2. Polymers

2.1. Traditional and modern applications
2.2. From chemistry to statistical description
2.3. Polymer solutions and polymer blends
2.4. Amorphous polymers
2.5. The glass transition
2.6. Crystalline polymers
2.7. Polymer networks
2.8. Polymer nanocomposites
2.1 Traditional and modern applications of polymers

Traditional applications

Soft and light materials

good heat and electrical insulators

problem: waste / recycling

www.basf.de

ENTROPY !!!
Block copolymer thin films as gas sensors

- array of well-ordered conducting polymer nanowires
- etch mask consisting of cylinder-forming diblock copolymers
- wires act as sensor for ethanol vapor


high degree of order achieved by treatment with toluene vapor
Drug delivery from nanogels


thermoresponsive nanogels
diameter 600 nm

release of cancer drug
5-Fluorouracil

cumulative amount of 5-FU
released from nanogels

Nanostructured polymer particles
for enhanced drug uptake in the cell
Controllable ultrafiltration


coating with switchable P(S-\textit{b}-NIPAM-\textit{b}-S)

poly(\textit{styrene-\textit{b}-NIPAM-\textit{b}-\textit{styrene})

118 kg/mol, \( f_{\text{PNIPAM}} = 0.77 \)

• permeable only für small molecules
• permeability decreases strongly upon collapse
2.2. From chemistry to statistical description

Polymers are chain-like macromolecules consisting of a LARGE number \( N \) of monomers (= repeat units).

**degree of polymerization** \( N \): number of polymerized monomers
Degree of polymerization

<table>
<thead>
<tr>
<th>Number of Carbons in Chain</th>
<th>State and Properties of Material</th>
<th>Use, Dependent on Chain Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–4</td>
<td>Simple gas</td>
<td>Bottled gas for cooking</td>
</tr>
<tr>
<td>5–11</td>
<td>Simple liquid</td>
<td>Gasoline</td>
</tr>
<tr>
<td>9–16</td>
<td>Medium-viscosity liquid</td>
<td>Kerosene</td>
</tr>
<tr>
<td>16–25</td>
<td>High-viscosity liquid</td>
<td>Oil and grease</td>
</tr>
<tr>
<td>25–50</td>
<td>Simple solid</td>
<td>Paraffin wax candles</td>
</tr>
<tr>
<td>1000–3000</td>
<td>Tough plastic solid</td>
<td>Polyethylene bottles and containers</td>
</tr>
</tbody>
</table>

$N$ may be very high

→ solid materials (entanglements)

→ description by statistical means
A few polymers

- poly(1,4-butadiene) *rubber tires*
- polypropylene *plastic bags*
- poly(dimethylsiloxane) *silicone*
- poly(ethylene oxide) *PEG*
- poly(p-phenylene-terephthalamide) *Kevlar*
The radius of gyration

characteristic size of a single polymer

characteristic length scales / sizes:

• mean-square end-to-end distance $\langle R^2 \rangle^{1/2}$

• radius of gyration

$$R_g^2 \equiv \frac{1}{N} \sum_{i=1}^{N} (\bar{R}_i - \bar{R}_{cm})^2$$

$\bar{R}_i$ : monomer position

$\bar{R}_{cm}$ : polymer's center of mass

calculation in lecture
A close look at the chain

- bond vector $\vec{r}_i$ between atoms $C_{i-1}$, $C_i$ = axis of rotation for $\vec{r}_{i+1}$
- bond angle $\theta_i$ constant
Various single chain models

ideal chain model:
• no interactions between monomers
• rotations around bonds unhindered
• bond length and angle fixed

\[ \langle \mathbf{R}_g^2 \rangle = \frac{1}{6} nl^2 \]

\( n \): number of monomers
\( l \): monomer length

freely rotating chain:
1. all bond lengths \( b \) and angles \( \theta \) fixed
2. all rotation angles \( \varphi \) equally probable

\[ \langle \mathbf{R}_g^2 \rangle = \frac{1}{6} nl^2 \cdot \frac{1 + \cos \theta}{1 - \cos \theta} \]

hindered rotation model:
1. all bond lengths and angles fixed
2. potential of rotation not constant

\[ \langle \mathbf{R}_g^2 \rangle = \frac{1}{6} n l^2 \cdot \frac{1 + \cos \theta}{1 - \cos \theta} \cdot \frac{1 + \langle \cos \varphi \rangle}{1 - \langle \cos \varphi \rangle} \]
The characteristic ratio $C_\infty$

all corrections are comprised in $C_\infty$  \[ \langle \vec{R}_g^2 \rangle = \frac{1}{6} n l^2 \cdot C_\infty \]

e.g. for hindered rotation model  \[ C_\infty = \frac{1+\cos \theta}{1-\cos \theta} \cdot \frac{1+\langle \cos \varphi \rangle}{1-\langle \cos \varphi \rangle} \]

$C_\infty$ is found in tables for all common polymers

<table>
<thead>
<tr>
<th>polymer</th>
<th>$C_\infty$</th>
<th>$b$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-polybutadiene</td>
<td>5.5</td>
<td>9.9</td>
</tr>
<tr>
<td>polypropylene</td>
<td>6.0</td>
<td>11</td>
</tr>
<tr>
<td>poly(dimethylsiloxane)</td>
<td>6.8</td>
<td>13</td>
</tr>
<tr>
<td>polyethylene</td>
<td>7.4</td>
<td>14</td>
</tr>
<tr>
<td>atactic polystyrene</td>
<td>9.5</td>
<td>18</td>
</tr>
</tbody>
</table>

$b$: Kuhn segment length
Coarse-graining: The equivalent freely jointed chain

true chain: $n$ monomers of length $l$
equivalent chain: $N$ monomers of length $b$
Kuhn monomers

(i) contour length: $N \cdot b = R_{\text{max}}$
(ii) end-to-end distance: $\langle R^2 \rangle = N \cdot b^2 = C_\infty \cdot n \cdot l^2$

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

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

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

→ coarse-grained chain with $b$, $N$ follows simple scaling law
Free energy of an ideal chain → force needed to pull on a chain  

Helmholtz free energy \( F = U - TS \)

\( U(N, \vec{R}) = 0 \) no interactions \( \rightarrow F = -TS \)

entropy  
\[ S(N, \vec{R}) = k_B \cdot \ln \Omega(N, \vec{R}) \]

\( \Omega(N, \vec{R}) \) : number of conformations of freely jointed chain of \( N \) monomers with end-to-end vector \( \vec{R} \)

Gaussian distribution of end-to-end vectors

\[ \Rightarrow F(N, \vec{R}) = \frac{3}{2} k_B T \frac{\vec{R}^2}{Nb^2} + F(N,0) \]

free energy of a single chain having an end-to-end-vector \( \vec{R} \)
elastic force
when separating the chain ends by $R_x$ in $x$ direction

$$f_x = \frac{\partial F(N, \vec{R})}{\partial R_x} = \frac{3k_B T}{Nb^2} \cdot R_x$$

$$\Rightarrow \vec{f} = \frac{3k_B T}{Nb^2} \cdot \vec{R}$$

the lower $T$,
the lower the spring constant,
the softer the chain

elastic spring constant

force $\sim$ elongation: looks like Hookes' law
but origin is different from normal spring:
solid: enlarged distance between atoms
polymer: unfolding of bonds

„entropic elasticity“ $\rightarrow$ origin of rubber elasticity
chain = „entropy spring“

http://www.youtube.com/watch?v=A25LHIMK_v8
2.3. Polymer solutions

**Solvent quality:**
interaction monomer – solvent

**good solvent:**
maximization of monomer-solvent contacts → chain expansion, „swollen chain“

\[
\left\langle R_g^2 \right\rangle^{1/2} \sim N^\nu
\]
\[
\nu = 0.588 \equiv 3/5
\]

**theta solvent:**
balanced interactions → unperturbed (ideal) chain

\[
\left\langle \overline{R}_g^2 \right\rangle^{1/2} = N^{1/2} \cdot \frac{bC_{\infty}^{1/2}}{6^{1/2}}
\]
\[
\nu = 1/2
\]

**poor solvent:**
minimization of monomer-solvent contact → chain collapse, clustering, precipitation
Transition good solvent – poor solvent

Poly(N-isopropylacrylamide) (PNIPAM) in water
- below cloud point H-bonds with H$_2$O (cage structure)
- above cloud point H-bonds with adjacent amide group
- 'zipper' effect

$T < 32^\circ C$
H$_2$O is good solvent

$T > 32^\circ C$
H$_2$O is poor solvent

cloud point = 32$^\circ$C
Good solvent – theta solvent

from Rubinstein, Colby.

polystyrene in benzene (good solvent)
\[ \left\langle R_g^2 \right\rangle^{1/2} \sim N^{0.59} \]

polystyrene in cyclohexane (theta solvent)
\[ \left\langle R_g^2 \right\rangle^{1/2} \sim N^{0.50} \]

The swelling of the chain in good solvent results as a balance of the
- repulsion energy between monomers and
- the entropy loss due to increased end-to-end vector
Concentration regimes in polymer solutions

if intermolecular bonds present (e.g. hydrogen bonds, vulcanization) → gelation from concentrated solution

(a) $c < c^*$
dilute solution
characteristic lengthscale:
$R_g \propto N^{3/5}$

(b) $c \approx c^*$
semidilute
chains start to overlap

(c) $c > c^*$
concentrated solution
characteristic lengthscale:
mesh size $\xi$
Phase behavior of polymer solutions

From Rubinstein, Colby: Polymer Physics. Data from N. Takano et al., *Polym. J.* 1985

polyisoprene solutions in dioxane:

- for 133 000 g/mol at 22°C: miscibility only for \( \phi < \sim 0.02 \) and \( \phi > 0.20 \)
- for 53 300 g/mol at 22°C: miscibility for all \( \phi \)

→ first-order phase transition from 1-phase to 2-phase system

transition temperature depends on polymer molar mass and on polymer volume fraction

\[ \phi_A: \text{volume fraction of polymer in solvent} \]

\[ \phi_A = \frac{c}{\rho} = c \cdot \frac{v_{\text{mon}} N_{Av}}{M_{\text{mon}}} \]

- \( c \): polymer concentration
- \( \rho \): polymer mass density
- \( v_{\text{mon}} \): monomer volume
- \( M_{\text{mon}} \): monomer molar mass
- \( N_{Av} \): Avogadro’s constant