprene



cis

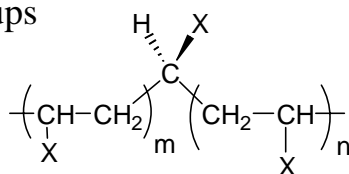
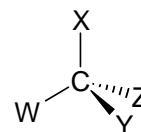


trans

- cis*-polyisoprene is a good elastomer, possesses a low crystallinity & lower melting point
- trans*-polyisoprene is less rubbery, has a higher crystallinity & melting point
- Both are found in nature; *Hevea* rubber (98% *cis*) & *gutta percha* (mostly *trans*)

# Stereoisomerism

- Due to “chiral centers” such as asymmetric carbons
- Occurs in polymers when chain has pendant groups

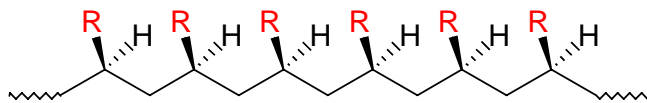


*m* & *n* are, in effect, never equal

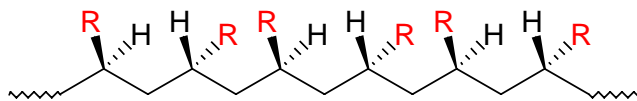
- Rather than chirality, when applied to polymers is called “**tacticity**”.

# Tacticity

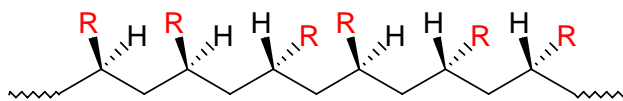
View chain as planar zigzag...



**Isotactic** – all R groups on same side



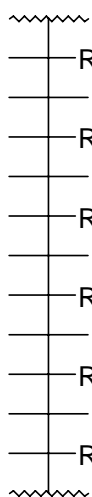
**Syndiotactic** – R groups alternate



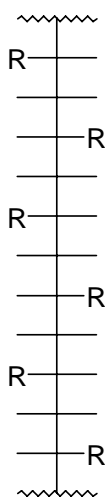
**Atactic** – random arrangement

Iso- & syndiotactic are termed **stereoregular** polymers.

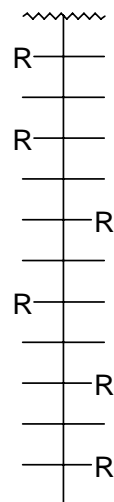
## An Alternative View



**Isotactic**



**Syndiotactic**



**Atactic**

# Stereoregularity

- Affects ability of polymer to form ordered (crystalline) regions.
- Stereoregular polymers show higher crystallinity which leads to:
  - higher melting/softening points
  - higher physical strength
  - increased solvent resistance
  - increased chemical resistance
- Atactic polymers tend to be tacky with little or no physical strength

# Stereoregular Polymers

Polypropylene (PP) –

Atactic – rubbery, amorphous

$T_m \sim 75^\circ$

few applications

Isotactic – high strength-to-weight ratio

$T_m \sim 183^\circ$

stress crack resistant

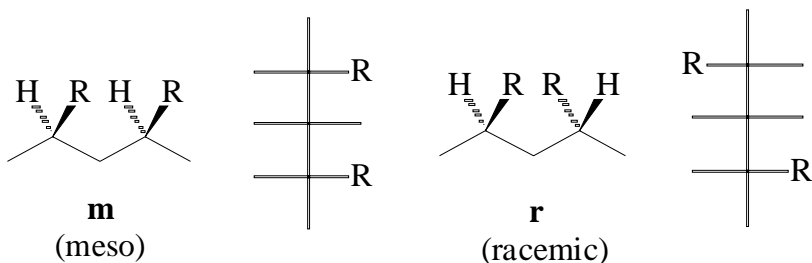
good electrical resistance

used as both plastic & fiber

used in place of HDPE at higher T

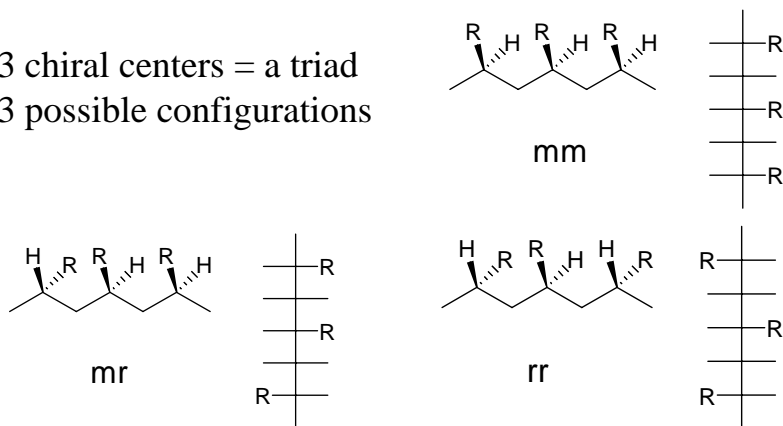
# Stereoregular Segments

- Completely tactic or atactic polymers are rare.
- Regions of tacticity can be detected by NMR.
- The type & extent of the region are designated by the number of “chiral centers” and their relationship.
- 2 centers is termed a “dyad” & can be ...



## Dyads & triads & tetrads, oh my!

3 chiral centers = a triad  
3 possible configurations



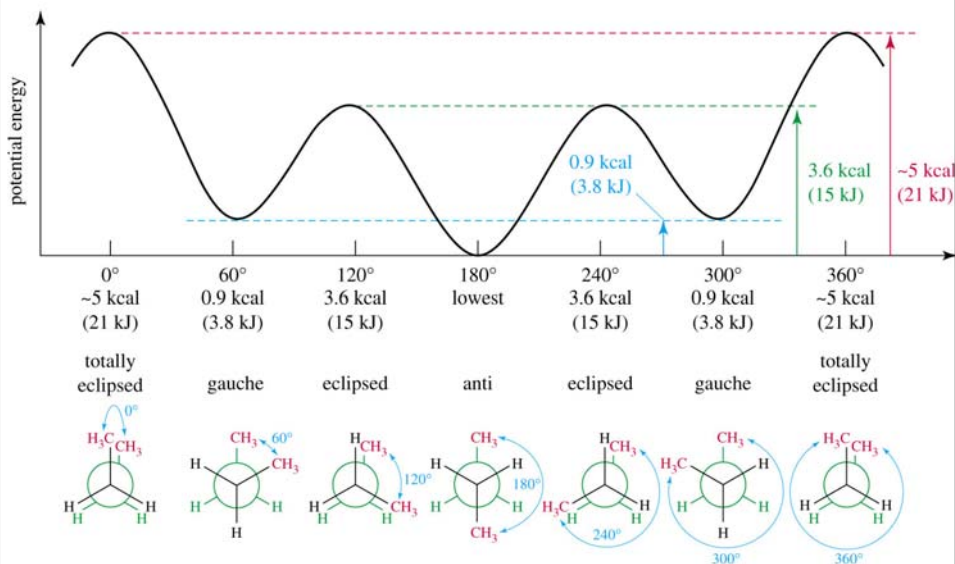
4 chiral centers = a tetrad, 6 possible configurations  
(mmm, rrr, rrm, rmr, mrm, mmr)

# Polymer Conformation

- Considers “rotational isomers” of polymer backbone
- Twisting, bending, & entanglement of polymer chains occurs through multiple rotations of this type.
- Rate & ease of this motion determines
 

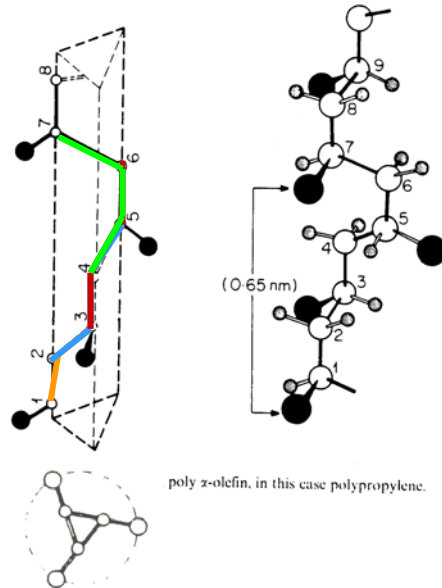
melt viscosity	mechanical properties
rate of crystallization	thermal behavior
- Rotational behavior can be modeled on that of butane

## Rotational Conformers of Butane



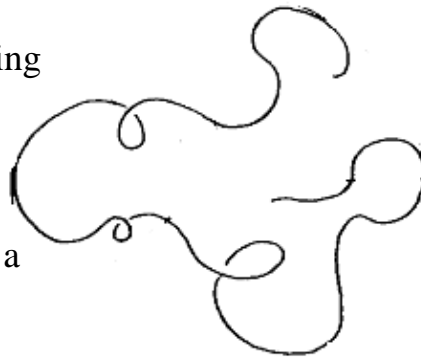
## Polymer Conformation

- Crystal conformation depends on both low energy and packing efficiency.
- HDPE forms all *trans* chains
- Isotactic polymers tend to form an  $f_j$  helical conformation
- $f$  is the monomer units per  $j$  turns
- Iso-PP forms a *trans/gauche/trans/gauche* conformation
- Leading to a  $3_1$  helix

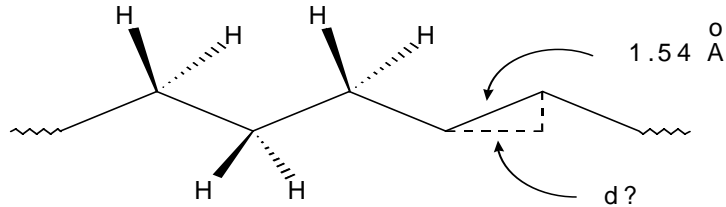


## Amorphous Conformation

- In liquid or solution phase, polymer chain not restricted by crystal packing
- $\Delta E$  between *gauche* & *trans* is small, easily less than thermal energy
- Equilibrium form will be a distribution of *gauche* & *trans* termed the **RANDOM COIL**



## Polymer Dimensions



Consider a poly(methylene)  $-(\text{CH}_2)_n$   $M_n = 160,000$

Number of units (DP) =  $M_n/M_o = 160,000/14 = 11,420$

Chain length =  $11,420 \times d =$

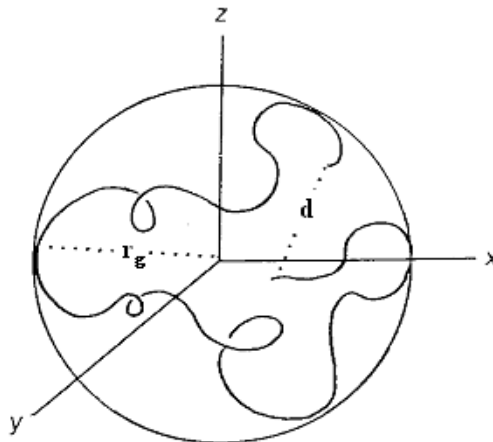
$11,420 \times 0.154 \text{ nm} \times \sin(109.5/2) =$

**1436 nm**

(and only 0.3 nm in diameter!)

## Random Coil Dimensions

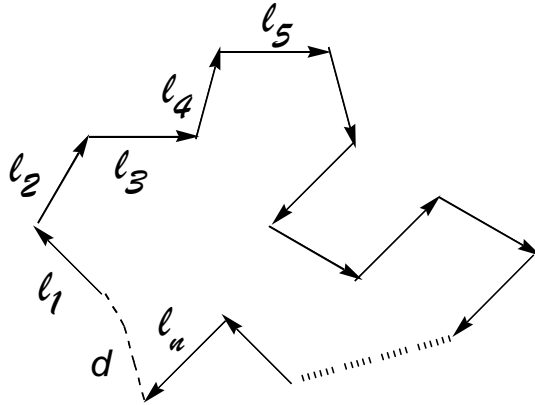
- Random coil polymers are NOT all *trans* as assumed
- Dimensions are expressed by...
  - $d$  – average distance between chain ends
  - $r_g$  – radius of gyration, average distance from center of mass



Can these be predicted from our understanding of conformation?

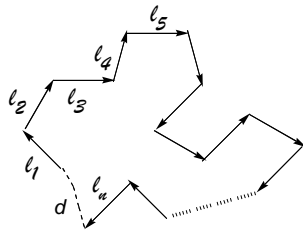
## The Random Walk Model

- A theoretical approach which treats each repeat unit as a random vector ( $\ell$ ).
- The overall dimensions are determined from an average of these vectors
- Multiple models of increasing sophistication



## Random Walk Variations

- Freely jointed –
  - Bond lengths are fixed, but vector may turn in any direction, at any angle



For this simple approach, the sum of all vectors  $d = 0$ .  $d^2$  is calculated since it Removes vector direction.

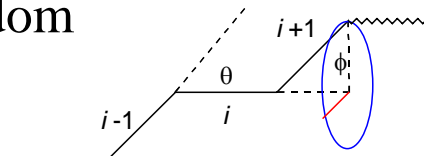
$$\langle d^2 \rangle = \sum \ell_i^2 = \sigma \ell_o^2$$

$\ell_o$  = vector magnitude  
 $\sigma$  = number of units  
 (Eqn 4-15)

## More Real, Less Random

- Freely rotating –

- Bond lengths fixed, vector turns freely, but angle ( $\theta$ ) is restricted to value consistent with molecular bonds



$$\langle d^2 \rangle = \sigma \ell^2 \left( \frac{1 + \cos \theta}{1 - \cos \theta} \right) \quad \text{Eqn 4-16}$$

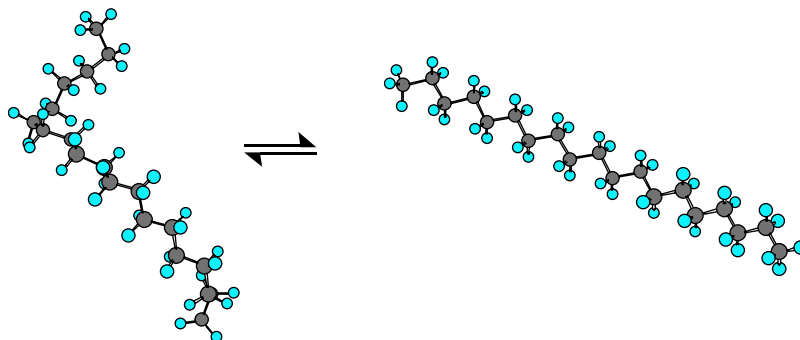
- Hindered rotor

- Bond lengths fixed, both bond angle ( $\theta$ ) and rotational angle ( $\phi$ ) are restricted.  $\cos \phi$  is averaged.

$$\langle d^2 \rangle = \sigma \ell^2 \left( \frac{1 + \cos \theta}{1 - \cos \theta} \right) \left( \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right) \quad \text{Eqn 4-17}$$

## Elastic Behavior

- Flow & deformation results from twisting and bending of small segments of the chains.
- Elasticity stems from the ability of these chains to regain the coiled shape rapidly.



## Cross-Linked Elastomers

- Elastic behavior of cross-linked polymers, such as vulcanized rubber, is dependent on the

Cross-link density ( $\Gamma$ )

$$\Gamma = \frac{\left(\overline{M}_n\right)_o}{\left(\overline{M}_n\right)_c}$$

$(M_n)_o$  – number avg MW of uncrosslinked polymer  
 $(M_n)_c$  – number avg MW between crosslinks

- Typical vulcanized rubber has < 5% S (~ 20K between links)
- 30 % S yields a rigid, inelastic material called ebonite

## Molecular Characteristics of Elastomers

- 1) Material must be a high polymer.
- 2) Molecules must remain flexible at usage temperatures.
- 3) Must be amorphous in unstressed state.
- 4) Must be possible to introduce crosslinks to bond into continuous network.

## How Do Rubber Bands Work?

- In relaxed state, molecule occurs as mixed *trans/gauche* forms.
- When stretched, chain assumes the more highly ordered, all-*trans* conformation.
- Increasing entropy drives chain to contract back to random coil.

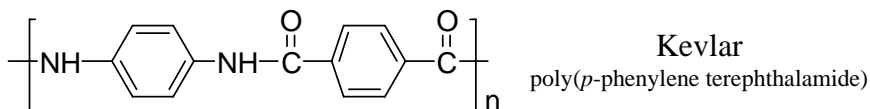


A rubber band is an “entropy spring”.

- *Trans* is lower enthalpy than *gauche*... as band extends, heat is released.
- Increasing T shifts the equilibrium to higher enthalpy, chain contracts.

## Rigid Rod Molecules

- Molecules with aromatic backbones do not exhibit the flexibility of vinyl polymer.



- These form stiff, rigid chains, which act like logs, rather than coils.
- Molecules of this sort can form strong, oriented fibers. Used in composite materials.
- They also display liquid crystal properties.