

Chemical Engineering 160/260
Polymer Science and Engineering

Lecture 2 - Polymer Chain
Configuration and Conformation

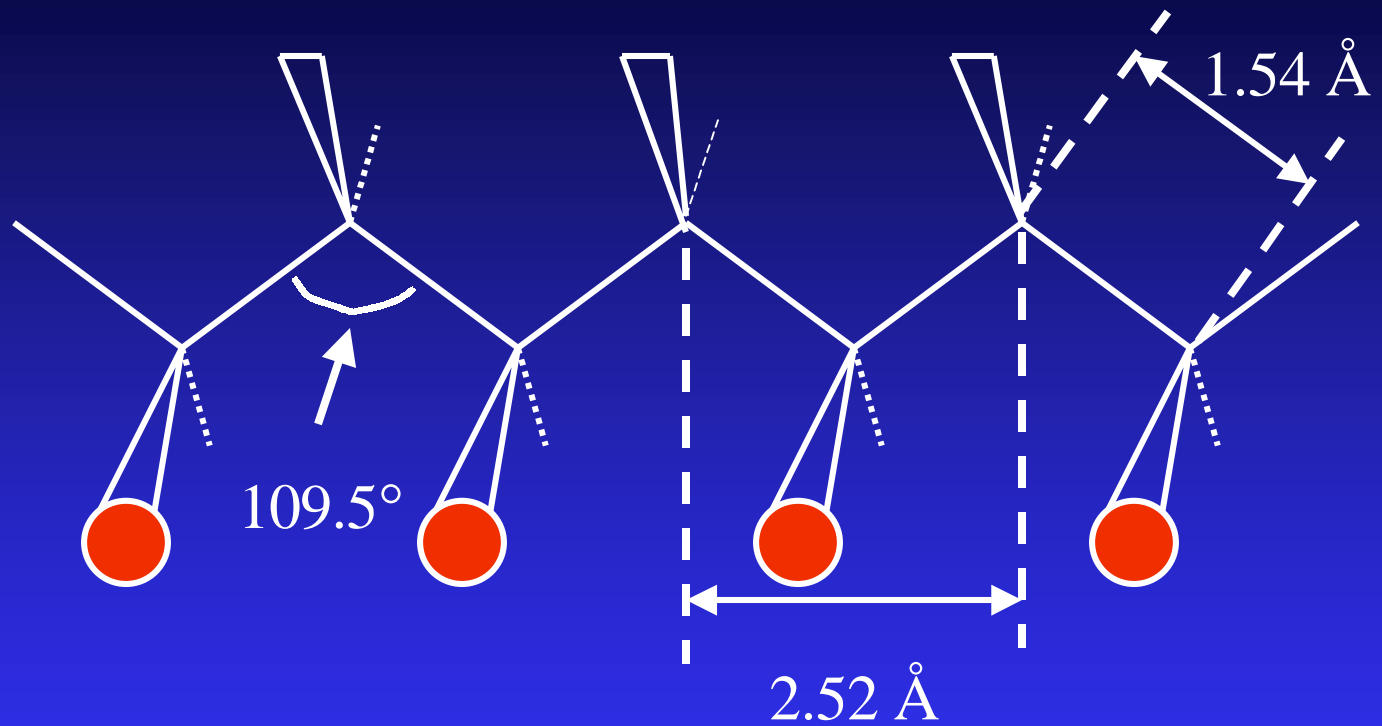
January 12, 2001

Sperling, Ch 2

Outline

- **Polymer Isomerism for All-carbon Backbones**
 - ◆ Constitutional
 - ◆ Configurational
 - ◆ Conformational
- Spatial Parameters for Polymer Chains
 - ◆ End-to-end distance
 - ◆ Radius of gyration
 - ◆ Freely-jointed model chain

Spatial Parameters for All-carbon Backbones



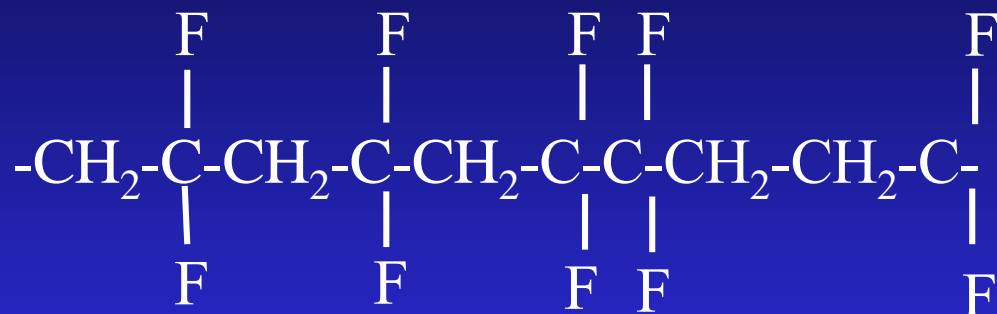
Contour length of the fully extended chain = nl

n = number of repeat units

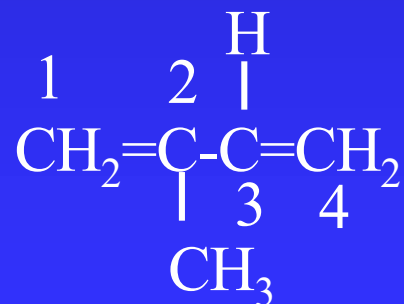
l = length of repeat unit

Constitutional Isomerism

Head-to-head defects



Dienes: H/H, H/T, addition mode, cis/trans

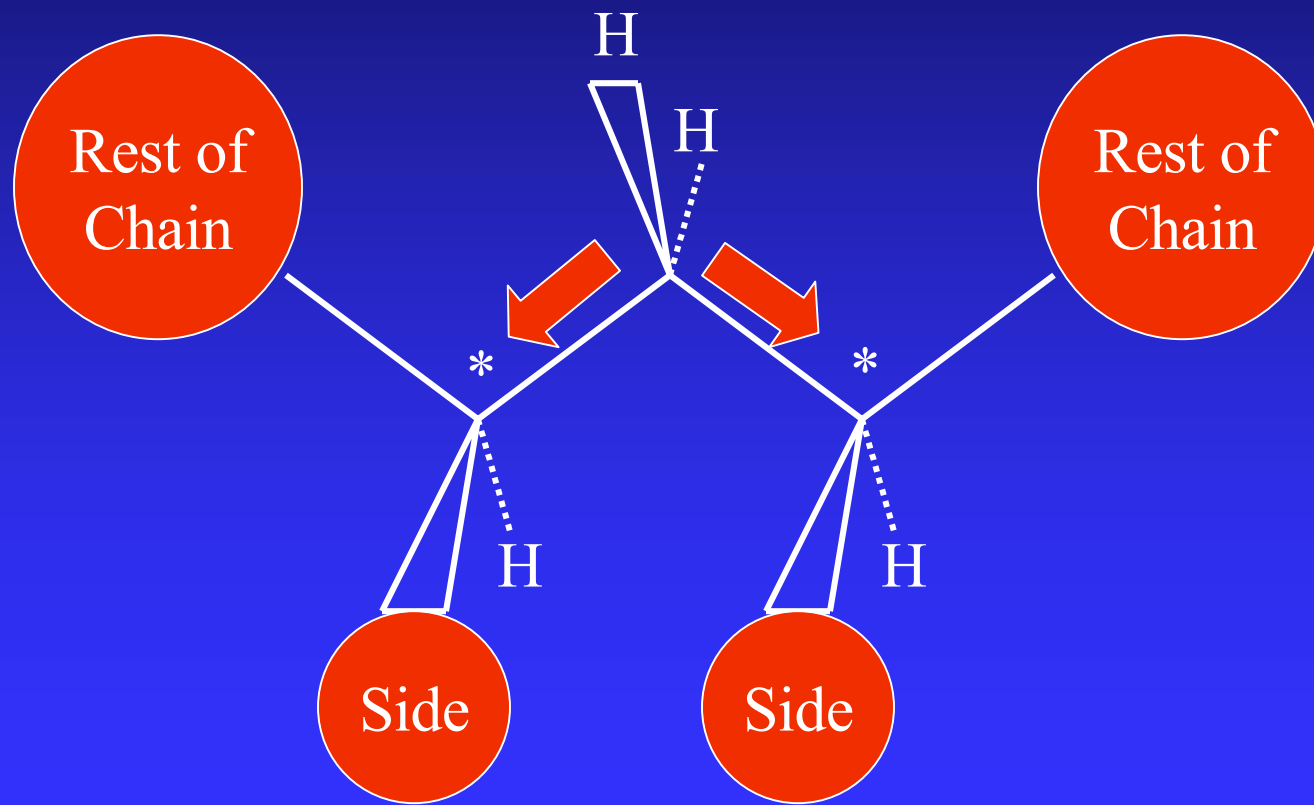


1,2-addition

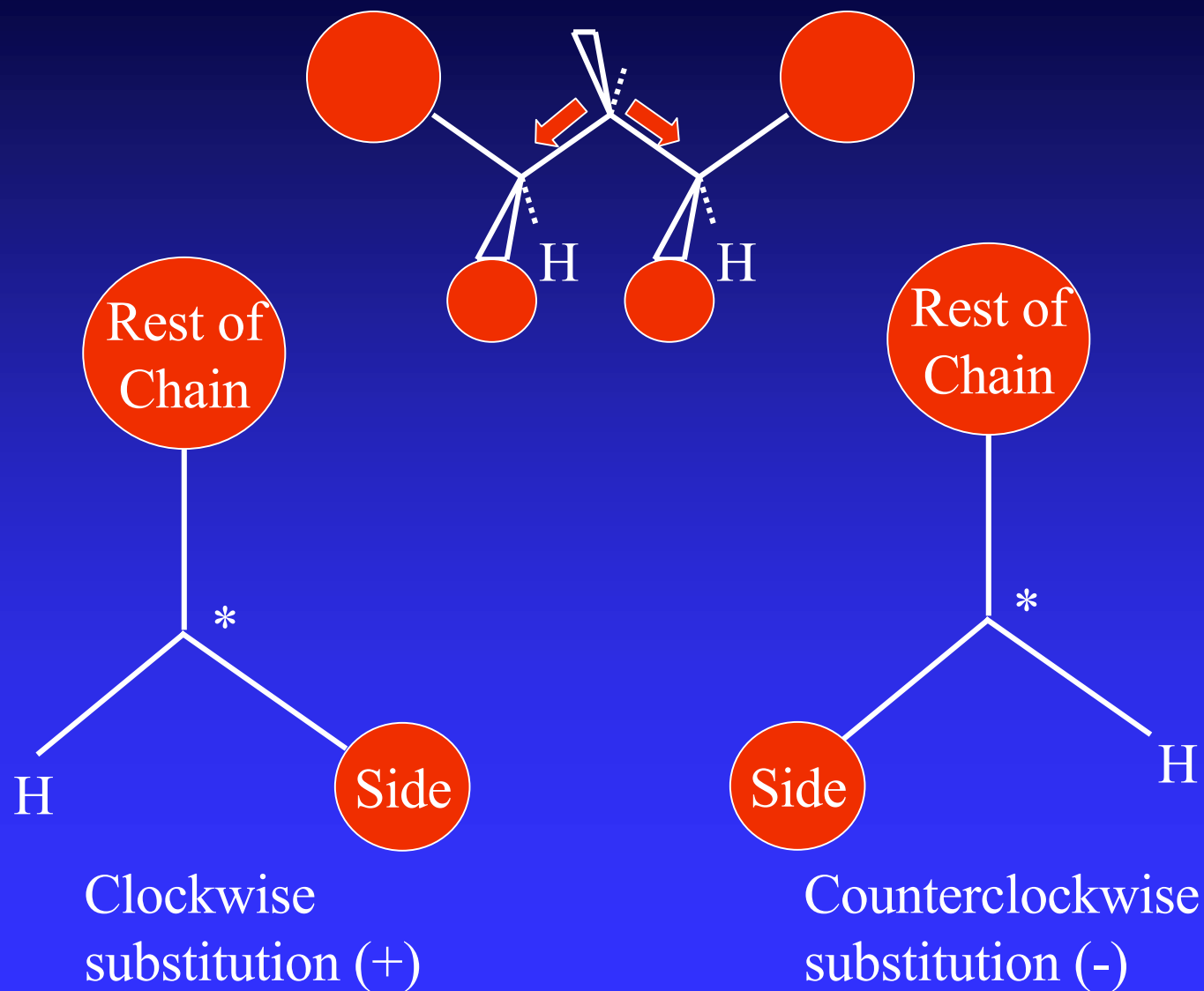
3,4-addition

1,4-addition

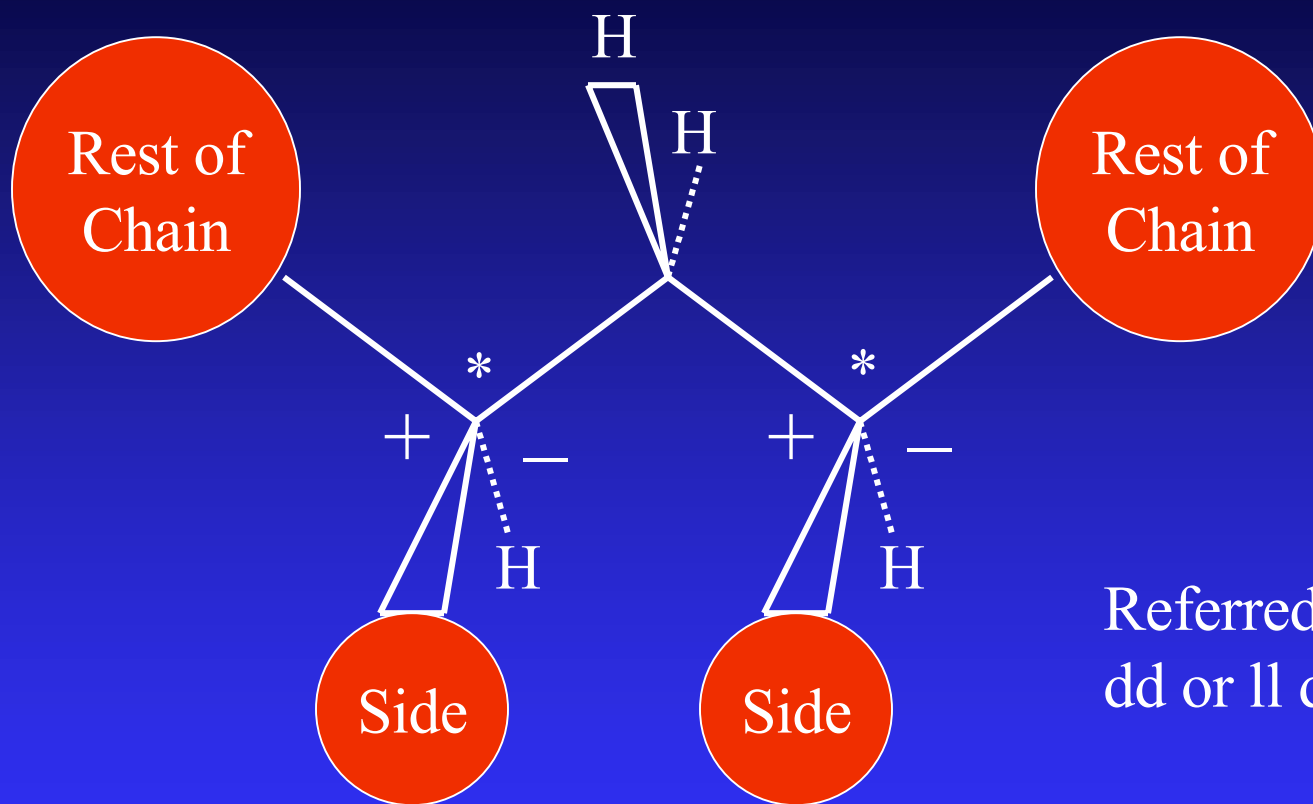
Configuration of Pseudoasymmetric Carbon



Stereoconfiguration



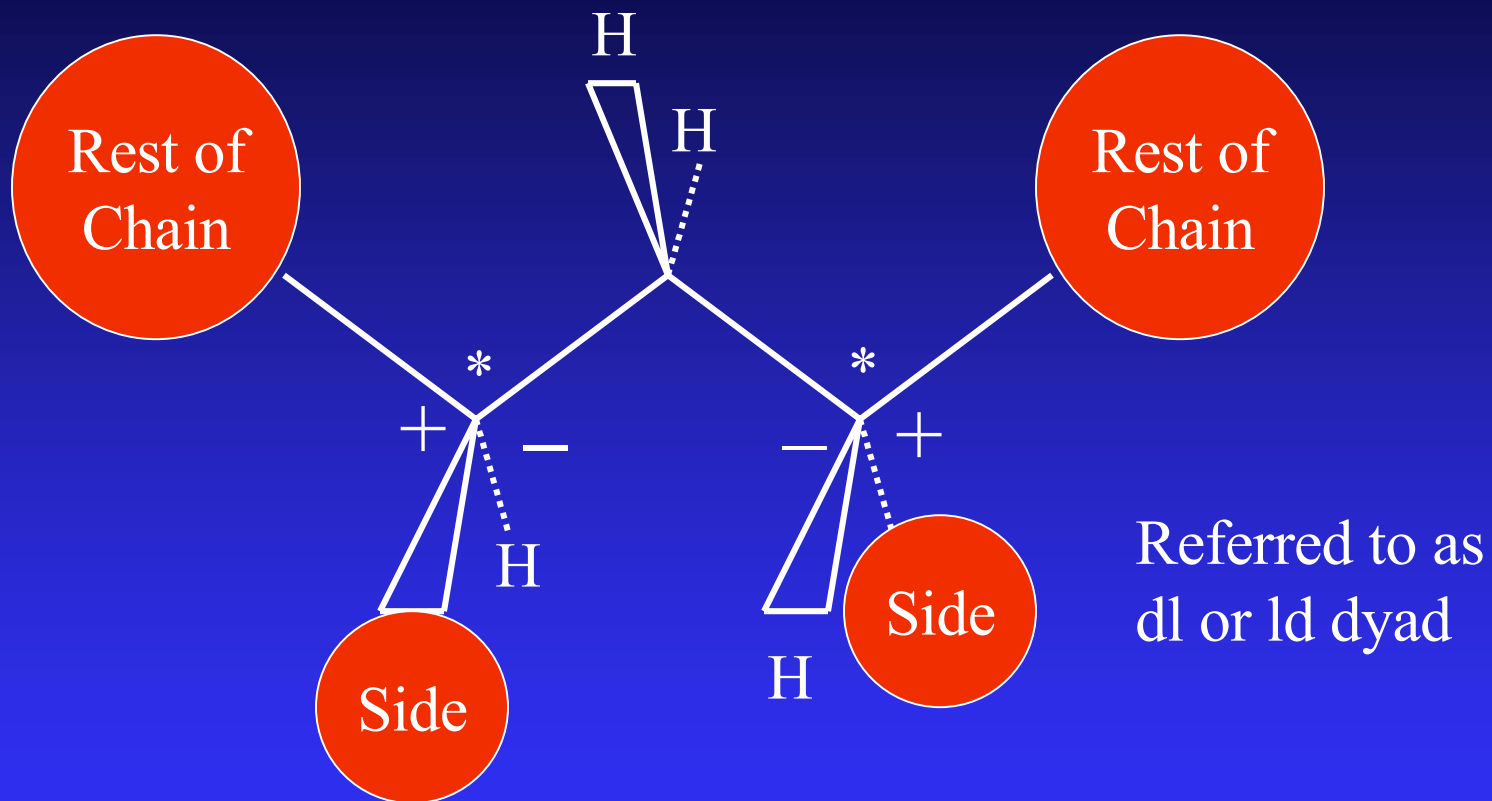
Pseudoasymmetric Carbons: Meso Dyad



Referred to as
dd or ll dyad

The stereochemical configuration is the **same** for each pseudoasymmetric carbon for a **meso** dyad.

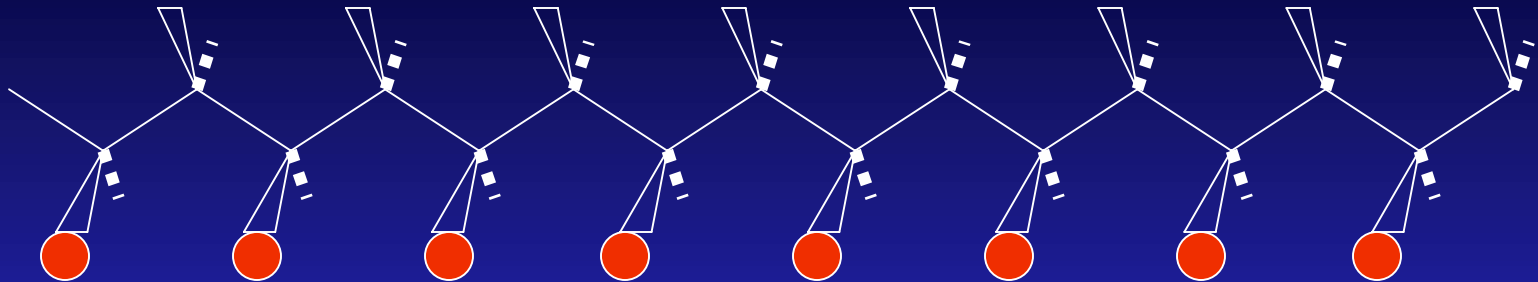
Pseudoasymmetric Carbons: Racemic Dyad



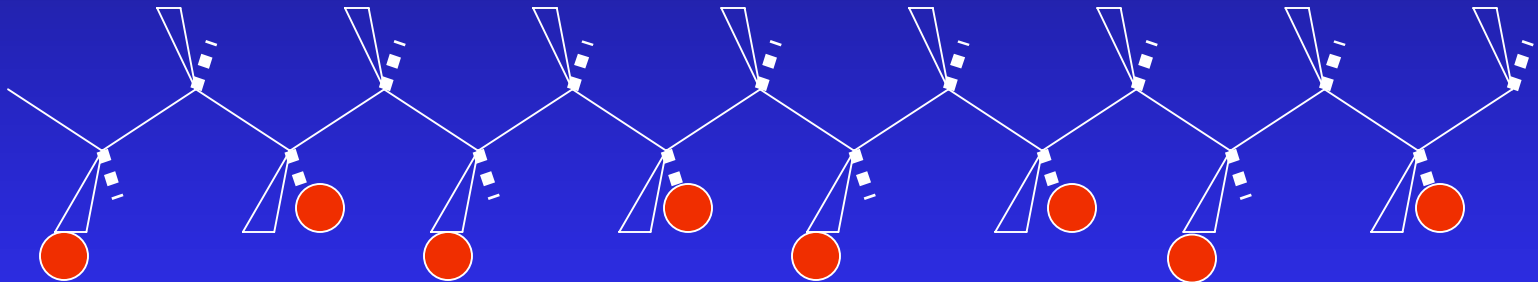
The stereochemical configuration **alternates** for each pseudoasymmetric carbon for a **racemic** dyad.

Configurational Isomerism

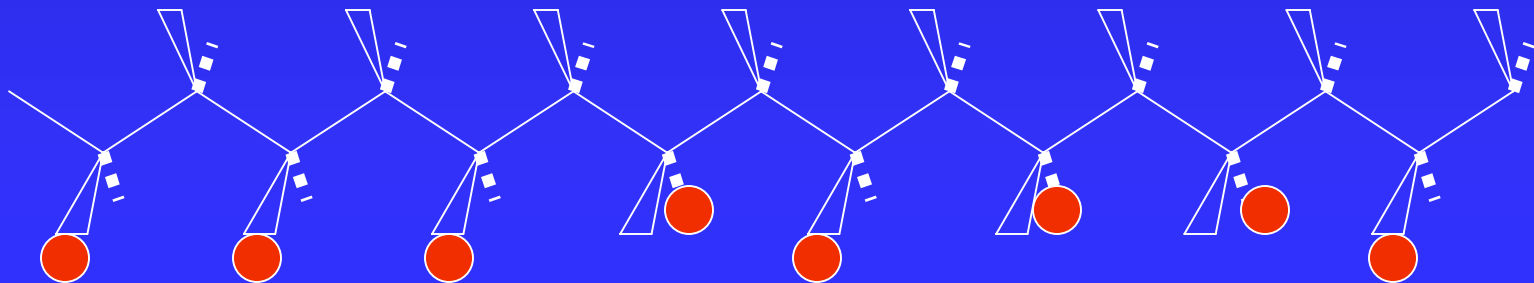
Isotactic: $(+-)(+-)(+-)(+-)(+-)(+-)(+-)(+-)$



Syndiotactic: $(+-)(-+)(+-)(-+)(+-)(-+)(+-)(-+)$

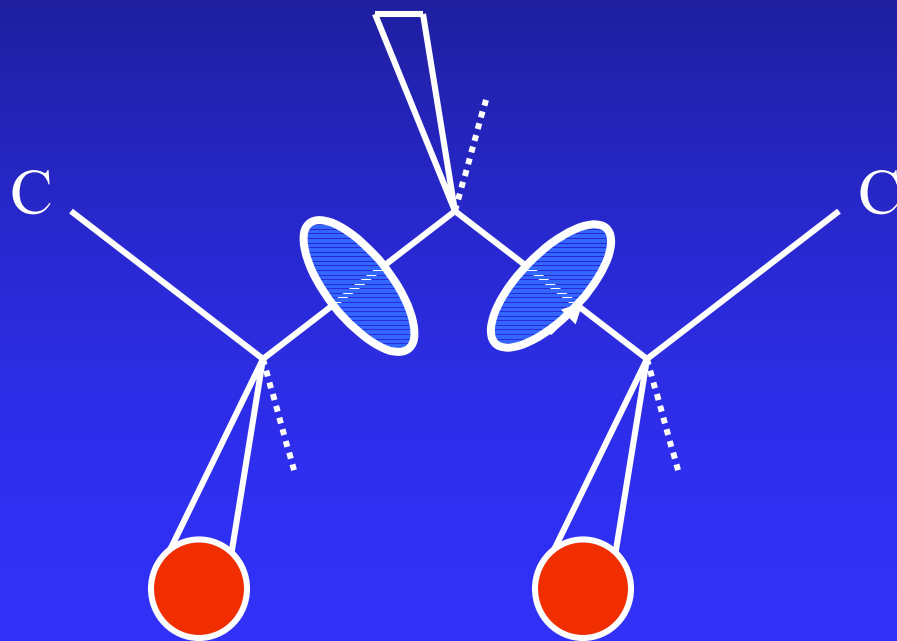


Atactic: $(+-)(+-)(+-)(-+)(+-)(-+)(-+)(+-)$ for example



Conformational Isomerism

Although the **configurational** state (tacticity) is fixed by the chemical reaction, many possible **conformational** isomers result from rotations about carbon-carbon backbone bonds. Each backbone bond has a rotational state [**trans, gauche (+), or gauche (-)**]. These are denoted t, g⁺, g⁻.

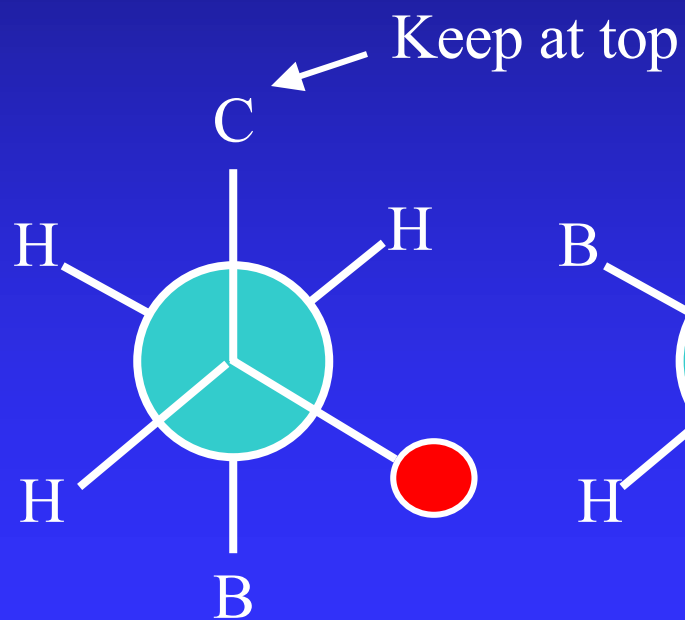
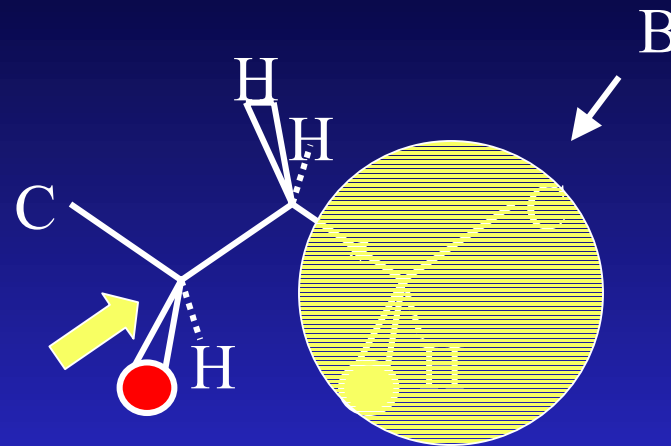


“C” refers to the rest of the chain.

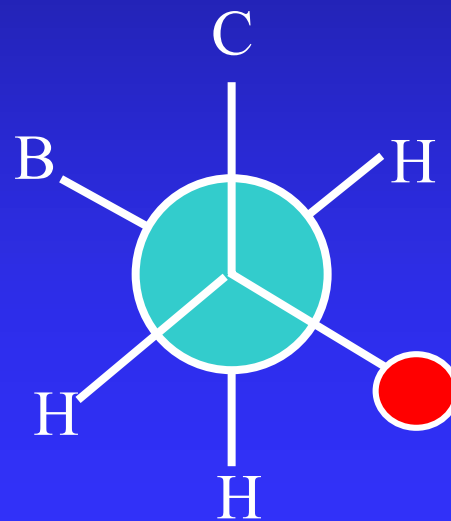
Conformational Isomerism

Consider Newman projections of an **internal** bond.

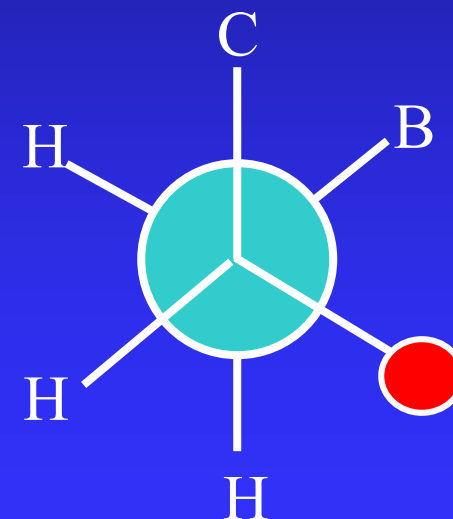
Look along the direction of the first internal bond in this meso dyad.



trans

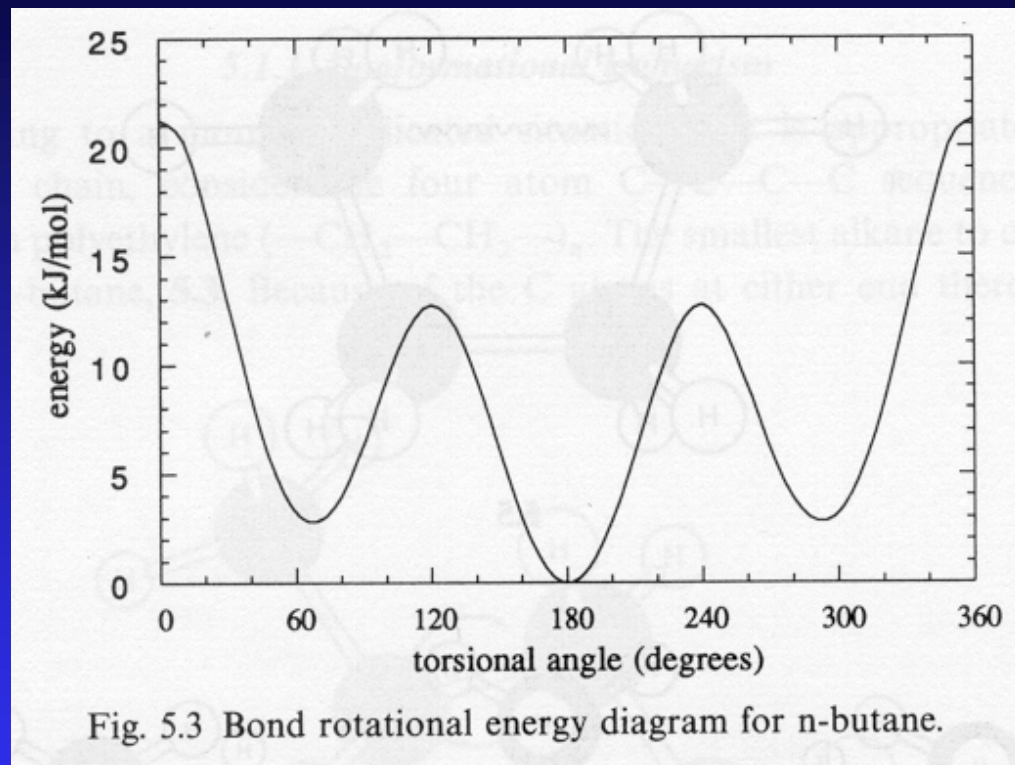


gauche (+)



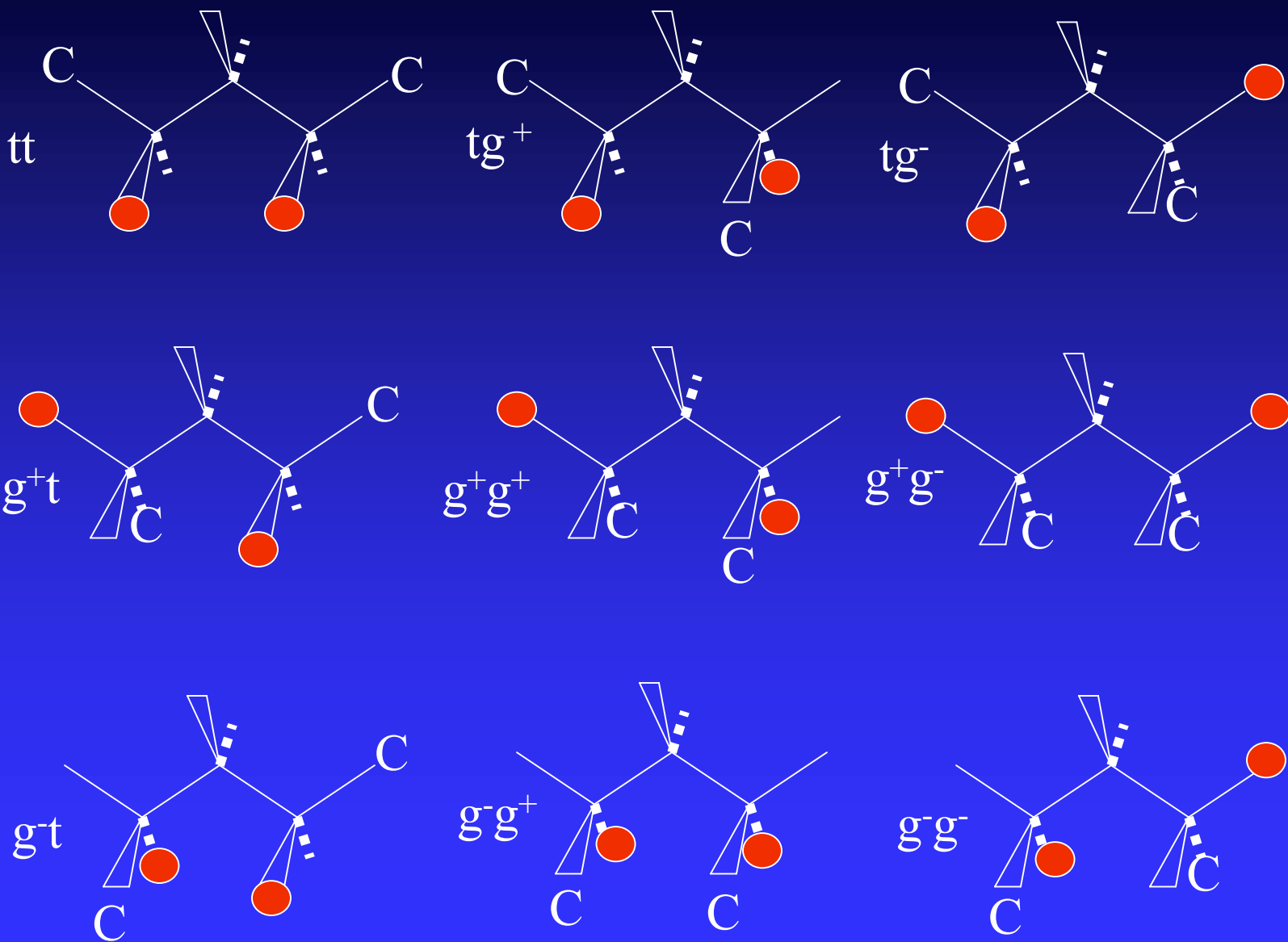
gauche (-)

Conformational Isomerism in Butane

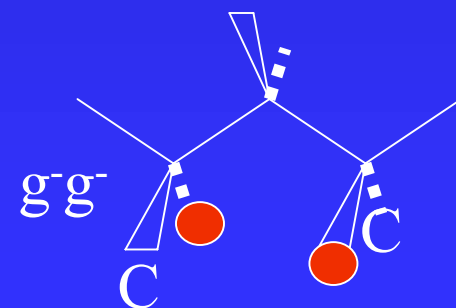
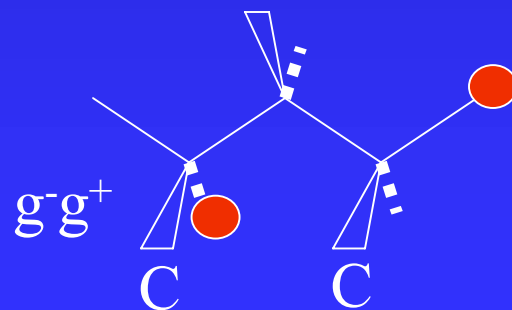
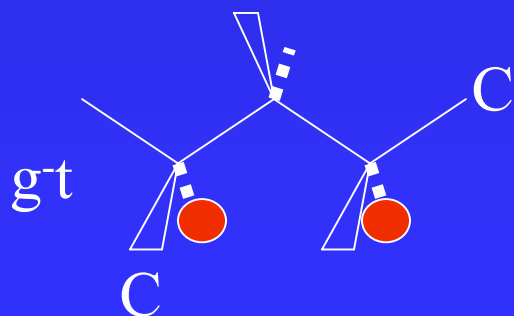
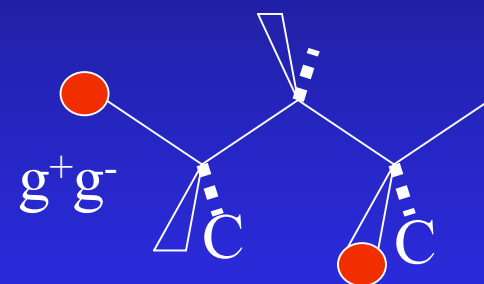
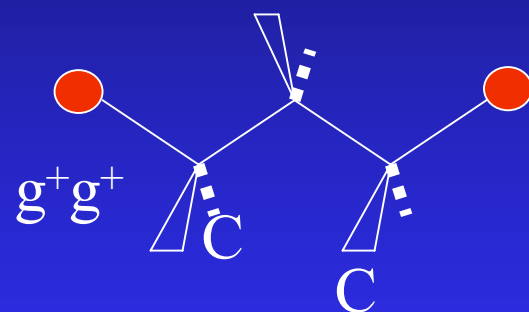
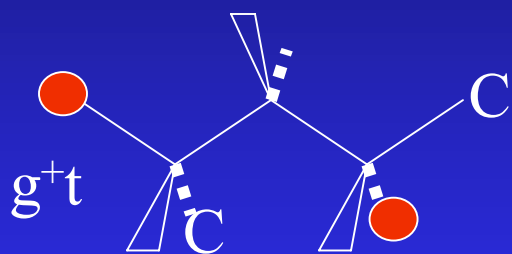
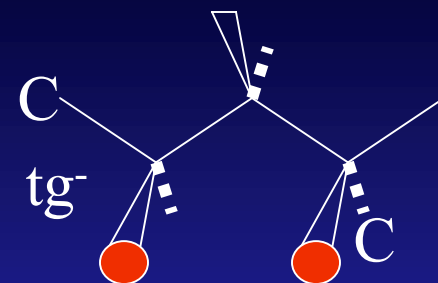
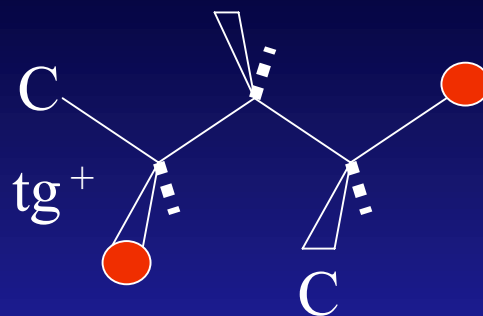
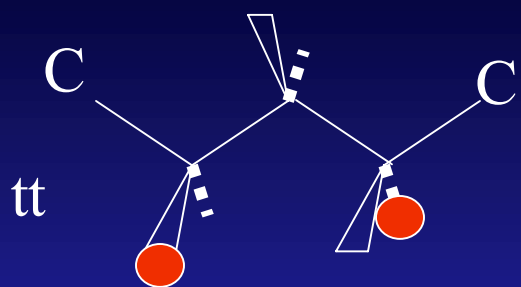


From The Science of Polymer Molecules,
R.H. Boyd and P.J. Phillips, 1993, p 160.

Meso (dd, ll) Rotational Dyad



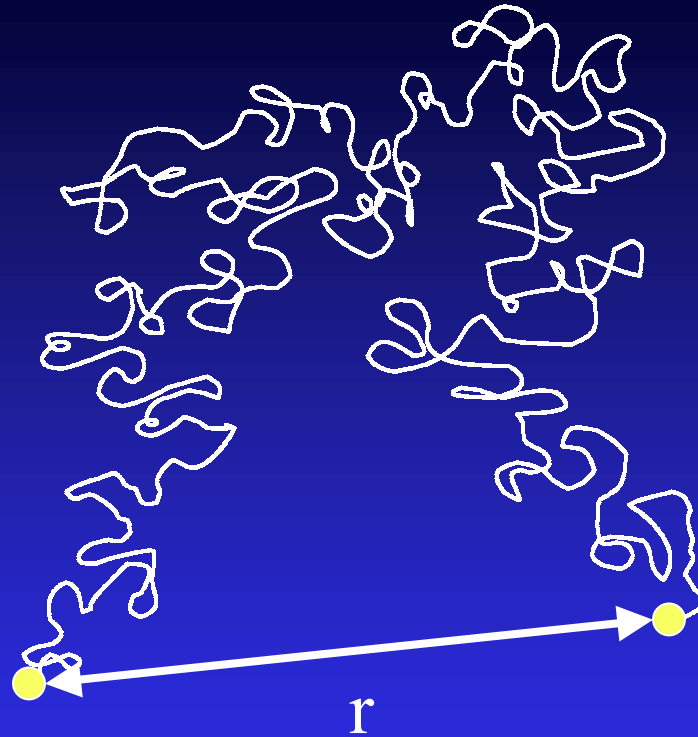
Racemic (dl, ld) Rotational Dyad



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 - ◆ Radius of gyration
 - ◆ Freely-jointed model chain

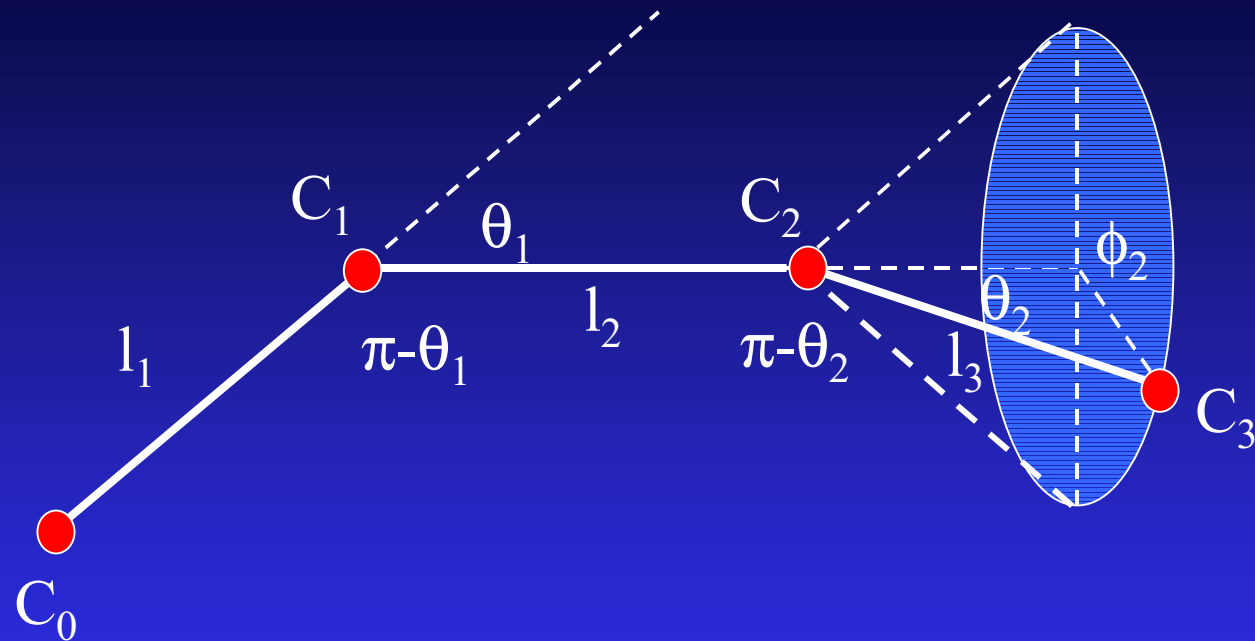
End-to-end Distance of a Random Coil



In general, we will express the end-to-end distance in terms of the root-mean-square statistical average.

$$\langle r^2 \rangle^{1/2}$$

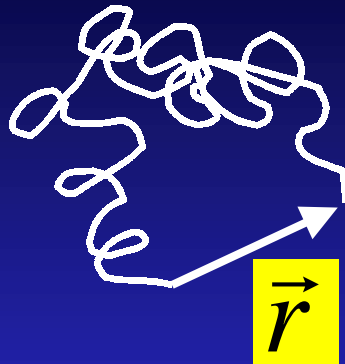
Freely Jointed Model Polymer Chain



Assume that the bond length l_i is fixed, as is realistic.

No restrictions are imposed on the valence bond angle ($\pi - \theta_i$) or on the dihedral angle (ϕ_i), contrary to physical reality.

Freely Jointed Model Polymer Chain: Mean-squared End-to-end Distance



$$\vec{r} = \sum_{i=1}^n \vec{l}_i$$

Vector

$$r^2 = \vec{r} \cdot \vec{r} = \sum_{i,j} \vec{l}_i \cdot \vec{l}_j = \sum_i l_i^2 + 2 \sum_{0 < i < j \leq n} \vec{l}_i \cdot \vec{l}_j$$

Average over
configurations.

$$\langle r^2 \rangle = \sum_i \langle l_i^2 \rangle + 2 \sum_{0 < i < j \leq n} \langle \vec{l}_i \cdot \vec{l}_j \rangle$$

$$\langle r^2 \rangle = nl^2 + 2 \sum_{i < j} \langle \vec{l}_i \cdot \vec{l}_j \rangle = nl^2$$

There is no
correlation.

Freely Jointed Model Polymer Chain: Mean-squared End-to-end Distance

Relationship to molecular weight

$$\langle r^2 \rangle = nl^2 \approx M$$

Characteristic ratio

$$C_n = \frac{\langle r^2 \rangle_o}{nl^2}$$

The subscript refers to the unperturbed reference state in which there are no external forces or solvent effects.

$C_n = 1$ for a freely rotating model chain.

Equivalent Chain

One may account for fixed bond angles and hindered rotation by letting several real bonds be represented by a longer equivalent bond.

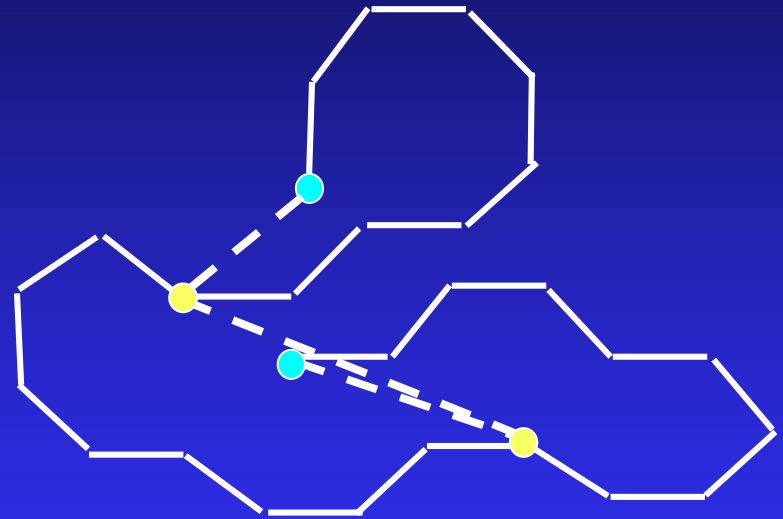
Real chain: n, l

Equivalent chain: n', l'

$n' < n, l' > l$

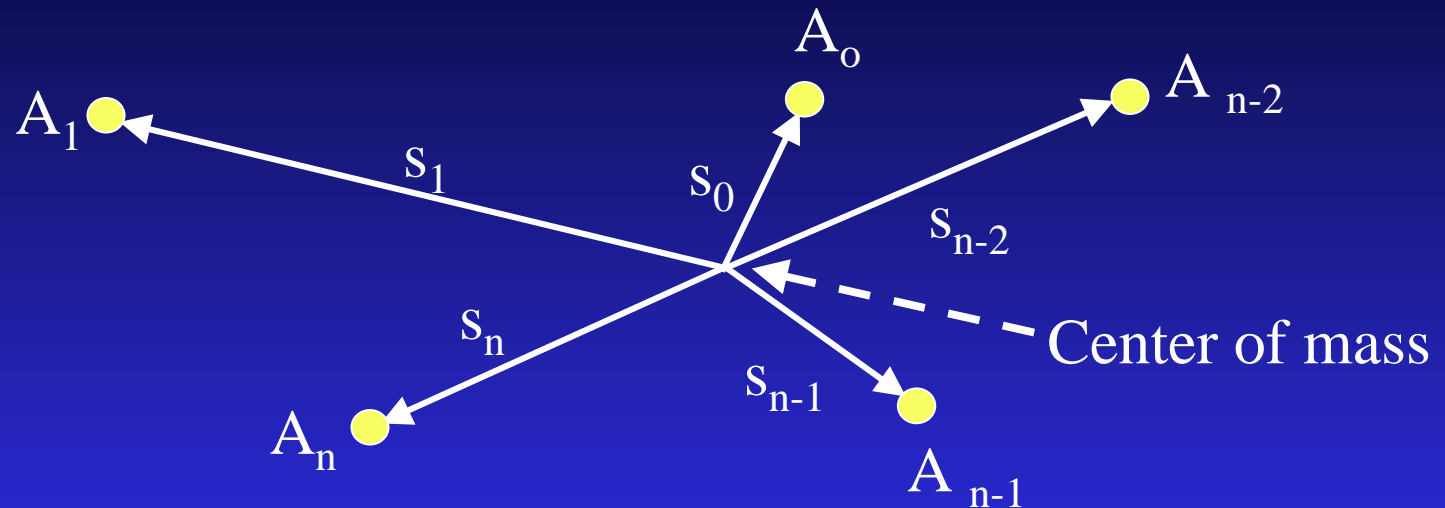
$$\langle r^2 \rangle = nl^2 = n'(l')^2$$

$$C = \frac{n'(l')^2}{nl^2}$$



$$n' \propto M^{1/2}$$

Mean-squared Radius of Gyration



$$s^2 = \frac{\sum_0^n m_i s_i^2}{\sum_0^n m_i} = \frac{m \sum_0^n s_i^2}{m(n+1)} = \frac{1}{n+1} \sum_0^n s_i^2$$

$$\langle s^2 \rangle^{1/2} \equiv R_g$$

Mean-squared Radius of Gyration

The mean-squared radius of gyration is related to the mean-squared end-to-end distance by

$$\langle s^2 \rangle_o = \frac{nl^2}{6} \left(\frac{n+2}{n+1} \right)$$

Details of this calculation may be found in Statistical Mechanics of Chain Molecules, P.J. Flory, 1969, pp 16-17.

In the limit as $n \rightarrow \infty$

$$\langle s^2 \rangle = \frac{\langle r^2 \rangle_o}{6} = R_g^2$$

R_g may be determined from light, x-ray, or neutron scattering.