►Higher frequency (elastic) gives higher Tg. (See stress-strain curve at different extension rate.)

►Empirically

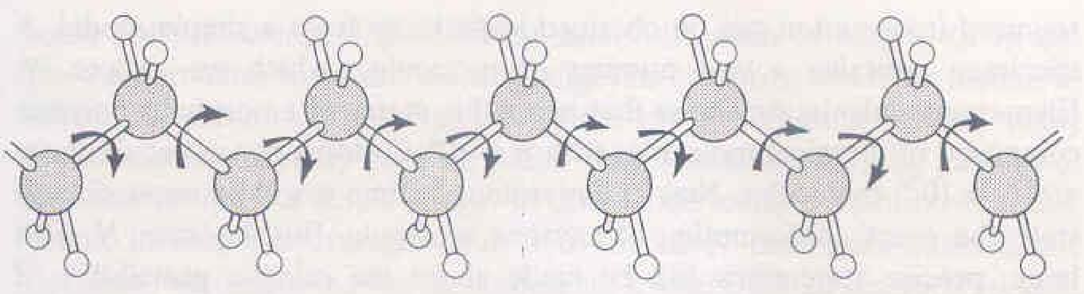
$$T_g = 0.6\ T_m \qquad (2.4)$$

►Remember the Tg of copolymer (Fox eq) - Inverse additivity

2.7 Molecular Conformation in the Amorphous Polymer

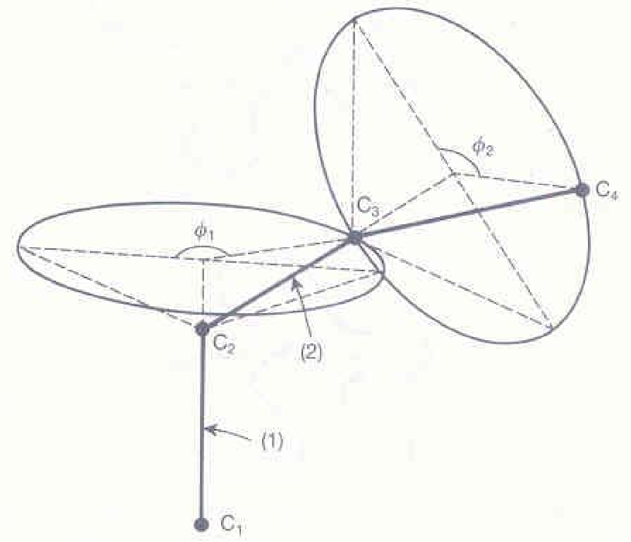
►Molecular conformation in crystal:
Well defined by the crystalline structure.
Ex. Fully extended planar zig-zag conformation, being caged in by its neighbors (See Figure 2.1b) for PE.

►In amorphous state (glassy, rubbery state) or in dilute solution, molecule assumes a random conformation (See the rotation C-C b in Figure 2.13).



2.13 The rotation around C—C bonds which causes the polyethylene planar zigzag conformation to be changed into one of the enormous number of random conformations typical of the amorphous polymer.

Number of random conformation (Figure 2.14)



2.14 Rotational freedom in an idealized chain of four carbon atoms.

Figure 2.14

Assume bond (1) is fixed.

Position of C_3 = $f(\phi_1)$, $0 \le \phi_1 \le 2\pi$

Position of C_4 = $f(\phi_1, \phi_2)$, $0 \le \phi_2 \le 2\pi$

.....

Position of C_n = $f(\phi_1, \phi_2, \ldots \phi_{n-2})$, $0 \le \phi_{n-2} \le 2\pi$

The position of last C atom (C_n) depends on $\phi_1, \phi_2, \ldots \phi_{n-2}$, each varies from 0 to 2π.

Typical value of n = $O(10^3) \sim O(10^4)$

►Number of random conformation → ∞

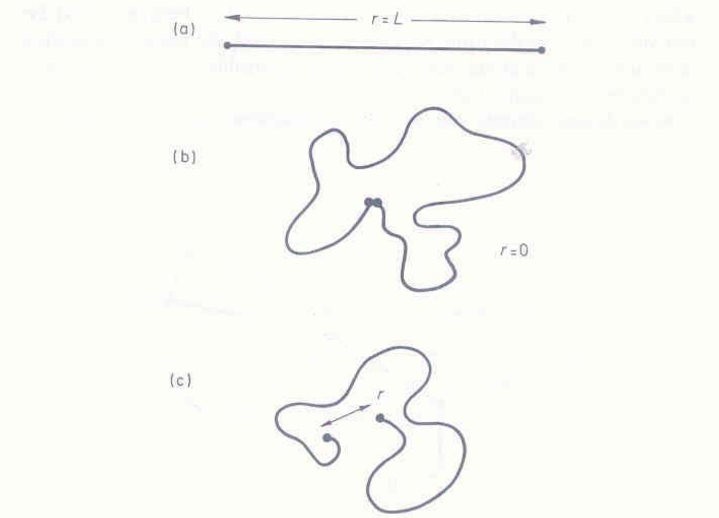
So, statistical analysis applies.

Ideas for polymer molecular size

▶Radius of gyration

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

▶End to end distance (r) (See Figure 2.15)



2.15 Illustration of the characterization of a molecular conformation by the end-to-end distance r: (a) the maximum value of $r = L$, the contour length; (b) the minimum value, $r = 0$, the ends coincident; (c) a more a priori likely value of r, $0 < r < L$.

$0 \leq r \leq L$ (=Contour length, fully extended length)

We are interested in the average value of r.

Two types of average r:

i) Time average of one polymer molecule (rubbery, melt state)

ii) Average over N molecules at a specific instance (glassy polymer)

For statistically large number of samples, i) = ii)

2.8 Freely Jointed Chain

Contour length

$$L = n\,l \qquad \circ\circ\ (2.5)$$

n = # of segment
l = length of one segment (Same for all segments.)

The n rigid segments are joined flexibly one to another ($0 \leq \Theta_{ij} \leq 180°$)

(Θ_{ij} = bond angle between segments i and j).

Then the end-to-end vector

$\mathbf{r} = \sum l_i \qquad \circ$ (2.6)

Magnitude of a vector is obtained by taking its scalar product.
So,

$$\begin{aligned} r^2 &= \mathbf{r} \circ \mathbf{r} = (l_1 + l_2 + \circ\circ\circ\circ\circ\circ\circ\circ + ln) \circ (l_1 + l_2 + \circ\circ\circ\circ\circ\circ\circ\circ + ln) \\ &= (l_1 \circ l_1 + l_2 \circ l_2 + \circ\circ\circ\circ\circ\circ\circ\circ + ln \circ ln) \\ &\quad + 2(l_1 \circ l_2 + l_1 \circ l_3 + \circ\circ\circ\circ\circ\circ\circ\circ + ln \circ ln-1 \\ &= nl^2 + 2l^2(\cos\Theta_{12} + \cos\Theta_{13} + \circ\circ\circ\circ\circ\circ\circ\circ + \cos\Theta_{n,\ n-1}) \quad (2.7) \end{aligned}$$

(Note $l_1 = l_2 = \circ\circ\circ\circ = ln$)

For N molecules, the average r is obtained as:

$$\begin{aligned} \langle r^2 \rangle &= \frac{1}{N}\sum_1^N [nl^2 + 2l^2(\cos\Theta_{12} + \cos\Theta_{13} + \circ\circ\circ\circ\circ\circ\circ\circ + \cos\Theta_{n,\ n-1})] \\ &= nl^2 + \frac{2l^2}{N}\sum_1^N(\cos\Theta_{12} + \cos\Theta_{13} + \circ\circ\circ\circ\circ\circ\circ\circ + \cos\Theta_{n,n-1}) \quad (2.8) \end{aligned}$$

Note that

$$\sum_1^N(\cos\Theta_{12} + \cos\Theta_{13} + \circ\circ\circ\circ\circ\circ\circ\circ + \cos\Theta_{n,\ n-1}) = 0 \quad (2.9)$$

∵ Angle was taken randomly in the range of $0 \leq \Theta \leq 180°$ (See the cosine curve for the range.).

Then,

$$\langle r^2 \rangle = nl^2 \qquad (2.10)$$

The root mean square end-to-end distance (R)

$$R = \langle nl^2 \rangle^{1/2} = n^{1/2}\, l \qquad (2.11)$$

The ratio of R to the contour length

$$\frac{R}{L} = \frac{n^{\frac{1}{2}}}{nl} l = \frac{1}{n^{\frac{1}{2}}} \qquad (2.12)$$

As n increases ratio of end-to-end distance to contour length becomes small - The molecules exist in highly coiled state!!!

Note that Eq (2.10) in general form is:

$$\langle r^2 \rangle = C\, n\, l^2$$

$C=1$ for Freely jointed model
$C \geq 2$ for Freely rotating model
$C \geq 3$ for Hindered rotating model

Freely rotating model (See details in Lecture # 203)
Bond angle is fixed. ($\tau \sim 110°$ for C-C bond)

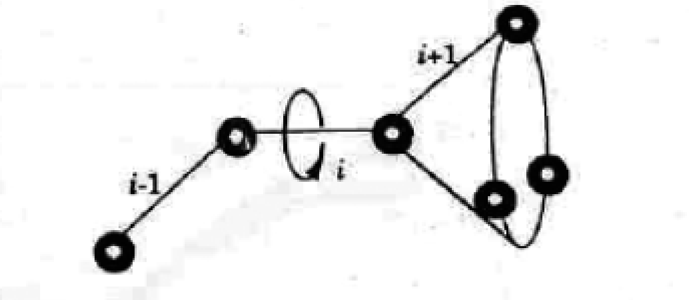


Figure 2.11 Three different rotational isomers are generated by torsion about bond *i*. If the three states are equally populated, the average vector of bond *i* + 1 has no component perpendicular to a vector parallel to the *i*th bond.

$$\langle r^2\rangle = nl^2\left(1+\frac{2\alpha}{1-\alpha}\right)= nl^2\left(\frac{1+\alpha}{1-\alpha}\right)$$
$$= nl^2\,\frac{1+\cos(180-\tau)}{1-\cos(180-\tau)} \qquad (2.19)$$

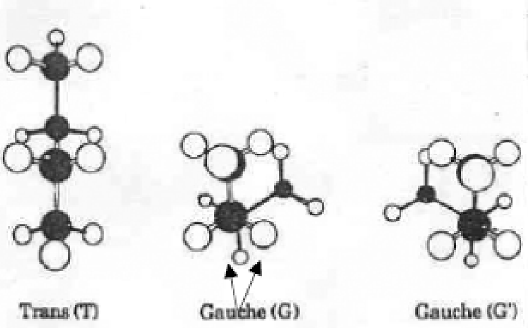


Figure 2.3 Conformational states of *n*-butane. Note that the views of the gauche conformers are along the middle carbon–carbon bond. Carbon – shaded; hydrogen – white.

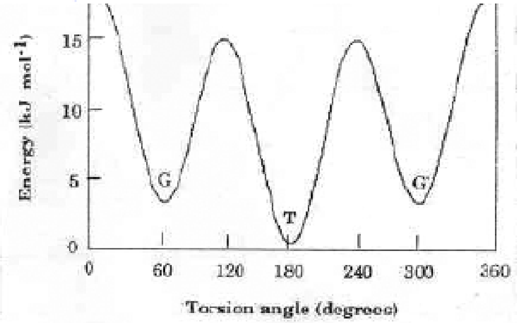


Figure 2.4 Conformational energy of *n*-butane as a function of torsion angle of the central carbon–carbon bond. The outer carbon–carbon bonds are assumed to be in their minimum energy states (staggered positions).

Subing τ~110° gives the value of the second term of RHS becomes approx 2.

Hindered rotating model

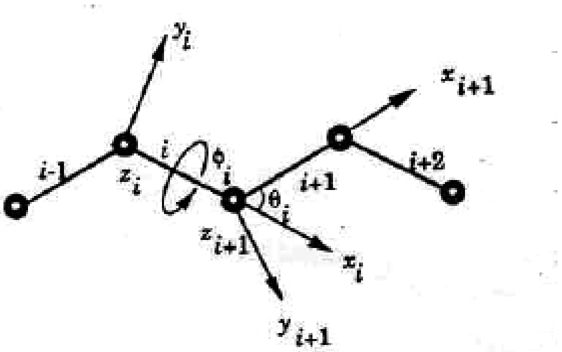


Figure 2.12 Definition of CS_i and CS_{i+1}; the torsion angle ϕ is set to zero for the planar trans conformation. Axis y_i is in the plane of bonds i and $i-1$, and z_i completes the right-handed Cartesian coordinate system.

$$\langle r^2\rangle = n\,l^2\left(\frac{1+\cos(180-\tau)}{1-\cos(180-\tau)}\right)\left(\frac{1+\langle\cos\phi\rangle}{1-\langle\cos\phi\rangle}\right) \qquad (2.29)$$

$$\langle\cos\phi\rangle = \textit{origin of temperature dependence}$$

This model assumes three rotational isomers, viz. T, G, and G'.