Molecular Liquids

- Flexible molecules: polymers
- Polymers are molecular fragments linked together by chemical bonds
- Simplest polymers contain the same fragments (monomers)
- Proteins contain mixtures of monomers taken from the twenty naturally occurring amino acids

Polymers

- History is typically divided into eras:
  - Stonge age
  - Bronze age
  - Iron age
  - In a similar way, in the 20th century we entered the "Polymer age"
- Naturally occurring polymers (biopolymers) have been in used for centuries
  - e.g. natural rubber (from the "rubber-tree" plant)

Polymers

- In the 1800's polymers were synthesized, but misidentified as small colloids with "mysterious" non-covalent bonds
  - In reality, they are formed by very large molecules
- In 1920, Staudinger proposed the **macromolecular hypothesis**
  - Polymers are molecules made of covalently bonded *monomers*
  - Colloidal properties are attributed solely to the sizes of these large molecules

Polymers

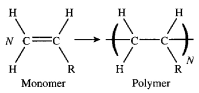
- By 1929 several polymers were synthesized with well-defined structures
  - Thus, the *Polymer Age* was born
- Between 1930 and 1960, main concepts of polymers were established:
  - **Macromolecular sizes (Kuhn)**
  - Swelling of a single chain in a good solvent (Flory)
  - Thermodynamics of mixtures (Huggins and Flory)
  - Gelation (Flory and Stockmayer)
  - Rubber elasticity (Kuhn, James, and Guth)
  - Single-molecule models of polymer dynamics (Rouse and Zimm)

Polymers

- Between 1960 to 1980 main principles of modern polymer physics were developed:
  - The polymer chain and its confining tube (Edwards)
  - Semidilute solutions (des Cloizeaux and de Gennes)
  - Reptation theory of chain diffusion (de Gennes)
  - Doi-Edwards theory for the flow properties of polymer melts
- Details are still far from a full understanding, e.g.:
  - Polymer with associating groups bonded to their chains, polymer crystallization, liquid crystallline polymers, charged polymers
  - With their applications to DNA, RNA, proteins, polysaccharides

Polymers

- (poly)-(mer) means (many)-(parts)
  - Molecules consisting of many elementary units, called **monomers**
  - **Monomers** are structural repeating units of a polymer that are connected to each other by covalent bonds
  - Two general types of monomers:
    - Chemical monomer (the actual molecules)
    - Kuhn monomer (conceptually defined - longer section of chain)
- Polymerization: chemical process by which monomers covalently bond to each other
  - # of monomers in a polymer is its **degree of polymerization** *N*
  - *(total) Molar mass* $M = N M_{monomer}$

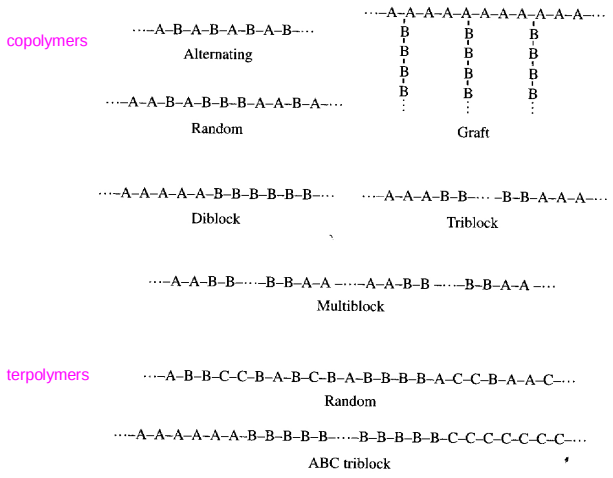


Polymers

- Homopolymers: Contain only one type of monomers

  ... -A-A-A-A-A-A- ...
- Heteropolymers: more types
  - Properties depend on fraction of each monomer type and sequence
  - Copolymers – two different types of monomers
  - Terpolymers – three types
  - Many biopolymers are heteropolymers
    - DNA – four different types of monomers (nucleotides)
    - Proteins – 20 different types (amino acids)

copolymers



terpolymers

Polymers

Major factors determining properties:

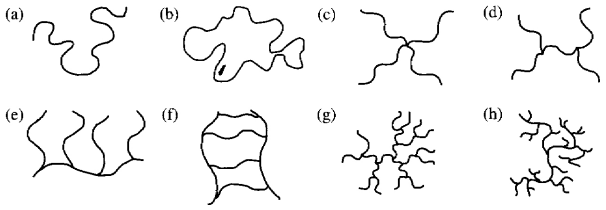
- Degree of polymerization *N*
  - N < 20 typically called oligomer
  - Linear polymers 20 < N < billions (chromosome)
- Linkage
  - Boiling point and melting point increase with # of bonds

Table 1.1 Properties and applications of alkane hydrocarbons (following Sperling)

Number of C atoms	State at 25 °C	Example	Uses
1–4	Simple gas	Propane	Gaseous fuels
5–15	Low-viscosity liquid	Gasoline	Liquid fuels and solvents
16–25	High-viscosity liquid	Motor oil	Oils and greases
20–50	Simple soft solid	Paraffin wax	Candles and coatings
>1000	Tough plastic solid	Polyethylene	Bottles and toys

Polymers

- Architecture
  - (a) linear, (b) ring, (c) star, (d) H, (e) comb, (f) ladder, (g) dendrimer, (h) randomly branched [used in bottles]



  - Interconnected polymers = polymer network

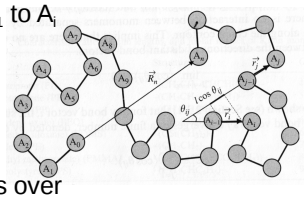
Ideal Chains

- An idealized model for polymers (the SHO of polymer physics)
  - Does not consider interactions between monomers, except the covalent neighbors
- "Real" chains:
  - Monomers interact with each other and with the solvent
  - Not entirely described by this model, although some may approximate it
  - Interactions could be effectively attractive or repulsive:
    - Dominant attractive (e.g. low T) → collapsed conformation
    - Dominant repulsive (e.g. high T) → swollen polymer
  - At the θ-temperature, real chains are in conformations described by ideal chain models
    - θ-temperature : intermediate T at which attraction and repulsion are balanced

Conformations of Ideal Chains

- Flexible polymer with n+1 atoms
- Define $\boldsymbol{r}_i$ vector from atom A_{i-1} to A_i
- With end-to-end vector

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



- has average value (average is over different conformations of the same chain or different chains – ensemble average)

$$\langle \vec{R}_n \rangle = 0$$

Conformations of Ideal Chains

- Simplest non-zero average is the mean-square end-to-end distance

$$\begin{aligned} \langle R^2 \rangle &\equiv \langle \vec{R}_n^2 \rangle \\ &= \langle \vec{R}_n \cdot \vec{R}_n \rangle \\ &= \left\langle \left(\sum_{i=1}^{n} \vec{r}_i \right) \cdot \left(\sum_{j=1}^{n} \vec{r}_j \right) \right\rangle \\ &= \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \vec{r}_i \cdot \vec{r}_j \rangle \end{aligned}$$

- If all bonds are the same length $l = |\boldsymbol{r}_i|$, use angle between bond vectors $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$

$$\vec{r}_i \cdot \vec{r}_j = l^2 \cos\theta_{ij} \qquad \text{so that} \qquad \langle R^2 \rangle = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \cos\theta_{ij} \rangle$$

Conformations of Ideal Chains

- Special Case: Freely Jointed Chain Model
  - Constant bond length *l*
  - No correlations between directions of bond vectors

$$\langle \cos\theta_{ij} \rangle = 0 \text{ for } i \neq j$$
$$\langle \cos\theta_{ij} \rangle = 1 \text{ for } i = j$$

  - thus

$$\langle R^2 \rangle = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \cos\theta_{ij} \rangle = n l^2$$

Conformations of Ideal Chains

- Typical polymer chains, however, have angle correlations – at least between nearest neighbors

$$\langle \cos\theta_{ij} \rangle \neq 0$$

From restricted bond angles and steric hindrance

- But because in ideal chains there are no interactions between far neighbors, in general

$$\lim_{|i-j| \to \infty} \langle \cos\theta_{ij} \rangle = 0$$

- Can show that for any bond vector *i*, (C'_i finite)

$$C'_i \equiv \sum_{j=1}^{n} \langle \cos\theta_{ij} \rangle$$

Conformations of Ideal Chains

- Typical polymer chain

$$\langle R^2 \rangle = l^2 \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \cos\theta_{ij} \rangle = l^2 \sum_{i=1}^{n} C'_i = C_n n l^2$$

- Where C_n is Flory's *characteristic ratio*

$$C_n = \frac{1}{n} \sum_{i=1}^{n} C'_i$$

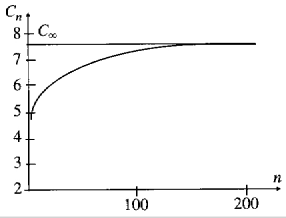
- The fact that <R²> is proportional to nl² is the <u>main property</u> of *ideal chains*

Conformations of Ideal Chains

- Properties of C_n
  - An infinite chain has a value of C_∞
  - Real chains with finite length have a lower value of C'_i
  - $C_n > 1$ for all polymers
  - Ideal chain models ignore steric hindrance for far away bonds, resulting in C_n saturating at a value of C_∞ for long chains

$$\langle R^2 \rangle \simeq C_\infty n l^2$$

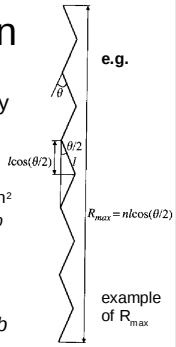
  - Typical values of C_∞ are between 7 to 9



Equivalent Description

- Ideal polymers can be described in a unified way (independent of chemical structure)
- Define the **equivalent freely jointed chain**
  - Purpose is to describe with <R²> = number X length²
  - Define *N* = freely-jointed effective bonds of length *b*
  - Where *b* is the effective bond length called **Kuhn length**
- Recipe:
  - Given R_{max} (max end-to-end), define $R_{max} = N b$
  - And $\langle R^2 \rangle = N b^2$
  - But because

$$\langle R^2 \rangle = N b^2 = b R_{max} = C_\infty n l^2$$



Equivalent Description

- Then, for the **Kuhn monomers**

$$N = \frac{R_{max}^2}{C_\infty n l^2}$$

with **Kuhn lengths**

$$b = \frac{\langle R^2 \rangle}{R_{max}} = \frac{C_\infty n l^2}{R_{max}}$$

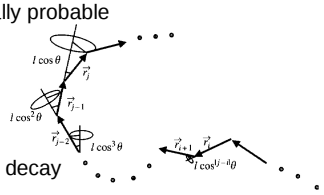
then, the root-mean-square end-to-end distance

$$R_0 = \sqrt{\langle R^2 \rangle} = b N^{1/2}$$

valid for all flexible linear polymers in the ideal state with N>>1. All chemical specific characteristics are contained in the Kuhn length and monomer

Models of Ideal Chains

- Freely Rotating Chain Model
  - All bond lengths and bond angles are fixed
  - All torsion angles are equally probable
  - In this case
    $$C_\infty = \frac{1+\cos\theta}{1-\cos\theta}$$
  - scale at which correlations decay
    $$s_p = -\frac{1}{\ln(\cos\theta)}$$



notes

Models of Ideal Chains

- Worm-like Chain Model
  - Special case of the freely rotating model for small values of the bond angle
  - Good for stiff polymers, such as DNA
  - In this case $C_\infty = \frac{1+\cos\theta}{1-\cos\theta} \simeq \frac{2-(\theta^2/2)}{(\theta^2/2)} \simeq \frac{4}{\theta^2}$ $\qquad s_p \simeq \frac{2}{\theta^2}$
  - With *persistence length* $l_p \equiv s_p l = l\frac{2}{\theta^2}$
  - With a Kuhn length
    $$b = l\frac{C_\infty}{\cos(\theta/2)} \simeq l\frac{4}{\theta^2} = 2l_p$$

In DNA, $l_p \approx 50$ nm; b ≈ 100 nm