II. Structure of Polymer Chain

Polymer molecules have many *conformations* and might have different *configurations*. Conformations can be changed by rotation about the backbone, while configurations can only be changed by breaking the bonds.

**Chain Isomerism:**

*I. Positional isomerism:* Example head-to-head and head-to-tail (e.g. PP)

*II. Stereo isomerism:* Isotactic, Syndiotactic and Atactic, (e.g. PMMA)

*III. Geometrical isomerism:* 1,2 or 1,4; etc.; cis- and trans-; (e.g. polybutadiene, polyisoprene)
Role of **tacticity and microstructure**. Tacticity of polymer chain can affect flexibility of the chain, packing of chains (free volume) and in this way will influence glass transition temperature. Tacticity strongly affects crystallization of polymers.

**Example of PMMA:**

<table>
<thead>
<tr>
<th>Syndiotactic</th>
<th>Isotactic</th>
</tr>
</thead>
</table>
| \[
\begin{array}{c}
\text{OCH}_3 \\
\text{CO} \\
\text{CH}_3 \\
\text{H}_3\text{C}
\end{array}
\] |
| \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C} \\
\text{C} \\
\text{CO} \\
\text{OCH}_3 \\
\text{H}_3\text{C} \\
\text{C} \\
\text{C} \\
\text{CO} \\
\text{OCH}_3
\end{array}
\] |

Microstructure of polymers also affect Tg significantly. An example is 1,4 and 1,2 poly(butadiene). Presence of the double bond in the back-bone reduces Tg drastically.

\[
\begin{array}{c}
\text{C} \equiv \text{C} \\
\text{C} \equiv \text{C} \\
\text{C} \equiv \text{C} \\
\text{C} \equiv \text{C}
\end{array}
\]

1,4-PB, Tg~175K

1,2-PB, Tg~270K

Tg in polybutadienes is a smooth function of vinyl content [Hofmann, et al. *Macromolecules* **29**, 129 (1996)]. This is an example of Tg in a random co-polymer.
Chain configuration is formed during the synthesis. It is often characterized in the number of dyads. There are *meso* and *rasemic* dyads

\[
\begin{array}{c}
\text{X} & \text{H} & \text{X} \\
\text{H} & \text{X} \\
\end{array}
\quad
\begin{array}{c}
\text{X} & \text{H} & \text{X} \\
\text{H} & \text{X} \\
\end{array}
\]

Let’s assume \( p_m \) and \( p_r \) are the probability of addition occurring in the meso or in the racemic modes. \( p_m + p_r = 1 \). \( p_m = \frac{k_i}{k_i + k_s} \), here \( k \) is the rate constant for isotactic or syndiotactic additions. Assuming \( p \) is independent of a prior addition, we can have various triads:

**Isotactic triad;** \( p_i = p_m^2 \)

\[
\begin{array}{c}
\text{X} & \text{X} & \text{X} \\
\text{m} & \text{m} \\
\end{array}
\]

**Syndiotactic triad;** \( p_s = (1-p_m)^2 \)

\[
\begin{array}{c}
\text{X} & \text{X} & \text{X} \\
\text{r} & \text{r} \\
\end{array}
\]

**Heterotactic triad;** \( p_h = 2p_m(1-p_m) \)

\[
\begin{array}{c}
\text{X} & \text{X} & \text{X} \\
\text{m} & \text{r} \\
\end{array}
\]

Fraction of iso-, syndio- and hetero- triads

Control of chain stereoregularity is usually achieved by using right catalysts (e.g. Ziegler-Natta catalysts). In many cases they regulate particular way the monomer and the chain will orient.
Spectroscopic techniques to characterize chain structure

Optical absorption: Electronic transitions depend on structure and sometimes even on sequence of microstructures.

Vibrational Spectroscopy (Raman scattering, Infrared spectroscopy):
Characteristic vibrational frequency depend on microstructure

*Examples of Raman spectra of polymers*

Conformational changes in PB

\[ \text{trans} \quad \left( \begin{array}{c} \text{CH} \\
\text{CH=CH} \\
\text{CH}_2 \end{array} \right) \]

\[ \text{vinyl} \quad \left( \begin{array}{c} \text{CH}_2 \\
\text{CH} \\
\text{CH}_2 \end{array} \right) \]

\[ \text{cis} \quad \left( \begin{array}{c} \text{CH}_2 \\
\text{CH=CH} \\
\text{CH}_2 \end{array} \right) \]
NMR SPECTROSCOPY:

Nuclei have a nuclear spin number $I$, which is zero for the common isotopes $^{12}$C and $^{16}$O, and 1/2 for $^1$H (natural abundance 99.98%) and $^{13}$C (natural abundance 1.11%).

In a uniform external magnetic field, the nucleus has $2I+1$ discrete orientations. If $I = 1/2$, the orientations have two energy levels $\pm \mu H_0$, where $\mu$ is the magnetic moment and $H_0$ is the external magnetic field. The transition between them requires $E = h\nu = 2\mu H_0$, which depends on the size of the external magnetic field. The higher the magnetic filed – the higher the frequency (NMR spectrometers are called accordingly, e.g. 900 MHz …).

The Chemical Shift

The local field sensed by a nucleus is modified slightly (but measurable) by shielding by nearby electrons. The size of this effect is proportional to $H_0$. This proportionality to $H_0$ is removed when the frequencies are converted to chemical shifts,

$$\delta = \frac{(H_{\text{reference}} - H_{\text{sample}})}{H_{\text{reference}}}$$

Given the small size of the effect, $\delta$ is usually reported in ppm. Typical ranges for $\delta$ are 10 ppm for $^1$H and 600 ppm for $^{13}$C. Tetramethylsilane (TMS) is a common reference.
In proton NMR, the signal intensity is proportional to the number of protons. In low resolution spectrum, ethanol (CH$_3$CH$_2$OH) has three resonances with areas in the ratio 3:2:1.

The ratio of the signal intensities of $^1$H is determined by chemical composition. Analysis of intensities can be used to determine chemical composition.

**Example:** The chemical composition of a copolymer of methyl methacrylate (MMA) and hexyl methacrylate (HMA) can be determined by using the intensities of resonances due to:

- The three hydrogen atoms in the methyl group in the methyl ester of MMA, -COO-CH$_3$.
- The two hydrogen atoms in the methylene group bonded to the ester in HMA, -COO-CH$_2$-(CH$_2$)$_4$-CH$_3$
Spin-Spin Interactions

Spin-spin interactions are seen in higher resolution NMR spectra. They arise from the interaction of spins on hydrogen atoms bonded to neighboring carbon atoms. The multiplicity from $n$ hydrogen atoms is $n+1$, with the intensities being 1:1, 1:2:1, 1:3:3:1 for doublets, triplets, and quadruplets, respectively.

At high resolution, the NMR spectrum of ethanol becomes a triplet (CH$_3$, due to spin-spin interaction with CH$_2$), quadruplet (CH$_2$, due to spin-spin interaction with CH$_3$), and a singlet (OH), with the areas of triplet:quadruplet:singlet in the ratio 3:2:1.

The spacing in a multiplet (spin-spin coupling constant $J$) is independent of $H_0$ (only at small $J$).
**$^{13}$C NMR**

- Spin-spin interactions are insignificant (due to the low abundance of $^{13}$C), unless enriched materials are used. The $^{13}$C spectra often appear simpler (fewer peaks) than $^1$H spectra.
- Signals from particular nuclei in a structure can be identified by materials selectively enriched in $^{13}$C.
- The $\delta$ occur over a much wider (50 times larger) range for $^{13}$C than for $^1$H.
- Signals in $^{13}$C NMR are intrinsically weaker (~64 times) than in $^1$H NMR, and their intensities are not proportional to the number of nuclei.

Example of $^{13}$C NMR spectrum
Observation of Tacticity: Poly(methyl methacrylate)

PMMA can be synthesized as atactic (common, from free radical polymerization), isotactic, or syndiotactic. **Methylene (CH\(_2\)) protons** in the backbone

\[
\begin{array}{ccc}
\text{CH}_3 & \text{H} & \text{CH}_3 \\
\text{CH}_3 & \text{H} & \text{COOR} \\
\end{array}
\]

**Isotactic (m)**

\[
\begin{array}{ccc}
\text{CH}_3 & \text{H} & \text{COOR} \\
\text{H} & \text{COOR} & \text{AB pattern} \\
\end{array}
\]

**Syndiotactic (r)**

\[
\begin{array}{ccc}
\text{COOR} & \text{H} & \text{CH}_3 \\
\end{array}
\]

<table>
<thead>
<tr>
<th>Distinguishable</th>
<th>Indistinguishable</th>
</tr>
</thead>
</table>

Atactic: Shows both characteristics. A physical mixture of isotactic and syndiotactic looks like atactic, because the CH\(_2\) protons only feel dyads.

**Backbone methyl (CH\(_3\)) protons**

\[
\begin{array}{ccc}
\text{CH}_3 & \text{H} & \text{CH}_3 \\
\text{CH}_3 & \text{H} & \text{CH}_3 \\
\text{CH}_3 & \text{H} & \text{COOR} \\
\text{COOR} & \text{H} & \text{COOR} \\
\text{COOR} & \text{H} & \text{CH}_3 \\
\text{COOR} & \text{H} & \text{COOR} \\
\text{COOR} & \text{H} & \text{COOR} \\
\end{array}
\]

**Isotactic triad**

\[
\begin{array}{ccc}
\text{CH}_3 & \text{H} & \text{CH}_3 \\
\end{array}
\]

\(mm\)

CH\(_3\) protons are sensitive to *triads*. **Singlet**, but with a *chemical shift* that is different in *mm*, *mr* (=*rm*), and *rr* triads.

**Heterotactic triad**

\[
\begin{array}{ccc}
\text{CH}_3 & \text{H} & \text{COOR} \\
\end{array}
\]

\(mr (=rm)\)

Mixture of isotactic and syndiotactic *distinguishable* from atactic.

**Syndiotactic triad**

\[
\begin{array}{ccc}
\text{COOR} & \text{H} & \text{CH}_3 \\
\text{COOR} & \text{H} & \text{COOR} \\
\text{CH}_3 & \text{H} & \text{COOR} \\
\end{array}
\]

\(rr\)
Example of proton NMR spectra of PMMA with different tacticity

Example of $^{13}$C NMR spectra of polypropylene
Synthesis of copolymers

To achieve particular properties copolymers can be synthesized. Example SBR (styrene-butadiene rubber), where by changing S/B monomer ratio Tg can be shifted from ~180K up to ~370K, changing the polymer at room temperature from very soft rubber to a brittle solid polymer.

Copolymer can be alternating, random or block. The copolymer composition depends on the rate of specific monomer addition, concentration of monomers, etc.

We will consider a simplified situation:

➢ Only two monomers \( M_1 \) and \( M_2 \);

➢ Only radical chain end influences the rate constant for propagation (terminal control mechanism)

\[
\begin{align*}
-\cdot M_1 + M_1 & \xrightarrow{k_{11}} -M_1M_1 \\
-\cdot M_1 + M_2 & \xrightarrow{k_{12}} -M_1M_2 \\
-\cdot M_2 + M_1 & \xrightarrow{k_{21}} -M_2M_1 \\
-\cdot M_2 + M_2 & \xrightarrow{k_{22}} -M_2M_2
\end{align*}
\]

Here \( k_{ij} \) is a propagation constant with \( i \) index corresponding to terminal monomer, and \( j \) index is the added monomer

Important parameter is reactivity ratio: \( r_1 = \frac{k_{11}}{k_{12}} \) \( r_2 = \frac{k_{22}}{k_{21}} \)

The relative rates of the two monomer additions, that defines the ratio of the two kinds of repeat units in the copolymer

\[
\begin{align*}
\frac{d[M_1]}{dt} &= \frac{[M_1]}{[M_2]} \left( \frac{k_{11}}{k_{12}} \right) [M_1] + [M_2] = \frac{1 + r_1[M_1]/[M_2]}{1 + r_2[M_2]/[M_1]}
\end{align*}
\]
Composition vs Feedstock:

$F_i$ is the mole fraction of the component $i$ in the polymer; $f_i$ is the mole fraction of component $i$ in the monomer solution.

Copolymer composition equation:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

### Table 5.1 Values of Reactivity Ratios $r_1$ and $r_2$ and the Product $r_1 r_2$ for a Few Copolymers at 60°C

<table>
<thead>
<tr>
<th>$M_1$</th>
<th>$M_2$</th>
<th>$r_1$</th>
<th>$r_2$</th>
<th>$r_1 r_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile</td>
<td>Methyl vinyl ketone</td>
<td>0.61</td>
<td>1.78</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>Methyl methacrylate</td>
<td>0.13</td>
<td>1.16</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>$\alpha$-Methyl styrene</td>
<td>0.04</td>
<td>0.20</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>Vinyl acetate</td>
<td>4.05</td>
<td>0.061</td>
<td>0.25</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>Styrene</td>
<td>0.46</td>
<td>0.52</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>Methacrylic acid</td>
<td>1.18</td>
<td>0.63</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>Vinyl acetate</td>
<td>20</td>
<td>0.015</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>Vinylidene chloride</td>
<td>2.53</td>
<td>0.24</td>
<td>0.61</td>
</tr>
<tr>
<td>Styrene</td>
<td>Vinyl acetate</td>
<td>55</td>
<td>0.01</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>Vinyl chloride</td>
<td>17</td>
<td>0.02</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>Vinylidene chloride</td>
<td>1.85</td>
<td>0.085</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>2-Vinyl pyridine</td>
<td>0.55</td>
<td>1.14</td>
<td>0.63</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>1-Butene</td>
<td>2.0</td>
<td>0.34</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>Isobutylene</td>
<td>2.15</td>
<td>0.31</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>Vinyl chloride</td>
<td>0.23</td>
<td>1.68</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Vinylidene chloride</td>
<td>0.05</td>
<td>6.7</td>
<td>0.34</td>
</tr>
</tbody>
</table>

$r_1$ and $r_2$ define the structure of copolymer:

1. Alternating structure when $r_1 \rightarrow 0$ and $r_2 \rightarrow 0$;
2. Random when $r_1 r_2 \rightarrow 1$
3. “Blocky” when $r_1 r_2 \gg 1$.

Usually radical activity ($k_{12}$) goes in opposite direction with monomer activity, mostly because the monomers lose (gain) stability by converting to radicals.

<table>
<thead>
<tr>
<th>Table 5.2</th>
<th>Values of the Cross-Propagation Constants $k_{12}$ (L mol$^{-1}$ s$^{-1}$) for Four Monomer–Radical Combinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>Radical</td>
</tr>
<tr>
<td></td>
<td>Styrene</td>
</tr>
<tr>
<td>Styrene</td>
<td>145</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>435</td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>203</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>2.9</td>
</tr>
</tbody>
</table>
III. Conformations of Polymer Chain, Chain Statistics

Issues in Averaging over all Conformations in an Ensemble

• Are bond lengths fixed or variable?
• Are bond angles free, or are they fixed?
• Are torsions hindered or unhindered?
  o If hindered, symmetric or asymmetric?
  o If hindered, independent or interdependent?
• Linear chain? Cyclic Chain? Branched?

End-to-end distance
\[ \langle R_n^2 \rangle = \left\langle \left( \sum_{i=1}^{n} r_i \right) \left( \sum_{j=1}^{n} r_j \right) \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle r_i r_j \rangle = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \cos \theta_{ij} \rangle \]  

(1)

Freely Jointed (Random Walk) Chain Model

No correlations between directions of different bond vectors, \( \langle \cos \theta_{ij} \rangle = 0 \) for \( i \neq j \).

Substituting this into the eq.1:
\[ \langle R_n^2 \rangle = n l^2 \]  

(2)

The tetrahedral angle \( \theta \) in real chain is fixed (e.g. PE \( \theta \sim 68^\circ \))

For any long enough \( (n \rightarrow \infty) \) flexible unperturbed chain, \( \langle R_n^2 \rangle_0 \propto n \). However, proportionality constant \( (l^2 \text{ in this model}) \) depends on the local structure and short-range interactions in the chain
Long random walk chains (in the limit as \( n \to \infty \)) have a simple relationship between the mean square unperturbed end-to-end distance and mean square unperturbed radius of gyration.  
\[
\langle R_n^2 \rangle_0 = 6 \langle R_g^2 \rangle_0 
\]
- This relationship is obeyed by any flexible unperturbed homopolymer if it contains a sufficient number of bonds.
- Experimental “measurements” of \( \langle R_n^2 \rangle_0 \) usually are measurements of \( \langle R_g^2 \rangle_0 \) that have been converted using the above equation.

The mean square radius of gyration for freely jointed chains of any number of bonds is  
\[
\langle R_g^2 \rangle_0 = (n+2)(n+1)^{-1} \langle R_n^2 \rangle_0 / 6 
\]

In the limit where \( n \to \infty \), the ratio \( \langle R_n^2 \rangle_0 / \langle R_g^2 \rangle_0 \to 6 \).

<table>
<thead>
<tr>
<th>( N )</th>
<th>( \langle R_n^2 \rangle_0 / \langle R_g^2 \rangle_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5.5</td>
</tr>
<tr>
<td>100</td>
<td>5.94</td>
</tr>
<tr>
<td>1000</td>
<td>5.99</td>
</tr>
</tbody>
</table>

Macrocycles:  
\[
\langle R_g^2 \rangle_0, \text{cyclic} / \langle R_g^2 \rangle_0, \text{linear} = 1/2 
\]
Freely Rotating Chain Model

Torsion angle $\phi$ is random, while tetrahedral angle $\theta$ is fixed.

\[ \langle R_n^2 \rangle = nl^2 \frac{1 + \cos \theta}{1 - \cos \theta} \quad (3) \]

For $\theta=68^\circ$: $\langle R_n^2 \rangle \approx 2nl^2$

**Characteristic Ratio**

The dimensionless characteristic ratio is defined as the ratio of the mean square unperturbed end-to-end distance for a real (or model) chain to the value expected for a freely jointed chain with the same number of bonds, of the same length

\[ C_n = \frac{\langle R^2 \rangle_0}{nl^2} \quad (4) \]

- By definition, $C_n = 1$ for a freely jointed chain.
- $C_n = (1+\cos \theta)/(1-\cos \theta)$ for the freely rotating chain.
- Nearly all real chains have $C_n > 1$, due to restrictions on bond angles and torsion angles.
- For long enough chain, $C_\infty = C_n$ at $n \to \infty$.

For any real long enough chain

\[ \langle R_n^2 \rangle = C_\infty nl^2 \quad (5) \]
Kuhn Segment

In order to bring real chain to the freely jointed chain:

\[ \left< R_n^2 \right> = C_\infty n l^2 = N b^2 \]

here \( N \) is the number of random steps (Kuhn segments) and \( b \) is the length of the random steps (Kuhn segment length).

The contour length of the chain \( L = N b \), so the Kuhn length

\[ b = \frac{\left< R_n^2 \right>}{L} \]

The assumption in many textbooks: \( L = R_{\text{max}} \approx \alpha nl \); e.g. for all trans PE \( \alpha \approx 0.83 \). Then

\[ b = \frac{\left< R_n^2 \right>}{R_{\text{max}}} = C_\infty l \]

This is not correct (will be discussed later).

Parameters for known polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>( C_\infty )</th>
<th>( b ) (Å)</th>
<th>( \rho ) (g/cm(^3))</th>
<th>( M_0 ) (g/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-polyisoprene (PI)</td>
<td>-(CH(_2)CH=CHCH(CH(_3)))-</td>
<td>4.6</td>
<td>8.2</td>
<td>0.830</td>
<td>113</td>
</tr>
<tr>
<td>1,4-polybutadiene (PB)</td>
<td>-(CH(_2)CH=CHCH(_2))-)</td>
<td>5.3</td>
<td>9.6</td>
<td>0.826</td>
<td>105</td>
</tr>
<tr>
<td>polypropylene (PP)</td>
<td>-(CH(_2)CH(_2)(CH(_3)))-</td>
<td>5.9</td>
<td>11</td>
<td>0.791</td>
<td>180</td>
</tr>
<tr>
<td>poly(ethylene oxide) (PEO)</td>
<td>-(CH(_2)CH(_2)O)-</td>
<td>6.7</td>
<td>11</td>
<td>1.064</td>
<td>137</td>
</tr>
<tr>
<td>poly(dimethyl siloxane) (PDMS)</td>
<td>-(OSi(CH(_3))(_2))-</td>
<td>6.8</td>
<td>13</td>
<td>0.895</td>
<td>381</td>
</tr>
<tr>
<td>polyethylene (PE)</td>
<td>-(CH(_3)CH(_2))-</td>
<td>7.4</td>
<td>14</td>
<td>0.784</td>
<td>150</td>
</tr>
<tr>
<td>poly(methyl methacrylate) (PMMA)</td>
<td>-(CH(_2)C(CH(_3))(COOCH(_3)))-</td>
<td>9.0</td>
<td>17</td>
<td>1.13</td>
<td>655</td>
</tr>
<tr>
<td>atactic polystyrene (PS)</td>
<td>-(CH(_2)CHC(_6)H(_5))-</td>
<td>9.5</td>
<td>18</td>
<td>0.969</td>
<td>720</td>
</tr>
</tbody>
</table>
The Simple Chain with Hindered Rotation

In real chains θ and l are constant and also torsion angle rotation is hindered by a potential \( U(\phi_i) \). It might have just a few minima \( i \).

\[
C_\infty = \left( \frac{1 + \cos \theta}{1 - \cos \theta} \right) \left( \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right)
\]

Here the average cosine of torsion angle is

\[
\langle \cos \phi \rangle = \frac{\int_0^{2\pi} \exp(-U(\phi)/kT) \cos \phi \, d\phi}{\int_0^{2\pi} \exp(-U(\phi)/kT) \, d\phi}
\]

If the torsion potential energy function \( U(\phi) \):

- Favors torsion angles near the *trans* placement, the value of \( C_\infty \) increases
- Favors torsion angles near the *cis* placement, the value of \( C_\infty \) decreases
- Makes all torsion angles equally probable, \( \langle \cos \phi \rangle = 0 \) and we recover the freely rotating chain
- Causes \( U(\pi - \phi) = U(\phi) \), \( \langle \cos \phi \rangle = 0 \) and \( C_\infty \) is the same as the freely rotating chain.
**Temperature Coefficient**

This model is the first one presented here that explicitly allows a *temperature dependence* for $\langle R_n^2 \rangle_0$ because $\langle \cos \phi \rangle$ can depend on $T$.

The temperature coefficient of the unperturbed dimensions is usually reported as $\partial \ln C_\infty / \partial T$, equivalent to $\partial \ln \langle R_n^2 \rangle_0 / \partial T$. For ordinary flexible chains, the order of magnitude is typically $\pm 10^{-3}$ K$^{-1}$. For polyethylene it is $-1.1 \times 10^{-3}$ K$^{-1}$.

**Simple Examples of the C-C Bond**

**Ethane CH$_3$–CH$_3$**

The molecule has $C_{3v}$ symmetry. The torsion potential is *symmetric* and *threelfold*, with a barrier $E_b$ separating minima spaced at 120°.

$E = (E_b/2)(1 + \cos 3\phi)$

With this potential, $\langle \cos \phi \rangle = 0$ at all $T$.

The size of $E_b$ (about 12 kJ/mol) is *large* compared to $kT$ at ordinary temperatures. The C-C bond in ethane strongly prefers three equivalent, staggered rotational isomeric states that are separated by torsions of 120°. The lifetime of a rotational isomer is $10^2$–$10^4$ times longer than the lifetime for a vibration.
**n-Butane CH₃CH₂–CH₂CH₃**

Interaction of the terminal CH₃ groups causes the torsion potential at the internal C-C bond to have one maximum (cis) that is higher than the other two maxima (skew), and one minimum (trans) that is lower than the other two minima (gauche).

The normalized populations of the three discrete rotational isomeric state (trans and gauche±) are:

\[ p_t = \frac{1}{Z}; \quad p_{g^+} = p_{g^-} = \frac{\sigma}{Z}; \quad Z = 1 + 2\sigma; \quad \sigma = \exp \left[ -\frac{(E_g - E_t)}{kT} \right] \]

- The value of \( E_g - E_t \) is about 2 kJ/mol
- \( \sigma \) is the temperature-dependent statistical weight of a g state, relative to a t state. It is about 0.4 at 300K.
- \( Z \), the conformational partition function, is the sum of the statistical weights for all conformations. \( Z = 1 + 2\sigma \) for butane.
- The population of any conformation is the ratio of its statistical weight to \( Z \)
- \( \langle \cos \phi \rangle = p_t (1) + p_{g^+} (-1/2) + p_{g^-} (-1/2) \)

\( \langle \cos \phi \rangle \) is ~1/3 for butane near 300K. If the restriction on the torsion angle in n-butane were an appropriate model for the C-C bond in PE, \( C_\infty \sim 4 \). The temperature coefficient would be negative.
The considered so far models assumes independent bonds. Independent bonds imply the same probabilities for the $g^+g^+$ and $g^+g^-$ sequences. In $n$-pentane, CH$_3$CH$_2$–CH$_2$–CH$_2$CH$_3$, the $g^+g^-$ states are actually an order of magnitude less probable than the $g^+g^+$ states, due to repulsive interactions of the two methyl groups. This interdependence of the bonds produces an additional extension of the chain. It brings the prediction for $C_\infty$ for polyethylene into the observed range.

**Interdependent Bonds in $n$-Pentane** CH$_3$CH$_2$–CH$_2$–CH$_2$CH$_3$

Distances (nm) between methyl carbon atoms in $n$-pentane.

- $tt$: 0.50
- $tg$: 0.43
- $g^+g^+$: 0.35
- $g^+g^-$: 0.25

The last distance, 0.25 nm, is so short that it generates a strong repulsion (about 8 kJ/mol) between the methyl group. This strong repulsion does not exist in the other conformations.

Nearly all *real* chains have interdependent bonds !! But most simple *model* chains assume independent bonds !!

Simple models cannot accurately account for all of the physical properties of real chains. They are useful nevertheless, because they do account for some of the observed properties … and they are easily used models, because they are simple.
Rotation Isomeric State (RIS) Model

Each molecule is assumed to exist only in discrete torsional states corresponding to the energy minima (value of $\phi_i$ are close to the minima $t,g^+,g^-$). A conformation of a chain with $n$ main-chain bonds is presented by a sequence of $n-2$ torsion angles: $\ldots$ $tg$-$tg^+$-$tg^+$ $\ldots$

Each of these $n-2$ $\phi$ can be in one of 3 states ($t,g^-,g^+$). Therefore the whole chain has $3^{n-2}$ states. These states are not equally probable. The relative probabilities of different states are taken into account.

<table>
<thead>
<tr>
<th>Models</th>
<th>FJC</th>
<th>FRC</th>
<th>HR</th>
<th>RIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond Length $l$</td>
<td>fixed</td>
<td>fixed</td>
<td>fixed</td>
<td>fixed</td>
</tr>
<tr>
<td>Bond Angle $\theta$</td>
<td>free</td>
<td>fixed</td>
<td>fixed</td>
<td>fixed</td>
</tr>
<tr>
<td>Torsion Angle $\phi$</td>
<td>free</td>
<td>free</td>
<td>controlled by $U(\varphi)$</td>
<td>$t,g^+,g^-$</td>
</tr>
<tr>
<td>Next $\varphi$ Independent?</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>$C_\infty$</td>
<td>1</td>
<td>$\frac{1+\cos \theta}{1-\cos \theta}$</td>
<td>$\frac{1+\langle \cos \varphi \rangle}{1-\langle \cos \varphi \rangle}$</td>
<td>specific</td>
</tr>
</tbody>
</table>

Radius of Gyration (nm) for Polyethylene Chains

<table>
<thead>
<tr>
<th>$M$</th>
<th>$R_{min}$</th>
<th>FJC</th>
<th>FRC</th>
<th>HR</th>
<th>RIS</th>
<th>$R_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^4$</td>
<td>1.4</td>
<td>1.7</td>
<td>2.4</td>
<td>3.2</td>
<td>3.6</td>
<td>26</td>
</tr>
<tr>
<td>$10^5$</td>
<td>3.0</td>
<td>5.3</td>
<td>7.5</td>
<td>9.9</td>
<td>14</td>
<td>260</td>
</tr>
<tr>
<td>$10^6$</td>
<td>6.4</td>
<td>17</td>
<td>24</td>
<td>31</td>
<td>44</td>
<td>2600</td>
</tr>
</tbody>
</table>
The Persistence Length

For a freely rotating chain with \( n \) bonds of length \( l \), the average projection of \( \mathbf{R} \) onto the direction of the first bond is

\[
\langle \mathbf{R} \cdot \mathbf{l}_1 \rangle / l_1 = l[1-(\cos \theta)^n](1 - \cos \theta)^{-1}
\]

The persistence length, \( a \), is the limit of this projection for a long chain.

\[ a = l/(1 - \cos \theta) \]

For other chains, \( a \) is similarly defined. If the chain is flexible and all bonds are of the same length,

\[ a = (l/2)(C_\infty + 1) \]

The Kuhn length is twice the persistence length, \( b \approx 2a \).

The Worm-Like Chain

Special case of the freely rotating chain for very small values of the bond angle \( \theta \). This is a good model for very stiff polymers, such as DNA, for which the flexibility is due to fluctuations of the contour of the chain from a straight line rather than trans-gauche bond rotation.

The resulting wormlike chain has continuous curvature, with no correlation in the direction of curvature at any two points along the chain. It is characterized by only two parameters:

- \( a \), which characterizes the stiffness, independent of \( M \)
- \( R_{\text{max}} \), which is proportional to \( M \)
The mean square unperturbed dimensions of the worm-like chain
\[ \langle R_n^2 \rangle_0 = 2aR_{\text{max}} \{1 - (a/R_{\text{max}})[1 - \exp (-R_{\text{max}}/a)]\} \]

- The flexible chain limit: \( a/R_{\text{max}} \to 0 \) \( \langle R_n^2 \rangle_0/R_{\text{max}} \approx 2a \approx b \)
- The stiff chain limit: \( R_{\text{max}}/a \to 0 \) \( \langle R_n^2 \rangle_0 \approx R_{\text{max}}^2 \)

The same model (with different numerical assignment of its two parameters) can represent either a stiff chain or a flexible chain.

For the model with small values of the bond angle (\( \theta << 1 \)): \( a \approx 2l/\theta^2 \); \( C_\infty \approx 4/\theta^2 \).

Depending on the length of the chain relative to the persistent length, chain can be considered as Rod, Worm-like chain or a Coil.
Characteristic ratio first increases with number of bonds $n$, and then saturates at the level of $C_\infty$. The level of $C_\infty$ and $n$ at which it is reached depend on structure of the chain, its rigidity.

Analysis of $C_n$ in three polymers with similar $C_\infty$ demonstrated that PDMS ($C_\infty \sim 6.3$) approaches the asymptotic limit much faster than PIB ($C_\infty \sim 6.6$) and PE ($C_\infty \sim 6.8$) [Mattice, et al, Macromolecules 36, 9924 (2003)].

This creates a problem for the traditional description of chain statistics through the Kuhn segment.
Deficiency of the Traditional Definition of the Kuhn Segment

\[ \langle R^2 \rangle = N_R l_R^2 = C_\infty n l_0^2 = C_\infty \frac{M}{m_0} l_0^2 \]

\[ R_{\text{max}} = N_R b \times n l_0 \] assumes that the chain is extended (all trans for PE) inside of the each bead (Kuhn segment).

\[ b \times C_\infty l_0 \]

\[ R_{\text{max}} = N_R l_R = \frac{M}{m_R} l_R < n l_0 \]

\[ b^2 = l_R^2 = C_\infty \frac{m_R}{m_0} l_0^2 \]

\( C_\infty \) is the parameter that characterizes the size of the chain, but one needs more than one parameter to characterize the chain statistics.
The average polymer conformation can be described by the mean-squared end-to-end distance (or $<R_g^2>$). Much more information is contained in the distribution of end-to-end vectors than in $<R_n^2>$.

$P(N,R)$ is the probability distribution function for the end-to-end distance $R$ of a chain with $N$ random steps (bonds of freely jointed chain). For long enough chain ($N>>1$), it can be well approximated by a Gaussian distribution function:

$$P(N, R) = \left(\frac{3}{2\pi\langle R_n^2 \rangle}\right)^{3/2} \exp\left(-\frac{3R^2}{2\langle R_n^2 \rangle}\right) = \left(\frac{3}{2\pi Nb^2}\right)^{3/2} \exp\left(-\frac{3R^2}{2Nb^2}\right)$$

The probability to find a chain with the end-to-end distance $R$:

$$W(N, R)dR = P(N, R) \times 4\pi R^2 dR =$$

$$= 4\pi R^2 \left(\frac{3}{2\pi\langle R_n^2 \rangle}\right)^{3/2} \exp\left(-\frac{3R^2}{2\langle R_n^2 \rangle}\right) dR$$

This distribution function is not accurate when $R$ is approaching $Nb$, and it will be wrong at $R>Nb$. 

![Graph of the probability density function](image)
Good, Poor, and $\Theta$ Solvents

What fraction of the space inside the domain of an unperturbed random coil is actually occupied by segments from that chain? Does the answer depend on $M$?

Approximate as the cube of the ratio of two radii of gyration: $(R_{\text{min}} / \langle R_g^2 \rangle_0^{1/2})^3$

Example of polyethylene

<table>
<thead>
<tr>
<th>$M$</th>
<th>$R_{\text{min}}$, nm</th>
<th>$\langle R_g^2 \rangle_0^{1/2}$, nm</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^4$</td>
<td>1.4</td>
<td>3.6</td>
<td>0.06</td>
</tr>
<tr>
<td>$10^5$</td>
<td>3.0</td>
<td>14</td>
<td>0.01</td>
</tr>
<tr>
<td>$10^6$</td>
<td>6.4</td>
<td>44</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Fraction will be smaller in a good solvent.

In dilute solution, a flexible polymer will expand in a good solvent (to maximize interaction with the solvent), and contract in a poor solvent (to minimize interaction). This effect is represented by an expansion factor.

$$\alpha^2 = \langle R^2 \rangle / \langle R^2 \rangle_0$$

The ranges for $\alpha^2$ in three types of solvents are:

- Good solvent: $\alpha^2 > 1$
- Ideal ($\Theta$ solvent): $\alpha^2 = 1$
- Poor solvent: $\alpha^2 < 1$. 
The molecular weight dependence of the mean square dimensions depends on the solvent quality
\[ \langle R_n^2 \rangle \propto n^{2\nu}, \text{ and therefore } \alpha \propto n^{(2\nu-1)/2} \]
The limiting values for the exponents are:
- **Good** solvent: \( \nu = \frac{3}{5} \)
- **Ideal** (\( \Theta \) solvent): \( \nu = \frac{1}{2} \)
- **Poor** solvent: \( \nu = \frac{1}{3} \)
These \( \nu \) are the limiting slopes of \( \ln \langle R_n^2 \rangle^{1/2} \) vs. \( \ln M \).
The mean square dimensions become more sensitive to solvent as \( M \) increases.

The \( \Theta \) state is achieved in
- Carefully selected solvents at specified temperatures
- The *bulk amorphous polymer (Flory hypothesis)*
This result tells us which solvent should be selected if we want to learn about the conformations of the polymer in the bulk amorphous state by making measurements in dilute solution. The principal experimental validation of the Flory hypothesis is via measurements of \( \langle R_g^2 \rangle \). The measurements in dilute solution are usually obtained by the angular dependence of light scattering (LS). The measurements in the bulk employ mixtures of normal and deuterated polymers, studied by the scattering of neutrons (SANS).