

Chapter 2. Chain Conformations in Polymers

2.1 Introduction

Conformation : Due to degree of freedom for rotation about σ bonds

- Rotational positions of ethane ($\text{CH}_3\text{-CH}_3$)

Staggered position

Eclipsed position ~ energy barrier : 11.8 kJ/mol

Intermediate position cf.) At room temp., $RT \doteq 2.5$ kJ/mol

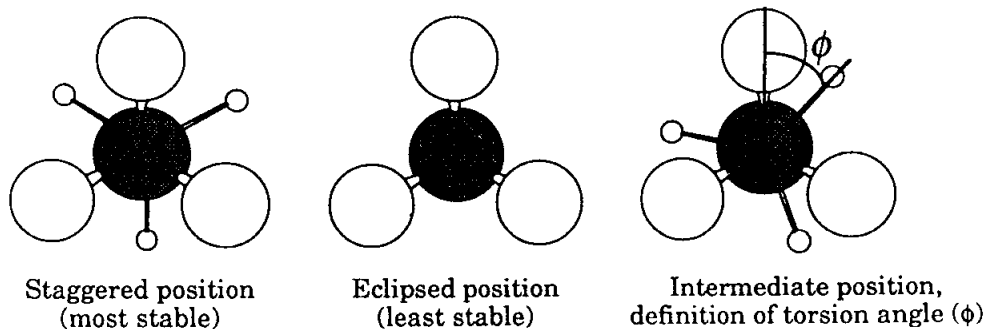


Figure 2.1 Rotational isomers of ethane from a view along the C–C bond: carbon – shaded; hydrogen – white.

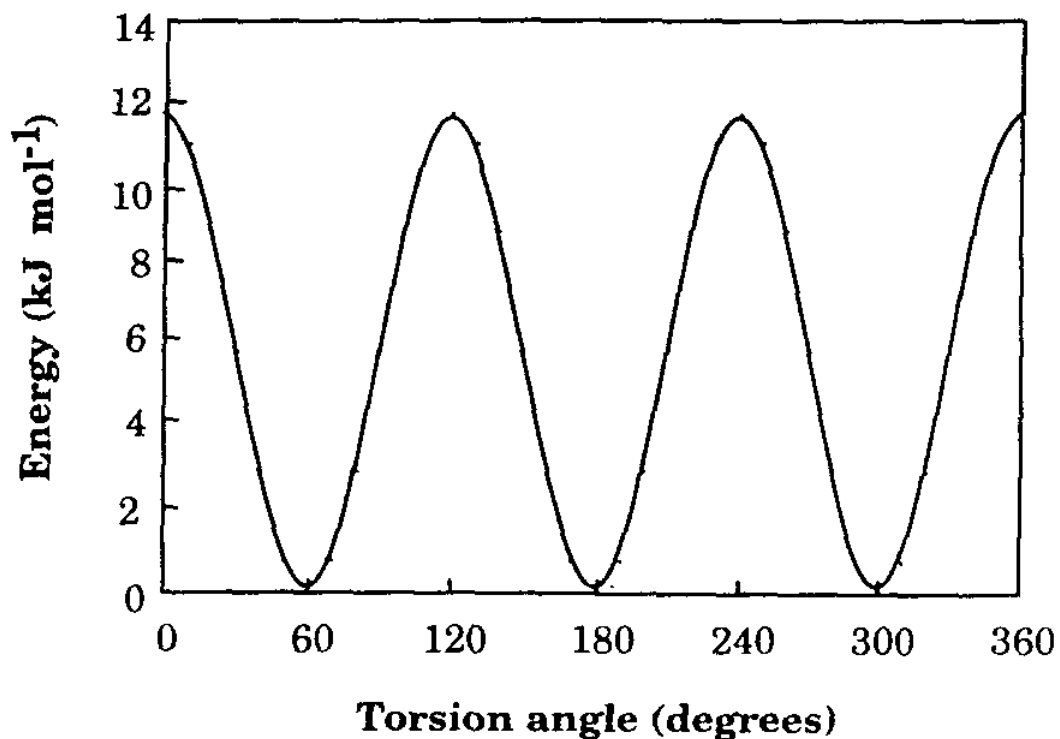


Figure 2.2 Conformational energy of ethane as a function of torsion angle.

- n-butane ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$)
stable states : trans(T), gauche(G, G')

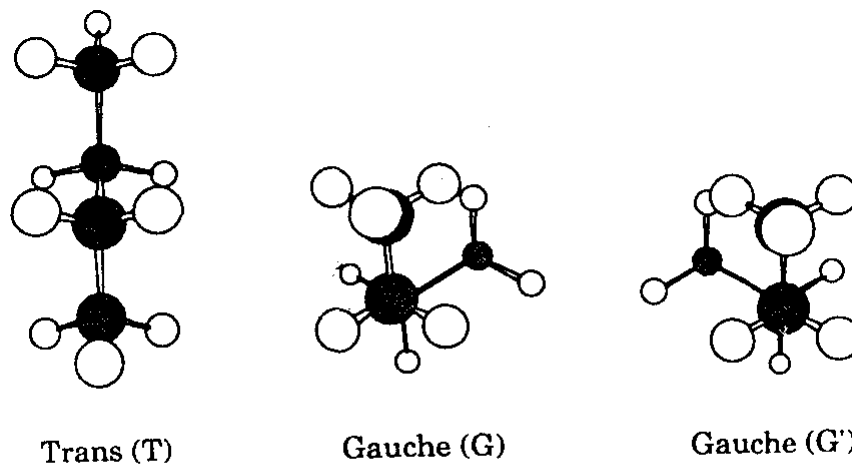
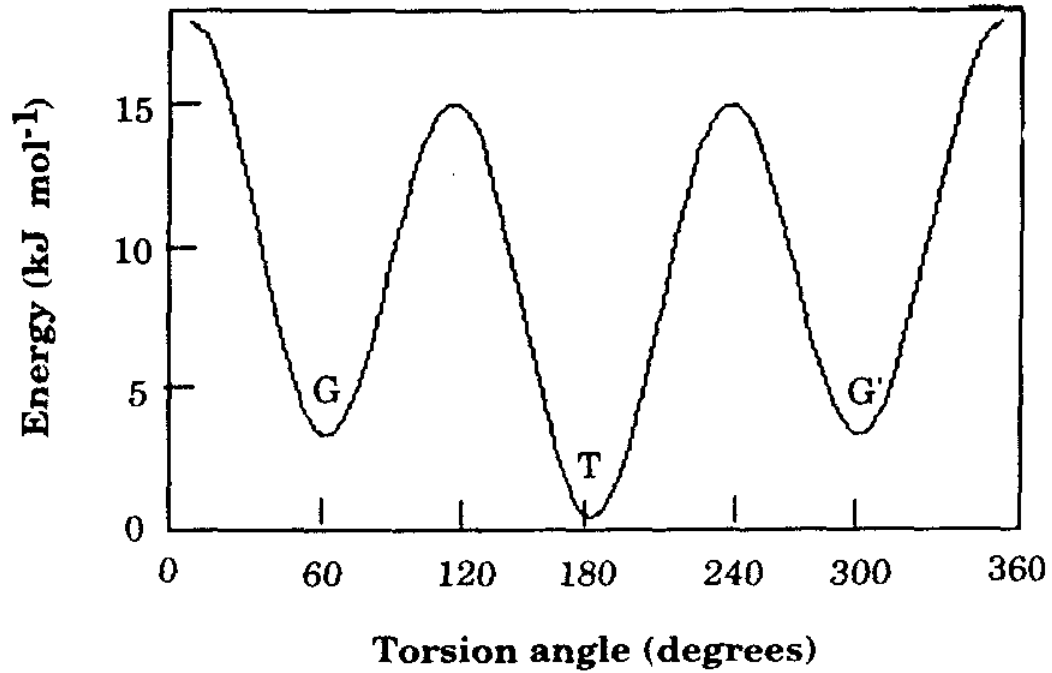


Figure 2.3 Conformational states of *n*-butane. Note that the views of the gauche conformers are along the middle carbon-carbon bond. Carbon – shaded; hydrogen – white.



- An alkane with n carbons

How many different conformations ?

$n-1$ σ main-chain bonds $\rightarrow 3^{n-3}$

typical polymer molecule : 10,000 carbons : $3^{9997} \approx 10^{4770}$ conformations

실제로는 이보다 작다. (\because symmetry, E of certain conformations is very high!)

ex) GG' conformation in n -pentane

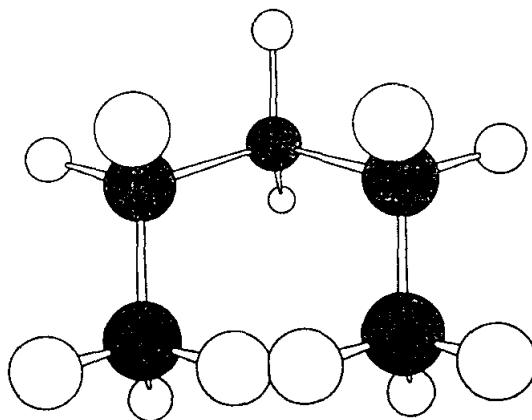


Figure 2.5 Illustration of the steric repulsion in the high-energy GG' conformer in n -pentane: carbon – shaded; hydrogen – white.

- Characteristic dimension of the random chain

: **end-to-end distance** (양단간거리) r or **radius of gyration** (회전반경) s

→ function of MW, chain flexibility & T

$$s^2 = \frac{\sum_{i=1}^n m_i \overline{r_i^2}}{\sum_{i=1}^n m_i} = \frac{\sum_{i=1}^n \overline{r_i^2}}{n} \quad \text{if all } m_i \text{'s are the same}$$

$\overline{r_i}$: vector from the center of gravity to atom i

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

2.2 Experimental determination of dimensions of chain molecules

Size of the molecular coils : dependent on the solvent

Good solvent ($\alpha > 1$) ~ expands the coil

Poor solvent ($\alpha < 1$) ~ shrinks the coil

Theta solvent ($\alpha = 1$) ~ intermolecular & interamolecular interactions are similar

α : coil expansion factor

Common methods for determining the coil size : *light scattering & viscometry*

- *Light scattering* of polymer solutions as a function of coil size

$$\frac{Kc}{R_\theta} = \frac{1}{M} + 2A_2c + 3A_3c^2 + \dots$$

$$\frac{c}{R_\theta} \propto \frac{1}{M_w}, \quad \frac{1}{P(\theta)} = 1 + \frac{16}{3} \pi^2 \frac{\langle r^2 \rangle}{6\lambda^2} \sin^2 \frac{\theta}{2}$$

$$\frac{Kc}{R_\theta} = \frac{1}{M_w P(\theta)} + 2A_2c + \dots$$

$$\Rightarrow \frac{Kc}{R_\theta} = \frac{1}{M_w} + \frac{1}{M_w} \frac{16}{3} \pi^2 \frac{\langle r^2 \rangle}{6\lambda^2} \sin^2 \frac{\theta}{2} + 2A_2c$$

θ : scattering angle, λ : wave length, c : concentration

A_2 : second virial coefficient, K : optical constant (굴절률에 관련)

$P(\theta)$: particle scattering function (effect of chain size & conformation)

R_θ : Rayleigh's ratio (reduced scattered intensity), $I_\theta r^2 / I_0$

I_θ : intensity of observed light

I_0 : intensity of incident light

r : distance between sample and source

Separate determination of \overline{M}_w & $\langle r^2 \rangle$: Zimm plot

$$\lim_{\theta \rightarrow 0} \frac{Kc}{R_\theta} = \frac{1}{\overline{M}_w} + 2A_2c$$

$$\lim_{c \rightarrow 0} \frac{Kc}{R_\theta} = \frac{1}{\overline{M}_w} + \frac{1}{\overline{M}_w} \frac{16}{3} \pi^2 \frac{\langle r^2 \rangle}{6\lambda^2} \sin^2 \frac{\theta}{2}$$

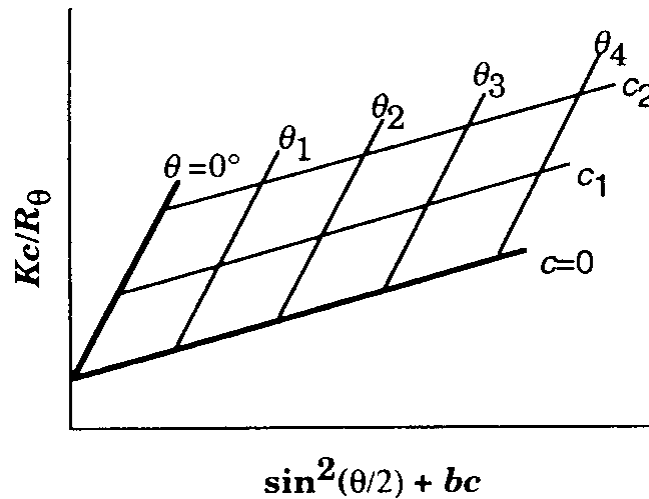


Figure 2.8 Schematic Zimm plot.

- *Viscometry*

$$[\eta] = \frac{\Phi \langle r^2 \rangle^{3/2}}{M} = \left(\frac{\eta_r - 1}{c} \right)_{c \rightarrow 0}$$

$[\eta]$ in dl/g, M in \overline{M}_n \longrightarrow r in cm

$\Phi = 2.6 \times 10^{21} \text{ dl/mol cm}^3$ for near-theta conditions (Flory constant)

η_r : relative viscosity $\left(\frac{\eta}{\eta_0} \right)$,

$\eta_r - 1 \equiv \eta_{sp}$ (specific viscosity)

2.3 Characteristic dimensions of 'Random Coil' polymers

Polymers dissolved in theta solvent,

$$\langle r^2 \rangle_0 = Cnl^2$$

l : chain length

n : number of chain

C : polymer related constant (depends on the nature of polymer)

0 : θ condition

Table 2.1 C values for some polymers under theta conditions

Polymer	$C (M = \infty)^a$
Polyethylene	6.7
Polyethyleneoxide	4.0
Polystyrene, atactic	10.0

Source: Flory (1989)

^a See eq. (2.7).

Flexible backbones exhibit low C .

$$\langle r^2 \rangle = \alpha^2 \langle r^2 \rangle_0$$

α : linear expansion factor

$$\alpha^5 - \alpha^3 = C\Psi\sqrt{n}\left(1 - \frac{\theta}{T}\right)$$

θ : θ -temperature

Ψ : interaction entropy (Chap. 4). In a good solvent ($T > \theta$), $\alpha \propto n^{1/10}$

$$\Rightarrow \langle r^2 \rangle = C_1 n^{1/5} \langle r^2 \rangle_0$$

$$= C_2 n^{1/5} n = C_2 n^{6/5}$$

$\therefore r \propto n^{3/5}$ (실험치 $r \propto n^{0.59}$) for good solvents

$$\text{At } T = \theta, \langle r^2 \rangle = \langle r^2 \rangle_0$$

Molten polymer molecules are unperturbed as they are in θ -solvent. (by Flory)

2.4 Models for calculating average end-to-end distance

Mean square end-to-end distance

$$\bar{r} = \sum_{i=1}^n \bar{r}_i : \text{end-to-end vector}$$

$$r^2 = \sum_{i=1}^n \bar{r}_i \cdot \sum_{j=1}^n \bar{r}_j \dots$$

- *Freely jointed chain*

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

$$\langle r^2 \rangle = \alpha^2 Cnl^2$$

← including the short range (C)
and long range (α) interactions

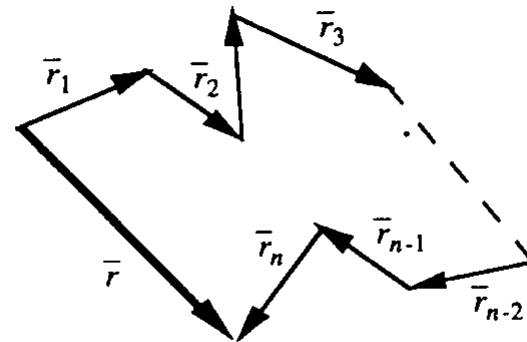


Figure 2.10 Definition of quantities in a jointed-chain model.

- Freely rotating chain

Bond angle (τ) is constant.

$$\begin{aligned}\langle r^2 \rangle &= nl^2 \left[\frac{1 + \cos(180 - \tau)}{1 - \cos(180 - \tau)} \right] \\ &= nl^2 \frac{1 - \cos \tau}{1 + \cos \tau}\end{aligned}$$

If $\tau = 90^\circ$, $\langle r^2 \rangle = nl^2$

If $\tau = 109.28^\circ$, $\langle r^2 \rangle = 2nl^2$

← methylene chain with free rotation

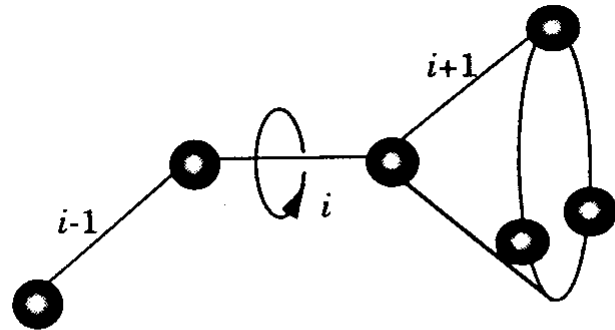


Figure 2.11 Three different rotational isomers are generated by torsion about bond i . If the three states are equally populated, the average vector of bond $i + 1$ has no component perpendicular to a vector parallel to the i th bond.

- **Equivalent chain**

$$\langle r^2 \rangle = Cnl^2 = n'l'^2$$

$$r_{\max} = n'l'$$

ex) For polyethylene with $r_{\max} = 0.83nl$

nl : contour length

$$\langle r^2 \rangle_0 = 6.7nl^2$$

$$\therefore \frac{n}{n'} = 9.73, \quad \frac{l'}{l} = 8.07$$

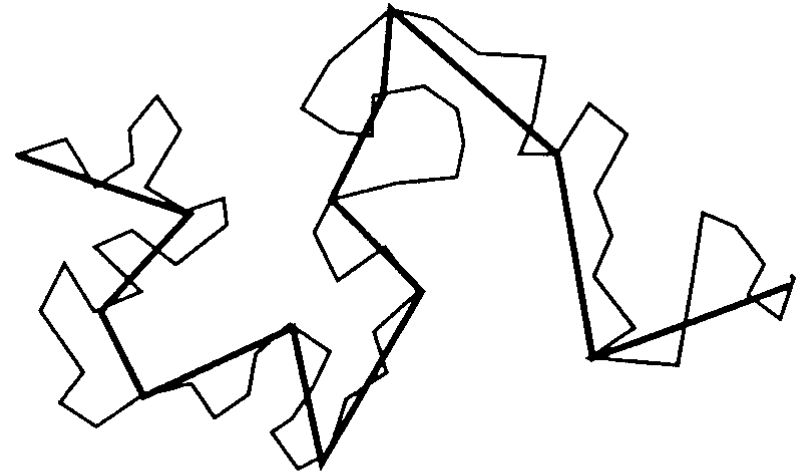


Figure 2.16 Schematic representation of the equivalent chain.

2.5 Distribution of the end-to-end distance

Expression for the distribution of the end-to-end distance

← Random-flight analysis

Probability of finding the chain end in the point (x, y, z) in a chain originating at the origin with the other chain end :

$$P(x, y, z)dx dy dz = \left(\frac{3}{2\pi \langle r^2 \rangle_0} \right)^{3/2} \exp\left(-3r^2/2\langle r^2 \rangle_0\right) dx dy dz$$

With radial distribution function, $P(r)dr$:

$$P(r)dr = 4\pi r^2 \left(\frac{3}{2\pi \langle r^2 \rangle_0} \right)^{3/2} \exp\left(-3r^2/2\langle r^2 \rangle_0\right) dr$$

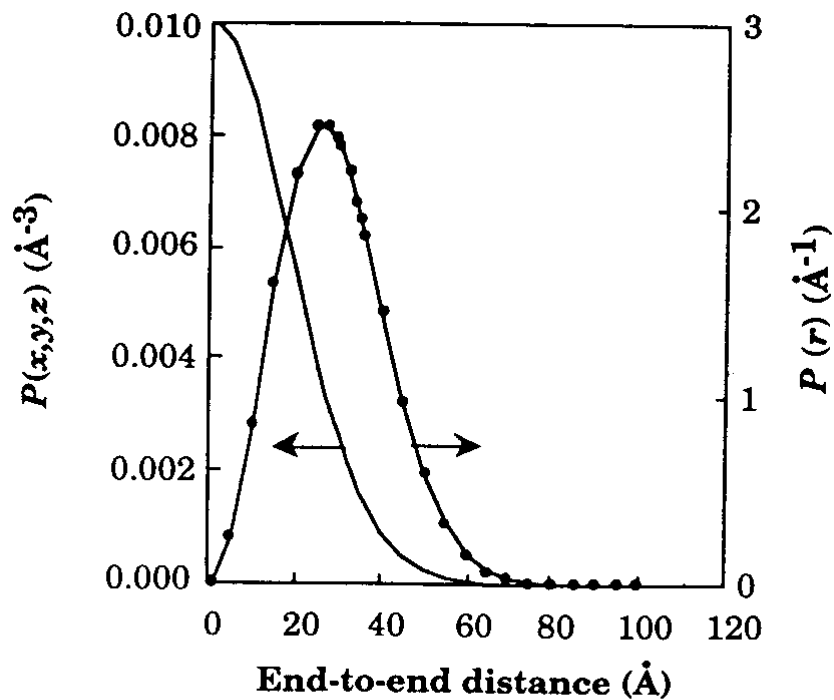


Figure 2.18 Schematic representation of distribution functions: $P(x, y, z)$ and $P(r)$.

2.6 Chains with preferred conformation

PE : all-trans conformation is the most stable (zigzag planar)

PP : Three polymer repeating units in one turn of the helix

POM : 9 repeating units in 5 turns

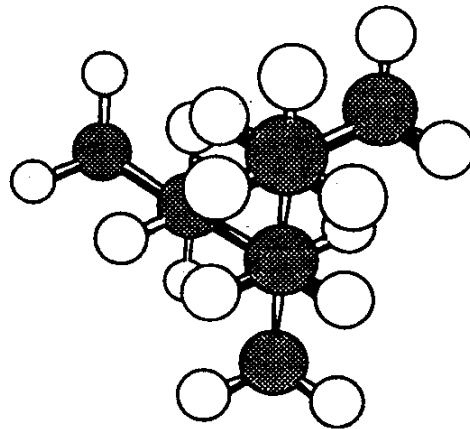


Figure 2.20 View along helical axis of 3_1 helix of isotactic polypropylene. The cross-section of the backbone part of the molecule is triangular and the pendant methyl groups are directed out from the corners of the triangle.