An introduction to polymer physics

6 hours

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3. Long range structure of polymer chains (8 hours)

contents

3.1 Conformation of polymer chains

3.2 Flexibility of polymer chains

3.3 statistical theories of conformation of polymer chains

required：
• concepts of conformation 、 flexibility and segments
• factors influencing the flexibility is also important

objective：

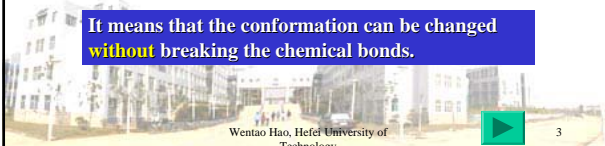to establish the concept of long chain molecule, random coil and segments

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3.1 conformation (构象)

3.1.1 Concept

Key point

The conformation of a macromolecule of given constitution and configuration specifies the spatial arrangements of the various atoms in the molecules that may occur due to the rotation about the single bonds.

由于单键内旋转而产生的分子在空间的不同形态称为构象

It means that the conformation can be changed without breaking the chemical bonds.

For the very long polymer chains, they are not always straightly extended, but in **curl state**.

Why polymer chains like to be curled?

As we know, many polymer chains are made up of carbon atoms linked by single bonds. And polymer chain can rotate around single bonds……
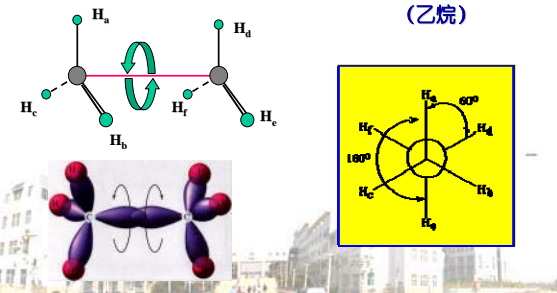
3.1.2 rotation of small molecules

A. Now let's see the conformation of ethane first.

（乙烷）
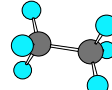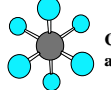
Rotational isomers of ethane

Staggered position or trans position
交叉式

Most stable

Carbon atoms

Eclipsed position
叠同式

Least stable

Hydrogen atoms

1

Slide 7

Potential energy* curve of ethane with different conformation
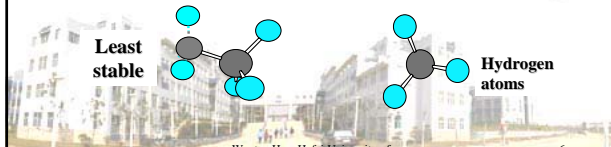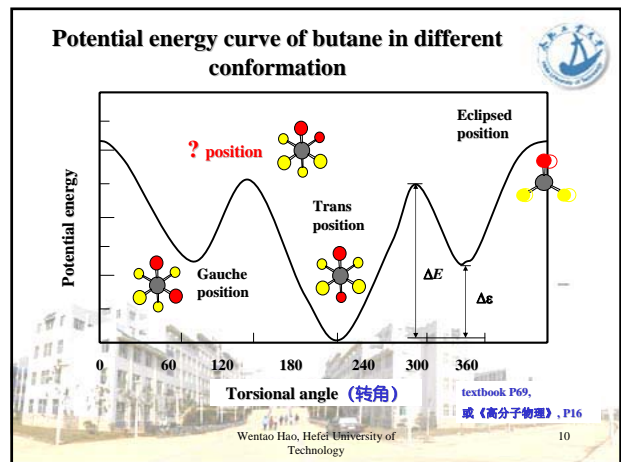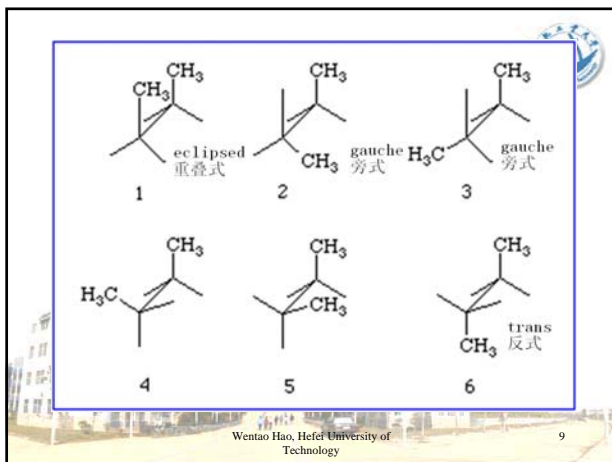
$$U = \frac{1}{2}U_0(1 - \cos 3\psi)$$

$$U_0 = 11.5 \, kJ/mol$$

Eclipsed position

U₀ → U_0

Potential energy (kJ/mol)

−180 −120 −60 0 60 120 180

Phi (degree)

* 势能

trans position

In most cases, ethane will stay in the **trans-position** to lower the potential energy of the whole system

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B. Butane 丁烷

g⁺（gauche）

g⁻（gauche）

ϕ

t（trans）

θ

1

The same bond

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CH₃ / CH₃ eclipsed 重叠式 1

CH₃ gauche 旁式 CH₃ 2

H₃C gauche 旁式 CH₃ 3

H₃C CH₃ 4

CH₃ CH₃ 5

CH₃ trans 反式 CH₃ 6

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Potential energy curve of butane in different conformation

Potential energy

? position

Eclipsed position

Trans position

Gauche position

ΔE

$\Delta \varepsilon$

0   60   120   180   240   300   360

Torsional angle（转角）

textbook P69, 或《高分子物理》, P16

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What does the potential energy curve of butane tell us?

- For polymer chains, they will have lots of confirmations. **(why?)**

- Rotation of single bonds on real polymer chains are **not free**.

- For polyethylene, the most stable (lowest energy) state is in the zigzag shape（之字形）.

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C. The Difference between the Conformation and the Configuration　　(key points)

The term **conformation** refers to the different arrangements of atoms and substitutes of the polymer chain brought about by **rotations** around the single bonds.

The term **configuration** refers to the organization of the atoms along the chain. It is used to describe those arrangements of atoms that cannot be altered except by breaking and re-forming primary **chemical bonds**.

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3.1.2 rotation of polymer chains

A. First look

Let's have a close and clear look on the rotation around a single bond.

Dotted lines means the possible position of carbon atoms.

(possible conformation)

C3

C2 $\sigma 2$ $\sigma 3$ C4

ϕ

α

$\sigma 1$ fixed

C1

高分子物理 P15

Slide 14
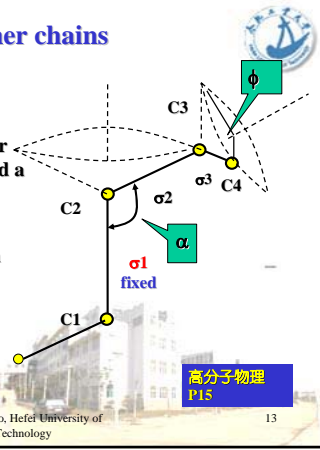
Rotation around single bonds

Slide 15
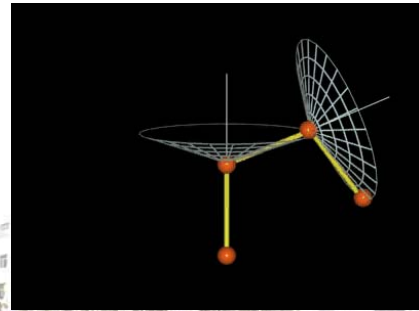
B. Random coil 无规线团
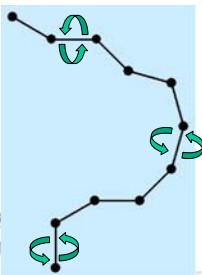
If the polymer chain is long enough, the position of the far end could be in **anywhere** in the space due to the rotation of single bonds.

That means, the polymer chain are very **flexible**.

Sometimes polymer chains are called the **random coils**

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Rotation of polymer chain

Slide 17
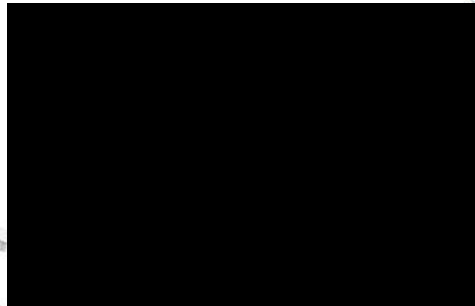
conformation of random polymer chain is like …

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Flory –

One of the founders of polymer science, contributed a lot to polymer physics, such as the concept of random coils, theories of polymer solution etc.

Paul J. Flory

1974 Nobel Chemistry prize

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P.J. Flory 简介

- 高分子科学家。
- 1910年6月19日生于伊利诺伊州斯特灵，1985年9月9日逝世。
- 1934年在俄亥俄州立大学获物理化学博士学位，后任职于杜邦公司，进行高分子基础理论研究。
- 1948年在康奈尔大学任教授。
- 1957年任梅隆科学研究所执行所长。
- 1961年任斯坦福大学化学系教授，1975年退休。
- 1953年当选为美国科学院院士。
- Flory在高分子物理化学方面的贡献，几乎遍及各个领域。他是实验家又是理论家，是高分子科学理论的主要开拓者和奠基人之一。著有《高分子化学原理》和《长链分子的统计力学》等。
- 1974年获诺贝尔化学奖。

http://www.salspolymer.com/show.asp?id=/s_history/paul_j_flory

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3.2 flexibility of polymer chains   Key point
柔性

3.2.1 concepts

The property that polymer chain can adjust their **conformation** by rotation is called **flexibility**.
构象

The stronger the ability to rotate,

the more the conformation,

the better the flexibility.

A. Flexibility at equilibrium state 平衡态柔性

- It refers to the flexibility at thermal equilibrium state.
- It depends on the **energy difference** between the <u>trans</u> and <u>gauche</u> conformation $\Delta\varepsilon$.   反式
  旁式

a. As $\Delta\varepsilon/kT \ll 1$, little hindrance, flexible

kT – thermal energy 热能

b. As $\Delta\varepsilon/kT \gg 1$, great hindrance, rigid

Higher $\Delta\varepsilon$
Less flexibility

Flexibility at equilibrium state reflects the ability of molecular chains to change their conformation.

$\Delta\varepsilon$ is very small   → $\Delta\varepsilon$ increases a little

What will happen?

Maybe only **part** of the single bonds is rotatable

Motion units   Single bonds   segments
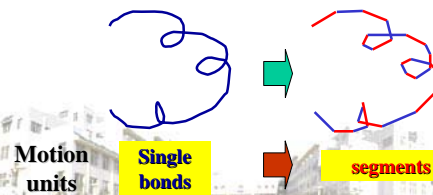
B. Segments 链段

Those short chains restricted in two rotatable single bonds are called segments.

构象变化是由分子链中单键内旋转引起的，但由于内旋转的发生需要克服内旋转位垒，并不是所有的单键都能克服位垒发生旋转，在某种条件和某一时刻只有部分单键能发生旋转，两个可旋转单键之间的一段链，称为链段。链段是随机的，链段长度是一种统计平均值。

C. Flexibility and Structure

Flexibility   ←   rotation   ←   structure

由于分子内旋转是导致分子链柔顺性的根本原因，而高分子链的内旋转又受其分子结构的制约，因而分子链的柔顺性与其分子结构密切相关。

3.2.2 Internal and External Factors

A   **Internal Factors**   内部因素

- I.   Structure of main chain
- II.   Substitutes (取代基)
- III.   Branching and cross-linking
- IV.   Length of polymer chain
- V.   Intermolecular force (分子间力)
- VI.   Crystallization (结晶)

B   **External Factors**   外部因素

- I.   Temperature
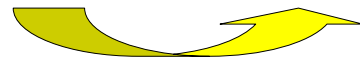- II.   External Force
- III.   Solvent

A. Internal factors   I. Structure of main chain

i. Carbon chain polymer; ii. Heterochain polymer
杂链高分子

—O—(CH₂)₆—O—C—(CH₂)₄—C—   **polyester**   **>**   —CH₂—CH₂—   **polyethylene**

PDMS   **>**   C—O—C   **POM**

C—O—C   **POM**   **>**   **PPO**

Summary：1) Bond length, 2) bond angle, 3) substitutes and (4) phenyl groups

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A. Internal factors   I. Structure of main chain

iii. Isolated double bonds; iv. Conjugate double bonds
孤立双键   共轭双键

Single bonds adjacent to the isolated double bonds are of STRONGER ability to rotate.

R4, R3—C=C—R1, R2

Why?

—CH=CH—CH=CH—

For conjugate double bonds, it is quite different. They can not rotate.

A. Internal factors
II. Substitute

i. Polarity of substitutes;

interaction   rotation

polarity   flexibility

polarity：-CN > Cl > CH₃; flexibility：PAN < PVC < PP

[—C—C—] with CN   **<**   [—C—C—] with Cl   **<**   [—C—C—] with CH₃

A. Internal factors
II. Substitute

ii. Symmetric substitution 对称取代

The better the symmetry, the better the flexibility. For example, the PIB and PP.

—C—C— (H, CH₃ / CH₃) **PIB**   **>**   —C—C— (H, H / H, CH₃) **PP**

Same potential energy for left and right gauche conformation   *different potential energy for left and right gauche conformation*

A. Internal factors
II. Substitute

iii. Distribution of substitutes

—C—C—C—C—C—C— (Cl, Cl, Cl)   —C—C—C—C—C—C— (Cl, Cl, Cl)

Chlorinated Polyethylene (CPE)   **Polyvinyl Chloride (PVC)**
氯化聚乙烯

CPE > PVC

Rubber-like   Plastic

A. Internal factors
II. Substitute
iv. Size of non-polar substitutes

Bigger substitutes

⬇

Greater hindrance

⬇

Little flexibility

Size:
$-C_6H_5 > CH_3 > H$ ➡ Flexibility:
PS < PP < PE

A. Internal factors
III. Branching and Crosslinking

Length of branched chains ⬆

➡ flexibility ⬇

crosslinking degree **(WHY?)**

➡ flexibility ⬇

A. Internal factors
IV. Length of polymer chain

L…e…n…g…t…h of molecular chain ⬇

➡ conformation ⬇

➡ flexibility ⬇

A. Internal factors
V. Intermolecular force

LARGER intermolecular forces

⬇

Less flexibility

A. Internal factors
VI. Crystallization

Crystallization of some flexible polymer chains, such as PE, PP and PEO will **freeze** the motion of molecule chain, so that the flexibility **can not be easily observed**.

B. External factors
I. Temperature- Enhance

Temperature ⬆ **rotation** ⬆ **flexibility** ⬆

B. External factors

II. Force – restrict

| mobility of molecular chains | ⬇ | ➡ | Flexibility | ⬇ |

III. Solvent – increase

| mobility of molecular chains | ⬆ | ➡ | Flexibility | ⬆ |

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Summery

1. **Rotation (conformation), flexibility, segments**

2. **the relationship between them**

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Summery

- **Small** hindrance, **Easy** to rotate;
- The **more** the Single bonds rotatable, the **more** the conformation;
- The **shorter** the segments, the **better** the flexibility.

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Time to ask questions
☺☺☺☺☺

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例1. 试从下列高聚物的链节结构，定性判断分子链的柔性或刚性，并分析原因。

(1) $-CH_2-C(CH_3)_2-$

(2) $-CH(R)-C(O)-N(H)-$

(3) $-CH_2-CH(CN)-$

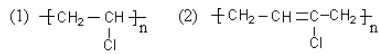(4) $-O-C_6H_4-C(CH_3)_2-O-C(O)-$

(5) $-C(C_6H_5)=C-C=C(C_6H_5)-$

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解：
　（1）柔性。因为两个对称的侧甲基使主链间距离增大，链间作用力减弱，内旋转位垒降低。
　（2）刚性。因为分子间有氢键作用，分子间作用力大，内旋转位垒高。
　（3）刚性。因为侧基极性大，分子间作用力大，内旋转位垒高。
　（4）刚性。因为主链上有苯环，内旋转较困难。
　（5）刚性。因为侧基体积大，妨碍内旋转，而且主链与侧链形成了大 π 键共轭体系，使链僵硬。

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例2. 比较以下两种聚合物的柔顺性，并说明为什么？
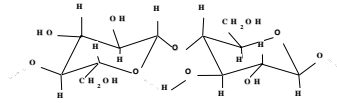
(1) $+CH_2-CH+_n$ 带Cl   (2) $+CH_2-CH=C-CH_2+_n$ 带Cl

解：

聚氯丁二烯的柔顺性好于聚氯乙烯，所以前者用作橡胶而后者用作塑料。

聚氯乙烯有极性的侧基Cl，有一定刚性。聚氯丁二烯虽然也有极性取代基Cl，但Cl的密度较小、极性较弱，另一方面主链上存在孤立双键，孤立双键相邻的单键的内旋转位垒较小，因为①键角较大（120°而不是109.5°），②双键上只有一个H原子或取代基，而不是两个。
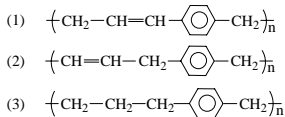

例3. 试分析纤维素的分子链为什么是刚性的。（提示：从纤维素链节结构分析阻碍内旋转的因素）

解：因为

(1) 分子有极性，分子链间相互作用力强。

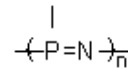(2) 六元吡喃环结构使内旋转困难。

(3) 分子内和分子间都能形成氢键，尤其是分子内氢键使糖苷键不能旋转，从而大大增加了刚性。

例4. 比较以下三个聚合物的柔顺性，从结构上简要说明原因。

(1) $+CH_2-CH=CH-\bigcirc-CH_2+_n$

(2) $+CH=CH-CH_2-\bigcirc-CH_2+_n$

(3) $+CH_2-CH_2-CH_2-\bigcirc-CH_2+_n$

解：

(1) 的刚性最大，因为双键与苯环共轭；(2) 的柔性最大，因为双键是孤立双键；(3) 介于中间。

例5. 评价主链带有间隔单键和双键的聚磷腈的柔顺性。其结构示意如下：

$+P=N+_n$

解：

这种结构是已知最有柔顺性的主链。

因为：

(1) 骨架键长为0.16nm，比C-C键长0.154nm略长，减少了短程分子间相互作用；

(2) N的键角从C=C双键的120°变为135°；

骨架的电子结构并无 π 键阻碍内旋转。

聚磷腈高分子的主链虽由交替的氮磷原子以单、双键交替连接而成，但未形成利于电荷转移的共轭体系，不具备导电或光导电的特性。其内在结构原因，目前尚未探明。一般认为，在形成 σ 键之后，每一个磷氮结构单元还剩下四个电子，其中两个电子为氮原子上的孤对电子，另外两个则占据由磷 d 轨道和氮 $2p$ 轨道杂化而成的 $d\pi-p\pi$ 轨道。但与有机分子不同的是 π 键的形成并没有对N-P键的旋转造成障碍（估计是在旋转时，磷原子上的五个分散的 d 轨道可以互相替换的缘故），因此，对称的 $d\pi-p\pi$ 轨道体系在每一个磷原子上均形成一个结点。也就是说，每一个 π 键都是一个孤立的体系，彼此之间没有相互作用，因此，整个主链也就没有形成长程共轭。这同时解释了为什么聚磷腈高分子主链具有很好的柔性。

3.3 statistical theory of the conformation of polymers chains

Contents: **P72-76, section 3.3.3**

- **The single freely jointed chains**
- **The freely rotatable chains**
- **The equivalent freely jointed chains**
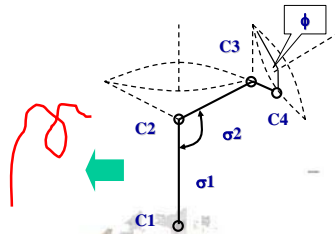
Requirements:

- **Calculation of mean square end-to-end length $\overline{h_0^2}$ under different conditions, application is important too.**

Objective:

- **To know the statistical theory**

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3.3.1 the single freely jointed chain
自由连接链/自由结合链

Single freely jointed chain is the simplified model of real polymer chains

C3
C2 σ2 C4
σ1
C1
φ

键长固定、键角不固定、内旋转自由

A. Some assumption:

✓ The real chain is replaced by a set of points jointed by *n* equal one-dimensional links of length *l*. The *contour* (轮廓线) or *fully extended length* of the chain is then *nl*.

✓ It is assumed that there is *no* restriction on the angles between the links; the angles are *not* restricted to lie on cones (圆锥).

✓ It is assumed that *no energy* is required to change the angles.
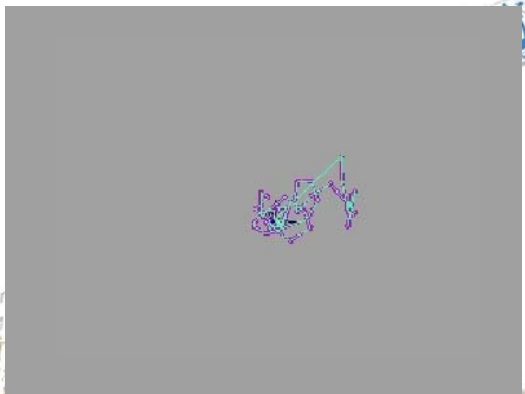
B. Root-mean-square (RMS) length of an unperturbed randomly coiled chain
无扰无规线团链的根均方长度，无扰链的根均方末端距

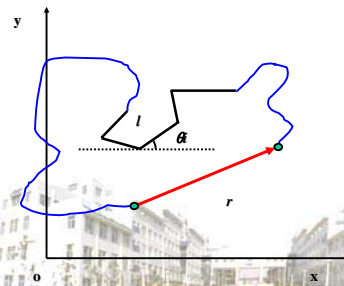**Fig. 3.6 Calculation of the RMS chain length.**

The thick lines – five actual links;

The curve – the other parts of polymer chain

The angle θ_i is the angle between the *i*th link and the OX axis.

Textbook p73

Calculation of *r*

- Let *r* to be the **end-to-end vector** of the chain

$$r_x = \sum_i l \cos\theta_i$$

$$r_x^{\,2} = l^2\left(\sum_i \cos^2\theta_i + \sum_{i\neq j}\cos\theta_i\cos\theta_j\right)$$

If $r_x^{\,2}$ is averaged over a large number of chains, the second term averages to be 0. Then …

$$\langle r_x^{\,2}\rangle = nl^2\langle\cos^2\theta_i\rangle = \frac{1}{3}nl^2$$

$<r_x^{\,2}>$ means the average of $r_x^{\,2}$

- **Due to**

$$\langle r^2\rangle = \langle r_x^{\,2}\rangle + \langle r_y^{\,2}\rangle + \langle r_z^{\,2}\rangle$$

- **and**

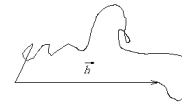$$\langle r_x^{\,2}\rangle = \langle r_y^{\,2}\rangle = \langle r_z^{\,2}\rangle$$

- **then**

$$\begin{cases}\langle r^2\rangle = nl^2 \\ r_{RMS} = \sqrt{\langle r^2\rangle} = n^{\frac{1}{2}}l\end{cases}$$

$$<r^2> \propto n$$

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C. Comparison between RMS length and fully extended length

- $r_{RMS} = n^{1/2}l$
- Fully extended length $= nl$
- $n^{1/2}l \ll nl$

That means the chains are generally in curled state rather than in extended state.

也可用"均方末端距"表征分子链的尺寸。

均方 – 平方的平均 $\overline{h_0^2} = r^2_{RMS} = nl^2$

分子尺寸 ➡ 均方末端距

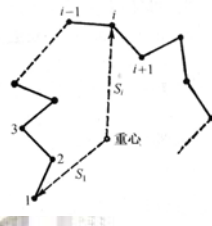内旋转容易 ➡ 链段短 ➡ 线团蜷缩

➡ 线团尺寸小 ➡ 末端距小

D. Radius of gyration (回旋半径)

r_g is the RMS distance of the atoms on the chain from the center of gravity of the chain.

$$r_g = r_{RMS}/\sqrt{6}$$

$$\overline{r_g^2} = \frac{\overline{h^2}}{6}$$

高分子物理, p30

3.3.2 freely rotatable chains 自由旋转链

（键长固定、键角固定、内旋转自由）

$$\overline{h_{f,r}^2} = \sum_{i=1}^{n}\sum_{j=1}^{n} l_i \cdot l_j \approx nl^2 \frac{1+\cos\theta}{1-\cos\theta}$$

The subscript f, r indicates freely rotatable

$$\Theta \cos\theta = \cos(180^o - 109.5^o) \approx \frac{1}{3},$$

$$\therefore \overline{h_{f,r}^2} = nl^2 \frac{1+\cos\theta}{1-\cos\theta} = 2nl^2$$

键角限定后，与自由结合链相比，自由旋转链不算太自由，均方末端距增大一倍

For the freely rotatable chains

$$\overline{h_{f,r}^2} = nl^2 \frac{1+\cos\theta}{1-\cos\theta} = 2nl^2$$

$$\overline{h_{f,r}^2} \propto n$$
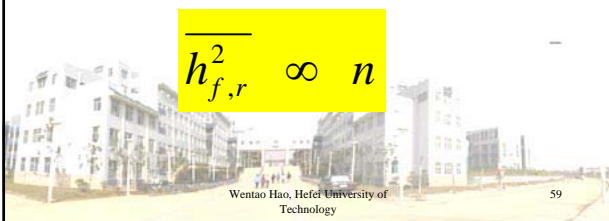
If the interaction between the non-adjacent atoms was considered……

$$\overline{h^2} = nl^2 \frac{1+\cos\theta}{1-\cos\theta} \cdot \frac{1+\alpha}{1-\alpha}$$

$$\alpha = \overline{\cos^2\varphi} = \frac{\int_0^{2\pi} e^{-U(\varphi)/kT}\cos\varphi d\varphi}{\int_0^{2\pi} e^{-U(\varphi)/kT}d\varphi}$$

$$\overline{h^2} \propto n$$

设内旋转位能函数为偶函数
U(+φ) = U(-φ)

For isotactic & syndiotactic polymer

$$\overline{h^2} = nl^2 \frac{1+\cos\theta}{1-\cos\theta} \cdot \frac{1-\alpha^2-\beta^2}{(1-\alpha^2)+\beta^2} \qquad \text{isotactic}$$

$$\overline{h^2} = nl^2 \frac{1+\cos\theta}{1-\cos\theta} \cdot \frac{1-(\alpha^2+\beta^2)^2}{(1-\alpha^2)+(\alpha-\alpha^2-\beta^2)^2} \qquad \text{syndiotactic}$$

$$\overline{h^2} \ \infty \ n \qquad \beta = \overline{\sin^2\varphi} = \frac{\int_0^{2\pi} e^{-U(\varphi)/kT}\sin\varphi\, d\varphi}{\int_0^{2\pi} e^{-U(\varphi)/kT}d\varphi}$$

Generally, for a flexible polymer of *n* links

$$\overline{h^2} = nG_0(l,\theta,\alpha,\beta) \ \infty \ n$$

3.3.4 Gaussian chain (高斯链)

- **If a chain has such a property that the actual end-to-end distance is much less than the fully extended length, *r << nl*, it is called the Gaussian chain.**

- 如果某聚合物的均方末端距正比于其聚合度或分子量，则该聚合物分子链也可被认为是高斯链。

3.3.4 Gaussian chain (高斯链)

dxdydz P

z

OP << *nl*

o   y

x

the Gaussian chain with one end free and another coincide with the origin

Fig. 3.7, textbook p74
图1-13, 高分子物理, p25

Gaussian error function or normal distribution （高斯误差函数或正态分布）

- **The probability that P lies in the small element of volume dxdydz at (x,y,z) is**

- **p(x,y,z) dxdydz = (b³/ π ³/²)exp(-b²r²)dxdydz**
- **Where b² = 3/(2nl²), r² = x² +y² +z²**

- **p(x,y,z) = (b³/ π ³/²)exp(-b²r²) – Gaussian error function or normal distribution**

简称"高斯分布函数"   http://lyceum.blog.sohu.com/19390390.html

The probability *P(r)dr* that the end P lies somewhere in the spherical shell of radius *r* and thickness *dr* is

$$P(r)dr = p(r)\cdot 4\pi r^2 dr = 4\pi r^2(b^3/\pi^{3/2})\exp(-b^2 r^2)dr$$

$$p(r) = p(x,y,z) = (b^3/\pi^{3/2})\exp(-b^2 r^2)$$

$$P(r) = p(r)\cdot 4\pi r^2 = 4\pi r^2(b^3/\pi^{3/2})\exp(-b^2 r^2)$$

The mean square end-to-end distance of Gaussian chain

$$\langle r^2 \rangle = \int_0^\infty r^2 P(r)\,dr = \int_0^\infty r^2 4\pi r^2 \left(b^3/\pi^{3/2}\right)\exp\left(-b^2 r^2\right)dr$$

$$\Rightarrow \quad \langle r^2 \rangle = \frac{3}{2b^2}$$

$$\Theta\, b^2 = \frac{3}{2nl^2}, \therefore \langle r^2 \rangle = nl^2$$

Coincide with the calculation by geometrical methods

关于高斯链及统计理论

- 关于高斯链的计算实际上是以自由结合链为基础的计算，前提是n很大
- 首先推导出一端固定的高斯链自由端在空间某点处的几率函数，然后推导出末端距为r时的几率函数，最后求出均方末端距，结果当然应该一致
- 对于实际的高分子链，高斯函数是否还能适用？

3.3.4 equivalent freely jointed chains
等效自由结合链

Key point

1. What is " equivalent freely jointed chains"?

2. How to calculated it?

3. "Segments", what's the meaning here?

高分子物理，p27

Q1. What is " equivalent freely jointed random chains"?

- If the chain is long enough, it maybe considered as Gaussian chain though **NO** real chains are freely jointed random chains.
- Suppose chains are composed of n_e segments with length of l_e .

$$L_{\max} = n_e l_e$$

In the form of freely jointed chains

$$\overline{h_0^{\,2}} = n_e l_e^{\,2}$$

Q2. How to calculate it?

$$L_{\max} = n_e l_e$$

$$\overline{h_0^{\,2}} = n_e l_e^{\,2}$$

$$n_e = \frac{L_{\max}^2}{\overline{h_0^{\,2}}}, \quad l_e = \frac{\overline{h_0^{\,2}}}{L_{\max}}$$

Example of polyethylene

Fully extended chain length

$$L_{\max} = nl\cos\left(\frac{\theta}{2}\right)$$

Since and

$$\cos^2\left(\frac{\theta}{2}\right) = \left(\frac{1+\cos\theta}{2}\right)$$
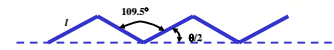
$$\cos\theta \approx \frac{1}{3}$$

Then and

$$\cos\left(\frac{\theta}{2}\right) = \left(\frac{2}{3}\right)^{\frac{1}{2}}$$

$$L_{\max} = \left(\frac{2}{3}\right)^{\frac{1}{2}} nl$$

Suppose polyethylene chain is freely rotatable chain

$$\overline{h^2} = 2nl^2$$

$$n_e = \frac{L_{\max}^2}{\overline{h^2}} = \frac{n}{3}$$

$$l_e = \frac{\overline{h^2}}{L_{\max}} = 2.45l$$

Q.3 "Segments", what does it the mean?

- Segments here replaced the single bonds to function as the smallest rotatable units.

3.3.5 Characterization of Flexibility

1. Rigidity factor 刚性因子

$$\sigma = [\overline{h_0^2} / \overline{h_{f,r}^2}]^{1/2}$$

By experiments   **By calculation**

键数和键长一定时，链越柔顺，其均方末端距愈小。因此可以用实测的无扰均方末端距与自由旋转的均方末端距之比－刚性因子，作为分子链柔顺性的度量。

Bigger σ, less flexibility；

smaller σ, better flexibility.

---

2. Characteristic ratio 特征比

$$C_n = \overline{h_0^2} / nl^2$$

By experiments   **By calculation**

Freely jointed chains
$$C_n = \overline{h_0^2} / nl^2 = 1$$

Fully extended chains
$$C_n = \overline{h_0^2} / nl^2 = n$$

The smaller the C_n is, the more flexible the chain is.

---

3. length of segments l_e

- If we use equivalent freely jointed chain to describe the molecular size, the more flexible the chain is, the smaller the l_e (length of segments) is; the larger the l_e value, the more rigid the chain is.
- 若以等效自由连接链描述分子尺寸，则链愈柔顺，链段愈短，因此链段长度也可以表征链的柔顺性。链段长度l_e愈大，柔性差。

Summery I
三种均方末端距的表示方法：

1. **Freely jointed chains**：
$$\overline{h_{f,j}^2} = nl^2$$

2. **Freely rotatable chains**：
$$\overline{h_{f,r}^2} \approx nl^2 \frac{1+\cos\theta}{1-\cos\theta}$$

3. **Equivalent freely jointed chains**：
$$\overline{h^2} = n_e l_e^2$$

Summery II
三种分子链柔顺性的表示方法：

1. **Rigidity factor**
$$\sigma = [\overline{h_0^2} / \overline{h_{f,r}^2}]^{1/2}$$

2. **Characteristic ratio**
$$C_n = \overline{h_0^2} / nl^2$$

3. **Length of segments**
$$l_e$$

Time to ask questions


例1. 近程相互作用和远程相互作用的含义及它们对高分子链的构象有何影响？

解：

所谓"近程"和"远程"是根据沿大分子链的走向来区分的，并非为三维空间上的远和近。事实上，即使是沿高分子长链相距很远的链节，也会由于主链单键的内旋转而会在三维空间上相互靠的很近。

高分子链节中非键合原子间的相互作用——近程相互作用，主要表现为斥力，如中两个C原子上的H原子，两个H原子的范德华半径之和为0.240nm，当两个H原子为反式构象时，其间的距离为0.247 nm，处于顺式构象时为0.226nm。因此，H原子间的相互作用主要表现为斥力，至于其它非键合原子间更是如此。

近程相互排斥作用的存在，使得实际高分子的内旋转受阻，使之在空间可能有的构象数远远小于自由内旋转的情况。受阻程度越大，构象数就越少，高分子链的柔性就越小。远程相互作用可为斥力，也可为引力。当大分子链中相距较远的原子或原子团由于单键的内旋转，可使其间的距离小于范德华距离而表现为斥力，大于范德华距离为引力。无论哪种力都使内旋转受阻，构象数减少，柔性下降，末端距变大。

高分子链占有体积及交联和氢键等都属于远程相互作用。
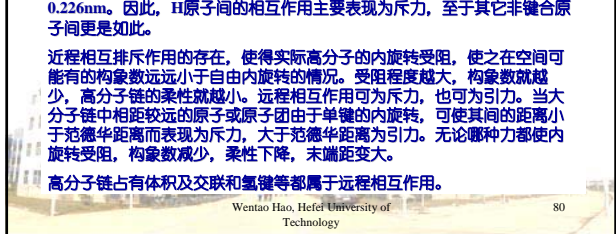
例2. C－C键键长为0.154nm，求聚合度1000的自由结合链的**均方根**末端距。

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

$$\langle h^2 \rangle^{1/2} = 4.87 \times 10^{-9}\, m$$

例3. 链的尺寸扩大10倍，则聚合度需扩大多少倍？

$$10\langle h^2 \rangle^{1/2} = \left(100nl^2\right)^{1/2}$$

所以聚合度应扩大100倍。

例4. 假定聚乙烯的聚合度为2000，键角为109.5°，求伸直链的长度Lmax与自由旋转链的根均方末端距之比值。并由分子运动观点解释某些高分子材料在外力作用下可以产生很大变形的原因。

解：对于聚乙烯链

$$L_{\max} = \left(\frac{2}{3}\right)^{\frac{1}{2}} nl \qquad \left(\overline{h_{f,r}^2}\right)^{\frac{1}{2}} = \sqrt{2}nl$$

n = 2 × 2000 = 4000 （严格地说应为3999）

所以
$$L_{\max}\Big/\left(\overline{h_{f,r}^2}\right)^{\frac{1}{2}} = \sqrt{n/3} = \sqrt{4000/3} = 36.5$$

可见高分子链在一般情况下是相当卷曲的，在外力作用下链段运动的结果是使分子趋于伸展。于是某些高分子材料在外力作用下可以产生很大形变，理论上，聚合度2000的聚乙烯完全伸展可形变36.5倍。

注意：公式中的n为键数，而不是聚合度，本题中n为4000，而不是2000。